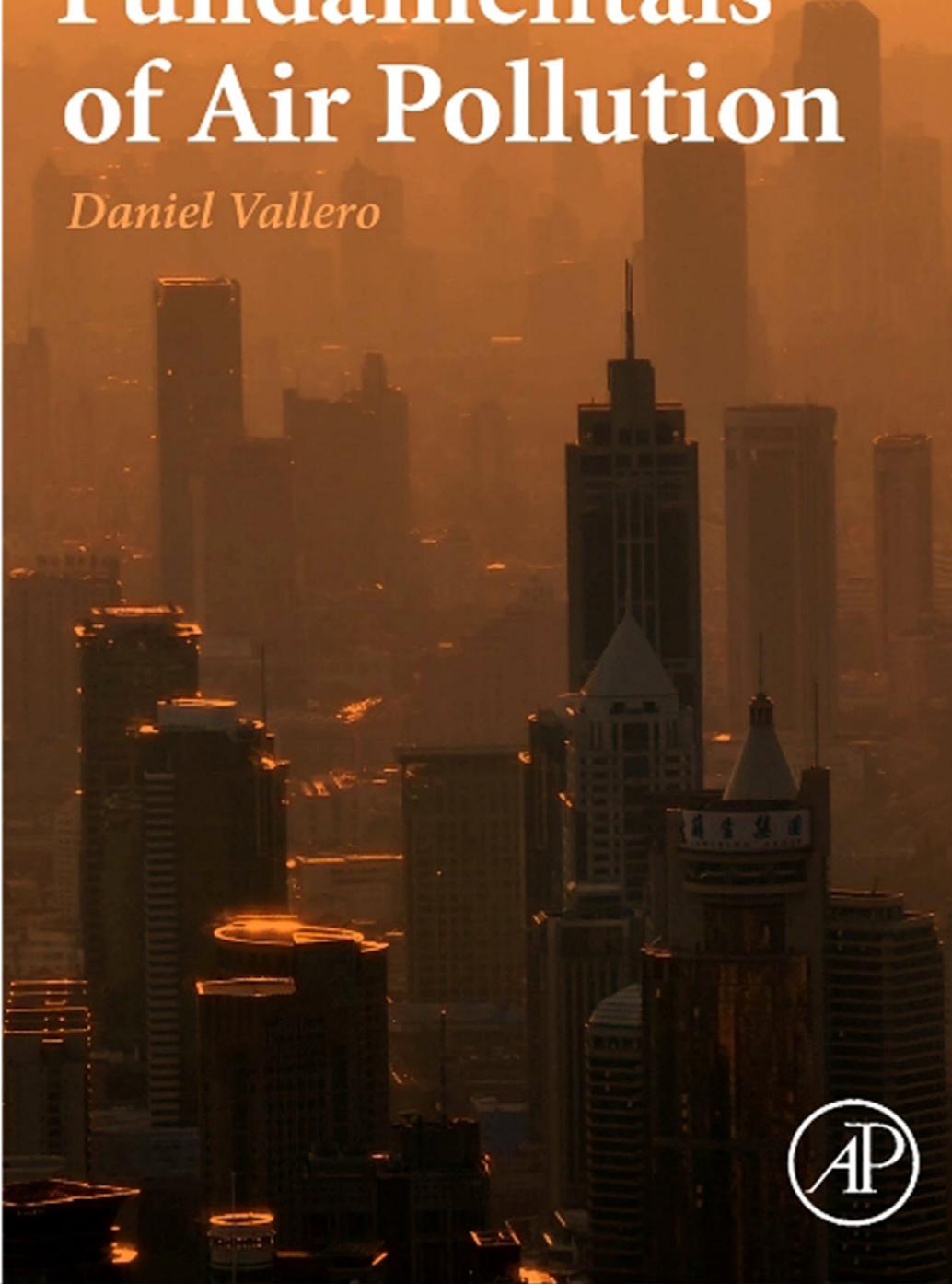




FIFTH EDITION

# Fundamentals of Air Pollution

*Daniel Vallero*



# FUNDAMENTALS OF AIR POLLUTION

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# FUNDAMENTALS OF AIR POLLUTION

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FIFTH EDITION

DANIEL VALLERO



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# Preface

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Air pollution is a very complex societal problem. It has been recognized as such for centuries. Unlike the evolution of many scientific phenomena, its cause and effect relationships have been reasonably deductive. For example, in the fourteenth century, King Edward II decreed that the cause of London's air pollution problem was attributed to burning coal, and incidentally, anyone found burning coal while Parliament was meeting would be executed. That is a supreme example of a science-based decision followed by strong execution; literally!

Of course, scientific cause and effect relationships have greatly improved since. Present-day air pollution expertise came into its own in the middle of the twentieth century, when air pollution episodes in Europe and the United States were becoming all too common; in several instances leading to immediate disease and death. The experts at that time likely would not have even referred to themselves as air pollution experts; preferring to be called meteorologist, engineer, physicist, chemist, or earth scientist. The scientific disciplines of atmospheric science, and more specifically atmospheric physicist or chemist or environmental engineer, have grown in expertise and confidence exponentially since the first edition of this book. In the years since, the information on air quality and knowledge of how and why the atmosphere becomes polluted have allowed for continuously improving decisions that have led to a much cleaner atmosphere.

Air pollution was a seemingly intractable problem for most of the developed world in the previous century. The improvement has been remarkable, especially for the health-related criteria air pollutants. More recently, substantial and sustained progress has also been made decreasing atmospheric concentrations of hazardous air pollutants, better known as the air toxics.

In spite of the exponential growth of information, knowledge, and technologies to address air pollution, scientists and policy makers continue to be confronted with many daunting problems. For example, much of the progress has been in the developed and richest parts of the world. Considerable numbers of people of the developing and poorer parts of the world have seen little improvement. Indeed, in the fastest growing economies and the regions with the greatest increases in industrialization, the problems have worsened dramatically.

These growing economies in many instances are retracing the steps taken by the United States, Japan, and Europe during the petrochemical revolution after World War II, which led to so many pollution problems and episodes. Repeating the problems is unnecessary for most of the known air pollutants, if viewed from a scientific and control technology perspective. The challenge for criteria pollutant prevention may largely be geopolitical and cultural. Thus, this edition recognizes these obstacles by updating and increasing attention substantially to the technical solutions that can prevent repeating poor decision making that plagued the developed nations in the previous century.

Indeed, I have modified the fifth edition of Fundamentals of Air Pollution substantially. These changes were necessary, given the changes in how air pollution is being addressed.

First, the book includes much more detail related to the effects on the three types of receptors, i.e. humans, ecosystems, and materials. In particular, the fifth edition takes the view that air pollution knowledge begins with the adverse outcome, with separate chapters devoted to the major effects, i.e. respiratory, cardiovascular, endocrinological, neurological, and cancer. Previous editions addressed these in a more cursory manner, but this edition gives details on how the effects from various air pollutants occur.

The fourth edition introduced the concept of systems science and sustainability to air quality. The fifth edition integrates this perspective throughout. For example, a separate chapter on life cycle analysis (LCA) in energy production, i.e. Chapter 4, has been added to demonstrate the difference between typical command and control technologies vs preventive and regenerative approaches. The LCA is revisited throughout the text, with an overarching desire to prevent the pollution rather than treat it.

Another major change is the addition of biogeochemical cycling. This was added in the fourth edition during specific topics, especially discussions of sulfur and nitrogen. However, for a complete view of air pollution, separate chapters have now been added on water, carbon, nitrogen, sulfur, and metal and metalloid cycles. Other substances, e.g. phosphorous and potassium, which did not require separate chapters but share similarities to the substances being discussed, are addressed in these cycling discussions as well.

Another major enhancement is air pollutant exposure. This book incorporates very recent changes in the state of exposure science, including attention to human activities and models. The air quality and emission standards have changed substantially for many air pollutants since the fourth edition. I have painstakingly updated these for North America and Europe, but they will continue to change with demands for cleaner air throughout the world. They are also changing as new compounds are added to the lists of chemicals of concern. The six criteria pollutants will continue to be extremely important, but numerous other air pollutants, notably the air toxics, will have to be addressed. Thus, this new addition places added emphasis on the person and microenvironments, where the lion's share of exposure to air pollutants occurs.

The control technology discussions have also been completely updated, with expanded use of illustrations and inclusion of modifications and improvements. The laws of thermodynamics and motion that underpin the technologies are now addressed in these discussions, e.g. heat and energy transfer, drag and buoyancy, gravitation, electromagnetic principles, and diffusion and Brownian forces.

Another systems approach is an update to the partitioning discussions that had been added in the fourth edition. There are now separate chapters for inherent properties of air pollutants and the kinetics and equilibria associated with these pollutants in the environment. Although air pollution is correctly most concerned about the air pollutant's behavior in the atmosphere, other media (e.g. water, soil, and biota) are now discussed in more detail to demonstrate the interconnectedness of these compartments. For example, the air pollution expert needs to know how a pollutant may have formed in soil or how it may find its way to biotic tissue, in addition to how it behaves in the troposphere.

These enhancements and additions allow the fifth edition to be more representative of the entire life cycle of air pollution. As such, it can be used as the text for two semesters of air pollution engineering, as well as two semesters of air pollution science (perhaps using every chapter, but with less emphasis on chapters 30 and 31).

The text may also be used for a single semester of an introduction to air pollution risk assessment and management:

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<b>Part I</b>	<b>Foundations of Air Pollution</b>
Chapter 1	The State of the Atmosphere
Chapter 3	The Science of Air Pollution
Chapter 4	Air Pollution Decision Tools
Chapter 5	Life Cycle Analysis of Air Pollutants

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<b>Part II</b>	<b>The Risks of Air Pollution</b>
Chapter 6	Inherent Properties of Air Pollutants
Chapter 7	Hazard Assessment of Air Pollutants
Chapter 8	Exposure Assessment of Air Pollutants
Chapter 9	Respiratory Effects of Air Pollutants
Chapter 10	Cardiovascular Effects of Air Pollutants
Chapter 11	Cancer and Air Pollution
Chapter 12	Reproductive and Hormonal Effects of Air Pollutants
Chapter 13	Neurological Effects of Air Pollutants
Chapter 14	Air Pollution's Impact on Ecosystems
Chapter 15	Air Pollution's Impact on Materials and Structures
<b>Part III</b>	<b>Tropospheric Pollution</b>
Chapter 16	Scale and Complexity of Air Pollution
Chapter 19	Air Pollutant Persistence and Bioaccumulation
<b>Part V</b>	<b>Addressing Air Pollution</b>
Chapter 25	Methods for Measuring Air Pollutants
Chapter 26	Air Quality Monitoring
Chapter 27	Modeling Applications
Chapter 28	Air Quality Status and Trends
<b>Part VI</b>	<b>The Future for Air Pollution Science and Engineering</b>
Chapter 32	Sustainable Approaches
Chapter 33	Grand Challenges

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The text may also be used for a single semester of an introduction to air pollution engineering:

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<b>Part I</b>	<b>Foundations of Air Pollution</b>
Chapter 1	The State of the Atmosphere
Chapter 3	The Science of Air Pollution
Chapter 4	Air Pollution Decision Tools
Chapter 5	Life Cycle Analysis of Air Pollutants
<b>Part II</b>	<b>The Risks of Air Pollution</b>
Chapter 6	Inherent Properties of Air Pollutants
Chapter 7	Hazard Assessment of Air Pollutants
Chapter 8	Exposure Assessment of Air Pollutants
<b>Part III</b>	<b>Tropospheric Pollution</b>
Chapter 16	Scale and Complexity of Air Pollution
Chapter 17	Kinetics of Air Pollutant Transformation
Chapter 18	Air Pollutant Equilibrium and Fate
Chapter 19	Air Pollutant Persistence and Bioaccumulation

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—cont'd

<b>Part IV</b>	<b>Biogeochemistry of Air Pollutants</b>
Chapter 21	The Carbon Cycle
Chapter 22	The Nitrogen and Sulfur Cycles
Chapter 23	Metal and Metalloid Cycles
<b>Part V</b>	<b>Addressing Air Pollution</b>
Chapter 24	Source Sampling and Emissions Measurement
Chapter 25	Methods for Measuring Air Pollutants
Chapter 26	Air Quality Monitoring
Chapter 29	Air Pollutant Emissions
Chapter 30	Air Pollution Control Technologies
Chapter 31	Controlling Air Pollution from Sources
<b>Part VI</b>	<b>The Future for Air Pollution Science and Engineering</b>
Chapter 32	Sustainable Approaches
Chapter 33	Grand Challenges

The text may also be used for a single semester of an introduction to air pollution science, with a selection of chapters dependent on the specific discipline. For example, if the emphasis is chemistry, Parts III and IV could provide the core readings. If the emphasis is physics, Chapter 16 is particularly useful, and could be melded with all of the chapters in Part V.

The text is also now updated and enhanced to address the needs of the practitioner. Those engaged in air pollution engineering, science, policy, and other careers should find this new edition to be very useful handbook in their daily work.

Finally, this book has been made to be much more easily searchable. It now includes numerous links that will allow the reader to be up-to-date on the ever-changing world of air quality and air pollution. The addition of numerous color slides is now more feasible than it was for previous editions to use electronic formats, as in the connection between the Elsevier companion site and this book.

The companion site should also allow for the sharing of recent changes in technologies, applications, and scientific advances, with its discussion forum. I welcome the readers' ideas and applications and uses of this book. For example, if a professor would like to share a solution to a problem or answer to a question, please do so. Likewise, an engineer who has a unique application or control technology that is different from or is an enhancement to one described here, please post this. Scientists engaged in research in any of the numerous aspects of air pollution should feel free to suggest changes in the state of the science. Policy makers and

regulators are also invited to share changes in their jurisdictions with regard to air pollution rules, regulations, guidelines, and standards, as well as innovative ways of achieving improved air quality other than by rules, such as emissions banking.

Air pollution has been thriving and continues to thrive on technological, engineering, and regulatory paradigm shifts. We are now able to stay abreast of these advancements and enhancements. This edition has added many, but more are certain to come in the next decade.

I have had the great privilege to work with many gifted scientists, engineers, and policy experts during a career that has spanned four decades (so far). Too many to name individually, but all to whom I am grateful for the abundant knowledge and wisdom they have shared.

I would like to acknowledge those who have coauthored and contributed to my previous books. Jeff Peirce at Duke encouraged me to write my first book, to which he made a substantial contribution. My mentor from Kansas, Ross McKinney wrote a wonderful foreword to that book. Aarne Vesilind, who has retired from Duke and subsequently from Bucknell, introduced me to engineering ethics as a separate and crucial part of my professional and academic experience. This perspective has permeated almost all of my academic writings. John Ahearne of Sigma Xi, Duke and formerly the U.S. Nuclear Regulatory Commission, wrote the foreword to Aarne's and my socially responsible engineering book, wherein he reminded us of the quote by the famous engineer Norm Augustine, that "Engineers who make bad decisions often don't realize they are confronting ethical issues". How true!

My interest in sustainability and systems thinking began many years ago, in the 1970s, shortly after the passage of the National Environmental Policy Act. I was working with an energetic and forward-thinking faculty member of Southern Illinois University Edwardsville, Charles Hess, who was doing work with the U.S. Army Corps of Engineers in St Louis. We considered the pros and cons of a Corps lake in Southern Illinois, which was readily justified by a benefit–cost ratio, but which Charles asked me to take a more systematic view (e.g. possible indirect impacts of population shifts and access brought on by the new lake). Since then, my work and writings have attempted to go beyond the obvious benefits and costs and to look for possible systems failures in the future.

My appreciation for sustainability grew with my preparation of environmental impact statements for seemingly environmentally benign or beneficial projects. Even these had substantial drawbacks when viewed from a perspective of sustainability. My latest works have been enhanced by ongoing collaborations with the coauthor of my sustainable design book, Chris

Brasier. Chris has been doing great work assimilating architecture with engineering at Duke, and has introduced me to different perspectives beyond green engineering, including regenerative systems and a greater appreciation for the importance of place. Indeed, Chris and I coined the term “synthovation” to try to capture the need to innovate and look for design synergies.

More recently, I have collaborated with the gifted chemist, Trevor Letcher. Trevor has added so much to the inclusion of first principles, especially thermodynamics, in environmental systems. Our books have addressed every environmental compartment from the perspective of waste management and, most recently,

the scientific analysis of how and why environmental disasters occur.

I am exceedingly humbled by the experiences of working with these talented people. I must admit, however, that my most recent collaborations have been the most rewarding and edifying. I am learning and thoroughly enjoying my collaborations with Chloe Jayne Randall, coauthor of my most recent book, *Coco's Earth Day Surprise*. Her perspective of the next generation and the need for continuous improvement in environmental quality is invaluable. It is even more gratifying to be her grandfather.

DAV

## P A R T I

# FOUNDATIONS OF AIR POLLUTION

Planet earth's abundant resources are composed of slightly over 100 elements; yet its environment supports life by delicately blending these few elements into compounds. Living creatures depend on these compounds being present in quantities that fall within relatively small ranges and in the presence of environmental conditions of temperature, oxygen content, nutrients, light, and other essential combinations of mass and energy. Without nutrient compounds in the soil and air becoming food for all living things, life could not last more than a few weeks. Without water from the hydrosphere, life could not last more than a few days. However, without appropriate amounts of molecular oxygen in the atmosphere, humans and other air-breathing animals could not last more than a few minutes.

The first part of this book describes the conditions of the atmosphere, but in a manner somewhat different from meteorological, geological, and other scientific texts. Every discussion's purpose relates to air pollution. Thus, when the mix of gases comprising the troposphere is discussed, it is not so much for the inherent interest in the atmosphere, but more in the way the relative quantities of these gases provide a baseline from which to compare the quality of the air. Discussions of carbon dioxide or carbonic acid, for example, are carried out with an eye toward what is considered "normal air" *versus* "polluted air".

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# The State of the Atmosphere

## 1.1 INTRODUCTION

Discussions about air pollution often begin with the composition of the atmosphere. In particular, the discussion often focuses on how a particular part of the troposphere or stratosphere deviates in quality from a norm. Popular perceptions of air pollution are driven largely by fear. After all, the most notorious air pollution events have often been associated with dramatic atmospheric visuals, such as smoke billowing from industrial stacks into the air, smog hanging over large cities, dead trees from acid rain, and disasters with plumes of contaminants reaching upward and outward into the troposphere, the lowest atmospheric layer where humans and other organisms reside. Other mental pictures have been more abstract, yet just as dramatic, e.g. increasing levels of greenhouse gases in the troposphere or the so-called “hole” in the ozone layer higher up in atmosphere, the stratosphere.

Like many perceptions, those of the atmosphere are frequently correct, but incomplete. For example, the atmosphere is studied at every scale from planetary to molecular. The portion of atmosphere influencing a single cell organism may be a few cubic nanometers in volume, whereas the atmosphere influencing and being influenced by biome shift is planetary in scale, with pollution encompassing many cubic kilometers. Indeed, much of a human being’s exposure to air pollutants occurs in comparatively small parcels of the atmosphere, especially in the home. These small compartments, known as microenvironments, are indeed subdivisions of the atmosphere. In fact, humans are frequently exposed at highest rates to many of the most harmful air pollutants in what is known as a “personal cloud”.<sup>1</sup>

## 1.2 PHYSICAL AND CHEMICAL PROPERTIES OF THE ATMOSPHERE

By dry volume, 99.997% of the atmosphere consists of four gases, molecular nitrogen and oxygen ( $N_2$  and  $O_2$ ,

respectively), argon (Ar), and carbon dioxide ( $CO_2$ ). Chemically, Ar is inert (nonreactive) since it is a noble gas. The other three compounds are also very stable and nonreactive under most atmospheric conditions of temperature and pressure, so they remain very stable components of the atmosphere. Approximately 99% of the mass of the atmosphere lies within 50 kilometers (km) of the earth’s surface, i.e. in the troposphere and stratosphere. This is where the air pollution occurs.

The earth’s atmospheric temperature varies with altitude (Figure 1.1), as does the density of the substances comprising the atmosphere.<sup>2</sup> The earth is warmed when incoming solar radiation is absorbed at or near the earth’s surface and reradiated at longer electromagnetic wavelengths (infrared). In general, the air grows progressively less dense with increasing altitude moving upward from the troposphere through the stratosphere and the chemosphere to the ionosphere. In the upper reaches of the ionosphere, the gaseous molecules are few and far between as compared with the troposphere.

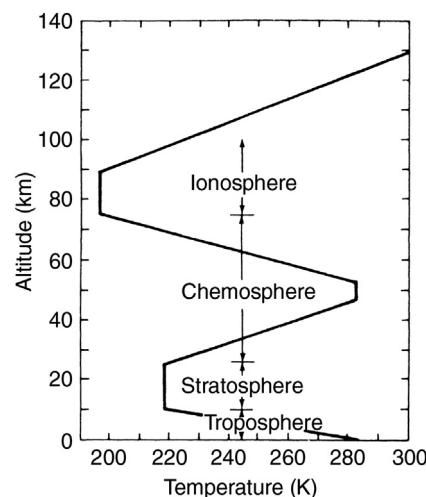


FIGURE 1.1 Temperature profile of the earth’s atmosphere.

The ionosphere and chemosphere are of interest to space scientists because they must be traversed by space vehicles en route to or from the moon or the planets, and they are also regions in which satellites travel in the earth's orbit. These regions are also of interest to communications scientists because of their influence on radio communications. However, these layers are of interest to air pollution scientists primarily because of their absorption and scattering of solar energy, which influence the amount and spectral distribution of solar energy and cosmic rays reaching the stratosphere and the troposphere.

The stratosphere is of interest to aeronautical scientists because it is traversed by airplanes; to communications scientists because of radio and television communications; and to air pollution scientists because global transport of pollution, particularly the debris of aboveground nuclear testing atomic bomb tests and volcanic eruptions, occurs in this region and because absorption and scattering of solar energy also occur there. The lower portion of this region contains the stratospheric ozone layer, which absorbs harmful ultraviolet (UV) solar radiation. This layer may also be undergoing modifications by long-term accumulation of chlorofluorocarbons (CFCs) and other gases released at the earth's surface or by high-altitude aircraft.

The troposphere is the region in which we live and is the primary focus of this book; however, we will discuss stratospheric ozone formation and destruction in some detail in Chapter 11.

### 1.2.1 Tropospheric Composition

Gaseous composition of the so-called "unpolluted" tropospheric air is given in [Table 1.1](#). Unpolluted air is a conception, i.e. the composition of the air without human influence. There is really no place on the planet that presently meets this criterion. Even at the most remote locations at sea, at the poles, and in the deserts and mountains, the air contains pollutants, albeit at extremely low concentrations.

Note that the gaseous concentrations are mean values for the atmosphere and do not actually exist as reported in the table in any region of the atmosphere, especially near the earth's surface. The atmosphere is more complex than a dry mixture of permanent gases. It has other constituents—especially varying concentrations of water vapor and other vapors (e.g. organic liquids), as well as liquid and solid phase constituents (aerosols or particulate matter (PM) held in suspension).

The distinction between gases and vapors is often academic. However, in this book, as in many environmental texts and handbooks, the difference has to do with how substances are partitioned among environmental compartments. In this case, vapors are the

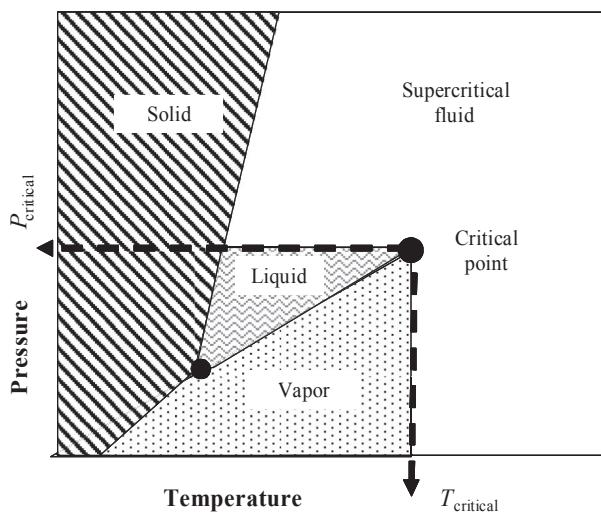
**TABLE 1.1** Gaseous Composition of the Atmosphere (Dry, Unpolluted Air)

	ppm (vol.)	$\mu\text{g m}^{-3}$
Nitrogen	780,000	$8.95 \times 10^8$
Oxygen	209,400	$2.74 \times 10^8$
Water	—	—
Argon	9300	$1.52 \times 10^7$
Carbon dioxide	315	$5.67 \times 10^5$
Neon	18	$1.49 \times 10^4$
Helium	5.2	$8.50 \times 10^2$
Methane	1.0–1.2	$6.56\text{--}7.87 \times 10^2$
Krypton	1.0	$3.43 \times 10^3$
Nitrous oxide	0.5	$9.00 \times 10^2$
Hydrogen	0.5	$4.13 \times 10^1$
Xenon	0.08	$4.29 \times 10^2$
Organic vapors	c. 0.02	—

gas phase fraction of those substances that would be liquids under most environmental conditions, especially commonly found temperatures and pressure. This is the subject matter of thermodynamics, the study of the relationships among properties of matter and the changes that occur to these properties. A change in physical state may result spontaneously or from interactions with other materials. Thermodynamics concerns itself with the thermal systems, including ecosystems and organic systems in humans, especially how these systems work. In thermodynamics, a system is simply a sector or region in space or some parcel that has at least one substance that is ordered into phases.

The phase diagram in [Figure 1.2](#) is an example of the phases that are available in this ordering. The more general understanding of scientists and technicians is that a "system" is a method of organization, e.g. from smaller to larger aggregations. At a basic thermodynamic level, systems are a means for understanding how matter and energy move and change within a parcel of matter.

Matter in the solid phase has a fixed volume and shape. Solid substances' component particles (i.e. atoms, molecules, or ions) are confined and fixed into place. Liquids maintain a fixed volume, but their shape changes to fit their container. Liquid particles are denser than those of the vapor of the same substance (e.g. liquid water *versus* water vapor), but move freely. Gases have both variable volume and shape, filling the container. Gas particles are neither close together nor fixed in place. Plasmas have a substantial number of ions and free electrons, along with neutral atoms. Like gases,



**FIGURE 1.2 Phase diagram for a hypothetical substance.** All of the polygons shown in the diagram will exist, but their shapes and slopes of the polygon sides and points of phase changes will differ. The vapor–liquid boundary line temperature is the boiling point and the pressure is the vapor pressure. The line between the vapor and solid phases is known as the sublimation point (i.e. a phase change from solid to gas, or gas to solid, without first becoming a liquid). The liquid–solid boundary line temperature is freezing and melting point.  $P_{\text{pressure}}$  and  $T_{\text{temperature}}$  are the pressure and temperature, respectively, of a fluid at its critical point; i.e. the point at which a gas cannot be liquefied by an increase of pressure.

plasmas have no definite volume or shape since the ions and electrons move freely.

Air pollution terminology generally breaks matter down into two phases, particulate and gas. Particulates and aerosols are generally synonymous terms in air pollution literature, i.e. liquid and solid phase. They are distinguished from gases and vapors.<sup>a</sup>

For air pollutants, gases are distinguished from vapors in that they exist entirely within the vapor phase of Figure 1.2 under environmental conditions, i.e. not under extremely high pressure and extremely low temperature. That is, gases are those that would be in the physical gaseous state under conditions ranging from the arctic temperatures to the largest pressures found in the atmosphere.

At higher orders important to air pollution, systems include the “ecosystem” and the “organism” ordering systems. These consist of physical phases and order. For example, ecosystems ordering systems include producer–consumer–decomposer, predator–prey, and individual–association–community. Ordering within organisms includes cell–tissue–organ–system.

Thermodynamic systems are classified into two major types: closed and open. Both exist and are important in the environment. A closed system does not allow material to enter or leave the system (engineers refer to a closed system as a “control mass”). The open system allows material to enter and leave the systems (such a system is known as a *control volume*).

Another thermodynamic concept is that of the “property”. As will be covered in more detail in Section 1.4 discussions of fluid properties of contaminants, a property is some trait or attribute that can be used to describe a system and to differentiate that system from the others. A property must be able to be stated at a specific time independently of its value at any other time and unconstrained by the process that induced the condition (state). An intensive property is independent of the system’s mass (such as pressure and temperature). An extensive property is proportional to the mass of the system (such as density or volume). Dividing the value of an extensive property by the system’s mass gives a “specific property”, such as *specific heat, specific volume, or specific gravity*.

The thermodynamic term for the description of the change of a system from one state (e.g. equilibrium) to another is known as a “process”. Processes may be reversible or irreversible; they may be adiabatic (no gain or loss of heat, so all energy transfers occur through work interactions) or non-adiabatic (See Chapter 2). Other processes include isometric (constant volume), isothermal (constant temperature), isobaric (constant pressure), isentropic (constant entropy), and isenthalpic (constant enthalpy).

This discussion introduces the concept of phase partitioning, which is covered in detail in Chapter 18. Partitioning simply means the substance will exist in one or more physical phases. An important partitioning coefficient for air pollution is Henry’s Law, which states that the partial pressure of a compound can be related to its equilibrium concentration in a dilute aqueous solution through a constant of proportionality. In other words, a varying number of molecules will find their way into the air, even though most of the molecules remain in the water, i.e. dissolved in water. Even a small amount of partitioning can account for large amounts of vapor phase compounds in the atmosphere.

One of the earth’s nicknames is the “water planet”, so the predominant vapor in the air is, not surprisingly, water vapor. In the atmosphere, above their temperature of condensation, vapor molecules act just like permanent gas molecules in the air. Below its condensation

<sup>a</sup> Although the plasma is the most common state of matter in the universe, plasmas are not often mentioned in air pollution. Perhaps they should be since fires are plasmas, which are a major source of pollutants. Lightning produces plasmas, a major source of nitrogen exchange between the earth’s surface and the atmosphere. The upper portion (85–600 km altitude) of the atmosphere, i.e. the ionosphere, is the plasma resulting from solar radiation.

TABLE 1.2 Gaseous Composition of the Atmosphere (Wet Basis; Unpolluted Air)

	ppm (vol.)	$\mu\text{g m}^{-3}$
Nitrogen	756,500	$8.67 \times 10^8$
Oxygen	202,900	$2.65 \times 10^8$
Water	31,200	$2.30 \times 10^7$
Argon	9000	$1.47 \times 10^7$
Carbon dioxide	305	$5.49 \times 10^5$
Neon	17.4	$1.44 \times 10^4$
Helium	5.0	$8.25 \times 10^2$
Methane	0.97–1.16	$6.35\text{--}7.63 \times 10^2$
Krypton	0.97	$3.32 \times 10^3$
Nitrous oxide	0.49	$8.73 \times 10^2$
Hydrogen	0.49	$4.00 \times 10^1$
Xenon	0.08	$4.17 \times 10^2$
Organic vapors	c. 0.02	—

temperature, if the air is saturated, water changes from vapor to liquid. This phenomenon gives rise to fog or mist in the air and condensed liquid water on cool surfaces exposed to air. The quantity of water vapor in the air varies greatly from almost complete dryness to supersaturation, i.e. between 0 and 4% by weight (see Table 1.2). If Table 1.1 is compiled on a wet air basis at a time when the water vapor concentration is 31,200 parts by volume per million parts by volume of wet air (Table 1.2), the concentration of condensable organic vapors is seen to be so low compared to that of water vapor that for all practical purposes the difference between wet air and dry air is its water vapor content.

Gaseous composition in Tables 1.1 and 1.2 is expressed as parts per million by volume—ppm (vol.) or ppmV. (When a concentration is expressed simply as ppm, it is unclear whether a volume or weight basis is intended.) To avoid confusion caused by different units, air pollutant concentrations in this book are generally expressed as micrograms per cubic meter of air ( $\mu\text{g m}^{-3}$ ) at an environmental temperature (e.g. 20 ° or 25 °C) and 760 mmHg, i.e. in metric units. To convert from units of ppm (vol.) to  $\mu\text{g m}^{-3}$ , it is assumed that the ideal gas law is accurate under ambient conditions. A generalized formula for the conversion at 25 °C and 760 mmHg is:

$$\begin{aligned} 1 \text{ ppm (vol.) pollutant} &= \frac{1 \text{ l pollutant}}{10^6 \text{ l air}} \\ &= \frac{(1 \text{ l}/22.4) \times \text{MW} \times 10^6 \mu\text{g} \times \text{g m}^{-3}}{10^6 \text{ l} \times 298 \text{ K}/273 \text{ K} \times 10^{-3} \text{ m}^3 \times 1^{-1}} \quad (1.1) \\ &= 40.9 \times \text{MW} \mu\text{g m}^{-3} \end{aligned}$$

TABLE 1.3 Conversion Factors between Volume and Mass Units of Concentration (25 °C, 760 mmHg)

Pollutant	To Convert from	
	ppm (vol.) to $\mu\text{g m}^{-3}$ , multiply by	$\mu\text{g m}^{-3}$ to ppm (vol.), multiply by ( $\times 10^{-3}$ )
Ammonia ( $\text{NH}_3$ )	695	1.44
Carbon dioxide	1800	0.56
Carbon monoxide	1150	0.87
Chlorine	2900	0.34
Ethylene	1150	0.87
Hydrogen chloride	1490	0.67
Hydrogen fluoride	820	1.22
Hydrogen sulfide	1390	0.72
Methane (carbon)	655	1.53
Nitrogen dioxide	1880	0.53
Nitric oxide	1230	0.81
Ozone	1960	0.51
Peroxyacetyl nitrate	4950	0.20
Sulfur dioxide	2620	0.38

where MW equals molecular weight ( $\text{g mol}^{-1}$ ). For convenience, conversion units for common pollutants are shown in Table 1.3. The rationale for Eqn (1.1) is discussed in Section 1.4.1.

Extra care must be taken for conversions of pollutant classes. For example, the units of the air pollutant, nitrogen dioxide ( $\text{NO}_2$ ), can be converted using Eqn (1.1). However, when addressing smog and ozone in the troposphere, the oxides of nitrogen, not  $\text{NO}_2$  specifically, are the major concern. The concentrations of  $\text{NO}_2$  and nitric oxide (NO) are commonly expressed in ppm (vol.) and expressed as a sum, known as " $\text{NO}_x$ ". Thus, the conversion from ppm (vol.) to  $\mu\text{g m}^{-3}$  must be carried out separately for  $\text{NO}_2$  and NO before the two species are added together.

### 1.3 ATMOSPHERIC CHEMICAL CONCENTRATIONS

As mentioned, molecular nitrogen ( $\text{N}_2$ ), molecular oxygen ( $\text{O}_2$ ), water ( $\text{H}_2\text{O}$ ), argon (Ar), and carbon dioxide ( $\text{CO}_2$ ) make up most of the atmosphere (Tables 1.1 and 1.2). Most other compounds and substances exist only in trace amounts. Note that of the remaining most abundant gases by volume, all but two are also quite reactive; the exceptions being hydrogen ( $\text{H}_2$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ). Neon (Ne), helium (He), krypton (Kr), and

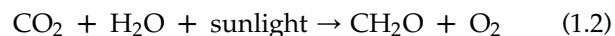
xenon ( $Xe$ ) are noble gases; and methane ( $CH_4$ ) is quite stable under atmospheric conditions.

Hydrogen is highly reactive, but exists only in trace amounts in the lower troposphere. Its relative abundance, i.e. seventh most abundant gas in dry air, is mainly because of the high energy conditions in the upper atmosphere (altitude > 500 km), where the solar radiation dissociates molecules of  $H_2O$ ,  $CH_4$ , and  $H_2$ , producing H atoms. Since concentrations of  $H_2O$  and  $CH_4$  molecules are highly variable in the atmosphere, the amount of H produced in this manner is also highly variable. Incidentally, the same is true for ozone ( $O_3$ ) which is also produced photochemically in the upper atmosphere (15–50 km altitude) and why there is a distinctive  $O_3$  layer in the stratosphere. This is also the reason that atomic oxygen, which is almost nonexistent in the lower layers, is also much more abundant in the upper atmosphere.<sup>3</sup>

It should be noted from a mass balance perspective that nitrogen (N) and oxygen (O) exist in numerous chemical compounds in the atmosphere. As will be discussed in detail in Chapter 22, nitrogen's compounds include a number of air pollutants, especially nitrogen dioxide ( $NO_2$ ), and many essential compounds, e.g. nitrates, nitrites, and ammonia. However,  $N_2$  is the dominant atmospheric N-constituent, i.e.  $3.9 \times 10^{18}$

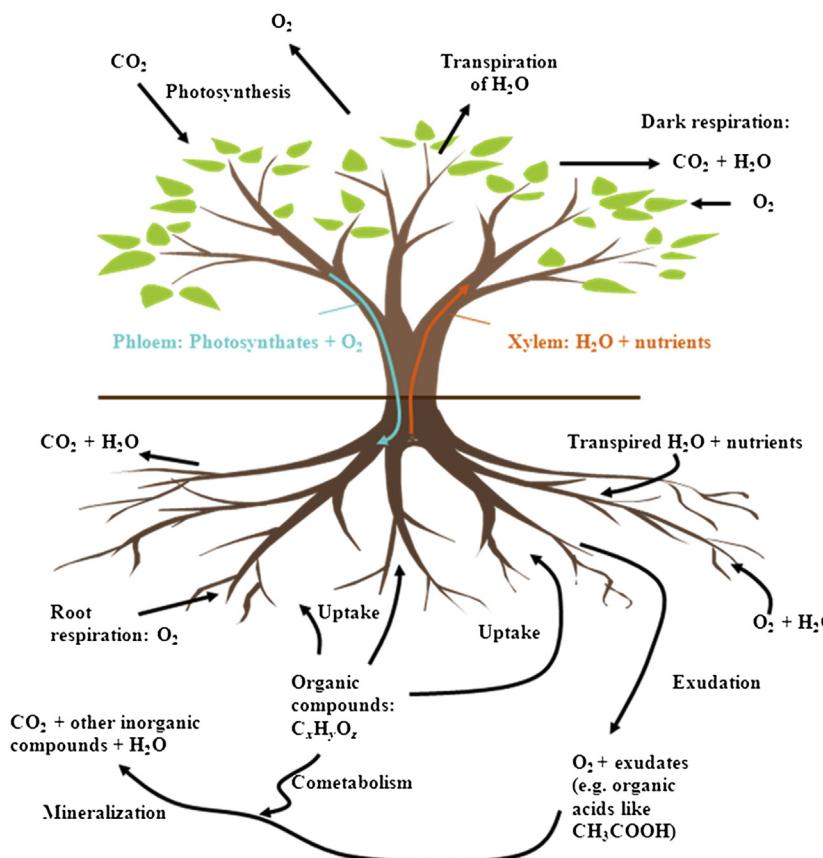
kilograms (kg) being six orders of magnitude larger than the second,  $N_2O$ . The movement to and from the atmosphere, i.e. flux, of N in its many species is massive. The flux of  $N_2$  between the earth's surface and the atmosphere is about  $10^{11}$  kg annually.<sup>3</sup>

Oxygen is a part of myriad compounds, including most organic compounds. Photosynthesis provides most of the atmospheric  $O_2$ , predominant from terrestrial plants and aquatic microbes, especially phytoplankton (see Figure 1.3).<sup>3</sup> Using light energy from incoming solar radiation, photosynthesis converts vapor phase  $CO_2$  and water into solid phase carbohydrates and  $O_2$ . Although there are numerous intermediate steps, the reaction is summarized as:



In the upper altitudes, water vapor and  $N_2O$  undergo photodissociation via UV solar radiation, additional  $O_2$  is formed providing between 1 and 2 percent of atmospheric oxygen.

Respiration is the chemical counterpart to photosynthesis, i.e. the transport of  $O_2$  from the atmosphere into cells and the transport of  $CO_2$  away from cells into the atmosphere. Respiration is the process by which organisms use  $O_2$  for energy and to build cells, with  $CO_2$  as the



**FIGURE 1.3 Photosynthesis and respiration processes in a tree.** Note that there are several sites at which  $O_2$ ,  $H_2O$ , and  $CO_2$  are exchanged, both above and below ground. Although photosynthesis is the dominant process for plant life, there is also respiration (i.e. dark respiration) in the absence of sunlight. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Kamath R, Rentz JA, Schnoor JL, Alvarez PJJ. Phytoremediation of hydrocarbon-contaminated soils: principles and applications. *Stud Surf Sci Catal* 2004;151:447–78.

waste product. Conversely, air breathing organisms come in many forms, but the basic respiration chemistry is similar. Humans and other mammals, as well as birds, reptiles for their entire lives, and amphibians for parts of their lives use lungs to exchange the O<sub>2</sub> in the air mixture. Fish similarly use gills to exchange the O<sub>2</sub> in the water mixture (i.e. dissolved oxygen). Other organisms in air and water use similar mechanisms to extract O<sub>2</sub> for respiration. The only exceptions are the anaerobic organisms, which use electron acceptors other than O<sub>2</sub>. These electron acceptors include sulfate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), sulfur (S), and fumarate (HO<sub>2</sub>CCH=CHCO<sub>2</sub>H).

Carbon (C) is the distinguishing element for organic compounds, i.e. those with C–C and/or H–C bonds, but it is also part of many inorganic compounds, including CO<sub>2</sub> and carbon monoxide (CO). Organic compounds include those that comprise cells in organisms and other biochemical substances. Carbon is a major constituent of many air pollutants, including CO, PM in various forms, as well as many of the most toxic air pollutants, e.g. dioxins, polychlorinated biphenyls (PCBs), and many pesticides. Of recent interest are greenhouse gases, of which, most are carbon compounds, e.g. CO<sub>2</sub>, CH<sub>4</sub>, and chlorofluorocarbons (HCHs). Thus, C, O, N, and H are the principal elements involved in air pollution.

Several of the abundant compounds in the atmosphere are greenhouse gases, most notably CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O. Indeed, H<sub>2</sub>O is also a greenhouse gas since, by definition, it traps heat in the atmosphere. That is, the portion of the incoming solar radiation that is reradiated as infrared wavelengths is either trapped by greenhouse gases or is allowed to leave the atmosphere. In particular, as the most abundant greenhouse gas, CO<sub>2</sub> has been the focus of much recent interest in both scientific communities and the public at large. The amount has steadily increased in recent decades (see Figure 1.4).

Methane (CH<sub>4</sub>), the most abundant organic molecule in the atmosphere, also increased in concentration dramatically after the industrial revolution, but is no longer increasing. It is produced from anaerobic processes. These include agriculture, e.g. livestock and rice paddies; landfills; fossil fuel extraction and gas distribution; and biomass burning.<sup>3</sup> These anthropogenic sources produce about the same amounts of CH<sub>4</sub> as natural sources, which include reduced, anoxic portions of wetlands and portions of ecosystems undergoing organic decomposition. CH<sub>4</sub> is a much more potent greenhouse gas than CO<sub>2</sub>, absorbing 22 times energy per unit mass. However, at about nine years, its atmospheric residence could be far less than that of CO<sub>2</sub>, which is estimated to range between 5 and 100 years (see Table 1.4). No unique lifetime can be defined for CO<sub>2</sub> given the varying rates of uptake by different

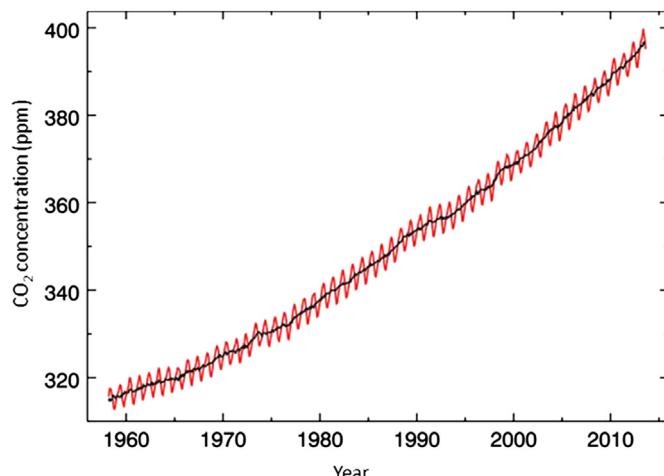


FIGURE 1.4 Monthly mean atmospheric carbon dioxide concentrations (ppm by volume) at Mauna Loa Observatory, Hawaii. The CO<sub>2</sub> data (red curve) are presented as the mole fraction in dry air, on Mauna Loa constitute the longest record of direct measurements in the atmosphere. The black curve represents the seasonally corrected data. Data are reported as a dry mole fraction defined as the number of molecules of CO<sub>2</sub> divided by the number of molecules of dry air multiplied by one million (ppm). (For interpretation of the references to color in this figure legend, the reader is referred to the online version of this book.) National Oceanic and Atmospheric Administration. Trends in atmospheric carbon dioxide. <http://www.esrl.noaa.gov/gmd/ccgg/trends/>; 2013 [accessed 23.09.13].

production and removal processes and exchanges occurring between the atmosphere, ocean, and land surfaces.

More than 90% of the degradation of methane is by oxidation, mainly by reactions with the hydroxyl radical in the stratosphere which accounts for more than 90% of methane loss. The equilibria and fate of CO<sub>2</sub>, CH<sub>4</sub>, and other carbon compounds are discussed in detail in Chapter 21.

It is important to note that the gases listed in the tables vary in concentration throughout the atmosphere. Each gas mixes in the air at different altitudes, i.e. they have unique mixing ratios (see Figure 1.5). The mixing ratio is the number density of the gas divided by number density of all gases in dry air. Only N<sub>2</sub> and the noble gases have nearly constant mixing ratios below 100 km, given their chemical stability. Since most CH<sub>4</sub> and N<sub>2</sub>O are destroyed at the stratosphere, their mixing ratios start decreasing at about 20 km altitude. The mixing ratio of water vapor, with a highly temperature-dependent concentration, decreases sharply with altitude and decreasing temperatures in the troposphere. The stratospheric O<sub>3</sub> layer is also apparent at 35 km from Figure 1.5.

The trace amounts of thousands of compounds in the atmosphere include both essential compounds and air pollutants. The physics, chemistry, and biology of these substances comprise the bulk of scientific interest in air pollution.

TABLE 1.4 Approximate Concentrations (ppb) and Rate of Concentration Change (ppb year<sup>-1</sup>) of Select Greenhouse Gases That Are Affected by Human Activities

	CO <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub> O	CFC-11 (Chlorofluorocarbon-11)	HFC-23 (Hydrofluorocarbon-23)	CF <sub>4</sub> (Perfluoro methane)
Preindustrial concentration	$2.8 \times 10^5$	700	270	0	0	$4.0 \times 10^{-2}$
Concentration in 1998	$3.7 \times 10^5$	1745	314	0.27	14	$8.0 \times 10^{-2}$
Rate of concentration change <sup>§</sup>	$1.5 \times 10^{6*}$	7.0*	0.8	$-1.4 \times 10^{-3}$	$5.5 \times 10^{-4}$	$1.0 \times 10^{-3}$
Atmospheric lifetime (years)	5 to 200 <sup>¶</sup>	12 <sup>  </sup>	114 <sup>  </sup>	45	260	$>5.0 \times 10^4$

\* Rate has fluctuated between 0.9 and 2.8 ppm/year for CO<sub>2</sub> and between 0 and 13 ppb/year for CH<sub>4</sub> over the period 1990–1999.

§ Rate is calculated over the period 1990–1999.

\* No single lifetime can be defined for CO<sub>2</sub> because of the different rates of uptake by different removal processes.

|| This lifetime incorporates the indirect effect of the gas on its own residence time.

Source: Folland CK, Karl TR, Christy JR, Clarke RA, Griggs GV, Jouzel J, et al. Observed climate variability and change. In: Houghton JT, Ding Y, Griggs DJ, Noguer M, van der Linden PJ, Dai X, et al., editors. Climate change 2001: the scientific basis. Contribution of working group I to the third assessment report of the intergovernmental panel on climate change. Cambridge (United Kingdom) and New York (NY): Cambridge University Press; 2001.

Essential compounds include micronutrients needed by plant life and other organisms in the ecosystems. However, even essential substances can become pollutants in the wrong concentrations. Thus, expression of chemical concentration is crucial to understanding atmospheric science generally and the fundamentals of air pollution specifically.

Constituents of air are expressed as densities. Many earth and atmospheric science texts and references express the larger constituents (i.e. N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O) in percent volume of air. Thus, this is a unitless expression, i.e. volume of constituent per volume of air. However, smaller air constituents, including all air pollutants, are expressed either as a number density, i.e. molecules per unit volume, such as molecules cm<sup>-3</sup>; or as a mass density, such as µg m<sup>-3</sup>. An example of a number density expression of an air pollutant would be  $1.2 \times 10^{12}$  formaldehyde (CH<sub>2</sub>O) molecules per cm<sup>3</sup> =  $1.2 \times 10^{18}$  molecules per m<sup>3</sup>.

Unitless density (e.g. parts per billion [ppb]) and mass density are the most common expressions of air pollutant concentration. A number density can be converted to mass density by the use of gram molecular weight (mole) per volume. Avogadro's constant, the

number of constituent particles (molecules or atoms), informs us about the number of moles. That is, 1 mole (mol) of any particle contains  $6.022 \times 10^{23}$  molecules. Thus, since we know the number density of formaldehyde, we can find its mass density from its number of moles per volume:

$$[1.2 \times 10^{18} \text{ CH}_2\text{O molecules per m}^3] \div 6.022 \times 10^{23} \text{ molecules} \approx 2 \times 10^{-6} \text{ mol m}^{-3}$$

Therefore, the number density can be converted to a mass density. In this case, the number density of  $1.2 \times 10^{12}$  formaldehyde (CH<sub>2</sub>O) molecules per cm<sup>3</sup> is the same as the mass density  $2 \times 10^{-6}$  mol m<sup>-3</sup> or 2 micromoles (µmol) per cubic meter.

The 2 µmol formaldehyde per m<sup>3</sup> of air can be converted to the more common units of µg m<sup>-3</sup>. The atomic mass of carbon (C) is 12, hydrogen (H) is 1, and oxygen (O) is 16, so the atomic mass of CH<sub>2</sub>O is 30. Thus, 1 mol CH<sub>2</sub>O = 30 g =  $3 \times 10^{-5}$  µg.

Since 1 µmol =  $10^{-6}$  mol, then 2 µmol formaldehyde =  $2 \times 30 \times 10^{-6}$  g =  $6 \times 10^{-5}$  g = 60 µg. Expressed as a mass density, 2 µmol per m<sup>3</sup> CH<sub>2</sub>O in air is the same as a chemical concentration of 60 µg m<sup>-3</sup>. Mass

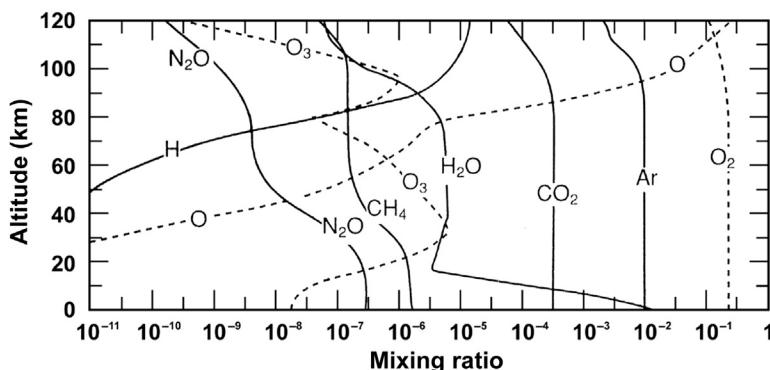


FIGURE 1.5 Atmospheric mixing ratios for ozone and abundant atmospheric gases, other than molecular nitrogen and noble gases (given they are well mixed up to 100-km altitude). With permission from Goody RS. *Nat Med.* 1995 Jun;1(6):519–520.

density is more commonly used than number density to express air pollutant concentrations. However, the expression of mass density is highly variable, especially with regard to standards and regulations. Even in the same standards, different units are used (e.g. ppb and  $\mu\text{g m}^{-3}$ ).

### 1.3.1 Chemical Concentration

The chemical concentrations in [Tables 1.2 and 1.3](#) are mean atmospheric concentrations. Concentration can be expressed as combinations of mass and volume, usually volume per volume or mass per volume. Note that the tables include at the bottom what would appear to be a small amount of compounds under the classification of "organic vapors". Actually, this seemingly small group of compounds comprises a very large amount of air pollutants. It includes any compound with at least one carbon-to-carbon or carbon-to-hydrogen bond that emits molecules into the atmosphere. These molecules are emitted as vapors. Generally, the higher the vapor pressure of a substance, the more of the molecules of that substance finds its way to the atmosphere. This exchange among solid, liquid, and gas phases, including vaporization, is discussed in detail in Chapter 18.

Indeed, formaldehyde would be included among the organic vapors that in total comprise about 0.02 ppm. However, formaldehyde concentrations are highly variable, depending on the unique environmental conditions where it exists. There is both spatial and temporal variability, such as the differences in ambient concentrations in various urban areas and seasonal differences in the same urban area ([Figure 1.6](#)). For example, formaldehyde concentrations in urban areas are generally higher in summer; whereas, the concentrations of benzene, another organic vapor, are generally higher in the winter ([Figure 1.7](#)). Atmospheric concentrations can vary even more in different microenvironments than in the ambient air (see [Table 1.5](#)).

Formaldehyde is not unique. All other organic vapor concentrations also vary significantly in different parts of the atmosphere; as do inorganic compounds, for that matter. Thus, although the total amount of substances under the category "organic vapors" is somewhat constant on a global atmospheric scale, it is highly variable in the ambient air (e.g. much higher concentrations near a wood processing facility) and even more variable between ambient and indoor air, as indicated in [Table 1.5](#).

The variability in chemical concentrations can be even greater among various types of indoor environments. For example, the two types of homes listed in [Table 1.5](#) have very different mean and maximum

concentrations, with manufactured homes much higher than conventional homes. This likely indicates that manufactured homes include sources of formaldehyde that are greater than those of conventional homes, e.g. higher ratios of formaldehyde-containing building materials to non-formaldehyde-containing materials in manufactured homes. It may also be the result of smaller air exchange rates in manufactured homes.

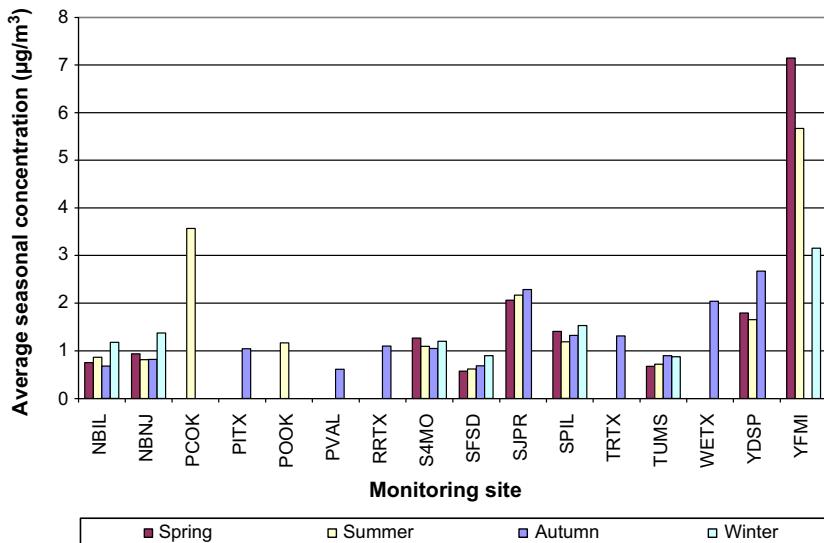
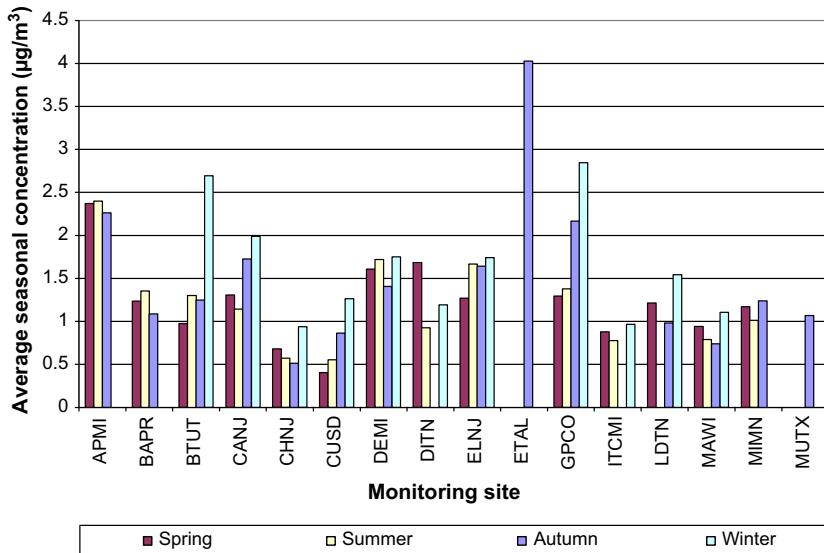
Some microenvironments contain concentrations of compounds that are several orders of magnitude higher than these mean values. For example, workplace microenvironments may contain levels far higher than atmospheric means and even higher than those found in highly polluted urban air; especially if air pollution control devices are not deployed. Thus, the concentration of an air pollutant that is expected and permitted will vary according to the protection needed in ambient air and various personal and workplace microenvironments (see [Figure 1.8](#)). This type of figure is used frequently in this text, especially in Chapter 7. It is quite useful in comparing allowable amounts of toxic air pollutants.

Higher concentrations of air pollutants are often permitted in workplace environments than in the general environment. This is because workplace environments often require personal protection equipment (PPE), which is enforced by occupational regulatory agencies. In addition, exposures in workplace environments are generally much shorter in duration and frequency, e.g. 8 h per day, five days per week for 30 years, compared to general exposures, e.g. 24 h per day, seven days per week for a lifetime. Thus, both the cancer and minimum risk level (MRL) are much lower than the occupational levels on the right-hand side of [Figure 1.8](#). The MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse noncancer health effects over a specified duration of exposure.<sup>4</sup>

The recommended or regulated amount of exposure to air pollutants varies by scenario and activity. In the United States, the Occupational Safety and Health Administration's (OSHA) workplace exposure standard is the permissible exposure limit (PEL) for each air pollutant. The PEL is set to protect workers day in and day out for their entire career, i.e. a long-term exposure.

There are three types of PELs:

1. The Time-Weighted Average (TWA) is the average employee exposure over a time period that a person is expected to work. This is usually 8 h, so the 8-h TWA is very commonly used. It is based on the measurements taken near or on the worker, i.e. personal exposure. The measured pollutant concentration may exceed the TWA value at times during the 8-h period but the 8-h average concentration must be below the PEL.



2. The Ceiling Limit (PEL-C) is the maximum allowable concentration, not an average. Thus, any exceedence is considered a violation of the PEL, even for a very short time.
3. The Short-Term Exposure Limit (STEL) is the concentration that must not be exceeded when averaged over a specified short period of time (usually 15 min). When there is an STEL for a substance, exposure still must never exceed the PEL-C or the 8-h TWA.

The majority of air pollutants with PELs have a published TWA value. Some air pollutants also have ceiling or short-term exposure limits (STELs). Others have ceilings and STELs instead of TWA values.

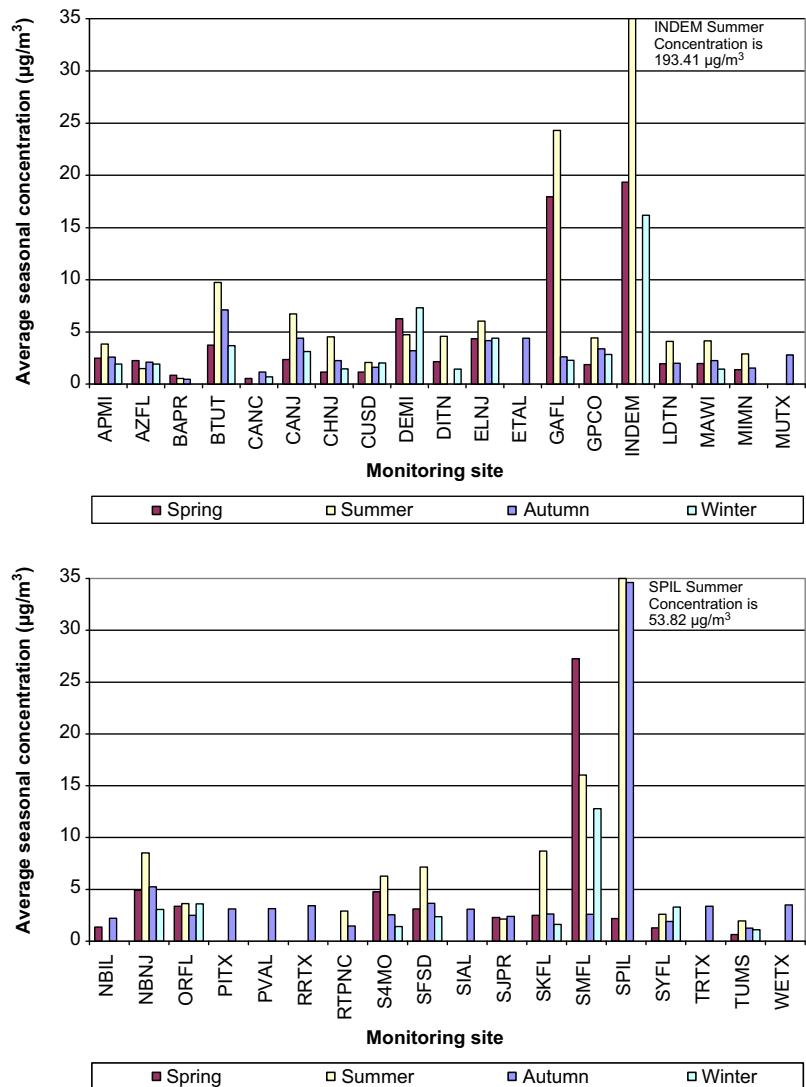
The science behind recommended levels of workplace exposure comes from governmental research; e.g.

the National Institute of Occupational Safety and Health (NIOSH) publishes air quality limits for substances to provide guidance on safe worker exposures. The recommendations can also come from professional and scientific associations. For example, the American Conference of Governmental Industrial Hygienists publishes occupational exposure guidelines, i.e. the threshold limit values (TLV). Both, the TLV and Recommended Exposure Level (REL) are advisory, but the PEL is a legal requirement that carries penalties when exceeded.

NIOSH publishes four types of exposure recommendations, structured similarly to the PELs:

1. The REL-TWA: 8-hour time-weighted average concentration.
2. The REL-TWA: 15-min time-weighted average concentration.

**FIGURE 1.7 Measured concentrations of benzene in several urban areas during four seasons of the year 2005.** APMI, Allen Park, Detroit, MI; AZFL, Azalea Park, St. Petersburg, FL; BAPR, Barcelona, Puerto Rico; BTUT, Bountiful, UT; CANC, Candor, NC; CANJ, Camden, NJ; CHNJ, Chester, NJ; CUSD, Custer, SD; DITN, Dickson, TN; ELNJ, Elizabeth, NJ; ETAL, East Thomas, Birmingham, AL; FLFL, Davie, FL; GAFL, Gandy in Tampa, FL; GRMS, Grenada, MS; INDEM, Gary, IN; ITCMI, Sault Sainte Marie, MI; LDTN, Loudon, TN; MAWI, Madison, WI; MIMN, Minneapolis, MN; MUTX, Murchison Middle School in Austin, TX; NBAL, North Birmingham, AL; NBNJ, New Brunswick, NJ; ORFL, Winter Park, FL; PCOK, Site 1 in Ponca City, OK; PGMS, Pascagoula, MS; PITX, Pickle Research Center, Austin, TX; POOK, Site 2 in Ponca City, OK; PVAL, Providence, RI; RRTX, Round Rock, TX; RTPNC, Research Triangle Park, NC; SFSD, Sioux Falls, SD; SIAL, Sloss Industries, Birmingham, AL; SJPR, San Juan, Puerto Rico; SMFL, Simmons Park in Tampa, FL; SPIL, Schiller Park in Chicago, IL; TRTX, Travis High School in Austin, TX; TUMS, Tupelo, MS; WETX, Webberville Road in Austin, TX; YDSP, El Paso, TX; YFMI, Yellow Freight in Detroit, MI. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. 2005 Urban Air Toxics Monitoring Program (UATMP). Final report. Report No. EPA-454/R-07-001; 2006.



**TABLE 1.5 Formaldehyde Concentrations Measured at Various Locations in California**

Location	Mean— $\mu\text{g m}^{-3}$ (ppb)	Maximum— $\mu\text{g m}^{-3}$ (ppb)
Conventional homes	11.3 (9.1)	38.8 (31.3)
Manufactured homes	45 (36.3)	282 (227)
Public & commercial buildings	16 (12.9)	32 (25.8)
Industrial plant	16 (12.9)	32 (25.8)
School	26.2 (21.1)	121.5 (98.0)
In-vehicle (Sacramento)	9.3 (7.5)	18.5 (14.9)
In-vehicle (Los Angeles)	15.3 (12.3)	23.6 (19.0)
Outdoor	3.6 (2.9)	14.3 (11.5)

Source: California Office of Environmental Health Hazard Assessment. Formaldehyde. Prioritization of toxic air contaminants. Children's Environmental Health Act. [http://oehha.ca.gov/air/toxic\\_contaminants/pdf\\_zip/formaldehyde\\_final.pdf](http://oehha.ca.gov/air/toxic_contaminants/pdf_zip/formaldehyde_final.pdf); 2001 [accessed 20.09.13].

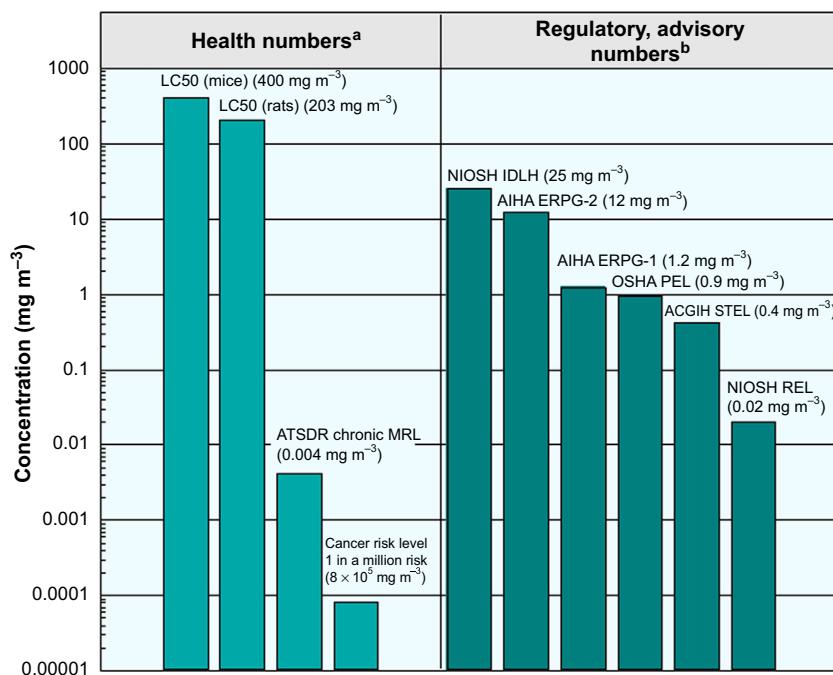
3. REL-C: Ceiling concentration—not to be exceeded.
4. IDHL: 30-min concentration that is Immediately Dangerous to Life and Health.

Table 1.6 shows the PELs and RELs for some important workplace air pollutants.

### 1.3.2 Concentration Unit Example

The REL-TWA concentration of ammonia ( $\text{NH}_3$ ) is 25 ppm. The ceiling REL is 5 ppm for hydrogen chloride (HCl). The ammonia TLV is also 25 ppm. The PEL-TWA for ammonia is 50 ppm, and the ceiling PEL for HCl is 5 ppm, the same as its REL. For ammonia, the time for which the concentration is averaged is often 8 h (i.e. 8-h TWA), but the TWA can also be calculated for extended work periods, e.g. a 10-h TWA, or for short-term exposures.

Suppose that a work area is monitored to show an 8-h TWA  $\text{NH}_3$  concentration of  $23 \text{ mg m}^{-3}$  and  $3 \text{ mg m}^{-3}$  for HCl. Are the workplace concentrations meeting NIOSH and OSHA recommendations?



**FIGURE 1.8 Health data for inhalation exposure to formaldehyde as of 1999.** To convert concentrations in air (at 25 °C) from ppm to mg m<sup>-3</sup>: mg m<sup>-3</sup> = (ppm) × (molecular weight of the compound)/(24.45). For formaldehyde: 1 ppm = 1.23 mg m<sup>-3</sup>. AIHA ERPG, American Industrial Hygiene Association's emergency response planning guidelines. ERPG 1 is the maximum airborne concentration below which it is believed nearly all individuals could be exposed up to 1 h without experiencing other than mild transient adverse health effects or perceiving a clearly defined objectionable odor; ERPG 2 is the maximum airborne concentration below which it is believed nearly all individuals could be exposed up to 1 h without experiencing or developing irreversible or other serious health effects that could impair their abilities to take protective action. ACGIH STEL: American Conference of Governmental and Industrial Hygienists' short-term exposure limit expressed as a time-weighted average exposure; the concentration of a substance which should not be exceeded at any time during a workday; LC<sub>50</sub> (Lethal Concentration-50): A calculated concentration of a chemical in air to which exposure for a specific length of time is expected to cause death in 50% of a defined experimental animal population—this is a common expression of acute hazard; NIOSH IDLH: National Institute of Occupational Safety and Health's immediately dangerous to life or health limit; NIOSH recommended exposure limit to ensure that a worker can escape from an exposure condition that is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from the environment; NIOSH REL: NIOSH's recommended exposure limit; NIOSH recommended exposure limit for an 8- or 10-h time-weighted average exposure and/or ceiling; OSHA PEL: Occupational Safety and Health Administration's permissible exposure limit expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effect averaged over a normal 8 h workday or a 40 h workweek.<sup>a</sup>Health numbers are toxicological values derived from animal testing or risk assessments developed by the U.S. government.<sup>b</sup>Regulatory values have been incorporated in U.S. government regulations, whereas advisory values are non-regulatory, but based on advice from the U.S. government or other groups as advice. OSHA numbers are regulatory, whereas NIOSH, ACGIH, and AIHA numbers are advisory.<sup>5–11</sup>(For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Formaldehyde. <http://www.epa.gov/ttnatw01/hltheff/formalde.html>; 2013 [accessed 21.09.13].

From Table 1.3, the conversion factor if  $\mu\text{g m}^{-3}$  is known is  $1.44 \times 10^{-3}$  for NH<sub>3</sub> and  $0.67 \times 10^{-3}$  for HCl.

$$23 \text{ mg} = 23,000 \text{ } \mu\text{g}.$$

$$23,000 \text{ } \mu\text{g m}^{-3} \times 1.44 \times 10^{-3} = 33.12 \text{ ppm NH}_3.$$

This means that the readings are higher than the REL, but lower than the PEL (50 ppm). Although the PEL is not being violated, there may still be concern, since it exceeds the recommended levels. Due diligence would call for finding ways to reduce the workplace concentrations to be closer to the REL and TLV.

For HCl, applying the 0.67 conversion factor gives:

$$3 \text{ mg} = 3000 \text{ } \mu\text{g}.$$

$$3000 \text{ } \mu\text{g m}^{-3} \times 0.67 \times 10^{-3} = 2 \text{ ppm}.$$

Given that 2 ppm < 5 ppm, would OSHA deem that this facility is not violating the PEL standard of 5 ppm if this area requires workers to be present? Note that Table 1.6 indicates that HCl is not a TWA PEL, but is a C-PEL. The C-PEL cannot be exceeded, even instantaneously. Thus, the average HCl concentration is not the appropriate measure. The actual measurements would have to be used instead to determine compliance with the C-PEL. Let us assume that the monitor provides 5-min intervals of data and that during the sampling period there were 15 intervals above 5 ppm. The peak concentration measured was 20 mg m<sup>-3</sup>:

$$20 \text{ mg} = 20,000 \text{ } \mu\text{g}.$$

$$20,000 \text{ } \mu\text{g m}^{-3} \times 0.67 \times 10^{-3} = 13.4 \text{ ppm}.$$

TABLE 1.6 U.S. Permissible Exposure Levels (PELs) and Recommended Exposure Levels (RELs) for Selected Workplace Air Pollutants

Air Pollutant	Permissible Exposure Level	Recommended Exposure Level
Acetaldehyde	TWA 200 ppm ( $360 \text{ mg m}^{-3}$ )	Treated as a carcinogen* Careful consideration given to reducing exposures to nine related aldehydes
Acetone	TWA 1000 ppm ( $2400 \text{ mg m}^{-3}$ )	TWA 250 ppm ( $590 \text{ mg m}^{-3}$ )
Acrolein	TWA 0.1 ppm ( $0.25 \text{ mg m}^{-3}$ )	TWA 0.1 ppm ( $0.25 \text{ mg m}^{-3}$ ) ST 0.3 ppm ( $0.8 \text{ mg m}^{-3}$ ) Careful consideration given to reducing exposures to nine related aldehydes
Ammonia	TWA 50 ppm ( $35 \text{ mg m}^{-3}$ )	TWA 25 ppm ( $18 \text{ mg m}^{-3}$ ) ST 35 ppm ( $27 \text{ mg m}^{-3}$ )
<i>n</i> -Butane	None	TWA 800 ppm ( $1900 \text{ mg m}^{-3}$ )
2-Butanone	TWA 200 ppm ( $590 \text{ mg m}^{-3}$ )	TWA 200 ppm ( $590 \text{ mg m}^{-3}$ ) ST 300 ppm ( $885 \text{ mg m}^{-3}$ )
Chlorine	C 1 ppm ( $3 \text{ mg m}^{-3}$ )	C 0.5 ppm ( $1.45 \text{ mg m}^{-3}$ ) (15 min)
Chlorine dioxide	TWA 0.1 ppm ( $0.3 \text{ mg m}^{-3}$ )	TWA 0.1 ppm ( $0.3 \text{ mg m}^{-3}$ ) ST 0.3 ppm ( $0.9 \text{ mg m}^{-3}$ )
Diethyl phthalate	None	TWA 5 $\text{mg m}^{-3}$
Ethyl benzene	TWA 100 ppm ( $435 \text{ mg m}^{-3}$ )	TWA 100 ppm ( $435 \text{ mg m}^{-3}$ ) ST 125 ppm ( $545 \text{ mg m}^{-3}$ )
Formaldehyde	TWA 0.75 ppm ( $0.9 \text{ mg m}^{-3}$ ) ST 2 ppm ( $2.5 \text{ mg m}^{-3}$ )	NIOSH Potential Occupational Carcinogen. RELs for asbestos, formaldehyde, benzene, and ethylene oxide are quantitative values based primarily on analytical limits of detection or technological feasibility. C 0.1 ppm ( $0.1 \text{ mg m}^{-3}$ ) (15 min)
Gasoline	None	Treated as a carcinogen*
<i>n</i> -Heptane	TWA 500 ppm ( $2000 \text{ mg m}^{-3}$ )	TWA 85 ppm ( $350 \text{ mg m}^{-3}$ ) C 440 ppm ( $1800 \text{ mg m}^{-3}$ ) (15 min)
<i>n</i> -Hexane	TWA 500 ppm ( $1800 \text{ mg m}^{-3}$ )	TWA 50 ppm ( $180 \text{ mg m}^{-3}$ )
Hydrogen bromide	TWA 3 ppm ( $10 \text{ mg m}^{-3}$ )	3 ppm ( $10 \text{ mg m}^{-3}$ )
Hydrogen chloride	C 5 ppm ( $7 \text{ mg m}^{-3}$ )	C 5 ppm ( $7 \text{ mg m}^{-3}$ )
Hydrogen fluoride	TWA 3 ppm	TWA 3 ppm ( $2.5 \text{ mg m}^{-3}$ ) C 6 ppm ( $5 \text{ mg m}^{-3}$ ) (15 min)
Hydrogen sulfide	C 20 ppm 50 ppm (10-min maximum peak)	C 10 ppm ( $15 \text{ mg m}^{-3}$ ) (10 min)
Isobutane	None	TWA 800 ppm ( $1900 \text{ mg m}^{-3}$ )
Hg vapor	TWA 0.1 $\text{mg m}^{-3}$	Hg vapor: TWA 0.05 $\text{mg m}^{-3}$ (skin) Other: C 0.1 $\text{mg m}^{-3}$ (skin)
Mercury (organo) alkyl compounds (as Hg)	TWA 0.01 $\text{mg m}^{-3}$ C 0.04 $\text{mg m}^{-3}$	TWA 0.01 $\text{mg m}^{-3}$ ST 0.03 $\text{mg m}^{-3}$ (skin)
Methyl alcohol	TWA 200 ppm ( $260 \text{ mg m}^{-3}$ )	TWA 200 ppm ( $260 \text{ mg m}^{-3}$ ) ST 250 ppm ( $325 \text{ mg m}^{-3}$ ) (skin)
Methyl chloride	TWA 100 ppm C 200 ppm 300 ppm (5-min maximum peak in any 3 h)	Treated as a carcinogen*
Methyl chloroform	TWA 350 ppm ( $1900 \text{ mg m}^{-3}$ )	C 350 ppm ( $1900 \text{ mg m}^{-3}$ ) (15 min) Along with 1,1-dichloroethane, ethyl chloride, pentachloroethane, and 1,1,1,2-tetrachloroethane should be treated in the workplace with caution because of their structural similarity to the four chloroethanes shown to be carcinogenic in animals
Naphthalene	None	TWA 0.040 $\text{mg m}^{-3}$ (0.005 ppm) C 0.170 $\text{mg m}^{-3}$ (0.020 ppm) (10 min)
Nitric acid	TWA 2 ppm ( $5 \text{ mg m}^{-3}$ )	TWA 2 ppm ( $5 \text{ mg m}^{-3}$ ) ST 4 ppm ( $10 \text{ mg m}^{-3}$ )

**TABLE 1.6** U.S. Permissible Exposure Levels (PELs) and Recommended Exposure Levels (RELs) for Selected Workplace Air Pollutants—cont'd

Air Pollutant	Permissible Exposure Level	Recommended Exposure Level
Nitrogen dioxide	C 5 ppm ( $9 \text{ mg m}^{-3}$ )	ST 1 ppm ( $1.8 \text{ mg m}^{-3}$ )
Octane	TWA 500 ppm ( $2350 \text{ mg m}^{-3}$ )	TWA 75 ppm ( $350 \text{ mg m}^{-3}$ ) C 385 ppm ( $1800 \text{ mg m}^{-3}$ ) (15 min)
Ozone	TWA 0.1 ppm ( $0.2 \text{ mg m}^{-3}$ )	C 0.1 ppm ( $0.2 \text{ mg m}^{-3}$ )
Sodium hydroxide	TWA 2 $\text{mg m}^{-3}$	C 2 $\text{mg m}^{-3}$
Styrene	TWA 100 ppm C 200 ppm 600 ppm (5-min maximum peak in any 3 h)	TWA 50 ppm ( $215 \text{ mg m}^{-3}$ ) ST 100 ppm ( $425 \text{ mg m}^{-3}$ )
Sulfur dioxide	TWA 5 ppm ( $13 \text{ mg m}^{-3}$ )	TWA 2 ppm ( $5 \text{ mg m}^{-3}$ ) ST 5 ppm ( $13 \text{ mg m}^{-3}$ )
Tetrachloroethylene	TWA 100 ppm C 200 ppm (for 5 min in any 3-h period), with a maximum peak of 300 ppm	Treated as a carcinogen*
Titanium dioxide	TWA 15 $\text{mg m}^{-3}$	Treated as a carcinogen*
Toluene	TWA 200 ppm C 300 ppm 500 ppm (10-min maximum peak)	TWA 100 ppm ( $375 \text{ mg m}^{-3}$ ) ST 150 ppm ( $560 \text{ mg m}^{-3}$ )
1,2,3-Trimethylbenzene	None	TWA 25 ppm ( $125 \text{ mg m}^{-3}$ )
1,2,4-Trimethylbenzene	None	TWA 25 ppm ( $125 \text{ mg m}^{-3}$ )
1,3,5-Trimethylbenzene	None	TWA 25 ppm ( $125 \text{ mg m}^{-3}$ )
Vinyl acetate	None	C 4 ppm ( $15 \text{ mg m}^{-3}$ ) (15 min)
Vinyl bromide	None	Treated as a carcinogen*
Vinyl chloride	TWA 1 ppm C 5 ppm (15 min)	Treated as a carcinogen*
Welding fumes	None	Treated as a carcinogen*
<i>o</i> -Xylene	TWA 100 ppm ( $435 \text{ mg m}^{-3}$ )	TWA 100 ppm ( $435 \text{ mg m}^{-3}$ ) ST 150 ppm ( $655 \text{ mg m}^{-3}$ )
<i>m</i> -Xylene	TWA 100 ppm ( $435 \text{ mg m}^{-3}$ )	TWA 100 ppm ( $435 \text{ mg m}^{-3}$ ) ST 150 ppm ( $655 \text{ mg m}^{-3}$ )
<i>p</i> -Xylene	TWA 100 ppm ( $435 \text{ mg m}^{-3}$ )	TWA 100 ppm ( $435 \text{ mg m}^{-3}$ ) ST 150 ppm ( $655 \text{ mg m}^{-3}$ )
Zinc chloride fume	TWA 1 $\text{mg m}^{-3}$	TWA 1 $\text{mg m}^{-3}$ ST 2 $\text{mg m}^{-3}$
Zinc oxide	TWA 5 $\text{mg m}^{-3}$ (fume) TWA 15 $\text{mg m}^{-3}$ (total dust) TWA 5 $\text{mg m}^{-3}$ (respirable dust)	Dust: TWA 5 $\text{mg m}^{-3}$ C 15 $\text{mg m}^{-3}$ Fume: TWA 5 $\text{mg m}^{-3}$ ST 10 $\text{mg m}^{-3}$

\* For these substances, NIOSH will project a no-effect exposure, as well as exposure levels at which there may be residual risks. This policy applies to all workplace hazards, including carcinogens, and is responsive to Section 20(a)(3) of the Occupational Safety and Health Act of 1970, which charges NIOSH to "...describe exposure levels that are safe for various periods of employment, including but not limited to the exposure levels at which no employee will suffer impaired health or functional capacities or diminished life expectancy as a result of his work experience."

TWA, time-weighted average; C, ceiling concentration; ST, short-term exposure level (STEL), ppm, parts per million;  $\text{mg m}^{-3}$ , milligram per cubic meter.

Source: National Institute of Occupational Safety and Health. NIOSH pocket guide to chemical hazards. <http://www.cdc.gov/niosh/npg/pgintro.html>; 2013 [accessed 09.09.13].

Sometimes, industrial operations can be conducted entirely within a sealed area, e.g. using robots. However, several industrial operations may require work in higher workplace exposures. This is permitted if the workers wear appropriate PPE, especially respirators.

Assigned protection factors (APFs) are published by OSHA.<sup>12</sup> An APF defines the level of respiratory protection expected to be provided by a respirator or class of respirators. The APFs range from 5 to 10,000 (see Table 1.7). Similarly, the maximum use concentration

(MUC) is the highest atmospheric concentration of a hazardous substance from which a worker would be expected to be protected when wearing the respirator. The relationship between the MUC and APF informs the decision on the type of respirator needed:

$$\text{MUC} = \text{PEL} \times \text{APF} \quad (1.3)$$

If the phase of concern of HCl is a vapor, Table 1.7(B) describes the appropriate respirator. Several respirators equipped with appropriate gas/vapor cartridges would

TABLE 1.7 Assigned Protection Factors for Particulate (A) and Gas/Vapor (B) Respirators

Assigned Protection Factor	Respirator Type
<b>A. PARTICULATE RESPIRATORS</b>	
5	<ul style="list-style-type: none"> <li>Quarter mask respirator</li> </ul>
10	<ul style="list-style-type: none"> <li>Any air-purifying elastomeric half-mask respirator equipped with appropriate type of particulate filter (filter medium must provide protection against the particulate in question).</li> <li>Appropriate filtering facepiece respirator filter medium must provide protection against the particulate in question; APF of 10 can only be achieved if the respirator is qualitatively or quantitatively fit tested on individual workers.</li> <li>Any air-purifying full facepiece respirator equipped with appropriate type of particulate filter (filter medium must provide protection against the particulate in question).</li> <li>Any negative pressure (demand) supplied-air respirator equipped with a half-mask.</li> </ul>
25	<ul style="list-style-type: none"> <li>Any powered air-purifying respirator equipped with a hood or helmet and a high-efficiency (HEPA) filter.</li> <li>Any continuous flow supplied-air respirator equipped with a hood or helmet.</li> </ul>
50	<ul style="list-style-type: none"> <li>Any air-purifying full facepiece respirator equipped with N-100, R-100, or P-100 filter(s).</li> <li>Any powered air-purifying respirator equipped with a tight-fitting facepiece (half- or full facepiece) and a high-efficiency filter.</li> <li>Any negative pressure (demand) supplied-air respirator equipped with a full facepiece.</li> <li>Any continuous flow supplied-air respirator equipped with a tight-fitting facepiece (half or full facepiece).</li> <li>Any negative pressure (demand) self-contained respirator equipped with a full facepiece.</li> </ul>
1000	<ul style="list-style-type: none"> <li>Any pressure-demand supplied-air respirator equipped with a half-mask.</li> </ul>
2000	<ul style="list-style-type: none"> <li>Any pressure-demand supplied-air respirator equipped with a full facepiece.</li> </ul>
10,000	<ul style="list-style-type: none"> <li>Any pressure-demand self-contained respirator equipped with a full facepiece.</li> <li>Any pressure-demand supplied-air respirator equipped with a full facepiece in combination with an auxiliary pressure-demand self-contained breathing apparatus.</li> </ul>
<b>B. GAS/VAPOR RESPIRATORS</b>	
10	<ul style="list-style-type: none"> <li>Any air-purifying half-mask respirator equipped with appropriate gas/vapor cartridges (select a cartridge/canister certified to be used for the specific class of chemicals or the specific gas/vapor found in the workplace).</li> <li>Any negative pressure (demand) supplied-air respirator equipped with a half mask.</li> </ul>
25	<ul style="list-style-type: none"> <li>Any powered air-purifying respirator with a loose-fitting hood or helmet equipped with appropriate gas/vapor cartridges (select a cartridge/canister certified to be used for the specific class of chemicals or the specific gas/vapor found in the workplace).</li> <li>Any continuous flow supplied-air respirator equipped with a hood or helmet.</li> </ul>
50	<ul style="list-style-type: none"> <li>Any air-purifying full facepiece respirator equipped with appropriate gas/vapor cartridges<sup>2</sup> or gas mask (canister respirator) (select a cartridge/canister certified to be used for the specific class of chemicals or the specific gas/vapor found in the workplace).</li> <li>Any powered air-purifying respirator equipped with a tight-fitting facepiece (half or full facepiece) and appropriate gas/vapor cartridges or canisters (select a cartridge/canister certified to be used for the specific class of chemicals or the specific gas/vapor found in the workplace).</li> <li>Any negative pressure (demand) supplied-air respirator equipped with a full facepiece.</li> <li>Any continuous flow supplied-air respirator equipped with a tight-fitting facepiece (half or full facepiece).</li> <li>Any negative pressure (demand) self-contained respirator equipped with a full facepiece.</li> </ul>
1000	<ul style="list-style-type: none"> <li>Any pressure-demand supplied-air respirator equipped with a half-mask.</li> </ul>
2000	<ul style="list-style-type: none"> <li>Any pressure-demand supplied-air respirator equipped with a full facepiece.</li> </ul>
10,000	<ul style="list-style-type: none"> <li>Any pressure-demand self-contained respirator equipped with a full facepiece.</li> <li>Any pressure-demand supplied-air respirator equipped with a full facepiece in combination with an auxiliary pressure-demand self-contained breathing apparatus.</li> </ul>

Source: Centers for Disease Control and Prevention. National Institute for Occupational Safety and Health. NIOSH Respirator Selection Logic. DHHS (NIOSH) Publication No. 2005-100; 2004.

provide an APF of 10. That is,  $MUC = 5 \times 10 = 50$  ppm. If the measured 13.4 ppm peak concentration represents the highest HCl levels expected in this workplace, respirators providing an APF of 10 should be sufficient protection, if worn and used properly.

Monitoring must continue; but let us assume that the equipment being used does not display ppm units, but gives units of  $\mu\text{g m}^{-3}$ . Since the peak (ceiling PEL) concentration not to be exceeded using the APF 10 respirator is 50 ppm, what is this in units of  $\mu\text{g m}^{-3}$ ? Returning to [Table 1.3](#), the conversion factor for HCl to use when ppm is known is 1490:

$$1490 \times 50 = 74,500 \mu\text{g m}^{-3} = 74.5 \text{ mg m}^{-3}$$

If concentrations begin to approach  $70 \text{ mg m}^{-3}$ , a more protective respirator may be needed (e.g. the supplied-air respirator with an APF of 1000 would be much more protective).

To ensure that the unit conversions for  $\text{NH}_3$  and HCl are correct, the molecular weight (MW) of each can be inserted in to [Eqn \(1.1\)](#):

$$\begin{aligned} 33.12 \text{ ppm } \text{NH}_3 &= 33.12 \times [40.9 \times \text{MW}] \mu\text{g m}^{-3} \\ 33.12 \text{ ppm } \text{NH}_3 &= 33.12 \times [40.9 \times 17.0] \mu\text{g m}^{-3} \\ 33.12 \text{ ppm } \text{NH}_3 &= 23,028 \mu\text{g m}^{-3} \\ 13.4 \text{ ppm HCl} &= 13.4 \times [40.9 \times \text{MW}] \mu\text{g m}^{-3} \\ 13.4 \text{ ppm HCl} &= 13.4 \times [40.9 \times 36.5] \mu\text{g m}^{-3} \\ 13.4 \text{ ppm HCl} &= 20,004 \mu\text{g m}^{-3} \end{aligned}$$

Both unit conversions are within rounding error at three significant figures.

## 1.4 FLUID PROPERTIES AND DYNAMICS

Gases and liquids are fluids. Since the air is a mixture of gases, with varying amounts of suspended liquids and solids, it possesses fluid properties.<sup>b</sup> In addition to the complex and changing chemical composition of the atmosphere, the air's fluid properties and dynamics must be understood at various scales, from the movement of air masses at a global scale to the movement of contaminants and essential nutrients among and within an organism's cells. Air is the most prominent fluid when considering air pollutants, but it is not the only fluid involved in air pollution. Water is arguably equally important for numerous reasons, including as a component of the atmosphere and as the transport and transformation medium of bodily fluids during intake, adsorption, metabolism, distribution, and excretion of air pollutants and their byproducts within an organism. Many other fluids are

important to air pollution. Indeed, the pollutants themselves are often fluids under environmental conditions, e.g. alcohols, solvents, and oils.

The first law of motion states that every object in a state of uniform motion tends to remain in that state of motion unless an external force is applied to it, i.e. inertia. The most common external force that changes the state of uniform motion is friction.

The second law of motion describes the relationship between an object's mass  $m$ , its acceleration  $a$ , and the applied force:

$$F = ma \quad (1.4)$$

Acceleration and force are vectors; wherein the direction of the force vector is the same as the direction of the acceleration vector. For example, if the mass of the pollutant, the mass of the fluid where it resides (i.e. air mass), and applied force (e.g. generated by the wind) are known, then the acceleration of a particle can be calculated, as well as the acceleration of the entire plume from one point to another.

The third law of motion states that for every action there is an equal and opposite reaction. Like the first law, this means that movements are dynamic and actions taken to change the velocity or direction of a pollutant (e.g. baffles, vents, and barriers) will be met with resistance and will result in changes in flow and direction of the pollutants. This comes into play when designing pollution control equipment.

The laws of chemistry remind us that what we put into a reaction always leads to a specific product. Thus, science tells us that so long as we understand the variables and parameters of any system, the outcome is predictable. This is obviously not completely possible when designing air pollution control equipment, for example, but lessons learned from successes and failures in previous designs lead to improved control technologies. There are numerous ways to identify, characterize, and analyze air pollution and to determine how the exposure to a pollutant has led and can lead to health and environmental impacts. Accurate descriptions of fluid properties and fluid dynamics are an essential part of this.

### 1.4.1 Atmospheric Fluid Properties

Air pollution involves fluids. The term "fluid" includes all liquids and gases. A liquid is a form of matter that is composed of molecules that move freely among themselves without separating from each other. A gas is a form of matter that is composed of molecules that

<sup>b</sup> Even solids can be fluids at a very large scale. For example, in plate tectonics and other expansive geological processes, solid rock will flow, albeit very slowly.

move freely and are infinitely able to occupy the space in which they are contained at a constant temperature. Engineers define a fluid as a substance that will deform continuously upon the application of a shear stress; i.e. a stress in which the material on one side of a surface pushes on the material on the other side of the surface with a force parallel to the surface.

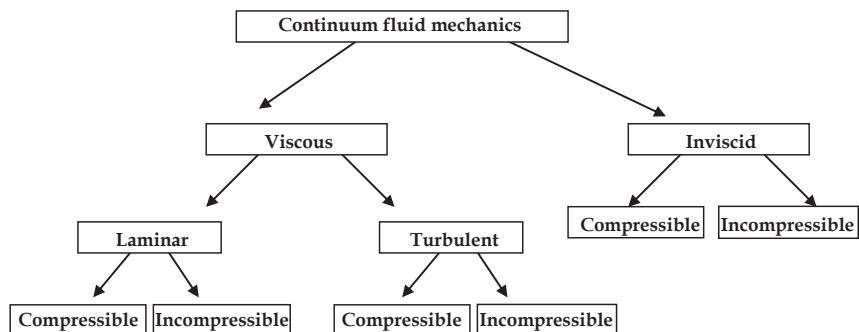
The medium itself, i.e. air, is a fluid. So are some of the pollutants (gases like carbon monoxide, vapors like benzene, and liquid aerosols). Also, water is a key fluid, such as its vapor phase (e.g. clouds, fog, and steam) and its liquid phase (e.g. droplets, surface and groundwater interactions with the atmosphere). Indeed, many other fluids must be considered to describe air pollution fully, notably after exposure, blood, lipids, and other bodily fluids transport air pollutants and their metabolites within organisms.

As mentioned, fluids are either liquid or gaseous. Fluid properties, along with fluid dynamics determine the extent and severity of a disaster. For example, contaminant's fluid properties will determine how soluble it will be in water droplets that are transported and deposited differently from air pollutants having lower aqueous solubility. A substance that is insoluble in water is often quite soluble in fats, meaning that exposures will lead to buildup in lipids. If a chemical is easily absorbed, the hazard may be higher.

The fluid properties of an agent, whether chemical or biological (e.g. bacteria and viruses), determine where the agent is likely to be found in the environment after release (e.g. in the air as a vapor, sorbed to a particle, dissolved in water, or accumulated in biota).

As science becomes less reductionist and more systematic, certain long-held boundaries between disciplines are becoming blurred. For example, physical transport is not only a function of the mechanics of fluids, but it is also a chemical process, such as when and under what conditions transport and chemical transformation processes become a steady state or nearly steady state, e.g. sequestration and storage in the environment. Thus, transport and transformation of air pollutants depends on the characteristics of environmental fluids.

**FIGURE 1.9** Classification of fluids based on continuum fluid mechanics. *Research and Education Association. The essentials of fluid mechanics and dynamics I. Piscataway (NJ): REA; 1987.*



Fluids can be classified according to observable physical characteristics of flow fields. A continuum fluids mechanics classification is shown in [Figure 1.9](#). Laminar flow is in layers, while turbulent flow has random movements of fluid particles in all directions. In incompressible flow, the variations in density are assumed to be constant, while the compressible flow has density variations, which must be included in flow calculations. Viscous flows must account for viscosity while inviscid flows assume viscosity is zero.

The time rate of change of a fluid particle's position in space is the fluid velocity ( $\mathbf{V}$ ). This is a vector field quantity. Speed ( $V$ ) is the magnitude of the vector velocity  $\mathbf{V}$  at any given point in the fluid, and average speed ( $\bar{V}$ ) is the mean fluid speed through a control volume's surface. Therefore, velocity is a vector quantity (magnitude and direction), while speed is a scalar quantity (magnitude only). The standard units of velocity and speed are meter per second ( $\text{m s}^{-1}$ ).

Velocity is important in determining pollution properties and mechanisms, such as mixing rates after an effluent is discharged to a stream, how rapidly an aquifer will become contaminated, and the ability of liners to slow the movement of leachate from a landfill toward the groundwater. The distinction between velocity and speed is seldom made, even in technical discussions.

Another important fluid property is pressure. A force per unit area is pressure ( $p$ ):

$$p = \frac{F}{A} \quad (1.5)$$

So,  $p$  is a type of stress that is exerted uniformly in all the directions. It is common to use pressure instead of force to describe the factors that influence the behavior of fluids. The standard unit of  $p$  is the pascal (Pa), which is equal to  $1 \text{ N m}^{-2}$ . The preferred pressure unit in this book is the kilopascal (kPa), since the standard metric unit of pressure is the pascal, which is quite small.

Potential and kinetic energy discussions must consider the fluid acceleration due to gravity. In many ways, it seems that acceleration was a major reason for

Isaac Newton's need to develop the calculus.<sup>13</sup> Known as the mathematics of change, calculus is the mathematical means of describing acceleration and addressed Newton's need to express mathematically his new law of motion. Acceleration is the time rate of change in the velocity of a fluid particle. In terms of calculus, it is a second derivative. That is, it is the derivative of the velocity function. And a derivative of a function is itself a function, giving its rate of change. This explains why the second derivative must be a function showing the rate of change of the rate of change, which is readily apparent from the units of acceleration: length per time per time ( $\text{m s}^{-2}$ ).

Unfortunately, in the United States and some other countries, pollution rules, regulations, and standards are not used consistently and uniformly. For example, the regulations for ozone ( $\text{O}_3$ ) are expressed volumetrically in parts per billion, but aerosols are usually mass per volume. Since volume is directly proportional and temperature indirectly proportional to density (combined gas law), some assumptions must be made before converting volumetric units (ppm, volume) to concentration units ( $\mu\text{g m}^{-3}$ ). Unless otherwise stated, the first simplifying assumption is that the ideal gas law is expected to apply to environmental conditions in this book:

$$pV = nR'T \quad (1.6)$$

where  $n$  is the number of moles and  $R'$  is the gas constant,  $R' = 8.315 \text{ J K}^{-1} \text{ mol}^{-1}$ .

An ideal gas is one in which the atoms or molecules are moving randomly and not interacting with one another. Under environmental conditions, e.g. standard temperature and pressure, most gases in the atmosphere behave like ideal gases. However, at decreasing temperatures and pressures, gases begin to deviate from ideal behavior, especially due to molecular size (i.e. less space between molecules means the ratio of molecule to void space increases) and intermolecular forces (i.e. the ratio of kinetic energy to intermolecular forces decreases).

Since the density ( $\rho$ ) of a fluid is its mass per unit volume (e.g.  $\mu\text{g m}^{-3}$ ), the density of an ideal gas is found using the gas constant specific to that molecule and applying the ideal gas law:

$$\rho = p(RT)^{-1} \quad (1.7)$$

where,

$p$  = gas pressure

$R$  = specific gas constant

$T$  = absolute temperature.

The specific gas constant must be known to calculate the gas density. For example, the  $R$  for air is  $287 \text{ J kg}^{-1} \text{ K}^{-1}$ . The specific gas constant for methane ( $R_{\text{CH}_4}$ ) is  $518 \text{ J kg}^{-1} \text{ K}^{-1}$ .

Applying these assumptions, at  $25^\circ\text{C}$  and  $760 \text{ mmHg}$ , ppb (vol.) can be converted to  $\mu\text{g m}^{-3}$ :

$$\begin{aligned} 1 \text{ ppb (vol.) pollutant} &= \frac{1 \text{ l pollutant}}{10^9 \text{ l air}} \\ &= \frac{(1 \text{ l}/22.4) \times \text{MW} \times 10^9 \mu\text{g} \times \text{g m}^{-3}}{10^9 \text{ l} \times 298 \text{ K}/273 \text{ K} \times 10^{-3} \times \text{l}^{-1}} \quad (1.8) \\ &= 4.09 \times 10^4 \text{ MW } \mu\text{g m}^{-3} \end{aligned}$$

where MW equals the molecular weight. Thus, Equations 1.1 and 1.8 can be used to convert any molecule volumetric concentration to mass per volume concentration.

Several air pollutants are considered as classes or collections of compounds (e.g. coke oven emissions, oxides of sulfur, and oxides of nitrogen). Thus, it is important to keep in mind that a published concentration will often be an average or total. To be completely correct, each chemical species must be converted separately, since the density of each compound in the group differs. For example, it is a common practice to add concentrations of nitrogen dioxide and nitric oxide in ppm (vol.) and express the sum as "oxides of nitrogen". In metric units, conversion from ppm (vol.) to  $\mu\text{g m}^{-3}$  must be calculated separately for nitrogen dioxide and nitric oxide prior to addition.

Density is a very important fluid property for any air pollution situation. If a pollutant is very dense, such as a heavy particle, it will stay aloft for a much shorter time and distance than will a lighter particle of the same shape and size. For first responders, the density in part determines the response. For example, whether a burning substance is of greater or lesser density than water will be one of the factors on how to extinguish the fire. If the substance is less dense than water, the water will likely settle below the layer of water, making water a poor choice for fighting the fire. So, any flammable liquid with a density less than water (see Table 1.8), such as benzene or acetone, will require fire-extinguishing substances other than water. For substances heavier than water, like carbon disulfide, water may be a good choice.

The reciprocal of a substance's density is known as its specific volume ( $v$ ). This is the volume occupied by a unit mass of a fluid. The units of  $v$  are reciprocal density units ( $\text{m}^3 \text{ kg}^{-1}$ ). Stated mathematically, this is:

$$v = \rho^{-1} \quad (1.9)$$

The weight of a fluid per unit volume is known as the specific weight ( $\gamma$ ). Scientists and engineers sometimes use the term interchangeably with density. Geoscientists frequently refer to a substance's specific weight. A substance's  $\gamma$  is not an absolute fluid property as it depends upon the fluid itself and the local gravitational force:

$$\gamma = gp \quad (1.10)$$

TABLE 1.8 Densities of Some Important Environmental Fluids

Fluid	Density ( $\text{kg m}^{-3}$ ) at 20 °C unless Otherwise Noted
Air at standard temperature and pressure (STP) = 0 °C and 101.3 N m <sup>-2</sup>	1.29
Air at 21 °C	1.20
Ammonia	602
Diethyl ether	740
Ethanol	790
Acetone	791
Gasoline	700
Kerosene	820
Turpentine	870
Benzene	879
Pure water	1000
Seawater	1025
Carbon disulfide	1274
Chloroform	1489
Tetrachloromethane (carbon tetrachloride)	1595
Lead (Pb)	11,340
Mercury (Hg)	13,600

Specific weight units are the same as those for density, e.g.  $\text{kg m}^{-3}$ . Specific weight is not often used by air pollution practitioners and researchers, but it can be an important property when characterizing fugitive dust and for source apportionment. For example, a particle's specific weight may be a way to distinguish dust from soil erosion or surface mining or from other sources.

The fractional change in a fluid's volume per unit change in pressure at constant temperature is the fluid's coefficient of compressibility. Any fluid can be compressed in response to the application of pressure ( $p$ ). For example, water's compressibility at 1 atm is  $4.9 \times 10^{-5} \text{ atm}^{-1}$ . This compares to the lesser compressibility of mercury ( $3.9 \times 10^{-6} \text{ atm}^{-1}$ ) and the greater compressibility of hydrogen ( $1.6 \times 10^{-3} \text{ atm}^{-1}$ ). A fluid's bulk modulus,  $E$ , is a function of stress and strain on the fluid, and is a description of its compressibility, and is defined according to the fluid volume ( $V$ ):

$$E = \frac{\text{stress}}{\text{strain}} = -\frac{dp}{dV/V_1} \quad (1.11)$$

TABLE 1.9 Surface Tension (Contact with Air) of Selected Environmental Fluids

Fluid	Surface Tension, $\sigma$ ( $\text{N m}^{-1}$ at 20 °C)
Acetone	0.0236
Benzene	0.0289
Ethanol	0.0236
Glycerin	0.0631
Kerosene	0.0260
Mercury	0.472
<i>n</i> -Octane	0.0270
Tetrachloromethane	0.0236
Toluene	0.0285
Water	0.0728

$E$  is expressed in units of pressure (e.g. kPa). Water's  $E = 2.2 \times 10^6 \text{ kPa}$  at 20 °C.

Surface tension effects occur at liquid surfaces (interfaces of liquid–liquid, liquid–gas, liquid–solid). Surface tension,  $\sigma$ , is the force in the liquid surface normal to a line of unit length drawn on the surface. Surface tension decreases with temperature and varies depending on the contact fluid. Surface tension is involved in capillary rise and drop. Water has a very high  $\sigma$  value ( $0.0728 \text{ N m}^{-1}$  at 20 °C). Of the environmental fluids, only mercury has a higher  $\sigma$  (see Table 1.9). The high surface tension creates a type of skin on a free surface, which is how an object that is denser than water (e.g. a steel needle) can "float" on a still water surface. It is the reason insects can sit comfortably on water surfaces. Surface tension is somewhat dependent upon the gas that is in contact with the free surface. If not indicated, it is usually assumed that the gas is air.

The composition and fluid properties of the atmosphere provide the setting and context for the discussion of air pollution. The following chapters consider various ways of characterizing air pollution and air pollutants, beginning with the physical processes at work in the atmosphere, followed by discussions of society's expectations of scientists and professionals who must apply scientific principles to address air pollution.

## QUESTIONS

- What is the mixing ratio? What advantage is there to using this as opposed to concentrations of gases in the atmosphere?
- Explain why the mixing ratio below 100 km altitude in the atmosphere is highly variable for most

- substances other than molecular nitrogen and the noble gases.
3. Why do the mixing ratios for methane and nitrous oxide decrease beginning at about 20 km of altitude?
  4. What is a standard atmosphere?
  5. What is air density?
  6. What is density of air at 1 atm and 20 °C? How about in the Nevada desert in summer, if the atmospheric pressure is 0.92 atm and  $T = 40^\circ\text{C}$ ?
  7. If the number density of benzene in a garage is  $2.4 \times 10^{18}$  molecules per  $\text{m}^3$ , what is the mass density in  $\mu\text{mol}$ ? In  $\mu\text{g m}^{-3}$ ?
  8. Give some possible reasons for the differences in formaldehyde concentrations shown in Figure 1.6 and benzene concentrations in Figure 1.7?
  9. Assume the average weight of a passenger vehicle is 1800 kg and the average gas mileage is 10 km  $\text{L}^{-1}$ , and that gasoline weighs an average of 0.7 kg  $\text{L}^{-1}$ , with 85% of this weight as carbon. Does the average vehicle emit its own weight in  $\text{CO}_2$  each year?
  10. Using the data from the previous question, if there are 1 billion vehicles in the world, estimate the annual global carbon emissions from vehicles. Give your answer in tons, tonnes, and teragrams.
  11. If the average vehicle lowers its emissions of  $\text{NO}_x$  (i.e.  $\text{NO} + \text{NO}_2$ ) from 17 to  $0.64 \text{ kg year}^{-1}$  and volatile organic compounds from 35 to  $1 \text{ kg year}^{-1}$ , how would the global emissions of these compounds change? What effect might this have on smog?
  12. What would the answers to the three previous questions be if the average gas mileage were 15 and 25 km  $\text{L}^{-1}$ ? Based on these calculations, make a statement about the relationship between air pollution and efficiency.
  13. Why might formaldehyde concentrations be higher in manufactured homes *versus* conventional homes, such as the data shown in Table 1.5? How might time since construction affect these data?
  14. Explain why the bars for acute toxicity ( $\text{LC}_{50}$ ) are so much taller than those for chronic toxicity (MRL and cancer risk) in Figure 1.8.
  15. At 25 °C and 760 mmHg, express 15 ppm benzene, 180 ppb ozone and 500 ppm of sulfuric acid in  $\mu\text{g m}^{-3}$ .
  16. What may cause the above calculations of benzene and sulfuric acid to be incorrect?
  17. Explain why a first responder needs to know the density of substances that may be in a building? Why do the different densities between air and those of carbon disulfide and ammonia matter for a first responder?
  18. How is the formation of  $\text{CO}_2$  different in respiration *versus* combustion?
  19. A 200 scfm gas stream from the ground consisting of 60% by volume methane and 40% carbon dioxide is to be treated by an incinerator. The gas is to be burned with 20% excess air at 980 °C. Find the stoichiometric amount of air required, the total auxiliary air required, the total influent gas flow rate to the incinerator, and the total emission rate from the incinerator. What could be a likely source of this gas stream? In the real-world, what else is likely to be in this gas stream?
  20. Why do concentrations of  $\text{H}_2\text{O}$  vapor and  $\text{CO}_2$  vary so much in the atmosphere compared to most other substances?
  21. Name two atmospheric gases that absorb incoming (shortwave) solar radiation.
  22. Name two gases that absorb outgoing thermal (infrared) radiation.
  23. Why does such a small amount of the atmosphere's gases not drift off into space?
  24. Which principal atmospheric gas changes the most in concentration with altitude?
  25. Describe the major changes in temperature profile in the troposphere and stratosphere. Explain.
  26. What is the spectral range of thermal radiation?
  27. At what spectral range is the atmosphere transparent to IR energy (i.e. heating)?
  28. Define atmospheric pressure.
  29. What causes the fluid dynamics (i.e. movement of air) in the atmosphere?
  30. What are the major sources of  $\text{CH}_4$  and  $\text{CO}_2$  in the environment? How do these two compounds relate to each other?
  31. Why has the preindustrial concentration of  $\text{N}_2\text{O}$  changed so little as of 1998 compared to that of methane and carbon dioxide?
  32. What were the sources of perfluoromethane before the industrial revolution? Why has it doubled since then?
  33. What are some of the possible air pollutants that can be released by confined animal feeding operations? What can be done to address them?
  34. Why was asbestos used so commonly in the twentieth century?

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13. Newton actually co-invented the calculus with Wilhelm Leibniz in the 17th century. Both are credited with devising the symbolism and the system of rules for computing derivatives and integrals, but their notation and emphases differed. A debate rages on who did what first, but both of these giants had good reason to revise the language of science; i.e. mathematics, to explain motion.

# The Physics of the Atmosphere

The atmosphere is the environmental compartment into which air pollutants are emitted and serves as the medium through which air pollutants are transported and dispersed. While being transported, the pollutants may undergo chemical reactions that transform the released pollutants into new substances. These transformation products may be more or may be less polluting than the emitted pollutants. In addition, the emitted and transformed compounds, may be removed by physical processes such as gravitational settling, impaction, and wet removal.

This chapter provides an introduction to the basic concepts of meteorology and other aspects of physics that apply to air pollution.

## 2.1 ENERGY

All of the energy that drives the atmosphere is derived from the sun. During its elliptical orbit, the earth is at an average of 150 million km from the sun. In spite of this great distance the radiant energy, i.e. electromagnetic radiation, is sufficient to support life and the myriad human activities. The electromagnetic spectrum is shown in Figure 2.1. After reaching the earth's atmosphere and surface, the solar radiation is converted to various forms, including mechanical energy that moves the molecules in the atmosphere, chemical energy via photosynthesis and respiration, and potential energy stored in fossil fuels.

Although this energy is, in part, furnished directly to the atmosphere, it is primarily received at the earth's surface and redistributed by several processes. The earth's gravity keeps the thin layer of gases that constitute the atmosphere from escaping. The combination of solar heating and the spin of the earth causes internal pressure forces in the atmosphere, resulting in numerous atmospheric motions. The strength of the sun's radiation, the distance of the earth from the sun, the mass and diameter of the earth, and the existence

and composition of the atmosphere combine to make the earth habitable. This particular combination of conditions would not be expected to occur frequently throughout the universe.

The volume of the atmosphere consists approximately of 76% nitrogen, 20% oxygen, 3% water, 0.9% argon, and 0.03% carbon dioxide; the rest mainly made up of inert and relatively non-reactive gases such as neon, helium, methane, krypton and xenon, and other gases including nitrous oxide and hydrogen. Compared with the average radius of the earth, 6370 km, the atmosphere is an incredibly thin veil; 90% of its mass is below 12 km and 99% below 30 km. In spite of its thinness,

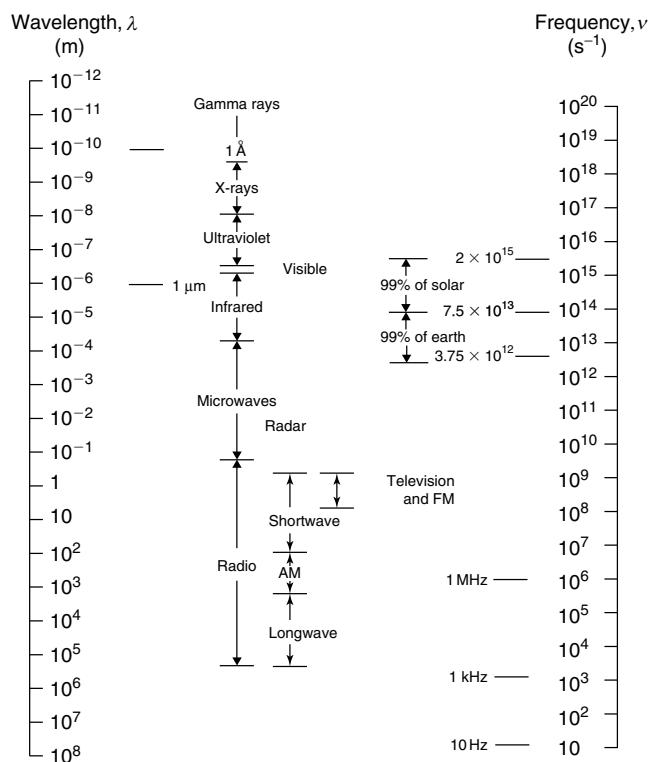


FIGURE 2.1 Electromagnetic spectrum, with regions of solar and earth radiation denoted.

however, the total mass of the atmosphere is about  $5 \times 10^{18}$  kg. Therefore, its heat content and energy potential are very large.

### 2.1.1 Radiation from a Blackbody

Physics applies the term blackbody to an object that is a perfect emitter and absorber of radiation at all wavelengths. Although no such object exists in nature, the properties are useful for comparison with materials found in the real world. The amount of radiation, or radiant flux over all wavelengths ( $F$ ), from a unit area of a blackbody is dependent on the temperature of that body and is given by the Stefan–Boltzmann law:

$$F = \sigma T^4 \quad (2.1)$$

where  $\sigma$  is the Stefan–Boltzmann constant and equals  $8.17 \times 10^{-11} \text{ cal cm}^{-2} \text{ min}^{-1} \text{ deg}^{-4}$  and  $T$  is the temperature in K. Radiation from a blackbody ceases at a temperature of absolute zero, 0 °K.

In comparing the radiative properties of materials to those of a blackbody, the terms absorptivity and emissivity are used. Absorptivity is the amount of radiant energy absorbed as a fraction of the total amount that falls on the object. Absorptivity depends on both frequency and temperature; for a blackbody it is 1. Emissivity is the ratio of the energy emitted by an object to the emission energy of a blackbody at the same temperature. It depends on both the properties of the substance and the frequency. Kirchhoff's law states that for any substance, its emissivity at a given wavelength and temperature equals its absorptivity. Note that the absorptivity and emissivity of a given substance may be quite variable for different frequencies.

As seen in Eqn (2.1), the total radiation from a blackbody is dependent on the fourth power of its absolute temperature. The frequency of the maximum intensity of this radiation is also related to temperature through Wien's displacement law (derived from Planck's law):

$$\nu_{\max} = 1.04 \times 10^{11} T \quad (2.2)$$

where frequency  $\nu$  is in inverse second units ( $\text{s}^{-1}$ ) and the constant is in  $\text{s}^{-1} \text{ K}^{-1}$ .

The radiant flux can be determined as a function of frequency from Planck's distribution law for emission:

$$E_\nu d\nu = c_1 \nu^3 [\exp(c_2 \cdot \nu \cdot T^{-1}) - 1]^{-1} d\nu \quad (2.3)$$

where

$$\begin{aligned} c_1 &= 2\pi \cdot h \cdot c^{-2} \\ h &= 6.62 \times 10^{-27} \text{ erg s} \text{ (Planck's constant)} \\ c &= 3 \times 10^8 \text{ m s}^{-1} \text{ (speed of light)} \\ c_2 &= h \cdot k^{-1} \end{aligned}$$

and

$$k = 1.37 \times 10^{-16} \text{ erg K}^{-1} \text{ (Boltzmann constant)}$$

The radiation from a blackbody is continuous over the electromagnetic spectrum. The use of the term black in blackbody, is quite misleading, as a number of nonblack materials approach blackbodies in behavior. The sun behaves almost like a blackbody; snow radiates in the infrared nearly as a blackbody. At some wavelengths, water vapor radiates very efficiently. Unlike solids and liquids, many gases absorb (and reradiate) selectively in discrete wavelength bands, rather than smoothly over a continuous spectrum.

### 2.1.2 Incoming Solar Radiation

As mentioned, the sun radiates approximately as a blackbody, with an effective temperature of about 6000 K. The total solar flux is  $3.9 \times 10^{26}$  W. Using Wien's law, it has been found that the frequency of maximum solar radiation intensity is  $6.3 \times 10^{14} \text{ s}^{-1}$  (wavelength ( $\lambda$ ) = 0.48 μm), which is in the visible part of the spectrum; 99% of solar radiation occurs between the frequencies of  $7.5 \times 10^{13} \text{ s}^{-1}$  ( $\lambda = 4 \mu\text{m}$ ) and  $2 \times 10^{15} \text{ s}^{-1}$  ( $\lambda = 0.15 \mu\text{m}$ ) and about 50% in the visible region between  $4.3 \times 10^{14} \text{ s}^{-1}$  ( $\lambda = 0.7 \mu\text{m}$ ) and  $7.5 \times 10^{14} \text{ s}^{-1}$  ( $\lambda = 4 \mu\text{m}$ ). The intensity of this energy flux at the distance of the earth is about  $1400 \text{ W m}^{-2}$  on an area normal to a beam of solar radiation. This value is known as the solar constant. Due to the eccentricity of the earth's orbit as it revolves around the sun once a year, the earth is closer to the sun in January (perihelion) than in July (aphelion). This results in about a 7% difference in radiant flux at the outer limits of the atmosphere between these two times.

Since the area of the solar beam intercepted by the earth is  $\pi E^2$ , where  $E$  is the radius of the earth. As the earth rotates, the energy falling within this circle is spread over the area of the earth's sphere,  $4\pi E^2$ , in 24 h, the average energy reaching the top of the atmosphere is one-fourth of the solar constant, i.e.  $338 \text{ W m}^{-2}$ . This accounts for the angle of solar radiation striking the earth's surface and the fact that only one-half of the earth is illuminated at any time. The average radiant energy reaching the outer limits of the atmosphere is depleted as it attempts to reach the earth's surface. Ultraviolet radiation with a wavelength less than 0.18 μm is strongly absorbed by molecular oxygen in the ionosphere 100 km above the earth; shorter X-rays are absorbed at even higher altitudes above the earth's surface. At 60–80 km above the earth, the absorption of 0.2–0.24 μm wavelength radiation leads to the formation of ozone; below 60 km there is so much ozone that much of the 0.2–0.3 μm wavelength radiation is absorbed. This ozone layer in the lower mesosphere and the top of the stratosphere shields life from much of the harmful ultraviolet radiation. The various layers warmed by the absorbed radiation reradiate in wavelengths dependent on their temperature

and spectral emissivity. Approximately 5% of the total incoming solar radiation is absorbed above 40 km. Under clear sky conditions, another 10–15% is absorbed by the lower atmosphere or scattered back to space by the atmospheric aerosols and molecules; as a result, only 80–85% of the incoming radiation reaches the earth's surface. With average cloudiness, only about 50% of the incoming radiation reaches the earth's surface, because of the additional interference of the clouds.

### 2.1.3 Albedo and Angle of Incidence

The portion of the incoming radiation reflected and scattered back to space is the albedo (unitless, between 0 and 1). The albedo of clouds, snow, and ice-covered surfaces is around 0.5–0.8, i.e. between 50 and 80% of the incoming solar radiation is reflected. The albedo of fields and forests is 0.03–0.3, and that of water is 0.02–0.05 except when the angle of incidence becomes nearly parallel to the water surface.<sup>1</sup> Table 2.1 shows the albedo of a water surface as a function of the angle of incidence. The albedo averaged over the earth's surface is about 0.35. Table 2.2 provides albedo values for various surfaces.

The albedos of communities can vary considerably, depending on vegetative cover, materials used and amount of paved surfaces. Albedo is a very important factor in microclimatology, e.g. it has a major impact on the urban heat island effect, because of which downtown areas have higher average summer temperatures than surrounding suburban and rural areas. Materials that reflect more and absorb less shortwave radiation can be used to ameliorate this heat island effect (see Figure 2.2). For example, dark asphalt has albedo between 5 and 8%; whereas grass has between 18 and 22% albedo. Some roofing materials have albedos greater than 70%.<sup>3</sup>

TABLE 2.1 Percent of Incident Radiation Reflected by a Water Surface (Albedo of Water)

Angle of Incidence	Percent Reflected	Percent Absorbed
90	2.0	98.0
70	2.1	97.9
50	2.5	97.5
40	3.4	96.6
30	6.0	94.0
20	13.0	87.0
10	35.0	65.0
5	58.0	42.0

Adapted from: Ref. 1.

TABLE 2.2 Albedo Values as Percentage of Incoming Shortwave Radiation for Various Surfaces and Locations

Surface	Albedo
Black soil, dry	14
Black soil, moist	8
Plowed field, moist	14
Sand, bright, fine	37
Dense, dry, and clean snow	86–95
Sea ice, slightly porous milky bluish	36
Ice sheet, covered by a water layer of 15–20 cm	26
Woody farm covered with snow	33–40
Deciduous forest	17
Tops of oak	18
Pine forest	14
Desert shrub land	20–29
Swamp	10–14
Prairie	12–13
Winter wheat	16–23
Heather	10
Yuma, Arizona	20
Washington, DC (September)	12–13
Winnipeg, Manitoba (July)	13–16
Great Salt Lake, Utah	3

Source: Ref. 2.

Although events taking place on the sun, such as sunspots and solar flares, alter the amount of radiation, the alteration is almost entirely in the X-ray and ultraviolet regions and does not affect the amount in the wavelengths reaching the earth's surface. Therefore, the amount of radiation from the sun that can penetrate to the earth's surface is remarkably constant.

In addition to the effect of albedo on the amount of radiation that reaches the earth's surface, the angle of incidence of the radiation compared to the perpendicular to the surface affects the amount of radiation flux on an area.<sup>4</sup> The flux on a horizontal surface  $S_h$  is as follows:

$$S_h = S \cos Z \quad (2.4)$$

where  $S$  is the flux through an area normal to the solar beam and  $Z$  is the zenith angle (between the local vertical, the zenith, and the solar beam).

Because of the tilt of the earth's axis by 23.5° with respect to the plane of the earth's revolution around the sun, the north pole is tilted toward the sun on June 22 and away from the sun on December 21 (see Figure 2.3). This tilt causes the solar beam to have

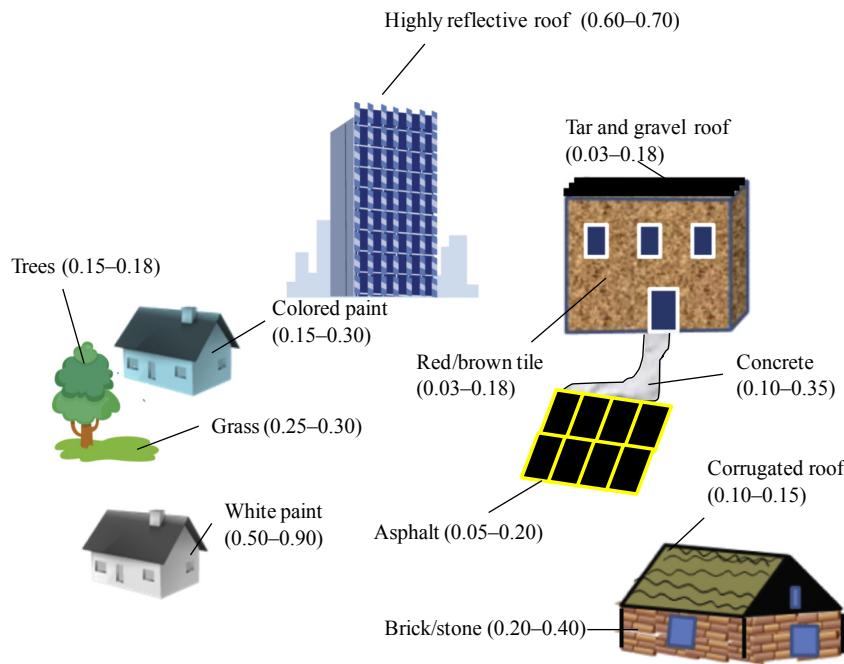


FIGURE 2.2 Albedos of various materials in urban areas. (For color version of this figure, the reader is referred to the online version of this book.) Data source: Ref. 3.

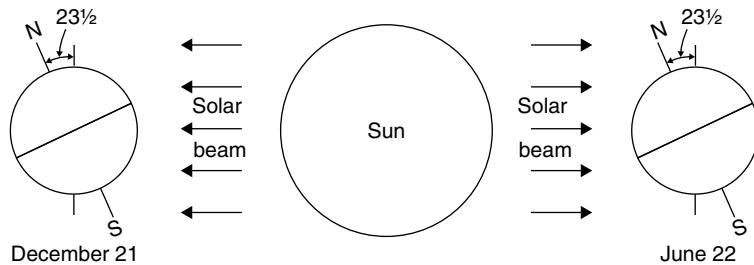


FIGURE 2.3 Orientation of the earth to the solar beam at the extremes of the earth's revolution around the sun.

perpendicular incidence at different latitudes depending on the date. The zenith angle  $Z$  is determined from:

$$\cos Z = \sin \varphi \sin \delta + \cos \varphi \cos \delta \cos \eta \quad (2.5)$$

where  $\varphi$  is latitude (positive for northern hemisphere, negative for southern hemisphere),  $\delta$  is solar declination (see Table 2.3), and  $\eta$  is hour angle,  $15^\circ \times$  the number of hours before or after local noon.

The solar azimuth  $\omega$  is the angle between south and the direction toward the sun in a horizontal plane:

$$\sin \omega = (\cos \delta \sin \eta) / \sin Z \quad (2.6)$$

Since many surfaces receiving sunlight are not horizontal, a slope at an angle  $i$  from the horizontal facing an azimuth  $\omega'$  degrees from south experiences an intensity of sunlight (neglecting the effects of the atmosphere) of

$$S_s = S[\cos Z \cos i + \sin Z \sin i \cos(\omega - \omega')] \quad (2.7)$$

Here  $\omega$  and  $\omega'$  are negative to the east of south and positive to the west.

At angles away from the zenith, solar radiation must penetrate a greater thickness of the atmosphere. Consequently, it will encounter more scattering due to

TABLE 2.3 Solar Declination

Date	Declination Degree	Date	Declination Degree
January 21	-20.90	July 21	20.50
February 21	-10.83	August 21	12.38
March 21	0.0	September 21	1.02
April 21	11.58	October 21	-10.42
May 21	20.03	November 21	-19.75
June 21	23.45	December 21	-23.43

Adapted from Ref. 4.

the presence of particles and greater absorption due to this greater thickness.

### 2.1.4 Outgoing Longwave Radiation

Because most ultraviolet radiation is absorbed from the solar spectrum and does not reach the earth's surface, the peak of the solar radiation which reaches the earth's surface is in the visible part of the spectrum. The earth reradiates nearly as a blackbody at a mean temperature of 290 K. The resulting infrared radiation extends over wavelengths of 3–80  $\mu\text{m}$ , with a peak at around 11  $\mu\text{m}$ . The atmosphere absorbs and reemits this longwave radiation primarily because of water vapor but also because of carbon dioxide in the atmosphere. Because of the absorption spectrum of these gases, the atmosphere is mostly opaque to wavelengths less than 7  $\mu\text{m}$  and greater than 14  $\mu\text{m}$  and partly opaque between 7 and 8.5  $\mu\text{m}$  and between 11 and 14  $\mu\text{m}$ . The atmosphere loses heat to space directly through the nearly transparent window between 8.5 and 11  $\mu\text{m}$  and also through the absorption and successive reradiation by layers of the atmosphere containing these absorbing gases.

Different areas of the earth's surface react quite differently to heating by the sun. For example, although a sandy surface reaches fairly high temperatures on a sunny day, the heat capacity and conductivity of sand are relatively low; the heat does not penetrate more than about 0.2–0.3 m and little heat is stored. In contrast, in a body of water, the sun's rays penetrate several meters and slowly heat a fairly deep layer. In addition, the water can move readily and convection can spread the heat through a deeper layer. The heat capacity of water is considerably greater than that of sand. All these factors combine to allow considerable storage of heat in water bodies compared to that of land.

### 2.1.5 Heat Balance

Because of the solar beam's more direct angle of incidence in equatorial regions, considerably more radiation penetrates and is stored by water near the equator than water nearer the poles. This excess is not compensated for by the outgoing longwave radiation, yet there is no continual buildup of heat in equatorial regions. The first law of thermodynamics requires that the energy entering the system (earth's atmosphere) be balanced with that exiting the system. Figure 2.4 shows the annual mean incoming and outgoing radiation averaged over latitude bands. There is a transfer of heat poleward from the equatorial regions to make up for a net outward transfer of heat near the poles. This heat is transferred by air and ocean currents as warm currents move poleward and cool currents move equatorward.<sup>4</sup> Considerable heat

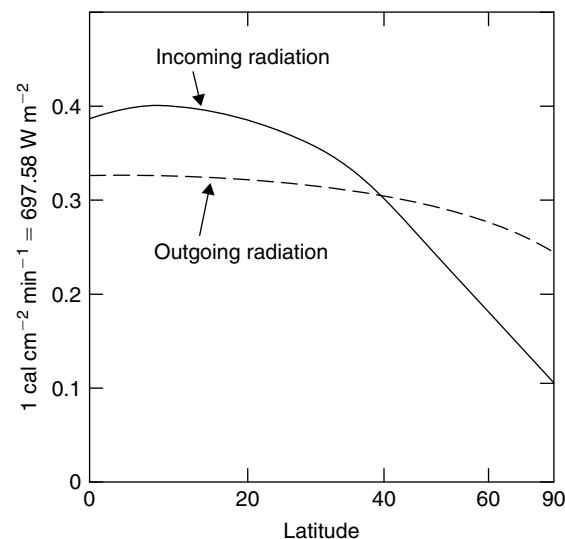


FIGURE 2.4 Annual mean radiation by latitude. Note that the latitude scale simulates the amount of the earth's surface area between the latitude bands. Incoming radiation is that absorbed by earth and atmosphere. Outgoing radiation is that leaving the atmosphere. ( $1 \text{ cal cm}^{-2} \text{ min}^{-1} = 697.58 \text{ W m}^{-2}$ ). Adapted from: Ref. 4.

transfer occurs by the evaporation of water in the tropics and its condensation into droplets farther poleward, with the release of the heat of condensation. Enough heat is transferred to result in no net heating of the equatorial regions or cooling of the poles.<sup>5</sup> The poleward flux of heat across various latitudes is shown in Table 2.4.

Taking the earth as a whole over a year or longer, because there is no appreciable heating or cooling, there is a heat balance between the incoming solar radiation and the radiation escaping to space.<sup>6</sup> This balance is depicted as bands of frequency of electromagnetic radiation in Figure 2.5.

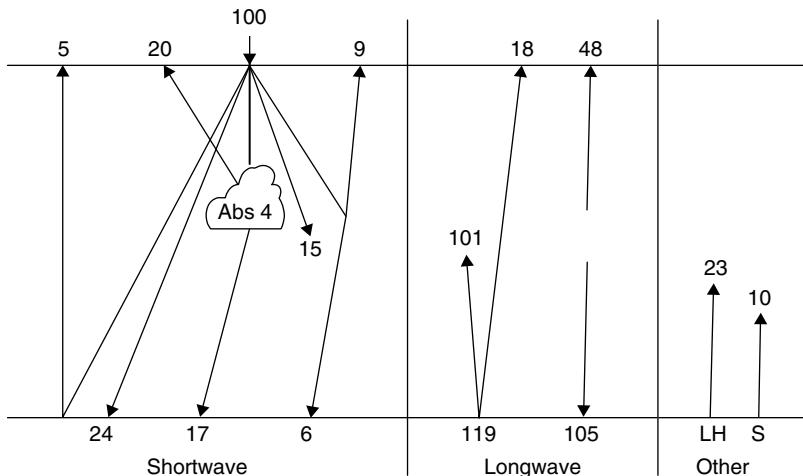
For every 100 units of energy entering the atmosphere, 51 units are absorbed by the earth's surface, 19 units are absorbed by the atmosphere, and 30 units are reflected back into space. Thus, there are 70 units that will be eventually reradiated as longwave radiation. Thermodynamically, the earth operates as a large heat engine, with hot–cold contrasts that generate power. Heat may be transferred with or without matter's movement. Heat is

TABLE 2.4 Poleward Flux of Heat across Latitudes ( $10^{19} \text{ kcal year}^{-1}$ )

Latitude	Flux	Latitude	Flux
10	1.21	50	3.40
20	2.54	60	2.40
30	3.56	70	1.25
40	3.91	80	0.35

Adapted from: Ref. 5.

**FIGURE 2.5 Radiation heat balance.** The 100 units of incoming shortwave radiation are distributed: reflected from earth's surface to space, 5; reflected from cloud surfaces to space, 20; direct reaching earth, 24; absorbed (Abs) in clouds, 4; diffuse reaching earth through clouds, 17; absorbed in atmosphere, 15; scattered to space, 9; and scattered to earth, 6. The longwave radiation comes from (1) the earth radiating 119 units: 101 to the atmosphere and 18 directly to space, and (2) the atmosphere radiating 105 units back to earth and 48 to space. Additional transfers from the earth's surface to the atmosphere consist of latent heat (LH), 23; and sensible (S) heat, 10. Ref. 7.



transported by conduction, convection, and advection. During conduction, heat is transferred through matter without transferring the matter itself. Due to heat-induced density differentials, heat is transferred with matter moving vertically (i.e. conduction) or horizontally (i.e. advection).<sup>2</sup>

The heat exchange involves the two most abundant fluids, air and water, and can be seen as an ocean–atmosphere interaction. About 60% of the heat exchange is attributed to air movements, and approximately 40% is the result of ocean currents. In the oceans, warm water flows poleward along the western side of an ocean basin and cold water flows toward the equator on the eastern side. At higher latitudes, warm water moves poleward in the eastern side of the ocean basin and cold water flows toward the equator on the western side.<sup>7</sup>

## 2.2 MOTION

Vertical air motions affect both weather and the mixing processes of importance to air pollution. Upward vertical motions can be caused by lifting over terrain, lifting over weather fronts, and convergence toward low-pressure centers. Downward vertical motions can be caused by sinking to make up for divergence near

high-pressure centers. When the atmosphere resists vertical motions, it is called stable; when the atmosphere enhances vertical motions, it is called unstable or in a state of instability.

In incompressible fluids<sup>a</sup>, such as water, the vertical structure of temperature very simply reveals the stability of the fluid. When the lower layer is warmer and thus less dense than the upper layer, the fluid is unstable so that convective currents will cause it to overturn. When the lower layer is cooler than the upper layer, the fluid is stable and vertical exchange is minimal. However, because air is compressible, the determination of stability is somewhat more complicated. The temperature and density of the atmosphere normally decrease with elevation. Air compressibility and convection is further complicated since density is also affected by the amount of moisture in the air.

The relationship between pressure  $p$ , volume  $V$ , mass  $m$ , and temperature  $T$  is given by the equation of state:

$$pV = RmT \quad (2.8)$$

where  $R$  is a specific gas constant, which is equal to the universal gas constant divided by the gram molecular weight of the gas. Since the density  $\rho$  is  $m/V$ , the equation can be rewritten as:

$$p = R\rho T \quad (2.9)$$

<sup>a</sup>For atmospheric purposes, many liquids, including water, are usually considered to be “incompressible”. In fact, water compressibility has been published, i.e. at 0 °C, its compressibility is  $5.1 \times 10^{-10} \text{ Pa}^{-1}$ , reaching a minimum of  $4.4 \times 10^{-10} \text{ Pa}^{-1}$  at approximately 45 °C, after which the compressibility again increases with increasing temperature. See: Fine RA, Millero FJ. Compressibility of water as a function of temperature and pressure. *J Chem Phys* 1973;59(10):5529. <http://dx.doi.org/10.1063/1.1679903>. Water’s compressibility, expressed as change of volume per volume ( $\Delta V/V$ ), is  $4.6 \times 10^{-5}$  per atm in the vicinity of 1 atm dropping to  $4.0 \times 10^{-5} \text{ atm}^{-1}$  around 250 atm. Pressure increases about 1 atm per 10 m depth. So, even under 4 km of ocean water (the mean ocean depth), i.e. 400 atm, the water only decreases by about 1.8% volume (The top 250 atm:  $250 \times (4.6 \times 10^{-5} \text{ atm}^{-1}) = 0.0115$ , and the lower 150 atm:  $150 \times (4.0 \times 10^{-5} \text{ atm}^{-1}) = 0.006$ ; total compression = 0.0175). Other liquids have similar compressibilities, e.g. phenol =  $5.0 \times 10^{-5} \text{ atm}^{-1}$ , aniline =  $4.5 \times 10^{-5} \text{ atm}^{-1}$  and benzene =  $9.5 \times 10^{-5} \text{ atm}^{-1}$ .

or considering specific volume  $\alpha = \rho^{-1}$  it may also be rewritten as:

$$\alpha p = RT \quad (2.10)$$

These equations combine the principles of two gas laws: Boyle's law, which states that when temperature is held constant the volume varies inversely with the pressure; and the law of Gay-Lussac, which states that when pressure is held constant the volume varies in proportion to the absolute temperature.

### 2.2.1 First Law of Thermodynamics

If a volume of air is held constant and a small amount of heat  $\Delta h$  is added, the temperature of the air will increase by a small amount  $\Delta T$ . This can be expressed as

$$\Delta h = c_v \Delta T \quad (2.11)$$

where  $c_v$  is the specific heat at constant volume. In this case, all the heat added is used to increase the internal energy of the volume affected by the temperature. From the equation of state (Eqn (2.8)), it can be seen that the pressure will increase.

If, instead of being restricted, the volume of air considered is allowed to remain at an equilibrium constant pressure and expand in volume, as well as change temperature in response to the addition of heat, this can be expressed as

$$\Delta h = c_v \Delta T + p \Delta v \quad (2.12)$$

By using the equation of state, the volume change can be replaced by a corresponding pressure change:

$$\Delta h = c_p \Delta T + v \Delta p \quad (2.13)$$

where  $c_p$  is the specific heat at constant pressure and equals  $c_v + R_d$ , where  $R_d$  is the gas constant for dry air.

### 2.2.2 Adiabatic Processes

An adiabatic process is one with no loss or gain of heat to a volume of air. Conversely, if heat is supplied or withdrawn, the process is diabatic or nonadiabatic. Near the earth's surface, where heat is exchanged between the earth and the air, the processes are diabatic.

However, at increasing altitude from the surface, processes frequently are adiabatic. For example, if a volume (parcel) of air is forced upward over a ridge, the upward-moving air will encounter decreased atmospheric pressure and will expand and cool. If the air is not saturated with water vapor, the process is called dry adiabatic. Since no heat is added or subtracted,  $\Delta h$  in Eqn (2.13) can be set equal to zero, and introducing

the hydrostatic equation, the change in pressure can be expressed as:

$$-\Delta p = \rho g \Delta z \quad (2.14)$$

Furthermore, combining equations results in:

$$-\Delta T \Delta z^{-1} = g c_p^{-1} \quad (2.15)$$

Thus air cools as it rises and warms as it descends. Since this assumes an adiabatic process,  $-\Delta T \Delta z^{-1}$  defines  $\gamma_d$ , the dry adiabatic process lapse rate, which is a constant equal to  $0.0098 \text{ K m}^{-1}$ . This is nearly  $1 \text{ K } 100 \text{ m}^{-1}$  or  $5.4^\circ\text{F } 1000 \text{ ft}^{-1}$ .

If an ascending air parcel reaches saturation, the addition of latent heat from condensing moisture will partially overcome the cooling due to expansion. Therefore, the saturated adiabatic lapse rate (of cooling)  $\gamma_w$  is smaller than  $\gamma_d$ .

### 2.2.3 Determining Stability

By comparing the density changes of a rising or descending parcel of air in relation to the density of the surrounding environment, the enhancement or suppression of the vertical motion can be determined. Since pressure decreases with height, there is an upward-directed pressure gradient force. The force of gravity is downward. The difference between these two forces is the buoyancy force. Using Newton's second law of motion, which indicates that a net force equals an acceleration, the acceleration  $a$  of an air parcel at a particular position is given by

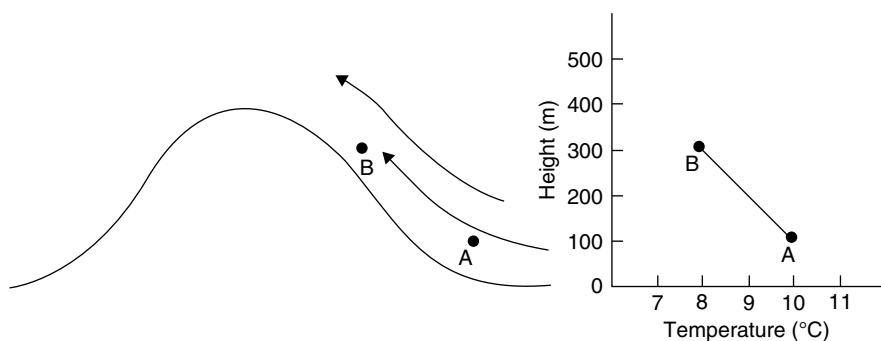
$$a = g(T_p - T_e) T_p^{-1} \quad (2.16)$$

where  $g$  is the acceleration due to gravity ( $9.8 \text{ m s}^{-2}$ ),  $T_p$  is the temperature of an air parcel that has undergone a temperature change according to the process lapse rate, and  $T_e$  is the temperature of the surrounding environment at the same height. (Temperatures are expressed in degrees Kelvin.)

Figure 2.6 shows the temperature change undergone by a parcel of air forced to rise 200 m over a ridge. Assuming that the air is dry, and therefore that no condensation occurred, this figure also represents the warming of the air parcel if the flow is reversed so that the parcel moves downslope from B to A.

Comparing the temperature of this parcel to that of the surrounding environment (see Figure 2.7), the ascension from 100 to 300 m changes the parcel temperature at the dry adiabatic process lapse rate. The dashed line is a dry adiabatic line or dry adiabat. Suppose that the environmental temperature structure is shown by the solid curve. Since the lapse rate of the surrounding environment in the lowest 150–200 m is steeper than the adiabatic lapse rate (superadiabatic)—that is, since the

**FIGURE 2.6 Cooling of ascending air.** Dry air forced to rise 200 m over a ridge cools adiabatically by 2 °C.



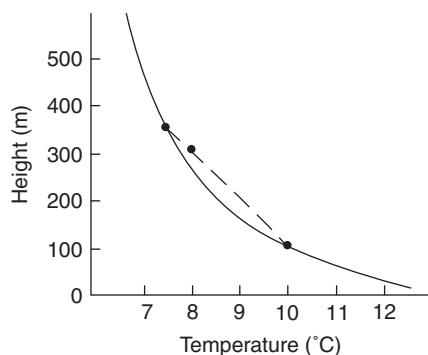
temperature drops more rapidly with height—this part of the environment is thermally unstable. At 300 m the parcel is 0.2 °C warmer than the surrounding environment, the resulting acceleration is upward, and the atmosphere is enhancing the vertical motion, so it is unstable. The parcel of air continues to rise until it reaches 350 m, where its temperature is the same as that of the environment and its acceleration drops to zero. However, above 350 m the lapse rate of the surrounding environment is not as steep as the adiabatic lapse rate (subadiabatic), and this part of the environment is thermally stable (it resists upward or downward motion).

If the temperature structure, instead of being that of Figure 2.7, differs primarily in the lower layers, it resembles Figure 2.8, where a temperature inversion exists, i.e. an increase rather than a decrease of temperature with height. In the forced ascent of the air parcel up the slope, dry adiabatic cooling produces parcel temperatures that are everywhere cooler than the environment; acceleration is downward, resisting displacement; and the atmosphere is stable. In this situation, pollutants can be trapped in stable layers near the earth's surface, which can prolong exposures and lead to the unhealthy conditions of air pollution episode.

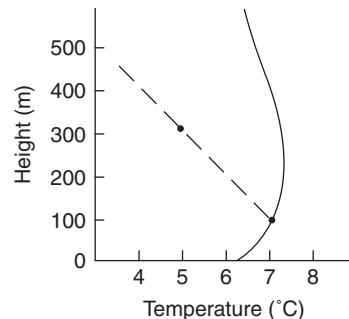
Thermodynamic diagrams which show the relationships between atmospheric pressure (rather than altitude), temperature, dry adiabatic lapse rates, and moist adiabatic lapse rates are useful for numerous

atmospheric thermodynamic estimations. Standard meteorology provides additional details. In air pollution meteorology, the thermodynamic diagram may be used to determine the current mixing height, i.e. the top of the neutral or unstable layer. The mixing height at a given time may be estimated by use of the morning radiosonde ascent plotted on a thermodynamic chart. The surface temperature at the given time is plotted on the diagram. If a dry adiabat is drawn through this temperature, the height aboveground at the point where this dry adiabat intersects the morning sounding is the mixing height for that time. The mixing height for the time of maximum temperature is the maximum mixing height. Use of this sounding procedure provides an approximation because it assumes that there has been no significant advection since the time of the sounding.

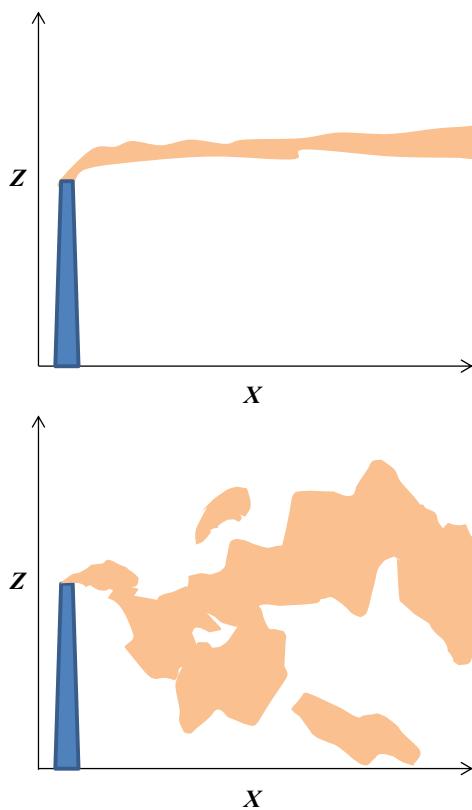
Stability is described as either static or dynamic. The former does not account for wind speed. However, increasing wind speed increases vertical mixing of air parcels. Thus, static stability is based on buoyancy forces resulting from density differences; whereas dynamic stability is based on shear forces. Describing the stability of an air parcel must include these and other factors. For example, if the wind speed is  $<2 \text{ m s}^{-1}$  and incoming solar radiation is strong, the atmosphere would be very unstable. Conversely, on a clear night, the same calm winds would make for a stable air mass. These conditions induce very different air pollution plumes (see Figure 2.9).



**FIGURE 2.7 Temperature of a parcel of air forced to rise 200 m compared to the superadiabatic environmental lapse rate.** Since the parcel is still warmer than the environment, it will continue to rise.



**FIGURE 2.8 Temperature of a parcel of air forced to rise 200 m compared to an inversion environmental lapse rate.** Since the parcel is cooler than the environment, it will sink back to its original level.



**FIGURE 2.9** Air pollution plumes (side views) under stable (top) and unstable (bottom) atmospheric conditions. (For color version of this figure, the reader is referred to the online version of this book.)

To address these complexities, meteorologists have devised atmospheric stability classifications, which are addressed in detail in Chapter 27.

#### 2.2.4 Potential Temperature

The atmosphere is very dynamic in terms of temperature and pressure, which calls for a benchmark to compare conditions at a specific time and place to other conditions. This is particularly important for stability, i.e. determining the extent to which one layer of the atmosphere is more or less stable than another, given various temperatures and pressures.

Potential temperature ( $\theta$ ) provides a benchmark, i.e. a means of identifying the dry adiabat to which a particular given atmospheric combination of temperature and pressure is related. Potential temperature is the temperature of the air if the measured temperature were at sea level and 1 atm pressure, i.e. the temperature that an unsaturated parcel of air would have if brought adiabatically and reversibly from its initial standard pressure ( $p_0$ ):

$$\theta = T \left[ \frac{p_0}{p} \right]^k \quad (2.17)$$

where  $T$  = temperature (in K) and  $k$  is known as the Poisson constant, which is usually assumed to be  $2/7 \approx 2.86$ , i.e. the ratio of the gas constant ( $R = 8.316963 \text{ J mol}^{-1} \text{ K}^{-1}$ ) to the specific heat capacity at constant pressure for an ideal diatomic gas.

The potential temperature  $\theta$  can be calculated from the temperature ( $T$ ) at a given pressure  $p$ :

$$\theta = T \left[ \frac{1 \text{ atm}}{p} \right]^{0.286} \quad (2.18)$$

Or, if  $p$  is in millibars (mb), Eqn (2.17) would be:

$$\theta = T \left[ \frac{1000}{p} \right]^{0.286} \quad (2.19)$$

This value is the same as the temperature that a parcel of dry air would have if brought dry adiabatically to a pressure of 1000 mb.

If the potential temperature decreases with height, the atmosphere is unstable. If the potential temperature increases with height, the atmosphere is stable. The average lapse rate of the atmosphere is about  $6.5 \text{ }^{\circ}\text{C km}^{-1}$ ; that is, the potential temperature increases with height and the average state of the atmosphere is stable.

If the atmosphere is in a dry adiabatic, hydrostatic condition, its  $\theta$  does not vary vertically:

$$\frac{\partial \theta}{\partial z} = 0 \quad (2.20)$$

This means that in a dry adiabatic atmosphere,  $T$  must decrease with height.

It is important to keep in mind that near the earth's surface the atmosphere is continuously undergoing heating and cooling. Thus, the adiabatic assumptions are rarely fulfilled. Neither are the hydrostatic, dry conditions. That is, the lower portions of the troposphere are seldom neither adiabatic nor dry. Thus, near the surface the atmosphere's slope of  $\frac{dT}{dz}$  does not equal the dry adiabatic lapse rate. Parcels of air can be assumed to be under local adiabatic conditions, since they are commonly transported locally by a turbulent atmosphere, which does not allow much energy exchange during these short times of transport.

#### 2.2.5 Effect of Mixing

The mixing of air in a vertical layer produces constant potential temperature throughout the layer. Such mixing is usually mechanical, such as air movement over a rough surface. In Figure 2.10 the initial temperature structure is subadiabatic (solid line). The effect of mixing is to achieve a mean potential temperature throughout the layer (dashed line), which in the lower part is dry adiabatic. The bottom part of the layer is warmed; the top is cooled. Note that above the vertical extent of the mixing, an

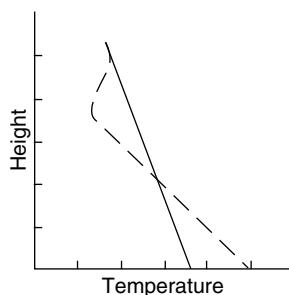


FIGURE 2.10 Effect of forced mixing (dashed line) on the environmental subadiabatic lapse rate (solid line). Note the formation of an inversion at the top of the mixed layer.

inversion is formed connecting the new cooled portion with the old temperature structure above the zone of mixing. If the initial layer has considerable moisture, although not saturated, cooling in the top portion of the layer may decrease the temperature to the point where some of the moisture condenses, forming clouds at the top. An example of this is the formation of an inversion and a layer of stratus clouds along the California coast.

Inversions at the surface are caused frequently at night by radiational cooling of the ground, which in turn cools the air near it. Such inversions are known as radiation or nocturnal inversions.

### 2.2.6 Subsidence Inversions

There is usually some descent (subsidence) of air above surface high-pressure systems. This air warms dry adiabatically as it descends, decreasing the relative humidity and dissipating any clouds in the layer. A subsidence inversion forms as a result of this sinking. Since the descending air compresses as it encounters the increased pressures lower in the atmosphere, the top portion of the descending layer will be further warmed due to its greater descent than will the bottom portion of the layer (Figure 2.11). Occasionally a subsidence inversion descends all the way to the surface, but usually its base is well above the ground.

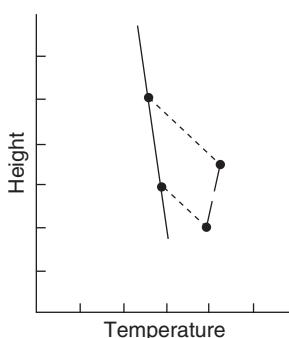


FIGURE 2.11 Formation of a subsidence inversion in subsiding (sinking) air. Note the vertical compression of the sinking layer which is usually accompanied by horizontal divergence.

Inversions are of considerable interest in relation to air pollution because of their stabilizing influence on the atmosphere, which suppresses the vertical motion that causes the vertical spreading of pollutants.

## 2.3 ENERGY–MOTION RELATIONSHIPS

The atmosphere is continuously in motion. The scales and magnitude of these motions extend over a wide range. Although vertical motions certainly occur in the atmosphere and are important to both weather processes and the movement of pollutants, for convenience the only horizontal component of velocity is often wind.

On the regional scale (hundreds to thousands of kilometers), the winds are most easily understood by considering the balance of various forces in the atmosphere. The applicable physical law is Newton's second law of motion,  $F = ma$ ; if a force  $F$  is exerted on a mass  $m$ , the resulting acceleration  $a$  equals the force divided by the mass. This can also be stated as the rate of change of momentum of a body, which is equal to the sum of the forces that act on the body. It should be noted that all the forces to be discussed are vectors; that is, they have both magnitude and direction. Although Newton's second law applies to absolute motion, it is most convenient to consider wind relative to the earth's surface. This assumption causes some slight difficulties, but they are usually easily managed.

### 2.3.1 Pressure Gradient Force

Three forces of importance to horizontal motion are the pressure gradient force, gravity, and friction. Atmospheric pressure equals mass times the acceleration of gravity. Considering a unit volume,  $p = \rho g$ ; the gravitational force on the unit volume is directed downward. Primarily because of horizontal temperature gradients, there are horizontal density gradients and consequently horizontal pressure gradients. The horizontal pressure gradient force  $p_h = \frac{\Delta p}{\rho \Delta x}$ , where  $\Delta p$  is the horizontal pressure difference over the distance  $\Delta x$ . The direction of this force and of the pressure difference measurement is locally perpendicular to the lines of equal pressure (isobars) and is directed from high to low pressure.

### 2.3.2 Coriolis Force

If the earth were not rotating, the wind would blow exclusively from high to low pressure. Close to the earth, it would be slowed by friction between the atmosphere and the earth's surface but would maintain the same direction with height. However, since the earth rotates on its axis, there is an apparent force acting on horizontal

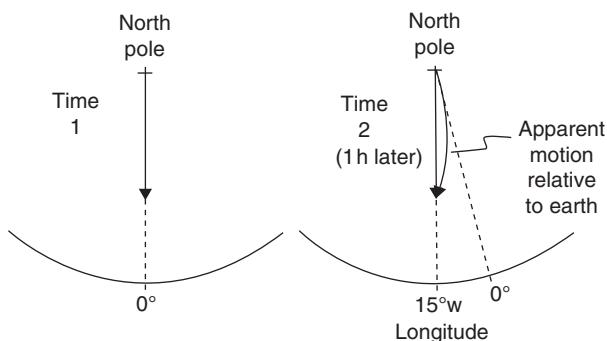


FIGURE 2.12 Effect of the Coriolis force. The path of air moving from the North Pole to the south as viewed from space is straight; as viewed from the earth's surface it is curved.

atmospheric motions when examined from a point of reference on the earth's surface. For example, consider a wind of velocity  $10 \text{ m s}^{-1}$  blowing at time 1 in the direction of the  $0^\circ$  longitude meridian across the north pole (see Figure 2.12). The wind in an absolute sense continues to blow in this direction for 1 h, and a parcel of air starting at the pole at time 1 travels 36 km in this period. However, since the earth turns  $360^\circ$  every 24 h, or  $15^\circ \text{ h}^{-1}$ , it has rotated  $15^\circ$  in the hour and we find that at time 2 (60 min after time 1) the  $15^\circ$  meridian is now beneath the wind vector.

As viewed from the absolute frame of reference (i.e. space), the flow has continued in a straight line. However, as viewed from the earth, the flow has undergone an apparent deflection to the right. The force required to produce this apparent deflection is the Coriolis force and is equal to  $D = vf$  where  $f$ , the Coriolis parameter, equals  $2\Omega \sin \varphi$ . Here,  $\Omega$  is the angular speed of the earth's rotation,  $\frac{2\pi}{24 \times 60 \times 60} = 7.27 \times 10^{-5} \text{ s}^{-1}$ , and  $\varphi$  is the latitude. The value of  $f$  is maximal at the poles and zero at the equator. The deflecting force is to the right of the wind vector in the northern hemisphere and to the left in the southern hemisphere. For the present example, the deflecting force is  $1.45 \times 10^{-3} \text{ m s}^{-2}$ , and the amount of deflection after the 36-km movement in 1 h is 9.43 km.

### 2.3.3 Geostrophic Wind

Friction between the atmosphere and the earth's surface may generally be neglected at altitudes of about 700 m and higher. Therefore, large-scale air currents closely represent a balance between the pressure gradient force and the Coriolis force. Since the Coriolis force is at a right angle to the wind vector, when the Coriolis force is equal in magnitude and opposite in direction to the pressure gradient force, a wind vector perpendicular to both of these forces occurs, with its direction along the lines of constant pressure (Figure 2.13). In the northern hemisphere, the low pressure is to the left of the wind vector (Buy's Ballot's law); in the

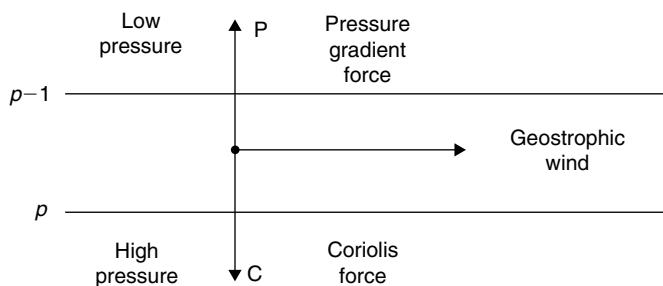


FIGURE 2.13 Balance of forces resulting in geostrophic wind.

southern hemisphere, low pressure is to the right. The geostrophic velocity is:

$$v_g = \frac{-\Delta p}{\rho f \Delta d} \quad (2.21)$$

When the isobars are essentially straight, the balance between the pressure gradient force and the Coriolis force results in a geostrophic wind parallel to the isobars.

### 2.3.4 Gradient Wind

When the isobars are curved, an additional force, a centrifugal force outward from the center of curvature, enters into the balance of forces. In the case of curvature around low pressure, a balance of forces occurs when the pressure gradient force equals the sum of the Coriolis and centrifugal forces (see Figure 2.14) and the wind continues parallel to the isobars. In the case of curvature around high pressure, a balance of forces occurs when the sum of the pressure gradient and centrifugal forces equals the Coriolis force (see Figure 2.15). To maintain a given gradient wind speed, a greater pressure gradient force (tighter spacing of the isobars) is required in the flow around low-pressure systems than in the flow around high-pressure systems.

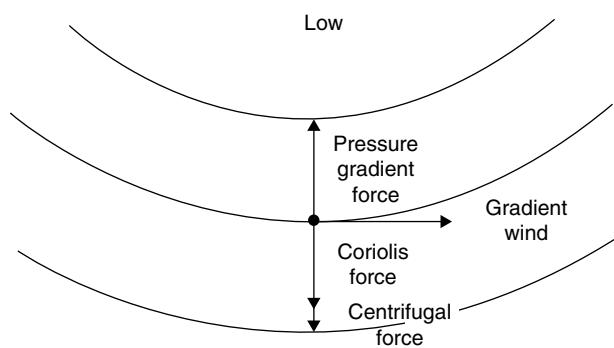


FIGURE 2.14 Balance of forces resulting in gradient wind around low pressure.

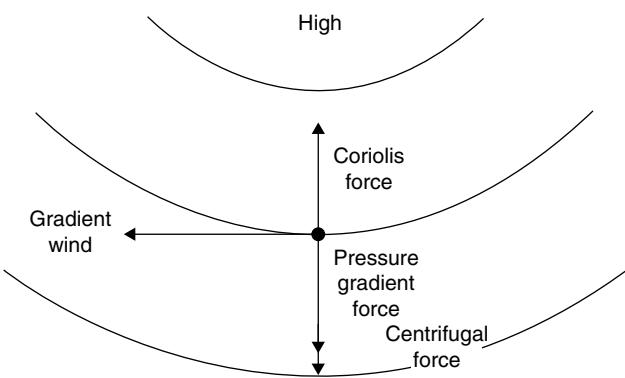


FIGURE 2.15 Balance of forces resulting in gradient wind around high pressure. Note that the wind speed is greater for a given pressure gradient force than that around low pressure.

### 2.3.5 Friction

The frictional effect of the earth's surface on the atmosphere increases as the earth's surface is approached from aloft. Assuming geostrophic balance aloft, the effect of friction with distance approaching the earth's surface is to slow the wind velocity, which in turn decreases the Coriolis force. The wind then turns toward low pressure until the resultant vector of the frictional force and the Coriolis force balances the pressure gradient force (see Figure 2.16). The greater the friction, the slower the wind and the greater the amount of turning toward low pressure. The turning of the wind

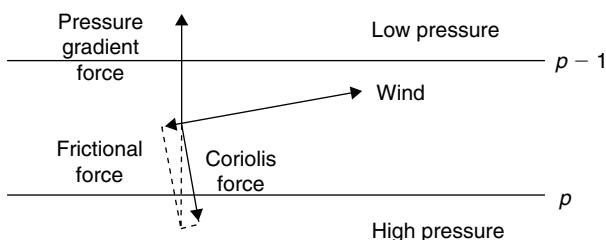


FIGURE 2.16 Effect of friction on the balance of forces causing wind to blow toward low pressure.

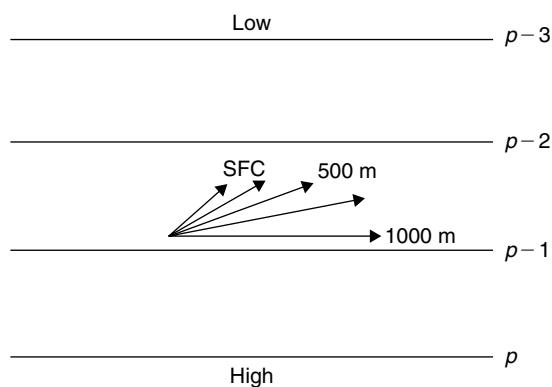


FIGURE 2.17 Hodograph showing variation of wind speed and direction with height aboveground. SFC, surface wind.

from the surface through the friction layer is called the *Ekman spiral*. A radial plot, or hodograph, of the winds through the friction layer is shown diagrammatically in Figure 2.17.

Note that this frictional effect will cause pollutants released at two different heights to tend to move in different directions. This is particularly important when predicting the path and expected destination of long-range transport of a plume.

In the friction layer where the isobars are curved, the effect of frictional drag is added to the forces discussed under gradient wind. The balance of the pressure gradient force, the Coriolis deviating force, the centrifugal force, and the frictional drag in the vicinity of the curved isobars results in windflow around low pressure and high pressure in the northern hemisphere, as shown in Figure 2.18.

### 2.3.6 Divergence

So far in discussing motion in the atmosphere, horizontal motions have been emphasized. Although of much smaller magnitude than horizontal motions, vertical motions are important both to daily weather formation and to the transport and dispersion of pollutants.

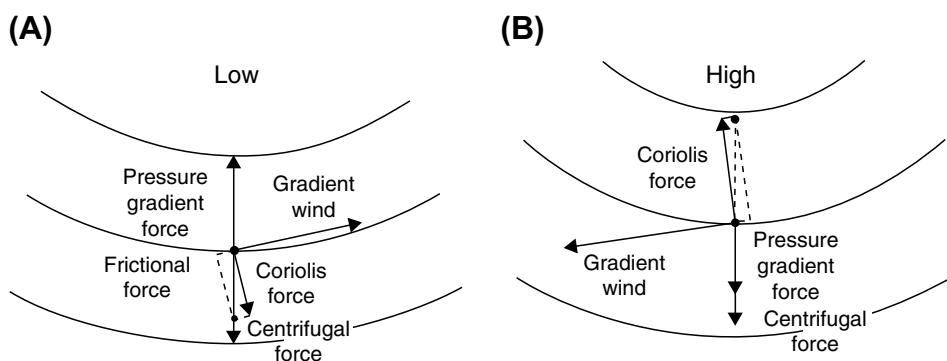


FIGURE 2.18 Effect of friction upon gradient wind around (A) low and (B) high pressures.

Persistent vertical motions are linked to the horizontal motions. If there is divergence (spreading) of the horizontal flow, there is sinking (downward vertical motion) of air from above to compensate. Similarly, converging (negative divergence) horizontal air streams cause upward vertical motions, producing condensation and perhaps precipitation in most air masses, as well as transport of air and its pollutants from near the surface to higher altitudes.

## 2.4 LOCAL WIND SYSTEMS

Frequently, local wind systems are superimposed on the larger-scale wind systems just discussed. These local flows are especially important to air pollution since they determine the amount of a pollutant that will come in contact with the receptor. In fact, local conditions may dominate when the larger-scale flow becomes light and indefinite. Local wind systems are usually quite significant in terms of the transport and dispersion of air pollutants.

### 2.4.1 Sea and Land Breezes

The sea breeze is a result of the differential heating of land and water surfaces by incoming solar radiation. Since solar radiation penetrates several meters of a body of water, it warms very slowly. In contrast, only the upper few centimeters of land are heated, and warming occurs rapidly in response to solar heating. Therefore, especially on clear summer days, the land surface heats rapidly, warming the air near the surface and decreasing its density. This causes the air to rise over the land, decreasing the atmospheric pressure near the surface relative to the pressure at the same altitude over the water surface. The rising air increases the pressure over the land relative to that above the water at altitudes of approximately 100–200 m. The air that rises over the land surface is replaced by cooler air from over the water surface. This air, in turn, is replaced by subsiding air from somewhat higher layers of the atmosphere over the water. Air from the higher-pressure zone several hundred meters above the surface then flows from over the land surface out over the water, completing a circular or cellular flow (see Figure 2.19). Any general flow due to large-scale pressure systems will be superimposed on the sea breeze and may either reinforce or inhibit it. Ignoring the larger-scale influences, the strength of the sea breeze will generally be a function of the temperature excess of the air above the land surface over that above the water surface.

Just as heating in the daytime occurs more quickly over land than over water, the radiational cooling at

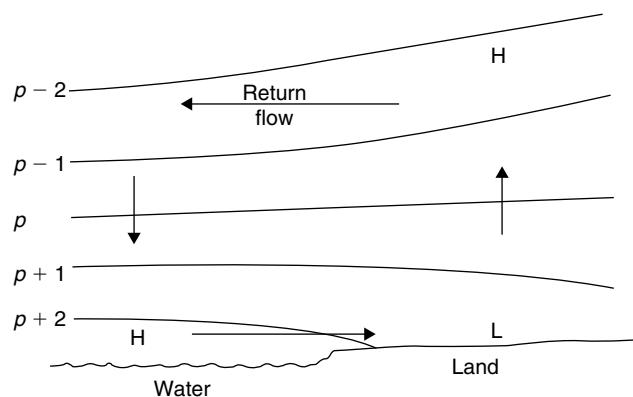


FIGURE 2.19 Sea breeze due to surface heating over land, resulting in thermals, and subsidence over water.

night occurs more quickly over land. The pressure pattern tends to be the reverse of that in the daytime. The warmer air tends to rise over the water, which is replaced by the land breeze from land to water, with the reverse flow (water to land) completing the circular flow at altitudes somewhat aloft. Frequently at night, the temperature differences between land and water are smaller than those during the daytime, and therefore the land breeze has a lower speed.

### 2.4.2 Mountain and Valley Winds

Solar heating and radiational cooling influence local flows in terrain situations. Consider midday heating of a south-facing mountainside. As the slope heats, the air adjacent to the slope warms, its density is decreased, and the air attempts to ascend (see Figure 2.20). Near the top of the slope, the air tends to rise vertically. Along each portion of the slope farther down the mountain, it is easier for each rising parcel of air to move upslope, replacing the parcel ahead of it rather than rising vertically. This upslope flow is the valley wind.

At night when radiational cooling occurs on slopes, the cool dense air near the surface descends along the

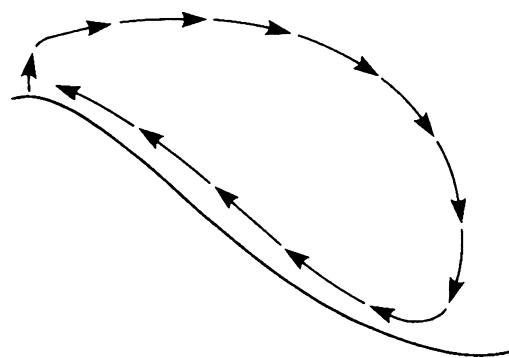


FIGURE 2.20 Upslope wind (daytime) due to greater solar heating on the valley's side than in its center.

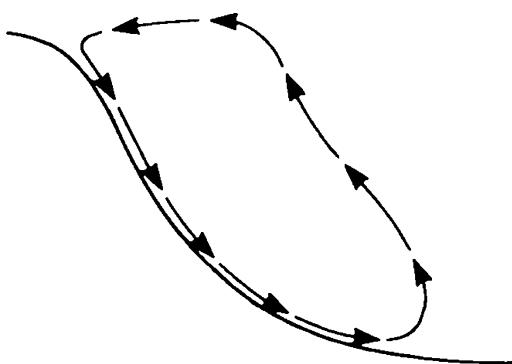


FIGURE 2.21 Downslope wind (night) due to more rapid radiational cooling on the valley's slope than in its center.

slope (see Figure 2.21). This is the downslope wind. To compensate for this descending air, air farther from the slope that is cooled very little is warmer relative to the descending air and rises, frequently resulting in a closed circular path. Where the downslope winds occur on opposite slopes of a valley, the cold air can accumulate on the valley floor. If there is any slope to the valley floor, this pool of cold air can move down the valley, resulting in a drainage or canyon wind.

Different combinations of valley and mountain slope, especially with some slopes nearly perpendicular to the incoming radiation and others in deep shadow, lead to many combinations of wind patterns, many nearly unique. Also, each local flow can be modified by the regional wind at the time which results from the current pressure patterns. Table 2.5 gives characteristics of eight different situations depending on the orientation of the

ridgeline and valley with respect to the sun, wind direction perpendicular or parallel to the ridgeline, and time of day. Figure 2.22 shows examples of some of the mountain and valley winds listed in Table 2.5. These are rather idealized circulations compared to observed, real-world flows at any one time.

The effect of solar radiation is different with valley orientation. An east–west valley has only one slope that is significantly heated—the south-facing slope may be near normal with midday sunshine. A north–south valley will have both slopes heated at midday. The effect of flow in relation to valley orientation is such that flows perpendicular to valleys tend to form circular eddies and encourage local flows; flows parallel to valleys tend to discourage local flows and to sweep clean the valley, especially with stronger wind speeds.

Air flows result from the combination of the general and local flows; the lighter the general flow, the greater the opportunity for generation of local flows.

Complicated terrain such as a major canyon with numerous side canyons will produce complicated and unique flows, especially when side canyon drainage flows reinforce the drainage flow in the main valley.

#### 2.4.3 Urban–Rural Circulations

Urban areas have surface roughness and thermal characteristics different from those of their rural surroundings. Although the increased roughness affects both the vertical wind profile and the vertical temperature profile, the effects due to the thermal features are dominant. The asphalt, concrete, and steel of urban

TABLE 2.5 Generalized Mesoscale Windflow Patterns Associated with Different Combinations of Wind Direction and Ridgeline Orientation

Wind Direction Relative to Ridgeline	Time of Day	Ridgeline Orientation	
		East–West	North–South
Parallel	Day	1. South-facing slope is heated—single helix	2. Upslope flow on both heated slopes—double helix
	Night	3. Downslope flow on both slopes—double helix	4. Downslope flow on both slopes—double helix
Perpendicular	Day	South-facing slope is heated	6. Upslope flow on both heated slopes—stationary eddy on one side of valley
	Night	5a. North wind—stationary eddy fills valley  5b. South wind—eddy suppressed, flow without separation  7. Indefinite flow—extreme stagnation in valley bottom	8. Indefinite flow—extreme stagnation in valley bottom

Examples of these ridgeline orientations at different times of day are shown in Figure 2.22.

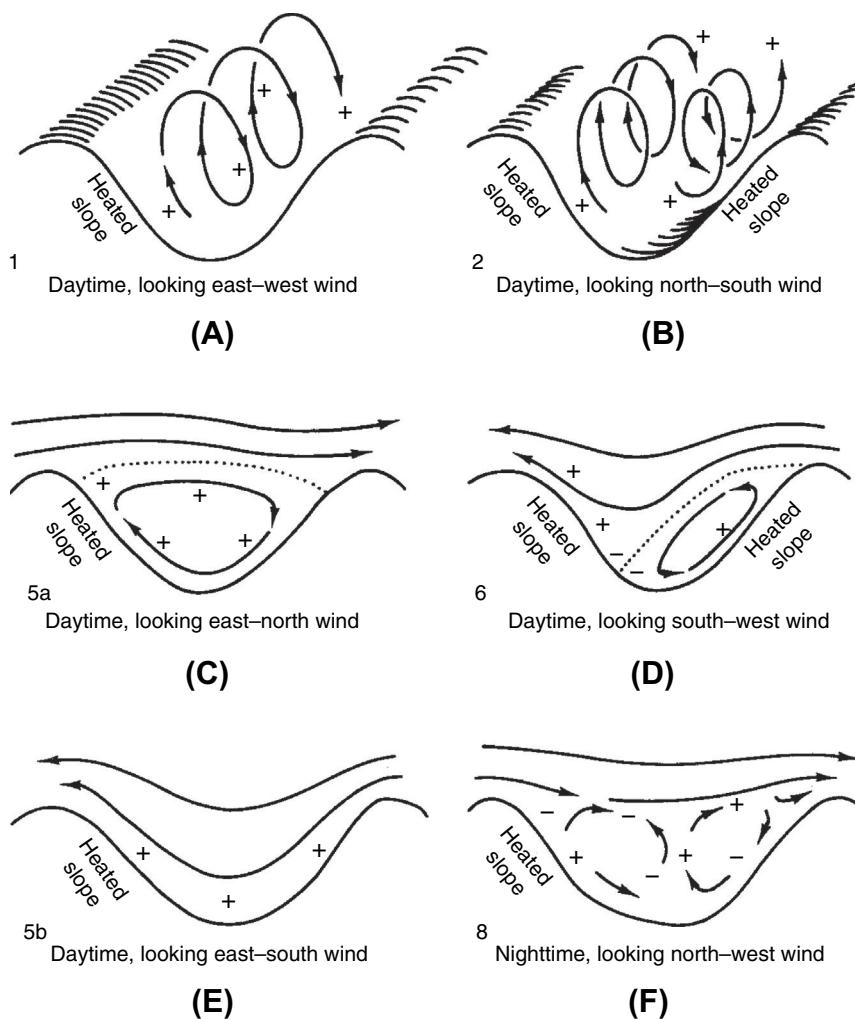


FIGURE 2.22 Local valley–ridge flow patterns. Numbers refer to Table 2.5.

areas heat quickly and have a high heat-storing capability compared to the soil and vegetation of rural areas. Also, some surfaces of buildings are normal to the sun's rays just after sunrise and also before sunset, allowing warming throughout the day. The result is that the urban area becomes warmer than its surroundings during the day and stores sufficient heat so that reradiation of the stored heat during the night keeps the urban atmosphere considerably warmer than its rural surroundings throughout most nights with light winds.

Under the lightest winds, the air rises over the warmest part of the urban core, drawing cooler air from all directions from the surroundings (see Figure 2.23).

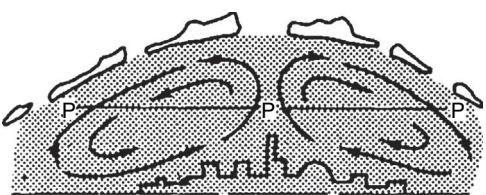


FIGURE 2.23 Urban heat island (light regional wind).

Subsidence replaces this air in rural areas, and a closed torus (doughnut)-shaped circulation occurs with an outflow above the urban area. This circulation is referred to as the urban heat island, mentioned during the discussion of albedo. The strength of the resulting flow is dependent on the difference in temperature between the urban center and its surroundings.

When the regional wind allows the outflow to take place in primarily one direction and the rising warm urban air moves off with this regional flow, the circulation is termed the urban plume (see Figure 2.24). Under this circumstance, the inflow to the urban center near the

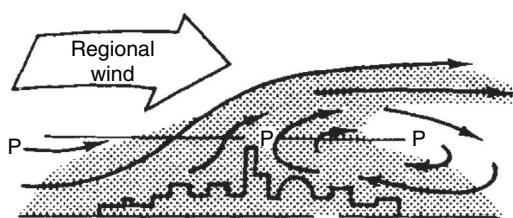


FIGURE 2.24 Urban plume (moderate regional wind).

surface may also be asymmetric, although it is more likely to be symmetric than the outflow at higher altitudes.

The urban area also emits heat through the release of gases from combustion and industrial processes. Compared to the heat received through solar radiation and subsequently released, the combustion and process heat is usually quite small, although it may be greater than 10% in major urban areas. Heating from these sources can be substantial in the vicinity of a specific local source, such as a steam power plant (where the release of heat is large over a small area) and during light-wind winter conditions.

#### 2.4.4 Flow around Structures

When the wind encounters objects in its path, such as an isolated structure, the flow usually is strongly perturbed and a turbulent wake is formed in the vicinity of the structure, especially downwind of it. If the structure is semistreamlined in shape, the flow may move around it with little disturbance. Since most structures have edges and corners, generation of a turbulent wake is quite common. [Figure 2.25](#) shows schematically the flow in the vicinity of a cubic structure. The disturbed flow consists of a cavity with strong turbulence and mixing, a wake extending downwind from the cavity a distance equivalent to a number of structure side lengths, a displacement zone where flow is initially displaced before entering the wake, and a region of flow that is displaced away from the structure but does not get caught in the wake. Wind tunnels, water channels, and/or towing tanks are extremely useful in studying building wake effects.<sup>8</sup>

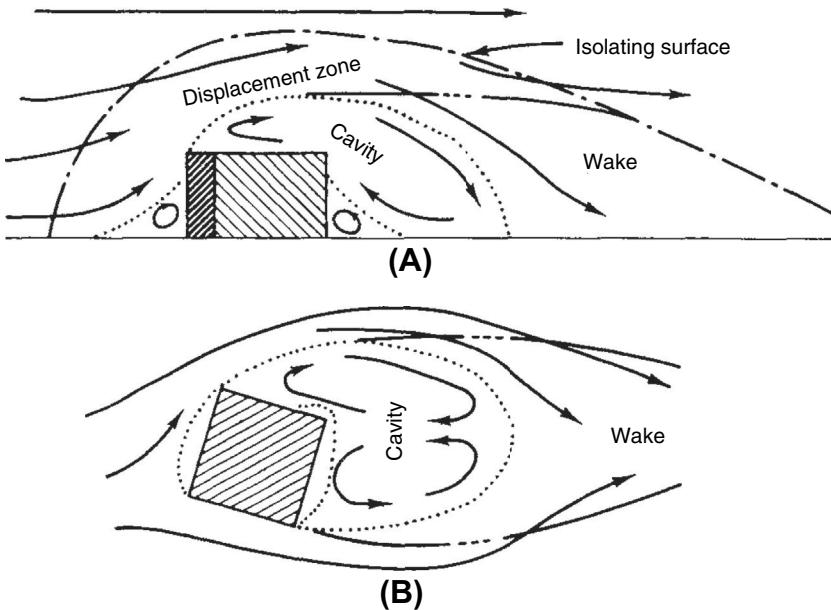
Such micrometeorological phenomena as flow around structures is very important to estimating micro-environmental exposures to air pollutants, including street canyon effects and penetration of pollutants into structures.

## 2.5 GENERAL CIRCULATION

Atmospheric motions are driven by the heat from incoming solar radiation and the redistribution and dissipation of this heat to maintain constant temperatures on the average. The atmosphere is inefficient, because only about 2% of the received incoming solar radiation is converted to kinetic energy, that is, air motion; even this amount of energy is tremendous compared to that which humans are able to produce. As was shown in [Section 2.1.5](#), a surplus of radiant energy is received in the equatorial regions and a net outflux of energy occurs in the polar regions. Many large-scale motions serve to transport heat poleward or cooler air toward the equator.

If the earth did not rotate or if it rotated much more slowly than it does, a meridional (i.e. along meridians) circulation would take place in the troposphere (see [Figure 2.26](#)). Air would rise over the tropics, move poleward, sink over the poles forming a subsidence inversion, and then stream equatorward near the earth's surface. However, since the earth's rotation causes the apparent deflection due to the Coriolis force, meridional motions are deflected to become zonal (along latitude bands) before moving more than 30°. Therefore, instead of the single cell consisting of dominantly meridional motion, meridional transport is accomplished by three

**FIGURE 2.25** Aerodynamic flow around a cube:  
(a) side view and (b) plan view. *Adapted from: Ref. 8.*



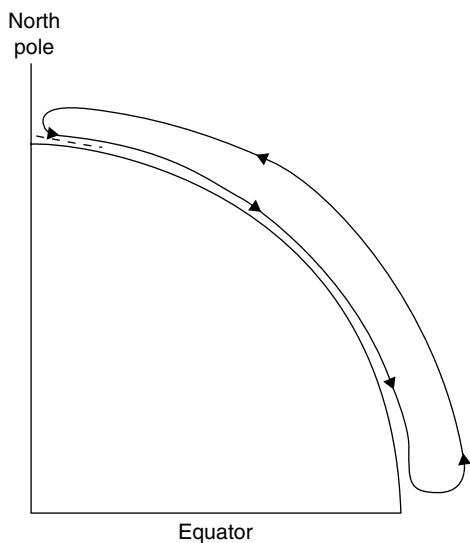


FIGURE 2.26 Meridional single-cell circulation (on the sunny side of a nonrotating earth).

cells between the equator and the pole (see Figure 2.27). This circulation results in subsidence inversions and high pressure where there is sinking toward the earth's surface and low pressure where there is upward motion.

### 2.5.1 Tropics

Associated with the cell nearest the equator are surface winds moving toward the equator which are deflected toward the west. In the standard terminology of winds, which uses the direction from which they come, these near-surface winds are referred to as easterlies (see Figure 2.28), also called trade winds. Since most of the earth's surface near the equator is ocean, these winds absorb heat and moisture on their way to the equator.

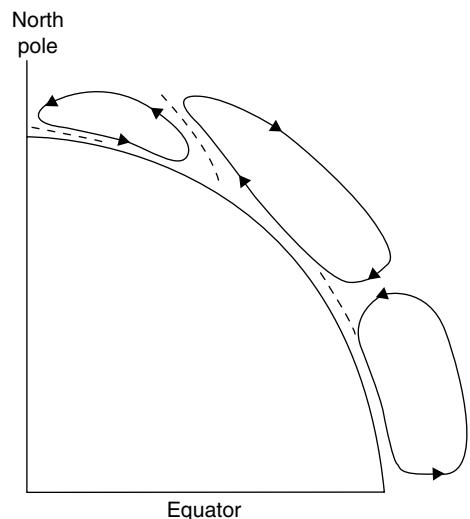


FIGURE 2.27 Meridional three-cell circulation (rotating earth).

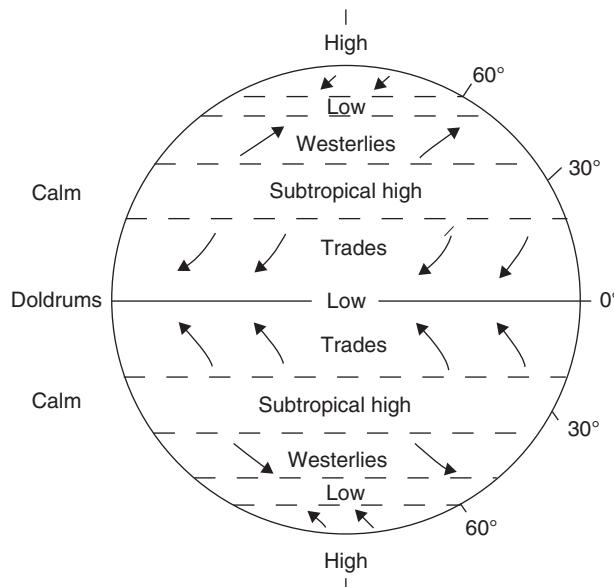


FIGURE 2.28 Near-surface winds for various latitude belts.

Where the trade winds from each hemisphere meet is a low-pressure zone, the intertropical convergence zone. This zone of light winds or doldrums shifts position with the season, moving slightly poleward into the summer hemisphere. The rising air with high humidity in the convective motions of the convergence zone causes heavy rainfall in the tropics. This giant convective cell, or Hadley cell, absorbs heat and the latent heat of evaporation at low levels, releasing the latent heat as the moisture condenses in the ascending air. Some of this heat is lost through infrared radiation from cloud tops. The subsiding air, which warms adiabatically as it descends in the vicinity of 30° latitude (horse latitudes), feeds warm air into the midlatitudes. Although the position of the convergence zone shifts somewhat seasonally, the Hadley cell circulation is quite persistent, resulting in a fairly steady circulation.

### 2.5.2 Midlatitudes

Because at higher latitudes the Coriolis force deflects wind to a greater extent than in the tropics, winds become much more zonal (flow parallel to lines of latitude). Also in contrast to the persistent circulation of the tropics, the midlatitude circulations are quite transient. There are large temperature contrasts, and temperature may vary abruptly over relatively short distances (frontal zones). In these regions of large temperature contrast, potential energy is frequently released and converted into kinetic energy as wind. Near the surface there are many closed pressure systems—cyclones and anticyclones, which are quite mobile, causing frequent changes in weather at any given location. In contrast

to the systems near the earth's surface, the motions aloft (above about 3 km) have few closed centers and are mostly waves moving from west to east.<sup>1</sup> The core where speeds are highest in this zonal flow is the jet stream at about 11–14 km aboveground (see Figure 2.29).

Where the jet stream undergoes acceleration, divergence occurs at the altitude of the jet stream. This, in turn, promotes convergence near the surface and encourages cyclogenesis (formation of cyclonic motion). Deceleration of the jet stream conversely causes convergence aloft and subsidence near the surface, intensifying high-pressure systems. The strength of the zonal flow is determined by the zonal index, which is the difference in average pressure of two latitude circles such as 35° and 55°. A high index thus represents strong zonal flow; a low index indicates weak zonal flow. A low index is frequently accompanied by closed circulations which provide a greater degree of meridional flow. In keeping with the transient behavior of the midlatitude circulation, the zonal index varies irregularly, cycling from low to high in periods ranging from 20 to 60 days.

The jet stream is caused by strong temperature gradients, so it is not surprising that it is frequently above the polar front, which lies in the convergence zone between the midlatitude loop of the general circulation and the loop nearest the poles (see Figure 2.27). The positions of both the polar front and the jet stream are

quite variable, shifting poleward with surface surges of warm air and moving toward the equator with outbreaks of cold air.

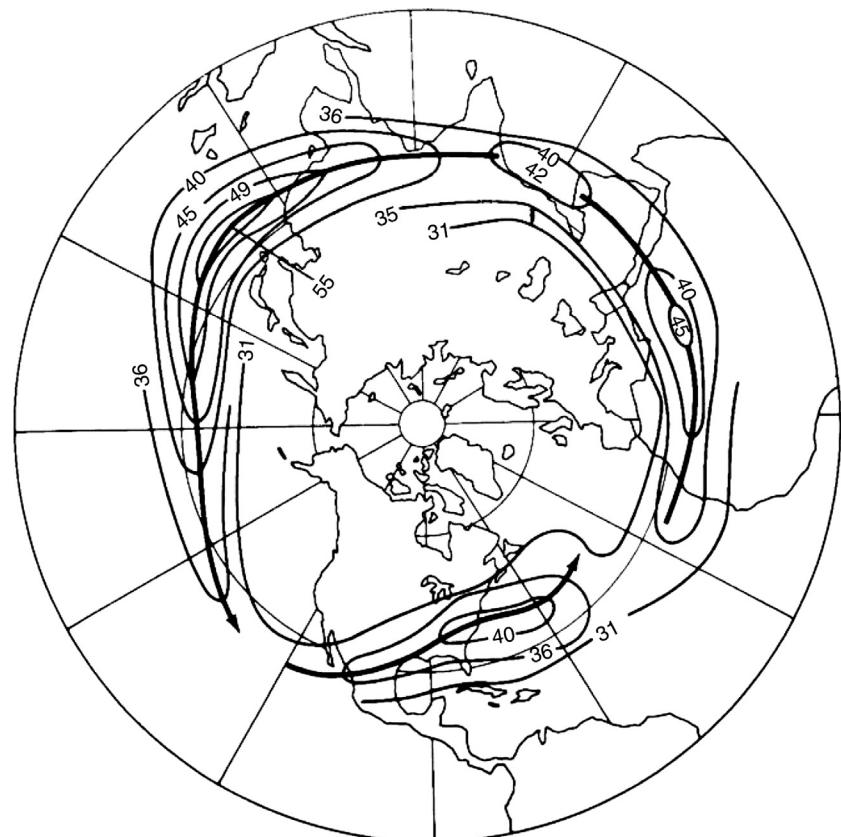
### 2.5.3 Polar Region

The circulation cells nearest the poles include rising air along the polar front, movement toward the poles aloft, sinking in the polar regions causing subsidence inversions, and flow toward the equator near the earth's surface. These motions contribute to the heat balance as the moisture in the air rising over the polar front condenses, releasing the heat that was used to evaporate the water nearer the equator. Also, the air moving toward the equator is cold and will be warmed as it is moved toward the tropics.

### 2.5.4 Other Factors

Of considerable usefulness in transporting heat toward the poles are the ocean currents. They are particularly effective because of the high heat content of water. Significant poleward-moving currents are the Brazil, Kuroshio, and Gulf Stream currents. Currents returning cold water toward the equator are the Peru and California currents.

**FIGURE 2.29** Average position and strength of the jet stream in January between 11 and 14 km above the earth's surface (speeds in  $\text{m s}^{-1}$ ).  
Adapted from: Ref. 1.



The pressure pattern changes from winter to summer in response to temperature changes. Because most of the southern hemisphere consists of ocean, the summer-to-winter temperature differences are moderated. However, the increased landmass in the northern hemisphere allows high continental temperatures in summer, causing small equator-to-pole temperature differences; cooling over the continents in winter produces more significant equator-to-pole temperature differences, increasing the westerly winds in general and the jet stream in particular.

## QUESTIONS

1. List four factors governing the amount of incoming solar radiation.
2. Which molecule stores more heat energy than all other atmospheric constituents combined?
3. If an air mass moves from the northern part of France to southern Italy, carrying elevated concentrations of particulate matter, describe the heating process(es) that cause(s) such movement.
4. If an air parcel rises from the surface at the Ruhr to 1000 m altitude and falling to 500 m altitude before reaching the surface near Frankfurt, carrying elevated concentrations of particulate matter, describe the heating process(es) that cause(s) such movement.
5. Verify the intensity of the energy flux from the sun in  $\text{cal cm}^{-2} \text{ min}^{-1}$  reaching the outer atmosphere of the earth from the total solar flux of  $5.6 \times 10^{27} \text{ cal min}^{-1}$  and the fact that the earth is  $1.5 \times 10^8 \text{ km}$  from the sun. (The surface area of a sphere of radius  $r$  is  $4\pi r^2$ .)
6. Compare the difference in incoming radiation on a horizontal surface at noon on June 22 with that at noon on December 21 at a point at  $23.5^\circ\text{N}$  latitude.
7. What is the zenith angle at 1000 h local time on May 21 at  $36^\circ\text{N}$  latitude?
8. At what local time is sunset on August 21 at  $40^\circ\text{S}$  latitude?
9. Show the net heating of the atmosphere, on an annual basis, by determining the difference between heat entering the atmosphere and heat radiating to the earth's surface and to space (see Figure 2.5).
10. If the universal gas constant is  $8.31 \times 10^{-2} \text{ mb m}^{-3} (\text{g mol})^{-1} \text{ K}^{-1}$  and the gram molecular weight of dry air is 28.9, what is the mass of a cubic meter of air at a temperature of 293 K and an atmospheric pressure of 996 mb?
11. On a particular day, temperature can be considered to vary linearly with height between  $28^\circ\text{C}$  at 100 m aboveground and  $26^\circ\text{C}$  at 500 m aboveground. Do you consider the layer between 100 and 500 m aboveground to be stable or unstable?
12. A parcel of air is heated by infrared reradiation from the earth's surface with two types of materials. To the north, the albedo is 0.3. To the south the albedo is 0.7. Which half of the air mass will be warmer, assuming all other variables are constant?
13. Is the scenario in the above question undergoing an adiabatic process?
14. At 800 m altitude, the air mass is 280 K at a pressure of 890 mb and at 10 m altitude the air mass is 278 K at a pressure of 970 mb. What are the potential temperatures at each height? Which layer is likely to be more stable?
15. Using Wien's displacement law, determine the mean effective temperature of the earth-atmosphere system if the resulting longwave radiation peaks at  $11 \mu\text{m}$ . Contrast the magnitude of the radiant flux at  $11 \mu\text{m}$  with that at  $50 \mu\text{m}$ .
16. What accompanies horizontal divergence near the earth's surface? What effect is this likely to have on the thermal stability of this layer?
17. At what time of day and under what meteorological conditions is maximum ground-level pollution likely to occur at locations several kilometers inland from a shoreline industrial complex whose pollutants are released primarily from stacks of moderate height (about 40–130 m)?
18. When the regional winds are light, at what time of day and what location might high ground-level concentrations of pollutants occur from the low-level sources (less than 20 m) of a town in a north-south-oriented valley whose floor slopes down to the north? Can you answer this question for sources releasing in the range 50–70 m aboveground?
19. Consider the air movement in the northern hemisphere (see Figure 2.29). Explain how persistent organic compounds, such as polychlorinated biphenyls might be found in the tissues of polar bears and in human mother's milk in the arctic regions.
20. New York City is located in a complex geographic and meteorological situation. Explain how local wind systems and heat balances may account for air pollution in and around the city.
21. Following the World Trade Center attacks on September 11, 2001, the use of wind information from the three major airports was not representative of conditions at Ground Zero. Give reasons for these variations.

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## Suggested Reading

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# The Science of Air Pollution

## 3.1 AIR POLLUTION IN PERSPECTIVE

There are numerous ways to approach air pollution. Biologists may think of how contaminants in the air affect living things. Within biology, the subdisciplines vary in their interests. Ecologists are often interested in how exposures to air pollutants affect biodiversity and overall ecosystem health. Biomedical scientists are concerned about the diseases associated with various air contaminants. Toxicologists, in particular, are interested in how these effects differ from one species to another and from one type of contaminant to another. For example, the same compound may rapidly cause mutations in bacteria at relatively low doses and cancer in humans at even lower doses, but over decades of exposure. Toxicologists are also interested in the length of time that it takes to observe the effects, contrasting those that appear right away, i.e. acutely toxic, with those that take several years to elicit effects, i.e. chronically toxic. Differences and similarities of effects are important within a species (e.g. adults *versus* children) and among species. It is not unusual for a compound to be acutely toxic at low doses for fish, but acutely toxic in mammals only at much higher doses.

Other biological specialists have myriad concerns about air pollution, such as geneticists' interest in how pollutants may change genetic material in organisms or how genetically modified organisms may be transported into the atmosphere and potentially reach human populations and ecosystems.

Epidemiologists are interested in how the exposure and effects of air pollutants differ in time and space. They may observe a cluster of diseases and associate this with a source of air pollution. Or, they may observe a change in disease occurrence over time that tracks with changes in the type and amount of pollution released in an area.

Chemists are often concerned about the various types of pollutants. For example, they may be interested in how reactive or persistent certain compounds are after they are released from a stack, vent, or tailpipe. They are also interested in how the compounds change after

release, i.e. what reactions occur in the atmosphere after release. This is also the concern of physicists, who want to explain the thermodynamics and motion that is involved in this transfer and the fate of air pollutants as they are created and after they are released. That is why air pollution experts often lump these concerns together as physicochemical properties and behavior. Indeed, this book gives ample attention to these throughout.

The first inclination of engineers may be to look for innovative ways to control and treat the various types of pollutants, using the physical sciences. They tend to divide air pollutants into aerosols (liquid and solid) and vapors (gas), since the technologies needed to remove and treat these substances differ. A good example of this is if you knew that you would be exposed to high levels of dust in a room, you would want to make sure your personal protection equipment included filters to collect the dust particles. However, if you knew there would also be toxic vapors, you must be aware that this filter would be inadequate and that other technologies would be needed to trap the gas phase pollutants.

Engineers and scientists must now take the systematic view. They must consider the entire life cycle of processes that have led or could lead to air pollution. The fundamentals of air pollution in the first part of the twenty-first century differs from that of the end of the twentieth century with the presently greater focus on preventing air pollution and attention to the green chemistry and green engineering. Pollution characterization, prediction, and control remain fundamentals of air pollution and receive much attention in this edition. However, considerably greater attention is devoted to the fundamentals of green chemistry, green engineering, and sustainability.

The extent of interest, awareness, and concern about air pollution varies by many factors, including where people and those they care about live, their age, their health status, their world view, and their knowledge level. People living near an industrial complex likely will see frequent, visible signs of pollution, such as dark plumes emitted from smoke stacks or hazy

conditions on certain days. Conversely, if they live near a nearly pristine park or forest, they may be particularly leery of any change in air quality. Both observations call for action, but different approaches, i.e. cleaning polluted air and preventing air pollution. A person with asthma may be more concerned about certain air pollutants than those who have never experienced breathing problems. Students who have taken a few earth science or meteorology courses, hopefully, will be more aware of even subtle forms of pollution than are lesser informed people. A farmer experiencing crop damage is likely to be concerned that the conditions leading to the damage are not repeated.

One's level of awareness and concern is enhanced with a sufficient amount of scientifically sound and reliable information and knowledge about air pollution specifically. This book is designed to provide such information and to enhance the reader's knowledge of air pollution.

Air pollution to some extent is in the eye of the beholder (actually it is also in the beholder's ears, nose, mouth, skin, and, most prominently, lungs). Each person perceives a difference between polluted and unpolluted air. Science requires a more objective distinction. To understand the fundamentals of air pollution requires knowledge of the pollutant and of the air in which the pollutant is found.

The U.S. Environmental Protection Agency (EPA) defines air pollution as the presence of contaminants or pollutant substances in the air that interfere with human health or welfare, or produce other harmful environmental effects.<sup>1</sup> The key verb in the definition is "interfere". Thus, we obviously have a desired state, but these substances are keeping us from achieving that state. So, then, what is that state? The second part of the definition provides some clues; namely, air must be of a certain quality to support human and other life.

Like many scientific concepts, there is a general understanding of air pollution that includes the essence of the scientific definition, but differs in detail from the more technical delineation between polluted and unpolluted air. Technical definitions and characterizations require clarity of meaning, with as little ambiguity as possible. For centuries people knew that something was amiss when their air was filled with smoke or when they smelled an unpleasant odor. They relied on their unaided senses to determine whether a pollutant existed and to perceive its unpleasantness. However, most pollutants cannot be sufficiently and accurately detected solely by the five human senses. Many are odorless, colorless, and otherwise undetectable. Even those that are inherently detectable with unaided human senses, such as hydrogen sulfide's ( $H_2S$ ) rotten egg odor or orange color of lead oxide ( $PbO$ ), are sensed only at concentrations well above thresholds of harm. Unfortunately, the

adage, "what you don't know won't harm you" is not true for most air pollutants.

Generally, environmental agencies must take action if the expected exposure concentration of a pollutant is within the range of where it may cause harm. Thus, the state of the science has had to advance to begin to address air pollution properly. Sound science was needed to identify those constituents in the air that might be causing problems. Science was also needed to measure such agents. Biomedical sciences had to advance to discern which adverse health events were being caused by these agents. Indeed, a baseline had to be set to begin to take action.

Another way to look at the interferences mentioned in the EPA definition is to place them within the context of "harm". The recipients of the harm have undergone varying levels of interest. In the 1960s, harm to ecosystems, including threats to the very survival of certain biological species was paramount. This concern was coupled with harm to humans, especially in terms of diseases directly associated with obvious episodes, such as respiratory diseases and even death associated with combinations of weather and pollutant releases.

Other emerging concerns were also becoming apparent, including anxiety about nuclear power plants, particularly the possibilities of meltdown and the continuous generation of large volumes of cancer-causing nuclear wastes. The petrochemical revolution was also causing concerns, such as the increasing production and release of ominous-sounding chemicals like dichloro-diphenyl-trichloroethane (DDT) and other pesticides, as well as spills of oil and chemicals. These apprehensions would increase in the next decade, with the public's growing wariness about "toxic" chemicals added to the more familiar "conventional" pollutants like soot, carbon monoxide, and oxides of nitrogen and sulfur. The major new concern about toxics was that of cancer. The next decades kept these concerns, but added new ones, including threats to hormonal and reproductive systems in humans and wildlife, neurotoxicity (especially in children), and immune system disorders.

Growing numbers of studies in the last quarter of the twentieth century provided evidence linking disease and adverse effects to extremely low levels of certain particularly toxic substances. For example, exposure to dioxin at almost any level above what science could detect could be associated with numerous adverse effects in humans. During this time, other recipients of pollution were identified, including the loss of aquatic diversity in lakes due to deposition of acid rain. Acid deposition was also increasingly associated with the corrosion of materials, including some of the most important human-made structures, such as the pyramids in Egypt and monuments to democracy in Washington, DC. Somewhat later, global pollutants became

the source of public concern, such as those that seemed to be destroying the stratospheric ozone layer or those that appeared to be affecting the global climate.

This escalation of awareness of the multitude of pollutants complicated matters. For example, many pollutants under other circumstances would be “resources”, such as compounds of nitrogen. In the air, these compounds can cause respiratory problems directly or, in combination with hydrocarbons and sunlight indirectly can form ozone and smog. But, in the soil, nitrogen compounds are essential nutrients. So, it is not simply a matter of “removing” pollutants, but one of managing systems to ensure that optimal conditions for health and environmental quality exist. Science must be able to explain the conditions under which something in our air that is at first harmless or even beneficial becomes harmful. Impurities are common, but in excessive quantities and in the wrong places they become harmful. One of the most interesting definitional quandaries about pollution has come out of the water pollution literature, especially by the language in the Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500). The objective of this law was to restore and maintain the chemical, physical, and biological integrity of the U.S. waters. To achieve this objective, the law set two goals: the elimination of the discharge of all pollutants into the navigable waters of the United States by 1985; and to provide an interim level of water quality to protect fish, shellfish, and wildlife and recreation by 1983.<sup>2</sup> Could the Congress have realistically expected all sources that drained into U.S. lakes and rivers to be completely free of pollutants in 13 years? Or did this goal hinge upon the definition of a pollutant? In other words, even toxic substances are not necessarily “pollutants” if they exist below a threshold of harm. In light of the fact that this same law established so-called “effluent limitations”, there is a strong likelihood that the definition called for in this goal was concentration-based.<sup>3</sup>

This paradigm spilled over into air pollution. More recently, the term “zero emission” has been applied to vehicles, as the logical next step following low emission vehicles (LEVs) and ultralow emission vehicles (ULEVs) in recent years. However, zero emissions of pollutants will not be likely for the foreseeable future, especially if one considers that even electric cars are not emission free, but are actually an example of emission trading, since the electricity is generated at a power plant that is emitting pollutants as it burns fossil fuels or is generating thermal and radioactive wastes if it is a nuclear power plant. Even hydrogen, solar and wind systems are not completely pollution free since the parts and assemblages require energy and materials that may even include hazardous substances.

These definitional uncertainties beg the question, then, of when does an impurity become a pollutant?

Renaissance thinking may help us here. Paracelsus, the sixteenth century scientist is famous for his contention that “dose alone makes a poison.... All substances are poisons; there is none which is not a poison. The right dose differentiates a poison and a remedy”.<sup>4</sup> Paracelsus’ quote illuminates a number of physical, chemical, and biological concepts important to understanding air pollution. Notably, the poisonous nature, i.e. the toxicology, of a substance must be related to the circumstances of exposure. In other words, to understand a pollutant, one must appreciate its context. Air pollutants become a problem when they come into contact with the receptor. This leads to some important questions that must be answered to address air pollution:

1. What is the physical, chemical, and biological nature of the air pollutant and what are the conditions surrounding the receptor (e.g. a person, an endangered species, or an entire population or ecosystem)?
2. What is the exposed or potentially exposed person’s existing health status; including vulnerabilities and susceptibilities that differ from the general population (e.g. a baby, an asthmatic child, an elderly person)?
3. What is the condition of the ecosystem?
4. What are the chemical composition and physical form of the air contaminant?
5. How has the person or organism been exposed to the pollutant; from inhalation of air, eating food contaminated by air pollutants in the home, or dermally from people touching settled dust with their skin?
6. Does the pollution involve one substance or is it present along with other, possibly synergistic contaminants?

These and other characterizations of a contaminant must be known to determine the extent and degree of harm.

Another concept highlighted by Paracelsus is that dose is related to response. This is what scientists refer to as a biological gradient or a *dose-response* relationship (See Chapter 7). Under most conditions, the more poison to which one is exposed the greater the harm.

The classification of harm is an expression of *hazard*, which is a component of risk. The terms hazard and risk are frequently used interchangeably in everyday parlance, but hazard is actually a component of risk. As we will see throughout this text, hazard is expressed as the potential of unacceptable outcome, while risk is the likelihood (i.e. probability) that such an adverse outcome will occur. A hazard can be expressed in numerous ways. For chemical or biological agents, the most important hazard is the potential for disease or death (referred to in medical literature as “morbidity”

and “mortality”, respectively). So, the hazards to human health are referred to collectively in the medical and environmental sciences as “toxicity”. Toxicology is chiefly concerned with health outcomes and their potential causes.

To scientists and engineers, risk is a straightforward mathematical and quantifiable concept. Risk equals the probability of some adverse outcome. Any risk is a function of probability and consequence.<sup>5</sup> The consequence can take many forms. In environmental sciences, a consequence is called a “hazard”. Risk, then, is a function of the particular hazard and the chances of person (or neighborhood or workplace or population or a part or all of an ecosystem) being exposed to the hazard. For air pollution, this hazard often takes the form of toxicity, although other public health and welfare hazards abound (such as corrosivity to materials; See Chapter 15).

### 3.2 EMERGENCE OF AIR POLLUTION SCIENCE, ENGINEERING, AND TECHNOLOGY

Environmental science and engineering are young professions compared to many other disciplines in the physical and natural sciences and engineering. In a span of just a few decades, advances and new environmental applications of science, engineering, and their associated technologies have coalesced into a whole new way to see the world. Science is the explanation of the physical world, while engineering encompasses applications of science to achieve results. Thus, what we have learned about the environment by trial and error has incrementally grown into what is now standard practice of environmental science and engineering. This heuristically attained knowledge has come at a great cost in terms of the loss of lives and diseases associated with mistakes, poor decisions (at least in retrospect), and the lack of appreciation of environmental effects.

Environmental awareness is certainly more “mainstream” and less a polarizing issue than it was in the 1970s, when key legislation reflected the new environmental ethos. The number of laws intended to protect natural resources, including air quality, grew steadily throughout the 20th century. Following the 1960s, the growth of such legislation grew exponentially with increased public awareness and concern. Notably, the 1970 Clean Air Act codified the national need to decrease air pollution by requiring federal standards for ambient air quality. This was accomplished by requiring state and local jurisdictions to implement plans to achieve air quality standards and to require sources of air pollution to decrease emissions. There has been a steady march of advances in environmental science and engineering for several decades, as

evidenced by the increasing number of Ph.D. dissertations and credible scientific journal articles addressing a myriad of environmental issues. Corporations and government agencies, even those whose missions are not considered to be “environmental”, have established environmental programs.

Arguably, a more complete understanding of atmospheric processes is one of the more emergent areas of environmental science and technology; growing from the increasing awareness of air pollution and advances of control technologies in the twentieth century. However, the roots of the science of air pollution can be traced to the Ancients.

The environmental sciences, including its subdisciplines specializing in air pollution, apply the fundamentals of chemistry, physics, and biology, and their derivative sciences such as meteorology, to understand these abiotic<sup>6</sup> and biotic relationships. Expanding these observations to begin to control outcomes is the province of environmental engineering.

As scientists often do, systematic and specific explanations must be applied to practical knowledge. So, biologists and their subdisciplines began to specialize in what came to be known as the environmental sciences. Health scientists, like Paracelsus and William Harvey, provided insights into how the human body interacts with and reacts to environmental stimuli. In fact, Paracelsus' studies of metal contamination and exposure to miners may well be among the earliest examples of environmental epidemiology.

Not only are the environmental disciplines young, but also many of the environmental problems faced today differ from those throughout most of human history. The difference is in both kind and degree. For example, the synthesis of chemicals, especially organic compounds has grown exponentially since the mid-1900s. Most organisms lack mechanisms to metabolize and eliminate these new compounds. Also, stresses put on ecosystems prior to the Industrial Revolution were comparatively small in extent of damage. Pollutants have been emitted into the atmosphere throughout human history, but only recently were such emissions so large and long-lasting, or of pollutants with such high toxicity, that they have diminished the quality of entire airsheds.

### 3.3 WHAT IS AIR POLLUTION?

In spite of its vastness, the atmosphere can be and has been polluted. But, when does science consider the atmosphere to be unpolluted *versus* polluted? Sometimes, the best that can be done is to compare the condition of the atmosphere currently against some type of baseline, e.g. preindustrialized atmosphere prior to the nineteenth century. Another approach is to consider the

principles by which materials are released into the atmosphere, move, transform, and are removed from the atmosphere, and based on this assessment determine the extent of atmospheric pollution.

The definition of an air pollutant or air pollution depends on the context of time, space, and impact for a particular set of circumstances. Earlier discussions attempted to distinguish unpolluted from polluted air. However, the same chemical compounds or particles from a natural source (e.g. a volcano) elicit the same adverse effects as when they are emitted by anthropogenic sources.

Thus, unpolluted air is merely a benchmark to show the extent and trends of air pollution. Governments around the world have established and are continuously evaluating the impact of elevated levels of myriad gaseous and particulate material in the atmosphere.

Air pollution implies acceptability. The difference between acceptable and unacceptable air quality is the focus. Over the past few decades the central feature of air pollution has been its association with harm, especially harm to humans in terms of diseases, such as respiratory diseases associated with air pollutants. Harm implies a value; i.e. something that society values is lost or diminished.

Air pollutants affect both human health and ecosystems. The United Nations Environmental Programme estimates that indoor and outdoor air pollution are responsible for nearly 5% of the global disease burden, including excess cases of asthma and other allergic respiratory diseases, adverse pregnancy outcomes (e.g. stillbirth and low birth weight).<sup>2</sup> People in developing countries are particularly vulnerable to air pollution. Approximately two million people in rural areas die each year from exposure to high concentrations of particulate matter (PM) suspended in the indoor air. Excess mortality due to outdoor PM and sulfur dioxide contribute to mortality of about 500,000 people annually.<sup>3</sup>

In the United States, a handful of commonly found air pollutants are known to cause three specific types of harm. They impair health, destroy and adversely affect environmental resources, and damage property. To address these harms, as mentioned in Chapter 1, legislation has been passed around the world. In the United States, the Clean Air Act of 1970 established the National Ambient Air Quality Standards (NAAQS) to address six so-called “criteria air pollutants”:

1. particulate matter (PM)
2. ozone ( $O_3$ )
3. carbon monoxide (CO)
4. sulfur dioxide ( $SO_2$ )
5. nitrogen dioxide ( $NO_2$ )
6. lead ( $Pb$ )

These pollutants are called criteria air pollutants because agencies around the world, such as the U.S.

EPA, Health Canada, and Environment Directorate General of the European Union regulate them by using two sets of criteria for pollutant standards. The first set of standards is designed to protect public health based on sound science. This set of limits (known as *primary standards*) protects health. A second set of limits (known as *secondary standards*) aims to prevent environmental and property damage. When an urban area or other geographic area has concentrations of a criteria pollutant below the standard it is said to be “in attainment” and the area is declared to be an “attainment area”. Conversely, any area that has concentrations of a criteria pollutant above the standard is called a “nonattainment area”. Such a designation is not only problematic because of the potential health and environmental effects, but also because it means that the local and state governments will have to take actions to bring the area into attainment. The Clean Air Act gives the federal government a range of possible sanctions to encourage these actions, including withholding certain federal funds (e.g. road-building and other transportation projects). At present, many urban areas are classified as nonattainment for at least one criteria air pollutant. In fact, about 90 million Americans live in nonattainment areas.<sup>3</sup>

The public’s apprehensions, however, extend beyond the criteria pollutants and increase with the growing wariness about “toxic” chemicals added to the more familiar “conventional” pollutants. The clearest association of toxic air pollutants in recent decades has been with cancer, although neurotoxicity (especially in children) from lead and mercury grew in importance in the 1970s and 1980s. By the end of the twentieth century, new toxic pollutants also competed for the public’s attention, including air pollutants that threaten hormonal systems in humans and wildlife, as well as those associated with immune system disorders.

### 3.3.1 Particulate Matter

Neither Table 1.1 nor Table 1.2 lists among the constituents of the air the PM that is always suspended in various concentrations in the troposphere. Each gas or vapor exists as an individual molecule in random motion that exerts its proportionate partial pressure in the air. However, particles are aggregates of many molecules, sometimes of similar molecules, often of dissimilar ones. They form and transform in the air by several processes. Some particles serve as nuclei upon which vapors condense. Some particles react chemically with atmospheric gases or vapors to form different compounds. When two particles collide in the air, they tend to adhere to each other because of attractive surface forces, thereby forming progressively larger and larger particles by agglomeration. The larger a particle becomes, the greater its weight and the greater its likelihood of falling

to the ground rather than remaining airborne. The process by which particles fall out of the air to the ground is called *sedimentation*. Washout of particles by snowflakes, rain, hail, sleet, mist, or fog is a common form of agglomeration and sedimentation. Still other particles leave the air by impaction onto and retention by the solid surfaces of vegetation, soil, and buildings. The particulate mix in the atmosphere is dynamic, with continual injection into the air from sources of small particles; creation of particles in the air by vapor condensation or chemical reaction among gases and vapors; and removal of particles from the air by agglomeration, sedimentation, or impaction.

Before the advent of humans and their works, there must have been particles in the air from natural sources. These certainly included all the particulate forms of condensed water vapor; the condensed and reacted forms of natural organic vapors; salt particles resulting from the evaporation of water from sea spray; wind-borne pollen, fungi, molds, algae, yeasts, rusts, bacteria, and debris from live and decaying plant and animal life; particles eroded by the wind from beaches, desert, soil, and rock; particles from volcanic and other geothermal eruption and from forest fires started by lightning; and particles entering the troposphere from outer space. As mentioned earlier, the true natural background concentration will never be known because when it existed humans were not there to measure it, and by the time humans started measuring PM levels in the air, these particles had already been polluting the atmosphere for eons. The best that can be done now is to assume that the particulate levels at remote places—the middle of the sea, the poles, and the mountaintops—approach the true background concentration. The very act of going to a remote location to make a measurement implies some change in the atmosphere of that remote location attributable to the means people used to travel and to maintain themselves while obtaining the measurements. PM is measured on a dry basis, thereby eliminating from the measurement not only water droplets and snowflakes but also all vapors, both aqueous and organic, that evaporate or are desiccated from the PM during the drying process. Since different investigators and investigative processes employ different drying procedures and definitions of dryness, it is important to know the procedures and definitions employed when comparing data.

Although many of the air pollutants discussed in this book are best classified by their chemical composition, particles are first classified according to their physical properties. PM is a common physical classification of particles found in the air, such as dust, dirt, soot, smoke, and liquid droplets.<sup>4</sup> Unlike other U.S. criteria pollutants ( $O_3$ , CO,  $SO_2$ ,  $NO_2$ , and lead [Pb]), PM is not a specific chemical entity but is a mixture of particles from

different sources and of different sizes, compositions, and properties. The chemical composition of PM is very important and highly variable. In fact, knowing what a particle is made of tells us much about its source, e.g. receptor models use chemical composition and morphology of particles as a means to trace pollutants back to the source.

The chemical composition of tropospheric particles includes inorganic ions, metallic compounds, elemental carbon, organic compounds, and crustal substances (e.g. carbonates and compounds of alkali and rare earth elementals). For example, the mean 24 h PM<sub>2.5</sub> concentration measured near Baltimore, Maryland in 1999 was composed of 38% sulfate, 13% ammonium, 2% nitrate, 36% organic carbon, 7% elemental carbon, and 4% crustal matter.<sup>5</sup> In addition, some atmospheric particles can be hygroscopic, i.e. they contain particle-bound water. The organic fraction can be particularly difficult to characterize, since it often contains thousands of organic compounds.

Particles range from ultrafine to coarse (see [Figure 3.1](#)). The size of a particle is determined by how the particle is formed. For example, combustion can generate very small particles, while coarse particles are often formed by mechanical processes (see [Figure 3.2](#)).

If particles are sufficiently small and of low mass, they can be suspended in the air for long periods of time. Larger particles (e.g. 10  $\mu\text{m}$  aerodynamic diameter) are found in smoke or soot (see [Figure 3.3](#)), while very small particles (<2.5  $\mu\text{m}$ ) may be apparent only indirectly, such as the manner in which they diffuse, diffract, absorb, and reflect light (see [Figure 3.4](#)).

Sources of particles are highly variable. They may be emitted directly to the air from stationary sources, such as factories, power plants, and open burning, and from moving vehicles (known as “mobile sources”), first by direct emissions from internal combustion engines, but also when these and other particles are re-entrained due to the movement of vehicles (e.g. in a “near-road” situation). Area or nonpoint sources of particles include construction, agricultural activities such as plowing and tilling, mining, and forest fires.

Numerous physical processes are at work in the formation of particles in the troposphere. These processes give a clue as to how to control particle emissions. By measuring each portion of the particle size spectrum by the most appropriate method, a composite diagram of the size distribution of the atmospheric aerosol can be produced. [Figure 3.5](#) shows that there are separate size distributions with respect to the number, surface area, and volume (or mass) of the particles. The volume (mass) distribution is called *bimodal* because of its separate maxima at about 0.2 and 10  $\mu\text{m}$ , which result from different mechanisms of particle formation. The mode with the 0.2- $\mu\text{m}$  maximum results from coagulation

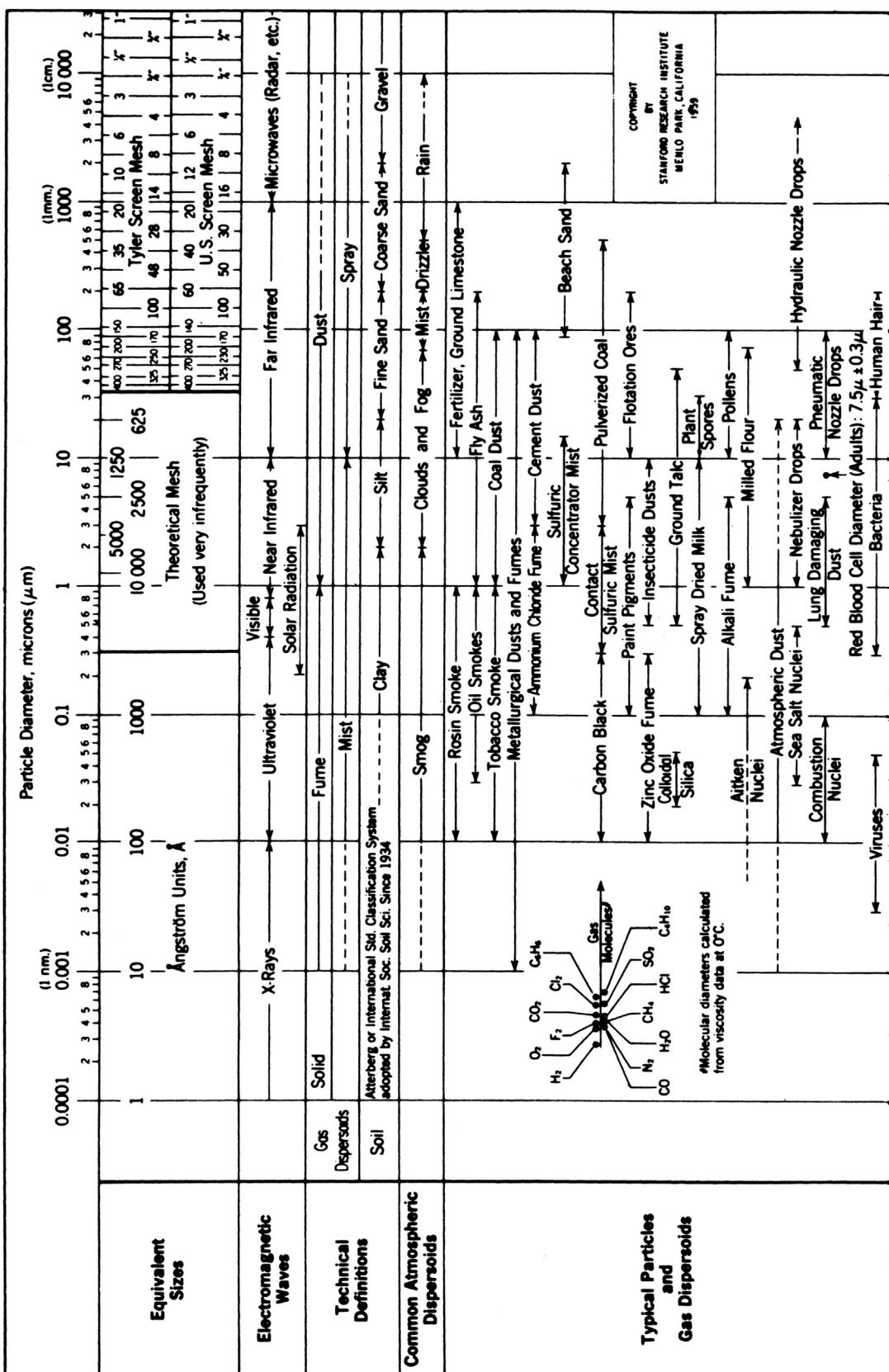


FIGURE 3.1 Characteristics of particles and particle dispersoids. Adapted from figure reproduced by permission from SRI International, Menlo Park (CA); 1959.

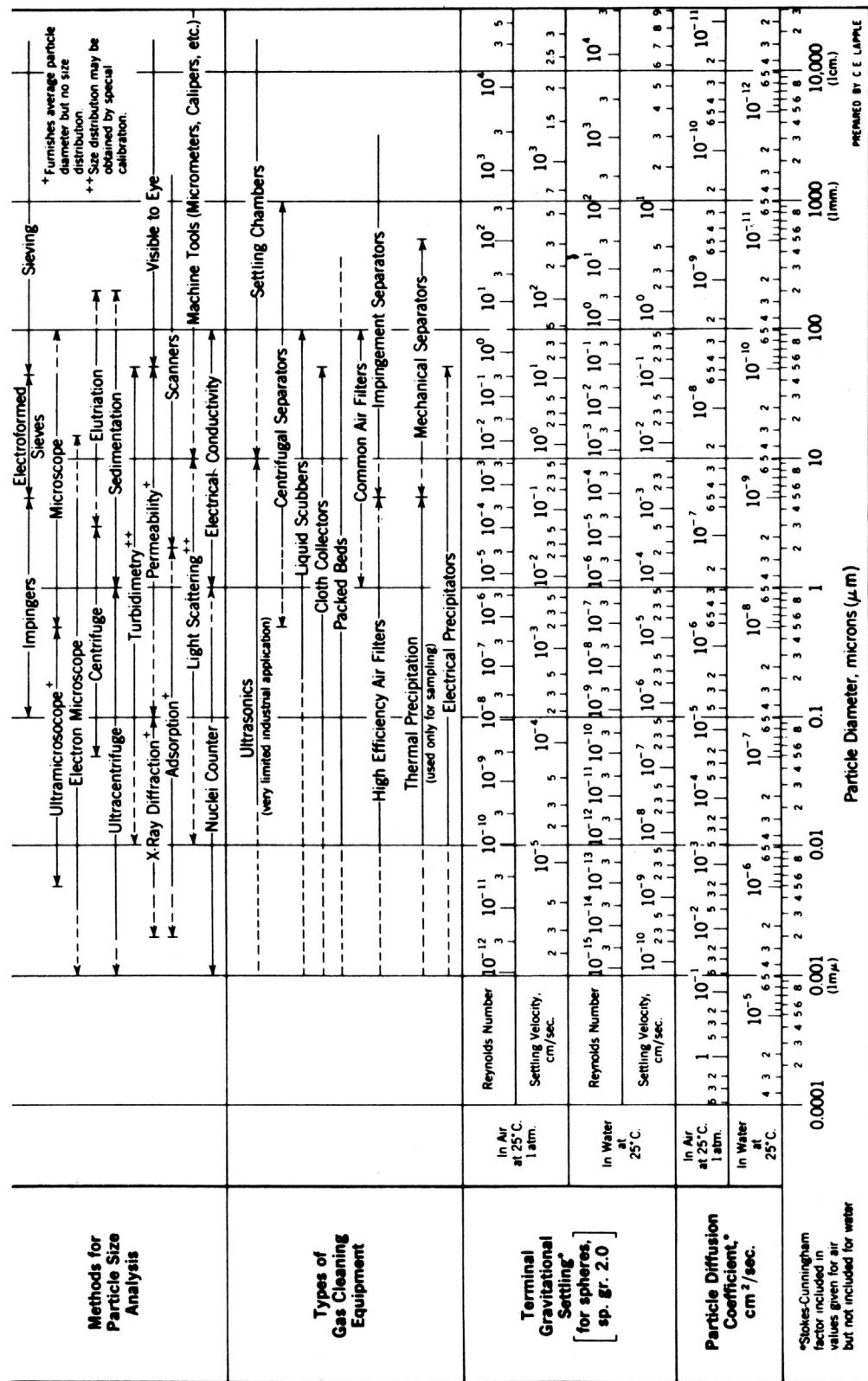
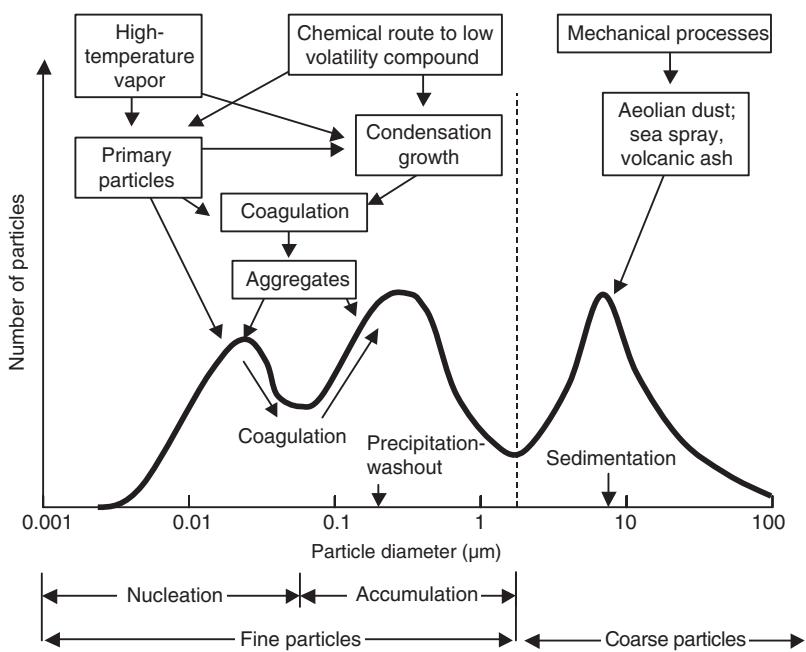
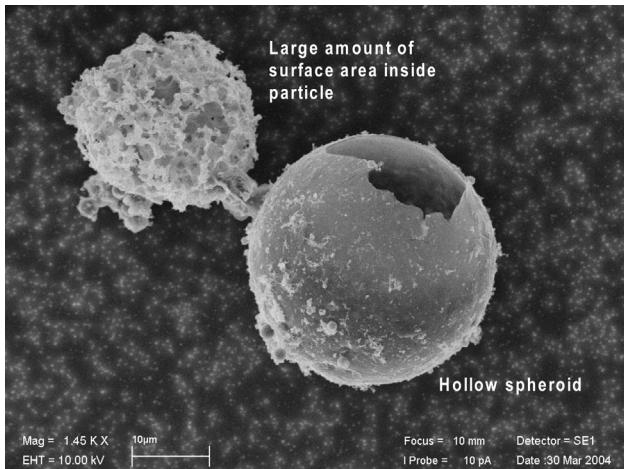


FIGURE 3.1 cont'd.

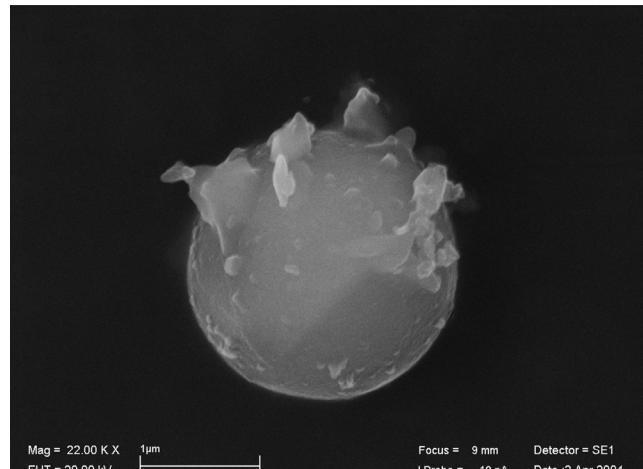


**FIGURE 3.2** Prototypical size distribution of tropospheric particles with selected sources and pathways of how the particles are formed. Dashed line is approximately 2.5  $\mu\text{m}$  diameter. Adapted from: United Kingdom Department of Environment, Food, and Rural Affairs, Expert Panel on Air Quality Standards. Airborne particles: what is the appropriate measurement on which to base a standard? A discussion document; 2004.



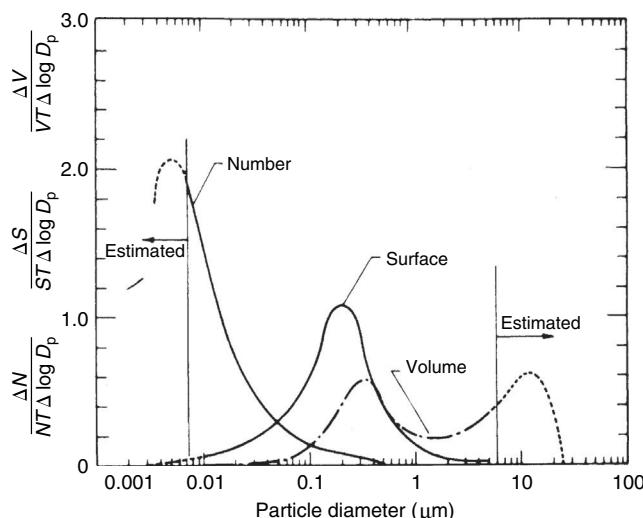
**FIGURE 3.3** Scanning electron micrograph of coarse particles emitted from an oil-fired power plant. Diameters of the particles are greater than 20  $\mu\text{m}$  optical diameter. Both particles are hollow, so their aerodynamic diameter is significantly smaller than if they were solid. Source characterization study by Stevens R, Lynam M, Proffitt D, 2004. Photo courtesy of Willis R, U.S. Environmental Protection Agency.

and condensation formation mechanisms. As mentioned, these particles are created in the atmosphere by chemical reactions among gases and vapors. They are called *fine* particles to differentiate them from the particles in the 10- $\mu\text{m}$  maximum mode, which are called *coarse*. These fine particles are primarily sulfates, nitrates, organics, ammonium, and lead compounds. The



**FIGURE 3.4** Scanning electron micrograph of spherical alumino-silicate fly ash particle emitted from an oil-fired power plant. Diameter of the particle is approximately 2.5  $\mu\text{m}$ . Photo courtesy of Willis R, U.S. Environmental Protection Agency.

mode with the 10- $\mu\text{m}$  maximum are particles introduced to the atmosphere as solids from the surface of the earth and the seas, plus particles from the coagulation-condensation mode which have grown larger and moved across the trough between the modes into the larger size mode. These are primarily silicon, iron, aluminum, sea salt, and plant particles. Thus, there is a dynamism that creates small particles, allows them to



**FIGURE 3.5 Grand average number ( $N$ ), surface area ( $S$ ), and volume ( $V$ ) distribution of Los Angeles smog.** The linear ordinate normalized by total number ( $NT$ ), area ( $ST$ ), or volume ( $VT$ ) is used so that the apparent area under the curves is proportional to the quantity in that size range. *Corn M. Properties of non-viable particles in the air. In: Stern AC, editor. Air pollution. 3rd ed., vol. 1. New York: Academic Press; 1976. p. 123.*

grow larger, and eventually allows the large particles to be scavenged from the atmosphere by sedimentation (in the absence of precipitation), plus washout and rainout when there is precipitation.

The majority of particles in the atmosphere are spherical in shape because they are formed by condensation or cooling processes or they contain core nuclei coated with liquid. Liquid surface tension draws the material in the particle into a spherical shape. Other important particle shapes exist in the atmosphere; e.g. asbestos is present as long fibers and fly ash can be irregular in shape. The amount of each element or radical, anion, or cation that is present in the mixture can be determined. Specific organic compounds may be separated and identified. The shapes of individual particles may be analyzed by electron microscopy.

Particle size is important for many reasons. They dictate the necessary control technologies. They determine the types of health and environmental problems to be expected when particles are inhaled and retained by the human respiratory system and when particles absorb and scatter incoming solar radiation.

### 3.4 ATMOSPHERIC TRANSPORT AND FATE

A number of scientific concepts apply to the movement of air pollutants and other airborne substances in the atmosphere. Air pollutants are studied from at least

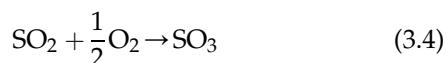
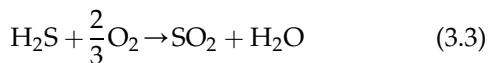
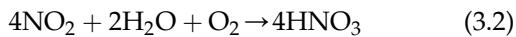
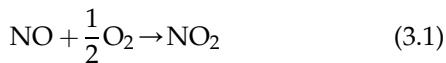
three perspectives: the sources, the movement, and the receptors. The sources of air pollutants vary in size (e.g. tons emitted per year), type (e.g. stationary or mobile) and composition (e.g. coke oven emissions include thousands of compounds, but many smelters include a handful of metals). Movement can range from molecular diffusion to continental and global transport in winds aloft. Receptors include humans, ecosystems, and materials. Following are a few concepts that underpin most discussions about air pollution.

#### 3.4.1 Sources and Sinks

The places from which pollutants emanate are called *sources*. There are natural as well as anthropogenic sources of the particles and gases considered to be pollutants. These include plant and animal respiration and the decay of what was once living matter. Volcanoes and naturally caused forest fires are other natural sources. A special type of natural sources are *biogenic*, which are living things that release a variety of pollutants, both organic (e.g. volatiles like pinene) and inorganic (e.g. carbon dioxide [ $\text{CO}_2$ ] and methane [ $\text{CH}_4$ ]). The places to which pollutants disappear from the air are called *sinks*. Sinks include the soil, vegetation, structures, and water bodies, particularly the oceans. The mechanisms whereby pollutants are removed from the atmosphere are called *scavenging mechanisms*, and the measure used for the aging of a pollutant is its *half-life*—the time it takes for half of the quantity of a pollutant emanating from a source to disappear into its various sinks. Fortunately, most pollutants have a rather short half-life (i.e. days rather than decades) that prevents their accumulation in the air to the extent that they substantially alter the composition of unpolluted air shown in Table 1.1. Several gases do appear to be accumulating in the air to the extent that measurements have documented the increase in concentration from year to year. The best-known example is  $\text{CO}_2$ . Other accumulating gases are nitrous oxide ( $\text{N}_2\text{O}$ ),  $\text{CH}_4$ , CFCs, and other halocarbons. All of these gases have complex roles in climate change processes, and thus are at the center of discussions about global warming concerns. CFCs are chemically very stable compounds in the troposphere and have half-lives from tens of years to over hundreds of years. One of the sinks for CFCs is transport to the stratosphere, where shortwave UV radiation photodissociates the molecules, releasing chlorine (Cl) atoms. When in excess, these Cl atoms decrease the steady-state stratospheric ozone concentration, in turn increasing the penetration of harmful UV radiation to the earth's surface.

Oxidation, either atmospheric or biological, is a prime removal mechanism for inorganic as well as organic gases. Inorganic gases, such as nitric oxide (NO),

nitrogen dioxide ( $\text{NO}_2$ ), hydrogen sulfide ( $\text{H}_2\text{S}$ ), sulfur dioxide ( $\text{SO}_2$ ), and sulfur trioxide ( $\text{SO}_3$ ), may eventually form corresponding acids:



Oxidation of  $\text{SO}_2$  is slow in a mixture of pure gases, but the rate is increased by light,  $\text{NO}_2$ , oxidants, and metallic oxides which act as catalysts for the reaction. The formed acids can react with PM or ammonia to form salts.

### 3.4.2 Receptors

A *receptor* is something that is adversely affected by polluted air. A receptor may be a person or animal that breathes the air and whose health may be adversely affected thereby, or whose tissue may be irritated, or whose surfaces (e.g. skin, leaf cover, roof) may be coated or discolored. It may be a tree or plant that dies, or the growth yield or appearance of which is adversely affected. It may be some material such as paper, leather, cloth, metal, stone, or paint that is affected. Some properties of the atmosphere itself, such as its ability to transmit radiant energy, may be affected. Aquatic life in lakes and some soils are adversely affected by acidification via acidic deposition.

### 3.4.3 Transport and Dispersion

Transport is the mechanism that moves the pollution from a source to a receptor. The simplest source–receptor combination is that of an isolated point source and an isolated receptor. A point source may best be visualized as a chimney or stack emitting a pollutant into the air; the isolated point source might be the stack of a smelter standing by itself in the middle of a flat desert next to the body of ore it is smelting. The isolated receptor might be a resort hotel 5 mi distant on the edge of the desert. The effluent from the stack will flow directly from it to the receptor when the wind is along the line connecting them (Figure 3.6). The wind is the means by which the pollution is transported from the source to the receptor. However, during its transit over the 5 mi between the source and the receptor, the plume does not remain a cylindrical tube of pollution of the same diameter as the interior of the stack from which it was emitted. Instead, as it travels over the 5-mile distance, turbulent eddies in the air and in the plume move parcels from the edges of the plume into the surrounding air and move parcels of surrounding air into the plume. If the wind speed is greater than the speed of ejection from the stack, the wind will stretch out the plume until the plume speed equals wind speed. These two processes—mixing by turbulence and stretch-out of the plume, plus a third one, meandering (which means that the plume may not follow a true straight line between the source and the receptor but may meander somewhat about that line as wind direction fluctuates from its mean value over the time of transit between the two points)—tend to make the concentration of the plume as it arrives at the receptor less than its concentration on release from the stack. The sum of all these processes is called *diffusion*. However, the term diffusion has a substantially different meaning in chemistry. Substances diffuse

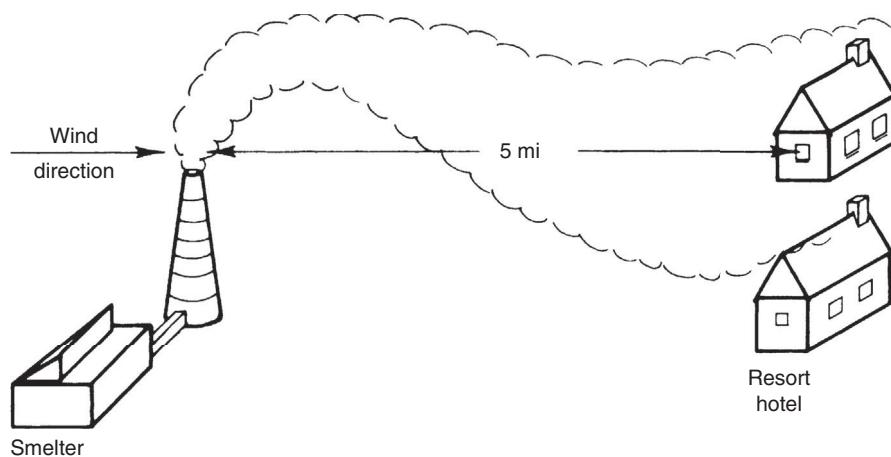


FIGURE 3.6 Transport and dispersion of air pollutants in a plume, connecting an air pollution source to a receptor.

according to Fick's law of diffusion, wherein the concentration diminishes with distance from the source. This is known as a concentration gradient. Therefore, dispersion is the preferred term when discussing atmospheric transport at a scale larger than molecular.

If the plume carrying air pollutants is above the height where ground-based convective and turbulent processes will bring it down to the ground reasonably close to its origin, it may travel for hundreds of miles at that height before being brought to earth by these processes in a remote community. This is known as long-range or long-distance transport.

### 3.4.4 Polluted Atmosphere

Most atmospheric constituent data presented in meteorological and atmospheric science references are assumed to reflect the composition of an "unpolluted" atmosphere.

Air pollution exists within the context of time, space, and impact for a particular set of circumstances. The same chemical compounds or particles from a natural source (e.g. a volcano) elicit the same adverse effects as when they are emitted by anthropogenic sources. Thus, the source does not define air pollution. The receptor is a better reference point for determining whether air is polluted or unpolluted.

A substance in the same concentration in one scenario could be a pollutant, but not in another. For example, schools now must be careful to ensure that highly allergic children are not exposed to allergens, such as those emitted by certain legumes, such as peanuts (*Arachis hypogaea*). Most children would not be affected by the volatilization of small concentrations of vapors or aerosols from opening a package of peanut products. However, highly sensitive children might suffer a severe respiratory response. For this sensitive subpopulation, the indoor air in the school cafeteria would be "polluted". In this case, the school air may be deemed polluted by a substance that is not even regulated by environmental and occupational health agencies.

Thus, unpolluted air is merely a benchmark to show the extent and trends of air pollution. Governments around the world have established and are continuously evaluating the impact of elevated levels of myriad gases and particulate material in the atmosphere. Clearly, these agencies are charged with addressing polluted air so that it is healthy to breathe, supports ecosystems, and supports other welfare uses, such as visibility and integrity of buildings and other structures. This leads to the need to consider the risks brought about by a polluted atmosphere.

Although, air pollution is a scientific concept, during the second half of the twentieth century, air pollution definitions progressively joined the legal parlance. For example, the State of Florida defines air pollution as

"the presence of any substances in the atmosphere in quantities which are or may be harmful or injurious to human health, welfare, animal or plant life, or property or unreasonably interfere with the enjoyment of life or property".<sup>4</sup> Similarly, the State of Victoria, Australia, says that "air pollution occurs when the air contains gases, dust, fumes or odor in harmful amounts. That is, a substance is an air pollutant only in amounts which could be harmful to the health or comfort of humans and animals or which could cause damage to plants and materials".<sup>5</sup> Terms like "unreasonably" and "could be" are problematic for scientists, since such words are quite subjective. Unfortunately, this is often the case for debates as to what air pollution is and is not. When a substance is deemed to be an air pollutant, the governments are compelled to set standards and to require prevention, control, and other actions to decrease the pollution to a concentration considered acceptable from a public health or environmental perspective. The decision of when air is considered to be polluted never completely rests within the bounds of science.

Air quality control agencies must decide when a concentration of a substance is acceptable and when it is unacceptable. This leads to the need to consider the risks brought about by a polluted atmosphere.

As the peanut allergy example illustrates, even if the atmosphere is not generally polluted, the atmosphere is often compartmentalized so that parts of the atmosphere can still be polluted. Indeed, average pollution is not nearly as important as pollution in particular microenvironments. For example, indoor air pollution is extremely important, since in most parts of the world people spend more time indoors than out. Thus, if ambient conditions are acceptable, but microenvironmental air is polluted, the public health is harmed.

Air pollutants are a type of "contaminant". Contamination often is a call to arms for regulators. Contamination implies that something must be cleaned up. For example, if a community were told that their yards, homes, neighborhoods, or air is contaminated, it is very likely that the residents would be greatly troubled. They would probably want to know the extent of the contamination, its source, what harm they may have already suffered from it, and what they can do to reduce it. Contamination is also a term that is applied differently by scientists and the general public, as well as among scientists from different disciplines.

The dictionary<sup>7</sup> definition of the verb "contaminate" includes "to corrupt by contact or association", or "to make inferior, impure, or unfit". These are fairly good descriptions of air pollutants. When they come into contact with people, ecosystems, crops, materials, or anything that society values, they cause harm. They make resources less valuable or less fit to perform their useful purposes. From an air quality perspective, contamination

is usually meant to be “chemical contamination” and this most often is within the context of human health. However, air pollution abatement laws and programs have recognized that effects beyond health are also important, especially *welfare* protection. Thus, public health is usually the principal driver for assessing and controlling environmental contaminants, but ecosystems are also important receptors of contaminants. As mentioned, contaminants also impact structures and other engineered systems, including historically and culturally important monuments and icons, such as the contaminants in rainfall (e.g. nitrates and sulfates) that render it more corrosive than would normally be expected (i.e. acid rain).

Contaminants are not limited to abiotic chemical substances, but can be biological (viruses, molds, etc.) and physical, such as the energy from ultraviolet (UV) light. In some instances, the physical contamination, this exposure is realized by chemical contamination. For example, the release of chemicals into the atmosphere, in turn react with ozone in the stratosphere, decreasing

the ozone concentration and increasing the amount of UV radiation at the earth’s surface. This has meant that the mean UV dose in the temperate zones of the world has increased. Higher UV dosage has been associated with an increase in the incidence of skin cancer, especially the most virulent form, melanoma. The disease is the result of UV exposure, but the UV exposure has been increased due to chemical reactions in the stratosphere, decreasing the absorption of UV.

The characteristics of the pollutant *and* the characteristics of the place where the chemical is found determines the extent and severity of pollution. This place is known as the “environmental medium”. The major environmental media are air, water, soil, sediment, and even biota. This book is principally concerned with the air medium, but every medium affects or is affected by air pollution actions and inactions, as demonstrated by the fuel additive methyl tertiary-butyl ether (MTBE) (see Discussion Box: Cure Worse than the Disease: The Case of MTBE).

## CURE WORSE THAN THE DISEASE: THE CASE OF MTBE

Automobiles generally rely on the internal combustion engine to supply power to the wheels.<sup>8</sup> Gasoline is the principal fuel source for most cars. The exhaust from automobiles is a large source of air pollution, especially in densely populated urban areas. To improve fuel efficiency and to provide a higher octane rating (for antiknocking), most gasoline formulations have relied on additives. Up to relatively recently, the most common fuel additive to gasoline was tetraethyl-lead. But with the growing awareness of lead’s neurotoxicity and other health effects, tetraethyl-lead has been banned in most parts of the world, so suitable substitutes were needed.

Methyl tertiary-butyl ether (MTBE) was one of the first replacement additives, first used to replace the lead additives in 1979. It is manufactured by reacting methanol and isobutylene, and has been produced in very large quantities (more than 200,000 barrels per day in the United States in 1999). MTBE is a quite volatile (vapor pressure = 27 kPa at 20 °C), so that it is likely to evaporate readily. It also readily dissolves in water (aqueous solubility at 20 °C = 42 g l<sup>-1</sup>) and is very flammable (flash point = 230 °C).

MTBE is a member of the chemical class of oxygenates. The Clean Air Act called for greater use of oxygenates in an attempt to help to reduce the emissions of carbon monoxide (CO), one of the most important air pollutants. So in 1992, MTBE began to be used at higher concentrations in some gasoline to fulfill the oxygenate requirements.

Even before the national mandate, some cities, notably Denver, used MTBE at higher concentrations during the wintertime in the late 1980s.

The rationale was noble, given that CO toxicity results by interfering with the protein hemoglobin’s ability to carry oxygen. Hemoglobin absorbs CO about 200 times faster than its absorption rate for oxygen. The CO-carrying protein is known as carboxyhemoglobin and when sufficiently high it can lead to acute and chronic effects. This is why smoking cigarettes leads to cardiovascular problems, i.e. the body has to work much harder because the normal concentration of oxygen in hemoglobin has been displaced by CO. CO is also a contributing factor in the photochemistry that leads to elevated levels of ozone (O<sub>3</sub>) in the troposphere. In addition, oxygenates decrease the emissions of volatile organic compounds (VOCs), which along with oxides of nitrogen are major precursors to the formation of tropospheric O<sub>3</sub>. This is one of the most important roles of oxygenates, since unburned hydrocarbons can largely be emitted before catalytic converters start to work.

From an air pollution control perspective, the use of MTBE was a success by providing oxygen and helping gasoline burn more completely, resulting in less harmful exhaust from motor vehicles. The oxygen also dilutes or displaces compounds such as benzene and its derivatives (e.g. toluene, ethyl benzene, and xylene), as well as sulfur. The oxygen in the MTBE molecule also

(Continued)

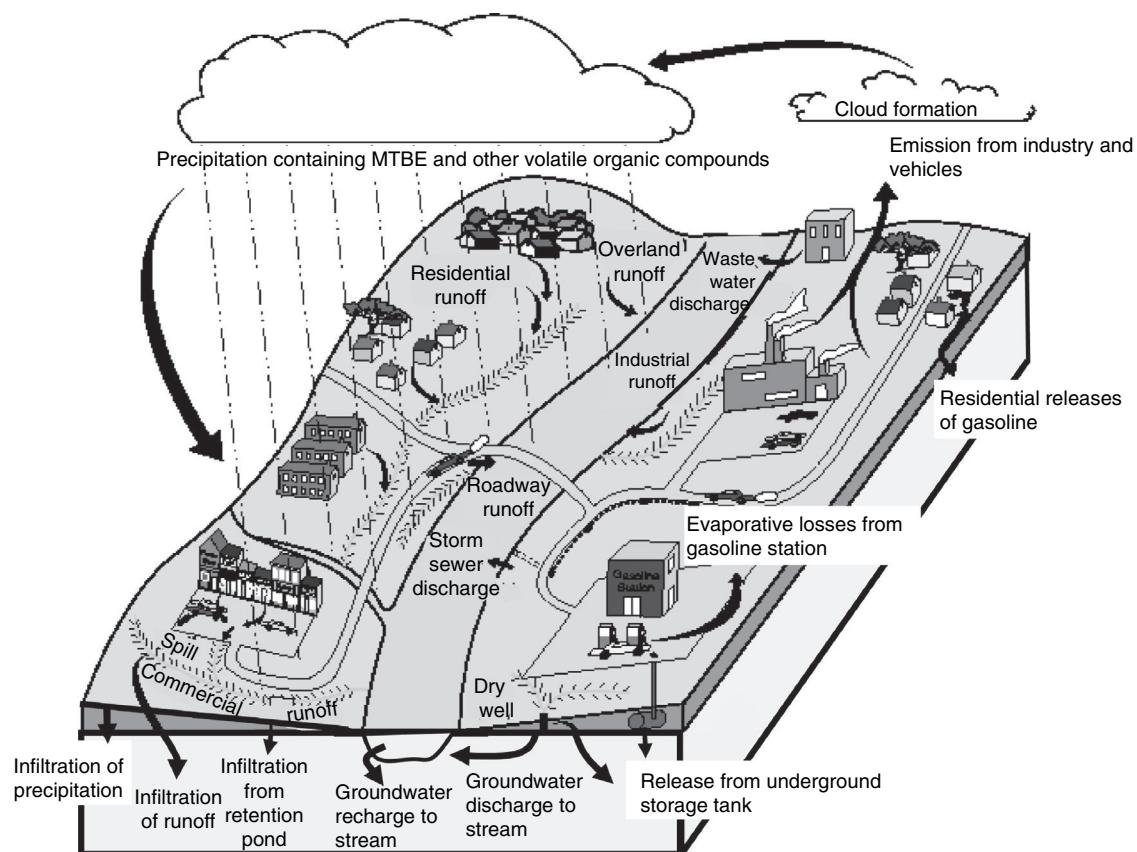
### CURE WORSE THAN THE DISEASE: THE CASE OF MTBE (cont'd)

enhances combustion (recall that combustion is oxidation in the presence of heat). MTBE was not the only oxygenate, but it has very attractive blending characteristics and is relatively cheap compared to other available compounds. Another widely used oxygenate is ethanol.

Unfortunately, MTBE exposure has been linked to certain health effects, including cancer in some animal studies. In addition, MTBE has subsequently been found to pollute water, especially groundwater in aquifers. Some of the pollution comes from unburned MTBE emitted from tailpipes, some from fueling, but a large source is underground storage tanks (USTs) at gasoline stations or other fuel operations (see Figure 3.7). A

number of these tanks have leaked into the surrounding soil and unconsolidated media and have allowed the MTBE to migrate into the groundwater. Since it has such a high aqueous solubility, the MTBE is easily dissolved in the water.

When a pollutant moves from one environmental compartment (e.g. air) to another (e.g. water), as it has for MTBE, this is known as cross-media transfer. The problem has not really been eliminated, just relocated. It is also an example of a risk trade-off, albeit unknown at the time. The risks posed by the air pollution were traded for the new risks from exposure to MTBE-contaminated waters. These trade-offs are discussed as part of the discussion of life cycles in Chapter 5.



**FIGURE 3.7 Migration of MTBE in the environment.** Delzer GC, Zogorski JS, Lopes TJ, Bosshart RL. Occurrence of the gasoline oxygenate MTBE and BTEX in urban stormwater in the United States, 1991–95. US Geological Survey. Water Resources Investigation Report 96-4145, Washington (DC); 1996.

### 3.5 AIR POLLUTION ENGINEERING

When air pollution engineering first became recognized as a unique discipline, most of the engineers involved called themselves sanitary engineers, but now they are usually considered to be environmental engineers. “Environmental engineering” for the most part has replaced “sanitary engineering” in the United States. Sanitary engineering has existed as a field since at least as early as the nineteenth century. The School of Military Engineering at Chatham, Kent, England, held a series of lectures given by J. Bailey Denton in 1876.<sup>6</sup> By that time, Denton had already written extensively on sanitary engineering concepts and practices, including wastewater, potable water, drainage, and town planning. In the preface of the book capturing these lectures, Denton stated his desire “to place before the engineering student the character of information which will qualify him for Sanitary duties, being much impressed with the conviction that, until all those who are charged with the *execution of works* upon which the public health depends, fully appreciate the principles which guide the Medical Officer in his opinions and reports, and comprehend the data which govern the Chemist in his analyses and deductions, they will be placed at a great disadvantage, and cannot entirely command the confidence of the public”. (capitalization and italics are Denton’s).

Denton’s view of sanitary engineering continues to be emblematic of professionals and scientists engaged in addressing air pollution. First, he reminds the engineer this, to paramount the safety, health, and welfare of the public even before professional conduct had been codified as the first canon of engineering ethics. Thus, to the sanitary engineer first and the environment engineer later, the public places its trust in the engineer to ensure the air is healthful. Denton also ties the work of the engineer to the health profession (i.e. the medical officer). Engineers must understand and connect their work with that of the biomedical community, e.g. health-based air quality standards. Finally, Denton reminds us that public health officials and engineers must base their decisions and designs on physicochemical principles.

Although sanitary engineering generally and Denton specifically focused on water quality and quantity, his first lecture addressed air. His description of the constituents was quite accurate: “Air in its normal condition consists of about four-fifths, by volume, nitrogen, and one-fifth oxygen”. He also accurately estimated that the air contains carbonic acid (the source of reduced pH in unpolluted air).

In an early scientific definition of air pollution, Denton concluded that altering the constituents, e.g. “increase of carbonic acid, and mixture of other foreign

matters”, leads to unhealthy air (although he quotes his colleague, Angus Smith, as attributing this mainly to the reduction in oxygen content, rather than to the toxicity of the “foreign matters”). An interesting observation is that since carbonic acid has a sour taste, and nitrogen and oxygen have no taste, the fouling of the air can be largely attributed to increased carbonic acid. This is interesting because Denton and Smith appear to indicate that combustion is somehow tied to air pollution; a fact we now accept, but was less obvious in the nineteenth century.

In the United States, the field of environmental engineering can be traced back to the early part of the twentieth century, with the first mention in 1890 by the War Department’s Chief of Engineers’ Report of the Examination and Survey of the Savannah River above Augusta (Georgia). The U.S. Public Health Service’s Division of Environmental Engineering and Food Protection was established in 1961.<sup>9</sup>

There were many reasons for the name change from “sanitary” to “environmental”. One certainly is the growing appreciation for the interconnections among abiotic and biotic systems in the protection of ecosystems and human health. Starting with the New Deal in second quarter of the twentieth century, engineers engaged in “public works” projects, which in the second half of the century evolved to include sanitary engineering projects, especially wastewater treatment plants, water supplies, and sanitary landfills. Meanwhile, sanitary engineers were designing cyclones, electrostatic precipitators, scrubbers, and from other devices to remove air pollutants from industrial emissions.

The realization that there was much more that engineers design beyond these structures and devices has led to comprehensive solutions to environmental problems. Certainly, structural and mechanical solutions are still the foundation of air pollution engineering, but these are now seen as a part of an overall set of solutions. Thus, systems engineering, optimizations, and the application of more than physical principles (adding chemical and biological foundations) are better reflected in “environmental engineering” than in sanitary engineering. Air pollution engineering has the problem in that “everything seems to matter”.<sup>10</sup> The challenge for the engineer is to choose wisely the variables to be optimized.

By the mid-1970s, many universities had replaced sanitary engineering majors with environmental engineering (see [Figure 3.8](#)). This could in part be because “sanitary” implies human health, while “environmental” brings to mind ecological and welfare as well as human health as primary objectives of the profession. Sanitation is the province of industrial hygienists and public health professionals. The protection of the environment is a broader mandate for engineers.

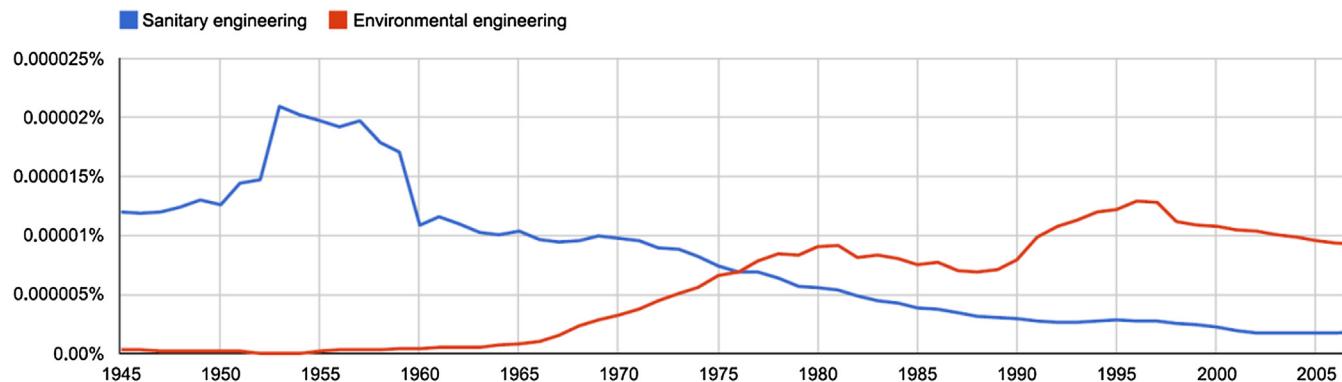


FIGURE 3.8 Books addressing sanitary engineering and environmental engineering, from 1945 through 2008. Sanitary engineering peaked in the early 1950s, with a cross-over in 1976, after which environmental engineering became the principal subject of engineering books. *Google Books, Ngram Viewer; //Aa.ad.epa.gov/ord/RTP/Users/A-D/dvallero/net mydocuments/Sanitary Environ Enviro ngram.nht*; [accessed 06.08.13]. (For color version of this figure, the reader is referred to the online version of this book.)

The historical “inertia” may help to explain why environmental engineering, and its subdiscipline air pollution engineering, is commonly considered to be a civil rather than chemical engineering field. This can be in part due to chemical engineering’s concern with the design and building of systems (e.g. “reactors”) that convert raw materials into useful products. So, in a way, chemical engineering is the mirror image of pollution engineering, which strives to remove and treat substances, e.g. converting complex chemicals to simpler compounds (ultimately  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$ ). So, one could view the two fields as a chemical equilibrium within which reactions in each direction are equal. Chemical engineers design reactors to synthesize compounds and air pollution engineers design systems to collect and degrade compounds.

Actually, both fields are crucial in addressing air pollution and contribute in unique ways. Treatment systems are indeed reactors. Toxic and harmful reagents enter and, hopefully, innocuous products exit. In addition, chemical engineers improve processes within industry so that less pollution results, i.e. “green engineering”.

### 3.6 SOCIAL ASPECTS OF AIR POLLUTION

Environmental quality is important to everyone. This book stresses the importance of sound science, but it should always be understood that when it comes to the environment and public health, the social sciences can never be ignored. Certain social values have been passed down for generations, while others have been recently adapted to changes. For example, if a person or neighborhood has just experienced a nasty battle with an industry or governmental organization regarding an environmental decision, such as the location of landfill or prohibition of a certain type of use of their own land, they may be reticent to trust the environmental professional who

promises that it will be different this time. The second half of the twentieth century, particularly the time from the mid-1960s through the 1970s ushered in a new environmental ethos, or at least memorialized the fact that most, if not all, people expect certain quality of the environment. The laws and policies stemming from these years are still evolving.

Environmental awareness grew in the second half of the twentieth century. With this awareness, the public demand for environmental safeguards and remedies to environmental problems was an expectation of a greater role for government. A number of laws were on the books prior to the 1960s, such as early versions of federal legislation to address limited types of water and air pollution, and some solid waste issues, such as the need to eliminate open dumping. The real growth, however, followed the tumultuous decade of the 1960s. Environment had become a social cause, akin to the civil rights and antiwar movements. Major public demonstrations on the need to protect “spaceship earth” encouraged elected officials to address environmental problems, exemplified by air pollution “inversions” that capped polluted air in urban valleys, leading to acute diseases and increased mortality from inhalation hazards, the “death” of Erie Canal and rivers catching on fire in Ohio and Oregon.

### 3.7 AIR POLLUTION LAWS

The increased awareness and public demand for improved environmental quality led to exponential growth of laws, rules, and policies around the world to address air pollution. Some directly target air pollutants, e.g. the Clean Air Act in the United States, the Clean Air and Climate Act in Canada, and similar laws in Europe and Asia. As indicated in Table 3.1, the

TABLE 3.1 Comparison of US Clean Air Act Provisions to European Air Quality Policies and Measures

US	EU
Geographical areas covered	Each state has primary responsibility for assuring air quality within its entire geographic area. AQ is managed on the basis of air quality control regions (AQCRs), usually counties, US EPA may redesignate any interstate or major intrastate areas into one AQCR if necessary or appropriate for AQM
What triggers the planning requirement	States must submit state implementation plans (SIPs) covering each of the NAAQs for the AQCRs within their areas. The SIP is either an attainment-maintenance SIP (if the AQCR is designated as in attainment) or an attainment demonstration SIP (if the AQCR is designated as nonattainment).
Consequences related to status of attainment	Requirements for control measures & deadlines for achieving attainment are differentiated according to the severity (degree) of nonattainment.
Who makes the plans	Agency(s) differ from state to state due to various geographic spans of AQCRs. A SIP can be prepared by the state authority or a local or regional government.
What is required to be in the plans	SIPs are required to include a list of local, state, regional, and federal air quality control measures in accordance with the pollutant-specific requirements provided by the Clean Air Act (CAA).
Transboundary aspects	Downwind states can petition EPA to have upwind contribution recognized & force upwind state to take action (NO <sub>x</sub> SIP call resulted in upwind states being given caps for LCP emissions)
Regulatory oversight during the review process of the plans	Once SIPs are developed, they are submitted to EPA to check if the plan meets requirements. If EPA approves the SIP, it becomes enforceable as a matter of federal & state law (& subject to lawsuits if failure to comply).
Consequences of inadequate plans	EPA can disapprove a SIP if it does not meet the procedural and substantive requirements & require a resubmission with revisions. If a state fails to generate a SIP, EPA has the power to control the AQM programs for that state. In extreme cases, EPA can replace an inadequate SIP with a federal implementations plan (FIP).
Consequences of noncompliance and/or nonattainment	If AQCRs fail to demonstrate attainment by deadline, the following measures can be applied: (1) sanctions: (a) 2-to-1 emission offset sanctions before allowing any new or expanded major stationary sources; (b) withholding of federal funding for highway projects, except for projects to improve safety, transit, & AQ; (c) federal funding, authorization, or approval of any project or program that does not conform with the SIPs withheld; (2) "bump-up" provision: reclassification of a failed ozone nonattainment area to a higher classification, triggering more stringent requirements; and (3) penalty fee (severe & extreme ozone nonattainment areas only): each major source in area required to pay \$5000 per ton of VOC or NO <sub>x</sub> emitted in excess of 80% of the stationary source's permitted level of emissions until attainment is demonstrated.
	<ol style="list-style-type: none"> <li>Under the AQFD, each member state is responsible for ensuring air quality within its territory, and for designating agglomerations and zones on the basis of AQ management considerations.</li> <li>The NECD also places responsibility on each member state to reduce emissions within its territory.</li> </ol> <p>The AQFD requires plans only for those zones and agglomerations with pollutant levels higher than the AQLVs, and not if a zone is in attainment.</p> <p>The NECD requires MS to draw up national-level programs for progressive reduction of pollutants as required to achieve ceilings by 2010.</p> <p>No differentiation in terms of requirements for control measures or attainment deadlines on the basis of severity of nonattainment.</p> <ol style="list-style-type: none"> <li>MS designate at the appropriate levels the competent authorities and bodies responsible for implementing the AQFD requirements.</li> </ol> <p>The AQFD requires plans to list main emission sources, total emissions from these sources (tonnes/year), pollution imported from other regions, description of measures; estimated improvement of AQ &amp; time to attain the objectives.</p> <ol style="list-style-type: none"> <li>Member states required to consult each other when level of pollution due to significant pollution originating in another member state.</li> <li>NECs set at levels aimed at reducing regional pollutant transport problems.</li> </ol> <p>AQFD requires MS to report to Commission on the plans &amp; programs prepared in order to attain the target value, &amp; to inform the Commission every 3 years on the progress of any such plan or program.</p> <ol style="list-style-type: none"> <li>AQFD does not specify. In general, if an MS is not in compliance with EU law, the Commission can decide to initiate an infringement action (see below).</li> </ol> <ol style="list-style-type: none"> <li>The Commission publishes an annual list of the zones &amp; agglomerations in exceedance of AQLVs.</li> <li>The Commission is obliged to submit reports in 2004 &amp; 2008 to the Council &amp; European Parliament on progress toward meeting the NECs. The reports, if appropriate, are to be accompanied by proposals for modifications to the NECs, possible further emission reductions, and/or measures to ensure compliance with the ceilings.</li> </ol> <p>If an MS does not comply with the AQLVs or the NEC, the Commission may pursue an infringement action, including an action before the European Court of Justice, under its general power of enforcement over the MS.</p>

Source: Danish National Environmental Research Institute and the European Commission, Center for Clean Air Policy. [http://ec.europa.eu/environment/archives/cafe/activities/pdf/case\\_study2.pdf](http://ec.europa.eu/environment/archives/cafe/activities/pdf/case_study2.pdf); 2004 [accessed 25.09.13].

goals and approaches are similar. Other laws and regulations address environmental quality more generally, but include provisions for air quality.

### 3.7.1 The National Environmental Policy Act

The movement was institutionalized in the United States by a series of new laws and legislative amendments. The National Environmental Policy Act (NEPA) was in many ways symbolic of the new federal commitment to environmental stewardship. It was signed into law in 1970 after contentious hearings in the U.S. Congress. NEPA was not really a technical law. It did two main things. It created the Environmental Impact Statement (EIS) and established the Council on Environmental Quality (CEQ) in the Office of the President. Of the two, the EIS represented a sea change in how the federal government was to conduct business. Any federal agency was required to prepare EISs on any major action that it was considering that could “significantly”<sup>a</sup> affect the quality of the environment. From the outset, the agencies had to reconcile often-competing values; i.e. their mission and the protection of the environment.

The CEQ was charged with developing guidance for all federal agencies regarding NEPA compliance, especially when and how to prepare an EIS. The EIS process combines scientific assessment with public review. The process is similar for most federal agencies. Agencies often strive to receive a so-called “FONSI” or the finding of no significant impact, so that they may proceed unencumbered on a mission-oriented project.<sup>11</sup> Whether a project either leads to a full EIS or a waiver through the FONSI process, it will have to undergo an evaluation. This step is referred to as an “environmental assessment”. An incomplete or inadequate assessment will lead to delays and increases the chance of an unsuccessful project, thus sound science is needed from the outset of the project design. The final step is the record of decision (ROD). The ROD describes the alternatives and the rationale for final selection of the best alternative. It also summarizes the comments received during the public reviews and how the comments were addressed. Many states have adopted similar requirements for their RODs.

The EIS documents were supposed to be a type of “full disclosure” of actual or possible problems if a federal project is carried out. This was accomplished by looking at all of the potential impacts to the environment from any of the proposed alternatives, and comparing those outcomes to a “no action” alternative. At first,

many tried to demonstrate that their “business as usual” was in fact very environmentally sound. In other words, the environment would be better off with the project than without it (action is better than no action). Too often, however, an EIS was written to justify the agency’s mission-oriented project. One of the key advocates for the need for a national environmental policy, Lynton Caldwell, is said to have referred to this as the federal agencies using an EIS to “make an environmental silk purse from a mission-oriented sow’s ear!”<sup>12</sup> The courts adjudicated some very important laws along the way, requiring federal agencies to take NEPA seriously. Some of the aspects of the “give and take” and evolution of federal agencies’ growing commitment to environmental protection were the acceptance of the need for sound science in assessing environmental conditions and possible impacts, and the very large role of the public in deciding on the environmental worth of a highway, airport, dam, waterworks, treatment plant, or any other major project sponsored by or regulated by the federal government. This change provided a major impetus in the growth of the environmental disciplines since the 1970s. Experts were needed who not only would “do the science” but who could communicate what their science means to the public.

All federal agencies must follow the CEQ regulations<sup>13</sup> to “adopt procedures to ensure that decisions are made in accordance with the policies and purposes of the Act”. This process must be set up in advance, early in an agency’s planning stages. For example, if waste remediation or reclamation is a possible action, the NEPA process must be woven into the remedial action planning processes, beginning with the identification of the need for and possible kinds of actions being considered. Noncompliance or inadequate compliance with NEPA rules and regulations has led lawsuits, increased project costs, delays, and the loss of the public’s loss of trust and confidence, even if the project is designed to improve the environment, and even if the compliance problems seem to be only “procedural”.

The U.S. EPA is responsible for reviewing the environmental effects of all federal agencies’ actions. This authority was written as Section 309 of the Clean Air Act. The review must be followed with the EPA’s public comments concerning the environmental impacts of any matter related to the duties, responsibilities, and authorities of EPA’s administrator, including EISs. The EPA’s rating system (see Table 3.2) is designed to determine whether a proposed action by a federal agency is unsatisfactory from the standpoint of public health, environmental quality, or public welfare. This determination is

<sup>a</sup> This is the actual adjective used in NEPA. It is unfortunate given its ambiguity. Also, “significant” is a term with clear meaning in the sciences, i.e. unlikely to occur by chance at a defined level of confidence (e.g. 0.05%); which is not the meaning in NEPA.

TABLE 3.2 Summary of the US Council on Environmental Quality Guidance for Compliance with the National Environmental Policy Act of 1969

Title of Guidance	Summary of Guidance	Citation	Relevant Regulation/ Documentation
Forty most often asked questions concerning CEQ's NEPA regulations	Provides answers to 40 questions most frequently asked concerning implementation of NEPA.	46 FR 18026, dated March 23, 1981	40 CFR parts 1500–1508
Implementing and explanatory documents for Executive Order (EO) 12114, environmental effects abroad of major federal actions	Provides implementing and explanatory information for EO 12114. Establishes categories of federal activities or programs as those that significantly harm the natural and physical environment. Defines which actions are excluded from the order and those that are not.	44 FR 18672, dated March 29, 1979	EO 12114, environmental effects abroad of major federal actions
Publishing of three memoranda for heads of agencies on: <ul style="list-style-type: none"> <li>• Analysis of impacts on prime or unique agricultural lands (Memoranda 1 and 2)</li> <li>• Interagency consultation to avoid or mitigate adverse effects on rivers in the Nationwide Inventory (Memorandum 3)</li> </ul>	1 or 2 Discusses the irreversible conversion of unique agricultural lands by Federal Agency action (e.g. construction activities, developmental grants, and federal land management). Requires identification of and cooperation in retention of important agricultural lands in areas of impact of a proposed agency action. The agency must identify and summarize existing or proposed agency policies, to preserve or mitigate the effects of agency action on agricultural lands. 3 "Each Federal Agency shall, as part of its normal planning and environmental review process, take care to avoid or mitigate adverse effects on rivers identified in the Nationwide Inventory prepared by the Heritage Conservation and Recreation Service in the Department of the Interior". Implementing regulations includes determining whether the proposed action: affects an Inventory river; adversely affects the natural, cultural, and recreation values of the Inventory river segment; forecloses options to classify any portion of the Inventory segment as a wild, scenic, or recreational river area, and incorporates avoidance/mitigation measures into the proposed action to maximum extent feasible within the agency's authority.	(45 FR 59189, dated September 8, 1980)	1/2 Farmland Protection Policy Act (7 USC §4201 et seq.) 3 The Wild and Scenic Rivers Act of 1965 (16 USC §1271 et seq.)
Memorandum for heads of agencies for guidance on applying Section 404(r) of the Clean Water Act at Federal projects which involve the discharge of dredged or fill materials into waters of the United States including wetlands	Requires timely agency consultation with U.S. Army Corps of Engineers (COE) and the U.S. EPA before a Federal project involves the discharge of dredged or fill material into U.S. waters, including wetlands. Proposing agency must ensure, when required, that the EIS includes written conclusions of EPA and COE (generally found in Appendix).	CEQ, dated November 17, 1980	Clean Water Act (33 USC §1251 et seq.) EO 12088, Federal compliance with pollution control standards
Scoping guidance	Provides a series of recommendations distilled from agency research regarding the scoping process. Requires public notice; identification of significant and insignificant issues; allocation of EIS preparation assignments; identification of related analysis requirements in order to avoid duplication of work; and the planning of a schedule for EIS preparation that meshes with the agency's decision-making schedule.	46 FR 25461, dated May 7, 1981	40 CFR parts 1500–1508
Guidance regarding NEPA regulations	Provides written guidance on scoping, CatEx's, adoption regulations, contracting provisions, selecting alternatives in licensing and permitting situations, and tiering.	48 FR 34263, dated July 28, 1983	40 CFR parts 1501, 1502, and 1508

(Continued)

TABLE 3.2 Summary of the US Council on Environmental Quality Guidance for Compliance with the National Environmental Policy Act of 1969—cont'd

Title of Guidance	Summary of Guidance	Citation	Relevant Regulation/ Documentation
NEPA implementation regulations, Appendices I, II, and III	Provides guidance on improving public participation, facilitating agency compliance with NEPA and CEQ implementing regulations. Appendix I updates required NEPA contacts, Appendix II compiles a list of Federal and Federal-State Agency Offices with jurisdiction by law or special expertise in environmental quality issues; and Appendix III lists the Federal and Federal-State Offices for receiving and commenting on other agencies' environmental documents.	49 FR 49750, dated December 21, 1984	40 CFR part 1500
Incorporating biodiversity considerations into environmental impact analysis under the NEPA	Provides for "acknowledging the conservation of biodiversity as national policy and incorporates its consideration in the NEPA process"; encourages seeking out opportunities to participate in efforts to develop regional ecosystem plans; actively seeks relevant information from sources both within and outside government agencies; encourages participating in efforts to improve communication, cooperation, and collaboration between and among governmental and nongovernmental entities; improves the availability of information on the status and distribution of biodiversity, and on techniques for managing and restoring it; and expands the information base on which biodiversity analyses and management decisions are based.	CEQ, Washington, DC, dated January 1993	Not applicable
Pollution prevention and NEPA	Pollution-prevention techniques seek to reduce the amount and/or toxicity of pollutants being generated, promote increased efficiency of raw materials and conservation of natural resources and can be cost-effective. Directs Federal agencies that to the extent practicable, pollution prevention considerations should be included in the proposed action and in the reasonable alternatives to the proposal, and to address these considerations in the environmental consequences section of an EIS and EA (when appropriate).	58 FR 6478, dated January 29, 1993	EO 12088, Federal Compliance with Pollution Control Standards
Considering cumulative effects under NEPA	Provides a "framework for advancing environmental cumulative impacts analysis by addressing cumulative effects in either an environmental assessment (EA) or an environmental impact statement". Also provides practical methods for addressing coincident effects (adverse or beneficial) on specific resources, ecosystems, and human communities of all related activities, not just the proposed project or alternatives that initiate the assessment process.	January 1997	40 CFR §1508.7
Environmental justice guidance under NEPA	Provides guidance and general direction on EO 12898 which requires each agency to identify and address, as appropriate, "disproportionately high and adverse human health or environmental effects of its programs, policies, and activities on minority populations and low-income populations".	CEQ, Washington, DC, dated December 10, 1997	EO 12898, Federal actions to address environmental justice in a minority populations and low-income populations

Source: National Aeronautics and Space Administration. Implementing the National Environmental Policy Act and Executive Order 12114; 2001 [chapter 2].

published in the *Federal Register* (for significant projects) and referred to the CEQ.

### 3.7.2 Clean Air Act and Amendments

The year 1970 was a watershed year in environmental awareness.<sup>b</sup> The 1970 amendments to the Clean Air Act (CAA) arguably ushered in the era of environmental legislation with enforceable rules. The 1970 version was enacted to provide a comprehensive set of regulations to control air emissions from area, stationary, and mobile sources.

The CAA's goal, from its beginning, has been to protect public health and the environment from air pollution. In the more recent versions, air pollutants are classified into categories, with distinction between "conventional" as opposed to "toxic" pollutants: ambient concentrations of vapors and particulate matter (PM), including those to reduce photochemical oxidant smog or ozone (see Discussion Box: Smog and Ozone). The six conventional or "criteria" pollutants that are covered under the NAAQS are summarized in Table 3.3.

Note that the NAAQS are continuously evaluated, with the possibility of adding criteria pollutants (the

TABLE 3.3 US National Ambient Air Quality Standards under the Clean Air Act Amendments

Criteria Pollutant	Primary/Secondary		Averaging Time	Level	Standard Description	
Carbon monoxide	Primary		8 h	9 ppm	Not to be exceeded more than once per year	
			1 h	35 ppm		
Lead	Primary and secondary		Rolling 3 month average	0.15 $\mu\text{g m}^{-3}$ *	Not to be exceeded	
Nitrogen dioxide <a href="http://www.epa.gov/airquality/nitrogenoxides/">http://www.epa.gov/airquality/nitrogenoxides/</a>	Primary		1 h	100 ppb	98th Percentile, averaged over 3 years	
	Primary and secondary		Annual	53 ppb <sup>§</sup>	Annual mean	
Ozone	Primary and secondary		8 h	0.075 ppm <sup>¶</sup>	Annual fourth-highest daily maximum 8-hr concentration, averaged over 3 years	
Particle pollution <a href="http://www.epa.gov/airquality/particlepollution/">http://www.epa.gov/airquality/particlepollution/</a>	PM <sub>2.5</sub>	Primary	Annual	12 $\mu\text{g m}^{-3}$	Annual mean, averaged over 3 years	
		Secondary	Annual	15 $\mu\text{g m}^{-3}$	Annual mean, averaged over 3 years	
	Primary and secondary		24 h	35 $\mu\text{g m}^{-3}$	98th Percentile, averaged over 3 years	
	PM <sub>10</sub>	Primary and secondary	24 h	150 $\mu\text{g m}^{-3}$	Not to be exceeded more than once per year on average over 3 years	
Sulfur dioxide	Primary		1 h	75 ppb <sup>  </sup>	99th Percentile of 1-h daily maximum concentrations, averaged over 3 years	
	Secondary		3 h	0.5 ppm	Not to be exceeded more than once per year	

\* Final rule signed October 15, 2008. The 1978 lead standard ( $1.5 \mu\text{g m}^{-3}$  as a quarterly average) remains in effect until one year after an area is designated for the 2008 standard, except that in areas designated nonattainment for the 1978, the 1978 standard remains in effect until implementation plans to attain or maintain the 2008 standard are approved.

† The official level of the annual NO<sub>2</sub> standard is 0.053 ppm, equal to 53 ppb, which is shown here for the purpose of clearer comparison to the 1-h standard.

¶ Final rule signed March 12, 2008. The 1997 ozone standard (0.08 ppm, annual fourth-highest daily maximum 8-h concentration, averaged over 3 years) and related implementation rules remain in place. In 1997, EPA revoked the 1-h ozone standard (0.12 ppm, not to be exceeded more than once per year) in all areas, although some areas have continued obligations under that standard ("antibacksliding"). The 1-h ozone standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is less than or equal to one.

|| Final rule signed June 2, 2010. The 1971 annual and 24-h SO<sub>2</sub> standards were revoked in that same rulemaking. However, these standards remain in effect until one year after an area is designated for the 2010 standard, except in areas designated nonattainment for the 1971 standards, where the 1971 standards remain in effect until implementation plans to attain or maintain the 2010 standard are approved.

Source: U.S. Environmental Protection Agency. <http://www.epa.gov/air/criteria.html>; 2013 [accessed 25.09.13].

<sup>b</sup> Perhaps we should say "airshed" year.

metal lead was the last to be added, but CO<sub>2</sub> is currently under discussion).

Existing NAAQS requirements are also revised when supported by sound science. For example, the particulate standard was changed to address finer particles; i.e. particles with diameters <2.5 µm (PM<sub>2.5</sub>), in response to research showing that exposure to these smaller particles is more likely to lead to health problems than do exposures to larger particles (see Chapters 9 and 10). Smaller particles are able to penetrate further into the lungs and likely are more bioavailable than the larger PM<sub>10</sub>. Recently, however, concerns about larger particles (e.g. PM<sub>10</sub>) have increased, particularly as research is beginning to link coarse particles to chronic diseases like asthma. Other provisions, such as averaging times, are evaluated and changed if they are deemed to be a better reflection of potential exposures and health effects.

The original goal was to set and to achieve NAAQS in every state by 1975. These new standards were combined with charging the 50 states to develop state implementation plans (SIPs) to address industrial, transportation, and other sources in the state. The ambient atmospheric concentrations are measured at over 4000 monitoring sites across the United States. The ambient concentrations have continuously decreased, as shown in Table 3.4.

The improvements in Table 3.3 correlate directly with reductions in emissions. Emission trends can be derived using on a combination of actual measurements and

**TABLE 3.4** Percent Change in Air Quality in the United States as Reflected by Trends in the Six National Ambient Air Quality Standard (NAAQS) Pollutants

	Time Period for Trend		
	1980 versus 2012	1990 versus 2012	2000 versus 2012
Carbon monoxide (CO)	-83	-75	-57
Ozone (O <sub>3</sub> ) (8 h)	-25	-14	-9
Lead (Pb)	-91	-87	-52
Nitrogen dioxide (NO <sub>2</sub> ) (annual)	-56	-50	-38
Nitrogen dioxide (NO <sub>2</sub> ) (1 h)	-60	-46	-29
PM <sub>10</sub> (24 h)	ND	-39	-27
PM <sub>2.5</sub> (annual)	ND	ND	-33
PM <sub>2.5</sub> (24 h)	ND	ND	-37
Sulfur dioxide (SO <sub>2</sub> ) (1 h)	-78	-72	-54

Notes: 1. ND = Trend data not available; 2. Negative numbers indicate improvements in air quality; 3. In 2010, EPA established new 1 h average NAAQS for NO<sub>2</sub> and SO<sub>2</sub>.

Source: U.S. Environmental Protection Agency; 2013.

models based on industrial activity, technologies, fuel consumption, vehicle miles traveled, etc. From these calculations, carbon monoxide and SO<sub>2</sub> emissions have each decreased by 70% since 1980. Nitric oxide (NO) and NO<sub>2</sub> together are known as NO<sub>x</sub>. Since 1980, NO<sub>x</sub> emissions have been halved. Emissions of volatile organic compounds (VOCs), which are precursors to O<sub>3</sub>, are a third of what they were in 1980. Dust and other particle emissions have also dropped by more than half. In spite of these improvements, about 90 million tons of NAAQS pollutants are still released annually in the United States.<sup>7</sup>

The Clean Air Act Amendments (CAAA) of 1977 mandated new dates to achieve attainment of NAAQS (many areas of the country had not met the prescribed dates set in 1970). Other amendments were targeted at insufficiently addressed types of air pollution, including acidic deposition (so-called "acid rain"), tropospheric ozone pollution, depletion of the stratospheric ozone layer, and a new program for air toxics, the National Emission Standards for Hazardous Air Pollutants (NESHAPs).

The 1990 Amendments to the Clean Air Act (CAAA90) profoundly changed the law, by adding new initiatives and imposing dates to meet the law's new requirements.

### 3.7.2.1 State Implementation Plans

The CAA's *criteria air pollutants* require measures to limit their concentrations in ambient air. Nonattainment areas those parts of the country where the air exceeds the NAAQS for any of the six criteria pollutants. Each state in the United States establishes a SIP to engage control strategies for reducing air pollution in nonattainment areas. These plans are periodically reviewed for effectiveness.

The SIP addresses mobile sources, including baselines and projection inventories of pollutants from automobiles and other mobile sources. The inventories are tools in targeting control strategies for on-road and off-road mobile sources. The SIP also addresses stationary sources by requiring control strategies to address pollutants from industrial facilities and other stationary sources. As for mobile sources, the SIP also requires stationary source inventories based on emissions data from major regulated facilities, as well as calculated emissions from minor stationary sources (i.e. area source calculations).<sup>8</sup>

### 3.7.2.2 Prevention Strategies: Source Review

The CAA includes provisions to keep clean air clean under the New Source Review (NSR). The NSR embodies sets of rules that apply to a proposed construction, either new or substantially modifications to an existing site. The two categories of NSR rules are: (1)

## SMOG AND OZONE

The term *smog* is a shorthand combination of “smoke—fog”. However, it is really the code word for photochemical oxidant smog, the brown haze that can be seen when flying into Los Angeles, St. Louis, Denver, and other metropolitan areas around the world (see [Figure 3.9](#)). Point-of-fact is that to make smog, at least three ingredients are needed: light, hydrocarbons, and radical sources,



**FIGURE 3.9** Photo of smog episode in Los Angeles, CA, taken in May of 1972. *Documerica, US Environmental Protection Agency's Photo Gallery; Photographer: Gene Daniels.*

such the oxides of nitrogen. Therefore, smog is found most often in the warmer months of the year, not because of temperature, but because these are the months with greater amounts of sunlight. More sunlight is available for two reasons, both attributed to the earth’s tilt on its axis. In the summer, the earth is tilted toward the sun, so the angle of inclination of sunlight is greater than when the sun tipped away from the earth leading to more intensity of light per earth surface area. Also, the days are longer in the summer, so these two factors increase the light budget.

Hydrocarbons come from many sources, but the fact that internal combustion engines burn gasoline, diesel fuel, and other mixtures of hydrocarbons makes them a ready source. Complete combustion results in carbon dioxide and water, but anything short of complete combustion will be a source of hydrocarbons, including some of the original ones found in the fuels that are released during refining, transport, and during refueling, as well as new ones formed during combustion. The compounds that become free radicals, like the oxides of nitrogen, are also readily available from internal combustion engines, since the three quarters of the troposphere is made up of molecular nitrogen ( $N_2$ ). Although  $N_2$  is relatively not chemically reactive, with the high temperature and pressure conditions in the engine, it does combine with the  $O_2$  from the fuel/air mix and generates oxides that can provide electrons to the photochemical reactions.

The pollutant most closely associated with smog is ozone ( $O_3$ ), which forms from the photochemical reactions mentioned above. In the early days of smog control efforts,  $O_3$  was used more as a surrogate or *marker* for smog, since one could not really take a sample of smog. Later,  $O_3$  became recognized as a pollutant in its own right since it was increasingly linked to respiratory diseases.

### Nonattainment NSR and (2) Prevention of Significant Deterioration (PSD).

The nonattainment NSR rules are designed to assist in efforts to attain and maintain compliance with the NAAQS, applying to pollutants for which an area has been designated as not meeting one or more of the NAAQS, i.e. a nonattainment area. These standards are summarized in [Table 3.3](#). The nonattainment NSR rules assumes that minor sources and minor modifications do not significantly affect the attainment status, nor do they interfere with plans to achieve

compliance with the NAAQS. Some of the key provisions are Lowest Achievable Emission Rate (LAER), offsets, alternative site analysis, and compliance certification.<sup>14</sup>

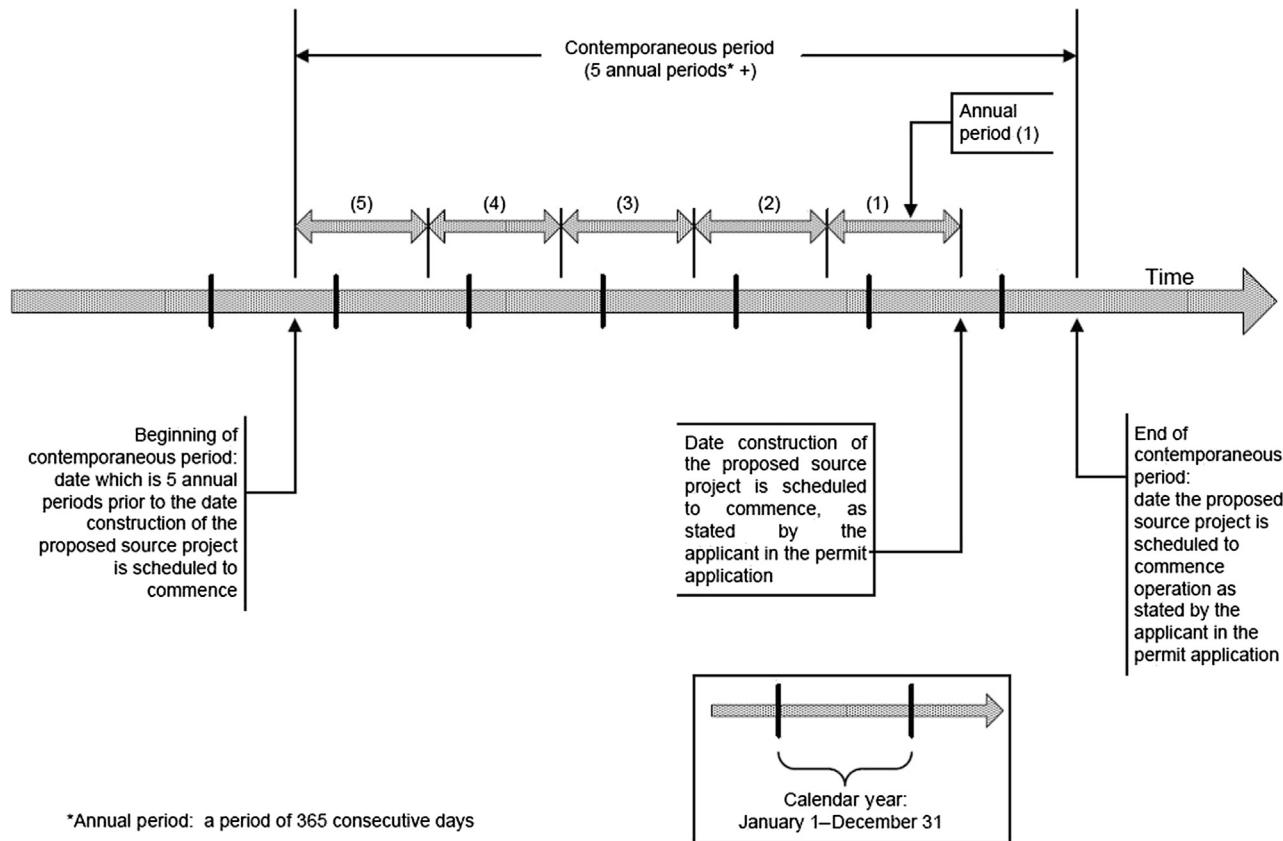
In the United States, PSD rules are designed to curtail transport of pollution to areas whose air is presently meeting standards. The CAAA90 defines the amount of deterioration that can be considered insignificant. PSD is needed to protect public health and welfare; and to preserve, protect, and enhance the air quality in national parks, national wilderness areas, national

monuments, national seashores, and other areas of special national or regional natural, recreational, scenic, or historic value. PSD also requires that economic growth will occur in a manner consistent with the preservation of existing clean air resources.

The PSD provisions also ask that regulatory actions be viewed in a manner that allows for certain levels of air pollutant releases from the perspective of the cumulative impact in any area. This provision is analogous to a virtual bubble over a group of stacks and vents, addressing the total releases under the bubble instead of emissions from each of the sources. The permit applicant can conduct a netting exercise, i.e. the demonstration that by aggregating emission changes which have occurred at a source over a contemporaneous time period (see [Figure 3.10](#)). These resulting emission changes are then reviewed to determine if the proposed project must undergo NSR. The key is to account for other emission decreases and increases which have

occurred and are expected to occur over the contemporaneous timeframe. The applicant must demonstrate that the overall net increase in emissions would not be “significant”.<sup>c</sup> The provisions governing netting differ for each attainment area, e.g. netting is more stringent in serious, severe, and extreme ozone nonattainment areas.<sup>11</sup>

Basically, PSD rules must be followed when a company adds a new source or modifies an existing source in an area designated as attainment of the NAAQS under CAAA90. The PSD rules need to be addressed for the pollutants for which the area is classified as attainment with the NAAQS. The rules are a safeguard for ensuring that compliance with the NAAQS continues in time. As with nonattainment NSR, the strategy with PSD rules assumes that minor new sources and minor modifications do not significantly affect the air quality. The distinctive requirements of PSD are Best Available Control Technology (BACT), air quality



**FIGURE 3.10** Contemporaneous period determination for severe/marginal/moderate ozone nonattainment areas and attainment portions of the ozone transport region (volatile organic compounds or oxides of nitrogen), and for PM<sub>10</sub> or PM<sub>2.5</sub> nonattainment areas. *New York Department of Environmental Conservation. Part 231 NSR for new and modified facilities—applicability flow charts. <http://www1.dec.state.ny.us/chemical/54330.html>; 2009 [accessed 26.09.13].*

<sup>c</sup> As in NEPA, “significant” does not necessarily mean the change must meet some level of statistical confidence (e.g. alpha level), but is the more general term (e.g. substantial or important).

analysis—modeling (allowable increments), and analysis of impacts of the project on visibility, vegetations, and soils.

Preserving air quality depends on knowing which sources are contributing to the deterioration. When the results of air pollution measurements are interpreted, one of the first questions asked by scientists, engineers, and policy makers is where did it come from? Sorting out the various sources of pollution is known as *source apportionment*. A number of tools are used to try to locate the sources of pollutants. A widely used approach is the “source–receptor model” or as it is more commonly known, the receptor model.

Using receptor models can be distinguished from the dispersion models in that dispersion models usually start from the source and estimate the direction and mixing of the plume and its contaminants is expected to move (see Chapter 21). Conversely, receptor models are based upon measurements taken in the ambient environment and from these observations, make use of algorithms and functions to determine pollution sources.

### **3.7.2.3 Urban Air Pollution**

Cities that failed to achieve human health standards as required by NAAQS were required to reach attainment within 6 years of passage of CAAA90, although Los Angeles was given 20 years, since it was dealing with major challenges in reducing ozone concentrations.

Almost 100 cities failed to achieve ozone standards, and were ranked from *marginal* to *extreme*. The more severe the pollution, the more rigorous controls required, although additional time was given to those extreme cities to achieve the standard. Measures included new or enhanced inspection/maintenance (I/M) programs for autos; installation of vapor recovery systems at gas stations and other controls of hydrocarbon emissions from small sources; and new transportation controls to offset increases in the number of miles traveled by vehicles. Major stationary sources of nitrogen oxides were also required to reduce emissions.

The 41 cities failing to meet carbon monoxide standards were ranked *moderate* or *serious*; states may have to initiate or upgrade inspection and maintenance programs and adopt transportation controls. The 72 urban areas that did not meet PM<sub>10</sub> standards were ranked *moderate*; states will have to implement Reasonably Available Control Technology (RACT); use of wood stoves and fireplaces may have to be curtailed.

### **3.7.2.4 Mobile Sources**

As mentioned, SIPs must address mobile sources. However, mobile sources are problematic for both conventional and toxic air pollutants. Vehicular tailpipe

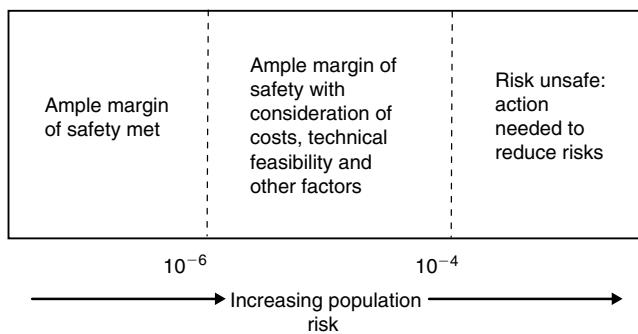
emissions of hydrocarbons, carbon monoxide, and oxides of nitrogen were to be reduced with the 1994 models. Standards now have to be maintained over a longer vehicle life. Evaporative emission controls were mentioned as a means for reducing hydrocarbons. Beginning in 1992, “oxyfuel” gasolines blended with alcohol began to be sold during winter months in cities with severe carbon monoxide problems. In 1995, reformulated gasolines with aromatic compounds were introduced in the nine cities with the worst ozone problems; but other cities were also allowed to participate. Later, a pilot program introduced 150,000 low emitting vehicles to California that met tighter emission limits through a combination of vehicle technology and substitutes for gasoline or blends of substitutes with gasoline. Other states are also participating in this initiative.

Air toxic emissions from vehicles and other mobile sources are a growing concern. Near-roadway environments can be substantial exposure pathways to benzene and other organic air pollutants. And, in nations that have not banned leaded gasoline, near-roadway exposures can be a major contributor to Pb body burden.<sup>11</sup> Air toxic exposure from mobile sources, therefore, is particularly worrisome for children, given the neurological, developmental, and cancer risks.

### **3.7.2.5 Toxic Air Pollutants**

In the 1990 amendments, the number of toxic air pollutants covered by the Clean Air Act was increased to 189 compounds in 1990. As of 2013, 187 hazardous air pollutants are listed. Most of these are carcinogenic, mutagenic, and/or toxic to neurological, endocrine, reproductive, and developmental systems. Actually, this list includes many more than 189 chemical compounds. For example, the coke oven emission category includes thousands of chemical species, and the metals are listed as metals and their compounds.

All 189 air toxic emissions were to be reduced within 10 years. The EPA published a list of source categories and issued Maximum Achievable Control Technology (MACT) standards for each category over a specified timetable. The next step beyond MACT standards was to begin to address chronic health risks that would still be expected if the sources meet these standards. This is known as residual risk reduction. The first step was to assess the health risks from air toxics emitted by stationary sources that emit air toxics after the technology-based, i.e. MACT, standards are in place. The residual risk provision sets additional standards if MACT does not protect public health with an “ample margin of safety”, as well as additional standards if they are needed to prevent adverse environmental effects.



**FIGURE 3.11 Ample margin of safety based on airborne contaminant's cancer risk.** The actual thresholds between the three risk categories can vary by pollutants, depending on available control technologies, as well as by jurisdiction, statutes and regulations. For example, the middle category could be much smaller than the other two if control technologies are not available or are quite expensive, e.g. ample margin of safety would be defined as a risk less than  $10^{-6}$ , but the unsafe category could be a risk greater than  $10^{-5.5}$ .

What an “ample margin of safety” means is still up for debate, but one proposal for airborne carcinogens is shown in Figure 3.11. That is, if a source can demonstrate that it will not contribute to greater than  $10^{-6}$  cancer risk, then it meets the ample margin of safety requirements for air toxics. The ample margin needed to protect populations from noncancer toxins, such as neurotoxins, is being debated, but it will involve the application of some type of hazard quotient (HQ). The HQ is the ratio of the potential exposure to the substance to the level at which no adverse effects are expected. An  $\text{HQ} < 1$  means that the exposure levels to a chemical should not lead to adverse health effects. Conversely, an  $\text{HQ} > 1$  means that adverse health effects are possible. Due to uncertainties and the feedback that is coming from the business and scientific communities, the ample margin of safety threshold is presently ranging from  $\text{HQ} = 0.2$  to  $\text{HQ} = 1.0$ . So, if a source can demonstrate that it will not contribute to greater than the threshold for noncancer risk (whether it is 0.2, 1.0, or some other level established by the federal government), it meets the ample margin of safety requirements for air toxics.

An air toxics source is designated as “major” if it emits 10 or more tons per year of any of the listed toxic air pollutants, or 25 or more tons per year of a mixture of air toxics. In addition to releases from stacks and vents, these emission totals include equipment leaks and releases during transfer. Area sources are those facilities that emit less than 10 tons per year of a single air toxic, or less than 25 tons per year of a combination of air toxics.<sup>12</sup>

The MACTs are customized for specific source categories. For example, semiconductor manufacturing, semiconductor packaging, printed wiring board

manufacturing, and display manufacturing, each with specific air toxics that apply (see Table 3.5). In this case, the list includes both organic contaminants and metals. In addition, the manufacturer must be aware of upcoming plans to use other chemicals used in its processes computer industry MACTs address. The company would be encouraged to find less hazardous substances as substitutes, if possible.

**TABLE 3.5** Chemicals Used in Semiconductor Manufacturing that are Scheduled for Maximum Achievable Control Technology (MACT) Standards

**A. SEMICONDUCTOR MANUFACTURING HAZARDOUS AIR POLLUTANTS**

Antimony compounds	Hydrochloric acid
Arsenic compounds	Hydrofluoric acid
Arsine	Methanol
Carbon tetrachloride	Methyl isobutyl ketone
Catechol	Nickel compounds
Chlorine	Phosphine
Chromium compounds	Phosphorus
Ethyl acrylate	1,1,1-Trichloroethane
Ethyl benzene	Trichloroethylene
Ethylene glycol	Xylene

**B. SEMICONDUCTOR PACKAGING HAZARDOUS AIR POLLUTANTS**

Chlorine	Methanol
Chromium	Methylene chloride
Ethyl benzene	Nickel compounds
Ethylene glycol	Toluene
Hydrochloric acid	1,1,1 Tricholoroethane
Hydrofluoric acid	Xylene
Lead compounds	

**C. PRINTED WIRE BOARD MANUFACTURING HAZARDOUS AIR POLLUTANTS**

Chlorine	Lead compounds
Dimethylformamide	Methylene chloride
Formaldehyde	Nickel compounds
Hydrochloric acid	Perchloroethylene
Hydrofluoric acid	1,1,1-Trichloroethane
Ethylene glycol	

A. Manufacturing; B. Packaging; C. Printed Wire Board Manufacturing.

Source: U.S. Environmental Protection Agency. Design for the environment.

Section A. Clean Air Act Amendments. [http://www.epa.gov/dfe/pubs/pub/tech\\_rep/fedregs/regsecta.htm](http://www.epa.gov/dfe/pubs/pub/tech_rep/fedregs/regsecta.htm); 2013 [accessed 26.09.13].

### 3.7.2.6 Acid Deposition

The introduction of acidic substances to flora, soil, and surface waters has been collectively called “acid rain” or “acid deposition”. Acid rain is generally limited to the so-called “wet” deposition (low pH precipitation), but acidic materials can also reach the earth’s surface by dry deposition (“acid aerosols”) and acid fog (e.g. airborne droplets of water that contains sulfuric acid or nitric acid). Generally, acid deposition is not simply materials of pH <7, but usually of pH <5.7, since “normal” rainfall has a pH of about 5.7, due to the ionization of absorbed carbon dioxide (see discussions in Chapters 5 and 21). There is much concern about acid deposition because aquatic biota can be significantly harmed by only slight changes in pH. The problem of acidified soils and surface waters is a function of both the increase in acidity of the precipitation and the ability of the receiving waters and soil to resist the change in soil pH. So, it is the contribution of the human-generated acidic materials, especially the oxides of sulfur and the oxides of nitrogen, which are considered to be the sources of “acid rain”.

The 1990 amendments introduced a two-phase, market-based system to reduce sulfur dioxide emissions from power plants by more than half. Total annual emissions were to be capped at 8.9 million tons, a reduction of 10 million tons from the 1980 baseline levels. Power facilities were issued allowances based on fixed emission rates set in the law, as well as their previous fossil-fuel use. Penalties were issued for exceedances, although the allowances could be banked or traded within the fuel burning industry. In Phase I, large, high-emission plants in eastern and midwestern regions of the United States were required to reduce emissions by 1995. Phase II began in 2000 to set emission limits on smaller, cleaner plants and further tightening of the Phase I plants’ emissions. All sources were required to install continuous emission monitors to assure compliance (see Chapter 24). Emissions of the oxides of nitrogen were also to be reduced; however, the approach differed from the oxides of sulfur, using EPA performance standards, instead of the two-phase system.

The 1990 amendments required a National-Scale Air Toxics Assessment (NATA) to evaluate air toxics, i.e. a state-of-the-science screening tool to prioritize pollutants, emission sources, and locations of interest for further study in order to gain a better understanding of risks. NATA provides estimates of the risk of cancer and other serious health effects from inhaling air toxics. NATA assessments use general information about sources to calculate estimates of risks, erring on the side of overestimating rather than underestimating risks. The estimates of cancer and noncancer health effects are

based on chronic exposure from outdoor sources, providing a snapshot of the outdoor air quality and the risks to human health that would result if air toxic emissions levels remain unchanged.

The NATA follows a four step process<sup>13</sup>:

1. Compiling a national air toxics emissions inventory of outdoor stationary and mobile sources (i.e. the National Emissions Inventory (NEI)).
2. Estimating ambient concentrations of air toxics based on air dispersion and photochemical models.
3. Calculating population exposure estimates using a screening-level inhalation exposure model.
4. Characterizing potential cancer and noncancer public health risks due to inhaling air toxics.

The first NATA was in 1996 and the most recent assessment is for 2005. The 2005 assessment addresses the inhalation of 178 air toxics, for cancer and noncancer risk, plus noncancer risk for diesel PM. The 2005 NATA results are summarized in [Figure 3.12](#). Note that the route of exposure is assumed to be inhalation, so the NATA does not include other routes (e.g. ingestion and dermal exposure to the same air toxic).

For cumulative cancer risks<sup>15</sup> from all air toxics compounds listed as carcinogenic or likely to be carcinogenic to humans are estimated by combining the risks at the census tracts level. In 2005, the combined upper bound lifetime cancer risk from these compounds exceeded 10 in 1 million risk and more than 2 million people live in census tracts where the combined upper bound lifetime cancer risk from these compounds exceeded 100 in 1 million risk. The overall national average risk in the United States is 36 in a million.

For cumulative noncancer risks,<sup>16</sup> HQs would ideally combine pollutants that cause the same adverse effects by the same toxic mechanism. However, because detailed information on mechanisms is unavailable for most air toxics, a simpler and more conservative method was used. Many of the pollutants in this assessment cause adverse effects in humans or animals by irritating the lining of the respiratory system or by causing various effects to the nervous system. Additive effects are represented by a “hazard index”, i.e. the sum of the HQs of the air toxics compounds that affect the respiratory or nervous system. In 2005, the respiratory hazard index was dominated by a single substance, acrolein. The respiratory hazard index exceeded 1.0 for nearly the entire U.S. population, and exceeded 10 for more than 22 million people. The neurological hazard index was similarly dominated by manganese compounds, with minor contributions by cyanide compounds, ethylene oxide, and mercury compounds. The neurological hazard index exceeded 1.0 for fewer than 350,000 people in the United States.

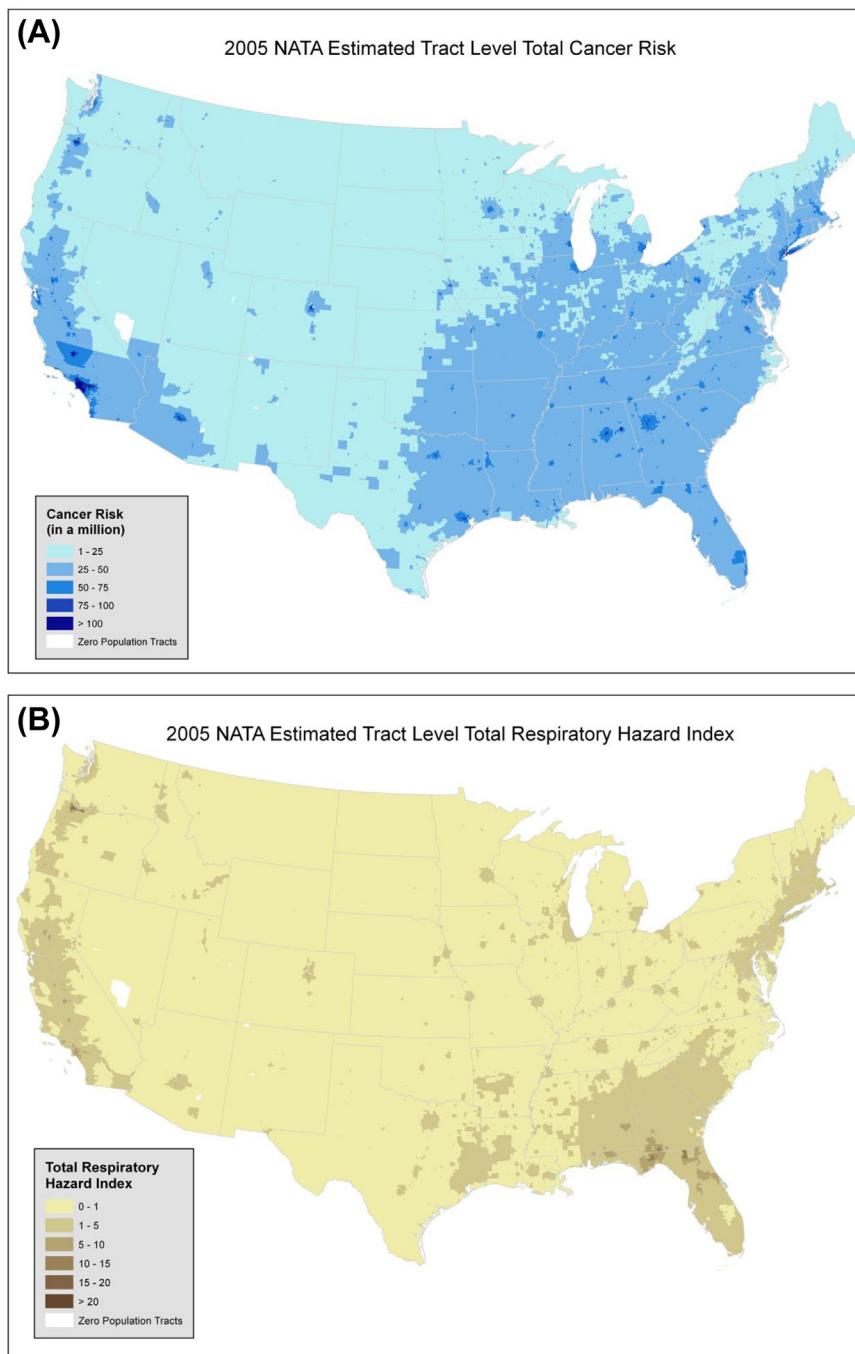


FIGURE 3.12 (A) 2005 National Air Toxics Assessment census tract level total cancer risk. (B) 2005 National Air Toxics Assessment census tract level total respiratory (noncancer) hazard index. (For color version of this figure, the reader is referred to the online version of this book.)

### 3.7.2.7 Protecting the Ozone Layer

The ozone layer filters out substantial amounts of UV radiation from the sun. This UV radiation can cause skin damage and lead to certain forms of cancer, including the most fatal form, melanoma. Therefore, the international scientific and policy communities have been concerned about the release of chemicals that find their way to stratosphere and accelerate the

breakdown of the ozone (see Discussion box: Good Ozone, Bad Ozone).

The 1990 Clean Air Act Amendments required a phase-out of the production and use of ozone-destroying chemicals. By 1996, the United States no longer produced many propellants and other chemicals that destroy the ozone layer, e.g. chlorofluorocarbons (CFCs), halons, and methyl chloroform.

## GOOD OZONE, BAD OZONE

Like the three rules of real estate, i.e. location, location, and location, where a chemical is found in the atmosphere can make a difference as to whether it is desirable or harmful. As shown in [Figure 3.13](#), ground-level (tropospheric) ozone ( $O_3$ ) concentrations are small, but increase in the stratosphere. Approximately 90% of the atmosphere's  $O_3$  lies in the layer between 10 and 17 km above the earth's surface up to an altitude of about 50 km. This is commonly known as the ozone layer. Most of the remaining ozone is in the lower part of the atmosphere, the troposphere. The stratospheric  $O_3$  concentrations must be protected, while the tropospheric  $O_3$  concentrations must be reduced.

The stratosphere ranges from 16 to 48 km above the earth's surface. Stratospheric ozone (the "good ozone") absorbs most of the biologically damaging UV sunlight (UV-B), allowing only a small amount to reach the earth's surface. The absorption of UV radiation by ozone generates heat, which is why [Figure 3.13](#) shows an increase in temperature in the stratosphere. Without the filtering action of the ozone layer, greater amounts of the sun's UV-B radiation would penetrate the atmosphere and would reach the earth's surface. Many experimental

studies of plants and animals and clinical studies of humans have shown the harmful effects of excessive exposure to UV-B radiation.

Scientists have been studying the stratospheric ozone layer since the 1970s. In the 1980s, scientific evidence overwhelmingly indicated that the ozone layer was being depleted. The so-called "ozone hole" above the South Pole has appeared each year during the Antarctic winter, growing larger in extent as the area of the continental United States. The concentration of  $O_3$  decreased by 5% from 1978 to 1997. Two of the largest ozone holes were observed in 2006, the largest of 29 million square kilometers (11.4 million square miles). These findings spurred over 190 nations, including the major industrialized nations in Europe and North America to sign Montreal Protocol in 1997, calling for the elimination of chemicals that destroy stratospheric ozone.<sup>[17](#)</sup>

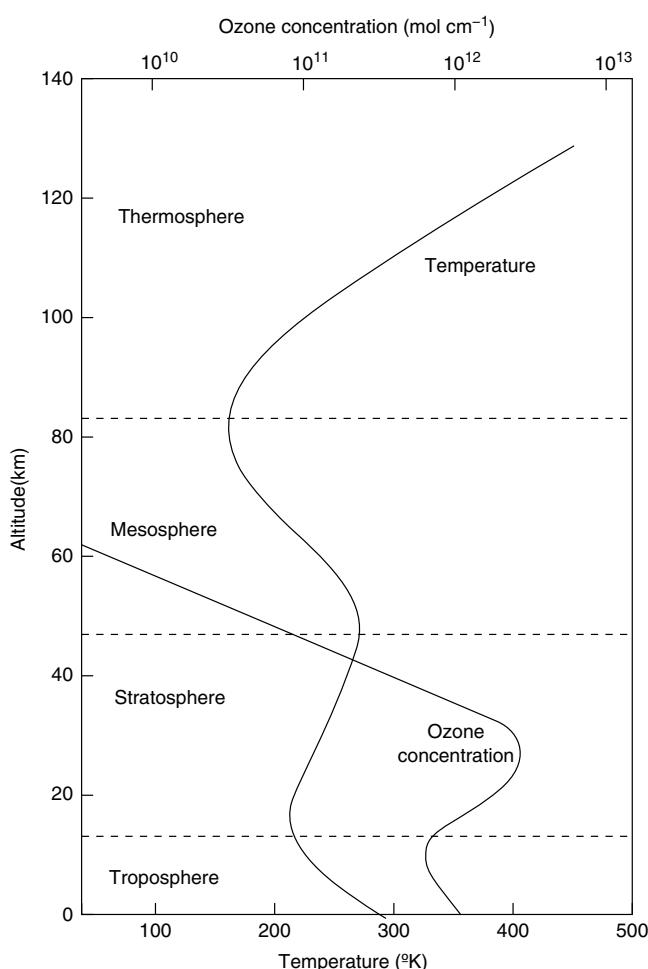
In the troposphere,  $O_3$  exposure is destructive ("bad ozone"), because it is highly reactive with tissues, leading to ecological and welfare effects, such as forest damage and reduced crop production, and human health effects, especially cardiopulmonary diseases.

These compounds are often highly persistent; in some cases, taking decades to degrade. This means that nearly 60 years will be needed to restore the stratospheric ozone layer to its preindustrial condition. Indeed, ending the production and use does not end the reaction of compounds with  $O_3$ . Ozone-destroying chemicals already in the stratosphere are still moving through the troposphere and will arrive within the next few years.

The CFCs, along with other chlorine- and bromine-containing compounds, can accelerate the depletion of stratospheric  $O_3$  layer. CFCs were first developed in the early 1930s for many industrial, commercial, and household products. They are generally compressible, nonflammable, and nonreactive, which led to many CFC uses, including as coolants for commercial and home refrigeration units, and aerosol propellants. In 1973, chlorine was found to catalyze ozone destruction. Catalytic destruction of ozone removes the odd-numbered oxygen species (atomic oxygen [ $O$ ] and ozone [ $[O_3]$ ]), but leaves the chlorine unaffected. A complex scenario involving atmospheric dynamics, solar radiation, and chemical reactions accounts for spring thinning of the ozone layer at the earth's poles. Global monitoring of ozone levels from space using National Aeronautics and Space Administration's (NASA) Total Ozone Mapping Spectrometer (TOMS) instrument has shown

profound downward trends in ozone concentrations at all of the earth's latitudes, except the tropics. In the high-energy stratosphere, the compounds undergo hundreds of catalytic cycles involving  $O_3$  before the CFCs are scavenged by other chemicals.

CAA90 built upon the Montreal Protocol on substances that deplete the ozone layer, the international treaty where nations agreed to reduce or eliminate ozone-destroying gas production and uses of chemicals that pose a threat to the ozone layer. The amendments further restricted the use, emissions, and disposal of these chemicals, including the phasing out of the production of CFCs, as well as other chemicals that lead to ozone attacking halogens, such as tetrachloromethane (commonly called carbon tetrachloride) and methyl chloride by the year 2000, and methyl chloroform by 2002. The act also will freeze the production of CFCs in 2015 and requires that CFCs be phased out completely by 2030. Companies servicing air conditioning for vehicles are now required to purchase certified recycling equipment and train employees. EPA regulations require reduced emissions from all other refrigeration sectors to lowest achievable levels. "Nonessential" CFC applications are prohibited. The act increases the labeling requirements of the Toxic Substances Control Act (TSCA) by mandating the placement of warning labels on all containers and products (such as cooling



**FIGURE 3.13 Ozone concentrations and temperature profile of the earth's atmosphere.** Watson RT, Geller MA, Stolarski RS, Hampson RF. *Present State of Knowledge of the Upper Atmosphere: An Assessment Report*, NASA Reference Publication; 1986.

equipment, refrigerators, and insulation) that contain CFCs and other ozone-depleting chemicals.

The Clean Air Act includes other steps to protect the ozone layer, including encouraging the development of “ozone-friendly” substitutes for ozone-destroying chemicals. Numerous systems, products, and processes have been redesigned, e.g. refrigerators manufactured in the United States and many other nations no longer use CFCs.

Indeed, the search for more environmentally benign substances has been underway for some time. One set of potential substitutes is the hydrochlorofluorocarbons (HCFCs). Obviously, the HCFC molecules contain Cl atoms, but the hydrogen increases the reactivity of the HCFCs with other tropospheric chemical species. These low altitude reactions decrease the probability of a Cl atom finding its way to the stratosphere. Hydrofluorocarbons (HFCs) are potential substitutes that lack chlorine.

There are still numerous challenges, such as finding substitutes for CFCs used in certain biomedical

applications. Agricultural substitutions can also be challenging. For example, ozone-depleting methyl bromide is still used because farmers have not yet found an effective alternative pesticide.

### 3.7.3 Solid and Hazardous Wastes Laws

Although the Clean Air Act and its amendments comprise the most notable example of U.S. legislation passed to protect air quality, other laws address air pollution more indirectly. For example, air pollution around solid and hazardous waste facilities can be problematic. The two principal U.S. laws governing solid wastes are the Resource Conservation and Recovery Act (RCRA) and Superfund. The RCRA law covers both hazardous and solid wastes, while Superfund and its amendments generally address abandoned hazardous waste sites. RCRA addresses active hazardous waste sites.

#### 3.7.3.1 Management of Active Hazardous Waste Facilities

With RCRA, the US EPA received the authority to control hazardous waste throughout the waste’s entire life cycle, known as the “cradle-to-grave”. This means that manifests must be prepared to keep track of the waste, including its generation, transportation, treatment, storage, and disposal. RCRA also set forth a framework for the management of nonhazardous wastes in Subtitle D.

The Federal Hazardous and Solid Waste Amendments (HSWA) to RCRA required the phase out of land disposal of hazardous waste. HSWA also increased the federal enforcement authority related to hazardous waste actions, set more stringent hazardous waste management standards, and provided for a comprehensive underground storage tank (UST) program.

The 1986 amendments to RCRA allowed the federal government to address potential environmental problems from USTs for petroleum and other hazardous substances.

#### 3.7.3.2 Addressing Abandoned Hazardous Wastes

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) is commonly known as Superfund. Congress enacted it in 1980 to create a tax on the chemical and petroleum industries and to provide extensive federal authority for responding directly to releases or threatened releases of hazardous substances that may endanger public health or the environment.

The Superfund law established prohibitions and requirements concerning closed and abandoned hazardous waste sites; established provisions for the liability of persons responsible for releases of hazardous waste at these sites; and established a trust fund to provide

for cleanup when no responsible party could be identified.

The CERCLA response actions include:

- Short-term removals, where actions may be taken to address releases or threatened releases requiring prompt response. This is intended to eliminate or reduce exposures to possible contaminants.
- Long-term remedial response actions to reduce or eliminate the hazards and risks associated with releases or threats of releases of hazardous substances that are serious, but not immediately life threatening. These actions can be conducted only at sites listed on EPA's National Priorities List (NPL).

Superfund also revised the National Contingency Plan (NCP), which sets guidelines and procedures required when responding to releases and threatened releases of hazardous substances.

CERCLA was amended by the Superfund Amendments and Reauthorization Act (SARA) in 1986. These amendments stressed the importance of permanent remedies and innovative treatment technologies in cleaning up hazardous waste sites. SARA required that Superfund actions consider the standards and requirements found in other state and federal environmental laws and regulations and provided revised enforcement authorities and new settlement tools. The amendments also increased state involvement in every aspect of the Superfund program, increased the focus on human health problems posed by hazardous waste sites, encouraged more extensive citizen participation in site cleanup decisions, and increased the size of the Superfund trust fund.

SARA also mandate that the Hazard Ranking System (HRS) be revised to ensure the adequacy of the assessment of the relative degree of risk to human health and the environment posed by uncontrolled hazardous waste sites that may be placed on the NPL.

### 3.7.4 Environmental Product and Consumer Protection Laws

Most authorizing legislation targeted at protecting and improving the environment is based on actions needed in specific media (i.e. air, water, soil, and sediment), however, certain laws have been written in an attempt to prevent environmental and public health problems by focusing on potential exposures to substances during product development, before hazardous ingredients reach the market, and during product usage. In this way, air pollution is prevented to some extent at the potential source, such as chemical ingredients in products that can be sources of indoor air pollution.

The predominant product laws designed to protect people and ecosystems in the United States from

contaminants before they reach the market and at the point of use are the Federal Food, Drug, and Cosmetics Act (FFDCA); the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA); and the Toxic Substances Control Act (TSCA). The European Union has similar measures that categorize product ingredients. Such laws differ from the previously discussed legislation in that they look at products in terms of potential risks for yet-to-be-released products and estimated risks for products already in use. If the risks are unacceptable, new products may not be released as formulated or the uses will be strictly limited to applications that meet minimum risk standards. For products already in the marketplace, the risks are periodically reviewed. For example, pesticides have to be periodically reregistered with the government. This reregistration process consists of reviews of new research and information regarding health and environmental impacts discovered since the product's last registration.

FIFRA's major mandate is to control the distribution, sale, and applications of pesticides. This not only includes studying the health and environmental consequences of pesticide usage, but also to require that those applying the pesticides register when they purchase the products. Commercial applicators must be certified by successfully passing exams on the safe use of pesticides. FIFRA requires that the EPA license any pesticide used in the United States. The licensing and registration makes sure that pesticide is properly labeled and will not cause unreasonable environmental harm.

An important, recent product production law is the Food Quality Protection Act (FQPA), including new provisions to protect children and limit their risks to carcinogens and other toxic substances. The law is actually an amendment to FIFRA and FFDCA that includes new requirements for safety standard—reasonable certainty of no harm—that must be applied to all pesticides used on foods. FQPA mandates a single, health-based standard for all pesticides in all foods; gives special protections for infants and children; expedites approval of pesticides likely to be safer than those in use; provides incentives for effective crop protection tools for farmers; and requires regular re-evaluation of pesticide registrations and tolerances so that the scientific data supporting pesticide registrations include current findings.

There is some ongoing debate about the actual routes and pathways that contribute the most to pesticide exposure. For example, certain pesticides seem to be most likely to be present in dietary pathways (e.g. the purchased food contains the pesticide), nondietary ingestion (e.g. the food is contaminated by airborne pesticides in the home or the people living in the home touch contaminated surfaces and then touch the food), and dermal exposure (people come into contact with

the pesticide and it infiltrates the skin). This seems to vary considerably by the type of pesticide, but it suffices to say that the air pathways are important.

Another product-related development in recent years is the screening program for endocrine disrupting substances. Research suggests a link between exposure to certain chemicals and damage to the endocrine system in humans and wildlife. Because of the potentially serious consequences of human exposure to endocrine disrupting chemicals, Congress added specific language on endocrine disruption in the FQPA and recent amendments to the Safe Drinking Water Act (SDWA). The FQPA mandated that the EPA develop an endocrine disruptor screening program, and the SDWA authorizes EPA to screen endocrine disruptors found in drinking water systems. In the United States, rapid screening programs are being used to detect and characterize the toxicity of chemicals. The scientific data needed for the estimated 87,000 chemicals in commerce does not exist to conduct adequate assessments of potential risks. The screening provides information to decide appropriate regulatory action by prioritizing chemicals for their potential to elicit toxic effects and their potential exposures in near-field scenarios (e.g. indoors, product use) and far-field scenarios (e.g. ambient air exposures).

Thousands of chemicals undergo sorting into four categories according to the available existing, scientifically relevant information:

1. Category 1 chemicals have sufficient, scientifically relevant information to determine that they are not likely to interact with the estrogen, androgen, or thyroid systems. This category includes some polymers and certain exempted chemicals.
2. Category 2 chemicals have insufficient information to determine whether they are likely to interact with the estrogen, androgen, or thyroid systems, thus will need screening data.
3. Category 3 chemicals have sufficient screening data to indicate endocrine activity, but data to characterize actual effects are inadequate and will need testing.
4. Category 4 chemicals already have sufficient data for the EPA to perform a hazard assessment.

TSCA gives the EPA the authority to track 75,000 industrial chemicals currently produced or imported to the United States. This is accomplished through screening the chemicals and requiring that reporting and testing be done for any substance that presents a hazard to human health or the environment. If a chemical poses a potential or actual risk that is unreasonable, the EPA may ban the manufacture and import of that chemical.

The EPA has tracked thousands of new chemicals being developed by industries each year, if those chemicals have either unknown or dangerous characteristics. This

information is used to determine the type of control that these chemicals would need to protect human health and the environment. Manufacturers and importers of chemical substances first submitted information about chemical substances already on the market during an initial inventory. Since the initial inventory was published, commercial manufacturers or importers of substances not on the inventory have been subsequently required to submit notices to the EPA, which has developed guidance about how to identify chemical substances in order to assign a unique and unambiguous description of each substance for the inventory. The categories include:

- polymeric substances;
- certain chemical substances containing varying carbon chains;
- products containing two or more substances, formulated, and statutory mixtures; and
- chemical substances of unknown or variable composition, complex reaction products, and biological materials ("UVCB" substance).

### 3.8 AIR POLLUTION BEFORE THE INDUSTRIAL REVOLUTION

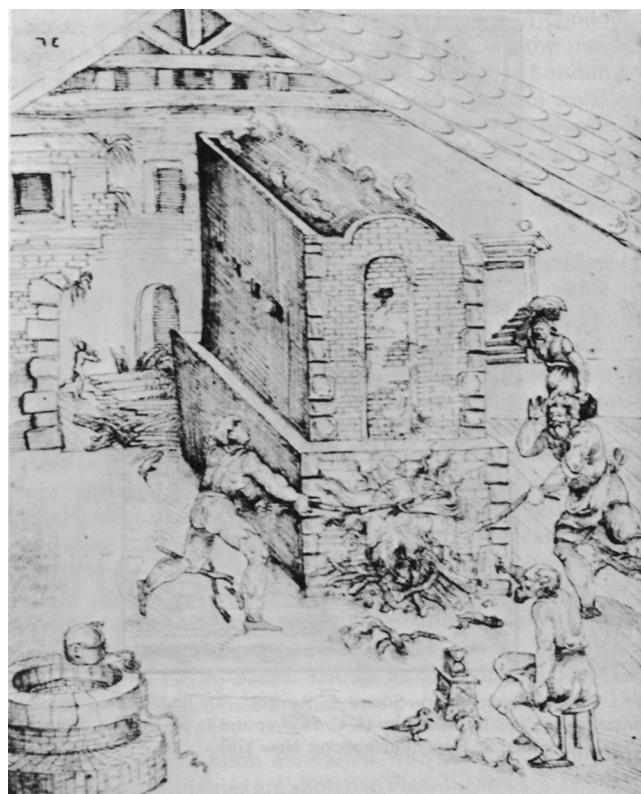
While the programs to address air pollution are recent, controlling air pollution is rooted in Antiquity. One of the reasons the tribes of early history were nomadic was to move periodically away from the stench of the animal, vegetable, and human wastes they generated. When the tribesmen learned to use fire, they used it for millennia in a way that filled the air inside their living quarters with the products of incomplete combustion. Examples of this can still be seen today in some of the more primitive parts of the world. After its invention, the chimney removed the combustion products and cooking smells from the living quarters, but for centuries the open fire in the fireplace caused both indoors and outdoors to be smoky. In AD 61, the Roman philosopher Seneca reported thus on conditions in Rome:

As soon as I had gotten out of the heavy air of Rome and from the stink of the smoky chimneys thereof, which, being stirred, poured forth whatever pestilential vapors and soot they had enclosed in them, I felt an alteration of my disposition.

Air pollution, associated with burning wood in Tutbury Castle in Nottingham, was considered "unendurable" by Eleanor of Aquitaine, the wife of King Henry II of England, and caused her to move in the year 1157. One hundred sixteen years later, coal burning was prohibited in London; and in 1306, Edward I issued a royal proclamation enjoining the use of *sea coal* in

furnaces. Elizabeth I barred the burning of coal in London when Parliament was in session. The repeated necessity for such royal action would seem to indicate that coal continued to be burned despite these edicts. By 1661, the pollution of London had become bad enough to prompt John Evelyn to submit a brochure "Fumifugium, or the Inconvenience of the Aer, and Smoake of London Dissipated (together with some remedies humbly proposed)" to King Charles II and Parliament. This brochure has been reprinted and is recommended to students of air pollution.<sup>18</sup> It proposes means of air pollution control that are still viable in the twenty-first century.

The principal industries associated with the production of air pollution in the centuries preceding the Industrial Revolution were metallurgy, ceramics, and preservation of animal products. In the bronze and iron ages, villages were exposed to dust and fumes from many sources. Native copper and gold were forged, and clay was baked and glazed to form pottery and bricks before 4000 BC. Iron was in common use and leather was tanned before 1000 BC. Most of the methods of modern metallurgy were known before AD 1. Early metalworkers relied on charcoal rather than coal or coke. However, coal was mined and used for fuel before AD 1000, although it was not made into coke until about



**FIGURE 3.15 A pottery kiln.** Cipriano Piccolpasso. The three books of the Potters's art, fol. 35C. [Rackham B, Van de Put A, Trans.]. London (UK): Victoria and Albert Museum; 1934 [1550].



**FIGURE 3.14 Sixteenth century etching of a lead smelting furnace.** Ref. 21.

1600; and coke did not enter metallurgical practice significantly until about 1700. These industries and their effluents as they existed before 1556 are best described in the book *De Re Metallica* published in that year by Georg Bauer, known as Georgius Agricola (Figure 3.14). This book was translated into English and published in 1912 by Herbert Clark Hoover and his wife.<sup>19</sup>

Combustion in kilns was problematic even before the Industrial Revolution. For example, ceramics and animal product preservation industries produced air pollution from the combustion of materials to heat kilns (see Figures 3.15 and 3.16, respectively).

### 3.9 AIR POLLUTION AND THE INDUSTRIAL REVOLUTION

The Industrial Revolution was the consequence of the harnessing of steam to provide power to pump water and move machinery. This began in the early years of the eighteenth century, when Savery, Papin, and Newcomen designed their pumping engines, and culminated in 1784 in Watt's reciprocating engine. The reciprocating steam engine reigned supreme until it was displaced by the steam turbine in the twentieth century.

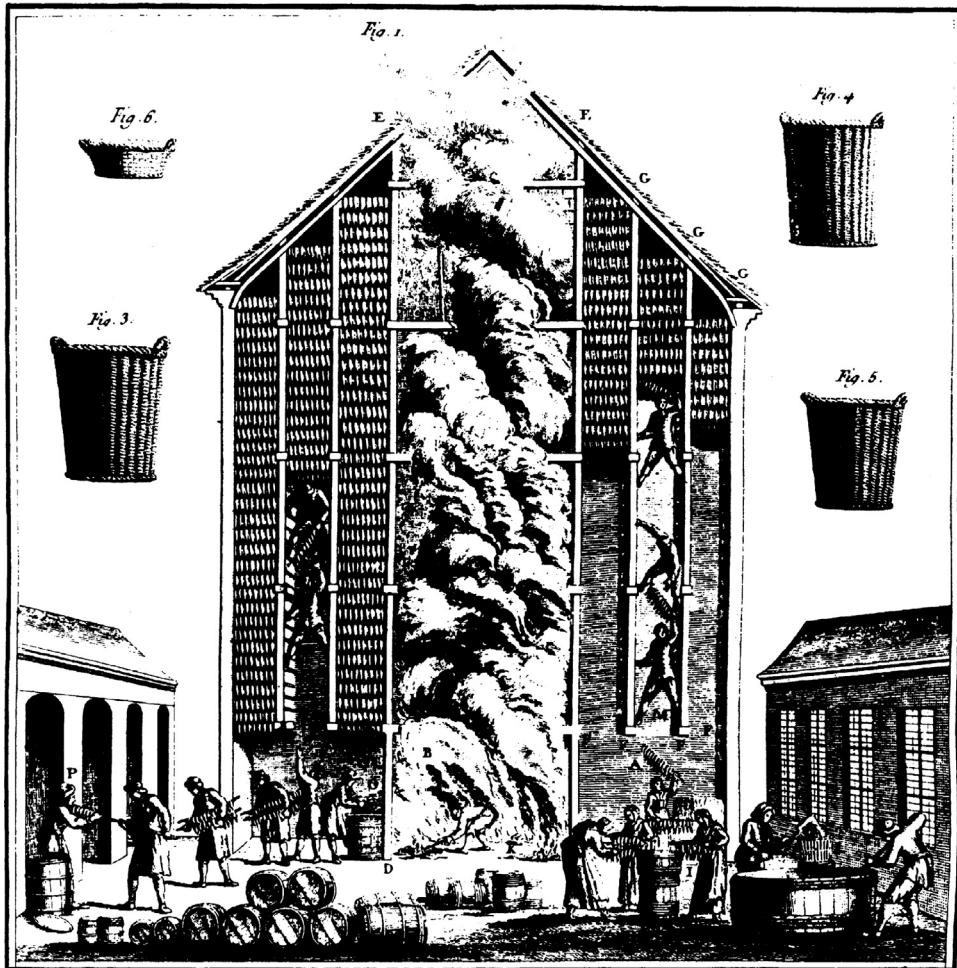


FIGURE 3.16 A kiln for smoking red herring. *Duhamel due Monceau HL. Traité général des pêches, vol. 2, Section III, Plate XV, Fig. 1, Paris (France); 1772.*

Steam engines and steam turbines require steam boilers, which, until the advent of the nuclear reactor, were fired by vegetable or fossil fuels. During most of the nineteenth century, coal was the principal fuel, although some oil was used for steam generation late in the century.

The predominant air pollution problem of the nineteenth century was smoke and ash from the burning of coal or oil in the boiler furnaces of stationary power plants, locomotives, and marine vessels, and in home heating fireplaces and furnaces. Great Britain took the lead in addressing this problem, and, in the words of Sir Hugh Beaver<sup>20</sup>:

By 1819, there was sufficient pressure for Parliament to appoint the first of a whole dynasty of committees "to consider how far persons using steam engines and furnaces could work them in a manner less prejudicial to public health and comfort". This committee confirmed the practicability of smoke prevention, as so many succeeding committees were to do, but as was often again to be experienced, nothing was done.

In 1843, there was another Parliamentary Select Committee, and in 1845, a third. In that same year, during the height of the great railway boom, an act of Parliament disposed of trouble from locomotives once and for all (!) by laying down the dictum that they must consume their own smoke. The Town Improvement Clauses Act 2 years later applied the same panacea to factory furnaces. Then 1853 and 1856 witnessed two acts of Parliament dealing specifically with London and empowering the police to enforce provisions against smoke from furnaces, public baths, and washhouses and furnaces used in the working of steam vessels on the Thames.

Smoke and ash abatement in Great Britain was considered to be a health agency responsibility and was so confirmed by the first Public Health Act of 1848 and the later ones of 1866 and 1875. Air pollution from the emerging chemical industry was considered a separate matter and was made the responsibility of the Alkali Inspectorate created by the Alkali Act of 1863.

In the United States, smoke abatement (as air pollution control was then known) was considered a municipal responsibility. There were no federal or state smoke

abatement laws or regulations. The first municipal ordinances and regulations limiting the emission of black smoke and ash appeared in the 1880s and were directed toward industrial, locomotive, and marine rather than domestic sources. As the nineteenth century drew to a close, the pollution of the air of mill towns the world over had risen to a peak; damage to vegetation from the smelting of sulfide ores was recognized as a problem everywhere it was practiced.

The principal technological developments in the control of air pollution by engineering during the nineteenth century were the stoker for mechanical firing of coal, the scrubber for removing acid gases from effluent gas streams, cyclone, and bag house dust collectors, and the introduction of physical and chemical principles into process design.

### 3.10 AIR POLLUTION EVENTS IN THE TWENTIETH AND TWENTY-FIRST CENTURIES

#### 3.10.1 Early Twentieth Century Events

During the period 1900–1925 there were great changes in the technology of both the production of air pollution and its engineering control, but no significant changes in legislation, regulations, understanding of the problem, or public attitudes toward the problem. As cities and factories grew in size, the severity of the pollution problem increased.

One of the principal technological changes in the production of pollution was the replacement of the steam engine by the electric motor as the means of operating machinery and pumping water. This change transferred the smoke and ash emission from the boiler house of the factory to the boiler house of the electric generating station. At the start of this period, coal was hand-fired in the boiler house; by the middle of the period, it was mechanically fired by stokers; by the end of the period, pulverized coal, oil, and gas firing had begun to take over. Each form of firing produced its own characteristic emissions to the atmosphere.

At the start of this period, steam locomotives came into the heart of the larger cities. By the end of the period, the urban terminals of many railroads had been electrified, thereby transferring much air pollution from the railroad right-of-way to the electric generating station. The replacement of coal by oil in many applications decreased ash emissions from those sources. There was rapid technological change in industry. However, the most significant change was the rapid increase in the number of automobiles from almost none at the turn of the century to millions by 1925 (Table 3.6).

The principal technological changes in the engineering control of air pollution were the perfection of the

**TABLE 3.6** Number of New Foreign and Domestic Trucks, Buses, and Automobiles Sold Annually in the United States. Sales for Years 2000, 2005, and 2010 Include Leases and Are Rounded to Nearest 1000

Year	Total Vehicles
1900	4192
1905	25,000
1910	187,000
1915	969,930
1920	2,227,347
1925	4,265,830
1930	3,362,820
1935	3,971,241
1940	4,472,286
1945	725,215
1950	8,003,056
1955	9,169,292
1960	7,869,221
1965	11,057,366
1970	8,239,257
1975	8,985,012
1980	8,067,309
1985	11,045,784
1990	9,295,732
2000	14,137,000
2005	17,445,000
2010	11,772,000

*Source: U.S. Census.*

motor-driven fan, which allowed large-scale gas-treating systems to be built; the invention of the electrostatic precipitator, which made particulate control in many processes feasible; and chemical engineering applications and the design of process equipment, which made the control of gas and vapor effluents feasible.

#### 3.10.2 Events during 1925–1950

In this period, present-day air pollution problems and solutions emerged. The Meuse Valley, Belgium, episode<sup>21</sup> occurred in 1930; the Donora, Pennsylvania, episode<sup>23</sup> occurred in 1948; and the Poza Rica, Mexico, episode<sup>23</sup> in 1950. Smog was first recorded in Los Angeles in the 1940s (Figure 3.8). The Trail, British Columbia, smelter arbitration<sup>24</sup> was completed in 1941. The first National Air Pollution Symposium in the United States was held in Pasadena, California<sup>25</sup> in

1949, and the first United States Technical Conference on Air Pollution<sup>26</sup> was held in Washington, DC, in 1950. The first large-scale surveys of air pollution were undertaken—Salt Lake City, Utah<sup>27</sup> (1926); New York City,<sup>28</sup> (1937); and Leicester, England<sup>29</sup> (1939).

Air pollution research got a start in California. The Technical Foundation for Air Pollution Meteorology was established in the search for means of disseminating and protecting against chemical, biological, and nuclear warfare agents. Toxicology came of age. The stage was set for the air pollution scientific and technological explosion of the second half of the twentieth century.

A major technological change was the building of natural gas pipelines, and where this occurred, there was rapid displacement of coal and oil as home heating fuels with dramatic improvement in air quality; as evidenced by the much publicized decrease in black smoke in Pittsburgh (Figure 3.17) and St. Louis. The diesel locomotive began to displace the steam locomotive, thereby slowing the pace of railroad electrification. The internal combustion engine bus started its displacement of the electrified streetcar. The automobile continued to proliferate (Table 3.6).

During this period, no significant national air pollution legislation or regulations were adopted anywhere in the world. However, the first state air pollution

law in the United States was adopted by California in 1947.

### 3.10.3 Events during 1950–1980

In Great Britain, a major air pollution disaster hit London in 1952, resulting in the passage of the Clean Air Act in 1956 and an expansion of the authority of the Alkali Inspectorate.<sup>30</sup> The principal changes that resulted were in the means of heating homes. Previously, most heating was done by burning soft coal on grates in separate fireplaces in each room. A successful effort was made to substitute smokeless fuels for the soft coal used in this manner, and central or electrical heating for fireplace heating. The outcome was a decrease in “smoke” concentration, as measured by the blackness of paper filters through which British air was passed, decreasing from  $175 \mu\text{g m}^{-3}$  in 1958 to  $75 \mu\text{g m}^{-3}$  in 1968.<sup>31</sup>

During these two decades, almost every country in Europe, as well as Japan, Australia, and New Zealand, experienced serious air pollution in its larger cities. As a result, these countries were the first to enact national air pollution control legislation. By 1980, major national air pollution research centers had been set up at the Warren Springs Laboratory, Stevenage, England; the

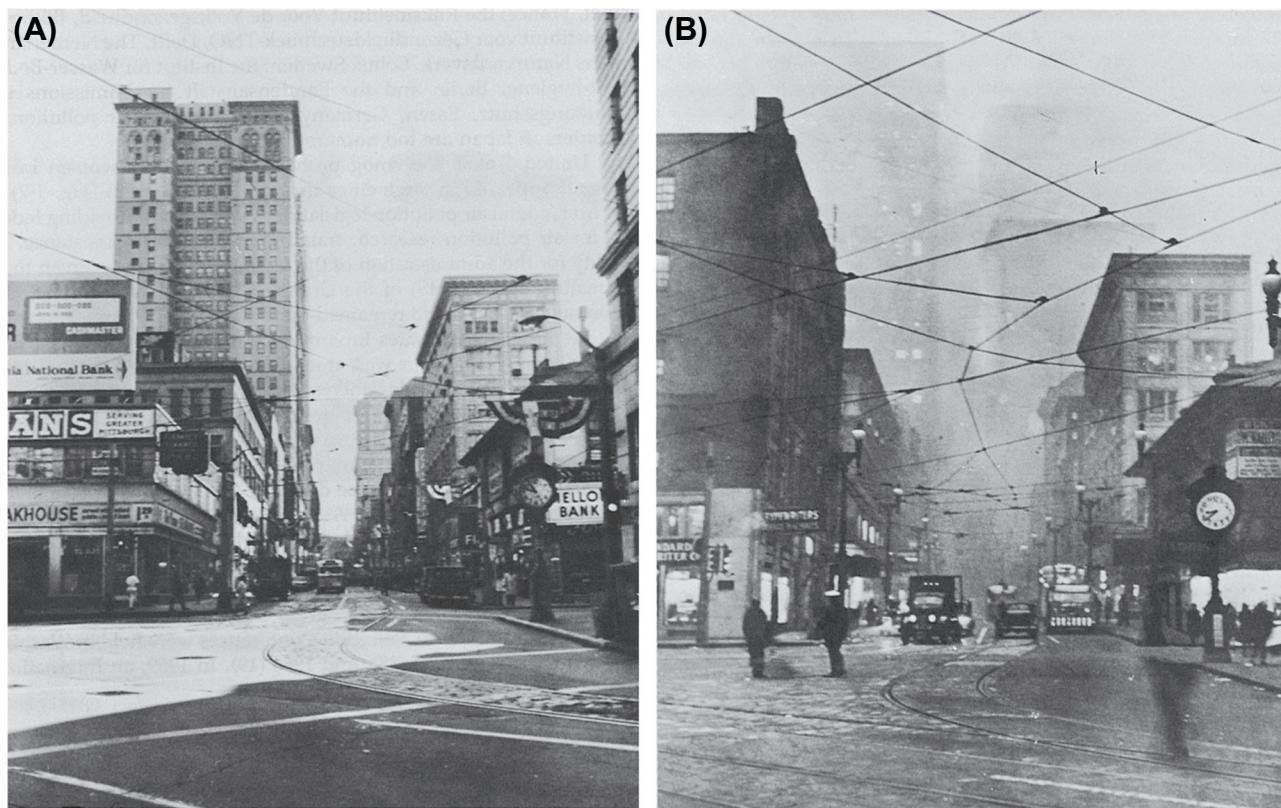


FIGURE 3.17 (A) Pittsburgh after the decrease in black smoke. (*Allegheny County, Pennsylvania.*) (B) Pittsburgh before the decrease in black smoke.

Institut National de la Santé et de las Recherche Médicale at Le Visinet, France; the Rijksinstituut Voor de Volksgezondheid, Bilthoven and the Instituut voor Gezondheidstechniek-TNO, Delft, The Netherlands; the Statens Naturvardsverk, Solna, Sweden; the Institut für Wasser-Bodenund Luft-hygiene, Berlin; and the Landesanstalt für Immissions und Bodennutzungsschutz, Essen, Germany. Many air pollution research centers were established in Japan.

In the United States, the smog problem continued to worsen in Los Angeles and appeared in large cities throughout the nation. In 1955, the first federal air pollution legislation was enacted, providing federal support for air pollution research, training, and technical assistance. Responsibility for the administration of the federal program was given to the Public Health Service (PHS) of the United States Department of Health, Education, and Welfare, and remained there until 1970, when it was transferred to the new US EPA. The initial federal legislation was amended and extended several times between 1955 and 1980, greatly increasing federal authority, particularly in the area of control.<sup>32</sup> Automobile ownership continued to grow, peaking in 2005 and declining substantially in 2009 and 2010, likely due to the economic recession (Table 3.6). However, the rest of the world has continued to increase vehicle ownership. Global production of motor vehicles increased from 54.4 million in 1997 to 84.4 million in 2012. In fact, China produced twice as many vehicles as either the United States or Japan in 2012 (19.3 million compared to 10.3 million in the United States and 9.9 million in Japan).<sup>33</sup>

As in Europe, air pollution research activity expanded tremendously in the United States during these three decades. The headquarters of federal research activity was at the Robert A. Taft Sanitary Engineering Center of the PHS in Cincinnati, Ohio, during the early years of the period and at the National Environmental Research Center in Triangle Park, North Carolina, at the end of the period.

An International Air Pollution Congress<sup>34</sup> was held in New York City in 1955. Three National Air Pollution Conferences were held in Washington, DC<sup>35</sup> in 1958, 1962, and 1966. In 1959, an International Clean Air Conference was held in London. In 1964, the International Union of Air Pollution Prevention Associations (IUAPPA) was formed.

Technological interest from the 1950s through the 1970s focused predominantly on automotive air pollution and its control, on sulfur oxide pollution and its control by sulfur oxide removal from flue gases and fuel desulfurization, and on control of nitrogen oxides produced in combustion processes.

Air pollution meteorology came of age, and by 1980 mathematical models of the pollution of the atmosphere were being energetically developed. The understanding

of the photochemistry of air pollution began at this time and has since greatly improved, but remains a major research challenge. Air quality monitoring systems became operational throughout the world. A wide variety of measuring instruments became available.

### 3.10.4 The 1980s

The highlight of the 1970s and 1980s was the emergence of the ecological, or total environmental, approach. Organizationally, this has taken the form of departments or ministries of the environment in governments at all levels throughout the world. In the United States, the federal EPA became well established during this time, and most states and populous counties and cities instituted and enhanced their counterpart organizations charged with responsibility for air and water quality, solid waste sanitation, noise abatement, and control of the hazards associated with radiation and the use of pesticides. This was paralleled in industry, where formerly diffuse responsibility for these areas became increasingly the responsibility of an environmental protection coordinator. Similar changes were evident in research and education.

Pollution controls were being built into pollution sources—automobiles, power plants, factories—at the time of original construction rather than later on. Also, for the first time, serious attention was directed to the problems caused by the “greenhouse” effect of carbon dioxide and other gases building up in the atmosphere, possible depletion of the stratospheric ozone layer by fluorocarbons, long-range transport of pollution, prevention of significant deterioration (PSD), and acidic deposition.

### 3.10.5 Recent History

The most sweeping change, in the United States at least, in the 1990s was the passage of the Clean Air Act Amendments<sup>36</sup> on November 15, 1990. This was the only change in the Clean Air Act since 1977, even though the U.S. Congress had mandated that the Act be amended much earlier.

The 1990s saw the emergence, in the popular media, of two distinct but closely related global environmental crises, uncontrolled global climate changes and stratospheric ozone depletion. The climate changes of concern were both the warming trends caused by the buildup of greenhouse gases in the atmosphere and cooling trends caused by PM and sulfates in the same atmosphere. Some researchers have suggested that these two trends will cancel each other. Other authors<sup>37,38</sup> have written that the concerns about global warming have been exaggerated.<sup>37</sup> The UN Conference of Environment and Development in Rio de Janeiro during June 1992 did little to resolve the problems, but it did indicate the

magnitude of the concern and the differences expressed by the nations of the world.

The other global environmental problem, stratospheric ozone depletion, was less controversial and more imminent. The US Senate Committee Report supporting the Clean Air Act Amendments of 1990 states, "Destruction of the ozone layer is caused primarily by the release into the atmosphere of chlorofluorocarbons (CFCs) and similar manufactured substances—persistent chemicals that rise into the stratosphere where they catalyze the destruction of stratospheric ozone. A decrease in stratospheric ozone will allow more UV radiation to reach earth, resulting in increased rates of disease in humans, including increased incidence of skin cancer, cataracts, and, potentially, suppression of the immune system. Increased UV radiation has also been shown to damage crops and marine resources".

The Montreal Protocol of July 1987 resulted in an international treaty in which the industrialized nations agreed to halt the production of most ozone-destroying CFCs by the year 2000. This deadline was hastily changed to 1996, in February 1992, after a U.S. NASA satellite and high-altitude sampling aircraft found levels of chlorine monoxide over North America that were 50% greater than that measured over Antarctica.

Global problems continue to hold sway. In the early years of the twenty-first century, global air pollution has taken on a greater urgency, both within the scientific community and the general public. Courts in the United States have mandated that carbon dioxide be considered and regulated as an air pollutant due to its radiant properties and link to global warming. The long-range atmospheric transport of persistent, bioaccumulative toxic substances (PBTs) has led to elevated concentrations in the tissues of marine and arctic mammals, as well as increased PBT levels in the mother's milk of indigenous people, such as the Inuit. Stratospheric ozone depletion is strongly suspected to have played a role in diminished biodiversity around the world.

The meltdown of the Fukushima nuclear power facility in Japan and the potential for attendant migration of radioisotopes created concern on the West Coast of North America. Like the PBT pollution of Inuit peoples, Fukushima served as another reminder that pollutants can travel thousands of miles in winds aloft. Wildfires in North America and biomass burning in South America have released large amounts of PM and other air pollutants. Even what would be considered water disasters, the huge oil spills in the Gulf of Mexico and around the world caused emissions of volatile organic compounds and other potential airborne contaminants.

Arguably, the most visible ongoing concern of late is that of global climate change. It is also one of the most controversial. Until relatively recently, most engineers would probably agree that ensuring complete

combustion is a very effective means of reducing pollution, since many very toxic and persistent air pollutants, such as carbon monoxide and polycyclic aromatic compounds, are products of incomplete combustion. More recently, however, the product of complete combustion, CO<sub>2</sub>, is a major concern as a greenhouse gas.

### 3.11 THE FUTURE

The air pollution problems of the future are predicated on the use of more and more fossil and nuclear fuel as the population of the world increases. During the lifetime of the students using this book, partial respite may be offered by solar, photovoltaic, geothermal, wind, nonfossil fuel (hydrogen and biomass), and oceanic (thermal gradient, tidal, and wave) sources of energy. Still, many of the agonizing environmental decisions of the next decades will involve a choice between fossil fuel and nuclear power sources and the depletion of future fuel reserves for present needs.

Industrial pollution is a worldwide and growing problem. Hopefully, developing nations will not repeat the twentieth century problems experienced by Western nations and will apply lessons without having to suffer the consequences of side effects from economic development (see Chapter 33). Air pollution was both a sad and a promising story of recent decades. Sad, because the pollutants have brought so much premature and avoidable harm to humans and ecosystems. Promising, because science, engineering, and technologies have advanced rapidly to address and to prevent air pollution; and because society reached a consensus that air pollution was not inevitable.

### QUESTIONS

1. Explain the difference between reductionist and systems science as it pertains to air quality.
2. Give two reasons for the crossover of the lines in [Figure 3.8](#) in 1976.
3. If hydrogen sulfide can be smelled in the low percent concentrations in the air, why would one want to use sophisticated detection equipment to detect it at concentrations several orders of magnitude lower?
4. What does the contention by Paracelsus that the dose makes the poison have to do with air pollution?
5. What is the difference between a primary and secondary standard for a criteria air pollutant?
6. If two urban areas, one in southern California and one in central Georgia, are designated as nonattainment for ground-level ozone, how might their approaches be similar in attempting to reach

- attainment status? How might their approaches differ?
7. Referring to **Table 3.1**, find a difference in how transboundary disputes between states is handled in the United States *versus* in the European Union.
  8. Physicists and air pollution experts both use the term “phase” to describe matter. How do they differ? Why?
  9. Give two reasons why particle size is important.
  10. Name the three types of receptors. If sulfur dioxide concentrations in the air are 10 ppb, how might its effects on these receptors differ?
  11. What were the major pollutants of concern in the mid-twentieth century? How has this changed as of the first part of the twenty-first century?

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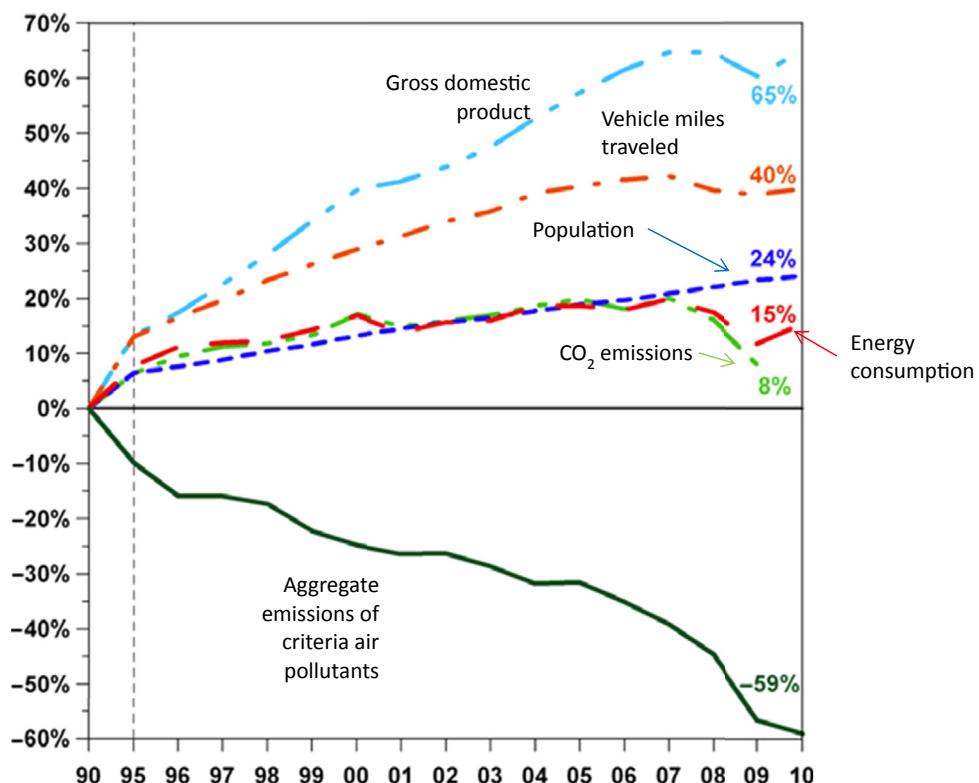
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# Air Pollution Decision Tools

## 4.1 INTRODUCTION

Air pollution results from myriad sources and processes. Air pollution and other atmospheric data come in many forms and of highly varying quality. This includes information about the agents (air pollutants), the media (layers of the atmosphere and components of the hydro-sphere), the modifiers (physical, chemical, and biological substances that transform and transport the agents within the media), and the receptors (human individuals, human populations, and ecosystems and their components).

This information must be evaluated and integrated to inform decision makers as to the best approaches for addressing the problems presented by polluted air. The myriad combinations of scientific and socioeconomic data make for extremely complex decisions (see Figure 4.1). As such, the fundamentals of air pollution includes both direct and indirect relationships among factors that must be understood systematically. The information in the figure indicates that air pollution is not a single-variable, linear relationship between sources and receptors. Indeed, activities that one may assume would



**FIGURE 4.1** Air pollution metrics compared to national socioeconomic metrics (1990–2010). During this period, US gross domestic product, total energy consumption, and total miles traveled by US vehicles increased substantially. The US population and total energy consumption increased, as did emissions of the carbon dioxide. However, emissions of criteria air pollutants (i.e. lead, tropospheric ozone, carbon monoxide, sulfur dioxide, nitrogen dioxide, and particulate matter) decreased markedly. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Office of Air & Radiation. *Our Nation's Air, status and trends through 2010.* [www.epa.gov/airtrends/2011/index.html](http://www.epa.gov/airtrends/2011/index.html); 2011 [accessed 24.09.13].

increase emissions, such as increased energy consumption and vehicle miles traveled, were accompanied by substantial decreases in the emissions of criteria air pollutants.

The relationships between risk from air pollutants and sources can only properly be explained systematically. That is, the harm that results from air pollution is a product of the life cycle of pollution. Air pollution is an outcome of the steps that involve energy and various types of matter, both living and nonliving. The life cycle includes not only time in the air, but also time in the water, on the land, in the soil, and within organisms. The emission of an agent is only one part of the life cycle. Indeed, it is not even the beginning, since certain processes always precede the emission.

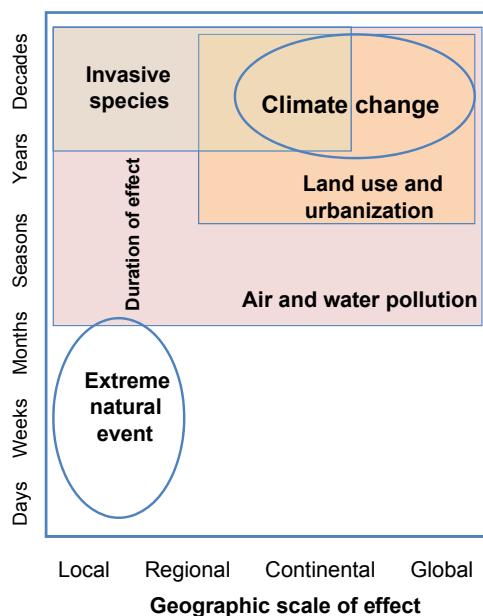
Presently, environmental and health policies are made from two broad perspectives: (1) evidence-based risk assessments and (2) precaution. The difference mainly lies in the onus of the decision. For evidence-based decisions, the onus is mainly placed on proving that a product or process causes harm, whereas in precaution-based decision making, the onus is placed on proving something is safe or will not cause harm. The precaution usually includes an element of irreversibility, i.e. even a slight chance that an agent will cause irreversible harm would lead to a decision not to allow

the agent, or at least only allow it at levels below which there is strong scientific information showing no harm.

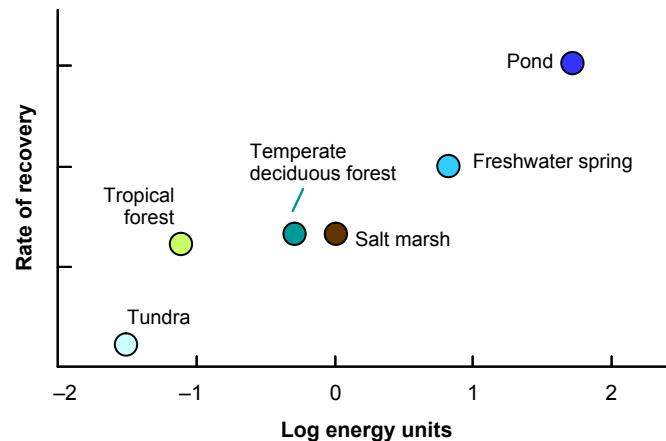
Both evidence-based and precaution-based decisions require the analysis of substantial amounts of data. Evidence-based risk assessments require information regarding both the hazard and the likelihood of exposure to that hazard (see Chapters 7 and 8, respectively). Thus, if this information is scarce or unreliable, the risk assessment is useless at best and dangerous at worst, since it either underestimates or overestimates the risk. For problems that may affect large numbers of people, large geographic areas, and/or that are irreversible, precaution is in order. This is the basis for factors of safety in engineering design and prudence. Therefore, precaution applies to global-scale air pollution, such as the long-range transport of pollutants, acid rain, and climate change (see Figure 4.2).

One of the arguments for taking actions to address climate change, for example, is that climate change could be irreversible (given the long wait for sufficient evidence) and that under many predicted scenarios such change likely would lead to widespread and severe damage to public health and ecosystems (the upper right-hand portion of Figure 4.2). The ecological effects include loss of diversity and productivity. Some habitats are particularly vulnerable to irreversibility.<sup>1</sup> In this sense, irreversibility is indirectly proportional to a system's resilience. For example, habitats shown in the lower left-hand portion of Figure 4.3 would more likely suffer severe and irreversible harm from exposure to air pollutants (e.g. SO<sub>2</sub> and low-pH precipitation, i.e. acid rain) than those in the upper portion.

Risk is commonly understood as the chance that something will go wrong or that some undesirable



**FIGURE 4.2** The response to stressors has temporal and spatial dependencies. Near-field stressors can result from a spill or emergency situation. At the other extreme, global climate change can result from chronic releases of greenhouse gases with expansive (planetary) impacts in direct proportion to significant changes in global climate (temperature increases in the troposphere and oceans, shifting biomes, sea level rise, and migratory patterns). (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Vallero D. *Environmental biotechnology: a biosystems approach*. Burlington (MA): Elsevier Academic Press; 2009. ISBN: 978-0-12-375089-1; based on a drawing by Smith, B. U.S. Environmental Protection Agency; used with permission.



**FIGURE 4.3** System resilience index calculated from bioenergetics for six community types. Rate of recovery units are arbitrary; energy units = energy input per unit standing vegetation. (For color version of this figure, the reader is referred to the online version of this book.) Vallero D. *Environmental biotechnology: a biosystems approach*. Burlington (MA): Elsevier Academic Press; 2009. ISBN: 978-0-12-375089-1. Data from: Ref. 1; and Begon M, Harper JL, Townsend CR. *Ecology*. 3rd ed. Oxford (United Kingdom): Blackwell Science, Ltd.; 1996.

event will occur. Every time a person engages in an activity, e.g. walking, working, jogging, etc., that activity introduces risk of some adverse outcome. The person may get hurt, injure others, or even die in a mishap. The understanding of the factors that lead to a risk is called risk analysis; whereas the reduction of this risk (e.g. by wearing helmet and staying on bike paths) is known as risk management. Risk management is often differentiated from risk assessment, which comprises the scientific considerations of a risk. Risk management includes the policies, laws, and other societal aspects of risk.<sup>a</sup>

Air pollution risk is increased in two very basic ways. The mix of substances may become inherently more harmful; or the amount of exposure to harmful substances may increase. The former is an increase in the hazard and the latter is an increase in exposure. Thus, air pollution actions must be based on reliable risk analysis and assessment. They must account for the interrelationships among factors that put people at risk to provide decision makers with thoughtful studies based upon the sound application of the physical sciences.<sup>2</sup> Air pollution engineers design systems to reduce risk and to enhance the reliability of these systems.<sup>3</sup>

Everyone to some extent, at least intuitively, assesses risks and determines the reliability of decisions every day. They desire safety, but this is a relative term. The “safe” label requires a value judgment and is always accompanied by uncertainties, but engineers frequently characterize the safety of a product or process in objective and quantitative terms. Air pollution safety is usually expressed by safety’s opposite term, risk.

## 4.2 INTERPRETING DATA

Events can be characterized in a number of ways. Events may be discrete or continuous. If the event is forced to occur as a finite set of outcomes (e.g. six sides of a die) the event is discrete. However, if the event can be of any value within a domain, e.g. size of a tumor, the event is continuous. Events can also be independent or dependent. An event is independent if the results are not influenced by previous outcomes. Conversely, if an event is affected by any previous outcome then the event is a dependent event.

Since air pollution usually involves numerous variables, joint probabilities are also calculated. For  $n$  mutually exclusive events as possible outcomes from  $E$  that have probabilities equal to  $P\{E_i\}$ , the probability of

these events in a trial equals the sum of the individual probabilities:

$$P\{E_1 \text{ or } E_2 \dots \text{ or } E_k\} = P\{E_1\} + P\{E_2\} + \dots + P\{E_k\} \quad (4.1)$$

Further this helps us to find the probabilities of events  $e_i$  and  $g_i$  for two independent sets of events,  $E$  and  $G$ , respectively:

$$P\{e_i \text{ or } g_i\} = P\{e_i\}P\{g_i\} \quad (4.2)$$

For example, a company record book indicates that a waste site has 10 unlabeled buried chemical drums. However, the drums were originally color coded according to the vapor pressures ( $P^\circ$ ) of the contents: five drums that contain a low vapor pressure ( $P^\circ = 10^{-6}$  kPa) substance ( $P_{low}$ ), two drums that contain a medium vapor pressure ( $P^\circ = 10^{-4}$  kPa) substance ( $P_{med}$ ), and three drums that contain a very high vapor pressure ( $P^\circ = 10^{-1}$  kPa) substance ( $P_{vh}$ ). Unfortunately, the color coding is no longer visible. The plant manager is hoping to remove the  $P_{low}$  and  $P_{med}$  drums before calling in special equip teams for the  $P_{low}$  drums that, if ruptured, would release the contents into the air more rapidly. The manager asks the environmental safety officer what is the likelihood of pulling up these drums. This can be accomplished by using joint probabilities. We can determine the probability of pulling up one of the drums that contains substances with a low or medium vapor pressure (i.e.  $P_{low}$  and  $P_{med}$ ). The two possible events ( $P_{low}$  drum or  $P_{med}$  drum) then, are mutually exclusive and come from the same sample space; so we can use Eqn (4.1):

$$P\{P_{low} \text{ or } P_{med}\} = P\{P_{low}\} + P\{P_{med}\} = \frac{5}{10} + \frac{2}{10} = \frac{7}{10}.$$

Thus we have a 70% probability of pulling up a drum with a low to moderate vapor pressure substance.

A nearby waste site also has 10 unlabeled, buried drums, but with known chemical formulations: three drums that contain dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and seven drums that contain trichloromethane ( $\text{CHCl}_3$ ). If there is a possibility that the  $P_{med}$  substance could be very dangerous in the presence of  $\text{CHCl}_3$ , and the need for special measures to segregate the  $P_{med}$  and  $\text{CHCl}_3$ , the plant manager wants to know the probability of pulling up a  $P_{med}$  drum from the first site and a  $\text{CHCl}_3$  drum from the second site. Since the two trials are independent, we can use Eqn (4.2):

$$\begin{aligned} P\{P_{med} \text{ and } \text{CH}_2\text{Cl}_2\} &= P\{P_{low}\} + P\{P_{med}\} \\ &= \frac{2}{10} \times \frac{3}{10} = \frac{6}{100}. \end{aligned}$$

<sup>a</sup> The segregation of risk assessment (science) from risk management (feasibility) is a recent approach. One of the first advocates for separating the two processes was William Ruckelshaus, who twice served as the Administrator of the U.S. EPA.

Thus we have 6% probability of extracting a medium vapor pressure substance drum and a dichloromethane drum on our first excavation. Since we do not know the chemical composition of the  $P_{med}$  drum, we must assume that a worst case scenario, i.e. the  $P_{med}$  contents are very dangerous when combined with  $CHCl_3$ . Thus, there will be a 6% probability of this scenario, unless other steps are taken (e.g. conducting removals on different days).

Another important concept for environmental data is that of conditional probability. If we have two dependent sets of events,  $E$  and  $G$ , the probability that event  $e_k$  will occur if the dependent event  $g$  has previously occurred is shown as  $p\{e_k|g\}$ , which is found using Baye's theorem:

$$p\{e_k|g\} = \frac{p\{e_k \text{ and } g\}}{p\{g\}} = \frac{p\{g|e_k\}p\{e_k\}}{\sum_{i=1}^n p\{g|e_i\}p\{e_i\}} \quad (4.3)$$

A review of this equation shows that conditional probabilities are affected by a cascade of previous events. Thus, the probability of what happens next can be highly dependent upon what has previously occurred. For example, the cumulative risk of cancer depends on the serial (dependent) outcomes. Similarly, reliability can also be affected by dependencies and prior events. Thus, characterizing any risk or determining the reliability of systems are expressions, at least in part, of probability.

Air pollution data can also be presented by a "probability density function" (PDF) for data. The PDF is created from a probability density; that is, when the data are plotted in the form of a histogram, as the amount of data increases, the graph increases its smoothness, i.e. the data appear to be continuous. The smooth curve can be expressed mathematically as a function,  $f(x)$ . This is the PDF. The probability distribution can take many shapes, so the  $f(x)$  for each distribution will differ accordingly. For example, in environmental matters, distributions commonly seen

are normal, log-normal, and Poisson. The normal (Gaussian) distribution is symmetrical and is best known as the "bell curve", given its shape (see Figure 4.4). The log-normal distribution is also symmetrical, but its  $x$ -axis is plotted as a logarithm of the values.

The Poisson distribution is a representation of events that happen with relative infrequency, but regularly.<sup>4</sup> Stated mathematically the Poisson distribution function expresses the probability of observing various numbers of a particular event in a sample when the mean probability of that event in any one trial is very small. So, the Poisson probability distribution characterizes discrete events that occur independently of one another during a specific period of time. This is useful for risk assessments, since exposure-related measurements can be expressed as a rate of discrete events, i.e. the number of times an event happens during a defined time interval, such as the frequency (times per week) that a person drives a car. The Poisson distribution describes events that take place during a fixed period of time (i.e. a rate), so long as the individual events are independent of one another.

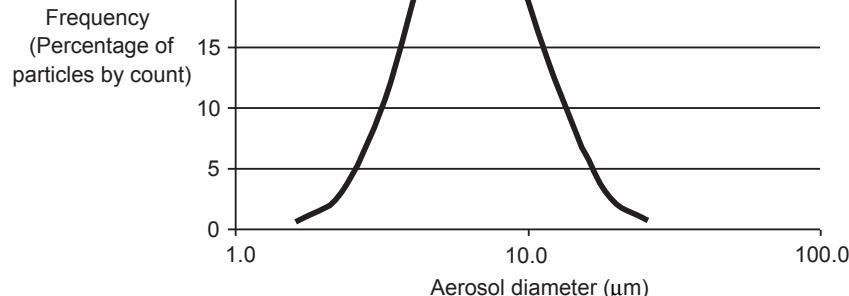
As the expected number of events or counts increases (i.e. the event rate increases), so does variability. Obviously, if we expect a count to equal 1, then an observation of 2 or 0 would be more reasonable than an observation between 500 and 0. If we expect a count to be equal to 50,000, counts of 49,700 and 50,300 are within reason. The range and variance of the latter, however, is actually larger by 100. The Poisson equation needed to compute the probability of a specific number of counts being observed over a defined time interval is

$$P_\lambda = \frac{e^{-\lambda} \lambda^n}{n!} \quad (4.4)$$

where,  $\lambda$  = average or expected counts or events per unit time and  $n$  = number of encounters

Thus, the Poisson distribution is useful in a risk assessment to estimate exposures. It may be used to characterize the frequency with which a person (or animal or ecosystem) comes into contact with a

**FIGURE 4.4 Distribution (log normal) of aerosols in the lower troposphere.** Silverman L, Billings CE, First MW. Particle size analysis in industrial hygiene. New York (NY): Academic Press; 1971.



substance (e.g. the number of times per day a person living near a wood treatment facility is exposed to pentachlorophenol atmospheric concentrations above  $100 \text{ ng m}^{-3}$ ). Assuming that based on existing data, the expected number of encounters is two per day, applying Eqn (4.4) with  $\lambda = 2$ , there is a 9% chance that an individual will have four (i.e.  $n = 4$ ) encounters with pentachlorophenol concentrations above  $100 \text{ ng m}^{-3}$  on a given day.

#### 4.2.1 Expressions of Air Pollution Risk

Stated mathematically, an event ( $e$ ) is one of the possible outcomes of a trial (drawn from a population). Risk is a probability. All probabilities, including risk, range from zero to unity, or are stated as a percentage, 0–100%. Note that risk is unitless, e.g. a one-in-five risk or a 20% risk. In a coin toss, we usually think of two possible outcomes, i.e. heads or tails. However, it is actually three, i.e. heads, tails, and edge. These three outcomes together form a finite “sample space”, designated as  $E = [e_1, e_2, e_s]$ . Thus, the sample space for any air pollution risk scenario can be stated as

$$E = [e_1, e_2, \dots, e_n] \quad (4.5)$$

The edge outcome in a coin toss is a very low probability event that is often, by convention, ignored. For example, at the beginning of overtime in a football game, a tossed coin determines who will receive the ball, and thus have the first opportunity to score a touchdown, which results in a win. When the referee tosses the coin, there is little concern about anything other than “heads or tails”. However, the National Football League undoubtedly has a protocol for the rare event of the coin not being a discernible heads or tails. In an air pollution scenario involving a carcinogen,  $e$  could represent a case of cancer. Consider, for example, a population of 1 million people exposed to a carcinogenic air pollutant over a specific time period, with one additional cancer diagnosed that can be attributed to that pollutant exposure. Thus, the probability of  $e$ , i.e.  $p\{e\} = 10^{-6}$ . This one-in-a-million event has the same probability as the hypothetical event of a coin landing on its edge. Even a rare event will occur in a sufficiently large population.

Risks in a population can be stated as the product of probability and an outcome. This can be stated as a frequency ( $F$ ) at which the adverse outcome occurs:

$$F = \frac{X}{N} \quad (4.6)$$

where,  $X$  = number of adverse events;  $N$  = number of individuals in the population. For example, if 100 people contract a disease randomly distributed in a popula-

tion of 100,000, frequency of the disease is  $\frac{10^2}{10^5} = 10^{-3}$ , or

one in a thousand. The  $F$  term is usually referred to as a probability ( $P$ ). Air pollution studies often compare populations, e.g. workers exposed to a particular air pollutant compared to the general population. This comparison is known as a relative risk (RR), which is calculated as

$$\frac{P_{\text{exposed}}}{P_{\text{unexposed}}} = \frac{X_{\text{exposed}} (N_{\text{exposed}})^{-1}}{X_{\text{unexposed}} (N_{\text{unexposed}})^{-1}} \quad (4.7)$$

RR for air pollutants is often stated as a ratio, particularly as a standard mortality ratio or a standard morbidity ratio (both abbreviated to “SMR”):

$$\text{SMR} = \frac{D_{\text{observed}}}{D_{\text{expected}}} = \frac{P_{\text{exposed}}}{P_{\text{unexposed}}} \quad (4.8)$$

where,  $D$  = number of deaths for standardized mortality rates or number of diseases for standardized morbidity rates.

For example, if 15 out of 10,000 workers who are exposed to air polluted with a metallic compound have died of a type of lung cancer that occurs at a rate of 15 per million, the SMR for this hypothetical cohort of exposed workers would be  $\frac{15(10^4)^{-1}}{15(10^6)^{-1}} = 10^2$ . This means that the worker’s RR is 100 times that of the general population of dying from this particular type of cancer.

The SMR is used as a specific measure of the strength of association between a population’s exposure to an air pollutant and deaths that may be attributed to that exposure. The mortality rate in a community without a specific exposure or intervention is called the *baseline rate*, which represents the *expected level* of the mortality. Note that the denominators in Eqns (4.7) and (4.8) include “unexposed” in their subscripts. Actually, these populations are seldom completely unexposed.

In the metallic compound example above, the workers live in the general population, so those 10,000 persons would have to be subtracted from the million. Also, unless the compound is exclusively found in the workplace, others in the general population would be exposed, albeit often at much lower concentrations. Workplaces may differ from the general environment not only in the concentrations of certain pollutants, but also in the ways people are exposed. For example, the toxic metal cadmium (Cd) is a pollutant released during the production of batteries (especially, nickel-cadmium [NiCd] types), paints, and coatings, as well as during metal work, e.g. welding, soldering, and plating. Air concentrations of Cd in the workplace can be much higher than in the general environment. As evidence, in the United States, inhalation is the major route of workplace exposure to Cd. The Occupational Safety and Health Administration has set the permissible exposure limit (PEL) for Cd fumes or

cadmium oxide ( $\text{CdO}$ ) as  $0.1 \text{ mg m}^{-3}$ . This is five orders of magnitude higher than average Cd concentrations in unpolluted air ( $1 \times 10^{-6} \text{ mg m}^{-3}$ ) and less than four orders of magnitude higher than average Cd concentrations in urban areas ( $4 \times 10^{-5} \text{ mg m}^{-3}$ ). Thus, in the case of Cd, the general population can be considered to be relatively unexposed compared to that of workers in certain industries.<sup>5,b</sup>

#### 4.2.2 Risk Factors and Confounders

Another way to think about Eqns (4.7) and (4.8) is that they show the difference between what is being observed *versus* what is expected in terms of death and disease. That is, how do the observed population compare to the expected population (Eqn (4.8))?

Thus, the denominator actually needs to be comparable from one study to the next, i.e. a “standard population” or “reference population”. So, the SMR is employed to compare mortality or morbidity risks of a study population to that of a standard population. Again, the standard population may or may not be an unexposed population. For most air pollutants, the standard population is indeed exposed, but usually are much lower levels than the study group. Sometimes, however, the standard population may actually be more highly exposed to certain air pollutants. For example, if a state or national exposure rate is used as the standard population, the standard population may have higher average exposures than a study group of infants for ozone ( $\text{O}_3$ ). Indoor concentrations of  $\text{O}_3$  are usually much lower than outdoor concentrations. Since newborns spend more time indoors than most other age groups in developed nations, their  $\text{O}_3$  exposures would be less than that of the standard population. The previous discussion of RR can be visualized as a two-by-two table (Table 4.1). The table shows that the incidence of an outcome when the risk factor is present, e.g. population exposed to Cd concentrations above PEL ( $\leq 0.1 \text{ mg m}^{-3}$ ) is  $\frac{A}{A+B}$ . The incidence when the risk factor is absent (e.g. Cd  $> 0.1 \text{ mg m}^{-3}$ ) is  $\frac{C}{C+D}$ :

$$\text{Relative risk} = \frac{\left(\frac{A}{A+B}\right)}{\left(\frac{C}{C+D}\right)} \quad (4.9)$$

The odds ratio can also be calculated from this table:

$$\text{Odd ratio} = \frac{(A \times D)}{(B \times C)} \quad (4.10)$$

TABLE 4.1 Two-by-two Table for Calculating Relative Risk of an Outcome When a Risk Factor is Present and Absent

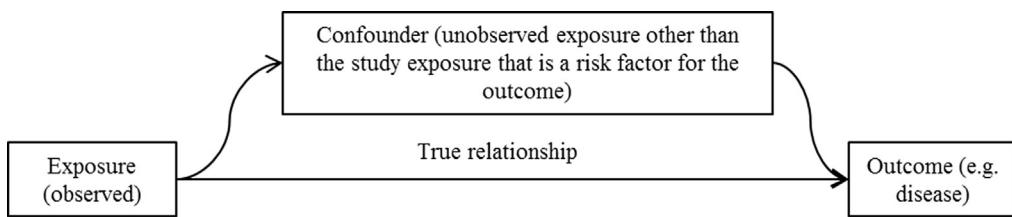
Risk Factor	Outcome: Disease	Outcome: No Disease	Total
Present	A	B	A + B
Absent	C	D	C + D
Total	A + C	B + D	A + B + C + D

The previous discussions point to the need for care in choosing the standard population. Smoking and other behaviors will confound the meaning of RR assessments. A confounder is an extraneous (third) variable that would influence the outcome of study or could be causing at least some of the outcome, instead of the variable being studied (see Figure 4.5). Thus, a confounder is a risk factor of the outcome, is associated with the exposure, is not an intermediate step in the link between the risk factor of interest and the outcome, and is not a surrogate of exposure.<sup>6</sup>

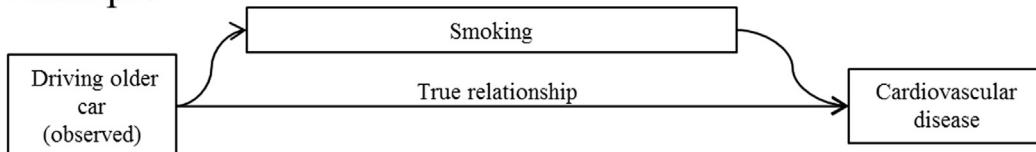
The confounder or third variable in Figure 4.5 provides an example of hypothesis testing. A hypothetical research project found that people who drive old cars appear to contract heart disease at a higher rate than the general public. Based on the crude data, there does indeed appear to be a strong association between driving an older car and cardiovascular problems, i.e. an odds ratio = 2.23. However, the common confounder of such studies is smoking, since numerous studies have shown the link between smoking and various cardiovascular problems (due in large part to the carbon monoxide inhalation and consequent decrease in oxygen carried by hemoglobin, i.e. carboxyhemoglobin, which stresses the heart and cardiovascular system). An astute researcher would look for risk factors other than the one being studied. In this case, when smoking is accounted for properly, the odds ratios drop to 1. That is, when the crude data are stratified by smokers and nonsmokers, driving an older car does not account for any increase in risk of cardiovascular disease. Odds ratios and RRs that equal 1 mean that the study group’s risk does not differ from the standard population (e.g. the US adult population). If they are greater than 1, the study group has an apparently greater risk, and less than 1 means an apparently lesser risk. In addition to smoking, study populations are often stratified by age, sex, socioeconomic status, education levels, and other risk factors that would bias results and mask the real risk factors.

Risk factors can be difficult to disentangle. In this hypothetical example, smoking may indeed be highly

<sup>b</sup> See Chapter 1 for a discussion of respirators and other personal protective equipment needed to decrease exposures in the workplace.



### Example



Crude odds ratio: data		
	Cardiovascular disease Yes	Cardiovascular disease No
Old car driver Yes	90 (A)	60 (B)
Non-old car driver No	60 (C)	90 (D)

$$\text{Crude odds ratio} = (A \cdot D) / (B \cdot C) = (90 \cdot 90) / (60 \cdot 60) = 8100 / 3600 = 2.25$$

Stratified data				
	Smokers		Nonsmokers	
	Cardiovascular disease Yes	Cardiovascular disease No	Cardiovascular disease Yes	Cardiovascular disease No
Old car driver	80	40	10	20
Non-old car driver	20	10	40	80

$$\text{Odds ratio for those who smoke} = (A \cdot D) / (B \cdot C) = (80 \cdot 10) / (40 \cdot 20) = 800 / 800 = 1.0$$

$$\text{Odds ratio for those who do not smoke} = (A \cdot D) / (B \cdot C) = (10 \cdot 80) / (20 \cdot 40) = 800 / 800 = 1.0$$

**FIGURE 4.5 Confounder flow chart.** Although the observed exposure appears to be associated with the disease, it is actually following the path through a confounder. In this case, the confounder is associated with the disease, so the relationship between the observed exposure and the outcome cannot be precisely known unless the confounder is removed from the flow. Ref. 6.

correlated with driving an older car. Had the odds ratio been greater than 1, it may have been plausible to investigate the matter further. For example, older vehicles do indeed emit, on average, much large amount of PM, volatile organic compounds, carbon monoxide, and other pollutants compared to newer models. Thus, even if the odds ratios do not bear this out in this particular study, it does not mean the drivers are not actually at higher risks of cardiovascular disease. It could be that the drivers of older cars who do not smoke are also more careful about keeping their cars well maintained, for example. Or, it could be that smoking has such a strong signal that swamps out the smaller signal from vehicle emissions. The bottom line is that one study is usually not enough and has limitations and flaws, whether the

findings are positive or negative. This is why science depends on numerous and varied studies of the linkage between air pollutant exposures and health effects.

The SMR can be calculated for any event or case, especially across population and geographic subdivisions, such as zip codes and census tracts. Air pollution maps often show concentrations of a pollutant compared to mortality and morbidity rates. The SMR can be stated as

$$\text{SMR} = \frac{D_{\text{observed}}}{D_{\text{expected}}} = \frac{\sum_{j=1}^J d_j}{\sum_{j=1}^J n_j \lambda_j^*} = \frac{\sum_{j=1}^J n_j \lambda_j}{\sum_{j=1}^J n_j \lambda_j^*} \quad (4.11)$$

where,  $d_j$  = number of cases in the observed population across  $j$  age groups;  $n_j$  = number of cases in the standard

population;  $\lambda_j^*$  = disease or death rate in the census tract; and  $\lambda_j$  = disease or death rate in the standard population.

In the cadmium example, Cd exposures are much higher in certain microenvironments than in the general environment. The distinction in this case is between the workplace and the ambient air. However, exposures are driven by activities, e.g. diet and smoking. The two principal pathways for Cd exposure in the general US population differ between its nonsmokers and smokers. For the nonsmoker, the major Cd exposure pathway is ingestion of food. For the smoker, it is the inhalation of tobacco smoke.<sup>7</sup> On average, a cigarette contains 2.0 µg Cd, of which 2–10% is transferred into smoke; accounting for twice the blood Cd in smokers than in nonsmokers.<sup>8</sup> Any comparison of the Cd-related diseases in workers to those in the general population must consider smoking. That is, there needs to be a method for including and excluding the confounder of effect of smoking in the denominator of Eqn (4.7) or (4.8).

Often, risk estimates are derived from physical, chemical, and biological factors that give rise to probabilities. Returning to our football coin flip example, the probability of the third outcome (a coin on edge) is higher if the coin lands in grass or artificial turf, compared to landing on a hard flat surface. Such factors are deterministic. Thus, the physical conditions increase the relative probability of the third event. This is analogous to a person who may have the same exposure to a carcinogen as the general population, but who may be genetically predisposed to develop cancer. The exposure is the same, but the probability of the outcome is higher for this “susceptible” individual. Thus, risk varies by both environmental and individual circumstances. In this instance, it is important to identify subpopulations with genetic predispositions to a disease that is being investigated for its linkage to an air pollutant.

#### 4.2.3 Causal Links between Risk Factors and Adverse Outcomes

To link air pollution to adverse outcomes in anything other than a purely academic discussion, air pollution decision making must infer causality. Risk of an adverse outcome is increased when risk factors are increased in number and size. Risk factors must be present before the onset of the adverse event. However, these associations must be supported by other information in order to find causes.

Two essential attributes of a risk factor is its strength of association and its temporality. Exposure to the air pollutant must correlate with the onset of the disease and the exposure must occur prior to the onset of the disease. The biomedical research and epidemiological communities use a number of criteria to determine the strength of an argument for causality. The first criteria

were first well articulated by A. Bradford Hill as a means of linking risk factors to cancer.<sup>9</sup> These criteria are

1. Strength of association
2. Consistency
3. Specificity
4. Temporality
5. Biologic gradient
6. Plausibility
7. Coherence
8. Experimentation
9. Analogy

Depending on the case, some of Hill’s criteria are more important than others. As mentioned, strength of association and temporality are essential. Others, like coherence and plausibility, are desirable in most cases, but could stifle hypotheses since they resist paradigm shifts, e.g. new hypotheses for diseases.

##### 4.2.3.1 Strength of Association

This chapter’s discussion up to now has mainly addressed how to associate a particular risk factor, especially an air pollutant, with an adverse outcome. For a chemical exposure to cause an effect, the exposure must be associated with that effect. Strong associations provide more certain evidence of causality than is provided by weak associations. Common epidemiological metrics used in association include risk ratio, odds ratio, and standardized mortality ratio.

Descriptive epidemiology is often a first step in air pollution studies. For example, even before hypotheses are made regarding what may be causing or contributing to a health problem, epidemiologists must characterize differences. Sex, race, ethnicity, age, and socioeconomic factors can show different outcomes for diseases in the same general population.

Recall from the discussions of confounders that calculating RRs can be visualized as a two-by-two table (Table 4.1), i.e.  $RR = \left(\frac{A}{A+B}\right)\left(\frac{C}{C+D}\right)^{-1}$ . The difference in age, sex, and whether one lives in a rural *versus* urban area can be among the first descriptive comparisons conducted by epidemiologists, as in a recent study of mortality rates for diseases in the Hubei Province in China (see Table 4.2).

The table shows differences between crude and standardized deaths. The standardization is accomplished by adjusting the crude death rate for differences in age composition between the study group (urban and rural) *versus* that of the standard population. This allows for comparisons of asymmetrical distributions within subpopulations, so that the risk factor being investigated is less influenced by other factors (i.e. confounders).

Standardization can be accomplished in two ways, i.e. directly and indirectly. If interested in standardizing

**TABLE 4.2** Mortality Rate of Chronic Disease among Men in Urban and Rural Areas in Hubei Province, China; 2008–2010

Diseases	Urban		Rural		Standardized Relative Risk (95% Confidence Interval)
	Crude Death Rate (per 100,000)	Standardized Death Rate (per 100,000)	Crude Death Rate (per 100,000)	Standardized Death Rate (per 100,000)	
<b>Circulatory system</b>	351.34	301.63	400.99	582.55	1.93(1.88–1.98)
Cerebrovascular disease	193.86	165.27	260.32	369.75	2.24(2.16–2.31)
Ischemic heart disease	118.33	102.80	86.81	128.44	1.25(1.19–1.31)
<b>Neoplasms</b>	257.23	220.77	240.01	286.61	1.30(1.26–1.34)
Lung	110.94	94.61	46.95	74.31	0.79(0.75–0.83)
Liver	39.26	34.34	49.02	53.44	1.56(1.44–1.68)
Stomach	26.98	22.81	45.16	56.22	2.47(2.25–2.70)
Colon and rectum	19.92	16.93	8.04	9.85	0.58(0.51–0.66)
Esophagus	22.54	19.69	13.80	23.00	1.17(1.05–1.30)
Breast	0.43	0.36	0.25	0.32	0.85(0.38–1.87)
<b>Respiratory system</b>	82.28	70.15	134.23	215.28	3.07(2.92–3.23)
Chronic lower respiratory disease	61.49	52.09	130.52	210.83	4.05(3.82–4.29)
<b>Digestive system</b>	26.76	23.25	21.03	24.62	1.06(0.96–1.17)
Diseases of liver	12.83	11.25	11.29	12.08	1.07(0.93–1.24)
<b>Endocrine, nutritional, and metabolic diseases (E00–E90)</b>	25.55	21.87	10.05	13.31	0.61(0.54–0.68)
Diabetes mellitus	24.44	20.91	9.64	12.80	0.61(0.55–0.69)

Source: Cheng L, Tan L, Zhang L, Wei S, Liu L, Long L, et al. Chronic disease mortality in rural and urban residents in Hubei Province, China, 2008–2010. *BMC Public Health* 2013; 13:713. <http://dx.doi.org/10.1186/1471-2458-13-713>.

for age using the direct standardization method would calculate a weighted average of the study group's age-specific mortality rates where the weights represent the age-specific sizes of the standard population. Each age-specific mortality rate for the study group is multiplied by the number of people in the age group of the standard population. These products are summed and divided by the number of people in the standard population. An example of standardization used by US Center for Disease Control and Prevention is shown in Table 4.3.

The indirect method applies age-specific mortality rates from the standard population to derive expected deaths in the region's population. For each age group, the age-specific mortality rate for the standard population is multiplied by the number of people in the age group of the study group and summed. This number of deaths in the entire study group is divided by this sum. The result is multiplied by the crude death rate.

Note that the last column in Table 4.2, relative risk, includes confidence intervals. This is an indication of the uncertainty in the estimates.

The odds ratio is the probability that an event will occur divided by the probability that it will not occur. It can also reflect the odds of an event for one group (e.g. urban dwellers) divided by the odds of a different group (e.g. rural population). Rather than presence or absence shown in Table 4.1, the information in Table 4.3 can be compared for urban and rural populations (see Table 4.4). In this case, the risk factor is a differentiation as to where people live. For some outcomes "urbanization" appears to be protective for several of the diseases listed in Table 4.2. The rural population of this Chinese province had higher RRs for cerebrovascular diseases, ischemic heart disease, stomach cancer, and liver cancer, whereas urban populations showed higher RRs for lung, colorectal, and breast cancers; endocrine diseases; and diabetes. Since some, but certainly not all, of these diseases share some risk factors, this descriptive epidemiology indicates the need to investigate what it is about urban and rural life that leads to these differences.

Descriptive information like that in Table 4.2 helps to generate hypotheses and provoke ideas. This is analytical epidemiology, i.e. possible explanations of why

TABLE 4.3 Example of Age-Adjusted Standardization of Mortality Rates

Crude Death Rate Comparison						
Age	Community A			Community B		
	Deaths	Population	Rate (per 1000)	Deaths	Population	Rate (per 1000)
0–34 years	20	1000	20	180	6000	30
35–64 years	120	3000	40	150	3000	50
65 years and over	360	6000	60	70	1000	70
Total	500	10,000	50	400	10,000	40

Age-Adjusted Death Rate Calculation					
Age	Community A			Community B	
	Standard Population	Rate (per 1000)	Rate × Population	Rate (per 1000)	Rate × Population
0–34 years	3000	20	60	30	90
35–64 years	3000	40	120	50	150
65 years and over	4000	60	240	70	280
Total	10,000	42	420	52	520

Source: Curtin LR, Klein RJ. Direct standardization (age-adjusted death rates). *Healthy People 2000. Statistical Notes. No. 6.* Atlanta (GA): National Center for Health Statistics. <http://www.cdc.gov/nchs/data/statnt/statnt06rv.pdf>; 2013 [accessed 10.08.13].

there are differences among the different segments. Since air pollution risk is a function of the pollutant's inherent hazard (e.g. cancer potency) and the exposures (e.g. inhaling air containing the pollutant), outcomes like those in the first column of Table 4.2 are usually low-probability events, such as the number of cancers added to what would otherwise be expected without the air pollution. Therefore, statistics are needed to express the linkages between the hazards and exposures. As mentioned, this often begins with the odds ratio for these events.

The odds ratio is a key step toward linking a risk factor to the adverse outcome, since it reflects the strength of the association between an exposure and an outcome, i.e. the odds that an outcome will occur given a particular exposure, compared to the odds of the outcome occurring in the absence of that exposure.<sup>10</sup> For example, the Children's Health Study in southern California used odds ratios to link indicators of respiratory problems in children with proximity to major roadways (mobile air pollutant exposure). Asthma medication usage (odds ratio = 1.50; 95% confidence interval, 1.16–1.95), wheezing (odds

ratio = 1.40; 95% confidence interval, 1.09–1.78), and lifetime asthma incidence (odds ratio = 1.29; 95% confidence interval, 1.01–1.86) for children residing in homes within 75 m of a major road.<sup>11</sup> The odds ratios of 1.50, 1.40, and 1.29 indicate that living near a roadway is associated with 50% more children using medication, 40% more children exhibiting wheezing, and 29% more children being diagnosed with asthma compared to those living in homes greater than 75 m from a major roadway. Note also that each odds ratio is expressed within a confidence interval. This is a way of expressing uncertainty and variability. That is, 95% of the time, for children living <75 m from a major road, the odds ratio for asthma medication usage will fall between 1.16 and 1.95. If the lower interval were less than 1, this would mean that the exposed and unexposed were not statistically different, i.e. living near or far from a roadway would have made no statistical difference for a variable if the confidence interval were less than 1.

Recall that risk is the probability of an adverse or unwanted outcome.<sup>12</sup> Probability is the mathematical expression that relates a particular outcome of an event to the total number of possible outcomes. Returning to our earlier coin example that flipping it should give very nearly a 50–50 chance of either a heads or tails. Actually, however, the 50% probability depends on every physical factor on each side being equal. Indeed, this is not the case for most coins, since the heads side usually has a head and the tail side has something other than a head. Thus, the aerodynamics differs due to shape, ridges, and valleys on the two sides. These are

TABLE 4.4 Two-by-two Table for Calculating Relative Risk of a Disease Outcome for Urban versus Rural

Risk Factor	Outcome: Disease	Outcome: No Disease	Total
Urban	A	B	A + B
Rural	C	D	C + D

deterministic features that may make the odds change ever so slightly.

We must keep in mind of the very rare chance (i.e. highly unlikely, but still possible) that the coin could land on its edge, i.e. the outcome is neither a heads nor a tails. Deterministic factors may increase the probability of this rare outcome, e.g. a thicker coin is more likely than a thinner coin to land on its edge. The total probability of all outcomes must be unity, i.e. the sum of the probabilities must be 1. In the case of the coin standing on end rather than being a heads or tails, we can apply a quantifiable probability to that rare event. Let us say that laboratory research has shown that one in a million times ( $\frac{1}{1,000,000} = 0.000001 = 10^{-6}$ ), the coin lands on edge. By difference, since the total probabilities must equal 1, the other two possible outcomes (heads and tails) must be  $1 - 0.000001 = 0.999999$ . Again, we are assuming that the aerodynamics and other physical attributes of the coin give it an equal chance of being either heads or tails, then the probability of heads = 0.4999995 and the probability of tails = 0.4999995. Air pollution statistics are similarly affected by deterministic features. Thankfully, many of the diseases caused by air pollutants are rare. For example, additional cancers attributable to air pollutants are often considered in one-in-a-million scenarios. Scientists ask what amount of exposure would lead to  $10^{-6}$  additional cancer risk in a population. As such, scientists must have objective and reliable ways to consider rare outcomes.

Deterministic factors, analogous to the features on the head side of the coin, can increase the risk of diseases and damage from air pollution. For example, children and the elderly may be particularly susceptible to respiratory effects resulting from exposures to air pollutants. Thus, risk is affected by features of both the agent (e.g. pollutant concentration, potency, and bioavailability) and the receptor population (e.g. genotype, age, sex, and race).

#### **4.2.3.2 Consistency**

Hill asked the question, "Has [the association] been repeatedly observed by different persons, in different places, circumstances and times?"<sup>9</sup> That is, even though there may be strong weight of evidence, if this is only from one type of study, e.g. laboratory experiments, the findings are not yet consistent. The exposure to an air pollutant must also be consistently associated with an adverse effect under different studies using diverse methods of study of assorted populations under varying circumstances by different investigators. Such consistency strengthens the link between exposure to an air pollutant and an adverse effect, e.g. lung cancer.

Consider an air pollutant that is positive for mutagenicity, is linked to cancer in mouse and Rhesus monkey experiments, and for which human epidemiological studies show increased cancer incidence. This is an example of consistency across study types. If another pollutant shows cancer only in animal studies, with just a few human studies that are inconclusive, the lack of consistency detracts from even strong associations between exposures and cancer in the animals.

#### **4.2.3.3 Specificity**

The specificity criterion holds that the cause should lead to only one disease and that the disease should result from only this single cause. This criterion is akin to the germ theory of microbiology, where a specific strain of bacteria and viruses elicits a specific disease. This is rarely the case in studying most chronic diseases, since a chemical can be associated with cancers in numerous organs, and the same chemical may elicit cancer, hormonal, immunological, and neural dysfunctions.

In addition, non-chemical stressors may elicit the same chronic effects as chemicals, such as psychological stress and genetic disorders. Thus, for air pollution studies, specificity is not to be expected for many diseases.

#### **4.2.3.4 Temporality**

Timing of exposure is critical to causality. This criterion requires that exposure to the chemical must precede the effect. For example, in a retrospective study, the researcher must be certain that the manifestation of a disease was not already present before the exposure to the chemical. If the disease were present prior to the exposure, it does not necessarily mean that the chemical in question is not a cause, but it does mean that it is not the sole cause of the disease (see "Specificity" above). For example, lung damage may have already begun due to exposure to tobacco smoke, but accelerates with the additional exposure to asbestos fibers.

For air pollutants, the exposure begins the disease progression process (Figure 4.6). If the disease occurs before the exposure, the pollutant cannot be considered a cause of the disease.

Whether the disease actually occurs and the severity of effects depend on other factors, as well, such as genetic predisposition. Although the temporality is required for causality, it does not assure causality. That is, if the exposure to the air pollutant occurred after the onset of the disease, that study cannot be used as evidence linking the air pollutant to the disease. However, if the exposure occurred prior to the disease, the study may be used, but only if other criteria support the causal link, since another agent or risk factor may be the actual cause of the disease (see the earlier discussion of confounders).

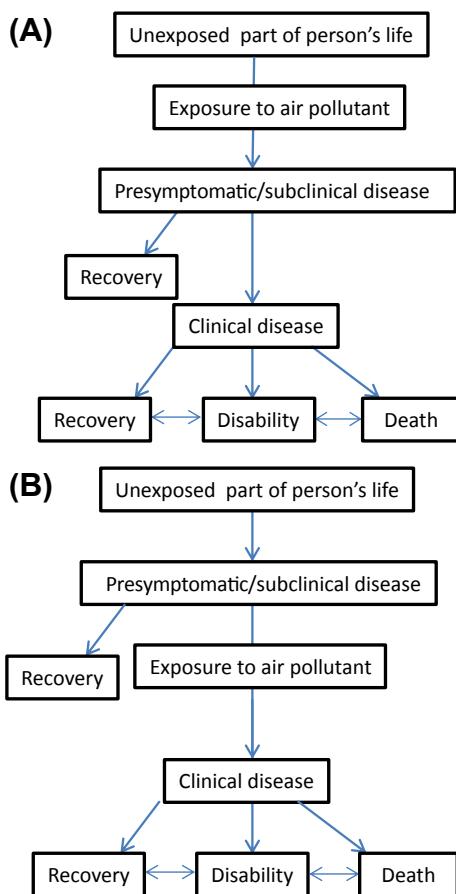


FIGURE 4.6 Air pollution exposure leading to the natural history of a disease (A) *versus* a disease that is caused by a factor other than exposure to the air pollutant (B). (For color version of this figure, the reader is referred to the online version of this book.)

#### 4.2.3.5 Biologic Gradient

Chemical hazard is usually determined from bioassays, animal studies, epidemiology, and models that generate a biological gradient, i.e. the higher the dose the greater the effect. In fact, this is known as the “dose–response” step in risk assessment. Dose–response is an essential part of an air pollutant’s inherent hazard. The comparison of the dose of an air pollutant to a biological response in humans, in other organisms, or in ecosystems is an important aspect of hazard. Dose–response curves point to thresholds above which air pollutant exposures are expected to elicit effects (e.g. above a “no observable adverse effect level”). Since it is a key component in chemical hazard assessment, dose–response is discussed in detail in Chapter 7.

Air pollution is hazardous to both human health and ecosystems, so the biological response may manifest

itself as diseases and death in human populations and as damage to habitats and organisms living in ecosystems. If the concentration, intensity, duration, or total level of chemical exposure is increased, then a concomitant, progressive increase should occur in the toxic effect.

#### 4.2.3.6 Plausibility

Generally, an association needs to follow a well-defined explanation based on known biological systems. The association must be consistent with physical, chemical, and biological principles. This is not to say that the principles cannot be reordered to explain an observation, since the “paradigm shifts” in the understanding of key scientific concepts do change. A noteworthy example is the change in the latter part of the twentieth century of the understanding of the functioning of and interrelationships among the endocrine, immune, and neural systems, from the view that these are exclusive systems to today’s perspective that in many ways they constitute an integrated chemical and electrical set of signals in an organism.<sup>13</sup>

#### 4.2.3.7 Coherence

The criterion of coherence suggests that all available evidence concerning the natural history and biology of the disease should “stick together” (cohere) to form a cohesive whole. By this logic, the proposed causal relationship should not conflict or contradict information from experimental, laboratory, epidemiologic, theoretical, or other knowledge sources.

For air pollution, temporal patterns of exposure and adverse effects must adhere to what is known about the associated biological effects. For example, animal data and human data (i.e. epidemiology) should support characterizations of an air pollutant. If animal data suggest that inhaling a substance leads to a respiratory effect, but human data do not, this is an example of lack of coherence. It should be noted that lack of coherence may be the result of paucity of human data<sup>c</sup>. Lack of coherence may also result from intraspecies differences for which human studies have not yet been properly designed. Lack of coherence, then, does not in itself eliminate a causal link. Conversely, if all studies are coherent, it very strongly suggests a causal link.

#### 4.2.3.8 Experimentation

Experimental evidence in support of a causal hypothesis may come in the form of community and

<sup>c</sup>Usually, animal data are the first to suggest the link between exposure to a pollutant and a chronic disease, which later is or is not supported by human data. However, a prominent example of human data showing a link in the absence of animal data was arsenic (As). Occupational and other epidemiology showed a link many years before human As data supported these findings in the 20th century.

clinical trials, *in vitro* and *in vivo* laboratory experiments, animal models, and natural experiments. Several major problems arise for air pollution experiments. First, the relationship between an air pollutant and an adverse outcome is usually multifaceted. For example, slight differences in chemistry, physical form, and biological makeup of the receptor organism cannot usually be duplicated with well-controlled experiments. Thus, the results are usually very specific to the independent and dependent variables in study and not easily extrapolated to actual, real-world situations.

Second, the strongest and most reliable data about human health is derived from human populations. However, large chamber studies are very expensive and burdensome to subjects. In addition, chamber studies must treat human subjects ethically, meaning that exposures to air pollutants must be at relatively low doses.

Third, the association between chronic diseases and low-concentration exposures to air pollutants might be missed. Latency periods for cancer, for example, can be decades. Animal experiments usually trade dose for time, e.g. a 3-month study with sufficiently high doses of a pollutant to elicit an effect. Acute effects could mask chronic effects. For example, if a substance is given at a dose that kills or causes an acute effect in an animal, the animal will not likely have sufficient time to exhibit chronic effects (e.g. tumors).

#### 4.2.3.9 Analogy

The term analogy implies a similarity in some respects among things that are otherwise different. It is thus considered one of the weaker forms of evidence. In a sense, the structural activity relationship (SAR) is an example of an analogy in the physical sciences. The SAR is a system that uses molecular structure of a known chemical to estimate how a similar chemical might behave in the environment or in an organism. For example, benzene, toluene, and phenol each have a single benzene ring, with toluene having one substituted methyl group and phenol having one substituted hydroxyl group. An SAR may suggest that these three compounds will have similar affinities for air, water, and soil. A more uncertain analogy is that the endogenous processes, e.g. metabolism, of the three compounds would be similar. Problems arise as a result of small differences, e.g. phenol's hydroxyl group makes it more polar and thus more likely to be removed in the first phases of metabolism compared to benzene. This does not mean that the SAR is not useful, only that caution is needed to avoid over-extrapolating absorption, distribution, metabolism, elimination, and other biological processes from similarities in molecular structure.

Another example of analogy is the highly exposed population. If a phenomenon is observed in coal miners over time, how might this phenomenon appear in the

general population? For example, miners in Eastern Europe who were exposed to radon ( $Rn$ ) had a much higher incidence of lung cancer compared to the general public. By analogy, if the miners have higher cancer rates because of  $Rn$ , others exposed to  $Rn$  in other scenarios may also have a similar lung cancer risk, albeit smaller (see "Biological Gradient" above).

An analogy's disadvantage is that there is no standard available for objectively evaluating the analogy's usefulness. For example, an imaginative scientist may posit an analogy that since small children are messier than adults, messiness may explain why children are more susceptible to indoor air pollution, especially allergens. Both statements are likely true, but the analogy may not hold since a third variable (physiology) may better explain this. However, such an analogy may be useful, even if wrong for a given scenario. In this case, the "hygiene hypothesis" is an analogy that goes back to the concept of hormesis, i.e. exposures to small, incremental amounts of bacteria helps prevent future diseases. The hypothesis is an analogy of gradual adaptation (e.g. muscle growth, learning, etc.). It is best explained as immune response, i.e. the immune system increases cells to combat foreign substances (bacteria). The analogy from other gradual adaptations may well have generated this thinking in medicine by Pasteur, Paracelsus, and others. However, the homesis analogy does not usually, if ever, hold for chemical agents. Being exposed to vinyl chloride, lead, or mercury does not make one immune. To the contrary, the chronic exposure lead to health effects, including weakening immune and neural systems (actually an "anti-homesis" argument).

## 4.3 RARE EVENTS: PERFECT STORMS AND BLACK SWANS

Two metaphors come to mind when discussing low-probability, high-impact outcomes, i.e. the black swan and the perfect storm. A "black swan" event is one in which the outcome would not have been predicted from past evidence due to the low probability of a possible confluence of events, but the event indeed occurred.

A "perfect storm" of a confluence of unlikely events is something that air pollution scientists and engineers must always consider, such as the combination of factors that led to the disaster from the toxic plume over Bhopal, India (see Discussion Box: The Bhopal and Lac-Mégantic Events).

Black swan events have occurred, but had not been known to occur before, nor had there been evidence that they could occur. It is an extremely low-probability event that did indeed occur. It can be argued at least in the abstract that air pollution disasters are not actually black swan events, since scientists understood

## THE BHOPAL AND LAC-MÉGANTIC EVENTS

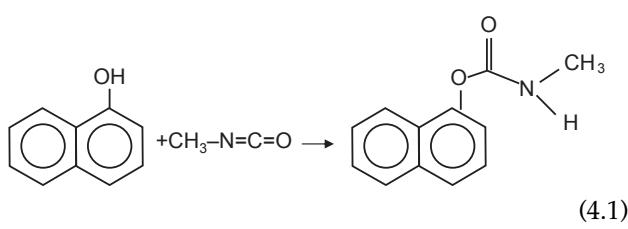
Although the toxic plume in Bhopal, India, and the Lac-Mégantic derailment have very different origins, they are dramatic examples of low-probability, high-impact events.

A newspaper account of the Bhopal incident, one of the worst air pollution tragedies in history, was as follows:

In the middle of the night of December 2-3, 1984, residents living near the Union Carbide pesticide plant in Bhopal, India awoke coughing, choking, gasping, and in the case of thousands, slowly dying. Half a day later, half a world away, company executives sleeping soundly near the Danbury, CT headquarters of Union Carbide Corporation awoke in the middle of the night yawning and grumbling at the sound of telephones ringing... shortcuts taken in the name of profit — authorized by the highest executives within the company — had just killed thousands of innocent citizens. It was the worst industrial disaster of the 20th century, forever changing the public's trust of the chemical industry. Union Carbide claimed it was sabotage by a disgruntled employee that led to the disaster, but how much did the company already know about the dangerous conditions its shortcuts and bottom-line focus had created?<sup>14</sup>

The toxic cloud that drifted over the city from the Union Carbide pesticide plant gas leak led to the death of 20,000 people and permanently injured 120,000. The event resulted from at least two types of engineering failures: (1) misapplication of science (e.g. a mathematical error and an incorrect extrapolation of a physical principle) and (2) human factors (e.g. misbehaviors, misdeeds, and mistakes).

Although the Union Carbide Company was headquartered in the United States, as of 1984, it operated in 38 different countries.<sup>15a,15b</sup> It was quite large (35th largest US company), and was involved in numerous types of manufacturing, most of which involved proprietary chemical processes. The pesticide manufacturing plant in Bhopal, India, had produced the insecticides Sevin and carbaryl since 1969, using the intermediate product, methyl isocyanate (MIC) in its gas phase. The MIC was produced by the following reaction:



This process was highly cost-effective, involving only a single reaction step. The schematic of the MIC process is shown in [Figure 4.7](#). MIC is highly water reactive (see [Table 4.5](#)); i.e. its reaction with water generating a very strong exothermic reaction that produces carbon dioxide. When MIC vaporizes it becomes a highly toxic gas that, when concentrated, is highly caustic and burns biological tissues. This can lead to scalding nasal and throat passages, blinding, and loss of limbs, as well as death. The acute and chronic health information is provided in [Figure 4.8](#).

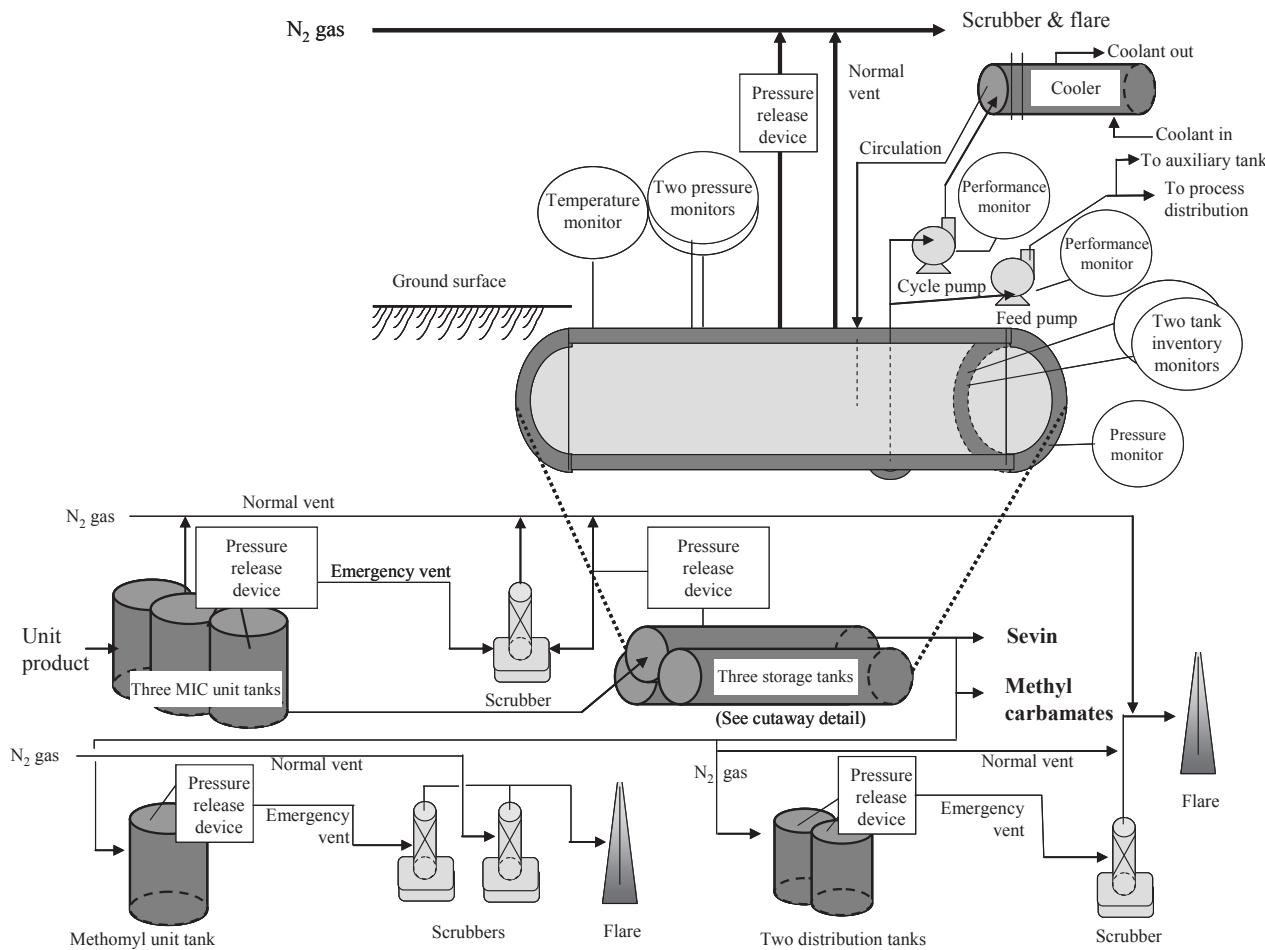
On December 3, 1984, the Bhopal plant operators became concerned that a storage tank containing MIC was showing signs of overheating and began to leak. The leak rapidly increased in size, and within 1 h of the first leakage, the tank exploded and released approximately 80,000 lbs ( $4 \times 10^4$  kg) of MIC into the atmosphere. The human exposure to MIC was widespread, with a half million people exposed. Nearly 3000 people died within the first few days after the exposure, 10,000 were permanently disabled. Ten years after the incident, 12,000 death claims had been filed, along with 870,000 personal injury claims. However, only \$90 million of the Union Carbide settlement agreement had been paid. As of 2001, many victims did receive compensation, averaging about \$600 each, although claims were still outstanding.

The CO<sub>2</sub> generated by the exothermic reaction likely led to the rapid increase in pressure, which caused the release of the MIC into the atmosphere.

Several human factors increased the likelihood of a disaster. The Indian government required that the plant be operated exclusively by Indian workers, so Union Carbide agreed to train them on-site at a sister plant in West Virginia. In addition, the company required that US engineering teams make periodic on-site inspections for safety and quality control, but these ended in 1982, when the plant decided that these costs were too high. So, instead, the US contingency was only responsible for budgetary and technical controls, but not safety. The last US inspection in 1982 warned of many hazards, including a number that have since been implicated as contributing to the leak and release.

From 1982 to 1984, safety measures declined, attributed to high employee turnover, improper and inadequate training of new employees, and low technical savvy in the local workforce. On-the-job experiences were often substituted for reading and understanding safety

### THE BHOPAL AND LAC-MÉGANTIC EVENTS (cont'd)



**FIGURE 4.7 Schematic of methyl isocyanate processes at the Bhopal, India, plant (c. 1984).** Adapted from: Worthy W. *Methyl isocyanate: the chemistry of a hazard*. *Chem Eng News* 1985;63(66):29.

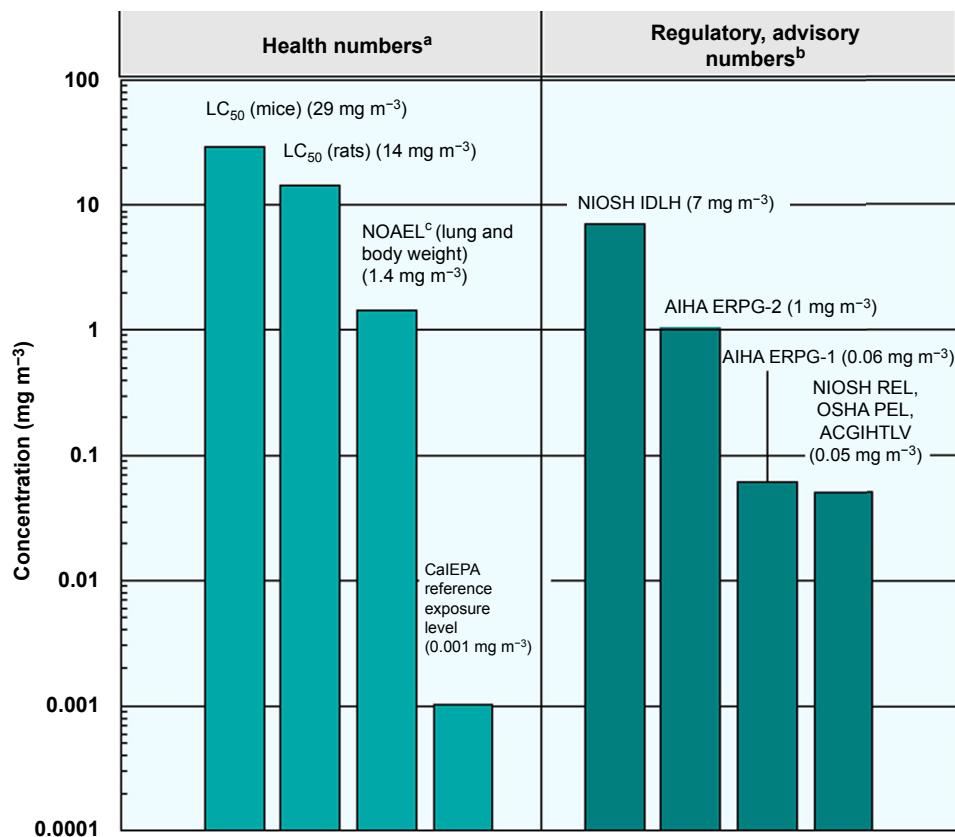
**TABLE 4.5 Properties of Methyl Isocyanate**

Common name	Isocyanic acid, methyl ester, and methyl carbylamine
Molecular mass	57.1
Properties	<ul style="list-style-type: none"> <li>Melting point: <math>-45^{\circ}\text{C}</math>; boiling point: <math>43\text{--}45^{\circ}\text{C}</math></li> <li>Volatile liquid</li> <li>Pungent odor</li> <li>Reacts violently with water and is highly flammable</li> <li>MIC vapor is denser than air and will collect and remain at low areas. The vapor mixes readily with air and explosive mixtures are formed</li> <li>May polymerize due to heating or under the influence of water and catalysts</li> <li>Decomposes on heating and produces toxic gases like hydrogen cyanide, nitrogen oxides, and carbon monoxide</li> </ul>
Uses	Used in the production of synthetic rubber, adhesives, pesticides, and herbicide intermediates. It is also used for the conversion of aldoximes to nitriles

Sources: U.S. Chemical Safety and Hazards Board, <http://www.chemsafety.gov/lib/bhopal.0.1.htm>; Chapman and Hall, *Dictionary of Organic Chemistry*, vol. 4, 5th ed. United States of America: Mack Printing Company; 1982; and Graham TW, *Organic Chemistry*, 6th ed. Canada: John Wiley and Sons, Inc.; 1996.

(Continued)

## THE BHOPAL AND LAC-MÉGANTIC EVENTS (cont'd)



**FIGURE 4.8** Health data, with regulatory and advisory limits for methyl isocyanate. Note: AIHA ERPG: American Industrial Hygiene Association's emergency response planning guidelines. ERPG 1 is the maximum airborne concentration below which it is believed nearly all individuals could be exposed up to 1 h without experiencing other than mild transient adverse health effects or perceiving a clearly defined objectionable odor; ERPG 2 is the maximum airborne concentration below which it is believed nearly all individuals could be exposed up to 1 h without experiencing or developing irreversible or other serious health effects that could impair their abilities to take protective action. ACGIH STEL: American Conference of Governmental and Industrial Hygienists' short-term exposure limit expressed as a time-weighted average exposure; the concentration of a substance that should not be exceeded at any time during a workday; LC<sub>50</sub> (lethal concentration-50): A calculated concentration of a chemical in air to which exposure for a specific length of time is expected to cause death in 50% of a defined experimental animal population—this is a common expression of acute hazard; NIOSH IDLH: National Institute of Occupational Safety and Health's immediately dangerous to life or health limit; NIOSH recommended exposure limit to ensure that a worker can escape from an exposure condition that is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from the environment; NIOSH REL: NIOSH's recommended exposure limit; NIOSH recommended exposure limit for an 8 or 10 h time-weighted average exposure and/or ceiling; OSHA PEL: Occupational Safety and Health Administration's permissible exposure limit expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effect averaged over a normal 8 h workday or a 40 h workweek.<sup>16–21</sup> (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Methyl isocyanate. <http://www.epa.gov/ttnatw01/hlthef/methylis.html>; 2013 [accessed 01.04.14]. To convert concentrations in air (at 25 °C) from parts per million to milligrams per cubic meter: mg m<sup>-3</sup> =  $\frac{(ppm) \times (\text{molecular weight of the compound})}{24.45}$ . For methyl isocyanate: 1 ppm = 2.34 mg m<sup>-3</sup>. <sup>ab</sup>

manuals<sup>c</sup>. In fact workers would complain of acute symptoms that commonly indicate of pesticide exposure, such as shortness of breath, chest pains, headaches, and vomiting, yet they would typically refuse to wear protective clothing and equipment. The refusal in part stemmed from the lack of air conditioning in this subtropical climate, where masks and gloves can be uncomfortable.

Indian, rather than the more stringent US, safety standards were generally applied at the plant after 1982. This likely contributed to overloaded MIC storage tanks (company manuals cite a maximum of 60% fill).

The release lasted about 2 h, after which the entire quantity of MIC was released. The highly reactive MIC arguably could have caused much less problems if it degraded and mixed before reaching human populations.

## THE BHOPAL AND LAC-MÉGANTIC EVENTS (*cont'd*)

However, over the years, tens of thousands of squatters had taken up residence just outside of the plant property, hoping to find work or at least take advantage of the plant's water and electricity. The squatters were not notified of hazards and risks associated with the pesticide manufacturing operations, with the exception of signs posted by a local journalist stating: "Poison Gas. Thousands of Workers and Millions of Citizens are in Danger". A "confluence of events" indeed led to this disaster.

- The tank that initiated the disaster was 75% full of MIC at the outset.
- A standby overflow tank for the storage tank contained a large amount of MIC at the time of the incident.
- A required refrigeration unit for the tank was shut down five months prior to the incident, leading to a three- to fourfold increase in tank temperatures over expected temperatures.
- One report stated that a disgruntled employee unscrewed a pressure gauge and inserted a hose into the opening.
- A new employee was told by a supervisor to clean out connectors to the storage tanks, so the worker closed the valves properly, but did not insert safety discs to prevent the valves from leaking. In fact, the worker knew the valves were leaking, but they were the responsibility of the maintenance staff. Also, the second-shift supervisor position had been eliminated.
- When the gauges started to show unsafe pressures, and even when the leaking gases started to sting mucous membranes of the workers, they found that evacuation exits were not available. There had been no emergency drills or evacuation plans.
- The primary fail-safe mechanism against leaks was a vent-gas scrubber, i.e. normally this release of MIC would have been sorbed and neutralized by sodium hydroxide (NaOH) in the exhaust lines, but on the day of the disaster, the scrubbers were not working. (The scrubbers were deemed unnecessary, since they had never been needed before).
- A flare tower to burn off any escaping gas that would bypass the scrubber was not operating because a section of conduit connecting the tower to the MIC storage tank was under repair.
- Workers attempted to mediate the release by spraying water 100 ft high, but the release occurred at 120 ft.

Thus, according to an audit, many checks and balances were in place, but the cultural considerations and human factors were ignored or given low priority such as, when the plant was sited, the need to recognize the differences

in land use planning and buffer zones in India compared to Western nations or the difference in training and oversight of personnel in safety programs. Every engineer and environmental professional needs to recognize that their work is affected by geopolitical realities and a global economy. This means that we must understand how cultures differ in their expectations of environmental quality. One cannot assume that a model that works in one setting will necessarily work in another without adjusting for differing expectations. Bhopal demonstrated the consequences of ignoring these realities.

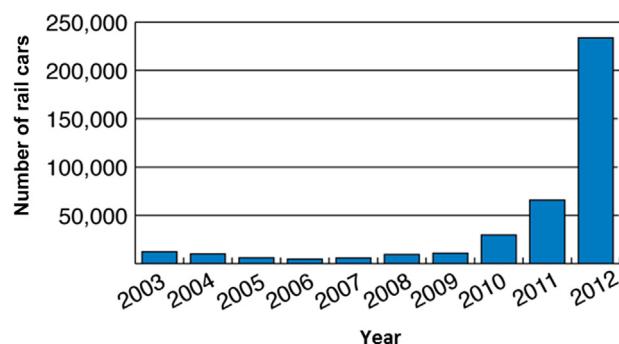
In Lac-Mégantic, a town in eastern Quebec, Canada, at approximately 01:15 a.m. Eastern Daylight Time on July 6, 2013, a 73-car freight train carrying crude oil broke away, derailed, and the crude oil it was carrying became inflamed and exploded. Forty-two people were confirmed dead with 5 more missing and presumed dead. More than 30 buildings, half of the downtown area, were destroyed.<sup>22</sup> The disaster site contains high concentrations of benzene and other hydrocarbons, so that soil and water will have to be decontaminated over a period of several years. Although this may not appear to be a threat to air quality, one of the major concerns in cleanups is that contaminants may move from one environmental compartment to another. Given the relatively high vapor pressures of many hydrocarbons, they have likely been emitted to the atmosphere since the disaster began.

The fact that the cars were carrying crude oil complicates the ongoing debates about fossil fuels and their transport. There are risk trade-offs among pipelines, ships, trucks, and rail. An estimated 140,000 carloads of crude oil were shipped in Canada by rail in 2013, whereas only 500 carloads were shipped by rail in 2009. In the first quarter of 2013, the United States shipped 97,000 carloads of crude oil by rail, an increase of 166% from the first quarter of 2012. The increase in rail shipping of crude oil has been dramatic (Figure 4.9). The risk trade-off question is whether pipelines are safer and more environmentally acceptable than rails for the movement of such large volumes of hazardous substances. From a life cycle perspective, the question is how to reduce society's overall reliance on fossil fuels for major economic sectors, including transportation, industry, and heating. In the meantime, however, transport of fossil fuels must be sufficiently safe and reliable.

Smaller versions of these types of incidents are more likely to occur. For example, two freight trains collided in Graniteville, South Carolina, just before 3:00 a.m. on January 6, 2005, resulting in the derailment of three tanker cars carrying chlorine (Cl<sub>2</sub>) gas and one tanker car carrying sodium hydroxide (NaOH) liquids. The highly toxic Cl<sub>2</sub>

*(Continued)*

## THE BHOPAL AND LAC-MÉGANTIC EVENTS (cont'd)



**FIGURE 4.9 Rail carloads carrying crude oil in the United States.** (For color version of this figure, the reader is referred to the online version of this book.) Institute for Energy Research. <http://www.instituteforenergyresearch.org/2013/07/24/rail-tragedy-in-quebec-highlights-need-for-keystone-xl/>; 2013 [accessed 10.08.13]. Data from AAR Quarterly Commodity Statistics Database.

gas was released into the atmosphere. The wreck and gas release resulted in hundreds of injuries and eight deaths.

In February of 2005, the District of Columbia City Council banned large rail shipments of hazardous chemicals through the US Capital, making it the first large metropolitan area in the United States to attempt to reroute trains carrying potentially dangerous materials. The railroad company has opposed the restrictions, arguing that they violate Constitutional protections and interstate commerce legislation and rules. Roadways and rails are in very close contact to where people live. The intersection of hazardous materials and human population has led to incidents that are not really all that rare. Seven months before the Graniteville incident, three people died after exposure to chlorine as a result of derailment in San Antonio, Texas. Fifty more people were hospitalized. One of the concerns is occupational safety, but another is community exposures.

Many metropolitan areas also have areas where rail, trucks, and automobiles meet, so there is an increased risk of accidents. Most industrialized urban areas have

the problematic mix of high-density population centers, multiple modes of transport, dense rail and road networks, and rail-to-rail and rail-to-truck exchange centers. Most cities are especially vulnerable if an accident were to involve hazardous chemicals, since they are major crossroads of various forms of transport near large numbers of people. And, rerouting trains is not feasible in many regions because transcontinental lines here run through most urban areas. So, other steps can be taken to reduce shipment risks from hazardous substances like chlorine and improvements in manifest reports are immediately available to first responders. At present, such information is not generally available. Following the September 11, 2001, attacks, rail companies have been reticent to disclose what is being shipped. One local fire department spokesman has stated that one "could almost assume there are several cars of hazardous materials every time we see a train".<sup>23</sup>

The lessons from Bhopal, Lac-Mégantic, and other low-probability, high-impact incidents are many. However, a major one is to be mindful that artifacts will occur. A number of these cannot be fully appreciated prospectively, so factors of safety must be built into the design. And, human factors must always be seen as design constraints. The plan is only as good as the way it is implemented. If this is sloppy, failure and, tragically, disaster can be the result.

<sup>a</sup> Health numbers are toxicological numbers from animal testing or risk assessment values developed by EPA.

<sup>b</sup> Regulatory numbers are values that have been incorporated in U.S. government regulations, while advisory numbers are non-regulatory values provided by the government or other groups as advice. OSHA numbers are regulatory, whereas NIOSH, ACGIH, and AIHA numbers are advisory. The NOAEL is from the critical study used as the basis for the CalEPA chronic inhalation reference exposure level.

<sup>c</sup> This is an important reminder for plant and human resource managers that there is often a sharp decline in safety vigilance after training. Thus, health and safety training must be updated regularly and safety drills be conducted according to the hazards at a specific facility.

most of the elements and contributing causes before the actual events, e.g. atmospheric inversions, chemical reactions, and some cause-and-effect relationships between pollutants and diseases. The extent and severity may not have been expected, especially in light of the many variables involved in the event. Thus, engineers and scientists must insert factors of safety to address such uncertainties for any adverse outcome, but especially for those that can lead to unacceptable harm.

Safety is a fundamental facet of all engineering codes of practice and ethics. As such, engineers rely on criteria that inform them when designs and projects are sufficiently safe. Four safety criteria are applied to test engineering safety:<sup>24</sup>

1. The design must comply with applicable laws.
2. The design must adhere to "acceptable engineering practice".

3. Alternative designs must be sought to see if there are safer practices.
4. Possible misuse of the product or process must be foreseen.

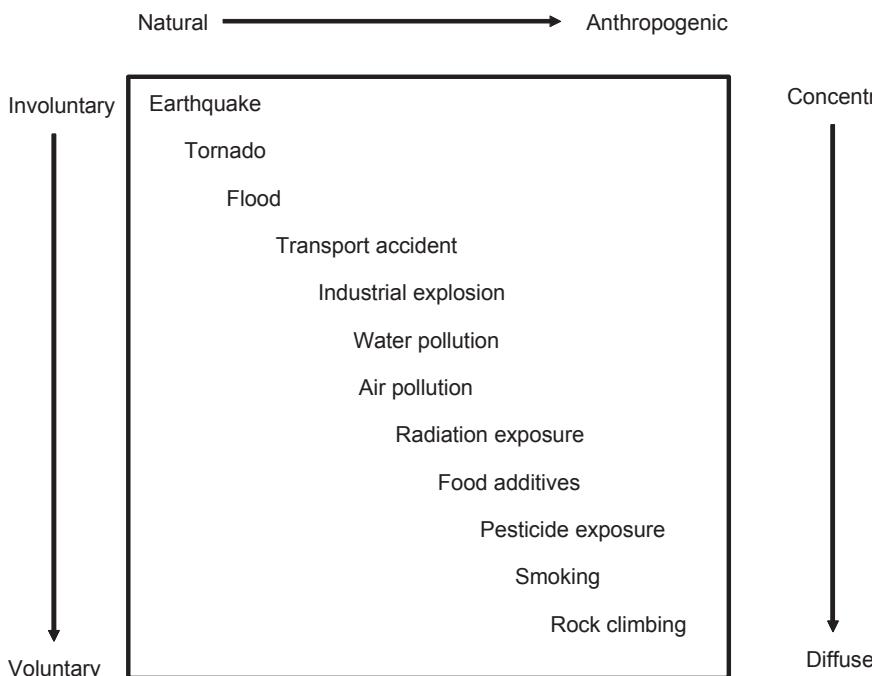
The first two criteria are usually more manageable than the latter two. The engineer can refer to handbooks and manuals for the physical, chemical, and biological factors to calculate tolerances and factors of safety for specific designs. Laws and regulations are promulgated to protect the public. Crossing these legal thresholds indicates the point at which the engineer has failed to provide adequate protection. Engineering practice standards go a step further. Much of the public and its lawyers would not be able to recognize this type of failure unless other engineers help to judge whether an ample margin of safety has been met. The margin is dictated by sound engineering principles and practice. Often, however, looking up answers is only the beginning. Solutions to air pollution problems also often need creativity and imagination. Like most decisions, air pollution risk management decisions consist of five components:

1. an inventory of relevant choices;
2. an identification of potential consequences of each choice;
3. an assessment of the likelihood of each consequence actually occurring;
4. a determination of the importance of these consequences; and
5. a synthesis of this information to decide which choice is the best.<sup>25</sup>

Risk management must also address risk perceptions, which vary according to psychological, social, and environmental factors. In addition, the specific air pollutants being addressed influence risk perception. For example, whether the hazard is intense or diffuse, or whether it is natural or human induced (see Figure 4.10) can greatly influence public acceptance of even the most scientifically sound air pollution action. In general, most people are more willing to accept of hazards that are natural in origin, voluntary, and concentrated in time and space.<sup>26</sup>

Note that air pollution is in the middle of the spectrum. It is more voluntary than most accidents, e.g. one can choose not to go into a smoke-filled room, but less voluntary than smoking, i.e. a person may chose to smoke or not to smoke. The damage from air pollution is more diffuse than rock climbing (the potential harm is very concentrated, i.e. the potential fall is part of the experience), and less concentrated than a tornado (a specific neighborhood in its path). And, air pollution includes both natural and human-induced pollutants. Interestingly, many of the hazards listed in the figure are directly or indirectly related to air pollution (e.g. ruptured tanks after earthquakes and tornados release air pollutants, and industrial explosions and transport accidents cause air pollutants to be emitted).

Pesticide exposure is often via inhalation. Choosing not to smoke may not protect one from tobacco smoke, i.e. environmental tobacco smoke or side stream smoke is a major source of indoor pollution. Radiation exposure can come about by airborne isotopes. Industrial accidents have exposed thousands to air toxins (see Discussion Box: The Bhopal and Lac-Mégantic Events later in this chapter).



**FIGURE 4.10 Spectrum of hazards.**  
Adapted from Smith K. *Environmental hazards: assessing risk and reducing disaster*. London (UK): Routledge; 1992. Ref. 2.

What people perceive as risks and how they prioritize those risks are only partly driven by science-based, objective assessment of risk, i.e. the severity of the hazard from an air pollutant must be combined with the magnitude, duration, and frequency of the exposure to the hazard. For example, a person may be generally aware that cigarette smoke contains carcinogens and other substances that cause heart disease, but is not directly aware of what these are (e.g. polycyclic aromatic hydrocarbons and carcinogenic metal compounds). Even after reading the conspicuous warning labels on the pack, the connection between the hazard and the self-imposed exposure may not have “rung true”. The person may have not met anyone with emphysema or lung cancer, or may not be concerned (yet) with the effects on the unborn (i.e. *in utero* exposure).

Psychologists have found this to be particularly problematic for adolescents contemplating high-risk activities, such as smoking, i.e. an unrealistic sense of invincibility. This is even more problematic in that the cause and effect can be separated by decades, i.e. the latency period between exposure and symptoms of cancer and other chronic diseases. Human beings can be conditioned by positive stimuli (e.g. nicotine euphoria and perception of being an adult) without immediate mental links to any negative consequences, since they are often far in the future.

Another interesting aspect of risk perception is how it varies in scale and scope. The author recalls sitting in a meeting in the late 1970s among a group of highly trained engineers and scientists from the US Environmental Protection Agency (EPA) and the Kansas Department of Health and Environment. These are the two principal federal and state agencies, respectively, charged with protecting the environment. The meeting was to determine the appropriate ways to reduce the ambient concentrations of pollutants, especially PM and carbon monoxide (CO). The meeting was held in a small room and almost every person, except the author, was smoking. It was indeed a proverbial, “smoke-filled” room. Here was a technical discussion regarding the best approaches for decreasing ambient levels to the parts per million range (high by today’s standards, but at detection limits in the 1970s) in a room with PM and CO concentrations that could have been reported as a percent rather than ppm. (i.e.  $10^{-6}$  versus  $10^{-2}$ ). The irony was lost on the participants, probably for good reason. They were not making personal decisions, they were making policy decisions. This is akin to saying “Do as I say, not as I do”.

No matter how technically sound and convincing an air pollution action is to engineers and scientists, the decision may be misunderstood or even resented by those expected to benefit. Thus, every effort must be made to make the scientific rationale clear and understandable to the specific audience.

The converse is also true. The air pollution expert may be completely persuaded based upon data, facts, and models that something clearly does not cause significant harm, but those that the expert is trying to convince may disagree. They may believe the expert has a vested interest, or that they find the expert guilty by association with a group they do not trust, i.e. a “hired gun” working for those with interests other than those of the community. This lack of trust is exacerbated if experts use jargon and do not clearly communicate.

Managing air pollution risks consists of balancing among alternatives. Usually, an air pollution problem can be addressed in numerous ways that vary in feasibility, cost, and effectiveness. Acceptable risk flows from decisions that ameliorate the adverse outcomes and/or decrease the chance that negative consequences will occur.<sup>27</sup> Indeed, “acceptable risk is the risk associated with the best of the available alternatives, not with the best of the alternatives which we would hope to have available”.<sup>28</sup>

Since risk involves chance, risk calculations are inherently constrained by three conditions:

1. The actual values of all important variables cannot be known completely and, thus cannot be projected into the future with complete certainty.
2. The physical and biological sciences of the processes leading to the risk can never be fully understood, so the physical, chemical, and biological algorithms written into predictive models will propagate errors in the model.
3. Risk prediction using models depend on probabilistic and highly complex processes that make it infeasible to predict many outcomes.<sup>29</sup>

The decision to accept an air pollution action is usually based upon a “risk-reward” paradigm, and should be a balance between benefits and costs.<sup>30</sup> This creates the need to have costs and risks substantially outweighed by societal benefits. The term “substantially” is preferable to “significantly”. Significance has two problems: (1) the uncertainty resulting from the three constraints described above and (2) the margin between good and bad. Significance is the province of statistics, i.e. it tells us just how certain we are that the relationship between variables cannot be attributed to chance. But, when comparing benefits to costs, we are not all that sure that any value we calculate is accurate. For example, a benefit/cost ratio of 1.3 with confidence levels that give at a range between 1.1 and 1.5 is very different from a benefit/cost ratio of 1.3 with a confidence range between 0.9 and 1.7. The former does not include any values below 1, while the latter does (i.e. 0.9). This value means that even with all the uncertainties, our calculation shows that the project could be unacceptable. This situation is compounded by the

second problem of not knowing the proper margin of safety. That is, we do not know the overall factor of safety to ensure that the decision is prudent. Even a benefit/cost ratio that appears to be mathematically high, i.e. well above one, may not provide an ample margin of safety given the risks involved.

The likelihood of unacceptable consequences can result from exposure processes, from effects processes, or both processes acting together. So, four possible permutations can exist:

1. Probabilistic exposure with a subsequent probabilistic effect
2. Deterministic exposure with a subsequent probabilistic effect
3. Probabilistic exposure with a subsequent deterministic effect
4. Deterministic exposure with a subsequent deterministic effect<sup>31</sup>

A risk outcome is deterministic if the output is uniquely determined by the input. A risk outcome is probabilistic if it is generated by a statistical method, e.g. randomly. Thus, the accuracy of a deterministic model depends on choosing the correct conditions, i.e. those that will actually exist during a project's life and correctly applying the principles of physics, chemistry, and biology. The accuracy of the probabilistic model

depends on choosing the right statistical tools and correctly characterizing the outcomes in terms of how closely the subpopulation being studied (e.g. a community or an ecosystem) resembles those of the population (e.g. do they have the same factors or will there be sufficient confounders to make any statistical inference incorrect). A way of looking at the difference is that deterministic conditions depend on how well one understands the science underpinning the system, while probabilistic conditions depend on how well one understands the chance of various outcomes (see Table 4.6).

The deterministic exposure/deterministic effect scenario is not actually a risk scenario because there is no "chance" involved. It would be like calculating the risk of a 50 kg anvil hitting the earth's surface after releasing it without any other forces acting on the anvil besides gravity. The first principles of science assure us that this will happen. The risk only comes into play when we must determine external consequences of the anvil falling. For example, if an anvil is suspended at the height of 1 m by steel wire and used by workers to perform some task (i.e. a deterministic exposure), there is some probability that it may fall (e.g. if studies have shown that the wires fail to hold one in 10,000 events, then the failure probability of 0.0001), Thus, this scenario would be an example of a deterministic exposure followed by a probabilistic effect (wire failure), i.e. permutation number two. An air pollution example

TABLE 4.6 Exposure and Effect Process Risk Management

	Probabilistic Exposure	Deterministic Exposure
<b>Probabilistic Effect</b>	Contracting the West Nile Virus Although many people are bitten by mosquitoes, most mosquitoes do not carry the West Nile virus. There is a probability that a person will be bitten and another, much lower probability that the bite will transmit the virus. A third probability of this bitten group may be rather high that once bitten by the West Nile virus-bearing mosquito that the bite will lead to the actual disease. Another conditional probability exists that a person will die from the disease. So, death from a mosquito bite (probabilistic exposure) leads to a very unlikely death (probabilistic effect).	Occupational Exposure to Asbestos Exposure to asbestos from vermiculite workers is deterministic because the worker chooses to work at a plant that processes asbestos-containing substances. This is not the same as the person choosing to be exposed to asbestos, only that the exposure results from an identifiable activity. The potential health effects from the exposures are probabilistic, ranging from no effect to death from lung cancer and mesothelioma. These probabilistic effects increase with increased exposures, which can be characterized (e.g. number of years in certain jobs, availability of protective equipment, and amount of friable asbestos fibers in the air).
<b>Deterministic Effect</b>	Death from Methyl isocyanate exposure Exposure to a toxic cloud of high concentrations of the gas methyl isocyanate (MIC) is a probabilistic exposure, which is very low for most people. But, for people in the highest MIC concentration plume, such as those in the Bhopal, India, tragedy, death was 100% certain. Lower doses led to other effects, some acute (e.g. blindness) and others chronic (e.g. debilitation that led to death after months or years). The chronic deaths may well be characterized probabilistically, but the immediate poisonings were deterministic (i.e. they were completely predictable based on the physics, chemistry, and biology of MIC).	Generating carbon dioxide from combusting methane The laws of thermodynamics dictate that a decision to oxidize methane, e.g. escaping from a landfill where anaerobic digestion is taking place, will lead to the production of carbon dioxide and water (i.e. the final products of complete combustion). Therefore, the engineer should never be surprised when a deterministic exposure (heat source, methane, and oxygen) lead to a deterministic effect (carbon dioxide release to the atmosphere). In other words, the production of carbon dioxide is 100% predictable from the conditions. The debate on what happens after the carbon dioxide is released (e.g. global warming) is the province of probabilistic and deterministic models of these effects.

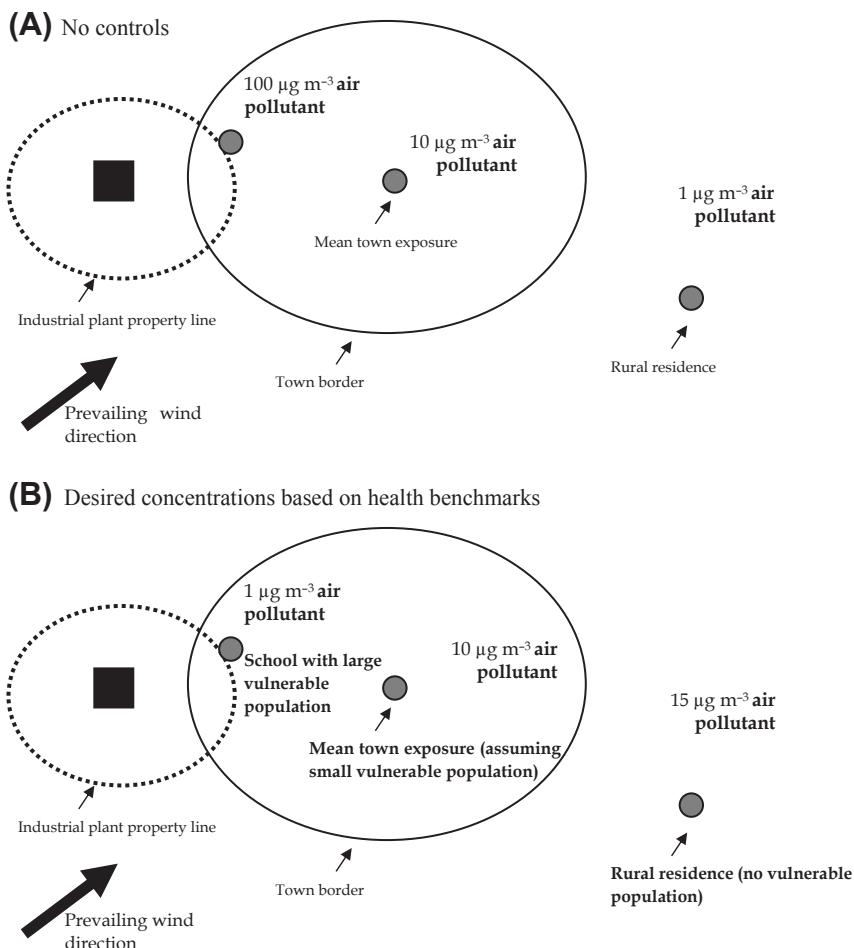
would be the potential release of a small amount of a very toxic air compound. If the toxic compound is included in a release from the facility's stack due to a chain of events that cause a release of the toxic compound in one of 10,000 events), then the failure probability is 0.0001 or  $10^{-4}$ , i.e. the deterministic exposure to the compound could then be calculated from the likelihood that populations would come into contact with them. Furthermore, if there is a 0.01 ( $10^{-2}$ ) likelihood of contact to this compound that is in dust suspended in air, which becomes re-entrained after settling that causes dermal contact, or exposure from food or drinking water, then the overall (contingent) exposure probability of this scenario is  $10^{-4} \times 10^{-2} = 10^{-6}$ . Note that this is not the risk, but the exposure. The risk is a function of the exposure and the hazard, e.g. the effect from receiving a dose of the air pollutant.

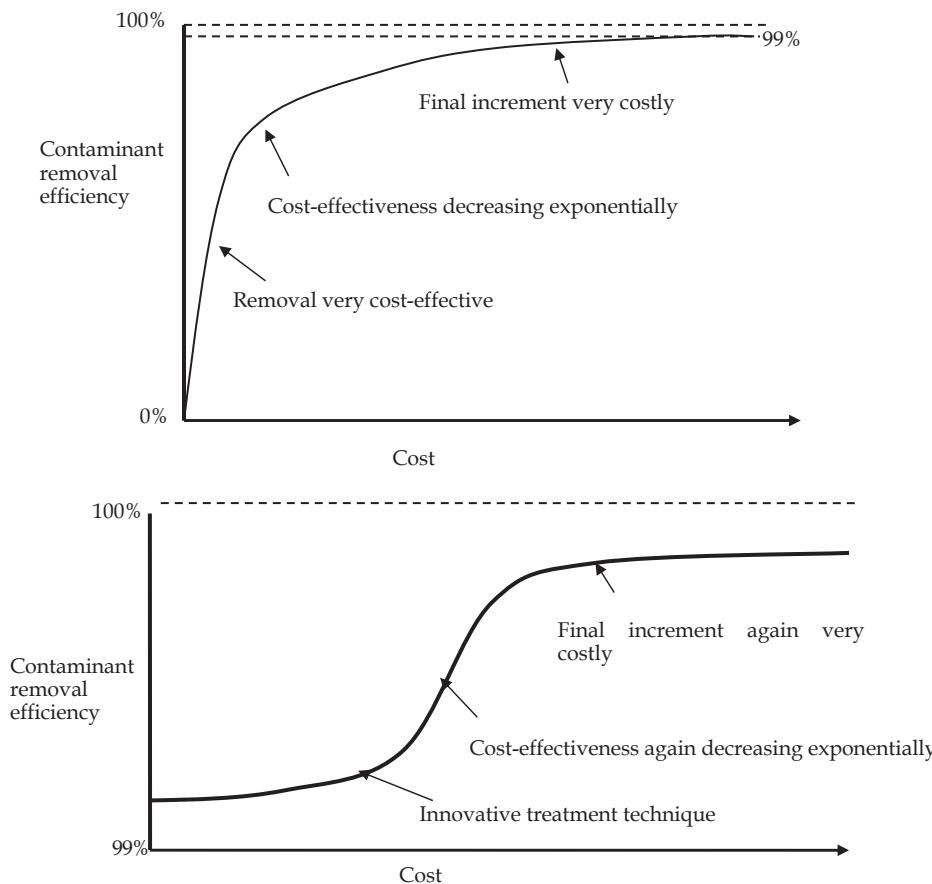
Estimating risk using a deterministic approach requires the application of various scenarios, e.g. a very likely scenario, an average scenario, or a worst case scenario. Very likely scenarios are valuable in some situations when the outcome is not life threatening or not one of severe effects, like cancer. The debate in the public

health arena is often between a mean or median (50th percentile) exposure and a worst case exposure (i.e. maximally exposed and highly sensitive individuals). The latter is more protective, but almost always more expensive and difficult to attain. For example, lowering the emissions of PM from a power plant stack to protect the mean population of the state from the effects of PM exposures is much easier to achieve than lowering the PM emissions to protect an asthmatic child, an immunocompromised person, or an elderly person living just outside of the power plant property line (see Figure 4.11).

In the hypothetical example depicted in Figure 4.11, the pollutant concentrations that would occur without controls (A) are the opposite of those needed to protect public health (e.g. a school near the industry boundary). The pollutant is diluted by dispersion, so that the concentrations fall dramatically with distance. Unfortunately, the most vulnerable population happens to attend the school near the industrial source. Indeed, the general population may not be adversely affected if the concentration of  $10 \mu\text{g m}^{-3}$  is actually the level below which no adverse effects are expected. However, this is a mean value, so there would be days when the  $10 \mu\text{g m}^{-3}$  level is

**FIGURE 4.11** (A) Concentrations of an air pollutant emitted from an industrial facility. (B) Hypothetical allowable amounts of an air pollutant based on benchmarks of health and welfare, e.g. the allowable concentrations are lower if the risks are based on a highly sensitive subpopulation (e.g. elderly, infants, and asthmatic). In this hypothetical example, the pollutant concentrations that would occur without controls (A) move in the opposite direction (lower with distance due to mixing) as those needed to protect public health (e.g. a school near the industry boundary).





**FIGURE 4.12** Prototypical contaminant removal cost-effectiveness curve. In the top diagram, during the first phase, a relatively large amount of a substance is removed at comparatively low costs, e.g. using gravity to collect coarse particulate matter (PM). Removal and control of the remaining portion of the substance (e.g. small fraction of ultrafine PM) increase in costs substantially. Costs increase with less benefit. The costs increase exponentially for each unit of substance removed, until the curve nearly reaches a steady state where the increment needed to reach complete removal is very costly. The top curve does not recognize innovations that, when implemented, as shown in the bottom diagram, can make a new curve that will again allow for a steep removal of the contaminant until its cost-effectiveness decreases. This concept is known to economists as the law of diminishing returns. Ref. 3.

exceeded. Also, the general population always includes vulnerable members, albeit in smaller numbers than the general population. The limits depend upon the effects elicited by the pollutant. For example, if the air pollutant is associated with cardiopulmonary effects in babies, an additional factor of safety may push the risk-based controls downward by an additional safety factor, e.g. from 10 to achieve  $0.1 \mu\text{g m}^{-3}$  to protect the maximally exposed, sensitive population.<sup>d</sup>

So, then, why not require zero risk from an air pollutant, or from any hazard for that matter? Selecting an allowable pollutant concentration is an exercise in optimization among variables and trade-offs among values. Of course, the most protective standards are best, but the feasibility of achieving them can be a challenge. The regulated standard can be very close to zero, especially if one assumes a worst case scenario for exposure and provides adequate or even more conservative factors of safety, for example, if the air pollutant causes

severe health effects even at very low exposures. Stated differently, putting controls and fail-safe measures in place to prevent an accidental release 99% of the time is much more feasible than the controls and fail-safe measures needed to prevent an accidental release 99.999% of the time (see Figure 4.12). Depending on the hazard, however, even the 99.999% may not meet engineering and risk standards. Some substances are so toxic, and some biological agents so poorly understood, that prevention of their releases may require numerous redundancies. The risk reduction measures are not only dependent on initial design, but also on retrofits, operation and maintenance, and decommissioning of air pollution control equipment (i.e. in life cycle terminology, “downstream” effects).

Actual or realistic values are input into the deterministic model. For example, estimating the risk of a tank explosion from one of several rail cars moving through and parked in a community would require a wide range

<sup>d</sup> This also demonstrates the importance of good planning. If the industry was there before the school, then this should have not been a factor in not locating the school nearby. Conversely, if the school was there first, it would have been poor planning and siting to allow the industrial plant so near.

of data about the number and size of cars, the flammability and vapor pressure of the contents, the ambient temperature, the vulnerability of the tank materials to rupture, the likelihood of derailment, and other physico-chemical, mechanical, and operational factors. In a semi-quantitative approach, these factors would be weighted and assigned numerical values, from which the risk of explosion is calculated. A probabilistic approach would require the identification of the initiating events and the plant operational conditions to be considered; analysis of the adverse outcome using statistical analysis tools, including event trees; application of fault trees for the systems analyzed using the event trees, collection of probabilistic data (e.g. probabilities of failure and the frequencies of initiating events based on past events and occurrences in similar domains); and the interpretation of results.

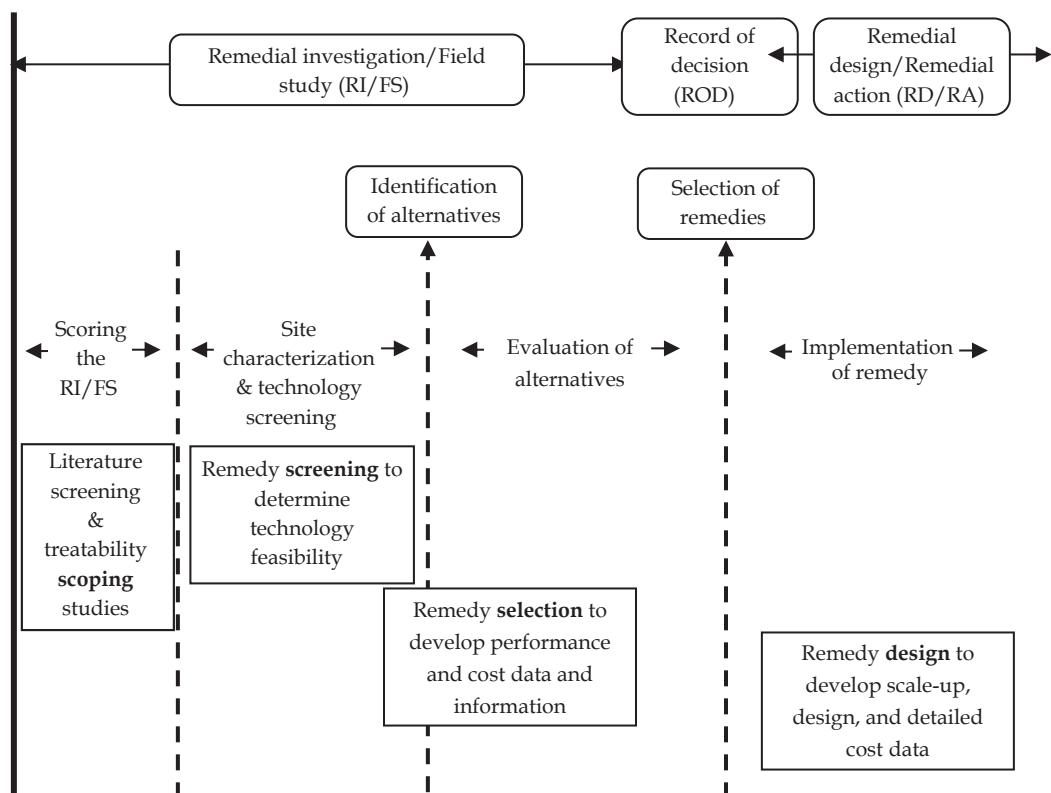
With regard to the precautionary approach to decisions, the no-action alternative is seldom completely innocuous. An action is warranted only if it is the optimal solution to the air pollution problem if it eliminates the pollution, but also avoids unwarranted financial costs, does not cause unnecessary disruption to normal activities, and is implemented in a manner that is socially acceptable to the community. This optimization is needed at all scales, from choosing one control

technology over another to decisions about national actions to address climate change (e.g. controls of greenhouse gas emission).

Due diligence must be applied to designs and plans for manufacturing processes that

1. limit, reduce, or prevent air pollution; to ways to reduce risks in operating systems,
2. assess sites and systems for possible human exposures to hazardous and toxic substances, and
3. evaluate and devise systems to reduce or eliminate these exposures.

Prevention is preferable, but an air pollution problem that already exists must be addressed to protect health, environment, and welfare. The environmental remedy process varies according to the particular environmental compartment of concern (i.e. air, water, or soil), the characteristics of contaminant of concern (e.g. toxicity, persistence in the environment, and likelihood to be accumulated in living tissues), and the specific legislation and regulations covering the project. However, it generally follows a sequence of preliminary studies, screening of possible remedies, selecting the optimal remedy from the reasonable options, and implementing the selected remedy (see [Figure 4.13](#)). The evaluation and selection of the best alternative is the stuff of risk management.



**FIGURE 4.13 Steps in cleaning up a contaminated site.** U.S. Environmental Protection Agency, 1992, *Guide for Conducting Treatability Studies under the Comprehensive Environmental Response, Compensation and Liability Act: Thermal Desorption*, EPA/540/R-92/074 B. The Comprehensive Environmental Response, Compensation and Liability Act is popularly known as "Superfund".

Sometimes organizational problems and demands put scientists and engineers in situations where the most scientifically sound and professional course of action is not supported by management. Working within an organization has a way of inculcating the “corporate culture” into professionals. The process is incremental and can “desensitize” employees to acts and policies that an outsider would readily see to be wrong. Much like the proverbial frog placed in water that gradually increases to the boiling pot, an environmental professional can work in gradual isolation, specialization, and compartmentalization that ultimately could lead to improper behavior, such as ignoring key warning signs that a decision to locate a facility in a certain area will have an unfair and disparate impact on neighborhoods, that health and safety are being compromised, and that political influence or the “bottom line” of profitability is disproportionately weighted in the recommendation.<sup>32</sup>

Another reason that optimization is difficult is that an engineer must deal with factors and information that may have not been adequately addressed during formal engineering training or even during career development. Although environmental and public health decisions must always give sufficient attention to the toxicity and exposure calculations, these quantitative results are tempered with feasibility considerations. Thus, engineering strengths lie to the far left and right of Figure 4.13, but the middle steps, i.e. feasibility and selecting the best alternative require information that is not “well behaved” in the minds of many engineers. For example, in 1980 the US Congress passed the Comprehensive Environmental Response, Compensation, and Liability Act, commonly referred to as Superfund.<sup>33</sup> The Superfund law authorizes the federal government to respond directly to releases or to the threat of releases of hazardous substances and enables the US EPA to take legal action to force parties responsible for causing the contamination to clean up those sites or to reimburse the Superfund for the costs of cleanup. If the responsible parties for site contamination cannot be found or are unwilling or unable to clean up a site, the EPA can use funds from the Superfund to clean up a site.

Air pollution decision making is “utilitarian”; that is, we are called upon “to produce the most good for the most people”.<sup>34a,34b</sup> In addition, all engineers are duty bound to codes of ethics, design criteria, regulations, and standards of practice. Engineers must, to the best of their abilities, consider all possible design outcomes, planned or otherwise. But this is not easy when the most appropriate “benchmarks” for success in air quality actions are moving targets. There is no consensus at the outset that even if the design is implemented to meet all specifications, the project could be

deemed a failure. For example, in environmental decisions regarding the level of cleanup of a hazardous waste can be based on the target health risk following cleanup. This remediation target cleanup has been based on what was called the “residential standard”. That is, immediately following the passage of key hazardous waste laws, regulators held the general view that a polluted site needed to be cleaned up to the point that no undue risk remained and the site could be returned to productive use, as if it had never been polluted. This closely follows the steps of hazard identification, dose-response relationships, exposure analysis, and effects assessment to characterize risks.<sup>35a,35b</sup>

In the United States, the cleanup of a hazardous waste begins with a feasibility study to address nine criteria that will determine the best approach for addressing the contamination, as well as the ultimate level of cleanup. They also directly apply to air pollution decisions:

1. Overall protection of human health and environment
2. Compliance with applicable or relevant and appropriate requirements
3. Long-term effectiveness and permanence
4. Reduction of toxicity, mobility, or volume through treatment
5. Short-term effectiveness
6. Ease of implementation
7. Cost
8. State acceptance
9. Community acceptance

The first and fourth criteria are clearly the product of a sound, quantitative risk assessment. The other criteria must also include semiquantitative and qualitative information. This illustrates the variety of data and information used in evaluating the environmental implications of air pollution.

With the large list of hazardous air pollutants and variety of sources, new and improved technologies must be developed to address them. When considering the potential impacts of any emerging technology, however, concerns about downstream impacts are crucial. Possible problems may not present themselves until sufficient time and space have been crossed. Products that contain dangerous materials like asbestos, lead, mercury, polybrominated compounds, and polychlorinated biphenyls were once considered acceptable and were even required by law or policy to protect the public safety and health, such as asbestos-containing and polybrominated materials to prevent fires, dichlorodiphenyltrichloroethane and other persistent pesticides to kill mosquitoes in an effort to prevent disease, and methyl *tert*-butyl ether as a fuel additive to prevent air pollution.

Also, as discussed in Chapter 5, downstream impacts may not involve the air pollutant of concern directly, but indirectly. The choice of end-of-life approaches can lead to the prevention or creation of an air toxin. The formation of dioxins, a highly toxic class of organic compounds, will differ according to the end-of-life options, including incineration, landfill, or reuse. At the other extreme, the choice of reactants and products during manufacturing and use can make for large amounts of dioxin precursors, such as preservatives. The amount of dioxins created is often a function of the amount of these available precursors and the type of end-of-life measures. If the precursors are present and combustion is part of the end-of-life step in the life cycle, the likelihood of producing dioxins is increased.

Predicting potential impacts of new technologies and new substances is difficult. Countless environmental problems are yet to be resolved and others are plagued with incomplete or nonexistent unanimity of thought as to their importance or even whether indeed they are problems, such as the cumulative health and environmental impacts of confined animal feeding operations on microbial populations.

The trade-off in such cases may be between two competing yet legitimate societal needs, such as a reliable food source and clean water. Sometimes the two needs are mutually exclusive, but others may be met by modifications of one or both solutions (unconfined, local, and more spatially distributed animal operations, along with the public's willingness to accept higher prices for meat). The key to good environmental decision making is that it be informed with reliable information and that it be transparent.

## QUESTIONS

1. Explain why the aggregate concentrations of criteria air pollutant have fallen since 1990, even as economic output, vehicle miles traveled, and energy consumption have increased.
2. What is the difference between risk-based and precaution-based decision making?
3. Give an example of local air pollution problem with a short-term duration, and an example of a global air pollution problem with a long-term (e.g. years) duration.
4. Is it possible to have a pollutant with a chemical half-life of 1 year that causes a short-term problem? Can a pollutant with a very short half-life (hours), cause a long-term problem? Explain.
5. What are two types of ecosystem effects from air pollution?

6. Of a temperate forest and a tropical rainforest, which ecosystem is more likely to suffer long-term, possibly irreversible damage from air pollution? Why?
7. Consider an area where 25% of the homes have slab foundations and that due to the geology and soil in this area, the unsealed slab foundations allow substantial penetration of radon (Rn) gas into the home. Studies have shown that 70% of homes in this area with slab foundations exceed recommended Rn concentration thresholds. Rn gas intrusion accounts for 90% of indoor Rn concentration, with the remaining 10% of the Rn coming from building materials (e.g. stone). What is the probability of a house in this area with a slab foundation having Rn above the recommended concentration?
8. What is the probability of a house without a slab foundation in this area, chosen at random, would have concentrations of Rn above recommended levels?
9. What is the probability of a house exceeding indoor Rn recommended levels no matter which type of foundation?
10. Calculate the SMR of lung, pancreatic, and kidney cancer in male workers for a battery manufacturing plant that, over a 40-year period, had 16 lung cancer deaths, 6 pancreatic cancer deaths, and 1 kidney cancer death, when the expected number of cancer deaths was 9.1, 4.0, and 2.5, respectively. Explain the meaning of these SMRs.
11. List some possible confounders in the study described in List 10.
12. Why is temporality an essential requirement by causality?
13. What are some of the reasons that animal data alone often cannot explain an air pollutant's cause and effect?
14. List at least five factors that led to the toxic plume in Bhopal.
15. Give an example of a diffuse event that is a voluntary exposure to air pollution.
16. Give two reasons that air pollution removal become increasingly costly when approaching 100%.
17. Describe two trade-offs that affect air quality.
18. Explain the science behind the phrase "Think globally, but act locally".
19. What are some of the major differences between how the Clean Air Act (NESHAPs) addresses hazardous chemicals and how they are addressed by the hazardous waste laws (RCRA and Superfund)?
20. Choose two chemicals from the list of 189 "air toxics" (visit: <http://www.epa.gov/ttn/atw/orig189.html>). Give at least three steps that a business can take to approach air pollution from these substances.

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# Life Cycle Assessment of Air Pollutants

## 5.1 SYSTEMS CONTEXT FOR AIR POLLUTION

Chapter 4 introduces the tools needed to support air pollution decision making. One increasingly useful and reliable tool is the life cycle assessment (LCA). Air pollution results from myriad sources and processes. As such, the fundamentals of air pollution embody not only the principles of the atmospheric sciences, but also those of many other scientific disciplines. Air pollution must be understood systematically and includes steps that involve energy and various types of matter, both living and nonliving. The life cycle perspective avoids arbitrary divisions among air pollution, water pollution, land pollution, and the like. Thus, to truly explore the subject of this book, consideration of an entire life cycle is needed.

Certainly, the fundamentals include a sound basis for designing and selecting the appropriate air pollution control equipment or understanding the chemical reactions that lead to the emission of air pollutants. However, the fundamentals also include what happened long before the stack releases and chemical reactions and long after the emitted substances do their damage. What may be good for the air may be detrimental to the soil and vice-versa.

Energy production is a major source of air pollution. Stacks and tailpipes releasing smoke and fumes are emblematic of the connections between fossil fuel combustion and air pollution. Indeed, energy concerns are at the forefront of political, policy, and scientific decisions. Questions loom about how to become less reliant on finite energy sources, like fossil fuels; how to balance economic growth with environmental stewardship; and whether to employ precaution to protect the environment, including the potential for climate change, endangered species, and chronic public health impacts.

To this end, this chapter provides an overview of the life cycles of energy systems and the damage incurred by the various stages, from extraction to disposal<sup>a</sup>. All energy production causes insults to the environment, differing in the amount and type of pollution.

## 5.2 ENERGY

Modern life depends on energy in all of its forms. Everyday activities rely on a mix of mechanical, thermal, chemical, acoustic, and nuclear energy. Most of the earth's available energy comes from the sun. The fusion and fission of the sun emits large amounts of electromagnetic radiation, some of which finds its way to the earth. Thus, our planet has been and continues to be bombarded by the sun's electromagnetic energy, i.e. sunlight. Plants use and store this energy by photosynthesis. Animals use the stored energy for respiration. The remains of these plants and animals are deposited, and under pressure and over vast periods of time, energy is captured in minerals, known as fossil fuels.

The sun is also the source of many so-called alternative energy sources. Most obvious is solar energy, in which the electromagnetic energy is used directly (e.g. to heat water) or indirectly, in photovoltaic systems that convert photons to electrons. Wind is actually a type of solar energy, since the heating of the atmosphere leads to air movements. Bioenergy systems, e.g. algae and wood, are also solar, given that they derive their energy from photosynthesis and respiration.

The only "nonsolar" energy source on the earth is nuclear energy. Radioactive elements have unstable nuclei that emit radiation as they decay. These are also sources of fuel for energy. Indeed, uranium and other radioactive elements in minerals can be processed to reach

<sup>a</sup> This chapter is adapted from: 1. Vallero, D.A. (2013). Chapter 25. Environmental Impacts of Energy Production, Distribution and Transport. Letcher, T. Editor (2013). *Future Energy: Improved, Sustainable and Clean Options for Our Planet*. Second Edition. Academic Press, Amsterdam, Netherlands and Boston MA. ISBN: 9780080994246. eBook ISBN: 9780080994222.

critical concentrations in a reactor. These reactions throw off enormous amounts of heat (i.e. nuclear energy converted to thermal energy).

Choosing the best energy source is complicated. Advocates for and against various sources invoke a number of criteria for what is “best”. Some argue for reliability of production. Others emphasize economics, e.g. based on a cost–benefit analysis. Arguably, however, the most contentious and important are the public health and environmental impacts of the various energy sources. Unfortunately, comparisons are often difficult given the differences in the steps needed to provide energy to the end user. For example, an electric car may appear to be much cleaner than a gasoline-powered car, based solely on tailpipe emissions. The comparison becomes more complicated when the major source of electricity is coal that, when burned, emits large amounts of pollution from a stationary source, i.e. the power plant. Next, the impacts from extraction (coal mine *versus* oil well), transport (rail *versus* pipeline), etc. need to be considered in any proper decision.

Thus, the best way to consider the air pollution impacts of energy production, distribution, and transport is to employ a life cycle assessment (LCA). Such analyses are only as good as the assumptions and data used. It is important to keep in mind that energy use is similar to all societal decisions in that it depends on what is valued.

The value placed on an activity or material determines the costs that will be tolerated. For much of the past century in the United States, for example, much of society highly valued personal transportation based on the internal combustion engine to be highly valued, even if that has meant urban smog and other environmental impacts. If there is a switch to substantially greater numbers of electric vehicles, this may entail a change to less mobile sources of pollution, but greater

centralized, stationary sources from fossil fuel-fired and nuclear power-generating stations.

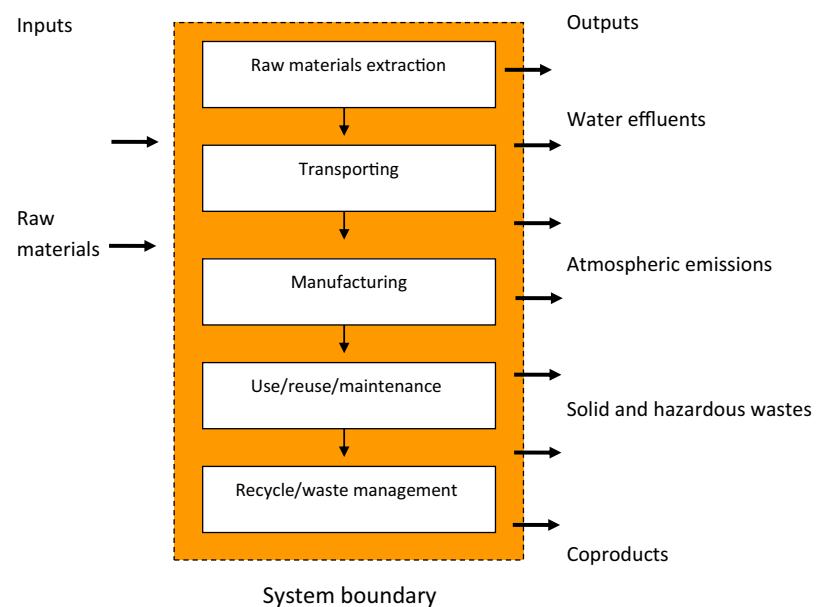
Whether such a transition is better depends on what is valued. In almost every large-scale energy plan, it is not a question of one option with much pollution and the other with no pollution. It is often a matter of the type of pollutant. In the electricity *versus* internal combustion example, the electric car system would emit large amounts of particulate matter (PM), sulfur dioxide ( $\text{SO}_2$ ), nitrogen dioxide ( $\text{NO}_2$ ), and heavy metals (including mercury [ $\text{Hg}$ ]) from a central source. Conversely, each gasoline-powered car would emit much smaller amounts of PM; volatile organic compounds (VOCs), like benzene; and other pollutants, but the overall emissions from millions of small mobile sources (vehicles) is what is important. Society may be willing to accept increased rates of diseases, even mortalities, as well as damage to ecosystems, if they place a higher value of what internal combustion engines provide or appear to provide (e.g. freedom of movement), *versus* less polluting options. Such trade-offs are common. The LCA is a tool for presenting the differences, but energy decisions depend on the willingness to make trade-offs. Incidentally, the status quo is difficult to change, even when facts show it to be less efficient and more costly than a new approach; that is, paradigms do indeed shift, but usually only after much resistance.<sup>1</sup>

### 5.3 ENERGY LIFE CYCLES

The environmental acceptability of any energy source must be evaluated systematically. This is demonstrated by the LCA (see Figure 5.1).

Consider the choice of whether to burn 100-L fuel A to manufacture 1000 kg of product Y releasing 100 kg of  $\text{SO}_2$

**FIGURE 5.1** Life cycle stages of a process must follow the conservation law, with material and energy balances. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Life cycle assessment: inventory guidelines and principles. EPA/600/R-92/245. Cincinnati (OH): Office of Research and Development; 1993.



per year *versus* burning 150 L of fuel B to manufacture the same amount of product Z, but releasing 300 kg of SO<sub>2</sub> per year. If this were the only criterion, fuel A would unquestionably be the best choice. It uses 50% less fuel (more energy efficient) and releases one-third of the pollutant. However, looking further back into the life cycle in [Figure 5.1](#), we find that fuel A requires that 1 t of earth is removed to produce 100 L of fuel A, but fuel B requires no extraction (it is generated from recycled food oils, e.g. biodiesel). It would appear that, early in the life cycle, fuel A has a much higher environmental cost (damage) than does fuel B. It could be that the extraction process does not emit a large amount of air pollutants, although such processes usually do, often in the form of fugitive dust (PM). Extraction activities almost always damage ecosystems, soil, and water systems. Furthermore, the two fuels will have different costs and benefits at the other levels in [Figure 5.1](#).

This demonstrates the complexity of most environmental problems. Environmental scientists and engineers are charged with providing credible information to inform decisions to address these problems. Indeed, the public has come to expect a modicum of environmental protection, placing much trust in scientists and engineers.

The public evaluates the actions of industry, governments, farmers, consumers, and everyone as to how much insult the action inflicts on the environment. An otherwise worthy endeavor may be too distasteful for the public if it adds or appears to add too much pollution in its achieving these otherwise commendable ends. In this sense, pollution prevention and control must be both prospective and systematic. Acceptable solutions are prospective in that they must adapt to a changing set of rules, both scientific and societal. They are systematic in that everything in the environment affects every other entity. The “entity” can be a material substance (e.g. a xenobiotic toxin) or an organism (both the agent and the receptor, e.g. a microbe and a human host for a contaminant or a microbe and ecosystem in a remediation project). The “entity” may also be a process or mechanism. K.W. Miller, editor of the *IEEE Technology and Society Magazine*, captured this prospective, systematic perspective, adding society’s expectation of scientific vigilance:

From stone spearheads to nanotubes, our artifacts can change how we live and, ultimately, who we are. The social significance of technological change requires us to take responsibility for the design, implementation, and deployment of the things we make... (I)t is clear that technology can change society. But sometimes we lose sight of the idea that society can change technology.<sup>2</sup>

As technological changes come at us thick and fast, we can be overwhelmed. Either consciously or unconsciously, we may start to accept some degree of technological determinism or Chandler’s inevitability thesis. The idea that technology is

going to happen no matter what we do is both tempting and highly dangerous, as many have pointed out. We have to keep reminding ourselves that we not only *can* steer technology but also that we *should*. Engineers especially must remember that part of our professional responsibility is to shape technology for the benefit of the public at large.

Identifying, characterizing, controlling, and reducing risks present an apparent cacophony or symphony (depending on one’s point of view) of multifaceted efforts to solve ill-posed problems. There is seldom a singular critical path to success. And, being human, even a well-designed, properly focused path to success is seldom followed as conceived, especially when living things are involved. Even the simplest of chemical compounds or the smallest of organisms does not completely behave as expected, particularly when a project is *scaled up* from the laboratory to the mesoscale pilot to the prototype and finally in the real world. Error, variability, and unexpected contingent events are missed or mischaracterized in a setting with additional and changing variables, even after applying the lessons from each scale-up step.

The challenge is to achieve something of importance, e.g. medical, agricultural, manufacturing, and environmental breakthroughs, without undue harm in space and time. Spatial harm occurs when a contaminant is released into the environment and causes immediate harm within a defined distance of the release. For example, an atmospheric plume may be transported to places where it causes additional harm. Within the plume, chemical transformation may occur by abiotic and biotic processes to form new compounds, which may be more or less reactive and toxic and which may build up in the environment after they are deposited from the atmosphere.

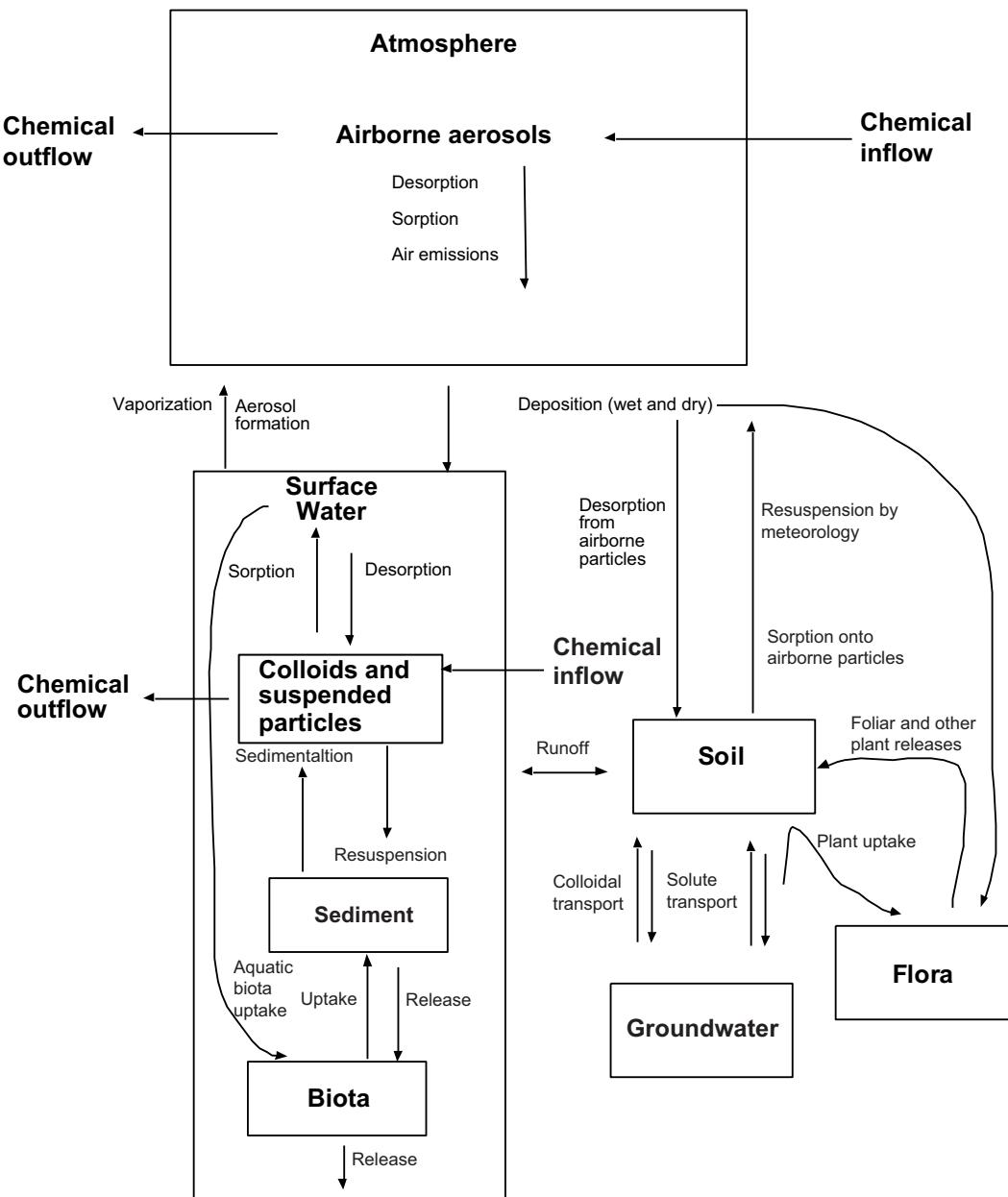
Temporal harm can take the form of short-term impacts. A substance is released into the environment, rendering an immediate, acute impact. Such a response can range from the highly circumscribed with little impact (e.g. release of a highly reactive substance in sufficiently low quantities and distance between the release and the receptor, so that it breaks down long before causing any harm) to disastrous (an immediate release of sufficiently large quantities of a substance that reach the receptor and elicit effects to a large population of receptors). The insult may be either isolated or episodic (e.g. one-time event like thermal inversion during a confluence of events, such as an explosion, where large amounts of contaminants are released and remain for a protracted time period), or it may be continuous, e.g. a water heater that releases carbon monoxide due to inadequate air-to-gas ratios, a leak from a propane tank valve into the atmosphere, or a slow release of gasoline (benzene–toluene–ethylbenzene–xylene) from an underground storage tank over decades into the groundwater and atmosphere. The simplest biochemodynamic

approach addresses each compartment where a contaminant is found in discrete phases of air, water, soil, sediment, and biota (see Figures 5.2 and 5.3).

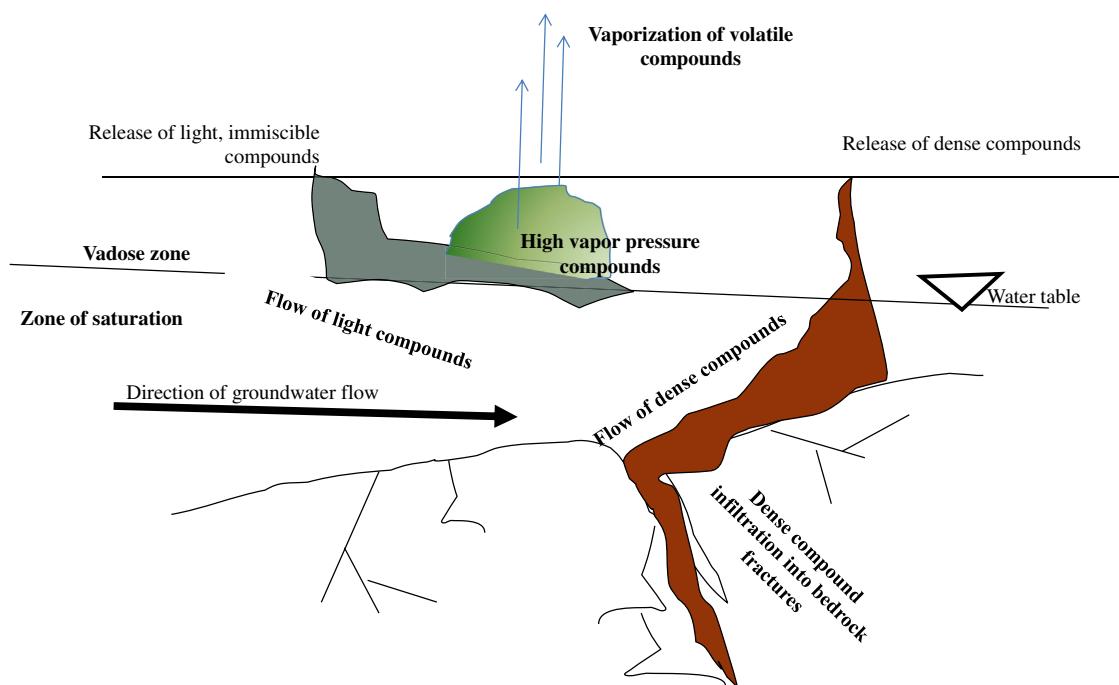
The top box in Figure 5.2 includes emissions from every step in the energy life cycle, from extraction (e.g. PM from mining and volatilization of compounds from crude oil and natural gas extraction) to releases of air pollutants from refining and processing to emissions from vehicles and other sources during

combustion to releases from landfills, incinerators, recycling, and other end-of-life systems.

The first law of thermodynamics states that the mass of the contaminant entering and the mass leaving a control volume must be balanced by what remains within the control volume. However, environmental systems are a cascade of control volumes. Within each control volume, an individual compartment may gain or lose mass of a substance, but the overall mass must balance.



**FIGURE 5.2** Substances move between and within environmental media, including compartmental uptake, transport, transformation, and various fates. Partitioning coefficients must be developed for each arrow and steady-state conditions may not be assumed; reaction rates and other chemical kinetics must be developed for each arrow and box. *Vallero DA. Environmental Biotechnology: A Biosystems Approach. Burlington (MA): Academic Press; 2011.*



**FIGURE 5.3 Air pollutants include more than those directly released into the environment.** For example, light (e.g. specific weight less than that of water) compounds may remain in the unsaturated (vadose) zone underground, with some eventually volatilizing to the atmosphere and others continuing to move in the groundwater plume. Light compounds that readily mix with water (miscible) will move further downgradient, and denser compounds may continue to flow perpendicular to the surface until reaching an impermeable layer, whereupon they move gravitationally. Even these may become air pollutants if they are pumped to the surface and partition. (For color version of this figure, the reader is referred to the online version of this book.) Vallero DA. Environmental Contaminants: Assessment and Control. Burlington (MA): Academic Press; 2004. ISBN: 0127100571.

The generally inclusive term for these compartmental changes is known as fugacity or the “fleeing potential” of a substance. Fugacity is a thermodynamic term for a substance’s propensity to escape from one environmental compartment to another (see Chapter 18). Combining the relationships between and among all the partitioning terms is one means of modeling chemical transport in the environment.<sup>3</sup> Even within a single compartment, a contaminant may exist in various phases (e.g. dissolved in water and sorbed to a particle in the solid phase). Interphase reactions, or the physical interactions of the contaminant at the interface between each compartment, determine the amount of any substance in the environment. Within a compartment, a contaminant may remain unchanged for a designated time period, may move physically, or may be transformed chemically into another substance. The measure of temporal harm is persistence. The measure of environmentally acceptable designs and operations is sustainability. For example, a recalcitrant chemical compound will have a high measure of persistence.

Certainly, all environmental decisions are technical in content, but they vary in the mix of skills and content needed. For example, both structural and mechanical engineers address the laws of motion and thermodynamics, but differ as to why. Mechanical engineers may be more

interested in finding better ways to make something move, whereas structural engineers are more likely to make sure something never moves over its designed life, or at least moves in nanometers rather than meters. Even this distinction is variable, since a mechanical engineer working on a braking system may share more in common with the structural engineer than his mechanical engineering colleagues working on increasing an engine’s torque and delivering more energy to turn the wheels. Often, however, the distinctions lie with the mix of physics, chemistry, and biology.

As mentioned, one of the key requirements of an energy system is that it be sustainable. More than simply meeting an environmental benchmark, a sustainable solution is one that assures that the benchmark will be met continuously for the foreseeable future. As such, engineering and science are becoming increasingly systems-oriented. Proper design must consider the raw materials, energy, labor, and other aspects of a project before extraction from the earth, manufacture, and operating life. The LCA for an energy decision should consider what is valuable about a site beyond its utility at hand. For example, how does an energy choice affect the fabric of the community, including the vitality, history, and connections within the neighborhood and the other neighborhoods to which it is connected? This is currently one of the

key concerns with hydraulic fracturing of shale and other rock strata to obtain natural gas and other fossil fuels. Even a technically sound and environmentally acceptable method is unacceptable if its adverse societal impacts are unacceptable. That is, before the project is evaluated for its environmental and operational utility, it should have already undergone the review by LCA to ensure fairness.

When considering the first canon of the engineering profession, i.e. to "hold paramount the safety, health and welfare of the public"<sup>4</sup>, the public is often perceived to be a broad and amorphous entity. However, since engineering must always incorporate sufficient margins of safety, good design must include the needs of persons who historically have been underrepresented. Unfortunately, the opposite has been the case all too often in the past. The path of least resistance to gain approval for infrastructures has often traversed the neighborhoods of disadvantaged neighborhoods. Entire communities have been displaced, historical treasures lost, and sacred land trampled as engineers and planners found far less resistance from these neighborhoods than from those with higher socioeconomic status (SES). Zoning has been used to pave the way and eminent domain to acquire the space for the factory, shopping center, and other private endeavors. Siting the power plant and other quasipublic projects; and selecting the best place for a landfill, wastewater treatment plant, highway, or other public infrastructural enterprises have been much easier to attain in neighborhoods with muted voices.

### 5.3.1 Upstream Impacts

Every energy source has upstream impacts. Obviously, coal and uranium must be mined, crude oil and natural gas drilled, and trees harvested. However, this also extends to "nonemitting" sources. Solar panels must be constructed of materials extracted from the earth (e.g. silica for glass and crude oil to make plastics). Wind turbines are made of steel and other metals that require extracting ores, as well as other manufactured materials (e.g. plastic insulation).

After extraction, the manufacturing processes are also part of the upstream stage of the life cycle for all energy sources. This applies to decentralized systems, such as solar panels and wind turbines installed on buildings, as well as to large, centralized, stationary sources, such as the construction, operation, and decommissioning of a coal or nuclear power generating facility. The footprint of these large systems can be substantial in terms of time, materials, and energy demands.

Environmental insult involves a stressor and a receptor. The stressor is a matter or energy that comes into contact with a receptor, causing harm. Most commonly for air pollution, the agent is chemical. An agent may also be biological, such as an organism (e.g. fungi,

bacteria, and viruses). An agent may also be physical, including direct and indirect effects from energy exposure. For example, ultraviolet light (physical stressor) reaches human skin cells (receptor), changing the deoxyribonucleic acid and leading to skin cancer (harm).

The principal upstream stressors result from mining and drilling. Mining alters habitats physically, chemically, and biologically. Physically removing large amounts of overburden completely changes the geomorphology of the mining region. This involves the removal of the soil and rocks and has caused environmental problems and sometimes loss of life.

#### 5.3.1.1 Mining stressors

Surface mining comes in many forms. Mining a seam of mineral by first removing a long strip of overburden is called strip mining and is often used in coal mining. It is also being used to extract the tar and oil from the sand at Athabasca in Alberta resulting in severe damage to the ecology and posing a threat to Alberta's boreal forest ecosystem. Open pit mining refers to mining from a huge open pit which can be very deep and large. This approach has been used to mine lignite in Germany and coal in Colombia.<sup>5,6</sup>

A more common and particularly physically and biologically stressful mining method is hilltop mining, i.e. stripping the overburden from the top of a mountain to expose the ore and then depositing the waste material in nearby valleys (see Figure 5.3). It seriously disturbs the ecosystem and changes the topography and even the flow of rivers and streams. One of the major problems with mountaintop mining is that head water streams are often buried, resulting in the loss of ecosystems. This technique leads to forest destruction, loss of biodiversity, and affects many species (see Figure 5.4).



**FIGURE 5.4 Mountaintop mining in West Virginia.** (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. <http://www.epa.gov/region03/mtntop/index.htm>; 2012 [accessed 16.03.12].

Hundreds of streams near US Appalachian coal fields have experienced:

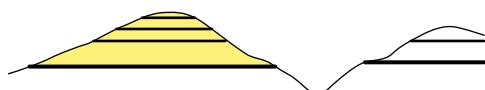
1. Increased concentrations of minerals in water, e.g. zinc, sodium, selenium, and sulfate which could have an impact on the fish and macroinvertebrates, and other streams in watersheds below valley fills tend to have greater base flow.
2. Wetlands destruction.
3. Forests broken into sections.
4. Impeded regrowth of trees and woody plants on regraded land in part due to compacted soils.
5. Increased populations of grassland birds and snakes on reclaimed mine, but reduced populations of amphibians.

Other impacts of surface mines include aesthetics, groundwater and surface water runoff contamination, noise, air quality (dust and mining pollutants), vibration, subsidence, as well as a devastating effect on the flora and fauna of the region.<sup>7</sup>

In addition to habitat destruction, mining activities lead to explosions, subsidence, slurry spills, and chemical pollution both above ground and through groundwater.

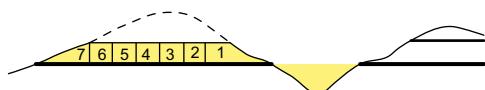
Chemical pollution results when soil and rock are broken, allowing migration of metals and other elements from the mining area in air (i.e. fugitive dust) and in water. One of the most common results from surface coal mines is an increase in acidity, in large part due to the sulfur being leached from the coal and overburden, and being oxidized.

The most direct and immediately obvious ecological effect of coal extraction has been acid mine drainage (see Figure 5.5). Acid drainage is caused by the oxidation of metallic compounds such as the mineral constituent of rocks and soils that is often present in coal mine wastes and overburden. Streams affected by coal mine drainage are typically acidic (pH 2.5–6.0) and are characterized by high iron and sulfate concentrations. In addition, the iron, as ferric hydroxide, often precipitates as a fine flock that may coat stream bottoms and further affect aquatic life. Acid mine drainage may also leach toxic concentrations of metals such as copper, aluminum, and zinc from rocks and soils. The oxidation, or weathering, of pyrite and other metal sulfides is a natural process that may occur spontaneously on exposure of minerals to air, or it may be mediated by bacteria.

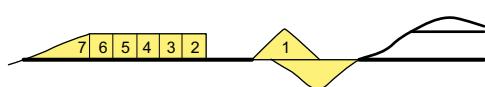


Step 1. Layers of rock and soil above the coal (called overburden) are removed

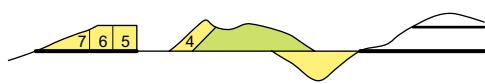
**FIGURE 5.5 Coal and overburden removal methods used in mountain top mining.** (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. <http://www.epa.gov/region03/mtntop/index.htm>; 2012 [accessed 16.03.12].



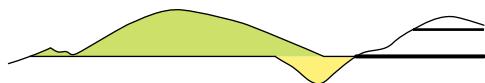
Step 2. The upper seams of coal are removed with spoils placed in an adjacent valley



Step 4. Draglines excavate lower layers of coal with spoils placed in spoil piles



Step 4. Re-grading begins as coal excavation continues



Weathering of pyritic rock formations has resulted in naturally acidic streams in some localized areas of the southeast United States.

By the mid-1960s, a century of US surface mining had disturbed<sup>8</sup> about 8000 km<sup>2</sup>, including 21,000 km of streams (totaling 550 km<sup>2</sup>), 281 natural lakes (419 km<sup>2</sup>), and 168 reservoirs (168 km<sup>2</sup>). Coal mining accounted for 41% of the total disturbed lands, the bulk of pollution being from acid mine drainage in the East and the Midwest portions of the United States. Current US surface mining regulations mandate the restoration of disturbed lands. Similar surface mining contamination has been observed in other parts of the world.

In addition to and exacerbated by decreasing pH, metal contamination also occurs from mining. For most metals, the chemical form determines just how toxic it is. The form also determines how readily the metal moves in the environment and how rapidly it is taken up and stored by organisms. The chemical form is determined by the oxidation state or valence of the metal. Metals form positive ions (cations), are reducing agents, have low electron affinities, and have positive valences (oxidation numbers). Metalloids have properties of both metals and nonmetals, but two environmentally important metalloids, arsenic (As) and antimony (Sb), behave much like metals in terms of their toxicity and mobility, so they are often grouped with the heavy metals.

At some concentration, all elements except those generated artificially by fission in nuclear reactors, are found in overburden and soils. This is true for toxic elements, such as the heavy metals, mercury (Hg), and lead (Pb), which are known to be neurotoxic and to cause other human health effects. The global mass balance of these metals, however, does not change; only their location and form (i.e. chemical species) can be changed. When concentrated and made bioavailable to humans and other organisms, such as from extraction and refining processes, metals and metalloids can present major threats to public health and the environment.

Contamination from fossil fuel mining is not limited to surface waters, but can reach ground water, a major source of drinking water for much of the world. Indeed, both the quality and quantity of groundwater are threatened. Groundwater, surface water, and the atmosphere must be considered as a single system, with contaminants moving and transforming physically and chemically within and between each level (see Figure 5.6). For example, fugitive dust blowing off the mine will become dissolved or suspended in water vapor. Droplets return to the earth as precipitation and reach surface water and groundwater. Metals in each compartment will change valency, making them more or less mobile and more or less toxic.

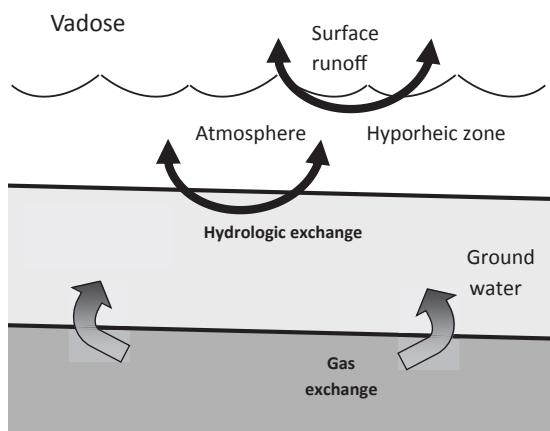


**FIGURE 5.6** Iron hydroxide precipitate in a Missouri stream receiving acid drainage from surface coal mining. (For color version of this figure, the reader is referred to the online version of this book.) Photo credit: U.S. Geological Survey and Hardesty D.

Underground or shaft coal mining also has environmental risks, including groundwater contamination, subsidence, and coal fires. A coal mine fire smolders, since oxygen levels are low, meaning it can burn for many years. This presents a serious problem from many aspects: economical (burning a vital commodity), environmental (emitting vast amounts of greenhouse gases—CH<sub>4</sub> and CO<sub>2</sub> and mercury), dangerous subsidence, and toxicity.

Underground fires are very difficult to extinguish since it is almost impossible to seal leaks to the surface over the entire room and pillar systems. Flooding the mines with water and slurries has been ineffective, since the fire simply follows pathways of available oxygen in the leaky underground strata. Even if technically possible, suffocating fires can introduce safety risks, e.g. miner safety and postignition fire suppression. To ensure sufficient oxygen levels and low toxic gas concentrations, the mine's ventilation systems require methane-drainage holes to control methane at the face. In many abandoned mines, cross-measure holes (see Figure 5.7) were the most common types. These systems are one reason that oxygen remains available to these fires.<sup>9</sup>

Internationally there are probably many hundreds of coal fires presently burning. Indeed, Australia,



**FIGURE 5.7 Atmospheric exchanges and reactions that originate in groundwater, sediment, and surface water.** Some of the stream water moves into and out of the sediment and in shallow groundwater (i.e. the hyporheic zone). The process can increase the mobility of dissolved metallic compounds. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from U.S. Geological Survey and Vallero DA. Environmental Contaminants: Assessment and Control. Burlington (MA): Academic Press; 2004.

Canada, China, Germany, India, Indonesia, New Zealand, Norway, South Africa, and the United States have documented details of ongoing fires. It has been estimated that these fires contribute to at least 3% of the world's annual carbon emissions. For example, fires from China's coal mines presently release about  $1 \times 10^9$  t (metric tons) of CO<sub>2</sub> to the atmosphere every year. Estimates put India's coal mine fire releases to be about  $50 \times 10^6$  t per year. This accounts for as much as 1% of all carbon greenhouse gas releases. This is about the same as the CO<sub>2</sub> emitted by all the gasoline fuel automobiles in the United States. Engineering solutions that reduce these emissions would actively improve the net greenhouse gas global flux. Unfortunately, the problem is persistent. Some US coal mine fires have burned for more than a century.

### 5.3.1.2 Uranium mining

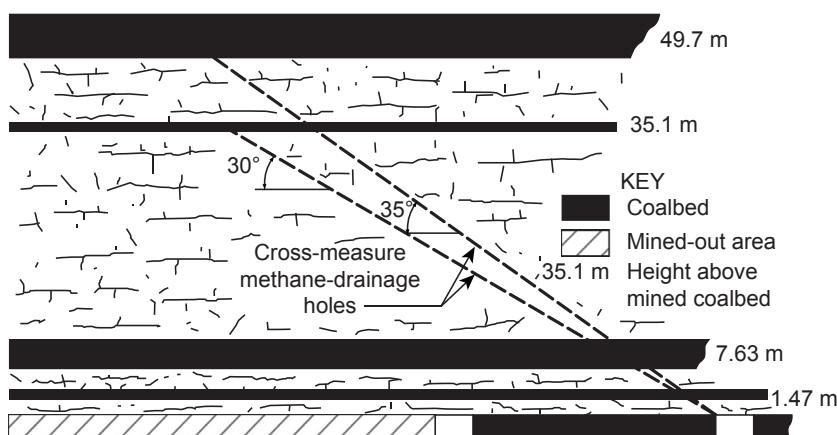
Fossil fuel extraction represents the largest contribution to environmental damage. Other energy-related extractions, however, can also be substantial. Considerable amounts of uranium continue to be mined in the United States (Figure 5.8) and around the globe (Table 5.1). Uranium and its decay products, radium and radon, can be inhaled. Uranium and radium inhalation exposures are usually as PM, and radon is a gas. Uranium miners and those near mining operations and tailings (solid waste left after concentrating the ore) have the highest potential exposures.

Environmental damage from uranium mining can be widespread. Most mining in the United States, predominantly in the Mountain West region, use *in situ* leaching, which needs large amounts of water, largely from wells and extensive pumping systems to transport ore and dissolve the minerals to concentrate the uranium content. These processes increase the risk of heavy metal and radioisotope contamination of air, soil, and water (particularly groundwater)<sup>10</sup> due to the mechanisms shown in Figure 5.8.

Besides uranium mining, various ore extractions are needed for other energy sources, such as copper and other metals for electronics in solar panels, wind turbines, and all heating and cooling systems; aluminum and iron extraction for numerous purposes (e.g. turbine housings for wind and hydroelectric energy); and nickel mining for batteries in electric cars and devices. The physical and chemical processes are similar to those described above. These must be included in any complete LCA.

### 5.3.1.3 Crude oil and natural gas drilling stressors

Oil and natural gas are extracted by drilling. Drilling activities pollute the water, soil, and air. Air pollutants can be aerosols (suspended liquid and/or solid particles) or vapor phase. Aerosols are released when soil is removed to install casings and rigs, as well as from vehicular activities. Gases and vapors include VOCs, such as benzene and



**FIGURE 5.8 Section view of cross-measure methane-drainage holes in a coal mine ventilation system.** Smith AC, Diamond WP, Organiscak JA. Bleederless ventilation systems as a spontaneous combustion control measure in U.S. coal mines; 1994. U.S. Department of the Interior, Bureau of Mines, Information Circular 9377, NTIS PB94-152816; McKensey BR, Rennie JW. Longwall ventilation with methane and spontaneous combustion-Pacific Colliery. Paper in Fourth International Mine Ventilation Congress (Brisbane, Australia, July 3–6, 1988); 1988. Melbourne (Australia): Aust. Inst. Min. and Met. p. 617–624.

TABLE 5.1 Global Uranium Production and Recoverable Resources

Nation	2010 Production from Mines (tons uranium)	Percent of World Production	2007 Known Recoverable Resources of Uranium (tons uranium)	Percent Total Resources (%)
Kazakhstan	17,803	33.17	817,000	14.94
Canada	9783	18.23	423,000	7.73
Australia	5900	11.00	1,243,000	22.73
Namibia	4496	8.37	275,000	5.03
Niger	4198	7.82	546,000	9.98
Russia	3562	6.63	274,000	5.01
Uzbekistan	2400	4.47	111,000	2.03
USA	1660	3.09	342,000	6.25
Ukraine (estimated)	850	1.58	200,000	3.66
China	827	1.54	68,000	1.24
Malawi	670	1.24	N/A	N/A
South Africa	583	1.08	435,000	7.95
India	400	0.74	73,000	1.33
Czech Republic	254	0.47	N/A	N/A
Brazil	148	0.27	278,000	5.08
Romania (est.)	77	0.14	N/A	N/A
Pakistan (est.)	45	0.08	N/A	N/A
France	7	0.01	N/A	N/A
Jordan	N/A	N/A	112,000	2.05
Mongolia	N/A	N/A	62,000	1.13
Other countries	N/A	N/A	210,000	3.84
World total	53,663		5,469,000	

Source: Fettus GH, McKinzie MG. Nuclear fuel's dirty beginnings: environmental damage and public health risks from uranium mining in the American west; 2012; Natural Resource Defense Council. <http://www.nrdc.org/nuclear/files/uranium-mining-report.pdf> [accessed 02.07.13]. Cited data source: World Nuclear Association Market Report data at [world-nuclear.org/info/inf23.html](http://world-nuclear.org/info/inf23.html) and, the Organisation for Economic Co-operation and Development (OECD), the Nuclear Energy Agency (NEA), and the International Atomic Energy Agency (IAEA), Uranium 2007: Resources, Production and Demand. N/A.

toluene. Both are aromatic in that they have a six-carbon ring. Benzene is carcinogenic and neurotoxic. Toluene is also neurotoxic and causes reproductive disorders. VOCs from drilling operations include numerous other aromatic and aliphatic carbon chains, which have health effects and contribute to smog (tropospheric ozone). Operations that produce these compounds include venting, flaring, and dehydration of natural gas.<sup>11</sup> Other drilling-related air pollutants include carbon monoxide, oxides of nitrogen, ozone, and sulfur dioxide, which are products of incomplete combustion (PICs). Methane and hydrogen sulfide occur naturally with and in the aquifers and are released during the drilling process.

Soil can be contaminated by hydrocarbons in the crude oil; soils also receive any impurities, including heavy metals, salts, and radioactive isotopes; as well as chemicals used in the development process, e.g. 2-butoxyethanol, 2-(2-methoxyethoxy) ethanol, and nonylphenol. All three have been linked to endocrine disruption, among other health effects in humans.<sup>12</sup>

Drilling operations pollute both groundwater and surface water. Groundwater is polluted when the oil or gas enters aquifers, especially drinking water aquifers, from leaks in casings and other means of penetration, such as cracks in confining strata, allowing the oil, gas, and their impurities to enter other strata. Indeed, *in situ* releases have accounted for the largest releases of crude oil, such as the Gulf War oil spill in the Persian Gulf in 1991, Deepwater Horizon in 2010, and the Ixtoc spill in Bay of Campeche, Mexico, in 1979 and 1980. Some areas have suffered continuous releases for decades, such as the thousands of separate incidents in the Niger River Delta of Nigeria that have collectively released about 220,000 m<sup>3</sup> of crude oil into surface waters and wetlands, including sensitive habitats.

Historically, crude oil drilling has mainly occurred at the rigs and derricks on land and offshore. However, unique risks are being introduced with deeper extractions further away from the shore, as evidenced by the recent devastating spill in the Gulf of Mexico (Figure 5.9). The Deepwater Horizon was a dynamically positioned, semi-submersible offshore oil drilling rig, designed to drill in ultradeep waters. In dynamic positioning, the vessel is kept in place using computerized thrusters and propellers. By April 14, 2010, BP Exploration & Production Inc. (BP) had nearly completed the exploratory phase of the Macondo well, with two well operation tasks remaining: running the well casing and preparing the well to be temporarily abandoned. The Deepwater Horizon was scheduled to depart the well once these tasks were completed. By this time, BP had verified the existence of a hydrocarbon reservoir but did not plan to immediately produce it; a different rig would commence completion operations for the operator at a later date.<sup>13</sup>

Casing is typically installed with two sets of cementing check valves: the float shoe, located on the very bottom of the casing string, and the float collar, usually installed from two to six casing joints above the bottom. BP's production casing design for the Macondo well called for only one cementing check device, consisting of a double valve and an autofill float collar.

The window for safe drilling between the fracture gradient and the pore pressure gradient decreases with drilling depth, so keeping the correct amount of equivalent circulating density had become increasingly difficult. This perturbed the integrity of the well and led to fluid losses. As this safety window narrowed, BP began to change plans by reducing the well's target depth, considering changes in well casings, reducing the circulating rate below the parameters specified to convert the

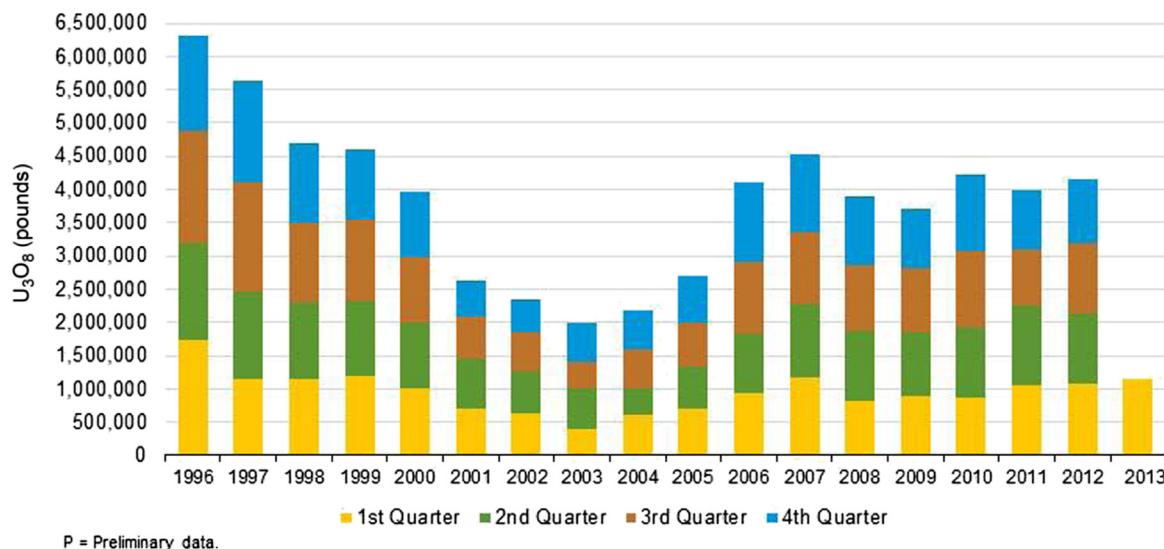


FIGURE 5.9 Uranium concentrate (U<sub>3</sub>O<sub>8</sub>) production in the United States. Here 1 pound = 0.454 kg. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Energy Information Administration. Domestic Uranium Production Report-Quarterly. <http://www.eia.gov/uranium/production/quarterly/>; 2013 [accessed 02.07.13].

float collar, decreasing the density of cement with nitrogen foam, using less cement, and ceasing to conduct complete bottoms-up cementing.

A negative pressure test was needed to make certain that the cement would stop flowing from the oil reservoir into the well after seawater replaced the drilling mud. The test should have been a red flag of trouble ahead; that is, the pressure readings on the drill pipe were abnormal. This should have been a warning that the cement barrier was not working. Pressure bypassed the cement and float equipment, so that the well was still connected to the oil formation. At the very least, this was a miscalculation, since the negative pressure test results were misinterpreted. The failure was compounded when BP decided to go ahead with the final displacement.

The BP oil spill flowed into the Gulf for 3 months and is the largest oil spill disaster in the history of the oil industry. The explosion on the rig killed 11 men and injured 17. The oil poured out of a leak on the seafloor bottom. It released 780,000 m<sup>3</sup> (4.9 million barrels) of oil into the Gulf of Mexico; about 800 km (500 miles) off the coastline of Louisiana, Mississippi, Florida, and Alabama was contaminated by BP oil. The spill affected every type of flora and fauna in the area, whales and dolphins died at twice their normal rate, wetland grass and flora died and fishing came to a halt, and an underwater plume, not visible on the surface, killed seafloor flora and fauna. BP admitted that it made mistakes and soon after the accident set up a \$20 billion fund to compensate victims of the oil spill.<sup>14</sup>

This disaster demonstrates the risks of deepwater drilling. It is quite difficult to quantify these risks for comparisons to other energy options, e.g. the mining options discussed earlier. In addition, applying these comparisons to societal trade-offs may not lend itself to quantification. For example, cycling is virtually free of fossil fuels, but the demand for individual and personal transportation may outweigh concerns for the environment.

## 5.4 ENVIRONMENTAL JUSTICE DURING EXTRACTION

As mentioned, a complete LCA consideration must include societal factors. A particularly illustrative example is justice. For example, coal, uranium, crude oil, and natural gas extraction occurs on Native American tribal land at a much higher rate than most of the North American population. Since risk is a function of

hazard and exposure, all other things being equal, risks from energy extraction are disproportionately high for Native Americans and are arguably an unjust outcome of deliberate and incidental decisions and events. "Environmental justice" communities have two characteristics:

1. They have experienced historical (usually multigenerational) exposures to disproportionately high doses of potentially harmful substances (the *environmental* part).
2. They have certain specified socioeconomic and demographic characteristics, including a low SES; are racial and ethnic; and are historically a disadvantaged people (the *justice* part).

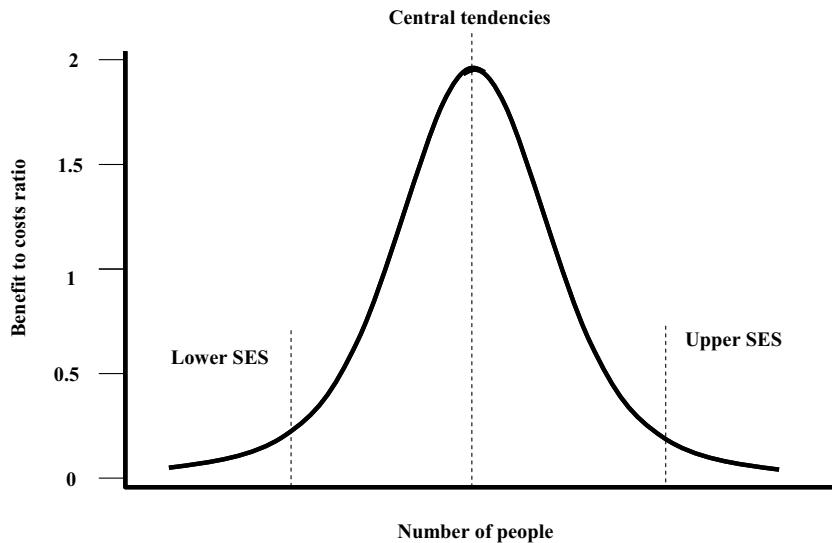
The determination of disproportionate impacts, i.e. diseases and other health endpoints, is fundamental to environmental justice. Epidemiologists look at clusters and other indications of elevated exposures and effects in populations. Certain cancers and neurological and other chronic diseases have been found to be significantly higher in minority communities and in socioeconomically depressed areas. Acute diseases, as indicated by hospital admissions, may also be higher in certain segments of society, such as pesticide poisoning in migrant workers. In addition, each person responds to an environmental insult uniquely and that person is affected differently at various life stages. For example, young children are at higher risk to neurotoxins. However, subpopulations can also experience different effects than that of the whole population, meaning that genetic differences seem to affect people's susceptibility to contaminant exposure. Scientists are very interested in genetic variation, so that genomic techniques<sup>15</sup> (e.g. identifying certain polymorphisms) are a growing area of inquiry.<sup>16</sup>

It appears that the tribes have borne disproportionate exposure to pollution and destruction of environmental resources. The disproportionate exposure demonstrates the weakness of the benefit to cost ratio (B/C), which is often considered for large populations, akin to the statistical concept of a normal distribution (Figure 5.10). Assuming that the benefits and costs<sup>b</sup> in a given situation are normally distributed within a population, the option with the average, largest benefits *versus* costs would be selected. This assures that subpopulations furthest from the mean would derive the least benefits, and that most of the population would get the most benefit. That is, the highest B/C ratios are those near the statistical measures of central tendency, i.e. the mean, median, and mode.

<sup>b</sup> Cost can be considered to be health and ecological risks when constructing a benefit/cost relationship. This is another weakness of the B/C, i.e. often the "environmental services" of an ecosystem are only a part of its value. This is often limited to those services valued by large segments of the population and is very anthropocentric (i.e. what good does this ecosystem provide to humans.) The distinction is often between instrumental *versus* inherent value, with many ecosystem service advocates most interested in the former.



**FIGURE 5.10 Deepwater Horizon drilling rig in flames.** A US Environmental Protection Agency photo. (For color version of this figure, the reader is referred to the online version of this book.)



**FIGURE 5.11 Hypothetical selection of a "fair" option from a utilitarian perspective when the benefits are normally distributed.** Vallero DA. Biomedical Ethics for Engineers. Burlington (MA): Elsevier Academic Press; 2007. ISBN: 978-0-7506-8227-5.

In the case of tribal lands, the normal distribution can lead to environmental injustices; it has placed a disproportionate environmental and potential health burden on the tribes. This may also demonstrate a type of “tyranny of the majority”.<sup>c</sup> Often, the curve is not normally distributed, but is skewed in favor of the higher socio-economic strata (Figure 5.11). As is often the case, the energy extraction disparity is doubly unfair in that many people assuming most of the costs and risks receive the fewest benefits and have had little voice in the decisions as to how and where to extract the minerals.

## 5.5 FUEL CYCLE IMPACTS

Once material is extracted, it must be converted to usable fuel. Some fuels are usable directly as extracted, e.g. natural gas and coal, but often need to be changed

physically to aid transport and combustion. For example, the natural gas may be compressed for ease in cross-oceanic transport. Coal will be crushed and even pulverized, depending on the combustion requirements.

Other materials will require processing and conversion. Processing uranium ore into usable fuel may require large amounts of energy, often from fossil fuels. Thus, even though the nuclear reactions themselves produce no greenhouse gases or other pollutants, the processing steps certainly will.

Crude oil processing and conversion is a substantial source of environmental pollution. Depending on the end product, varying amounts of energy is needed to refine crude oil into gasoline, diesel fuel, kerosene, etc. In addition, the life cycle must also consider the other needs of the final product. For example, both electric and gasoline-powered (and hybrid) vehicles need

<sup>c</sup> The phrase was coined by Alexis de Tocqueville and considered at some length by John Stuart Mills. In a democracy, the majority is very powerful. It can influence and even control the entire people, as what happened in Germany where elected officials, including Hitler gained and abused power. This was much on the mind of the framers of the United States Constitution, so that the duly elected do not become the tyrants and so that those with little power are not crushed.

lubricants for moving parts, but electric motors do not require motor oil to lubricate pistons and other parts of internal combustion engines. These lubricants are derived from crude oil, so when comparing energy demands, they must be included.

Another aspect of the fuel cycle is the transport of the raw material to the various sites. In its gaseous form, natural gas is transported by pipelines. The excavation, construction, and upkeep of these lines must be considered as part of natural gas life cycle. Indeed, pipelines can have major environmental impacts on ecosystems, such as bifurcating or truncating habitats, changing migration patterns, interfering with spawning and nesting, and even changing micrometeorology (e.g. warm pipelines changing caribou migration). Pipelines

also present human safety and health risks from explosion and fire, as methane ( $\text{CH}_4$ ) and other alkanes are highly explosive and flammable. As mentioned, natural gas may also be compressed and shipped as a liquid in tankers. Although they do not have the risk of oil spills, such long-range shipments require energy and pose potential threats to ecosystems, e.g. bilge issues.

### 5.5.1 Fuel Cycle Stressors

Environmental stressors introduced in the fuel cycle stages include many of those mentioned for upstream stages, since the extracted ores and substances are what are being transported and processed. Since crude oil presents very large environmental threats during

TABLE 5.2 Largest Oil Spills Since 1967, Ranked by Weight of Product Spilled

Position	Ship Name	Year	Location	Spill Size (t)
1	Atlantic Empress	1979	Off Tobago, West Indies	287,000
2	ABT Summer	1991	700 nautical miles off Angola	260,000
3	Castillo de Bellver	1983	Off Saldanha Bay, South Africa	252,000
4	Amoco Cadiz	1978	Off Brittany, France	223,000
5	Haven	1991	Genoa, Italy	144,000
6	Odyssey	1988	700 nautical miles off Nova Scotia, Canada	132,000
7	Torrey Canyon	1967	Scilly Isles, UK	119,000
8	Sea Star	1972	Gulf of Oman	115,000
9	Irenes Serenade	1980	Navarino Bay, Greece	100,000
10	Urquiola	1976	La Coruna, Spain	100,000
11	Hawaiian Patriot	1977	300 nautical Miles off Honolulu	95,000
12	Independenta	1979	Bosphorus, Turkey	95,000
13	Jakob Maersk	1975	Oporto, Portugal	88,000
14	Braer	1993	Shetland Islands, UK	85,000
15	Khark 5	1989	120 nautical Miles off Atlantic coast of Morocco	80,000
16	Aegean Sea	1992	La Coruna, Spain	74,000
17	Sea Empress	1996	Milford Haven, UK	72,000
18	Nova	1985	Off Kharg Island, Gulf of Iran	70,000
19	Katina P	1992	Off Maputo, Mozambique	66,700
20	Prestige	2002	Off Galicia, Spain	63,000
35	Exxon Valdez	1989	Prince William Sound, Alaska, USA	37,000

t = ton (metric ton).

Source: International Tanker Oil Owners Pollution Federation, Limited. Statistics. <http://www.itopf.com/information-services/data-and-statistics/statistics>; 2012 [accessed 14.03.12].

TABLE 5.3 Incidence of Spills 7–700 t by Operation at Time of Incidence and Primary Cause of Spill, 1970–2011

	Operations			
	Loading/Discharging	Bunkering	Other Operations	Unknown
	388	33	136	785
<b>Causes</b>				
Collisions	4	0	32	308
Groundings	0	0	16	253
Hull failures	36	4	10	50
Equipment failures	141	6	17	38
Fires/explosions	8	0	13	26
Other/unknown	199	23	48	110
Total	388	33	136	785

Source: International Tanker Oil Owners Pollution Federation, Limited. Statistics. <http://www.itopf.com/information-services/data-and-statistics/statistics>; 2012 [accessed 14.03.12].

transport, it is discussed in detail, followed by a discussion of raw material processing.

### 5.5.2 Crude Oil Transport Stressors

Crude oil is also transported via pipelines, with the same risks as above. In addition, when crude oil is leaked, it can have devastating impacts on ecosystems, both terrestrial and aquatic. Transport by tanker and barge presents substantial environmental threats. Notorious examples of liquid spills include oil from the wrecked Exxon Valdez off the Alaskan coast and the massive release of crude oil from the breach of the Deepwater Horizon piping in the Gulf of Mexico. These are all examples of immediate releases of a contaminant. In the case of the Exxon Valdez, the release itself was from a single vessel (i.e. a ship's hull or a tank). In the case of the Deepwater Horizon spill, the release continued for months.

The extent and duration of a leak or spill is determined by the available volume of a substance. Once the ship hull or tank is emptied, the spill itself ends, but the damage it causes can endure for decades. If the source is vast, such as the oil in rock strata under the Gulf of Mexico, the spill will end only after the pressure differential between the strata and the surface reaches equilibrium, or until the available substance is depleted. Thus, the properties of the fluid and the characteristics of the environment determine the amount and rate of a contaminant that is released in a disaster.<sup>17</sup>

There have been numerous oil spills since crude oil and oil products began to be shipped over large distances (see Table 5.2). The largest spill from a vessel at sea in terms of amount of release occurred in 1979 when the Atlantic Empress spilled 287,000 t of crude oil near Tobago in the West Indies. Oil spills result from many causes. Actually,

the Exxon Valdez was the most notorious spill prior to the Deepwater Horizon spill in the Gulf of Mexico. However, the Valdez stands in the 35th position in terms of weight (37,000 t). This illustrates that the amount spilled is only part of the criteria used to determine disaster status of an event. In the case of the Valdez, much of the problem had to do with where the spill occurred and the sensitivity of the habitat. Some organisms readily adapt to change, whereas other, more sensitive organisms may be irreversibly affected by very slight changes in habitat conditions.

The causes of spills vary widely, but there appears to be a difference between very large and smaller spills. Equipment and hull failures account for nearly half (46%) of all spills. The difference seems to lie in where the spills occur (see Tables 5.3 and 5.4). Most large spills occur in open water, whereas for the smaller spills (less than 7 t) where the cause is known, most occur in the port, e.g. loading and discharging the fluid.<sup>18</sup>

The Exxon Valdez oil spill is arguably the most infamous tanker disaster, having changed the consciousness of the vulnerability of sensitive coastal habitats and littoral ecosystems. The supertanker loaded oil from the trans-Alaska pipeline from the Valdez terminal to deliver it to West Coast states (see Figure 5.12). On March 24, 1989, it veered out of the normal tanker channel and spilled  $41.7 \times 10^3 \text{ m}^3$  ( $11 \times 10^6$  gallons) of oil after striking Bligh Reef in Prince William Sound. The oil slick expanded rapidly (see Figure 5.13).

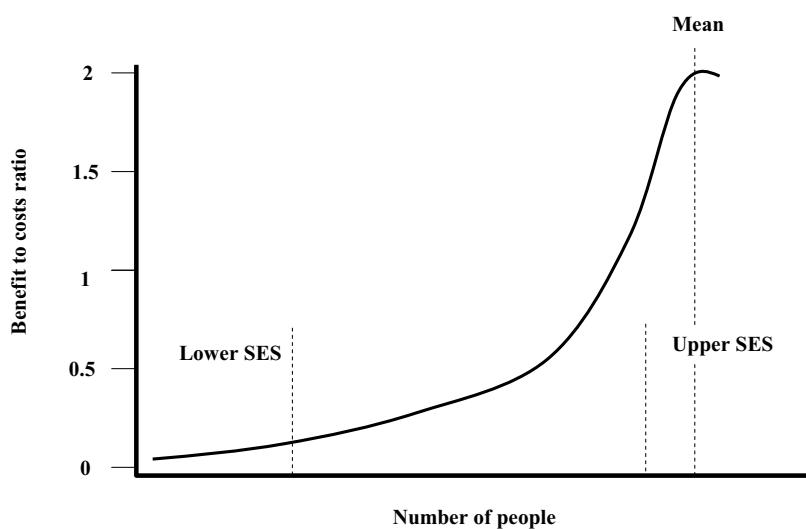
## 5.6 REFINING STRESSORS

After extraction, the large source of pollution in terms of total mass released to the environment occurs during processing of the raw materials. For example, petroleum

TABLE 5.4 Incidence of Spills &gt;7 t by Operation at Time of Incidence and Primary Cause of Spill, 1970–2011

	Operations						Other Operations/ Unknown
	At Anchor (Inland/ Restricted)	At Anchor (Open Water)	Underway (Inland/Restricted)	Underway (Open Water)	Loading/ Discharging	Bunkering	
	13	9	82	225	41	1	83
<b>Causes</b>							
Allisions (single moving vessel) collisions	6	5	33	65	1	0	24
Groundings	4	2	45	66	2	0	29
Hull failures	0	1	0	50	0	0	8
Equipment failures	0	0	0	7	11	0	1
Fires/explosions	1	1	3	25	14	1	9
Other/unknown	2	0	1	12	13	0	12
Total	13	9	82	225	41	1	83

Source: International Tanker Oil Owners Pollution Federation, Limited Statistics. <http://www.itopf.com/information-services/data-and-statistics/statistics>; 2012 [accessed 14.03.12].



**FIGURE 5.12** Conceptual model for selecting a "fair" option from a utilitarian perspective when the benefits are skewed in favor of the higher socioeconomic strata. *Vallero DA. Biomedical Ethics for Engineers. Burlington (MA): Elsevier Academic Press; 2007. ISBN: 978-0-7506-8227-5.*



**FIGURE 5.13** Valdez, Alaska oil transport terminal. (For color version of this figure, the reader is referred to the online version of this book.) Photo credit: National Oceanic and Atmospheric Administration.

refining releases PM ( $0.1\text{--}3 \text{ kg t}^{-1}$  of crude), oxides of sulfur ( $0.2\text{--}0.6 \text{ kg t}^{-1}$  of crude), oxides of nitrogen ( $0.06\text{--}0.5 \text{ kg t}^{-1}$  of crude), and VOCs (e.g. 2.5 g of benzene, toluene, and xylene in 1 t of crude). Refining also uses massive amounts of water (producing up to  $5 \text{ m}^3$  of wastewater for every 1 t of crude refined, even when recycling the water). When released to waterways, this waste can significantly lower dissolved oxygen (averaging  $150 \text{ mg L}^{-1}$  biochemical oxygen demand), presenting a large threat to aquatic life.<sup>19</sup>

Note that complete combustion yields water and carbon dioxide. Interestingly, both are greenhouse gases and both are essential to life on earth. Thus, the same substance that is essential can also be harmful, depending on its amount and location in time and space.

A pollutant source can be stationary or mobile. Combustion at stationary sources, like large power plants and factories, releases CO<sub>2</sub> and PICs. Combustion from mobile sources, such as automobiles, trucks, buses, aircraft, trains, and watercraft, also release pollutants. In fact, mobile sources can be worse than stationary sources in terms of the number of people exposed, since large populations live near roadways and other transportation routes. A relatively small number of people living near stationary sources, especially those with inadequate pollution controls, may have very high exposures relative to the general population. Thus, the environmental impacts of stationary sources *versus* those of mobile sources may call for decisions on whether it is worse to have a small, highly exposed subpopulation or a large, less exposed general population.<sup>d</sup>

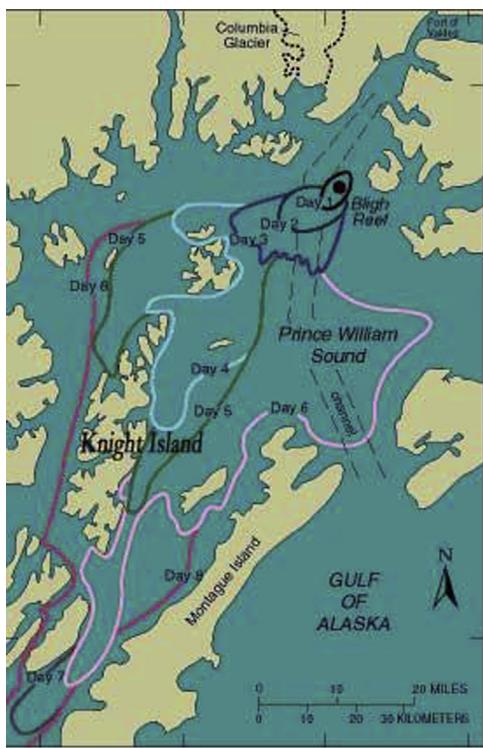
## 5.7 OPERATION STAGE

After extraction and fuel processing, each energy system is operated over its design life. During this life, fossil fuels are burned, nuclear reactions occur, and biota grow. The efficiency of these operations comprises a large component of energy use and sustainability.

<sup>d</sup>This is an example of the greatest good for the greatest number, a concept of utilitarian philosophy. Conversely, deontologists would hold that it is immoral to allow such exposures. The categorical imperative, for example, would hold that if the level of exposure of a few cannot be universalized, i.e. if everyone were exposed to the same pollutant at the same concentration, would this be acceptable. The answer would be "no". Indeed, the first canon of the engineering profession is to hold paramount the safety, health and welfare of the public. Arguably, allowing certain groups to be exposed at high levels does not meet this canon.

### 5.7.1 Combustion

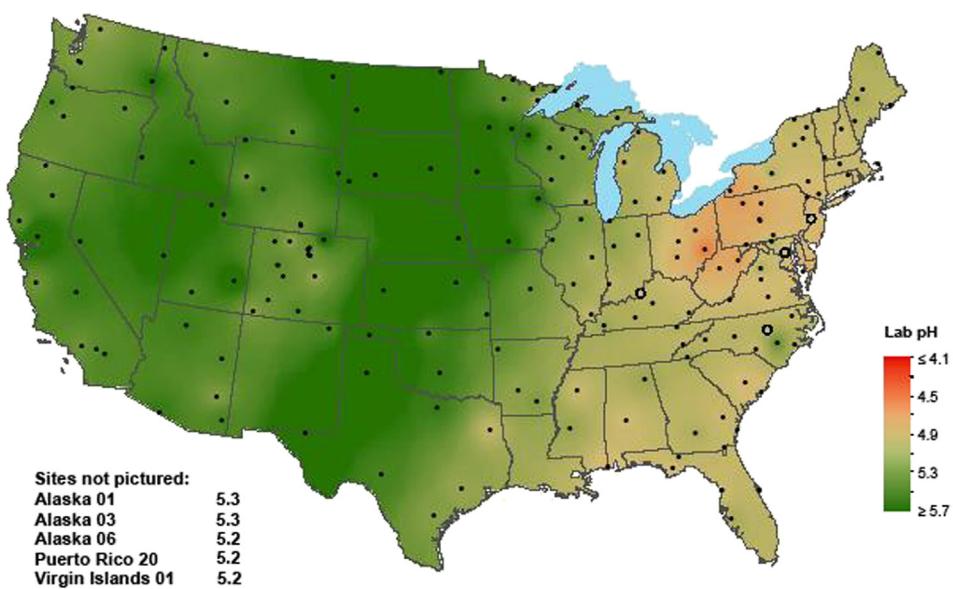
The largest human-induced source of many air pollutants is the combustion of fossil fuels to generate electricity. And the principal contributor to Hg, CO<sub>2</sub>, and SO<sub>2</sub> emissions has been coal-fired power plants. Eastern and midwestern coals contain significant quantities of sulfur, so their combustion reactions release large quantities of SO<sub>2</sub>, the major component of acid precipitation, to the atmosphere. Most of the high-sulfur coal consumed in the United States during this century has been used to make steel and to generate electricity in the east and midwest. From there, atmospheric pollutants responsible for acid precipitation are transported northward and eastward by prevailing winds and storms. These trends are reflected in the geographic distribution of rainfall pH (Figure 5.14). There are a number of sources contributing to acid precipitation, including those from automotive exhausts, but emissions from coal-fired electricity-generating plants presently constitute the largest source of atmospheric SO<sub>2</sub> in North America.



**FIGURE 5.14** The Exxon Valdez ran aground on Bligh Reef on March 24, 1989. The map shows the expansion of oil front from day 1 through day 8. (For color version of this figure, the reader is referred to the online version of this book.) *Map credit: U.S. Geological Survey from one to eight days after the spill. Map credit: U.S. Geological Survey; National Oceanic and Atmospheric Administration. Prince William's Oily Mess: A Tale of Recovery. [http://oceanservice.noaa.gov/education/stories/oilmess/oily07\\_time.html](http://oceanservice.noaa.gov/education/stories/oilmess/oily07_time.html); 2012 [accessed 06.03.12].*

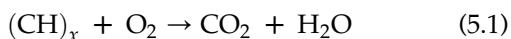
Areas with underlying crystalline rock, shale, and sandstone are more prone to acidification than those underlain by rock systems that buffer the acids, e.g. limestone and other carbonate-rich rock. Potentially sensitive areas are widely distributed in North America and include much of the Appalachian Mountains, where rainfall is most acidic (Figure 5.14); the Canadian Shield region of the upper Midwest (i.e. the northern parts of Michigan and Wisconsin, as well as eastern Minnesota and parts of eastern and central Canada); the higher elevations of the Sierra Nevada, Rocky Mountains, and Cascade Range; and parts of the Ozark and Ouachita uplands, mid-Atlantic Coastal Plain, and Florida. Buffering by ions in groundwater and constituents leached from watersheds makes large lakes and rivers at lower elevations less susceptible to acidification than smaller, higher elevation lakes and streams.

The interactions of ions in precipitation (i.e. H<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>) with organic and inorganic constituents of soil and water affect toxicity. Particularly important is the leaching of potentially toxic elements, especially aluminum, from rocks and soils by acidic precipitation. Toxicity attributable to pH and aluminum is often episodic, occurring during high surface water discharge in the spring months. During the Spring, spawning and larvae releases occur for many aquatic organisms, making them vulnerable to reduced pH conditions. By definition, acid rain is rainfall with a pH lower than about 5.0; the pH of distilled water in equilibrium with atmospheric CO<sub>2</sub> is 5.6, but other atmospheric constituents tend to make rainfall more acidic even in areas unaffected by air pollution. In addition to sulfur, the combustion of coal emits other potentially toxic elements, including arsenic, cadmium, lead, mercury, and selenium. Cadmium and selenium are concentrated in coal ash, from which they may be leached into surface waters and accumulated to toxic concentrations by aquatic organisms. Mercury, along with selenium, and other elements in coal are released into the atmosphere in stack emissions and can move long distances. Mercury and selenium readily bioaccumulate in birds, mammals, and predatory fishes. Mercury is generally released from point sources, e.g. caustic soda, i.e. sodium hydroxide (NaOH) plants and paper mills. Bioaccumulation of mercury in remote lakes in the northeast seems to indicate that atmospheric transport and natural chemical processes tend to keep mercury available for accumulation by organisms. According to the US Environmental Protection Agency (EPA), coal-fired electric generating plants are the greatest sources of atmospheric mercury, while other important sources include municipal and hospital waste incinerators.



**FIGURE 5.15** United States rainfall pH, 2011, as weighted mean values based on measurements at about 200 sites maintained by the National Acid Deposition Program. (For color version of this figure, the reader is referred to the online version of this book.) National Acid Deposition Program/National Trends Network. <http://nadp.sws.uiuc.edu/htn/annualmapsbyyear.aspx>; 2013 [accessed 02.07.13].

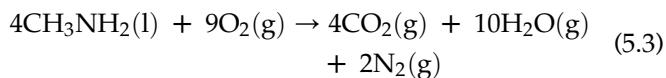
Complete or efficient combustion (thermal oxidation) converts hydrocarbons to carbon dioxide and water:



Combustion is the combination of O<sub>2</sub> in the presence of heat (as in burning fuel), producing CO<sub>2</sub> and H<sub>2</sub>O during complete combustion of organic compounds, such as the combustion of octane:



Complete combustion may also result in the production of molecular nitrogen (N<sub>2</sub>) when nitrogen-containing organics are burned, such as in the combustion of methylamine:



Incomplete combustion can produce a variety of compounds. Some are more toxic than the original compounds being oxidized, such as polycyclic aromatic hydrocarbons (PAHs), dioxins, furans, and CO. An alert reader will note at least two observations about these categories. First, all are kinetic, as denoted by the one-

directional arrow (→). Second, in the environment, many processes are incomplete, such as the common problem of incomplete combustion and the generation of new compounds in addition to carbon dioxide and water.

Incomplete combustion reactions are very important sources of air pollutants. For example, these reactions generate PICs, such as carbon monoxide (CO), PAHs, dioxins, furans, and hexachlorobenzene.

Consider the emissions of a 600 MW coal-fired power plant with a capacity factor<sup>e</sup> of 69% and a heat rate<sup>f</sup> of 10,415. Without controls, each year this plant would release<sup>20</sup> 500 t of fine PM (PM<sub>2.5</sub>), 14,100 t of SO<sub>2</sub>, 10,300 t of oxides of nitrogen (NO<sub>x</sub>), 220 t of VOCs (toxic and precursors to tropospheric ozone), 495 kg of arsenic (As), 370 kg of mercury (Hg), 251 kg of lead (Pb), 9 kg of cadmium (Cd), and other metals, including radioisotopes. All these emissions occur during the coal combustion stage of electricity generation from a single plant.

Globally, CO<sub>2</sub> emissions have been increasing since the Industrial Revolution, but at a faster rate in recent decades (see Figure 5.15). Energy supply contributes 26% of greenhouse gas emissions, the highest sector. Industry contributes 19%; forest and land activities, not including

<sup>e</sup>Capacity factor is the frequency that a plant is operating, i.e. the amount electricity produced at continuous full power operation during that period. For example, a 600-MW power plant produces 3.63 million megawatt-hours (MWh) for a year; its capacity factor is 69% because  $3.63 \times 10^6 \text{ MWh} = 69\%$  of the electricity that the generator would have produced if it operated for the entire year (i.e. 1 year = 8760 h) without pause at full capacity ( $600 \text{ MW} \times 8760 \text{ h} = 5.25 \times 10^6 \text{ MWh}$ ). That is  $\frac{3.63 \times 10^6 \text{ MWh}}{5.25 \times 10^6 \text{ MWh}} = 0.69$ .

<sup>f</sup>Heat rate is thermal unit per power-time. In this case, it is the British thermal unit (BTU) per kilowatt-hour. For example, in 2011, the average operating heat rate for coal was 10,444, compared to 10,829 for petroleum, 8152 for natural gas, and 10,464 for nuclear energy. Source: U.S. Energy Information Agency (2011). Form EIA-913. Plant operations report.

agriculture, contribute 17%; agriculture contributes 14%; transportation contributes 13%; and buildings contribute 8%.<sup>21</sup> Actually, total CO<sub>2</sub> emissions in the United States have been falling in recent years (see Figure 5.16). Unfortunately, several other countries' CO<sub>2</sub> emissions have more than compensated for the US decrease (see Figures 5.17 and 5.18 and Table 5.5).

All atmospheric releases of products of complete and incomplete combustion find sinks throughout the biogeochemical cycles (see Part IV). Each box in Figure 5.2 below the atmosphere is a sink for substances in the atmosphere. For example, in the carbon cycle, CO<sub>2</sub> becomes dissolved in surface waters. The largest reservoirs of surface water are the oceans, which have been dissolving increasing amounts of CO<sub>2</sub>. In turn, the oceans are experiencing decreasing pH, a worrying prospect for the

earth's vast oceanic ecosystems and food sources (see Ocean Acidification).

### 5.7.2 Operation

Operation is often the only or principal consideration when comparing environmental impacts of energy choices. For example, a vehicle's tailpipe emissions and fuel economies are compared to those of other vehicles. Indeed, these are important considerations, but as the previous discussion has shown, they are only part of the life cycle. Today, for instance, most electric cars are actually "coal-fired" or "nuclear-powered" vehicles. This will continue until alternative energy sources supplant fossil fuel and nuclear sources of electricity.

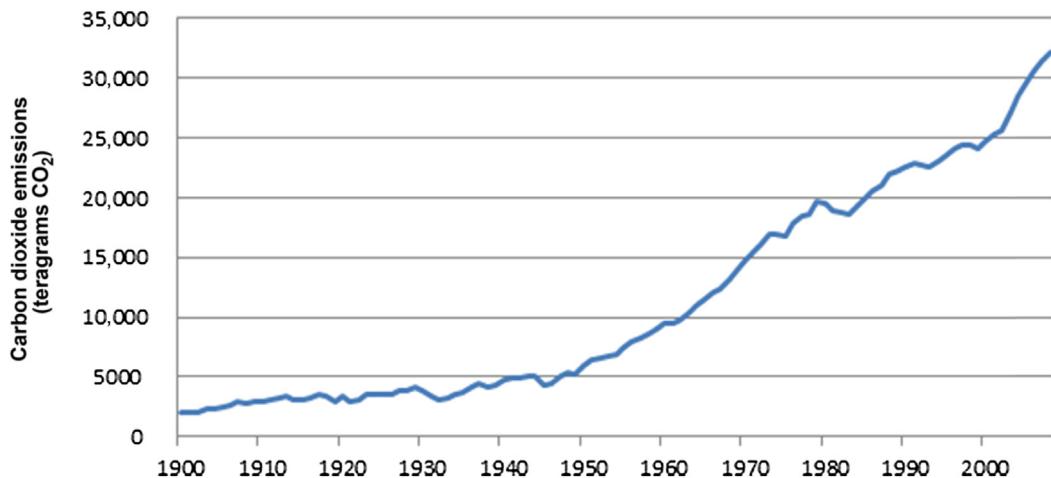


FIGURE 5.16 Global carbon dioxide emissions from fossil fuels. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Global greenhouse gas emissions data. <http://www.epa.gov/climatechange/ghgemissions/global.html>; 2013 [accessed 25.09.13].

## OCEAN ACIDIFICATION

The mean pH of ocean water has been decreasing, i.e. becoming more acidic, over recent decades, largely because of the ocean's uptake of CO<sub>2</sub> from the atmosphere. The decrease in ocean pH has co-occurred with the steady increase in the mean atmospheric concentration of CO<sub>2</sub> over the past three centuries from 280 ppm to nearly 400 ppm. Ocean acidification has potentially devastating ramifications for all ocean life, from the smallest, single-celled algae to the largest whales.

As a requirement of the Federal Ocean Acidification Research and Monitoring Act of 2009, the National Oceanic and Atmospheric Administration's (NOAA) Ocean Acidification Program was officially established in May 2011. The OAP is an integral part of a much

broader US research effort to increase our understanding about how (and how fast) the chemistry of the ocean is changing, how variable that change is by region, and what impacts these changes are having on marine life, people, and the local, regional, and national economies.

NOAA is coordinating closely with other federal agencies which have strong ocean acidification research or policy portfolios. These include the National Science Foundation, United States Geological Survey, National Aeronautical and Space Administration, Bureau of Energy Management, Department of State, US Fish and Wildlife Services, and the EPA. Visit: <http://oceanacidification.noaa.gov/IWGOA.aspx>.

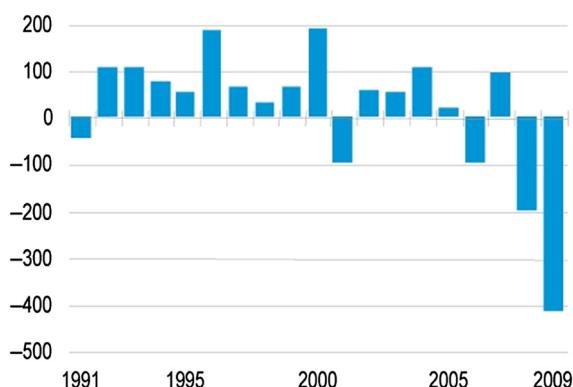


FIGURE 5.17 Annual change in total US emissions of carbon dioxide (million metric tons). Change compared to 1990 baseline; e.g. the 2009 emissions were 406 million metric tons (Mt) less than 1990 emissions, a 7.1% decrease ( $5041 \text{ Mt} - 5447 \text{ Mt} = 406 \text{ Mt}$ ). The decrease is even greater compared to 2005, the year of maximum CO<sub>2</sub> emissions (6055 Mt), i.e. a decrease of 608 Mt = -10% change. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Energy Information Administration. *Emissions of greenhouse gases in the U.S. Report No. DOE/EIA-073(2009); 2011.*

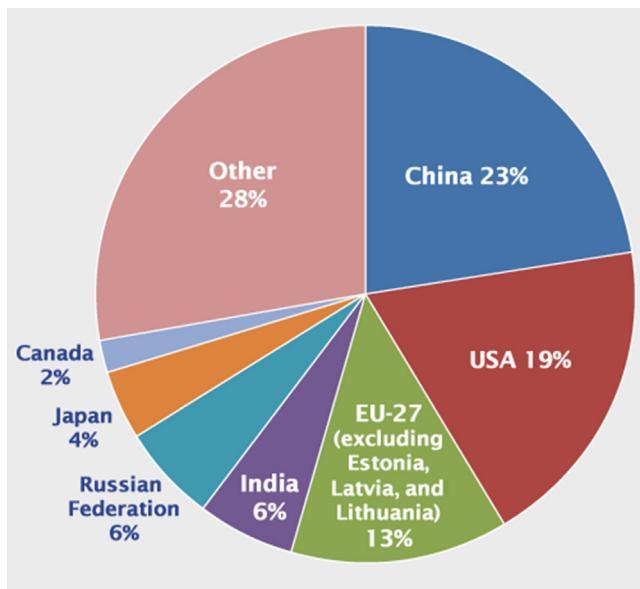


FIGURE 5.18 Global carbon dioxide emissions from fossil fuel combustion and select industrial process (million metric tons). (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Global greenhouse gas emissions data. <http://www.epa.gov/climatechange/ghgemissions/global.html>; 2013 [accessed 25.09.13].

The same goes for home and other building heating and cooling. Units have improved their energy efficiencies dramatically in recent decades.

## 5.8 DOWNSTREAM IMPACTS

Evaluating the effects of energy choices must also consider the problems brought on by dismantling, decommissioning, disposing, and recycling. The key is to prevent the pollution in the first place. For example, if the demand for fossil fuels and other energy sources declines, less environmental damage would occur due to decreased need for extraction, fuel processing, and disposal of hazardous wastes associated with the operations. Energy conservation can go a long way to decrease the release of toxic pollutants and greenhouse gases, as well.

Also, choices of materials can greatly affect downstream impacts. For example, chemicals injected underground are among the controversial aspects of horizontal drilling and hydraulic fracturing to obtain natural gas and other fossil fuels from previously unproductive strata. If safer, biodegradable chemicals are used, at least one concern would be lessened, i.e. potential contamination of water supplies. And, the problems of decommissioning fracture sites would be ameliorated if no toxic substances have been used during the useful life of the project. Conversely, if recalcitrant and toxic substances are used, these would have to be removed and treated during and after the project.

Automobile manufacturers are increasingly being called upon to design vehicles so that nothing from that vehicle finds its way to the landfill. All materials must be used up, recycled, or reused. Developing nations that are increasingly extracting, refining, and processing ores and crude must consider the problems of developed nations only a few decades ago. Many energy activities were shortsighted, extracting and processing as much as possible, believing they would simply move on to other sites. However, abandoned and active hazardous wastes sites became more widespread and more difficult to clean up. Many energy companies, if they had a chance to do it over, would likely not repeat these mistakes, given the lawsuits, public health issues, and costs in the billions of dollars, not to mention the wrath of shareholders. Many are still addressing and will continue for the foreseeable future to pay the costs legally, financially, politically, and environmentally for these dreadful decisions.

To date, air pollution science and engineering have focused mainly on emissions of pollutants during separate processes, not from a comprehensive life cycle perspective. Mining emissions were not necessarily connected to refining emissions. Indeed, the different companies doing the mining and the refining receive separate permits. The same is true for distributors of ores, crude oil, and fuel. Pipelines are regulated differently than rail, which has different requirement than trucks. Finally, operators and users of the fuel are

**TABLE 5.5** Ranking of Carbon Dioxide Emissions for the 20 Largest Emitting Countries in 2010

Country	Total CO <sub>2</sub> Emissions (million metric tons)
People's Republic of China	2,259,856
United States of America	1,481,608
India	547,811
Russian Federation	474,714
Japan	319,257
Germany	203,268
Islamic Republic of Iran	155,880
Republic of Korea	154,777
Canada	136,116
United Kingdom	134,580
Saudi Arabia	126,665
South Africa	125,477
Mexico	120,991
Indonesia	118,350
Brazil	114,468
Italy (including San Marino)	110,801
Australia	101,740
France (including Monaco)	98,520
Poland	86,516
Ukraine	83,121

Source: Boden TA, Marland G, Andres RJ. Global, regional, and national fossil-fuel CO<sub>2</sub> emissions. Oak Ridge (Tennessee, U.S.A.): Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy; 2013. [http://dx.doi.org/10.3334/CDIAC/00001\\_V2013](http://dx.doi.org/10.3334/CDIAC/00001_V2013).

regulated separately and differently than those who provide the fuel. The system is segmented not only between air, water, and other environmental media but also within the air medium. LCA is a step toward a more comprehensive and systematic approach to environmental quality and air quality specifically.

## QUESTIONS

- Where does air pollution show up in a life cycle assessment?
- What are the limiting factors on the reliability of a life cycle assessment?
- What is Chandler's inevitability thesis?
- What is the difference between an episodic event and a continuous air pollution problem?
- Three compounds are found to be leaking into the groundwater from an underground tank.

Compound A has a vapor pressure of 12 kPa and density of 1.6 g m<sup>-3</sup>. Compound B has a vapor pressure of 59 kPa and density of 0.7 g m<sup>-3</sup>. Compound C has a vapor pressure of 0.003 kPa and density of 1.1 g m<sup>-3</sup>. These values are all at 20 °C. Based on these data alone, give the order of each compound likely to be emitted to the atmosphere through the soil.

- What other properties could change this order?
- What is fugacity?
- List some of the contaminants released during coal mining.
- List some of the contaminants released during crude oil extraction.
- Describe the two aspects of environmental justice.
- Give an example of when a benefit–cost ratio is inadequate for an environmental decision.
- In the past four decades, during which types of operations have the most incidents of tanker spillage of greater than 7 tonnes occurred?
- What is the capacity factor for a 500 MW coal-fired power plant generating 2.1 million megawatt-hours in a year?
- If the same power plant above stated that they expected it to generate 4.2 million megawatt-hours next year with the same system, do you believe them? Why or why not?
- About 25,000 metric tons of 4% sulfur-content coal was burned during the deadly London smog episode of 1952. A thermal inversion occurred at about 0.15 km altitude over an area of 1200 km<sup>-2</sup>, so the mixing occurred beneath this layer. Calculate the SO<sub>2</sub> concentration contributed by coal combustion to this air column. How does this compare to current standards?
- Which nation emits the most CO<sub>2</sub>?
- What is the cause of ocean acidification?

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## P A R T   I I

# THE RISKS OF AIR POLLUTION

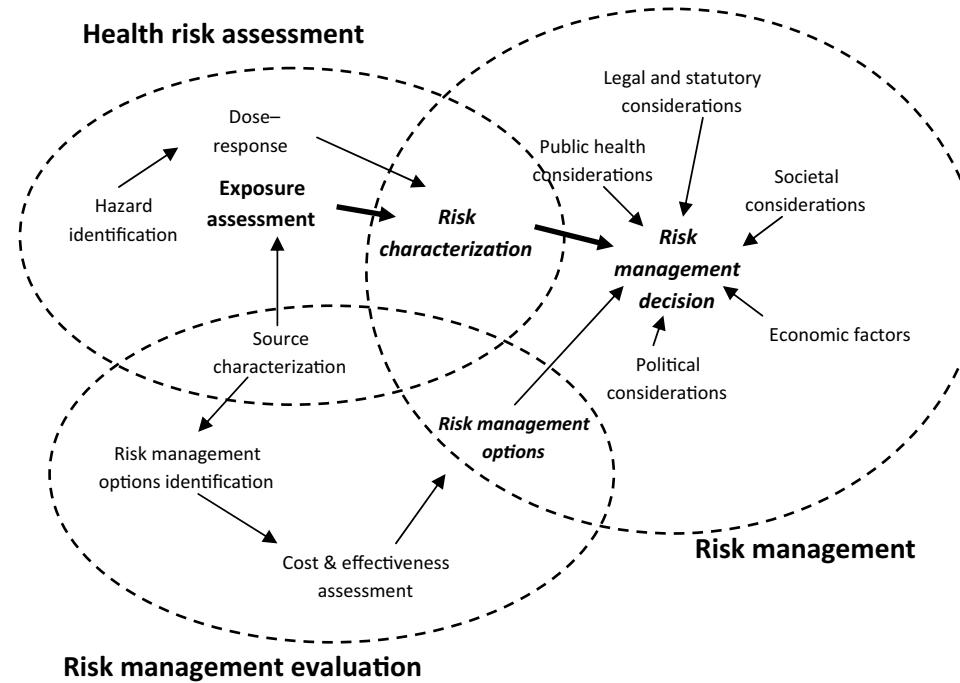
Most people have a working definition of “risk”. The term is generally used with a negative connotation, i.e. the chance that some unwelcome event will occur. In this sense, it is the opposite of “reward”, i.e. the chance of some pleasant outcome, such as designing a new air pollution technology, e.g. a scrubber to remove sulfur dioxide ( $\text{SO}_2$ ), which leads to the reward of cleaner air to breathe. Risk and reward, then, have an inverse relationship. The risk of a disease resulting from exposure to an air pollutant is ameliorated by the rewards of installing the scrubber, i.e. the reward of a healthier population results from the reduced risks that would have resulted from the exposure to  $\text{SO}_2$ .

The means of understanding which factors and the weighting of these factors that lead to a risk is known as risk analysis. The reduction of this risk (for example, by installing pollution control equipment or passing regulations that reduce ambient concentrations of an air pollutant) is risk management. Risk management is often differentiated from risk assessment, which comprises the scientific considerations of a risk. Risk management includes the policies, laws, and other societal aspects of risk.

Until the last quarter of the twentieth century, the processes for environmental risk assessment and risk management were not differentiated and almost always occurred simultaneously. The rise in discovery of hazardous waste sites like those at Love Canal in New York and Times Beach in Missouri caused the scientific community and others to question this practice. Indeed, science needed to precede decisions and decisions needed a solid scientific foundation. As the carpenter’s adage recommends, “measure twice, cut once”, reliable data and information are needed before choosing the best approach for solving a problem. As mentioned, the separation of risk assessment from risk management officially began in the late 1970s, when the proliferation of the waste sites emphasized the folly of making environmental decisions using a hodgepodge of policy, politics, finance, engineering, and technology. People living near these sites dreaded being exposed to ominous, yet often not clearly characterized, hazards. It was becoming obvious that ignoring sound science or making science acquiescent to other factors leads to poor environmental decisions. Although toxic waste sites were a primary motivation, air pollution decisions were also the target of the National Research Council’s<sup>1a,1b</sup> (NRC) recommendation that federal agencies separate the science (risk assessment) from the policy decisions (risk management). The now-familiar paradigm is depicted in [Figure II.1](#). The new paradigm was incorporated into the next amendment of the Clean Air Act (CAA) in 1990, which requires credible risk assessment approaches. As evidence, the final step of the NRC risk assessment process was referred to as “characterization” to mean that “both quantitative and qualitative elements of risk analysis, and of the scientific uncertainties in it, should be fully captured by the risk manager”.<sup>2</sup>

One of the goals of the new hazardous waste laws that were passed prior to the 1990 CAA amendments was that risk management decisions had to be based on the sound science provided by risk assessments conducted in scientifically sound ways. In the United States, these laws are the Resource Conservation and Recovery Act and the Comprehensive Environmental Response, Compensation and Liability Act (better known as Superfund). After the mid-1980s, other subsequent environmental legislation (including air and water quality, pesticides, products, and emergency response laws) in the United States and in most other countries adopted risk paradigms similar to the National Academy of Sciences (NAS) recommendations.

For several decades in the United States and numerous other nations, risk analysis has been conducted according to the chemical risk assessment paradigm formalized by the NAS in 1981. Those risks that differ from chemical risks may follow certain steps in the risk process, but may need special attention in others (e.g. rather than inducing a disease, the release of a biotechnological product



**FIGURE II.1** Risk assessment/risk management paradigm. Adapted from the Ref. 1a; and National Research Council. Science and judgment in risk assessment. Washington (DC): National Academy Press; 1994.

may upset the delicate ecological balances as a result of gene flow; or the release of greenhouse gas may cause atmospheric changes that indirectly introduce health risks due to warmer temperatures). Therefore, this book follows the general chemical risk paradigm, but highlights differences, depending on the type of pollutant.

To ascertain possible risks from air pollution, the first step is to identify a general hazard (a potential threat) and then to develop a scenario of events that could take place to unleash the potential threat and lead to an effect. To assess the importance of a given scenario, the severity of the effect and the likelihood that it will occur in that scenario are calculated. This combination of the hazard particular to that scenario constitutes the risk.

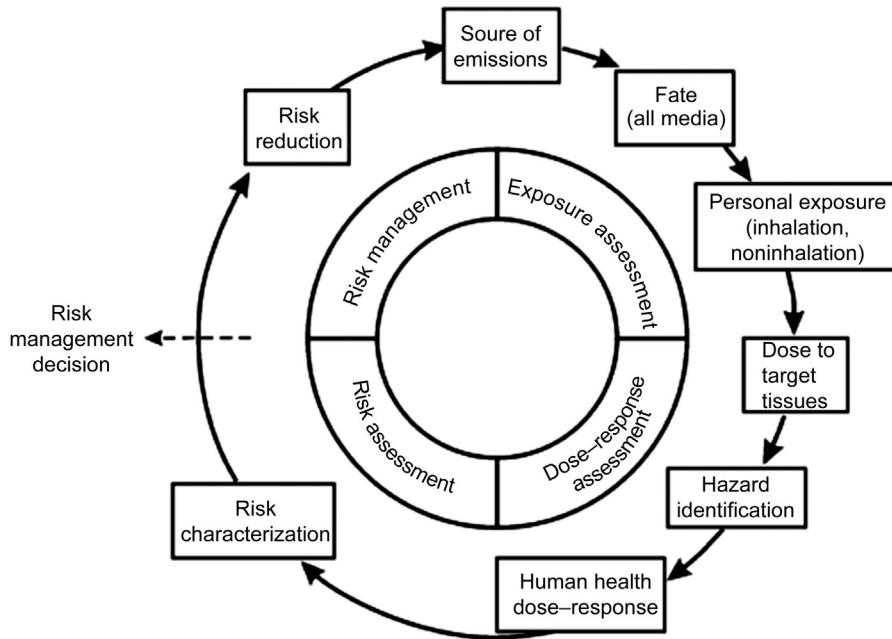
The relationship between the severity and probability of a risk follows a general equation<sup>3</sup>:

$$R = f(S, P) \quad (\text{II.1})$$

where risk ( $R$ ) is a function ( $f$ ) of the severity ( $S$ ) and the probability ( $P$ ) of harm. The risk equation can be simplified to be a product of severity and probability:

$$R = S \times P \quad (\text{II.2})$$

Equations (II.1) and (II.2) indicate that risk is expressed as a probability. Probabilities range from 0 to 1. Stated as percentage, the range is 0–100%, or from completely unlikely (impossible) to completely certain to happen. Notwithstanding the common suffix “im-” in “improbable”, an “improbable” risk, in its general connotation, a particular health or ecological risk is almost never impossible at most atmospheric concentrations, but rather is a very small probability (above zero, but very low). This is a reminder that text is often less reliable than numerical and quantitative expressions. That is why scientists state risk in engineering notation, e.g. a chemical compound that is suspected of causing cancer, i.e. a carcinogen, may have elicited the cancer in laboratory animals above a certain dose. This animal dose is then extrapolated to humans. This derived dose must account for differences between the laboratory study and human populations (e.g. differences in the animal species’ physiology and rates of absorption, distribution, metabolism, and excretion of the compound) and other uncertainties (small numbers of animals, short study time frames compared to human lifetime exposures, etc.). Then, the product of the toxic dose and the exposure will indicate the potential human population risk. This is reported as a quantitative range, e.g.



**FIGURE II.2** Risk assessment and management paradigm as employed by environmental agencies in the United States. The inner circle includes the steps recommended by the National Research Council. (NRC. *Risk assessment in the federal government*. Washington (DC): National Academy of Sciences; 1983.) The outer circle indicates the activities (research and assessment) that are currently used by regulatory agencies to meet these required steps.

$2.0 \times 10^{-5}$ – $5.0 \times 10^{-4}$ . In other words, under these conditions, the study suggests that this carcinogen will be expected to add between 0.002 and 0.04% to the population's cancer risk.

Since risk is a function of hazard and exposure, the first two chapters in this part address each individually. The term “hazard” refers exclusively to the substance of concern. It is an inherent property of the substance. Indeed, environmental scientists and engineers refer to chemical inherency of a substance or mixture (see Chapter 6). Some substances are inherently problematic, owing to their chemical and physical properties. For example, vinyl chloride causes cancer in mammals *and* has other properties, e.g. vapor pressure and lipophilicity, which add to its potential risk. The inherent properties, then, determine both how hazardous a substance can be and how likely humans and other organisms may be exposed to the substance.

Recently, scientists and regulators have viewed the process to be more cyclical than linear (see Figure II.2). Exposure and effects sciences are complementary. For example, biomarkers can indicate exposures to air pollutants long before tissue damage. Biomarkers may also indicate genetic damage (i.e. toxicogenomics), which allows for more predictive assessments. Other increasingly important risk assessment tools include computational chemistry and improved structure–activity relationships and quantitative structure–activity relationships, which have incrementally been quantified in terms of molecular structure of pollutants along with other chemical descriptions. Biomedical sciences increasingly focus on a person’s entire life, rather than the presence or absence of diseases. This medical paradigm shift provides early indicators of outcome, making it possible to shorten the time between exposure and observation of an effect.<sup>4</sup> Air pollution exposure and toxicology is rapidly changing as a result of these and other systems approaches.

The World Health Organization estimates that air pollution causes about 1.5 million premature deaths.<sup>5</sup> A recent study at Cornell University estimates that air pollution causes closer to 3 million deaths.<sup>6</sup> Each is likely an underestimate, since air pollution also contributes indirectly to many public health problems. For example, tropospheric ozone ( $O_3$ ) can greatly damage crop yields by hastening senescence and abscission of leaves, reducing stomatal aperture and thereby carbon uptake, and decreasing photosynthetic carbon fixation (see Figure II.3).<sup>7</sup> Indeed, high concentrations of  $O_3$  is presently depressing yields of crops important to global food supply (for example, average global yield reductions as high as 5.5% for corn, 14% for wheat, and 15% for soybeans). And, since

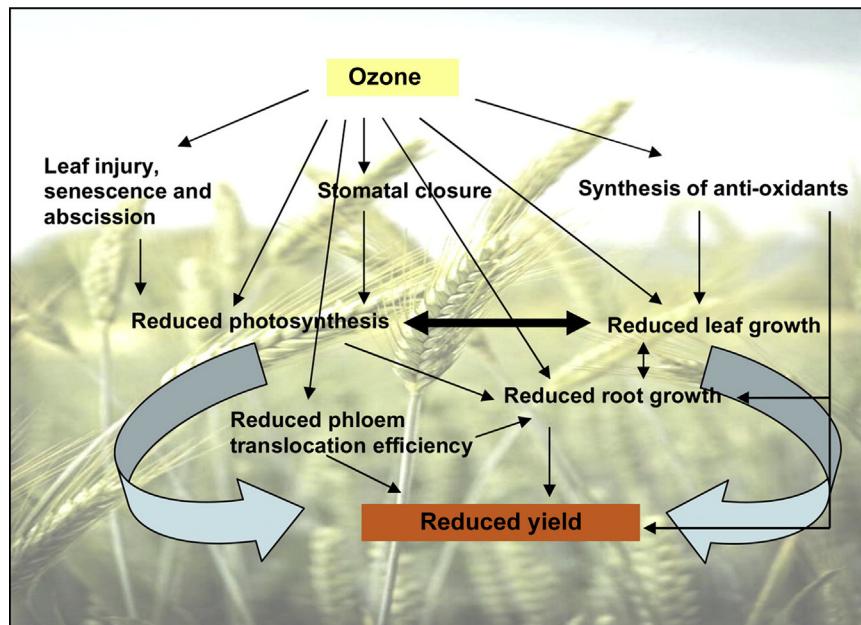


FIGURE II.3 Effects of ozone on carbon gain and carbon use that impact on crop yield. Ref. 7. (For color version of this figure, the reader is referred to the online version of this book.)

climate change may lead to emission increases of hydrocarbon and oxides of nitrogen in many areas, tropospheric O<sub>3</sub> concentrations may well increase in future decades, exacerbating the food supply stress. Ozone causes visible injury symptoms to foliage; it can moderate biomass growth via carbon availability or more directly; it can decrease translocation of fixed carbon to edible plant parts (grains, fruits, pods, and roots) due to reduced availability at the source, redirection to synthesis of chemical protectants, or reduced transport capabilities via phloem; decreased carbon transport to roots reduces nutrient and water uptake and affects anchorage; ozone can moderate or bring forward flowering and induce pollen sterility; it induces ovule and/or grain abortion; and finally it reduces the ability of some genotypes to withstand other stresses such as drought, high vapor pressure deficit, and high photon flux density via effects on stomatal control. This is doubly troubling given the predictions that atmospheric conditions conducive to drought formation will also give rise to intense precursor emission events that will become more severe over the coming decades.

Thus, Part II considers the air pollution risk from the perspective of the pollutant (i.e. the hazard) and the receptor (i.e. the exposure). This is followed by chapters addressing the prominent health effects, as well as damage to ecosystems and materials.

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# Inherent Properties of Air Pollutants

## 6.1 INHERENCY

The physical and chemical properties inherent to a molecule determine whether it is likely to be an air pollutant. The toxicity and other hazards of the molecule are also driven by these inherencies. The rates of generation, transport, transformation, and fate of an air pollutant are a function of its inherent properties. Inherent properties of a substance can be combined with the properties of the medium where it resides to estimate its fate in the environment (see Chapter 7). A distinguishing aspect of inherent properties in the environmental and biomedical sciences is that there are few “absolutes”. That is, inherent properties must always be considered with respect to the substrate, matrices, and environments where the substance resides. Hazards, exposures, and risks from an air pollutant are driven by, or at least influenced by, environmental conditions. How an air pollutant behaves in the atmosphere, in the hydrosphere, on surfaces, in tissues, and in cells is determined by physicochemical inherency and thermodynamic properties of the environment.

Inherency indicates the pollutant's potential to move and change. Inherency also gives a strong clue as a pollutant's affinity for various substrates in the environment. Thus, an air pollutant will have to have some affinity for the atmosphere for at least part of its or its precursor's existence. If a substance's properties elicit movement to the atmosphere, it is more likely to be inhaled and, thus, present a respiratory hazard and risk. However, even if a substance has little affinity for the air, its inherent properties may still cause it to become an air pollutant. For example, a substance with a low vapor pressure but high affinity to sorb to small particles would become an air pollutant as a component of aerosols.

### 6.1.1 Basic Chemical Concepts

Environmental chemistry is the discipline that concerns itself with how chemicals are formed, how they are introduced into the environment, how they change

after being introduced, the extent to which they enter and where they end up in organisms and other receptors, and the effects they have (usually the damage they do) once they get there. To cover these concepts, environmental chemistry must address the processes in effect in every environmental compartment. This is evident by the diverse subdisciplines within environmental chemistry, including atmospheric chemistry. There are even fields such as environmental physical chemistry (such as environmental photochemistry), environmental analytical chemistry (including environmental separation sciences and chromatography), and environmental chemical engineering (including fields addressing environmental thermodynamics).

When a material substance has decomposed chemically to its simplest form, it is an element, i.e. what appears on the periodic table of elements (Figure 6.1). Elements may be further broken down only by nuclear reactions, where they are released as subatomic particles. Such particles are important sources of pollution, e.g. downwind from a leaking nuclear power plant. An atom is the smallest part of an element that can enter into a chemical reaction. The molecule, which may also be an atom, is the smallest subdivision of an element that is able to exist as a natural state of matter. The nucleus of an atom, consisting of protons and neutrons (hydrogen has only one proton in its nucleus), accounts for virtually all of the atomic mass, or the atomic mass unit (amu). The term nucleon is inclusive of protons and neutrons (i.e. the particles comprising the atom's nucleus). An amu is defined as one-twelfth of the mass of carbon ( $C^{12}$ ), or  $1.66 \times 10^{-27}$  kg. The atomic weight of an element listed in most texts and handbooks is the relative atomic weight, which is the total number of nucleons in the atom. So, for example, oxygen (O) has an atomic mass of 16. The atomic number ( $Z$ ) is the number of protons in the nucleus. The chemical nomenclature for atomic weight  $A$  and number of element  $E$  is in the form:

$${}^A_Z E \quad (6.1)$$

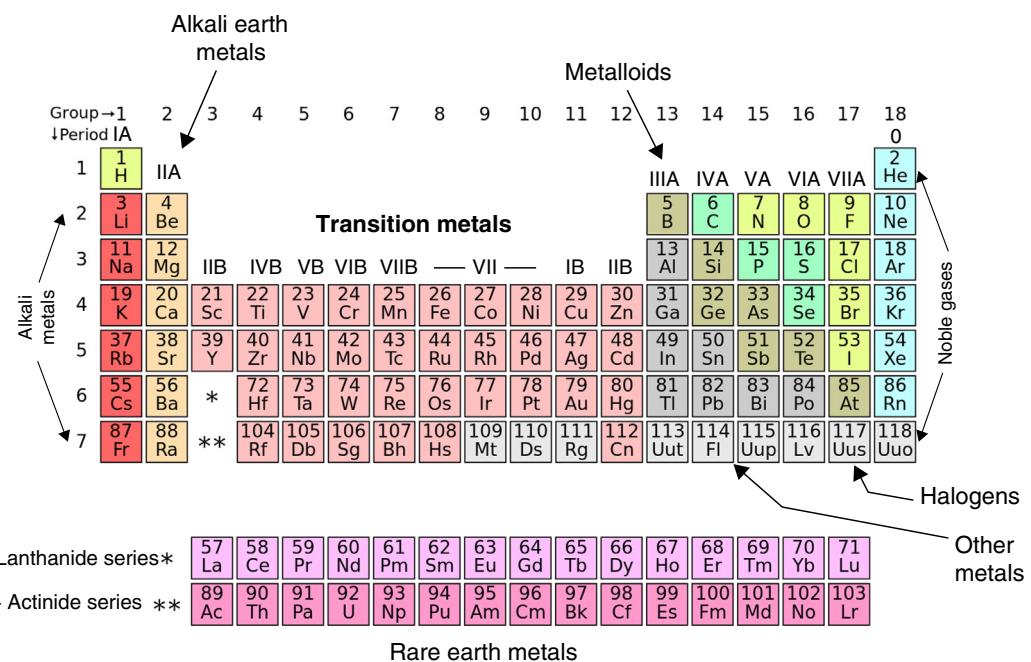


FIGURE 6.1 Periodic table of elements. (For color version of this figure, the reader is referred to the online version of this book.)

However, since an element has only one atomic number, Z is usually not shown. For example, the most stable form of carbon is seldom shown as  $^{12}\text{C}$ , and is usually indicated as  $^{12}\text{C}$ .

Elements may have different atomic weights if they have different numbers of neutrons (the number of electrons and protons of stable atoms must be the same). Elements having different atomic weights are known as *isotopes*. All atoms of a given element have the same atomic number, but atoms of a given element may contain different numbers of neutrons in the nucleus. An element may have numerous isotopes. Stable isotopes do not undergo natural radioactive decay, whereas radioactive isotopes involve spontaneous radioactive decay, as their nuclei disintegrate. This decay leads to the formation of new isotopes or new elements. The stable product of an element's radioactive decay is known as a radiogenic isotope. For example, lead (Pb; Z = 82) has four naturally occurring isotopes of different masses ( $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$ ). Only the isotope  $^{204}\text{Pb}$  is stable. The isotopes  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$  are daughter (or progeny) products from the radioactive decay of uranium (U), while  $^{208}\text{Pb}$  is a product from thorium (Th) decay. Owing to the radioactive decay, the heavier isotopes of lead will increase in abundance compared to  $^{204}\text{Pb}$ .

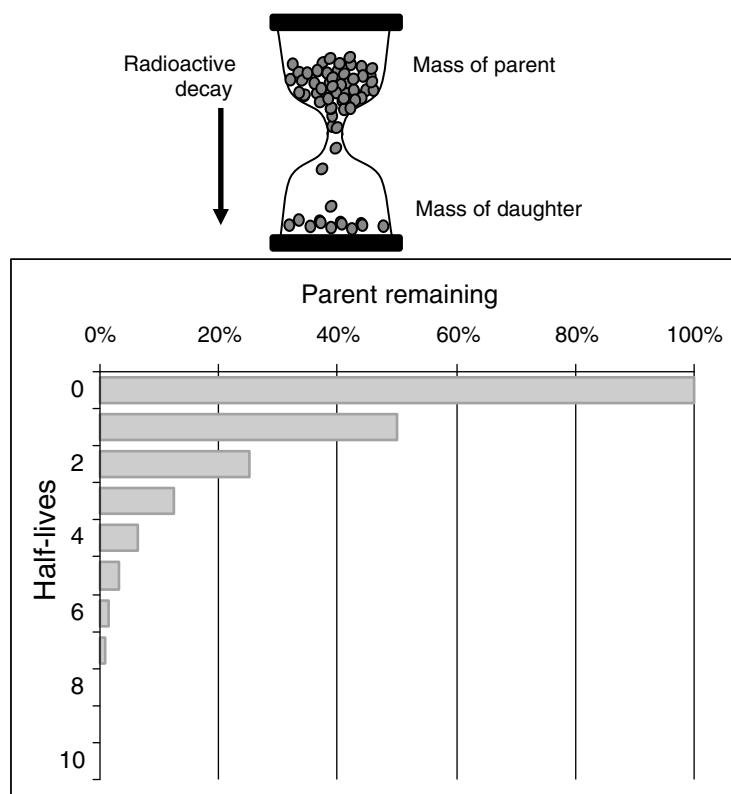
The kinds of chemical reactions for all isotopes of the same element are the same. However, the rates of reactions may vary. This can be an important factor, for example, in dating material. Such processes have been used to ascertain the sources of pollution (see Discussion Box: Carbon Dating).

Radiogenic isotopes are useful in determining the relative age of materials. The length of time necessary for the original number of atoms of a radioactive element in a rock to be reduced by half (*radioactive half-life*) can range from a few seconds to billions ( $10^9$ ) of years. Scientists use these "radioactive clocks" by the following procedure<sup>a</sup>:

1. Extracting and purifying the radioactive parent and progeny from the rock or other material.
2. Measuring variations in the masses of the parent and progeny isotopes.
3. Combining the abundances with the known rates of decay to calculate an age.

Radiogenic isotopes are commonly used as *tracers* to indicate the movement of substances through the environment. Radiogenic isotope tracer applications using Pb, strontium (Sr), and neodymium (Nd), among others make use of the fact that these are heavy isotopes, in

<sup>a</sup> US Geological Survey. *Radiogenic isotopes and the eastern mineral resources program of the US Geological Survey*; 2003.



**FIGURE 6.2 Radio-dating is a function of the radioactive decay of specific isotopes in a substance.** The hourglass analogy holds, where the number of grains of sand in the top reservoir represents the parent isotope and the sand in the bottom reservoir represents the daughter isotopes. A measurement of the ratio of the number of sand grains in the two reservoirs will give the length of time that the sand has been flowing (radioactive decay). US Geological Survey. Short-lived isotopic chronometers: a means of measuring decadal sedimentary dynamics, FS-073-98, 2003.

contrast to lighter isotopes such as hydrogen (H), oxygen (O), and sulfur (S). Heavy isotopes are relatively unaffected by changes in temperature and pressure during transport and accumulation, variations in the rates of chemical reactions, and the coexistence of different chemical species available in the environment. Chemical reactions and processes involving Pb, for example, will not discriminate among the naturally occurring isotopes of this element on the basis of atomic mass differences ( $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$ ).

Long-term monitoring data are frequently not available for environmental systems, so indirect methods, like radiogenic isotope calculations must be used. For example, in sediments, chronological scales can be determined by the distribution of radioactive isotopes in the sediment, based on the isotopes' half-lives.<sup>1</sup> The age of the sediment containing a radioactive isotope with a known half-life can be calculated by knowing the original concentration of the isotope and measuring the percentage of the remaining radioactive substance. For this process to work, the chemistry of the isotope must be understood, the half-life known,

and the initial amount of the isotope per unit substrate accurately estimated. The change in concentration of the isotope must be entirely attributable to radioactive decay. The effective range covers approximately eight half-lives. The four isotopes which presently meet these criteria ( $^{137}\text{Cs}$ ,  $^7\text{Be}$ ,  $^{14}\text{C}$ , and  $^{210}\text{Pb}$ ) are being used to measure the movement (e.g. deposition and lateral transport) for the past 150 years. The following summarizes the uses and potential uses of these four radioisotopes in dating recent sediment. This process also lends itself to differentiating sources of air pollutants (e.g. that caused by recent human activities is distinguished from that of geological or biological origins, as discussed in the box below).

The process is analogous to an hourglass (see Figure 6.2), where the number of grains of sand in the top reservoir represents the parent isotope and the sand in the bottom reservoir represents the progeny isotopes. A measurement of the ratio of the number of sand grains in the two reservoirs will give the length of time that the sand has been flowing, which represents the process of radioactive decay. For

deposited material like an aerosol deposited from the troposphere onto the soil or taken up by flora, the counting begins when the aerosol is deposited so that the carbon or other element is taken up into the

plant ( $t_0$ ), and the exchange between the water and particle ceases. As the particles and plant life are subsequently buried, the parent isotope decays to the progeny products.

### SOURCE APPORTIONMENT, RECEPTOR MODELS, AND CARBON DATING

When the results of air pollution measurements are interpreted, one of the first questions asked by scientists, engineers, and policy makers is where did it come from? Sorting out the various sources of pollution is known as *source apportionment*. A number of tools are used to try to locate the sources of pollutants. A widely used approach is the "source–receptor model" or as it is more commonly known, the *receptor model*.

Receptor models are often distinguished from the atmospheric and hydrologic dispersion models. For example, dispersion models usually start from the source and estimate the extent of mixing and the distance that the plume and its contaminants will travel. Conversely, receptor models are based on measurements taken in the ambient environment and from these observations, make use of algorithms and functions to determine pollution sources. One common approach is the mathematical "back trajectory" model. Often, chemical co-occurrences are applied. So, it may be that a certain fuel is frequently contaminated with a conservative and, hopefully, unique element. Some fuel oils, for example, contain trace amounts of the element vanadium. Since there are few other sources of vanadium in most ambient atmospheric environments, its presence is a strong indication that the burning of fuel oil is a most likely source of the plume.

The model, if constructed properly, can even quantify the contribution. So, if measurements show that sulfur dioxide ( $\text{SO}_2$ ) concentrations are found to be  $10 \mu\text{g m}^{-3}$  in an urban area, and vanadium is also found at sufficient levels to indicate home heating systems are contributing a certain amount of the  $\text{SO}_2$  to the atmosphere, the model will correlate with the amount of  $\text{SO}_2$  coming from home heating systems. If other combustion sources, e.g. cars and power plants, also have unique trace elements associated with their  $\text{SO}_2$  emissions, further  $\text{SO}_2$  source apportionment can occur, so that the total may look something like in [Table 6.1](#).

Receptor models need tracers that are sufficiently sensitive and specific to identify sources. We also mentioned that they be "conservative". This, perhaps, needs some explanation. A conservative tracer is a chemical that strongly resists chemical reactions but has transport properties similar to those of other, more reactive chemicals (i.e. the contaminant of concern). A good tracer is one that moves exactly with the fluid (i.e. the air), so if a chemical is reactive, its mass diminishes and does not allow direct interpretation of the advective movement of the plume in an air mass. A conservative tracer also makes for a sufficiently stable compound to sample from the atmosphere and to analyze it in the laboratory.

TABLE 6.1 Hypothetical Source Apportionment of Measured Sulfur Dioxide Concentrations

Source	Distance from Measurement (km)	$\text{SO}_2$ Concentration Contributed to Ambient Measurement ( $\mu\text{g m}^{-3}$ )	Percent Contribution to Measured $\text{SO}_2$
Coal-fired electric generating station	25	3.0	30
Coal-fired electric generating station	5	2.0	20
Mobile sources (cars, trucks, trains, and planes)	0–10	1.5	15
Oil refinery	30	1.5	15
Home heating (fuel oil)	0–1	1.0	10
Unknown	Not applicable	1.0	10
Total		10.0	100

## SOURCE APPORTIONMENT, RECEPTOR MODELS, AND CARBON DATING (cont'd)

Since combustion involves the oxidation of organic matter, which always contains carbon, it stands to reason that if there were a way to distinguish "old carbon" from "new carbon" this would provide a reliable means of differentiating fossil fuels from *biogenic* hydrocarbon sources (e.g. volatile organic carbons released from coniferous trees, including pinene). As the name implies, fossil fuels are made up of carbon deposited long ago and until now the carbon has been sequestered. During that time, the ratio of the isotopes of carbon has changed. So, the ratios reflect whether the carbon being measured had been first sequestered a few years ago or many thousands of years ago.

Naturally occurring radioactive carbon ( $^{14}\text{C}$ ) is present at very low concentrations in all biotic (living) matter. The  $^{14}\text{C}$  concentrations result from plants' photosynthesis of atmospheric carbon dioxide ( $\text{CO}_2$ ), which contains all of the natural isotopes of carbon. However, no  $^{14}\text{C}$  is found in fossil fuels since all of the carbon has had sufficient time to undergo radioactive decay. Studies now can take advantage of this dichotomy in ratios. For example, they can address an elusive contributor to particulate matter (PM), i.e. *biogenic* hydrocarbons. In the summer months, biogenic aerosols are formed from gas-to-particle atmospheric conversions of volatile organic compounds (VOCs) that are emitted by vegetation<sup>b</sup>. Reliable methods for estimating the contribution of biogenic sources of VOCs and PM are needed because current estimates of the importance of biogenic aerosols as contributors to total summertime PM have very large ranges (from negligible to dominant). There are large uncertainties in both the conversion mechanisms, and the amount and characteristics of biogenic VOC emissions.

Direct experimental estimates can be ascertained by measuring the quantity of  $^{14}\text{C}$  in a PM sample. The method depends on the nearly constant fraction of  $^{14}\text{C}$  relative to ordinary carbon ( $^{12}\text{C}$ ) in all living and recently living material, and its absence in fossil fuels. The fine fraction of PM (PM<sub>2.5</sub>) summertime samples are available from numerous locations in the United States, from which  $^{14}\text{C}$  measurements, can be conducted. Some recent studies have shown that the carbonaceous biogenic fraction may be contributing as much as one-half of the particles formed from VOCs.

The method for measuring and calculating the isotope ratios is straightforward. The percent of modern carbon (pMC) equals the percentage of  $^{14}\text{C}$  in a sample of unknown origin relative to that in a sample of living material, and this pMC is about equal to the percentage of

carbon in a sample that originated from nonfossil (i.e. biogenic) sources. So, for sample X:

$$\text{pMC}_x = \frac{\left(\frac{^{14}\text{C}}{^{13}\text{C}}\right)_X}{0.95 \cdot \left(\frac{^{14}\text{C}}{^{13}\text{C}}\right)_{\text{SRM4990B}}} \times 100 \quad (6.2)$$

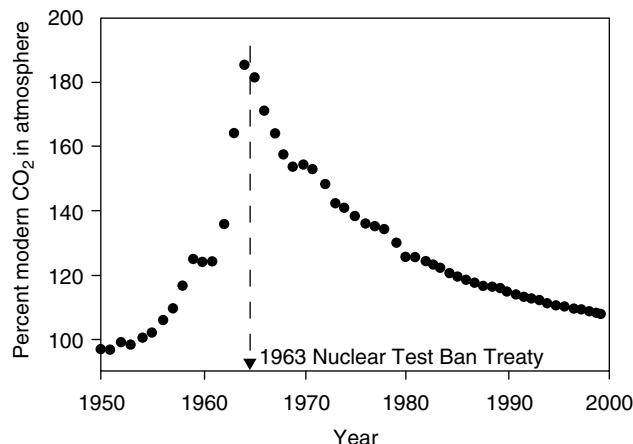
where the numerator is the ratio measured in the PM<sub>2.5</sub> sample, and the denominator is the ratio measured using the method specified by the National Institute of Standards and Testing for modern carbon.<sup>d</sup> Further:

$$\text{pMC}_{\text{Fossilfuel}} = 0 \quad (6.3)$$

Thus, for a sample X, the biogenic fraction is:

$$\% \text{Biogenic C}_x = \frac{\text{pMC}_x}{\text{pMC}_{\text{Biogenic}}} \times 100 \quad (6.4)$$

The 0.95 correction is needed to address the increase in radiocarbon due to nuclear weapons testing in the 1950s and 1960s (see Figure 6.3) and to calibrate the measurements with the standard used for radiocarbon dating



**FIGURE 6.3 Biospheric  $^{14}\text{C}$  enhancement of atmospheric modern carbon as a result of radiocarbon additions from nuclear testing and nuclear power generation.** The plot indicates the time record of  $^{14}\text{C}$  in the biosphere. The  $^{14}\text{C}$  content of northern hemisphere biomass carbon was doubled in 1963, but since the cessation of atmospheric nuclear testing, the excess  $^{14}\text{C}$  is now nearing natural, cosmic ray background levels. Fraction of modern carbon relative standard uncertainties are typically 0.5%. *National Institute of Standards and Technology. A critical evaluation of interlaboratory data on total, elemental, and isotopic carbon in the carbonaceous particle reference material, NIST SRM 1649a. 2002;107(3); and Lewis C, Klouda G, Ellenson W. Cars or trees: which contribute more to particulate matter air pollution?. Washington (DC): US Environmental Protection Agency, Science Forum; 2003.*

(Continued)

## SOURCE APPORTIONMENT, RECEPTOR MODELS, AND CARBON DATING (cont'd)

(i.e. wood from 1890).<sup>e</sup> Although the levels have dropped since the 1963 test ban treaty, they are still elevated above the pre-1950s background level.

<sup>b</sup> Lewis C, Klouda G, Ellenson W. *Cars or trees: which contribute more to particulate matter air pollution?*. Washington (DC): US Environmental Protection Agency, Science Forum; 2003.

<sup>c</sup>This is the carbon component of a fine particulate sample (PM<sub>2.5</sub>), such as those measured at ambient air monitoring stations. The ratios are calculated according to the National Bureau of Standards, Oxalic Acid Standard Reference Method SRM 4990B.

<sup>d</sup>National Bureau of Standards, Oxalic Acid Standard Reference Method SRM 4990B.

<sup>e</sup>The defined reference standard for <sup>14</sup>C is 0.95 times the <sup>14</sup>C specific activity of the original NBS Oxalic Acid Standard Reference Material (SRM 4990B), adjusted to a <sup>13</sup>C delta value of -19.09‰. This is "modern" carbon. It approximates wood grown in 1890 that was relatively free of CO<sub>2</sub> from fossil sources. Due to the anthropogenic release of radiocarbon from nuclear weapons testing and nuclear power generation, oxalic acid from plant material grown after World War II is used currently to standardize <sup>14</sup>C measurements contains more <sup>14</sup>C than 1890 wood.

### 6.1.2 Expressions of Chemical Characteristics

The gravimetric fraction of an element in a compound is the fraction by mass of the element in that compound. This is found by a gravimetric (or ultimate) analysis of the compound. The empirical formula of a compound provides the relative number of

atoms in the compound. The empirical formula is found by dividing the gravimetric fractions (percent elemental composition) by atomic weights of each element in the compound, and dividing all of the gravimetric fraction-to-atomic weight ratios by the smallest ratio.

### EMPIRICAL FORMULA DEVELOPMENT EXAMPLE

An air sampling stainless steel canister was evacuated by the local fire department and brought to the environmental laboratory for analysis. The person who brought in the sample said that the sample was taken near a site where a rusty 55-gallon drum was found by some children in creek near their school. The children and neighbors reported an unpleasant smell near the site where the drum was found.

The gravimetric analysis of the gas in the canister indicated the following elemental compositions:

Carbon: 40.0%  
Hydrogen: 6.7%  
Oxygen: 53.3%

#### Solution

First, divide the elemental percentage compositions by the respective atomic weights:

$$\text{C : } \frac{40.0}{12} = 3.3$$

$$\text{H : } \frac{6.7}{1} = 6.7$$

$$\text{O : } \frac{53.3}{16} = 3.3$$

Next, divide every ratio by the smallest ratio (3.3):

$$\text{C : } \frac{3.3}{3.3} = 1$$

$$\text{H : } \frac{6.7}{3.3} = 2$$

$$\text{O : } \frac{3.3}{3.3} = 1$$

So, the empirical formula is CH<sub>2</sub>O or HCHO. This is formaldehyde, a toxic substance.

#### Preliminary Interpretation

The challenge of formaldehyde, however, is that it comes from many sources, including emissions from factories and automobiles, and even natural sources. However, since the drum seems to be a likely source, the liquid contents should be analyzed (and a search for additional drums should begin immediately—the illegal dumping often is not limited to a single unit).

The first likelihood is that the liquid is formalin, a mixture that contains formaldehyde. The high vapor pressure of the formaldehyde may be causing it to leave the solution and move into the air.

Since children are in the area and there may be a relatively large amount of the substance, steps must be taken to prevent exposures and to remove the formaldehyde immediately.

### 6.1.2.1 The Periodic Table

The periodic table (Figure 6.1) follows the periodic law, which states that the properties of elements depend on the atomic structure and vary systematically according to atomic number. The elements in the table are arranged according to increasing atomic numbers from left to right.

An element shares many physicochemical properties with its vertical neighbors, but differs markedly from its horizontal neighbors. For example, oxygen (O) will chemically bind and react similarly to sulfur (S) and selenium (Se), but behaves very differently from nitrogen (N) and fluorine (F). Elements in the horizontal rows, known as periods, grow increasingly different with the distance moved to the left or right. So, O differs physically and chemically more from boron (B) than O does from F, and O is a very different from lithium (e.g. O is a nonmetal and Li is a light metal).

The groups (vertical columns) are designated by numerals (often Roman numerals). For example, O is a group VIA element and gold (Au) is in group IB. The A and B designations are elemental families. Elements within families share many common characteristics. Within families, elements with increasing atomic weights become more metallic in their properties.

Metals (elements to the left of the periodic table) form positive ions (*cations*), are reducing agents, have low electron affinities, and have positive valences (oxidation numbers). Nonmetals (on the right side of the periodic table) form negative ions (*anions*), are oxidizing agents, have high electron affinities, and have negative valences. Metalloids have properties of both the metals and nonmetals. However, two environmentally important metalloids, arsenic (As) and antimony (Sb) are often addressed as heavy metals in terms of fate, transport, treatment and control technologies, and toxicity.

Some common periodic table chemical categories are:

- *Metals*: Every element except the nonmetals
- *Heavy metals*: Metals near the center of the table
- *Light metals*: Groups I and II
- *Alkaline earth metals*: Group IIA
- *Alkali metals*: Group IA
- *Transition metals*: All Group VIII and B families
- *Actinons*: Elements 90–102
- *Rare earths*: Lanthanons (Lanthanides), Elements 58–71
- *Metalloids*: Elements separating metals and nonmetals, Elements 5, 14, 32, 33, 51, 52, and 84

- *Nonmetals*: Elements 2, 5–10, 14–18, 33–36, 52–54, 85, and 86
- *Halogens*: Group VIIA
- *Noble gases*: Inert elements, Group 0

Every element in the table has environmental relevance. In fact, at some concentration, every element except those generated artificially by fission in nuclear reactors is found in the environment, especially in soils, in varying concentrations. Thus, it would be absurd to think of how to “eliminate” them. This is a common misconception, especially with regard to heavy metal and metalloid contamination. For example, mercury (Hg) and lead (Pb) are known to be important contaminants that cause neurotoxic and other human health effects and environmental pollution. However, the global mass balance of these metals does not change, only their locations and forms (i.e. *speciation*). So, protecting health and ecological resources is a matter of decreasing and eliminating exposures and changing the form of the compounds of these elements so that they are less mobile and less toxic. The first place to potential air pollutants is to consider the oxidation states, or valence, of elements.

### 6.1.3 Electromagnetic Radiation, Electron Density, Orbitals, and Valence

According to quantum mechanics, the energy of a photon of light can cause an electron to change its energy state, so that the electron is disturbed from its original state. *Electromagnetic radiation* (EMR) is related to atomic structure. Much that is known about atomic structure, especially an atom's arrangement of electrons around its nucleus, is from what scientists have learned about the relationship between matter and different types of EMR. One principle is that EMR has properties of both a *particle* and a *wave*. Particles have a definite mass and occupy space (i.e. they conform to the classic description of matter). Waves have no mass but hold energy with them as they travel through space. Waves have four principle characteristics, i.e. speed ( $v$ ), frequency ( $\nu$ ), wavelength ( $\lambda$ ), and amplitude. These are demonstrated in Figure 6.4.

Measuring  $\nu$  in cycles per second (hertz, Hz) and  $\lambda$  in meters, the product gives the velocity of the wave moving through space:

$$v = \nu\lambda \quad (6.5)$$

For example, if a certain light's  $\lambda$  is  $10^{-7}$  m and its  $\nu$  is  $10^{15}$  Hz, then the velocity of that light is  $10^8$  m s<sup>-1</sup>.

## ELECTROMAGNETIC RADIATION

Most of the time, when someone mentions the term “environmental contaminant”, it calls to mind some chemical compound. However, contaminants may also come in the form of biological or physical agents. Biological contaminants may be pathogenic bacteria or viruses that adversely affect health, or introduced species (e.g. the zebra mussel or kudzu) that harm ecosystems. Physical agents are often the least likely to come to mind. A common physical contaminant is energy. Life depends on energy, but like most resources, when it comes in the wrong form and quantity, it may be harmful. EMR is comprised of wave functions that are propagated by simultaneous periodic variations in electrical and magnetic field intensities (see [Figure 6.3](#)). Natural and many anthropogenic sources produce EMR energy in the form of waves, which are oscillating energy fields that can interact with an organism’s cells. The waves are described according to their wavelength and frequency, and the energy that they produce.

Wave frequency is the number of oscillations that passes a fixed point per unit of time, measured in cycles per second (cps). 1 cps = 1 hertz (Hz). Thus, the shorter the wavelength, the higher is the frequency. For example, the middle of the amplitude modulated radio broadcast band has a frequency of one million hertz (i.e. 1 megahertz = 1 MHz) and a wavelength of about 300 m. Microwave ovens use a frequency of about 2.5 billion hertz (i.e. 2.5 GHz) and a wavelength of 12 cm. So, the microwave, with its shorter wavelength has a much higher frequency.

An EMR wave is made of tiny packets of energy called photons. The energy in each photon is directly proportional to the frequency of the wave. So the higher the frequency, the more energy there will be in each photon. Biological tissue and cellular material is affected in part by the intensity of the field and partly by quantity of energy in each photon.<sup>f</sup>

At low frequencies EMR waves are known as electromagnetic fields and at high frequencies EMR waves are referred to as electromagnetic radiations. Also, the frequency and energy determines whether an EMR will be ionizing or nonionizing radiation. Ionizing radiation consists of high frequency electromagnetic waves (e.g. X-rays and gamma rays), having sufficient photon energy to produce ionization (producing positive and negative electrically charged atoms or parts of molecules) by breaking bonds of molecules. The general term nonionizing radiation is for the portion of the electromagnetic spectrum where photon energies are not strong enough to break atomic bonds. This segment of the spectrum includes ultraviolet (UV) radiation, visible light, infrared radiation, radio waves, and microwaves, along with static electrical and magnetic fields. Even at high intensities, nonionizing radiation cannot

ionize atoms in biological systems, but such radiation has been associated with other effects, such as cellular heating, changes in chemical reactions and rates, and the induction of electrical currents within and between cells.

Of course, not every EMR effect causes harm to an organism; such as when a mammal may respond to EMR by increasing blood flow in the skin in response to slightly greater heating from the sun. Life as we know it depends on various EMR wavelengths and frequencies, including the conversion of visible and UV wavelengths to infrared by the earth’s surface which warms the planet. Photosynthesis depends on the incoming light. EMR also induces positive health effects, such as the sun’s role in helping the body to produce vitamin D. Unfortunately, certain direct or indirect responses to EMR may lead to adverse effects, including skin cancer.

The data supporting UV as a contaminant are stronger than those associated with more subtle fears that sources, like high-energy power transmission lines and cell phones, may be producing health effects. The World Health Organization (WHO) is addressing the health concerns raised about exposure to radio frequency (RF) and microwave fields, intermediate frequencies (IF), extremely low frequency (ELF) fields, and static electric and magnetic fields. IF and RF fields produce heating and the induction of electrical currents; so it is highly plausible that this is occurring to some extent in cells exposed to IF and RF fields. Fields at frequencies above about 1 MHz primarily cause heating by transporting ions and water molecules through a medium. Even very low energy levels generate a small amount of heat, but this heat is carried away by the body’s normal thermoregulatory processes. However, some studies indicate that exposure to fields too weak to cause heating may still produce adverse health consequences, including cancer and neurological disorders (i.e. memory loss).

Since, electrical currents already exist in the body as a normal part of the biochemical reactions and metabolic process, the fear is that additional energy from electromagnetic fields could induce sufficiently high currents to overload the system and engender adverse biological effects.

ELF electric fields exist when a charge is generated, but almost none of the electric field penetrates into the human body. At very high field strengths they can feel like one’s skin is “crawling” or their hair is raised. Some studies, however, have associated low-level ELF electric fields with elevated incidence of childhood cancer or other diseases, whereas other studies have not been able to establish a relationship. The WHO is recommending that more focused research be conducted to improve health risk assessments. ELF magnetic fields also exist whenever an electric current is flowing. However, unlike the ELF

## ELECTROMAGNETIC RADIATION (cont'd)

electric fields, magnetic fields readily penetrate an organism's tissue with virtually no attenuation. Again the epidemiology is mixed, with some studies associating ELF fields with cancer, especially in children, and others finding no such association.

The primary action in biological systems by these static electrical and magnetic fields is by inducing electrical and magnetic energy. However, there is a paucity of reliable data to come to any conclusions about chronic effects associated with long-term exposure to static magnetic fields at levels found in the working environment.

The challenge of EMR is similar to that of chemical contamination. The exposure and risks associated with this hazard is highly uncertain. The key decision is

whether sufficient scientific evidence exists to encourage limits on certain types of activities (either as an individual choice or regulated by a public agency) where adverse effects may be occurring. Almost anywhere in the world, one can observe a number of people using cell phones. Many neighborhoods have visible overhead power lines. EMR sources are ubiquitous. The challenge is deciding what level of evidence linking EMR to adverse effects would be sufficient to require actions to protect public health.

<sup>f</sup>Photons are also extremely important in air pollutant transformation, since many contaminants and free radicals in the atmosphere owe their existence, at least in part, to photochemical reactions. Like other mechanisms, photochemical reactions are also beneficial, such as in photosynthesis, endogenous process (e.g. vitamin D formation), and the formation of the ozone layer in the stratosphere.

Quantum mechanics is the basis for numerous chemical analyses (e.g. mass spectrometry) of air pollutants. An atom's electrons occupy orbitals where the electrons contain various amounts of energy. Electrons vary in the spatial orientations and average distances from the nucleus, so that electrons occupying inner orbitals are closer to the nucleus (see Figure 6.5). The electron's velocity or position changes. If we can measure the electron's position we will not know its velocity, and if we measure the electron's velocity, we will not be able to know its position. We are uncertain about the electron's simultaneous position and velocity. This is the basis for the Heisenberg Uncertainty Principle, which states that the more that is

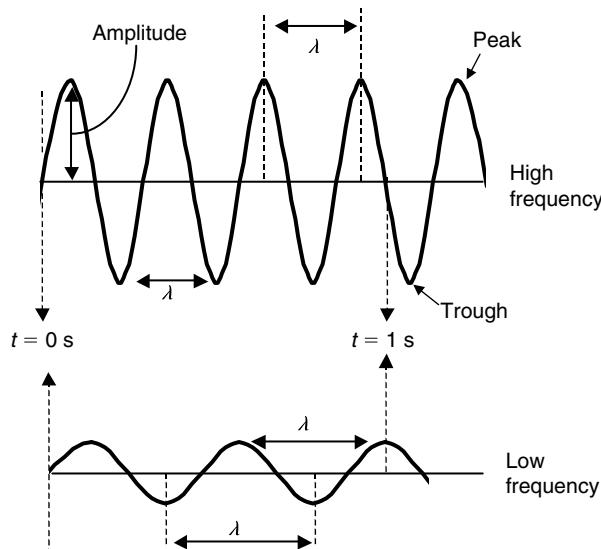


FIGURE 6.4 EMR. The amplitude of the wave in the top chart is higher than that in lower chart. The bottom wave is 2.5 cycles per seconds (2.5 Hz). The top wave is 3.5 Hz, so the bottom wave has a 1 Hz lower frequency and emits less energy than the top wave.

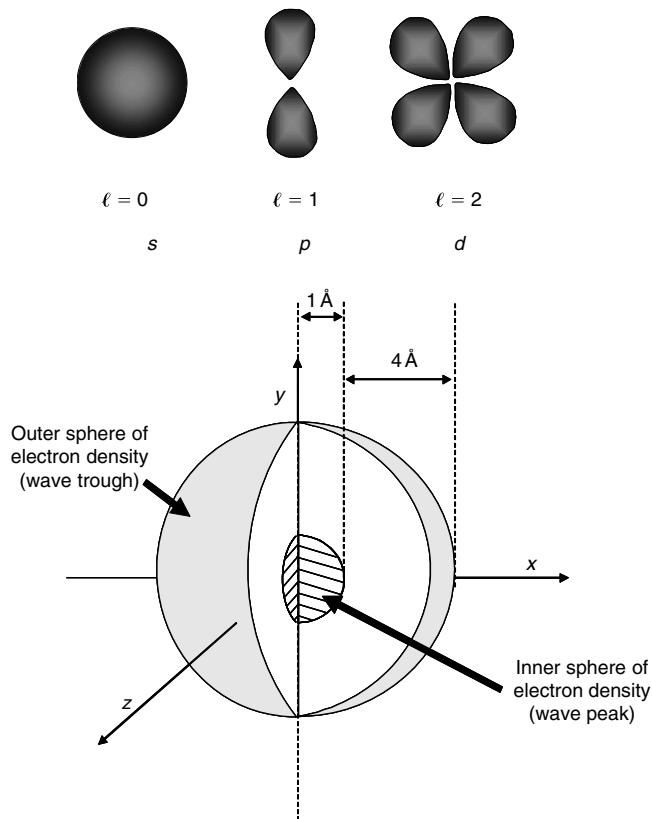


FIGURE 6.5 Two-dimensional orbital shapes, showing three angular quantum numbers ( $\ell$ ) and subshells  $s$ ,  $p$ , and  $d$  (top). The three-dimensional 2s orbital (bottom) is shown as a cutaway view into the atom, the peak (inner sphere) and trough (outer concentric sphere) of the electron wave. The orbital is two concentric spheres of electron densities. Adapted from Loudon G. Organic Chemistry. 3rd ed. Redwood City (CA): Benjamin/Cummings Publishing Company, Inc.; 1995.

known about the electron's position, the less that can be known about its velocity. Further, to keep an electron from escaping from an atom, the electron must maintain a minimum velocity, which corresponds back to the uncertainty of the electron's position in the atom. Since, the uncertainty of the position is actually the whole atom, i.e. the electron can be anywhere in the atom, chemists refer to an electron as a "cloud of electron density" within the atom rather than describing an electron as a finite particle. So, the electron orbitals are envisioned as regions in space where the electrons are statistically most likely to be located. We do not know where an electron is, but we know where it might be; that is, somewhere in the electron cloud.<sup>g</sup>

The Schrödinger model applies three coordinates to locate electrons, known as quantum numbers. The coordinates are principal ( $n$ ), angular ( $l$ ), and magnetic ( $m_l$ ) quantum numbers. These characterize the shape, size, and orientation of the electron cloud orbitals of the atom. The principal quantum number  $n$  gives the size of the orbital. A relative size of  $n = 2$  is larger than a cloud with the size  $n = 1$ . Energy is needed to excite an electron to make it move from a position closer to the nucleus (e.g.  $n = 1$ ) to a position further from the nucleus ( $n = 2, 3$ , or higher). So,  $n$  is an indirect expression of an orbital's energy level.

The angular quantum number  $l$  maps the shape of the cloud. A spherical orbital has an  $l = 0$ . Polar shaped orbitals have  $l = 1$ . Cloverleaf orbitals have  $l = 2$ . See [Figure 6.4](#) for renderings of these shapes. The magnetic quantum number  $m_l$  describes the orientation of the orbital in space. Orbitals with the same value of  $n$  form a shell. Within a shell, orbitals are divided into subshells labeled by their  $l$  value. The commonly used two-character description of shells (e.g.  $2p$  or  $3d$ ) exemplifies the shell and subshell. For example,  $2p$  indicates the shell ( $n = 2$ ) and the subshell ( $p$ ). Subshells are indicated by:

- $s: l = 0$
- $p: l = 1$
- $d: l = 2$
- $f: l = 3$
- $g: l = 4$
- $h: l = 5$

The number of subshells in any shell will equal the  $n$  for the shell. So, for example, the  $n = 2$  shell contains two subshells (i.e.  $2s$  and  $2p$ ) and  $n = 5$  shell contains five subshells (i.e.  $5s$ ,  $5p$ ,  $5d$ ,  $5f$ , and  $5g$  orbitals).

The electrons occupying the outermost shell are known as valence electrons. Valence is the number of bonds that an

element can form, which is related to number of electrons in the outermost shell. The arrangement of the electrons in the outermost (i.e. valence) band determines the ultimate chemical behavior of the atom. The outer electrons become involved in transfer to and sharing with shells in other atoms, i.e. forming new compounds and ions. Note that the number of valence electrons in an "A" group in the periodic table (except helium, whose shell is filled with 2) is equal to the group number. So, sodium (Na), a Group 1A element, has one valence electron. Carbon (C) is a Group 4A compound, so it has four valence electrons. Chlorine (Cl), fluorine (F), and the other halogens of Group 7A have seven valence electrons. The noble gases, except He, in Group 8A, have eight valence electrons.

The noble gases are actually the only elements that exist as individual atoms, because the noble gases have no valence electrons. Conversely, carbon has four electrons in its outermost shell, so it has just as many electrons to gain or to lose (i.e. 4 is just as close to 8, for a newly filled shell, as it is to 0, for the loss of a shell), so there are many ways for it to reach chemical stability. This is one of the reasons that so many subtly, but profoundly different carbon-based compounds, i.e. organic compounds, are in existence. Most atoms combine by chemical bonding to other atoms, creating molecules.

Thus, the outermost electrons explain how readily an element will engage in a chemical reaction and the type of reaction that will occur. The oxidation number is the electrical charge assigned to an atom. The sum of the oxidation numbers is equal to the net charge. [Table 6.2](#) shows the oxidation numbers of certain atoms that form contaminants and nutrients in the environment. [Table 6.3](#) gives the oxidation numbers for environmentally important radicals, i.e. groups of atoms that combine and behave as a single chemical unit. An atom will gain or lose valence electrons to form a stable ion that has the same number of electrons as the noble gas nearest the atom's atomic number. For example, Na with a single valence electron and a total of 11 electrons, will tend to lose an electron to form  $\text{Na}^+$ , the sodium cation. This ion has the same number of electrons (eight) as the nearest noble gas, neon (Ne). Fluorine, with 7 valence electrons and 9 total electrons, tends to gain (accept) an electron to form a 10-electron fluorine anion,  $\text{F}^-$  that, like the sodium ion, has the same number of electrons as Ne (eight).

Noble gases have an octet (i.e. group of eight) of electrons in their valence shells, meaning that the tendency of an atom to gain or to lose its valence electrons to form ions in the noble gas arrangement is called the "octet rule".<sup>h</sup>

<sup>g</sup> Note that this configuration is very different from the popular depiction of an atom, which is still shown even in the logos of nuclear agencies and warning labels. This depiction is the Rutherford atom, after Ernest Rutherford direction of the work by Hans Geiger and Ernest Madsen. The model was refined by Niels Bohr using quantum theory to visualize the electron cloud.

<sup>h</sup> Obviously, for the atoms near He, it is the "duet rule".

**TABLE 6.2** Oxidation Numbers for Atoms Important to Air Pollution

Atom	Chemical Symbol	Oxidation Number(s)
Aluminum	Al	+3
Antimony	Sb	-3, +3, +5
Arsenic	As	-3, 0, +3, +5
Barium	Ba	+2
Boron	B	+3
Calcium	Ca	+2
Carbon	C	+2, +3, +4, -4
Chlorine	Cl	-1
Chromium	Cr	+2, +3, +6
Cobalt	Co	+2, +3
Copper	Cu	+1, +2
Fluorine	F	-1
Gold	Au	+1, +3
Hydrogen	H	+1
Iron	Fe	+2, +3
Lead	Pb	0, +2, +4
Lithium	Li	+1
Magnesium	Mg	+2
Manganese	Mn	+2, +3, +4, +6, +7
Mercury	Hg	0, +1, +2
Nickel	Ni	+2, +3
Nitrogen	N	-3, +2, +3, +4, +5
Oxygen	O	-2
Phosphorus	P	-3, +3, +5
Plutonium	Pu	+3, +4, +5, +6
Potassium	K	+1
Radium	Ra	+2
Radon	Rn	0 (Noble gas)
Selenium	Se	-2, +4, +6
Silver	Ag	+1
Sodium	Na	+1
Sulfur	S	-2, +4, +6
Tin	Sn	+2, +4
Uranium	U	+3, +4, +5, +6
Zinc	Zn	+2

**TABLE 6.3** Oxidation Numbers for Radicals Important to Air Pollution

Radical	Chemical Symbol	Oxidation Number(s)
Acetate	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	-1
Acrylate	CHCO <sub>2</sub>	-1
Ammonium	NH <sub>4</sub>	+1
Bicarbonate	HCO <sub>3</sub>	-1
Borate	BO <sub>3</sub>	-3
Carbonate	CO <sub>3</sub>	-2
Chlorate	ClO <sub>3</sub>	-1
Chlorite	ClO <sub>2</sub>	-1
Chromate	CrO <sub>4</sub>	-2
Cyanide	CN	-1
Dichromate	Cr <sub>2</sub> O <sub>7</sub>	-2
Hydroperoxide	HO <sub>2</sub>	-1
Hydroxide	OH	-1
Hypochlorite	ClO	-1
Nitrate	NO <sub>3</sub>	-1
Nitrite	NO <sub>2</sub>	-1
Perchlorate	ClO <sub>4</sub>	-1
Permanganate	MnO <sub>4</sub>	-1
Phosphate	PO <sub>4</sub>	-3
Sulfate	SO <sub>4</sub>	-2
Sulfite	SO <sub>3</sub>	-2
Thiocyanate	SCN	-1
Thiosulfate	S <sub>2</sub> O <sub>3</sub>	-2

Chemical species of atoms are particularly stable when their outermost shells contain eight electrons.

Elements combine to form compounds. Two-element compounds are known as binary compounds. Three-element compounds are ternary or tertiary compounds. The representation of the relative numbers of each element is a chemical formula. Compounds are formed according to the law of definite proportions. That is, a pure compound must always be composed of the same elements that are always combined in a definite proportion by mass. Also, compounds form in accordance with the law of multiple proportions, which states that when two elements combine to make more than one compound, the combining mass of each element must always exist as small integer ratios to one another. The sum of all oxidation numbers must equal zero in a stable, neutral compound. The simplest example is water. Oxygen's -2 valence is balanced by the two hydrogen's +1 valences.

## COMPOUND FORMATION EXAMPLE

Is  $\text{PbC}_2\text{H}_3\text{O}_2$  a valid compound?

### Answer

Consulting Tables 6.2 and 6.3, we find that lead (Pb) has two common oxidation numbers (+2 and +4), and that acetate ( $\text{C}_2\text{H}_3\text{O}_2$ ) has an oxidation number of -1, so the molecular formula given is *not* valid.

Lead acetate is  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ . Two atoms of acetate are needed to balance the +2 valence of Pb. The molecule is

often called lead (II) acetate to show that in this instance it is the “divalent” form of lead that has reacted with the acetate radical. Incidentally, lead (II) compounds are suspected human carcinogens, based on experiments conducted on laboratory animals. Lead acetate is also very acutely toxic and may be fatal if swallowed, and is harmful if inhaled or absorbed through the skin. Like other lead compounds, long-term exposure may harm the central nervous system, blood, and gastrointestinal tract.

### 6.1.3.1 Physicochemical Processes in the Formation of Air Toxics

Atoms and molecules combine in many ways, according to the reactions described in this chapter. Let us consider some of the important processes under which selective toxic compounds are formed.

#### 6.1.3.1.1 COMBUSTION REACTIONS

Dioxins and furans are important air pollutants. Dioxin formation is illustrative of the complex set of combustion reactions that can generate toxic air pollutants. Chlorinated dioxins have 75 different forms and there are 135 different chlorinated furans, simply by different number and arrangement of chlorine atoms in the molecules. The compounds can be separated

into groups that have the same number of chlorine atoms attached to the furan or dioxin ring. Each form varies in its chemical, physical, and toxicological characteristics (see Figure 6.6).

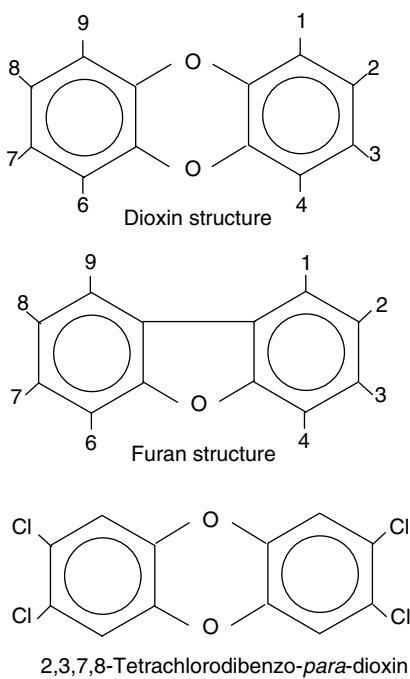
Dioxins are highly toxic compounds that are created unintentionally during combustion processes. The most toxic form is the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) isomer. Other isomers with the 2,3,7,8 configuration are also considered to have higher toxicity than the dioxins and furans with different chlorine atom arrangements (see Table 6.4).

What is currently known about the conditions needed to form these compounds has been derived from studying full-scale municipal solid waste incinerators, and the experimental combustion of fuels and feeds in the

**TABLE 6.4** De Novo Formation of Chlorinated Dioxins and Furans after Heating Mg-Al Silicate, 4% Charcoal, 7% Cl, 1%  $\text{CuCl}_2 \cdot \text{H}_2\text{O}$  at 300 °C

Compound	Concentrations (ng g <sup>-1</sup> )				
	0.25	0.5	1	2	4
Tetrachlorodioxin	2	4	14	30	100
Pentachlorodioxin	110	120	250	490	820
Hexachlorodioxin	730	780	1600	2200	3800
Heptachlorodioxin	1700	1840	3500	4100	6300
Octachlorodioxin	800	1000	2000	2250	6000
Total chlorinated dioxins	3342	3744	7364	9070	17,020
Tetrachlorofuran	240	280	670	1170	1960
Pentachlorofuran	1360	1670	3720	5550	8300
Hexachlorofuran	2500	3350	6240	8900	14,000
Heptachlorofuran	3000	3600	5500	6700	9800
Octachlorofuran	1260	1450	1840	1840	4330
Total chlorinated furans	8360	10,350	17,970	24,160	38,390

Source: Stieglitz L, Zwick G, Beck J, Bautz H, Roth W. Chemosphere 1989;19:283.



**FIGURE 6.6 Molecular structures of dioxins and furans.** Bottom structure is of the most toxic dioxin congener, tetrachlorodibenzo-*p*-dioxin (TCDD), formed by the substitution of chlorine for hydrogen atoms at positions 2, 3, 7, and 8 on the molecule. The toxic forms of dioxins and furans often are chlorinated, but may also include other halogen substitutions, especially bromine.

laboratory. Most of the chemical and physical mechanisms identified by these studies can relate to combustion systems in which organic substances combusted in the presence of chlorine (Cl). Incinerators of chlorinated wastes are the most common environmental sources of dioxins, accounting for about 95% of the volume.

The emission of dioxins and furans from combustion processes may follow three general physicochemical pathways. The first pathway occurs when the feed material going to the incinerator contains dioxins and/or furans and a fraction of these compounds survives thermal breakdown mechanisms, and pass through to be emitted from vents or stacks. This is not considered to account for a large volume of dioxin released to the environment, but it may account for the production of dioxin-like, coplanar polychlorinated biphenyls (PCBs).

The second process is the formation of dioxins and furans from the thermal breakdown and molecular rearrangement of precursor compounds, such as the chlorinated benzenes, chlorinated phenols (such as pentachlorophenol), and PCBs, which are chlorinated aromatic compounds with structural resemblances to the chlorinated dioxin and furan molecules. Dioxins appear to form after the precursor has condensed and adsorbed onto the surface of particles, such as fly ash.

This is a heterogeneous process, where the active sorption sites on the particles allow for the chemical reactions, which are catalyzed by the presence of inorganic chloride compounds and ions sorbed to the particle surface. The process occurs within the temperature range, 250–450 °C, so most of the dioxin formation under the precursor mechanism occurs away from the high-temperature zone in the incinerator, where the gases and smoke derived from combustion of the organic materials have cooled during conduction through flue ducts, heat exchanger and boiler tubes, air pollution control equipment or the vents and the stack.

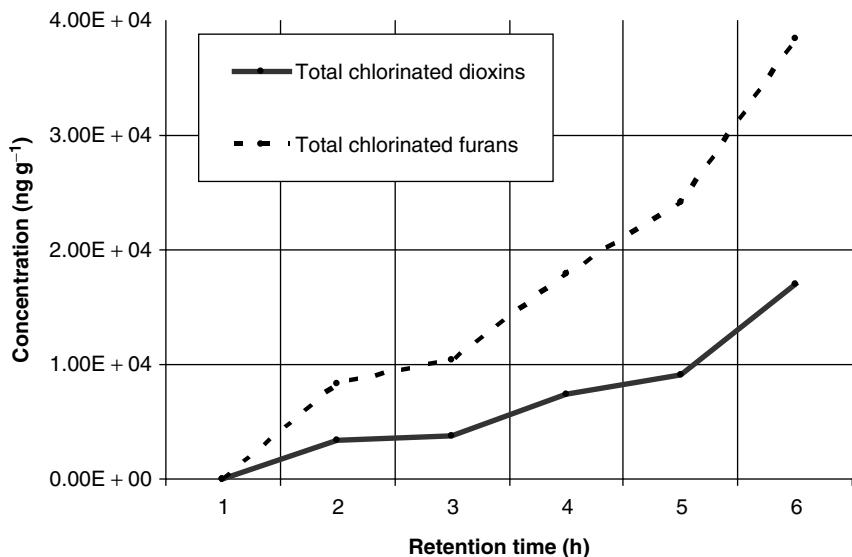
The third means of synthesizing dioxins is *de novo* within the so-called “cool zone” of the incinerator, wherein dioxins are formed from moieties different from those of the molecular structure of dioxins, furans, or precursor compounds. Generally, these can include a wide range of both halogenated compounds like polyvinyl chloride (PVC), and nonhalogenated organic compounds like petroleum products, nonchlorinated plastics (polystyrene), cellulose, lignin, coke, coal, and inorganic compounds like particulate carbon, and hydrogen chloride gas. No matter which *de novo* compounds are involved, however, the process needs a chlorine donor (a molecule that “donates” a chlorine atom to the precursor molecule). This leads to the formation and chlorination of a chemical intermediate that is a precursor. The reaction steps after this precursor is formed can be identical to the precursor mechanism discussed in the previous paragraph.

*De novo* formation of dioxins and furans may involve even more fundamental substances than those moieties mentioned above. For example, dioxins may be generated<sup>i</sup> by heating of carbon particles absorbed with mixtures of magnesium–aluminum silicate complexes when the catalyst copper chloride (CuCl<sub>2</sub>) is present (see Table 6.4 and Figure 6.7). The *de novo* formation of chlorinated dioxins and furans from the oxidation of carbonaceous particles seems to occur at around 300 °C. Other chlorinated benzenes, chlorinated biphenyls, and chlorinated naphthalene compounds are also generated by this type of mechanism.

The three processes that lead to the formation of dioxins and furans are also found in the formation of numerous other air pollutants by thermal mechanisms. Thus, air pollution engineers must take care to ensure that conditions in reactors, stacks, and other processes are not generating byproducts that will be released. Indeed, pollution control equipment itself may create conditions that would otherwise not generate these pollutants, e.g. injection of sorbing materials, ignorance of precursor compounds in carrier air, and operating temperatures in regions of the equipment that induce

<sup>i</sup>Stieglitz L, Zwick G, Beck J, Bautz H, Roth W. *Chemosphere* 1989;19:283.

**FIGURE 6.7** *De novo* formation of chlorinated dioxins and furans after heating Mg-Al silicate, 4% charcoal, 7% Cl, 1% CuCl<sub>2</sub>·H<sub>2</sub>O at 300 °C. Stieglitz L, Zwick G, Beck J, Bautz H, Roth W. Chemosphere 1989;19:283.



pollutant formation (similar to the cool zones of the incinerator).

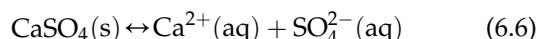
Other processes generate dioxin pollution. A source that has been greatly reduced in the last decade is the paper production process, which formerly used chlorine bleaching. This process has been dramatically changed, so that most paper mills no longer use the chlorine bleaching process. Dioxin is also produced in the making of PVC plastics, which may follow chemical and physical mechanisms similar to the second and third processes discussed above.

Like many other halogenated organic compounds, dioxin and dioxin-like compounds are lipophilic and persistent, which means that they often readily accumulate in soils, sediments, and organic matter where they can persist for decades.<sup>j</sup> These compounds are also semivolatile, so they may migrate away from these sites and be transported in the atmosphere either as aerosols (solid and liquid phase) or as gases (the portion of the compound that volatilizes). Therefore, great care must be taken during removal and storage of sludge, filtrate, and other materials collected from air pollution control equipment, as well as during remediation efforts to avoid unwittingly emitting these contaminants via volatilization or aerosolization, as well as via perturbations, such as from ash piles and pits.

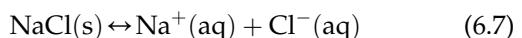
Dioxin demonstrates the complexity of air pollution's physicochemical processes. At the most basic level only a few types of chemical reactions dominate in the environment. These include ionization, acid–base, precipitation, and oxidation–reduction (redox).

#### 6.1.3.1.2 IONIZATION

When a salt is dissolved in water, it dissociates into ionic forms. Notwithstanding their variability in doing so, under the right conditions all complexes can become dissolved in water, e.g. in droplets in the atmosphere. Ions that are dissolved in a solution can react with one another, and can form solid complexes and compounds. Strictly speaking, a salt compound does not exist in water. For example, when the salts calcium sulfate and sodium chloride are added to water, it is commonly held that CaSO<sub>4</sub> and NaCl are in the water. However, what is really happening is that the metals and nonmetals are in chemical equilibrium:



and

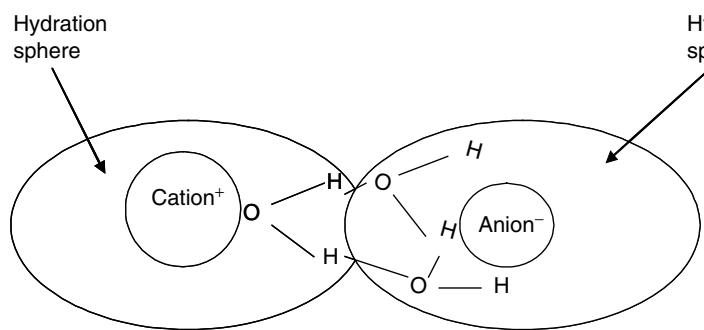


Thus, all four of the dissociated ions are free and no longer associated with each other. That is, the Na, Ca, Cl, and SO<sub>4</sub> ions are “unassociated” in the water. The Na and the Cl are no longer linked to each other as they were before the compound was added to the water.

Even though atoms are neutral, in the process of losing or gaining electrons, they become electrically charged, i.e. they become *ions*. An atom that loses one or more electrons is positively charged, and is known as a *cation*. For example, the potassium atom loses one electron and becomes the monovalent potassium cation:



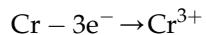
<sup>j</sup>For discussion of the transport of dioxins, see Koester CJ, Hites RA. Wet and dry deposition of chlorinated dioxins and furans. *Environ Sci Technol* 1992;26:1375–82; and Hites RA. *Atmospheric transport and deposition of polychlorinated dibenz-p-dioxins and dibenzofurans*, EPA/600/3-91/002. Research Triangle Park (NC); 1991.



When the mercury atom loses two electrons, it becomes the divalent mercury cation:



When the chromium atom loses three electrons it becomes the trivalent chromium cation:



Conversely, an atom that gains electrons becomes a negatively charged ion, and is known as an *anion*. For example, when chlorine gains an electron it becomes the chlorine anion:



When sulfur gains two electrons, it becomes the divalent sulfide anion:



Note that the Greek prefix (mono-, di-, tri-, etc.) denoting the valence is the number of electrons by which the ion differs from neutrality.

Reactions between ions, known as ionic reactions, frequently occur as ions of water-soluble salts that can react in aqueous solution to form salts that are nearly insoluble in water. This causes them to separate into insoluble precipitates:



#### 6.1.3.1.3 SOLUBILITY AND ELECTROLYTES

The aqueous solubility of contaminants ranges from completely soluble in water to virtually insoluble. Solubility equilibrium is the phenomenon that keeps

**FIGURE 6.8** Ion pairs. Evangelou V. Environmental soil and water chemistry: principles and applications. New York (NY): John Wiley & Sons; 1998.

molecules dissolved in a solvent. Solubility and precipitation are in a way, two sides of the same coin. There is truth in the old chemists' pun, "If you're not part of the solution, you are part of the precipitate!" Solubilities typically are quantitatively expressed as mass of solute per volume of solvent (e.g. mg l<sup>-1</sup>), and sometimes expressed by the adjectives "soluble", "slightly soluble", or "insoluble".

In the solid phase, a salt is actually a collection of ions in a lattice, where the ions are surrounded by one another. However, when the salt is dissolved in water, the ions become surrounded by the water, rather than by the other ions. Each ion now has its own coordinating water envelope or "hydration sphere", i.e. a collection of water molecules surrounding it. An ion-association reaction is an ion–ion interaction between the ions in an electrolyte (i.e. ion-containing) solution.<sup>k</sup> So, when the salt lattice enters the water, the ions assemble into couples of separate oppositely charged ions, i.e. cations and anions, the so-called "ion pairs". The pairs are held together by electrostatic attraction. Ion association is the reverse of dissociation where the ions separate from a compound into free ions. Ions (or molecules) surrounded by water exist in the aqueous phase. So, ionic compounds that are soluble in water break apart (i.e. dissociate) into their ionic components, i.e. anions and cations (see Figure 6.8).

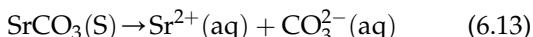
Solutions may contain nonelectrolytes, strong electrolytes, and/or weak electrolytes. Nonelectrolytes do not ionize. They are nonionic molecular compounds that are neither acids nor bases. Sugars, alcohols, and most other organic compounds are nonelectrolytic. Some inorganic compounds are also nonelectrolytes.

Weak electrolytes only partially dissociate in water. Most weak electrolytes dissociate less than 10%, i.e.

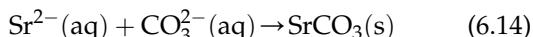
<sup>k</sup> The Swedish chemist, Svante Arrhenius, is credited with establishing the relationship between electrical and chemical properties of molecules. He observed that particular chemical compounds (later to be known as electrolytes) conduct electricity when they are dissolved in water, while other chemicals do not. He also saw that certain chemicals are involved in seemingly instantaneous reactions, while others took much longer to react. Finally, he observed that particular chemical compounds showed extremely strange colligative properties while others were consistent with Raoult's Law, which states that the solvent's vapor pressure in an ideal solution is equal to the product of the mole fraction of the solvent and the vapor pressure of the pure solvent. The four colligative properties of solutions are the elevation of boiling point, the depression of freezing point, the decreasing of vapor pressure, and osmotic pressure.

greater than 90% of these substances remain undissociated. Organic acids, such as acetic acid, are generally weak electrolytes.

An example of dissociation is strontium carbonate dissolved in water:



Conversely, the reverse reaction forms a solid; that is, it returns from the solution to re-form the lattice of ions surrounding ions. This is a precipitation reaction. In our Sr example, the carbonate species is precipitated:



The *ionic product* ( $Q$ ) is a measure of the ions present in the solvent. The *solubility product constant* ( $K_{\text{sp}}$ ) is the ionic product when the system is in equilibrium. So, solubility is often expressed as the specific  $K_{\text{sp}}$ , the equilibrium constant for dissolution of the substance in water. Since  $K_{\text{sp}}$  is an expression of chemical equilibrium, it is a quantitative way of describing the balance of opposing reversible chemical reactions which proceed at constant and equal rates, thus resulting in no net change in the system (hence the symbol,  $\leftrightarrow$ ). Like sorption, Henry's law and other equilibrium constants that are discussed in detail in Chapter 18, solubility follows Le Chatelier's Principle, which states that in a balanced equilibrium, if one or more factors change, the system will readjust to reach equilibrium.  $K_{\text{sp}}$  values and the resulting solubility calculations for four important compounds are shown in Table 6.5.  $K_{\text{sp}}$  constants for many compounds can be found in engineering handbooks.

Since  $\text{SrCO}_3$  is a highly insoluble salt (aqueous solubility =  $6 \times 10^{-3}$  mg l<sup>-1</sup>), its equilibrium constant for the reaction is quite small:

$$K_{\text{sp}} = [\text{Sr}^{2+}][\text{CO}_3^{2-}] = 1.6 \times 10^{-9} \quad (6.15)$$

TABLE 6.5 Solubility Product Constant versus Solubility for Four Types of Salts

Salt	Example	Solubility Product ( $K_{\text{sp}}$ )	Solubility (S)
AB	$\text{CaCO}_3$	$[\text{Ca}^{2+}][\text{CO}_3^{2-}]$ $= 4.7 \times 10^{-9}$	$(K_{\text{sp}})^{1/2} = 6.85 \times 10^{-5} \text{ M}$
$\text{AB}_2$	$\text{Zn(OH)}_2$	$[\text{Zn}^{2+}][\text{OH}^-]^2$ $= 4.5 \times 10^{-17}$	$(K_{\text{sp}}/4)^{1/3} = 2.24 \times 10^{-6} \text{ M}$
$\text{AB}_3$	$\text{Cr(OH)}_3$	$[\text{Zn}^{3+}][\text{OH}^-]^3$ $= 6.7 \times 10^{-31}$	$(K_{\text{sp}}/27)^{1/4} = 1.25 \times 10^{-8} \text{ M}$
$\text{A}_3\text{B}_2$	$\text{Ca}_3(\text{PO}_4)_2$	$[\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$ $= 1.3 \times 10^{-32}$	$(K_{\text{sp}}/108)^{1/5} = 1.64 \times 10^{-7} \text{ M}$

Source: US Army Corps of Engineers. Engineering and design: precipitation/coagulation/flocculation. Chapter 2, EM 1110-1-4012, 2001.

The small  $K_{\text{sp}}$  value of the constant reflects the low concentration of dissolved ions. So, as the number of dissolved ions approaches zero, the compound is increasingly insoluble in water. This does not mean that that an insoluble product cannot be dissolved, but it will require additional chemicals to induce solubility. In this case, strontium carbonate requires the addition of an acid to *solubilize* the  $\text{Sr}^{2+}$  ion.

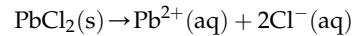
To precipitate a compound, the product of the concentration of the dissolved ions in the equilibrium expression must exceed the value of the  $K_{\text{sp}}$ . The concentration of each of these ions does not need to be the same. For example, if  $[\text{Sr}^{2+}]$  is  $1 \times 10^{-5}$  M, the carbonate ion concentration must exceed  $0.0016$  M for precipitation to occur because  $(1 \times 10^{-5}) \times (1.6 \times 10^{-4}) = 1.6 \times 10^{-9}$  (i.e. the  $K_{\text{sp}}$  for strontium carbonate).

### DISSOCIATION AND PRECIPITATION REACTION EXAMPLE

An environmental analytical chemist adds 100 ml of 0.050 M NaCl to 200 ml of 0.020 M  $\text{Pb}(\text{NO}_3)_2$ . Will the lead chloride that is formed precipitate from the 300 ml sample?

#### Solution

Calculate the *ion product* ( $Q$ ) and compare it to the  $K_{\text{sp}}$  for the reaction:



When the two solutions are mixed, the unassociated ions are formed as:

$$[\text{Pb}^{2+}] = 0.21 \times 2.0 \times 10^{-2} \text{ M} / 0.31 = 1.3 \times 10^{-2} \text{ M}$$

and

$$[\text{Cl}^-] = 0.11 \times 5.0 \times 10^{-2} \text{ M} / 0.31 = 1.7 \times 10^{-2} \text{ M}$$

The value for the ion product is calculated as:

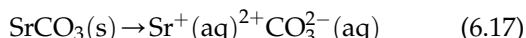
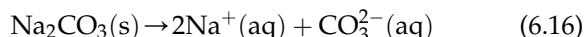
$$Q = [\text{Pb}^{2+}][\text{Cl}^-]^2 = [1.3 \times 10^{-2}][1.7 \times 10^{-2}]^2 \\ = 3.8 \times 10^{-7}$$

The  $K_{\text{sp}}$  for this reaction is  $1.6 \times 10^{-5}$ .

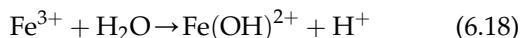
$Q < K_{\text{sp}}$ , so no precipitate will be formed. If the ion product were greater than the  $K_{\text{sp}}$  a precipitate would have been formed.

Environmental conditions can affect solubility. One such instance is the *common ion effect*. Compared to a solution in pure water, an ion's solubility is decreased in an aqueous solution that contains a common ion (i.e. one of the ions that make up the compound).

This allows a precipitate to form if the  $K_{sp}$  is exceeded. For example, soluble sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in solution with strontium ions can cause the precipitation of strontium carbonate, since the carbonate ions from the sodium salt are contributing to their overall concentration in solution and reversing the solubility equilibrium of the “insoluble” compound, strontium carbonate:



Also, a complexing agent or *ligand* may react with the cation of a precipitate, enhancing the solubility of the compound. In addition, several metal ions are weakly acidic and readily hydrolyzed in solution. For example, hydrolyzing ferric ion ( $\text{Fe}^{3+}$ ) forms a hydroxide and hydrogen ion:



When such metal ions hydrolyze, they produce a less soluble complex. The solubility of the salt is inversely related to the pH of the solution, with solubility increasing as the pH decreases. The minimum solubility is found under acidic conditions when the concentrations of the hydrolyzed species approach zero.

### 6.1.3.2 Environmental Acid and Base Chemistry

For many air pollution situations, an acid is considered to be any substance that causes hydrogen ions to be produced when dissolved in water. Conversely, a base is any substance that produces hydroxide ions when dissolved in water. Acids are proton donors and bases are proton acceptors (this is known as the Brönsted–Lowry model). Acids are electron-pair acceptors and bases are electron-pair donors (following the Lewis model). Actually, the  $\text{H}^+$  is a bare proton, having lost its electron, so it is highly reactive. In reality, the acid produces a hydronium ion:



When acids react with bases, a double-replacement reaction takes place, resulting in neutralization. The products are water and a salt. One mole of acid neutralizes precisely 1 mol of base. Being electrolytes, a strong acid dissociates and ionizes 100% into  $\text{H}_3\text{O}^+$  and anions. These anions are the acid’s specific conjugate base. A strong base also dissociates and ionizes completely. The ionization results in hydroxide ions and cations, known as the base’s conjugate acid. Weak acids and weak bases dissociate less than 100% into the respective ions.

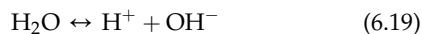
There are four strong acids that are important in air pollution. These are hydrochloric acid (HCl), nitric

### IONIZATION EXAMPLE

What exactly is the pH scale? Why do pH values range from 0 to 14?

#### Answer

Water ionizes. It does not exist only as molecular water ( $\text{H}_2\text{O}$ ), but also includes hydrogen ( $\text{H}^+$ ) and hydroxide ( $\text{OH}^-$ ) ions:



The negative logarithm of the molar concentration of hydrogen ions, i.e.  $[\text{H}^+]$  in a solution (usually water in the environmental sciences), is referred to as pH. This convention is used because the actual number of ions is extremely small. Thus pH is defined as:

$$\text{pH} = -\log_{10}[\text{H}^+] = \log_{10}[\text{H}^+]^{-1} \quad (6.20)$$

The brackets refer to the molar concentrations of chemicals, and in this case it is the ionic concentration in moles of hydrogen ions per liter. The reciprocal relationship of molar concentrations and pH means that the more hydrogen ions in solution the lower the pH value will be.

Likewise, the negative logarithm of the molar concentration of hydroxide ions, i.e.  $[\text{OH}^-]$  in a solution is pOH:

$$\text{pOH} = -\log_{10}[\text{OH}^-] = \log_{10}([\text{OH}^-])^{-1} \quad (6.21)$$

The relationship between pH and pOH is constant. At 25 °C, this constant is:

$$K = [\text{H}^+] [\text{OH}^-] = 10^{-14} \quad (6.22)$$

When expressed as a negative log, one can see that the pH and pOH scales are reciprocal to one another and that they both range from 0 to 14. Thus, a pH 7 must be neutral (same number of hydrogen ions as hydroxide ions).

Upon further investigation, the log relationship means that for each factor pH unit change there is a factor of 10 change in the molar concentration of hydrogen ions. Thus, a pH 2 solution has 100,000 times more hydrogen ions than neutral water (pH 7), or  $[\text{H}^+] = 10^{12}$  versus  $[\text{H}^+] = 10^7$ , respectively.

acid ( $\text{HNO}_3$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and perchloric acid ( $\text{HClO}_4$ ). Many weak acids are particularly important, such as carbonic acid, acetic acid, and phosphoric acid.

Strong bases include sodium hydroxide ( $\text{NaOH}$ ) and potassium hydroxide ( $\text{KOH}$ ). Weak bases include ammonia ( $\text{NH}_3$ ), which dissolves in water to become ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) and organic amines (i.e. compounds with the radical:  $-\text{NH}$ ).

Nonmetal oxides, such as carbon dioxide ( $\text{CO}_2$ ) and sulfur dioxide ( $\text{SO}_2$ ), are generally acidic (forming carbonic acid and sulfuric acid, respectively in water), while metal oxides like those of calcium (e.g.  $\text{CaO}$ ) and magnesium (e.g.  $\text{MgO}$ ), are generally basic. These two metal oxides, for example, form calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ] and magnesium hydroxide [ $\text{Mg}(\text{OH})_2$ ] in water, respectively.

The principal environmental metric for acidity and basicity in assessing and controlling air pollution is pH. As mentioned, the “p” in pH represents the negative log and the “H” represents the hydrogen ion or hydronium ion molar concentration:

$$\text{pH} = -\log[\text{H}^+] \text{ and } [\text{H}^+] = 10^{-\text{pH}} \quad (6.24)$$

The autoionization of water into its hydrogen ion and hydroxide ions is an equilibrium constant, i.e. the water dissociation equilibrium constant ( $K_w$ ). At  $25^\circ\text{C}$ , the molar concentration of the product of these ions is  $1.0 \times 10^{-14}$ . That is:

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad (6.25)$$

Thus, pH ranges from 0 to 14, with 7 being neutral. Values below 7 are acidic and values above 7 are basic.

### STRONG ACID/BASE EXAMPLE 1

An air pollution analytical laboratory is using an aqueous solution of sulfuric acid, which is 0.05 M. What is the hydrogen ion and chloride ion molar concentration of the solution?

#### Answer

Since this is a strong acid, it should ionize and dissociate completely. Thus:

$[\text{H}^+] = 0.05$  and  $[\text{Cl}^-] = 0.05$ , so none of the associated acid remains.

### STRONG ACID/BASE EXAMPLE 2

What is the pH of the solution in the earlier example? What is the  $[\text{OH}^-]$  of the solution in the earlier example?

#### Answer

Since  $[\text{H}^+] = 0.05$ , and  $\text{pH} = -\log[\text{H}^+] = -\log 0.05 \text{ M} = 1.3$ .

Also, recall that:

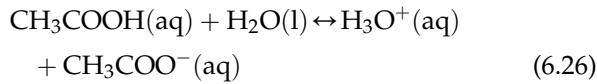
$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

$$\text{So, } [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{0.05} = 2.0 \times 10^{-13}$$

Thus, even with a very high relative concentration of hydrogen ions in the acidic solution, there is still a small amount of hydroxide ion concentration.

Characterizing an acid or base as strong or weak has nothing to do with the concentration (i.e. molarity) of the solution, and everything to do with the extent to which the acid or base dissociates when it enters water. In other words, whether at a concentration of 6.0 M or at 0.00001 M, sulfuric acid will completely ionize in the water, but acetic acid will not completely ionize at any concentration. To demonstrate this, Table 6.6 shows the pH for a number of acids and bases, all with the same molar concentration. The strongest acids are at the top and the strongest bases are at the bottom. The weak acids and bases are in the middle of the table.

Most acid–base reactions in the atmosphere involve weak substances. In fact, the amount of ionization in most environmental reactions, especially those in the ambient air (as opposed to those in chemical engineering and laboratory reactors), are quite weak, usually well below 10% dissociation.<sup>1</sup> So, for every 1000 molecules of a weak acid, only a few, say 50, molecules of the acid will dissociate into hydronium ions in the water. Thus, taking acetic acid as an example, the acid–base equilibrium reaction is:



<sup>1</sup>Note that by this definition, water itself is a weak acid in that it autoionizes into  $10^{-14}$  molar concentration of ions, which means that some of the water ionizes into hydroxide and hydronium ions. Hydronium is the hydrogen ion bound to a water molecule. The importance of water's ionization in virtually all biological processes should not be underestimated. At  $25^\circ\text{C}$ , there are 55.35 mol water per liter. So, since half of the ions are hydronium ions in neutral water, this means there are:  $\frac{1.0 \times 10^{-7} \text{ M H}_3\text{O}^+}{55.35 \text{ M H}_2\text{O}} = 1.8 \times 10^{-9}$  hydronium ions per water molecule. Even this small ratio provides enough  $\text{H}^+$  given the amount of water available in the hydrological cycle and the highly reactive nature of each hydrogen ion.

**TABLE 6.6** The Experimentally Derived pH Values for 0.1 M Solutions of Acids and Bases at 25 °C

Compound	pH
HCl	1.1
H <sub>2</sub> SO <sub>4</sub>	1.2
H <sub>3</sub> PO <sub>4</sub>	1.5
CH <sub>3</sub> COOH	2.9
H <sub>2</sub> CO <sub>3</sub> (in saturated solution)	3.8
HCN	5.1
NaCl	6.4
H <sub>2</sub> O (distilled)	7.0
NaCH <sub>3</sub> CO <sub>2</sub>	8.4
NaSO <sub>3</sub>	9.8
NaCN	11.0
NH <sub>3</sub> (aqueous)	11.1
NaPO <sub>4</sub>	12.0
NaOH	13.0

Source: Spencer J., Bodner G., Rickard L. Chemistry: structure and dynamics. 2nd ed. New York (NY): John Wiley & Sons; 2003.

The acetate ion (CH<sub>3</sub>COO<sup>-</sup>) is the reaction's conjugate base and the hydronium ion is the active acid chemical species. Because the reaction is in equilibrium with all four species, another equilibrium constant can be established for acid reactions, i.e. the acid constant ( $K_a$ ):

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \quad (6.27)$$

At 25 °C, the  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$  (see Table 6.7). If the percent dissociation in an acid reaction is known, the product of this percentage and the initial acid concentration will give the molar concentration of hydrogen ions, [H<sup>+</sup>]. For example, if 0.1 M solution of cyanic acid (HOCN) is 2.8% ionized, the [H<sup>+</sup>] can be found. We know that HOCN is a weak acid because the percent ionization is less than 100. In fact, it is well below 10%. This means that the hydrogen ion molar concentration is

$$[H^+] = 2.8\% \times 0.1 \text{ M} = 0.0028 \text{ or } 2.8 \times 10^{-3}$$

Published  $K_a$  constants show that the HOCN constant at 25 °C is  $3.5 \times 10^{-3}$ , so environmental conditions, likely temperature, are slightly affecting the pH of the

**TABLE 6.7** Equilibrium Constants for Selected Environmentally Important Weak Monoprotic (Single H Atom) Acids and Bases at 25 °C

Monoprotic Acid	Dissociation Reaction	$K_a$
Hydrofluoric acid	HF + H <sub>2</sub> O ⇌ H <sub>3</sub> O <sup>+</sup> F <sup>-</sup>	$7.2 \times 10^{-4}$
Nitrous acid	HNO <sub>2</sub> + H <sub>2</sub> O ⇌ NO <sub>2</sub> + H <sub>3</sub> O <sup>+</sup>	$4.0 \times 10^{-4}$
Lactic acid	CH <sub>3</sub> CH(OH)CO <sub>2</sub> H + H <sub>2</sub> O ⇌ CH <sub>3</sub> CH(OH)CO <sub>2</sub> <sup>-</sup> + H <sub>3</sub> O <sup>+</sup>	$1.38 \times 10^{-4}$
Benzoic acid	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H + H <sub>2</sub> O ⇌ C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> <sup>-</sup> + H <sub>3</sub> O <sup>+</sup>	$6.4 \times 10^{-5}$
Acetic acid	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> + H <sub>2</sub> O ⇌ C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup> + H <sub>3</sub> O <sup>+</sup>	$1.8 \times 10^{-5}$
Propionic acid	CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> H + H <sub>2</sub> O ⇌ CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> + H <sub>3</sub> O <sup>+</sup>	$1.3 \times 10^{-5}$
Hypochlorous acid	HOCl + H <sub>2</sub> O ⇌ OCl <sup>-</sup> + H <sub>3</sub> O <sup>+</sup>	$3.5 \times 10^{-8}$
Hypobromous acid	HOBr + H <sub>2</sub> O ⇌ OBr + H <sub>3</sub> O <sup>+</sup>	$2 \times 10^{-9}$
Hydrocyanic acid	HCN + H <sub>2</sub> O ⇌ CN <sup>-</sup> + H <sub>3</sub> O <sup>+</sup>	$6.2 \times 10^{-10}$
Phenol	HOC <sub>6</sub> H <sub>5</sub> + H <sub>2</sub> O ⇌ OC <sub>6</sub> H <sub>5</sub> <sup>-</sup> + H <sub>3</sub> O <sup>+</sup>	$1.6 \times 10^{-10}$
Base	Dissociation Reaction	$K_b$
Dimethylamine	(CH <sub>3</sub> ) <sub>2</sub> NH + H <sub>2</sub> O ⇌ (CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup> + OH <sup>-</sup>	$5.9 \times 10^{-5}$
Methylamine	CH <sub>3</sub> NH <sub>2</sub> + H <sub>2</sub> O ⇌ CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup> + OH <sup>-</sup>	$7.2 \times 10^{-4}$
Ammonia	NH <sub>3</sub> + H <sub>2</sub> O ⇌ NH <sub>3</sub> <sup>+</sup> + OH <sup>-</sup>	$1.8 \times 10^{-5}$
Hydrazine	H <sub>2</sub> NNH <sub>2</sub> + H <sub>2</sub> O ⇌ H <sub>2</sub> NNH <sub>3</sub> <sup>+</sup> + OH <sup>-</sup>	$1.2 \times 10^{-6}$
Aniline	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> + H <sub>2</sub> O ⇌ C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup> + OH <sup>-</sup>	$4.0 \times 10^{-10}$
Urea	H <sub>2</sub> NCONH <sub>2</sub> + H <sub>2</sub> O ⇌ H <sub>2</sub> NCONH <sub>3</sub> <sup>+</sup> + OH <sup>-</sup>	$1.5 \times 10^{-14}$

Source: Casprian A. Chemistry. In: Olia M., editor. How to prepare for the fundamentals of engineering (FE/EIT) exam. Hauppauge (NY): Barron's Educational Series, Inc.; 2000.

TABLE 6.8 Equilibrium Constants for Selected Environmentally Important Polyprotic (Two or More H Atom) Acids at 25 °C

Acid	Dissociation Reactions	$K_{a1}$	$K_{a2}$	$K_{a3}$
Sulfuric acid	$\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \leftrightarrow \text{HSO}_4^- + \text{H}_3\text{O}^+$	$1.0 \times 10^3$	$1.2 \times 10^{-2}$	
	$\text{HSO}_4^- + \text{H}_2\text{O} \leftrightarrow \text{SO}_4^{2-} + \text{H}_3\text{O}^+$			
Hydrogen sulfide	$\text{H}_2\text{S} + \text{H}_2\text{O} \leftrightarrow \text{HS}^- + \text{H}_3\text{O}^+$	$1.0 \times 10^{-7}$	$1.3 \times 10^{-13}$	
	$\text{HS}^- + \text{H}_2\text{O} \leftrightarrow \text{S}^{2-} + \text{H}_3\text{O}^+$			
Phosphoric acid	$\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \leftrightarrow \text{HPO}_4^- + \text{H}_3\text{O}^+$	$7.1 \times 10^{-3}$	$6.3 \times 10^{-8}$	
	$\text{HPO}_4^- + \text{H}_2\text{O} \leftrightarrow \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$			
	$\text{HPO}_4^{2-} + \text{H}_2\text{O} \leftrightarrow \text{PO}_4^{3-} + \text{H}_3\text{O}^+$			$4.2 \times 10^{-13}$
Carbonic acid	$\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+$	$4.5 \times 10^{-7}$	$4.7 \times 10^{-11}$	
	$\text{HCO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+$			

Source: Caspary A. Chemistry. In: Olia M, editor. How to prepare for the fundamentals of engineering (FE/EIT) exam. Hauppauge (NY): Barron's Educational Series, Inc.; 2000.

solution. Remember that all equilibrium constants are temperature dependent.

Weak bases follow precisely the same protocol as weak acids, with a base equilibrium constant,  $K_b$ . Some important acid and base equilibrium constants are provided in Tables 6.7 and 6.8.

Because the atmosphere contains relatively large amounts of carbon dioxide (on average about 350 ppm), the  $\text{CO}_2$  becomes dissolved in surface water and in soil water (because  $\text{CO}_2$  is a common soil gas). Thus, one of the most important environmental acid–base reactions<sup>m</sup> is the dissociation of  $\text{CO}_2$ :

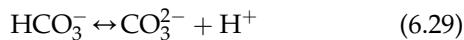


The asterisk (\*) denotes that this compound is actually the sum of two compounds, i.e. the dissolved  $\text{CO}_2$  and the reaction product, carbonic acid  $\text{H}_2\text{CO}_3$ .

Since the carbonic acid that is formed is a diprotic acid (i.e. it has two hydrogen atoms), an additional equilibrium step reaction occurs in water. The first reaction forms bicarbonate and hydrogen ions:



Followed by a reaction that forms carbonate and hydrogen:

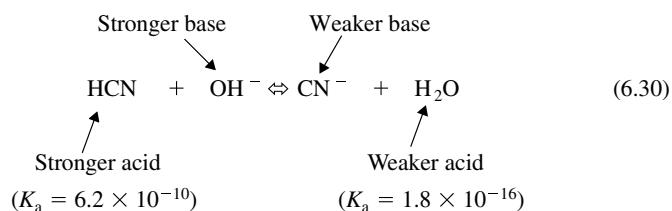


Each of the two-step reactions has its own acid equilibrium constant ( $K_{a1}$  and  $K_{a2}$ , respectively), as shown in Table 6.8. For a triprotic acid, there would be

three unique constants. Note that the constants decrease substantially with each step. In other words, most of the hydrogen ion production occurs in the first step.

Numerous reactions can be predicted from the relative strength of acids and bases, since their strength results from how well the protons via the hydronium ion are transferred from the acid and the electrons are transferred via the hydroxide ion from the base. If an acid is weak, its conjugate base must be strong, and if an acid is strong, its conjugate base must be weak. Likewise, if a base is weak, its conjugate acid must be strong, and if the base is strong, its conjugate acid must be weak. The tables show actual  $K_a$  and  $K_b$  constants; however, many sources publish values for  $pK_a$  and  $pK_b$ . Since the “p” denotes negative logarithm, the larger the  $pK_a$ , the weaker the acid, and the larger the  $pK_b$ , the weaker the base.

An example of how the  $K_a$  is an indicator of relative strength of reactants and products is that of hydrocyanic acid (HCN):



The ratio of the  $K_a$  constant values of the two acids is a direct way to quantify the equilibrium. In the

<sup>m</sup> For an excellent discussion of carbon dioxide equilibrium in water see Hemond HF, Fechner-Levy EJ. *Chemical fate and transport in the environment*. San Diego (CA): Academic Press; 2000.

hydrocyanic acid instance above, the ratio is  $\frac{6.2 \times 10^{-10}}{1.8 \times 10^{-16}} \approx 4 \times 10^6$ .

This large quotient indicates that the equilibrium is quite far to the right. So, if HCN is dissolved in a hydroxide solution (e.g. NaOH), the resulting reaction will produce much greater amounts of the cyanide ion ( $\text{CN}^-$ ) than the amount of both the hydroxide ion ( $\text{OH}^-$ ) and molecular HCN. Conversely, for an aqueous solution of sodium cyanide (NaCN), the water will only react with a tiny amount of  $\text{CN}^-$ .

Among the properties of water, one of the most environmentally important is that it can behave as either an acid or a base, i.e. water is an amphoteric compound. That is one of the reasons that water is sometimes shown as HOH. When water acts as a base its  $\text{pK}_b = -1.7$ . When water acts as an acid its  $\text{pK}_a = 15.7$ .

Many air pollution reactions occur in water (e.g. in droplets, on aerosols, and even in the water within organisms), so the relationship between conjugate acid–base equilibrium and pH is important. The Henderson–Hasselbalch equation states this relationship:

$$\text{p}K_a = \text{pH} + \log \frac{[\text{HA}]}{[\text{A}^-]} \quad (6.31)$$

Thus, Henderson–Hasselbalch tells us that when the pH of an aqueous solution equals the  $\text{p}K_a$  of an acidic component, the concentrations of the conjugate acids and bases must be equal (since the log of 1 = 0). If pH is 2 or more units lower than  $\text{p}K_a$ , the acid concentration will be greater than 99%. Conversely, when pH is greater than  $\text{p}K_a$  by 2 or more units, the conjugate base concentration will account for more than 99% of the solution.<sup>n</sup>

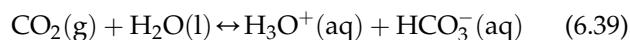
This means that mixtures of acidic and nonacidic compounds can be separated with a pH adjustment, which has strong implications for the design and operation of air pollution control equipment. The application of this principle is also important to the transformation of environmental contaminants in the form of weak organic acids or bases, because these compounds in their nonionized form are much more lipophilic, meaning they will be absorbed more easily through the skin than when they exist in ionized forms. As a general rule, the smaller the  $\text{p}K_a$  for an acid and the larger the  $\text{p}K_b$  for a base, the more extensive will be the dissociation in aqueous environments at normal

pH values, and the greater compound's electrolytic nature.

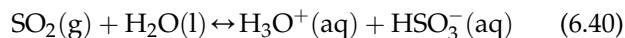
#### 6.1.3.2.1 HYDROLYSIS

All of the acid–base reactions involve chemical species reacting with water. It is worth noting that even some so-called neutral compounds have acidic or basic properties. For example, metal<sup>o</sup> acetates ((MeC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>x</sub>) can dissolve in water and actually react with the water to form weak acids and hydrogen ions. The resulting solutions are generally slightly basic (pH < 7), since the acetate ion is conjugate base of the weak acid. This process is known as hydrolysis (i.e. lysis or breaking apart water molecules).

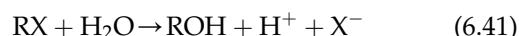
Likewise, some compounds produce weak bases when dissolved in water. For example, when ammonium chloride (NH<sub>4</sub>Cl) is dissolved in water, the solution becomes more acidic. The NH<sub>4</sub><sup>+</sup> cation serves as the conjugate base of ammonium hydroxide (NH<sub>4</sub>OH), or molecular ammonia (NH<sub>3</sub>) is the conjugate base of the NH<sub>4</sub><sup>+</sup> cation. Oxide gases (e.g. carbon dioxide and sulfur dioxide) can be hydrolyzed to form hydronium ions and anions:



and,



These reactions also take place in organic compounds, where the organic molecule, RX, reacts with water to form a covalent bond with OH and cleaves the covalent bond of the leaving group (X) in RX, which displaces X with the hydroxide ion and an ion formed from the leaving group:



Amides, epoxides, carbonates, esters, organic halides, nitriles, urea compounds, and esters of organophosphate compounds are functional groups that are susceptible to hydrolysis. The process involves an electron-rich nucleus seeker (i.e. a nucleophile) attacking an electron-poor electron seeker (i.e. an electrophile) to displace the leaving group (such as a halogen). This is why hydrolysis is one of the methods of dechlorination, a detoxification process for hazardous chlorinated hydrocarbons.

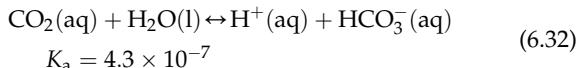
Environmental engineers use hydrolysis to eliminate or to reduce the toxicity of hazardous contaminants by

<sup>n</sup> US Environmental Protection Agency. *Dermal exposure assessment: principles and applications*. Interim Report. EPA/600/8-91/011B. Washington (DC); 1992.

<sup>o</sup>The abbreviation "Me" is commonly used for "metals" when a number of metals exhibit identical or similar properties and behavior (e.g. Hg, Cd, Pb, and Mn may behave similarly on an aerosol's surface, catalyzing certain reactions, or they may also exhibit similar physiological processes, such as interferences with neurons and calcium gates in the brain and central nervous system). Rather than listing every metal, the chemical formulae will display Me.

## ACID RAIN EXAMPLE

Acid–base reactions are demonstrated by the acid rain problem. Dissolved CO<sub>2</sub> causes most rainfall to be slightly acidic:



Acidic precipitation, popularly known as “acid rain” contains the strong acids H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, mainly from the combustion of fossil fuels that contain sulfur (the air contains molecular nitrogen that is oxidized during internal combustion in engines, i.e. “mobile sources” and in any high temperature furnaces, like those in power plants). The sulfuric acid is stepped process. Recall that the contaminant released from stacks is predominantly sulfur dioxide when the elemental sulfur is oxidized:



The sulfur dioxide in turn is oxidized to sulfur trioxide:



The sulfur trioxide then reacts with atmospheric water (vapor, clouds, on particles) to form sulfuric acid:



The net result is to increase the acidity of the rain, which is a threat to aquatic life, and metallic and carbonate materials (including artwork, statues, and buildings). Near pollution sources, rainwater pH can be found to be less than 3 (i.e. 10,000 times more acidic than neutral).

What are the molar concentrations of [H<sup>+</sup>] and [OH<sup>-</sup>] of rainwater at pH 3.7 at 25 °C? When SO<sub>2</sub> dissolves in water, sulfurous acid (H<sub>2</sub>SO<sub>3</sub>, K<sub>a1</sub> = 1.7 × 10<sup>-2</sup>, K<sub>a2</sub> = 6.4 × 10<sup>-8</sup>) is formed. What is the reaction when sulfurous acid donates a proton to a water molecule? What are the Brønsted–Lowry acid and base in this reaction?

Surface waters have a natural buffering capacity, especially in regions where there is limestone which gives rise to dissolved calcium (e.g. central Kansas is less at risk of acid rain’s effects than are the Finger Lakes of New York). What is the reaction of a minute amount of acid rain containing sulfuric acid reaching a lake containing carbonate (CO<sub>3</sub><sup>2-</sup>) ions?

### Solution

Since, pH = −log [H<sup>+</sup>], then [H<sup>+</sup>] = 10<sup>−pH</sup> × 10<sup>−3.7</sup> 2.0 × 10<sup>−4</sup> M in aqueous solution at 25 °C.

The sulfurous acid proton donation reaction is:



H<sub>3</sub>O<sup>+</sup> is the stronger acid (i.e. K<sub>a+</sub> < 1) and HSO<sub>3</sub><sup>-</sup> is the stronger base.

Regarding the buffered water system, CO<sub>3</sub><sup>2-</sup> is the conjugate base of the weak acid HCO<sub>3</sub><sup>-</sup>, so the former can react with the strong acid H<sub>3</sub>O<sup>+</sup> in the sulfuric acid solution:



The K = 1/K<sub>a2</sub> of H<sub>2</sub>CO<sub>3</sub> (making for a large K).

Similarly HSO<sub>4</sub><sup>-</sup> also reacts with CO<sub>3</sub><sup>2-</sup>:



The K = (K<sub>a2</sub> of H<sub>2</sub>SO<sub>4</sub>)/(K<sub>a2</sub> of H<sub>2</sub>CO<sub>3</sub>) (thus, large K). So, an HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> buffer is produced.

An excess of acid rain will consume all the CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>, converting all to H<sub>2</sub>CO<sub>3</sub> (and completely eliminating the buffer).

These are important and representative reactions of the challenging global problem of acid rain.

abiotic transformation and biotransformation, especially bacterial. For example, the highly toxic methyl isocyanate, infamous as the contaminant that led to loss of life and health effects in the Bhopal, India incident, can be transformed hydrolytically.

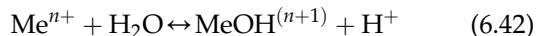
Two factors are particularly enhancing to hydrolysis. Microbial mediation, including enzymatic activity can catalyze hydrolytic reactions. This occurs both in the ambient environment, such as the hydrolysis of inorganic and organic compounds by soil bacteria, as well

as in engineered systems, such as acclimating those same bacteria to the treatment of chlorinated organic compounds in solid and liquid wastes.

The second factor is pH. Hydrolysis can be affected by specific acid and base catalysis. In acid catalysis, the H<sup>+</sup> ion catalyzes this reaction; and in base catalysis the OH<sup>-</sup> ion serves as the catalyst. The effect of temperature on hydrolysis can be profound. Each 10 °C incremental temperature increase results in a hydrolysis rate constant change by a factor of 2.5.<sup>P</sup>

<sup>P</sup> Knox R, Sabatini D, Canter L. *Subsurface transport and fate processes*. Boca Raton (FL): Lewis Publishers; 1993.

Metal (Me) hydrolysis is a special case. Cations in water act like Lewis acids in that they are prone to accept electrons, while water behaves like a Lewis base because it makes its oxygen's two unshared electrons available to the cations. When strong water–metal (acid–base) interactions take place, H<sup>1</sup> dissociates and hydronium ions form in a prototypical reaction:



Although reactions such as these have obvious applications to contaminant transformations in surface water, soil water, and ground water, they occur in any medium where water is present. Water is present in the atmosphere, so hydrolysis occurs in clouds and fog, as well as in the water fraction hygroscopic nuclei. Water is also present in all living things, so hydrolysis is a common process in metabolism (particularly in the first phase, as discussed later) and other organic processes. Thus, hydrolysis is important in numerous environmental and toxicological processes.

#### 6.1.3.2.2 PHOTOLYSIS

The sun's EMR at UV and visible wavelengths can induce chemical reactions directly and indirectly. Direct photolysis is the process where sunlight adds activation energy needed to transform a compound. Indirect photolysis is the process by which an intermediate

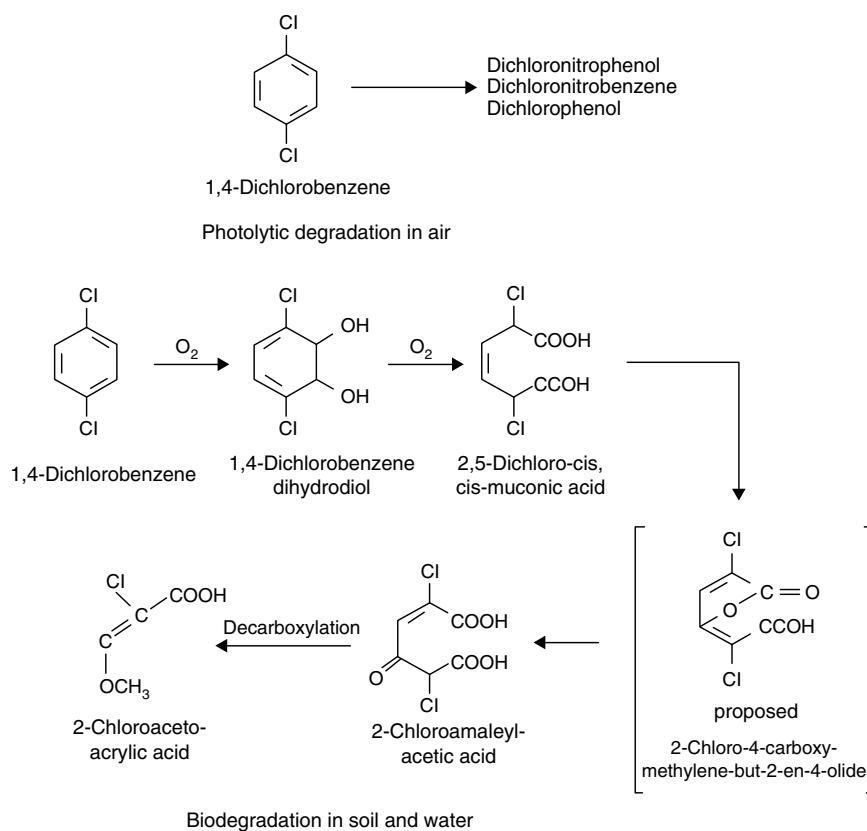
compound is energized, which in turn transfers energy to another compound.

Contaminants are photochemically degraded in both atmospheric and aquatic environments. Photolysis can combine or interchange with other processes, such as in the degradation pathways for chlorinated organic contaminants. For example, the degradation pathway for 1,4-dichlorobenzene in air is a reaction with photochemically generated OH<sup>-</sup> radicals and oxides of nitrogen. However, in soil and water, the degradation is mainly microbial biodegradation, leading to very different end products (see [Figure 6.9](#)).

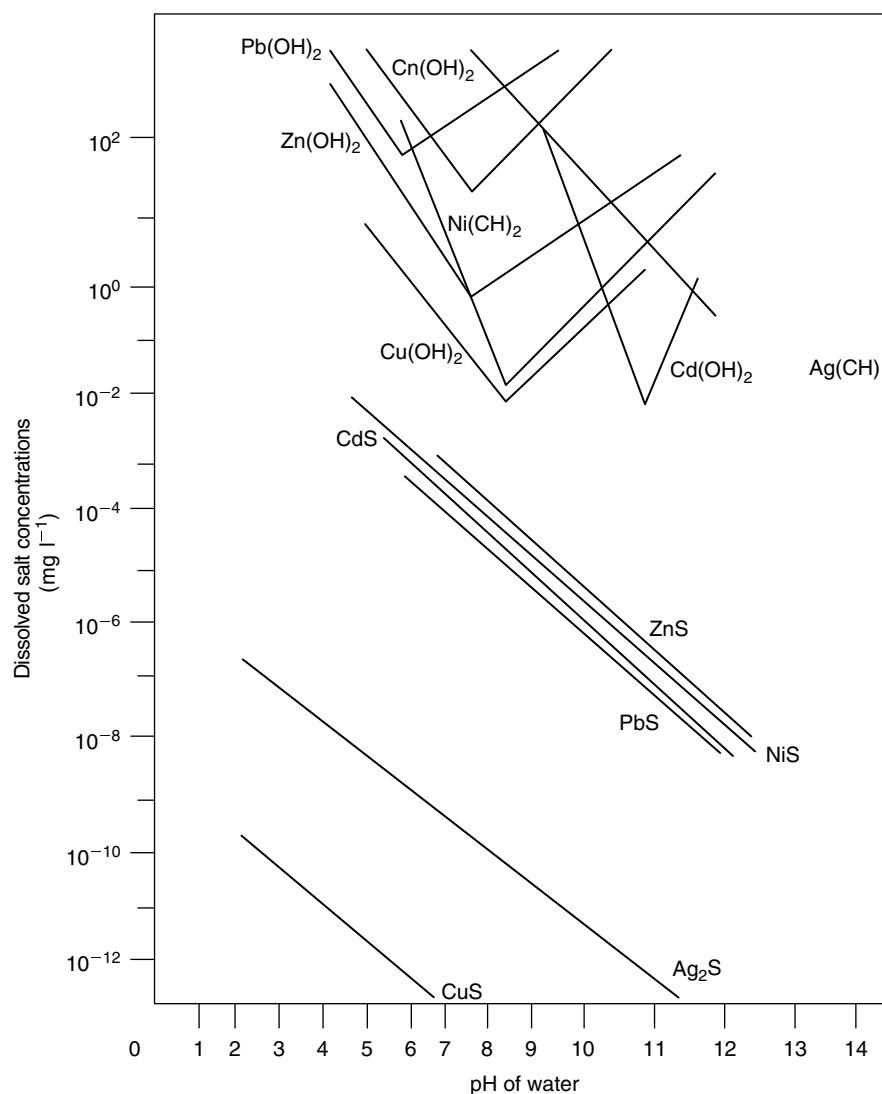
#### 6.1.3.2.3 PRECIPITATION REACTIONS

Dissolved ions may react with one another to form a solid phase compound under environmental conditions of temperature and pressure. Salts are compounds that form when metals react with nonmetals, such as sodium chloride (NaCl). They may also form from cation and anion combinations, such as ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>). Precipitation is both a physical and chemical process, wherein soluble metals and inorganic compounds change into insoluble metallic and inorganic salts. In other words, the dissolved forms become solids. Such reactions in which soluble chemical species become insoluble products are known as "precipitation reactions".

**FIGURE 6.9** Different 1,4-dichlorobenzene reactions according to environmental media. Agency for Toxic Substances and Disease Registry. Toxicological Profile for 1,4-Dichlorobenzene. <http://www.atsdr.cdc.gov/toxprofiles/tp10.html>; 1998.



**FIGURE 6.10** Effect of pH on the solubility of metal hydroxides and sulfides. US Environmental Protection Agency. Summary report: control and treatment technology for the metal finishing industry; sulfide precipitation. Report No. EPA 625/8-80-003. Washington (DC); 1980.



Chemical precipitation occurs within a defined pH and temperature range unique for each metallic salt. Usually in such reactions, an alkaline reagent is added to the solution, thereby raising the solution pH. The higher pH often decreases the solubility of the metallic constituent, bringing about the precipitation (see Figure 6.10). For example, adding caustic soda ( $\text{NaOH}$ ) decreases the amount of soluble nickel, producing the much less water-soluble species nickel hydroxide precipitate (recall that “s” denotes a solid precipitate):



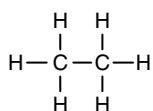
#### 6.1.4 Organic Chemistry

Carbon is an amazing element. It can bond to itself and to other elements in a myriad of ways. In fact, it can form single, double, and triple bonds with itself. This makes for millions of possible organic compounds. An organic compound is a compound that includes at least one carbon-to-carbon or carbon-to-hydrogen covalent bond.

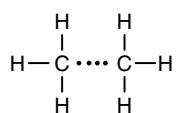
The majority of air pollutants are organic.<sup>q</sup> Organic compounds can be further classified into two basic groups: aliphatics and aromatics. Hydrocarbons are

<sup>q</sup>This is true in terms of the actual number of chemical compounds. By far, most contaminants are organic. However, in terms of total mass of reactants and products in the biosphere, inorganic compounds represent a greater mass. For example, most hazardous waste sites are contaminated with organic contaminants, but large-scale waste represented by mining, extraction, transportation, and agricultural activities have larger volumes and masses of metals and inorganic substances.

the most fundamental type of organic compounds. Unsubstituted hydrocarbons contain only the elements carbon and hydrogen. Aliphatic compounds are classified into a few chemical families. Each carbon normally forms four covalent bonds. Alkanes are hydrocarbons that form chains with each link comprised of the carbon. A single link is  $\text{CH}_4$ , methane. The carbon chain length increases with the addition of carbon atoms. For example, ethane's structure is:



And the prototypical alkane structure is:



The alkanes contain a single bond between each carbon atoms, and include the simplest organic compound, methane ( $\text{CH}_4$ ), and its derivative "chains" such as ethane ( $\text{C}_2\text{H}_6$ ) and butane ( $\text{C}_4\text{H}_{10}$ ). Alkenes contain at least one double bond between carbon atoms. For example, 1,3-butadiene's structure is  $\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2$ . The numbers "1" and "3" indicate the position of the double bonds. The alkynes contain triple bonds between carbon atoms, the simplest being ethyne,  $\text{CH}\equiv\text{CH}$ , which is commonly known as acetylene (the gas used by welders).

The aromatics are all based on the six-carbon configuration of benzene ( $\text{C}_6\text{H}_6$ ). The carbon–carbon bond in this configuration shares more than one electron, so that benzene's structure allows for resonance among the double and single bonds, i.e. the actual benzene bonds flip locations. Benzene is the average of two equally contributing resonance structures.

The term "aromatic" comes from the observation that many compounds derived from benzene are highly fragrant, such as vanilla, wintergreen oil, and sassafras. Aromatic compounds, thus, contain one or more benzene rings. The rings are planar, that is, they remain in the same geometric plane as a unit. However, in compounds with more than one ring, such as the highly toxic PCBs, each ring is planar, but the rings that are bound together may or may not be planar. This is actually a very important property for toxic compounds. It has been shown that some planar aromatic compounds are more toxic than their nonplanar counterparts, possibly because living cells may be more likely to allow planar compounds to bind to them and to produce nucleopeptides that lead to biochemical reactions associated with cellular dysfunctions, such as cancer or endocrine disruption.

Both the aliphatic and aromatic compounds can undergo substitutions of the hydrogen atoms. These substitutions render new properties to the compounds, including changes in solubility, vapor pressure, and toxicity. For example, halogenation (substitution of a hydrogen atom with a halogen) often makes an organic compound much more toxic. Thus, trichloroethane is a highly carcinogenic liquid that has been found in drinking water supplies, whereas nonsubstituted ethane is a gas with relatively low toxicity. This is also why one of the means for treating chlorinated hydrocarbons and aromatic compounds involves dehalogenation techniques.

The important functional groups that are part of many organic compounds are shown in Table 6.9.

Structures of organic compounds can induce very different physical and chemical characteristics, as well

TABLE 6.9 Structures of Organic Compounds

Chemical Class	Functional Group
Alkanes	$\begin{array}{c}   &   \\ -\text{C} & -\text{C}- \\   &   \end{array}$
Alkenes	$\begin{array}{c} >\text{C}=\text{C}< \end{array}$
Alkynes	$\begin{array}{c} -\text{C}\equiv\text{C}- \end{array}$
Aromatics	$\begin{array}{c} \text{C}_6\text{H}_6 \end{array}$
Alcohols	$\begin{array}{c}   \\ -\text{C}-\text{OH} \\   \end{array}$
Amines	$\begin{array}{c}   \\ -\text{C}-\text{N} \\   \end{array}$
Aldehydes	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{H} \end{array}$
Ether	$\begin{array}{c}   &   \\ -\text{C} & -\text{O}-\text{C}- \\   &   \end{array}$
Ketones	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{C}-\text{C}- \\   &   \end{array}$

(Continued)

TABLE 6.9 Structures of Organic Compounds—cont'd

Chemical Class	Functional Group
Carboxylic acids	
Alkyl halides*	
Phenols (aromatic alcohols)	
<b>SUBSTITUTED AROMATICS (SUBSTITUTED BENZENE DERIVATIVES)</b>	
Nitrobenzene	
Monosubstituted alkylbenzenes	
Toluene (simplest monosubstituted alkylbenzene)	
<b>POLYSUBSTITUTED ALKYLBENZENES</b>	
1,2-Alkyl benzene (also known as ortho or <i>o</i> -...)	
1,2-Xylene or <i>ortho</i> -xylene ( <i>o</i> -xylene)	

TABLE 6.9 Structures of Organic Compounds—cont'd

Chemical Class	Functional Group
1,3-Xylene or <i>meta</i> -xylene ( <i>m</i> -xylene)	
1,4-Xylene or <i>para</i> -xylene ( <i>p</i> -xylene)	
<b>HYDROXYPHENOLS DO NOT FOLLOW GENERAL NOMENCLATURE RULES FOR SUBSTITUTED BENZENES</b>	
Catechol (1,2-hydroxiphenol)	
Resorcinol (1,3-hydroxiphenol)	
Hydroquinone (1,4-hydroxiphenol)	

\* The letter "X" commonly denotes a halogen, e.g. fluorine, chlorine, or bromine, in organic chemistry. However, in this text, since it is an amalgam of many scientific and engineering disciplines, where "x" often means an unknown variable and horizontal distance on coordinate grids, this rule is sometimes violated. Note that when consulting manuals on the physicochemical properties of organic compounds, such as those for pesticides and synthetic chemistry, the "X" usually denotes a halogen.

as change the bioaccumulation and toxicity of these compounds. For example, the differences between the estradiol and a testosterone molecule may seem small but they cause significant differences in the growth and reproduction of animals. The very subtle differences between an estrogen and an androgen, female and male hormones respectively, can be seen in these structures.

But look at the dramatic differences in sexual and developmental changes that these compounds induce in organisms!

Incremental to a simple compound, such as substituting chlorine atoms for three hydrogen atoms on the ethane molecule, can make for large differences (see [Table 6.10](#)). Replacing two or three hydrogen atoms with chlorine atoms makes for differences in toxicities between the nonhalogenated form and the chlorinated form. The same is true for the simplest aromatic, benzene. Substituting a methyl group for one of the hydrogen atoms forms toluene.

The lessons here are many. There are uncertainties in using surrogate compounds to represent whole groups of chemicals (since a slight change can change the molecule significantly). However, this points to the importance of “green chemistry” and computational chemistry, as tools to prevent dangerous chemicals reaching the marketplace and the environment before they are manufactured. Subtle differences in molecular structure can render molecules safer, while maintaining the characteristics that make them useful in the first place, including their market value.

### 6.1.4.1 Isomers

Isomers are compounds with identical chemical formulas, but different structures. They are very important in air pollution chemistry, because even slightly different structures can evoke dramatic differences in chemical and physical properties. So, isomers may exhibit different chemodynamic behavior and different toxicities. For example, the three isomers of pentane ( $C_5H_{12}$ ) are shown in [Figure 6.14](#). The difference in structure accounts for significant physical differences. For example, the boiling points for *n*-pentane, isopentane, and neopentane at 1 atm are 36.1, 27.8, and 9.5 °C, respectively. Thus, neopentane’s lower boiling point means that this isomer has a lower vapor pressure, which makes it is more likely to enter the atmosphere than the other two isomers under the same environmental conditions.

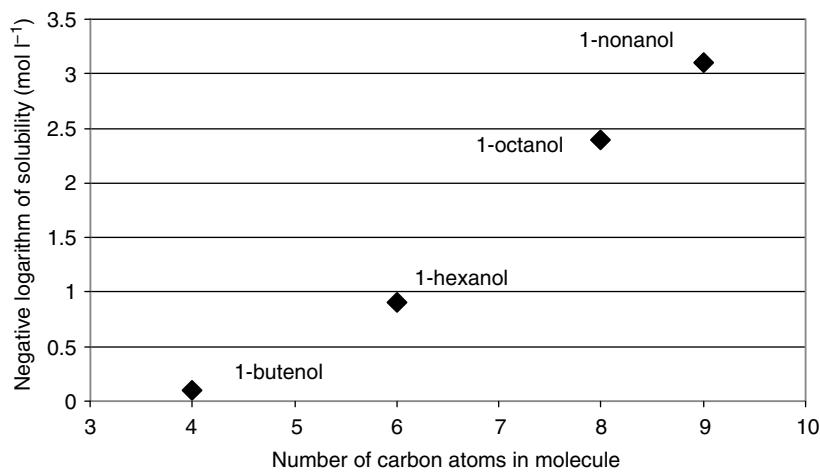
Optical isomers or chiral forms of the same compound are those that are mirror images to each other. These differences may make one, e.g. the left-handed form, virtually nontoxic and easily biodegradable, yet the right-handed form may be toxic and persistent.

## ORGANIC STRUCTURE EXAMPLE 1

### Answer and Discussion

If the aqueous solubility, which is expressed as  $-\log S$  (in  $\text{mol l}^{-1}$ ), of 1-butanol, 1-hexanol, 1-octanol, and 1-nonanol are 0.1, 0.9, 2.4, and 3.1, respectively, what does this tell you about the length of carbon chains and the solubility of alcohols? (Remember that this expression of solubility is a negative log!)

Recall that solubility is expressed as a negative logarithm, so lengthening the carbon chain *decreases polarity and, therefore, aqueous solubility* since “like dissolves like” and water is very polar. Thus, as shown in [Figure 6.11](#), butanol is orders of magnitude more hydrophilic than is nonanol.



**FIGURE 6.11** Aqueous solubility of four alcohols.

## ORGANIC STRUCTURE EXAMPLE 2

Consider the polarity of the four alcohols in #2 above. If aqueous solubilities, which is expressed as  $-\log P^0$ , of *n*-butane, *n*-hexane, *n*-octane, and *n*-nonane are, respectively, 3.0, 3.8, 5.2, and 5.9 mol l<sup>-1</sup>, what effect does the substitution of a hydroxyl functional group for the hydrogen atom have on an alkane's polarity? Can this effect also be observed in aromatics? (*Hint:* Compare *S* for benzene, toluene to phenol in the table in #1 above; and recall that phenol is a hydroxylated benzene.)

### Answer

There is a direct relationship (see Figure 6.12) between the increase in polarity and hydrophilicity when alkanes are hydroxylated into alcohols. This is why alcohols are miscible in water. This can be an important fact, especially in anaerobic treatment processes where microbes reduce organic compounds and in the process generate alcohols (and ultimately methane and water). Hydroxylation of an aromatic, as indicated by comparing the solubilities of benzene and phenol, also increases polarity and hydrophilicity.

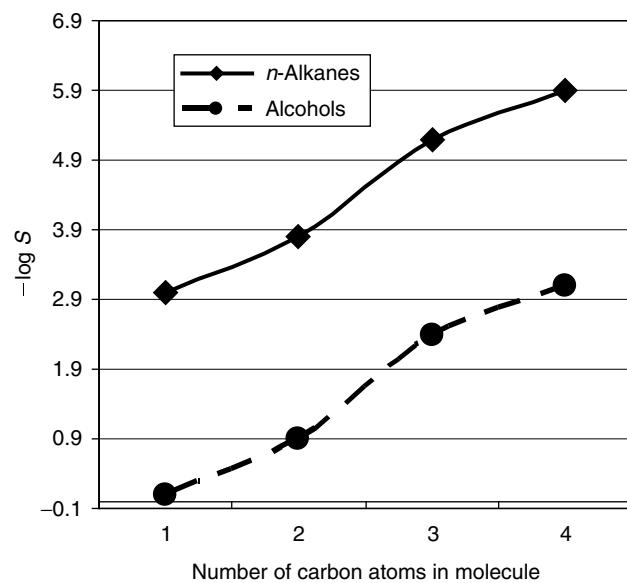


FIGURE 6.12 Aqueous solubility of selected aliphatic compounds.

It should be noted that solubility may be modified in environmental systems by using compounds known as "surfactants" (see Figure 6.13). Surfactants can be very effective in solubilizing adsorbed hydrophobic compounds in soils. The increased solubility and dispersion of hydrocarbons and aromatic compounds with very low aqueous solubility enhances desorption and bioavailability. Unfortunately, a widely used group of surfactants, i.e. alkylphenolethoxylates (APEs) have been banned in Europe because their breakdown products can be very toxic to aquatic organisms. The APEs have been particularly of concern because of their hormonal effects, particularly their estrogenicity. So, one must keep in mind not only the physical and chemical advantages of such compounds, but also any ancillary risks that they may introduce. This is a classic case of competition among values (i.e. easier and more effective cleanup *versus* additive health risks from the cleanup chemical).

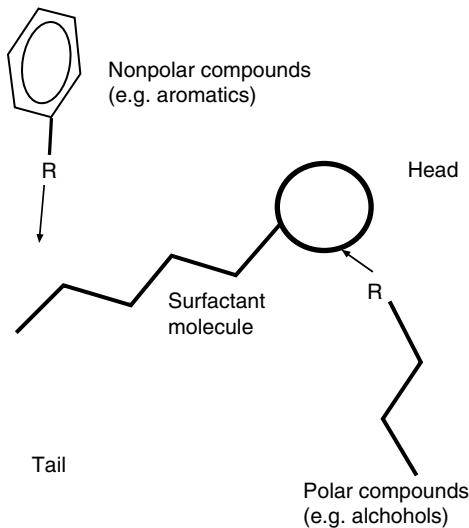


FIGURE 6.13 Structure of a surfactant prototype. The head of the molecule is relatively polar and the tail is relatively nonpolar, so in the aqueous phase the more hydrophilic compounds will react with the surfactant molecule at the head position, while the more lipophilic compounds will react at the tail position. The result is that a greater amount of the organic compounds will be in solution when surfactants are present. *Vallero D. Engineering the risks of hazardous wastes. Boston (MA): Butterworth-Heinemann; 2003.*

TABLE 6.10 Incremental Differences in Molecular Structure Leading to Changes in Physicochemical Properties and Hazards

Compound	Physical State at 25 °C	−log $P^0$ Solubility in H <sub>2</sub> O at 25 °C (mol l <sup>-1</sup> )	−log Vapor Pressure at 25 °C (atm)	Worker Exposure Limits (parts per million)	Regulating Agency
Methane, CH <sub>4</sub>	Gas	2.8	−2.4	25	Canadian Safety Association
Tetrachloromethane (carbon tetrachloride), CCl <sub>4</sub>	Liquid	2.2	0.8	2 Short-term exposure limit (STEL) = 60 min	National Institute of Occupation Health Sciences
Ethane, C <sub>2</sub> H <sub>6</sub>	Gas	2.7	−1.6	None (simple asphyxiant)	Occupational Safety and Health Administration (OSHA)
Trichloroethane, C <sub>2</sub> H Cl <sub>3</sub>	Liquid	2.0	1.0	450 STEL (15 min)	OSHA
Benzene, C <sub>6</sub> H <sub>6</sub>	Liquid	1.6	0.9	5 STEL	OSHA
Phenol, C <sub>6</sub> H <sub>5</sub> O	Liquid	0.2	3.6	10 ppm	OSHA
Toluene, C <sub>7</sub> H <sub>8</sub>	Liquid	2.3	1.4	150 STEL	UK Occupational & Environmental Safety Services

### 6.1.5 Introduction to Atmospheric Chemistry

Atmospheric chemistry encompasses all of the chemical transformations occurring in the various atmospheric layers from the troposphere to beyond the stratosphere. Air pollution chemistry represents the subset of these atmospheric chemical processes which have a direct impact on human beings, vegetation, and surface water bodies. Classification of atmospheric chemical processes as either human made (anthropogenic) or natural is useful but not precise. For example, the trace gases nitric oxide (NO) and sulfur dioxide (SO<sub>2</sub>) have

both anthropogenic and natural sources, and their atmospheric behavior is independent of their source. A vivid example was the 1980 Mt. St. Helen's volcanic eruption in Washington, a gigantic point source for SO<sub>2</sub> and PM in the atmosphere. This natural source was of such magnitude as to become first a regional air pollution problem and subsequently a global atmospheric chemical problem.

#### 6.1.5.1 Types of Atmospheric Chemical Transformations

The chemical transformations occurring in the atmosphere are best characterized as oxidation processes. Reactions involving compounds of carbon (C), nitrogen (N), and sulfur (S) are of most interest. The chemical processes in the troposphere involve oxidation of hydrocarbons, NO, and SO<sub>2</sub> to form oxygenated products such as aldehydes, nitrogen dioxide (NO<sub>2</sub>), and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). These oxygenated species become the secondary products formed in the atmosphere from the primary emissions of anthropogenic or natural sources (Figure 6.15).

Solar radiation influences the chemical processes in the atmosphere by interacting with molecules that act as photoacceptors. Free radicals are formed by the photodissociation of certain types of molecules. Free radicals are neutral fragments of stable molecules and are very reactive. Examples are O, atomic oxygen; H, atomic hydrogen; OH, the hydroxyl radical; and HO<sub>2</sub>, the hydroperoxy radical. In areas with photochemical smog, the principal photoacceptors are aldehydes, NO<sub>2</sub>, nitrous acid (HNO<sub>2</sub>), and ozone. The

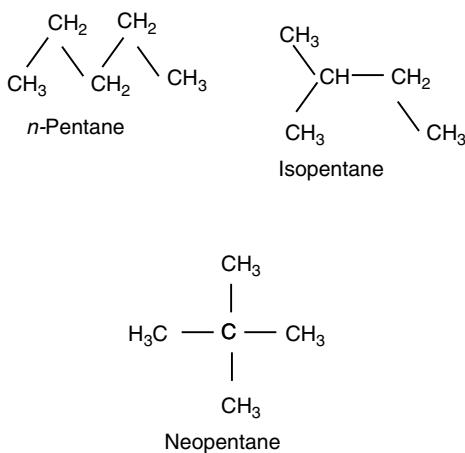
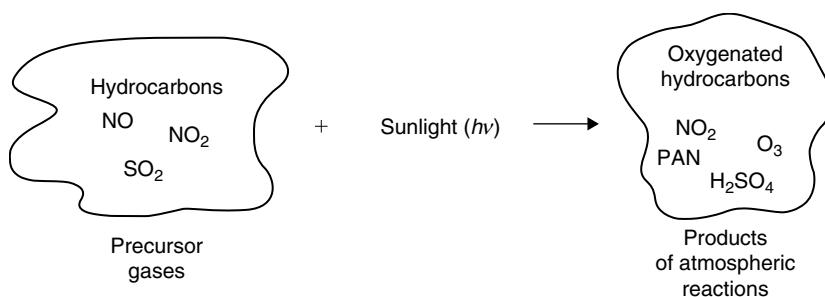


FIGURE 6.14 Isomers of pentane. Although the chemical composition is identical, the different molecular arrangements result in molecules that exhibit very dissimilar physical, chemical, and biological properties. *Vallero D. Environmental contaminants: assessment and control. Burlington (MA): Academic Press; 2004.*

**FIGURE 6.15** Precursor–product relationship of atmospheric chemical reactions.



photodissociation process is energy dependent, and only photons with sufficient energy are capable of causing photodissociation. The wavelength dependence of solar radiation is discussed in Chapter 5.

The reactivity of chemical compounds will differ because of their structure and molecular weight. Hydrocarbon compounds have been ranked according to their rate of reaction with various types of oxidizing species such as OH, NO<sub>3</sub>, and O<sub>3</sub>.<sup>t</sup> The role of hydrocarbons, along with oxides of nitrogen, in the formation of ozone is very complex. Ozone formation is a function of the mixture of hydrocarbons present and the concentration of NO<sub>x</sub>, [NO<sub>x</sub>] (= [NO] + [NO<sub>2</sub>]). The concept of an incremental reactivity scale permits assessing the increment of ozone formation per incremental change in a single hydrocarbon component.<sup>s</sup> Incremental reactivity is determined by calculating the ozone formation potential in a baseline scenario using a simple mixture of hydrocarbons representing an urban atmosphere. Then for each hydrocarbon species of interest, the ozone formation is recalculated with incremental hydrocarbons added to the mixture. From this approach, the Δ[O<sub>3</sub>]/Δ[HC] values represent the impact of a specific hydrocarbon on urban photochemical smog formation.

The vapor pressure of a compound is important in determining the upper limit of its concentration in the atmosphere. High vapor pressures will permit higher concentrations than low vapor pressures. Examples of organic compounds are methane and benzo[a]pyrene. Methane, with a relatively high vapor pressure, is always present as a gas in the atmosphere; in contrast, benzo[a]pyrene, with a relatively low vapor pressure, is adsorbed on PM and is therefore not present as a gas. Vapor pressure also affects the rate of evaporation of organic compounds into the atmosphere and the

conversion of atmospheric gases to PM, e.g. SO<sub>2</sub> to the aerosol H<sub>2</sub>SO<sub>4</sub>.<sup>t</sup>

Atmospheric chemical reactions are classified as either photochemical or thermal. Photochemical reactions are the interactions of photons with species which result in the formation of products. These products may undergo further chemical reaction. These subsequent chemical reactions are called *thermal* or *dark* reactions.

Finally, atmospheric chemical transformations are classified in terms of whether they occur as a gas (homogeneous), on a surface, or in a liquid droplet (heterogeneous). An example of the last is the oxidation of dissolved sulfur dioxide in a liquid droplet. Thus, chemical transformations can occur in the gas phase, forming secondary products such as NO<sub>2</sub> and O<sub>3</sub>; in the liquid phase, such as SO<sub>2</sub> oxidation in liquid droplets or water films; and as gas-to-particle conversion, in which the oxidized product condenses to form an aerosol.

### 6.1.5.2 Role of Solar Radiation in Atmospheric Chemistry

The time required for atmospheric chemical processes to occur is dependent on chemical kinetics. Many of the air quality problems of major metropolitan areas can develop in just a few days. Most gas-phase chemical reactions in the atmosphere involve the collision of two or three molecules, with subsequent rearrangement of their chemical bonds to form molecules by combination of their atoms. Consider the simple case of a bimolecular reaction of the following type:



$$\text{Rate of reaction} = k[B][C] \quad (6.45)$$

<sup>t</sup> Pitts Jr JN, Winer AM, Darnall KR, Lloyd AC, Doyle GJ. In: Dimitriades B, editor. *Proceedings of the international conference on photochemical oxidant pollution and its control*, vol. II, EPA-600/3-77-OOl. Research Triangle Park (NC): US Environmental Protection Agency; 1977. p. 687–707.

<sup>s</sup> Carter WPL. *Development of ozone reactivity scales for volatile organic compounds*. EPA 600/3-91-050. US Environmental Protection Agency; August 1991.

<sup>t</sup> National Research Council. *Ozone and other photochemical oxidants*. Washington (DC): National Academy of Sciences; 1977.

TABLE 6.11 Values of  $\exp(-E_a/RT)$  as a Function of the Activation Energy for  $T = 298 \text{ }^\circ\text{K}$ <sup>\*</sup>

$E_a$	$\exp(-E_a/RT)$
1.0	0.67
3.0	0.30
10.0	0.0177
30.0	$5.51 \times 10^{-6}$
100.0	$2.95 \times 10^{-18}$
300.0	$2.56 \times 10^{-53}$

\* In SI units,  $R = 8.31434 \text{ joules per mole degree kelvin (J}^\circ\text{ k}^{-1} \text{ mol}^{-1}\text{)}$ .

where  $k = A \exp(-E_a/RT)$  and  $k$ , the rate constant, is dependent on the frequency factor ( $A$ ), the temperature ( $T$ ), the activation energy of the reaction ( $E_a$ ) and the ideal gas constant ( $R$ ). The frequency factor,  $A$ , is of the same order of magnitude for most gas reactions. For  $T = 298 \text{ K}$  the rate of reaction is strongly dependent on the activation energy  $E_a$  as shown in Table 6.11.<sup>u</sup> When  $E_a$  is  $>30 \text{ kJ mol}^{-1}$  the rates become very small, limiting the overall rate of reaction. Table 6.12 lists the activation energies for bimolecular collisions of different molecular species. For the first three reactions between molecular species,  $E_a > 100 \text{ kJ}$ , but for the last three reactions  $E_a < 10 \text{ kJ}$ . The last three reactions involve the participation of free radical or atomic species. The activation energies of reactions involving atomic or free radicals are very small, permitting chemical transformations on a short timescale.

TABLE 6.12 Activation Energies for Atmospheric Reactions

Reaction	$E_a (\text{kJ mol}^{-1})$
$\text{N}_2 + \text{O}_2 \rightarrow \text{N}_2\text{O} + \text{O}$	538
$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$	251
$\text{SO}_2 + \text{NO}_2 \rightarrow \text{SO}_3 + \text{NO}$	106
$\text{O} + \text{H}_2\text{S} \rightarrow \text{OH} + \text{HS}$	6.3
$\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$	<1
$\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}$	<1

Source: Campbell IM. *Energy and the atmosphere*. New York: Wiley; 1977:212–13.

<sup>u</sup> Campbell IM. *Energy and the atmosphere*. New York: Wiley; 1977.

<sup>v</sup> Lonneman WA, Seila RL, Bufalini JJ. *Environ Sci Technol* 1978;12:459–63.

<sup>w</sup> Data obtained from the 1976 data file of the Regional Air Pollution Study Program. US Environmental Protection Agency. Research Triangle Park (NC); 1976.

<sup>x</sup> Akimoto H, Sakamaki F, Hoshino M, Inoue G, Oduda M. *Environ Sci Technol* 1979;13:53–58.

<sup>y</sup> Graedel TE, Hawkins DT, Claxton LD. *Atmospheric chemical compounds: sources, occurrence, and bioassay*. Orlando (FL): Academic Press; 1986.

### 6.1.5.3 Gas-Phase Chemical Reaction Pathways

The complexity of the atmospheric chemical reactions occurring in major metropolitan areas can be staggering. Urban atmospheres are characterized as complex mixtures of hydrocarbons and oxides of sulfur and nitrogen. Table 6.13 show the hydrocarbons identified in the urban air of St. Petersburg, Florida.<sup>v</sup> The interactions among this large number of compounds can be understood by studying simpler systems. Figure 6.16 shows the diurnal patterns of NO, NO<sub>2</sub>, and O<sub>3</sub> for St. Louis, Missouri.<sup>w</sup> These diurnal patterns are interrelated. The concentration profiles of Figure 6.16 are the result of a combination of atmospheric chemical and meteorological processes. To uncouple this combination of factors, laboratory (smog chamber) studies such as those of the propene–NO<sub>x</sub> system (Figure 6.17) have been undertaken.<sup>x</sup> These profiles show chemical transformations separated from meteorological processes.

Similar chemical steps occur in the ambient air and in laboratory smog chamber simulations. Initially, hydrocarbons and nitric oxide are oxidized to form nitrogen dioxide, ozone, and other oxidation products such as peroxyacetyl nitrate (PAN) and aldehydes. The complete process is very complicated, with many reaction steps.

The principal components of atmospheric chemical processes are hydrocarbons, oxides of nitrogen, oxides of sulfur, oxygenated hydrocarbons, ozone, and free radical intermediates. Solar radiation plays a crucial role in the generation of free radicals, whereas water vapor and temperature can influence particular chemical pathways. Table 6.14 lists a few of the components of each of these classes. Although more extensive tabulations may be found in *Atmospheric Chemical Compounds*,<sup>y</sup> those listed in Table 6.14 are sufficient for an understanding of smog chemistry. The major undesirable components of photochemical smog are NO<sub>2</sub>, O<sub>3</sub>, SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, PAN, and aldehydes. Air quality standards have been established in several countries for SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub>; H<sub>2</sub>SO<sub>4</sub> contributes to acidic deposition and reduction in visibility; and PAN and aldehydes can cause eye irritation and plant damage if their concentrations are sufficiently high.

TABLE 6.13 Hydrocarbon Compounds Identified in Ambient Air Samples from St. Petersburg, Florida

Acetaldehyde	<i>m</i> -Ethyltoluene	Methylcyclohexane	Propene
Acetylene	<i>o</i> -Ethyltoluene	3-Methylhexane	<i>n</i> -Propylbenzene
1,3-Butadiene	<i>p</i> -Ethyltoluene	2-Methylpentane	Toluene
<i>n</i> -Butane	<i>n</i> -Heptane	Nonane	2,2,4 Trimethylpentane
<i>trans</i> -2-Butene	Isobutane	<i>n</i> -Pentane	<i>m</i> -Xylene
Cyclopentane	Isobutylene	1-Pentene	<i>o</i> -Xylene
<i>n</i> -Decane	Isopentane	<i>cis</i> -2-Pentene	<i>p</i> -Xylene
2,3-Dimethylpentane	Isopropyl benzene	<i>trans</i> -2-Pentene	1,2,4-Rimethylbenzene
Ethane	Limonene	<i>alpha</i> -Pinene	1,3,5-Rimethylbenzene
Ethylbenzene	Methane	<i>beta</i> -Pinene	
Ethylene	2-Methyl-1-Butene	Propane	

Source: Lonneman WA, Seila RL, Bufalini JJ. Environ Sci Technol 1978;12:459–63.

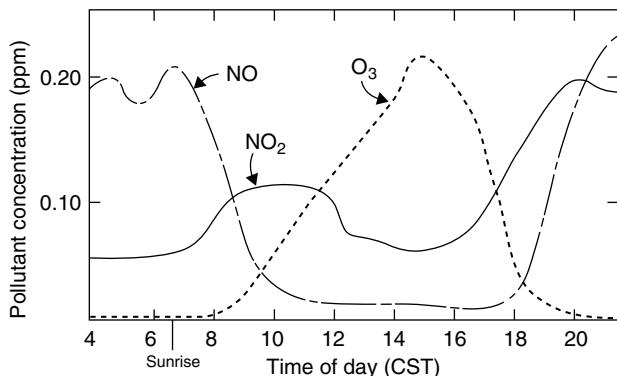


FIGURE 6.16 NO-NO<sub>2</sub>-O<sub>3</sub> ambient concentration profiles from average of four regional air monitoring stations (RAPS) in downtown St. Louis, Missouri (USA) on October 1, 1976 (CST stands for central standard time). RAPS, Data obtained from the 1976 data file for the Regional Air Pollution Study Program. US Environmental Protection Agency. Research Triangle Park (NC); 1976.

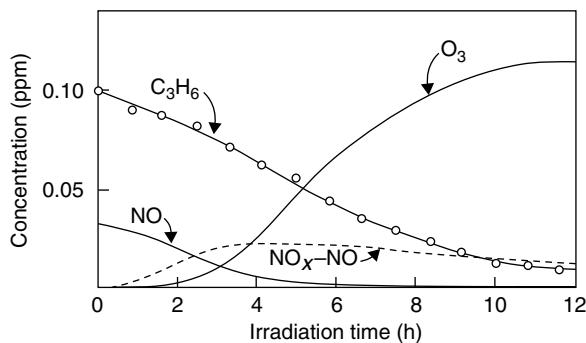


FIGURE 6.17 Concentration versus time profiles of propene, NO, NO<sub>x</sub>-NO, and O<sub>3</sub> from smog chamber irradiation;  $k_1 = 0.16 \text{ min}^{-1}$ . Akimoto H, Sakamaki F, Hoshino M, Inoue G, Oduda M. Environ Sci Technol 1979;13:53–58.

### 6.1.5.3.1 PHOTOABSORPTION OF SOLAR RADIATION

Solar radiation initiates the formation of free radicals. According to the elementary quantum theory of atoms and molecules, the internal energy of molecules is composed of electronic energy states. Molecules interact with solar radiation by absorbing photons. This absorption process causes the molecule to undergo a transition from the ground electronic state to an excited state. The change in energy between the two states corresponds to a quantum or photon of solar radiation. The frequencies  $v$  of absorption are expressed by Planck's law:

$$E = hv = hc/\lambda \quad (6.46)$$

where  $h$  is Planck's constant,  $c$  is the speed of light, and  $v$  and  $\lambda$  are the frequency and wavelength of the light of the photon, respectively. The spectrum of solar radiation in the lower troposphere starts at  $\sim 295 \text{ nm}$  and increases. Photons of shorter wavelength and higher energy are absorbed in the upper atmosphere and therefore do not reach the lower troposphere.

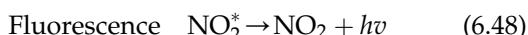
Molecules and atoms interact with photons of solar radiation under certain conditions to absorb photons of light of various wavelengths. Figure 16.18 shows the absorption spectrum of NO<sub>2</sub> as a function of the wavelength of light from 240 to 500 nm. This molecule absorbs solar radiation from 295 nm through the visible region. The absorption of photons at these different wavelengths causes the NO<sub>2</sub> molecule to enter an excited state. For longer wavelengths, transitions only in the rotational-vibrational states occur, whereas for shorter wavelengths changes in electronic states may occur. The process of photoabsorption for NO<sub>2</sub> is expressed as



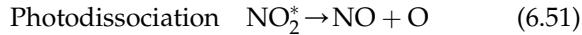
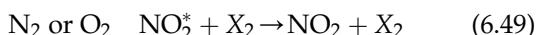
TABLE 6.14 Classes and Examples of Atmospheric Compounds

Hydrocarbons	Oxygenated Hydrocarbons
Alkenes	Aldehydes
Ethene C <sub>2</sub> H <sub>4</sub>	Formaldehyde HCHO
Propene C <sub>3</sub> H <sub>6</sub>	Acetaldehyde CH <sub>3</sub> CHO
<i>trans</i> -2-Butene	Other aldehydes RCHO
Alkanes	Acids
Methane CH <sub>4</sub>	Formic acid HCOOH
Ethane C <sub>2</sub> H <sub>6</sub>	Acetic acid CH <sub>3</sub> COOH
Alkynes	Alcohols
Acetylene C <sub>2</sub> H <sub>2</sub>	Methanol CH <sub>3</sub> OH
Aromatics	
Toluene C <sub>6</sub> H <sub>6</sub>	
<i>m</i> -Xylene C <sub>6</sub> H <sub>10</sub>	
Oxides of nitrogen	Oxides of sulfur
Nitric oxide NO	Sulfur dioxide SO <sub>2</sub>
Nitrogen dioxide NO <sub>2</sub>	Sulfur trioxide SO <sub>3</sub>
Nitrous acid HNO <sub>2</sub>	Sulfuric acid H <sub>2</sub> SO <sub>4</sub>
Nitric acid HNO <sub>3</sub>	Ammonium bisulfate (NH <sub>4</sub> )HSO <sub>4</sub>
Nitrogen trioxide NO <sub>3</sub>	Ammonium sulfate (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
Dinitrogen pentoxide N <sub>2</sub> O <sub>5</sub>	
Ammonium nitrate NH <sub>4</sub> NO <sub>3</sub>	
Free radicals	Oxidants
Atomic oxygen O	PAN CH <sub>3</sub> COO <sub>2</sub> NO <sub>2</sub>
Atomic hydrogen H	Ozone O <sub>3</sub>
Hydroxyl OH	
Hydroperoxy OH <sub>2</sub>	
Acyl RCO	
Peroxyacetyl RCOO <sub>2</sub>	

where  $h\nu$  represents the photon of solar radiation of energy and NO<sub>2</sub>\* is the NO<sub>2</sub> molecule in the excited state. The excited NO<sub>2</sub> molecule can follow several pathways:



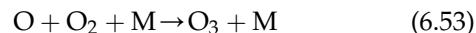
Collisional deactivation where X<sub>2</sub> is



In the case of NO<sub>2</sub>, for each photon absorbed below 400 nm, photodissociation occurs. For other photoabsorbers, HNO<sub>2</sub> and aldehydes, the photodissociation process leads to the formation of free radicals.

### 6.1.5.3.2 NITRIC OXIDE, NITROGEN DIOXIDE, AND OZONE CYCLES

Three relatively simple reactions can describe the interrelationships among these components.



Equation (6.52) shows the photochemical dissociation of NO<sub>2</sub>. Equation (6.53) shows the formation of ozone from the combination of O and molecular O<sub>2</sub> where M is any third-body molecule (principally N<sub>2</sub> and O<sub>2</sub> in the atmosphere). Equation (6.54) shows the oxidation of NO by O<sub>3</sub> to form NO<sub>2</sub> and molecular oxygen. These three reactions represent a cyclic pathway (Figure 6.18) driven by photons represented by  $h\nu$ . Throughout the daytime period, the flux of solar radiation changes with the movement of the sun. However, over short-time periods ( $\sim 10$  min) the flux may be considered constant, in which case the rate of Eqn (6.52) may be expressed as

$$\text{Rate} = k_1[\text{NO}_2] \quad (6.55)$$

where  $k_1$  is a function of time of day. Expressions for the time rate of change for each of the components may be written. If this cycle reaches a steady state, the change in concentration with time no longer occurs, so that d [conc]/dt is equal to zero.

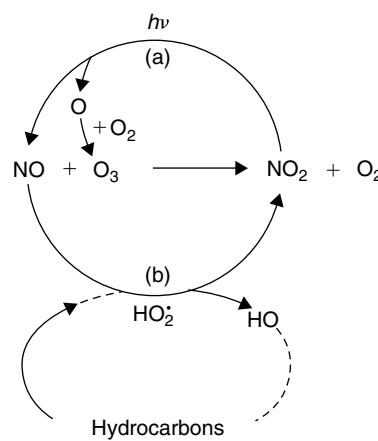
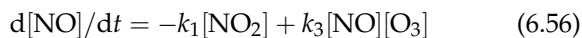


FIGURE 6.18 Photochemical cycle of NO, NO<sub>2</sub>, O<sub>3</sub>, and free radicals.

TABLE 6.15  $[O_3]$  Predicted from Photostationary State Approximation as a Function of Initial  $[NO_2]^*$

$[NO_2]$ (ppm)	$[NO_2]_{final}$ (ppm)	$[O_3]_{final}$ (ppm)	$[NO_2]/[NO]$
0.1	0.064	0.036	1.78
0.2	0.145	0.055	2.64
0.3	0.231	0.069	3.35
0.4	0.319	0.081	3.94
0.5	0.408	0.092	4.43

\*  $k_1 = 0.5 \text{ min}^{-1}$ ;  $k_3 = 24.2 \text{ ppm}^{-1} \text{ min}^{-1}$ .

$$\frac{d[O]}{dt} = k_1[NO_2] - k_2[O][O_2][M] \quad (6.57)$$

$$\frac{d[O_3]}{dt} = k_2[O][O_2][M] - k_3[NO][O_3] \quad (6.58)$$

From Eqn (6.56), it is possible to obtain an expression for the relationship among NO,  $NO_2$ , and  $O_3$ :

$$\frac{d[NO]}{dt} = O; \quad k_1[NO_2] = k_3[NO][O_3] \quad (6.59)$$

$$[O_3] = k_1[NO_2]/k_3[NO] \quad (6.60)$$

Equation (6.60) is called the *photostationary state expression* for ozone. Upon examination, one sees that the concentration of ozone is dependent on the ratio  $NO_2/NO$  for any value of  $k_1$ . The maximum value of  $k_1$  is dependent on the latitude, time of year, and time of day. In the United States, the range of  $k_1$  is from 0 to  $0.55 \text{ min}^{-1}$ . Table 6.15 illustrates the importance of the  $NO_2/NO$  ratio with respect to how much ozone is required for the photostationary state to exist. The conclusion to be drawn from this table is that most of the NO must be converted to  $NO_2$  before  $O_3$  will build up in the atmosphere. This is also seen in the diurnal ambient air patterns shown in Figure 6.15 and the smog chamber simulations shown in Figure 6.16. It is apparent that without hydrocarbons, the NO is not converted to  $NO_2$  efficiently enough to permit the build up of  $O_3$  to levels observed in urban areas (Table 6.16).

The cycle represented by Eqns (6.52–6.54) is illustrated by the upper loop (a) in Figure 6.17. In this figure, the photolysis of  $NO_2$  by a photon forms an NO and an  $O_3$  molecule. If no other chemical reaction is occurring, these two species react to form  $NO_2$ , which can start the cycle over again. In order for the  $O_3$  concentration to build up, oxidizers other than  $O_3$  must participate in the oxidation of NO to form  $NO_2$ . This will permit the  $NO_2/NO$  ratio to build up and steady-state  $O_3$  concentrations as represented by Eqn (6.60) to achieve

typical ambient values. The other oxidizers in the atmosphere are free radicals. In the lower loop (b) of Figure 6.17, a second pathway for NO oxidation is shown, with free radicals participating. These free radicals are derived from the participation of hydrocarbons in atmospheric chemical reactions.

#### 6.1.5.3.3 ROLE OF HYDROCARBONS

The important hydrocarbon classes are alkanes, alkenes, aromatics, and oxygenates. The first three classes are generally released to the atmosphere, whereas the fourth class, the oxygenates, is generally formed in the atmosphere. Propene will be used to illustrate the types of reactions that take place with alkenes. Propene reactions are initiated by a chemical reaction of OH or  $O_3$  with the carbon–carbon double bond. The chemical steps that follow result in the formation of free radicals of several different types which can undergo reaction with  $O_2$ , NO,  $SO_2$ , and  $NO_2$  to promote the formation of photochemical smog products.

**6.1.5.3.3.1 OZONE REACTION WITH PROPENE** A schematic diagram of the  $O_3$  reaction with propene (Figure 6.19) is based on the work of Atkinson and Lloyd.<sup>z</sup> The molozonide formed by addition of ozone to the double bond decomposes to form an aldehyde and an energy-rich ( $\ddagger$ ) biradical. In the case of propene, two sets of products are formed. Along the pathway on the right, approximately 40% of the biradicals ( $H\dot{C}HO\cdot\ddagger$ )<sup>‡</sup> form a thermalized biradical ( $\dot{C}H_2OO\cdot$ ).<sup>A</sup> The remainder undergo rearrangement to form energy-rich formic acid ( $HCOOH\cdot\ddagger$ ), which subsequently decomposes to form  $H_2O$ , CO,  $CO_2$ ,  $H_2$ , H, and  $HCO_2$  radicals with percentages assigned to each pathway. The larger biradical ( $CH_3\dot{C}HO\cdot\ddagger$ ) follows a slightly different pathway. Approximately 40% forms a thermalized biradical ( $CH_3CHO\cdot$ ). Of the remaining 60%, a portion decomposes to  $CH_4$  and  $CO_2$  and two additional energy-rich species ( $CH_3COOH\cdot\ddagger$  and  $(CHOOCH_3)\cdot\ddagger$ ). These two unstable species decompose as shown to form  $CH_3$ , OH, H,  $HCO$ ,  $CH_3O$ , CO, and  $CO_2$ .

Alkyl radicals, R, react very rapidly with  $O_2$  to form alkylperoxy radicals. H reacts to form the hydroperoxy radical  $HO_2$ . Alkoxy radicals, RO, react with  $O_2$  to form  $HO_2$  and  $R'CHO$ , where  $R'$  contains one less carbon. This formation of an aldehyde from an alkoxy radical ultimately leads to the process of hydrocarbon chain shortening or clipping upon subsequent reaction of the aldehyde. This aldehyde can undergo photodecomposition forming R, H, and CO; or, after OH attack, forming  $CH(O)OO$ , the peroxyacetyl radical.

<sup>z</sup> Atkinson R, Lloyd AC. *J Phys Chem Ref Data* 1984;13:315–444.

<sup>A</sup> The dots represent unpaired electrons.

TABLE 6.16 Air Mass Origin, PM<sub>2.5</sub> Total Carbon Concentration, Organic to Elemental Carbon Ratio (OC/EC), and Percent Modern Carbon (pMC), and Biogenic Percentage for Total Carbon (Bio TC)

Start Date 1999	Start Time (h)	Duration (h)	Direction of Air Mass Origin	TC* ( $\mu\text{g m}^{-3}$ )	OC/EC <sup>§</sup>	pMC <sub>TC</sub> <sup>§,¶</sup> (%)	Bio TC <sup>§,**</sup> (%)
June 21	1900	11.5	ENE	8.2	12.6 ± 1.9	75 ± 1	69 ± 1
June 22	0700	11.5	S	8.0	15.5 ± 2.7	66 ± 1	61 ± 1
June 28	0700	10.5	SW	2.9	10.3 ± 3.0	66 ± 2	61 ± 2
June 29	0700	11.5	NW	3.2	15.8 ± 5.6	80 ± 2	73 ± 2
June 29	1900	11.5	NW	4.3	5.4 ± 0.8	56 ± 1	51 ± 1
July 1	0700	5.5	S	3.9	10.2 ± 4.0	68 ± 3	62 ± 3
July 1	1250	5.7	S	3.9	29.2 ± 27.3 <sup>§§</sup>	67 ± 3	61 ± 3
July 1	1900	11.5	SSW	2.8	9.9 ± 2.7	75 ± 2	69 ± 2
July 4	1900	11.5	S	7.6	3.6 ± 0.4	64 ± 1	59 ± 1
						66 ± 1 <sup>¶¶</sup>	61 ± 1 <sup>¶¶</sup>
July 5	0700	5.5	S	7.7	11.8 ± 2.1	63 ± 1	58 ± 1
July 5	1300	5.5	S	7.9	13.1 ± 3.5	64 ± 1	59 ± 1
July 6	1900	11.5	WNW	4.6	5.7 ± 0.8	65 ± 1	60 ± 1
July 7	0700	11.5	N	5.6	14.0 ± 2.9	66 ± 1	61 ± 1
July 8	1900	11.5	S	5.0	8.4 ± 1.4	70 ± 1	64 ± 1
July 9	0700	11.5	SW	4.8	17.5 ± 4.8	78 ± 1	72 ± 1
July 10	1900	11.5	N	3.8	11.2 ± 2.7	75 ± 1	69 ± 1
July 11	0700	5.5	NE	3.5	7.1 ± 2.3	70 ± 3	64 ± 3
July 11	1300	5.5	NE	4.1	7.1 ± 2.3	78 ± 3	72 ± 3
July 12	1900	11.5	NNE	5.7	15.0 ± 2.2	79 ± 1	72 ± 1
July 13	0700	5.5	N	3.6	7.9 ± 2.8	65 ± 3	60 ± 3
July 13	1300	5.5	NNW	4.1	15.1 ± 7.7	67 ± 2	61 ± 2

\* Estimated uncertainty, ±15%.

§ Uncertainty calculated by usual error propagation using the standard deviations of the measured value and the blank used to correct the measured value.

¶ Corrected for TC composite ( $n = 3$ ) filter blank: pMC =  $43 \pm 1$ , concentration =  $1.7 \pm 0.2 \mu\text{g TC cm}^{-2}$ .

\*\*  $(\text{pMCTC}/108) \times 100$

§§ The magnitude of (OC/EC) and its uncertainty are dominated by the near detection limit EC measurement.

¶¶ Duplicate analysis

Source: Lewis CW, Klouda GA, Ellenson WD. Radiocarbon measurement of the biogenic contribution to summertime PM<sub>2.5</sub> ambient aerosol in Nashville, TN. *Atmos Environ*;39(35):6053–61.

**6.1.5.3.3.2 HYDROXYL RADICAL ADDITION TO PROPENE** As shown in Figure 6.20, hydroxyl radicals primarily add to either of the carbon atoms which form the double bond. The remaining carbon atom has an unpaired electron which combines with molecular oxygen, forming an RO<sub>2</sub> radical. There are two types of RO<sub>2</sub> radicals labeled C<sub>3</sub>OHO<sub>2</sub> in Figure 6.20. Each of these RO<sub>2</sub> radicals reacts with NO to form NO<sub>2</sub>, and an alkoxy radical reacts with O<sub>2</sub> to form formaldehyde, acetaldehyde, and HO<sub>2</sub>.

**6.1.5.3.3.3 ALDEHYDE PHOTOLYSIS AND REACTIONS** Aldehydes undergo two primary reactions: photolysis and reaction with OH radicals. These reactions lead to formation of CO, H, and R radicals.

**6.1.5.3.3.4 RADICAL REACTIONS WITH NITRIC OXIDE AND NITROGEN DIOXIDE** Alkylperoxy (RO<sub>2</sub>) and peroxyacetyl (RC(O)OO) radicals react with NO to form NO<sub>2</sub>. The alkylperoxy radicals (RO<sub>2</sub>) react with NO<sub>2</sub> to form pernitric acid-type compounds, which decompose thermally as the temperature increases. The peroxyacetyl radical reacts with NO<sub>2</sub> to form PAN-type compounds, which also decompose thermally.

**6.1.5.3.3.5 RADICAL OXIDATION OF SULFUR DIOXIDE** Sulfur dioxide is oxidized in the atmosphere eventually to form sulfate compounds. The oxidation process includes both homogeneous and heterogeneous pathways. The free radicals produced from the degradation of hydrocarbons can and do react with SO<sub>2</sub> in the

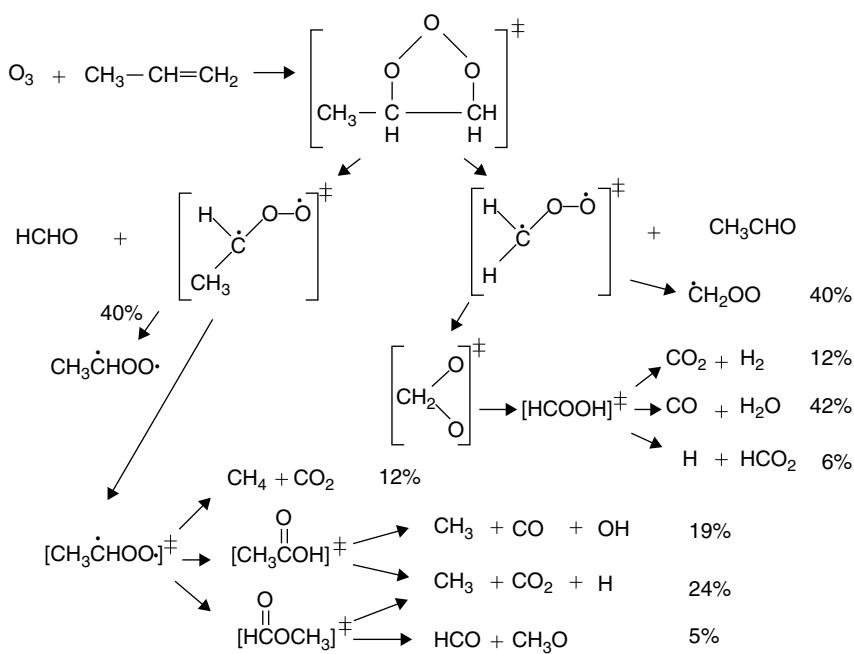


FIGURE 6.19 Ozone-propene reaction pathways showing oxidation products.

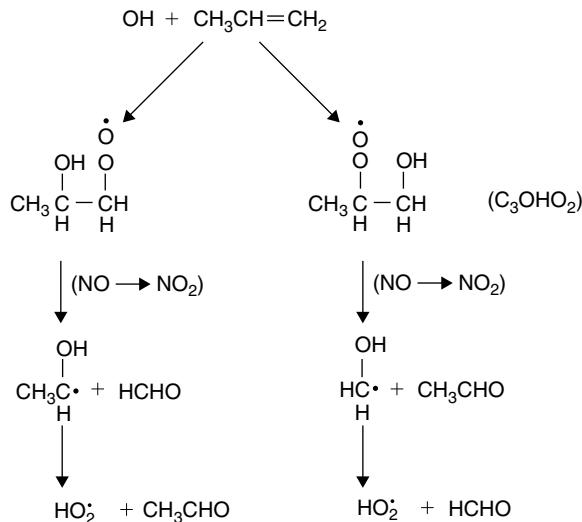


FIGURE 6.20 OH-propene reaction pathways showing oxidation products.

gas phase. Both  $OH$  and  $HO_2$  oxidize  $SO_2$  to reactive intermediates such as  $HSO_3$  and  $SO_3$ .<sup>B</sup> These intermediates combine rapidly with water vapor in the atmosphere to form sulfuric acid aerosol. This type of process is dependent on atmospheric conditions. In urban areas with existing photochemical smog problems,

the homogeneous oxidation of  $SO_2$  by free radicals is probably dominant during the daytime.

### 6.1.6 Heterogeneous Reactions

Heterogeneous reactions are defined as those involving the gas–liquid or gas–solid phases. The chemistry of  $NO_2$  and  $SO_2$  has a heterogeneous component in the atmosphere. Heterogeneous reactions involve the dissolving of  $NO_2$  and  $SO_2$  in water droplets, with subsequent chemical reactions occurring to form  $HNO_3$  and  $H_2SO_4$  in the liquid phase. The heterogeneous oxidation of  $SO_2$  in liquid droplets and water films is also a major pathway for conversion to sulfate in wet plumes and during humid or foggy conditions.

### 6.1.7 Scavenging and Removal from the Atmosphere

The atmosphere is a dynamic system, with gases and PM entering, undergoing transformation, and leaving. Atmospheric chemical processes of oxidation transform gases into more highly oxidized products, e.g.  $NO$  to  $NO_2$  to  $HNO_3$ , hydrocarbons to aldehydes, and  $SO_2$  to sulfate particles. The removal of material from the atmosphere involves two processes: wet and dry deposition.

<sup>B</sup> Calvert JG, Su F, Bottenheim JW, Strausz OP. *Atmos Environ* 1978;12:197–226.

The water solubility of gases influences the extent of removal by wet *versus* dry deposition. Gases such as SO<sub>2</sub> and NO<sub>2</sub> are sufficiently soluble to dissolve in water associated with in-cloud formation of rain droplets. These soluble gases may be removed by wet deposition of liquid droplets in the form of rain or fog. Less soluble gases such as O<sub>3</sub> and hydrocarbon vapors are removed by transport to the surface of the earth, where they diffuse to vegetation, materials, or water bodies (see Chapter 14).

## 6.2 VAPOR PRESSURE

For most air pollutants, vapor pressure is arguably their most important inherent property. Air pollutants exist in various physical states under environmental conditions. In particular, substances of low molecular weight and certain molecular structures have sufficiently high vapor pressures that they can exist in either the liquid or gas phase under environmental conditions. The vapor pressure ( $P^0$ ) of a contaminant in the liquid or solid phase is the pressure that is exerted by its vapor when the liquid and vapor are in dynamic equilibrium (see Figure 6.21).

Although vapor pressure is indeed an inherent property, the  $P^0$  value itself is an expression of the partial pressure of a chemical substance in a gas phase that is in equilibrium with the nongaseous phases. Thus, it is

both an inherent and partitioning property. For many vapors under environmental conditions, a fraction of the molecules will be in liquid phase and a fraction in the gaseous phase. Thus, under identical conditions, if molecule A has a  $P^0$  higher than the  $P^0$  of molecule B, molecule A's liquid:gas ratio will be less than molecule B's liquid:gas ratio.

With the caveats given in Chapter 1, gases are often assumed to behave according to the ideal gas law. The thermodynamic "equation of state" expresses the relationships of pressure ( $p$ ), volume ( $V$ ), and thermodynamic temperature ( $T$ ) in a defined quantity ( $n$ ) of a substance. For gases, the ideal gas law states this relationship as:

$$pV = nRT \quad (6.61)$$

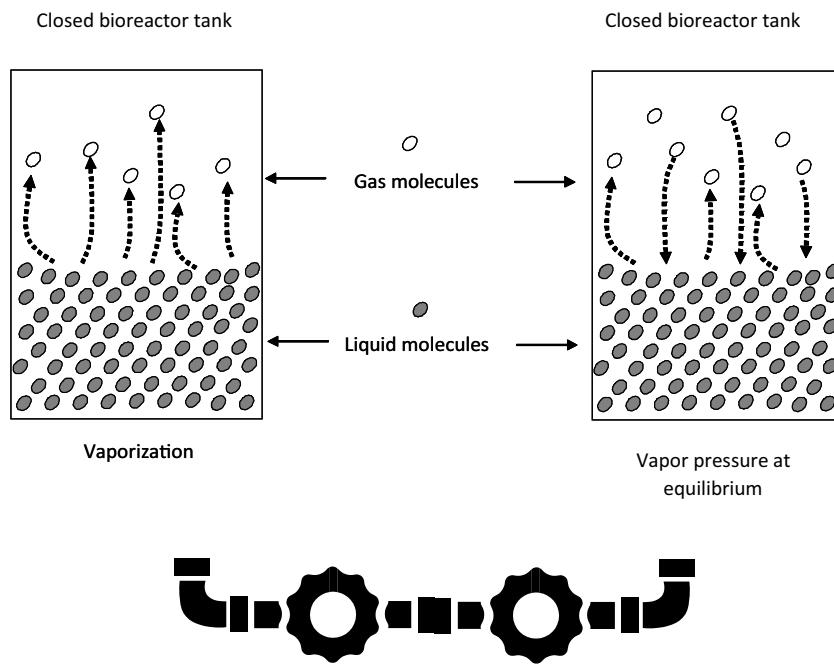
where  $R$  is the universal gas constant or molar gas constant = 8.31434 J mol<sup>-1</sup> K<sup>-1</sup>.

The ideal gas law can be used to convert  $P^0$  into moles of vapor per unit volume:

$$\frac{n}{V} = \frac{P^0}{RT} \quad (6.62)$$

where  $V$  is the volume of the container;  $n$ , number of moles of the chemical;  $R$ , molar gas constant;  $\frac{n}{V}$ , the gas phase concentration (mol l<sup>-1</sup>) of the chemical.

The  $P^0$  that is published in texts and handbooks is an expression of a chemical in its pure form; that is,  $P^0$  is expressed as the force per unit area exerted by a vapor in an equilibrium state with its pure solid, liquid, or



**FIGURE 6.21** Reactor vapor pressure of a fluid during vaporization and at equilibrium. A portion of a substance in an evacuated, closed container with limited headspace will vaporize. The pressure in the space above the liquid increases from zero and eventually stabilizes at a constant value. This value is what is known as the vapor pressure of that substance. Substances not in a closed container (i.e. infinitely available headspace) will also vaporize, but will continue to vaporize until all of the substance has partitioned to the gas phase.

TABLE 6.17 Vapor Pressures at 20 °C for Some Selected Pollutants

Chemical	Vapor Pressure (kPa) at 0 °C	Vapor Pressure (kPa) at 20 °C	Vapor Pressure (kPa) at 25 °C	Vapor Pressure (kPa) at 50 °C
Atrazine		$4.0 \times 10^{-8}$		
Benzene	3.3		12.7	36.2
Chlorobenzene			1.6	
Cyclohexane			13.0	36.3
1,1-Dichloroethane	9.6		30.5	79.2
1,2-Dichloroethane	2.8	9.2	10.6	31.4
Ethanol	1.5		7.9	29.5
Toluene			3.8	
Vinyl chloride	170	344	355	
Tetrachlorodibenzo- <i>para</i> -dioxin (TCDD)		$4.8 \times 10^{-9}$	$5.6 \times 10^{-3}$	

Source: Column 2: Hemond H, Fechner-Levy E. Chemical fate and transport in the environment. San Diego (CA): Academic Press; 2000; Columns 3 and 4: Lide D, editor. CRC handbook of chemistry and physics. 76th ed. Boca Raton (FL): CRC; 1995; TCDD data from the NTP Chemical Repository, National Environmental Health Sciences Institute; 2003 and US Environmental Protection Agency. Technical Fact Sheet on Dioxin (2,3,7,8-TCDD); 2003.

solution at a given temperature (see Table 6.17). This situation is seldom encountered in the real world of environmental engineering, so adjustments have to be made to estimates based on the published  $P^0$  values.

Note that the ideal gas law only applies to ideal gases, those that are made up of molecules taking up negligible space, with negligible spaces between the gas molecules. So, for real gases, the equilibrium relationship is:

$$(p + k)(V - nb) = nRT \quad (6.63)$$

where  $K$  is the factor for the decreased pressure on the walls of the container due to gas particle attractions;  $nb$ , volume occupied by gas particles at infinitely high pressure.

Further, the van der Waals equation of state is:

$$k = \frac{n^2 a}{V^2} \quad (6.64)$$

where  $a$  is a constant.

Gas reactions, therefore, depend upon partial pressures. The gas equilibrium  $K_p$  is quotient of the partial pressures of the products and reactants, expressed as:

$$K_p = \frac{p_C^z p_D^w}{p_A^x p_E^y} \quad (6.65)$$

Thus,  $K_p$  can also be expressed as:

$$K_p = K_{eq}(RT)^{\Delta v} \quad (6.66)$$

where  $\Delta v$  is defined as the difference in stoichiometric coefficients.

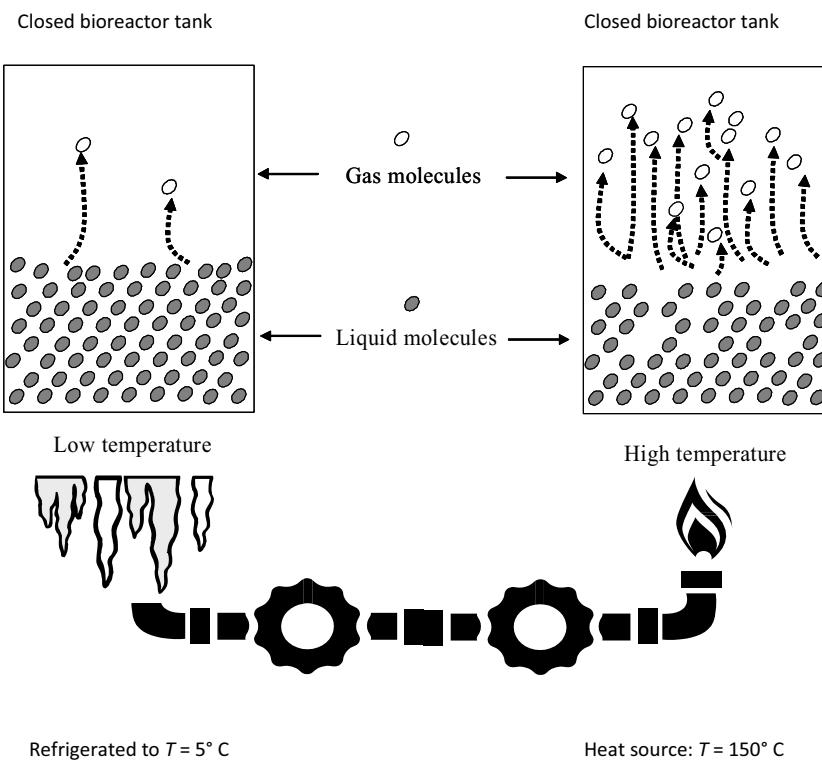
Therefore,  $P^0$  is a measure of a substance's propensity to evaporate (Figure 6.1), increasing exponentially with

an increase in temperature (see Figure 6.22), which means that a statement of  $P^0$  must always be accompanied by a temperature for that  $P^0$ . For example,<sup>2</sup> the  $P^0$  of trichloroethene at 21.0 °C is about 7.5 kPa, but at 25.5 °C rises to about 9.5 kPa. As such,  $P^0$  is a component of partitioning coefficients and volatilization rate constants.

VOCs have  $P^0$  values greater than  $10^{-2}$  kPa; semivolatile organic compounds have  $P^0$  values between  $10^{-5}$  and  $10^{-2}$  kPa, and the so-called "nonvolatile organic compounds" have  $P^0$  values less than  $10^{-5}$ .

Any substance, depending upon the temperature, can exist in any phase. However, in many environmental contexts, many compounds can be excluded from certain phases. For example, molecular nitrogen ( $N_2$ ) certainly exists in a liquid phase; however, it must be cooled below its boiling point (-196 °C). Nowhere on earth do ambient conditions meet this temperature requirement, so  $N_2$  will be considered an atmospheric gas. Conversely, a vapor is a substance that is in its gas phase but under typical environmental conditions exists as a liquid or solid under a given set of conditions. Although the pressure in the closed container in Figure 6.21 is constant and below the boiling point, molecules of the vapor will continue to condense into the liquid phase and molecules of the liquid will continue to evaporate into the vapor phase. However, the rate of these two processes is equal, meaning no net change in the amount of vapor or liquid. This is an example of dynamic equilibrium, or equilibrium vapor pressure.

At the boiling point temperature, a liquid's vapor pressure is equal to the external pressure. Generally, as vapor pressure increases for substances, boiling points



**FIGURE 6.22** Reactor vapor pressure increases in direct proportion with increasing temperature. Readings of vapor pressure values must always be accompanied by the temperature at which each measured vapor pressure is occurring.

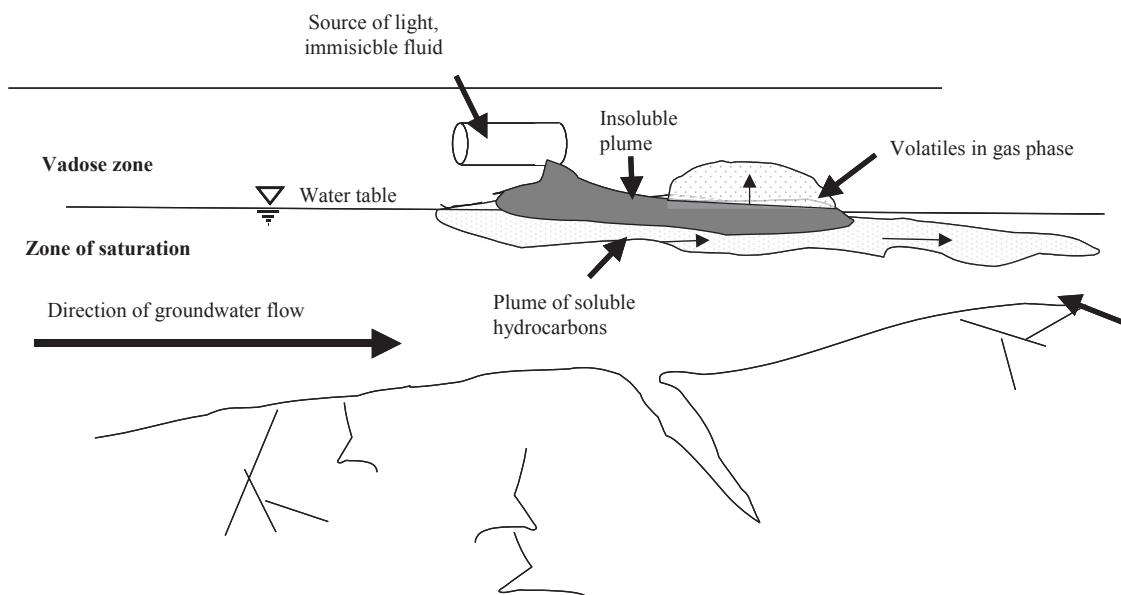
at a given pressure decrease. So, compounds with high vapor pressures are classified as “volatile”. Volatility is a measure of the propensity of a substance to form concentrations of vapor above the liquid.<sup>c</sup> This means that volatile compounds are potential air pollutants when they are stored in tanks, etc. and it also means that they can present problems to the first responders. For example, if a volatile compound is also flammable, there is a fire and explosion hazard higher than if the substance were less volatile. This is one of the reasons that lower explosive limits are so important for first responders, since volatile compounds that may have been released can concentrate in the air (e.g. inside a confined space or room) to a point where they are dangerously close to exploding.

Volatility can combine with other inherent properties of a substance, which is important to know in air pollution source characterization. For example, ground water can be contaminated with nonaqueous phase liquids (NAPLs) of varying densities. Light NAPLs (LNAPLs) are more likely to remain in the upper reaches of

aquifers than dense NAPLs (DNAPLs). The contaminated soil and ground water can become an air pollution source if an LNAPL includes a relatively insoluble substance that distributes between liquid and gas phases (see Figure 6.23). The LNAPL can infiltrate and move along the water table near the top of the zone of saturation, just above the capillary fringe. However, some of the contaminant fluid lags behind the plume and slowly solubilizes in the pore spaces of the soil and unconsolidated material. These more soluble forms of the fluid find their way to the zone of saturation and move with the general ground water flow. The higher vapor pressures of portions of the plume will lead to upward movement of volatile compounds in the gas phase.

Thus, a water contamination scenario becomes an air pollution scenario as a result of the interplay of inherent properties, i.e. vapor pressure, solubility, and density of the fluid components. As always, the extent and severity of the pollution must also account for environmental conditions, including temperature, atmospheric pressure, relative humidity, soil type (e.g. more permeable

<sup>c</sup> This is an important aspect in chromatography, as well. The lower boiling point compounds, i.e. the VOCs, usually come off the column first. That is, as the gas chromatograph's oven increases the temperature of the column, the more volatile compounds leave the column first, and they hit the detector first, so their peaks show up before the less volatile compounds. Other chemical factors such as halogenation and sorption affect this relationship, so this is not always the case, but as a general rule, a compound's boiling point is a good first indicator of residence time on a column.



**FIGURE 6.23 Hypothetical plume of hydrophobic fluid.** Adapted from: Sara MN. Ground water monitoring system design. In: Nielsen DM, editor. Practical handbook of ground-water monitoring. Chelsea (MI): Lewis Publishers; 1991.

soil allows increased contaminant transfer), concentration of pollutant, and presence of other substances. For example, if surfactants are present, the organic contaminant may have more affinity of the water and be less likely to escape to the atmosphere.

### 6.2.1 Henry's Law

The Henry's Law constant ( $K_H$ ) can be more powerful than simple vapor pressures for predicting an air pollutant entry of compounds into the atmosphere. It is the ratio at equilibrium of the gas phase concentration to the liquid phase concentration of a gas. Since it is an equilibrium relationship, it is discussed in detail in Chapter 17. However, it is also an inherent property of chemical compounds, since it combines two inherent properties, i.e. vapor pressure and solubility to estimate the likelihood that a substance will be exchanged between air and a liquid, especially water. Thus, under prescribed conditions of pressure and temperature, the vapor pressure and solubility in water of a compound can be known. However, the method used to calculate  $K_H$  affects the estimate. For example, the  $K_H$  for benzene for solubility in water at 298.15 K has varied from 0.12 to 0.22 mol kg<sup>-1</sup> bar<sup>-1</sup>, with even more variability using a temperature dependent method, i.e. 2200–5300 (unitless Henry's Law Constant).<sup>3</sup>

## 6.3 SOLUBILITY

The measure of the amount of chemical that can dissolve in a liquid is called solubility. It is usually

expressed in units of mass of solute (that which is dissolved) in the volume of solvent (that which dissolves). Usually, when scientists use the term "solubility" without any other attributes, they mean the measure of the amount of the solute in water, i.e. aqueous solubility. Otherwise, the solubility will be listed along with the solvent, such as solubility in benzene, solubility in methanol, or solubility in hexane. Solubility may also be expressed in mass per mass or volume per volume, represented as parts per million (ppm), parts per billion (ppb), or parts per trillion (ppt). Occasionally, solubility is expressed as a percent or in parts per thousand; however, this is uncommon for contaminants, and is usually reserved for nutrients and essential gases (e.g. percent carbon dioxide in water or ppt water vapor in the air).

The solubility of a compound is very important to the extent and type of pollutant transport. The inherent solubility is also a reasonably reliable indication of a compound's affinity for various substrates, e.g. in precipitation. As such, solubility in water and other solvents is an indication of where one is likely to find the compound in the environment. For example, the most toxic form of dioxin, TCDD, has low aqueous solubility and very high solubility in organic solvents (see Table 6.18). Based on these solubility differences, if a source is releasing dioxins, one would expect TCDD to have a much greater affinity for PM that contains organic compounds. After being emitted, it may precipitate sorbed to PM. After deposition, it may strongly bond to lipophilic compounds in sediment, organic particles, and the organic fraction of soils. Low aqueous solubility indicates that dissolved TCDD in the water column should be at only

TABLE 6.18 Solubility of Tetrachlorodibenzo-*para*-dioxin in Water and Organic Solvents

Solvent	Solubility (mg l <sup>-1</sup> )	Reference
Water	$1.93 \times 10^{-5}$	Podoll et al. Environ Sci Technol 1986;20:490–92
Water	$6.90 \times 10^{-4}$ (25 °C)	Fiedler et al. Chemosphere 1990;20:1597–602
Methanol	10	International Agency for Research on Cancer (IARC)
Lard oil	40	IARC
n-Octanol	50	IARC
Acetone	110	IARC
Chloroform	370	IARC
Benzene	570	IARC
Chlorobenzene	720	IARC
Orthochlorobenzene	1400	IARC

extremely low concentrations. But, as will be seen in the discussion regarding co-solvation, for example, other processes may override any single process, e.g. dissolution, in an environmental system.

A number of physicochemical characteristics of a substance come into play in determining its solubility. A principal property is a substance's polarity. The polarity of a molecule is its unevenness in charge. Since the water molecule's oxygen and two hydrogen atoms are aligned so that there is a slightly negative charge at the oxygen end and a slightly positive charge at the hydrogen ends, and since "like dissolves like", polar substances have an affinity to become dissolved in water, and nonpolar substances resist being dissolved in water.

Increasing temperature, i.e. increased kinetic energy, in a system increases the velocity of the molecules, so that intermolecular forces are weakened. With increasing temperature, the molecular velocity becomes sufficiently large so as to overcome all intermolecular forces, so that the liquid boils (vaporizes). Intermolecular forces may be relatively weak or strong. The weak forces in liquids and gases are often called van der Waals forces.

The same air pollutant exists in various physical states under environmental conditions. In particular, substances of low molecular weight and certain molecular structures have high enough vapor pressures that they can exist in either the liquid or gas phase under environmental conditions. Volatilization, solubility, and other inherent properties of a chemical compound lead to net partitioning. A contaminant's physical properties may make for an affinity for a suspended particle, but the particle may consist

of organic compounds with their own properties. The net result is that sorption, the organic-aqueous phase partitioning, and bioconcentration all taking place at the same time. These and other partitioning factors are discussed in Chapter 17. The net result of the inherent properties may be that the contaminant remains in and on the particle. Researchers are interested in the fraction of these and other mechanisms that accounts for the fugacity. In the real-life environment, however, it often suffices to understand the net effect. That is why there are so many "black boxes" in environmental models. There is often only incomplete understanding of reason the fugacity is occurring, but relatively high confidence that the first principles of science as expressed by the partitioning coefficients will occur unless there is some yet to be explained other factors affecting them. In other words, we will have to live with an amount of uncertainty, but scientists are always looking for ways to increase certainty.

Models are important tools for estimating the movement of contaminants in the environment. They do not obviate the need for sound measurements. In fact, measurements and models are highly complementary. Compartmental model assumptions must be verified in the field. Likewise, measurements at a limited number of points depend on models to extend their meaningfulness. Having an understanding of the basic concepts of a contaminant transport model, we are better able to explore the principle mechanism for the movement of contaminants throughout the environment.

## 6.4 PERSISTENCE

The inverse of a molecule's reactivity is its persistence. The more persistent the air pollutant, the more likely it will come into contact with humans and other receptors. Persistent compounds are slow to degrade, i.e. breakdown into simpler compounds, in the environment. This includes residence time not only in the atmosphere but also in other parts of the environment which serve as sources and reservoirs of air pollutants. For example, if a compound is persistent, its rate of build up in soil equals the rate of deposition onto and into soil particles minus its degradation rate.

The soil, water, and other media can become air pollutant reservoirs over time. For example, if mean rate of deposition of benzo(a)pyrene to the soil is  $100 \text{ ng kg}^{-1} \text{ year}^{-1}$  and its mean degradation rate is  $10 \text{ ng kg}^{-1} \text{ year}^{-1}$  the mean accumulation rate for benzo(a)pyrene concentrations would be  $90 \text{ ng kg}^{-1} \text{ year}^{-1}$ . This means that if the soil in this area already contains  $200 \text{ ng kg}^{-1}$ , in 10 years, the soil will contain  $1100 \text{ ng kg}^{-1}$  or  $1.1 \mu\text{g kg}^{-1}$ . To complete the understanding of a reservoir, the rate at which benzo(a)pyrene exits

the soil would also need to be known. For example, a chemical compound leaves the soil to the atmosphere in two basic ways, by volatilization and by particle entrainment. Indeed, many persistent compounds are lipophilic, i.e. highly soluble in fats and oils, which means that they bind tightly to the organic soil matter and resist volatilization and dissolution. However, the soil<sup>D</sup> may become dislodged, emitted into the atmosphere and transported. Since the compounds are persistent, they can remain suspended for long distances. Fugacity and other such partitioning are discussed in Chapter 17.

A chemical compound's ability to resist reactions, i.e. persist, especially photochemical reactions, dictates in large part its half-life, i.e. the time required to degrade one-half of the mass of a compound.<sup>4</sup>

#### 6.4.1 Photochemical Reactivity

The two principal photochemical reactions in the atmosphere are photodissociation and photo-oxidation. Photodissociation is a chemical reaction that degrades compounds by bombarding the molecule with photons. Photolysis is the type of photodissociation wherein a compound is decomposed by light or other forms of radiant energy. During photo-oxidation in the atmosphere, photodissociation combines with oxidation to breakdown chemicals in the presence of sunlight. The oxidation reactions involve the exchange of electrons between the pollutant molecule and other reactive compounds.

If the only concern for air pollutants were the pollutant's residence time in the atmosphere, the degradation processes would mainly be photolysis and photo-oxidation. However, since the life cycle of the air pollutant includes most environmental compartments, other processes need to be discussed, especially redox, biodegradation, and hydrolysis (see Figure 6.24).

#### 6.4.2 Reduction–Oxidation Potential

Oxidation, i.e. loss of electrons, and reduction, i.e. gain of electrons, occur simultaneously as a redox reaction. The amount of electrons shared defines the oxidation state or oxidation number. As discussed earlier in this chapter, a pure element has an oxidation number = 0. For example, Hg<sup>0</sup> is known as "elemental" mercury or "zero valent" mercury.

Monatomic ions, i.e. those of a single element, have oxidation numbers that are the charge of the ion. For example, the oxidation number of mercury (II) chloride or mercuric chloride (HgCl<sub>2</sub>) is +2, since it must have a

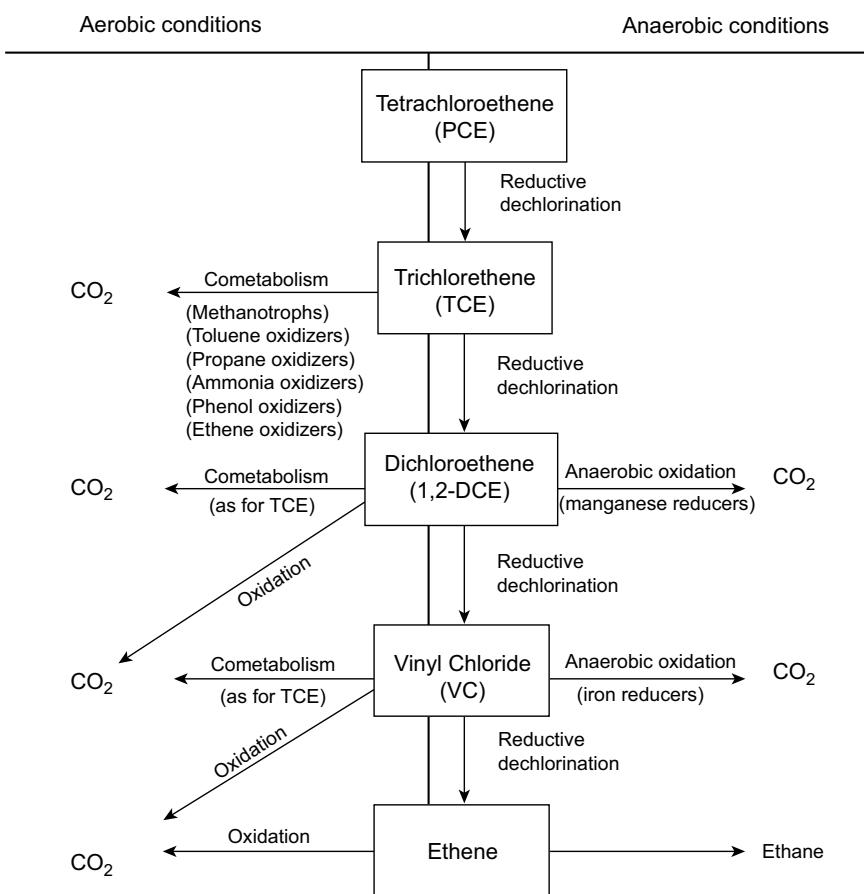
positive charge of 2 to match -2 of the two chlorine (Cl<sup>-</sup>) ions. Note that this is an inorganic form of mercury, since it lacks any carbon-to-carbon or carbon-to-hydrogen bond. An example of organic mercury is methylmercuric chloride (CH<sub>3</sub>HgCl), which has an oxidation number of +2 to match the total of the -1 for the methyl (CH<sub>3</sub><sup>-</sup>) and the -1 for Cl<sup>-</sup>. These different oxidation states completely change the physical and chemical characteristics of the compound. For example, the aqueous solubility of Hg<sup>0</sup> =  $5.6 \times 10^{-5}$  g l<sup>-1</sup> at 25 °C. The aqueous solubility<sup>5</sup> is higher for CH<sub>3</sub>HgCl at 0.10 g l<sup>-1</sup> at 21 °C; and much higher for HgCl<sub>2</sub> at 69 g l<sup>-1</sup> =  $5.6 \times 10^{-5}$  g l<sup>-1</sup> at 20 °C. In addition, the organic forms of Hg are readily absorbed by tissue, making their direct health and environmental impacts greater than elemental and inorganic forms.

#### 6.4.3 Biodegradation

Molecules, especially organic compounds, are broken down by organisms, usually involving catalysis by enzymes. This degradation is most often associated with microorganisms, especially bacteria and fungi. Aerobic biodegradation occurs when microbes decompose complex organic compounds in the presence of oxygen and use the liberated energy for reproduction and growth. Anaerobic biodegradation occurs when microorganisms use a chemical other than oxygen as an electron acceptor. Common substitutes for oxygen are nitrate, sulfate, iron, carbon dioxide, and other organic compounds (fermentation).

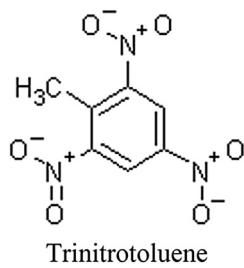
Compounds vary in their ability to resist the different types of biodegradation. For example, some compounds break down. Metabolism can occur incidentally when a microbe breaks down another substance to obtain carbon, which makes for degradation that is catalyzed by an enzyme that is fortuitously produced by the organisms for other purposes. The microbe does not directly benefit from the degradation of the compound.<sup>6</sup> In fact, the biotransformation of the compound could actually be harmful or can inhibit the growth and metabolism of the microbe. Engineers take advantage of this process, known as cometabolism, in biological treatment of persistent compounds. By adding additional carbon sources (e.g. unsubstituted alkanes) biodegradation of the targeted pollutant (e.g. a more resistant chlorinated alkane) is stimulated. This process has been used successfully to degrade halogenated compounds that are inherently more recalcitrant than their nonhalogenated counterparts by stimulating soil bacteria with the addition of O<sub>2</sub> and CH<sub>4</sub> to the subsoil strata.

<sup>D</sup> Persistent compounds behave similarly in sediment in surface waters, i.e. bind to the organic fraction, but are released into water through various mechanisms.



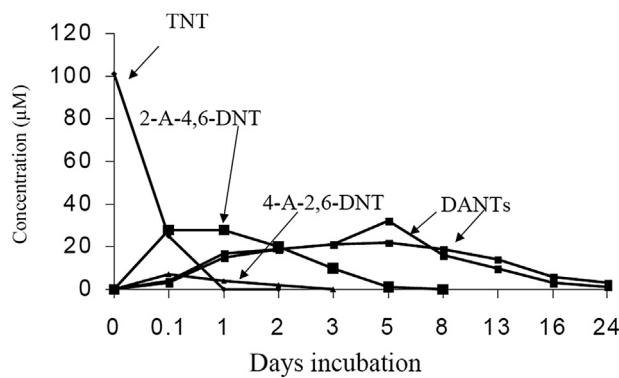
**FIGURE 6.24** Degradation pathways of chlorinated ethers that involve various types of reactions. The different chemical species vary in persistence. Note that vinyl chloride accumulates as a result of anaerobic digestion, i.e. reductive dechlorination of a degradation product, i.e. 1,2-DCE. *Environmental Security Technology Certification Program. White paper: bioaugmentation for remediation of chlorinated solvents: technology development, status, and research needs. Prepared by GeoSyntec Consultants; 2004.*

Cometabolism has been used to treat other toxics, like trinitrotoluene (TNT). Obviously, the compound degrades extremely fast when ignited, i.e. the explosion from the addition of oxygen in the presence of a heat source. This extremely rapid oxidation produces CO<sub>2</sub>, H<sub>2</sub>O, and oxides of nitrogen. Scientists also observed that in the environment TNT can be reduced slowly. In laboratory studies, the majority of the TNT degrades to monoaminodinitrotoluene and diaminonitrotoluene isomers within a few days (see Figure 6.25).



The persistence of TNT in the environmental systems is quite different. When released into the atmosphere it is degraded by predominantly direct photolysis, with an estimated atmospheric half-life ranging from

18.4 days to 184 days.<sup>6</sup> These  $T_{1/2}$  estimates are based on the expected reactions with hydroxyl radicals in the atmosphere. The transformation of TNT in surface waters by microbial metabolism is much slower than photolysis. Under anaerobic and aerobic environments, the predicted biodegradation  $T_{1/2}$  of TNT in surface water ranges between 1 and 6 months.<sup>7</sup>



**FIGURE 6.25** Degradation of trinitrotoluene (TNT) biodegradation in serum bottles incubated under reduced (methanogenic) conditions. Note: 2-A-4,6-DNT, 2-amino-4,6-dinitrotoluene; 4-A-2,6-DNT, 4-amino-2,6-dinitrotoluene; and DANTs, diaminonitrotoluene isomers. Ref. 12.

These rates do not represent environmental biodegradation, however, since environmental fate depends on more than mere abiotic chemistry. In addition to redox reactions, the TNT is sorbed to clay and organic molecules (e.g. humic acid) in the soil, with the intermediate degrades formed along the way. That is, TNT initially undergoes oxidation to form a variety of reduction products, culminating in the formation of triaminotoluene, which can be irreversibly adsorbed to soil's clay and organic matter content (see Figure 6.26). These chemical and physical mechanisms, i.e. redox

and soil binding, call for a series of aerobic, and then anaerobic degradation processes (see Figure 6.27) to completely remove and degrade TNT when it is in soil.<sup>7</sup> The reduction of one nitro ( $-NO_2$ ) group of TNT is quite fast by aerobes. Conversely, the reduction of 2-amino-4,6-dinitrotoluene requires a lower redox potential, and reduction of 2,4-diamino-6-nitrotoluene requires a very low redox potential (i.e.  $<-200$  mV), due to the electron-donating properties of the amino ( $-NH_2$ ) group's decreasing the electron deficiency of the molecule.<sup>8</sup>

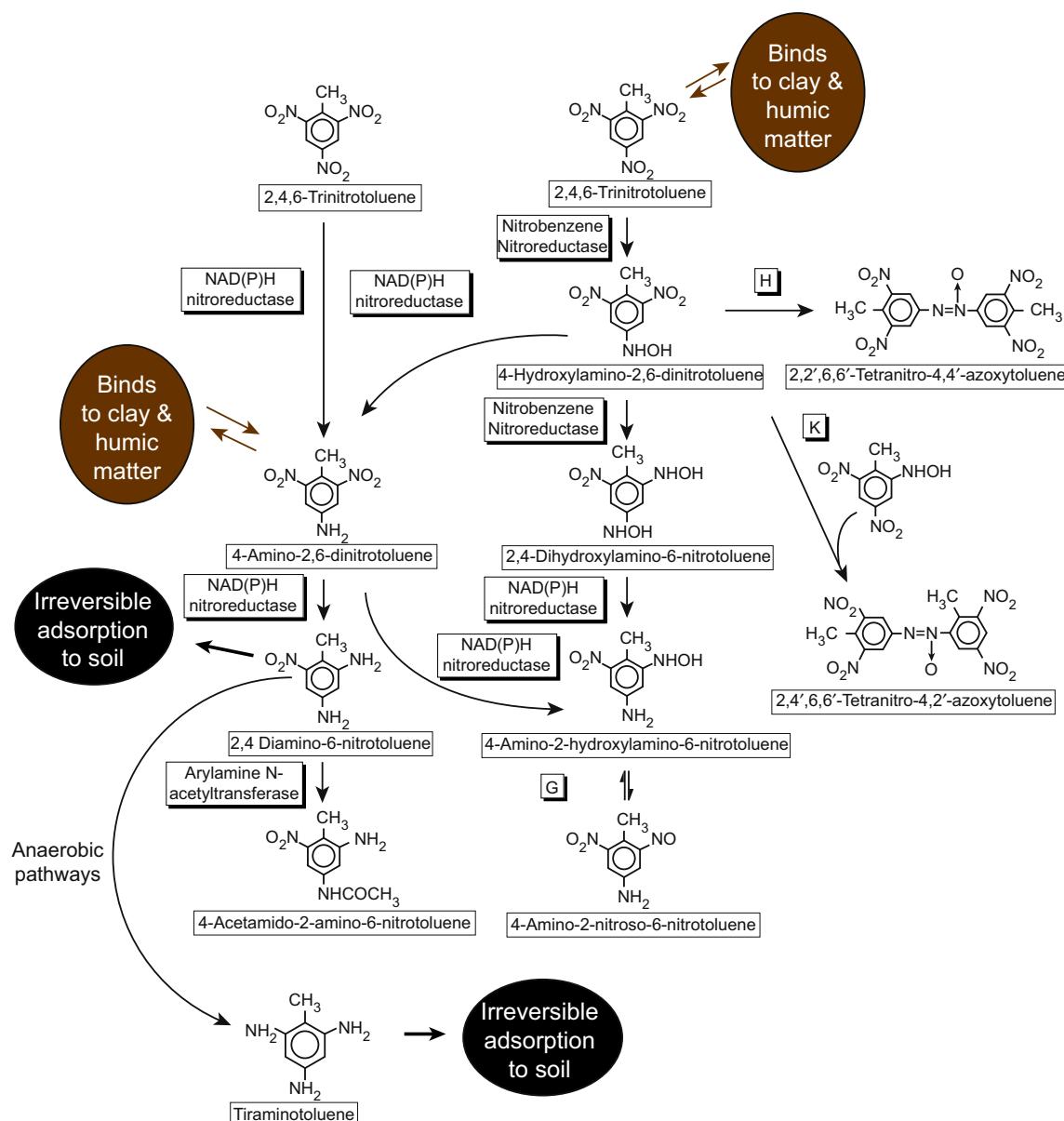
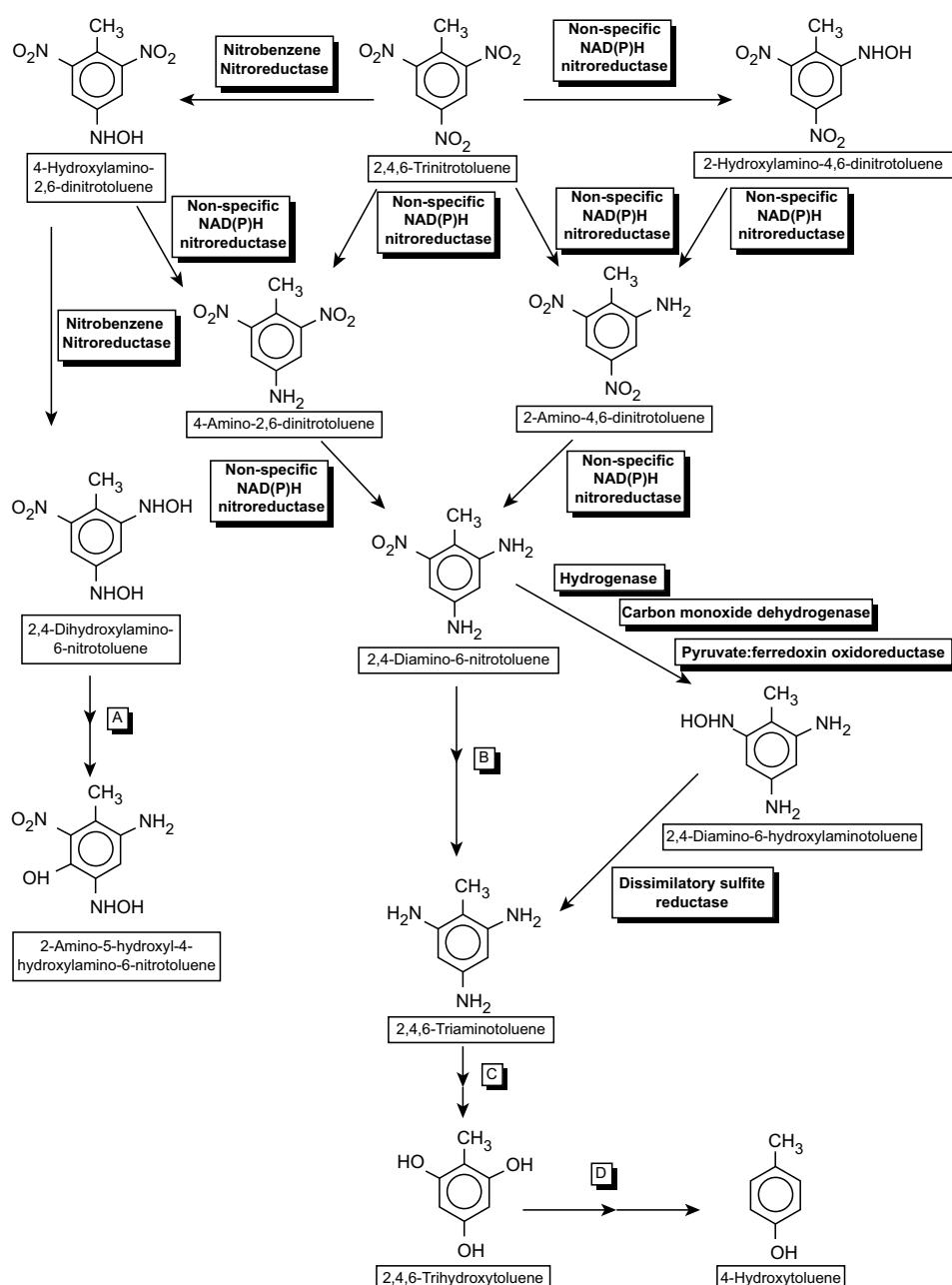


FIGURE 6.26 One set of aerobic (e.g. *Pseudomonas savastanoi*) biodegradation pathways of trinitrotoluene, including influence of soil binding. Anaerobic pathway details are shown in Figure 12.22. (For color version of this figure, the reader is referred to the online version of this book.) Scragg A. Environmental biotechnology. 2nd ed. Oxford (United Kingdom): Oxford University Press; 2004 and McFarlan S. 2,4,6-Trinitrotoluene pathway map. University of Minnesota Biocatalysis/Biodegradation Database; 2009.



**FIGURE 6.27 Anaerobic biodegradation pathway for trinitrotoluene.** Most reactions are catalyzed by nonspecific NAD(P)H dependent nitroreductases. The last reduction steps to produce triaminotoluene occur only under anaerobic conditions catalyzed by enzymes in *Desulfovibrio* spp., *Clostridium pasteurianum*, and *Moorella thermoacetica*. These nitro group reductions are also catalyzed by purified xenobiotic reductase enzyme. McFarlan S, Yao G. Anaerobic trinitrotoluene pathway map. University of Minnesota Biocatalysis/Biodegradation Database; 2009.

TNT is biodegraded aerobically by a number of organisms, including fungi (*Phanerochaete chrysosporium* and *Irpex lacteus*), yeasts (*Candida* and *Geotrichum* spp.), and bacteria (e.g. *Actinomycetes* spp., *Pseudomonas* spp. and *Alcaligenes* 1–15), and anaerobically by bacteria (e.g. *Methanococcus* spp. B strain,<sup>9a,9b</sup> *Desulfovibrio* spp., *Clostridium pasteurianum* and *Moorella thermoacetica*).<sup>10</sup>

Incidentally, cometabolism appears to enhance TNT's degradation rates (see Table 6.19). The cosubstrates' presence may enhance the TNT degradation rates by

serving as H<sub>2</sub> donors. Complex substrates can be fermented by microorganisms in a bacterial consortium, thus generating H<sub>2</sub> as one of the products, which in turn becomes available to the TNT degrading bacteria.<sup>11</sup>

#### 6.4.4 Hydrolysis

Hydrolysis is a very important chemical process in air pollution, as in any environmental system. It is the

TABLE 6.19 Enhancement of Biodegradation of Trinitrotoluene (TNT) by Addition of Cosubstrates

Electron Donor	TNT Degradation Rate ( $\mu\text{M day}^{-1}$ )
None	2.2
Acetate	2.7
Ethanol	4.2
Glucose	6.3

Source: Ref. 12.

degradation of a compound by reaction with water. A hydrolyzed compound degrades into compounds that are less toxic. Conversely, it may be transformed to more toxic metabolites, a process known as bioactivation. Figure 6.28A illustrates the forms that the pesticide methyl parathion can take after it is released into the environment, and Figure 6.28B shows the metabolism of methyl parathion in rodents, including pathways that produce compounds that may be more toxic than the parent compound. The latter is known as bioactivation.

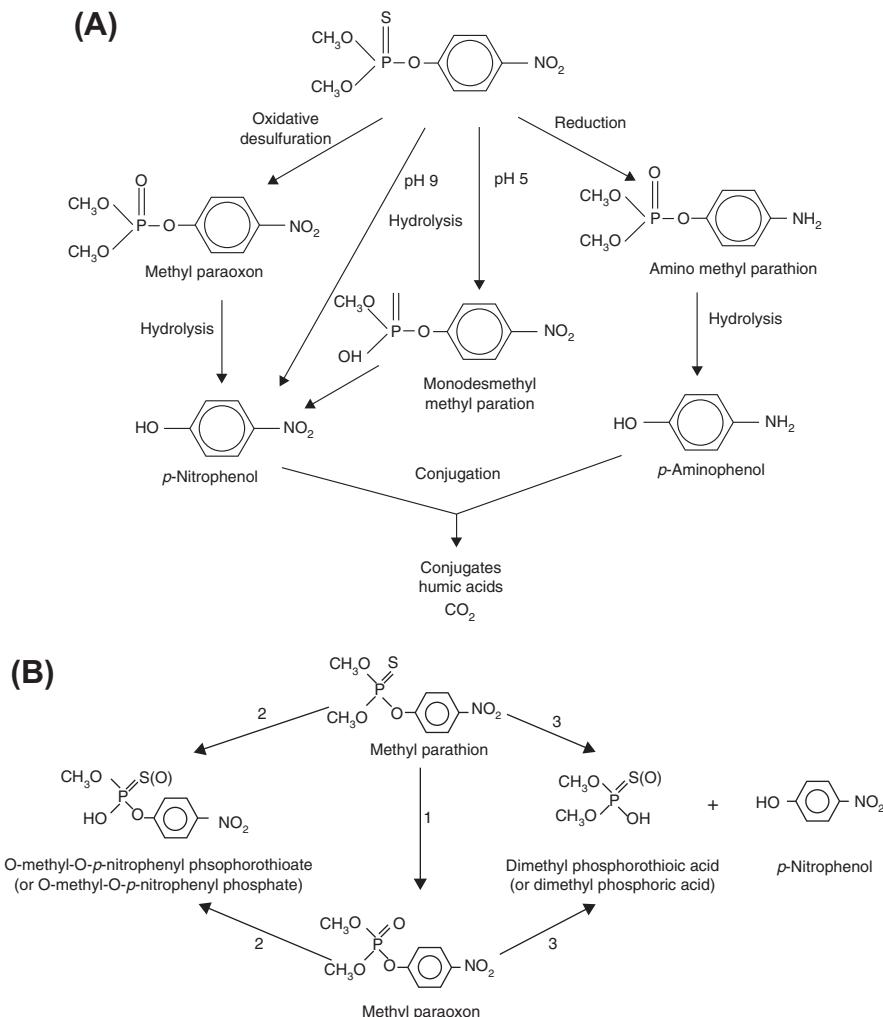
FIGURE 6.28 (A) Proposed pathway of methyl parathion in water. Environmental factors, including pH, available oxygen and water, determine the pathway. (B) Sometimes, chemicals become more toxic as a result of an organism's (in this instance, rodents) metabolism. For example, methyl parathion's toxicity changes according to the degradation pathway. During metabolism, the biological catalysts (enzymes) make the molecule more polar by hydrolysis, oxidation and other reactions. Bioactivation (pathway 1) renders the metabolites more toxic than the parent compound, while detoxification (pathways 2 and 3) produces less toxic metabolites. The degradation product, methyl paraoxon may be metabolized in the same pathways as those for methyl parathion. World Health Organization, International Programme on Chemical Safety. (1993) Environmental health criteria 145: methyl parathion, Geneva (Switzerland); Bourquin AW, Garnas RL, Pritchard PH, Wilkes FG, Cripe CR, Rubinstein NI. Interdependent microcosms for the assessment of pollutants in the marine environment. Int J Environ Stud 1979;13(2): 131–40; and Wilmes R. Parathion-methyl: Hydrolysis Studies. Leverkusen (Germany): Bayer AG, Institute of Metabolism Research; 1987:34 pp. (Unpublished report No. PF 2883, submitted to WHO by Bayer AG) 1987; International Agency for Research on Cancer, Methyl parathion, in *Miscellaneous Pesticides*, pp. 131–152. Lyon, France, 1983 (IARC Monographs on the evaluation of the carcinogenic risk of chemicals to humans, Volume 30).

## II. THE RISKS OF AIR POLLUTION

## 6.5 PHYSICAL PHASE

In air pollution science, the two “phases” of concern are particles and gases. Particle-phase substances include both liquid and solid phases. Gas phase substance includes gases and vapors; the latter are generally considered substances that are not gases at standard temperature and pressure, i.e. atmospheric conditions at 1 atm pressure (760 mm Hg) and 25 °C (298.15 K).<sup>12</sup>

The term “aerosol” is often used synonymously with PM. An aerosol can be a suspension of solid or liquid particles in a gas. In environmental sciences this gas is usually air, but not always. For example, liquid and gas phase pollutants of concern can be suspended in reactors, stacks, and flue gases. Generally, regulators usually consider a substance to be a “potential air pollutant” until it reaches the air. The amount exiting the stack, vent, or flue is what is usually regulated as stack emissions. And, the amount of a pollutant actually in the atmosphere is what is measured by pollution control agencies at the local, state, provincial, and federal levels. Once in the atmosphere, it is an actual air pollutant. Thus, the class of



air pollutants known as PM is an expression of all liquid and solid matters suspended in air. PM is an important vector for pollutant transport (e.g. moved by advection, or dissolved in or sorbed to aerosols).

Although the regulations are oriented toward emissions and ambient concentrations of pollutants, recent trends toward green engineering and pollution prevention should serve as impetus for addressing potential air pollutants more aggressively. Using different reagents in a reactor, changing pressure, temperature, and other operational conditions in industrial processes, other mechanisms are optimized; the potential air pollutants could be eliminated or greatly reduced. As such, the actual air pollutant would never exist. For example, adjusting operational conditions could greatly reduce the formation of particulates or change the size of the PM, allowing it to be more easily captured and/or treated.

The gases and vapors in air exist as individual molecules in random motion. Each gas or vapor exerts its proportionate partial pressure. The particles are aggregates of many molecules, sometimes of similar molecules, often of dissimilar ones. They age in the air by several processes. Some particles serve as nuclei upon which vapors condense. Some particles react chemically with atmospheric gases or vapors to form different compounds. When two particles collide in the air, they tend to adhere to each other because of attractive surface forces, thereby forming progressively larger and larger particles by agglomeration. The larger a particle becomes, the greater its weight and the greater its likelihood of falling to the ground rather than remaining airborne. The process by which particles fall out of the air to the ground is called *sedimentation*. Washout of particles by snowflakes, rain, hail, sleet, mist, or fog is a common form of agglomeration and sedimentation. Still other particles leave the air by impaction onto and retention by the solid surfaces of vegetation, soil, and buildings. The particulate mix in the atmosphere is dynamic, with continual injection into the air from sources of small particles; creation of particles in the air by vapor condensation or chemical reaction among gases and vapors; and removal of particles from the air by agglomeration, sedimentation, or impaction.

Air pollution is generally associated with industry, transportation, energy production, and other human activities, i.e. anthropogenesis. However, many harmful substances are natural in origin. For example, particles are emitted into the atmosphere from both human activities and natural sources. Particulate forms emitted naturally include condensed water vapor; the condensed and reacted forms of natural organic vapors; salt particles resulting from the evaporation of water from sea spray; wind-borne pollen, fungi, molds, algae, yeasts, rusts, bacteria, and debris from live and decaying plant and animal life; particles eroded by the wind from beaches, desert, soil, and rock; particles from volcanic

and other geothermal eruption and from forest fires started by lightning; and particles entering the troposphere from outer space.

The precise, prehuman (unpolluted) background concentrations of PM and other airborne substances can only be estimated indirectly. By the time humans started measuring PM levels in the air, they had already been polluting the atmosphere with particles resulting from their presence on earth for several million years. The best that can be done now is to assume that the particulate levels at remote places—the middle of the sea, the poles, and the mountaintops—approach the true background concentrations.

The debate over what the air quality may have been is a less meaningful benchmark than comparing PM concentrations, or those of any air pollutant, to health and environmental benchmarks. That is, how close is a given measurement to a safe level of exposure? Another important consideration is of trends. Are concentrations improving and at what rate?

Particulates are measured on a dry basis, thereby eliminating from the measurement not only water droplets and snowflakes but also all vapors, both aqueous and organic, that evaporate or are desiccated from the PM during the drying process. Since different investigators and investigative processes employ different drying procedures and definitions of dryness, it is important to know the procedures and definition employed when comparing data.

Although many of the air pollutants discussed in this book are best classified by their chemical composition, particles are first classified according to their physical properties. PM is a common physical classification of particles found in the air, such as dust, dirt, soot, smoke, and liquid droplets.<sup>4</sup> Unlike other US criteria pollutants [O<sub>3</sub>, CO, SO<sub>2</sub>, NO<sub>2</sub>, and lead (Pb)], PM is not a specific chemical entity but is a mixture of particles from different sources and of different sizes, compositions, and properties. However, the chemical composition of PM is very important and highly variable. In fact, knowing the chemical composition of a particle can indicate its source, e.g. receptor models use chemical composition and morphology of particles as a means to trace pollutants back to the source.

The chemical composition of tropospheric particles includes inorganic ions, metallic compounds, elemental carbon, organic compounds, and crustal (e.g. carbonates and compounds of alkali and rare earth elementals) substances. For example, the mean 24 h PM<sub>2.5</sub> concentration measured near Baltimore, Maryland in 1999 was composed of 38% sulfate, 13% ammonium, 2% nitrate, 36% organic carbon, 7% elemental carbon, and 4% crustal matter.<sup>5</sup> In addition, some atmospheric particles can be hygroscopic, i.e. they contain particle-bound water. The organic fraction can be particularly difficult to

characterize, since it often contains thousands of organic compounds.

Unless a particle is spherical its actual, i.e. physical, diameter is the same as its “aerodynamic diameter”. However, this is seldom the case, since particles vary in morphology (e.g. platy, irregular, etc.) and density (e.g. solid *versus* hollow). The aerodynamic diameter is an adjustment from the spherical shape and normalized density, i.e. the diameter of the sphere at a specified density (usually 1000 kg m<sup>-3</sup>), with the same settling velocity as the irregularly shaped particle. These features are discussed in detail in Chapters 30 and 31. Throughout this text, unless otherwise noted, particle diameter is assumed to be aerodynamic diameter.

The size of a particle is determined by how the particle is formed. For example, combustion can generate very small particles, while coarse particles are often formed by mechanical processes. If particles are sufficiently small and of low mass, they can be suspended in the air for long periods of time. Larger particles (e.g. 0.10 µm aerodynamic diameter) are found in smoke or soot, while very small particles (2.5 µm) may be apparent only indirectly, such as the manner in which they diffuse, diffract, absorb, and reflect light.

Sources of particles are highly variable. They may be emitted directly to the air from stationary sources, such as factories, power plants, and open burning, and from moving vehicles (known as “mobile sources”), first by direct emissions from internal combustion engines, but also when these and other particles are re-entrained due to the movement of vehicles (e.g. in a “near-road” situation). Area or nonpoint sources of particles include construction, agricultural activities such as plowing and tilling, mining, and forest fires.

Particles may also form from gases that have been previously emitted, such as when gases released from burning fuels react with sunlight and water vapor. A common production of such “secondary particles” occurs when gases undergo chemical reactions in the atmosphere involving O<sub>2</sub> and water vapor (H<sub>2</sub>O). Photochemistry can be an important step in secondary particle formation, resulting when chemical species like ozone (O<sub>3</sub>) are involved in step reactions with radicals, e.g. the hydroxyl ('OH) and nitrate (NO<sub>3</sub><sup>-</sup>) radicals. Photochemistry also occurs in the presence of air pollutant gases like sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), and organic gases emitted by anthropogenic and natural sources. In addition, nucleation of particles from low-vapor pressure gases emitted from sources or formed in the atmosphere, condensation of low-vapor pressure gases on aerosols already present in the atmosphere, and coagulation of aerosols can contribute to the formation of particles. The chemical composition, transport, and fate of particles are directly associated with the characteristics of the surrounding gas.

## 6.5.1 Particulate Matter Size and Mass

Since very small particles may remain suspended for some time, they are/can be particularly problematic from a pollutant transport perspective because their buoyancy allows them to travel longer distances. Smaller particles are also challenging because they are associated with numerous health effects (mainly because they can penetrate more deeply into the respiratory system than larger particles).

Generally, the mass of PM falling in two size categories is measured, i.e. <2.5 µm diameter, and >2.5 µm and <10 µm diameter. These measurements are taken by instruments with inlets using size exclusion mechanisms to segregate the mass of each size fraction (i.e. “dichotomous” samplers). Particles with diameters >10 µm are generally of less concern, since these particles rarely travel long distances; however, they are occasionally measured if a large particulate emitting source (e.g. a coal mine) is nearby.

Mass can be determined for a predominantly spherical particle by microscopy, either optical or electron, by light scattering and Mie theory, by the particle’s electrical mobility, or by its aerodynamic behavior. However, since most particles are not spherical, PM diameters are often described using an equivalent diameter, i.e. the diameter of a sphere that would have the same fluid properties. Another term, optical diameter, is the diameter of a spherical particle that has an identical refractive index as the particle. Optical diameters are used to calibrate the optical particle sizing instruments, which scatter the same amount of light into the solid angle measured. Diffusion and gravitational settling are also fundamental fluid phenomena used to estimate the efficiencies of PM transport, collection, and removal processes, such as in designing PM monitoring equipment and ascertaining the rates and mechanisms of how particles infiltrate and deposit in the respiratory tract.

Only for very small diameter particles is diffusion sufficiently important that the Stokes diameter is often used. The Stokes diameter for a particle is the diameter of a sphere with the same density and settling velocity as the particle. The Stokes diameter is derived from the aerodynamic drag force caused by the difference in velocity of the particle and the surrounding fluid. Thus, for smooth, spherical particles, the Stokes diameter is identical to the physical or actual diameter. The aerodynamic diameter ( $D_{pa}$ ) for all particles greater than 0.5 µm can be approximated<sup>6</sup> as the product of the Stokes particle diameter ( $D_{ps}$ ) and the square root of the particle density ( $\rho_p$ ):

$$D_{pa} = D_{ps} \sqrt{\rho_p} \quad (6.67)$$

The units of the diameters are in µm and the units of density are in g cm<sup>-3</sup>.

Fine particles ( $<2.5\text{ }\mu\text{m}$ ) generally come from industrial combustion processes and from vehicle exhaust. As mentioned, this smaller sized fraction has been closely associated with increased respiratory disease, decreased lung functioning, and even premature death, probably due to their ability to bypass the body's trapping mechanisms, such as cilia in the lungs, and nasal hair filtering. Some of the diseases linked to PM exposure include aggravation of asthma, chronic bronchitis, and decreased lung function.

In addition to health impacts, PM is also a major contributor to reduced visibility, including near national parks and monuments. Also, particles can be transported long distances and serve as vehicles on which contaminants are able to reach water bodies and soils. Acid deposition, for example, can be as dry or wet precipitation. Either way, particles play a part in acid rain. In the first, the dry particles enter ecosystems and potentially reduce the pH of receiving waters. In the latter, particles are washed out of the atmosphere and, in the process, lower the pH of the rain. The same transport and deposition mechanisms can also lead to exposures to persistent organic contaminants like dioxins and organochlorine pesticides, and heavy metals like mercury that have sorbed in/on particles.

Particles can function as vehicles for transporting and transforming chemical contaminants. For example, compounds that are highly sorptive (e.g. those with large  $K_{oc}$  partitioning coefficients) can use particles as a means for long-range transport. Also, charge differences between the particles and ions (particularly metal cations) will also make particles a means by which contaminants are transported.

There are ways of measuring PM other than by weight per unit volume of air. They include a count of the total number of particles in a unit volume of air, a count of the number of particles of each size range, the weight of particles of each size range, and similar measures based on the surface area and volume of the particles rather than on their number or weight. Some particles in the air are so small that they cannot be seen by an optical microscope, individually weighing so little that their presence is masked in gravimetric analysis by the presence of a few large particles.

The mass of a spherical particle is

$$\omega = \frac{4}{3}\pi \cdot \rho \cdot r^3 \quad (6.68)$$

where  $\omega$  is the particle mass (g),  $r$  is the particle radius (cm), and  $\rho$  is the particle density ( $\text{g cm}^{-3}$ ).

The size of small particles is measured by its diameter in microns ( $\mu\text{m}$ ). One micron is one-millionth of a meter or  $10,000\text{ }\text{\AA}$  (angstrom units)—the units used to

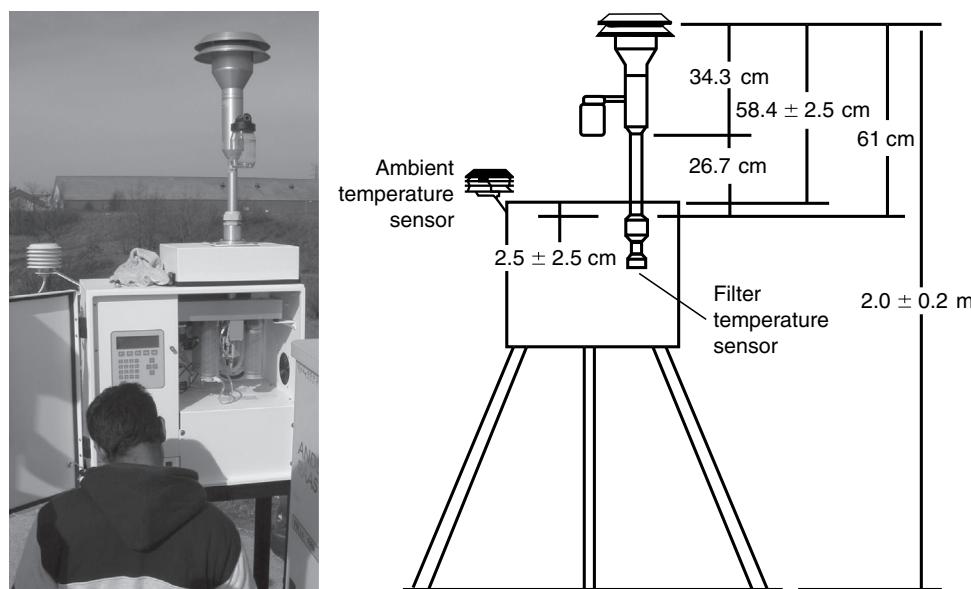
measure the wavelength of light (visible light is between  $3000$  and  $8000\text{ }\text{\AA}$ ). Compare the weight of a  $10\text{-}\mu\text{m}$  particle near the upper limit of those found suspended in the air and a  $0.1\text{-}\mu\text{m}$  diameter particle which is near the lower limit. If both particles have the same density ( $\rho$ ), the smaller particle will have one-millionth the weight of the larger one. This is because the radius term is cubed. The usual gravimetric procedures can scarcely distinguish a  $0.1\text{-}\mu\text{m}$  particle in the presence of a  $10\text{-}\mu\text{m}$  particle. To measure the entire size range of particles in the atmosphere, several measurement techniques must therefore be combined, each one most appropriate for its size range (Table 6.20). Thus, the smallest particles—those only slightly larger than a gas molecule—are measured by the electric charge they carry and by electron microscopy. The next larger size range is measured by electron microscopy or by the ability of these particles to act as nuclei upon which water vapor can be condensed in a cloud chamber. (The water droplets are measured rather than the particles themselves.) The still larger size range is measured by electron or optical microscopy; and the largest size range is measured gravimetrically, either as suspended particles separated from the air by a sampling device or, with sedimentation, particles falling out of the air into a receptacle.

Particles can form from gases that have been previously emitted, such as when gases released from burning fuels react with sunlight and water vapor. A common production of such "secondary particles" occurs when gases undergo chemical reactions in the atmosphere involving  $\text{O}_2$  and water vapor ( $\text{H}_2\text{O}$ ). An aerosol can be a suspension of solid or liquid particles in air, and aerosol concentration is often described as the mass of the particles suspended in the total volume of vapor or gas phase components of air. As mentioned, fine aerosol particles are problematic because they may remain suspended and the buoyancy allows them to travel longer distances, and because these particles are associated with numerous health effects (mainly because they can penetrate more deeply into the respiratory system than larger particles).

Generally, the mass of PM is currently regulated as either fine or coarse particles. In North America and Europe, the distinction is between particles with diameters  $<2.5\text{ }\mu\text{m}$  and particles with diameters  $>2.5\text{ }\mu\text{m}$  and  $<10\text{ }\mu\text{m}$ . These measurements are taken by instruments (see Figure 6.29) with inlets using size exclusion mechanisms to segregate the mass of each size fraction (i.e. "dichotomous" samplers). Particles with diameters  $>10\text{ }\mu\text{m}$  are generally of less concern, since these particles rarely travel long distances; however, they are occasionally measured if a large particulate emitting source (e.g. a coal mine) is nearby, since these particles that are emitted at sufficiently high altitudes (e.g. from tall

TABLE 6.20 Particle Size Ranges and Their Methods of Measurement

Particle Size Range ( $\mu\text{m}$ )	Ions	Nuclei	Visibility	Suspended or Settleable; Nonairborne	Dispersion Aerosol	Condensation Aerosol	Pollen and Spores	Sedimentation, Diffusion, and Settling
$10^{-4}\text{--}10^{-3}$	Small	—	—	Suspended	—	Gas molecules	—	Diffusion
$10^{-3}\text{--}10^{-2}$	Intermediate and large	Aitken nuclei	Electron microscope	Suspended	—	Vapor molecules	—	Diffusion
$10^{-2}\text{--}10^{-1}$	Large	Aitken and condensation nuclei	Electron microscope	Suspended	—	Fume-mist	—	Diffusion
<b>AIR POLLUTION</b>								
$10^{-1}\text{--}10^0$	—	Condensation nuclei	Microscope: electron and optical	Suspended	Dust-mist	Fume-mist	—	Diffusion and sedimentation
$10^0\text{--}10^1$	—	—	Microscope: optical	Suspended and settleable	Dust-mist	Fume-mist	—	Sedimentation
$10^1\text{--}10^2$	—	—	Eye, sieves	Settleable	Dust-mist	Mist-fog	Pollen and spores	—
$10^2\text{--}10^3$	—	—	Eye, sieves	Nonairborne	Dust-spray	Drizzle-rain	—	Sedimentation
$10^3\text{--}10^4$	—	—	Eye, sieves	Nonairborne	Sand-rocks	Rain	—	Sedimentation



**FIGURE 6.29 Photo and schematic of sampling device used to measure particles with aerodynamic diameters  $<2.5 \mu\text{m}$ .** Each sampler has an inlet (top) that takes in particles  $<10 \mu\text{m}$ . An impactor downstream in the instrument cuts the size fraction to  $<2.5 \mu\text{m}$ , which is collected on Teflon filter. The filter is weighed before and after collection. The Teflon allows construction for other analyses, e.g. X-ray fluorescence to determine inorganic composition of the particles. Quartz filters would be used if any subsequent carbon analyses are needed. *Photo and schematic courtesy of US EPA.*

stacks) reach human populations at concentrations to cause concern. If so, sampling devices with inlets larger than  $10 \mu\text{m}$  would be needed.

If spherical, the mass of a particle can be estimated using microscopy, either optical or electron, by light scattering and Mie theory, by the particle's electrical mobility, or by its aerodynamic behavior. However, since most particles are not spherical, PM diameters are often described using an equivalent diameter, i.e. the diameter of a sphere that would have the same fluid properties. The optical diameter is the diameter of a spherical particle that has an identical refractive index as the physical particle. Optical diameters are used to calibrate the optical particle sizing instruments, which scatter the same amount of light into the solid angle measured. Diffusion and gravitational settling are also fundamental fluid phenomena used to estimate the efficiencies of PM transport, collection, and removal processes, such as in designing PM monitoring equipment and ascertaining the rates and mechanisms of how particles infiltrate and deposit in the respiratory tract.

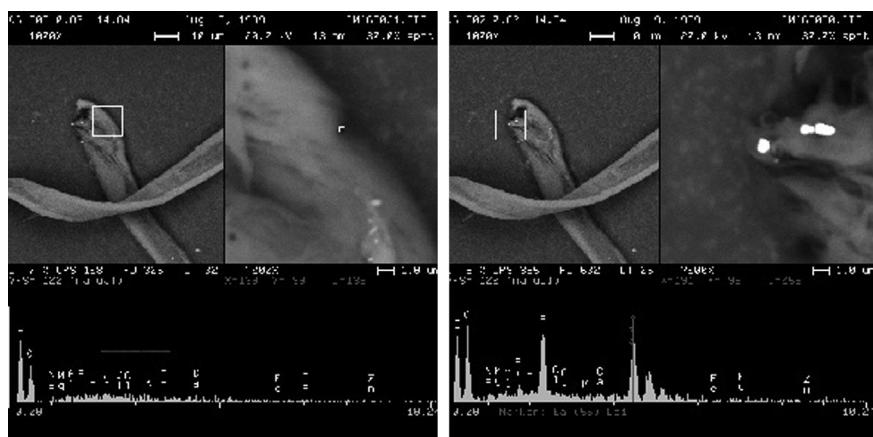
A typical means of indirect measurement of PM is by light scattering. A nephelometer includes a light source (lamp) that sends light through a lens after which an aperture focuses the light waves to a specific wavelength. The light that passes unscattered is assumed to contain no PM, and the light that is scattered at some angle (e.g.  $90^\circ$ ) is detected by the instrument detector. The amount of scattering is calibrated against known

PM concentrations, e.g. collocating one of the direct-measurement instruments with the nephelometer and comparing results. The concentration of particulates is proportionate to the amount of scattering detected, which means that the effectiveness of the instrument as an indirect measure of  $\text{PM}_{2.5}$  concentration can be determined by a ratio of scattering to  $\text{PM}_{2.5}$  concentrations compared at several sites and over time. Environmental conditions, especially relative humidity, can increase variability and uncertainty. Also, nephelometers do not collect PM, so analysis of particles for chemical composition is not possible, as it is for direct measurements of PM using filters.<sup>13</sup>

## 6.5.2 Fibers

Generally, when environmental scientists discuss particles, they mean those that are somewhat spherical or angular like soil particles. Particles that are highly elongated are usually differentiated as "fibers". Such elongation is expressed as a particle's aspect ratio, i.e. the ratio of the length to width. Fibers generally have aspect ratios greater than 3:1. Environmentally important fibers include fiberglass, fabrics, and minerals (see Figures 6.30 and 6.31). Exposure to fiberglass and textile fibers is most commonly found in industrial settings, such as it has been associated with the health problems of textile workers exposed to fibrous matter in high doses for many years. For example, chronic exposure to cotton fibers has led to the ailment,

**FIGURE 6.30 Scanning electron micrograph of cotton fibers.** Acquired using an Aspex Instruments, Ltd., Scanning electron microscope. US Environmental Protection Agency, 2004. Note the different chemical composition at different locations of the same fiber as indicated by X-ray diffraction (XRD) spectrometry. Each peak at the bottom of the left and right micrographs indicates a different chemical element; the higher the peak, the greater the concentration of that element. Photo courtesy of T. Conner, U.S. Environmental Protection Agency.



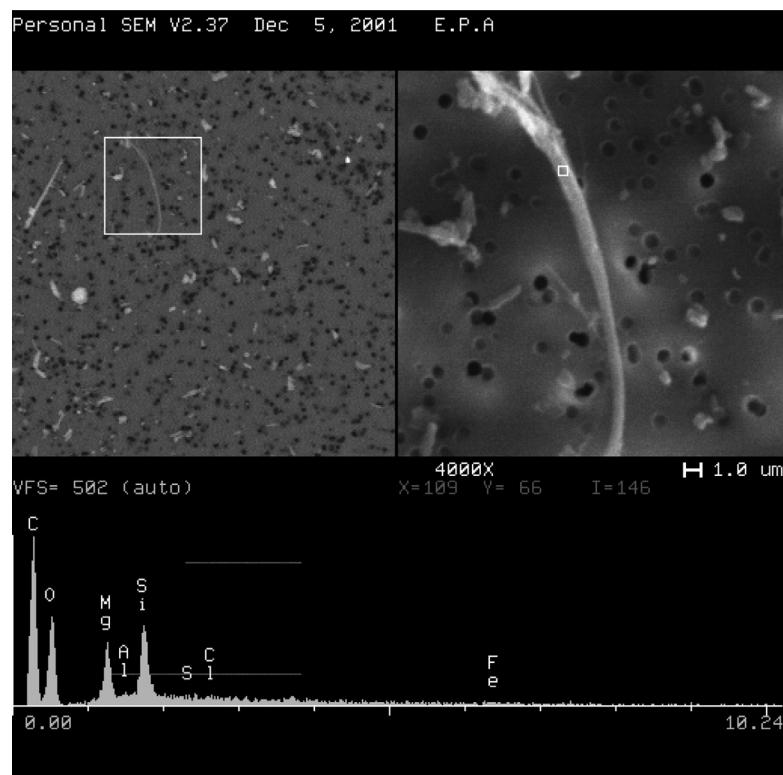
byssinosis, also referred to as “brown lung disease”, which is characterized by the narrowing of the lung’s airways. However, when discussing fibers, it is highly likely that first contaminant to come to mind is asbestos, a group of highly fibrous minerals with separable, long, and thin fibers. Separated asbestos fibers are strong enough and flexible enough to be spun and woven. Asbestos fibers are heat resistant, making them useful for many industrial purposes. Because of their durability, asbestos fibers that get into lung tissue will remain for long periods of time.

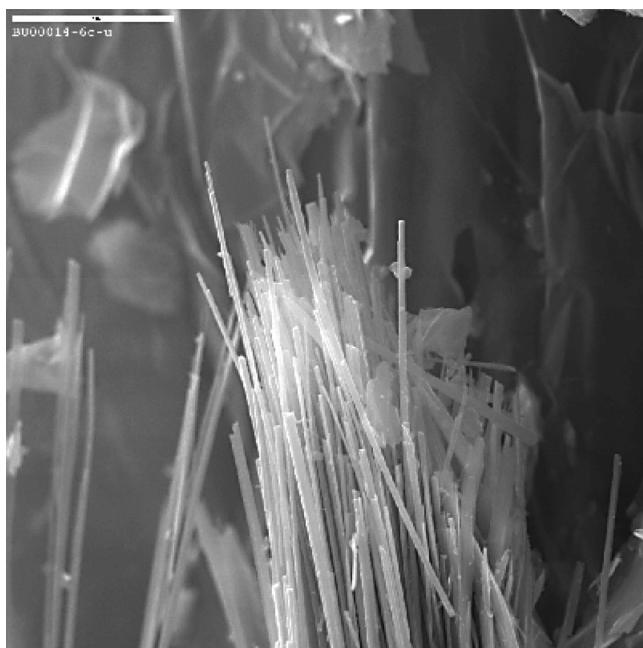
### 6.5.2.1 Asbestos: The Fiber of Concern

There are two general types of asbestos, amphibole and chrysotile. Some studies show that amphibole fibers stay in the lungs longer than chrysotile, and this tendency may account for their increased toxicity.

Generally, health regulations classify asbestos into six mineral types: chrysotile, a serpentine mineral with long and flexible fibers; and five amphiboles, which have brittle crystalline fibers. The amphiboles include actinolite asbestos, tremolite asbestos, anthophyllite asbestos, crocidolite asbestos, and amosite asbestos (see Figure 6.32).

**FIGURE 6.31 Scanning electron micrograph of fibers in dust collected near the World Trade Center, Manhattan, NY, in September 2001.** Acquired using an Aspex Instruments, Ltd., Scanning electron microscope. The bottom of the micrograph represents the elemental composition of the highlighted 15- $\mu\text{m}$  long fiber by energy dispersive spectroscopy (EDS). This composition (i.e. O, Si, Al, and Mg) and the morphology of the fibers indicate they are probably asbestos. The EDS carbon peak results from the dust being scanned on a polycarbonate filter. Photo courtesy of T. Conner, U.S. Environmental Protection Agency.





**FIGURE 6.32** Scanning electron micrograph of asbestos fibers (amphibole) from a former vermiculite-mining site near Libby, Montana. US Geological Survey and US Environmental Protection Agency, Region 8, Denver, CO. In: Agency for Toxic Substances and Disease Registry. What is asbestos? [http://www.atsdr.cdc.gov/asbestos/more\\_about\\_asbestos/what\\_is\\_asbestos/](http://www.atsdr.cdc.gov/asbestos/more_about_asbestos/what_is_asbestos/); 2013 [accessed 25.09.13].

Typical ambient air concentrations of asbestos fibers longer than 5  $\mu\text{m}$  range from about  $10^{-5}$  to  $10^{-4}$  fibers per milliliter ( $\text{fibers ml}^{-1}$ ), depending on the location. Human exposure to concentrations much higher than  $10^{24}$  fibers  $\text{ml}^{-1}$  is suspected of causing health effects.<sup>14</sup> Asbestos fibers are very persistent and resist chemical degradation (i.e. they are inert under most environmental conditions) so their vapor pressure is nearly zero. The fibers not only resist volatilization but also have extremely low aqueous solubility. This could erroneously indicate that exposure is unlikely. Indeed, segments of fibers do enter the air and water as asbestos-containing rocks and minerals that are weathered naturally or when extracted during mining operations. One of the most important exposures is when manufactured products (e.g. pipe wrapping and fire-resistant materials) begin to wear down. Small diameter asbestos fibers may remain suspended in the air for a long time and be transported advectively by wind or water before sedimentation.

Like lower aspect ratio (more spherical) particles, heavier fibers settle more quickly. Asbestos seldom moves substantially via soil. The fibers are generally not broken down to other compounds in the environment and will remain virtually unchanged over long periods. Although most asbestos is highly persistent, chrysotile, the most commonly encountered form, may breakdown slowly in acidic environments.

Asbestos fibers may break into shorter strands and, therefore, increase number of fibers, by mechanical processes (e.g. grinding and pulverization). Inhaled fibers may become trapped in the lungs and with chronic exposures build up over time. Some fibers, especially chrysotile, can be removed from or degraded in the lung with time.

### 6.5.2.2 Particulate Morphology

Generally, when environmental scientists discuss particles, they mean those that are somewhat spherical or angular like soil particles. As mentioned, particles that are highly elongated are usually differentiated as fibers. Note that the U.S. National Ambient Air Quality Standard (NAAQS) for particulates only designates size (<2.5 and <10 micron aerodynamic diameter). The standards do not consider the shape of the particles. This does not mean that shape is not considered. Indeed, one of the most important groups of regulated particles from a health perspective is asbestos, which is regulated elsewhere in the Clean Air Act (Section 112, National Emission Standards for Hazardous Air Pollutant, NESHAPS) and several other laws.

### 6.5.2.3 Particle Characteristics and Air Pollution Technology

Numerous physical processes are at work in the formation of particles in the troposphere. These processes give clues both to ways to measure PM, as well as to how to control particle emissions. By measuring each portion of the particle size spectrum by the most appropriate method, a composite diagram of the size distribution of the atmospheric aerosol can be produced. Figure 3.6 indicates that particle size distributions vary according to the number, surface area, and volume (or mass) of the particles. The volume (mass) distribution is called *bimodal* because of its separate maxima at about 0.2 and 10  $\mu\text{m}$ , which result from different mechanisms of particle formation. The mode with the 0.2- $\mu\text{m}$  maximum results from coagulation and condensation formation mechanisms. These particles are created in the atmosphere by chemical reaction among gases and vapors. They are called *fine* particles to differentiate them from the particles in the 10- $\mu\text{m}$  maximum mode, which are called *coarse*. These fine particles consist primarily of sulfates, nitrates, organics, ammonium, and lead compounds. The mode with the 10- $\mu\text{m}$  maximum is made up of particles introduced to the atmosphere as solids from the land and sea surfaces of the earth, plus particles from the coagulation-condensation mode which have grown larger and moved across the saddle between the modes into the larger size mode. These consist primarily of silicon, iron, aluminum, sea salt, and biogenic (e.g. detritus, pollen, cysts, and spores) particles. Thus, there is a dynamism that creates

small particles, allows them to grow larger, and eventually allows the large particles to be scavenged from the atmosphere by sedimentation (in the absence of precipitation), plus washout and rainout when there is precipitation.

Understanding these mechanisms is the key to controlling air pollution. Designing and operating pollution control equipment effectively must account for the number, surface characteristics, volume, and shape of particles.

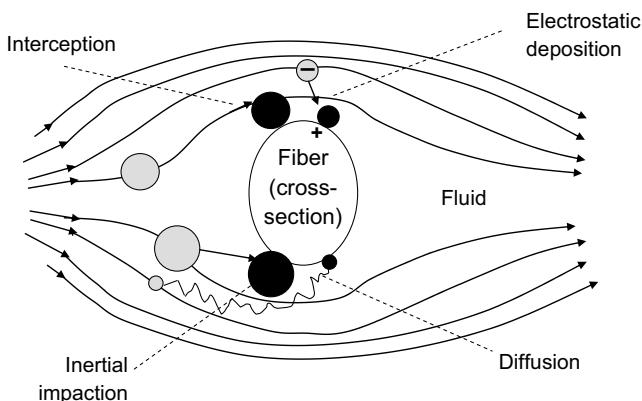
The majority of particles in the atmosphere are spherical in shape because they are formed by condensation or cooling processes or they contain core nuclei coated with liquid. Liquid surface tension draws the material in the particle into a spherical shape. Other important particle shapes exist in the atmosphere, e.g. asbestos is present as long fibers and fly ash can be irregular in shape.

The methods just noted describe the physical characteristics of atmospheric PM but not chemical composition. One can seek this kind of information for either individual particles or all particles *en masse*. Analysis of particles *en masse* involves analysis of a mixture of particles of many different compounds. How much of each element or radical, anion, or cation is present in the mixture can be determined. Specific organic compounds may be separated and identified. Individual particles may be analyzed by electron microscopy.

Much of the concern about PM in the atmosphere arises because particles of certain size ranges can be inhaled and retained by the human respiratory system. There is also concern because PM in the atmosphere absorbs and scatters incoming solar radiation.

After passage of the Clean Air Act of 1970, the U.S. EPA required measurements of total suspended particulates (TSP) based on particle collection using a high volume sampler, i.e. a device that collected a large range of sizes of particles (aerodynamic diameters up to 50  $\mu\text{m}$ ). Smaller particles are more likely to be inhaled than larger particles, so in 1987 the U.S. EPA changed the standard for PM from TSP to  $\text{PM}_{10}$ , i.e. particle matter  $\leq 10 \mu\text{m}$  diameters. The NAAQS for  $\text{PM}_{10}$  became a 24-h average of  $150 \mu\text{g m}^{-3}$  (not to exceed this level more than once per year), and an annual average of  $50 \mu\text{g m}^{-3}$  arithmetic mean. However, subsequent research showed the need to protect people breathing even smaller PM in air, since most of the particles that penetrate deeply into the air–blood exchange regions of the lung are very small (see Chapter 9). Thus, in 1997, the U.S. EPA added a new fine particle (diameters  $\leq 2.5$ ), known as  $\text{PM}_{2.5}$ .<sup>15</sup>

Aerosols are collected using equipment that separates out the size fraction of concern. Filtration is an important technology in every aspect of environmental engineering, i.e. air pollution, waste water treatment, drinking

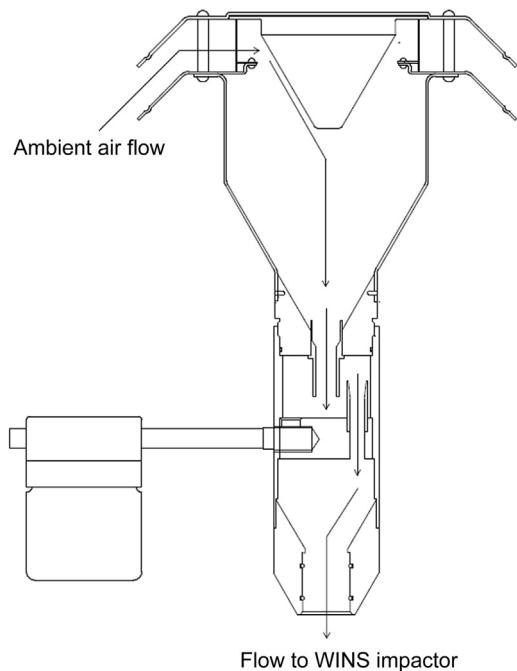


**FIGURE 6.33 Mechanical processes involved in collecting particulate matter.** Vallero DA. Fundamentals of air pollution. 4th ed. Burlington (MA): Elsevier Academic Press; 2008; Adapted from: Rubow KL. "Filtration: fundamentals and applications" In: Aerosol and particle measurement short course. Minneapolis (MN): University of Minnesota; August, 2004. 16–18.

water, and even hazardous waste and sediment cleanup. Basically, filtration consists of four mechanical processes: (1) diffusion; (2) interception; (3) inertial impaction; and (4) electrostatics (see Figure 6.33). These physical mechanisms are applied in the design and operation of air pollution control equipment, as discussed in detail in Chapters 29 and 30.

Diffusion is important only for very small particles ( $\leq 0.1 \mu\text{m}$  diameter) because the Brownian motion allows them to move in a “random walk” away from the air stream. Interception works mainly for particles with diameters between 0.1 and 1  $\mu\text{m}$ . The particle does not leave the air stream but comes into contact with the filter medium (e.g. a strand of fiberglass). Inertial impaction collects particles that are sufficiently large to leave the air stream by inertia (diameters  $\geq 1 \mu\text{m}$ ). Electrostatics consist of electrical interactions between the atoms in the filter and those in the particle at the point of contact (Van der Waal’s forces), as well as electrostatic attraction (charge differences between particle and filter medium). Other important factors affecting filtration efficiencies include the thickness and pore diameter of the filter, the uniformity of particle diameters and pore sizes, the solid volume fraction, the rate of particle loading onto the filter (e.g. affecting particle “bounce”), the particle phase (liquid or solid), capillarity and surface tension (if either the particle or the filter media are coated with a liquid), and characteristics of air or other carrier gases, such as velocity, temperature, pressure, and viscosity.

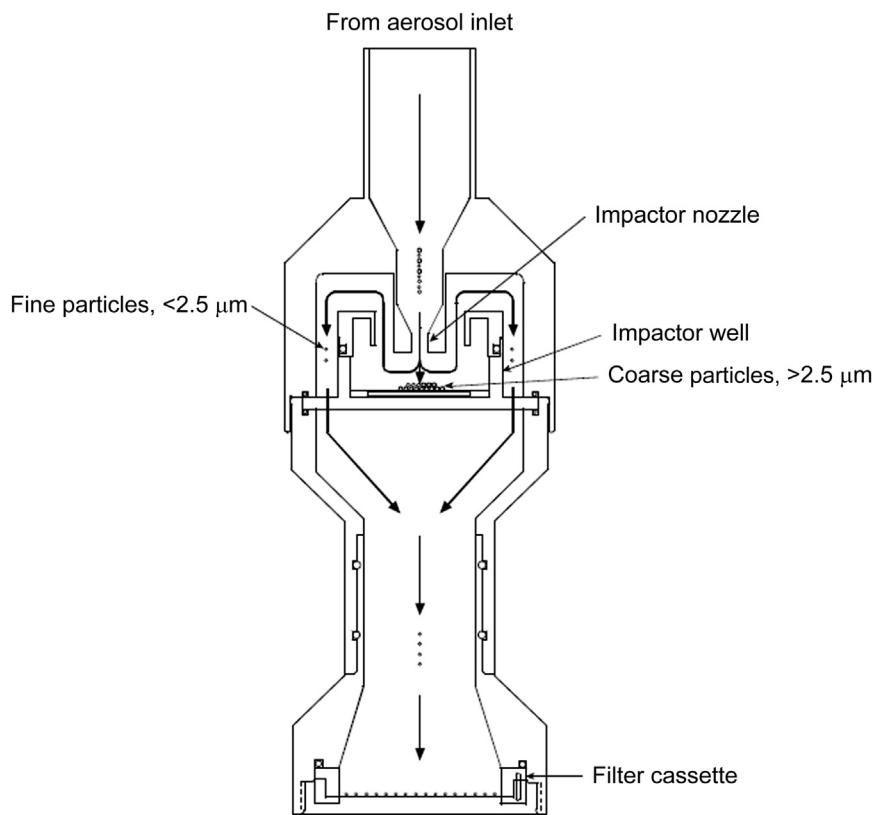
As mentioned, aerosol measurement is an expression of the mass of a particle size range, so collection devices must be selective and include only the particles within a specified size range. This is accomplished using differently sized inlets. Figure 6.34



**FIGURE 6.34** Flow of air through a sampler inlet head used to collect particulate matter with aerodynamic diameters  $<2.5\text{ }\mu\text{m}$  ( $\text{PM}_{2.5}$ ). WINS = well impactor ninety-six, i.e. the design of the particle impactor specified by the U.S. EPA for reference method samplers for  $\text{PM}_{2.5}$ . Ref. 13.

shows an inlet of the  $\text{PM}_{2.5}$  sampler that is designed to extract ambient aerosols from the surrounding air stream, remove particles with aerodynamic diameters  $>10\text{ }\mu\text{m}$ , and move the remaining smaller particles to the next stage. Figure 6.35 illustrates the impactor and filter assembly for removing those particles less than  $10\text{ }\mu\text{m}$  but greater than  $2.5\text{ }\mu\text{m}$  in diameter but allows particles of  $2.5\text{ }\mu\text{m}$  in diameter to pass and be collected on a filter surface. Particles  $<10\text{ }\mu\text{m}$  but  $<2.5\text{ }\mu\text{m}$  are removed downstream from the inlet by a single-stage, single-flow, single-jet impactor assembly. Aerosols are collected on filters which are weighed before and after sampling. This system uses  $37\text{ mm}$  diameter glass filters immersed in low volatility, low viscosity diffusion oil. The oil is added to reduce the impact of “bounce”, i.e. particle hit the filter and are not reliably collected.<sup>15</sup>

This chapter introduced the properties of gas-phase and particle-phase pollutants. These inherent properties provide the basis for the potential for substances to become air pollutants. The following chapters discuss how these inherent properties combine with the atmospheric and environmental conditions that lead to the transport, transformation, and fate of these substances.



**FIGURE 6.35** Flow of air through an impactor well and filter holder used to collect particulate matter with aerodynamic diameters  $<2.5\text{ }\mu\text{m}$  ( $\text{PM}_{2.5}$ ). Ref. 12.

## QUESTIONS

1. What are three ways that a hazardous air pollutant, like dioxin, can be formed during combustion?
2. If the pOH of a water droplet is 5 at 25 °C, what is the molar concentration of hydrogen ions in the droplet?
3. What is the solubility of silver chloride ( $K_{sp} = 1.8 \times 10^{-10}$ ) in water?
4. What is vapor pressure? What is the Antoine equation? Why is it important to air pollution?
5. What are the Antoine equation parameters for acetone? For 1,4-dioxane? For vinyl chloride (also known as chloroethene)? For mercury?
6. Based on these parameters, calculate the vapor pressure of each of the four compounds at 20 °C. What does this tell you about these substances?
7. What two inherent properties distinguish LNAPLs and DNAPLs?
8. The previous question simply mentioned mercury's vapor pressure. Is this a sufficient question? If not, what should be stipulated?
9. What is Raoult's Law and why is it important to air quality?
10. After a derailment, two rail cars emptied their contents onto a clay soil near the track. The spill occurred in autumn just outside of a large city in central Asia with the diurnal temperature ranging from 14 to 22 °C. The first car contained the pesticide atrazine in a solid form and the second car, a tanker, spilled vinyl chloride. Which spill is most likely to result in the most chemical released to the atmosphere, assuming identical wreckage (e.g. same number and size of ruptures, same size and position of cars, same amount of chemical compound in soil, etc.)?
11. Explain why the vapor pressure for MTBE is 51 mm Hg higher than that of chloroform, but the Henry's Law constant for MTBE is an order of magnitude lower than that of chloroform. Why is the vapor pressure of methylethylketone (MEK) about the same as that of benzene, but benzene's Henry's Law constant is 1.5 orders of magnitude greater than that of MEK. Why is methanol's Henry's Law constant so low? All of these relationships are at 25 °C.
12. What adjustments would have to be made if a nonconservative tracer were used to characterize a plume? Why might such a tracer need to be used instead of a conservative tracer?
13. Review the Table 6.16 with data from a southeastern US city. What is the contribution of nonfossil-fuel sources to particulate-laden carbon during the summer? Why are concurrent measurements of OC/EC ratios important to characterizing biogenic secondary organic aerosols, especially as an indicator of biogenic sources (i.e.

from other than human activities) being a significant nonfossil-fuel contributor?

14. Carbon monoxide is used to indicate the extent of combustion, since it is one the most stable products of incomplete combustion. Since CO<sub>2</sub> is one of the products of complete combustion, combustion efficiency (CE) is a relationship between CO<sub>2</sub> and CO:
- $$CE = D_{pa} = D_{ps} \sqrt{\rho_p}$$
- What is the combustion efficiency if there is no CO in the emission gas stream? What if there were no CO<sub>2</sub> in the gas stream and 0.001 mol CO?
15. Propane is being combusted at 80% theoretical air, i.e. 20% air deficiency. What is the combustion efficiency of this reaction?
  16. Consider a combustion reaction other than the ones described in this chapter and explain how products of incomplete combustion may form.
  17. Consider an acid–base reaction other than those described in this chapter and explain how an air toxic may form in a water droplet.
  18. What wavelength band of solar radiation leads to photodissociation of nitrogen dioxide? What determines the lower limit?
  19. How are free radicals formed and why are they so reactive?
  20. What are the two basic ways that a compound exits the soil to become an air pollutant?
  21. What are the two principal types of photochemical reactions important to air pollution?
  22. If the particles collected on filter A are mainly large particles (mean aerodynamic diameters >50 µm), and the particles on filter B are mainly fine particles (mean aerodynamic diameters <2 µm), which is most likely to be formed by mechanical processes?
  23. How does PM size generally relate to health risk?
  24. Why is PM often measured using dichotomous samplers?
  25. What is the advantage of using nephelometer for PM measurements? What is its disadvantage?
  26. What is a fiber?
  27. What are the six types of asbestos that are usually regulated as air pollutants?
  28. A company claims that its filter uses diffusion to capture 2.5 micron diameter PM. Is this likely?
  29. A company claims that its filter sieves PM. Is this likely?

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# Air Pollutant Hazards

## 7.1 HAZARDS

The first step in assessing air pollution risk is to identify the hazard. The hazards associated with air pollution are generally differentiated as to whether the agent causes harm to human health, impairs ecosystems, or damages socially important resources, such as monuments, buildings, and infrastructure.

As discussed in Chapter 3, air pollutants are divided into the so-called criteria pollutants and hazardous air pollutants. Both types are “hazardous”, but the criteria pollutants are those that are used to designate the air quality of a region. That is, the amounts measured in ambient air determine whether a region is meeting air quality standards, i.e. is in “attainment” status. Conversely, hazardous air pollutants, known as “air toxics”, are chemical compounds suspected of causing cancer and other chronic ailments in humans, even at very low doses. These are usually found in highest concentrations near particular industries, roadways, and other specific sources.

Air pollutant hazard primarily focuses on the toxicity of a chemical compound. For example, a compound that causes cancer or elicits respiratory problems in rats would be suspected of doing the same in humans, albeit at lower doses and over longer time frames than what laboratory rats have been exposed. However, toxicity to humans is not the only hazard that must be identified. The toxicity to other species is also of concern. For example, some species are sensitive to substances that may have low human toxicity, e.g. copper compounds can be highly toxic to fishes.

Ecosystem toxicity, i.e. ecotoxicity, is the hazard that a compound may cause to various species within an ecosystem. For example, a substance may have low toxicity to a particular fish species, but high toxicity to an organism on which the fish feeds. This would not kill the fish directly, but would diminish the abundance and diversity of fish species in the ecosystem.

Besides toxicity, chemical hazards include other potential harm, including fire hazard, explosiveness, corrosivity, and chemical reactivity. Hazards may also

be biological (biohazards) and physical (e.g. radioactive). Air pollution experts are primarily interested in chemical hazards, but must be aware of these other hazards, particularly in first response and emergency situations. Indeed, spills and accidents may at first be physical hazards, e.g. a highly reactive compound leaking from a ruptured tank. The reactions may form highly toxic vapors and gases that threaten human populations. In addition to stopping the leak, the immediate actions may be to evacuate nearby residences to prevent exposures to these toxic gases.

Health officials and occupational and environmental scientists and engineers often refer to *thresholds* of chemical compounds. The threshold level is the lowest amount needed to induce harmful effects in an organism. In addition to this inherent toxicity of the compound (e.g. cyanide and dioxin are highly and acutely toxic, whereas the metal iron is usually only acutely toxic in high doses), the hazard is also influenced by factors such as a chemical’s mobility in environmental media and tissues (how quickly does it move through the environment or across cellular membranes), its persistence or recalcitrance (remaining in the environment for years without being altered, e.g. a chlorinated compound is inherently more difficult to break down than its nonhalogenated counterpart), and its likelihood to accumulate in living tissue (e.g. mercury and lead can build up in tissue over years and decades with long-term exposures).

### 7.1.1 Chemical Hazards

The traditional risk assessment paradigm for chemicals in the environment (Figure II.1) is generally a step-wise process. It begins with the identification of a hazard, which is composed of a summary of an agent’s physicochemical properties and routes and patterns of exposure and a review of toxic effects. The tools for hazard identification take into account the chemical structures that are associated with toxicity, metabolic and pharmacokinetic properties, short-term animal and cell tests, long-term animal (*in vivo*) testing, and human

studies (e.g. epidemiology, such as longitudinal and case-control studies). These comprise the core components of hazard identification; however, additional hazard identification methods have been emerging that increasingly provide improved reliability of characterization and prediction.

Biological information is useful in identifying hazards since it will appear before tissue damage. Hazard identification is also being advanced by computational chemistry. This enhances the understanding of hazards resulting from slight differences in molecular structures. Even similar substitutions on molecules (e.g. one *versus* two methyl groups, methyl *versus* ethyl substitutes, or halogenations (Cl *versus* F) can lead to quite different hazards. Computational tools based on structure-activity relationships (SARs) known as quantitative SARs are increasingly used to model hazards. They also provide clues to subtle and presymptomatic hazard information akin to the biomedical sciences' increasing focus on a person's entire life, rather than the presence or absence of diseases.<sup>1</sup> Numerous new methods are being developed to identify and to characterize air pollutant hazards.

Regulatory agencies generally distinguish cancer from noncancer hazard and risk. Cancer hazards, i.e. carcinogens, are classified according to the extent to which sound science supports or rejects a chemical compound's link to cancer (see Table 7.1).

Thus, carcinogen classifications combine the amount of certainty and quality of the dose-response information, the type of information (e.g. animal *versus* human) and the potency of the carcinogen. Unlike the cancer dose-response curve, which has no threshold, noncancer hazard is generally based on a dose above which there is a potential for an adverse outcome (e.g. neurological damage, reproductive and developmental disorder, and endocrine disruption). This threshold is known as the no observable adverse effect concentration (NOAEC),<sup>a</sup> which is discussed under the Section 7.2.

As a precaution, it is generally assumed in cancer risk assessments that there is no safe level of exposure, i.e. there is no "threshold" below which an exposure is acceptable. In addition to the NOAEC, the "lowest observed adverse effect concentration" (LOAEC) is the area of the dose-response curve where studies have actually linked a dose to an effect. Thus, the precautionary principle renders the NOAEC and LOAEC irrelevant to cancer risk. Instead, cancer slope factors (CSFs) are used to calculate the estimated probability of increased cancer incidence over a person's lifetime (the so-called excess lifetime cancer risk). Like the reference doses and concentrations (RfDs and RfCs, respectively;

TABLE 7.1 Cancer Classifications in the United States

Cancer Classification	Description
A	The chemical considered to be a human carcinogen
B	The chemical is a probable human carcinogen, with two subclasses
B1	Chemicals that have limited human data from epidemiological studies supporting their carcinogenicity
B2	Chemicals for which there is sufficient evidence from animal studies but for which there is inadequate or no evidence from human epidemiological studies
C	The chemical is a possible human carcinogen
D	The chemical is not classifiable as to human carcinogenicity
E	There is evidence that the chemical does not induce cancer in humans

Carcinogens fall into the above-mentioned classes (strength in descending order based on type and certainty of weight of evidence).

*U.S. Environmental Protection Agency.*

see Section 7.2), slope factors follow exposure pathways, i.e. they will differ based on whether they are ingested, inhaled, or come into contact with the skin. CSFs are discussed in detail in Chapter 11.

## 7.1.2 Biological Hazards

Although most air pollutants discussed in this book address chemical hazards, there is a growing concern about nonchemical air pollutants, especially biological agents. These may include microbial organisms, e.g. viruses, bacteria, and fungi. They may also include parts of larger organisms, e.g. pet dander and insect antigens (as triggers for asthma), as well as pollen and spores. The concern has recently grown to include genetically modified organisms (GMOs). Risks and hazards from biological agents are often different from those posed by chemicals, so the risk assessment process is commensurately different. As evidence, the Safety in Biotechnology Working Party of the European Federation of Biotechnology<sup>1</sup> has identified four risk classes for GMOs:

Risk class 1: No adverse effect, or very unlikely to produce an adverse effect. Organisms in this class are considered to be safe.

Risk class 2: Adverse effects are possible but are unlikely to represent a serious hazard with respect to the

<sup>a</sup> The NOAEC is used for inhalation, so is most appropriate for air pollutants. For dermal, ingestion, and other exposure pathways, no observable adverse effect level (NOAEL) is commonly used as the threshold.

value to be protected. Local adverse effects are possible, which can either revert spontaneously (e.g. owing to environmental elasticity and resilience) or be controlled by available treatment or preventive measures. Spread beyond the application area is highly unlikely.

Risk class 3: Serious adverse local effects are likely with respect to the value to be protected, but spread beyond the area of application is unlikely. Treatment and/or preventive measures are available.

Risk class 4: Serious adverse effects are to be expected with respect to the value to be protected, both locally and outside the area of application. No treatment or preventive measures are available.

These classes indicate that even the safest genetic modifications carry some risk and that with more uncertainty about an organism, one cannot assume it to be safe. Thus, risk scenarios include not only the effects resulting from the intended purpose of the environmental application but also downstream and side effects that are not part of the desired purpose.

The biological agent risk classes are analogous to the hazard classes of various human health risk paradigms, e.g. carcinogen listings or extremely hazardous designations. Thus, a genetically modified microbe can be assigned to the appropriate risk class based on its physical, chemical, and biological properties, “independent of the technique used to select or generate the particular variant, and then scoring it against a set of values to be protected”.<sup>1</sup> Like the hazard identification process for chemicals, the microbe is classified according to its inherent properties. It is in the next stage that environmental conditions are taken into account, i.e. the characterization of administered dose to various responses in different populations. Both the hazard identification and dose-response information are based on research that is used in the risk analysis. For microbes, the highest score for any one determines the overall risk class for environmental application.

Another similarity of the risk classification of microbes to the chemical hazard identification processes is that it is not uncommon to extrapolate from available knowledge to other microbes with similar characteristics or to yet untested, but similar environmental conditions (e.g. a field study’s results in one type of field extrapolated to a different agricultural or environmental remediation setting). In chemical hazard identification, this is accomplished by SARs.

### 7.1.3 Ecological Hazards

In the United States, ecological risk assessment paradigms have differed from human health risk assessment paradigms. The ecological risk assessment framework (see Figure II.2) is based mainly on characterizing

exposure and ecological effects. Both exposure and effects are considered during problem formulation.<sup>2</sup>

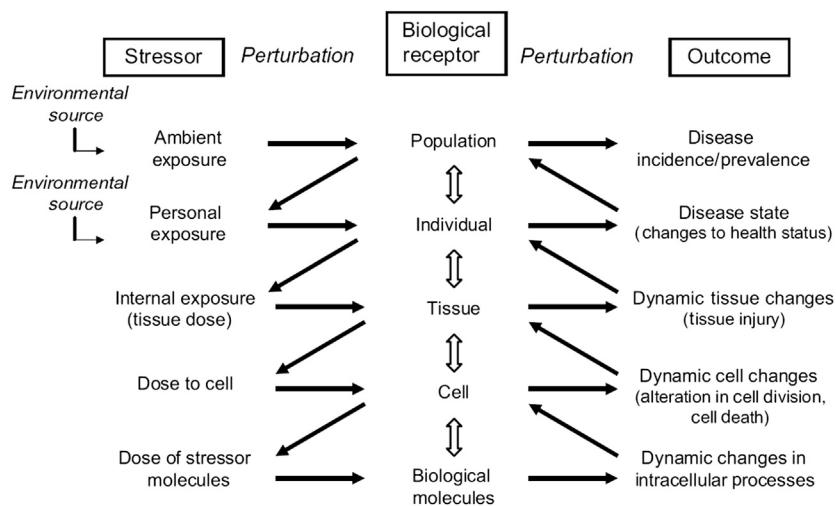
Increasingly, human risk assessment is following the ecological risk framework. The process shown in the inner circle of Figure II.2 actually does not target the technical analysis of risk so much as it provides coherence and connections between risk assessment and risk management. As mentioned, in the early 1980s there was confusion and mixing of the two processes. For example, a share of the criticism of the federal response to environmental disasters, such as those in Love Canal, New York, and Times Beach, Missouri, related to the mixing of scientifically sound studies (risk assessment) and decisions whether to pursue certain actions (risk management). This led to actual and perceived political and financial motivations for buyouts and remediation, in the absence of or, worse, in spite of sound science. In fact, the final step of the improved risk assessment process is referred to as “characterization” to mean that “both quantitative and qualitative elements of risk analysis, and of the scientific uncertainties in it, should be fully captured by the risk manager”.<sup>3</sup> In particular, the process allows for an integration of research with risk assessment, which could underpin risk management decisions. The problem formulation step in the ecological framework has the advantage of providing an analytic-deliberative process early on. That is, it combines sound science with input from various stakeholders inside and outside of the scientific community. The looming threat of this integration, however, is the risk of repeating the previous problems of biasing of sound science.

The ecological risk framework calls for the characterization of ecological effects instead of hazard identification used in human health risk assessments. This is because the term “hazard” has been used in chemical risk assessments to connote either intrinsic effects of a stressor (*chemical inherency*) or a *margin of safety* by comparing an ecological effect with an estimate of exposure concentration. In the latter connotation of hazard, the hazard is at a level in the environment that could be expected to induce adverse outcome.

Consider a hypothetical compound that is found at 10 ppm to reduce the ability of a species to reproduce, which in turn changes the predator-prey aspects of the ecosystem, leading to diminished biodiversity. This is an example of an ecological hazard. However, the threshold concentration denoting the hazard would not simply be 10 ppm, due to uncertainties in the data and science (e.g. measurement and modeling error and variability) underlying this hazard threshold. With an ample margin of safety, the hazard threshold is adjusted lower, e.g. to 5 ppm, to account for these uncertainties.

Another aspect of ecological hazard is that of the food chain, which incorporates human health and ecosystem condition. A hazard to an ecosystem must be considered

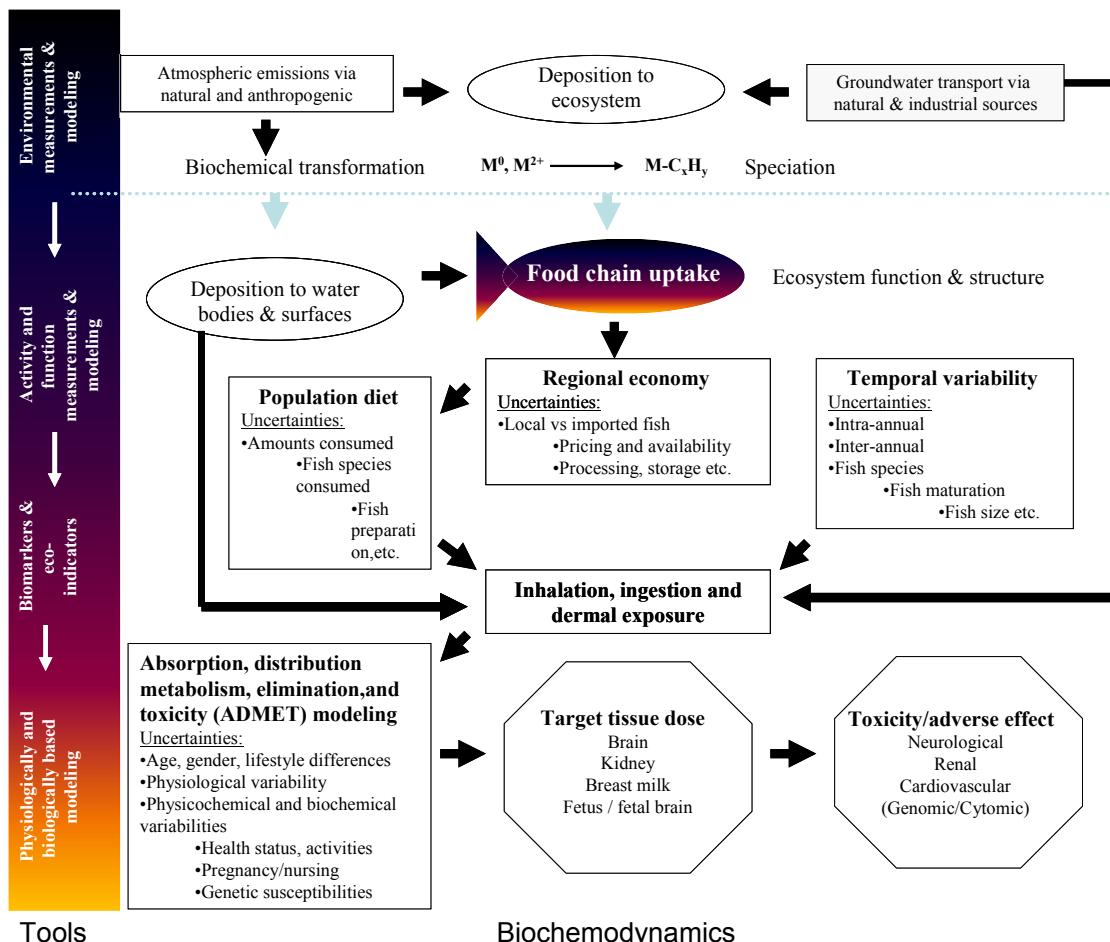
**FIGURE 7.1 Systems cascade of exposure-response processes.** In this instance, scale and levels of biological organization are used to integrate exposure information with biological outcomes. The stressor (chemical or biological agent) moves both within and among levels of biological organization, reaching various receptors, thereby influencing and inducing outcomes. The outcome can be explained by physical, chemical, and biological processes (e.g. toxicogenomic mode-of-action information). Ref. 5.



at multiple levels of biological organization (see Figure 7.1).<sup>4</sup> The food chain or web is, therefore, a means by which an ecological hazard becomes a human health hazard. It is also the means by which a hazard can

change physicochemical forms to become more hazardous, such as the methylation of mercury (Figure 7.2).

Although biological hazards are more complicated than purely chemical hazards, similar thresholds could



**FIGURE 7.2 Biochemodynamic pathways for a substance (in this case a single chemical compound).** After transport and transformation in the food web, the fate is mammalian tissue. Various modeling tools are available to characterize the movement, transformation, uptake, and fate of the compound. Similar biochemodynamic paradigms can be constructed for multiple chemicals (e.g. mixtures) and microorganisms. Vallero DA. *Environmental biotechnology: a biosystems approach*. Amsterdam, NV: Elsevier Academic Press; 2010. (For color version of this figure, the reader is referred to the online version of this book.)

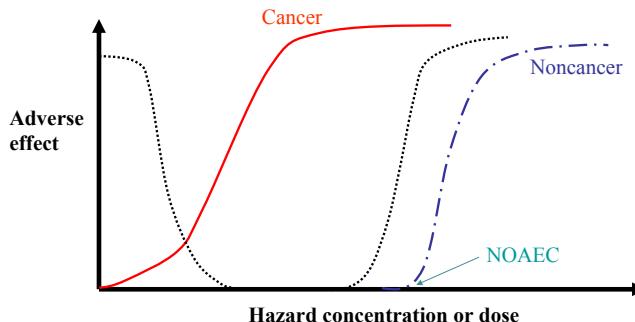
exist. For example, an introduced species may overwhelm another species in an ecosystem if introduced at some air pollution level (e.g. number of seeds, spores, or cysts). In such cases, the biological hazard would be identical to chemical hazard approach.

As mentioned, human risk assessment is becoming less sequential and stepwise, and more systematic. As such, human hazards are being approached more like ecosystem hazards.

## 7.2 DOSE-RESPONSE

Usually, the health hazard of a chemical compound is expressed as a gradient of the damage that can be caused by that compound, i.e. the dose. Dose is the amount (often mass) of a chemical administered to an organism (so-called applied dose), the amount of the chemical that enters the organism ("internal dose"), the amount of the chemical that is absorbed by an organism over a certain time interval ("absorbed dose"), or the amount of the chemical or its metabolites that reach a particular "target" organ ("biologically effective dose"), such as the amount of a hepatotoxin (liver damaging chemical) that reaches the liver. Increasing the concentration of a substance in an organism should also increase the severity of the expected adverse outcome. The classic demonstration of this gradient is the so-called dose-response curve (Figure 7.3). If one increases the amount of the substance, a greater incidence of the adverse outcome would be expected.

The three curves in Figure 7.3 represent those generally found for hazardous wastes. Curve A is the classic



**FIGURE 7.3** Prototypical dose response curve for a carcinogen, essential nutrient, and noncancer hazard. Note the cancer dose-response curve (solid line) has no safe level of exposure, i.e. it is a "no-threshold" curve. The essential substance (dotted line) has two regions separated by an optimal dose region. The region of deficiency is found at concentrations below the optimal dose and closer to zero. Above the optimal range is the range of toxicity. The noncancer dose response curve (dashes and dots) represents toxicity above a certain threshold, i.e. the NOAEC is the concentration below which no response is expected. Adapted from Vallero DA. *Environmental contaminants: assessment and control*. Burlington, MA: Elsevier Academic Press; 2004. (For color version of this figure, the reader is referred to the online version of this book.)

cancer dose-response curve. Regulatory agencies generally subscribe to the precautionary principle that any amount of exposure to a cancer-causing agent may result in an expression of cancer at the cellular level. Thus, the curve intercepts the  $x$ -axis at 0. Metals can be toxic at high levels, but several are essential to the development and metabolism of organisms. Thus, curve B represents an essential chemical (i.e. a "nutrient") that will cause dysfunction at low levels (below the minimum intake needed for growth and metabolism) and toxicity at high levels. The segment of curve B that runs along the  $x$ -axis is the "optimal range" of an essential substance. The extent to which a metal is toxic or essential depends on its oxidation state and is specific to each metallic compound. Curve C is the classic noncancer dose-response curve. The steepness of the three curves represents the potency or severity of the toxicity. For example, curve C is steeper than curve A, so the adverse outcome (disease) caused by the chemical in curve C is more potent than that of the chemical in curve A. This simply means that the response rate is higher. However, if the diseases in question are cancer (curve A) and a relatively less important disease for curve C, such as short-lived headaches, the steepness simply represents a higher incidence of the disease, not greater importance.

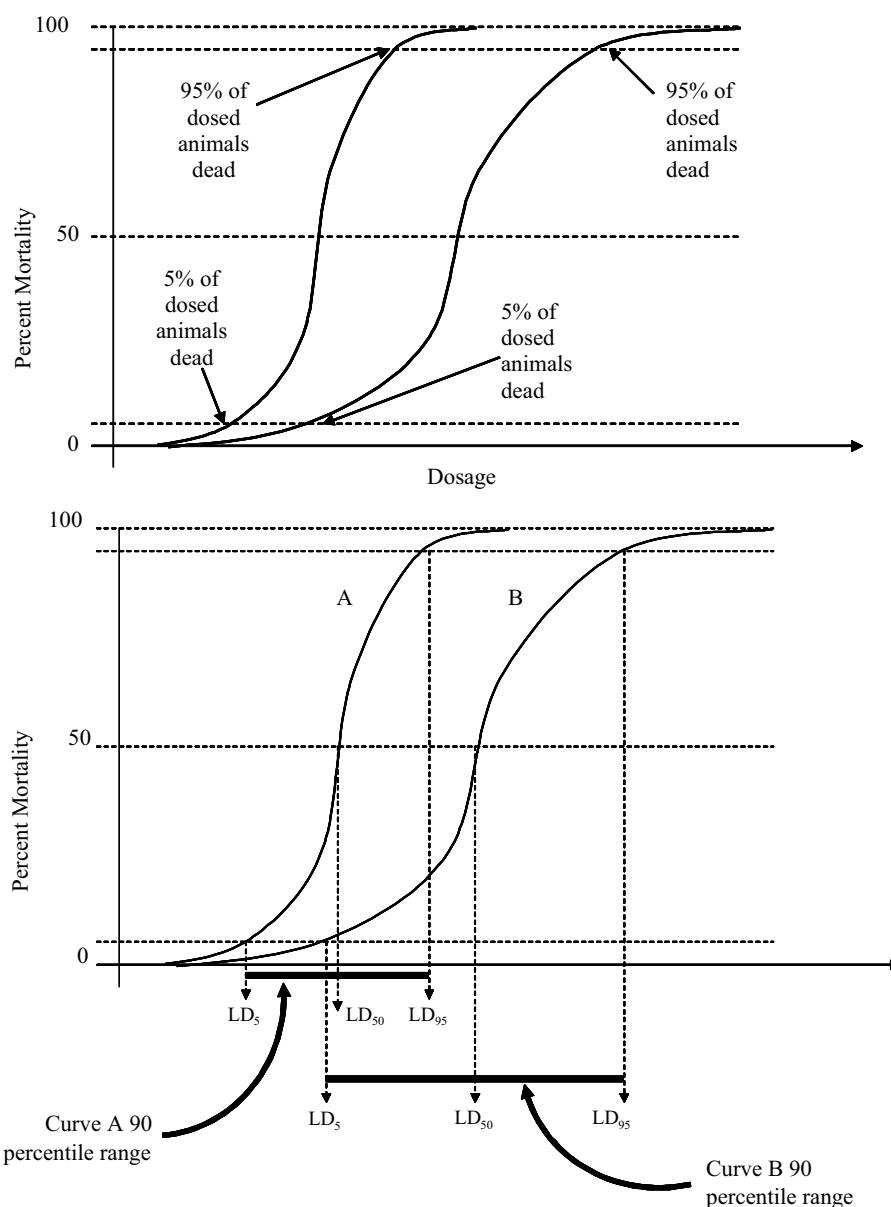
The shape and slope of the curve are formed according to available data. There are a number of uncertainties associated with these data. Often, the dose-response relationship is based on comparative biology from animal studies. These are usually high-dose, short-duration (at least compared to a human lifetime) studies. From these animal data, models are constructed and applied to estimate the dose-response that may be expected in humans. Thus, the curve may be separated into two regions: observed dose and modeled dose.

When environmental exposures do not fall within the range of observation, extrapolations must be made to establish a dose relationship. Generally, extrapolations are made from high to low doses, from animal to human responses, and from one route of exposure to another. The first step in establishing a dose-response relationship is to assess the data from empirical observations. To complete the dose-response curve, extrapolations are made either by modeling or by employing a default procedure based on information of the chemical's biochemical characteristics.

Dose-response models may be biologically based with parameters calculated from curve-fitting of data. If data are sufficient to support a biologically-based model specific to a chemical, and significant resources are available, this is usually the model of choice. Biologically-based models require large amounts of data.

Case-specific models employ model parameters and information gathered from studies specific to a particular chemical. Often, however, neither the biologically-based

**FIGURE 7.4** The greater the potency or severity of response (i.e. steepness of the slope) of dose-response curve, the smaller the range of toxic response (90 percentile range shown in bottom graph). Also, note that both curves have thresholds and that curve B is less acutely toxic based on all three reported lethal doses ( $LD_5$ ,  $LD_{50}$ , and  $LD_{95}$ ). In fact, risk is calculated by multiplying the slope of the dose-response curve by the actual contact with the substance, i.e. exposure. If either term is zero, the risk is zero. The risk of even the most toxic substance is zero if there is no exposure. If there is an extremely toxic substance on the planet Saturn, one's risk on the earth is zero. The risk will only increase if the substance finds its way to the earth or if we find our way to Saturn. Indeed, when the first man walked on the Moon, he changed the exposure paradigm for the planet earth. Never before was it possible to be exposed to lunar substances. However, if the substance were brought to the earth within or on the spacecraft, what was a zero risk of lunar substances became greater than zero risk, not because the substance's inherent toxicity changed, but because the exposure to the substance increased from zero.



nor the case-specific model is selected because the state-of-the-science is unsufficient, the necessary data are not available, or the significant costs cannot be justified.

Curve fitting is another approach used to estimate dose-response relationships for chemicals. Such models are used when response data in the observed range are available. A so-called point of departure for extrapolation is estimated from the curve. The point of departure is a point that is either a data point or an estimated point that can be considered to be in the range of observation, without the need for much extrapolation. The dose at which 10% of the test organisms die ( $LD_{10}$ ) in Figure 7.4 conceptually represents the lower 95% confidence limit on a dose associated with 10% extra risk. This is an example of such a point and, in fact, is often the standard

point of departure. Other hazard metrics are also used, e.g. estimates of increased adverse response, such as the  $ED_{10}$  (the estimate of a 10% increased response), which indicates a relative hazard and potency ranking.

The policies of many regulatory agencies and international organizations treat cancer differently than non-cancer effects, particularly in how the dose-response curves are drawn. As discussed in the dose-response curves, there is no safe dose for carcinogens. Cancer dose-response curve is almost always a nonthreshold curve, i.e. no safe dose is expected, while, theoretically at least, noncancer outcomes can have a dose below which the adverse outcomes do not present themselves. So, for all other diseases, safe doses of compounds can be established. If the substance is inhaled, the safe

dose is known as the reference concentration (RfC). For other exposure pathways, it is the reference dose (RfD). These references are calculated from thresholds below which no adverse effect is observed in animal and human studies. If the models and data were perfect, the safe level would be the threshold, i.e. RfC = NOAEC.

Incidentally, the term “noncancer” has a completely different meaning than the term “anticancer” or “anticarcinogens”. Anticancer procedures include radiation and drugs used to attack tumor cells. Anticarcinogens are chemical substances that work against the processes that lead to cancer, such as antioxidants and essential substances that help the body’s immune, hormonal, and other systems to prevent carcinogenesis.

Any hazard identification or dose-response research is never perfect, which means that the data derived from these investigations are often beset with various forms of uncertainty. The chief reasons for this uncertainty include variability among the organisms and between nonhuman and human organisms being tested. Interspecies uncertainties are the result of differences in response to the compound by different species (e.g. one mammal may have decreased adrenal gland activity, while another may show thyroid effects). Although interspecies uncertainty is usually associated with chemical risk, these uncertainties can also be part of microbial data sets. For example, certain immunocompromised subpopulations may respond adversely to microbial exposures that are below thresholds for the general population.

Another source of uncertainty occurs when studies only indicate the lowest concentration of a contaminant that causes the effect, i.e. the LOAEC, but the NOAEC is unknown. If the LOAEC is used, one is less certain how close this is to a safe level where no effect is expected. Often, there is temporal incongruence, since most of the studies take place in a shorter timeframe than in the real world. Thus, in lieu of long-term human studies, hazards and risks may have to be extrapolated from acute or subchronic studies of the same or similar agents. In a sense, dose replaces time (e.g. chronic exposure in a human over 30 years is estimated from high doses administered to hundreds of animals over a few months). Likewise, routes and pathways of exposure used to administer the agent to subjects may differ from the likely real-world exposures. For example, if the dose of substance in a research study is administered orally, but the pollutant is more likely to be inhaled by humans, this route-to-route extrapolation adds uncertainty. Finally, the hazard and exposure data themselves may be weak because the studies from which they have been gathered lack sufficient quality or the precision, accuracy, completeness, and representativeness, or they may not be directly relevant to the risk assessment at hand.

The factors underlying the uncertainties are quantified as specific uncertainty factors (UFs). The uncertainties in the RfD are largely due to the differences between results found in animal testing and expected outcomes in human population. As in other bioengineering operations, a factor of safety must be added to calculations to account for UFs. For air pollution risk analyses and assessments, the safe level is expressed in RfC, or in air the RfC. This is the dose or concentration below which regulatory agencies do not expect a specific unacceptable outcome. Thus, all the UFs adjust the actual measured levels of no effect (i.e. NOAECs and LOAECs) in the direction of a zero concentration. This is calculated as:

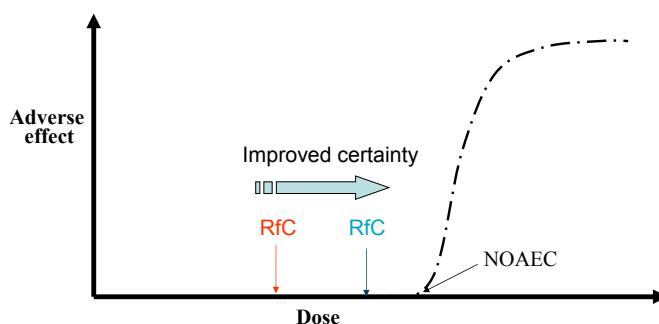
$$RfC = \frac{NOAEC}{UF_{inter} \times UF_{intra} \times UF_{other}} \quad (7.1)$$

The first of the three types of uncertainty is the previously mentioned difference between the response to a pollutant in the species tested *versus* in *Homo sapiens* ( $UF_{inter}$ ). Humans may be more or less sensitive than the tested species to a particular compound. The second UF is associated with the fact that certain human subpopulations are more sensitive to the effects of a compound than the general human population. These are known as intraspecies uncertainty/variability factors ( $UF_{intra}$ ). The third type of uncertainties ( $UF_{other}$ ) results when the available data and science is lacking.

The UFs are generally 10-fold, default factors used in operationally deriving the RfD and RfC from experimental data. The main classifications of UFs include: (1) accounting for variation in susceptibility among the members of the human population (i.e. intraspecies variability); (2) addressing the uncertainty in extrapolating animal data to humans (i.e. interspecies uncertainty); (3) accounting for the uncertainty in extrapolating from data obtained in a study with less-than-lifetime exposure (i.e. extrapolating from subchronic to chronic exposure); (4) uncertainty in extrapolating from an LOAEC rather than an NOAEC—i.e. data show a dose at which an effect is observed, but the “no effect” threshold has to be extrapolated; and (5) accounting for the uncertainty associated with extrapolation when the database is incomplete.<sup>5</sup> Since the NOAEC<sup>b</sup> is the numerator and the UFs are in the denominator, the larger the uncertainty, the closer the safe concentration (i.e. RfC) is to zero.

Note what occurs in Figure 7.5 as the UFs decrease, i.e. with better data and knowledge about the hazard. The UF values decrease. If all three UF values equal 1, i.e. complete certainty, the NOAEC and RfC become equal. Conversely, with very large uncertainties, the RfC approaches zero, i.e. the only “safe” dose is no dose.

<sup>b</sup> LOAEC if NOAEC has not been established.



**FIGURE 7.5** Reference concentrations (RfCs) on the noncancer dose-response curve (Figure 7.3), showing the movement of the RfC with improved scientific certainty. Adapted from Vallerio DA. *Environmental contaminants: assessment and control*. Burlington, MA: Elsevier Academic Press; 2004. (For color version of this figure, the reader is referred to the online version of this book.)

A hazard may be particularly severe for children, since they are growing and tissue development is much more prolific than in older years. To address these sensitivities, the Food Quality Protection Act includes what is known as the “10X” rule. This rule requires that the RfD for products regulated under FQPS, e.g. pesticides, must include an additional factor of 10 of protection of infants, children, and females between the ages of 13 and 50 years. This factor is included in the RfD denominator along with the other three UF values. The RfD that includes the UFs and the 10X protection is known as the population-adjusted dose (PAD). A risk estimate that is less than 100% of the acute or chronic PAD does not exceed the regulatory agency’s risk concern. An example of the use of an RfD as a factor of safety can be demonstrated by the US Environmental Protection Agency’s reregistration process for the organophosphate pesticide, chlorpyrifos. The acute dietary scenario had an NOAEL of  $0.5 \text{ mg kg}^{-1}\text{day}^{-1}$  and the three UF values equaled 100. Thus, the acute RfD =  $5 \times 10^{-3} \text{ mg kg}^{-1}\text{day}^{-1}$  but the more protective acute PAD =  $5 \times 10^{-4} \text{ mg kg}^{-1}\text{day}^{-1}$ . The chronic dietary scenario is even more protective, since the exposure is long term. The chronic NOAEL was found distinction to be  $0.03 \text{ mg kg}^{-1}\text{day}^{-1}$ . Thus, the chronic RfD for chlorpyrifos =  $3 \times 10^{-4} \text{ mg kg}^{-1}\text{day}^{-1}$  and the more protective acute PAD =  $5 \times 10^{-5} \text{ mg kg}^{-1}\text{day}^{-1}$ . Therefore, had the NOAEL threshold been used alone without the safety adjustment of the RfD, the allowable exposure would have been three orders of magnitude higher.<sup>6</sup>

### 7.3 AIR POLLUTION HAZARDS

Every hazard mentioned thus far in this chapter can be an air pollution hazard. Chemicals and microbes can be airborne and reach receptors, causing diseases and other

harm. Physical hazards can result from air pollution, such as increased incidence of melanoma due to larger ultraviolet light exposures as a result of air pollutants that find their way to the stratosphere and react with ozone.

The Clean Air Act and other laws around the world make a distinction between hazardous air pollutants and criteria air pollutants. This distinction is a bit misleading, since all air pollutants are hazardous, i.e. they contain some potential for harm. The difference, as previously mentioned, is that “hazardous air pollutants” cause or are suspected to cause cancer or other serious, chronic health effects, such as reproductive effects or birth defects, as well as substantial adverse ecological damage. These substances are differentiated from the criteria air pollutants, which are widespread air pollutants reasonably expected to harm the public health or welfare. Criteria pollutants are commonly used to indicate overall ambient air quality, based on common standards; whereas hazardous air pollutants are usually restricted spatially to “hot spots”, such as industrial and urban areas. These distinctions are drawn further in the following sections.

### 7.4 AIR TOXICS

Hazardous air pollutants are often called “air toxics”. The US EPA is required to control 187 hazardous air pollutants listed in Table 7.2. They are found in numerous settings, such as benzene in gasoline, perchloroethylene<sup>c</sup> (“perc”) in dry cleaning, and methylene chloride in paint strippers. Most air toxics are anthropogenic, emitted from both stationary and mobile sources, as well as in local microenvironments, e.g. in indoor air pollutants from building materials, solvents, and cleaning products. A number of air toxics are also released from indoor sources (e.g. some building materials and cleaning solvents).

<sup>c</sup>The prefix “per” means that a compound contains the maximum about possible of an element. In this case, perchloroethylene is the result of complete substitution of the four H atoms of the ethylene molecule with four Cl atoms. Thus, it is also known as tetrachloroethylene.

**TABLE 7.2** National Emission Standards for Hazardous Air Pollutants as Designated by Section 112, Clean Air Act Amendments of 1990

CAS#	Chemical or Class
75070	Acetaldehyde
60355	Acetamide
75058	Acetonitrile
98862	Acetophenone
53963	2-Acetylaminofluorene
107028	Acrolein
79061	Acrylamide
79107	Acrylic acid
107131	Acrylonitrile
8107051	Allyl chloride
92671	4-Aminobiphenyl
62533	Aniline
90040	<i>o</i> -Anisidine
1332214	Asbestos
71432	Benzene (including from gasoline)
92875	Benzidine
98077	Benzotrichloride
100447	Benzyl chloride
92524	Biphenyl
117817	Bis(2-ethylhexyl) phthalate (known as DEHP)
542881	Bis(chloromethyl) ether
75252	Bromoform
106990	1,3-Butadiene
156627	Calcium cyanamide
105602	Caprolactam
133062	Captan
63252	Carbaryl
75150	Carbon disulfide
56235	Carbon tetrachloride
463581	Carbonyl sulfide
120809	Catechol
133904	Chloramben
57749	Chlordane
7782505	Chlorine

**TABLE 7.2—cont'd**

CAS#	Chemical or Class
79118	Chloroacetic acid
532274	2-Chloroacetophenone
108907	Chlorobenzene
510156	Chlorobenzilate
67663	Chloroform
107302	Chloromethyl methyl ether
126998	Chloroprene
19773	Cresols/cresylic acid (isomers and mixture)
95487	<i>o</i> -Cresol
108394	<i>m</i> -Cresol
106445	<i>p</i> -Cresol
98828	Cumene
94757	2,4-dichlorophenoxyacetic acid (2,4-D) and its salts and esters
3547044	Dichlorodiphenyldichloroethylene (DDE)
334883	Diazomethane
132649	Dibenzofurans
96128	1,2-Dibromo-3-chloropropane
84742	Dibutyl phthalate
106467	1,4-Dichlorobenzene(p)
91941	3,3'-Dichlorobenzidene
111444	Dichloroethyl ether (bis(2-chloroethyl) ether)
542756	1,3-Dichloropropene
62737	Dichlorvos
111422	Diethanolamine
121697	<i>N,N</i> -Diethyl aniline ( <i>N,N</i> -dimethylaniline)
64675	Diethyl sulfate
119904	3,3-Dimethoxybenzidine
60117	Dimethylaminoazobenzene
119937	3,3-Dimethylbenzidine
79447	Dimethylcarbamoyl chloride
68122	Dimethylformamide
57147	1,1-Dimethylhydrazine
131113	Dimethyl phthalate

(Continued)

TABLE 7.2—cont'd

CAS#	Chemical or Class
77781	Dimethyl sulfate
534521	4,6-Dinitro- <i>o</i> -cresol and salts
51285	2,4-Dinitrophenol
121142	2,4-Dinitrotoluene
123911	1,4-Dioxane (1,4-diethyleneoxide)
122667	1,2-Diphenylhydrazine
106898	Epichlorohydrin (l-chloro-2,3-epoxyp propane)
106887	1,2-Epoxybutane
140885	Ethyl acrylate
100414	Ethyl benzene
51796	Ethyl carbamate (urethane)
75003	Ethyl chloride (chloroethane)
106934	Ethylene dibromide (dibromoethane)
107062	Ethylene dichloride (1,2-dichloroethane)
107211	Ethylene glycol
151564	Ethyleneimine (aziridine)
75218	Ethylene oxide
96457	Ethylene thiourea
75343	Ethylidene dichloride (1,1-dichloroethane)
50000	Formaldehyde
76448	Heptachlor
118741	Hexachlorobenzene
87683	Hexachlorobutadiene
77474	Hexachlorocyclopentadiene
67721	Hexachloroethane
822060	Hexamethylene-1,6-diisocyanate
680319	Hexamethylphosphoramide
110543	Hexane
302012	Hydrazine
7647010	Hydrochloric acid
7664393	Hydrogen fluoride (hydrofluoric acid)
123319	Hydroquinone
78591	Isophorone
58899	Lindane (all isomers)

TABLE 7.2—cont'd

CAS#	Chemical or Class
108316	Maleic anhydride
67561	Methanol
72435	Methoxychlor
74839	Methyl bromide (bromomethane)
74873	Methyl chloride (chloromethane)
71556	Methyl chloroform (1,1,1-trichloroethane)
78933	Methyl ethyl ketone (2-butanone)
60344	Methyl hydrazine
74884	Methyl iodide (iodomethane)
108101	Methyl isobutyl ketone (hexone)
624839	Methyl isocyanate
80626	Methyl methacrylate
1634044	Methyl- <i>tert</i> -butyl ether
101144	4,4-Methylene bis(2-chloroaniline)
75092	Methylene chloride (dichloromethane)
101688	Methylene diphenyl diisocyanate
101779	4,4'-Methylenedianiline
91203	Naphthalene
98953	Nitrobenzene
92933	4-Nitrobiphenyl
100027	4-Nitrophenol
79469	2-Nitropropane
684935	N-Nitroso- <i>N</i> -methylurea
62759	N-Nitrosodimethylamine
59892	N-Nitrosomorpholine
56382	Parathion
82688	Pentachloronitrobenzene (quintobenzene)
87865	Pentachlorophenol
108952	Phenol
106503	<i>p</i> -Phenylenediamine
75445	Phosgene
7803512	Phosphine
7723140	Phosphorus
85449	Phthalic anhydride

TABLE 7.2—cont'd

CAS#	Chemical or Class
1336363	Polychlorinated biphenyls (aroclors)
1120714	1,3-Propane sultone
57578	$\beta$ -Propiolactone
123386	Propionaldehyde
114261	Propoxur (Baygon)
78875	Propylene dichloride (1,2-dichloropropane)
75569	Propylene oxide
75558	1,2-Propylenimine (2-methylaziridine)
91225	Quinoline
106514	Quinone
100425	Styrene
96093	Styrene oxide
1746016	2,3,7,8-Tetrachlorodibenzo-p-dioxin
79345	1,1,2,2-Tetrachloroethane
127184	Tetrachloroethylene (perchloroethylene)
7550450	Titanium tetrachloride
108883	Toluene
95807	2,4-Toluene diamine
584849	2,4-Toluene diisocyanate
95534	o-Toluidine
8001352	Toxaphene (chlorinated camphene)
120821	1,2,4-Trichlorobenzene
79005	1,1,2-Trichloroethane
79016	Trichloroethylene
95954	2,4,5-Trichlorophenol
88062	2,4,6-Trichlorophenol
121448	Triethylamine
1582098	Trifluralin
540841	2,2,4-Trimethylpentane
108054	Vinyl acetate
593602	Vinyl bromide
75014	Vinyl chloride
75354	Vinylidene chloride (1,1-dichloroethylene)
1330207	Xylenes (isomers and mixture)
95476	<i>o</i> -Xylenes

TABLE 7.2—cont'd

CAS#	Chemical or Class
108383	<i>m</i> -Xylenes
106423	<i>p</i> -Xylenes
NA	Antimony compounds
NA	Arsenic compounds (inorganic, including arsine)
NA	Beryllium compounds
NA	Cadmium compounds
NA	Chromium compounds
NA	Cobalt compounds
NA	Coke oven emissions
NA	Cyanide compounds*
NA	Glycol ethers§
NA	Lead compounds
NA	Manganese compounds
NA	Mercury compounds
NA	Mineral fibers¶
NA	Nickel compounds
NA	Polycyclic organic matter**
NA	Radionuclides (including radon) §§
NA	Selenium compounds

\* X'CN where X=H' or any other group where a formal dissociation may occur. For example, KCN or Ca(CN)<sub>2</sub>.

§ Includes mono- and diethers of ethylene glycol, diethylene glycol, and triethylene glycol R-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-OR' where n = 1, 2, or 3; R = alkyl or aryl groups; R'=R, H, or groups that, when removed, yield glycol ethers with the structure: R-(OCH<sub>2</sub>CH)<sub>n</sub>-OH. Polymers are excluded from the glycol category (see previous note regarding modification).

¶ Includes glass, rock, or slag fibers (or other mineral-derived fibers) of average diameter 1  $\mu\text{m}$  or less.

\*\* Includes organic compounds with more than one benzene ring and which have a boiling point greater than or equal to 100 °C.

§§ A type of atom that spontaneously undergoes radioactive decay. For modifications to this list, visit: <http://www.epa.gov/ttn/atw/pollutants/atwsmod.html> [accessed on 12.07.10]. To date, the modifications have included methyl ethyl ketone, glycol esters, caprolactam, and hydrogen sulfide. A joint resolution to remove hydrogen sulfide, which was inadvertently included in the original Section 112(b)(1) list, was passed by the Senate on August 1, 1991 (Congressional Record page S11799), and the House of Representatives on November 25, 1991 (Congressional Record pages H11217-H11219). The Joint Resolution was approved by the President on December 4, 1991. Hydrogen sulfide is included in Section 112(r) and is subject to the accidental release provisions. For all listings above that contain the word "compounds" and for glycol ethers, the following applies: unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemical (i.e. antimony, arsenic, etc.) as part of that chemical's infrastructure.

A few air toxics are also released from natural sources such as volcanic eruptions and forest fires.<sup>7</sup> For example, a recent study in South Queensland, Australia, found that 61.2% of the emissions of volatile organic compounds (VOCs) in that region came from biogenic sources (e.g. releases from tree leaves) and another 5.7% from bush fires and biomass burning.<sup>8</sup> Several air toxics are VOCs; their relatively high vapor pressures (usually  $> 0.01 \text{ kPa}$ ) mean that they are likely to be found in the troposphere.

Stationary air toxic sources include industrial factories, refineries, and fossil fuel-burning electric generating facilities, and are categorized as either major or area sources.

- “Major” sources emit at least 10 tons per year of any of the listed toxic air pollutants, or at least 25 tons per year of a mixture of air toxics.
- “Area” sources are smaller facilities that emit less than 10 tons per year of a single air toxic or less than 25 tons per year of a combination of air toxics. The major problem with area sources is that even small amounts of very toxic compounds become increasingly hazardous with increasing numbers of sources, i.e. the cumulative increase in hazard due to the collective emissions of air toxics.<sup>9</sup>

The 1990 amendments to the Clean Air Act (CAA) also included the means to address the National Emission Standards for Hazardous Air Pollutants. Section 112 requires that the US Environmental Protection Agency work with state, local, and tribal governments to reduce releases of these specific toxic air pollutants.

#### 7.4.1 Maximum Available Control Technology

After the 1990 amendments to the CAA, the U.S. EPA published a list of source categories and issued Maximum Achievable Control Technology (MACT) standards for each category over a specified timetable. The next step after MACT standards is now underway. This is to address chronic health risks that would still be expected if the sources meet these standards. This is known as residual risk reduction. The first step was to

assess the health risks from air toxics emitted by stationary sources that emit air toxics after technology-based (MACT) standards are in place. The residual risk provision sets additional standards if MACT does not protect public health with an “ample margin of safety”, as well as additional standards if they are needed to prevent adverse environmental effects.

The “ample margin of safety” applies to airborne carcinogens (see Figure 7.6). Best available and maximum available control technologies are not necessarily risk based. The difference between using these technologies and the risk posed by the remaining air pollution is known as “residual risk”. That is, if a source can demonstrate that it will not contribute to a defined risk goal (e.g.  $< 10^{-6}$  cancer risk), then this may provide an ample margin of safety requirements for that particular air toxic.

The ample margin might also apply to noncancer toxins, such as neurotoxins. This would involve the application of the hazard quotient (HQ). The HQ is the ratio of the potential exposure to the substance and the level at which no adverse effects are expected. An  $\text{HQ} < 1$  means that the exposure levels to a chemical should not lead to adverse health effects. Conversely, an  $\text{HQ} > 1$  means that adverse health effects are possible. Due to uncertainties and the feedback that is coming from the business and scientific communities, the ample margin of safety threshold is presently ranging from  $\text{HQ} = 0.2\text{--}1.0$ . So, if a source can demonstrate that it will not contribute to greater than the threshold (whether it is 0.2, 1.0, or some other level established by the federal government) for noncancer risk, it meets the ample margin of safety requirements for air toxics.

#### 7.4.2 Coke Oven Emissions: A Complex Hazardous Air Pollutant Class

The air toxics list in the United States includes many more compounds than the listing in Table 7.3 may imply. For example, the list includes coke oven emissions.<sup>10a–10f</sup> Coke is a solid fuel widely used in heavy industry, e.g. steel and other metal processing. Coke is produced by

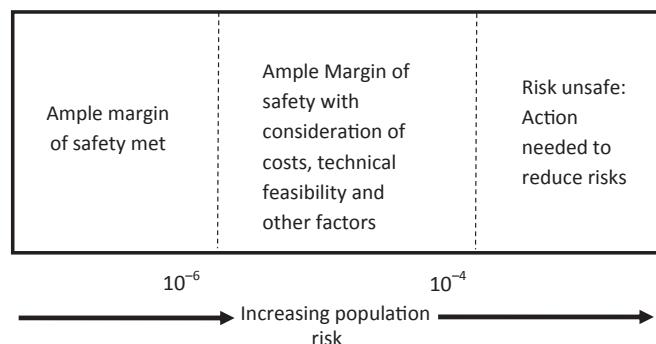


FIGURE 7.6 Ample margin of safety to protect public health and adverse environmental effects from an air pollutant. *Clean Air Act Amendments of 1990, Section 112(f)(2).*

TABLE 7.3 Air Quality Guide for Ozone

Air Quality Index	Protect Your Health
Good (0–50)	No health impacts are expected when air quality is in this range
Moderate (51–100)	Unusually sensitive people should consider limiting prolonged outdoor exertion
Unhealthy for sensitive Groups (101–150)	The following groups should limit prolonged outdoor exertion: <ul style="list-style-type: none"> <li>• People with lung disease, such as asthma</li> <li>• Children and older adults</li> <li>• People who are active outdoors</li> </ul>
Unhealthy (151–200)	The following groups should avoid prolonged outdoor exertion: <ul style="list-style-type: none"> <li>• People with lung disease, such as asthma</li> <li>• Children and older adults</li> <li>• People who are active outdoors</li> </ul> Everyone else should limit prolonged outdoor exertion
Very unhealthy (201–300)	The following groups should avoid all outdoor exertion: <ul style="list-style-type: none"> <li>• People with lung disease, such as asthma</li> <li>• Children and older adults</li> <li>• People who are active outdoors</li> </ul> Everyone else should limit outdoor exertion

For example, if a newspaper reports that ozone air quality is 120, people with lung disease, children, older adults, and those vigorously exercising should limit time spent outside engaging in exerting activities.

*U.S. Environmental Protection Agency. Air quality guide for ozone. EPA-456/F-08-001. Washington, DC; 2013.*

the pyrolysis of coal, i.e. by blending and heating bituminous coals to 1000° – 1400° C in the absence of oxygen. This drives off the most volatile compounds (those with the highest vapor pressures), leaving a much purer fuel than the original coal. However, from an air pollution perspective, it is this large fraction of volatile compounds that are the major concern.

Coke oven emissions include both vapor and aerosol phases, i.e. they are determined by measuring the benzene-soluble fraction of total particulate matter (PM) generated during coke production. Tars and light oils are distilled out of the coal, and gases are generated during this process. The emissions contain varying amounts of mixtures of particles, vapors, and gases that typically include organic compounds, such as phenol and polycyclic aromatic hydrocarbons (PAHs), VOCs (e.g. acrolein, aliphatic aldehydes, and formaldehyde), as well as inorganic compounds (e.g. ammonia, carbon monoxide, and nitrogen oxides). The emissions also include metals (e.g. cadmium, arsenic, and mercury)

and their compounds.<sup>11</sup> Thus, the single coke oven emission chemical listing includes many different compounds that make up coal tar, creosote, and coal tar pitch. As much as 1.6 million kg of coke oven emissions are generated annually in the United States.<sup>12</sup> By-products are collected in most coke-making operations, so the volatile compounds generally do not exit through the stack. However, the pollutants escape at various points in the coking process through openings due to structural defects around the doors or charging lids, improper controls, poor operation and maintenance of pollution control equipment, and operator error.<sup>13</sup>

Coke oven emissions include more than 60 organic compounds, notably more than 40 PAHs. One metric ton of coal yields approximately 545–635 kg (1200 to 1400 lb) of coke, 45–90 kg (100–200 lb) of coke breeze (large coke particulates), 7–9 kg (15–20 lb) of ammonium sulfate, 27.5–34 l (7.3–9.8 gal) of coke oven gas tar, 55–135 l (14.5–35.7 gal) of ammonia liquor, and 8–12.5 l (2.1–3.3 gal) of light oil. About 20–35% of the initial coal charge is emitted as gases and vapors, most of which are collected in by-product coke production. Coke oven gas includes hydrogen, methane, ethane, carbon monoxide, carbon dioxide, ethylene, propylene, butylene, acetylene, hydrogen sulfide, ammonia, oxygen, and nitrogen. Coke oven gas tar includes pyridine, tar acids, naphthalene, creosote oil, and coal tar pitch. Benzene, xylene, toluene, and solvent naphthas may be extracted from the light oil fraction.

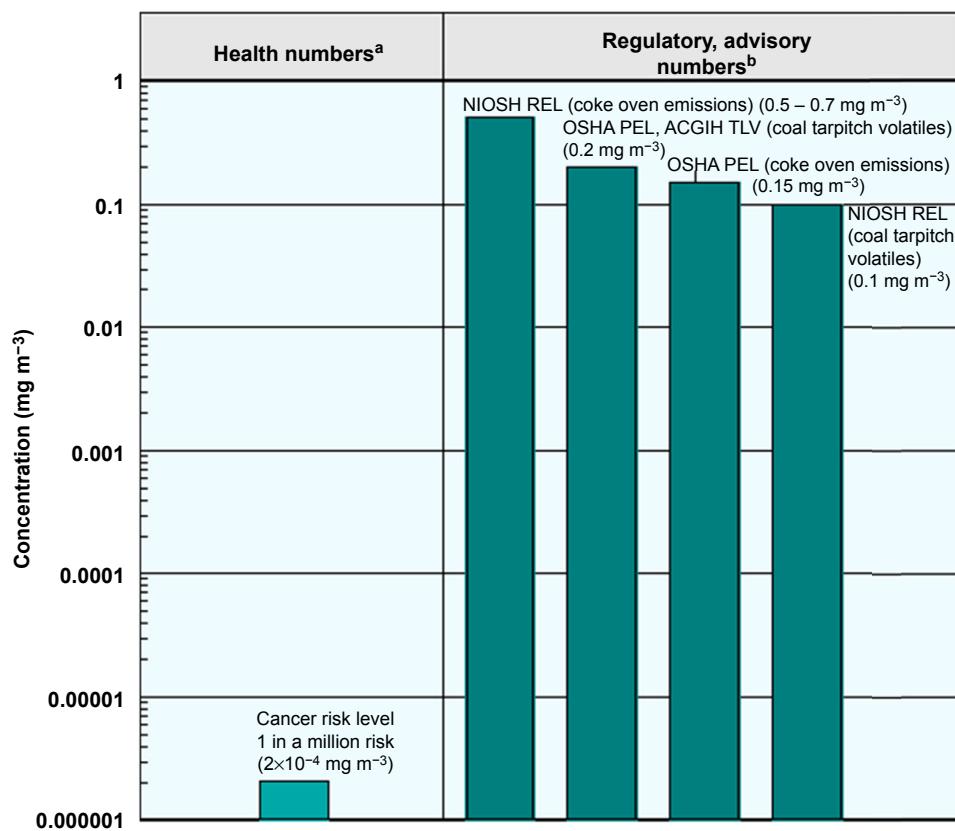
The chronic human health effects of coke oven emissions include disorders of the skin, respiratory, liver, and digestive systems. Human and animal data indicate that exposure to coke oven emissions leads to cancer of the lung, trachea, bronchus, kidney, prostate, and other sites. Indeed, these emissions are classified as known human carcinogens<sup>14</sup> (see Figure 7.7).

## 7.5 CRITERIA POLLUTANTS

The ambient air's concentrations of the criteria pollutants, i.e. PM, tropospheric ozone, carbon monoxide, nitrogen dioxide, sulfur dioxide, and lead, indicate the quality of the air in a region. The hazards posed by each are discussed below.

### 7.5.1 Particulate Matter

Particle pollution includes inhalable coarse particles, with aerodynamic diameters >2.5 µm but <10 µm and fine particles with diameters ≤2.5 µm. PM varies in size and shape (see Chapter 3). Primary particles are emitted directly from a source, such as construction sites, unpaved roads, fields, smokestacks, or fires. Secondary



**FIGURE 7.7 Health information for coke oven emissions.** ACGIH TLV, American Conference of Governmental and Industrial Hygienists' threshold limit value expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effects; NIOSH REL, National Institute of Occupational Safety and Health's recommended exposure limit; NIOSH-recommended exposure limit for an 8- or 10-h time-weighted average exposure and/or ceiling; OSHA PEL, Occupational Safety and Health Administration's permissible exposure limit expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effects averaged over a normal 8-h workday or a 40-h workweek. a = Health numbers are toxicological numbers from animal testing or risk assessment values developed by the U.S. EPA. b = Regulatory numbers are values that have been incorporated in government regulations, while advisory numbers are nonregulatory values provided by the U.S. government or other groups as advice. OSHA numbers are regulatory, whereas NIOSH and ACGIH numbers are advisory. U.S. Environmental Protection Agency. Coke oven emissions. <http://www.epa.gov/ttnatw01/hlthef/cokeoven.html>; 2013 [accessed 21.09.13]. (For color version of this figure, the reader is referred to the online version of this book.)

particles are generated by reactions in the atmosphere between sulfur dioxides, nitrogen oxides, and other compounds. Most fine PM are secondary particles.

Smaller diameter particles pose the greatest human health problems, as they penetrate deeply into lungs. Ecosystem hazards include decreased visibility due to haze caused by fine particles.

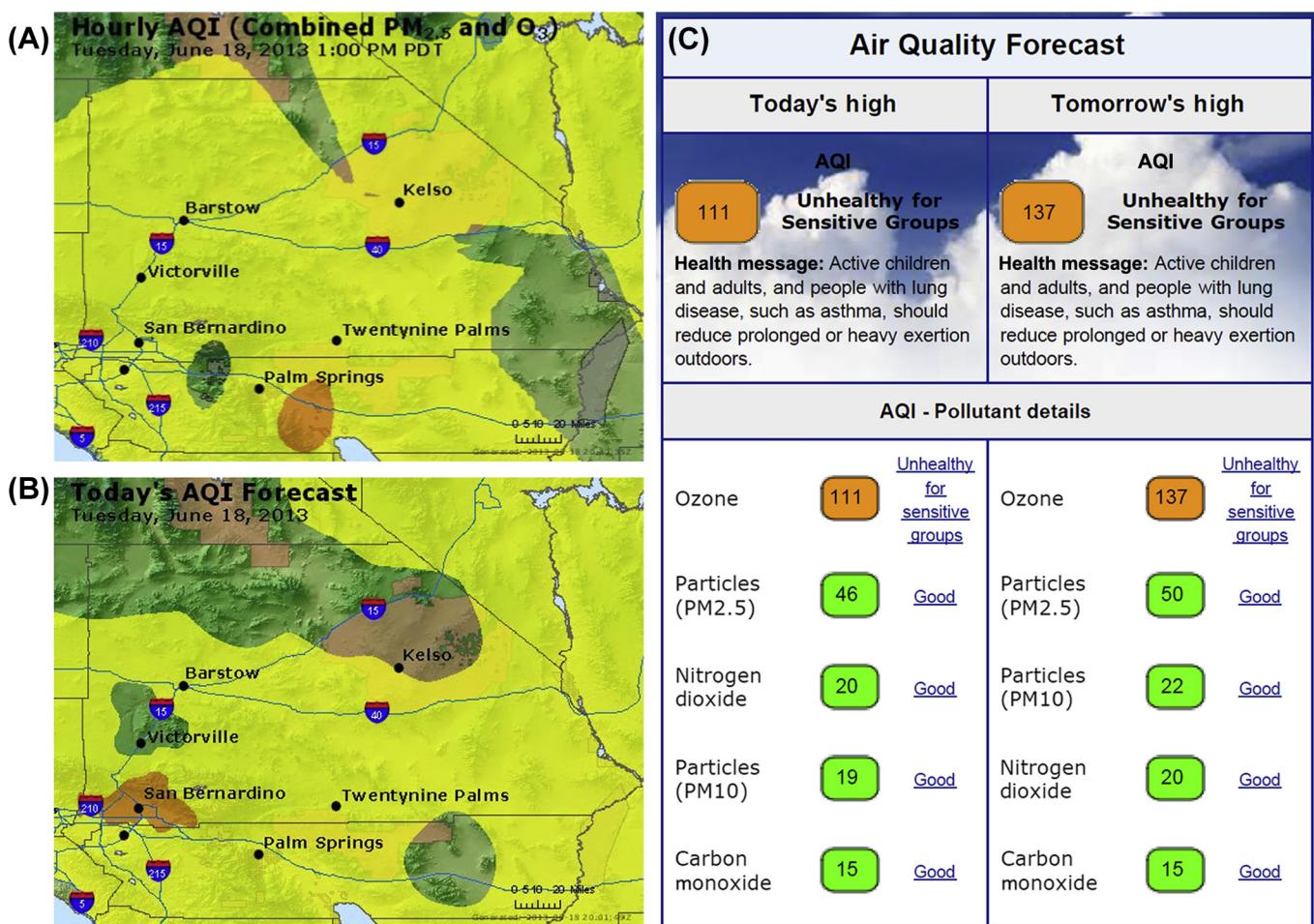
### 7.5.2 Tropospheric Ozone

The mix of VOCs and oxides of nitrogen ( $\text{NO}_x$ ) reacting in sunlight (i.e. photochemical reactions) leads to the formation of ozone ( $\text{O}_3$ ). These reactions occur in the lowest layer of the atmosphere, i.e. the troposphere. Since humans and other organisms live and breathe in the troposphere, ground-level ozone presents health problems in humans and causes damage to vegetation and wildlife.

Lung intake of elevated concentrations of  $\text{O}_3$  in air makes it difficult to breathe deeply and vigorously, leading to coughing, shortness of breath, and pain when taking a deep breath. These are short-term (acute) problems. Longer term problems include inflammation and damage to airways and lungs, leading to asthma, emphysema, bronchitis, and other chronic respiratory diseases. Increasing ambient  $\text{O}_3$  concentrations are associated with an increase in the frequency of asthma attacks, as well as increased susceptibility to infections.<sup>15</sup> Lung damage may continue after symptoms subside.

Although most incidents of elevated  $\text{O}_3$  occur as urban smog on warm, sunny days, the pollutant can also be transported *advectionally* (i.e. with the movement of an air mass) from one region to another. Thus,  $\text{O}_3$  levels can be elevated in areas of cooler, overcast regions if it is transported from where the pollutant was produced.

Local communities use air quality indices (AQIs) to warn residents of possible health conditions. These are



**FIGURE 7.8** Air Quality Index (AQI) map of southwestern California. The color codes on the forecast legend correspond to Table 7.3. A and B: on these days, ozone is the only reported pollutant to be at unhealthy levels. C: output from AQI. U.S. Environmental Protection Agency. AirNow. [http://airnow.gov/index.cfm?action=airnow.main; 2013 \[accessed 18.06.13\].](http://airnow.gov/index.cfm?action=airnow.main; 2013 [accessed 18.06.13].) (For color version of this figure, the reader is referred to the online version of this book.)

reported online and in media, e.g. newspaper (see Figure 7.8). In the summer, for example, the AQI can be strongly influenced by ozone concentrations. For example, on June 18, 2013, an area east of Palm Springs, California, reported an AQI value for ozone of 111, with a forecast for nearby San Bernardino of 137 the following day (see Figure 7.8(B)). Both scores are considered to be unhealthy for sensitive groups.

### 7.5.3 Nitrogen Dioxide and Oxides of Nitrogen

Nitrogen will be discussed in detail in Chapter 22. Nitrogen is a part of three of the six criteria pollutants, i.e. PM, NO<sub>2</sub>, and O<sub>3</sub>. Nitrogen dioxide (NO<sub>2</sub>) is a criteria pollutant under National Ambient Air Quality Standards (NAAQS).

Although the sum of nitric oxide (NO) and NO<sub>2</sub> is commonly called nitrogen oxides or NO<sub>x</sub>, other oxides of nitrogen including nitrous acid and nitric acid are included in the oxides of nitrogen category. In addition,

oxides of nitrogen play a major role in the formation of PM, when NO<sub>x</sub> reacts with ammonia and other compounds in the presence of water vapor to form fine aerosols.

From the perspective of direct health effects, NO<sub>2</sub> is the NO<sub>x</sub> compound of greatest concern. Short-term exposure to NO<sub>2</sub> (i.e. <24 h) can lead to respiratory effects, such as increased number and severity of asthma episodes and airway inflammation in healthy individuals. Inhalation of elevated short-term NO<sub>2</sub> concentrations has been associated with increased hospital emergency room visits for respiratory distress.<sup>16</sup>

Drivers and others who spend time on or near major roadways can experience short-term NO<sub>2</sub> exposures considerably higher than measured by the current network. Approximately 16% of US housing units are located within 300 ft of a major highway, railroad, or airport (approximately 48 million people). This population likely includes a higher proportion of nonwhite and economically disadvantaged people. Exposure to

elevated NO<sub>2</sub> concentrations near roadways<sup>d</sup> is of particular concern for susceptible individuals, including people with asthma, children, and the elderly. Thus, near-road environments present environmental justice issues, as well as threats to vulnerable populations.

#### 7.5.4 Sulfur Dioxide and Oxides of Sulfur

Sulfur dioxide (SO<sub>2</sub>) is a criteria pollutant under NAAQS in the United States. Exposure to SO<sub>2</sub> can lead to health effects. SO<sub>2</sub> and other oxides of sulfur form acids in the atmosphere, especially sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) which is a key component of acid rain. SO<sub>2</sub> also causes crop and material damage when acidic aerosols (liquid and solid) are deposited. These result from oxides of sulfur in stack emissions followed by chemical reactions in the atmosphere.

Controlling emissions of SO<sub>2</sub> and other oxides of sulfur (SO<sub>x</sub>) provides an example of the need to think systematically about air pollutants. One solution following the passage of the CAA of 1970 in the United States was to increase the height of stacks, so that the sulfur compounds would not deposit near the source. Certain industrial operations emit SO<sub>x</sub>, particularly those using sulfur-laden fuels for combustion processes. Notably sulfur dioxide (SO<sub>2</sub>) is a respiratory irritant, damages crops (foliar stress), and causes visibility problems, especially when sulfate particulates are suspended in the atmosphere. In the middle of the twentieth century, damage to crops was seen near facilities, like power plants. The paint of vehicles parked in the facilities' lots was commonly oxidized and damaged. People living near the facilities complained of respiratory problems and crop damage. Thus, a seemingly rational engineering solution was to increase the height of the stacks emitting SO<sub>2</sub>. Historically, the biggest decline in sulfur pollution was achieved simply by dispersion of pollutants from increasingly taller stacks (i.e. point of release is higher, so there is greater three-dimensional dispersion of the pollutant).<sup>17</sup> In fact, this seemed to work so well in terms of local crop and material damage, that when the Clean Air Act of 1970 required states to develop plans to meet the new standards, some states required that tall stacks at certain

facilities to dilute the local concentrations of SO<sub>2</sub>, as well as oxides of nitrogen (NO<sub>x</sub>).

Unfortunately, the taller stacks did more than disperse and dilute these pollutants. They allowed them to be captured by winds aloft and to reach higher regions of the troposphere. Moving advectively in these air streams, the pollutants can be transported long distances (hundreds and even thousands of kilometers). After release from mid-Western coal-fired power plants, the pollutants had sufficient time and atmospheric conditions, particularly the presence of water vapor, to generate acids. Thus, the taller stacks became a contributing factor to the acid rain problems in Northeastern states, Canada and Europe.

#### 7.5.5 Carbon Monoxide

Carbon monoxide (CO) is a product of incomplete combustion. Carbon monoxide elicits various health effects by binding and interfering with heme proteins (See Chapter 10). The amount of CO bound to hemoglobin as carboxyhemoglobin (COHb) is the key marker for health effects. The best studied health effect associated with CO levels of concern is reduced oxygen availability (i.e. hypoxia) as a result of the blood's increased COHb concentrations. That is, when COHb forms, it displaces the oxygen carrying capacity of the blood and decreases the release of oxygen to tissues. Vulnerable populations, e.g. persons with impaired cardiovascular systems are at greater risk to this hazard than the general public.

Other potential effects include damage to the central nervous system, reproduction and prenatal development, and the respiratory system. Of course, at sufficiently high concentrations, exposures to CO can be fatal.

#### 7.5.6 Lead

The principal direct hazard from Pb exposure is neurotoxicity. However, the original reason for removing lead (Pb) from gasoline is that it fouled catalytic converters, which presented an indirect smog hazard as a result of higher ambient concentrations of oxides of nitrogen and VOCs than would not have been released if Pb were absent in the fuel. Measures that were put in place to prevent the use of lead gasoline

<sup>d</sup> According to the US Environmental Protection Agency, NO<sub>2</sub> concentrations in vehicles and near roadways are generally much higher than average measurements. In-vehicle concentrations can be two to three times higher than measured at nearby area-wide monitors. Within 50 m of roadways, concentrations of NO<sub>2</sub> have been found to be 30–100% higher than at upwind locations. Thus, individuals who spend time on or near major roadways can experience elevated short-term NO<sub>2</sub> exposures. Approximately 16% of US housing units are located within 300 ft of a major highway, railroad, or airport (approximately 48 million people). Near-roadway neighborhoods have greater numbers of nonwhite and economically disadvantaged people than the US average. Source: U.S. Environmental Protection Agency (2013). Nitrogen oxide. <http://www.epa.gov/oaqps001/nitrogenoxides/index.html>; [accessed 01.10.13].

in vehicles equipped with catalytic converters worked well.

To meet mobile source emission standards beginning in the 1970s, older vehicles were continuously being replaced by newer ones that burned only lead-free gasoline. In addition to helping to lower atmospheric concentrations of criteria air contaminants, measurements of near-road environments also began to show a precipitous decline in Pb concentrations in soil and air. The National Health and Nutrition Examination Survey reported a 78% decrease in mean blood lead levels from 12.8 to  $2.8 \mu\text{g dl}^{-1}$  between the 5-year period from 1976 to 1980 and the 5-year period from 1988 to 1991.<sup>18a,18b</sup> This drop in blood lead levels has been attributed to the reduction of leaded gasoline and to the removal of lead from soldered cans. The removal of Pb from gasoline in the first place to address CO, NO<sub>x</sub>, and hydrocarbons, not Pb per se, was a fortuitous in decreasing Pb emissions in the air and the concomitant decrease in Pb in blood. This chain of events led to the addition of Pb as the sixth criteria air pollutant in 1978. The current NAAQS standard for lead is  $1.5 \mu\text{g m}^{-3}$ , maximum arithmetic mean during a calendar quarter.<sup>19</sup> In 1985, US federal mandates began to require reductions in the lead content of gasoline. The standard for lead content in gasoline was  $0.1 \text{ g Pb gal}^{-1}$  on January 1, 1986, with the complete ban on Pb in gasoline effective January 1, 1996.

The hazardous and criteria pollutants are discussed in greater detail in later chapters, including their health effects and methods of measuring and treating them. Chapter 8 provides information and examples of how to combine the hazard information with exposure estimates to characterize risk.

## QUESTIONS

1. What is a criteria air pollutant?
2. Draw a food chain diagram for a toxic air pollutant?
3. What is a no-threshold model?
4. On what part of the dose-response curve is the CSF usually derived?
5. What is an RfC and what are its uncertainties?
6. Calculate an RfC for a substance with a NOAEC =  $1.5 \text{ mg m}^{-3}$ , an interspecies uncertainty factor = 10, an intraspecies factor = 100 and other uncertainties = 10.
7. What would account for the relatively “other” uncertainty factor?
8. As science advances, if the above compound is neurotoxic, how might the RfC change?
9. If a stationary source in the United States annually emits 9 tons of a listed hazardous air pollutant is it a major source?

10. If a stationary source in the United States annually emits 3 tons of chemical A, 5 tons of chemical B, 8 tons of chemical C, 9 tons of chemical D and 100 lbs. of chemical E, all listed hazardous air pollutants, is it a major source?
11. Which metalloids are listed as hazardous air pollutants in the United States?
12. What are two bases for regulating the emissions of hazardous air pollutants?
13. In the United States, the air quality index for a metropolitan area is 105 on Wednesday and 48 on Thursday. What do these values indicate?
14. What is NO<sub>x</sub>? What is its hazard(s)?
15. What are the advantages and disadvantages of tall stacks?
16. Why does CO exposure contribute to cardiovascular problems?
17. What is the major health problem associated with lead (Pb) exposure?

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19. Lead can be present in the atmosphere as either a particle or gas. The NAAQS standard does not differentiate between phases, i.e. it is set for total Pb concentration.

# Air Pollutant Exposures

## 8.1 EXPOSURE

Thus far, we have considered hazard, which is half of what needs to be known to determine risk. As indicated in Figures II.1 and II.2, a complete characterization of the risk needs to be a complement of both the hazard of the pollutant and the extent and intensity of exposure of a receptor to the pollutant. The dominant focus of air pollution prevention and control has been on human health.

There is no clear consensus on the meaning of many risk assessment terms, and exposure assessment is one of those where researchers, engineers, and the general public use varying definitions. One definition of exposure assessment tracks closely with that of the World Health Organization (WHO):

The process of estimating or measuring the magnitude, frequency and duration of exposure to an agent, along with the number and characteristics of the population exposed. Ideally, it describes the sources, pathways, routes, and the uncertainties in the assessment.<sup>1</sup>

Unfortunately, the definition twice embeds the word being defined, i.e. exposure. Again, tracking with the WHO definition, a good working definition within the realm of air pollution is:

The contact between an agent and a target. Such contact occurs at an exposure surface over an exposure period.<sup>1</sup>

Exposure scientists characterize and predict the contact of an agent with a receptor for a specific duration of time.<sup>2</sup> This exposure is quantifiable. An air pollutant is an example of an agent, but it may be any chemical, biological, or physical entity that contacts a receptor, i.e. a biological entity that receives an exposure or dose.

The contact between an agent and a receptor occurs at an exposure surface over an exposure period. An exposure surface is the surface on a receptor where an agent

is present. Examples of exposure surfaces include the exterior of the skin and eyeball, as well as a virtual outer surface, such as the interface surface over the nose and open mouth. Virtual surfaces are not physical surfaces, but are two-dimensional areas across which the flux of an agent traverses. Examples of inner exposure surfaces include the linings of the gastrointestinal tract, respiratory tract, and urinary tract. Many of the features of exposure apply to organisms other than humans and even systems of organism, e.g. ecosystems and their subdivisions.

When a receptor is exposed to a specific agent or stressor from all sources across all routes and pathways, it is known as an aggregate exposure. For example, if a person is exposed to lead (Pb) by ingesting food and breathing air, this is an aggregate Pb exposure. The total exposure to multiple agents and/or stressors that causes a common toxic effect to human health by the same, or similar, sequence of major biochemical events is known as a cumulative exposure. For example, if a population is exhibiting neurological effects, it could be due to cumulative exposures to polychlorinated biphenyls (PCBs), Pb, mercury (Hg), and other neurotoxic substances. The exposures would be via inhalation, ingestion of food and nonfood substances, dermal contact through the skin, and nasal exposures almost directly to the brain.

Exposure assessment is the process of characterizing, estimating, measuring, and modeling the magnitude, frequency, and duration of contact with an agent as well as the number and characteristics of the population exposed. The assessment must consider not only the concentrations of an agent in the air and other media but also the factors related to human behavior and characteristics that help to determine an individual's exposure to an agent. These are known as exposure factors. An exposure pathway is the course taken by an agent from the source to the receptor. The exposure route is the way an agent enters a receptor after contact (e.g. by ingestion, inhalation, dermal application). The time

of continuous contact between the agent and receptor is known as the exposure duration.

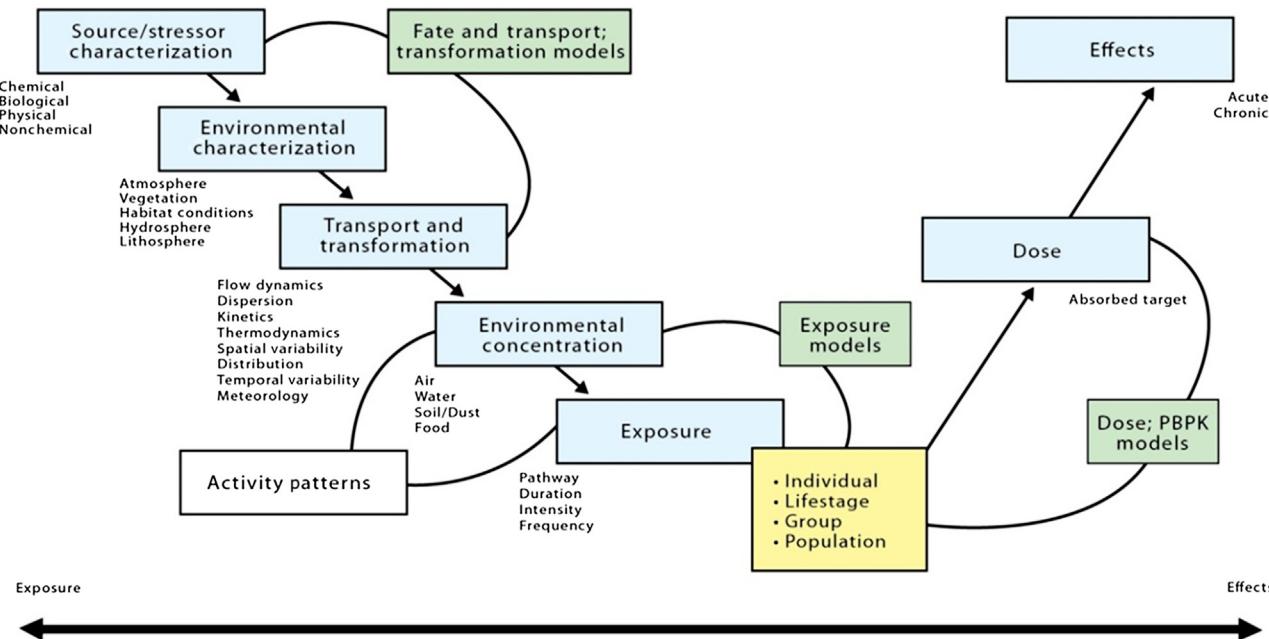
Exposure can be envisaged as a number of steps after an agent has been released into the environment and before it elicits harm. This is a source-to-outcome framework (Figure 8.1). Agents are released into the environment from a source. The actual exposure can be to the emitted air pollutant or a different compound that has been transformed by the environment. Contaminants or their transformation products move through the atmosphere and other compartments in the environment and can be found in many types of environmental media. Exposure results from the transfer of a contaminant from an environmental medium to a receptor. An exposure becomes a dose when the contaminant is taken up into the receptor. The endpoint for exposure science is the dose received endogenous site where the adverse health effect can occur. For example, the exposure endpoint for a neurological agent is the central or peripheral nervous system, whereas the exposure endpoint for a respiratory agent is the lung and/or other sites in the respiratory system. This endpoint serves as the starting point for the health effects discussed in the next chapters.<sup>3</sup>

As mentioned, an exposure is any contact between a receptor and an agent. The receptor can be human, other species, ecosystems, or even inanimate objects, e.g. buildings and monuments (see Chapter 15). For chemical and biological agents, this contact can come about from a number of exposure pathways (e.g. air, water,

and soil) and routes (e.g. inhalation, ingestion, dermal, nasal). Physical agents, such as ionizing, ultraviolet (UV), and electromagnetic radiation, may also come in contact via these pathways, but the exposure often has to be extrapolated from the energy that the radiation imparts to tissues. The absorbed dose is the amount of energy absorbed per unit weight of tissue. One gray dose is equivalent to 1 J radiation energy absorbed per kilogram of organ or tissue weight.

For chemicals, dose is the amount of agent that enters a target organ within a specified period of time after crossing a contact boundary. An exposure does not necessarily lead to a biologically effective dose. Conversely, there can be no dose without an exposure. Thus, the chemical undergoes two steps. First, the receptor is exposed, i.e. comes into contact with the agent. Next, an agent entering the body may or may not find its way to the target organ.

The exposure process begins with the release of a substance. As mentioned, the substance may be an air pollutant when it is released or it may become one during its path toward the receptor. Thus, there are three possibilities after release: (1) an air pollutant is released and remains an air pollutant when it reaches the receptor; (2) a nontoxic substance is released but due to physical, chemical, and biological conditions in the atmosphere is transformed into an air pollutant; and (3) an air pollutant is released but due to physical, chemical, and biological conditions in the atmosphere is transformed into a nontoxic substance. Although its



**FIGURE 8.1 Source-to-dose continuum.** Exposure occurs after an agent is released into the environment until an adverse effect occurs (e.g. disease and disruption). Steps toward the right approach the adverse effect. Steps toward the left approach the source of the agent (e.g. air pollutant emission). PBPK models, physiologically based pharmacokinetic models. Models are shown in green. Yellow box is the focus of the exposure assessment. White box is the necessary psychosocial data to be combined with physical science data. Terms outside of boxes represent the physical, chemical, and biological data needed for each step. (For interpretation of the references to color in this figure legend, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency, adapted from National Research Council. 1997.

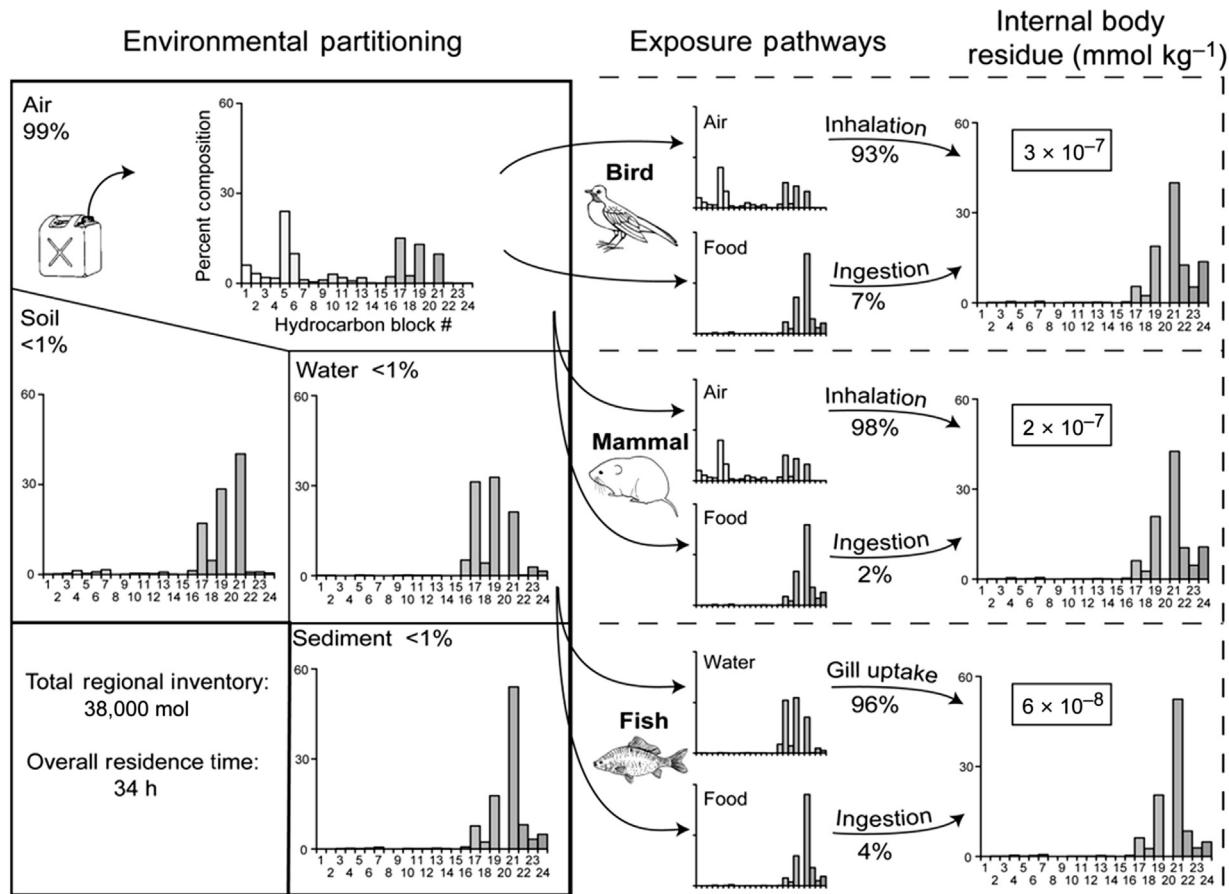
primary pathway is air, the pollutant may spend time in other environmental compartments like surface waters and soil before becoming re-entrained in the air and reaching the receptor. The primary route of air pollutant exposure is inhalation, but other routes are often involved. For example, suspended dust may be inhaled, but settled dust may be ingested when it deposits on food, or semivolatile air pollutants may sorb to surfaces whereupon a person's skin, eyes, and nose come into contact with what was previously an air pollutant.

Historically, air pollution exposure has often been assumed to be proportional to the chemical concentration of the pollutant. Certainly, if the chemical concentration is zero, there is no exposure. However, the concentration of the pollutant must always be combined with a person's activity pattern to determine the magnitude, frequency, and duration of the exposure. The amount of pollutant that crosses an absorption barrier (e.g. skin, lungs, and gut) is known as the absorbed dose. Following absorption, the chemical is distributed by the circulatory and other systems to various sites in the organism where it will be metabolized to obtain energy and to build cells.

A substance may completely avoid metabolism, become less toxic, or become more toxic as a result of biochemical reactions. When the parent compound or its metabolites interact with a target tissue, this is the dose that leads to the adverse health outcome (e.g. headache, lung damage, liver damage, or cancer).<sup>4</sup>

Populations can be exposed. Individuals can be exposed. The science and statistics needed to estimate and predict exposures varies by the receptor of interest. That is, very different methods are needed to determine the extent to which a population is exposed *versus* one of its subpopulation's exposures *versus* an individual's personal exposure. Thus, exposure science must take into account every step of the life cycle of an air pollutant from its source to its ultimate fate (i.e. a target organ, e.g. liver).

Exposure results from sequential and parallel processes in the environment, from release to environmental partitioning to movement through pathways to uptake and fate in the organism (see Figure 8.2). The substances often change to other chemical species as a result of the body's metabolic and detoxification processes. Thus, the air pollutant emitted from a stack,



**FIGURE 8.2** Processes leading to organismal uptake and fate of chemical and biological agents after release into the environment. In this instance, the predominant sources are air emissions, and the predominant pathway of exposure is inhalation. However, due to deposition in surface waters and the agent's affinity for sediment, the ingestion pathways are also important. Dermal pathways, in this case, do not constitute a large fraction of potential exposure. *McKone T, Maddalena R, Riley W, Rosenbaum R, Vallero D. Significance of partitioning, kinetics, and uptake at biological exchange surfaces. In: International conference on environmental epidemiology & exposure analysis. Paris, France; 2006.*

tailpipe, or other source may very well not be the chemical compound of exposure. The transformation products, i.e. the new substances, can be degradation products from abiotic processes (e.g. hydrolysis, redox, and photolysis) or metabolites that occur in the exposed organisms that are produced as their cells use the parent compounds as food and energy sources. Metabolism may also occur among different organisms, such as when bacteria and other microbes convert air pollutants, e.g. one species may be exposed and in turn metabolizes the parent compound into compounds with different chemical properties.

Humans will then be exposed to these newly formed compounds, which may be more toxic and/or more readily bioaccumulated than the parent compounds. Mercury, for example, is a highly toxic air pollutant, causing neurological and other health effects. However, like other metals the form of Hg determines its toxicity and ability to accumulate in tissue. Mercury is present in trace concentrations in coal, but so much coal is burned that coal-fired power generation contributes at least 60% of all Hg emissions. Since mercury is readily vaporized during combustion, there is a direct correlation of Hg concentrations in flue gas with the precombustion Hg concentrations in coal. A recent study<sup>5</sup> at one power plant in China found that coal Hg content of about  $10 \mu\text{g kg}^{-1}$  correlated with Hg emissions of about  $2 \mu\text{g m}^{-3}$ ,  $150 \mu\text{g kg}^{-1}$  correlated with Hg emissions of about  $10 \mu\text{g m}^{-3}$ ,  $250 \mu\text{g kg}^{-1}$  correlated with Hg emissions of about  $20 \mu\text{g m}^{-3}$ , and,  $400 \mu\text{g kg}^{-1}$  correlated with Hg emissions of about  $27 \mu\text{g m}^{-3}$ . The actual emissions will vary depending on the type of coal (e.g. anthracite releases greater Hg concentrations than does bituminous, when normalized), as well as combustion conditions, such as the amount and types of catalysts and fly ash concentrations. However, these and other studies show a direct correlation between Hg concentrations in fuel and Hg emission rates.

When combusted, Hg in the coal vaporizes and is released as elemental mercury ( $\text{Hg}^0$ ). Even before leaving the stack, however, the Hg again changes forms as it is oxidized in the hot flue gases, which contain acidic compounds (e.g. hydrochloric acid (HCl)) and oxides (e.g. sulfur dioxide ( $\text{SO}_2$ )) that can react heterogeneously on particulate matter (fly ash) thermochemically.<sup>5</sup> This changes some of mercury's valence to  $2^+$ , but some  $\text{Hg}^0$  and Hg aerosols may also be present in varying proportions. When organisms come into contact with the Hg, they will often alkylate the Hg into organic forms (e.g. dimethyl mercury). These organic forms are often much more toxic with greater bioaccumulation potentials. For example, anaerobic or facultative bacteria may reduce the oxidized Hg in methylated forms, which accumulates in the food chain. So, recent concerns about fish and shellfish mercury contamination is likely more

of an air pollution than a water pollution problem, even though the exposure pathway is food and the exposure route is ingestion of the food.

Physical agents, such as electromagnetic radiation, UV light, and noise, do not follow this pathway exactly. Contact with these sources of energy can elicit a physiological response that may generate endogenous chemical changes that behave somewhat like the metabolites discussed earlier. For example, UV light may infiltrate and damage skin cells. UV light helps to promote skin tumor formation by activating the transcription factor complex activator protein-1 (AP-1) and enhancing the expression of the gene that produces the enzyme cyclooxygenase-2 (COX2). Noise, i.e. acoustical energy, can also elicit physiological responses that affect an organism's chemical messaging systems, i.e. endocrine, immune, and neural systems.

The exposure pathway also includes the manner in which humans and other organisms can come into contact with the agent. The pathway has five parts:

1. The source of contamination (e.g. release from stack or vent).
2. An environmental medium and transport mechanism (e.g. pharmaceutical substrate or soil with water moving through it).
3. A point of exposure (such as a well used for drinking water).
4. A route of exposure (e.g. inhalation, dietary ingestion, nondietary ingestion, dermal contact, and nasal).
5. A receptor population (those who are actually exposed or who are where there is a potential for exposure).

If all five parts are present, the exposure pathway is known as a completed exposure pathway. The exposure may be short-term, intermediate, or long-term. Short-term contact, also known as an acute exposure, occurs as a single event or for only a short period of time (up to 14 days). An intermediate exposure is one that lasts from 14 days to less than 1 year. Long-term or chronic exposures are greater than 1 year in duration.

Determining the exposure for a neighborhood can be complicated. For example, even if all the contaminants of concern and its possible source are properly identified, the extent to which the receptor population has come into contact with these contaminants (steps 2 through 4) may be highly uncertain. Thus, assessing exposure involves not only the physical sciences but also the social sciences, e.g. psychology and behavioral sciences. People's activities greatly affect the amount and type of exposures. That is why exposure scientists use a number of techniques to establish activity patterns, such as asking potentially exposed individuals to keep diaries, videotaping, and using telemetry to monitor vital information, e.g. heart and ventilation rates.

General ambient measurements, such as those obtained using air pollution monitoring equipment located throughout cities, are often not good indicators of actual population exposures. For example, metals and their compounds comprise the greatest mass of toxic substances *released* into the US environment. This is largely due to the large volume and surface areas involved in metal extraction and refining operations. However, this does not necessarily mean that more people will be exposed at higher concentrations or more frequently to these compounds than to others. A substance that is released or even that resides in the ambient environment is not tantamount to its coming in contact with a *receptor*. Conversely, even a small amount of a substance under the right circumstances can lead to very high levels of exposure (e.g. handling raw materials and residues).

A study by the Lawrence Berkley National Laboratory demonstrates the importance of not simply assuming that the released or even background concentrations are a good indicator of actual exposure.<sup>6</sup> The researchers were interested in how sorption may affect microenvironments, so they set up a chamber constructed of typical building materials and furnished with actual furniture like that found in most residential settings. A number of air pollutants were released into the room and monitored (see Figure 8.3). With the chamber initially sealed, the observed decay of xylene, a volatile organic compound (VOC), in vapor phase concentrations results from adsorption onto surfaces (walls, furniture, etc.). The adsorption continues for hours, with xylene concentrations reaching a quasi-steady state. At this point the chamber was flushed with clean air to free the vapor phase xylene. The xylene concentrations shortly after the flush began to rise again

until reaching a new steady state. This rise must be the result of desorption of the previously sorbed xylene, since the initial source is gone. Sorption is one of the bio-chemodynamic processes that must be considered to account for differences in the temporal pattern of microenvironmental (e.g. occupational) and ambient concentrations.

The simplest quantitative expression of exposure is:

$$E = Dt^{-1} \quad (8.1)$$

where

$E$  = human exposure during the time period,  $t$  [units of concentration (mass per volume) per time] ( $\text{mg} (\text{kg}\cdot\text{day})^{-1}$ )

$D$  = mass of pollutant per body mass ( $\text{mg kg}^{-1}$ )

$t$  = time (day)

Usually, to obtain  $D$  the chemical concentration of a pollutant is measured near the interface of the person and the environment, during a specified time period. This measurement is sometimes referred to as the potential dose (i.e. the chemical has not yet crossed the boundary into the body, but is present where it may enter the person, such as on the skin, at the mouth, or at the nose).

Expressed quantitatively, exposure is a function of the concentration of the agent and time. It is an expression of the magnitude and duration of the contact. That is, exposure to a contaminant is the concentration of that contact in a medium integrated over the time of contact:

$$E = \int_{t=t_1}^{t=t_2} C(t) dt \quad (8.2)$$

where,

$E$  = exposure during the time period from  $t_1$  to  $t_2$  and  
 $C(t)$  = concentration at the interface between the organism and the environment, at time  $t$ .

Since the amount of a chemical agent that penetrates from the ambient atmosphere into a control volume affects the concentration term of the exposure equation, a complete mass balance of the contaminant must be understood and accounted for; otherwise exposure estimates will be incorrect. The mass balance consists of all inputs and outputs, as well as chemical changes to the contaminant:

Accumulation or loss of contaminant A

$$\begin{aligned} &= \text{Mass of A transported in} \\ &\quad - \text{Mass of A transported out} \pm \text{Reactions} \end{aligned} \quad (8.3)$$

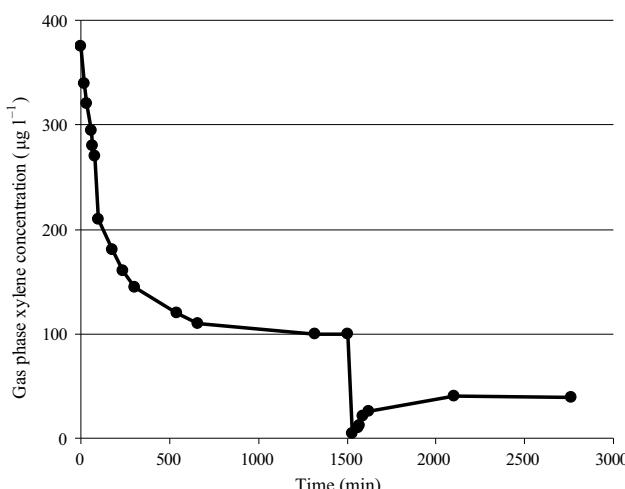


FIGURE 8.3 Concentrations of xylene measured in its vapor phase in a chamber sealed during adsorption and desorption periods. Ref. 6.

Often the reaction term is considered a loss term, i.e. only a negative sign. This assumes that there are no other compounds in the control volume. However, the reactions may be either those that generate substance A (i.e. sources) or those that destroy substance A (i.e. sinks). For example, if contaminant A is a hydrocarbon, it may actually be produced in the control volume by larger organic compounds degrading to this simpler hydrocarbon. Thus, the amount of mass transported in is the inflow to the system that includes pollutant discharges, transfer from other control volumes, and other media (e.g. if the control volume is a cubic meter parcel of air, additional mass of the pollutant may enter the parcel from adjacent parcels of soil; water and biota outdoors; and painted walls, carpet, and adjacent rooms indoors).

The contributed mass of chemical A, therefore, may come from adjacent sources and the formation of chemical A by abiotic chemistry and biological transformation. Conversely, the outflow is the mass transported out of the control volume, which includes uptake, by biota; transfer to other compartments (e.g. volatilization to the atmosphere); and abiotic and biological degradation of chemical A.

Thus, the rate of change of mass in a control volume is equal to the rate of chemical A transported in less the rate of chemical A transported out, plus the rate of production from sources, and minus the rate of elimination by sinks. Stated as a differential equation, the rate of change for contaminant A is:

$$\frac{d[A]}{dt} = -v \cdot \frac{d[A]}{dx} + \frac{d}{dx} \left( \Gamma \cdot \frac{d[A]}{dx} \right) \pm r \quad (8.4)$$

where

$v$  = fluid velocity

$\Gamma$  = a rate constant specific to the environmental medium

$\frac{d[A]}{dx}$  = concentration gradient of chemical A

$r$  = internal sinks and sources within the control volume

The  $r$  term is important for compounds that react within the control volume. As mentioned, term is usually considered to be a loss term, i.e. the mass of the compound exiting the control volume is decreased by the amount of reactivity. This is usually true for the parent compound, although some may be generated in the control volume by the synthesis and degradation of other simpler and larger compounds, respectively. However, it is important to keep in mind that these mass balance equations are only providing information about the parent compound and not the compounds created. Each of these has its own control volume with its own unique mass balance equation, e.g. if

chemical A' is produced during the  $r$  process for chemical A, its mass balance would be:

$$\frac{d[A']}{dt} = -v \cdot \frac{d[A']}{dx} + \frac{d}{dx} \left( \Gamma \cdot \frac{d[A']}{dx} \right) \pm r \quad (8.5)$$

These equations would occur for each compound generated, either from the parent compound A or from its degradation products and their own degradation products as shown in Figure 8.4.

These processes occur in the atmosphere and other environmental media, as well as within an organism. Those that occur within an organism are known as pharmacokinetics. The pharmacokinetic mass balance equations are often accompanied by enzymes, i.e. biological catalysts, and other biochemical and biomechanical processes, such as the distribution of the chemical from one organ to another in the body or clearance from the blood (i.e. half-life,  $t_{1/2}$ ).

Another challenge of the  $r$  term is that reactive compounds can be particularly difficult to measure. For example, many VOCs in the air can be measured by first collecting air in stainless-steel canisters and analyzed by chromatography in the laboratory. However, some of these compounds, like the carbonyls (notably aldehydes like formaldehyde and acetaldehyde) are prone to react inside the canister, meaning that by the time the sample is analyzed a portion of the carbonyls are degraded (under-reported). Therefore, other methods must be used when sampling for reactive vapors, such as trapping the compounds with dinitrophenylhydrazine-treated silica gel tubes that are frozen until being extracted for chromatographic analysis. The purpose of the measurement is to see what is in the air, water, soil, sediment, or biota at the

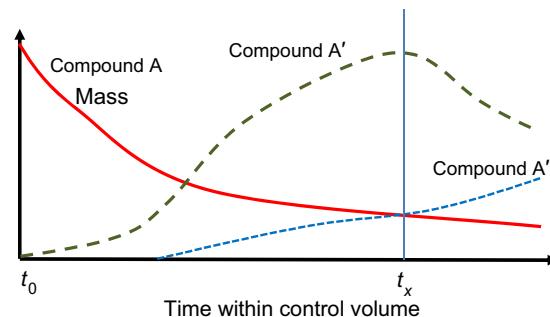


FIGURE 8.4 Hypothetical degradation of parent compound A and its degradation products, A' and A''. As compound A degrades in the control volume, the mass of its degradation product, compound A', increases. However, A' has its own degradation product A''. The mass of A'' increases as it is produced by the degradation of A'. At  $t_x$ , the mass of A has almost reached steady state and the mass of A' begins to decline at the expense of A''. This illustrates that the reaction variable in mass balance equations applies only to each compound at a specific time within the control volume. (For color version of this figure, the reader is referred to the online version of this book.)

**TABLE 8.1** Preservation and Holding Times for Anion Sampling and Analysis

Analyte	Preservation	Holding Time
<b>PART A: COMMON ANIONS</b>		
Bromide	None required	28 days
Chloride	None required	28 days
Fluoride	None required	28 days
Nitrate-N	Cool to 4 °C	48 h
Nitrite-N	Cool to 4 °C	48 h
Ortho-Phosphate-P	Cool to 4 °C	48 h
Sulfate	Cool to 4 °C	28 days
<b>PART B: INORGANIC DISINFECTION BY-PRODUCTS</b>		
Bromate	50 mg l <sup>-1</sup> EDA	28 days
Bromide	None required	28 days
Chlorate	50 mg l <sup>-1</sup> EDA	28 days
Chlorite	50 mg l <sup>-1</sup> EDA, cool to 4 °C	14 days

Source: U.S. Environmental Protection Agency. EPA method 300.1: determination of inorganic anions in drinking water by ion chromatography, Revision 1.0; 1997. EDA = ethylenediamine

time of sampling, so any reaction before the analysis gives measurement error.

Remember that the chemical that is released may or may not be the one that ultimately needs to be measured. If the released chemical is reactive, some or all of it may have changed into another form (i.e. speciated) by the time it is measured. Even relatively nonreactive compounds may speciate between when the sample is collected (e.g. in a water sample, an air canister, a soil core, or a bag) and when the sample is analyzed. In fact, each contaminant has unique characteristics which vary according to the type of media in which it exists, and extrinsic conditions like temperature and pressure. Sample preservation and holding times for the anions according to Environment Protection Agency Method 300.1, Determination of Inorganic Anions in Drinking Water by Ion Chromatography, are shown in Table 8.1. These methods vary according to the contaminant of concern and the environmental medium from which it is collected.

## 8.2 EXPOSURE CALCULATIONS

Exposure can be calculated by multiplying the concentration of the agent (e.g. air pollutant) by the

duration of the contact. Exposure occurs immediately when the agent contacts the receptor at a single point in time and space.<sup>7</sup>

Note in Eqn 8.2 that dividing the time-integrated exposure by the exposure duration, results in the time-averaged exposure. For example, if the time-integrated exposure for benzene in a workshop is  $E = 100 \mu\text{g m}^{-3}$  for a person who has been exposed 2 per day for 100 days ( $t_2 - t_1 = (2/24) \times 100 = 8.33$  days), the time-averaged exposure is  $100 \mu\text{g m}^{-3} \times 8.33 \text{ day} = 833 \mu\text{g benzene (m}^3\text{-day)}^{-1}$  or  $833 \mu\text{g m}^{-3} \text{ day}^{-1}$  benzene exposure.

The target may be the receptor (e.g. the amount of the contaminant applied or absorbed by a person). The target may also be an organ or other tissue in the receptor (e.g. the amount of the contaminant that reaches the bloodstream). It may be indicated by a biomarker, such as the concentration of benzene in urine. For example, if benzene is found in urine, this is the amount that has been eliminated following intake, absorption, distribution, and metabolism. The biomarker is not the exposure, but is merely an indicator of exposure.

A hypothetical, oversimplified example would be that if the only exposure route in the above benzene example were by inhalation, the losses to absorption, distribution, metabolism, and elimination (ADME) must be considered. Assuming that 50% of the benzene is absorbed, 10% of the benzene is sequestered in bone and other organs during distribution, and 10% is metabolized, the percentage that is eliminated is 70%. Assuming that half of the 30% that is excreted is in the urine, the biomarker would only receive 15% of the exposure amount. In our example, the time-averaged benzene exposure of  $833 \mu\text{g m}^{-3} \text{ d}^{-1}$  would appear as  $833 \times 0.15 = 125 \mu\text{g m}^{-3} \text{ d}^{-1}$  benzene in the urine. That is, the ADME urine normalizing factor for benzene in this case would be 6.7 (i.e. urine biomarker measurements would have to be multiplied by 6.7 to address the losses to ADME).

Dose can be an intake dose or an absorbed dose.<sup>8</sup> Dose equations can be derived by applying a general integral equation for exposure and defining boundary assumptions.<sup>4</sup> One such dose metric is the average daily dose (ADD) which is often used for noncancer effects, averages exposures, and doses during exposure duration periods. The ADD is ascertained by averaging an intake dose according to body weight and an averaging time:

$$\text{ADD} = \frac{I}{W \times t_{\text{averaging}}} \quad (8.6)$$

where  $I$  is the intake dose,  $W$  is the body weight (kilograms), and  $t_{\text{averaging}}$  is the averaging time (days). For

inhalation,  $I$  equals the concentration of the air pollutant times the inhalation rate (IR) times the exposure duration. Thus, if the concentration of the pollutant is  $10 \mu\text{g m}^{-3}$ , the IR is  $20 \text{ m}^{-3} \text{ day}^{-1}$ , and the exposure duration is 500 days, the intake dose is  $10 \times 20 \times 500 = 10^5 \mu\text{g m}^{-3}$ .

Note that the concentration is the mass of the agent in the medium (air, food, soil, etc.) per unit volume contacting the body and has units of mass/volume or mass/mass. For air pollutants, this is generally mass per volume (e.g.  $\mu\text{g m}^{-3}$ ).

The intake rate is expressed differently for the various routes, i.e. it can be the rate of inhalation, ingestion, and dermal contact.

It is important to keep in mind that inhalation is the dominant exposure route for air pollutants (the intake rate is that at which contaminated air is inhaled), but is not the only route. For example, after particulate matter settles on food, ingestion becomes a very important route of exposure (see Figure 8.5). For ingestion, the intake rate is simply the amount of contaminated food ingested by a person during some specific time period (units of mass/time). This is true for both dietary and nondietary ingestion, since the concentration in the food includes the total amount of the contaminant. For example, if the concentration of pesticide A in lettuce at the time it is brought home from the grocery store is  $10 \text{ ng kg}^{-1}$  but in a house that recently sprayed the same pesticide, the indoors have a concentration of  $50 \text{ ng kg}^{-1}$  when it is eaten, the additional  $40 \text{ ng kg}^{-1}$  would be part of the total  $50 \text{ ng kg}^{-1}$  in the intake dose calculation. Similarly, people can also be exposed dermally to air pollutants that deposit onto surfaces (including factors such as skin surface area and estimates of

the amount of solids that adhere to the skin, film thickness of liquids that adhere to the skin, transfer of residues, and skin thickness and chemical-specific absorption factors (AFs)).

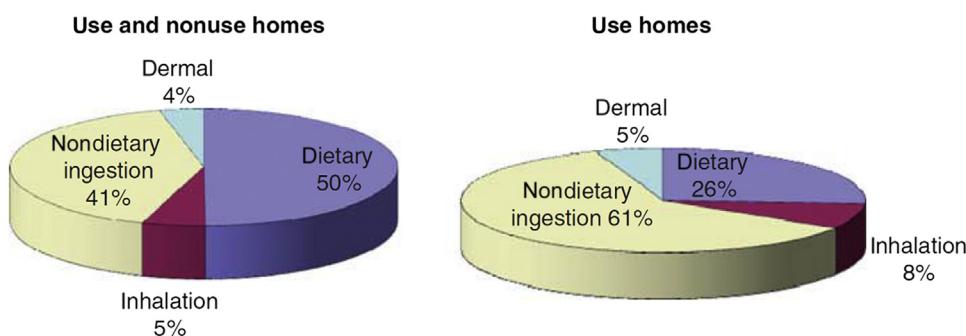
The exposure duration is the length of time of contact with an agent, which is more complicated than in the examples above. A thorough exposure duration value includes many time-related activity factors, such as the length of time a person lives in an area, frequency of bathing, time spent indoors *versus* outdoors, and time spent in various microenvironments.

When the above parameter values IR and ED remain constant over time, they can be substituted directly into the dose equation. When they change with time, calculations of dose must apply a summation approach. In both situations, however, the exposure duration is the length of time exposure occurs at the concentration and the intake rate specified by the other variables in the equations above.

Age groupings call for separate ADDs to be calculated for each age group that is exposed. Rather than a single average population value and/or a lifetime average value, this allows for chronic exposures to be calculated by summing across each life stage-specific ADD.

As mentioned in Chapter 7, cancer risks have traditionally been calculated using a linear nonthreshold model. This assumes in terms of lifetime probabilities by utilizing dose values presented in terms of lifetime average daily doses (LADDs).<sup>8</sup>

Exposure can be expressed for an individual, for certain groups (e.g. neighborhoods or children living in a county), or for entire populations. For example, one may want to calculate the exposure to a hazardous air pollutant for a geographic area, which includes the



**FIGURE 8.5 Differences in exposure route in homes where a pesticide has been recently applied *versus* other homes.** Exposure pathway contributions to annual average daily permethrin dose for 3- to 5-year-old children (simulated, i.e. including those residing in permethrin use and nonuse households) in the US population; based on means, the major contributing exposure route in use and nonuse homes was found to be nondietary ingestion at 41%, but this increased to 61% in use homes. Inhalation also increased from 5 to 8% in use homes. Nondietary ingestion includes household dust. (For color version of this figure, the reader is referred to the online version of this book.) Zartarian V, Xue J, Glen G, Smith L, Tulve N, Tornero-Velez R. Quantifying children's aggregate (dietary and residential) exposure and dose to permethrin: application and evaluation of EPA's probabilistic SHEDS-Multimedia model. *J Exp Sci Environ Epidemiol* 2012;22:267–73.

various microenvironments and age groups. This can be calculated as an inhalation exposure ( $E_j$ ):

$$E_j = \sum_{i=1}^n C_i \times IR_{ij} \times t_{ij} \quad (8.7)$$

where,  $E_j$  = daily exposure for the  $j$ th group ( $\text{mg day}^{-1}$ );  $n$  = settings (e.g. different microenvironmental and outdoor locations);  $i = 1, 2, 3, \dots n$  is the type of each different setting (e.g.  $i = 1$  is indoors,  $i = 2$  is driving in traffic,  $i = 3$  is outdoors, etc.);  $j = 1, 2, 3$ , referring to different age groups (e.g.  $j = 1$  is adults,  $j = 2$  is children, and  $j = 3$  is infants);  $C_i$  = air pollutant concentration in the  $i$ th setting ( $\text{mg m}^{-3}$ );  $IR_{ij}$  = inhalation rate in the  $i$ th setting of the  $j$ th group ( $\text{m}^3 \text{h}^{-1}$ ); and  $t_{ij}$  = daily exposure time span in the  $i$ th environment of the  $j$ th group ( $\text{h day}^{-1}$ ).

Consider a census tract located downwind from a wood processing facility  $E_j$  in which the concentrations of formaldehyde have been measured in three settings, i.e. indoors, outdoors near home, and while driving in traffic, as well as one that is called "other outdoors" which is assumed to make up the remainder of all the other settings (Table 8.2). The daily exposure can be calculated using Eqn (8.7).

Thus, a child's mean daily exposures by setting are:

- Indoors:  $0.5 \times 0.4 \times 18 = 3.6 \text{ mg day}^{-1}$
- Outdoors near home:  $0.4 \times 0.5 \times 4 = 0.8 \text{ mg day}^{-1}$
- In car:  $0.2 \times 0.4 \times 1 = 0.08 \text{ mg day}^{-1}$
- Other outdoors:  $0.7 \times 0.5 \times 1 = 0.35 \text{ mg day}^{-1}$

TABLE 8.2 Information Needed to Calculate Formaldehyde Daily Exposures in Four Hypothetical Settings

Setting	Indoors	Outdoors Near Home	In Car While Driving	Other Outdoors
Formaldehyde concentration ( $\text{mg m}^{-3}$ )	0.5	0.4	0.2	0.7
Child mean inhalation rate (IR) ( $\text{m}^3 \text{h}^{-1}$ )	0.4	0.5	0.4	0.5
Adult mean IR ( $\text{m}^3 \text{h}^{-1}$ )	0.6	0.7	0.5	0.8
Time spent in setting by child ( $\text{h day}^{-1}$ )	18	4	1	1
Time spent in setting by adult ( $\text{h day}^{-1}$ )	16	4	1	3

Thus, the mean daily exposure of children in the census tract, based on the measurements would be the sum of these microenvironmental exposures:

$$3.6 + 0.8 + 0.08 + 0.35 = 4.83 \text{ mg day}^{-1}$$

The calculated adult mean daily exposure is:

- Indoors:  $0.5 \times 0.6 \times 16 = 4.8 \text{ mg day}^{-1}$
- Outdoors near home:  $0.4 \times 0.7 \times 4 = 1.12 \text{ mg day}^{-1}$
- In car:  $0.2 \times 0.5 \times 1 = 0.1 \text{ mg day}^{-1}$
- Other outdoors:  $0.7 \times 0.8 \times 3 = 1.68 \text{ mg day}^{-1}$

Thus, the mean daily exposure of children in the census tract, based on the measurements would be the sum of these microenvironmental exposures:

$$4.8 + 1.12 + 0.1 + 1.68 = 7.7 \text{ mg day}^{-1}$$

The adult exposures appear to be higher than those of children. These daily estimates are expressed as mass per time, but exposure is usually normalized by body weight. The normal exposure units are  $\text{mg kg}^{-1} \text{ day}^{-1}$ . Thus, assuming the mean body weight of children in this census tract is 20 kg and that of adults is 80 kg, the exposures would be:

$$\begin{aligned} \text{Children: } & 4.83 \text{ mg day}^{-1} / 20 \text{ kg} = 0.24 \text{ mg kg}^{-1} \text{ day}^{-1} \\ \text{Adults: } & 7.7 \text{ mg day}^{-1} / 80 \text{ kg} = 0.10 \text{ mg kg}^{-1} \text{ day}^{-1} \end{aligned}$$

Thus, children's body-weight normalized exposure is more than twice as high as that of adults in this community.

Note that these hypothetical examples are based on very limited data and imprecise designations of settings and activities. For example, the IRs would need to represent more specific age groups, such as those in Table 8.3. This is because respiration rates are much lower for very young children. Also, infants and very young children are much more vulnerable to pollution and their exposures need to be known to determine risks to this vulnerable subpopulation.

Body weight is another very important exposure factor. For a given amount of contaminant intake, the lower the body weight, the larger the dose will be. The example of normalizing for body weight for children and adults was much too broad. As was true for IRs, body weight by age estimates are also available (see Table 8.4).

Decision makers can use the types of exposure estimates in these examples to evaluate the potential effects of locating a facility that would be a source of a pollutant. For example, the exposure estimates for children in this hypothetical scenario appear high. However, most of the exposure is indoors at home. This can mean either that substantial amounts of formaldehyde are penetrating the home from outdoors or that there are large indoor sources. In this case, the "outdoor

TABLE 8.3 Inhalation Rates by Age

Age	Mean Rate (m <sup>3</sup> day <sup>-1</sup> )	95th Percentile Rate (m <sup>3</sup> day <sup>-1</sup> )
Birth–1 month	3.6	7.1
1–<3 months	3.5	5.8
3–<6 months	4.1	6.1
6–<12 months	5.4	8.0
1–<2 years	5.4	9.2
Birth–<1 year	8.0	12.8
2–<3 years	8.9	13.7
3–<6 years	10.1	13.8
6–<11 years	12.0	16.6
11–<16 years	15.2	21.9
16–<21 years	16.3	24.6
21–<31 years	15.7	21.3
31–<41 years	16.0	21.4
41–<51 years	16.0	21.2
51–<61 years	15.7	21.3
61–<71 years	14.2	18.1
71–<81 years	12.9	16.6
≥81 years	12.2	15.7

Source: Ref. 4.

other” category has the highest concentrations of the four settings, so penetration appears plausible. However, formaldehyde has numerous indoor sources (e.g. furniture and processed wood panels), so more investigation is likely needed.

TABLE 8.4 Body Weight by Age

Age	Mean Body Weight (kg)
Birth–1 month	4.8
1–<3 months	5.9
3–<6 months	7.4
6–<12 months	9.2
1–<2 years	11.4
2–<3 years	13.8
3–<6 years	18.6
6–<11 years	31.8
11–<16 years	56.8
16–<21 years	71.6
Adult	80

Source: Ref. 4.

### 8.3 CHEMICAL INTAKE AND EXPOSURE

Exposure occurs via the inhalation route when a person inhales a substance. The substance may directly affect the respiratory tract. This is known as point-of-entry effect. The substance may also enter the bloodstream after being transferred from the air to the lungs so that it can harm other systems of the body. This is known as target organ effect. Generally, inhalation exposure is assumed to equal “dose” for gases, aerosols, and respirable particulate matter (<2.5 µm). Larger particles are less likely to reach the alveoli, i.e. the lowest parts of the lung. These can be removed by upward movement of cilia in the lungs and swallowed. Thus, estimating dose from inhaled air pollutant estimates is complicated.<sup>9</sup>

Inhalation exposure for a given exposure event is equal to the average chemical concentration in the air at the person’s breathing zone multiplied by the IR<sup>10</sup>:

$$E_{\text{inh}} = C_a \cdot k_{\text{inh}} \quad (8.8)$$

where,  $E_{\text{inh}}$  is the inhalation exposure (mass per time),  $C_a$  is the airborne concentration of the air pollutant contacted (mass of pollutant per volume of air in the breathing zone), and  $k_{\text{inh}}$  is the IR (volume of air per unit time).

Thus, a person engaged in physical work breathing at a rate of 20 m<sup>3</sup> day<sup>-1</sup> in air that contains 5 mg carbon monoxide per cubic meter would have an inhalation exposure of 100 mg day<sup>-1</sup>.

Irrespective of the type of risk assessment, the general exposure Eqn (8.2) must be rewritten to address each route of exposure, accounting for chemical concentration and the activities that affect the time of contact. In numerous regulatory and cleanup situations, the exposure calculated from these equations is actually the chemical intake ( $I$ ) in units of concentration (mass per volume or mass per mass) per time, which is mg kg<sup>-1</sup> day<sup>-1</sup>:

$$I = \frac{C \cdot CR \cdot EF \cdot ED \cdot AF}{BW \cdot AT} \quad (8.9)$$

where

$C$  = chemical concentration of contaminant (mass per volume)

$CR$  = contact rate (mass per time)

$EF$  = exposure frequency (number of events, dimensionless)

$ED$  = exposure duration (time)

These factors are further specified for each route of exposure and for different durations of exposure, such as the LADD, which is a maximum, chronic, long-term exposure for an individual (see Table 8.5). The first two equations in the table, i.e. inhaling aerosols and inhaling vapors, are the ones most often associated with air pollutants. However, as evidenced by the Hg

TABLE 8.5 Equations for Calculating Lifetime Average Daily Dose (LADD) for Various Routes of Exposure

Route of Exposure	LADD (in $\text{mg kg}^{-1} \text{ day}^{-1}$ )	Definitions
Inhaling aerosols (particulate matter)	$\frac{(C) \cdot (PC) \cdot (IR) \cdot (RF) \cdot (EL) \cdot (AF) \cdot (ED) \cdot (10^{-6})}{(BW) \cdot (TL)}$	$C$ = concentration of the contaminant on the aerosol/particle ( $\text{mg kg}^{-1}$ ) $PC$ = particle concentration in air ( $\text{g m}^{-3}$ ) $IR$ = inhalation rate ( $\text{m}^{-3} \text{ h}^{-1}$ ) $RF$ = respirable fraction of total particulates (dimensionless, usually determined by aerodynamic diameters, e.g. $2.5 \mu\text{m}$ ) $EL$ = exposure length ( $\text{h day}^{-1}$ ) $ED$ = duration of exposure (day) $AF$ = absorption factor (dimensionless) $BW$ = body weight (kg) $TL$ = typical lifetime (day). $10^{-6}$ is a conversion factor (kg to mg)
Inhaling vapor phase contaminants	$\frac{(C) \cdot (IR) \cdot (EL) \cdot (AF) \cdot (ED)}{(BW) \cdot (TL)}$	$C$ = concentration of the contaminant in the gas phase ( $\text{mg m}^{-3}$ ) Other variables the same as above
Drinking water	$\frac{(C) \cdot (CR) \cdot (ED) \cdot (AF)}{(BW) \cdot (TL)}$	$C$ = concentration of the contaminant in the drinking water ( $\text{mg l}^{-1}$ ) $CR$ = rate of water consumption ( $\text{l day}^{-1}$ ) $ED$ = duration of exposure (day) $AF$ = portion (fraction) of the ingested contaminant that is physiologically absorbed (dimensionless) Other variables are the same as above
Contact with soil-borne contaminants	$\frac{(C) \cdot (SA) \cdot (BF) \cdot (FC) \cdot (SDF) \cdot (ED) \cdot (10^{-6})}{(BW) \cdot (TL)}$	$C$ = concentration of the contaminant in the soil ( $\text{mg kg}^{-1}$ ) $SA$ = skin surface area exposed ( $\text{cm}^{-2}$ ) $BF$ = bioavailability (percent of contaminant absorbed per day) $FC$ = fraction of total soil from contaminated source (dimensionless) $SDF$ = soil deposition, the mass of soil deposited per unit area of skin surface ( $\text{mg cm}^{-2} \text{ day}^{-1}$ ) Other variables are the same as above

Source: Derelanko M. Risk assessment. In: Derelanko MJ, Hollinger MA, editors. CRC handbook of toxicology. Boca Raton (FL): CRC Press; 1999.

exposure discussion above, other exposure routes and pathways must be applied for air pollutants. Indeed, exposure to many persistent, bioaccumulating air pollutants comes through routes other than inhalation (e.g. ingestion and dermal).

Acute and subchronic exposures require different equations, since the ED is much shorter. For

example, instead of LADD, acute exposures to non-carcinogens may use maximum daily dose to calculate exposure. Nevertheless, even these exposures follow the general model given in Eqn (8.8). The discussion box, Exposure Calculation Example, provides a hypothetical example of an exposure to a toxic air pollutant.

### EXPOSURE CALCULATION EXAMPLE

In the process of synthesizing pesticides over an 18-year period, a polymer manufacturer has contaminated the soil on its property with vinyl chloride. The plant closed 2 years ago but vinyl chloride vapors continue to reach the neighborhood surrounding the plant at an average concentration of  $1 \text{ mg m}^{-3}$ . Assume that people are breathing at a ventilation rate of  $0.5 \text{ m}^3 \text{ h}^{-1}$  (about the average of adult males and females are older than 18 years<sup>11</sup>). The legal settlement allows neighboring residents to evacuate and sell their homes to the company. However, they may also stay. The neighbors have asked for advice on whether to stay or leave, since they have already been exposed for 20 years.

Vinyl chloride is highly volatile, so its phase distribution will be mainly in the gas phase rather than in the aerosol phase. Although some of the vinyl chloride may be sorbed to particles, use only vapor phase LADD equation, since the particle phase is likely to be relatively small. Also, assume that outdoor concentrations are the exposure concentrations. This is unlikely, however, since people spend commonly spend less time outdoors compared to indoors, so this may provide an additional factor of safety. To determine how much vinyl chloride penetrates living quarters, indoor air studies would have to be conducted. Likewise, to compare exposures, indoor air measurements should be taken.

(Continued)

### EXPOSURE CALCULATION EXAMPLE (cont'd)

Find the appropriate equation in [Table 8.5](#) and insert values for each variable. Absorption rates are published by the US EPA and the Oak Ridge National Laboratory's Risk Assessment Information System ([http://risk.lsd.ornl.gov/cgi-bin/tox/TOX\\_select?select=nrad](http://risk.lsd.ornl.gov/cgi-bin/tox/TOX_select?select=nrad)). Vinyl chloride is well absorbed, so for this exercise assume that AF = 1. Also assume that the person staying in the neighborhood is exposed at the average concentration 24 h day<sup>-1</sup> (EL = 24), and that a person lives the remainder of the entire typical lifetime exposed at the measured concentration.

Although the ambient concentrations of vinyl chloride may have been higher when the plant was operating, the only measurements we have are those taken recently. Thus, this is an area of uncertainty that must be discussed with the clients. The common default value for a lifetime is 70 years, so assume the longest exposure would be 70 years (25,550 days). [Table 8.6](#) gives some of the commonly used default values in exposure assessments.

The exposure of a person now 20 years of age who already been exposed for that time, and lives the remaining 50 years exposed at 1 mg m<sup>-3</sup> is:

$$\begin{aligned} \text{LADD} &= \frac{(C) \cdot (\text{IR}) \cdot (\text{EL}) \cdot (\text{AF}) \cdot (\text{ED})}{(\text{BW}) \cdot (\text{TL})} \\ &= \frac{(1) \cdot (0.5) \cdot (24) \cdot (1) \cdot (25,550)}{(70) \cdot (25,550)} \\ &= 0.2 \text{ mg kg}^{-1} \text{ day}^{-1} \end{aligned}$$

If the 20-year-old leaves today, the exposure duration would be for the 20 years that the person lived in the neighborhood. Thus, only the ED term would change, i.e. from 25,550 to 7300 days (i.e. 20 years).

Thus, the LADD falls to 2/7 of its value:

$$\text{LADD} = 0.5 \text{ mg kg}^{-1} \text{ day}^{-1}$$

**TABLE 8.6** Commonly Used Human Exposure Factors

Exposure Factor	Adult Male	Adult Female	Child (3–12 years old) <sup>12</sup>
Body weight (kg)	70	60	15–40
Total fluids ingested (l day <sup>-1</sup> )	2	1.4	1.0
Surface area of skin, without clothing (m <sup>2</sup> )	1.8	1.6	0.9
Surface area of skin, wearing clothes (m <sup>2</sup> )	0.1–0.3	0.1–0.3	0.05–0.15
Respiration/ventilation rate (l min <sup>-1</sup> ): resting	7.5	6.0	5.0
Respiration/ventilation rate (l min <sup>-1</sup> ): light activity	20	19	13
Volume of air breathed (m <sup>3</sup> day <sup>-1</sup> )	23	21	15
Typical lifetime (years)	70	70	NA
National upper-bound time (90th percentile) at one residence (years)	30	30	NA
National median time (50th percentile) at one residence (years)	9	9	NA

Source: U.S. Environmental Protection Agency. Exposure factor handbook; 2003 and Agency for Toxic Substances and Disease Registry. ATSDR public health assessment guidance manual; 2003<sup>13</sup>.

Recall that even though the predominant pathway is air and that inhalation is the major exposure route, other exposure pathways and routes contribute to total exposure to a pollutant, especially as exposure duration increases. For a persistent pollutant, which may build up in fats or other tissue, the aggregate exposure must be considered, i.e. every route and

pathway by which a person is exposed to the same chemical agent.

Body burden is an important exposure consideration, especially for toxic chemicals that are sufficiently persistent and that can bioaccumulate (see Chapter 19). These compounds include metals, e.g. lead (Pb), mercury (Hg), and cadmium (Cd); metalloids,

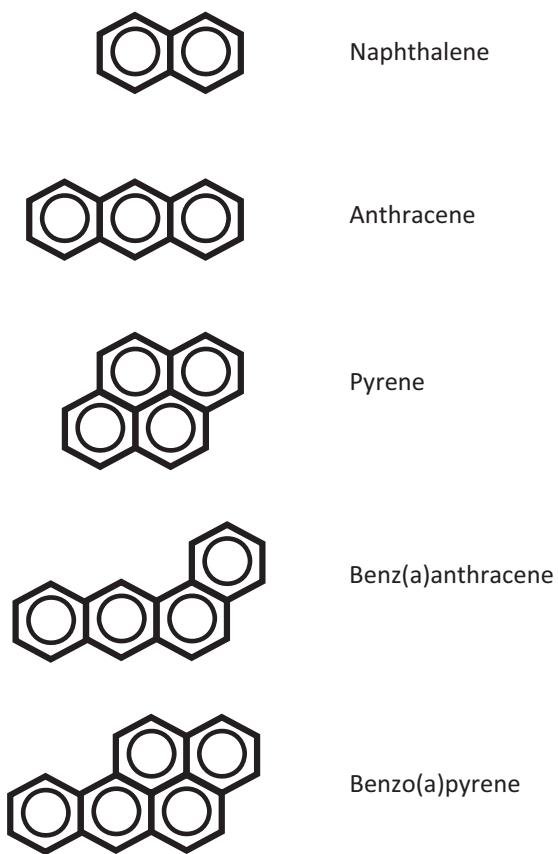


FIGURE 8.6 Structures of select polycyclic aromatic hydrocarbons.

e.g. arsenic (As); and organic compounds. Two important classes of persistent, bioaccumulating organic compounds are the products of incomplete combustion and compounds with halogen substitutions. Polycyclic aromatic hydrocarbons (PAHs) (see Figure 8.6) are some of the most toxic and bioaccumulating organic products of incomplete combustion. Persistent and bioaccumulating halogenated aromatic compounds include PCBs, polybrominated biphenyls, and the organochlorine pesticides, such as dichlorodiphenyltrichloroethane (DDT).

Consider a 100-kg person who is exposed to DDT over 20 years, predominantly as an air pollutant as a result of years of occupational exposure, but who is also exposed by ingesting food and dermal exposure from applying the compound as an insecticide against mosquitos.<sup>a</sup> If the exposure is  $325 \text{ ng } 100 \text{ kg}^{-1} \text{ year}^{-1}$  from inhaling air,  $25 \text{ ng } 100 \text{ kg}^{-1} \text{ year}^{-1}$  from ingesting food, and  $50 \text{ ng } 100 \text{ kg}^{-1} \text{ year}^{-1}$  from contact through

skin, the person's total accumulation for the 20 year period would be:  $(325 + 25 + 50) \text{ ng} \times 20 = 700 \text{ ng}$ .

This person's body would have built up  $7 \mu\text{g}$  of DDT over this 20-year span. However, to know the actual DDT dose during that period, the toxicokinetics need to be considered (see Figure 8.7). The AF in Eqn (8.9) indicates this. In fact, toxicokinetics includes not only the absorption rate but also the distribution, metabolism and elimination rates. From 70% to 80% of ingested DDT is absorbed from the gastrointestinal tract.<sup>14</sup> The extent of inhalation absorption seems to depend on the particulate characteristics of the DDT aerosol. Often, the aerosol is coarse, which means that inhalation is not as important compared to ingestion and dermal routes. However, if the particulates are fine, they can penetrate deeply and become absorbed. The particles may be cleared by the mucociliary mechanisms, with much of this subsequently ingested. DDT is stored in adipose tissue.

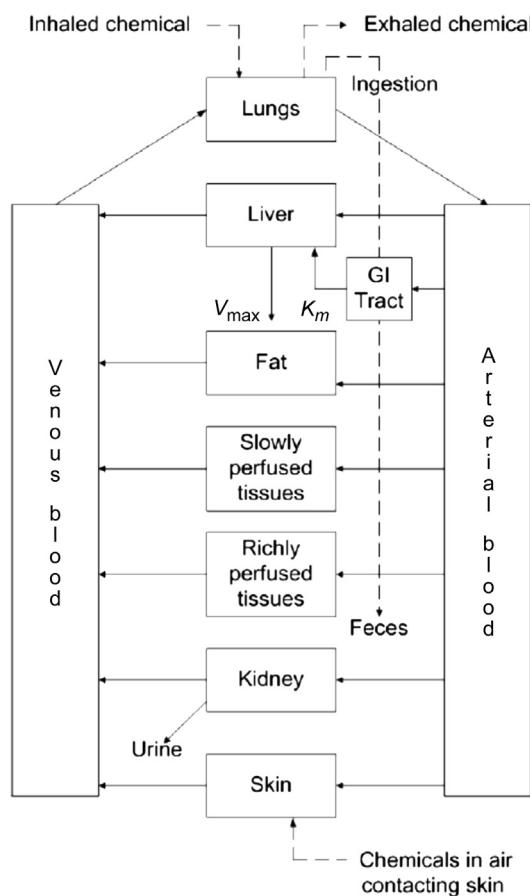
The actual body burden, however, is determined by the amount of a substance that is absorbed and the amount that is cleared. Assuming that on an average 80% of the DDT is absorbed after exposure and that 90% of this amount is cleared from the person's body each year, the net amount is the product of the accumulated amount, the absorption rate, and the remaining amount after clearance (i.e.  $1 - \text{clearance rate}$ ):  $7 \mu\text{g} \times 0.8 \times (1 - 0.9) = 0.56 \mu\text{g}$ .

Thus, the person has  $0.56 \mu\text{g}$  per  $100 \text{ kg}$  of DDT body burden after 20 years of exposure.

Of course, this calculated body burden would increase if the absorption rate increased. The body burden would decrease if the clearance rate increased. The high  $K_{\text{ow}}$  of DDT ( $\log K_{\text{ow}} = 6.9$ ; see Chapter 18) and its metabolites would suggest a strong potential for accumulation in lipid-rich tissues. Thus, the clearance rate could be decreased in proportion to the amount of a compound that is stored in lipids, i.e. lipophilic compounds generally have much longer half-lives than hydrophilic compounds in mammals.

A nonpersistent, nonbioaccumulating compound would have a 100% clearance rate, i.e. none of the compound is stored. However, this does not necessarily mean that the person has no risk. Indeed, many nonpersistent compounds are highly acutely toxic, so the long-term exposure to a toxic compound could be causing incremental harm. Secondly, even if the body burden of the parent compound is zero, its metabolites may accumulate and must be considered in exposure calculations. The person exposed to DDT would have

<sup>a</sup> Although the use of DDT has been banned in the United States, Canada, and much of Europe, it continues to be used in countries, especially in tropical and subtropical countries where mosquitoes are the principal vector for malaria. Reliable insecticides have been difficult to find as substitutes for DDT.



**FIGURE 8.7** Toxicokinetics for a hypothetical chemical substance. GI, gastrointestinal. Agency for Toxic Substances and Disease Registry. Toxicological profile for DDT, DDE, and DDD. U.S. Department of Health and Human Services. Public Health Service; 2002.

a body burden of not only the parent DDT but also its metabolites, dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) which are

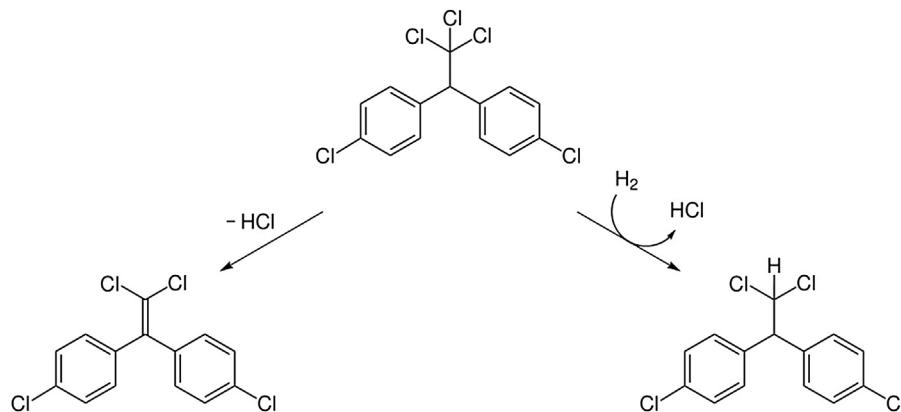
also persistent and bioaccumulate. In fact, the metabolite body burden may be much higher than that of the parent compound (see Figure 8.8). Incidentally, these metabolites have their own toxicities, e.g. DDE is highly disruptive to the endocrine system (i.e. antiandrogenic), that may differ from the parent. Indeed, the metabolites can be more toxic and otherwise problematic than the parent compound to which a person is exposed.

As mentioned, another important group of persistent, bioaccumulating compounds are the PAHs. In fact, these may be more illustrative of an inhalation exposure than the organochlorine pesticides, since the major pathway for PAHs is the air and the major route of exposure is inhalation. Like the organochlorine compounds, PAHs are highly soluble in lipids and are absorbed from the lung, gut, and skin of mammals and seem to be readily cleared from the lungs (e.g. rat studies show clearance in days).

The PAH clearance process involves two phases, i.e. a biphasic process involving the vapor and particulate phases. PAHs are predominantly adsorbed onto particles. After these are deposited in the airways, they can be eliminated by bronchial clearance. PAHs may then be partly desorbed from the particles during transport on the ciliated mucosa. From there, the PAHs may penetrate into the bronchial epithelium cells, whereupon metabolism begins.<sup>15</sup>

The chemical class of PAHs consists of compounds with two or more aromatic rings which are fused together when a pair of carbon atoms is shared between them (see Chapter 6). The difference between PAHs and other aromatic compounds is that the aromatic rings of PAHs are fused (Figure 8.9), whereas most other aromatic compounds are linked by bonds (compare Figures 8.8 and 8.9). These fused rings increase environmental persistence, as indicated by their

**FIGURE 8.8** Top: two degradation pathways for DDT. Right: reductive dechlorination to form dichlorodiphenyldichloroethane. Left: elimination of HCl (H<sub>2</sub> addition) to form dichlorodiphenyldichloroethylene.

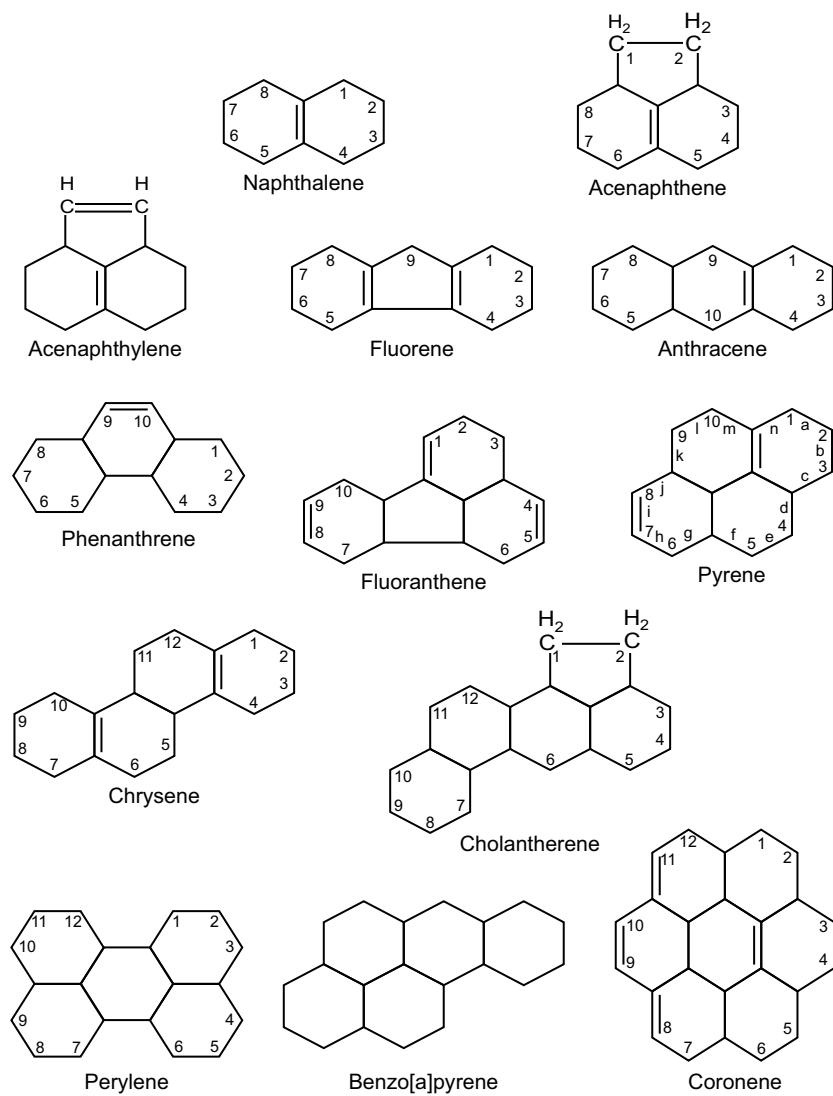


very low vapor pressures and aqueous solubilities (see Table 8.7).

The major PAH of concern to air pollution is arguably benzo[a]pyrene (BaP), which is also the PAH most studied and, thus, is associated with the highest quality data for exposure and toxicity. When BaP is adsorbed on particles, the respiratory uptake rate is subdued because the particles are retained for an extended period of time in the respiratory tract.<sup>16</sup> The initial clearance is rapid, with about half of the BaP mass removed in less than 1 h. However, the second, long-term clearance can be slow (e.g. animal studies have indicated 18 days to clear half of the BaP mass).<sup>17</sup> Once the BaP and other PAHs reach the

gastrointestinal tract they are readily absorbed. The absorption is facilitated by liver excretions.<sup>18a,18b</sup>

As is true for DDT and other halogenated organic compounds, dermal exposure must always be considered to be an important route for PAHs, since absorption through human skin has also been demonstrated.<sup>19</sup> Also, like DDT and other persistent organic compounds, the PAH metabolites have their own physicochemical properties and toxicities. Indeed, BaP metabolites are thought to be the main triggers for cancer. That is, the parent compound is less carcinogenic than the compound formed from mammalian metabolism. It becomes even more toxic by a process known as biological activation (see Figure 19.20).



**FIGURE 8.9** Structures of select polycyclic aromatic hydrocarbons known to be air pollutants. Note the fused aromatic rings. Province of British Columbia. Ambient water quality criteria for polycyclic aromatic hydrocarbons (PAHs). Ministry of Environment, Lands and Parks; 1993. <http://www.env.gov.bc.ca/wat/wq/BCguidelines/pahs/> [accessed 13.10.13].

TABLE 8.7 Physical and Chemical Properties of Polycyclic Aromatic Hydrocarbons

Compound	Molecular Weight (g)	Solubility at 25 °C ( $\mu\text{g l}^{-1}$ )	Vapor Pressure at 25 °C (mm Hg)	$\log K_{ow}$ ( $\log K_{oc}$ )
Naphthalene	128.2	$1.25 \times 10^5$ – $3.40 \times 10^5$	$1.8 \times 10^{-2}$	3.37
Acenaphthylene	152.2	$3.42 \times 10^4$	$10^{-3}$ – $10^{-4}$	4.07 (3.40)
Acenaphthene	154.2			3.98 (3.66)
Fluorene	166.2	800		4.18 (3.86)
Anthracene	178.2	59	$2.4 \times 10^{-4}$	4.5 (4.15)
Phenanthrene	178.2	435	$6.8 \times 10^{-4}$	4.46 (4.15)
Acridine	179.2			(4.48)
2-Methylanthracene	192.3	21.3		4.77
9-Methylphenanthrene	192.3	261		4.77
1-Methylphenanthrene	192.3	269		4.77
Fluoranthene	202.3	260		4.90 (4.58)
9,10-Dimethylanthracene	206.3	56		5.13
Benzo[a]fluorene	216.3	45		5.34
Benzo[b]fluorene	216.3	29.6		5.34
Pyrene	202.1	133	$6.9 \times 10^{-7}$	4.88 (4.58)
Benz[a]anthracene	228.3	11.0	$1.1 \times 10^{-7}$	5.63 (5.30)
Naphthacene	228.3	1.0		5.65
Chrysene	228.3	1.9		5.63 (5.30)
Triphenylene	228.3	43		5.63
Benzo[b]fluoranthene	252.3	2.4		6.04 (5.74)
Benzo[j]fluoranthene	252.3	2.4		6.21
Cholanthrene	254.3	2.0		6.28
7,12-Dimethylbenz[a]anthracene	256.3	1.5		6.36
Dibenzo[a,h]fluorene	266.3	0.8		6.57
Dibenzo[a,g]fluorene	266.3	0.8		6.57
Dibenzo[a,c]fluorene	266.3	0.8		6.57
3-Methylcholanthrene	267.3	0.7		6.64
Benzo[ghi]fluoranthene	214.2	0.5		6.78
Benzo[a]pyrene	252.3	3.8	$5.5 \times 10^{-9}$	6.06 (5.74)
Benzo[e]pyrene	252.3	2.4	$5.5 \times 10^{-9}$	6.21
Perylene	252.3	2.4		6.21
Indeno(1,2,3-cd)pyrene	276.3	—		6.58 (6.20)
Dibenz[a,h]anthracene	278.3	0.4		6.86 (6.52)
Benzo[ghi]perylene	276.4	0.3	$1.0 \times 10^{-10}$	6.78 (6.20)
Coronene	300.3	0.14	$1.5 \times 10^{-11}$	7.36

See Chapter 18 for an explanation of the partitioning coefficients,  $K_{ow}$  and  $K_{oc}$ .

Source: Province of British Columbia. Ambient water quality criteria for polycyclic aromatic hydrocarbons (PAHs). Ministry of Environment, Lands and Parks; 1933. <http://www.env.gov.bc.ca/wat/wq/BCguidelines/pahs/> [accessed 13.10.13].

## 8.4 EXPOSURE DATA

Exposure assessments are only as good as the data upon which they are based. The data must meet several criteria<sup>20</sup>:

1. Data must be sound: extent to which the scientific and technical procedures, measures, methods, or models generate the information are reasonable for and consistent with the intended application.
2. Data must be relevant: extent to which the information applies to the intended use.
3. Data and metadata must be clear and complete: the degree of clarity and completeness of documentation of the data, assumptions, methods, quality assurance process, sponsoring organizations, and analyses to generate the information.
4. Data must be accompanied with stated uncertainty and variability: the extent to which the uncertainty and variability (quantitative and qualitative) in the information or in the procedures, measures, methods, or models are evaluated and characterized.
5. Data must be evaluated and reviewed: the extent of independent verification and validation of the exposure information.

Data quality objectives express the minimum performance and acceptance criteria. For example, air pollution sampling might be conducted as part of a network to track pollution trends, but these data can also represent exposure concentrations. During a field study and its analysis, blank samples and duplicates need to be collected and used in data validation. Blank samples (e.g. field blanks, laboratory blanks) are samples known to be free of contamination that are carried through the sampling program. Contamination in these blanks during analysis indicates that sampling or analytical procedures are not meeting good field and laboratory practice. Duplicate samples, i.e. two samples collected in one location using identical sampling techniques, are expected to provide two samples that yield identical analytical results. In reality, analysis results are rarely identical, since instrument variability and error are never zero. However, the duplicates should meet comparability criteria, i.e. be near enough to the known value as to fall within the acceptable range.

All analytical methods have sensitivity limitations. Detection limit (DL), quantification limit, method DL, and reporting limit are common expressions of sensitivity standards. Analytical chemistry data sets should have some indication of all values that are lower than limits deemed reliable enough to report as numerical values (i.e. nondetects). These values should not be

expressed as "zero". Indeed, the actual concentration is unknown. Nondetects can be addressed using simple substitution methods, distributional methods, and robust methods.<sup>21</sup>

Simple substitution methods use a single value as a surrogate, e.g. the DL or half the DL, for each nondetect value. These methods can introduce biases into the data, particularly if zero is chosen, since measures of central tendencies would be skewed toward lower concentrations. For example, consider the following data set from a field sample of an air pollutant ( $\mu\text{g m}^{-3}$ ), with a DL of  $10 \mu\text{g m}^{-3}$  and the air quality standard of  $12 \mu\text{g m}^{-3}$ :

Date	Concentration as Reported in $\mu\text{g m}^{-3}$ (ND = nondetects)	Concentration in $\mu\text{g m}^{-3}$ when Nondetects = 0	Concentration in $\mu\text{g m}^{-3}$ when Nondetects = 0.5 DL
10/1	15	15	15
10/2	ND	0	5
10/3	25	25	25
10/4	ND	0	5
10/5	ND	0	5
10/6	20	20	20
10/7	17	17	17
Mean for the week	Unknown	11	13

If the nondetects are treated as 0, the standard is met. If the nondetects are treated as one-half of the DL, the standard is not met. This is particularly important for air toxics that are associated with adverse effects at very low concentrations, e.g. chronic diseases like cancer associated with concentrations in the parts per billion range.

Distributional methods are a type of internal approach that uses the detected values from which to extrapolate values for the nondetects. Statistics such as log-probit analysis are available to extrapolate data. The data set needs a sufficient number of data points above the DL to define the distribution function (e.g. log-normal) for exposure values with an acceptable degree of confidence. Regression is used to derive the non-detect values. These methods only assume that data below the DL follow a defined distribution, not the whole data set.

Data sets cannot always be combined. Metadata are crucial, including the circumstances under which each set of data were collected (e.g. target population, sampling design, location, and time) and quality (e.g. precision, accuracy, representativeness, and completeness).

This applies to both measurements and data sets derived from models.

#### 8.4.1 Environmental Data Needed for Air Pollution Exposure Calculations

Environmental data are used to characterize either chemical concentrations of an agent in a medium (e.g. particulate matter in a plume) or at an exposure point (e.g. VOCs in the breathing zone). Environmental data also describe the physical media in which an agent is present (e.g. stability of an atmospheric layer, inversion characteristics, and relative humidity).

Environmental data are used throughout an exposure assessment process. During the planning and scoping stage, they can direct the development of a conceptual model by providing information about the chemical source, types of releases, and potential transport mechanisms through the environment. Exposure assessors also use environmental data when quantitatively estimating exposure. These data serve as fundamental inputs, either directly as exposure concentrations or indirectly in exposure models that estimate likely exposure concentrations. For example, the concentration of a solvent in a drinking water supply could directly represent an exposure concentration for the population served by the water supply. The concentration of a solvent detected in ground water that is upgradient of a drinking water well, on the other hand, could serve indirectly as an input value for a model used to predict potential contamination based on parameters such as ground water flow, well pumping rates, and ground water velocity.

##### 8.4.1.1 Biomonitoring Data

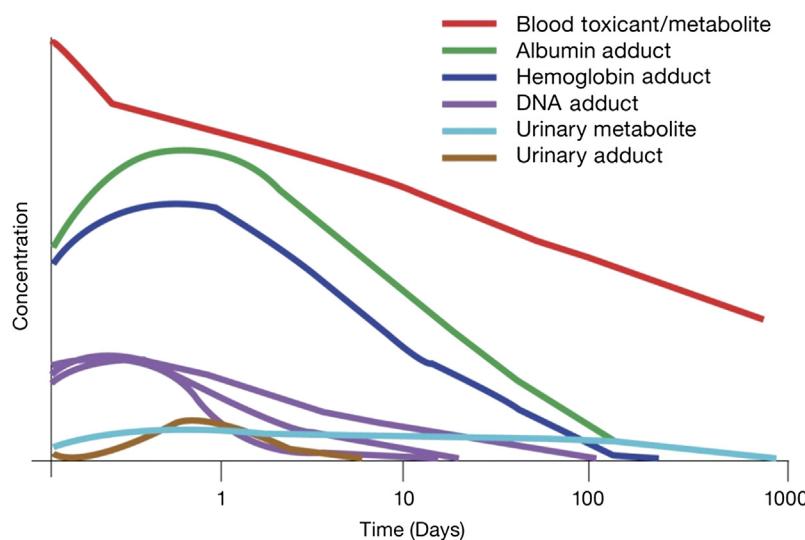
Biomarkers are becoming increasingly reliable for exposure assessment, especially for body burden information.

These are cellular, biochemical, analytical, or molecular measures of chemical exposure. Measurements are taken from samples of various biological media, e.g. tissues, cells, and fluids, which is known as biomonitoring. Biomarkers are used for both effects (see Chapter 7) and exposure. The difference is that exposure biomarkers record the concentration of the chemical or its metabolites in biological media, but effect biomarkers are indications of damage or other cellular, biochemical, or molecular changes that have resulted from the exposure to the chemical.<sup>22</sup> To be useful for exposure assessments, the biomarker must be sufficiently sensitive, specific, biologically relevant, and feasible to collect and analyze (e.g. have unique and identifiable chromatographic peaks). Its toxicokinetics must allow for the substance to persist in the body long enough to be detected.<sup>23</sup> Figure 8.10 shows some of the variability in the residence time of a parent compound or its metabolite in human tissue after a single exposure.

Any of the biomarkers in Figure 8.10 can be used, depending on the residence time of the body burden. For example, if daily changes in chemical exposure are needed, any of the biomarkers will suffice, so long as they are collected, stored, and analyzed properly. However, if biomonitoring is conducted every 150 days, the blood toxicant/metabolite test would be the only reliable biomarker (i.e. fewer nondetects and higher concentrations). This points to the problem of “false negatives” in biomonitoring. If a person is exposed periodically, many biomarkers would not detect the exposure because the chemical would have been cleared between the exposure and the test. If this is interpreted as “zero exposure”, this error is known as a false negative.

Biomonitoring studies help to close data gaps associated with possible exposures, baseline conditions, and internal chemical or metabolite concentrations. Biomonitoring

**FIGURE 8.10 Possible residence types for biomarkers following a single exposure to a persistent chemical.** (For color version of this figure, the reader is referred to the online version of this book.) Ref. 23.



data alone usually cannot link a chemical in the environment with an effect, but they are quite useful complements to environmental data in estimating exposure, especially as inputs to exposure models. These data are useful in establishing a baseline and reference concentration for air pollutants. They give indications of the prevalence of people's chemical body burdens, and highlight those above established toxicity benchmarks. They can be stratified to estimate the extent to which exposures are higher among certain life stages (e.g. Are children exposed differently than adults or are certain socioeconomic classes differentially exposed?).

As mentioned, biomonitoring data have several limitations. Chemical analytical methods are available only for some chemicals. Exposure estimates may be difficult to calculate due to background concentrations, confounding coexposures (see Chapter 4), metabolic uncertainties (e.g. "black boxes" in metabolic pathways), and limited information needed to correlate exposures to chemical concentrations of parent and metabolite. Many biomarkers are nonspecific, i.e. they are triggered by several different chemicals and various endogenous processes. Indeed, biomarkers range from highly specific, such as an enzyme of the heme pathway, i.e. the inhibition of amino-levulinic acid dehydratase, which indicates previous Pb exposure. Some biomarkers are collectively specific, e.g.

for a whole class of compounds, such as the inhibition of acetylcholine esterase (AChE), which is a specific biomarker for organophosphorus (OP) and carbamate pesticides. However, this biomarker cannot indicate the exposure to a specific pesticide, e.g. chlorpyrifos. Even more nonspecific are changes in the immune system or deoxyribonucleic acid (DNA) that could result from a wide range of agents (chemical and biological).

The less-specific biomarkers that indicate exposures to classes of chemicals can actually be quite useful. Often, the specific chemical is less important than the class. For example, enzyme activity can be present in numerous tissues, but AChE inhibition generally is determined from blood samples (whole blood or plasma) and the brain. This makes a biomarker useful not only in human exposure and toxicology but also for ecological exposure and toxicology. These AChE inhibitions occur in mammals, birds, and aquatic biota. With algorithms and models, these biomarkers can be used to predict internal body residues of classes of organic and metallic compounds in various species, e.g. OP pesticides in sentinel species like earthworms, *Eisenia fetida* and *Lumbricus terrestris* (see [Figure 8.2](#) and Discussion Box: Bioindicators of Ecosystem Exposures). These species are used to indicate overall exposures and stressors in habitats.

## BIOINDICATORS OF ECOSYSTEM EXPOSURES

The presence, condition, and diversity of plants, animals, and other living things can be used to assess air pollutant exposures in an ecosystem, such as a stream, lake, estuary, wetland, or forest. Such organisms are referred to as *biological indicators* or *bioindicators*.

An indicator is in a sense an "integrating" tool that incorporates highly complex information in an understandable manner. The iconic bioindicator is the famous canary in the coal mine. Miners were aware that if they hit a vein that contained "coal gas" (actually high concentrations of methane and carbon monoxide) they had little time to evacuate before inhalation of the gas would lead to death. However, they realized that due to its small mass, a smaller animal would succumb to the toxic effects before a human would be affected. The miners did not really care so much how it worked (i.e. the dose-response relationships and routes of exposure); they only cared that it worked. Actually the canary is an example of a *bioassay*, which is a test of toxicity or other adverse effect on one or a few organisms to determine the overall expected effect on a system.

Using an indicator or sentry organism can uncover a cumulative effect that occurs from relatively low-dose, chronic exposures, which are more common and realistic than laboratory studies that rely on short-duration, high-dose administrations to a relatively small number of test species, from which the results must be mathematically modeled. Living organisms, as natural biological integrators, represent numerous locations (wherever the organism has been) and realistic behaviors (what the organism ordinarily does, so long as the sensor is not disruptive).

In biomonitoring, a fluid or tissue sample reveals the contaminants to which these people have been exposed, as well as to the metabolites produced by pathways yielding breakdown products. In addition, an organism's endogenous chemicals respond to the exposure to the parent and breakdown products. Thus, there is a combination of the xenobiotic compound and its metabolites, as well as a change in the concentrations of the chemicals that are always produced by the organism. Metabolomics measures the metabolic status of the whole organism, connecting

(Continued)

## BIOINDICATORS OF ECOSYSTEM EXPOSURES (cont'd)

genomics and proteomics (genetic and cellular responses to the xenobiotic exposure, respectively) with histopathology (i.e. the tissue damage). This reveals a "fingerprint" of the organism's response to the uptake and metabolism of a substance. In other words, the "omics" tools characterize the expected chemical progeny of the parent compound and the profile of the organism's own endogenous compounds as a response to the exposure to the parent xenobiotic compound and its degradation products. In addition, these omics tools can be used at the population and higher trophic levels, so they may be applied in biological indication studies.

Indicators of effects are also available. Biological effects at the cellular level range from acute cellular toxicity to changes in the cellular ribonucleic and DNA structures, leading to cellular (and tissue) mutations, including cancer. The cells are also homes to chemical signaling processes such as those in the stimulus-response systems in microbes and plants, as well as the endocrine, immune, and neural systems in animals. The presence of enzymes and other chemicals can indicate stress at various biological levels. Metabolonomics is also a valuable computational tool for effects studies.

An ecological indicator can be a single measure, an index that embodies a number of measures, or a model that characterizes an entire ecosystem or components of that ecosystem. An indicator integrates the physical, chemical, and biological aspects of ecological condition. It is used to determine the status and to monitor or predict trends in environmental conditions and possible sources of contamination and stress on systems.

Biocriteria are metrics of a system's biological integrity. A system must be able to support communities of organisms in a balanced manner.<sup>24</sup> One means of determining biological integrity is to compare the current condition of an ecosystem to that of pristine or undisturbed conditions. The threshold is the condition below which a system suffers from dysfunction or impairment. A reference condition is frequently associated with biological integrity. However, few systems have not been in some way affected by humans, so the "pristine" system is rare indeed. So the environmental scientist will more often refer to a reference system as one that is "minimally impaired", i.e. one with high biological integrity. Ecosystems and environmental compartments can be degraded by chemical contamination, as well as by physical changes that alter habitats, such as the withdrawal of irrigation water from aquifers and surface waters, overfishing and overgrazing, and introduction of opportunistic exotic species. Biota are selectively sensitive to all forms of pollution.

Estimating ecosystem condition requires the application of direct or indirect evaluations of a system's attributes. Indirect evaluations can have the advantage of being cheaper than the direct approaches, but will not often be as robust. An attribute of natural systems to be protected, e.g. a fish population, is an example of an assessment endpoint, whereas an attribute that is quantified with actual measurements, e.g. age classes of the fish population, is known as a measurement endpoint. Reliable and representative assessment and measurement endpoints are needed to reflect a system's biological integrity (see Table 8.8).

An ecosystem's condition follows the hierarchy of a system's organization, including its various structures and functions. The metabolism of individual organisms is at one extreme. Population processes, e.g. reproduction, recruitment, dispersal, and speciation, are the next level. The highest level of organization, i.e. the communities or ecosystems, processes include nutrient cycling, interspecies interactions, and energy flows. Only a representative amount of biota needs to be sampled. Such selections must aggregate an optimal number of attributes with sufficient precision and sampling efficiency, to provide robust indicators of ecosystem well-being.

Biosensors make use of biological principles to give information about physicochemical agents that may be present. Such devices can be designed to detect the presence and, with calibration, concentrations of contaminants, or they may be used to sense certain physicochemical properties (solubility, polarity, partitioning, and bioavailability) of a whole sample. Compared to conventional methods, biosensors can improve sensitivity (i.e. the biosensor reliably indicates when the agent or class of compounds is present).

TABLE 8.8 Type of Data Essential or Desirable to Ecosystem Exposure Assessments

Biospheric Elements	Ecosystem Processes
Genetics	Mutation, recombination
Individual	Metabolism, growth, reproduction
Population/species	Age-specific birth and death rates Evolution/speciation
Assemblage (community and ecosystem)	Interspecies interactions Energy flow
Landscape	Water cycle Nutrient cycles Population sources and sinks Migration and dispersal

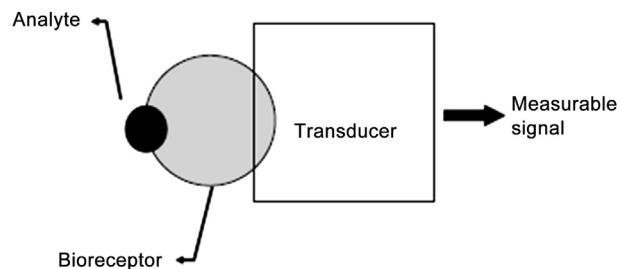
Source: U.S. Environmental Protection Agency.

## BIOINDICATORS OF ECOSYSTEM EXPOSURES (cont'd)

Biosensors can also be specific (only respond to a stimulus elicited by a single or well-defined set of contaminants) and portable (e.g. results known in the field, with no need to collect samples and return to the laboratory for "wet chemistry" at the bench). In contrast with chemical or physical analyses, elaborate and expensive instrumentation is not usually necessary when using biosensors.

To date, enzymes, antibodies, subcellular components, and microbes have dominated the types of biological components in biosensors. Enzymes tend to be unstable and expensive to use, so enzyme-based biosensors are more common in medical applications than in environmental biotechnology. Whole microbes are showing promise, as the biological component of biosensors, owing to their diversity and rapid reproduction, in addition to their well-understood culture collections. Whole-cell biosensors also take advantage of the biological integration that a microorganism undergoes. As such, the whole cell represents numerous enzymatic reactions, including those involved in cellular respiration and fermentation.<sup>25</sup>

The chemical being detected is transported in a sample to a sensor (e.g. O<sub>2</sub> electrode), from which the biological response is ascertained. This molecular response is what makes biosensor. The transducer simply provides a specific response to the biochemical activity (see Figure 8.11).<sup>26</sup>



**FIGURE 8.11 Schematic of a biosensor.** This is a whole-cell biosensor if the bioreceptor is a microbe. Otherwise, the bioreceptor can consist of a biomolecule, e.g. an antibody. Ref. 28.

The simplicity of this design provides good specificity, sensitivity, and portability, eliminating the need for expensive instrumentation, except for calibrations at the laboratory bench. Several types of whole-cell bacterial biosensors using recombinant DNA technology are now available. The bacteria are genetically engineered to respond to the presence of chemicals or physiological stresses by synthesizing a reporter protein, such as β-galactosidase, or green fluorescent protein.<sup>25</sup> A biosensor is evaluated on the basis of its:

1. *Sensitivity*: response of the sensor to per unit change in analyte concentration.
2. *Selectivity*: ability of the sensor to respond only to the target analyte; that is, lack of response to other interfering chemicals is the desired feature.
3. *Range*: concentration range over which the sensitivity of the sensor is good (also referred to as dynamic range or linearity).
4. *Response time*: time needed for the sensor to indicate a certain percentage of its final response due to a step change in analyte concentration.
5. *Reproducibility*: accuracy with which the sensor's output is obtained.
6. *DL*: lowest concentration of the analyte to which there is a measurable response.
7. *Useful life*: time period over which the sensor can be used without significant deterioration in performance characteristics.
8. *Stability*: change in its baseline or sensitivity over a fixed time period.<sup>26</sup>

Biosensors have been used for some time. Immunoassays, in particular, have been used in environmental applications. The improvements to these biotechnologies will allow for improved environmental and public health assessments.

Biomonitoring generally is not very helpful in identifying and apportioning air pollution sources of exposure, given the number of transport and transformation steps in the environment and within the organism (see Figures 8.1 and 8.7). Finally, the data on biologically equivalent doses that result in toxic effects are limited, making the comparisons necessary to assess health risks difficult.

### 8.4.2 Exposure Factors

Exposure factors are those that relate to human behavior and characteristics that are used to quantify a person's exposure to an agent in their environment. One of the most comprehensive compilations of these factors is the *Exposure Factors Handbook*.<sup>27</sup> The handbook summarizes the available data on a range of exposure factors,

including consumption of drinking water; breast milk intake; consumption of fruits, vegetables, dairy products, grain products, beef, and fish; soil ingestion; IRs; skin surface area; soil adherence; body weight; residential building characteristics; and consumer product use. Exposure factors also include data related to people's average body weight, age, and other physical characteristics.

A key set of exposure factors is activity pattern (or time use) data, which are a person's activities, length of time spent performing various activities, locations where a person spends time, and length of time spent within those various environments. Activity data include the types of activities, the length of time people practice the activity, and where and when the activity occurs. Activity patterns can be derived from time—activity diaries, electronic devices (e.g. global positioning systems), questionnaires, or surveys.

Exposure scenarios can be developed using these factors combined with activity patterns. As in this chapter's examples above, exposure factors are also used to estimate contact rates for different media, e.g. the amount of air inhaled in a breath and breathing rates.

#### 8.4.3 Observational Studies

Observational human exposure measurement studies quantify people's exposures to agents in their environments during their normal daily activities. This requires measurements of chemical, biological, or physical agents or other stressors in environmental media; collection of information about the study participants and their homes, work environments, and activities; and collection of personal exposure and biomarker samples.<sup>28</sup>

Observational human exposure measurement studies are used to identify the stressors to which people are exposed; exposure concentrations; important sources, routes, and pathways of exposure; and the factors that have the greatest impact on exposure. In addition, results from observational human exposure measurement studies are used to determine whether mitigation measures have been successful and whether regulatory standards have been exceeded. Data generated in observational human exposure measurements can be used as inputs to exposure and dose models. Unfortunately, these studies are often complex and costly, so large observational data sets are less likely to be conducted than in recent decades. Thus, other means of acquiring exposure data are needed.

#### 8.4.4 Acquiring Data for an Exposure Assessment

The data needed for an exposure assessment may be available from existing resources. Table 8.9 provides information on a variety of data sources that can be used in an exposure assessment. It contains examples of sources for

exposure factor, epidemiologic (e.g. health conditions, risk behaviors), demographic, activity, toxicological, physiochemical, observational human exposure (including occupational), environmental, and meteorological data. Sources from other government agencies, international and professional organizations, and peer-reviewed scientific literature are included, along with US EPA databases.

Each of the data types in Table 8.9 has unique characteristics that need to be evaluated and matched to a particular exposure assessment. These include environmental sampling, biomonitoring, compiling exposure factor information, and conducting questionnaires, surveys, and observations.

Environmental data are collected for many reasons, using a variety of sampling methods. Sources of environmental data include location-specific environmental sampling; regional or national monitoring databases; regulatory submittals for new and/or existing products; local, state and federal agency studies; and peer-reviewed scientific literature. Table 8.10 illustrates a number of aspects of common environmental data measurements, including typical measurement objectives, target media, and examples of sources of existing data.

Environmental sampling may be needed to fill data gaps associated with chemical concentrations or exposure point concentrations; and physical conditions (e.g. terrain). These data can help to define an exposure point concentration (e.g. personal monitoring in the breathing zone) and to support modeling to characterize possible exposure routes.

##### 8.4.4.1 Evaluation of Environmental Data

For an exposure assessment, evaluation of environmental data focuses primarily on the spatial and temporal conditions that affect how well the existing data represent the conditions addressed in the exposure assessment. These include the location of data collection, environmental conditions under which the data were collected, temporal variation in concentrations, and representativeness of microenvironmental data. These evaluation questions are discussed in detail below.

The exposure assessor needs to consider whether the data were collected close to an exposure point of concern in space and time. Media measurements that were collected close to the point of contact for the population or individual in space and/or time are preferable to measurements far removed geographically and/or temporally. The certainty with which the data represent the point of contact tends to decrease as the distance in space and/or time from the point of contact increases. For example, an outdoor air measurement alone cannot adequately characterize indoor exposure. Likewise, shelf studies of consumer products or market basket studies of foods that use regional or national sample groups can provide only a limited understanding of

TABLE 8.9 Examples of Sources of Data for an Exposure Assessment

Data Source	Data Type	Scale	Description	Link
Agency for Toxic Substances and Disease Registry (ATSDR)	Toxicological (primarily) Biological (infrequently) Environmental (rarely)	Local State Regional National	The ATSDR website features profiles on toxic substances, educational materials and current events updates relating to harmful substances. In some instances, the ATSDR will conduct an exposure investigation to study chemical exposures in a community in detail.	<a href="http://www.atsdr.cdc.gov">http://www.atsdr.cdc.gov</a>
ATSDR—National Toxic Substance Incidents Program (NTSIP)	Environmental	Local State National	The NTSIP gathers information about substance incidents into a central place.	<a href="http://www.atsdr.cdc.gov/ntsip/">http://www.atsdr.cdc.gov/ntsip/</a>
Bureau of Labor Statistics—American Time Use Survey (ATUS)	Activity	National	The ATUS measures the amount of time individuals spend doing various activities, such as paid work, childcare, volunteering, and socializing.	<a href="http://www.bls.gov/tus/">http://www.bls.gov/tus/</a>
Centers for Disease Control and Prevention (CDC)—Behavioral Risk Factor Surveillance System (BRFSS)	Biological	State National	The BRFSS is an ongoing telephone health survey system. It has tracked health conditions and risk behaviors in the United States yearly since 1984. Currently, data are collected monthly in all 50 states; Washington, D.C.; Puerto Rico; the Virgin Islands; and Guam. The BRFSS website makes its resources available to the public, including interactive databases, maps and raw annual survey data. The site also features data usage statistics by state.	<a href="http://www.cdc.gov/BRFSS/">http://www.cdc.gov/BRFSS/</a>
CDC—National Health and Nutrition Examination Survey (NHANES) <sup>29</sup>	Dietary Health Biomonitoring Demographics	National	The NHANES interview includes demographic, socioeconomic, dietary, and health-related questions. The examination component consists of medical, dental, and physiological measurements.	<a href="http://www.cdc.gov/nchs/nhanes.htm">http://www.cdc.gov/nchs/nhanes.htm</a>
CDC—National Health Interview Survey (NHIS)	Biological	State National	The NHIS conducts a continuing survey and special studies to secure accurate and current statistical information on the amount, distribution and effects of illness and disability in the United States. Supplemental questionnaires are administered every year with topics such as cancer prevalence, alternative medicine, immunization, and arthritis.	<a href="http://www.cdc.gov/nchs/nhis.htm">http://www.cdc.gov/nchs/nhis.htm</a>

(Continued)

TABLE 8.9 Examples of Sources of Data for an Exposure Assessment—cont'd

Data Source	Data Type	Scale	Description	Link
Census Bureau	Demographics	Census tract State Regional National	The Census Bureau has a number of powerful data sources, including its decennial censuses (compiling demographic, employment, housing, and other data), the American Community Survey (an annual survey that includes much of the decennial information but on a higher geographic scale) and the County Business Patterns (an annual collection of detailed business and employment data that is available at the ZIP code level).	<a href="http://www.census.gov/">http://www.census.gov/</a>
Census Bureau—American FactFinder	Demographics	Census tract State Regional National	The Census Bureau's American FactFinder provides fact sheets and data on population demographics, housing, and businesses.	<a href="http://factfinder2.census.gov/faces/nav/jsf/pages/index.xhtml">http://factfinder2.census.gov/faces/nav/jsf/pages/index.xhtml</a>
Census Bureau—Equal Employment Opportunity (EEO) Data Tool	Demographics	Census tract State Regional National	The Census Bureau's census 2000 EEO Data Tool is a Web-based tool that allows users to select tabulations of residence or workplace information at varying levels of geographic specificity. The data present available information for a variety of occupations categorized by race/ethnicity and sex.	<a href="http://www.census.gov/eeo2000/">http://www.census.gov/eeo2000/</a>
US EPA—Aggregated Computational Toxicology Resource (ACToR)	Toxicological Physicochemical	Local State Regional National	ACToR is US EPA's online warehouse of all publicly available chemical toxicity data. ACToR aggregates data from public sources on environmental chemicals. It includes chemical structure, physicochemical values, <i>in vitro</i> assay data and <i>in vivo</i> toxicology data. The database includes high- and medium-production volume industrial chemicals, pesticides (active and inert ingredients), and potential ground and drinking water contaminants.	<a href="http://www.epa.gov/actor/">http://www.epa.gov/actor/</a>
US EPA—Air Quality System (AQS)	Environmental	Local State Regional National	The AQS contains ambient air pollution data collected by US EPA, state, local and tribal air pollution control agencies from thousands of monitoring stations. AQS also contains meteorological data, descriptive information about each monitoring station (including its geographic location and operator), and data quality assurance (QA)/quality control (QC) information.	<a href="http://www.epa.gov/ttn/airs/airsaqs/">http://www.epa.gov/ttn/airs/airsaqs/</a>

US EPA—Children's Total Exposure to Persistent Pesticides and Other Persistent Organic Pollutants study (CTEPP)	Observational human exposure	State Regional	CTEPP was an observational human exposure study designed to determine what commonly used chemicals are found in home or day-care environments and if children in these environments encountered those chemicals. Chemicals included pesticides (such as bug spray), cleaners and household products. The research sought to identify the major pathways and sources through which children come in contact with chemicals.	<a href="http://www.epa.gov/heasd/research/ctepp.html">http://www.epa.gov/heasd/research/ctepp.html</a>
US EPA—Consolidated Human Activity Database (CHAD)	Activity	Local State National	CHAD is a database that contains data obtained from pre-existing human activity studies that were collected at city, state and national levels. CHAD is intended to be an input file for exposure/intake dose modeling and/or statistical analysis. The CHAD website offers two different ways to search, browse and download datasets.	<a href="http://www.epa.gov/heasd/chad.html">http://www.epa.gov/heasd/chad.html</a>
US EPA—ExpoCastDB	Observational human exposure Environmental Biological	Local State Regional National	ExpoCastDB captures results from observational studies measuring potential exposure to environmental chemicals. It contains data from studies in which chemicals were measured in environmental and biological media. The database also provides access to data on chemical structure and physicochemical values.	<a href="http://www.epa.gov/ncct/expocast/">http://www.epa.gov/ncct/expocast/</a>
US EPA—Exposure Factors Handbook	Exposure factors	State Regional National	The National Center for Environmental Assessment (NCEA) prepared this handbook to provide information on various physiological and behavioral factors commonly used in exposure assessments for various life stages. This document provides a summary of the available data on dietary consumption; soil ingestion; inhalation rates; skin surface area; soil adherence; lifetime activity patterns; body weight; consumer product use; and building characteristics.	<a href="http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=209866">http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=209866</a>
US EPA—Human Exposure Database System (HEDS)	Observational human exposure	National	HEDS is an integrated database system that contains chemical measurements, questionnaire responses, documents and other information related to US EPA research studies of the exposure of people to environmental contaminants. The HEDS website contains a list of studies. Project information includes actual datasets, metadata and relevant documentation describing the studies.	<a href="http://www.epa.gov/heds/index.htm">http://www.epa.gov/heds/index.htm</a>

TABLE 8.9 Examples of Sources of Data for an Exposure Assessment—cont'd

Data Source	Data Type	Scale	Description	Link
US EPA—National Human Adipose Tissue Survey (NHATS)	Biomonitoring	Local Regional National	The NHATS measures baseline levels and trends of exposure to toxic chemicals for the US population and selected subpopulations using human adipose tissue specimens collected in an annual survey conducted from 1970 to 1989.	<a href="http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=55204">http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=55204</a>
US EPA—National Emissions Inventory	Environmental	Local State National	The NEI is a comprehensive and detailed estimate of air emissions of both criteria and hazardous air pollutants from all air emissions sources. It is prepared every 3 years by US EPA and based primarily upon emission estimates and emission model inputs provided by state, local and tribal air agencies for sources in their jurisdictions and supplemented by data developed by US EPA.	<a href="http://www.epa.gov/ttn/chief/einformation.html">http://www.epa.gov/ttn/chief/einformation.html</a>
US EPA—National Human Exposure Assessment Survey (NHEXAS)	Observational human exposure	Local State Regional	NHEXAS evaluates comprehensive human exposure to multiple chemicals on a community and regional scale. The NHEXAS website describes the program's pilot projects, its strategic plan for the future and results from its data analysis workshop.	<a href="http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=22424">http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=22424</a>
US EPA—National-Scale Air Toxics Assessment (NATA)	Noncancer health risk Cancer risk	Local State Regional National	NATA provides estimates of the risk of cancer and other serious health effects from breathing (inhaling) air toxics. US EPA has completed four assessments (1996, 1999, 2002, and 2005) that characterize nationwide chronic cancer risk estimates and noncancer hazards from inhaling air toxics.	<a href="http://www.epa.gov/nata/">http://www.epa.gov/nata/</a>
US EPA—Pesticide Handlers Exposure Database (PHED)	Observational human exposure (occupational)	Regional National	PHED is a database containing empirical exposure monitoring data for workers involved in the handling or application of pesticides in the field. The website features information on the data, worker exposure considerations and a PHED Users Guide.	<a href="http://www.epa.gov/pesticides/science/handler-exposure-data.html">http://www.epa.gov/pesticides/science/handler-exposure-data.html</a>

US EPA—Relationship between Indoor, Outdoor and Personal Air Study (RIOPA)	Observational human exposure	Regional	Riopa quantified indoor and outdoor inhalation exposure to agents in three different areas of the United States. During the study, integrated indoor, outdoor and personal gas-phase and fine PM (2.5 µm or smaller) air samples were collected and analyzed. Questionnaire and time-activity information also were collected from residents.	<a href="http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/5837/report/F">http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/5837/report/F</a>
US EPA—Total Exposure Assessment Methodology Study (TEAM)	Observational human exposure	Local	TEAM, which started in 1979 and was completed in 1985, sought to develop methods for collecting individual exposure information and applying these methods, along with statistical analyses, to estimate exposures and body burdens for people living in several urban areas.	<a href="http://nepis.epa.gov/Exe/ZyNET.exe/2000TTY7.TXT?ZyActionD=ZyDocument&amp;Client=EPA&amp;Index=1986 + Thru+1990&amp;Docs=&amp;Query=&amp;Time=&amp;EndTime=&amp;SearchMethod=1&amp;TocRestrict=n&amp;Toc=&amp;TocEntry=&amp;QField=&amp;QFieldYear=&amp;QFieldMonth=&amp;QFieldDay=&amp;IntQFieldOp=0&amp;ExtQFieldOp=0&amp;XmlQuery=&amp;File=D%3A%5Czyfiles%5CIndex%20Data%5C86thru90%5CTxt%5C00000009%5C2000TTY7.txt&amp;User=ANONYMOUS&amp;Password=anonymous&amp;SortMethod=h%7C-&amp;MaximumDocuments=1&amp;FuzzyDegree=0&amp;ImageQuality=r75g8/r75g8/x150y150g16/i425&amp;Display=p%7Cf&amp;DefSeekPage=x&amp;SearchBack=ZyActionL&amp;Back=ZyActionS&amp;BackDesc=Results%20page&amp;MaximumPages=1&amp;ZyEntry=1&amp;SeekPage=x&amp;ZyPURL">http://nepis.epa.gov/Exe/ZyNET.exe/2000TTY7.TXT?ZyActionD=ZyDocument&amp;Client=EPA&amp;Index=1986 + Thru+1990&amp;Docs=&amp;Query=&amp;Time=&amp;EndTime=&amp;SearchMethod=1&amp;TocRestrict=n&amp;Toc=&amp;TocEntry=&amp;QField=&amp;QFieldYear=&amp;QFieldMonth=&amp;QFieldDay=&amp;IntQFieldOp=0&amp;ExtQFieldOp=0&amp;XmlQuery=&amp;File=D%3A%5Czyfiles%5CIndex%20Data%5C86thru90%5CTxt%5C00000009%5C2000TTY7.txt&amp;User=ANONYMOUS&amp;Password=anonymous&amp;SortMethod=h%7C-&amp;MaximumDocuments=1&amp;FuzzyDegree=0&amp;ImageQuality=r75g8/r75g8/x150y150g16/i425&amp;Display=p%7Cf&amp;DefSeekPage=x&amp;SearchBack=ZyActionL&amp;Back=ZyActionS&amp;BackDesc=Results%20page&amp;MaximumPages=1&amp;ZyEntry=1&amp;SeekPage=x&amp;ZyPURL</a>
US EPA—Toxics Release Inventory	Environmental	Local Regional National	The TRI program compiles the TRI data submitted by regulated facilities each year and makes the data available through the Internet. The TRI represents the largest database of emissions data from point sources in the United States and includes more than 650 chemicals.	<a href="http://www.epa.gov/tri/">http://www.epa.gov/tri/</a>
Department of Health and Human Services—National Toxicology Program (NTP)	Toxicological	National	The NTP website presents NTP technical reports on toxicological and carcinogenic studies. The NTP also has compiled answers to frequently asked questions from the public.	<a href="http://ntp.niehs.nih.gov/">http://ntp.niehs.nih.gov/</a>
NIOSH (National Institute for Occupational Safety and Health)—Health Hazard Evaluations (HHEs)	Observational human exposure Environmental Biological	Local	An HHE is a report on whether workers are exposed to hazardous materials or harmful conditions at a particular workplace. It can include interviews or surveys of employees, measurements of exposures and medical testing.	<a href="http://www.cdc.gov/niosh/hhe/">http://www.cdc.gov/niosh/hhe/</a>

(Continued)

TABLE 8.9 Examples of Sources of Data for an Exposure Assessment—cont'd

Data Source	Data Type	Scale	Description	Link
NIOSH—National Occupational Exposure Survey (NOES)	Observational human exposure	National	The NOES collected data on potential occupational exposures to chemical, physical and biological agents. The survey involved onsite visits to 4490 establishments in 522 industry types employing approximately 1,800,000 workers in 377 occupational categories.	<a href="http://www.cdc.gov/noes/">http://www.cdc.gov/noes/</a>
NIOSH—Workplace Data and Statistics Gateway	Observational human exposure Environmental Biological	Local	NIOSH's <i>Workplace Data and Statistics Gateway</i> is a central repository for the latest NIOSH surveillance data and statistical resources as well as important NIOSH historic surveillance information.	<a href="http://www.cdc.gov/niosh/data/">http://www.cdc.gov/niosh/data/</a>
OSHA (Occupational Safety and Health Administration)—Industry Profile for an OSHA Standard	Observational human exposure	State National	This database compiles OSHA citations for each OSHA standard issued by the federal or state OSHA during a specified fiscal year for particular industries.	<a href="http://www.osha.gov/pls/imis/industryprofile.html">http://www.osha.gov/pls/imis/industryprofile.html</a>
US Department of Agriculture—Continuing Survey of Food Intakes by Individuals	Exposure factors	National	The survey measures the kinds and amounts of foods eaten by individuals in the United States.	<a href="http://www.ars.usda.gov/Services/docs.htm?docid=14392">http://www.ars.usda.gov/Services/docs.htm?docid=14392</a>
USDA—Food Commodity Intake Database	Exposure factors	National	The database is a companion data set to the <i>Continuing Survey of Food Intakes by Individuals</i> in which intakes are presented in terms of food commodities rather than foods as consumed.	<a href="http://www.ars.usda.gov/services/docs.htm?docid=14514">http://www.ars.usda.gov/services/docs.htm?docid=14514</a>
USGS (US Geological Survey)—National Stream Quality Accounting Network (NASQAN)	Environmental	Local Regional	The NASQAN program reports on the concentrations and loads of selected constituents delivered by major rivers to the coastal waters of the United States and selected inland sub-basins in priority river basins.	<a href="http://water.usgs.gov/nasqan/">http://water.usgs.gov/nasqan/</a>

The sources of the information in this table include discussions with H. Ozkaynak, N. Tulle, and P. Egeghy, U.S. EPA, National Exposure Research Laboratory.

TABLE 8.10 Common Air Pollution Data Measurements

Type of Measurement	Measurement Objectives	Sources of Existing Data
Fixed-location media monitoring	Establish long-term trends at specific sampling locations Identify changes in existing conditions	<ul style="list-style-type: none"> <li>Air quality monitoring programs</li> </ul>
Short-term media monitoring	Characterize conditions at a location for a relatively short period of time	<ul style="list-style-type: none"> <li>Remedial investigation sampling under the Comprehensive Environmental Response, Compensation and Liability Act (Superfund)</li> <li>Special studies of environmental media</li> <li>Indoor air monitoring</li> </ul>
Source monitoring	Track chemical release rates to the environment from sources Characterize the relationships between release amounts and various source operating parameters Ensure regulatory compliance Identify disposal options for waste streams	<ul style="list-style-type: none"> <li>Emissions monitoring programs</li> <li>Stack sampling</li> <li>Incinerator ash sampling</li> <li>Fugitive emission sampling</li> <li>Pollution control device sampling</li> </ul>
Microenvironmental sampling	Evaluate ambient conditions in a defined area Identify exposure concentrations	<ul style="list-style-type: none"> <li>Special studies of residences</li> <li>Radon measurements</li> <li>Office building monitoring</li> </ul>
Personal monitoring (e.g. breathing zone samples)	Assess exposure to airborne chemicals Characterize dermal exposure	<ul style="list-style-type: none"> <li>Epidemiologic surveys</li> <li>Industrial hygiene studies</li> <li>Pesticide applicator surveys</li> </ul>

point-of-contact concentrations for localized areas or population groups.

The environmental conditions under which the data were collected are important. Data characterizing environmental conditions (e.g. ground water flow, soil composition, prevailing wind direction) are more representative when measured closer to the point of contact. Again, as the distance from the point of contact or location increases, the uncertainty about how well the data represent local conditions also increases. For instance, an aquifer might have an overall flow to the east, but local topography (e.g. streams, hills) might alter the direction of the flow.

The chemical concentrations vary over space and time. Chemical concentrations can vary considerably from place to place, seasonally and over time because of changing use patterns, degradation and migration. Changes are of particular concern when the measured data will be used to extrapolate trends over long time periods, such as a lifetime. Exposure assessors frequently use transport and dispersion models to understand how chemical concentrations vary over space and time.

If data were collected from a microenvironmental study, representativeness must be assured. Microenvironmental measurement approaches define specific zones that are thought to be relatively homogeneous and then characterize conditions in that zone. For example, microenvironments include the whole or parts of the home, office or other indoor settings as well as a moving vehicle. Microenvironments can also be divided

into time segments (e.g. garage-day, garage-night). This approach can produce measurements that are closely linked with the point of contact in both location and time. Because these studies represent a very limited environment, exposure assessments must ensure that measurements are representative of the population of interest.

An exposure assessment can have many sources of data uncertainty and variability (see Table 8.11). Care must be taken to consider how data uncertainty and variability can impact the outcome of the exposure assessment. The assessment needs to use only the data that are adequate for the decision being made and to state whether further data collection is necessary. Uncertainties include exposure scenario uncertainty, sampling or measurement uncertainty, and observational or modeling uncertainty.

Scenario uncertainty is the uncertainty that the exposure scenario being used is consistent with the scope and purpose of the assessment. Exposure scenario uncertainty results when information regarding the exposure scenario is limited or inadequate. For example, using an exposure assessment relying on information from a study conducted in the southwestern United States may not apply directly to activity patterns in the Midwestern United States. Sampling or measurement uncertainty is associated with data collection or analysis methods. Sample location, sample number, and analysis methods each can add to sampling uncertainty. As a result of these sources of uncertainty, sampling methods and analyses are unlikely to produce the same results

TABLE 8.11 Types of Uncertainty and Contributing Errors

Type of Uncertainty	Type of Error Causing Uncertainty	Description or Example
Exposure scenario	Misclassification	Failure to adequately identify exposure routes, exposure media, and exposed population
Sampling or measurement (parameter uncertainty)	Measurement: random	Random errors in analytical devices (e.g. imprecision of continuous monitors that measure stack emissions)
	Measurement: systemic	Systemic bias (e.g. estimating inhalation from indoor ambient air without considering the effect of volatilization of contaminants from hot water during showers)
	Surrogate data	Use of alternate data for a parameter instead of direct analysis of exposure (e.g. use of population figures as a surrogate for population exposure)
	Misclassification	Incorrect assignment of exposures of subjects in historical epidemiologic studies resulting from faulty or ambiguous information
	Random sampling error	Use of a small sample of individuals to estimate risk to exposed workers
	Nonrepresentativeness	Developing exposure estimates for a population in a rural area based on exposure estimates for a population in a city
Observational or modeling	Relationship errors	Incorrectly inferring the basis of correlations between environmental concentrations and urinary output
	Oversimplification	Misrepresentations of reality (e.g. representing a three-dimensional aquifer with a two-dimensional mathematical model)
	Incompleteness	Exclusion of one or more relevant variables (e.g. relating a biomarker of exposure measured in a biological matrix without considering the presence of the metabolite in the environment)
	Surrogate variables	Use of alternate variables for ones that cannot be measured (e.g. using wind speed at the nearest airport as a proxy for wind speed at the facility site)
	Failure to account for correlations	Not accounting for correlations that cause seemingly unrelated events to occur more frequently than expected by chance (e.g. two separate components of a nuclear plant are missing a particular washer because the same newly hired assembler put them together)
	Model disaggregation	Extent of (dis)aggregation used in the model (e.g. separately considering subcutaneous and abdominal fat in the fat compartment of a physiologically based pharmacokinetic model)

Source: U.S. Environmental Protection Agency. An examination of EPA risk assessment principles and practices. EPA/100/B-04/001. Washington (DC): OSA, US EPA; 2004. <http://www.epa.gov/OSA/pdfs/ratf-final.pdf> [accessed 14.10.13].

every time even when measuring the same sample. Sampling uncertainty is also introduced when surrogate data are used to represent an exposure or when data are not representative of the exposures.<sup>30</sup> This is sometimes called parameter uncertainty.

Observational or modeling uncertainty represents gaps in the scientific theory that are required to make predictions on the basis of causal inferences.

Every data set adds variability to an exposure assessment by all data sets. For example, environmental data represent a sample of the range of chemical concentrations that exist in the environment, and activity information represents a sample of the range of possible activities that can occur in a population. Air pollution data vary temporally, i.e. seasonally

(i.e. intra-annually) and year-to-year (interannually), as well as spatially (e.g. latitudinal, winds aloft, and land cover).

Metadata, i.e. qualitative or quantitative information about the level of uncertainty and variability associated with a data set, are not always available with the data sets. Unavailable metadata can be addressed somewhat by statistical analyses, such as standard deviations (SDs) and upper confidence limit calculations, to represent uncertainty and variability quantitatively. A larger SD is associated with a greater level of uncertainty or variability in the data. Computational techniques are increasingly being used to address model data uncertainty and variability.

## QUESTIONS

1. What is the difference between aggregate and cumulative exposure?
2. What is the difference between dose and exposure?
3. A monitoring station at the intersection of 18th and Vine Streets shows CO concentrations of 8 ppm for July 4. The local newspaper says that people are being exposed to 8 ppm in the town. Is this statement correct? Support your answer.
4. What are the major routes of air pollutant exposure?
5. Numerous activities change exposures to air pollutants. For example, showering can increase inhalation exposure to chlorinated compounds. A water sample is taken from a shower in a bathroom on January 2, with  $50 \text{ mg L}^{-1}$  EDA added immediately after collection and stored at  $4^\circ \text{ C}$ . It is analyzed on January 12 to determine chloride and chlorite ions as part of an indoor volatile organic compound study. Is this likely to be a reliable sample for laboratory analysis?
6. The home uses a cistern to collect rainwater. There is a phosphate fertilizer plant 2 km upwind from the home, so the technician collected a sample on January 2 and sent it to the lab for analysis on January 12. Can the sample be analyzed for ortho-phosphate-P?
7. A canister collects air samples from 6:00 am to 6:00 pm (day) and 6:00 pm to 6:00 am (night) each day for three days, with the following results:  
 June 1, Day: Benzene = 1.2 ppbv; 1,3-butadiene = 0.15 ppbv  
 June 1, Night: Benzene = 0.10 ppbv; 1,3-butadiene = ND  
 June 2, Day: Benzene = 2.2 ppbv; 1,3-butadiene = 0.39 ppbv  
 June 2, Night: Benzene = 0.15 ppbv; 1,3-butadiene = 0.03 ppbv  
 June 3, Day: Benzene = 2.5 ppbv; 1,3-butadiene = 0.47 ppbv  
 June 3, Night: Benzene = ND; 1,3-butadiene = 0.03 ppbV

What are the time-integrated exposures to benzene (ND = not detected)?

8. Suggest possible sources of the two compounds above.
9. Should the ND values be used to calculate concentrations and exposures? If so, how?
10. Why is cotinine a better indicator of exposure to environmental tobacco smoke than nicotine?
11. Give two differences between human exposure and ecosystem exposure.
12. If a sensor can reliably measure total volatile organic compounds at concentrations greater than 5 ppm and

- another sensor can detect benzene at 1 ppm, what can be said about the sensitivity and specificity of these two sensors?
13. Why is biomonitoring limited in identifying and apportioning sources of air pollutants?
14. Give some reasons that the mean inhalation rates for 6- to 11-year olds are about the same as those over 81-year olds.
15. The mean air exchange rate for building in the U.S. is 0.45 air exchanges per hour; whereas the 10th percentile is 0.18 air exchanges per hour. What factor would put a building into this lower exchange rate category?
16. In the U.S., the mean time waiting at a bus or train stop varies by race, age, educational level, part-time vs full-time work schedule, and other factors. How should such information be used in estimating possible exposures to air pollutants, as well as how to reduce these exposures?
17. If the measurement objective is to estimate emission rates to the atmosphere from sources, what types of monitoring can be used?
18. If the measurement objective is to assess personal exposures to air pollutants, what types of monitoring can be used?
19. A study to determine the total amount of polycyclic aromatic hydrocarbons inhaled by people in townhomes omits the amount released from the carpet. Also, the classification of whether a home is a townhome is based on home size and whether the street address has a letter in it (e.g. 210A, Carson Street or 1212D Wilson Drive). What types of error are contributing to the uncertainty in this study?
20. If a power plant burns coal that has  $10 \mu\text{g Hg kg}^{-1}$  emits  $2 \mu\text{g m}^{-3}$  and later burns coal with  $150 \mu\text{g Hg kg}^{-1}$  emits  $10 \mu\text{g m}^{-3}$ , estimate the emissions at this power plant for coal containing  $400 \mu\text{g Hg kg}^{-1}$ . What important assumptions must you make for this estimate?

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# Respiratory Effects of Air Pollutants

## 9.1 RESPIRATION IN HUMANS

In the previous chapter, the discussion of exposure to air pollutants began with two equations for the inhalation route of exposure, which reflect the two major respiratory phases, particulate and vapor:

$$E = \frac{(C) \cdot (PC) \cdot (IR) \cdot (RF) \cdot (EL) \cdot (AF) \cdot (ED) \cdot (10^{-6})}{(BW) \cdot (TL)} \quad (9.1)$$

$$E = \frac{(C) \cdot (IR) \cdot (EL) \cdot (AF) \cdot (ED)}{(BW) \cdot (TL)} \quad (9.2)$$

The first equation addresses inhalation of particulate matter (PM) and the second equation the inhalation of vapors and gases.<sup>a</sup>

Both equations include an inhalation rate (IR). In addition, Eqn (9.1) includes a respirable fraction, since exposure to particles needs to reflect the amount that actually penetrates into the respiratory system. Equation (9.2) lacks this term. Vapors do not need this fractionation because vapors are assumed to be completely respirable, given the gas laws. Thus, respiration is arguably the most important means by which humans and other breathing animals encounter air pollutants. By extension, respiratory effects are the most direct health outcomes associated with air pollutants.

The human body and other biological systems have a tremendous capacity for the uptake of myriad types of chemicals; thereafter either utilizing them for some bodily function or eliminating them from the body. As analytical capabilities have improved, increasingly lower concentrations of chemicals have been observed in various parts of the body. Some of these chemicals enter the body by inhalation.

The primary function of the human respiratory system is to deliver O<sub>2</sub> to the bloodstream and to remove CO<sub>2</sub> from the body. These two processes occur concurrently as the breathing cycle is repeated. Air containing O<sub>2</sub> flows into the nose and/or mouth and down through the upper airway to the alveolar region, where O<sub>2</sub>

diffuses across the lung wall to the bloodstream. The counterflow involves transfer of CO<sub>2</sub> from the blood to the alveolar region and then up the airways and out the nose and mouth. Because of the extensive interaction of the respiratory system with the surrounding atmosphere, air pollutants or trace gases can be delivered to the respiratory system.

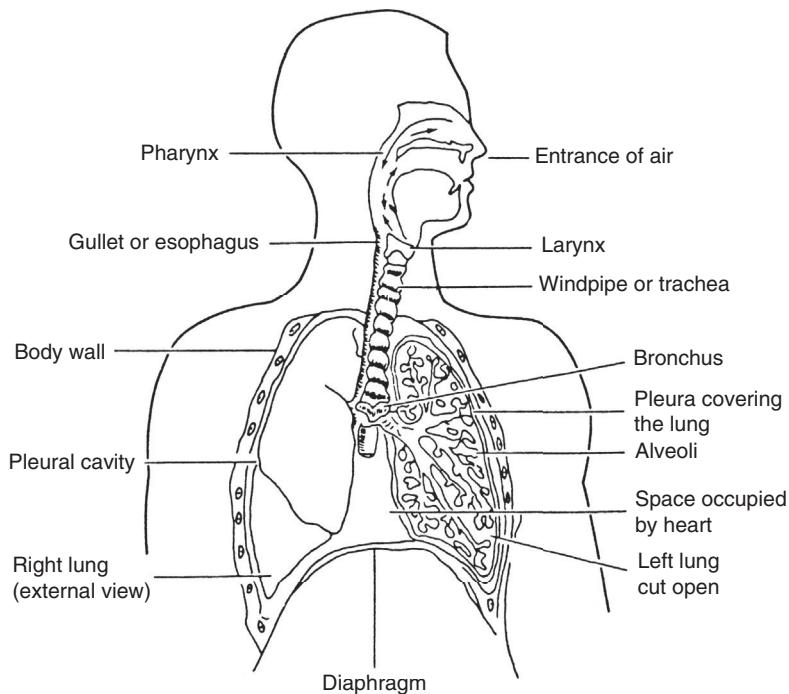
The anatomy of the respiratory system is shown in Figure 9.1. This system may be divided into three regions: the nasal, tracheobronchial, and pulmonary. The nasal region is composed of the nose and mouth cavities and the throat. The tracheobronchial region begins with the trachea and extends through the bronchial tubes to the alveolar sacs. The pulmonary region is composed of the terminal bronchi and alveolar sacs, where gas exchange with the circulatory system occurs. Figure 9.1 illustrates the continued bifurcation of the trachea to form many branching pathways of increasingly smaller diameter through which air moves to the pulmonary region. The trachea branches into the right and left bronchi. Each bronchus divides and subdivides at least 20 times; the smallest units, bronchioles, are located deep in the lungs. The bronchioles end in about 3 million air sacs, the alveoli.

The behavior of particles and gases in the respiratory system is greatly influenced by the region of the lung in which they are located.<sup>1</sup> Air passes through the upper region and is humidified and brought to body temperature by gaining or losing heat. After the air is channeled through the trachea to the first bronchi, the flow is divided at each subsequent bronchial bifurcation until very little apparent flow is occurring within the alveolar sacs. Mass transfer is controlled by molecular diffusion in this final region. Because of the very different flows in the various sections of the respiratory region, particles suspended in air and gaseous air pollutants are treated differently in the lung.

Particle behavior in the lung is dependent on the aerodynamic characteristics of particles in flow streams. In contrast, the major factor for gases is the solubility of

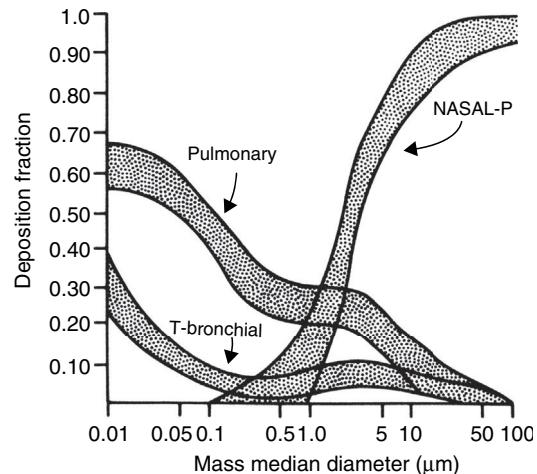
<sup>a</sup>See Chapter 8 for definitions of these terms.

**FIGURE 9.1 Anatomy of the human respiratory system.** Vallero DA. *Fundamentals of air pollution*. 4th ed. Burlington (MA): Elsevier Academic Press; 2008.



the gaseous molecules in the linings of the different regions of the respiratory system. The aerodynamic properties of particles are related to their size, shape, and density. The behavior of a chain type or fiber may also be dependent on its orientation to the direction of flow. The deposition of particles in different regions of the respiratory system depends on their size. The nasal openings permit very large dust particles to enter the nasal region, along with much finer airborne PM. Particles in the atmosphere can range from less than  $0.01\text{ }\mu\text{m}$  to more than  $50\text{ }\mu\text{m}$  in diameter.<sup>b</sup> The relationship between the aerodynamic size of particles and the regions where they are deposited is shown in Figure 9.2. Larger particles are deposited in the nasal region by impaction on the hairs of the nose or at the bends of the nasal passages. Smaller particles pass through the nasal region and are deposited in the tracheobronchial and pulmonary regions. Particles are removed by impacts with the walls of the bronchi when they are unable to follow the gaseous streamline flow through subsequent bifurcations of the bronchial tree. As the airflow decreases near the terminal bronchi, the smallest particles are removed by Brownian motion, which pushes them to the alveolar membrane.

The respiratory system has several mechanisms for removing deposited aerosols. The walls of the nasal and tracheobronchial regions are coated with a mucous fluid. Nose blowing, sneezing, coughing, and swallowing help to remove particles from the upper airways.



**FIGURE 9.2 Particle deposition as a function of particle diameter in various regions of the lung.** The nasopharyngeal region consists of the nose and throat; the tracheobronchial (T-bronchial) region consists of the windpipe and large airways; and the pulmonary region consists of the small bronchi and the alveolar sacs. *Task group on lung dynamics. Health Phys* 1996;12:173.

The tracheobronchial walls have fiber cilia, which sweep the mucous fluid upward, transporting particles to the top of the trachea, where they are swallowed. This mechanism is often referred to as the mucociliary escalator. In the pulmonary region of the respiratory system, foreign particles can move across the epithelial lining of the alveolar sac to the lymph or blood systems,

<sup>b</sup> Particles larger than  $50\text{ }\mu\text{m}$  deposit soon after emission, so are seldom found in ambient measurements.

or they may be engulfed by scavenger cells called alveolar macrophages. The macrophages can move to the mucociliary escalator for removal. For gases, solubility controls removal from the airstream. Highly soluble gases such as SO<sub>2</sub> are absorbed in the upper airways, whereas less soluble gases such as NO<sub>2</sub> and ozone (O<sub>3</sub>) may penetrate to the pulmonary region. Irritant gases are thought to stimulate neuroreceptors in the respiratory walls and cause a variety of responses, including sneezing, coughing, bronchoconstriction, and rapid, shallow breathing. The dissolved gas may be eliminated by biochemical processes or may diffuse to the circulatory system.

Since the location of particle deposition in the lungs is a function of a particle's aerodynamic diameter and density, changing the characteristics of aerosols can greatly affect their likelihood to elicit an effect. Larger particles (>5 µm) tend to deposit before reaching the lungs, especially being captured by ciliated cells that line the upper airway. Moderately sized particles (1–5 µm) are more likely to deposit in the central and peripheral airways and in the alveoli but are often scavenged by macrophages. Particles with an aerodynamic diameter less than 1 µm remain suspended in air and are generally exhaled. Recent studies have shown that large drug particles may be able to evade macrophages past the ciliated cells of the upper respiratory tract and deep into the lungs.

Air pollution respiration can be viewed as the opposite of drug delivery. That is, it is desirable to limit and eliminate the respiratory transport of an air pollutant into the lungs, whereas it is desirable to maximize the amount of a drug's respiratory transport. Thus, characteristics that are desirable from a drug delivery perspective, e.g. small aerodynamic diameter, are undesirable for an air pollutant.

Drug delivery attempts to avoid processes that override and pass by anatomical and physiological mechanisms. Optimal particle size, shape, and density, as well as porosity of the particles have been changed to deliver drug aerosols sufficiently large to evade macrophages past the ciliated cells of the upper respiratory tract, so that the drug may penetrate deeply into the lungs.<sup>2</sup> Pharmaceutical aerosol design has usually sought a standard size range of 1–5 µm, but a recent study used particles of nonstandardized density and aerodynamic diameter. Specifically, the researchers expect that large porous particles would have the mass and dynamics of smaller particles but since they are bigger they would more effectively evade scavenging macrophages in the alveoli. Thus, doses would be less frequent, since more of the medicine would penetrate to the desired, deeper locations in the lungs.<sup>3</sup> Air pollutant particles with these properties would have to be removed since they are so bioavailable.

## 9.2 LUNG KINETICS

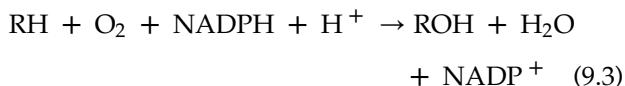
Respiratory pharmacokinetics is complex. Absorption is essential to drug delivery, but needs to be avoided in air pollution (e.g. respirators to prevent intake and absorption). The same is true for distribution. Distribution of more drug and less pollutant is desirable. However, metabolism is not so binary. For drugs, metabolism is only desirable for drugs that are designed to break down in target tissue, but earlier metabolism is to be avoided since less of the drug can find its way to the target. Also, metabolism at sites other than the target tissue can produce toxic products, e.g. side effects. For pollutants, metabolism is usually desirable since the first phases often increase aqueous solubility of pollutants, which increases elimination. However, metabolism may also lead to bioactivation, i.e. producing a metabolite that is more toxic than the parent or a previous metabolite.

The lung is quite capable of biologically transforming compounds in an attempt to detoxify them. In some instances, the biotransformation of a compound can result in producing more chemically reactive metabolites of rather persistent molecules. Unfortunately, this lung metabolism sometimes produces metabolites that are more toxic than the parent compound. Indeed, lung tissue is known to activate procarcinogens, i.e. compounds that only become carcinogenic after being metabolized. These include the polycyclic aromatic hydrocarbons and N-nitrosamines. The reactive intermediate metabolites increase the formation of DNA adducts. The adduct is a part of the DNA molecule that becomes covalently bonded to a cancer-causing compound, which is the initiation of a cancer cell. As mentioned in Chapter 8, DNA adducts are used as exposure biomarkers.

Bioactivation in the lungs occurs by the expression of enzymes to break down air pollutants that enter. Prominent among the enzymes is the cytochrome P450 enzyme, which catalyzes oxidative metabolism in many organic compounds, but can also induce bioactivation of certain classes, including substances that promote cancer, i.e. procarcinogens. Cytochrome P450 is the most prominent member of the superfamily (CYP) of a large and assorted group of enzymes (i.e. biological catalysts that accelerate oxidation of organic compounds). These reactions usually involve metabolic intermediates, e.g. lipids and steroid hormones, as well as toxic chemicals that have entered an organism. CYPs account for about three-fourths of the total number of different metabolic reactions.<sup>4</sup>

The most common reaction catalyzed by cytochrome P450 is the insertion of an oxygen atom from molecular oxygen into an organic substrate (RH) while reducing

the other oxygen atom (i.e. a monooxygenase reaction):



NADP is nicotinamide adenine dinucleotide phosphate, which is a coenzyme occurring in most living cells. It is similar to nicotinamide adenine dinucleotide, i.e. another coenzyme that also exists in cells. Both are oxidizing or reducing agents involved in various metabolic processes, but generally for different classes of organic compounds. A coenzyme is an organic molecule that binds with the protein molecule to form the active enzyme. NADPH is the reduced form of NADP. Pollutant-metabolizing P450 enzymes are expressed in bronchial and bronchiolar epithelium, Clara cells, type II pneumocytes, and alveolar macrophages.<sup>5</sup>

Metabolism occurs in three phases (see Figure 9.3):

1. Phase I—Modification
2. Phase II—Conjugation
3. Phase III—Advanced modification and excretion

Phase I includes the CYP reactions mentioned above. Phase I reactions include oxidation, reduction, hydrolysis, addition of oxygen or removal of hydrogen, and other reactions assisted by mixed-function oxidases. If the metabolites of phase I reactions are sufficiently polar, they may be readily excreted directly after phase I. However, many phase I products are slowly metabolized and need a subsequent reaction whereby the endogenous

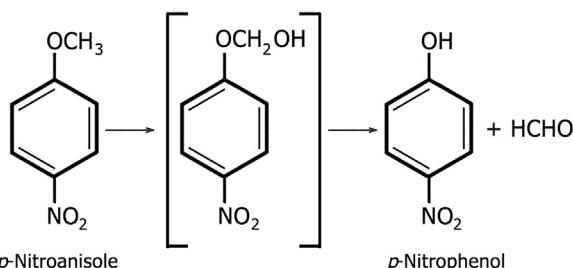


FIGURE 9.4 Phase I metabolism of *p*-nitroanisole. Ref. 6.

substrate combines with the newly incorporated functional group to form a highly polar conjugate.

These enzymatic reactions add or expose functional groups, e.g. —OH, —SH, —NH<sub>2</sub>, or —COOH, to organic compounds. These are the sites at which further reactions can occur, which is analogous to a hook on which numerous items can be attached. For example, *p*-nitroanisole is converted to *p*-nitrophenol by exposing the molecule to attack at the more polar —OCH<sub>2</sub>OH site (see Figure 9.4). Another common phase I reaction is by oxidation via conversion of a C—H bond to a C—OH, such as forming phenol during phase I metabolism of benzene (Figure 9.5). Thus, phase I metabolism consists of slight changes in molecular weight and increased polarity, setting up the molecule for subsequent phase II reactions.<sup>6</sup>

In subsequent phase II metabolism, enzymatic reactions result in the conjugation of large water-soluble, charged (polar) biomolecules. This occurs at a functional group site on either the parent compound or its phase I metabolite. These reactions are catalyzed by broadly specific transferases that enhance metabolism of lipophilic compounds with nucleophilic or electrophilic groups. The four primary phase II enzymes are glucuronosyltransferase, sulfotransferase, glutathione *S*-transferase and acetyltransferase. Their properties and mechanisms are similar to the CYP and other phase I enzymes. An example of phase II

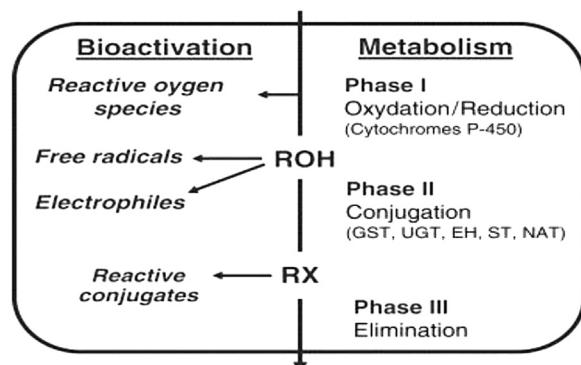


FIGURE 9.3 Metabolic transformation of an inhaled lipophilic pollutant. The process moves from right to left. Phase I modifies the compound chemically by oxidation, reduction, and/or hydrolysis, which increases the reactivity of metabolites so that they can be conjugated in phase II. This may be followed by additional processes that increase the metabolite's aqueous solubility, yet less chemically reactive metabolites that are more easily eliminated. However, these steps can also yield more toxic metabolites, i.e. bioactivation occurs. GST, glutathione *S*-transferase; UGT, UDP-glucuronyltransferase; EH, epoxide hydrolase; ST, sulfotransferase; NAT, *N*-acetyltransferase. Ref. 5.

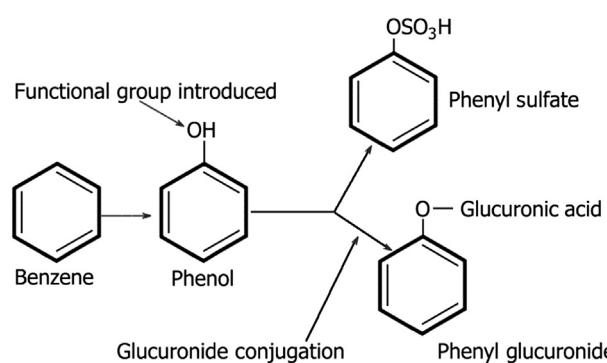
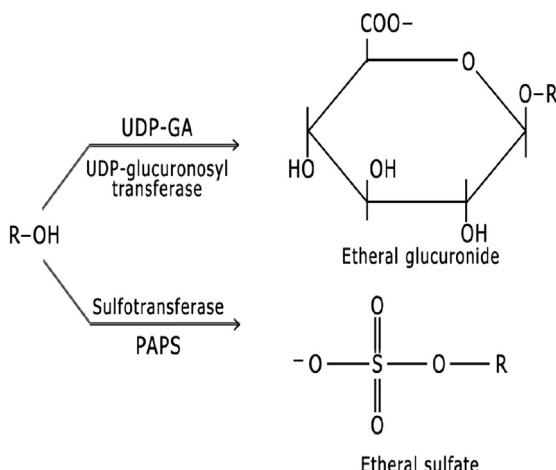


FIGURE 9.5 Metabolism of benzene by addition of the —OH group (hydrolysis), which allows for phase II conjugation. Ref. 6.



**FIGURE 9.6** Phase II metabolism of a phase I metabolite ( $\text{R}-\text{OH}$ ). The steps include glucuronidation (top right) and sulfation (bottom right) of a hydroxyl functional group. UDP-GA = Uridine diphosphate glucuronic acid; PAPS = 3'-Phosphoadenosine 5'-phosphosulfate. Ref. 6.

metabolism is shown in Figure 9.6. Following phase II, the conjugates may be further metabolized and excreted from cells in phase III.

### 9.3 AIR POLLUTANT PROPERTIES IMPORTANT TO RESPIRATION

The properties of air pollutants greatly influence their potential for respiration and the rate of exposure. For particulates, size, soluble fraction, and density are very important. For gaseous pollutants, vapor pressure, density, and solubility are key. For example, ultrafine particles (diameter  $<100 \text{ nm}$ ) can penetrate very deeply into the lungs. Air pollutants with high vapor pressures are more likely to stay aloft since they will be more likely to remain in the vapor phase compared to lower vapor pressure compounds.

Vapor pressure is the pressure exerted by a vapor in a confined space. Similarly vaporization is the change of a liquid or solid to the vapor phase. So, if a substance vaporizes it can enter a plume. Thus, a principal means of a substance being released as a plume is volatilization, which is a function of the concentration of a contaminant in solution and the contaminant's partial pressure. Henry's law states that the concentration of a dissolved gas is directly proportional to the partial pressure of that gas above the solution:

$$p_a = K_H [c] \quad (9.4)$$

where,

- $K_H$  = Henry's law constant
- $p_a$  = Partial pressure of the gas
- [ $c$ ] = Molar concentration of the gas

or,

$$p_a = K_H C_W \quad (9.5)$$

where  $C_W$  is the concentration of gas in water.

As is discussed in detail in Chapter 18, Henry's law is an expression of this proportionality between the concentration of a dissolved contaminant and its partial pressure in the headspace (including the open atmosphere) at equilibrium. A dimensionless version important to respiration is the air–water partition coefficient ( $K_{AW}$ ):

$$K_{AW} = \frac{C_A}{C_W} \quad (9.6)$$

where  $C_A$  is the concentration of a gas or vapor in air.

The relationship between the air/water partition coefficient and Henry's law constant for a substance is

$$K_{AW} = \frac{K_H}{RT} \quad (9.7)$$

where  $R$  is the gas constant ( $8.21 \times 10^{-2} \text{ J atm mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the temperature (K).

Henry's law presents a limiting factor for systems where a substance's partial pressure is approaching zero. At very high partial pressures, (e.g. 30 Pa—high by ambient atmospheric standards) or at very high contaminant concentrations (e.g.  $>1000 \text{ ppm}$ ), Henry's law assumptions cannot be met. Such vapor pressures and concentrations are seldom seen in ambient environmental situations, but may be seen in industrial and other source situations. Thus, in modeling and estimating the tendency for a substance's release in vapor form, Henry's law is a useful metric and is often used in compartmental transport models to indicate the fugacity from the water to the atmosphere. Fugacity, the tendency for a substance to leave one compartment (e.g. water) and join another (e.g. air), will be discussed in detail in Chapter 18.

It should be noted that air pollution is dynamic and that air pollutants are continuously undergoing physical and chemical changes. Indeed, the first two equations in this chapter may imply that pollutants are either particulate or vapor. Actually, the same substance can be both, as indicated by Henry's law. Some of the substance will be in liquid or solid phase and some in vapor phase. In the opposite phase partitioning, the vapor phase substance can be deposited or undergo aerosolization. In air pollution engineering and the environmental sciences, the use of the term "phase" is nuanced from that of physics. In atmospheric sciences the most important phase distribution is that of vapor *versus* particulate phase. The distinction between gases and vapors has to do with the physical phase that a substance would be under environmental conditions, e.g. at standard temperature and pressure.

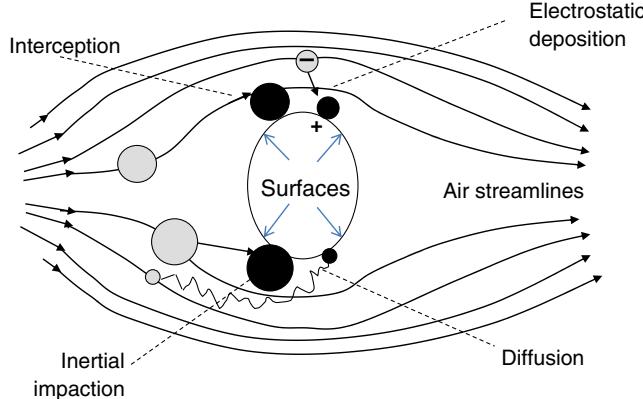
PM is inclusive of all particles, whether liquid or solid. An aerosol is a liquid or solid particle that is suspended in a gas; in environmental sciences this gas is usually air, but in reactors, stacks, and other nonambient conditions, this can be various flue gases. Standard atmospheric conditions can be defined as 1 atm pressure (760 mmHg) and 25 °C (298.15 K).<sup>7</sup>

PM is an important vector for pollutant transport (e.g. moved by advection, or dissolved in or sorbed to aerosols). As mentioned, in the United States, the Clean Air Act established the ambient standard (National Ambient Air Quality Standards (NAAQS)) for PM. In 1971, the US Environmental Protection Agency (EPA) required measurements of total suspended particulates (TSP) as measured by a high-volume sampler, i.e. a device that collected particles of a large range of sizes (aerodynamic diameters up to 50 µm). Smaller particles are more likely to be inhaled than larger particles, so in 1987 the US EPA changed the standard for PM from TSP to PM<sub>10</sub>, i.e. particle matter  $\leq 10 \mu\text{m}$  diameter. The diameter most often used for airborne particle measurements is the “aerodynamic diameter”. The aerodynamic diameter ( $D_{\text{pa}}$ ) for all particles greater than 0.5 µm can be approximated as the product of the Stokes particle diameter ( $D_{\text{ps}}$ ) and the square root of the particle density ( $\rho_p$ ):

$$D_{\text{pa}} = D_{\text{ps}} \sqrt{\rho_p} \quad (9.8)$$

If the unit of the diameters is micrometers, the unit of density is grams per cubic centimeter.

The Stokes diameter  $D_{\text{ps}}$  is the diameter of a sphere with the same density and settling velocity as the particle. The Stokes diameter is derived from the aerodynamic drag force caused by the difference in velocity



**FIGURE 9.7 Mechanical processes involved in the deposition of particulate matter.** Vallero DA. *Fundamentals of air pollution*. 4th ed. Burlington (MA): Elsevier Academic Press; 2008; adapted from: Rubow KL. *Filtration: fundamentals and applications*. In: *Aerosol and particle measurement short course*. Minneapolis (MN): University of Minnesota; 2004. August 16–18. (For color version of this figure, the reader is referred to the online version of this book.)

of the particle and the surrounding fluid. Thus, for smooth, spherical particles, the Stokes diameter is identical to the physical or actual diameter.

Following the passage of the Clean Air Act, the NAAQS for PM<sub>10</sub> was set as a 24 h average of 150 µg m<sup>-3</sup> (not to exceed this level more than once per year), and an annual average of 50 µg m<sup>-3</sup> arithmetic mean. However, subsequent research showed the need to protect people breathing even smaller PM in air, since most of the particles that penetrate deeply into the air–blood exchange regions of the lung are very small. Thus, in 1997, the US EPA added a new fine particle (diameters  $\leq 2.5$ ), known as PM<sub>2.5</sub>.<sup>8</sup>

Gases flow with the air, but aerosols deposit differentially within the airway by mechanical processes: (1) diffusion; (2) interception; (3) inertial impaction; and (4) electrostatics (see Figure 9.7). These same processes are at work in the respiratory system after the aerosol is inhaled.

## 9.4 RESPIRATORY SYSTEM TRANSPORT AND FLUID DYNAMICS

Air pollutants can damage the fluid dynamics in the respiratory system either directly (e.g. airway inflammation) or indirectly (e.g. by altering its immune response). Susceptibility to air pollutants differs among individuals, as exemplified by several diseases and conditions (e.g. asthma), but the fluid dynamics are the same, i.e. disruption of the movement of air into the lungs to provide oxygen.

The motion of air and gases in the respiratory system follow fundamental fluid dynamics theory.<sup>9</sup> The motion of these fluids is governed by the conservation of mass (continuity) equation and conservation of momentum (Navier–Stokes) equation. Under most conditions, the flow of air in the respiratory airways is assumed to be incompressible. For incompressible flow, the continuity equation is expressed as

$$\nabla \cdot V = 0 \quad (9.9)$$

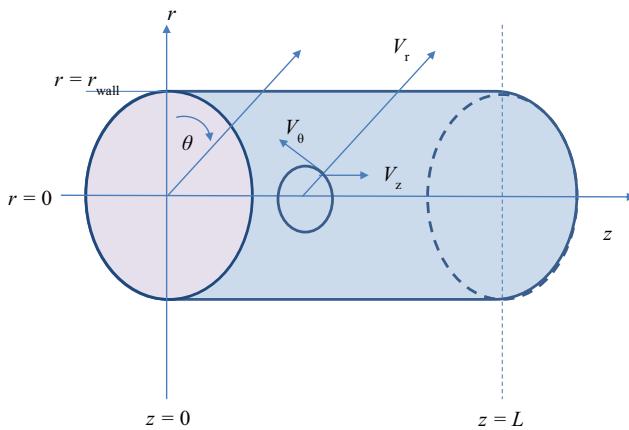
And, the continuity equation is

$$\left[ \frac{\partial V}{\partial t} + (V \cdot \nabla) V \right] = \rho f - \nabla p + \mu \nabla^2 V \quad (9.10)$$

where  $\nabla$  is a gradient operator;  $\nabla^2$  is a Laplacian operator;  $V$  is velocity;  $\rho$  is fluid density;  $\mu$  is absolute fluid viscosity;  $p$  is the hydrodynamic density; and  $f$  is a volumetric force that is applied externally, e.g. gravity.

For cylindrical profiles like bronchi, the gradient operator  $\nabla$  can be expressed in cylindrical coordinates:

$$\frac{\partial}{\partial r} + \frac{1}{r} \frac{\partial}{\partial \theta_0} + \frac{\partial}{\partial z} \quad (9.11)$$



**FIGURE 9.8** Coordinate system for an ideal cylindrical airway, depicting velocity component at an arbitrary point. Adapted from Ref. 9. (For color version of this figure, the reader is referred to the online version of this book.)

Thus, the continuity equation can also be expressed cylindrically:

$$\frac{1}{r} \frac{\partial}{\partial r} (r V_r) + \frac{1}{r} \frac{\partial}{\partial \theta} V_\theta + \frac{\partial}{\partial z} V_z = 0 \quad (9.12)$$

where,  $V_r$ ,  $V_\theta$ , and  $V_z$  are the components of the fluid velocity, which are depicted in Figure 9.8, i.e. radial ( $r$ ), circumferential ( $\theta$ ), and axial ( $z$ ) directions, respectively. Thus, the momentum equations in these directions can be expressed as

$$\begin{aligned} \frac{\partial V_r}{\partial t} + (\mathbf{V} \cdot \nabla) V_r - \frac{1}{r} V_\theta^2 &= -\frac{1}{\rho} \frac{\partial p}{\partial r} + f_r \\ &+ \frac{\mu}{\rho} \left( \nabla^2 V_r - \frac{V_r}{r^2} - \frac{2}{r^2} \frac{\partial V_\theta}{\partial \theta} \right) \end{aligned} \quad (9.13)$$

$$\begin{aligned} \frac{\partial V_\theta}{\partial t} + (\mathbf{V} \cdot \nabla) V_\theta + \frac{V_r V_\theta}{r} &= -\frac{1}{\rho r} \frac{\partial p}{\partial \theta} + f_\theta \\ &+ \frac{\mu}{\rho} \left( \nabla^2 V_\theta - \frac{V_\theta}{r^2} + \frac{2}{r^2} \frac{\partial V_r}{\partial \theta} \right) \end{aligned} \quad (9.14)$$

$$\frac{\partial V_z}{\partial t} + (\mathbf{V} \cdot \nabla) V_z = -\frac{1}{\rho} \frac{\partial p}{\partial z} + f_z + \frac{\mu}{\rho} \nabla^2 V_z \quad (9.15)$$

where,

$$\mathbf{V} \cdot \nabla = V_r \frac{\partial}{\partial r} + \frac{1}{r} V_\theta \frac{\partial}{\partial \theta} + V_z \frac{\partial}{\partial z} \quad (9.16)$$

The time derivatives (i.e. first terms) in these three equations can be ignored under steady state conditions.

The Laplacian operator can be defined in cylindrical airways as

$$\nabla^2 = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2} \quad (9.17)$$

Airway velocities are complicated by numerous factors including lung and other tissue morphologies, and the airway generations (branching level) through which the air is flowing. Equations can be tailored to these conditions or idealized velocity profiles can be assumed for the cascade of generations. These include parabolic flow (laminar fully developed), plug flow (laminar undeveloped), and turbulent flow.<sup>10</sup> For example, the upper tracheobronchial airways may be assumed to be turbulent, but in the pulmonary region, plug and parabolic profiles may be assumed.

The right and left lungs are connected via their primary bronchi to the trachea and upper airway of the nose and mouth (see Figure 9.1). From there, the bronchi, i.e. airways, subdivide into a branching network of many levels. Each level, called a generation, is designated with an integer. The trachea are generation  $n = 0$ , the primary bronchi are generation  $n = 1$ , and so forth. Thus, theoretically there are  $2n$  airway tubes at generation  $n$ . For generations  $0 \leq n \leq 16$ , known as the conducting zone, gas flow is restricted to entry and exit in the airway.<sup>11</sup> That is, air is moving, but there is no air–blood gas exchange of O<sub>2</sub> and CO<sub>2</sub>.

The generations  $n > 16$  comprise the respiratory zone, where air exchange takes place. Generations  $17 \leq n \leq 19$  are where air sacs (alveoli), which range from 75 to 300 μm in diameter, become present on the airway walls. Alveoli are thin-walled and owing to the rich capillary blood supply are designed for gas exchange. These are the respiratory bronchioles. For generations  $20 \leq n \leq 22$ , the walls of the tubes or ducts consist entirely of alveoli. At generation  $n = 23$ , terminal alveolar sacs are made up clusters of alveoli.

Two principal factors relevant to gas exchange are the airway volume ( $V_{aw}$ ) and airway surface area ( $A_{aw}$ ), which are proportional to the size of the person. Air exchange increases in proportion to  $A_{aw}$ . The  $V_{aw}$  (milliliters) for children is proportional to height and is approximated as<sup>12</sup>

$$V_{aw} = 1.018 \times \text{Height(cm)} - 76.2 \quad (9.18)$$

$V_{aw}$  (milliliters) can be estimated for adults by adding the ideal body weight (pounds) plus age in years.<sup>13</sup> For example, a 40-year-old adult whose ideal body weight is 160 pounds has an estimated  $V_{aw}$  of 200 ml.<sup>14</sup>

Alveoli are abundant in the lung, i.e. the average lung has from 300 to 500 million of these air sacs. In an average adult lung, the total alveolar surface area is

$70\text{ m}^2$ . This large  $A_{aw}$  allows not only for efficient gas exchange to supply  $O_2$  for normal respiration but also for large increases in gas exchange needed when a person is stressed (e.g. during exercise, injury, or illness). The Reynolds number (see Chapters 1 and 6) varies by generation (very high in the trachea, but low in the alveoli).<sup>11</sup> Airways have liquid lining, with two layers in the first generations (up to about  $n = 15$ ). A watery (Newtonian), serous layer is next to the airway wall. This layer has cilia that pulsate toward the mouth. Atop the serous layer is a mucus layer that possesses several non-Newtonian fluid properties, e.g. viscoelasticity, shear thinning, and a yield stress.

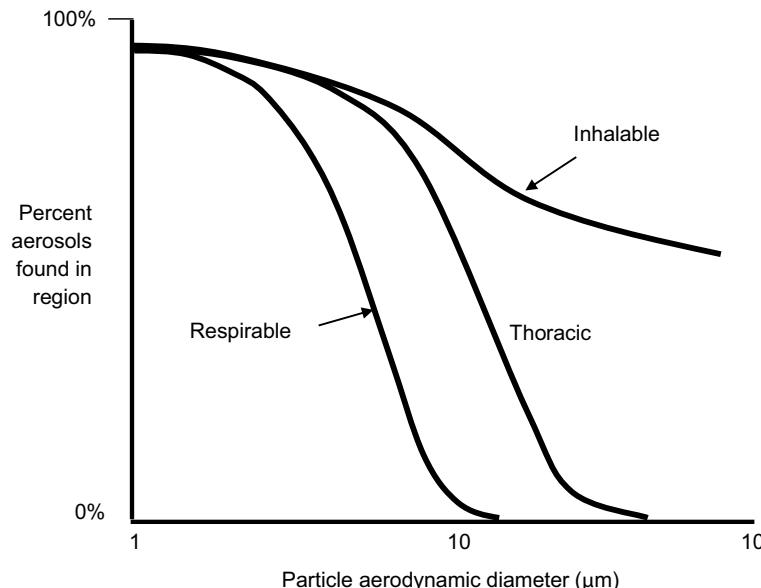
Alveolar cells produce surfactants that orient at the air–liquid interface and reduce the surface tension significantly. Air pollutants can adversely affect the surfactant chemistry, which can make the lungs overly rigid, thus hindering inflation.<sup>11</sup>

A pulmonary surfactant is a surface-active lipoprotein complex (phospholipoprotein) produced by type II pneumocytes also called alveolar type II cells. These pneumocytes are granular and comprise 60% of the alveolar lining cells. Their morphology allows them to cover smaller surface areas than type I pneumocytes. Type I cells are highly attenuated, very thin (25 nm) cells that line the alveolar surfaces and cover 97% of the alveolar surface. Surfactant molecules have both a hydrophilic head and a lipophilic tail. Surfactants adsorb to the air–water interface of the alveoli with the hydrophilic head in the water, while the hydrophobic tail is directed toward the air. The principal lipid component of surfactant, dipalmitoylphosphatidylcholine, is responsible for the decreasing surface tension.

The actual surface tension decrease depends on the surfactant's concentration on the interface. This concentration's saturation limit depends on temperature and the presence of other compounds in the interface. Surface area of the lung varies during compliance (i.e. lung and thorax expansion and contraction) during ventilation. Thus, the surfactant's interface concentration is seldom at the level of saturation. During lung expansion (inspiration), the surface increases, opening space for new surfactant molecules to join the interface mixture. During expiration, lung surface area decreases, compressing the surfactant and increasing the density of surfactant molecules, thus further decreasing the surface tension. Therefore, surface tension varies with air volume in the lungs, which protects the lungs from atelectasis at low air volume and tissue damage at high air volume.<sup>15a–15c</sup>

The size of the particle is indirectly proportional to its depth of lung penetration. Aerosol measurement is usually an expression of the mass of a particle and size of particle. Prior to 1997, the primary (health) standard for  $PM_{10}$  was a 24 h average of  $150\text{ }\mu\text{g m}^{-3}$  (not to exceed this level more than once per year), and an annual average of  $50\text{ }\mu\text{g m}^{-3}$  arithmetic mean. However, this standard did not provide sufficient protection for people breathing PM-contaminated air, since most of the particles that penetrate deeply into the air–blood exchange regions of the lung are quite small, with aerodynamic diameters much smaller than 10 microns (see Figure 9.9). The smallest particles, known as the respirable fraction, required additional attention. Thus, in 1997, the US EPA added a new fine particle (diameter  $\leq 2.5$ ), known as  $PM_{2.5}$ .<sup>8</sup>

**FIGURE 9.9 Three regions of the respiratory system where particle matter is deposited.** The inhalable fraction remains in the mouth and head area. The thoracic fraction is the mass that penetrates the airways of the respiratory system, while the smallest fractions, i.e. the respirable particulates, are those that can infiltrate most deeply into the alveolar region.



Basically, lung filtration consists of four mechanical processes:<sup>c</sup> (1) diffusion; (2) interception; (3) inertial impaction; and (4) electrostatics (see Figure 9.7). Diffusion is important only for very small particles ( $\leq 0.1 \mu\text{m}$  diameter) because the Brownian motion allows them to move in a “random walk” away from the airstream. Interception works mainly for particles with diameters between 0.1 and  $1 \mu\text{m}$ . The particle does not leave the airstream but comes into contact with matter (e.g. lung tissue). Inertial impaction collects particles sufficiently large to leave the airstream by inertia (diameter  $\geq 1 \mu\text{m}$ ). Electrostatics consist of electrical interactions between the atoms in a surface and those in the particle at the point of contact (Van der Waal’s force), as well as electrostatic attraction (charge differences between particle and surface). Other important factors affecting lung filtration are surface stickiness, uniformity of particle diameters, the solid volume fraction, the rate of particle loading onto tissue surfaces, the particle phase (whether liquid or solid), capillarity and surface tension, and characteristics of air in the airway, such as humidity, velocity, temperature, pressure, and viscosity.

## **9.5 RESPIRATORY HEALTH EFFECTS**

Air pollutants cause many respiratory diseases, both acute and chronic. Acute diseases include a range from mild irritations to inflammation to allergic reactions to impaired lung function to complete respiratory failure depending on the level of exposure. Chronic diseases include chronic obstructive pulmonary diseases (COPD), cardiovascular diseases, asthma, and lung and other cancers. Oxidative stress initiated by air pollutants appears to play a large role in such chronic diseases.

Principal vapor phase air pollutants that are associated with non-cancer effects of the respiratory system include ozone, sulfur oxides, carbon monoxide, nitrogen oxides, as well as PM. Numerous organic compounds, e.g. polycyclic aromatic hydrocarbons, have been linked to respiratory system cancers (e.g. lung cancer).

PM in various forms has been associated with cancer, including the organic fraction of the aerosol. Asbestos and other fibers have been linked to long-term effects, including mesothelioma, lung cancer, and asbestosis. Dust from coal has been associated with pneumoconiosis (so-called black lung disease). Dust from crushing silica-containing rocks has been linked to silicosis. Textile fiber exposures have led to byssinosis (so-called brown lung disease), which may result from bacteria in cotton (thus, a combined physical–chemical–biological air pollutant).

Exposure to elevated concentrations of tropospheric (ground-level) ozone is particularly harmful to people with asthma or lung disease and children who are more likely than adults to have asthma, which is aggravated by ozone. Chronic, continuous exposure to ozone for even short periods may cause children to have more breathing problems as adults. Older adults are more susceptible to lung disease. People engaged in heavy work or exercise are also at risk, since their ventilation rates and thus respiratory exposure doses are elevated. Infants are particularly vulnerable since their lungs continue to develop after birth and prolific tissue is more easily affected by air pollutants.

Tobacco smoke has been identified as a key factor in North America and Europe in the development and progression of COPD. Numerous air pollutants in the home and workplace can be synergistic with one another and with genetic factors and respiratory infections to increase the incidence and severity of COPD. In developing nations, indoor air quality plays a large role in the development and progression of COPD.<sup>16</sup>

Both conventional pollutants and air toxins are associated with respiratory effects. In addition to effects in the respiratory system, the conveyance and distribution of air pollutants and their metabolites lead to problems in other parts of the body, especially cardiovascular problems. These are the subject of the next chapter.

## **QUESTIONS**

1. Highlight the differences between [Equation 9.1](#) and [Equation 9.2](#).
2. If a person inhales air with  $10 \mu\text{g m}^{-3}$  aerosols with a mean aerodynamic diameter of  $5 \mu\text{m}$  at a rate of  $0.007 \text{ m}^3 \text{ min}^{-1}$ , approximately how much of PM will be deposited in tracheobronchial region in an 8-hour day? How much would be trapped nasally? How much would make it to small bronchi and alveolae?
3. At another location, a person inhales air with  $25 \mu\text{g m}^{-3}$  aerosols with a mean aerodynamic diameter of  $10 \mu\text{m}$  at a rate of  $0.007 \text{ m}^3 \text{ min}^{-1}$ . What are the approximate amounts of this size PM that will in the various regions after an 8-hour day?
4. The operations change at the location, so that a person now inhales air with  $10 \mu\text{g m}^{-3}$  aerosols with a mean aerodynamic diameter of  $2.5 \mu\text{m}$  at a rate of  $0.007 \text{ m}^3 \text{ min}^{-1}$ . What are the approximate amounts of this size PM that will in the various regions after an 8-hour day?
5. What if another person, about the same age and size, is working with the person above, but her job

<sup>c</sup>These are the same processes employed in filtration systems used to collect PM. They are discussed in detail in Part V.

- required more exertion, so that she her respiration rate is  $0.0085 \text{ m}^3 \text{ min}^{-1}$  and she has to remain there for 10 hours?
6. Based on your calculations of the previous four questions, what conclusions can be drawn about particulate size and respiratory exposures?
  7. Given their solubilities, where in the respiratory system would ozone and sulfur dioxide likely largely be absorbed?
  8. List three irritating gases. How might they elicit a physiological response?
  9. Why might water-soluble gases be less problematic if leaked indoors than less soluble gases?
  10. What atom is inserted into an organic substrate during the most common cytochrome P450 catalysis?
  11. Which phase of metabolism is most likely to produce electrophiles?
  12. Which metabolic phase is most likely to convert a C-H bond to a C-OH bond? What does this do to the compound being metabolized?
  13. How is lung tissue similar to a filter? How does it differ?
  14. What is an airway generation? Which generations comprise the conducting zone and the respiratory zone?
  15. Why is airway surface area important?
  16. Estimate the airway volume of a child 50 inches tall.
  17. Estimate the airway volume of a large-frame 25 year old man who is 70 inches tall.
  18. What is the difference in phase in layers of generations  $n = 0$  through 15 compared to higher generations?
  19. What type of pulmonary surfactant is produced by type II pneumocytes? How may air pollutants adversely affect lung flexibility?
  20. What physiological mechanism is associated with chronic, respiratory diseases?

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# Cardiovascular Effects of Air Pollutants

## 10.1 HUMAN CARDIOVASCULAR SYSTEM

Chapter 9 describes the mechanisms by which the respiratory system (Figure 9.1) provides oxygen to the body. All air-breathing animals need oxygen for metabolism. After intake, the molecular oxygen ( $O_2$ ) must be distributed throughout the body for energy exchange and building cells. This is the purpose of the cardiovascular system. In a way, all the effects discussed in Chapter 9 also damage the cardiovascular system. Reduced  $O_2$ -carrying capacity, e.g. increased carboxyhemoglobin and decreased hemoglobin levels resulting from CO, damages the cardiovascular system generally and the heart specifically. Also, toxicity to lung and other respiratory system cells and tissue from hazardous air pollutants cause additional damage to the cardiovascular system.

This chapter addresses specific types of cardiovascular damage caused by air pollutants. However, it should

be kept in mind that every system within an organism is interrelated. Thus, damage to the respiratory, endocrine, neurological, reproductive, and immunological systems will often be accompanied by effects in the cardiovascular system.

## 10.2 CARDIOVASCULAR DISEASE AND AIR POLLUTION ASSOCIATIONS

Rigorous studies of the association of short-term cardiovascular effects in human populations can be traced to a number of episodes in industrialized urban areas in the twentieth century (see Discussion Box: Infamous Air Pollution Episodes). This led to the passage of legislation and regulations around the world to address air pollution, notably the Clean Air Act of 1970 in the United States. Recent decades have seen a growth in the evidence and number of studies linking air pollution to cardiovascular diseases.<sup>1,2</sup>

### INFAMOUS AIR POLLUTION EPISODES

#### Meuse Valley, Belgium

During the period December 1–5, 1930, an intense fog occupied the heavily industrialized Meuse Valley between Liege and Huy (about 24 km apart) in eastern Belgium.<sup>3</sup> Several hundred persons had respiratory attacks primarily beginning on December 4, with 63 persons dying on December 4 and 5 after a few hours of sickness. On December 6, the fog dissipated; the respiratory difficulties improved and, in general, rapidly ceased.

The fog began on December 1 under anticyclonic conditions. What little air motion occurred was from the east, causing air to drift up-valley, moving smoke from the city of Liège and from the large factories southwest of it into the narrow valley. The valley sides

extend to about 100 m, and the width of the valley is about 1 km. A temperature inversion extended from the ground to a height of about 90 m, transforming the valley essentially into a tunnel deeper than the height of the stacks in the valley, which were generally around 60 m tall. Much of the particulate matter (PM) had 2–6  $\mu\text{m}$  aerodynamic diameters, i.e. readily respirable (see Chapter 7). The fog was cooled by radiation from the top and warmed by contact with the ground. This caused a gentle convection in the “tunnel”, mixing the pollutants uniformly and resulting in nearly uniform temperature with height.

The symptoms of the first patients began on the afternoon of December 3 and seemed to occur simultaneously

(Continued)

## INFAMOUS AIR POLLUTION EPISODES (*cont'd*)

along the entire valley. Deaths took place only on December 4 and 5, with the majority at the Liege end of the valley. Those affected were primarily elderly persons who had lung or heart problems. However, some previously healthy persons were among the seriously ill. There were no measurements of pollutants during the episode, but the five Liège University professors who participated in the subsequent inquiry indicated that part of the sulfur dioxide was probably oxidized to sulfuric acid. Of the 27 factories in the area, 15 were capable of releasing gaseous fluorine compounds and suggested that the release of these compounds was of significance.<sup>4</sup>

During the 30 years prior to the episode, fogs lasting for more than 3 days had occurred only five times, always in winter, in 1901, 1911, 1917, 1919, and 1930. Some respiratory problems were noted in 1911. Industrial activity was at a low level in 1917 and 1919.

J. Firket,<sup>3</sup> professor at the University of Liège, warned that if the episode were replicated in larger populations, the consequences would be magnified: "This apprehension was quite justified, when we think that proportionately, the public services of London, for example, might be faced with the responsibility of 3200 sudden deaths if such phenomenon occurred there". His fear was realized in 1952, when such a catastrophe occurred, as described in "London, England" section below.

### Donora, Pennsylvania

A severe episode of atmospheric pollution occurred in Donora, Pennsylvania, during the period October 25–31, 1948.<sup>5</sup> Twenty persons died, 17 of them within 14 h on October 30.

During this period, a polar high-pressure area remained nearly stationary, with its center in the vicinity of northeastern Pennsylvania. This caused the regional winds, both at the ground and through the lowest layers, to be extremely light. Donora is southeast of Pittsburgh and is in the Monongahela River valley. Cold air accumulated in the bottom of the river valley and fog formed, which persisted past midday for four consecutive days. The top of the fog layer has a high albedo (See Chapter 2), and reflects solar radiation, so that only part of the incoming radiation is available to heat the fog layer and eliminate it (Figure 10.1(a)). During the night, longwave radiation leaves the top of the fog layer, further cooling and stabilizing the layer (Figure 10.1(b)). Wind speeds at Donora were less than  $3.1 \text{ ms}^{-1}$  ( $7 \text{ miles h}^{-1}$ ) from the surface up to 1524 m (5000 ft) for three consecutive days, so that pollutants emitted into the air within the valley were not transported far from their point of emission.

Maximum temperatures at Donora at an elevation of 232 m (760 ft) mean sea level were considerably lower than those at the Pittsburgh airport, elevation 381 m (1250 ft), indicating the extreme vertical stability of the atmosphere. Thus, the pollutants were trapped within a stagnant air parcel in the valley. In the vicinity of Donora, there were sources of sulfur dioxide, PM, and carbon monoxide. Previous recorded periods of stagnation had occurred in Donora during October 5–13, 1923, and October 7–18, 1938.

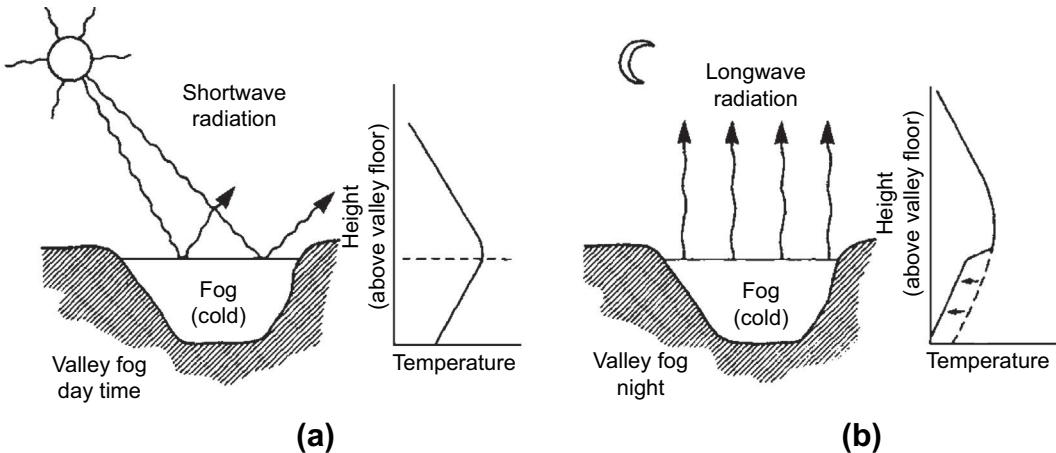
### London, England

A dense 4-day fog occurred in London and its surroundings during December 5–9, 1952.<sup>7,8</sup> The fog began as the area came under the influence of an anticyclone approaching from the northwest early on December 5. This system became stationary, so that there was almost no wind until milder weather spread into the area from the west on December 9. Temperatures remained near freezing during the fog. The visibility was unusually restricted, with a 4-day average of less than 20 m over an area approximately 20 by 40 km and visibility of less than 400 m over an area 100 by 60 km. The density of the fog was enhanced by the elevated concentrations of small particles in the air available for condensation of fog droplets. The result was a very large number of very small fog droplets, which make for a more opaque and persistent fog than one that is formed in cleaner air. The depth of the fog layer was variable with diameters, but was generally 100 m or less.

Measurements of PM with diameters less than  $20 \mu\text{m}$  and of sulfur dioxide were made at 12 sites in the greater London area. The measurements were made by pumping air through a filter paper and then through a hydrogen peroxide solution. The smoke deposit on the filter was analyzed by reflectometer; the sulfur dioxide was determined by titrating the hydrogen peroxide with standard alkali, thus eliminating interference by carbon dioxide. Using the sampling procedure, sulfur dioxide was measured in two phases, i.e. the gas phase and dissolved in fine fog droplets. Any sulfur dioxide associated with larger fog droplets or adsorbed on particles collected on the filter not measured.

During this time, "smoke" was, by today's standards, a crude indicator of PM. Smoke concentrations ranged from 0.3 to more than  $4 \text{ mg m}^{-3}$ . Daily means of the sampling stations are shown in Figure 21.4. Sulfur dioxide measurements ranged from less than  $0.1 \text{ ppm}$  ( $260 \mu\text{g m}^{-3}$ ) to  $1.34 \text{ ppm}$  ( $3484 \mu\text{g m}^{-3}$ ). Also, 4 of the 11 stations had at least one daily value in excess of 1 ppm, and 9 of the 11

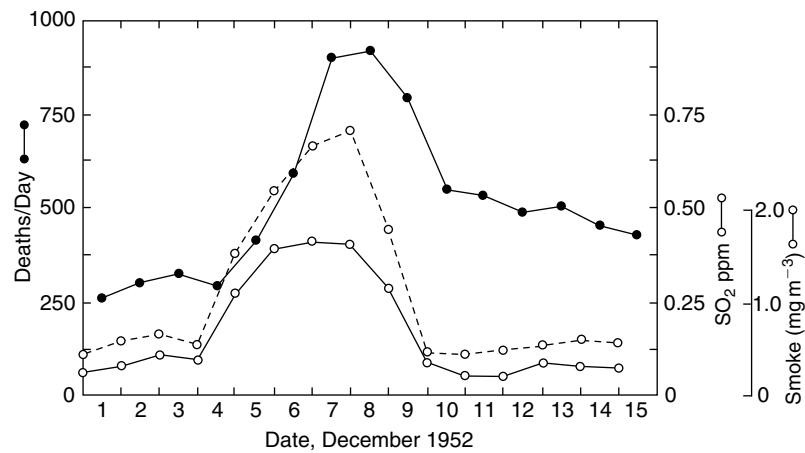
## INFAMOUS AIR POLLUTION EPISODES *(cont'd)*



**FIGURE 10.1** Dense fog maintaining stability in a valley. It reflects shortwave radiation during the day and radiates heat from the top of the fog at night. *Source:* Adapted from Ref. 6.

stations had at least one daily value in excess of 0.5 ppm. These concentrations indicated unhealthy conditions, e.g. the US primary (health) standard for sulfur dioxide, which is a maximum 24 h concentration of  $365 \mu\text{g m}^{-3}$  (0.14 ppm), must not be exceeded more than once per year. Daily means are shown in Figure 10.2. The smoke and  $\text{SO}_2$  means rose and later decreased in concomitantly. Daily concentrations of smoke averaged over all stations rose to about five times normal levels for London at that time and sulfur dioxide to about six times normal, peaking on December 7 and 8, respectively. In addition to the daily measurements at 12 sites, monthly measurements at 117 sites were made using lead peroxide candles. This allowed determination of the spatial pattern. The December 1952 concentrations were about 50% higher than those of December 1951.

From the commencement of the fog and low visibility, many people experienced difficulty in breathing; the effects generally occurring simultaneously over a large area of hundreds of square kilometers. The rise in the number of deaths (Figure 10.2) paralleled the mean daily smoke and sulfur dioxide concentrations; daily deaths reached a peak on December 8 and 9, with many of them related to respiratory troubles. Although the deaths decreased with decreasing concentrations, the deaths per day remained considerably above the pre-episode level for some days. A question that needs to be answered is whether most of the persons who died would have died soon afterward anyway. If this were the case, a below-normal death rate would have occurred following the episode. This situation did not seem to exist, but detailed analysis was complicated by increased deaths in January and February 1953,



**FIGURE 10.2** Daily air pollution ( $\text{SO}_2$  and smoke) and deaths during the 1952 London episode. Source: Adapted from Ref. 7.

*(Continued)*

## INFAMOUS AIR POLLUTION EPISODES (*cont'd*)

which were attributed primarily to an influenza outbreak. This also raises the possibility that exposures to air pollutants could have impaired immunity in sensitive groups, which made them more vulnerable to respiratory and cardiovascular diseases.

Those who analyzed these excess deaths (the number of deaths above the normal number for each calendar day) asserted that the level of sulfur dioxide was not near the toxic limit of 10 ppm necessary to affect healthy persons. They attributed the deaths to the synergistic effect of fine particles and sulfur dioxide combined. They believed that considerable sulfuric acid mist was formed from the oxidation of sulfur dioxide, but since no measurements were made, its amount was speculative.

In the Meuse Valley, Donora, and London episodes, the areas were influenced by high pressure with nearly nonexistent surface air motion. Surface inversions caused the condensation of fog, which, once formed, persisted throughout the day, even during midafternoon. In each case the fog layer was relatively shallow, extending only about 100 m. The persistence of the fog past the third day and the lack of any air transport out of the region, as well as the existence of considerable emissions of pollutants, seem to separate these episodes from more common meteorological occurrences. Both the Meuse Valley and Donora had topography constraining the volume in which the pollutants were confined. This constraint apparently resulted from the lack of any transport wind in the London 1952 episode. Measurements of pollutant concentrations were made only in London.

A previous air pollution episode responsible for approximately 300 deaths occurred in London between November 26 and December 1, 1948. Concentrations of smoke and sulfur dioxide were 50–70% of the values during the 1952 episode.

### Other Episodes

The co-occurrence of sulfur compounds and particulates appear to elicit greater air pollution problems. For example, just before the infamous London incident, a fog occurred during the period December 3–7, with sulfur dioxide as high as during the 1952 episode, but with particulate concentrations considerably lower due to the partial implementation of the 1956 British Clean Air Act. Excess deaths numbered 340.

High pollution levels were measured in the eastern United States between November 27 and December 5, 1962, notably in Washington, DC, Philadelphia, New York, and Cincinnati. Between December 2 and 7, elevated pollution levels were found in Rotterdam;

Hamburg, Frankfurt, and the Ruhr area; Paris; and Prague. Pollution levels were high in Osaka between December 7 and 10, and mortality studies, which were under way, indicated 60 excess deaths. An accident under similar meteorological conditions to those of the London incidents, i.e. complicated by fog, weak winds, and a surface inversion, occurred in Poza Rica, Mexico, in the early morning of November 24, 1950, when hydrogen sulfide was released from a plant for the recovery of sulfur from natural gas. There were 22 deaths, and 320 persons were hospitalized.

### Recent Air Pollution Emergencies

Government authorities increasingly are facing emergencies that may require rapid lifesaving decisions by those on the scene. Of particular concern are transportation accidents involving the movement of volatile hazardous materials. A railroad derailment accident of a tank car carrying liquefied chlorine on February 26, 1978, at Youngstown, Florida, caused seven people to die. An accident in Houston, Texas, involving a truck carrying anhydrous ammonia on May 11, 1976, also claimed seven lives. There are also many near-misses. Two potentially dangerous situations involved barges with tanks of chlorine: one that sank in the lower Mississippi River and another that came adrift and rested on the Ohio River dam at Louisville, Kentucky; neither resulted in release of material. Just one or a few differences in variables can mean the difference between disaster and prevention.

In 1978, US firefighters and other first responders<sup>9</sup> fought a fire in Chester, Pennsylvania, at a site with large quantities of illegally stored chemicals, among them highly flammable, extremely toxic, and highly volatile materials. This is a potentially deadly combination of physical and chemical factors. Volatile organic compounds (VOCs) were stored at the site. Given their high vapor pressure, even without a fire, ruptured tanks and other storage devices would likely see large releases of these toxic substances. In addition, the site contained a particularly toxic group of semivolatile compounds (vapor pressures in the range of  $10^{-5}$ – $10^{-2}$  kPa), the polychlorinated biphenyls (PCBs). Semivolatile compounds present special challenges during disasters. Although under normal conditions, they do not vaporize readily, during combustion they can be released in large quantities in aerosol form and be advectively transported within the plume. They may also be transformed to even more toxic compounds, e.g. halogenated dioxins and furans. Both mechanisms increase the danger to first responders and surrounding communities. The fire and

## INFAMOUS AIR POLLUTION EPISODES *(cont'd)*

explosion hazards were greater than if the substances were merely flammable, but less volatile.

The intense fire destroyed one building and caused extensive damage to two others used for stockpiling drummed wastes. Forty-seven firefighters were hospitalized. In the fire's aftermath, there remained a controversial three-acre site, located on the west bank of the Delaware River and in a light industrial area. Residential neighborhoods were within 300 m from the site. From the 1950s to the 1970s, the site had been used as a rubber recycling facility, but was later converted to an illegal industrial waste storage and disposal facility until 1978. Numerous 55 gallon drums were stored on the site, or dumped their contents either directly onto the ground or into trenches, severely contaminating soil and groundwater. In addition to the PCBs, the site stored acids and cyanide salts. Burned building debris, exploded drums, tires, shredded rubber, and contaminated earth littered the property. About 150,000 gallons of waste materials remained on site after the fire. Most of the wastes were in drums stored in the fire-damaged buildings. Because of the dumping of contaminants, and the fire, the groundwater and soil were contaminated with heavy metals including arsenic, chromium, mercury, and lead; these were in addition to the organic contaminants, e.g. PCBs; plastic resins; and VOCs from past disposal activities. Besides the public health menace, the fire and latent effects of the stored contaminants occurred in an ecologically sensitive area, including nearby wetlands and other habitat for wildlife and marine animals. Several cleanup actions were conducted until it was ultimately removed from the Superfund list of most hazardous sites. The site is now a parking area.

### **Bhopal, India**

On December 2, 1984, the contents of a methyl isocyanate (MIC) storage tank at the Union Carbide India plant in Bhopal became hot. Pressure in the tank became high. Nearly everything that could go wrong did. The refrigerator unit for the tank, which would have slowed the reactions, was turned off. After midnight, when the release valve blew, the vent gas scrubber that was to neutralize the gas with caustic soda failed to work. The flare tower, which would have burned the gas to harmless by-products, was down for repairs. As a result many tons of MIC were released from the tank. The gas spread as a foglike cloud over a large, highly populated area to the south and east of the plant<sup>10,11</sup>. The number of fatalities was in excess of 2000 people with thousands of others injured. Although little meteorological information is

available, it is assumed that winds were quite light and that the atmosphere at this time of day was relatively stable. Thus, stable atmospheric conditions made for longer exposure to elevated MIC concentrations.

### **Nuclear Accidents**

Releases of radioactive materials from nuclear power plants have occurred, with concentrations sufficient to require evacuation of residents.

On April 26, 1986, shortly after midnight local time, a serious accident occurred at a nuclear power plant in Chernobyl in the Ukraine. It is estimated that 4% of the core inventory was released between April 26 and May 6. Quantities of Cs-137 (cesium) and I-131 (iodine) were released and transported, resulting in contamination, primarily by wet deposition of cesium, in Finland, northern Sweden and Norway, the Alps, and the northern parts of Greece. Because of temperatures of several thousand kelvin during the explosion-like release, the resulting pollutant cloud is assumed to have reached heights of 2000 m or more. The estimated southeast winds at plume level initially moved the plume toward Finland, northern Sweden, and northern Norway. As winds at plume level gradually turned more easterly and finally north and northwesterly, contaminated air affected the region of the Alps and northern Greece. Modeling the long-range transport including wet and dry removal processes confirmed the regions affected.<sup>12</sup> Elevated levels of radioactivity were measured throughout the Northern Hemisphere. Because of the half-life of about 30 years for Cs-137, the contamination will endure.

More recently, in March of 2011, a tsunami and its aftermath led to large scale releases of radioactive material. The plume from the Fukushima nuclear disaster did not have the initial energy of the Chernobyl plume and the heavy elements appeared to remain in the reactor, whereas the volatiles, especially I-131, were transported advectively with the plume. Iodine from Fukushima was detected in Scotland a few days after the disaster. The initial winds blew towards the East, but after 2 days the winds changes rotation towards the southwest for a day, before becoming westerlies. A reason for the small exclusion zone of only 20 km in the case of Fukushima was as a result of the low energy of the explosion. Relatively little heavy material was ejected from the reactor. As in most nuclear power plant releases, I-131 and Cs-137 were transported in the plume. Radioactive iodine was detected in California, but by the time the plume reached the US West coast the level of radioactivity was very low. A large

*(Continued)*

## INFAMOUS AIR POLLUTION EPISODES (*cont'd*)

number of evacuees had decamped to an area southwest of Fukushima. Radiation levels there, 2 days after the accident, were apparently higher than at the boundary of the accident site. The heavier cesium in the plume was deposited in a line southwest of Fukushima. The accident contaminated 8% of Japanese land with Cs-137 (half-life is 30 years).

### World Trade Center, New York

On September 11, 2001, terrorists intentionally crashed fully fueled Boeing 767 jets into the twin towers of the heavily populated World Trade Center (WTC; [Figure 10.3](#)). The burning fuel, building materials, and building contents, as well as the fibers and particles released during the collapse were the source of dangerous gas and particle-phase pollutants released throughout the city. In addition to the immediate threat, the fire smoldered for months following the attack. The fire was a source of a variety of pollutants ([Figure 10.3](#)). A number of air pollutants and indicators of air pollution were measured at monitoring sites around the site.

Concentrations of all measured pollutants were generally highest in September and October and declined to levels more typical for New York City by November and December. Concentrations of pollutants were highest near the site of the twin towers, known as Ground Zero, decreasing with distance, showing a significant decrease at a measurement site 0.5 km away. Dust composition differed among samples from

the initial collapse, near underground fires, and during demolition/debris removal. Concentrations were highest until the fires were extinguished (December 19, 2001), after which the concentrations dropped and remained lower during the subsequent monitoring through February 2002. The analyses of air pollutants following the disaster are provide in [Table 10.1](#).

Concentrations of PM<sub>2.5</sub> and lead (Pb), for which there are 24 h daily observations at the Ground Zero and downwind sites were highly variable through the end of October. The highest PM<sub>2.5</sub> concentrations occurred at Ground Zero in October (400 µg m<sup>-3</sup>), dropping after November (<100 µg m<sup>-3</sup>). The particle concentrations decreased with distance from Ground Zero, as evidenced by only one reading at remote sites in October near 100 µg m<sup>-3</sup>, and the rest of the measurements consistently below 50 µg m<sup>-3</sup>.

Concentrations of coarse PM (particles between 2.5 and 10 µm) were initially equivalent to PM<sub>2.5</sub> at the downwind site, but steadily decreased until the fires were extinguished. After December, coarse PM concentrations dropped to approximately 30% of PM<sub>10</sub>, which is typically observed. This is supported by the number of particles in discrete size intervals (i.e. the particle size distribution from 0.3 to 10 µm).

The trends for Pb were similar. The highest Pb concentrations occurred at Ground Zero in September and October (6 µg m<sup>-3</sup>), dropping in November (about 0.1 µg m<sup>-3</sup>). As for PM, the lowest overall Pb concentrations were observed with distance from Ground Zero, highest in October and November (<1 µg m<sup>-3</sup>) and the rest of the measurements consistently below 0.3 µg m<sup>-3</sup>, through January 2002.

The difference in PM<sub>2.5</sub> and Pb concentrations was less marked between the Ground Zero sites and the downwind site after December. However, metals associated with steel, i.e. manganese (Mn) and iron (Fe), exhibited a different temporal trend. From October to December, concentrations of Mn and Fe steadily increased at Ground Zero and to a lesser degree at the downwind site. These Mn and Fe increases were likely due to the increased cutting of steel beams during debris removal. As these activities decreased, i.e. after December, Mn and Fe concentrations also declined.

Concentrations of especially those VOCs, vapor-phase compounds that are potential markers for combustion, also decreased substantially after September and October. As evidence, concentrations of benzene at Ground Zero were greater than 25 ppb in September, decreasing to 16 ppb in October, falling below 5 ppb thereafter



**FIGURE 10.3** Burning debris pile following World Trade Center attack. (For color version of this figure, the reader is referred to the online version of this book.) *Photo credit: U.S. Environmental Protection Agency.*

TABLE 10.1 Outdoor Monitoring Conducted in Response to the WTC Disaster

Lead Organization	Location	Parameters	Type	Start Date
EPA-Office of Research and Development	Ground Zero, <sup>1</sup> lower Manhattan <sup>2</sup>	PM <sub>2.5</sub> , PM <sub>10</sub> , metals, EC/OC, VOCs, SVOCs, continuous PM and EC, meteorology	Outdoor air and settled dust	9/21/01
EPA Region 2	Ground Zero, lower Manhattan, landfill <sup>3</sup>	Asbestos, PM <sub>2.5</sub> , PM <sub>10</sub> , CO, dioxins, furans	Outdoor air, worker protection	9/15/01
EPA Emergency Response Team	Ground Zero, lower Manhattan, landfill	Metals, VOCs, PCBs, freon, phosgene, H <sub>2</sub> S, CO, SO <sub>2</sub> , PM	Outdoor air, worker protection	9/15/01
NY State Department of Environmental Conservation	Ground Zero, Manhattan <sup>4</sup>	Asbestos, PM <sub>2.5</sub> , PM <sub>10</sub>	Outdoor air	Asbestos 10/1/01; PM prior to 9/11
NY State Department of Occupational Health	Lower Manhattan	VOCs, aldehydes, acids, TSP	Outdoor air	9/28/01
NY State Department of Labor	Ground Zero	Asbestos, metals, aldehydes, CO	Worker exposure	9/26/01
NY City Department of Environmental Protection	Manhattan	Asbestos	Outdoor air	9/14/01
Occupational Safety and Health Administration	Ground Zero, financial district <sup>5</sup>	VOCs, asbestos, PCBs, CO, silica	Worker exposure	9/13/01
Port Authority	Ground Zero	VOCs	Worker exposure	9/28/01
US Geological Survey	Ground Zero	Metals, asbestos	Settled dust	9/16/01
US Department of Interior	Ground Zero	Meteorology	Outdoor	10/15/01
Columbia University	Manhattan	Metals	Outdoor air, sediment cores	9/01; ongoing
Environmental and Occupational Health Sciences Institute	Ground Zero	Metals, SVOCs, dioxins, furans, asbestos	Settled dust	9/16/01–9/19/01
Johns Hopkins University	Ground Zero	PM, asbestos, metals	Outdoor air, worker exposure	10/01
New York University	Lower Manhattan	PM <sub>2.5</sub> , metals	Outdoor air, settled dust	9/01
University of California, Davis	Manhattan	PM (various sizes), metals, PAHs, SVOCs	Outdoor air	10/3/01
University of North Carolina	Ground Zero, lower Manhattan	PAHs	Outdoor air	9/21/01

<sup>1</sup>Ground Zero is the site of the WTC complex. Monitoring took place either on the rubble pile or in the immediate vicinity (~100 m).<sup>2</sup>Lower Manhattan is approximately south of Canal Street.<sup>3</sup>Landfill is the Fresh Kills Landfill located on Staten Island.<sup>4</sup>Manhattan is approximately north of Canal St.<sup>5</sup>Financial District is located in the southeast quadrant of lower Manhattan.

Note: CO = carbon monoxide; VOC = volatile organic compound; SVOC = semivolatile organic compound; EC = elemental carbon; OC = organic carbon; PAH = polycyclic aromatic hydrocarbon; PCB = polychlorinated biphenyl; PM = particulate matter; TSP = total suspended particulate (subscript indicates aerodynamic diameter in microns).

Source: A. Vette.

### INFAMOUS AIR POLLUTION EPISODES (*cont'd*)

(although increasing to above 5 ppb in one reading in January 2002).

Concentrations of airborne dioxins were monitored away from Ground Zero. Dioxins are semivolatile products of incomplete combustion. Thus, as expected, dioxin concentrations were highest in October and November (as high as 10 picogram per cubic meter ( $\text{pg m}^{-3}$ )) and decreasing after the fires were extinguished to less than 1  $\text{pg m}^{-3}$ . Other semivolatile organic compounds were measured downwind, also showing compounds associated with combustion, including one not previously observed in ambient monitoring, diphenylpropane (likely due to burning plastics).

All measured pollutants displayed similar spatial and temporal trends, i.e. highest near the fires and highest in September and October 2001.

In such emergencies, it is most important to know the local wind direction at the accident site, to determine the extent of the area to be immediately evacuated. The next important factor is the wind speed, so that the pollutant transport time to various areas can be determined. Both can be estimated on-site by simple means, such as watching the drift of bubbles released by a bubble machine. It would be well to keep in mind that wind speeds increase with height above the surface and that wind direction is different at height

than at the surface. In fact, the WTC episode dramatically demonstrated the importance of local meteorology. The wind directions at Ground Zero were almost always different than those measured at any of the three nearby, major airports. And, the three airports often have meteorological conditions different from one another.

As evacuation is taking place, it is important to determine whether meteorological events will cause a wind direction shift later on, requiring a change in the evacuation scenario. Particularly in coastal areas, or areas of complex terrain, and slopes, authorities should be alert to a possible change in wind direction between night and day. Useful advice may be obtained from the nearest weather forecaster, although accurate forecasting of wind direction for specific locations is not easy. Accurate air movement measurements and predictions are a matter of safety, even life and death. Portable meteorological stations are becoming increasingly accurate, precise, and reasonably available. These should be deployed during any emergency involving airborne contaminants, or the potential for such.

If the situation is one of potential rather than current release, specific concentrations at various distances and localities may be estimated for various conditions by using atmospheric dispersion models.

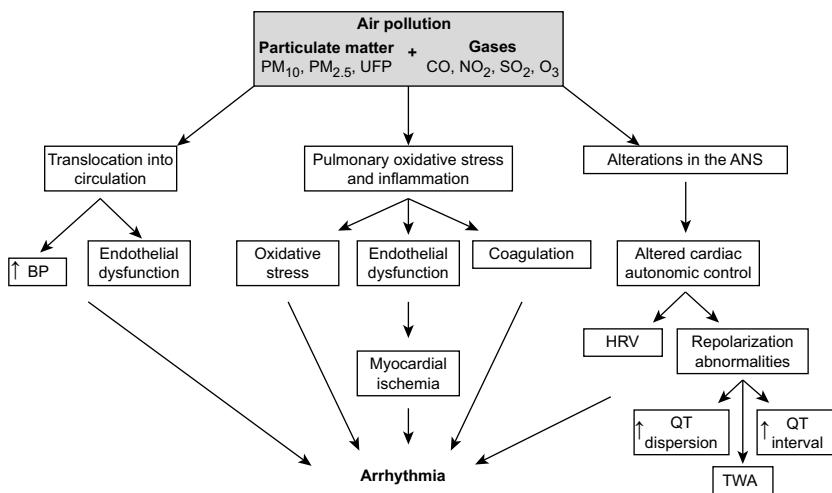
### **10.3 CARDIOVASCULAR EFFECTS**

There are a number of mechanisms and steps between exposure to an air pollutant and cardiovascular effects. For example, three mechanistic pathways have been proposed to link aerosol and gas-phase air pollutants to arrhythmia (see [Figure 10.4](#)). The pollutant may be translocated, whereupon it raises blood pressure and causes endothelial dysfunction, which in time leads to arrhythmia. The pollutant may induce oxidative stress and inflammation that increase coagulation, which in turn leads to myocardial ischemia. The oxidative stress, myocardial ischemia, and coagulation then lead to arrhythmia. Finally, the pollutant may alter the autonomic nervous system, which changes cardiac autonomic control. This can lead to heart rate variability (HRV) and repolarization abnormalities and changes to rhythm, which lead to arrhythmia.<sup>13</sup>

Most of the interest in ambient air pollution's role in cardiovascular disease has focused on chronic effects, e.g. the effects of long-term exposure to PM and

second-hand smoke (SHS) on heart disease. However, short-term, acute effects have also been associated with certain air pollutants, especially when a person has other risk factors, such as obesity, hypertension, and dyslipidemia (i.e. abnormal amounts of cholesterol, fats, and other lipids in blood).

Particulate matter is a primary air pollutant that has been associated with both acute and chronic cardiovascular disease. As evidence, beginning in 1987 the National Mortality and Morbidity Air Pollution Study (NMMAPS) has compared ambient concentrations of  $\text{PM}_{10}$  with morbidity and mortality in the largest US cities. The data indicate that daily mortality increased 0.21% ( $\pm 0.06$  standard error (SE)) and cardiopulmonary mortality increased 0.31% ( $\pm 0.09$  SE). These increases indicate that with each  $10 \mu\text{g m}^{-3}$  increase in daily ambient  $\text{PM}_{10}$  concentrations, there is a concomitant increase in total mortality and cardiovascular mortality rates. Conversely, each incremental decrease in  $\text{PM}_{10}$  concentrations would translate into improved cardiovascular health.<sup>14</sup> The effect is even more dramatic for



**FIGURE 10.4** Possible biological mechanisms linking air pollution with cardiac arrhythmia. ANS, autonomic nervous system; BP, blood pressure; CO, carbon monoxide; HRV, heart rate variability; O<sub>3</sub>, ozone; NO<sub>2</sub>, nitrogen dioxide; PM, particulate matter; SO<sub>2</sub>, sulfur dioxide; TWA, T wave alternans; UFP, ultrafine particles. Ref. 13.

finer particles. As evidence, an American Cancer Society<sup>11,15</sup> cohort study found that each 10 µg m<sup>-3</sup> increase in annual average PM<sub>2.5</sub> ambient concentration was associated with a 4% increase in mortality from all causes, as well as a 6% increase in cardiopulmonary-related mortality.

There appears to be a link between acute and chronic exposure to PM and cardiovascular events. These may be related to increases in heart rate and blood pressure, fibrinogen, and blood coagulation factors; arterial vasoconstriction; inflammatory mediators (e.g. C-reactive protein); endothelial injury/dysfunction; and decreases in heart rate variability.<sup>16</sup> These can then lead to myocardial ischemia, malignant ventricular arrhythmias, increased plaque vulnerability, and enhanced potential for acute thrombosis triggering acute coronary syndromes.<sup>17</sup> Further support for these changes has been drawn from studies of SHS, also known as environmental tobacco smoke, which is the single largest contributor to indoor PM when a smoker is present.<sup>18</sup> Exposure to SHS increases platelet activation, rapidly deteriorates endothelial function, promotes atherosclerotic plaque development, and increases the likelihood of infarct expansion.<sup>17</sup>

These and other studies indicate that even low doses of air pollution over time induce changes in coronary morphology and circulation, which lead to cardiovascular problems, i.e. air pollutant exposure accelerates the development of coronary atherosclerosis and worsens its sequelae.

Indeed, cardiovascular effects are both acute (quite abrupt, e.g. arrhythmia or myocardial infarction by acute inflammatory responses, altered platelet adhesiveness, or perhaps vascular endothelial dysfunction) and chronic (e.g. acceleration of the progression

of atherosclerosis). High concentrations of ambient particles can trigger the onset of acute myocardial infarction, but the stress caused by exposure to even low doses over time has been associated with chronic cardiovascular diseases.

### 10.3.1 Carbon Monoxide: a Cardiovascular Agent

Carbon monoxide (CO) exposure is a profound example of a mechanism of chronic cardiovascular effects induced by an air pollutant. The CO molecule binds to hemoglobin at a much higher preferential rate compared to oxygen ( $\approx 240:1$ ).<sup>19</sup> Tying up the oxygen carrier in the blood, hemoglobin results in COHb not easily releasing the carbon monoxide. Therefore, hemoglobin will not be available to transport oxygen from the lungs to the rest of the body. High concentrations of COHb are referred to as carboxyhemoglobinemia, which if sufficiently high leads to death. Carbon monoxide also decreases O<sub>2</sub> storage in muscle cells by binding to the O<sub>2</sub> and displacing the O<sub>2</sub> from myoglobin. All tissues are vulnerable to carbon monoxide-induced hypoxic injury, but those having the highest O<sub>2</sub> demand are particularly vulnerable. The brain and heart are particularly vulnerable, and the fetus may also be a sensitive target of carbon monoxide, through hypoxic and/or nonhypoxic mechanisms.<sup>20</sup>

At lower COHb concentrations, the continuous oxygen deprivation stresses the cardiovascular system. Exposure to CO and elevated COHb blood concentrations have been associated with blood clotting, which may be the mechanistic link of smoking and thromboembolism. Likewise, COHb crosses the placental membranes, causes vasoconstriction of the placenta,

which lowers birth weight. Since unborn children absorb CO faster and more efficiently than adults, this could lead to hypoxia, with resulting developmental problems.

The kinetics of carbon monoxide is fairly straightforward. For example, blood COHb concentrations can be compared to specific categories of health effects. Knowing the CO respiratory exposure dose can be used to estimate COHb in the blood. Table 10.2 can be even used to convert the reported ambient air carbon monoxide concentrations into equivalent predicted blood COHb levels. There is much uncertainty with such dose interconversions. Predicted COHb levels and corresponding exposure concentrations may have greater relevance to outcomes mediated through hypoxic mechanisms than to those mediated through nonhypoxic mechanisms. In addition, steady state requires exposure durations of approximately 16–24 h. Exposures to lower levels of carbon monoxide for longer durations and exposures to higher levels for shorter durations that achieve similar blood COHb levels likely will not indicate similar results.<sup>21</sup>

**TABLE 10.2** Predicted Steady State Blood Carboxyhemoglobin (COHb) Levels

Carbon Monoxide Exposure Concentration (ppm)	Steady State Blood COHb (%)
0.1	0.25
0.5	0.32
1	0.39
2	0.50
5	1.0
10	1.8
15	2.5
20	3.2
40	6.1
60	8.7
80	11
100	14
200	24
400	38
600	48
800	56
1000	61

Source: Agency for Toxic Substances and Disease Registry. Toxicological Profile for Carbon Monoxide. <http://www.atsdr.cdc.gov/ToxProfiles/tp.asp?id=1145&tid=253>; 2012 [accessed on 15.10.13].

### 10.3.2 Co-occurring Pollutants and Cardiovascular Effects

Some of the cardiovascular effects from CO exposure are tachycardia, tachypnea rhabdomyolysis, palpitations, cardiac dysrhythmias, hypotension, myocardial ischemia, and cardiac arrest.<sup>22</sup> However, CO concentrations in the ambient air are somewhat difficult to link directly to health effects since CO exposure tends to be strongly correlated with other air quality variables that can affect cardiovascular function, either directly or indirectly (e.g. via respiratory effects discussed in Chapter 9). Typical variables that correlate with CO concentrations include PM<sub>10</sub>, PM<sub>2.5</sub>, NO<sub>2</sub>, O<sub>3</sub>, and SO<sub>2</sub>. That is, in the ambient environment, CO is seldom the only air pollutant that is detected. Near-road environments also have cardiovascular air pollutants such as PM, NO<sub>2</sub>, benzene, and 1,3-butadiene. Urban areas often have O<sub>3</sub>, PM, numerous air toxins, oxides of nitrogen, and oxides of sulfur. Even in the instance of SHS (environmental tobacco smoke), CO is one of myriad cardiovascular pollutants, including polycyclic aromatic hydrocarbons.

These co-exposures present a statistical dilemma. Ignoring co-variables that contribute to risk in regression models (e.g. single-pollutant models) will bias risk assessments upwardly (false positives). However, assuming that strongly correlated co-variables are independent in multipollutant models introduces downward bias. The conservative approach would be to avoid false negatives, since there may be synergism among the co-occurring pollutants. Not all studies have explored multipollutant models, but most of those that have tend to support evidence similar to the results of clinical studies that have shown CO to exacerbate coronary vascular disease.<sup>21</sup>

Air pollutants that affect cardiovascular systems are most problematic for sensitive subpopulations, including unborn children, infants, asthmatics, the elderly, and the immunocompromised. For many air pollutants, exposure concentrations correspond to levels that may have relatively small impacts on the general population, but dramatic effects on these sensitive groups. This is true for acute impacts where highly susceptible individuals exhibit serious outcomes following increases in exposures to pollutants. For these and other reasons, cardiovascular epidemiologic studies often focus on highly susceptible populations. A typical design has been to examine associations between temporal trends in ambient pollution concentrations and hospital admissions or emergency department visits for which the reported diagnosis was some form of cardiovascular and/or respiratory disease of impairment. For example, worldwide hospital admissions appear to increase following an episode of elevated SO<sub>2</sub> ambient air concentrations.<sup>23</sup>

Although PM, CO, and other air pollutants linked to cardiovascular effects have been decreasing in developed countries, they have not shown these trends in many developing nations. People around the world are exposed to unhealthy concentrations of PM, CO, SO<sub>2</sub>, and other pollutants that stress cardiovascular systems. For example, indoor air contaminants pose a risk to the health of over half of the world's population. In homes where biomass fuels and coal are used for cooking and heating, PM levels may be 10–50 times higher than the guideline values.<sup>24</sup>

### 10.3.3 Indirect Cardiovascular Effects

The major steps between air pollutant exposure and cardiovascular effects involve inhalation of the air pollutant, followed by physiological mechanisms that lead to cardiovascular and cardiopulmonary disease (Figure 10.4). There are two other types of air pollution-linked cardiovascular paradigms: exposure routes other than inhalation and effects from changes in the environment induced by air pollution.

#### 10.3.3.1 Nonrespiratory Routes

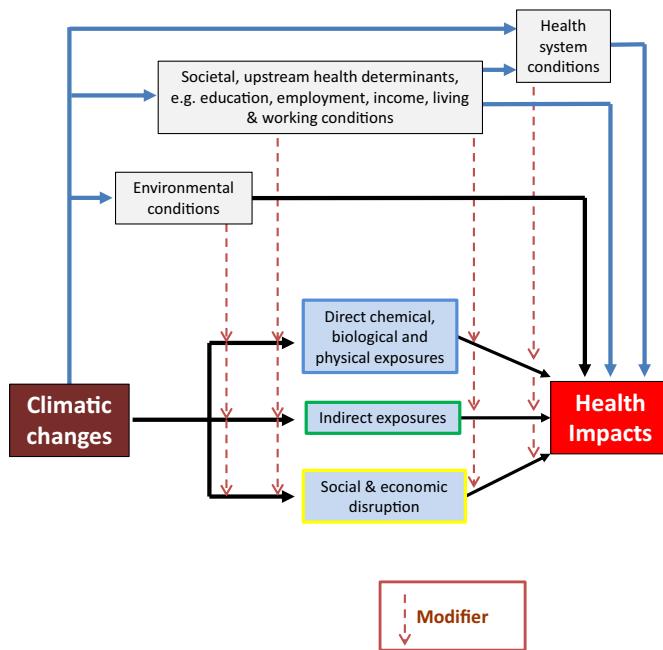
As discussed in Chapter 8, inhalation is the dominant exposure route for air pollutants, but is not the exclusive pathway to effects. Household dust, for example, is a major pathway for exposure to air pollutants. Following PM deposition onto food translates into an ingestion pathway (see Figure 8.5). Deposition onto surfaces can lead to dermal exposures.

These different routes would change the biological mechanisms linking air pollution with cardiovascular and other effects. This is because absorption into the gastrointestinal tract or through skin may change the kinetics and lead to different amounts and types of metabolites. These have their own mechanisms, which may or may not resemble those that begin with a pollutant entry via respiration.

#### 10.3.3.2 Environmental Changes Leading to Effects

The cardiovascular system works best under optimal environmental conditions, including acceptable ambient temperature and oxygen. Relatively small changes that alter environmental conditions so that an organism is outside of the optimal range that supports life will stress the cardiovascular system in humans and other animals.

Meteorological conditions certainly affect health. Previous discussions in this chapter addressed the more direct effects from air pollutants. Even within the category of climate change-induced health effects, cardiovascular and other outcomes can be brought about directly or indirectly, through multiple causal pathways (see Figure 10.5).



**FIGURE 10.5 Human health causal pathways possibly resulting from global climate change.** Direct chemical exposures could include increased bioavailability of chemical contaminants, e.g. higher temperatures increase transformation; it would also include increased use of chemicals to address problems, e.g. change in insect and microbial populations. Indirect exposures can include changes in water, air, and food quality, as well as changes in vector ecology, ecosystem conditions, agricultural operations, and industry. Indirect exposure may also include releases from contaminant sinks, such as sediments. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Ref. 25.

Any increase in the number and severity of other events, such as flooding, will also increase psychological stress and concomitant cardiovascular response (e.g. indicated by increased hospital admissions).

Changes in environmental conditions, e.g. warmer temperatures and altered hydrological cycle, can also lead to changes in ecosystems that in turn affect human health. Climate change can alter seasonality of some allergenic species and disease vectors. Insect and other vector populations could lead to increases in the number and severity of vector-borne diseases. These include changes in spatial and temporal distributions of malaria, dengue, tick-borne diseases, cholera, and some other diarrheal diseases.<sup>25</sup> These diseases can be expected to increase cardiovascular and other stress in human populations. Thus, opportunistic diseases brought on by environmental change that is induced by air pollutants (e.g. greenhouse gases) can result in increased cardiovascular effects in populations.

One of the considerations of global climate change is the extent to which the release of air pollutants may create extreme heat events. Heat waves are generally characterized by several days of warm, stable air

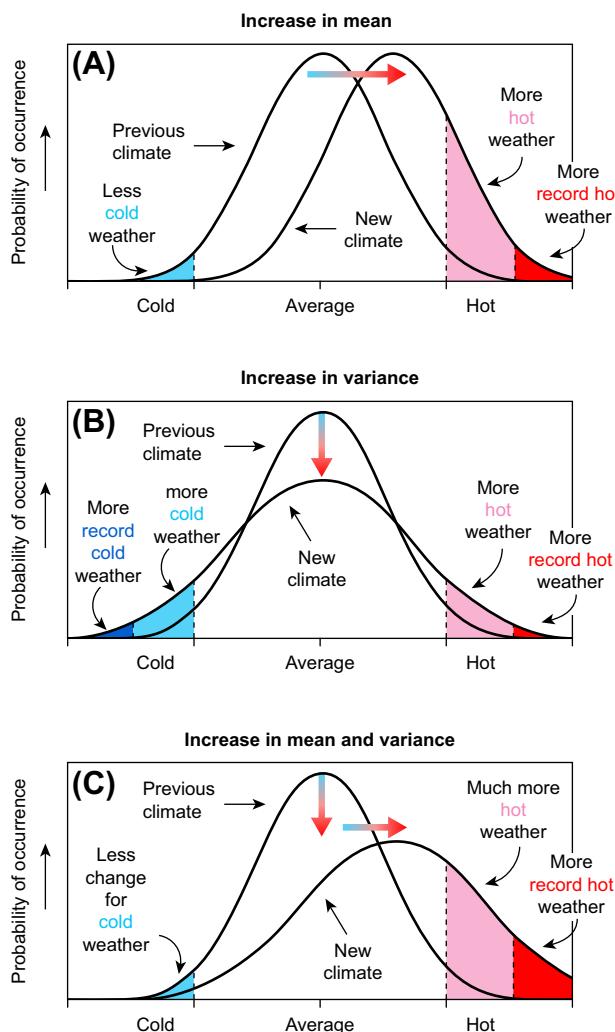
masses, with daytime temperatures  $>32^{\circ}\text{C}$ , and consecutive nighttime temperatures above normal. If climate change does indeed increase the number of and severity of heat waves in the temperate zones, this will be met by greater cardiovascular effects (see Figure 10.6).

Heat waves presently are the most deadly weather-related exposure in the United States, leading to a greater number of deaths annually than those attributed to hurricanes, tornadoes, floods, and earthquakes combined. Like direct air pollutant exposures, heat-sensitive subpopulations include children and the elderly. Climate change will bring more heat waves to the United States. Increases in the number of people living in cities, as well as population aging, will further increase heat-related health risks. Studies suggest that, if

current emissions hold steady, excess heat-related deaths in the United States may increase from the present average of about 700 each year to as many as 5000 per year by 2050.<sup>26</sup>

The indirect health effects demonstrate the complexity of causal links between emissions of air pollutants and health. This applies not only to cardiovascular effects but also to most other adverse health and ecological outcomes. This is important to keep in mind when reading the previous chapter and the next four chapters.

## QUESTIONS



**FIGURE 10.6** Potential shifts in the distribution of cold and hot weather as a result of climate change, showing the probabilities of greater hot weather with increases in mean temperature and variance around the mean. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 26.

1. Give an example of an air pollutant that causes direct cardiovascular damage.
2. Give an example of an air pollutant that indirectly leads to cardiovascular damage.
3. How did the Bhopal and Chester incidents differ from the other episodes in the discussion box?
4. How do emergency situations affect the behavior of semivolatile organic compounds?
5. What types of air pollutants were released and transported from the Chernobyl incident?
6. What problem is there with using airport meteorological conditions to respond to emergencies?
7. What are three ways that an air pollutant exposure can lead to arrhythmia?
8. What is the preferential rate of CO compared to O<sub>2</sub> in binding to hemoglobin?
9. Predict the steady-state blood COHb concentration of a person exposed to 5 ppm, a person exposed to 100 ppm and a person exposed to 200 ppm of carbon monoxide. Where might such exposures occur? What does this tell you about exposure and risk from CO?
10. Does a conservative approach to studying air pollution and cardiovascular disease more likely avoid false positives or avoid false negatives? Why?
11. What are examples of nonchemical stressors that co-occur with chemical air pollutants associated with cardiovascular disease?
12. Are such nonchemical stressors always distinct from air pollution?

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9. As the name implies, first responders are the teams who first arrive on the scene of an emergency. They include firefighters, HAZMAT teams, police, and medical personnel. These people are particularly vulnerable to exposures. Often, the contents of items and areas needing response are not well known, so the wrong treatment or response can be dangerous, such as spraying water on low-density or water-reactive substances. Other vulnerabilities include the frenetic nature of an emergency response. For example, the first responders to the WTC attacks on September 11, 2001, had incompatible radios and, since cell phone networks collapsed, they were not able to communicate well with each other. This undoubtedly led to a number of deaths. The vulnerability has been articulated well by Captain Larry R. Collins, a 24 year member of the Los Angeles County Fire Department (Frontline First Responder, April 5, 2003):  
*A truly accurate assessment of the stability of damaged structures often requires the skill, experience, training, and knowledge of a certified structural engineer who is prepared to perform a risk analysis and make certain calculations about the weight of the material, the status of key structural members, how the loads have been redistributed after the event, and the need for stabilization or evacuation. Unfortunately, first responders typically do not have those capabilities, and when lives are hanging in the balance, they do not have the luxury of time to wait for a structural engineer. Someone needs to make immediate decisions about firefighting, search and rescue, and other emergency operations.*
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# Cancer and Air Pollutants

## 11.1 LINKING AIR POLLUTION TO CANCER

Since the most prominent type of cancer associated with air pollution is lung cancer and since cancer is a chronic effect, many texts include cancer in a discussion of chronic respiratory effects (Chapter 8). However, there are a number of different types of cancers associated with airborne carcinogens. Indeed, the major exposure route for airborne carcinogens is inhalation, but the cancer outcomes can occur at numerous sites in the body.

Ambient air pollutants include carcinogens in both the vapor and particulate phases with sorbed compounds, metals and metallic compounds, and other substances that are capable of causing oxidative stress, inflammation, and genetic defects. Even at low doses, airborne pollutant exposure is a major contributor to lung and other cancers. A recent study in Europe of more than 300,000 cohorts representing over 4 million person-years at risk found that following exposures to particulate matter (PM), the risks of lung cancer are elevated incrementally by PM concentration.<sup>1</sup> For example, when exposed to the coarse fraction of PM (aerodynamic diameters  $>2.5\text{ }\mu\text{m}$  and  $<10\text{ }\mu\text{m}$ , i.e.  $\text{PM}_{10}$ ) for every concentration increase of  $10\text{ }\mu\text{g m}^{-3}$  was associated with a 22% increase in the hazard ratio (HR) for lung cancer incidence (i.e. newly reported cases in a year). For the fine fraction of PM (aerodynamic diameters  $<2.5\text{ }\mu\text{m}$ , i.e.  $\text{PM}_{2.5}$ ), for every increase of  $5\text{ }\mu\text{g m}^{-3}$ , there was 18% increase in the HR for lung cancer. These associations between risk for lung cancer and PM are statistically significant:

- $\text{PM}_{10}$  HR = 1.22 (95% confidence interval (CI) 1.03–1.45) per  $10\text{ }\mu\text{g m}^{-3}$ ; and
- $\text{PM}_{2.5}$  HR = 1.18 (0.96–1.46) per  $5\text{ }\mu\text{g m}^{-3}$ .

The associations also hold for specific types of lung cancer. The  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  HRs for adenocarcinomas

of the lung were found to be 1.51 (1.10–2.08) and 1.55 (1.05–2.29), respectively. Since all of the CI values are greater than 1, the associations between increased cancer risk and PM concentrations in the ambient air are significant at a 95% level of confidence. Indeed, the study concluded that at PM concentrations even below European Union limit values, ambient PM plays a role in lung cancer development.

The cancer HR in this context is actually a type of relative risk (see Chapter 4). Generally, the difference between the HR and relative risk is that the HR is an instantaneous event whereas relative risk is cumulative, i.e. the relative risk can only be reported following the study, whereas the HR can be calculated during the study at different points in time. In this case, ambient PM concentration intervals were compared to cases of cancer over more than a decade. If the concentration made no difference in cancer incidence, the HR and relative risk would be 1. If cancer incidence increased in accordance with PM concentration, the values would be  $>1$ . If cancer incidence had increased, the values would have been  $<1$ .<sup>a</sup>

The study also found an association between lung cancer HR and the volume of road traffic, i.e. 4000 vehicle km per day within 100 m of the residence was associated with an HR for lung cancer of 1.09 (0.99–1.21), although the CI does fall below 1. This nonchemical variable (i.e. location, not chemical concentration) could indicate the presence of airborne carcinogens, including PM but others as well, near roadways in Europe.<sup>1</sup> For example, benzene and 1,3-butadiene are often detected in the air near roadways.

The actual reasons for the link between PM and cancer are not completely clear. PM is composed of various chemical compounds, among which there are often carcinogens. However, the properties of the aerosol itself also play a role since PM from various sources and numerous locations tend to be linked to cancer.

<sup>a</sup>If an HR or relative risk from a factor (e.g. healthy diet) decreases significantly, this is considered to be a protective factor.

### 11.1.1 Cancer Etiology

A prominent hypothesis in carcinogenesis is the “two hit” theory, suggested by A.G. Knudson<sup>2</sup> in 1971. The theory argues that cancer develops after genetic material (i.e. usually deoxyribonucleic acid, DNA) is damaged. The first damage is known as “initiation”. This step may, but does not necessarily, lead to cancer. The next step, “promotion”, changes the cell’s makeup and nature, such as the loss of normal homeostasis (cellular self-regulation), and the rapid division of clonal tumor cells. Promoters may or may not be carcinogens. Health researchers and regulating agencies usually do not assign a safe concentration of exposure to a carcinogen. They do, however, use the reference concentration (RfC)<sup>b</sup> to assign a level of exposure that is “safe” in terms of health hazard for all diseases except cancer.

The criteria for causality discussed in Chapter 4 were developed by A. Bradford Hill as a means of linking risk factors to cancer.<sup>3</sup> Recall that these criteria are:

1. Strength of association,
2. Consistency,
3. Specificity,
4. Temporality,
5. Biologic gradient,
6. Plausibility,
7. Coherence,
8. Experimentation,
9. Analogy.

Strength of association and biological gradient are established by the cancer dose–response curves. These curves are the source of the cancer slope factor (CSF) for individual carcinogenic substances. The CSF is the principal hazard characteristic for carcinogens. It is an upper bound estimate, approximating a 95% confidence limit, of the increased cancer risk from a lifetime exposure to an agent. This estimate, usually expressed in units of proportion (of a population) affected per  $\text{mg kg}^{-1} \text{ day}^{-1}$ , is generally reserved for use in the low-dose region of the dose–response relationship; that is, for exposures corresponding to risks less than 1 in 100.<sup>c</sup>

The slope factor can be related to risk as follows:

$$\text{CSF} = \text{risk per unit dose} = \text{risk per } \text{mg kg}^{-1} \text{ day}^{-1} \quad (11.1)$$

Table 11.1 provides the CSF values for a number of potential air pollutants. Both factors are developed from a mix of mutagenicity studies, animal testing,

and epidemiology. Public health policy often holds that there is no “safe” level of exposure for carcinogens, i.e. dose–response models include no threshold. That is, cancer dose–response curves often do not include a “no observable adverse effect level” (NOAEL) or a “lowest observed adverse effect level”. Instead, CSFs are used to calculate the estimated probability of increased cancer incidence over a person’s lifetime (the so-called “excess lifetime cancer risk”).

Cancer is a type of mutation of genetic material of normal cells, which changes the normal balance between proliferation and cell death in favor of uncontrolled tumor cell division. The process of producing uncontrolled and rapidly dividing cells is known as *tumorigenesis*. These may mutate into malignant tumors (cancer). Such tumors can metastasize into other organs, meaning that lung and other cancers associated with air pollutants can lead to cancers at other sites.

Cancer involves billions of cells that theoretically originate from an initial cell that is cloned, escapes apoptosis (i.e. normal, programmed cell death), and becomes genetically altered into a new cell. This process forms new cellular material (neoplasms) that may be benign or malignant. Next, the constituent cells of malignant neoplasia are the result of numerous biochemical processes, including neoplastic differentiation; insensitivity to antigrowth signals; tissue invasion and metastasis; limitless replicative potential; evasion of apoptosis; sustained angiogenesis (i.e. development of new blood vessels); expression of telomerase (i.e. enzyme for adding nucleotides to cancer cells); and self-sufficient growth signals.<sup>5</sup>

A series of several mutations to certain classes of genes is usually needed for a normal cell to transform into a cancer cell.<sup>6</sup> This can entail numerous “driver mutations” and “passenger” mutations.<sup>7</sup> Driver mutations give selective advantage to a clone, which leads to clonal expansion. Passenger mutations or “gene hitchhikers” do not necessarily give an advantage to the clone, but can increase the frequency of cell growth since they are closely linked to selectively advantageous genes. The mutation mechanism involves a number of steps before carcinogenesis (Figure 11.1).

The pathway to carcinogenesis varies both inside and outside of the body. The compounds released into the atmosphere may be parent carcinogens. They may also include precursors to carcinogens (top of Figure 11.1). These precursors may be transformed in the atmosphere into carcinogens. They may also be transformed into

<sup>b</sup> For ingestion and dermal routes of exposure, the reference dose (RfD) is used. It is applied in exactly the same manner as the RfC.

<sup>c</sup> This text makes an effort to avoid using the slash in units, preferring the use of exponents (e.g.  $\text{mg m}^{-3}$  is preferable to  $\text{mg m}^{-3}$ ). However, for environmental exposure calculations, most literature uses the slash, i.e.  $\text{mg} (\text{kg day})^{-1}$ , so these units are used for exposure and its inverse, i.e.  $(\text{mg kg}^{-1} \text{ day}^{-1})^{-1}$ , for cancer slope factors.

TABLE 11.1 Cancer Slope Factors for Selected Environmental Contaminants<sup>4</sup>

Contaminant	Inhalation Slope Factor ((mg kg <sup>-1</sup> day <sup>-1</sup> ) <sup>-1</sup> )	GI Absorption
Acephate	$1.74 \times 10^{-2}$	0.5
Acrylamide	4.55	0.5
Acrylonitrile	$2.38 \times 10^{-1}$	0.8
Aldrin	$1.71 \times 10^1$	1
Aniline	$5.70 \times 10^{-3}$	0.5
Arsenic	$1.51 \times 10^1$	0.95
Atrazine	$4.44 \times 10^{-1}$	0.5
Azobenzene	$1.09 \times 10^{-1}$	0.5
Benzene	$2.90 \times 10^{-2}$	0.9
Benz(a)anthracene	$3.10 \times 10^{-1}$	0.5
Benzo(a)pyrene	3.10	0.5
Benzo(b)fluoranthene	$3.10 \times 10^{-1}$	0.5
Benzo(k)fluoranthene	$3.10 \times 10^{-2}$	0.5
Beryllium	8.40	0.006
Benzotrichloride	$1.63 \times 10^1$	0.8
Benzyl chloride	$2.13 \times 10^{-1}$	0.8
Bis(2-chloroethyl)ether	1.16	0.98
Bis(2-chloroisopropyl)ether	$3.50 \times 10^{-2}$	0.8
Bis(2-ethyl-hexyl)phthalate	$1.40 \times 10^{-2}$	0.5
Bromodichloromethane	$6.20 \times 10^{-2}$	0.98
Bromoform	$3.85 \times 10^{-3}$	0.75
Cadmium	Not given	0.044
Chlordane	$3.50 \times 10^{-1}$	
Captan	$7.00 \times 10^{-3}$	0.5
Chlorodibromomethane	$8.40 \times 10^{-2}$	0.8
Chloroethane (Ethylchloride)	$2.90 \times 10^{-3}$	0.8
Chloroform	$8.05 \times 10^{-2}$	1
Chloromethane	$3.50 \times 10^{-3}$	0.8
Chromium(VI)	$3.50 \times 10^{-3}$	0.013
Chrysene	$3.10 \times 10^{-3}$	0.5
DDD	$2.40 \times 10^{-1}$	0.8
DDE	$3.40 \times 10^{-1}$	0.8
DDT	$3.40 \times 10^{-1}$	0.8
Dibenz(a,h)Anthracene	3.10	0.5
Dibromo-3-Chloropropane,1,2-	$2.42 \times 10^{-3}$	0.5
Dichlorobenzene,1,4-	$2.20 \times 10^{-2}$	1
Dichlorobenzidine,3,3-	$4.50 \times 10^{-1}$	0.5

(Continued)

TABLE 11.1 Cancer Slope Factors for Selected Environmental Contaminants<sup>4</sup>—cont'd

Contaminant	Inhalation Slope Factor ((mg kg <sup>-1</sup> day <sup>-1</sup> ) <sup>-1</sup> )	GI Absorption
Dichloroethane,1,2-	$9.10 \times 10^{-2}$	1
Dichloroethene (mixture),1,1-	$1.75 \times 10^{-1}$	
Dichloromethane	$7.50 \times 10^{-3}$	1
Dichloropropane,1,2-	$6.80 \times 10^{-2}$	1
Dichloropropene,1,3-	$1.30 \times 10^{-1}$	0.98
Dieldrin	$1.61 \times 10^1$	1
Dinitrotoluene, 2,4-	$6.80 \times 10^{-1}$	1
Dioxane, 1,4-	$2.20 \times 10^{-2}$	0.5
Diphenylhydrazine, 1,2-	$7.70 \times 10^{-1}$	0.5
Epichlorohydrin	$4.20 \times 10^{-3}$	0.8
Ethyl acrylate	$6.00 \times 10^{-2}$	0.8
Ethylene oxide	$3.50 \times 10^{-1}$	0.8
Formaldehyde	$4.55 \times 10^{-2}$	0.5
Heptachlor	4.55	0.8
Heptachlor epoxide	9.10	0.4
Hexachloro-1,3-butadiene	$7.70 \times 10^{-2}$	1
Hexachlorobenzene	1.61	0.8
Hexachlorocyclohexane, alpha	6.30	0.974
Hexachlorocyclohexane, beta	1.80	0.907
Hexachlorocyclohexane, gamma (lindane)	1.30	0.994
Hexachloroethane	$1.40 \times 10^{-2}$	0.8
Hexahydro-1,3,5-trinitro-1,3,5-traizine (RDX)	$2.22 \times 10^{-1}$	0.5
Indeno(1,2,3-cd)pyrene	$3.10 \times 10^{-1}$	0.5
Isophorone	$9.50 \times 10^{-4}$	0.5
Nitrosodi- <i>n</i> -propylamine, <i>n</i> -	7.00	0.475
Nitrosodiphenylamine, <i>n</i> -	$4.90 \times 10^{-3}$	0.5
Pentachloronitrobenzene	$5.20 \times 10^{-1}$	0.5
Pentachlorophenol	$1.20 \times 10^{-1}$	0.5
Phenylphenol, 2-	$3.88 \times 10^{-3}$	0.5
Polychlorinated biphenyls (Arochlor mixture)	$3.50 \times 10^{-1}$	0.85
Tetrachlorodibenzo- <i>p</i> -dioxin, 2,3,7,8	$1.16 \times 10^5$	0.9
Tetrachloroethane,1,1,1,2-	$2.59 \times 10^{-2}$	0.8
Tetrachloroethane,1,1,2,2-	$2.03 \times 10^{-1}$	0.7
Tetrachloroethene (PCE)	$2.00 \times 10^{-3}$	1
Tetrachloromethane	$5.25 \times 10^{-2}$	0.85
Toxaphene	1.12	0.63
Trichloroethane,1,1,2-	$5.60 \times 10^{-2}$	0.81
Trichloroethene (TCE)	$6.00 \times 10^{-3}$	0.945

TABLE 11.1 Cancer Slope Factors for Selected Environmental Contaminants<sup>4</sup>—cont'd

Contaminant	Inhalation Slope Factor ((mg kg <sup>-1</sup> day <sup>-1</sup> ) <sup>-1</sup> )	GI Absorption
Trichlorophenol, 2,4,6-	$1.10 \times 10^{-2}$	0.8
Trichloropropane, 1,2,3-	8.75	0.8
Trifluralin	$3.85 \times 10^{-3}$	0.2
Trimethylphosphate	$7.40 \times 10^{-2}$	0.5
Trinitrotoluene, 2,4,6- (TNT)	$6.00 \times 10^{-2}$	0.5
Vinyl chloride	$3.00 \times 10^{-1}$	0.875

Source: U.S. Environmental Protection Agency. 2002. Integrated Risk Information System; U.S. EPA. 1994. Health effects summary tables; 1994.

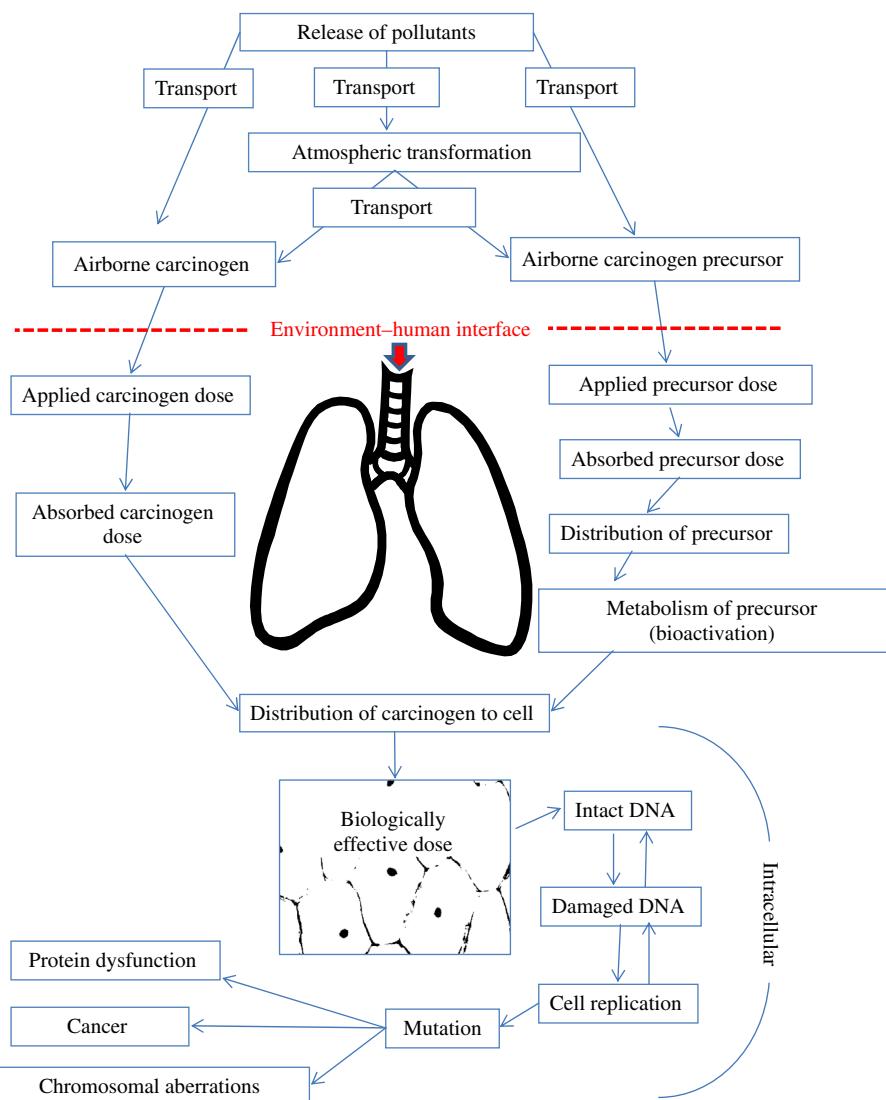


FIGURE 11.1 Pathway to carcinogenesis includes metabolic processes and endogenous chemicals, with a number of steps within the cell involving damage and repair of DNA. (For color version of this figure, the reader is referred to the online version of this book.) Bottom part of diagram adapted from Baltic University Programme. Chapter 14—How pollution affects life. In: Environmental science. [http://www.balticuniv.uu.se/environmentalscience/ch14/chapter14\\_g.htm](http://www.balticuniv.uu.se/environmentalscience/ch14/chapter14_g.htm); 2013 [accessed 17.10.13].

precursors that are not yet carcinogenic, but will become carcinogens as a result of endogenous processes within the organism (middle of [Figure 11.1](#)).

The process within the cell following distribution is the same, whether it is the parent compound that is carcinogenic, or one of the parent compound's atmospheric transformation products, or a metabolite of the parent compound or an exogenous transformation product that subsequently is bioactivated to become a carcinogen (bottom of [Figure 11.1](#)). Cancer is the result of mutation, but not all of these mutations become cancer. That is, all cancer begins with mutation, but not all mutation ends in cancer. The DNA damage and repair sequences could lead to cell death, protein dysfunction, chromosomal aberrations, or other expressions beside tumorigenesis.

As discussed in detail in Chapter 8, exposure is expressed as mass of an air pollutant per body mass per time, whereas slope factors are expressed in inverse exposure units since the slope of the dose-response curve is an indication of risk per exposure. Commonly, exposure is expressed in units of  $\text{mg kg}^{-1} \text{ day}^{-1}$  and the CSF is its inverse, i.e.  $(\text{mg kg}^{-1} \text{ day}^{-1})^{-1}$ .

The cancer slope indicates hazard (see Chapter 7). Since risk is the product of hazard and exposure, the product of the unit and the unit's inverse must be dimensionless. Risk is a unitless probability of the adverse outcome, i.e. cancer risk is the product of carcinogen hazard and the amount of exposure to that hazard. The CSF values are contaminant-specific and route-specific. Thus, one must not only know the contaminant, but how a person is exposed (e.g. via inhalation, via ingestion or through the skin).

Lifetime cancer risk can be defined as the theoretical probability of contracting cancer when continually exposed for a lifetime (e.g. 70 years) to a given concentration of a carcinogen. The probability is usually calculated as an upper confidence limit. The maximum estimated risk may be presented as the number of chances in a million of contracting cancer.

Two measures of risk are commonly reported. One is the individual cancer risk, i.e. the probability of a person developing cancer due to the exposure. This is often reported as a "residual" or increased probability above background. For example, to characterize the contribution of all the power plants in the United States to increased cancer incidence, the risk above background would be reported. The second way that cancer risk is reported is population risk, i.e. the annual excess

number of cancers in an exposed population. The maximum, worst case, individual risk might be calculated from exposure estimates based upon a "maximum exposed individual" or MEI. The hypothetical MEI lives an entire lifetime outdoors at the point where pollutant concentrations are highest. Assumptions about exposure greatly affect the risk estimates. For example, the cancer risk from power plants in the United States has been estimated to be to be 100- to 1000-fold lower for an average exposed individual than that calculated for the MEI.

## **11.2 ESTIMATING RISK FROM AIRBORNE CARCINOGENS**

Cancer risk varies by the potency of the carcinogen and the exposure to that carcinogen. As for any air pollution risk, cancer risk is a function of hazard and exposure. Since cancer is a chronic disease, the exposure must be long-term or at least must address the latency between exposure and cancer outcome. Thus, cancer risk assessments generally express hazard potency for the dose-response curves from animal research and human epidemiology. The quasi-linear segment of these curves provides what CSF and the long-term exposure is the lifetime average daily dose (LADD):

$$\text{Cancer risk} = \text{CSF} \times \text{LADD}$$

$$\text{LADD} = \frac{(C) \cdot (\text{IR}) \cdot (\text{EL}) \cdot (\text{AF}) \cdot (\text{ED})}{(\text{BW}) \cdot (\text{TL})} \quad (11.2)$$

Where C = chemical concentration (mass per volume); IR = inhalation rate (volume per time); EL = exposure length (time); AF = absorption factor (unitless); ED = exposure duration (time); BW = body weight (mass); and TL = typical lifetime (time). Usually, cancer occurs after prolonged exposure to a carcinogen. As such, the exposure setting must be characterized. This includes both the physical environment and the activities of the potentially exposed populations. From this assessment, sources of the air pollutant can be identified along with the possible routes of exposure. To quantify exposure, the concentration of the carcinogen and the intake variables must be assigned. Daily intake (DI) must be estimated or modeled:

$$\text{DI (mg per kg - day)} = \frac{\text{Concentration } (\text{mg volume}^{-1}) \times \text{Intake } (\text{volume day}^{-1})}{\text{body mass (kg)}} \quad (11.3)$$

Then, chronic daily intake can be estimated by averaging DI over long-term exposure (e.g. 70 years for LADD).

Exposure factors vary. For example, an average lifetime may be assumed to be 70 years, but the exposure duration (ED) may be for 25 years (e.g. the source may have only been operating for 25 years). Body weight may be assumed to be 70 kg; frequency of exposure may be <365 days a year (e.g. 250 days per year). The intake rate must account for time period and the amount of the air pollutant. For example, inhalation rates will vary by activity and person, so an average exposure inhalation rate may be used, e.g.  $2.5 \text{ m}^3 \text{ h}^{-1} \times 8 \text{ h day}^{-1}$ . However, as indicated in Table 11.2, inhalation rates can be age-dependent and highly variable.

As discussed in Chapter 8, an exposure equation<sup>8</sup> must account for both chemical concentration of the airborne carcinogen and a person's activities that affect the time of contact. The chemical intake ( $I$ ) is expressed in units of concentration (mass per volume or mass per mass) per time, such as  $\text{mg kg}^{-1} \text{ day}^{-1}$ . Since the intake of air pollutants is almost entirely via inhalation, the contaminant concentration in the air can be used exclusively.

$$I = C_A \times \frac{\text{IR}}{\text{BW}} \times \frac{\text{ET} \times \text{EF} \times \text{ED}}{\text{AT}} \quad (11.4)$$

Where  $C_A$  = contaminant concentration in air ( $\text{mg m}^{-3}$ )

IR = inhalation rate ( $\text{m}^3 \text{ h}^{-1}$ )

BW = body weight (kg)

ET = exposure time ( $\text{h day}^{-1}$ )

EF = exposure frequency ( $\text{days year}^{-1}$ )

ED = exposure duration (years)

AT = averaging time (days over which exposure is averaged).

Similarly, an exposure concentration (EC) is a time-weighted average concentration derived from measured or modeled concentrations of a contaminant in the air, but adjusted according to the characteristics of the exposure scenario. For an acute exposure, the EC and  $C_A$  values will almost be the same. However, estimating cancer risks from chronic exposure involves both the  $C_A$  measured at a point of exposure point as well as scenario-specific parameters, such as the EC and EF:

$$\text{EC} = \frac{C_A \times \text{ET} \times \text{EF} \times \text{ED}}{\text{AT}} \quad (11.5)$$

The value for AT for chronic exposures is ED in years  $\times$  365 days year $^{-1}$   $\times$  24 h day $^{-1}$ . Since this gives AT in hours, it is multiplied by 24 for an AT in days. Thus, EC usually is  $C_A$  that has been time-weighted over the duration of exposure and incorporates information on human activity patterns. The U.S. EPA cancer risk guidelines apply a linear extrapolation from exposures observed in animal studies or human occupational studies.<sup>9</sup> It is common to see EC combined with an inhalation unit risk (IUR), which is similar to the CSF, i.e. it is a predictive cancer risk potency estimate. The IUR is the upper bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of  $1 \mu\text{g m}^{-3}$  in air. For example, if the

TABLE 11.2 Tracheobronchial Region Default Values for Humans of Different Ages and Activity Patterns

	Minute Volume* ( $V_e$ ) ( $\text{l min}^{-1}$ )	Surface Area* (SA) ( $\text{cm}^2$ )	$(V_e/\text{SA}_{TB})$ ( $\text{l min}^{-1} \text{cm}^{-2}$ )	Tracheobronchial Regional Gas Dose Ratio	NOAEL (human equivalent concentration) ( $\text{mg m}^{-3}$ )
Outdoor worker M	17.5	2660	0.0066	0.94	0.15
Sedentary worker M	15.4	2660	0.0058	1.1	0.18
Sedentary worker F	12.6	2640	0.0048	1.3	0.21
15 year M	14.0	2520	0.0056	1.1	0.18
15 year F	10.9	2250	0.0048	1.3	0.21
10 Years	10.6	1830	0.0058	1.1	0.18
5 Years	6.1	1340	0.0046	1.4	0.22
1 Year	3.6	857	0.0042	1.5	0.24
3 Months	2.0	712	0.0028	2.2	0.35
Human equivalent concentration-default	13.8	3200	0.0043	1.4	0.22

\* These values are from International Commission on Radiological Protection (ICRP). ICRP publication 66: human respiratory tract model for radiological protection. Ann ICRP 1994;24:1–3.

Source: U.S. Environmental Protection Agency. Risk assessment guidance for superfund—volume I: human health evaluation manual (part E, supplemental guidance for inhalation risk assessment). Report No. EPA-540-R-070-002/OSWER 9285.7-82. Washington (DC); 2009.

$IUR = 2 \times 10^{-6}$  per  $\mu\text{g m}^{-3}$ , then two excess cancer cases (upper bound estimate) are expected to develop per 1,000,000 people if exposed daily for a lifetime to 1  $\mu\text{g}$  of the chemical in 1  $\text{m}^3$  air.<sup>d</sup>

The air pollution concentration in air ( $C_A$ ) must include all physical phases, i.e. both the pollutant in vapor phase and those in aerosol phase. The aerosol phase can simply be the same compound in liquid and solid phases, as well as any of the pollutant that is sorbed to particulate matter. For example, at equilibrium, benzene will exist in both gaseous and liquid phases, it can be sorbed on the surface of a particle (adsorbed), and it can be sorbed within the particle matrix (absorbed). The  $C_A$  value must account for all these phases and normalized, e.g. all expressed in units of mass per volume (e.g.  $\text{mg m}^{-3}$ ) or mass per mass (e.g.  $\text{mg kg}^{-1}$ ).

Many carcinogens and other toxic air pollutants are organic compounds with highly diverse physical

characteristics and chemical composition. Volatile organic compounds (VOCs), for example, exist in the ambient air almost entirely in the gas phase since their vapor pressures in the environment are usually  $>10^{-2}$  kPa. For VOCs, then,  $C_A$  may be almost equal to vapor phase concentrations. Conversely, relatively nonvolatile organic compounds (NVOCs) with vapor pressures  $<10^{-5}$  kPa are predominantly found in and on particles, unless significant energy is added to increase their volatility. Thus, the  $C_A$  for NVOCs can be estimated to equal the total amount of the air pollutant in PM collected. However, semivolatile organic compounds (SVOCs) with vapor pressures between  $10^{-2}$  and  $10^{-5}$  kPa can exist as in both the gas and particle phases in the ambient air. These values correspond to the classifications that are based upon observations of the compounds' behaviors during air sampling<sup>10</sup> (see Discussion Box: "Measuring SVOCs in the Air").

## MEASURING SVOCs IN THE AIR

Many airborne carcinogens are SVOCs, which have vapor pressures between  $10^{-5}$  and  $10^{-2}$  kPa under environmental conditions (temperature  $\approx 25^\circ\text{C}$ ; pressure  $\approx 1$  atm). This group includes the dioxins, furans, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and other persistent organic pollutants, including several organochlorine pesticides. These vapor pressures are low enough that the compounds may form particles and can sorb onto and into PM. The vapor pressures are high enough that they can also exist to some extent in the vapor phase in the troposphere. The compounds' phase distribution between gas and particle depends on environmental conditions, such as relative humidity and temperature. Measurements of phase distribution can be difficult due to the various inherent engineering features of the monitoring equipment, such as the need to maintain sampling flow rate, the pore size of filters, and the amount of time an organic compound resides on the filter or trap.<sup>11</sup> For example, a compound will sorb to a trapping material, such as a polymer (e.g. XAD) or polyurethane foam (PUF).

The general method for determining SVOCs in the air consists of several steps, such as those for PAHs<sup>12</sup>:

1. Filters and sorbent cartridges (containing sorbent media, e.g. PUF or XAD) are cleaned in solvents and vacuum dried. The filters and sorbent cartridges are

stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on the sampler.

2. Approximately  $300 - 400 \text{ m}^3$  of air is drawn through the filter and sorbent cartridge using a high-volume flow rate air sampler or equivalent.
3. The amount of air sampled through the filter and sorbent cartridge is recorded, and the filter and cartridge are placed in an appropriately labeled container and shipped along with blank filter and sorbent cartridges to the analytical laboratory for analysis.
4. The filters and sorbent cartridge are extracted by Soxhlet extraction with appropriate solvent. The extract is concentrated by Kuderna–Danish (K–D) evaporator (i.e. a system for concentrating materials dissolved in volatile solvents), followed by silica gel cleanup using column chromatography to remove potential interferences prior to analysis by gas chromatography/mass spectroscopy (GC/MS).
5. The eluent is further concentrated by K–D evaporation, then analyzed by GC/MS.
6. The analytical system is verified to be operating properly and calibrated with five concentration calibration solutions.

<sup>d</sup> The unit risk can also be applied to other exposure routes. For example, a similar calculation can be made for drinking water, with the assumption of continuous exposure to an agent at a concentration of 1  $\mu\text{g/L}$  in water. For example, if the unit risk =  $2 \times 10^{-6}$  per  $\mu\text{g/L}$ , 2 excess cancer cases (upper bound estimate) would be expected per 1,000,000 people if exposed daily for a lifetime to 1  $\mu\text{g}$  of the substance in 1 liter of drinking water.

## MEASURING SVOCs IN THE AIR (cont'd)

7. A preliminary analysis of the sample extract is performed to check the system performance and to ensure that the samples are within the calibration range of the instrument. If the preliminary analysis indicates nonperformance, then steps need to be taken, including recalibrating the instrument, adjusting the amount of the sample injected, adjusting the calibration solution concentration, and adjusting the data processing system to reflect observed retention times.
8. The samples and the blanks are analyzed and used (along with the amount of air sampled) to calculate the concentration of SVOCs in the air sample.

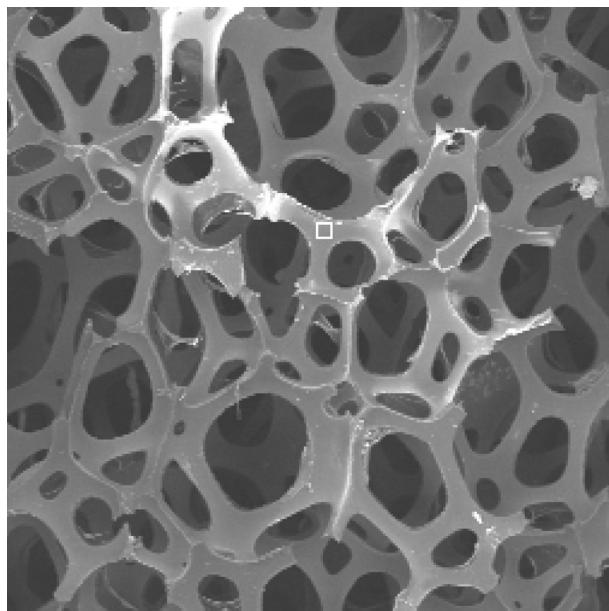
Systems for collecting, extracting, and analyzing SVOCs have been recommended by the American Society for Testing and Materials<sup>13</sup> and by the U.S. Food and Drug Administration.<sup>14</sup> Because of the relatively low concentrations of SVOCs in the environment, a large volume of air must pass through the filters and sorbents (e.g. for PAHs, the U.S. EPA recommends  $0.22 \text{ m}^{-3} \text{ min}^{-1}$ ) in order to acquire sufficient sample for analysis. Given the mid-range vapor pressures, efficient collection requires a filter backed up by sorbent cartridge (to collect aerosols and vapors, respectively).

Gas phase air pollutants are collected as they diffuse into media, such as PUF and XAD sorbant traps and denuders.<sup>15</sup> Denuders are devices that contain glass surfaces on which compounds are collected. Most of the gas volume, including the gas phase of SVOCs, immediately diffuses onto surfaces like those on the PUF, e.g. collection efficiencies<sup>16</sup> of the gas, sulfur dioxide ( $\text{SO}_2$ ), in a denuder have been found to be 99.2 and 99.6%. About 90% of the gas collected is in the first 10% of the denuder length.<sup>15</sup> The vapor phase of SVOCs would be expected to behave similarly.

The PUF is analogous to a “nest” of micro-denuders with its many crevices and large amount of surface area (Figure 11.2), so similar collection dynamics are assumed. Recently, similar findings have been found for PUF and the polymer collection media.<sup>17a,17b</sup>

If air flow volume is known (e.g. for SVOC monitoring, the target flow rate of air is about  $350 \text{ l min}^{-1}$ ), the concentration can be calculated. For example, if 20 mg of a compound is collected on the trap through which air has flowed for 24 h at  $350 \text{ l min}^{-1}$ , the integrated concentration of dioxins for that day would be

$$\frac{20 \text{ mg}}{24 \text{ h} \times \frac{60 \text{ min}}{\text{h}} \times \frac{350 \text{ l}}{\text{min}}} = 4 \times 10^{-5} \text{ mg l}^{-1} \text{ or } 40 \text{ ng l}^{-1}.$$



**FIGURE 11.2** Scanning electron micrograph (40× magnification) showing the void spaces in polyurethane foam (PUF) found in a semivolatile organic compound trap. Air flow is restricted to the void spaces, so if the flow is to remain constant, velocity within the trap is greater than the face velocity and greater than the velocity immediately after exit.

Converting liters to cubic meters ( $1000 \text{ l m}^{-3}$ ); the total concentration on this day would be  $40,000 \text{ ng m}^{-3}$  or  $40 \mu\text{g m}^{-3}$ .

There now exist integrated combined gas and particle sampling systems (Figure 11.2) that give both vapor and aerosol phase concentrations. An example of the results using this apparatus is provided in Table 11.3 and Figure 11.3, which show the mean concentrations of the PAHs observed during the sampling periods in September 2001. Several PAHs are suspected carcinogens.

Figure 11.4 shows the concentration of a number of PAHs collected by the various samplers. This is a gross indication of phase distribution between aerosols and gases. The lighter compounds to the left of the figure are fairly well distributed between the vapor and particle phases. This is indicated by their being captured in the gas phase by denuders and sorbant materials (i.e. the polymer XAD-4), and in the particle phase by the quartz filters. The heavier compounds to the right of the figure are mainly captured on quartz filters, that is, in the particle phase.

(Continued)

### MEASURING SVOCs IN THE AIR (cont'd)

TABLE 11.3 Total Concentrations ( $\text{ng m}^{-3}$ ) of PAHs Measured at Lower Manhattan, New York Using Equipment in Figure 11.3

Dates	09/26–09/27	10/04–10/05	10/06–10/07	10/12–10/13	10/20–10/21
	Total	Total	Total	Total	Total
Naphthalene <sup>§</sup>	699 (34)	824 (405)	109	22	42
2-Methyl naphthalene <sup>§</sup>	267 (6)	323 (37)	54	37	165
1-Methyl naphthalene <sup>§</sup>	178 (5)	212 (27)	29	11	103
Biphenyl <sup>§</sup>	182 (4)	224 (9)	11	90	190
2-Ethyl naphthalene*	42 (1)	42 (1)	7	30	46
1-Ethyl naphthalene*	17 (1)	24 (1)	4	10	26
2,6-dimethyl naphthalene*	81 (2)	77 (2)	19	75	99
1,6-dimethyl naphthalene*	44 (2)	63 (BD)	BD	45	75
Acenaphthylene	14 (BD)	3 (BD)	BD	6	2
Acenaphthene	49 (1)	55 (1)	9	37	46
2,3,6-Trimethyl naphthalene*	29 (1)	36 (1)	6	48	37
Fluorene	36 (1)	52 (1)	8	57	47
1-Methyl-9H-fluorene*	3 (BD)	9 (BD)	3	5	4
Dibenzothiophene*	12 (BD)	10 (BD)	1	12	10
Phenanthere	299 (6)	411 (8)	14	276	212
Anthracene	23 (BD)	13 (BD)	BD	14	8
Carbazole*	5 (BD)	5 (BD)	BD	2	1
Fluoranthene	111 (7)	179 (6)	4	61	52
Pyrene	59 (5)	93 (4)	2	32	27
Retene	9 (1)	10 (1)	BD	18	13
Benzo(a)anthracene	6 (3)	10 (3)	BD	2	2
Chrysene/triphenylene	15 (10)	30 (11)	BD	7	8
Benzo[b]fluoranthene	11 (11)	22 (20)	BD	4	6
Benzo[k]fluoranthene	4 (4)	8 (7)	BD	1	2
Benzo[a]pyrene	2 (2)	3 (3)	BD	1	1
Benzo[e]pyrene*	4 (4)	8 (8)	BD	1	2
Perylene*	BD (BD)	1 (1)	BD	BD	BD
Indeno[1,2,3-cd]pyrene	2 (2)	4 (4)	BD	BD	1
Dibenzo[a,h]anthracene	1 (1)	1 (1)	BD	BD	BD
Benzo[g,h,i]perylene	3 (3)	5 (5)	BD	1	1

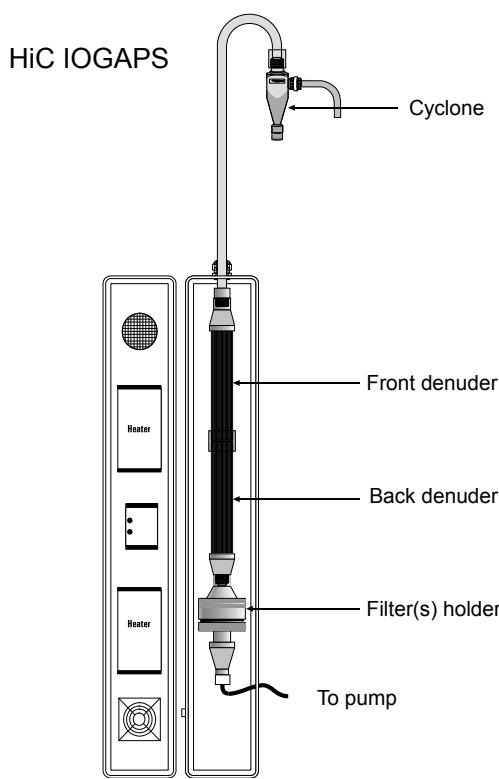
\* Estimated concentrations based on calibrations of similar compounds.

<sup>§</sup>Possible breakthrough of the species through the system.

Italicized data represents particle-only concentrations.

BD, below detection; NR, not reported.

### MEASURING SVOCs IN THE AIR (cont'd)



**FIGURE 11.3** Schematic of the high capacity Integrated Organic Gas and Particulate (HiC IOGAP) sampler with a 2.5 m cyclone inlet for particle discrimination was used in Lower Manhattan, NY to collect semivolatile gases and particles for speciation of organic compounds. The sampler utilizes two sorbant (XAD-4) coated eight-channel annular denuders (52 mm outer diameter, 285 mm length) to collect the gas phase species and a prebaked quartz filter followed by three XAD-4 impregnated quartz filters to collect the particle phase. The XAD-4 impregnated quartz filters were used to collect those compounds that desorb from the particles on the quartz filters and/or not removed by the denuders. The volumetric flow rate of the HiC IOGAP sampler was set to  $85 \text{ l min}^{-1}$  and temperature controlled at  $4^\circ\text{C}$  above ambient to prevent condensation of water. Drawing used with permission by URG Corporation.

The key to collecting and analyzing SVOCs lies in understanding their behavior in the environment. The sampling must consider the substrate. For example, is the compound bound to soil or sediment, does it need to be extracted from tissue, and how do the various phases differ in terms of sampling equipment? Sampling media varies with regard to the affinity they have for particular SVOCs. For example, most SVOCs are lipophilic, so the sampling media needs to have affinity for lipids. Most SVOCs are relatively large molecules, so the sampling material needs to be selected with that in mind.

There must also be a means of removing (extracting) the SVOC after collection. A material that is very good at collecting the SVOC, but from which extraction is almost impossible or inconsistent would not be a good sampling material. Usually, extraction is a means by which the analyte that was in the air, and then was trapped in sampling media, is now transferred to a solvent. For example, supercritical fluid extraction involves placing the sample (e.g. PUF) in a container which is exposed to supercritical  $\text{CO}_2$  which removes the analyte and transfers it to a known amount of solvent (e.g. hexane). The solvent is then injected into the chromatograph, which separates the various compounds and sends them to the detector, e.g. a mass spectrometer or ultraviolet detection.

The concentration of the analyte in the extract solution can be ascertained using a standard curve drawn from known amounts of the analyte injected into the chromatograph. Peak height or area is plotted linearly against concentration in nanograms per milliliter ( $\text{ng ml}^{-1}$ ). If the detector response is linear, a single point is used as a calculation constant. The quantity of the compound in the sample ( $A$ ) is calculated as:

$$A = 1000 \left( \frac{A_s \times V_e}{V_i} \right) \quad (11.6)$$

where,  $A$  is the total amount of analyte in the sample (ng);  $A_s$ , the calculated amount of material injected onto the chromatograph based on calibration curve for injected standards (ng);  $V_e$ , the final volume of extract (ml);  $V_i$ , the volume of extract injected ( $\mu\text{l}$ ); 1000, the factor for converting microliters to milliliters.

The extraction efficiency (EE) is determined from the recovery of surrogate spike:

$$\text{EE} = \frac{S}{S_a} (100) \quad (11.7)$$

where, EE is the extraction efficiency (percent);  $S$ , the amount of spike recovered (ng);  $S_a$ , the amount of spike added to plug (ng).

The EE (surrogate recovery) for an SVOC such as a PCB must fall between 60 and 120% to be acceptable. For example, if 200 ng of a PCB congener is added and 150 ng of the spike is recovered, the  $\text{EE} = (150/200) \times 100 = 75\%$ . This would be acceptable, so long as the recoveries are consistent. For example, if the next spike recovery is 65%, and the next is 85%, this is problematic. Even though all EE values are between 60 and 120%, they are so inconsistent that the concentrations being reported would have quite large uncertainties. The reason

(Continued)

## MEASURING SVOCs IN THE AIR (cont'd)

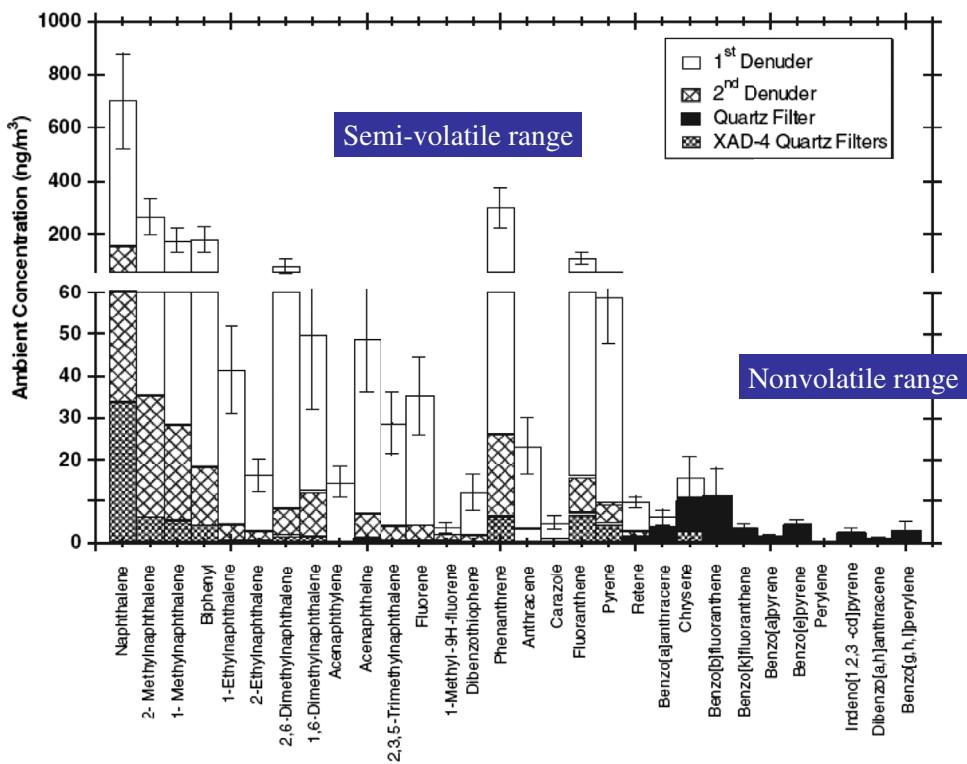


FIGURE 11.4 Average concentrations of polycyclic aromatic hydrocarbons sampled at lower Manhattan, September 26 and 27, 2001. Note broken bar between 60 and 200 ng m<sup>-3</sup> concentrations.

that these vary and that more than 100% of the spike appears to be recovered is related to instrument error and variability (e.g. there may have been drift and other changes in the GC after the calibration curve was drawn—following some runs, there may be other variations in the separation and detection equipment. Thus, the instrument needs to be recalibrated frequently, per instrument specifications and regulations). Arguably, within the acceptable range, lower but consistent EE (e.g. 65–70% range) is more acceptable than higher but inconsistent, i.e. less precise (e.g. 75–120% range) extraction.

The total volume of air sampled under ambient conditions is determined using the following equation<sup>18</sup>:

$$V_a = \frac{\sum_{i=1}^n (T_i \times F_i)}{1000 \text{ l/m}^3} \quad (11.8)$$

where,  $V_a$  is the total volume of air sampled (m<sup>3</sup>);  $T_i$ , the sampling period (min); and  $F_i$ , the average air flow during sampling period (l min<sup>-1</sup>).

This volume must be corrected to standard temperature (25 °C) and standard pressure (760 mm Hg):

$$V_s = V_a \left( \frac{P_b - P_w}{760 \text{ mm Hg}} \right) \left( \frac{298 \text{ K}}{t_A} \right) \quad (11.9)$$

where,  $V_s$  is the volume of air sampled at 25 °C and 760 mm Hg (m<sup>3</sup>);  $V_a$ , the total volume of air sampled;  $P_b$ , the mean ambient barometric pressure (mm Hg);  $P_w$ , the vapor pressure of water at calibration temperature (mm Hg); and  $t_A$ , the average ambient temperature (°C + 273).

A review of Eqns (11.4) and (11.5) indicates that intake and exposure increase with increasing pollutant concentration, along with the time, duration, and frequency of contact with the pollutant, but is indirectly proportionate to body weight and averaging time. The body weight proportionality reflects the decrease in dose, since the same mass of the chemical is present in a greater amount of tissue into which the pollutant is distributed and is metabolized. Similarly, a longer averaging time, with equal chemical uptake and all other factors held constant, simply dilutes the intake concentration and decreases exposure.

Human activity patterns vary over a lifetime, so it is recommended that a time-weighted average EC be calculated for each exposure period characterized by a specific activity pattern within each microenvironment (e.g. unique ECs for a school-aged child resident *versus* working adult residents *versus* adults at home for longer periods of time). All exposure period-specific ECs are then be combined into a longer term (e.g. lifetime) average EC by weighting the EC by the duration of each exposure period. An example is

$$EC_j = \sum_{i=1}^n (C_{Ai} \times ET_i \times EF_i) \times \frac{ED_j}{AT_j} \quad (11.10)$$

where,  $EC_j$  = average EC for exposure period  $j$ ;

$C_{Ai}$  ( $\mu\text{g m}^{-3}$ ) = contaminant concentration in air in  $ME_i$ ;

$ET_i$  (hours/day) = exposure time spent in  $ME_i$ ;

$EF_i$  (days/year) = exposure frequency for  $ME_i$ ;

$ED_j$  (years) = exposure duration for exposure period  $j$ ; and

$AT_j$  (hours) = averaging time =  $ED_j \times 24 \text{ h day}^{-1} \times 365 \text{ days year}^{-1}$ .

Once EC is calculated, it can be multiplied times a CSF or IUR to obtain a cancer risk estimate.

These factors are further specified for each route of exposure. The LADD is a commonly used metric of chronic, long-term exposure. Acute and subchronic exposures require different equations since the ED is much shorter. For example, instead of LADD, acute exposures to noncarcinogens may use maximum daily dose to calculate exposure (see Example Box: "Carcinogen Exposure Calculation").

## CARCINOGEN EXPOSURE CALCULATION

In the process of synthesizing pesticides over an 18-year period, a polymer manufacturer has contaminated the soil on its property with vinyl chloride. The plant closed 2 years ago but vinyl chloride vapors continue to reach the neighborhood surrounding the plant at an average concentration of  $1 \text{ mg m}^{-3}$ . Assume that people are breathing at a ventilation rate of  $0.5 \text{ m}^3 \text{ h}^{-1}$  (about the average of adult males and females over 18 years of age<sup>19</sup>). The legal settlement allows neighboring residents to evacuate and sell their homes to the company. However, they may also stay. The neighbors have asked for advice on whether to stay or leave since they have already been exposed for 20 years.

Vinyl chloride is highly volatile, so its phase distribution will be mainly in the gas phase rather than the aerosol phase. Although some of the vinyl chloride may be sorbed to particles, we will use only vapor phase LADD equation since the particle phase is likely to be relatively small. Also, we will assume that outdoor concentrations are the ECs. This is unlikely, however, since people spend very little time outdoors compared to indoors, so this may provide an additional factor of safety. To determine how much vinyl chloride penetrates living quarters, indoor air studies would have to be conducted. For a

scientist to compare exposures, indoor air measurements should be taken.

Absorption rates are published by the air quality agencies. For example, the EPA values for AF and CSF for a number of hazardous air pollutants are provided in Table 11.1. The appropriate equations in Table 11.4 must be selected based on the chemical's physical and chemical properties. In this case, most of the inhalation exposure will be vapor phase, given vinyl chloride's vapor pressure. Vinyl chloride is well absorbed, i.e.  $AF = 0.875$ . Assume an average person exposure, i.e. the person stays in the neighborhood is exposed at the average concentration  $24 \text{ h a day}$  ( $EL = 24$ ), and that a person lives the remainder of entire typical lifetime exposed at the measured concentration. However, these values can be adjusted if more specific human activity data are available (e.g. diaries).

Although the ambient concentrations of vinyl chloride may have been higher when the plant was operating, the only measurements we have are those taken recently. Thus, this is an area of uncertainty that must be discussed with the clients. The common default value for a lifetime is 70 years, so we can assume the longest exposure would be 70 years (25,550 days). These and other default values appropriate to the exposed population are given

(Continued)

## CARCINOGEN EXPOSURE CALCULATION (cont'd)

**TABLE 11.4** Equations for Calculating Lifetime Average Daily Dose (LADD) for Various Routes of Exposure

Route of Exposure	Equation LADD (in $\text{mg kg}^{-1} \text{ day}^{-1}$ )	Definitions
Inhaling aerosols (particulate matter)	$\frac{(C) \cdot (PC) \cdot (IR) \cdot (RF) \cdot (EL) \cdot (AF) \cdot (ED) \cdot (10^{-6})}{(BW) \cdot (TL)}$	$C$ = concentration of the contaminant on the aerosol/particle ( $\text{mg kg}^{-1}$ ) $PC$ = particle concentration in air ( $\text{gm m}^{-3}$ ) $IR$ = inhalation rate ( $\text{m}^{-3} \text{ h}^{-1}$ ) $RF$ = respirable fraction of total particulates (dimensionless, usually determined by aerodynamic diameters, e.g. $2.5 \mu\text{m}$ ) $EL$ = exposure length ( $\text{h day}^{-1}$ ) $ED$ = duration of exposure (day) $AF$ = absorption factor (dimensionless) $BW$ = body weight (kg) $TL$ = typical lifetime (day). $10^{-6}$ is a conversion factor (kg to mg)
Inhaling vapor phase contaminants	$\frac{(C) \cdot (IR) \cdot (EL) \cdot (AF) \cdot (ED)}{(BW) \cdot (TL)}$	$C$ = concentration of the contaminant in the gas phase ( $\text{mg m}^{-3}$ ) Other variables the same as above.
Contact with soil-borne contaminants	$\frac{(C) \cdot (SA) \cdot (BF) \cdot (FC) \cdot (SDF) \cdot (ED) \cdot (10^{-6})}{(BW) \cdot (TL)}$	$C$ = concentration of the contaminant in the soil ( $\text{mg kg}^{-1}$ ) $SA$ = skin surface area exposed ( $\text{cm}^{-2}$ ) $BF$ = bioavailability (percent of contaminant absorbed per day) $FC$ = Fraction of total soil from contaminated source (dimensionless) $SDF$ = soil deposition, the mass of soil deposited per unit area of skin surface ( $\text{mg cm}^{-1} \text{ day}^{-1}$ ) Other variables are the same as above.

Source: Derelanko M. Risk assessment. In: Derelanko MJ, Hollinger MA, editors. CRC handbook of toxicology. Boca Raton (Florida): CRC Press; 1999.

in Table 11.5. The ED is assumed to be for a person who is now 20 years of age and has already been exposed for that time, and lives the remaining 50 years exposed at  $1 \text{ mg m}^{-3}$ . Using the appropriate equation in Table 11.4 (inhaling vapor phase contaminants), LADD can be estimated as follows:

$$\begin{aligned}
 \text{LADD} &= \frac{(C) \cdot (IR) \cdot (EL) \cdot (AF) \cdot (ED)}{(BW) \cdot (TL)} \\
 &= \frac{(1) \cdot (0.5) \cdot (24) \cdot (0.875) \cdot (25,550)}{(70) \cdot (25,550)} \\
 &\approx 0.2 \text{ mg } (\text{kg} - \text{day})^{-1}
 \end{aligned}$$

If the 20 year old leaves today, the ED would be for the 20 years that the person lived in the neighborhood. Thus, only the ED term would change, i.e. from 25,550–7300 days (i.e. 20 years).

Thus, the LADD falls to 2/7 of its value:

$$\text{LADD} = 0.05 \text{ mg } (\text{kg} - \text{day})^{-1}.$$

Once the hazard and exposure calculations are done, risks can be characterized risk quantitatively. There are

two general ways that such risk characterizations are used in environmental problem solving, i.e. direct risk assessments and risk-based cleanup standards.

Using the LADD value, estimate the direct risk to the people living near the abandoned polymer plant. What information needs to be communicated?

Insert the calculated LADD values and the vinyl chloride inhalation slope factor of  $3.00 \times 10^{-1}$  from Table 11.1. The two LADD values under consideration, the cancer risk to the neighborhood exposed for an entire lifetime ( $ED = 70$  years) gives us  $0.2 \text{ mg kg}^{-1} \text{ day}^{-1} \times 0.3 (\text{mg kg}^{-1} \text{ day}^{-1})^{-1} = 0.06$ . This is an incredibly high risk! The threshold for concern is often 1 in a million ( $0.000001 = 10^{-6}$ ), while this is a probability of 6% or  $6 \times 10^{-2}$ .

Even at the shorter duration period (20 years of exposure instead of 70 years), the risk is calculated as  $0.05 \times 0.3 = 0.017$  or nearly a 2% risk. The combination of a very steep slope factor and very high lifetime exposures leads to a very high risk. Vinyl chloride is a liver carcinogen, so unless corrective actions significantly lower the ambient concentrations of vinyl chloride, the prudent course of action is that the neighbors accept the buyout and leave the area.

## CARCINOGEN EXPOSURE CALCULATION (cont'd)

**TABLE 11.5** Commonly Used Human Exposure Factors

Exposure Factor	Adult Male	Adult Female	Child (3–12 years of age) <sup>23</sup>
Body weight (kg)	70	60	15–40
Total fluids ingested (l day <sup>-1</sup> )	2	1.4	1.0
Surface area of skin, without clothing (m <sup>2</sup> )	1.8	1.6	0.9
Surface area of skin, wearing clothes (m <sup>2</sup> )	0.1–0.3	0.1–0.3	0.05–0.15
Respiration/ventilation rate (l min <sup>-1</sup> )—resting	7.5	6.0	5.0
Respiration/ventilation rate (l min <sup>-1</sup> )—light activity	20	19	13
Volume of air breathed (m <sup>3</sup> day <sup>-1</sup> )	23	21	15
Typical lifetime (years)	70	70	NA
National upper bound time (90th percentile) at one residence (years)	30	30	NA
National median time (50th percentile) at one residence (years)	9	9	NA

Source: U.S. Environmental Protection Agency. Exposure factor handbook; 2003; and Agency for Toxic Substances and Disease Registry. ATSDR public health assessment guidance manual; 2003.<sup>20</sup>

Incidentally, vinyl chloride has relatively high water solubility and can be absorbed to soil particles, so ingestion of drinking water (e.g. people on private wells drawing water from groundwater that has been contaminated) and dermal exposures (e.g. children playing in the soil) are also conceivable. The total risk from a single contaminant like vinyl chloride is equal to the sum of risks from all pathways (e.g. vinyl chloride in the air, water, and soil):

$$\text{Total Risk} = \sum \text{risks from all exposure pathways} \quad (11.11)$$

Equation 11.7 points to a recent observation about air pollutants, especially those that are ingredients in pesticides and other products. Although the pollutant may be airborne, some of the exposure may be through routes other than inhalation. For example, some pesticides are found in household dust that has settled on food, which is then eaten. This is an example of an air pollutant where the uptake is via food or nondietary ingestion, introducing the chemical into the gastrointestinal (GI) tract. This can be from pica (eating nonfood substance) or inadvertent ingestion of soil and dust. Thus, the chemical ingestion includes both food and nonfood items. Dietary (food and liquids) and/or nondietary (soil, dust, and other materials) exposure can be estimated as follows:

$$E_{\text{ing}} = (C_{\text{ing}}) \times (\text{IR}) \quad (11.12)$$

where

$E_{\text{ing}}$  = ingestion exposure (mass per time)

$C_{\text{ing}}$  = concentration of the chemical in food or other exposure media (mass of chemical per mass of medium or mass of chemical per volume of medium)

IR = ingestion rate (mass of medium ingested during the exposure per time).

Requirements and measures of success are seldom if ever as straightforward as this example. A number of actions are likely to be called for when carcinogens and other toxic compounds are found in elevated concentrations, including physical removal of the source and relocating people during the remediation.

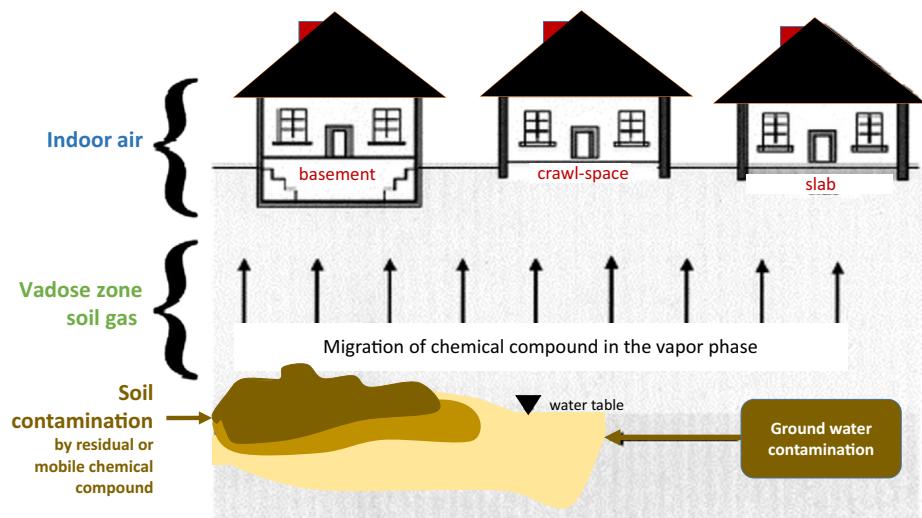
The actions will include documenting the amount of the chemical in the source and the amount moving into the air. Thus, the movement of the contaminant from soil to air must be estimated. Exposure to vinyl chloride may often occur from direct industrial releases, but has also been found in landfill gas and groundwater as a degradation product of chloroethylene solvents, particularly trichloroethylene. Vinyl chloride in contaminated groundwater can volatilize and contaminate indoor air, so is an important avenue of exposure (Figure 11.5). This volatilization is referred to as *vapor intrusion*, and should be considered in any volatile risk assessment.

Vapor intrusion into buildings presents an interesting perspective on exposure. Often, when groundwater is

(Continued)

## CARCINOGEN EXPOSURE CALCULATION (cont'd)

**FIGURE 11.5** Conceptualized schematic of the movement of a high vapor pressure substance, e.g. a VOC, from groundwater, through the unsaturated underground strata, through soil and into residences. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from U.S. Environmental Protection Agency (2002). OSWER Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance), Report No. EPA530-D-02-004, U.S. EPA, Office of Solid Waste and Emergency Response, Washington, DC.



contaminated, the principal exposure pathway is ingestion of well water. Thus, the logical action would be to find an alternate source of drinking water, e.g. bottled water. However, if the contaminant becomes an air pollutant, the inhalation pathway would remain. For example, consider a scenario where drinking water and vapor intrusion pathways led to exposure  $10 \mu\text{g m}^{-3} \text{ kg}^{-1} \text{ day}^{-1}$  and  $2.5 \mu\text{g m}^{-3} \text{ kg}^{-1} \text{ day}^{-1}$ , respectively. Using bottled water would eliminate the drinking water ingestion rate, but the exposure would only be reduced to  $2.5 \mu\text{g m}^{-3} \text{ kg}^{-1} \text{ day}^{-1}$  since the inhalation of vinyl chloride would continue.

Assessing the vapor intrusion pathway typically involves the use of indirect measurements and modeling, based on soil gas or groundwater data. In addition, sampling indoor air does not in itself account for contributions from "background" sources. For example, if the neighborhood is near a source of vinyl chloride emissions, some ambient concentrations will permeate the building. The measurements will indicate the total vinyl chloride concentrations, not whether they came from infiltration from ambient air or from vapor intrusion.<sup>21</sup>

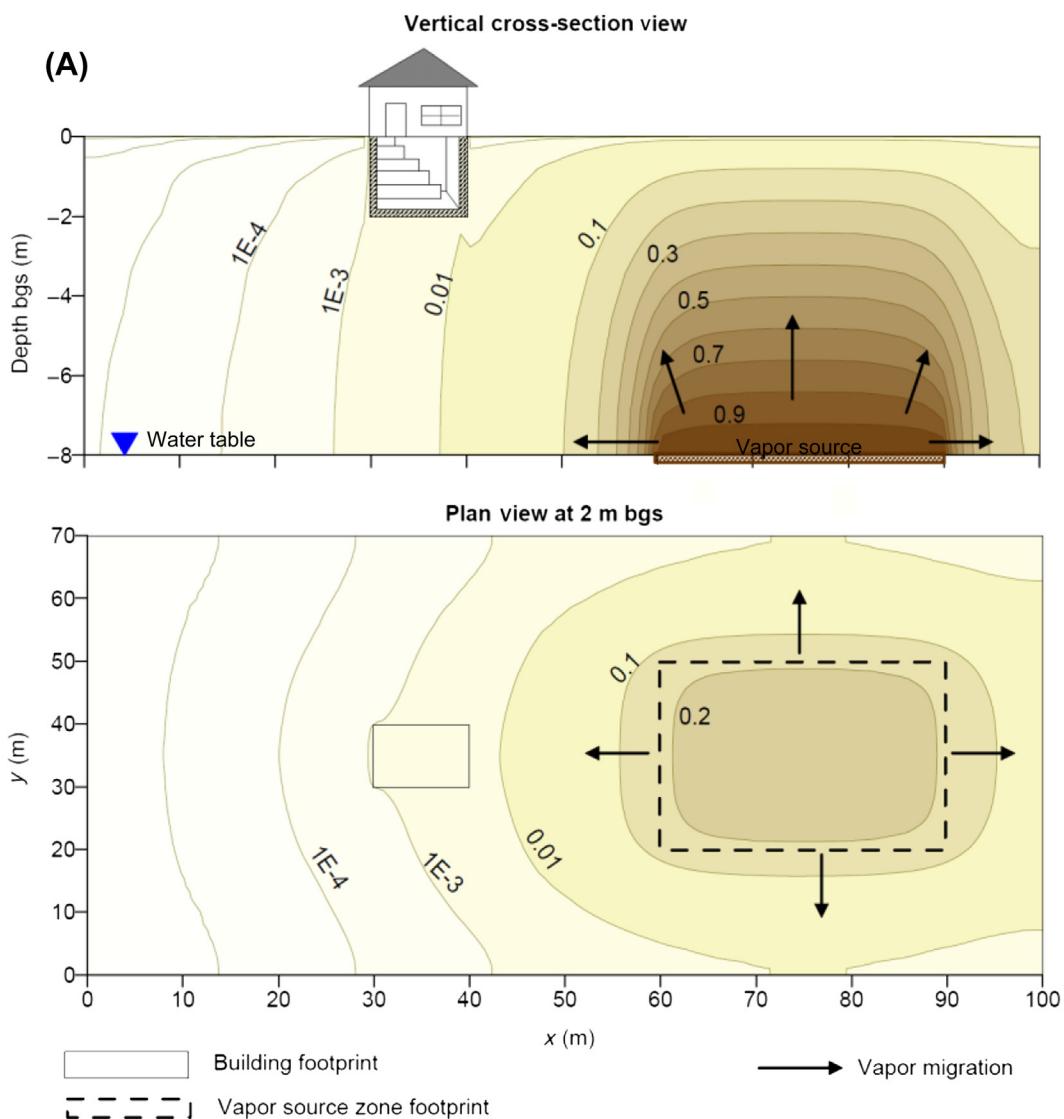
Concentrations of volatile substances in soil gas attenuate (i.e. decrease in concentration) as the substances move from the source through the soil and into indoor air (Figure 11.6). This occurs because the emissions into a building mix with the ambient air flow through the building. The extent of

attenuation depends on the emission rate into the building, which is affected by the following:

1. Subsurface features (e.g. fine-grained soils, high-moisture soil layers) that may hinder the diffusion and advection of VOCs
2. Biodegradation of contaminants, which leads to a decrease in the emissions along the vapor migration pathway
3. The integrity of the foundation and subgrade walls
4. Changes with time in groundwater level, source strength, and infiltration rates
5. Pressurization of the building (underpressurization draws soil gas into a building)
6. Air exchange into a building, which brings fresh air into the enclosed space and dilutes the concentration of VOCs that enter through the vapor intrusion pathway.<sup>22</sup>

Migration of chemical by diffusion occurs from a source (e.g. leaking tank or highly polluted area of higher concentration) to areas of lower concentration. The arrows in Figure 11.6(A) move from the groundwater source through the unsaturated (vadose) zone source (Figure 11.6(B)). Away from the building, the dominant contaminant transport mechanism through the water in the soil pore spaces from the building is commonly diffusion. Advection increases with

## CARCINOGEN EXPOSURE CALCULATION (cont'd)



**FIGURE 11.6** Direction of the vapor migration due to diffusion and resulting soil vapor concentration distribution for a ground-water vapor source (A). Direction of vapor migration and resulting soil vapor concentration distribution for a source in unsaturated soil (vadose zone) (B). The soil vapor concentration contour lines are normalized by the source vapor concentration. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Conceptual model scenarios for the vapor intrusion pathway. Report No. EPA530-D-10-103. Washington (DC): U.S. EPA, Office of Solid Waste and Emergency Response; 2012.

proximity to the building. Vapor phase air diffusion coefficients can be five orders of magnitude greater than water diffusion coefficients. Thus vapor diffusion through the air-filled pores of the soil matrix usually dominates for VOCs in the unsaturated zone. This is

not the case when a chemical has a very low Henry's Law constant (see Chapter 18). Also, vapor diffusion rates will decrease with increasing moisture content, so water diffusion becomes more dominant in very wet conditions.

## CARCINOGEN EXPOSURE CALCULATION (cont'd)

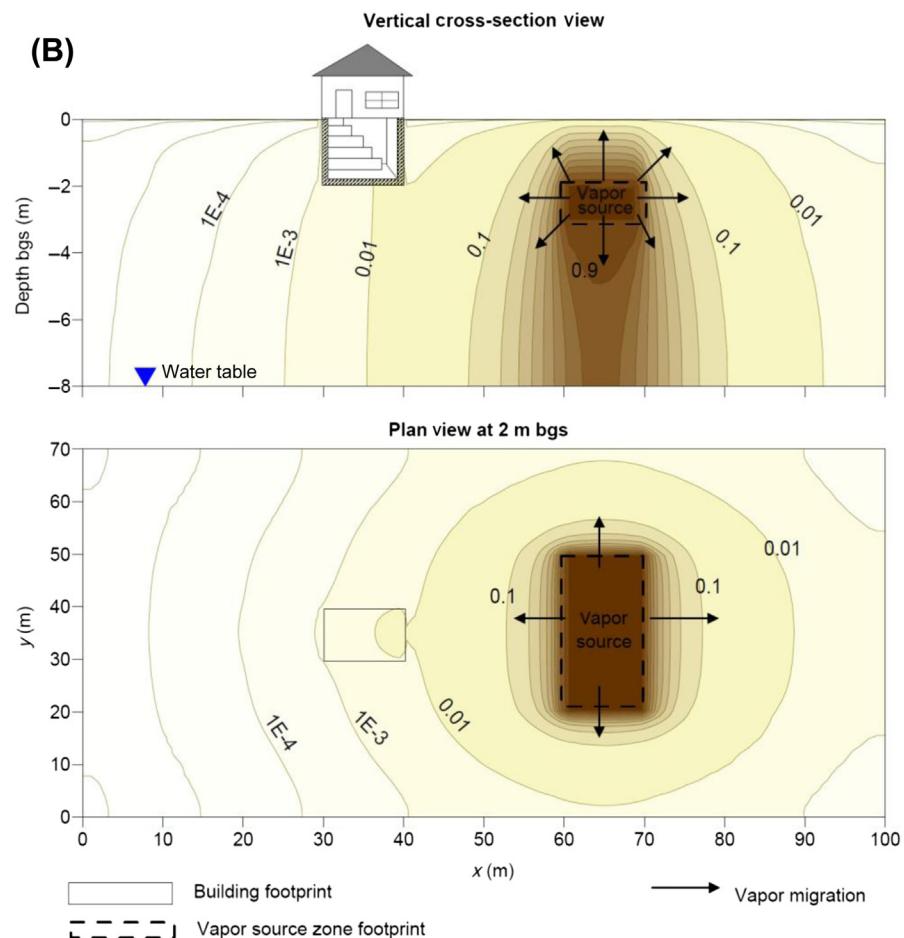


FIGURE 11.6 (Continued)

### **11.3 NATIONAL AIR TOXICS ASSESSMENT**

A very valuable tool for estimating air pollution cancer risks in the United States is the National Air Toxics Assessment (NATA). As discussed in Chapter 3, the 1990 amendments to the Clean Air Act required a U.S. national scale air toxics assessment to screen and prioritize pollutants, emission sources and locations of interest for further study in order to gain a better understanding of risks. NATA provides estimates of the risk of cancer and other serious health effects from inhaling air toxics. Assessments include estimates of cancer and noncancer health effects based on chronic exposure from outdoor sources, providing a snapshot of the outdoor air quality and the risks to human health that would result if air toxic emissions levels remained unchanged.

The assessment addresses the inhalation of 178 air toxics, for cancer and noncancer risk, plus noncancer risk for diesel PM. The 2005 NATA results are summarized in Figure 2.12. In addition to the national assessments, more focused reports can be generated. These include reports on a specific compound or the air toxics present in a specific state.

### **11.4 CANCER DOSE–RESPONSE**

The more potent the carcinogen, the larger the slope factor will be (i.e. the steeper the slope of the dose–response curve). Note, e.g. that when inhaled, ingested, or dermally exposed, the slope for the most carcinogenic dioxins, tetrachlorodibenzo-*p*-dioxin, is eight orders of magnitude steeper than the slope for aniline. Keep

in mind that this is the linear part of the curve. The curve is actually sigmoidal because at higher doses, the effect is dampened, i.e. the response is increasing at a decreasing dosage rate. This process is sometimes called the *saturation effect*. One way to think about this is to consider that if the dose-response curve comes from animal tests of various doses, there is a point at which increasing the dose of a chemical adds little to the onset of tumors. The dosage approaches an effective limit and becomes asymptotic. So, if chemical A is given to 1000 rats, at increasing dosages, an incremental increase in rats with tumors is seen. This is the linear range. Doubling dose doubles the effect. But, at some inflection point, the increased dosage, say after 50 rats with tumors, if the dose is doubled half as many additional rats with tumors are seen. The rate continues to decrease up to a point where even very large doses do not produce many additional tumors. This is one of the challenges of animal experiments and models. We are

trading dose for time; the assumed lifetime of humans is about 70 years and the doses to carcinogens are usually very small (e.g. parts per billion or trillion). Animal doses may last only a few months and use relatively high doses. We have to extrapolate long-term effects from limited data from short-term studies. The same is somewhat true for human studies, where we try to extrapolate effects from a small number of cases to a much larger population, e.g. a small study comparing cases to controls in one hospital or a retrospective view of risk factors that may have led to a cluster of cases of cancer.

It can be argued that addressing rare and chronic diseases like cancer, endocrine dysfunction, reproductive disorders, and neurological diseases is an effort in the controlling the variables to reduce the possibility of an improbable (thankfully!) event. In fact, new statistical devices are being developed to deal with rare events (see Discussion Box: Small Numbers and Rare Events).

### SMALL NUMBERS AND RARE EVENTS

In statistics, there is an interesting but logical observation that when one deals with rare events, small changes can be very profound. If you think about it, when you start with very small numbers, a slight change can make a huge difference. Stockbrokers and retailers use this phenomenon often. For example, a company may be the fastest growing company in its field this year. Upon investigation, its sales may have been only \$5.00 last year, but they grew to \$5000.00 this year. This is a 1000-fold increase, while real estate investors might say that sales grew 100,000% this year! Engineers and scientists often prefer absolute terms and might say that the growth rate was  $\$4.995 \times 10^3 \text{ year}^{-1}$ . These are all correct statements. But would you rather invest in a company that had \$10 million in sales last year and grew to \$20 million this year? That is only a 10-fold increase and only 100% growth. But, the absolute growth is  $\$1 \times 10^6 \text{ year}^{-1}$ , or three orders of magnitude greater than the small firm. What does this tell us about rare outcomes, like cancer?

First, one must know what the numbers mean. In reviewing epidemiological information, are the data given as incidence of disease or prevalence? Disease incidence is the number of new cases diagnosed each year, while prevalence is the number of cases at any given time. Next, we must be careful that to ascertain whether the values are absolute or relative. For example, are the values given a year-over-year change or are they simply a one-time event. In environmental and public health reports, especially risk assessments, the values are often presented as probabilities in engineering notation, e.g. a common target of cleanup of hazardous waste sites is that no more than

one additional case of cancer per million population should be result from the clean site, that is, the added risk is less than or equal to  $10^{-6}$ . Like all probabilities, this is simply a fraction and a decimal. However, if the environmental practitioner uses it in a public forum, it can be very disarming and not clearly understood. In fact, the whole concept of population risk is foreign to most people. The point is that when the environmental practitioner goes about explaining rare events like cancer, great care must be taken.

Toxicology deals with even smaller values and often very limited data. In fact, one of the raging toxicological debates is that of cancer dose-response, and where to literally "draw the line". As a matter of scientific policy, in what is known as the "precautionary principle", many health agencies around the world assume that a single molecule of a carcinogen *can* cause cancer. In other words, there is no threshold under which a dose, no matter how small, would be safe; "one hit potentially leads to a tumor". This approach is commonly known as the "one-hit model". Most other diseases have such a threshold dose, known as the "no observed adverse effect concentration" or the NOAEC (see Figure 7.3 and 7.5 in Chapter 7). The precautionary principle is in large part due to our lack of understanding of how things work at the molecular level. Toxicological models work better when they use observed data, but at level below this, we are guessing (albeit a very educated guess) as to what is happening. Since risk at very low doses is not directly measurable using animal experiments or from epidemiology, mathematical models are used to extrapolate from high to low doses.

(Continued)

## SMALL NUMBERS AND RARE EVENTS (cont'd)

Cancer dose-response curves do not have a threshold, i.e. there is no concentration at which cancer is not expected. This does not mean that one molecule of a carcinogen will cause cancer, but it does mean that there is no mathematical difference between a concentration at which cancer will occur and a lower concentration at which cancer will not occur. Thus, cancer risk models are usually considered to be "no threshold" models.

Various extrapolation models or procedures may reasonably fit the observed data; however, extremely large differences of risk at low doses can be calculated. Scientists must use different models depending on the particular chemical compound, as well as use information about how cancer seems to be occurring (i.e. the biological "mechanism of action" at work in the cell).<sup>24</sup> When such biological information is limited, the default is to assume linearity and since there is no threshold, the curve intersects the *y*-axis at 0. For example, the U.S. Environmental Protection Agency usually recommends a linearized multistage procedure as the default model unless sufficient information to the contrary exists. The linearized multistage procedure calls for the fitting of a multistage model to the data. Multistage models are exponential models approaching 100% risk at high doses, with a shape at low doses given by a polynomial function. If this is first degree, the model is equivalent to a so-called one-hit model, yielding almost a linear relationship between low dose and cancer risk. An upper bound risk is estimated by applying an appropriate linear term into the statistical bound for the polynomial. At sufficiently small exposures, any higher order terms in the polynomial are assumed to be negligible, and the graph of the upper bound will appear to be a straight line. The slope of this line is called *slope factor*, which is a measure of the cancer potency, the compound, i.e. the steeper the slope the more potent the carcinogen.<sup>25</sup>

Air pollution "treatment" is expressed as *pollutant removal efficiency*, such as "percent removal". For example, to determine how well an incinerator destroys a hazardous substance, the removal efficiency is employed. Environmental and chemical engineers use the "rule of six nines" for extremely hazardous compounds, i.e. the quantity (mass) of a compound in a waste stream must be reduced by 99.9999%. For instance, if the most toxic form of dioxin, tetrachlorodibenzo-*para*-dioxin (TCDD) is in a waste stream, the incinerator must destroy 99.9999% (six nines) of the TCDD. If the incinerator is destroying 99.9998%, then it theoretically is out of compliance (assuming the means to quantify the pollutant removal are within the range of six significant figures). Often, however, the removal is reported in units of mass or concentration. If a waste contains a total of 100 mg (mass), or 100 mg l<sup>-1</sup>

(concentration) of TCDD, after treatment in a properly operating incinerator, we are left with 0.0001 mg if we started with 100 mg (100 mg - 0.999999 × 100 mg). If the incinerator increases its efficiency seven nines (99.99999% removal), we would have 0.00001 mg TCDD left. That is, the improvement allowed us to remove only 0.00009 mg of TCDD. This leaves the engineer open to "spin". For example, the incinerator improvement may look better if the removal rate is reported as nanograms (ng) removed (10 ng better). To make the difference look insignificant, one could report the removal as grams removed (only 0.00001 g removed). But, both removal efficiencies are the same, only the units differ! Units can be challenging. For example, in hazardous waste engineering, we often use parts per billion (ppb). That is a small concentration. For example, in the language of bartending, 1 ppb is equivalent to a gin and tonic, where the shot of gin is added to a volume of tonic carried by train with 6 mi of tanker cars.<sup>26</sup>

A further problem is that removal efficiency is a relative measure of success. If a waste has a large amount of a contaminant, even relatively inefficient operations look good. Taking the TCDD example, if waste A has 100 g of TCDD (scary thought!) and waste B has 100 ng of TCDD and they both comply with the rules of six nines, the waste A incinerator is releasing 0.0001 g or 100 ng of the contaminant to the atmosphere, while the waste B incinerator is emitting only 0.0001 ng. That is why environmental laws also set limits on the maximum mass or concentration of a contaminant leaving the stack (or pipe for water discharges). In addition, the laws require that for some pollutants that ambient concentration not be exceeded. However, for many very toxic compounds that require elaborate and expensive monitoring devices, such ambient monitoring is infrequent and highly localized (e.g. near a known polluter). Regulators often depend on self-reporting by the facilities, with occasional audit (analogous to the IRS accepting a taxpayers self-reporting, which is verified to some extent by audits of a certain sample of taxpayers).

Statistics and probabilities for extreme and rare events can be perplexing. People want to know about trends and differences in exposures and diseases between their town or neighborhood and those of others. Normal statistical information about central tendencies, like the mean, median, and mode or ranges and deviations, fail us when we analyze rare events. Normal statistics allows us to characterize the typical behaviors in our data in terms of differences between groups and trends, focusing on the center of the data. Extreme value theory (EVT), conversely, lets us focus on the points far out on the tail of our data, with the intent of characterizing a rare event. For example, perhaps we have been

## SMALL NUMBERS AND RARE EVENTS (*cont'd*)

collecting health data for 10 years for thousands of workers exposed to a contaminant. What is special about those who have been most highly exposed (e.g. those at the 99th percentile)? What can we expect as the highest

exposures over the next 50 years? EVT is one means of answering these questions. The first question can be handled with traditional statistics, but the second is an extrapolation (50 years hence) beyond our data set.

## 11.5 AIRBORNE CARCINOGENS

There are three expansive categories of data from which the weight of evidence of cancer causality are drawn: (1) human data (primarily epidemiological); (2) results of long-term experimental animal bioassays; and (3) supporting data, including a variety of short-term tests for genotoxicity and other relevant properties, kinetic and metabolic studies, and structure–activity relationships. In hazard identification of carcinogens under the guidelines, human data, animal data, and supporting evidence are combined to characterize the weight-of-evidence (WOE) regarding the agent's potential as a human carcinogen. The general categories<sup>27</sup> used in the United States are the following:

- Carcinogenic to Humans
- Likely to be Carcinogenic to Humans
- Suggestive Evidence of Carcinogenic Potential
- Inadequate Information to Assess Carcinogenic Potential
- Not Likely to be Carcinogenic to Humans.

These closely track with an earlier U.S. classification system placed the cancer potential in a hierarchy of WOE. In descending order from strongest to weakest, the categories are as follows:

Group A (Strongest WOE)—Carcinogenic to Humans: Agents with adequate human data to demonstrate the causal association of the agent with human cancer (typically epidemiologic data).

Group B—Probably Carcinogenic to Humans: Agents with sufficient evidence (i.e. indicative of a causal relationship) from animal bioassay data, but either limited human evidence (i.e. indicative of a possible causal relationship, but not exclusive of alternative explanations; Group B1), or with little or no human data (Group B2).

Group C—Possibly Carcinogenic to Humans: Agents with limited animal evidence and little or no human data.

Group D (Weakest WOE)—Not Classifiable as to Human Carcinogenicity: Agents without adequate data either to support or refute human carcinogenicity.

Group E—Evidence of Noncarcinogenicity for Humans: Agents that show no evidence for carcinogenicity

in at least two adequate animal tests in different species or in both adequate epidemiologic and animal studies.

Table 11.6 shows both cancer classifications and the IUR for each hazardous air pollutant designated under Section 112 of the Clean Air Act. The IUR is the upper bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of  $1 \mu\text{g m}^{-3}$  in air. The WOE categories express the relative degree of certainty that these agents may cause cancer in humans. The categories specifically do not connote relative levels of hazard or degree of conservatism applied in developing a dose–response assessment. For example, a substance in group C (possible human carcinogen), under the 1986 guidelines, may have a greater cancer risk to a greater number of people than another substance in group A (known human carcinogen), yet there is a greater certainty with regard to the risk associated with the latter. EPA's WOE classifications are focused on the amount and quality of evidence regarding whether or not a substance is carcinogenic to humans, not on the level of risk a substance might present.

A number of chemical classes of air pollutants include carcinogens. These include both inorganic and organic compounds. Carcinogenic metals include both types of compounds. For example, a metal oxide is inorganic and a metal acetate is organic (i.e. an organometallic compound).

### 11.5.1 Carcinogenic Metals

The sensitivity of cells or tissues to metals appears to be related, at least in part, to their ability to produce metallothionein (MT), a protective protein that binds heavy metals. Activation of the MT gene in response to exposure results in production of metallothionein, which sequesters cadmium, thus limiting its genotoxic effects. The difference between rats and mice in sensitivity to a metal as a lung carcinogen appears, at least in part, to be due to differential expression of MT in lung tissue following inhalation exposure to cadmium. Other tissues in which some metals cause cancer in rodents also show minimal basal expression of the MT gene or limited activation of MT in response to metal (e.g. cadmium) exposure. There is no evidence to suggest that mechanisms by which a carcinogenic metal causes tumors in experimental animals would not also operate in humans.<sup>28</sup>

TABLE 11.6 Prioritized Chronic Dose–Response Values

Chemical Name	CAS No	IARC WOE	EPA WOE	IUR (( $\mu\text{g m}^{-3}$ ) $^{-1}$ )	MOA
Acetaldehyde	75-07-0	2B	B2	0.0000022	
Acetamide	60-35-5	2B		0.00002	
Acetonitrile	75-05-8		InI		
Acetophenone	98-86-2		D		
Acrolein	107-02-8	3	InI		
Acrylamide	79-06-1	2A	LH	0.0001	M*
Acrylic acid	79-10-7	3			
Acrylonitrile	107-13-1	2B	B1	0.000068	
Allyl chloride	107-05-1	3	C	0.000006	
Aniline	62-53-3	3	B2	0.0000016	
Antimony compounds	7440-36-0				
Antimony pentoxide	1314-60-9				
Antimony potassium tartrate	304-61-0				
Antimony tetroxide	1332-81-6				
Antimony trioxide	1309-64-4	2B			
Arsenic compounds	7440-38-2	1	A	0.0043	
Arsenic pentoxide	1303-28-2				
Arsine	7784-42-1				
Benzene	71-43-2	1	CH	0.0000078	
Benzidine	92-87-5	1	A	0.067	M*
Benzotrichloride	98-07-7	2B	B2		
Benzyl chloride	100-44-7	2B	B2	0.000049	
Beryllium compounds	7440-41-7	1	LH	0.0024	
Beryllium oxide	1304-56-9				
Biphenyl	92-52-4		D		
Bis(2-ethylhexyl)phthalate	117-81-7	2B	B2	0.0000024	
Bis(chloromethyl)ether	542-88-1	1	A	0.062	
Bromoform	75-25-2	3	B2	0.0000011	
1,3-Butadiene	106-99-0	1	CH	0.00003	
Cadmium compounds	7440-43-9	1	B1	0.0018	
Captan	133-06-2	3	B2		
Carbaryl	63-25-2				
Carbon disulfide	75-15-0				
Carbon tetrachloride	56-23-5	2B	LH	0.000006	
Chloramben	133-90-4				
Chlordane	57-74-9	2B	LH	0.0001	
Chlorine	7782-50-5				
Chloroacetic acid	79-11-8				
2-Chloroacetophenone	532-27-4				

TABLE 11.6 Prioritized Chronic Dose—Response Values—cont'd

Chemical Name	CAS No	IARC WOE	EPA WOE	IUR (( $\mu\text{g m}^{-3}\right)^{-1})$	MOA
Chlorobenzene	108-90-7		D		
Chlorobenzilate	510-15-6	3	B2	0.000078	
Chloroform	67-66-3	2B	LH		
Chloroprene	126-99-8	2B	LH	0.0003	M*
Chromium (III) compounds	16065-83-1	3	InI		
Chromium (VI) compounds	18540-29-9	1	CH	0.012	
Chromium (VI) trioxide, chromic acid mist	11115-74-5	1			
Cobalt compounds	7440-48-4	2B			
Coke oven emissions	8007-45-2		A	0.00062	
<i>m</i> -Cresol	108-39-4		C		
<i>o</i> -Cresol	95-48-7		C		
<i>p</i> -Cresol	106-44-5		C		
Cresols (mixed)	1319-77-3		C		
Cumene	98-82-8	2B	InI		
Cyanazine	21725-46-2		C		
Cyanide compounds	57-12-5		D		
Acetone cyanohydrins	75-86-5				
Calcium cyanide	592-01-8				
Copper cyanide	544-92-3				
Cyanogen	460-19-5				
Cyanogen bromide	506-68-3				
Cyanogen chloride	506-77-4				
Ethylene cyanohydrin	109-78-4				
Hydrogen cyanide	74-90-8				
Potassium cyanide	151-50-8				
Potassium silver cyanide	506-61-6				
Silver cyanide	506-64-9				
Sodium cyanide	143-33-9				
Thiocyanic acid, 2-(benzothiazolylthio) methyl est	21564-17-0				
Zinc cyanide	557-21-1				
2,4-D, salts and esters	94-75-7				
DDE	72-55-9		B2		
1,2-Dibromo-3-chloropropane	96-12-8	2B	B2	0.002	
Dibutylphthalate	84-74-2		D		
p-Dichlorobenzene	106-46-7	2B	C	0.000011	
3,3'-Dichlorobenzidine	91-94-1	2B	B2	0.00034	
Dichloroethyl ether	111-44-4	3	B2	0.00033	

(Continued)

TABLE 11.6 Prioritized Chronic Dose–Response Values—cont'd

Chemical Name	CAS No	IARC WOE	EPA WOE	IUR (( $\mu\text{g m}^{-3}$ ) $^{-1}$ )	MOA
1,3-Dichloropropene	542-75-6	2B	LH	0.000004	
Dichlorvos	62-73-7	2B	B2		
Diesel engine emissions	DIESEL EMIS.		LH		
Diethanolamine	111-42-2				
3,3'-Dimethoxybenzidine	119-90-4	2B	B2		
p-Dimethylaminoazobenzene	60-11-7	2B		0.0013	
3,3'-Dimethylbenzidine	119-93-7		B2		
Dimethyl formamide	68-12-2	3			
N,N-dimethylaniline	121-69-7	3			
1,1-Dimethylhydrazine	57-14-7	2B	B2		
2,4-dinitrophenol	51-28-5				
2,4-Dinitrotoluene	121-14-2	2B	B2	0.000089	
2,4/2,6-Dinitrotoluene (mixture)	25321-14-6	2B	B2		
1,4-Dioxane	123-91-1	2B	LH		
1,2-Diphenylhydrazine	122-66-7		B2	0.00022	
Epichlorohydrin	106-89-8	2A	B2	0.0000012	
1,2-Epoxybutane	106-88-7				
Ethyl acrylate	140-88-5	2B	B2		
Ethyl benzene	100-41-4	2B	D	0.0000025	
Ethyl carbamate	51-79-6	2A		0.00029	M*
Ethyl chloride	75-00-3	3			
Ethylene dibromide	106-93-4	2A	LH	0.0006	
Ethylene dichloride	107-06-2	2B	B2	0.000026	
Ethylene glycol	107-21-1				
Ethylene oxide	75-21-8	1	B1	0.000088	
Ethylene thiourea	96-45-7	3	B2	0.000013	
Ethyldene dichloride (1,1-Dichloroethane)	75-34-3		C	0.0000016	
Formaldehyde	50-00-0	1	B1	0.000013	
Diethylene glycol monobutyl ether	112-34-5				
Diethylene glycol monoethyl ether	111-90-0				
Ethylene glycol ethyl ether	110-80-5				
Ethylene glycol ethyl ether acetate	111-15-9				
Ethylene glycol methyl ether	109-86-4				
Ethylene glycol methyl ether acetate	110-49-6				
Heptachlor	76-44-8	2B	B2	0.0013	

TABLE 11.6 Prioritized Chronic Dose—Response Values—cont'd

Chemical Name	CAS No	IARC WOE	EPA WOE	IUR (( $\mu\text{g m}^{-3}\right)^{-1})$	MOA
Hexachlorobenzene	118-74-1	2B	B2	0.00046	
Hexachlorobutadiene	87-68-3	3	C	0.000022	
Hexachlorocyclopentadiene	77-47-4		NH		
Hexachlorodibenzo-p-dioxin, mixture	19408-74-3		B2	1.3	
Hexachloroethane	67-72-1	2B	LH		
Hexamethylene-1,6-diisocyanate	822-06-0				
n-Hexane	110-54-3		InI		
Hydrazine	302-01-2	2B	B2	0.0049	
Hydrochloric acid	7647-01-0	3			
Hydrofluoric acid	7664-39-3				
Hydrogen sulfide	7783-06-4		InI		
Hydroquinone	123-31-9				
Isophorone	78-59-1		C		
Lead compounds	7439-92-1	2B	B2		
Tetraethyl lead	78-00-2				
Lindane (gamma-HCH)	58-89-9	2B	B2—C	0.00031	
Alpha-Hexachlorocyclohexane (a-HCH)	319-84-6	2B	B2	0.0018	
Beta-Hexachlorocyclohexane (b-HCH)	319-85-7	2B	C	0.00053	
Technical Hexachlorocyclohexane (HCH)	608-73-1	2B	B2	0.00051	
Maleic anhydride	108-31-6				
Manganese compounds	7439-96-5		D		
Mercuric chloride	7487-94-7		C		
Mercury (elemental)	7439-97-6	3	D		
Methyl mercury	22967-92-6		C		
Phenylmercuric acetate	62-38-4				
Methanol	67-56-1				
Methoxychlor	72-43-5	3	D		
Methyl bromide	74-83-9		D		
Methyl chloride	74-87-3	3	InI		
Methyl chloroform (1,1,1-Trichloroethane)	71-55-6		InI		
Methyl isobutyl ketone	108-10-1	2B	InI		
Methyl isocyanate	624-83-9				
Methyl methacrylate	80-62-6		E		

(Continued)

TABLE 11.6 Prioritized Chronic Dose—Response Values—cont'd

Chemical Name	CAS No	IARC WOE	EPA WOE	IUR (( $\mu\text{g m}^{-3}$ ) $^{-1}$ )	MOA
Methyl tert-butyl ether	1634-04-4	3		0.00000026	
4,4'-MethylEne bis(2-chloroaniline)	101-14-4	1	B2	0.00043	
Methylene chloride	75-09-2	2B	LH	0.00000001	M*
Methylene diphenyl diisocyanate	101-68-8		InI		
4,4'-MethylEnedianiline	101-77-9	2B		0.00046	
Naphthalene	91-20-3		C	0.000034	
Nickel compounds	7440-02-0	1	A		
Nickel oxide	1313-99-1				
Nickel refinery dust	NI_DUST		A	0.00024	
Nickel subsulfide	12035-72-2		A	0.00048	
Nitrobenzene	98-95-3	2B	LH	0.00004	
2-Nitropropane	79-46-9	2B	B2	0.0000056	
Nitrosodimethylamine	62-75-9	2A	B2	0.014	M*
N-Nitrosomorpholine	59-89-2	2B		0.0019	
Parathion	56-38-2	3	C		
Polychlorinated biphenyls	1336-36-3	2A	B2	0.0001	
Aroclor 1016	12674-11-2				
Aroclor 1254	11097-69-1				
Pentachloronitrobenzene	82-68-8	3	C		
Pentachlorophenol	87-86-5	2B	B2	0.0000051	
Phenol	108-95-2	3	InI		
p-Phenylenediamine	106-50-3				
Phosgene	75-44-5		InI		
Phosphine	7803-51-2		InI		
Phosphorus, white	7723-14-0		D		
Phthalic anhydride	85-44-9				
Polybrominated biphenyls	59536-65-1	2B	B2		
Acenaphthene	83-32-9	3	D		
Acenaphthylene	206-96-8		D		
2-Aminoanthraquinone	117-79-3	3		0.0000094	
Anthracene	120-12-7	3	D		
Benzo(a)anthracene	56-55-3	2B	B2	0.00011	
Benzo(b)fluoranthene	205-99-2	2B	B2	0.00011	
Benzo[j]fluoranthene	205-82-3	2B		0.00011	
Benzo(k)fluoranthene	207-08-9	2B	B2	0.00011	
Benzo(g,h,i)perylene	191-24-2	3	D		
Benzo(a)pyrene	50-32-8	1	B2	0.0011	M*
Benzo(e)pyrene	192-97-2	3			

TABLE 11.6 Prioritized Chronic Dose—Response Values—cont'd

Chemical Name	CAS No	IARC WOE	EPA WOE	IUR (( $\mu\text{g m}^{-3}$ ) $^{-1}$ )	MOA
Carbazole	86-74-8	2B	B2		
beta-Chloronaphthalene	91-58-7				
Chrysene	218-01-9	2B	B2	0.000011	
Dibenz[a,h]acridine	226-36-8	2B		0.00011	
Dibenz[a,j]acridine	224-42-0	2A		0.00011	
Dibenz(a,h)anthracene	53-70-3	2A	B2	0.0012	M*
7H-Dibenzo[c,g]carbazole	194-59-2	2B		0.0011	
Dibenzo[a,e]pyrene	192-65-4	3		0.0011	
Dibenzo[a,h]pyrene	189-64-0	2B		0.011	
Dibenzo[a,i]pyrene	189-55-9	2B		0.011	
Dibenzo[a,l]pyrene	191-30-0	2A		0.011	
7,12-Dimethylbenz(a)anthracene	57-97-6			0.071	M*
1,6-Dinitropyrene	42397-64-8	2B		0.011	
1,8-Dinitropyrene	42397-65-9	2B		0.0011	
Fluoranthene	206-44-0	3	D		
Fluorene	86-73-7	3	D		
Indeno(1,2,3-cd)pyrene	193-39-5	2B	B2	0.00011	
3-Methylcholanthrene	56-49-5			0.0063	M*
5-Methylchrysene	3697-24-3	2B		0.0011	
1-Methylnaphthalene	90-12-0				
2-Methylnaphthalene	91-57-6		InI		
5-Nitroacenaphthene	602-87-9	2B		0.000037	
6-Nitrochrysene	7496-02-8	2B		0.011	
2-Nitrofluorene	607-57-8	2B		0.000011	
1-Nitropyrene	5522-43-0	2B		0.00011	
4-Nitropyrene	57835-92-4	2B		0.00011	
Octabromodiphenyl ether	32536-52-0		D		
Phenanthrene	85-01-8	3	D		
Pyrene	129-00-0	3	D		
1,3-Propane sultone	1120-71-4	2B		0.00069	
Propionaldehyde	123-38-6		InI		
Propoxur	114-26-1		B2		
Propylene dichloride	78-87-5		B2		
Propylene oxide	75-56-9	2B	B2	0.0000037	
Quinoline	91-22-5		LH		
Selenium compounds	7782-49-2	3	D		
Hydrogen selenide	7783-07-5				
Selenious acid	7783-00-8		D		
Selenium dioxide	7446-08-4				

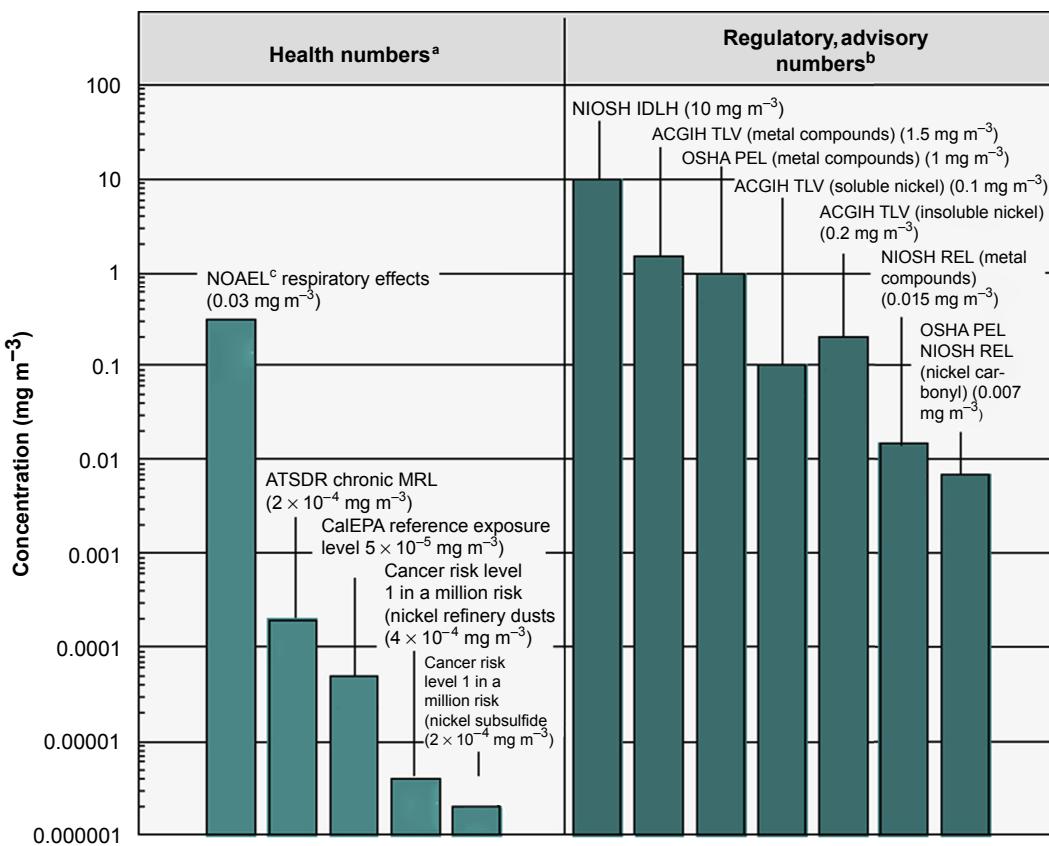
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TABLE 11.6 Prioritized Chronic Dose—Response Values—cont'd

Chemical Name	CAS No	IARC WOE	EPA WOE	IUR (( $\mu\text{g m}^{-3}$ ) $^{-1}$ )	MOA
Selenium disulfide	7488-56-4				
Selenium sulfide	7446-34-6		B2		
Selenourea	630-10-4				
Styrene	100-42-5	2B			
Styrene oxide	96-09-3	2A			
2,3,7,8-Tetrachlorodibenz-p-dioxin	1746-01-6	1	B2	33	
1,1,2,2-Tetrachloroethane	79-34-5	3	C	0.000058	
Tetrachloroethene	127-18-4	2A	LH	0.00000026	
Titanium tetrachloride	7550-45-0				
Toluene	108-88-3	3	InI		
2,4-Toluene diamine	95-80-7	2B	B2	0.0011	
2,4/2,6-Toluene diisocyanate mixture (TDI)	26471-62-5	2B		0.000011	
o-Toluidine	95-53-4	1	B2	0.000051	
Toxaphene	8001-35-2	2B	B2	0.00032	
1,2,4-Trichlorobenzene	120-82-1		D		
1,1,2-Trichloroethane	79-00-5	3	C	0.000016	
Trichloroethylene	79-01-6	2A	CH	0.0000041	M*
2,4,5-Trichlorophenol	95-95-4				
2,4,6-Trichlorophenol	88-06-2		B2	0.0000031	
Triethylamine	121-44-8				
Trifluralin	1582-09-8	3	C		
Uranium compounds	7440-61-1				
Uranium, insoluble salts	URANINSOLS				
Uranium, soluble salts	URANSOLS				
Vinyl acetate	108-05-4	2B			
Vinyl bromide	593-60-2	2A	B2	0.000032	
Vinyl chloride	75-01-4	1	CH	0.0000088	
Vinylidene chloride	75-35-4	3	SE		
m-Xylene	108-38-3				
o-Xylene	95-47-6				
Xylenes (mixed)	1330-20-7	3	InI		

IARC WOE = weight-of-evidence for carcinogenicity in humans (1, carcinogenic; 2A, probably carcinogenic; 2B, possibly carcinogenic; 3, not classifiable; 4, probably not carcinogenic). EPA WOE (2005 Guidelines) = weight of evidence for carcinogenicity under 2005 EPA cancer guidelines: CH, carcinogenic to humans; LH, likely to be carcinogenic; SE, suggestive evidence of carcinogenic potential; InI, inadequate information to assess carcinogenic potential; NH, not likely to be carcinogenic. EPA MOA (2005 Guidelines) = mode of action for carcinogenicity: M\*, mutagenic and early life data lacking; age-dependent adjustment factors should be applied when assessing risk for ages younger than 16 years per 2005 Supplemental Guidance. EPA WOE (1986 Guidelines) = weight of evidence for carcinogenicity under the 1986 EPA cancer guidelines: A, human carcinogen; B1, probable carcinogen, limited human evidence; B2, probable carcinogen, sufficient evidence in animals; C, possible human carcinogen; D, not classifiable E, evidence of noncarcinogenicity.

Source: U.S. Environmental Protection Agency. Dose-response assessment for assessing health risks associated with exposure to hazardous air pollutants. <http://www.epa.gov/airtoxics/toxsource/summary.html>; 2013 [accessed 18.10.13].



**FIGURE 11.7 Health data for inhalation exposure to nickel.** ACGIH TLV: American Conference of Governmental and Industrial Hygienists' threshold limit value expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effects. LC<sub>50</sub> (*Lethal Concentration*<sub>50</sub>): Concentration of a chemical in air to which exposure for a specific length of time is expected to cause death in 50% of a defined experimental animal population. NIOSH IDLH: National Institute of Occupational Safety and Health's immediately dangerous to life and health; NIOSH concentration representing the maximum level of a pollutant from which an individual could escape within 30 min without escape-impairing symptoms or irreversible health effects. OSHA PEL: Occupational Safety and Health Administration's permissible exposure limit expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effect averaged over a normal 8 h workday or a 40 h workweek. To convert concentrations in air (at 25 °C) from ppm to mg m<sup>-3</sup>: mg m<sup>-3</sup> = (ppm) × (molecular weight of the compound)/(24.45). For nickel: 1 ppm = 2.4 mg m<sup>-3</sup>. To convert concentrations in air from µg m<sup>-3</sup> to mg m<sup>-3</sup>: mg m<sup>-3</sup> = (µg m<sup>-3</sup>) × (1 mg/1000 µg). (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency.

Nickel (Ni) and its compounds are associated with several types of cancer, including cancers of the nasal cavity, lung, and possibly the larynx (Figure 11.7). Nickel has many uses used in steel, dental fillings, copper and brass, permanent magnets, storage batteries (along with Cd, i.e. NiCd batteries), and glazes. Exposure occurs by inhalation, ingestion, or dermally.

Occupational exposure to nickel (Ni) dust has been associated with lung and nasal cancers. The dust is a mixture of many nickel compounds, with nickel subsulfide (Ni<sub>3</sub>S<sub>2</sub>) being the major species. Both Ni refinery dust and Ni<sub>3</sub>S<sub>2</sub> are classified as human carcinogens (Group A) by the U.S. EPA. The calculated IUR estimate of  $2.4 \times 10^{-4}$  ( $\mu\text{g m}^{-3}$ )<sup>-1</sup> for Ni refinery dusts.<sup>29</sup> The IUR can be used to estimate the lifetime risk under various exposure scenarios:

$$\text{Cancer Risk} = \text{IUR} \times \text{Exposure} \quad (11.13)$$

For example, if a person were to continuously inhale air containing Ni refinery dust at an average rate of  $4 \times 10^{-3}$  µg m<sup>-3</sup> over an entire lifetime, the unit risk can be multiplied by this exposure (note that the IUR and exposure units are inverted, so they cancel):

$$\text{Cancer Risk} = (2.4 \times 10^{-4}) \times (4 \times 10^{-3}) \approx 1 \times 10^{-6}$$

Thus, this person would theoretically have a one-in-a-million increased chance of developing cancer as a direct result of breathing air containing this chemical.

The IUR is also a means of estimating the concentration that can be allowed based on a target risk. For example, assuming a person breathes the air near an abandoned smelter site that contains Ni refinery dust. What concentration of Ni dust in the air would be needed to ensure that person's lifetime cancer risk

from Ni dust does not exceed one-in-a-hundred thousand? Rearranging the equation gives

$$\text{Allowable exposure} = \frac{\text{Target risk}}{\text{IUR}}$$

$$\begin{aligned}\text{Allowable exposure} &= \frac{10^4}{2.4 \times 10^{-4}(\mu\text{g m}^{-3})^{-1}} \\ &\approx 4 \times 10^{-2} \mu\text{g m}^{-3} \quad (11.14)\end{aligned}$$

Thus, continuously breathing air containing  $4 \times 10^{-2} \mu\text{g m}^{-3}$  would be expected to result in no greater than a one-in-a-hundred thousand increased likelihood of developing cancer from the Ni exposure.

For nickel subsulfide,<sup>29</sup> the IUR estimate of  $4.8 \times 10^{-4} (\mu\text{g m}^{-3})^{-1}$ . Thus, if a person were to continuously breathe air containing this nickel compound at an average of  $0.002 \mu\text{g m}^{-3}$  an entire lifetime, that person would theoretically have no more than a one-in-a-million increased chance of developing cancer as a direct result of breathing air containing  $\text{Ni}_3\text{S}_2$ .

Nickel carbonyl [ $\text{Ni}(\text{CO})_4$ ] has been reported to produce lung tumors in rats exposed via inhalation. The U.S. EPA has classified  $\text{Ni}(\text{CO})_4$  as a Group B2, probable human carcinogen.

Beryllium (Be) compounds are known to cause lung cancer, as worker studies in beryllium production facilities have shown (Figure 11.8). Beryllium

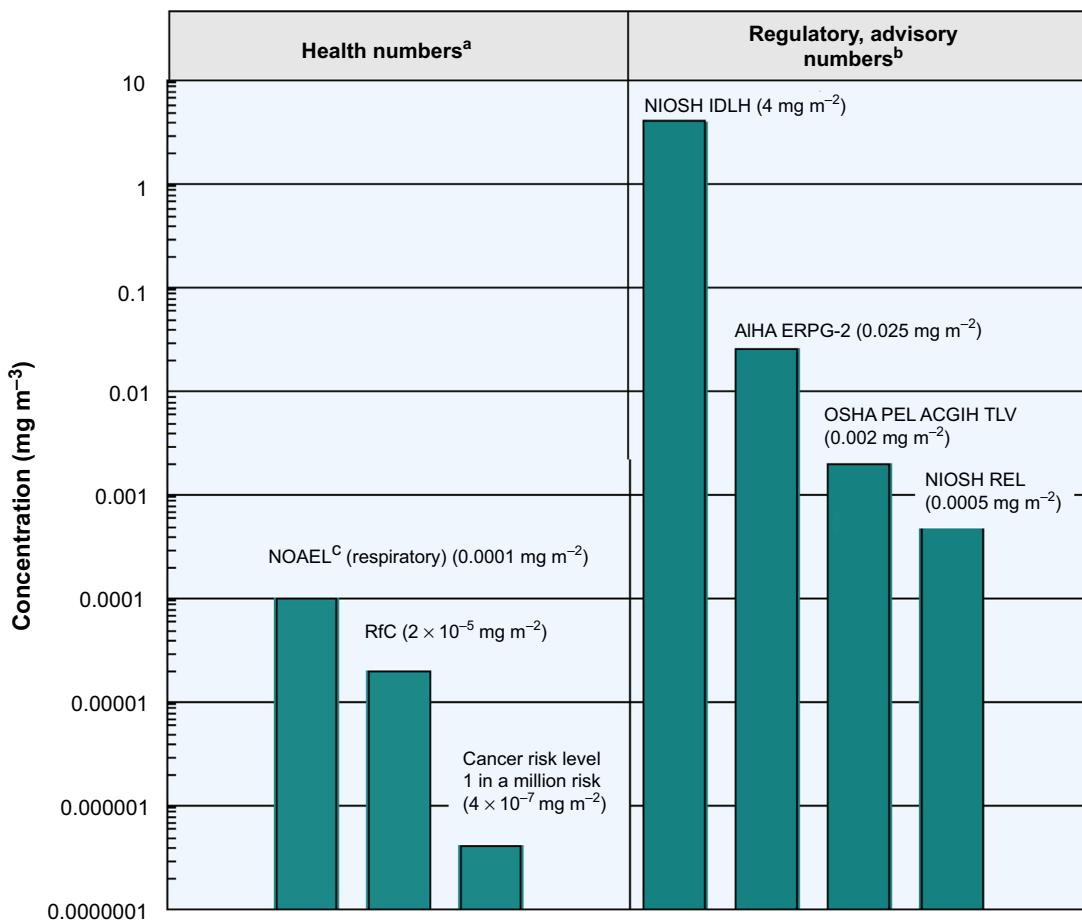


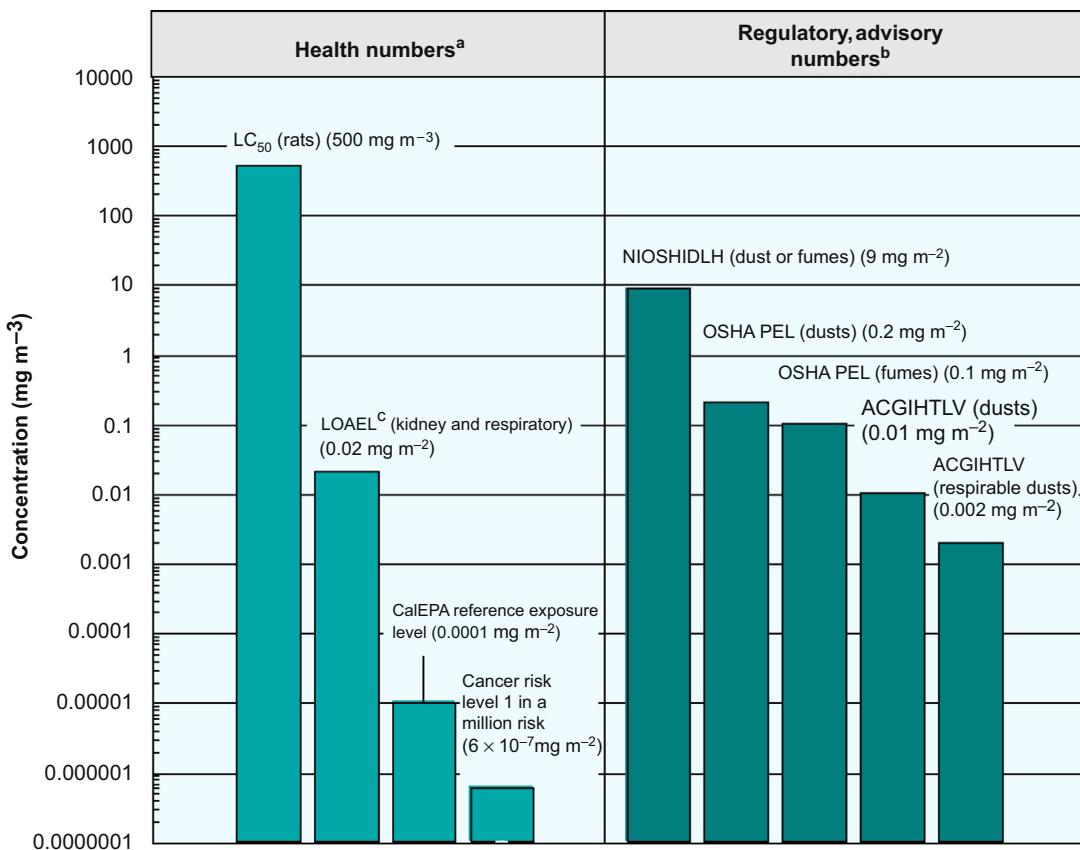
FIGURE 11.8 **Health data for beryllium related to inhalation exposure.** Beryllium and its compounds do not exist in the atmosphere in the vapor phase (in ppm); therefore, an air conversion factor is not applicable. ACGIH TLV: American Conference of Governmental and Industrial Hygienists' threshold limit value expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effects.  $LC_{50}$  (Lethal Concentration<sub>50</sub>): Concentration of a chemical in air to which exposure for a specific length of time is expected to cause death in 50% of a defined experimental animal population. NIOSH IDLH: National Institute of Occupational Safety and Health's immediately dangerous to life and health; NIOSH concentration representing the maximum level of a pollutant from which an individual could escape within 30 min without escape-imparing symptoms or irreversible health effects. OSHA PEL: Occupational Safety and Health Administration's permissible exposure limit expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effect averaged over a normal 8 h workday or a 40 h workweek. Be and its compounds do not exist in the atmosphere in the vapor phase (in ppm); therefore, an air conversion factor is not applicable. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency.

compounds are used as aerospace and defense industrial metals; in electrical components; in medical devices (e.g. X-ray tubes); in rocket fuel; in ceramic manufacturing; as additives to plastics and glass; in dental applications; and in sporting goods. Recently, Be has been used for fiber optics and cellular network communication systems. These have led to occupational exposures to Be. Atmospheric releases of Be occur primarily through the combustion of coal and fuel oil. The major routes of exposure for the general public is via inhalation of ambient air Be concentrations and tobacco smoke, as well as in food.<sup>30</sup>

Exposure to cadmium (Cd) and Cd compounds are associated with an increased risk of lung cancer (Figure 11.9). Occupational Cd exposure result from working near zinc and lead extraction and processing, producing cadmium powders, welding cadmium-coated steel, and working

with solders that contain cadmium. The primary use of Cd is as a metal coating to prevent corrosion, but it is also released in manufacturing plastic and synthetic products, in batteries, as stabilizers for polyvinyl chloride, and in fungicides. The industrial processes involved in making these products release cadmium into the air, surface water, groundwater, and topsoil where cadmium can be taken up by flora and sequentially transferred to consuming animals. Contaminated soil that allows uptake into tobacco plants possibly contributes the highest nonoccupational human exposure as the Cd is released from combustion of the plant material during smoking. Food is likely the main Cd source for nonsmokers.<sup>30</sup>

Cadmium compounds cause genetic damage, including gene mutations, DNA strand breaks, chromosomal damage, cell transformation, and disrupted DNA repair. Chromosomal aberrations have been observed in



**FIGURE 11.9 Health data for cadmium related to inhalation exposure.** ACGIH TLV: American Conference of Governmental and Industrial Hygienists' threshold limit value expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effects. LC<sub>50</sub> (Lethal Concentration<sub>50</sub>): Concentration of a chemical in air to which exposure for a specific length of time is expected to cause death in 50% of a defined experimental animal population. NIOSH IDLH: National Institute of Occupational Safety and Health's immediately dangerous to life and health; NIOSH concentration representing the maximum level of a pollutant from which an individual could escape within 30 min without escape-impairing symptoms or irreversible health effects. OSHA PEL: Occupational Safety and Health Administration's permissible exposure limit expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effect averaged over a normal 8 h workday or a 40 h workweek. To convert concentrations in air (at 25 °C) from ppm to mg m⁻³: mg m⁻³ = (ppm) × (molecular weight of the compound)/(24.45). For cadmium: 1 ppm = 4.6 mg m⁻³. To convert concentrations in air from µg m⁻³ to mg m⁻³: mg m⁻³ = (µg m⁻³) × (1 mg per 1000 µg). (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency.

the lymphocytes of workers occupationally exposed to cadmium. Ionic cadmium is the genotoxic form Cd and its compounds. Therefore, the carcinogenic potential of a given cadmium compound is expected to depend on the degree to which the compound releases ionic cadmium under the conditions of exposure.<sup>31</sup>

The calculated Cd IUR estimate of  $1.8 \times 10^{-3}$  ( $\mu\text{g m}^{-3}$ )<sup>-1</sup>. Thus, a continuously exposed individual inhaling air with an average of  $0.0006 \mu\text{g m}^{-3}$  over an entire lifetime would theoretically be a one-in-a-million increased chance of developing cancer as a direct result of this exposure.

Cadmium is regulated under numerous laws. It is listed as a hazardous air pollutant under the Clean Air Act's National Emissions Standards for Hazardous Air Pollutants, as well as regulations to limit cadmium emissions from

new municipal waste combustion units. Urban Air Toxics Strategy: Cadmium compounds have been identified as one of 33 hazardous air pollutants that present the greatest threat to public health in urban areas.

Hexavalent chromium ( $\text{Cr}^{6+}$ ) compounds are known to cause lung cancer (Figure 11.10). The steel, electroplating, and other industries have used Cd for protection against corrosion. Electroplating converts  $\text{Cr}^{6+}$ —the carcinogenic form—into a noncarcinogenic form (e.g.  $\text{Cr}^0$ ). The leather and textile industries have used the metal for tanning, coloring, and dyes. Workers who handle chromium VI are at greater risk than is the general population. Chromium is widely distributed in the air, water, soil, and food. Through some of these media, the entire population is probably exposed. The highest chromium exposure occurs in occupations related to

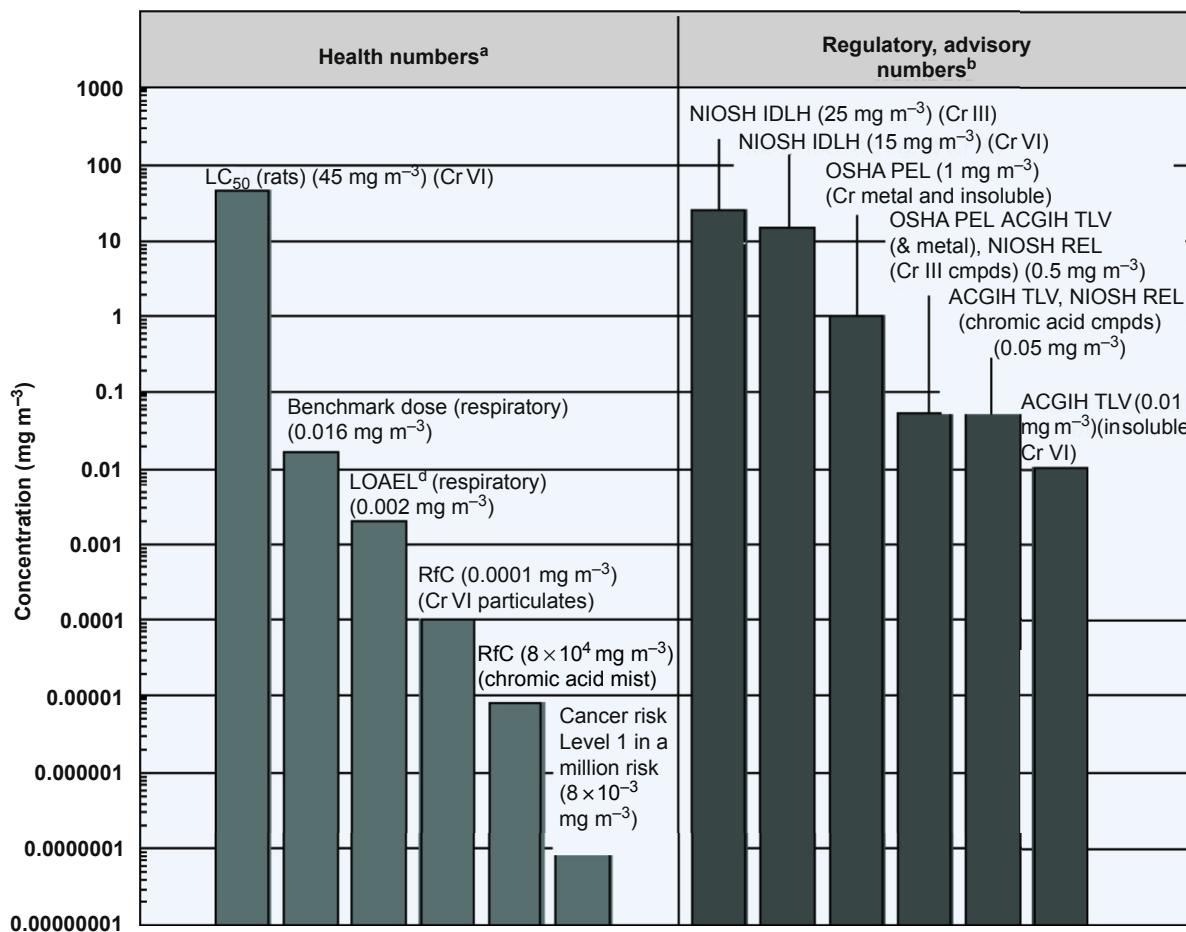


FIGURE 11.10 Health data from inhalation exposure to chromium. ACGIH TLV: American Conference of Governmental and Industrial Hygienists' threshold limit value expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effects.  $\text{LC}_{50}$  (Lethal Concentration<sub>50</sub>): Concentration of a chemical in air to which exposure for a specific length of time is expected to cause death in 50% of a defined experimental animal population. NIOSH IDLH: National Institute of Occupational Safety and Health's immediately dangerous to life and health; NIOSH concentration representing the maximum level of a pollutant from which an individual could escape within 30 min without escape-impairing symptoms or irreversible health effects. OSHA PEL: Occupational Safety and Health Administration's permissible exposure limit expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effect averaged over a normal 8 h workday or a 40 h workweek. To convert concentrations in air (at 25 °C) from ppm to  $\text{mg m}^{-3}$ :  $\text{mg m}^{-3} = (\text{ppm}) \times (\text{molecular weight of the compound}) / (24.45)$ . For chromium: 1 ppm =  $2.12 \text{ mg m}^{-3}$ . (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency.

stainless steel production, welding, chrome plating, and leather tanning.

Although lead (Pb) is most associated with neurotoxicity, two of its compounds, i.e. lead acetate and lead phosphate are likely human carcinogens. Lead acetate is used in cotton dyes; as a coating for metals; as a drier in paints, varnishes, and pigment inks; as a colorant in certain permanent hair dyes (progressive dyes); in explosives; and in washes to treat poison ivy. Lead phosphate is a stabilizer in certain plastics and specialty glass. Exposure to these compounds can occur by inhalation, ingestion, or dermally.

Occupational studies indicated that inhaled chromium is a human carcinogen, resulting in an increased risk of lung cancer. Although chromium-exposed workers were exposed to both Cr<sup>3+</sup> and Cr<sup>6+</sup> compounds, only the Cr<sup>6+</sup> compounds have been found to be carcinogenic in animal studies. Thus, the Cr<sup>6+</sup> species is the only Cr oxidation state that is classified by the U.S. EPA has as a human carcinogen (Group A).<sup>32,33</sup>

The calculated Cr<sup>6+</sup> IUR estimate is  $1.2 \times 10^{-2}$  ( $\mu\text{g m}^{-3}\right)^{-1}$ . Thus, a continuously exposed person breathing air containing Cr<sup>6+</sup> an average of  $8 \times 10^{-5}$   $\mu\text{g m}^{-3}$  over an entire lifetime would theoretically have no more than a one-in-a-million increased risk of developing cancer.

Compounds of the metalloid arsenic have been associated with many forms of skin, lung, bladder, kidney, and liver cancers (Figure 11.11). Occupational exposure to inhaled arsenic, especially in mining and copper smelting, has been consistently associated with an increased lung cancer risk. Arsenic is also used in wood preservatives, glass, insecticides, herbicides, among many processes. Exposure occurs mainly by inhalation air, and by ingestion of food and water.<sup>30</sup>

### 11.5.2 Fibers

Fibers were introduced in Chapter 6 as elongated particles, i.e. having aspect ratios greater than 3:1. Exposure to fibers of various chemical compositions, e.g. fiberglass, fabrics, and minerals has been linked to lung and other cancers. The major carcinogenic fiber is arguably asbestos, a group of highly fibrous minerals with separable, long, and thin fibers. These are discussed in detail in Chapter 5. Exposure to asbestos causes lung cancer and mesothelioma, which is a cancer of the linings of the lung, abdomen, and heart. It also causes asbestosis, a noncancer disease that progressively limits oxygen exchange.

Many of the occupational studies have reported that exposure to asbestos via inhalation causes lung cancer and mesothelioma (Figure 11.12). Smokers who are also exposed to asbestos have a greater than additive increased risk of developing lung cancer.<sup>34</sup> Asbestos exposure via ingestion has also been linked to GI

cancers. Fibers longer than 5  $\mu\text{m}$  appear to be more carcinogenic than short fibers (<5  $\mu\text{m}$ ). Asbestos to be a human carcinogen (cancer-causing agent) and has ranked it in the U.S. EPA's Group A.

The cancer mechanism for asbestos is complex. The synergistic effect of asbestos exposure and cigarette smoke observed for lung cancer has not been observed for mesothelioma in humans. Thus, the mechanisms induced solely by fibers *versus* those of fibers in concert with other carcinogens must be different. Fiber morphology, durability, and surface properties may be the key physicochemical properties that affect carcinogenicity. Asbestos appear to be both a cancer initiator and a promoter. Also, asbestos includes several different types of minerals, so it would appear that numerous mechanisms, the physical and chemical makeup of the different fibers would have different mechanisms.<sup>35</sup>

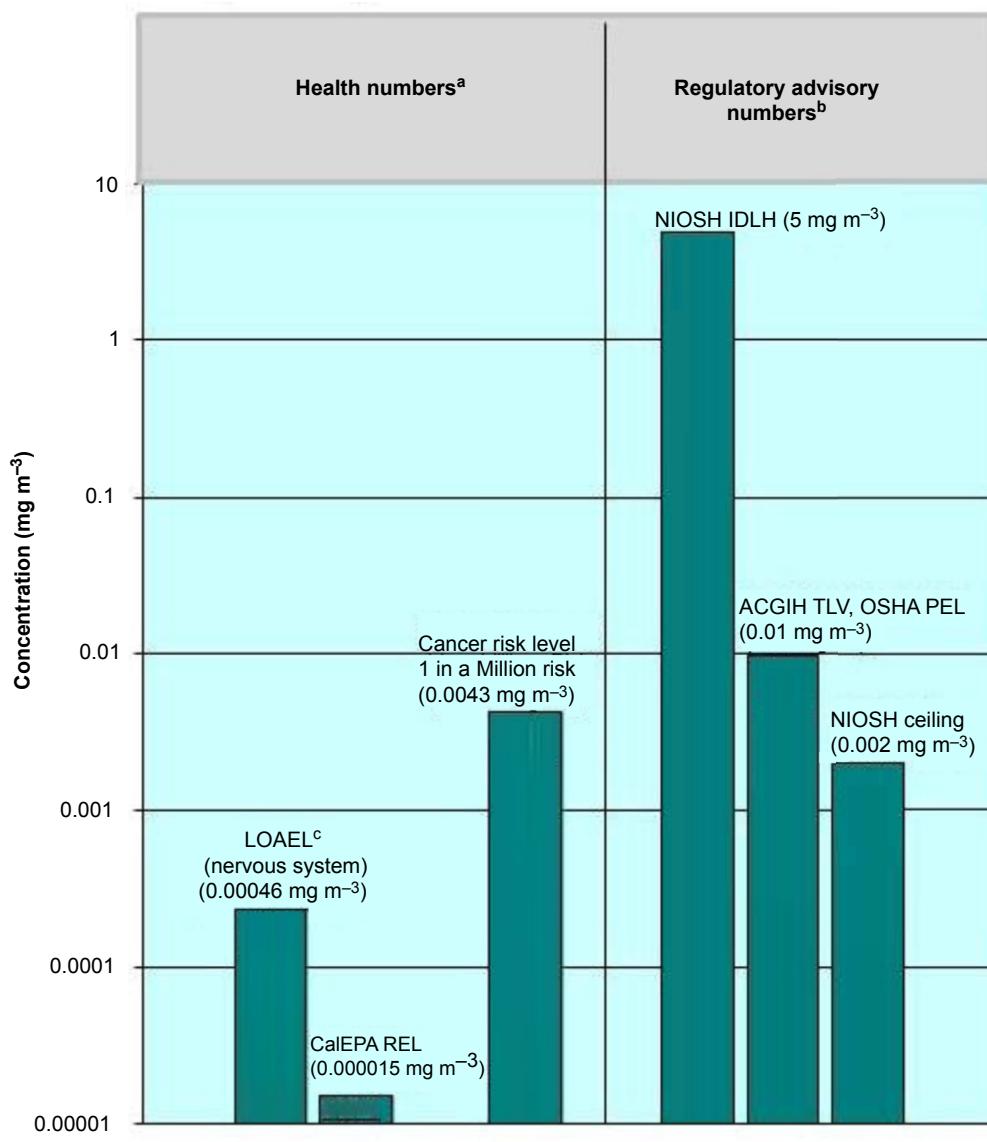
The calculated IUR estimate is  $2.3 \times 10^{-1}$  ( $\text{fibers cm}^{-3}\right)^{-1}$ . Thus, if an individual were to continuously breathe air containing asbestos at an average of 0.000004 fibers  $\text{cm}^{-3}$  over an entire lifetime, that person would theoretically have no more than a one-in-a-million increased chance of developing cancer as a direct result of breathing air containing this concentration of asbestos.<sup>36</sup>

Other fibers have been studied to determine cancer potential. The data are for the most part incomplete and not conclusive. This is not the same as saying they do not cause cancer, only that the weight of evidence is less than that of asbestos in designating them as carcinogenic fibers. Fiberglass, for example, has not been designated to be a carcinogen, but it may emit styrene, which is a possible carcinogen.<sup>38</sup>

Human-made fibers, such as carbon nanotubes, have properties that render them inhalable and potentially harmful, e.g. they may emulate some of asbestos' physical, chemical, and biological mechanisms.<sup>38</sup> Unfortunately, there is presently a paucity of reliable data from which to conduct a cancer risk assessment.

### 11.5.3 Carcinogenic Organic Compounds

Most of the hazardous air pollutants listed in Table 11.6 are organic compounds. These include both aromatics and aliphatic compounds, i.e. rings and chains, respectively. Their toxicity generally and carcinogenicity specifically depend on their chemical structure, especially the extent and types of substitutions (e.g. halogens and alkylated groups may make aromatic compounds more carcinogenic). The chemical conformation is also very important. For example, planar structures tend to increase the likelihood of docking to ligands on cell membranes, which could initiate mutations. As evidence, the planar PCBs appear to be more toxic than the nonplanar PCBs.

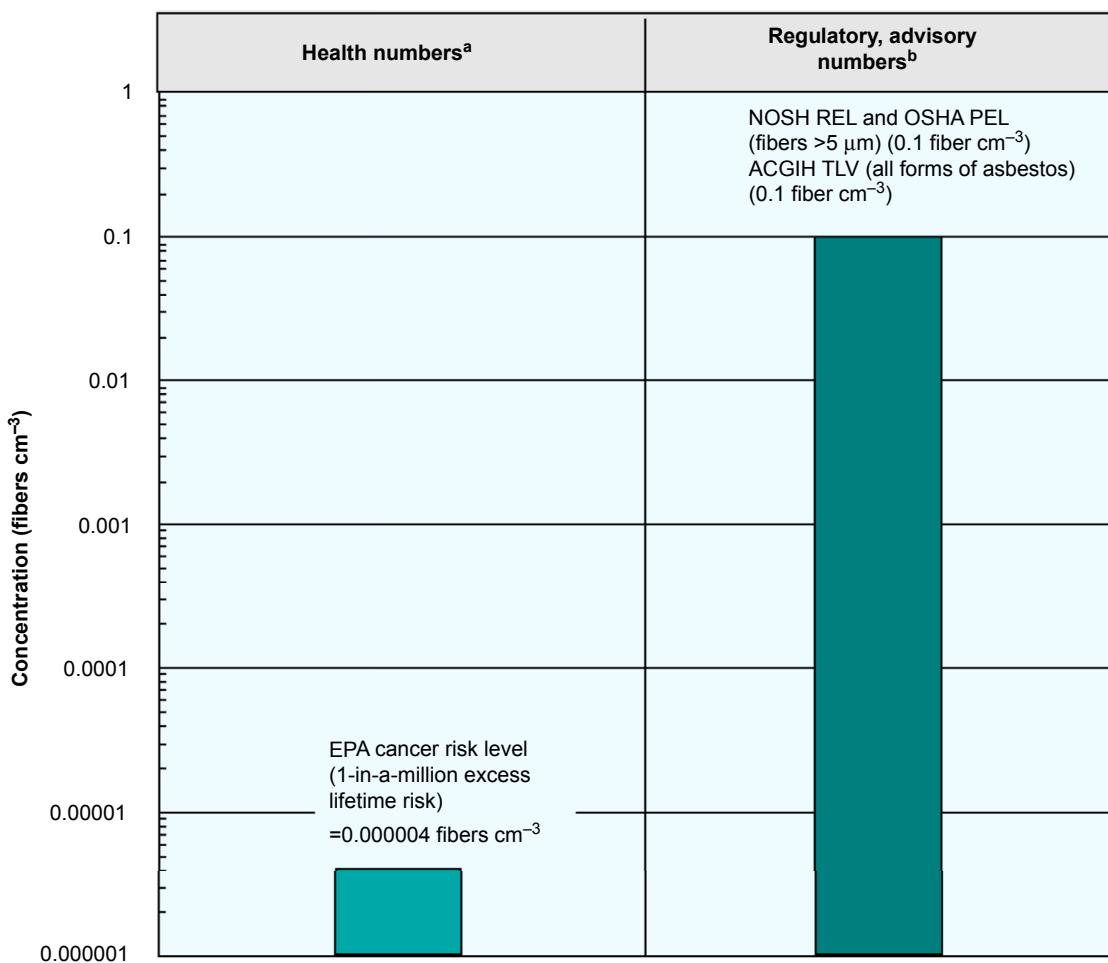


**FIGURE 11.11** Health data from inhalation exposure to inorganic arsenic. ACGIH TLV: American Conference of Governmental and Industrial Hygienists' threshold limit value expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effects.  $LC_{50}$  (Lethal Concentration<sub>50</sub>): Concentration of a chemical in air to which exposure for a specific length of time is expected to cause death in 50% of a defined experimental animal population. NIOSH IDLH: National Institute of Occupational Safety and Health's immediately dangerous to life and health; NIOSH concentration representing the maximum level of a pollutant from which an individual could escape within 30 min without escape-impairing symptoms or irreversible health effects. OSHA PEL: Occupational Safety and Health Administration's permissible exposure limit expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effect averaged over a normal 8 h workday or a 40 h workweek. To convert concentrations in air (at 25 °C) from ppm to mg m<sup>-3</sup>: mg m<sup>-3</sup> = (ppm) × (molecular weight of the compound)/(24.45). For inorganic arsenic: 1 ppm = 3.06 mg m<sup>-3</sup>. For arsine: 1 ppm = 3.19 mg m<sup>-3</sup>. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency.

Also, many of the properties that make for more persistence and bioavailability may also increase the potential carcinogenicity (see Chapter 18). For example, if a compound does not degrade rapidly or its bioactivated metabolite may have a strong likelihood of reaching the target tissue to initiate carcinogenesis.

The process of bioactivation, i.e. increasing carcinogenicity and other forms of toxicity endogenously in

PAHs, which are molecularly flat compounds with repeating benzene structures. The chemical structure, i.e. stereochemistry, renders most PAHs highly hydrophobic, i.e. fat soluble, and difficult for an organism to eliminate (since most blood and cellular fluids are mainly water). This property also enhances the PAHs' ability to insert themselves into the DNA molecule, interfering with transcription and replication. This is



**FIGURE 11.12 Health data from exposure to asbestos fibers.** ACGIH TLV: American Conference of Governmental and Industrial Hygienists' threshold limit value expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effects.  $LC_{50}$  (Lethal Concentration<sub>50</sub>): Concentration of a chemical in air to which exposure for a specific length of time is expected to cause death in 50% of a defined experimental animal population. NIOSH IDLH: National Institute of Occupational Safety and Health's immediately dangerous to life and health; NIOSH concentration representing the maximum level of a pollutant from which an individual could escape within 30 min without escape-impairing symptoms or irreversible health effects. OSHA PEL: Occupational Safety and Health Administration's permissible exposure limit expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effect averaged over a normal 8 h workday or a 40 h workweek. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency.

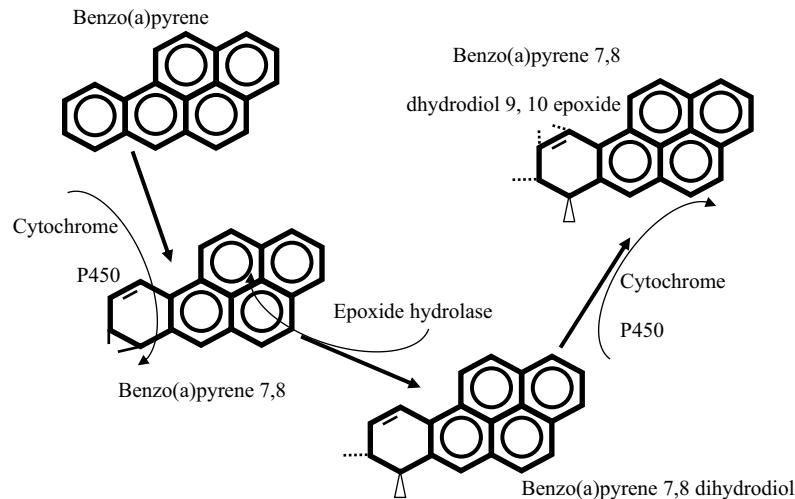
why some large organic molecules can be mutagenic and carcinogenic. One of the most toxic PAHs is benzo(a)pyrene, which is found in cigarette smoke, combustion of coal, coke oven emissions, and numerous other processes that use combustion. The compound likely produces an epoxide form compound that is even more toxic and carcinogenic than the parent PAH (Figure 11.13).

Note that these reactions, like many others involving carcinogenesis of organic compounds are catalyzed by cytochrome P450 is the most prominent member of the superfamily (CYP) of a large group of that accelerate oxidation of organic compounds (discussed in Chapter 9).<sup>39</sup> As also common for metabolism involved in carcinogenesis, other enzymes are

involved. In this series of reactions, the enzyme epoxide hydrolase is involved in hydrolyzing the metabolite benzo(a)pyrene 7,8 to benzo(a)pyrene 7,8 dihydrodiol, which is further metabolized to the suspected carcinogenic epoxide metabolite.

Carcinogens are a global concern. For example, the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) is a European Union regulation that lists chemicals of concern, including carcinogens (Table 11.7). REACH addresses the production and use of chemicals with regard to potential adverse impacts on human health and ecosystems. The European Chemicals Agency keeps a candidate list of substance of very high concern. The criteria are delineated in article 57 of the REACH Regulation.<sup>40</sup> A substance

**FIGURE 11.13** Biological activation of benzo(a)pyrene to form the carcinogenic active metabolite benzo(a)pyrene 7,8 dihydrodiol 9, 10 epoxide. During metabolism, the biological catalysts (enzymes) cytochrome P-450 and epoxide hydrolase are employed to make the molecule more polar, and in the process form diols and epoxides. These metabolites are more toxic than the parent compound.



may be proposed as an SVHC if it meets one or more of the following criteria:

- Carcinogenic
- Mutagenic
- Toxic for reproduction
- Persistent, bioaccumulative, and toxic
- Scientific evidence that the chemical presents probable, serious effects to human health or the environment which give rise to an equivalent level of concern (case-by-case decision).

material is damaged, but unlike the direct absorption of the chemical, the damage occurs after numerous reactions with the ozone in the stratosphere and the concomitant increase in UV radiation reaching the earth's surface that would have otherwise have been trapped (Figure 11.15).

Other free radicals besides O catalyze ozone destruction, including  $\text{Cl}\cdot$ ,  $\text{OH}\cdot$ ,  $\text{HOO}\cdot$ , and  $\text{NO}\cdot$ . Many reactions occur between  $\text{O}_3$  and various chemicals, but the net  $\text{O}_3$  depletion reaction is

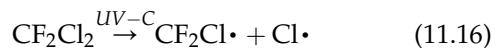


## 11.6 INDIRECT RELATIONSHIPS

As is the case for respiratory and cardiovascular effects discussed in the previous chapters, air pollution can lead to cancers in indirect ways. The most prominent indirect pathway is the depletion of the stratospheric ozone layer (Figure 11.14). In the late 1970s, the scientific community presented strong evidence of stratospheric ozone reacting with halogenated compounds found refrigerants, propellants, and other chemicals. As a result, laws and regulations were passed in many countries to decrease and eliminate the manufacture and use of several of these compounds, especially the halocarbons, which include the chlorofluorocarbons (CFCs).

Depletion of  $\text{O}_3$  begins with the release of chemicals into the atmosphere, i.e. air pollutants. Direct exposure is when a toxic chemical is absorbed, distributed, and metabolized to induce changes to genetic material in the cell, which then is expressed as clonal, tumor cells. Conversely, air pollutant carcinogenesis can be indirect, i.e. disease or damage results from earlier reactions that allow for exposures to other agents. In the case of  $\text{O}_3$  depletion, the agent is ultraviolet electromagnetic radiation. Like the direct exposure, the cellular genetic

Similar reaction reactions occur when CFCs release atomic Cl. While in the form of CFC, the chlorine and fluorine are tightly bound in stable compounds. This allows them to move up into stratosphere, where the high energy causes the molecules and fragments of their molecules to photodissociate to form radicals, including  $\text{Cl}\cdot$ ,  $\text{F}\cdot$ ,  $\text{FO}\cdot$ , and  $\text{ClO}\cdot$ . Catalysis is an important part of the process. That is, a molecule acts as the catalyst by reacting with an  $\text{O}_3$  molecule to remove one of the oxygen atoms, which generate molecular oxygen and the oxygenated form of the molecular catalyst. The oxygenated molecule then reacts with O to form another molecule of  $\text{O}_2$ . Many of these reactions involve free radicals, which are generally reactive given their odd number of electrons. For example, the refrigerant CFC-12 ( $\text{CF}_2\text{Cl}_2$ ) is an important ozone-depleting compound that releases  $\text{Cl}\cdot$ , in a reaction catalyzed photochemically. The CFC rises in the atmosphere until it reacts with ultraviolet light:



The chlorine atom is highly reactive and can undergo many reaction types that destroy  $\text{O}_3$ . In addition, the other product,  $\text{CF}_2\text{Cl}\cdot$  can then react with  $\text{OH}\cdot$ :



TABLE 11.7 Select Carcinogens Listed in Europe as Substances of Very High Concern

Substance Name	EC Number	CAS Number	Date of Inclusion	Reason for Inclusion
Cobalt(II) chloride (cobalt dichloride)	231-589-4	7646-79-9	October 28, 2008 June 20, 2011	Carcinogen
1,2,3-Trichloropropane	202-486-1	96-18-4	June 20, 2011	Carcinogen; toxic for reproduction
Hydrazine	206-114-9	302-01-2/7803-57-8	June 20, 2011	Carcinogen
Strontium chromate	232-142-6	7789-06-2	June 20, 2011	Carcinogen
Chromic acid, Oligomers of chromic acid and dichromic acid, Dichromic acid	231-805-1-236-881-5	7738-94-5-13530-68-2	December 15, 2010	Carcinogen
Chromium trioxide	215-607-8	1333-82-0	December 15, 2010	Carcinogen; mutagen
2-Methoxyethanol	203-713-7	109-86-4	December 15, 2010	Toxic for reproduction
Cobalt(II) diacetate	200-755-8	71-48-7	December 15, 2010	Carcinogen; toxic for reproduction
Cobalt(II) carbonate	208-169-4	513-79-1	December 15, 2010	Carcinogen; toxic for reproduction
Cobalt(II) dinitrate	233-402-1	10141-05-6	December 15, 2010	Carcinogen; toxic for reproduction
Cobalt(II) sulfate	233-334-2	10124-43-3	December 15, 2010	Carcinogen; toxic for reproduction
Sodium chromate	231-889-5	7775-11-3	June 18, 2010	Carcinogen; mutagen; toxic for reproduction
Potassium chromate	232-140-5	7789-00-6	June 18, 2010	Carcinogen; Mutagen
Ammonium dichromate	232-143-1	7789-09-5	June 18, 2010	Carcinogen; mutagen; toxic for reproduction
Potassium dichromate	231-906-6	7778-50-9	June 18, 2010	Carcinogen; Mutagen; toxic for reproduction
Boric acid	233-139-2/234-343-4	10043-35-3/11113-50-1	June 18, 2010	Toxic for reproduction
Trichloroethylene	201-167-4	79-01-6	June 18, 2010	Carcinogen
Acrylamide	201-173-7	79-06-1	March 30, 2010	Carcinogen; Mutagen
Aluminosilicate refractory ceramic fibres	—	Extracted from Index no. 650-017-00-8	January 13, 2010	Carcinogen
Zirconia aluminosilicate refractory ceramic fibres	—	Extracted from Index no. 650-017-00-8	January 13, 2010	Carcinogen
Pitch, coal tar, high temp.	266-028-2	65996-93-2	January 13, 2010	Carcinogen; PBT, vPvB

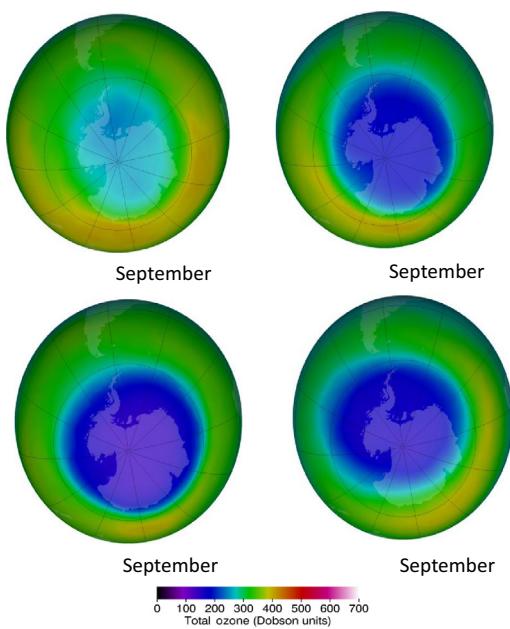
(Continued)

TABLE 11.7 Select Carcinogens Listed in Europe as Substances of Very High Concern—cont'd

Substance Name	EC Number	CAS Number	Date of Inclusion	Reason for Inclusion
2,4-Dinitrotoluene	204-450-0	121-14-2	January 13, 2010	Carcinogen;
Anthracene oil	292-602-7	90640-80-5	January 13, 2010	Carcinogen; PBT, vPvB
Anthracene oil, anthracene paste	292-603-2	90640-81-6	January 13, 2010	Carcinogen; mutagen; PBT, vPvB
Anthracene oil, anthracene paste, anthracene fraction	295-275-9	91995-15-2	January 13, 2010	Carcinogen; mutagen; PBT, vPvB
Anthracene oil, anthracene paste, distillation lights	295-278-5	91995-17-4	January 13, 2010	Carcinogen; mutagen; PBT, vPvB
Anthracene oil, anthracene-low	292-604-8	90640-82-7	January 13, 2010	Carcinogen; mutagen; PBT, vPvB
Lead chromate	231-846-0	7758-97-6	January 13, 2010	Carcinogen; toxic for reproduction
Lead chromate molybdate sulfate red (C.I. Pigment red 104)	235-759-9	12656-85-8	January 13, 2010	Carcinogen; toxic for reproduction
Lead sulfochromate yellow (C.I. Pigment yellow 34)	215-693-7	1344-37-2	January 13, 2010	Carcinogen; toxic for reproduction
Arsenic pentoxide (diarsenic pentaoxide)	215-116-9	1303-28-2	October 28, 2008	Carcinogen
Arsenic trioxide (diarsenic trioxide)	215-481-4	1327-53-3	October 28, 2008	Carcinogen
4,4'-Diaminodiphenylmethane (MDA)	202-974-4	101-77-9	October 28, 2008	Carcinogen
Lead hydrogen arsenate	232-064-2	7784-40-9	October 28, 2008	Carcinogen; toxic for reproduction
Sodium dichromate	234-190-3	7789-12-010588-01-9	October 28, 2008	Carcinogen; mutagen; toxic for reproduction
Triethyl arsenate	427-700-2	15606-95-8	October 28, 2008	Carcinogen

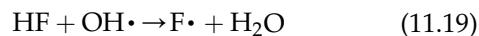
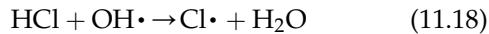
PBT, Persistent, Bioaccumulative and Toxic; vPvB, Very Persistent and Very Bioaccumulative.

Source: European Chemical Agency. Substances of very high concern. <http://echa.europa.eu/addressing-chemicals-of-concern/authorisation/substances-of-very-high-concern-identification>; 2013 [accessed 18.10.13].



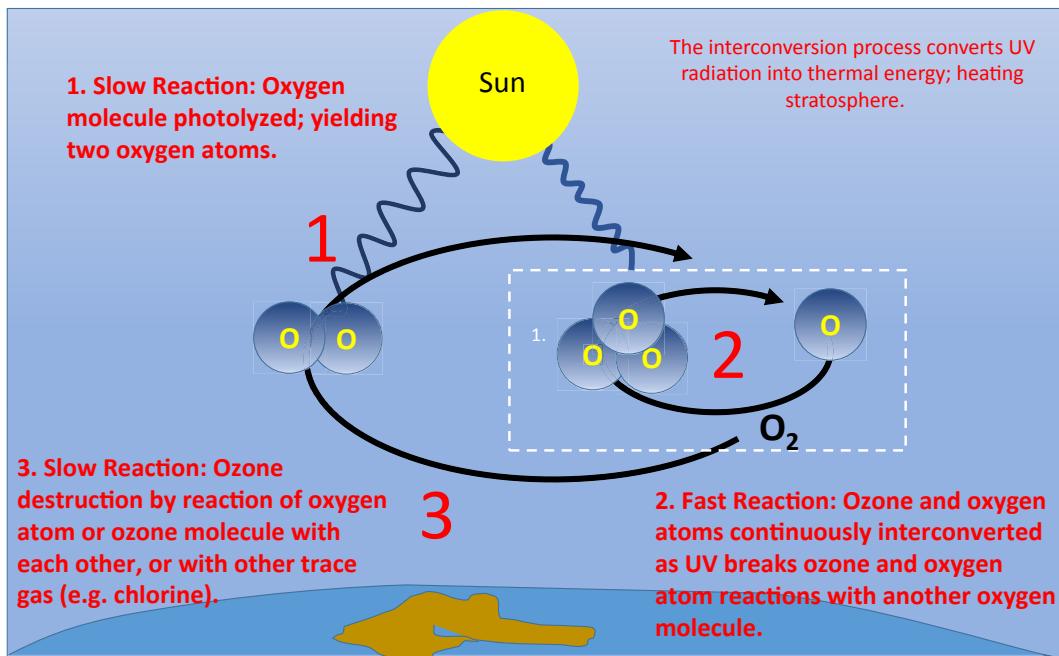
**FIGURE 11.14** Change in September monthly mean concentration of ozone ( $O_3$ ) in the stratosphere indicated by false-color view of total ozone over the Antarctic pole. The purple and blue colors indicate the lowest concentrations of ozone, and the yellows and reds show higher indications. Dobson unit = number of  $O_3$  molecules of ozone required to create a 0.01 mm layer of pure  $O_3$  at a 0 °C and 1 atm. (For color version of this figure, the reader is referred to the online version of this book.)

These products then react to form even more radicals.

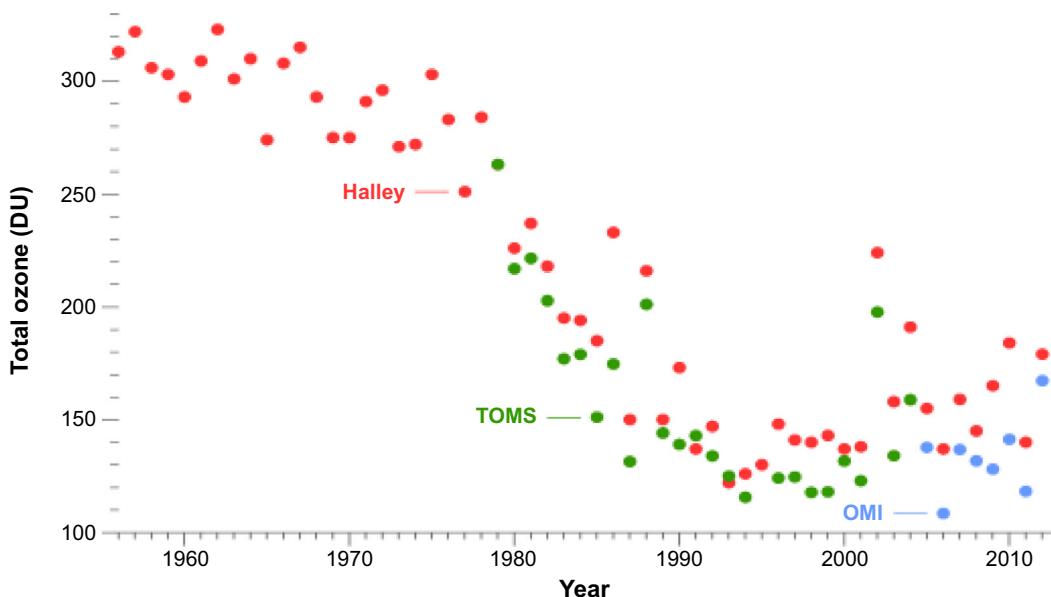


Thus, halocarbons are able to destroy ozone with numerous reactions. These decreasing ozone concentrations diminish the UV filter, which increases the amount of UV radiation at the earth's surface, thus increasing the global UV dose in the temperate zones (Figure 11.16). This change has been associated with an increase in the incidence of skin cancer, especially the most virulent form, melanoma. The disease is the result of UV exposure, but the UV exposure has been increased due to chemical reactions in the stratosphere, decreasing the absorption of UV. Indeed, the incidence of both nonmelanoma and melanoma skin cancers has been increasing over the past decades.

Globally each year, as many as 3 million persons contract nonmelanoma skin cancer and 132,000 persons contract melanoma. In the U.S. skin cancer represents a third of all diagnosed cancers, with about 20% of the population expected to contract skin cancer in their lifetimes. A 10% decrease in stratospheric  $O_3$  concentrations is projected to increase nonmelanoma skin cancer incidence by 26% worldwide. This would be associated with an additional 300,000 nonmelanoma and 4500 melanoma skin cancer cases annually.<sup>41</sup>



**FIGURE 11.15** Production and destruction of ozone in the stratosphere. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: *The process of ozone depletion*. <http://www.epa.gov/ozone/science/process.html>; 2013 [accessed 17.10.13]. U.S. Environmental Protection Agency.



**FIGURE 11.16** October monthly mean total ozone concentrations measured in Antarctica expressed in Dalton units (Dobson unit = number of  $O_3$  molecules of ozone required to create a 0.01 mm layer of pure  $O_3$  at 0 °C and 1 atm). The Halley Bay (Halley) instruments are deployed on the ground and other data points were collected by satellite above Antarctica (the Total Ozone Mapping Spectrometer (TOMS) and Ozone Monitoring Instrument (OMI)). Note the precipitous decline in total atmospheric ozone in the 1980s. (For color version of this figure, the reader is referred to the online version of this book.) National Aeronautics and Space Administration. Ozone facts: history of the ozone hole. <http://ozonewatch.gsfc.nasa.gov/facts/history.html>; 2013 [accessed 17.10.13].

## QUESTIONS

- What are the two steps in Knudson's theory of cancer etiology?
- Why do carcinogens not have a published RfC?
- Which of Hill's criteria most closely tracks with the dose-response curve?
- What is the principle hazard characteristic for a carcinogen? What are its units? How do these compare to the units for exposure?
- Calculate the additional lifetime cancer risk of a person living near a plant that emits chloroform, assuming the person breathes an average of  $0.09 \mu\text{g chloroform m}^{-3}$  in the gas phase and  $0.22 \text{ mg kg}^{-1}$  in the aerosol phase at work (8 h per day, 5 days per week for 50 weeks). The rest of the time the person breathes  $0.01 \mu\text{g chloroform m}^{-3}$  in the gas phase and  $0.1 \text{ mg kg}^{-1}$  in the aerosol phase. Also, assume that the only exposure is by inhalation. State all other assumptions needed to estimate this risk.
- Assuming that, in addition to the above exposure, some of the chloroform settles on food that is ingested by the person and that the person is exposed to chloroform in drinking water. The food ingestion exposure is  $0.001 \text{ ng kg}^{-1} \text{ day}^{-1}$  and the drinking water exposure is  $0.1 \text{ ng kg}^{-1} \text{ day}^{-1}$ . What is this person's total additional cancer risk from chloroform exposure? State any other assumptions you have to make in this estimate.

- Explain the difference in the weight of evidence values in Table 11.6 for allyl chloride, benzidine, 1,3-butadiene, and fluorene.
- Vinyl chloride, cadmium, nickel, benzene, CO, and  $\text{NO}_x$  all elicit health effects in humans. Which are carcinogens? Which are candidates to be designated "substances of very high concern" in Europe? See: <http://echa.europa.eu/web/guest/candidate-list-table>.
- Compare the role of MT for metals and cytochrome P450 for organic compounds.
- Explain bioactivation. Apply this to benzo(a)pyrene.
- Describe the link between emissions of halocarbons and melanoma. How does this differ from the link between emissions of vinyl chloride and angiogenesis of the liver?

## References

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# Reproductive and Hormonal Effects of Air Pollutants

## 12.1 REPRODUCTIVE AND DEVELOPMENTAL EFFECTS

A number of air pollutants can affect the female reproductive system's processes that produce eggs, as well as processes that affect how the sperm and egg combine to form a single cell (zygote), and the nurturing environment during gestation within the mother that allows the offspring to develop. Certain other air pollutants may also affect the developing, yet to be born child. Such chemicals are known as reproductive and developmental toxins. These chemical classes include teratogens, i.e. substances that induce birth defects, as well as mutagens and carcinogens that are discussed in Chapter 11.

The risks of reproductive problems from exposure to pollutants are very important because the time between conception and a child's birth is arguably the most vulnerable life stage threatened by air pollution. During this time, the unborn child is undergoing the most rapid growth of its entire lifetime, and whose organs are developing prolifically.<sup>1</sup> The child in the womb needs oxygen and nutrients provided by the mother, but the same processes that allow for entry of these essential chemicals also allow exposures, i.e. *in utero* exposures, to pollutants.

The actual effects during development have the same outcomes as in adults, e.g. respiratory dysfunction, cardiovascular problems, cancer, neurological damage, endocrine system changes, and compromised immunological systems. However, the prolific tissue development and vulnerability at early life stages exacerbates and increases the likelihood of these problems at substantially lower exposures and doses of the same pollutant. Thus, the timing of exposure to an air pollutant is crucial to the type and severity of a reproductive or developmental disorder (Figure 12.1). Developmental respiratory problems are particularly problematic (Figure 12.2).

The Agency for Toxic Substances Disease Registry lists reproductive toxics (Table 12.1). For most of these,

inhalation is a major exposure pathway. Note the variability of chemical classes, including substances that are highly volatile (e.g. the chlorinated solvents) to nearly nonvolatile (atrazine).

## 12.2 ENDOCRINE DISRUPTION

Developmental effects from air pollutants may also occur after birth. Other developmental toxins adversely affect any human life stage by altering the chemical messages between glands and receptors in cells throughout the body (Figure 12.3). These are collectively known as hormonally active agents or endocrine disruptors. These chemical compounds act in a number of ways at a number of sites (Table 12.2). The endocrine system consists of glands, i.e. specialized groups of cells that manufacture, store, and release hormones directly into the bloodstream. These chemical messengers regulate bodily functions. A number of air pollutants appear to disrupt the activity of glands, including the adrenals, chemoreceptor organs, gonads, hypothalamus, pancreatic islets, parathyroid, pineal, pituitary, and thyroid. Hormones that are affected include steroids, growth hormones, and thyroxine.<sup>2</sup>

The mode of action can be as an agonist, an antagonist, or as an indirect effect of another endogenous process (e.g. changes to the nervous or immune system that alter hormonal messages). This messaging system in animals and plants employs hormones, which chemical compounds that interact with receptor sites in the cell (usually on the membrane), which, in turn, initiate biochemical processes.

Endocrine disrupting chemicals (EDCs) provide a unique challenge since EDCs can mimic hormones, antagonize normal hormones, alter the pattern of synthesis and metabolism of natural hormones, or modify hormone receptor levels.<sup>3</sup> Anthropogenic EDCs that are of concern include pesticide residues (e.g. DDT,

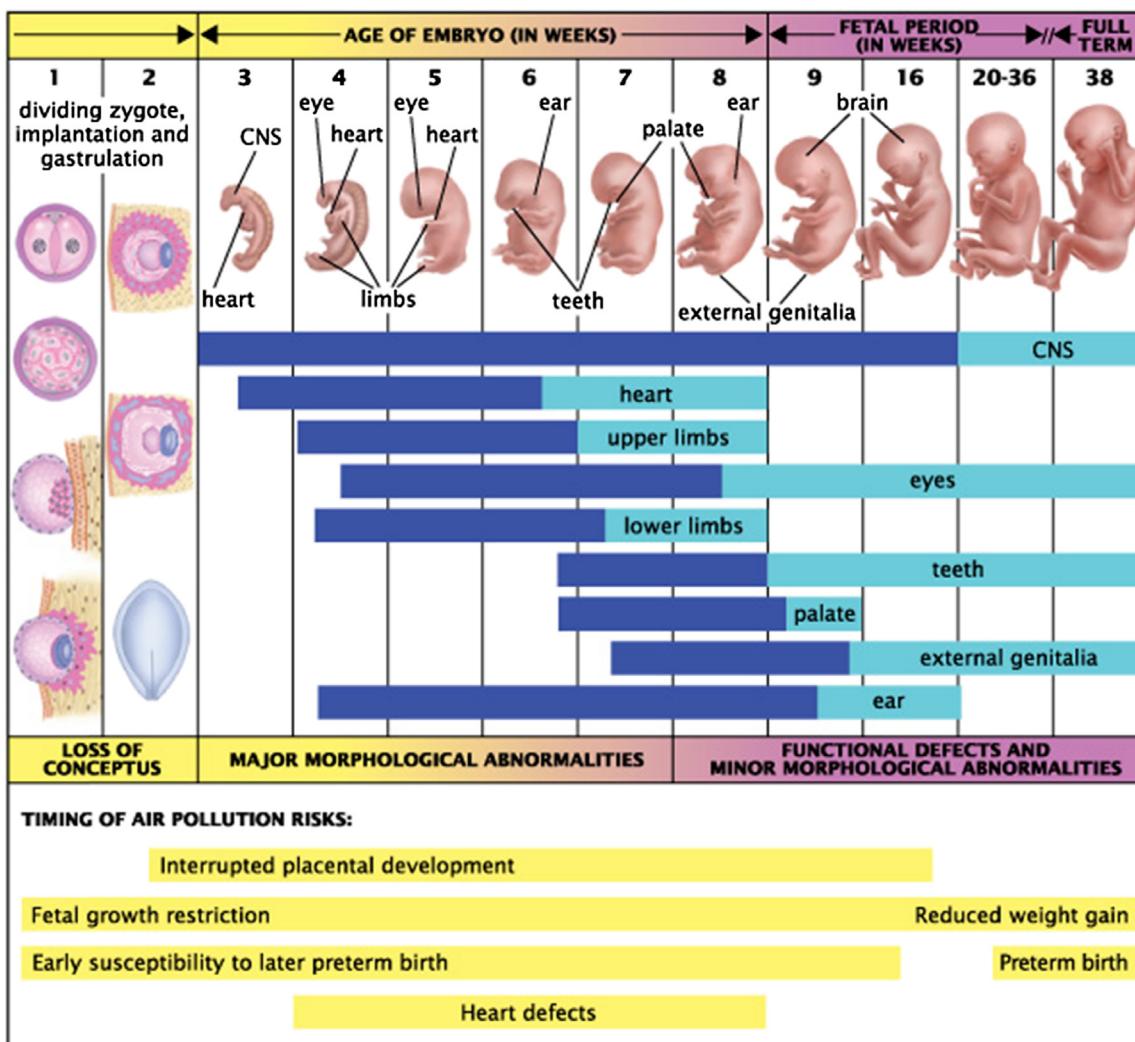


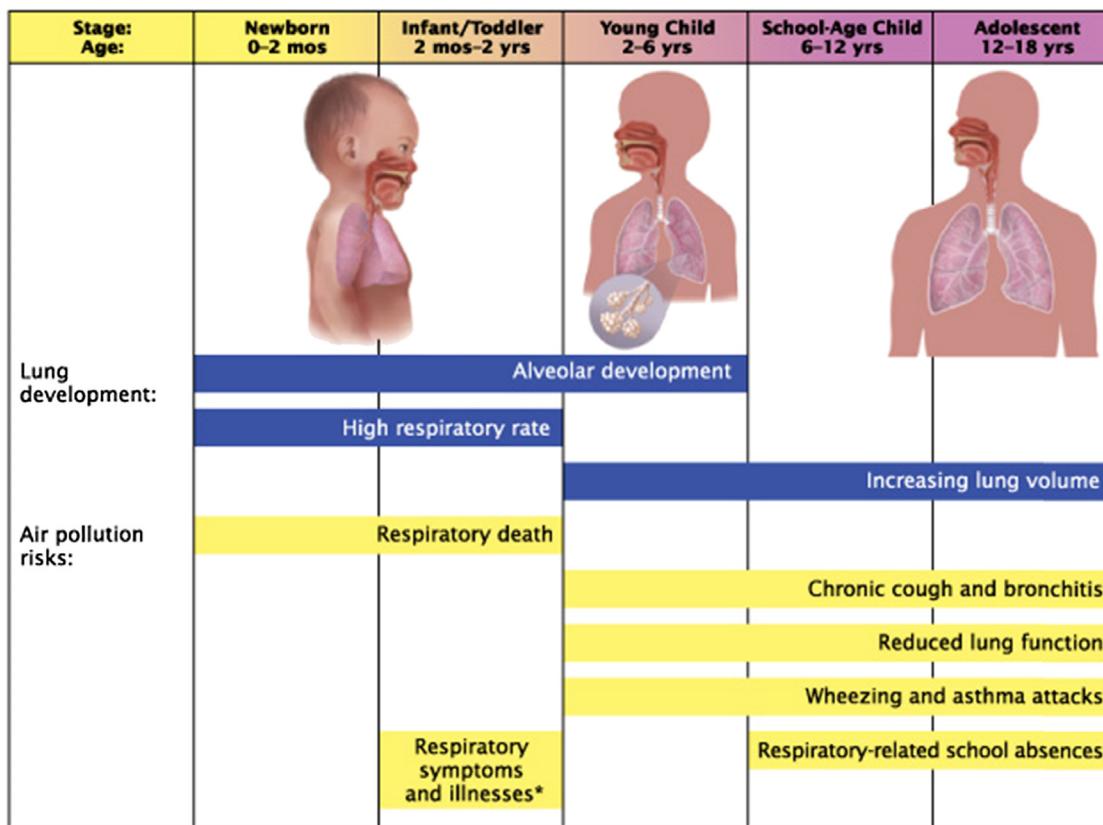
FIGURE 12.1 Life stages between conception and birth with associated air pollution risks from maternal and *in utero* exposures. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 1.

endosulfan, and methoxychlor), polychlorinated biphenyls (PCBs), dioxins, alkylphenols (e.g. nonylphenol), plastic additives (e.g. bisphenol A, diethyl phthalate), polycyclic aromatic hydrocarbons (PAHs), and pharmaceutical hormones (e.g. 17 $\beta$  estradiol, ethinyl estradiol).<sup>4</sup>

An endocrine disrupting molecule may react with a receptor molecule on the cell's surface. This reaction may signal the feminine or masculine responses (e.g. hair growth, testis or ova development) much like a hormone would do (Figure 12.4). In other words, the EDC and the natural hormone both bind to the cell's receptor. They are both ligands, i.e. molecules that travel through the bloodstream as chemical messengers that will bind to a target cell's receptor. Or, the new polypeptide that is formed from this receptor-contaminant interaction may react with DNA in the nucleus. The former reaction

is an example of an endocrine response, while the latter may lead to mutagenicity or cancer.

One of the first EDCs heavily researched was DDT.<sup>5</sup> Throughout the 1980s, exposure to this pesticide was associated with abnormal sexual differentiation in sea-gulls, and thinning and cracking of bald eagle eggs.<sup>6</sup> Numerous pesticides and chemicals have been associated with endocrine related abnormalities in wildlife, including the inducement of feminine traits, such as secretion of the egg laying hormone, vitellogenin, in males of numerous fish downstream for wastewater treatment plants (likely the result of chemicals used in homes, e.g. household chemicals and drugs) that bypassed treatment).<sup>7a,7b</sup> Numerous species of aquatic and terrestrial animals are affected by EDCs.<sup>8</sup> Recently, these problems have found their way to humans, such as those exposed to halogenated compounds and



\*Air pollution exposure has also been more recently linked to respiratory symptoms and illnesses in early life including cough, bronchitis, wheeze and ear infections.

FIGURE 12.2 Potential developmental respiratory problems resulting from *in utero* exposure to air pollutants. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 1.

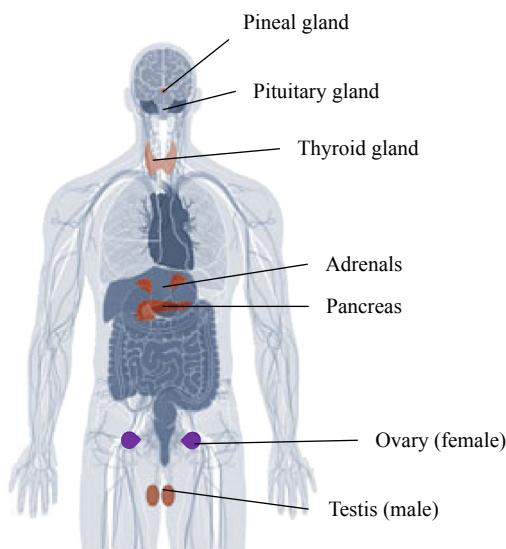
TABLE 12.1 Substances Listed as Reproductive Hazards by the Agency for Toxic Substances Disease Registry (2013)<sup>2</sup>

1,1-Dichloroethene
1,2-Dibromo-3-Chloropropane
1,2-Dibromoethane
1,3-Dinitrobenzene & 1,3,5-Trinitrobenzene
Acrylamide
Acrylonitrile
Atrazine
Barium
Cadmium
Chlordecone
Chlorinated dibenzodioxins
Chloroform
Cyanide
DDT, DDE, DDD

TABLE 12.1 Substances Listed as Reproductive Hazards by the Agency for Toxic Substances Disease Registry (2013)<sup>2</sup>—cont'd

Di(2-ethylhexyl)phthalate (DEHP)
Diethyl phthalate
Dinitrotoluenes
Hexachlorobenzene
Lead
Methoxychlor
<i>n</i> -Hexane
Pentachlorophenol
RDX (Cyclonite)
Selenium
Silver
Vanadium
White Phosphorus

(Continued)



**FIGURE 12.3 Endocrine system.** (For color version of this figure, the reader is referred to the online version of this book.) Ref. 2.

pesticides.<sup>9a–9c</sup> A recent nationwide survey of pharmaceuticals in US surface water found EDCs at nanogram per liter levels in 139 stream sites throughout the United States. Several of these EDCs even were found at microgram per liter levels, including nonylphenol ( $40 \mu\text{g l}^{-1}$ ), bisphenol A ( $12 \mu\text{g l}^{-1}$ ), and ethinyl estradiol ( $0.831 \mu\text{g l}^{-1}$ ).<sup>10</sup>

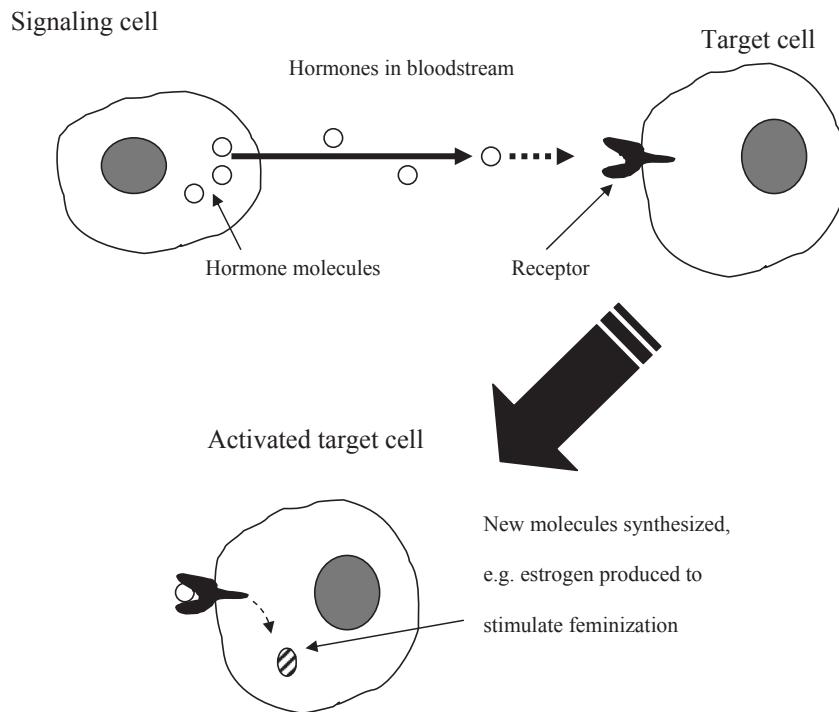
It is difficult to classify the chemicals that disrupt mammalian endocrine systems, given the different

**TABLE 12.2** Substances Listed as Endocrine Disruptors by the Agency for Toxic Substances Disease Registry (2013)<sup>2</sup>

Aldrin/Dieldrin
Atrazine
DDT, DDE, DDD
Endosulfan
Iodine
Malathion
Methoxychlor
Pentachlorophenol
Polybrominated biphenyls (PBBs) & polybrominated diphenyl ethers (PBDEs)
Polybrominated diphenyl ethers (PBDEs)
Polychlorinated biphenyls (PCBs)
Toxaphene

types of disruption, although those listed by one U.S. agency are largely represented by relatively low vapor pressure, lipophilic compounds.<sup>2</sup>

Most of the endocrine disruptors listed in Table 12.2 are semivolatile (vapor pressure ranging from  $10^{-5}$  to  $10^{-2} \text{ kPa}$  at  $20^\circ\text{C}$ ) and persistent organic pollutants



**FIGURE 12.4 Schematic of the process for endocrine signals between cells.** The signaling cell releases hormones into the bloodstream that reach the receptor of the target cell. When the receptor binds to the hormone, new molecules are synthesized in the activated target cell. Vallero DA. *Environmental biotechnology: a biosystems approach*. Burlington (MA): Elsevier Academic Press; 2009.

(POPs). The notable exceptions include iodine (0.04 kPa at 25 °C) and atrazine (vapor pressure =  $4 \times 10^{-8}$  kPa at 20 °C), given that iodine is not an organic compound and that atrazine can be considered virtually nonvolatile. Airborne POPs are particularly dangerous since they are often hormonally active and damage unborn children and neonates, as evidenced by their routinely being detected in breast milk<sup>11,12</sup> and in infant cord blood.<sup>13,14</sup> In the United States, biomonitoring results from the National Health and Nutrition Examination Survey show widespread human exposure to industrial chemicals, many of which have not been fully evaluated for adverse health effects but a number of which are likely EDCs.

### LONG-RANGE ATMOSPHERIC TRANSPORT AND THE INUIT

Indigenous peoples often subsist on traditional food for all or part of their diet. This is certainly true for the Inuit population who live in the Arctic and sub-Arctic climates. Ironically, these very remote Arctic regions have been chronically exposed to POPs, rendering these sub-populations vulnerable to the chronic health effects. Since POPs remain in the environment for long periods of time, they can be transported over great distances from their sources. The tendency of these compounds to be toxic, to bioaccumulate, and to biomagnify in food chains increases the risk to the Inuit populations.

In addition to the need for many indigenous people in the Arctic to rely on traditional diets for nourishment, the hunting and fishing are also an important part of their cultural identity. Indeed, alternative sources of food often do not exist. Exacerbating the problem, traditional diets are often high in fat. Since most POPs are lipophilic, they tend to accumulate in fatty tissue of the animals that are eaten. Due to these physicochemical properties, POPs can move many hundreds of kilometers away from their sources, either in the gas phase or attached to particles. They are generally moved by advection, i.e. along with the movement of air masses. Some of the routes of long-range transport of POPs are shown in Figure 12.5.

There is also a fairness problem. That is, most northern residents have not used or directly benefited from the activities associated with the production and use of these chemicals, yet indigenous peoples in the Arctic have some of the highest known exposures to these chemicals.

Lactating Inuit mother's breast milk, for example, contains elevated levels of PCBs, DDT, and its metabolites, chlorinated dioxins and furans, and brominated organics, such as residues from fire retardants, i.e. polybrominated diphenyl ethers (PBDEs), and heavy metals.<sup>1,15</sup> Infants are particularly vulnerable to persistent, bioaccumulating toxic compounds (PBTs) which, as mentioned, are

Much of the exposure to POPs is at distance from original sources and points of use. Due to their persistence, POPs can be transported to long distances. Long-range atmospheric transport can carry pollutants thousands of miles to what would otherwise be thought to be relatively pristine areas, e.g. arctic regions. POPs are a subset of the so-called "PBTs", which are compounds that are persistent, readily bioaccumulate in tissue, and are toxic at low doses. PBTs are composed of myriad compounds (see Discussion Box: The Inuit and Persistent Organic Pollutants).

Hormonally active pollutants actually include numerous chemical classes beyond those listed in

lipophilic and find their way to fat reserves in warm-blooded animals (Figure 12.6).

Although POPs are found in varying tissue concentrations among women in both industrially developed and developing nations, the Canadian Inuit have shown some of the highest levels of contaminants to be detected. Their diet consists of seal, whale, and other species high on the marine food chain, increasing the Inuit body burden of POPs.<sup>16</sup> These elevated exposures have been associated with reports of health effects similar to the effects of persons exposed to PCBs who also had evidence of other contaminants in body fluids.

A study of Inuit women from Hudson Bay<sup>17</sup> indicated very high levels of PCBs and dichlorodiphenylmethane (DDE) in breast milk; these results prompted an examination of the health status of Inuit newborns.<sup>18</sup> Correlation analysis revealed a statistically significant negative association between male birth length and levels of hexachlorobenzene, mirex, PCBs, and chlorinated dibenzodioxins (CDDs)/dibenzofurans (CDFs) in the fat of mothers' milk. No significant differences were observed between male and female newborns for birth weight, head circumference, or thyroid stimulating hormone. Immune system effects have also been detected in Inuit infants suspected of receiving elevated levels of PCBs and dioxins during lactation. These babies had a drop in the ratio of the CD4+ (helper) to CD8+ (cytotoxic) T cells at ages 6 and 12 months (but not at 3 months).<sup>18</sup>

The Inuit situation demonstrates the critical ties between humans and their environment and the importance of physical properties of contaminants (e.g. persistence, bioaccumulation, and toxicity potentials), the conditions of the environment (e.g. the lower Arctic temperatures increase the persistence of many POPs), and the complexities of human activities (e.g. diet and lifestyle) in order to assess risks and, ultimately, to take actions to reduce exposures. The combination of these factors leaves the Inuit

(Continued)

## LONG-RANGE ATMOSPHERIC TRANSPORT AND THE INUIT (cont'd)

in a tragic dilemma. Since they are subsistence anglers and hunters, they depend almost entirely on a tightly defined portion of the earth for food. Their lifestyle and diet dictate dependence on food sources high in POPs.

What makes this disaster even more complex and tragic is that it forces innocent people to make extremely difficult decisions. Pediatricians rightly encourage breast feeding for its many attributes, including enhancing the infant's immune system in the critical first weeks after birth. So, in terms of risk tradeoffs, it is dangerous to discourage breast feeding. This dilemma not only applies to the Inuit, or to subsistence farmers, hunters, and anglers, but to all of us. The key is to ensure that breast milk everywhere does not contain hazardous levels of PBTs and other contaminants. The only way to do this is to consider the entire life cycle of the pollutants and find ways to prevent their entry into the environment in the first place.

Another lesson is to pay attention to the properties of a compound before its use and to monitor for problems after the product reaches the marketplace. For example, all other things being equal, the recalcitrance of compounds is greater in the Arctic regions compared to temperate and tropical regions, as a direct result of lower ambient temperature. Toxicity properties of environmental contaminants are also affected by extrinsic conditions, such as whether the substances are found in the air, water, sediment, or soil, along with the conditions of these media (e.g. oxidation-reduction, pH, and grain size). For example, the metal mercury is usually more toxic in reduced and anaerobic conditions because it is more likely to form alkylated organometallic compounds, like monomethyl mercury and the extremely toxic dimethyl mercury. These reduced chemical

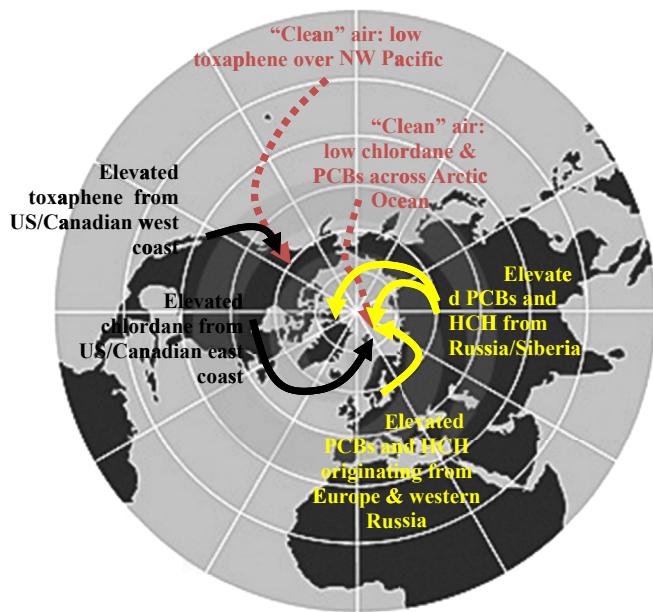
species are likely to form when buried under layers of sediment where dissolved oxygen levels approach zero. Ironically, engineers have unwittingly participated in increasing potential exposures to these toxic compounds. With the good intention of attempting to clean up contaminated lakes in the 1970s, engineers recommended and implemented dredging programs in the process of removing the sediment. However, the metals and other toxic chemicals that had been relatively inert and encapsulated in buried sediment were released to the lake waters. In turn, the compounds were also more likely to find their way to the atmosphere (see Figure 14.8 in Chapter 14).

The problem of long-range transport of persistent pollutants begins with the manufacture and use of a product, followed by contamination of soil and surface waters. Next the persistence allows the chemicals to reach the groundwater and to be sequestered in sediment. These are the reservoirs of the pollutants, which serve as sources of air pollutants. The pollutants are then transported many kilometers before they accumulate in the food chain. Along the way, humans and ecosystems are exposed, but the most damage to human populations may well occur in people who have not benefited from the use which occurred decades earlier. Unfortunately for the Inuit, the doses which cause the most reproductive, endocrine, neurotoxic, and other chronic effects are highest among a population separated in time and space from the benefits of pest control enjoyed by a previous generation of another population. These complexities are a lesson to environmental scientists and engineers to consider systematically the many physical, chemical, and biological characteristics of the compound and the environment where it exists.

**Table 12.2.** Another U.S. agency, the Environmental Protection Agency, includes a more expansive list of EDCs beyond the persistent organic pollutants ([Table 12.3](#)). This listing follows the process wherein chemicals are evaluated and screened for potential for endocrine disruption based on biological assays and potential exposure scenarios. This is a listing of the chemicals which were first screened as part of the Endocrine Disruptor Screening Program (EDSP) based on human exposure-related factors, not the actual biological mechanisms of endocrine disruption.<sup>19</sup> The factors include whether a chemical is produced in high volumes (i.e. high production volume [HPV] chemicals). This initial list focuses on active ingredients and inert ingredients

of products. Therefore, [Table 12.3](#) merely presents an alphabetized list of pesticide active ingredients and HPV/pesticide inert chemicals for screening in the EDSP. Because this list of chemicals was selected on the basis of exposure potential only, it was neither construed as a list of known nor likely endocrine disruptors.

After developing this first listing, the U.S. EPA issued a revised list of chemicals ([Table 12.4](#)) for screening. As in the first list ([Table 12.3](#)), these are merely candidates for potential endocrine disruptors, based on registration status and/or the likelihood of exposure (i.e. via drinking water).<sup>20</sup> Although the list is based on the ingestion pathway, the water being

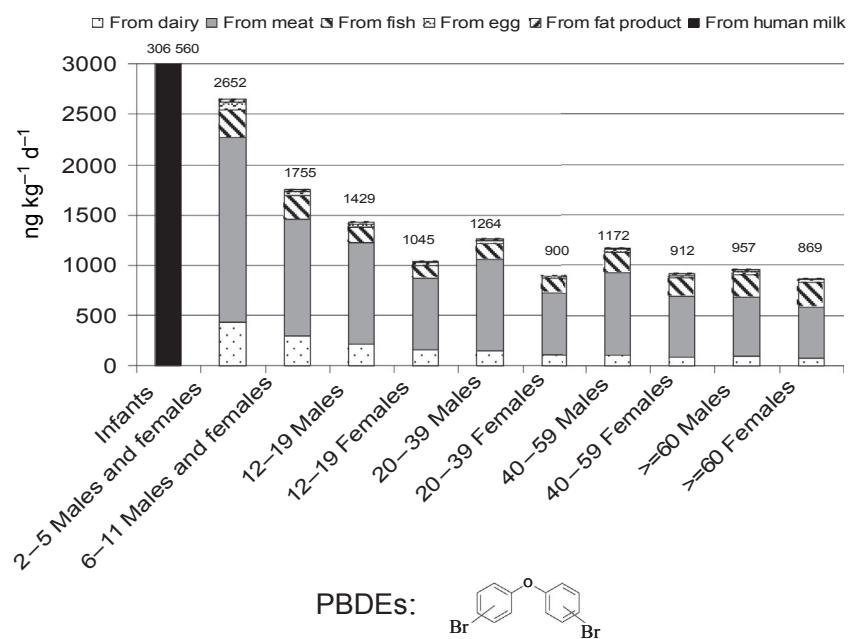


**FIGURE 12.5 Long-range transport of persistent organic pollutants in the Arctic regions.** (For color version of this figure, the reader is referred to the online version of this book.) Vallero DA. *Environmental biotechnology: a biosystems approach*. Burlington (MA): Elsevier Academic Press; 2009. Adapted from: Russian Chairmanship of the Arctic Council. Draft Fact Sheet; 2005.

ingested could indeed be contaminated by air pollutants which have migrated into surface and groundwater.

Comparing Tables 12.2–12.4 indicates the variation of possible exposure scenarios and modes of action that can lead to hormonal effects. As evidence, under environmental conditions, aqueous solubility of the compounds range 8 orders of magnitude and vapor pressures range 18 orders of magnitude. A third listing is a group of chemicals that have been associated with abnormal spermatogenesis, feminization of males, masculinization of females, dysfunction of adrenal, pineal, and thyroid glands, autoregulatory problems, and other hormonally related problems. They are diverse in molecular structure (Tables 12.4 and 12.5), come from a myriad of sources, and have been detected throughout the environment, i.e. food, water, air, soil, and in plant and animal tissues.

It is noteworthy that there is little overlap between the three tables. This is partially the result of the criteria for ranking endocrine disruptors. Table 12.3, for example, does not include the persistent pesticides that have been banned, such as DDT and aldrin. However, it does include dicofol, which is quite similar to DDT (Figure 12.7). In fact, DDT is one the intermediate chemicals produced in manufacturing dicofol. Some of the



**FIGURE 12.6 U.S. population's estimated daily dietary intake of polybrominated diphenyl ethers (PBDE) by age group and food source.** Units are picograms per kg ( $\text{pg kg}^{-1}$ ) of body weight per day. In all groups older than 1 year of age, total PBDE intake from meat is significantly higher than from any other food sources. The highest dietary intake values of PBDEs were found in nursing infants ( $307 \text{ ng kg}^{-1}$  body weight per day), which compares to  $1.0 \text{ ng kg}^{-1} \text{ day}^{-1}$  for men or  $0.9 \text{ ng kg}^{-1} \text{ day}^{-1}$  for women at  $\geq 60$  years of age. Data from Schecter A, Päpke O, Harris TR, Tung KC, Musumba A, Olson J, et al. Polybrominated diphenyl ether (PBDE) levels in an expanded market basket survey of U.S. food and estimated PBDE dietary Intake by age and sex. *Environ Health Perspect* 2006;114(10):1515–20.

TABLE 12.3 List of Chemicals for Screening under the Endocrine Disruptors Screening Program

Chemical	Aqueous Solubility at 25 °C (mg l <sup>-1</sup> )	Vapor Pressure (kPa)	Pesticide Active Ingredient?	HPV/ Inert?
4,7-Methano-1H-isoindole-1,3(2H)-Dione,2-(2-ethylhexyl)-3a,4,7,7a-tetrahydro-	11.78	2.4	Yes	
Piperonyl butoxide	0.64	0.696	Yes	
Dimethoate	6.6 × 10 <sup>4</sup>	4.64	Yes	
Carbaryl	416.20	2.79	Yes	
Acetone	2.2 × 10 <sup>5</sup>	3.09 × 10 <sup>7</sup>	Yes	
Isophorone	3010	5.84 × 10 <sup>4</sup>	Yes	
Methyl ethyl ketone	76,100	1.21 × 10 <sup>7</sup>	Yes	
Quintozene	0.58	100	Yes	
Diethyl phthalate	287	280		Yes
Dibutyl phthalate	2.35	2.68		Yes
Butyl benzyl phthalate	0.95	1.1		Yes
o-Phenylphenol	536	579	Yes	
2,4-D	336	152	Yes	
Toluene	573	3.79 × 10 <sup>6</sup>		Yes
Endosulfan	1.49	0.507	Yes	
Dicofol	0.78	0.176	Yes	
Di-sec-octyl phthalate	1.1 × 10 <sup>-3</sup>	1.89 × 10 <sup>2</sup>		Yes
Malathion	78	0.451	Yes	
Simazine	590	0.287	Yes	
Dimethyl phthalate	2014	411		Yes
Captan	50	0.391	Yes	
Folpet	47	0.667	Yes	
Methyl parathion	29	0.593	Yes	
Disulfoton	6.36	13	Yes	
Linuron	44	0.897	Yes	
Diazinon	6.46	12	Yes	
Phosmet	41	0.191	Yes	
Carbamothioic acid, dipropyl-, S-ethyl ester	90	3200	Yes	
Methidathion	157	0.619	Yes	
Glyphosate	0.77	3.55 × 10 <sup>-2</sup>	Yes	

(Continued)

TABLE 12.3 List of Chemicals for Screening under the Endocrine Disruptors Screening Program—cont'd

Chemical	Aqueous Solubility at 25 °C (mg l <sup>-1</sup> )	Vapor Pressure (kPa)	Pesticide Active Ingredient?	HPV/ Inert?
Dichlobenil	149	1330	Yes	
Carbofuran	354	141	Yes	
Trifluralin	0.21	10.5	Yes	
DCPA (or chlorthal-dimethyl)	1.76	6.44	Yes	
Benfluralin	0.23	22.1	Yes	
Chlorothalonil	26	12.8	Yes	
Atrazine	214	1.12	Yes	
Propachlor	523	100	Yes	
Propargite	0.33	0.04	Yes	
Chlorpyrifos	0.36	3.99	Yes	
Methamidophos	4 × 10 <sup>5</sup>	7.59	Yes	
Resmethrin	0.04	21.9	Yes	
Ethoprop	22.41	50.7	Yes	
Fenbutatin oxide	0.00	1.55 × 10 <sup>-12</sup>	Yes	
Methomyl	2.06 × 10 <sup>4</sup>	2.41	Yes	
Metribuzin	1304	0.579	Yes	
Gardona (cis-isomer)	4.79	0.0283	Yes	
Oxamyl	4287	173	Yes	
Propyzamide	25.74	1.12	Yes	
Norflurazon	159	2.27	Yes	
Acephate	2.83 × 10 <sup>4</sup>	0.952	Yes	
Iprodione	22	0.00627	Yes	
Triadimefon	57	0.00732	Yes	
Metolachlor	51	4.19	Yes	
Cypermethrin	1.56 × 10 <sup>-3</sup>	664	Yes	
Permethrin	9.75 × 10 <sup>-3</sup>	3.57 × 10 <sup>-3</sup>	Yes	
Metalaxyd	560	3.31	Yes	
Propiconazole	4.59	0.056	Yes	
Esfenvalerate	6.10 × 10 <sup>-3</sup>	4.39 × 10 <sup>-4</sup>	Yes	
Flutolanil	6.20	0.0397	Yes	
Cyfluthrin	8.43 × 10 <sup>-3</sup>	4.44 × 10 <sup>-5</sup>	Yes	
Abamectin	Insoluble	Negligible	Yes	
Bifenthrin	2.41 × 10 <sup>-4</sup>	0.0653	Yes	
Myclobutanil	23.9	0.536	Yes	

**TABLE 12.3** List of Chemicals for Screening under the Endocrine Disruptors Screening Program—cont'd

Chemical	Aqueous Solubility at 25 °C (mg l <sup>-1</sup> )	Vapor Pressure (kPa)	Pesticide Active Ingredient?	HPV/ Inert?
Pyridine, 2-(1-methyl-2-(4-phenoxy- phenoxy)ethoxy)-	0.17	0.469	Yes	
Tebuconazole	7.65	9.95 × 10 <sup>-3</sup>	Yes	
Imidacloprid	7172	3.6	Yes	

Those chemicals included on this "Tier 1" list are result from being a pesticide active ingredient or other ingredient that has high production volume (HPV/ Inert).

Sources: Ref. 20. Source of solubility and vapor pressure values is: U.S. Environmental Protection Agency, Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11. Washington (DC): United States Environmental Protection Agency; 2013. Note: Abamectin values are not available from this source, so its information was obtained from EXTOXNET. <http://extoxnet.orst.edu/pips/abamecti.htm>; 1996 [accessed 22.10.13].

**TABLE 12.4** Alphabetized List of Chemicals for Tier 1 Screening under the Endocrine Disruptor Screening Program

Chemical	Aqueous Solubility at 25 °C (mg l <sup>-1</sup> )	Vapor Pressure (kPa)	Pesticide Active Ingredient?
1,1,1,2-Tetrachloroethane	197	1.60 × 10 <sup>3</sup>	
1,1,1-Trichloroethane	666	1.65 × 10 <sup>4</sup>	
1,1,2-Trichloroethane	2.17 × 10 <sup>3</sup>	3.07 × 10 <sup>3</sup>	
1,1-Dichloroethane	3.49 × 10 <sup>3</sup>	3.03 × 10 <sup>4</sup>	
1,1-Dichloroethylene	1.81 × 10 <sup>3</sup>	8.45 × 10 <sup>4</sup>	
1,2,3-Trichloropropane	897	492	
1,2,4-Trichlorobenzene	20	61	
1,2-Dichloroethane	6.4 × 10 <sup>3</sup>	1.05 × 10 <sup>4</sup>	
1,2-Dichloropropane	2.17 × 10 <sup>3</sup>	7.11 × 10 <sup>3</sup>	
1,3-Dinitrobenzene	1.37 × 10 <sup>3</sup>	0.53	
1,4-Dioxane	2.14 × 10 <sup>5</sup>	5.08 × 10 <sup>3</sup>	
1-Butanol	7.67 × 10 <sup>4</sup>	893	
2-Methoxyethanol	1.12	1.27 × 10 <sup>3</sup>	
2-Propen-1-ol	3.18 × 10 <sup>5</sup>	3.48 × 10 <sup>3</sup>	
4,4'-MethylEnedianiline	1959	1.24 × 10 <sup>-3</sup>	
Acetaldehyde	2.57 × 10 <sup>5</sup>	1.20 × 10 <sup>5</sup>	
Acetamide	1.23	19	
Acetochlor	0.47	3.73 × 10 <sup>-3</sup>	Yes
Acetochlor ethanesulfonic acid ( $\times 10$ SA)	2.96 × 10 <sup>-5</sup>	1.17 × 10 <sup>-5</sup>	

**TABLE 12.4** Alphabetized List of Chemicals for Tier 1 Screening under the Endocrine Disruptor Screening Program—cont'd

Chemical	Aqueous Solubility at 25 °C (mg l <sup>-1</sup> )	Vapor Pressure (kPa)	Pesticide Active Ingredient?
Acetochlor oxanic acid (OA)	921	4.05 × 10 <sup>-4</sup>	
Acrolein	1.40 × 10 <sup>5</sup>	3.65 × 10 <sup>4</sup>	Yes
Acrylamide	5.04 × 10 <sup>5</sup>	3.61	
Alachlor	18	3.73 × 10 <sup>-3</sup>	Yes
Alachlor ethanesulfonic acid (ESA)	0.25	9.24 × 10 <sup>-8</sup>	
Alachlor oxanic acid (OA)	921	4.05 × 10 <sup>-4</sup>	
Alpha-Hexachlorocyclohexane	4.04	0.03	
Aniline	2.08 × 10 <sup>4</sup>	65	
Bensulide	0.82	1.32 × 10 <sup>-4</sup>	Yes
Benzene	2.00 × 10 <sup>3</sup>	1.26 × 10 <sup>4</sup>	
Benzo(a)pyrene (PAHs)	0.01	2.31 × 10 <sup>-5</sup>	
Butylated hydroxyanisole	213	0.54	
Carbon tetrachloride	280	1.53 × 10 <sup>4</sup>	
Chlorobenzene	401	1.60 × 10 <sup>3</sup>	
cis-1,2-Dichloroethylene	2.34 × 10 <sup>3</sup>	2.68 × 10 <sup>4</sup>	
Clethodim	1.36	3.55 × 10 <sup>-7</sup>	Yes
Clofentezine	27	4.64 × 10 <sup>-6</sup>	Yes
Clomazone	198	0.02	Yes
Coumaphos	1.54	6.08 × 10 <sup>-5</sup>	Yes
Cyanamide	6.52 × 10 <sup>5</sup>	0.77	Yes
Cyromazine	9.67 × 10 <sup>3</sup>	4.25 × 10 <sup>-5</sup>	Yes
Denatonium saccharide	169	1.41 × 10 <sup>-9</sup>	Yes
Di(2-ethylhexyl) adipate	5.45 × 10 <sup>-4</sup>	1.13 × 10 <sup>-4</sup>	
Dichloromethane	1.10 × 10 <sup>4</sup>	5.80 × 10 <sup>4</sup>	
Dicrotophos	2.78 × 10 <sup>4</sup>	0.02	Yes
Diuron	151	1.91 × 10 <sup>-4</sup>	Yes
Endothall	2.98 × 10 <sup>3</sup>	3.15 × 10 <sup>-7</sup>	Yes
Epichlorohydrin	5.06 × 10 <sup>4</sup>	2.19 × 10 <sup>3</sup>	
Erythromycin	0.52	1.56 × 10 <sup>-21</sup>	
Ethylbenzene	229	1.28 × 10 <sup>3</sup>	
Ethylene glycol	1.21	12	
Ethylene thiourea	2.11 × 10 <sup>5</sup>	0.02	
Ethylurethane	2.89 × 10 <sup>5</sup>	11	

(Continued)

(Continued)

**TABLE 12.4** Alphabetized List of Chemicals for Tier 1 Screening under the Endocrine Disruptor Screening Program—cont'd

Chemical	Aqueous Solubility at 25 °C (mg l <sup>-1</sup> )	Vapor Pressure (kPa)	Pesticide Active Ingredient?
Etofenprox	$4.08 \times 10^{-3}$	$3.57 \times 10^{-5}$	Yes
Fenoxaprop-P-ethyl	0.65	$1.53 \times 10^{-5}$	Yes
Flumetsulam	455	$6.52 \times 10^{-8}$	Yes
Fomesafen sodium	16	$3.03 \times 10^{-12}$	Yes
Fosetyl-Al (Aliette)	0.45	$2.53 \times 10^{-5}$	Yes
Glufosinate ammonium	0.74	$2.45 \times 10^{-6}$	Yes
HCFC-22	$2.75 \times 10^3$	$9.67 \times 10^5$	
Hexachlorobenzene	0.19	0.27	
Hexachlorocyclopentadiene	0.86	8.00	
Hexane	17	$2.01 \times 10^4$	
Hexythiazox	0.1	$2.27 \times 10^{-5}$	Yes
Hydrazine	1.49	$1.92 \times 10^3$	
Isoxaben	3.41	$1.77 \times 10^{-5}$	Yes
Lactofen	0.04	$1.47 \times 10^{-5}$	Yes
Lindane	4.04	$3.44 \times 10^{-2}$	
Methanol	1.49	$1.69 \times 10^4$	
Methyl tert-butyl ether	$1.98 \times 10^4$	$3.33 \times 10^4$	
Metolachlor ethanesulfonic acid (ESA)	0.26	$6.69 \times 10^{-8}$	
Metolachlor oxanilic acid (OA)	993	$3.12 \times 10^{-4}$	
Nitrobenzene	$1.05 \times 10^3$	33	
Nitroglycerin	$1.31 \times 10^3$	$5.33 \times 10^{-2}$	
N-Methyl-2-pyrrolidone	$2.48 \times 10^5$	46	
N-Nitrosodimethylamine (NDMA)	$4.10 \times 10^5$	360	
n-Propylbenzene	71	456	
o-Dichlorobenzene	92	196	
o-Toluidine	$8.29 \times 10^3$	35	
Oxydemeton-methyl	$1.06 \times 10^5$	$3.80 \times 10^{-3}$	Yes
Oxyfluorfen	0.2	$1.02 \times 10^{-4}$	Yes
Pacllobutrazol	25	$2.45 \times 10^{-5}$	Yes
p-Dichlorobenzene	90	429	Yes
Pentachlorophenol	3.09	0.44	Yes
Perchlorate	1.0	$4.36 \times 10^{-8}$	
Perfluoroctane sulfonic acid (PFOS)	0.1	1.51	

(Continued)

**TABLE 12.4** Alphabetized List of Chemicals for Tier 1 Screening under the Endocrine Disruptor Screening Program—cont'd

Chemical	Aqueous Solubility at 25 °C (mg l <sup>-1</sup> )	Vapor Pressure (kPa)	Pesticide Active Ingredient?
Perfluoroctanoic acid (PFOA)	0.48	139	
Picloram	629	$7.88 \times 10^{-7}$	Yes
Polychlorinated biphenyls	$2.50 \times 10^{-3}$	$1.32 \times 10^{-3}$	
Profenofos	0.45	$1.20 \times 10^{-4}$	Yes
Propionic acid	$1.74 \times 10^5$	471	Yes
Quinclorac	76	$2.92 \times 10^{-3}$	Yes
Quinoline	$1.71 \times 10^3$	8.00	
Quizalofop-P-ethyl	1.0	$2.80 \times 10^{-6}$	Yes
RDX	$6.06 \times 10^3$	$3.33 \times 10^{-5}$	
sec-Butylbenzene	11	233	
Styrene	343	853	
Terbufos	2.14	0.04	Yes
Terbufos sulfone	71	$3.09 \times 10^{-3}$	
Tetrachloroethylene	80	$2.47 \times 10^3$	
Thiophanate-methyl	439	$2.71 \times 10^{-4}$	Yes
Toluene diisocyanate	38	3.07	
trans-1,2-Dichloroethylene	$2.34 \times 10^3$	$2.68 \times 10^4$	
Trichloroethylene	779	$9.20 \times 10^3$	
Triflumizole	419	$4.48 \times 10^{-4}$	Yes
Trinexapac-ethyl	988	$2.77 \times 10^{-3}$	Yes
Triphenyltin hydroxide (TPTH)	8.00	NA*	Yes
Vinclozolin	33	$1.06 \times 10^{-4}$	Yes
Xylenes (total)	207	$1.11 \times 10^3$	Yes
Ziram	65	NA*	Yes

NA\* = Not available for TPTH and Ziram, which are metallic compounds. Vapor pressure information can be difficult to obtain using quantitative structure activity relationship (QSAR) tools that were originally designed for organic compounds, commonly for pharmaceuticals, so cannot be used for metals and inorganic compounds. It is not uncommon for metals and metal compound QSAR data to be lacking.

The listing of a chemical or substance does not necessarily mean that it interferes with the endocrine systems of humans or other species; rather these are candidates for screening purposes based only on their pesticide registration status and/or the likelihood that they may occur in sources of drinking water to which a substantial population may be exposed.

Sources: Ref. 21. Source of solubility and vapor pressure values is U.S. Environmental Protection Agency. Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11. Washington (DC): United States Environmental Protection Agency; 2013. Note: Abamectin values are not available from this source, so its information was obtained from EXTOXNET. <http://extoxnet.orst.edu/pips/abamecti.htm>; 1996 [accessed 22.10.13].

**TABLE 12.5** Selected Compounds Found in the Environment Suspected of Adversely Affecting Hormonal Function, Based on *In vitro*, *In vivo*, Cell Proliferation, or Receptor Binding Studies

Compound <sup>1</sup>	Endocrine Effect <sup>2</sup>	Potential Source
2,2',3,4',5,5'-Hexachloro-4-biphenylol and other chlorinated biphenylols	Anti-estrogenic	Degradation of PCBs released into the environment
4',7-Dihydroxy daidzein and other isoflavones, flavones, and flavonals	Estrogenic	Natural flora
Aldrin*	Estrogenic	Insecticide
Alkylphenols	Estrogenic	Industrial uses, surfactants
Bisphenol A and phenolics	Estrogenic	Plastics manufacturing
DDE (1,1-dichoro-2,2-bis( <i>p</i> -chlorophenyl)ethylene)	Anti-androgenic	DDT metabolite
DDT and metabolites	Estrogenic	Insecticide
Dicofol	Estrogenic or anti-androgenic in top predator wildlife	Insecticide
Dieldrin	Estrogenic	Insecticide
Diethylstilbestrol (DES)	Estrogenic	Pharmaceutical
Endosulfan	Estrogenic	Insecticide
Hydroxy-PCB congeners	Anti-estrogenic (competitive binding at estrogen receptor)	Dielectric fluids
Kepone (Chlorodecone)	Estrogenic	Insecticide
Lindane ( $\gamma$ -hexachlorocyclohexane) and other HCH isomers	Estrogenic and thyroid agonistic	Miticide, insecticide
Lutolin, quercetin, and naringen	Anti-estrogenic (e.g. uterine hyperplasia)	Natural dietary compounds
Malathion*	Thyroid antagonist	Insecticide
Methoxychlor	Estrogenic	Insecticide
Octachlorostyrene*	Thyroid agonist	Electrolyte production
Pentachloronitrobenzene*	Thyroid antagonist	Fungicide, herbicide
Pentachlorophenol	Anti-estrogenic (competitive binding at estrogen receptor)	Preservative
Phthalates and their ester compounds	Estrogenic	Plasticizers, emulsifiers
Polychlorinated biphenyls (PCBs)	Estrogenic	Dielectric fluid

(Continued)

**TABLE 12.5** Selected Compounds Found in the Environment Suspected of Adversely Affecting Hormonal Function, Based on *In vitro*, *In vivo*, Cell Proliferation, or Receptor Binding Studies—cont'd

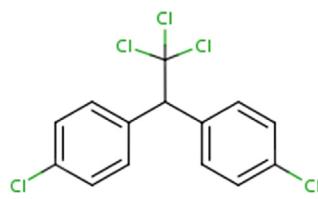
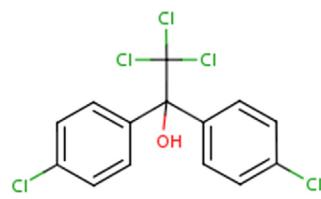
Compound <sup>1</sup>	Endocrine Effect <sup>2</sup>	Potential Source
Polybrominated diphenyl ethers (PBDEs)*	Estrogenic	Fire retardants, including <i>in utero</i> exposures
Polycyclic aromatic hydrocarbons (PAHs)	Anti-androgenic (Aryl hydrocarbon-receptor agonist)	Combustion byproducts
Tetrachlorodibenzo-p-dioxin and other halogenated dioxins and furans*	Anti-androgenic (Aryl hydrocarbon-receptor agonist)	Combustion and manufacturing (e.g. halogenation) byproduct
Toxaphene	Estrogenic	Animal pesticide dip
Tributyl tin and tin organometallic compounds*	Sexual development of gastropods and other aquatic species	Paints and coatings
Vinclozolin and metabolites	Anti-androgenic	Fungicide
Zineb*	Thyroid antagonist	Fungicide, insecticide
Ziram*	Thyroid antagonist	Fungicide, insecticide

<sup>1</sup>Not every isomer or congener included in a listed chemical group (e.g. PAHs, PCBs, phenolics, phthalates, and flavonoids) has been shown to have endocrine effects. However, since more than one compound has been associated with hormonal activity, the whole chemical group is listed.

<sup>2</sup>Note that the antagonists' mechanisms result in an opposite net effect. In other words, an anti-androgen feminizes and an anti-estrogen masculinizes an organism. Sources: For full list, study references, study types, and cellular mechanisms of action, see Chapter 2 of National Research Council. Hormonally Active Agents in the Environment. Washington (DC): National Academy Press; 2000. Source for asterisked (\*) compounds is: Colborn T, Dumanoski D, Myers JP. Our stolen future: are we threatening our fertility, intelligence and survival? <http://www.ourstolenfuture.org/Basics/chemlist.htm> [accessed 04.10.13].

DDT finds its way to the final product, although this amount has decreased to <1% in current formulations. Evidence suggests that dicofol is less endocrine disruptive than DDT and its metabolite, *p,p'*-dichlorodiphenyl-dichloroethylene (DDE; see Chapter 19).

The difference may be that dicofol can be more readily metabolized to less toxic chemicals, or that it has a shorter half-life ( $t_{1/2}$ ) than the  $t_{1/2}$  of DDT or DDE. It may also be because the parent compound of dicofol is less potent than DDT or DDE, or the reduced potency of the parent compound.<sup>21</sup> The chronic dietary reference dose (RfD, see Chapter 7), based on its endocrine effects is  $0.004 \text{ mg kg}^{-1} \text{ day}^{-1}$ . As a comparison, the oral RfD for DDT is  $0.0005 \text{ mg kg}^{-1} \text{ day}^{-1}$ , i.e. an order of magnitude greater hazard for DDT compared to dicofol.

*p,p'*-dichlorodiphenyltrichloroethane (DDT)

Dicofol

**FIGURE 12.7 Chemical structures of DDT and dicofol.** The dicofol molecule is hydrolyzed, so should have slightly higher aqueous solubility than the DDT, although both substances are very hydrophobic ( $<1 \text{ mg ml}^{-1}$ ). (For color version of this figure, the reader is referred to the online version of this book.)

The modes of action of endocrine disruption can be similar between mammals and other vertebrates. Thus, EDCs are also threats to ecosystems. Indeed, dicofol was the agent of a large spill into Lake Apopka, Florida. Studies of the consequences of the spill provided information about endocrine disruption of wildlife as a result of impaired physiology of reptiles, especially alligators, brought on by changes in their hormonal systems. Understanding of human endocrine disruption has also been enhanced from extrapolations from these and other “natural experiments” and other studies following spills and releases of toxic substances.

### 12.2.1 Endocrine Disruptor Characteristics

Some endocrine disruptors act directly on hormone receptors as hormone mimics or agonists.<sup>24</sup> Some EDCs block hormone receptors, i.e. antagonists. An estrogenic compound, for example, may lead to the same physiological outcome, i.e. feminization, as an anti-androgenic compound that blocks the estrogen receptor. The former is an estrogen agonist, the latter is an androgen antagonist. Others act directly on any number of proteins that control the delivery of a hormone to its normal target cell. The affinity of an endocrine disruptor to a hormone receptor is not directly equivalent to its potency, i.e. the dose-response of an EDC is one of the many factors within the endocrine system that determine the actual hormonal response. Based on *in vitro* and *in vivo* studies, most EDC dose-response curves are nonlinear. Endocrine disruptors are not necessarily specific, i.e. the same chemical can disrupt the activity of more than a single androgen, estrogen, or thyroid hormone. Indeed, some EDCs have been found to interact with multiple hormone receptors simultaneously. It appears that two different EDCs may act synergistically at low doses that would not have elicited an effect had each EDC acted alone.

As mentioned, EDCs often are also harmful to reproduction and development. Sensitivity to endocrine disruption is most severe during tissue development. The developmental effects occur at lower doses than

those required for the same effects in adults. Thus, any testing for endocrine disruption must consider exposures during a specific developmental period and the entire life, i.e. lifelong follow-up is needed to assess latent effects.

Endocrine disrupting compounds have been found to be transported from mother to child occurs through the placenta during pregnancy.<sup>23–25</sup> Indeed, there is much interest in the linking *in utero* exposures to air pollutants and other environmental contaminants to developmental outcomes.<sup>26,27</sup>

## QUESTIONS

- Mercury can accumulate in the unborn baby’s blood to concentrations higher than those in his or her mother. Newborns can be exposed to mercury during nursing. These exposures can lead to neurological damage during the child’s development. Why, then, is mercury not listed by ATSDR as a reproductive hazard?
- Describe an EDC.
- Describe a POP.
- Describe a PBT.
- Give an example of single substance that meets the criteria to be an EDC, a POP, and a PBT.
- Why do POPs and PBTs accumulate in fatty tissue?
- What are the likely sources of bisphenol-A in surface waters?
- Which U.S. demographic group receives the largest amount of PBDE dietary intake from meats? Which group receives the highest PBDE dietary exposure? Explain why.
- What role does the atmosphere play in exposures to PBDE, PCBs, and DDT?

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# Neurological Effects of Air Pollutants

## 13.1 NEUROTOXICITY

Neurotoxicants are ubiquitous in the environment. They range from the infamous toxic metals, lead and mercury, to complex organic compounds that were either designed and synthesized to insult nervous systems, e.g. the organochlorine and organophosphorus insecticides to other compounds that just happen to be neurotoxic, e.g. polycyclic aromatic hydrocarbons (PAHs) and halogenated compounds like the polychlorinated biphenyls (PCBs). These and other neurotoxicants move through the environment in many ways, but air transport is a key pathway that leads to human exposure.

Given the complexity of neural systems, the types of neurotoxicity elicited by air pollutants are varied. When taken up by humans and other organisms, they may either be detoxified or undergo bioactivation to become more toxic. Thus, the parent compounds may be intrinsically neurotoxic or they may be activated to become neurotoxic (Figure 13.1). Following the absorption and distribution of the neurotoxicant, the metabolic mechanism can be categorized. These general classifications of neurotoxic effects are discussed in the following sections.<sup>1</sup>

### 13.1.1 Demyelination

The support of myelin to signal transduction in the nervous system is analogous to an electrical insulator that prevents the loss of ionic currents. When xenobiotics<sup>a</sup> interfere with these processes in the peripheral nervous system (PNS), it can cause numbness, weakened muscles, poor coordination, and paralysis, known as myelinopathy. The effect of demyelination in the brain is known as toxic leukoencephalopathy, which ranges in severity from headaches to cognitive dysfunction to paralysis and death.

Pollutants can adversely affect the integrity of the myelin sheath either in the absence of or prior to damage to the myelinating cells and those that injure myelin-producing cells. The former group includes hexachlorophene, the organometallic species of tin (Sn) and other pollutants that cause reversible edema between the layers of myelin. Neurons (i.e. nerve cells; Figure 13.2) vary in susceptibility to different pollutants. For example, the optic nerve is highly susceptible to hexachlorophene, whereas other cranial nerves tend to have higher susceptibility to organic solvents, e.g. xylenes or trichloroethylene.

Conversely, long-term exposure to cyanide compounds ( $\text{CN}^-$ ) and carbon monoxide (CO) appears to cause direct injury to myelin-producing Schwann cell

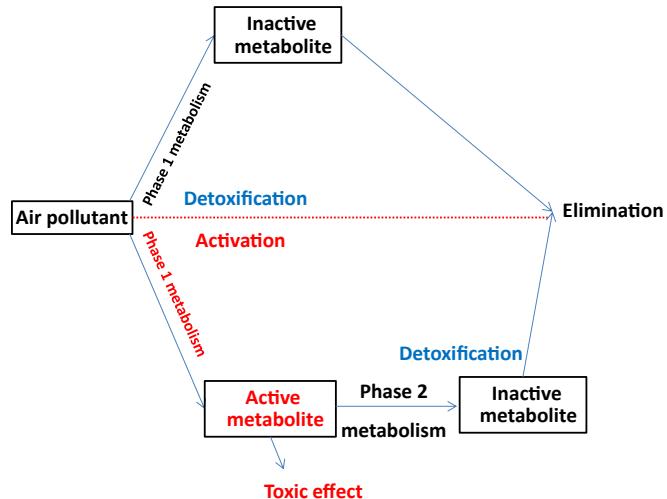
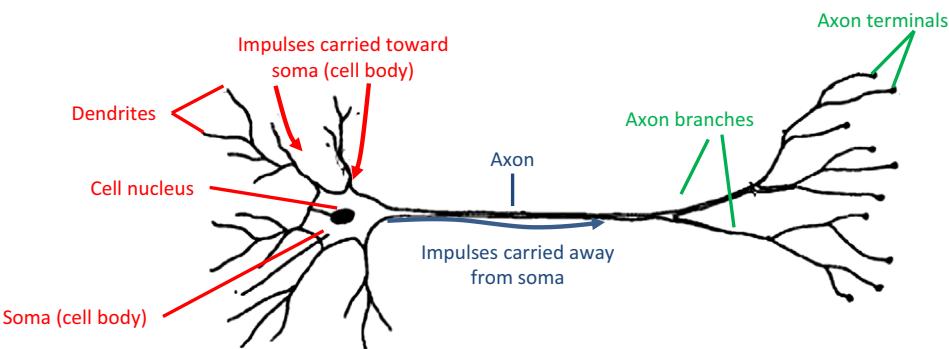


FIGURE 13.1 Metabolic pathways of detoxification and bioactivation of an air pollutant. (For color version of this figure, the reader is referred to the online version of this book.)

<sup>a</sup> Xenobiotic here is used to denote any substance foreign to the body. In other usage, a xenobiotic is one that is not only foreign, but is synthetic. The former would include any species of a metal, including naturally occurring forms, e.g. elemental lead or mercury. The latter definition would only include the chemical forms that are produced anthropogenically.



**FIGURE 13.2 The neuron.** The dendrites receive signals and the axon transmits signals to another neuron. Adapted from: National Institute on Drug Abuse. Neurons, brain chemistry and neurotransmission. <http://science.education.nih.gov/supplements/nih2/addiction/guide/lesson2-2.htm>; 2013 [accessed 25.10.13]. (For color version of this figure, the reader is referred to the online version of this book.)

bodies in the PNS and oligodendrocytes in the central nervous system (CNS). Inorganic lead (Pb) also damages myelin-producing cells. Oligodendrocytes seem to be more sensitive to Pb toxicity than do astrocytes or neurons. Indeed, the developmental effects of Pb exposure may result from the preferential inhibition of oligodendrocyte precursor cell differentiation.

### 13.1.2 Axonopathy

An axon can be degenerated while leaving the cell body intact, i.e. axonopathy, which can cause sensory and motor function deficits. Often, the greatest vulnerability to this type of neurotoxicity is at the most distal portions of the longest- and largest-diameter axon, which are the first parts to degenerate. The degeneration progresses with proximally and may eventually affect the entire neuron after long-term exposure, in a process known as “dying back neuropathy”. With axon degeneration, the myelin also degrades, but Schwann cells in the PNS may survive and guide PNS axon regeneration. Such regeneration does happen within the CNS.

The vulnerability of distal axons to toxic effects may be because these regions are more dependent on intact energy-dependent axonal transport mechanisms. Certain xenobiotics can transect an axon. Pollutants that interfere with the production of the coenzyme adenosine-triphosphate (ATP) may cause distal regions to degenerate first. Neurotoxicants that target the globular protein, tubulin, also induce this injury since tubulin-derived microtubules are critical for axonal transport.

### 13.1.3 Neuronopathy

Neuronopathy is a collective and general term related to damage to nerve cells, primarily in the body of the neuron. Airborne neurotoxicants can affect the normal

cycles of cellular generation and apoptosis, i.e. cell death, in neurons. For example, the most toxic dioxin congener, i.e. 2,3,7,8-dibenzo-*para*-dioxin, induces neurotoxicity and neuronal apoptosis in the brain cortex in part due to changes in neuronal apoptosis.<sup>2</sup>

Toxicity induced by glutamate and other excitatory amino acids, i.e. excitotoxicity, may cause ischemic and seizure-induced brain damage. For example, a toxin produced by algae in shellfish, i.e. domoic acid, binds to glutamate receptors, resulting in excitotoxic cell death. Although this is not a direct air pollution impact, pollutants that deposit into surface waters could change ecosystem diversity, with the indirect effect of preferential growth of certain toxin-producing microbes, e.g. algae, which could lead to human neurotoxicity.

### 13.1.4 Functional Neurotoxicity

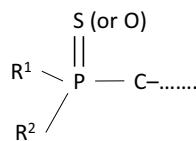
Neurotoxicants can interfere with nervous system signaling processes by activating or inhibiting receptors, or by altering the optimal quantities of a neurotransmitter available to activate receptors. For example, exposure to organophosphate and carbamate pesticides affects acetylcholine signaling.

### 13.1.5 Acetylcholinesterase Inhibition

Potential neurotoxicants are metabolized principally by oxidation, hydrolysis by esterases, and by transfer of portions of the molecule to glutathione. As discussed in Chapter 12, oxidation can detoxify or enhance toxicity by bioactivation. Many compounds are not directly neurotoxic, e.g. phosphorothioates, but become so as a result of oxidative metabolism to a neurotoxic compound.

One of the most obvious and widespread mechanism for environmental neurotoxicity is by inhibit the

endogenous production of the enzyme acetylcholinesterase (AChE). The function of AChE is to hydrolyze the neurotransmitter, acetylcholine, which is needed for synapses. Organophosphates inhibit AChE, which stops the enzyme's stimulation of the neural receptor activity. Following the release of acetylcholine into the synapse or the neuromuscular junction, AChE-catalyzed hydrolysis terminates the receptor-stimulating activity. Many pesticides include sulfur-phosphorous moieties, e.g. thiophosphates, thionophosphates, and thiophosphonates, which do not effectively inhibit AChE:



The R<sup>1</sup> and R<sup>2</sup> groups are either alkyl (carbon chain) or aryl (benzene ring) groups, which may be bonded directly to phosphorus (i.e. in phosphinates), or linked via —O—, or —S— (i.e. in phosphates). Also, the R<sup>1</sup> may be bonded directly and R<sup>2</sup> bonded via one of the above groups (phosphonates). In phosphoramidates, carbon is linked to phosphorus through an —NH group. The group C—... can be any of numerous substituted and branched aliphatic, aromatic, or heterocyclic groups linked to phosphorus by a bond (usually —O— or —S—), which is known as the leaving group. The double-bonded atom may be oxygen or sulfur. The P=O form of a thioate ester is referred to as the oxon, which is often part of the name of the derived compound (e.g. parathion is the parent P=S compound of paraoxon). Since the P=S form is intrinsically relatively stable, many insecticides are manufactured in this form which then is converted to the biologically active oxon in tissues. The substituent groups in R<sup>1</sup>, R<sup>2</sup>, and C—... may also be chemically transformed.<sup>3</sup>

These compounds are activated to phosphates or phosphonates by a CYP-dependent monooxygenase activity known as oxidative desulfuration (Chapter 12). The biologically active oxons bind to the active site of AChE, covalently phosphorylating the serine residue in the catalytic site of the enzyme. The phosphorylation of AChE creates a relatively stable inactive enzyme that persists for hours to days before hydrolysis of the phosphate moiety occurs spontaneously, and AChE activity is restored. An example of the bioactivation process is:

The precursor phosphorothioate in the pesticide parathion is bioactivated to the phosphate ester. This ester is directly responsible for the inhibition of AChE and for subsequent neurotoxicity.<sup>3</sup>

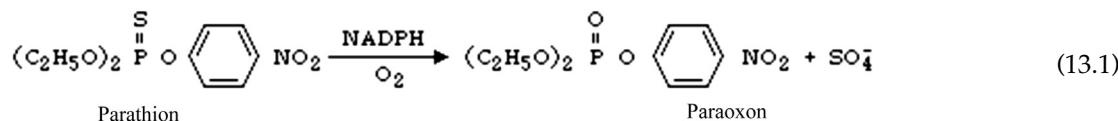
Carbamates similarly inhibit AChE, but by carbamylating the enzyme. The stability of the carbamylated enzyme is much less than the phosphorylated enzyme and spontaneous reactivation occurs much faster than with organophosphates. Whereas organophosphates enhance neurotransmitter activity by inhibiting the breakdown of acetylcholine, many toxins produce hyperstimulation of receptors by directly binding and activating them (agonism). Others reduce receptor stimulation by prohibiting the neurotransmitter from activating them (antagonism).

Certain chemical properties appear to increase the likelihood and severity of a neurotoxicant. Neurotoxicity increases with length of carbon chain and hydrophobicity of R<sup>1</sup> and R<sup>2</sup>, and when a leaving group is not sterically hindering (e.g. planar forms tend to be more toxic than nonplanar).

### 13.1.6 Developmental Neurotoxicity

The previous chapter discussed how exposures to air pollutants *in utero* and during early life can permanently alter physiology and metabolism. This not only applies to carcinogens, but to numerous other air pollutants, including those that adversely affect the nervous system, i.e. neurotoxins. Neonates are particularly vulnerable because of their rapid tissue growth, cell differentiation, immature metabolic pathways, and the development of vital organ systems. The CNS is particularly vulnerable, given its unprotected barriers and a large time of conformation.<sup>4</sup> The neurotoxic effects can be manifested immediately, or they may have latency periods of decades. For example, early life stage exposures to lead, mercury, and PAHs have been associated neurotoxic years or even decades after exposure.<sup>5</sup>

The U.S. Environmental Protection Agency (EPA) reviewed the scientific literature to assemble a list of chemicals that are toxic to the developing mammalian nervous system. Compounds were assigned one of three groups based on the strength of the evidence for developmental neurotoxicity: (1) no evidence: either there were no reports that met prescribed criteria for evidence, or there were reports which showed no developmental neurotoxicity; (2) minimal evidence: one report only or



**TABLE 13.1** Chemicals with Substantial Laboratory Evidence Supporting Developmental Neurotoxicity

1-Methyl-4-phenyl-1,2,3,6-tetrahydro-pyridine (MPTP)	2-Ethoxyethyl acetate	2-Methoxyethanol
5-Azacytidine	5-Bromodeoxyuridine	5-Flourouracil
6-Amino-nicotinamide	Acibenzolar-S-methyl	Acrylamide
Aldicarb	Allethrin	Aluminum ( $\text{AlCl}_3$ or $\text{C}_9\text{H}_{18}\text{AlO}_9$ )
Aminopterin	Arabinoside	Arsenic
Aspartame	Benomyl	Benzene
Bioallethrin	Bis( <i>tri-n</i> -butyltin) oxide	Bisphenol A
Butylated hydroxy anisol	Butylated hydroxytoluene	Cadmium
Caffeine	Carbamazepine	Carbaryl
Carbon monoxide	Chlordecone	Chlordiazepoxide
Chlorine dioxide	Chlorpromazine	Chlorpyrifos
Cocaine	Colcemid	Colchicine
Cypermethrin	Cytosine	D-Amphetamine
Deltamethrin	Dexamethasone	Di-(2-ethylhexyl)-phthalate
Diazepam	Diazinon	Dieldrin
Diethylstilbestrol	Diphenylhydantoin	Epidermal growth factor
Ethanol	Ethylene thiourea	Fluazinam
Fluoride	Griseofulvin	Haloperidol
Halothane	Heptachlor	Hexachlorobenzene
Hexachlorophene	Hydroxyurea	Imminodipropionitrile
Ketamine	Lead	Lindane
Lysergic acid	Maneb	Medroxyprogesterone
Mepivacaine	Methadone	Methanol
Methimazole	Methylazoxy-methanol	Methylmercury
Methylparathion	Monosodium glutamate	<i>N,N</i> -Diethyl-metatoluamide
Naltrexone	Nicotine	Ozone
Paraquat	Parathion (ethyl)	Penicillamine
Permethrin	Phenylacetate	Phenylalanine (d,l)
Polybrominated diphenyl ethers	Polychlorinated biphenyls	Propylthiouracil
Retinoids/vitamin A/isotretinoin	Salicylate	Tebuconazole

(Continued)

**TABLE 13.1** Chemicals with Substantial Laboratory Evidence Supporting Developmental Neurotoxicity—cont'd

Tellurium (salts)	Terbutaline	Tetrahydrocannabinol
Thalidomide	Toluene	Triamcinolone
Tributyltin chloride	Trichlorfon	Trichloroethylene
Triethyllead	Triethyltin	Trimethyltin
Trypan blue	Urethane	Valproate
Vincristine		

Source: Mundy W, Padilla S, Shafer T, Gilbert M, Breier J, Cowden J, et al. Building a database of developmental neurotoxicants: evidence from human and animal studies. *Toxicologist* 2009;108:284.

multiple reports from only one laboratory; or (3) substantial evidence: reports from more than one laboratory.

Those chemicals that have substantial evidence of developmental neurotoxicity are shown in Table 13.1. The list includes metals and their compounds, pesticides, industrial chemicals, pharmaceuticals, and other substances (e.g. nicotine and tetrahydrocannabinol, chemicals in tobacco and marijuana smoke, respectively). It also includes criteria air pollutants, i.e. ozone ( $\text{O}_3$ ) and CO.

## 13.2 NEUROTOXIC METALS

Metals have been known for centuries to induce neurotoxicity. Metal toxicity has been observed for millennia. The *Ebers papyrus* documented lead, copper, and the metalloid antimony over 3000 years ago. Hippocrates (460–377 BC) noted abdominal problems in miners of metallic ore.<sup>6</sup> Metals were important to ancient societies, but even then, their toxicity was somewhat known. The Romans, for example, knew of the danger of mercury exposure, so they used prisoners to mine the metal.<sup>7</sup> Since metals continue to be important part of society, it is inevitable that humans and ecosystems will be exposed to myriad metallic compounds.

After exposure, the parent metal, a salt, a cation, or one of its organometallic species is absorbed and distributed within the body. A fraction of the species or its transformation products may accumulate in lipids and other substrates and the rest is excreted. The difference results in accumulation and increased body burden. The metal and its metabolites thereafter induce neurotoxicity in various ways. For neurotoxicity to occur, a metal must reach a neural target (e.g. a neuron) at a concentration sufficient to alter mechanistically the normal functioning of the nervous system. Metal neurotoxicity can involve the types of membrane receptor–ligand disruptions discussed in Chapter 12. However, it may also involve intracellular receptors and ion channels. Metals

tend to react with nucleophilic macromolecules, e.g. proteins, amino acids, and nucleic acids. A nucleophile donates an electron pair to an electrophile, an electron pair acceptor, to form a chemical bond. Mercury, for example, reacts with sulfur (S) in thiols, cysteinyl protein residues, and glutathione and S in thiols and thiolates. However, other metals, e.g. lithium, calcium, and barium, preferentially react with harder nucleophiles, e.g. the oxygen in purines. Lead tends to fall between these two extremes, i.e. exhibits universal reactivity with all nucleophiles.<sup>6</sup>

### 13.2.1 Lead

Humans are exposed to lead (Pb) through numerous routes and pathways (Figure 13.3). In the United States, mean Pb population exposure has fallen with the elimination of leaded gasoline, Pb-based paint, and Pb solder in cans. With the decrease in Pb exposure, measured blood-Pb levels in the U.S. population has also occurred. The same phenomenon has been observed in other countries that eliminated gasoline Pb.<sup>8</sup> However, Pb exposures remains can remain elevated in areas near Pb sources, e.g. smelters, or for subpopulation exposed to Pb-based paint or Pb-contaminated drinking water.<sup>9</sup>

Like other metals, Pb can bioaccumulate in the tissues of aquatic organisms through ingestion of food and water, and adsorption from water, and can subsequently lead to adverse effects in contaminated tissue.

The metal lead (Pb) is arguably the most notorious and well-studied human neurotoxin. Many studies have indicated that an increase in Pb body burden, as indicated by blood Pb concentrations  $>10 \mu\text{g dl}$ , is associated with decreased cognitive functions<sup>10</sup> and increased behavioral problems<sup>11</sup> (Figure 13.4). Indeed, at elevated concentrations from acute exposure, Pb insults to the brain and CNS can result in coma, convulsions, and death. Surviving children from such acute Pb poisoning typically retain mental and behavioral disruptions. With lower concentrations, long-term exposures are associated with asymptomatic periods before observable neurotoxic effects, including diminished cognition, shortened attention span, behavioral changes, dyslexia, and attention deficit disorder. Other effects from chronic Pb exposure include hypertension, renal impairment, immunotoxicity, and toxicity to the reproductive organs. For the most part, these effects are permanent. Most of these ailments are irreversible and resist medical treatment.<sup>12</sup>

One of the first observations of a neurotoxic air pollutant was that of the Pb. Ingestion of nonfood items, i.e. pica, is known to be a major pathway to Pb exposure that leads to increase Pb concentrations in a child's blood, and ultimately to neurotoxic effects. However, other pathways contribute to the Pb body burden. In particular, interest has been given to near-road exposures to air pollutants. Like several other heavy metals, Pb interferes with physiological processes because, when ionized, divalent lead ( $\text{Pb}^{2+}$ ) acts like divalent

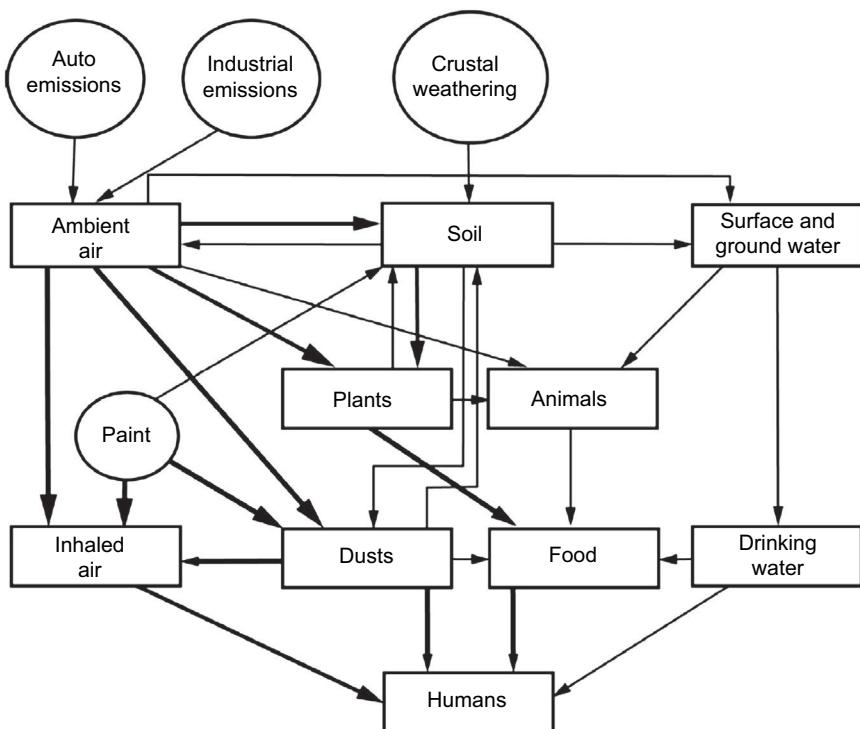
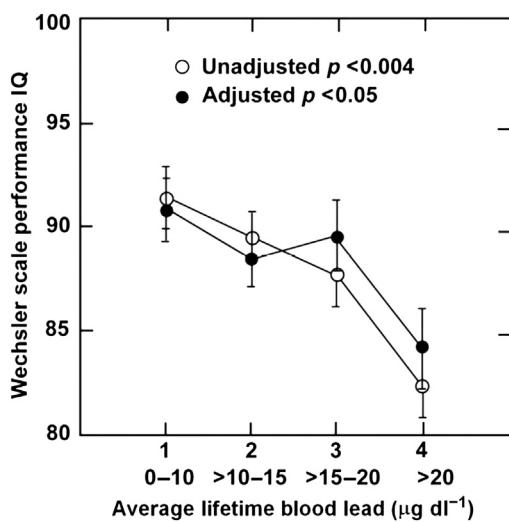


FIGURE 13.3 Pathways by which humans are exposed to lead. Adapted from Ref. 9.



**FIGURE 13.4** Relationship between intelligence indicators and blood lead (Pb) concentrations in a cohort of 253 Cincinnati 7-year-olds. Graph shows unadjusted relationship and relationship adjusted for home quality score, maternal intelligence quotient (IQ), birth weight, birth length, child gender, and cigarette consumption during pregnancy. The IQ is represented by the Wechsler Scale performance IQ test administered to the children. Mean  $\pm$  standard deviation of lifetime average blood Pb concentrations within each category: 0–10  $\mu\text{g dl}^{-1}$ ,  $7.7 \pm 1.4 \mu\text{g dl}^{-1}$  ( $n = 68$ ); >10–15  $\mu\text{g dl}^{-1}$ ,  $12.3 \pm 1.4 \mu\text{g dl}^{-1}$  ( $n = 89$ ); >15–20  $\mu\text{g dl}^{-1}$ ,  $17.1 \pm 1.2 \mu\text{g dl}^{-1}$  ( $n = 53$ ); and >20  $\mu\text{g dl}^{-1}$ ,  $26.3 \pm 5.0 \mu\text{g dl}^{-1}$  ( $n = 41$ ). Ref. 9. Data from Dietrich KN, Berger OG, Succop PA, Hammond PB, Bornschein RL. The developmental consequences of low to moderate prenatal and postnatal lead exposure: intellectual attainment in the Cincinnati lead study cohort following school entry. *Neurotoxicol Teratol* 1993a;15:37–44.

calcium ( $\text{Ca}^{2+}$ ). Due to its larger atomic size and other chemical differences, however,  $\text{Pb}^{2+}$  induces biological processes that differ from those of  $\text{Ca}^{2+}$ . For example, during gestation and in early childhood, the developing brain is harmed when  $\text{Pb}^{2+}$ , competing with  $\text{Ca}^{2+}$ , induces the release of a neurotransmitter in elevated amounts and at the wrong time (e.g. during basal intervals, when a person is at rest). Thus, at high lead exposures, a person may have abnormally high amounts of brain activity (when it should be lower) and, conversely, when a neural response is expected, little or no increase in brain activity is observed. This may induce chronic effects when synaptic connections in the brain are truncated during early brain development.

Lead also adversely affects the release of the transmitter, glutamate, which is involved in brain activities associated with learning. The *N*-methyl-D-aspartate

receptor seems to be selectively blocked when lead is present. Other lead effects include the activation of protein kinase C (known as “PKC”) because PKC apparently has a greater affinity for lead than for the normal physiological activator, divalent calcium. This interference complicates and exacerbates the other neurotransmitter effects and harms the cell’s chemical messaging (i.e. second-messenger systems), synthesis of proteins, and genetic expression.

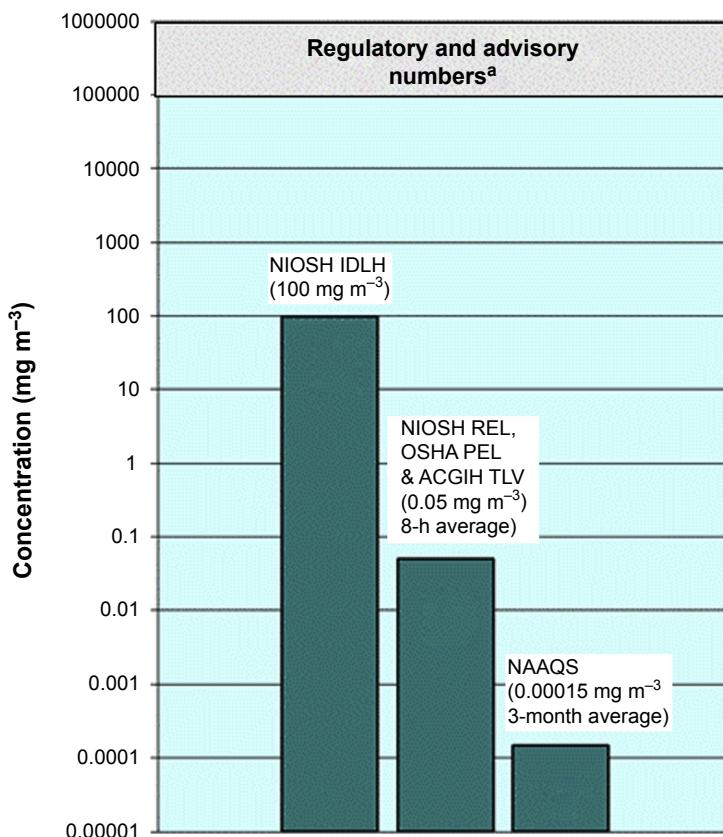
All of these neurological effects, especially in the developing brain, began to be documented in earnest by the medical community only within the last half century. Herbert Needleman, a pediatrician at the University of Pittsburgh Medical Center, discovered that a correlation existed between the amount of lead in the teeth of infants and their intelligence at age 16, as measured by their IQ scores.<sup>13</sup> This lead to research that has continued to show an inverse dose-response between lead dose and measured IQ. That is, the higher the lead content, the lower the IQ in these teenagers. In a series of follow-up studies, Needleman determined that lead poisoning had long-term implications for a child’s attentiveness, behavior, and school success.

Especially in poorer homes with older residences, this type of ingestion continues to be a major lead exposure pathway in young children. Other pathways include soil ingestion (another example of pica), inhalation of lead on dust particles (which can be very high when older homes are renovated, so not limited to lower socioeconomic status children), and Pb that has leached into food from glazes on cooking and dining ware into the food; common in some ethnic groups, e.g. Hispanic-Americans in the United States.

Needleman and other scientists called interventions even while the scientific evidence is still being gathered.<sup>b</sup> He was among the first to advocate the removal of tetraethyl lead from gasoline and to remove lead-based paints and to reduce exposure in houses where young children can chew on the paint chips. The results have been dramatic, with average blood lead levels in this country dropping an estimated 78% from 1976 to 1991.

Some important health thresholds are shown in Figure 13.5. It is important to note that chronic lead thresholds, e.g. the National Ambient Air Quality Standard (NAAQS), are several orders of magnitude lower than acute thresholds. As with other chronic disease, a

<sup>b</sup> At least on its face, this runs contrary to some of the measures calling for improved environmental risk-based science proposed in the 1980s, especially the separation of risk assessment and risk management. The National Academy of Sciences in 1983 (*Risk Assessment in the Federal Government: Managing the Process*; ISBN: 0309033497) issued risk assessment guidance with the intent to make risk science more objective and empirical. Thus, the scientific aspects of risks, i.e. risk assessment, are considered independently from the decision making aspects of risks, i.e. risk management.



**FIGURE 13.5 Health-related data for exposure to lead.** ACGIH TLV is the American Conference of Governmental and Industrial Hygienists' threshold limit value expressed as a time-weighted average; NIOSH REL is the National Institute of Occupational Safety and Health's recommended exposure limit; NIOSH-recommended exposure limit for an 8- or 10-h time-weighted-average exposure and/or ceiling. NIOSH IDLH is NIOSH's immediately dangerous to life or health concentration; NIOSH-recommended exposure limit to ensure that a worker can escape from an exposure condition that is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from the environment. NAAQS is National Ambient Air Quality Standard. The U.S. EPA sets NAAQS that protect public health and the environment for six commonly found pollutants: ozone, particle pollution, nitrogen oxides, sulfur dioxide, carbon monoxide and lead. The NAAQS for lead is  $0.15 \mu\text{g m}^{-3}$ . The rolling 3-month average of lead in total suspended particles may not exceed this concentration. OSHA PEL is the Occupational Safety and Health Administration's permissible exposure limit expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effect averaged over a normal 8-h workday or a 40-h workweek. Notes: The regulatory and advisory values cited in this factsheet were obtained in September 2011. Regulatory numbers are values that have been incorporated in Government regulations, while advisory numbers are nonregulatory values provided by the Government or other groups as advice. OSHA and NAAQS numbers are regulatory, whereas NIOSH and ACGIH numbers are advisory. a stands for health numbers are toxicological values derived from animal testing or risk assessments developed by the U.S government.<sup>14,15</sup> U.S. Environmental Protection Agency. Technology transfer network: air toxics: lead compounds. <http://www.epa.gov/ttn/atw/hlthef/lead.html>; 2011 [accessed 24.10.13]. (For color version of this figure, the reader is referred to the online version of this book.)

person exposed for a long time will experience neurotoxic effects at very lower concentrations.

### 13.2.2 Mercury

The neurotoxicity of the metal mercury (Hg) is the subject of both scientific and general concern. Notably, a mercury-based preservative used in vaccines has been implicated by certain advocacy group as contributing to the apparent increase in autism in recent decades. The metal has also been central to the debate about the safety of seafood and tradeoffs of hazards to unborn and nursing babies and the benefits of breast

feeding, given the prolific *in utero* and neonatal neural tissue development.

Like other metals, mercury is a natural component of the earth, with an average abundance of approximately  $0.05 \text{ mg kg}^{-1}$  in the earth's crust, with significant local variations. It is an unusual metal in that it is a liquid at room temperature (it melts at  $38.9^\circ\text{C}$  and boils at  $303^\circ\text{C}$ ) and is quite heavy with a density of  $13.5 \text{ g cm}^{-3}$  at  $25^\circ\text{C}$ . Studies have indicated that mercury can be a toxic substance and that one of its compounds methylmercury chloride is a highly toxic substance. Measurements have shown that because mercury persists in the environment and methylmercury

biomagnifies up the food chain, a wide variety of species and ecosystems may be exposed to excessive levels of mercury in the environment.<sup>16</sup>

Mercury ores that are mined generally contain about 1% mercury, but at the Almaden mine in Spain they are mining an ore which contains about 12% mercury. Although about 25 mercury minerals are known, virtually the only deposits that are being mined contain cinnabar ( $HgS$ ), a bright red substance which is also used to produce the color vermillion. Despite a decline in global mercury consumption, competing sources of mercury and low prices, the mining of mercury continues in a number of countries. Spain, China, Kyrgyzstan, and Algeria have dominated this activity in recent years. The last U.S. mine closed in 1982. There are reports of small mines in China, Russia (Siberia), Outer Mongolia, Peru, and Mexico. In the early 1980s, the annual production from mining (cinnabar) was 7000 tonnes, today it is less than half of that and is about 2000 tonnes.<sup>17</sup>

Mercury is also obtained: as a by-product of mining or refining of other metals (such as zinc, gold, silver) or minerals and even from natural gas; from recycling spent products; and reprocessing mine tailings containing mercury. In the United States, this recovery of mercury as a by-product of other metal mining (primarily gold) from recycling and from the decommissioning of chlor-alkali plants, amounts to about 250 tonnes per year.<sup>3</sup>

Concentrations of total mercury in the atmosphere of the northern hemisphere have recently been estimated at  $2\text{ ng m}^{-3}$ , those in the southern hemisphere being half this value. Values in urban areas are usually higher (e.g.  $10\text{ ng m}^{-3}$ ). Mercury has an appreciable vapor pressure ( $2 \times 10^{-3}\text{ mm Hg}$  or  $0.3\text{ Pa}$  at  $25^\circ\text{C}$ ) which is the reason for it being in the atmosphere.<sup>18,19</sup> It has been estimated that each year 2000–3000 tonnes<sup>20</sup> enter the atmosphere from natural and anthropogenic sources. Natural sources, such as volcanoes, are responsible for approximately half of atmospheric mercury emissions. The anthropogenic half can be divided into the following estimated percentages which excludes biomass burning, an important source in some regions<sup>21,22</sup>:

- 65% from stationary combustion, of which coal-fired power plants are the largest aggregate source (40% of U.S. mercury emissions in 1999). This includes power plants fueled with gas where the mercury has not been removed. Emissions from coal combustion are between one and two orders of magnitude higher than emissions from oil combustion, depending on the country.<sup>23</sup>
- 11% from gold production. The three largest point sources for mercury emissions in the United States are the three largest gold mines. Hydrogeochemical release of mercury from gold-mine tailings has been

accounted as a significant source of atmospheric mercury in eastern Canada.

- 6.8% from nonferrous metal production, typically smelters.
- 6.4% from cement production.
- 3.0% from waste disposal, including municipal and hazardous waste, crematoria, and sewage sludge incineration. This is a significant underestimate.
- 3.0% from caustic soda production.
- 1.4% from pig iron and steel production.
- 1.1% from mercury production, mainly for batteries.
- 2.0% from other sources.

Mercury vapor in laboratories can be a problem especially in laboratories that are heated. One way of reducing the evaporation (Hg vapor pressure is quite low; i.e.  $1.712619 \times 10^{-4}\text{ kPa}$  at  $20^\circ\text{C}$ ) is to cover the pool of mercury in a beaker with a layer of water. The diffusion of mercury through water is very slow and it effectively seals off the evaporation process (the diffusion coefficient of mercury in water is extremely low, i.e.  $6.3 \times 10^{-10}\text{ m}^2\text{ s}^{-1}$ ).<sup>24,25</sup>

The chemical species most easily absorbed through the gastrointestinal tract (about 95% absorbed) is methylmercury. Organic Hg species, especially methylmercury, impairs neurological development, especially in unborn children and infants. Methylmercury *in utero* exposure, which can result from a mother's consumption of fish and shellfish that contain methylmercury, can adversely affect a baby's growing brain and nervous system. Through the blood of a pregnant woman, Hg enters the blood of the developing child and then into the child's brain and other tissues. As with metallic mercury ( $Hg^0$ ), methylmercury can endogenously form inorganic mercury compounds. These compounds can accumulate and in the brain. Elimination of methylmercury occurs slowly over a period of several months, mostly as inorganic mercury in the feces. As with inorganic mercury, a fraction of the methylmercury in a nursing woman's body will pass into her breast milk.<sup>26</sup>

Cognitive skills, memory, attention, language, as well as fine motor and visual spatial skills have been observed in children exposed to methylmercury in the womb. More recent data from the U.S. Centers for Disease Control and Prevention (CDC) support this general finding.

Outbreaks of Hg poisonings provide strong evidence that adults, children, and unborn children are at risk from ingestion and inhalation exposures to mercury. During methylmercury poisoning outbreaks, infants were born with severe disabilities to some mothers who showed no symptoms of nervous system damage. These experiences demonstrated that the developing nervous system of the unborn child is likely much

TABLE 13.2 Percentage of Women Aged 16–49 Years with Blood Mercury Level  $\geq 5.8 \mu\text{g l}^{-1}$

Race/Ethnicity	No.	% with Hg Levels $\geq 5.8 \mu\text{g l}^{-1}$	(95% CI*)
Mexican American	1106	1.70	(1.04–2.79)
White, non-Hispanic	1377	5.77	(3.71–8.97)
Black, non-Hispanic	794	4.82	(2.55–9.11)
<b>Total</b>	<b>3637</b>	<b>5.66</b>	<b>(4.04–7.95)</b>

\* Confidence interval.

Source: National Health and Nutrition Examination Survey, U.S., 1999–2002.

Reported in Ref. 28.

more vulnerable to methylmercury exposure than is the adult nervous system.<sup>27</sup>

Mercury concentrations in human populations are being found above reference concentrations ( $\text{RfC} = 0.3 \mu\text{g m}^{-3}$ ), i.e. concentrations considered to be safe for exposures. For example, the U.S. National Health and Nutrition Examination Survey measurements of blood Hg levels in human populations from the years 1999 through 2002 confirm that blood Hg levels indicate that approximately 6% of childbearing-aged (i.e. 16–49 years old) women had levels at or above  $5.8 \mu\text{g l}^{-1}$  (Table 13.2).<sup>28</sup> This is the blood Hg concentration equivalent to the reference dose, which is  $0.1 \mu\text{g}$  per kilogram body weight per day ( $0.1 \mu\text{g kg}^{-1} \text{ day}^{-1}$ ). Based on this prevalence for the overall U.S. population of women of reproductive age and the number of U.S. births each year, 300,000 newborns each year may have increased risk of learning disabilities associated with *in utero* exposure to methylmercury.<sup>29</sup>

### 13.2.3 Manganese

As with lead and mercury, other metals are released to atmosphere not only as a result of mechanical processes during extraction and manufacturing, but also by combustion processes. Many organometallic molecules have been identified in the effluent from systems burning pure methane with pure oxygen. Inhibitors, such as tetraethyl lead and methylcyclopentadienyl manganese tricarbonyl (MMT), can greatly change the rate of reaction. That is their principal asset as gasoline additives. MMT ( $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$ ) is an octane enhancer, which was approved as a fuel additive in the US.

The element manganese (Mn) is ubiquitous in the environment. The metal and its compounds have been an important constituent of numerous manufacturing processes, including<sup>30</sup>:

- Metallic manganese primarily in steel production to improve hardness, stiffness, and strength. It is also

used in carbon steel, stainless steel, and high-temperature steel, along with cast iron and super alloys

- Manganese dioxide ( $\text{MnO}_2$ ) in the production of dry-cell batteries, matches, fireworks, and the production of other manganese compounds
- Catalyst manganese chloride ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) in the chlorination of organic compounds, in animal feed, and in dry-cell batteries
- Manganese sulfate as a fertilizer, livestock nutritional supplement, in glazes and varnishes, and in ceramics.

The average manganese levels in various environmental media are<sup>31</sup>:

- levels in drinking water are approximately 0.004 parts per million (ppm);
- average air levels are approximately 0.02 micrograms per cubic meter ( $\mu\text{g m}^{-3}$ );
- levels in soil range from 40 to 900 ppm;
- average daily intake from food ranges from 1 to 5 milligrams per day ( $\text{mg day}^{-1}$ ).

Workers where manganese metal is produced from manganese ore or where manganese compounds are used to make steel or other products are most likely to be exposed through inhalation to higher than normal levels of manganese.

Arguably, one of the most important current issues associated with manganese is as a fuel additive, especially MMT. In 1994, the EPA issued an exposure assessment based on some key assumptions in southern California:

- 100% unleaded gasoline contains 1/32 g of Mn per gallon of gasoline (about 14% of the gasoline in the Riverside area used MMT in 1990)
- About 30% of the total MMT combusted is emitted from the tailpipe as manganese-containing particle matter with an aerodynamic diameter of  $\leq 2.5$  microns ( $\text{PM}_{2.5}$ )
- 69% of the Mn in larger particles, that is  $\leq 4$  microns ( $\text{PM}_4$ ), was derived from automotive sources.

The exposure assessment concluded that 5–10% of the general population in Riverside might be exposed via inhalation to manganese annual average levels of approximately  $0.1 \mu\text{g m}^{-3}$   $\text{PM}_4$  or higher, indicating that possibly hundreds of thousands of persons in the Los Angeles area could experience such exposures at or greater than EPA's current inhalation health benchmark<sup>31</sup> for manganese RfC of  $0.05 \mu\text{g m}^{-3}$ . Decisions on the safety of Mn additive usage are still under consideration in the United States.

Manganese is essential for normal physiologic functioning in humans and animals. Unfortunately, Mn is also neurotoxic. Chronic inhalation exposure to high

concentrations of manganese in humans may result in CNS effects. The syndrome manganism may result from chronic exposure to higher levels, i.e. feelings of weakness and lethargy, tremors, a mask-like face, and psychological disturbances. Respiratory effects have also been noted in workers chronically exposed by inhalation. Impotence and loss of libido have been noted in male workers afflicted with manganism.<sup>32</sup> Chronic inhalation exposure of humans to manganese results primarily in effects on the nervous system. Slower visual reaction time, poorer hand steadiness, and impaired eye-hand coordination were reported in several studies of workers occupationally exposed to manganese dust in air. Other chronic effects reported in humans from inhalation exposure to manganese are respiratory effects such as an increased incidence of cough, bronchitis, dyspnea (difficult breathing) during exercise, and an increased susceptibility to infectious lung disease.<sup>33</sup>

The RfC for Mn is  $0.05 \text{ } \mu\text{g m}^{-3}$  based on impairment of neurobehavioral function in humans. The RfC is an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to

the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious noncancer effects during a lifetime. Although the RfC is not a direct estimator of risk, it serves as a reference point to gauge the potential effects. Thus, exposures increasingly greater than the RfC indicate a potential for adverse health effects increases (Figure 13.6).

Studies in human populations indicate neurological damage from Mn exposure. The lowest observable adverse effect concentration (LOAEC) is  $150 \text{ } \mu\text{g m}^{-3}$ , based on impairment of neurobehavioral function. Based on this LOAEC and other studies, the RfC for Mn is  $0.05 \text{ } \mu\text{g m}^{-3}$ .<sup>34</sup> Note that the LOAEC is likely higher than the no observable adverse concentration (NOAEC), since research could not show an Mn concentration threshold below which no neurotoxicity is observed. Thus, additional uncertainty factors had to be included in the RfC calculation (Chapter 7).

Manganese is one of a few contaminants that can be eliminated before even being absorbed. This process is known as “presystemic elimination” and can take place while the contaminant is being transferred from the

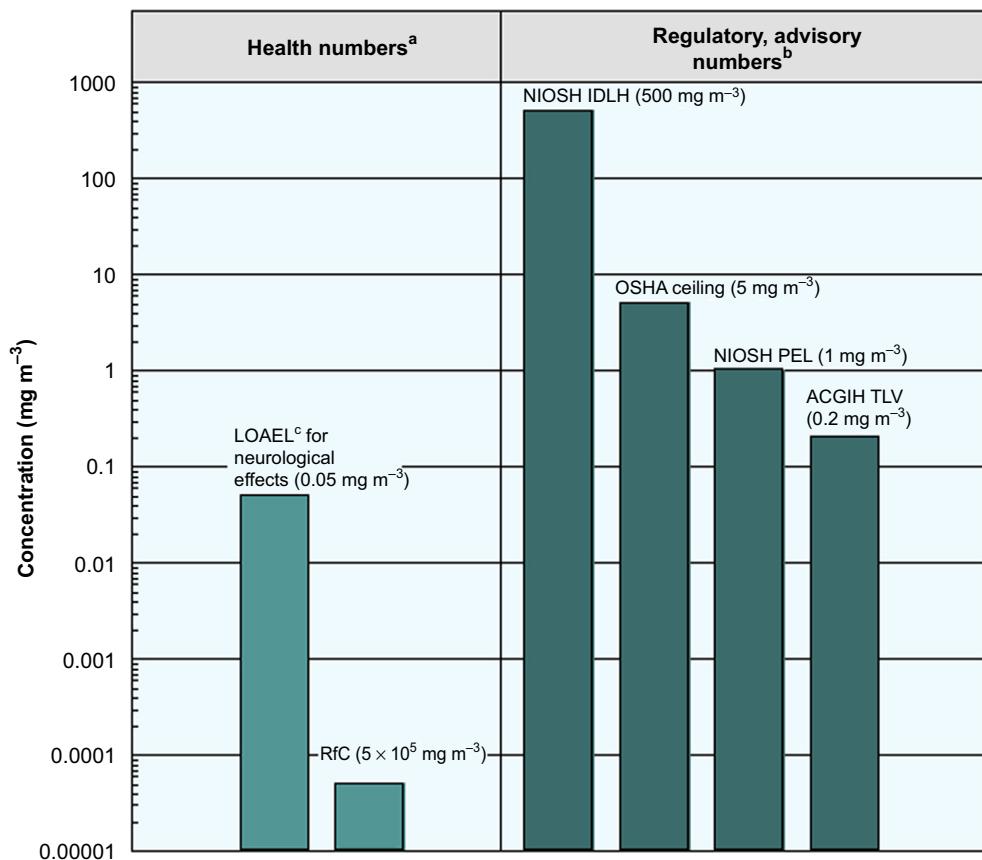


FIGURE 13.6 Health data from manganese inhalation exposure. To convert concentrations in air (at  $25^\circ\text{C}$ ) from ppm to  $\text{mg m}^{-3}$ :  $\text{mg m}^{-3} = (\text{ppm}) \times (\text{molecular weight of the compound}) / (24.45)$ . For manganese: 1 ppm =  $2.25 \text{ mg m}^{-3}$ . In figure, a stands for health numbers that are toxicological values derived from animal testing or risk assessments developed by the U.S government and b stands for Regulatory values that have been incorporated in the U.S. government regulations, whereas advisory values are non-regulatory, but based on advice from the U.S. government or other groups as advice. OSHA numbers are regulatory, whereas NIOSH, ACGIH, and AIHA numbers are advisory. Ref. 32, 36–39. (For color version of this figure, the reader is referred to the online version of this book.)

exposure site (e.g. the outer layer of the skin or the gastrointestinal (GI) tract). Manganese can be eliminated during uptake by the liver, even before it is absorbed into the bloodstream. Presystemic elimination, however, does not necessarily mean that an organism experiences no adverse effect. In fact, Mn exposure can damage the liver without ever being absorbed into the bloodstream. This is also one of the complications of biomarkers, since the body is protected against Mn toxicity by low rates of absorption or by the liver's presystemic Mn elimination.<sup>35</sup>

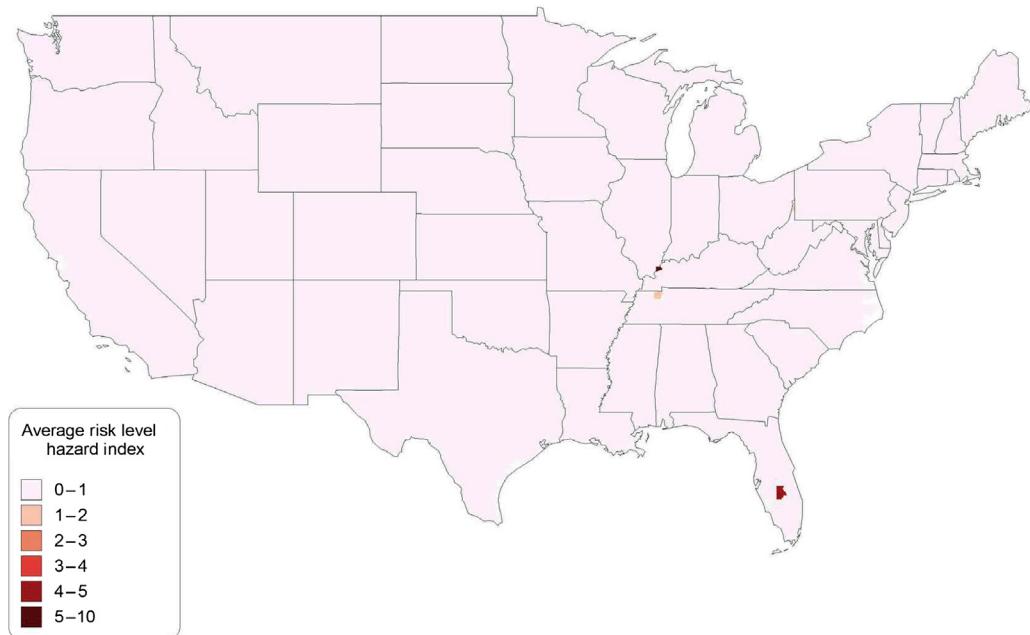
The inorganic forms include manganese chloride ( $MnCl_2$ ), manganese sulfate ( $MnSO_4$ ), manganese acetate [ $Mn(CH_3COO)_2$  or  $C_6H_9MnO_6 \cdot 2H_2O$ ], manganese phosphate ( $MnPO_4$ ), manganese dioxide ( $MnO_2$ ), manganese tetroxide ( $Mn_3O_4$ ), and manganese carbonate ( $MnCO_3$ ). Emphasis has been placed on the health effects of compounds containing inorganic manganese in the Mn(II), Mn(III), or Mn(IV) oxidation states, since these are the forms most often encountered in the environment and the workplace. There is evidence in animals and humans that adverse neurological effects can result from exposure to different manganese compounds; much of this information on toxicity differences between species of manganese is from reports and experiments of acute exposures to very high doses. Results from animal studies indicate that the solubility of inorganic manganese compounds can influence the bioavailability of manganese and subsequent delivery of manganese to critical toxicity targets such as the brain; however, the influence of manganese oxidation state

on manganese toxicity is not currently well understood. Manganese in the form of permanganate produces toxic effects primarily through its oxidizing capacity. However, because of its tendency to oxidize organic material, the permanganate ion is not stable in the environment; thus, the probability of exposure to this species around waste sites is considered very low.

As discussed in Chapter 3, the National Scale Air Toxics Assessment (NATA) screens U.S. emission sources and locations of interest for further study in order to gain a better understanding of risks. The NATA neurological hazard index was dominated by metals, specifically the manganese compounds, with minor contributions by cyanide compounds, ethylene oxide, and mercury compounds. The neurological hazard index exceeded 1.0 for fewer than 350,000 people in the United States (Figure 13.7).

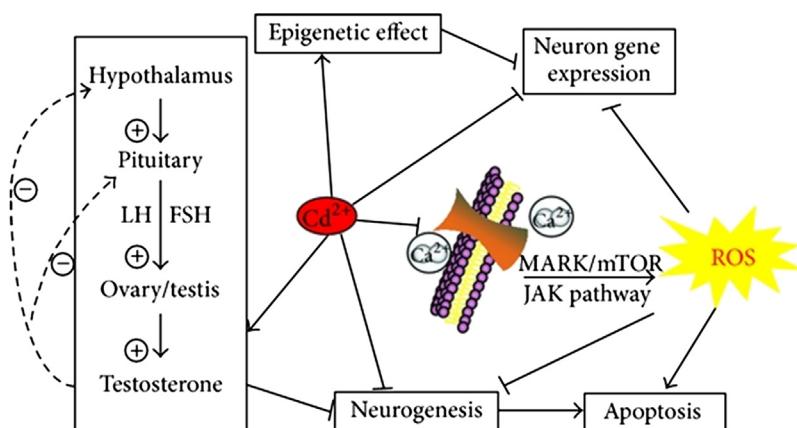
### 13.2.4 Other Neurotoxic Metals

A number of other metals are suspected of being neurotoxic, especially cadmium (Cd) and the metalloid arsenic (As). The biological mechanisms of Cd neurotoxicity are not well understood. It may involve oxidative damage and interaction with other metals, e.g. cobalt and zinc. It may also involve the endocrine system, i.e. Cd's hormonal activity may induce estrogenic endogenous changes that affect neurotransmissions.<sup>40</sup> As is the case for many pollutants, neurotoxic metals may also involve epigenetics and gene–environment interactions (Figure 13.8).



**FIGURE 13.7** 2005 National Air Toxics Assessment county level neurotoxic hazard index. U.S. Environmental Protection Agency. Summary of results for the 2002 national-scale assessment. <http://www.epa.gov/nata2002/risksum.html>; 2013 [accessed 25.10.13]. (For color version of this figure, the reader is referred to the online version of this book.)

**FIGURE 13.8 Potential mechanisms of cadmium (Cd) neurotoxicity.** (1) Cd-induced neuron cell apoptosis and formation of a reactive oxygen species (ROS) are mediated through  $\text{Ca}^{2+}$ -mitochondria signaling and  $\text{Ca}^{2+}$ -membrane channels. (2) Cd impaired neurogenesis. (3) Cd accumulation in the brain, which in turn alters gene expression and epigenetic effect. (4) Cd has estrogenic or anti-androgenic effect, which can disrupt hypothalamic–pituitary–gonadal (HPG) axis. These potential mechanisms have possible, simultaneous interactions. The solid black arrows represent the stimulation, the solid black line segments indicate the inhibition, and the dotted lines represent the negative feedback control of the HPG axis. Ref. 40. (For color version of this figure, the reader is referred to the online version of this book.)



Normally in adults, Cd seldom crosses the blood–brain barrier. Actually, Cd exposure may not necessarily follow the inhalation-adsorption model discussed in previous chapters, but can completely bypass the blood–brain route and follow a nasal exposure route. As such, Cd can move along the primary olfactory neurons to their terminations in the olfactory bulbs. The olfactory route is a plausible means of Cd reaching the brain. In addition, Cd has been shown to damage olfactory sensation.<sup>40</sup>

Upon entry into neurons, Cd induces a decrease in the activity of glutathione peroxidase catalase and super oxide dismutase, producing an increase in free radicals. This free radicals increase lipid peroxidation, which disrupts both cellular and mitochondrial membranes. This increases apoptosis and induces genetic damage. The net effect is a combination of these impacts and the extent to which metallothionein is activated, which scavenges free radicals and chelates Cd.<sup>41</sup> The degradation of membrane potentials stimulates the release of a cytochrome enzyme. Thus Cd neurotoxicity follows a path similar to other oxidative stress models.<sup>42</sup> Other metals are listed in Table 13.1. In addition to the Pb, Cd, and methylmercury, the specific compounds that are potentially neurotoxic include aluminum (Al) and tin (Sn). The specific compounds are aluminum chloride ( $\text{AlCl}_3$ ), aluminum lactate ( $\text{C}_9\text{H}_{18}\text{AlO}_9$ ), tributyltin chloride ( $\text{C}_{12}\text{H}_{27}\text{ClSn}$ ), and triethyltin [( $\text{C}_2\text{H}_5$ )<sub>3</sub>Sn].

Arsenic is also listed. Arsenic (As) is a metalloid that behaves in many ways like metals in the environment and within organisms, so in air pollution realms it is often grouped with metals.

### 13.3 NEUROTOXIC ORGANIC COMPOUNDS

In addition to the organometallic compounds mentioned in the previous section (e.g. alkylated Pb,

Hg, Mn, Al, and Sn compounds), numerous other organic compounds are known to affect mammalian nervous systems. Most of the chemicals listed in Table 13.1 are indeed organic compounds, having carbon-to-carbon and carbon-to-hydrogen bonds.

### 13.4 NEUROTOXIC PARTICULATES

Both conventional air pollutants and air toxics may have neurotoxic effects. The pathways of the chemicals sorbed to particles will be those discussed in this chapter. However, the pathways are complicated by the characteristics of particles. An ongoing area of investigation is which aspect of PM contributes to toxicity, including neurotoxicity. Indeed, if the PM constituents include the inherently toxic substances mentioned throughout this chapter, e.g. Pb, Hg, benzene, PAHs, PCBs, and dioxins, in which case the particulates simply serve as a delivery vehicle. However, the morphology and size must also play a role beyond toxicant delivery, e.g. contributing to endogenous changes to endocrine and immune signaling, which induce neurological responses. Diesel particles for example may follow an olfactory pathway similar to that described for Cd.

The organochlorine, organophosphate, and other pesticides modes of action often involve AChE, which is an extremely important mechanism for neurotoxicity (Section 13.1.5 above).

### 13.5 RELATIONSHIP TO OTHER EFFECTS

This chapter has discussed specific neurotoxic effects. It should be noted that respiratory, reproductive, developmental, endocrine, and neurotoxic effects are seldom unique endpoints, but involve and interact with one another. It should also be noted that many of the human effects described in these chapters relate directly to other

mammals, as well as other vertebrates. They also apply to invertebrates to the extent that their endogenous systems resemble those of humans (e.g. neurological and hormonal impacts can follow similar pathways for lower organisms to those of humans). As such, they should be kept in mind when discussing ecosystem effects in the next chapter.

## QUESTIONS

1. How might an air pollutant exposure lead to myelinopathy?
2. How might an air pollutant exposure lead to axonopathy?
3. Many pesticides are designed to inhibit AChE. Explain at least one mechanism brought on by exposure to an air pollutant, which decreases the activity of this enzyme.
4. What is the relationship between carbon chain length and neurotoxicity, in general?
5. Two compounds have similar molecular weight, structure, vapor pressure and persistence. They are chemical similar in every way, except that the aqueous solubility of compound A is  $0.1 \text{ mg L}^{-1}$  and the aqueous solubility of compound B is  $0.1 \text{ ng L}^{-1}$ . Which is more likely to be neurotoxic?
6. Three neurotoxic chemicals are similar in every way, except that the aqueous solubilities are:  
 Compound X =  $0.1 \text{ mg L}^{-1}$   
 Compound Y =  $0.1 \mu\text{g L}^{-1}$   
 Compound Z =  $0.1 \text{ ng L}^{-1}$   
 Give the expected ranking of severity of neurotoxicity.
7. What can be said about the chemicals listed in Table 13.1?
8. Explain the relationship between blood lead levels and adverse effects on cognitive ability, especially for children.
9. Why is the oxidative state or valence of a metal compound important in neurotoxicity?
10. Why is the NIOSH Pb exposure recommendation 6 orders of magnitude higher than the NAAQS (3-month average) for ambient Pb in the U.S.?
11. What is Hg's neurotoxicity RfC? What does this mean?
12. Why are the dose-response curves for some metals "U"-shaped?
13. Explain the large difference between manganese's LOEAL for neurological effects and its RfC.
14. What are the similarities of the neural, endocrine and immune systems? How may they be considered as a single system?

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# Air Pollution's Impact on Ecosystems

## 14.1 ECOSYSTEM RISK

The term “system” is included in “ecosystem”. Thus, air pollution’s impact on ecosystems must be considered in an integrated manner. The ecological risk assessment framework (Figure 14.1) is based mainly on characterizing exposure to a chemical, physical, or biological agent within the system, and the ecological effects resulting from this exposure. Both exposure and effects are considered during the problem formulation step.<sup>1</sup> The final step of the risk assessment process is referred to as “characterization” to mean that “both quantitative and qualitative elements of risk analysis, and of the scientific uncertainties in it, should be fully captured by the risk manager”.<sup>2</sup> In particular, the process allows for an

integration of research with risk assessment, which could underpin risk management decisions. The problem formulation step in the ecological framework has the advantage of providing an analytic-deliberative process early on. That is, it combines sound science with input from various stakeholders inside and outside of the scientific community.

The ecological risk framework calls for the characterization of ecological effects instead of hazard identification used in human health risk assessments (see Chapter 7). This is because the term “hazard” has been used in chemical risk assessments to connote either intrinsic effects of a stressor or a margin of safety by comparing a health effect with an estimate of exposure concentration.

## 14.2 ECOSYSTEM SUSCEPTIBILITY TO AIR POLLUTION

The earth includes a wide belt of ecosystems, including rain forests, temperate and arboreal forests, grasslands, coral reefs, riverine and lacustrine systems, and wetlands,<sup>a</sup> of magnificent diversity and productivity (Table 14.1).

Ecosystems can be harmed by numerous human activities that introduce stressors to the environment. As is the case for human health risk assessments, the stressors may be chemicals, but physical and biological stressors also exist. For example, the placement of a roadway or the changes brought about by bulldozers and earthmovers are considered to be physical stressors to habitats, e.g. by bifurcation and changes to buffer zones. The accidental or intentional introduction of invasive biota, e.g. grass carp, *Ctenopharyngodon idella*, (fauna) and kudzu, *Pueraria lobata*, (flora), in the southern United States are examples of biological stressors. Indeed, physical and biological stressors may arise as a result of chemical air pollutants,

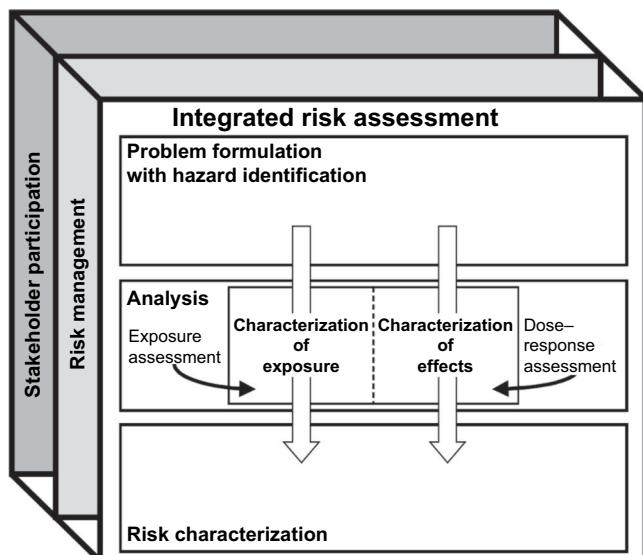
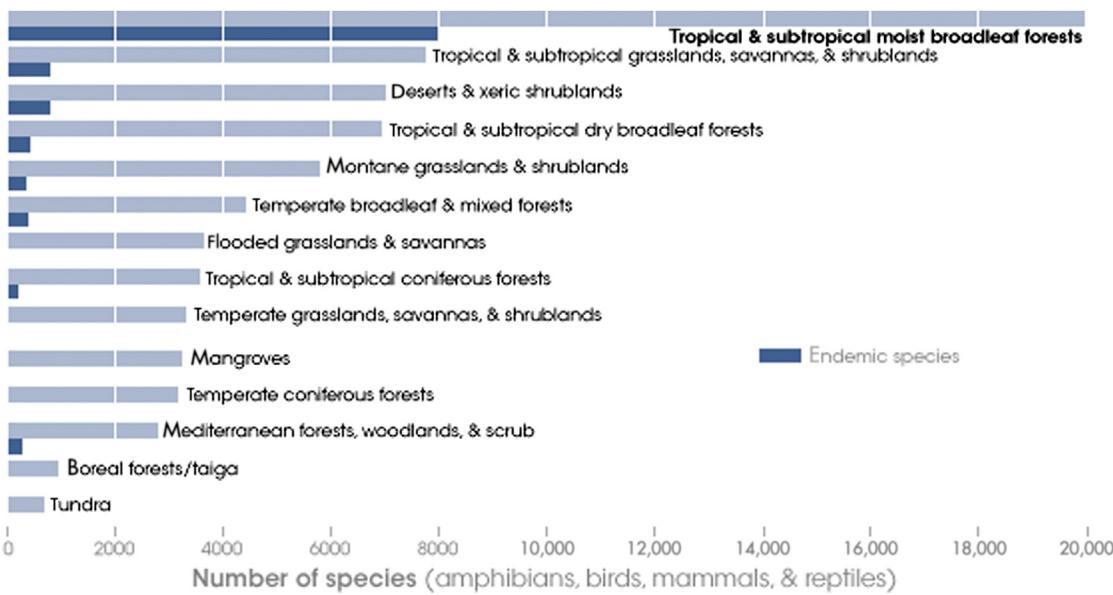


FIGURE 14.1 Framework for integrated human health and ecological risk assessment. World Health Organization and U.S. Environmental Protection Agency; 1998.

<sup>a</sup> Microbial ecologists would add those very small ecosystems that can be less than a few square centimeters.

TABLE 14.1 Species Abundance by Ecosystem Type



Tropical rain forests contain more species than any other ecosystem, as well as a higher proportion of species unique to a particular ecosystem (endemic).  
Source: Ref. 3; adapted from Simon R. Millennium ecosystem assessment. *Biodiversity Synthesis*; 2005.

such as shifting and shrinking habitats from climate change exacerbated by increasing concentrations of greenhouse gases or changes in ecosystem structure due to differential effects on certain species exposed to an air pollutant.

The identification of possible adverse outcomes is crucial. These outcomes alter essential structures or functions of an ecosystem. The severity of outcomes is characterized as to their type, intensity, and scale of the effect and the likelihood of an ecosystem to recover from the damage imposed by a single stressor or multiple stressors.

The characterization of adverse ecological outcomes can range from qualitative, expert judgments to statistical probabilities, to quantitative field measurements. The emergent fields of ecotoxicology and ecorisk have several things in common with human toxicology and risk assessment, such as concern about ambient concentration of contaminants and their uptake by biota in water, air, sediment, and soil. In some ways, however, ecological dose-response and exposure research differ from that in human systems. First, ecologists deal with many different species, some more sensitive than others to the effects of contaminants. Second, the means of calculating exposure are different, especially if one is concerned about the exposure of an entire ecosystem rather than the effects on one or a few biological species.

Ecosystems are complex. Ecologists characterize them by evaluating their composition, structure, and functions. Ecosystem composition is a listing, a taxonomy if you

will, of every living and nonliving part of the ecosystem. Ecological structure, as the term implies, is the manner in which all parts of the system are linked to form physical patterns of life forms from single forest stands to biological associations and plant communities. A single wetland or prairie, for example, is a much simpler structure than a multilayered forest, which consists of plant and microbial life in the detritus, herbs, saplings, newer trees, and canopy trees. Ecosystem functions include cycles of nitrogen, carbon, phosphorous, that lead to biotic processes such as production, consumption, and decomposition (see Part IV).

Indicators of an ecosystem's condition include the diversity of organisms living in the ecosystem. Another factor is the efficiency by which biota produce and store energy. Even for a healthy system, how sustainable is the condition given the stresses now and in the future?

Diversity is usually referred to as "biodiversity", which is the:

"... composition, structure, and function (that) determine, and in fact constitute, the biodiversity of an area. Composition has to do with the identity and variety of elements in a collection, and includes species lists and measures of species diversity and genetic diversity. Structure is the physical organization or pattern of a system, from habitat complexity as measured within communities to the pattern of patches and other elements at a landscape scale. Function involves ecological and evolutionary processes, including gene flow, disturbances, and nutrient cycling".<sup>4</sup>

The diversity of a community in an aquatic or wetland ecosystem can be found using the Shannon–Weiner index:

$$D = - \sum_{i=1}^m P_i \log_2 P_i \quad (14.1)$$

or

$$D = -1.44 \sum_{i=1}^m (n_i/N) \ln(n_i/N) \quad (14.2)$$

where,  $D$  = index of community diversity;  $P_i = n_i/N$ ;  $n_i$  = number (i.e. density) of the  $i$ th genera or species;  $N$  = total number (i.e. density) of all organisms in the sample;  $i = 1, 2, \dots, m$ ; and  $m$  = number of genera or species.

The larger the value of  $D$ , or community diversity, the greater is the stability of the ecosystem (see Example Box: Estimating Diversity of an Ecosystem).

Productivity is an expression of how economical a system is with its energy. How much biomass is produced from abiotic (e.g. nutrients and minerals) and biotic resources (from microbial populations to canopy plant species to top predator fauna)? One common measure is “net primary productivity”,<sup>b</sup> which is the difference between two energy rates:

$$P_1 = k_p - k_e \quad (14.3)$$

where  $P_1$  = net primary productivity;  $k_p$  = rate of chemical energy storage by primary producers; and  $k_e$  = rate at which the producers use energy (via respiration).

Sustainability describes the likelihood that the diversity and productivity will last. Even though an ecosystem appears to be diverse and highly productive, is there something looming that threatens the continuation of these conditions? For example, is an essential nutrient being leached out of the soil, or are atmospheric conditions changing that may threaten a key species of animal, plant, or microbe? Sustainability is difficult to quantify and even more difficult to predict precisely.

Ecological risk assessments may be prospective or retrospective, but often are both. The Florida Everglades provides an example of an integrated risk approach. The population of panthers, a top terrestrial carnivore in southern Florida, was found to contain elevated concentrations of mercury (Hg) in the 1990s. This was observed through retrospective eco-epidemiological studies. The findings were also used as scientists recommended possible measures to reduce Hg concentrations in sediment and water in Florida. Prospective risk assessments can help to estimate expected declines in Hg concentrations in panthers and other organisms in the food chain from a mass balance

perspective. That is, with decreasing Hg mass entering the environment through the air, water, and soil, how has the risk to sensitive species concomitantly been reduced? Integrated retrospective prospective risk assessments are employed where ecosystems have a history of previous impacts and have the potential for future effects from a wide range of stressors. This, for example, may be the case for ecosystems around and near hazardous waste sites.

### **14.3 AIR POLLUTION IMPACTS ON AQUATIC ECOSYSTEMS**

Various air pollutants induce a range of effects on aquatic ecosystems. Sulfur and nitrogen compounds can lead to acidification of surface waters via numerous mechanisms, such as hydrolysis, which cause gas-phase and particulate-phase pollutants to react in the atmosphere followed by deposition onto water surfaces and/or actual particulate phase pollutants that precipitate into water and thereafter react. Airborne nitrogen and phosphorus species can also enrich surface waters, which changes pH, dissolved oxygen, and other characteristics, which in turn change the species abundance and diversity. Although tropospheric ozone has very little effect in the water chemistry directly, it may change the biodiversity by stressing riparian and partially submerged plants or harming air-breathing animals.

Stress on aquatic ecosystems occurs at all spatial scales. Large and vulnerable systems can indicate the impact of pollutant loading on ecosystem condition. This is particularly true for coral reef systems.

#### **14.3.1 Coral Reefs**

Coral reefs are incredibly diverse and productive (Table 14.2). These so-called “rain forests of the ocean” cover a mere fraction of the ocean floor but are home to millions of organisms from thousands of species. They are threatened by natural and human events, e.g. warm ocean temperatures and high sea levels overfishing and development, but also by air pollution. For example, the corals off the coast of Florida, the world’s third largest barrier reef, have been highly stressed, with half of the live coral off the Florida coast lost in recent years. An additional indication is that fish feeding on these corals are developing deformities and experience premature mortality.<sup>6</sup> The addition of nitrogen species from the atmosphere contributes to these problems, since they serve as nutrients for aquatic microbes, respiration by which changes the oxygen content and

<sup>b</sup> Also known as “net primary production”. Either is abbreviated as NPP.

### EXAMPLE BOX: ESTIMATING DIVERSITY OF AN ECOSYSTEM<sup>5</sup>

An environmental assessment of microbes in a small stream near an industrial plant found a total of 1510 organisms, represented by seven different species. The actual number count of each microbial species in stream community was 10, 50, 75, 125, 200, 350, and  $750 \text{ ml}^{-1}$ .

#### Solution and Discussion:

Construct a table to derive the values needed to find  $D$ , using Eqn (14.1):

$$D = -1.44 \sum_{i=1}^m (n_i/N) \ln(n_i/N).$$

$i$	$n_i$	$n_i/N$	$-1.44 \ln(n_i/N)$	$-1.44(n_i/N) \ln(n_i/N)$
1	10	0.006623	7.224883	0.047847
2	50	0.033113	4.907292	0.162493
3	75	0.049669	4.323423	0.21474
4	125	0.082781	3.587834	0.297006
5	200	0.13245	2.911028	0.385567
6	350	0.231788	2.105182	0.487956
7	700	0.463576	1.10705	0.513202
$\Sigma$	1510	1		2.10881

Thus, the diversity index is approximately 2.1. The index is most useful when comparing systems. So, if the stream is 2.1 and surrounding streams are all around 4, there may be a problem. For example, further investigation is needed if these are biological indicators of the health of the stream and the facility is emitting pollutants that are known to stress ecosystems. Generally,  $D$  values range from about 1.5 to 4.5.

New pollution control equipment is installed and measurements are taken a year later with the following results, from which another index is calculated.

Construct a new table with four times each species:

$i$	$n_i$	$n_i/N$	$-1.44 \ln(n_i/N)$	$-1.44(n_i/N) \ln(n_i/N)$
1	40	0.006623	7.224883	0.047847
2	200	0.033113	4.907292	0.162493
3	300	0.049669	4.323423	0.21474
4	500	0.082781	3.587834	0.297006
5	800	0.13245	2.911028	0.385567
6	1400	0.231788	2.105182	0.487956
7	2800	0.463576	1.10705	0.513202
$\Sigma$	6040	1		2.10881

Even though the species abundance quadrupled, the index remains 2.1. The index indicates, correctly, that the total species abundance does not affect diversity.

Some new sources are located near the ecosystem, so a follow-up study is conducted 5 years later, which indicates the species density has changed to 3000, 50, 35, 40, 30, 70, and  $15 \text{ l}^{-1}$  of the same species of microbes as the early study. How had the numbers and diversity changed in 5 years?

Again, calculate  $D$  by constructing a new table:

$i$	$n_i$	$n_i/N$	$-1.44 \ln(n_i/N)$	$-1.44(n_i/N) \ln(n_i/N)$
1	3000	0.92593	0.11082	0.10261
2	50	0.01543	6.00668	0.0927
3	35	0.0108	6.52029	0.07044
4	40	0.01235	6.32801	0.07812
5	30	0.00926	6.74227	0.06243
6	70	0.0216	5.52216	0.11931
7	15	0.00463	7.7404	0.03584
$\Sigma$	3240	1		0.56144

After 5 years, the actual number of microbes is more than doubling, but the diversity has been drastically reduced ( $D = 0.6$  vs 2.1). This may indicate that conditions favorable to one species, e.g. the presence of a toxic chemical or a change in habitat (e.g. a road), are detrimental to the other six species.

A follow-up question must be asked. Were the measurements conducted in the same season (some microbes grow better in warmer conditions, while others may compete more effectively in cooler waters)? If the studies are comparable, further investigation is needed, but this certainly is an indication that things are amiss, since Shannon values usually range from about 1.5 to 4.5. Diversity, like productivity, is often an important indicator of change. If diversity as measured by the index shows a decline, it may well indicate than an ecosystem is under increasing stress.

**TABLE 14.2** Net Primary Productivity of Ecosystems (grams dry organic matter per square meter per year)

Ecosystem Type	Net Primary Productivity (g m <sup>-2</sup> year <sup>-1</sup> )
Open ocean water	100
Coastal seawater	200
Desert	200
Tundra	400
Upwelling area	600
Rice paddy	340–1200
Freshwater pond	950–1500
Temperate deciduous forest	1200–1600
Cropland (cornfield)	1000–6000
Temperate grassland	≤1500
Cattail swamp	2500
Tropical rain forest	≤2800
Coral reef	4900
Sugarcane field	≤9400

Source: Maier RM, Pepper IL, Gerba CP. Environmental microbiology. 2nd ed. Burlington (Massachusetts): Elsevier Academic Press; 2009.

pH of waters. These and other physicochemical changes contribute to coral reef destruction.

Disastrous coral reef losses are occurring from physical, chemical, and biological sources. The U.S. Coral Reef Task Force recently identified what it considers to be the most prominent threats that federal agencies and states must address to protect coral reefs in the United States<sup>7</sup>:

1. Pollution, including eutrophication and sedimentation from poor or overly intensive land use, chemical loading, oil and chemical spills, marine debris and invasive alien species.
2. Overfishing and exploitation of coral reef species for recreational and commercial purposes, and the collateral damage and degradation to habitats and ecosystems from fishing activities.
3. Habitat destruction and harmful fishing practices, including those fishing techniques that have negative impacts on coral reefs and associated habitats. This can include legal techniques such as traps and trawls used inappropriately, as well as illegal activities such as cyanide and dynamite fishing.
4. Dredging and shoreline modification in connection with coastal navigation or development.
5. Vessel groundings and anchoring that directly destroy corals and reef framework.

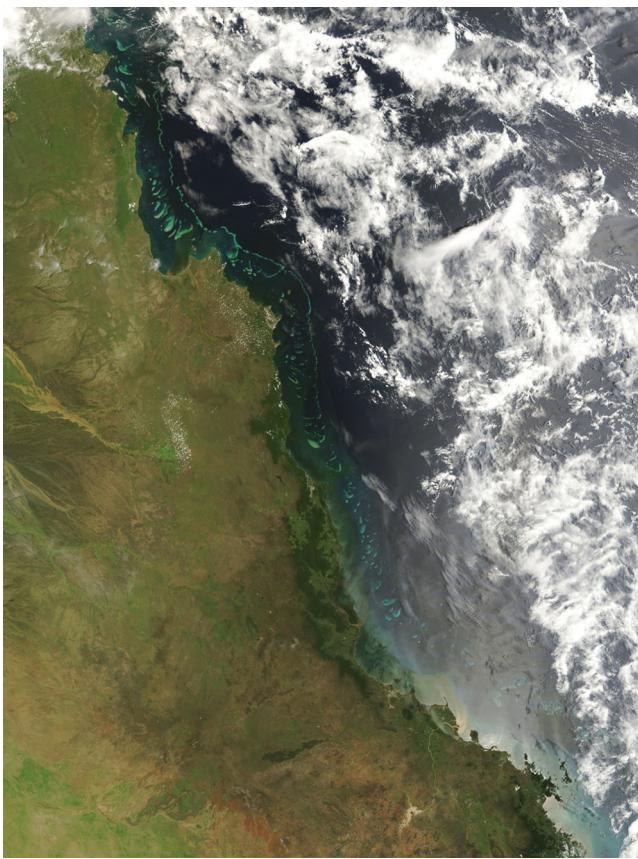
6. Disease outbreaks that are increasing in frequency and geographic range are affecting a greater diversity of coral reef species.
7. Global climate change and associated impacts including reduced rates of coral calcification, increased coral bleaching and mortality (associated with variety of stresses including increased sea surface temperatures), increased storm frequency, and sea level rise.

Air pollutant transport and impacts on coral reefs include biological agents. Microbes appear to be transported long distances in winds aloft. For example, some of the invasive bacteria that threaten coral reef habitats may be coming from Africa in the form of Saharan dust. Deserts commonly contain gravel and bedrock, along with some sand. The Sahara is the exception, with sand covering 20% of the spatial extent of the desert. This means that the Sahara often loses large amounts of dust by winds that advectively transport particles in plumes that can travel across the Atlantic Ocean, depositing dust along the way (Figure 14.2). Saharan dust carries disease-causing bacteria and fungi that have been associated with the destruction of coral reefs in the Caribbean Sea.

Scientists are investigating these phenomena to evaluate any linkages to the threats and possible interventions. For example, invasive species can include numerous organisms, but recently algae and bacteria have been highlighted as a much larger concern than had previously been thought. Some of these bacteria are likely arriving in the coral reef ecosystems by long-range, atmospheric transport.

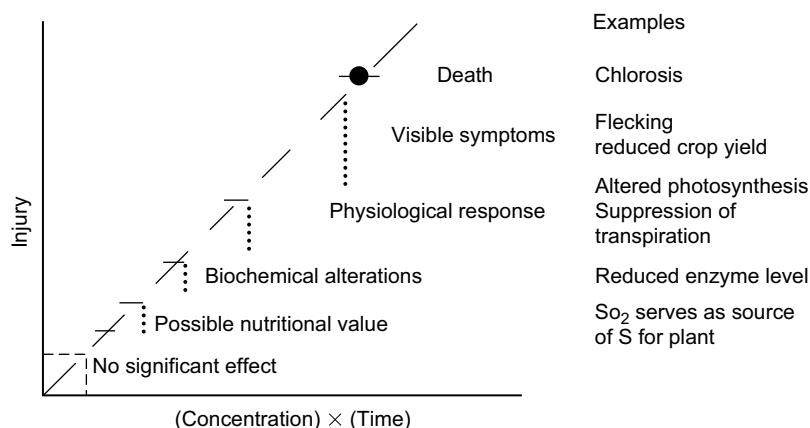
Physical threats include ultraviolet (UV) radiation, which have increased in the 20th century with the depletion of stratospheric ozone, i.e. an indirect effect of air pollution (Chapter 11). UV radiation can also increase locally when protective screens of organisms die off. UV radiation, therefore, is a ubiquitous stressor that is very likely impacting on human and ecological systems on a global scale. It has been implicated in observed shifts in polar plankton community composition, local and global declines in amphibian population abundance and diversity, coral bleaching syndrome, not to mention an increasing incidence of human skin cancer and other diseases. Disruption and loss of coral reef ecosystem communities due to coral bleaching/disease lead to coral mortality, changes in reef persistence, and formation dynamics, as well as cascading reef community interactions.<sup>8</sup>

Chemical contamination threatens both the integrity of coral reefs and the organisms need them for habitats. For example, several endocrine disrupting compounds discussed in Chapter 12 have found their way to the ocean. These compounds impair the reproduction and development of marine organisms by the same or similar



**FIGURE 14.2** February 9, 2007, deposition of sediment flowing into Princess Charlotte Bay on the east coast of Queensland's Cape York Peninsula in Australia. The plumes merge into a 12-km-wide river of sediment-laden water, moving northwardly and washing over the coral reef. The sediment makes the normally turquoise-colored reef look greenish-brown. The sediment integrates contaminants from various upstream sources, including atmospheric deposition onto watersheds. The plume veers northeastwardly from the inner reef and eventually reaches the outer reef. (For color version of this figure, the reader is referred to the online version of this book.) National Aeronautics and Space Administration. MODIS Rapid Response Team, Goddard Space Flight Center; 2007.

**FIGURE 14.3** Biological response spectrum for plants and air pollution. Note the similarities to the dose-response curves discussed in Chapter 7.



modes of actions as those for endocrine disruption in humans. Thus, living aquatic organisms in coral reef habitats could well be negatively impacted by interfering with the reproduction mechanisms in aquatic organisms. It is certainly likely that myriad organic and metallic compounds are transported and deposited into the ocean as air pollutants. The more volatile compounds are transported in the gas phase, and the semivolatile and nonvolatile organic compounds and metals sorbed to aerosols can be transported great distances in the atmosphere.

Contaminants may even reach reefs by leapfrogging from one medium to another, e.g. soil to air to water to air to biota, etc. For example, streams deposit their loads into reef systems (Figure 14.2). The streams themselves may receive loadings from nonpoint sources on land that had previously experienced atmospheric deposition. These loads contain contaminants from upstream sources, both natural (e.g. nutrients) and human activities (e.g. metallic and organic compounds from industrial and municipal facilities).

## 14.4 AIR POLLUTION IMPACTS ON TERRESTRIAL ECOSYSTEMS

As in aquatic ecosystems, those on land vary in vulnerability to air pollution. The effects on mammalian fauna are similar to those of humans. However, a terrestrial ecosystem consists of many more species. Various species of flora, fauna, and microbes respond differently to air pollutant exposure. In addition, ecosystems include abiotic components, e.g. soil, changes to which must also be considered as to their response to air pollution.

### 14.4.1 Effects on Flora

The effects of air pollution on plants range from subtle to catastrophic, as shown in Figure 14.3. Historically, these effects have been classified as visible symptoms

and nonvisual or subtle effects.<sup>9</sup> Visible symptoms are deviations from the normal healthy appearance of the leaves. For broadleaf plants, a healthy leaf has good color, with a normal cell structure in the various layers. Deviations from this healthy appearance include tissue collapse and various degrees of loss of color. Extensive tissue collapse or necrosis results from injury to the spongy or palisade cells in the interior of the leaf. The leaf becomes severely discolored and loses structural integrity. Dead tissue may fall out of the leaf, leaving holes in the structure. Less dramatic discolorations are caused by a decrease in the number of chloroplasts, a symptom referred to as chlorosis. Injury to the outer or epidermal layer is referred to as glazing or silvering of the leaf surface. When the pattern is spotty, the terms flecking and stippling are used to describe the injury.

Other forms of visible injury are related to various physiological alterations. Air pollution injury can cause early senescence or leaf drop. Stems and leaf structure may be elongated or misshapen. Ornamentals and fruit trees can also show visible injury to the blooms of the fruit, which can result in decreased yield.

The nonvisual or subtle effects of air pollutants involve reduced plant growth and alteration of physiological and biochemical processes, as well as changes in the reproductive cycle. Reduction in crop yield can occur without the presence of visible symptoms. This type of injury is often related to low-level, long-term chronic exposure to air pollution. Studies have shown that field plantings exposed to filtered and unfiltered ambient air have produced different yields when no visible symptoms were present.<sup>10</sup> Decreases in total biomass can lead to economic loss for forage crops or hay.

Physiological or biochemical changes have been observed in plants exposed to air pollutants, including alterations in net rates of photosynthesis, *stomata* response, and metabolic activity. Such exposure studies have been conducted under controlled laboratory conditions. An understanding of the processes involved will help to identify the cause of reduction in yield. Laboratory studies have also investigated the interaction of air pollutants and the reproductive cycle of certain plants. Subtle changes in reproduction in a few susceptible species can render them unable to survive and prosper in a given ecosystem.

The major air pollutants which are phytotoxic to plants are ozone, sulfur dioxide, nitrogen dioxide, fluorides, and peroxyacetyl nitrate (PAN).<sup>11</sup> Table 14.3 lists some of the types of plants injury resulting from exposure to these pollutants. The effects range from slight reduction in yield to extensive visible injury, depending on the level and duration of exposure. Examples of the distinction between air pollution injury and damage are also given in Table 14.3. Visible markings on plants

or crops such as lettuce, tobacco, and orchids caused by air pollution translate into direct economic loss (i.e. damage). In contrast, visible markings on the leaves of grapes, potatoes, or corn caused by air pollution will not result in a determination of damage if there is no loss in yield. Individual circumstances determine whether air pollution damage has occurred.

The costs of air pollution damage are difficult to estimate. However, estimates indicate crop losses are estimated to be billions of dollars in the United States alone.<sup>12</sup> When compared to the crop losses due to all causes, the air pollution loss percentages are small. Ozone ( $O_3$ ) is particularly damaging to flora, i.e. it is phytotoxic. It is well known that if  $O_3$  or its reaction products reach the target tissues in the plant cell, the cell will die. Recent studies have provided an increased understanding of how  $O_3$  interacts with the plant at the cellular level. Coupled with cost estimates, these types of studies give some indication of the crop loss and the costs associated with air pollutants. For example, although air quality has improved in most urban areas, it has not done so in numerous rural areas where most crops are grown.

Ground-level  $O_3$  exposures can impose huge financial and food supply costs. Sensitivity to ozone varies across species, with over 65 plant species. Many crop species exposed to  $O_3$  even at concentrations slightly lower than the U.S. standard experience decreased growth, lower biomass production, and thus, lower yields. Other effects include foliar injury, reduced plant vigor, increased susceptibility to environmental conditions (e.g. harsh weather, drought, and winds), diminished insect pest infestation, and reduced ability to compete with weed species.

#### 14.4.1.1 Forests

Forests are particularly vulnerable to air pollution. The risks are either direct or indirect. Direct damage to forests comes from damage to foliage and root systems as a result of chemical changes induced by air pollutants, e.g. acidic deposition onto trees and the soils from which the roots extract nutrients. This stresses the plant and damages its metabolic processes. Indirect damage can come about by changes in humidity and temperature regimes, brought on by emissions of greenhouse gases that lead to climate change. Actually, direct and indirect ecosystem risks often combine to exacerbate risks, such as when organisms that are already stressed from direct pollutant exposure (e.g. sulfur dioxide,  $SO_2$ ) are further stressed by changes in humidity and temperature.

Forests, particularly rain forests, are the oxygen factories of the earth. Tropical forests have particularly extensive species abundance. Other rain forests include seasonally moist forests, where rainfall is abundant for

TABLE 14.3 Examples of Types of Leaf Injury and Air Pollution

Pollutant	Symptoms	Maturity of Leaf Affected	Part of Leaf Affected	Injury Threshold			Sustained Exposure
				ppm (vol.)	$\mu\text{g m}^{-3}$		
Sulfur dioxide	Bleached spots, bleached areas between veins, chlorosis; insect injury, winter and drought conditions may cause similar markings	Middle-aged most sensitive; leaves oldest least sensitive	Mesophyll cells	0.3	785	8 h	
Ozone	Flecking, stippling, bleached spotting, pigmentation; conifer needle tips become brown and necrotic	Oldest leaves most sensitive; youngest least sensitive	Palisade or spongy parenchyma in leaves with no palisade	0.03	59	4 h	
Peroxyacetyl nitrate (PAN)	Glazing, silvering, or bronzing on lower surface of leaves	Youngest leaves most sensitive	Spongy cells	0.01	50	6 h	
Nitrogen dioxide	Irregular, white or brown collapsed lesions on intercostal tissue and near leaf margin	Middle-aged leaves most sensitive	Mesophyll cells	2.5	4700	4 h	
Hydrogen fluoride	Tip and margin burns, dwarfing, leaf abscission; narrow brown-red band separates necrotic from green tissue; fungal disease, cold and high temperatures, drought, and wind may produce similar markings; suture red spot on peach fruit	Youngest leaves most sensitive	Epidermis and mesophyll cells	0.1 (ppb)	0.08	5 weeks	
Ethylene	Sepal withering, leaf abnormalities; flower dropping, and failure of leaf to open properly; abscission; water stress may produce similar markings	Young leaves recover; older leaves do not recover fully	All	0.05	58	6 h	
Chlorine	Bleaching between veins, tip and margin burn, leaf abscission; marking often similar to that of ozone	Mature leaves most sensitive	Epidermis and mesophyll cells	0.10	290	2 h	
Ammonia	"Cooked" green appearance becoming brown or green on drying; overall blackening on some species	Mature leaves most sensitive	Complete tissue	~20	~14,000	4 h	
Hydrogen chloride	Acid-type necrotic lesion; tip burn on fir needles; leaf margin necrosis on broad leaves	Oldest leaves most sensitive	Epidermis and mesophyll cells	~5–10	~11,200	2 h	
Mercury	Chlorosis and abscission; brown spotting; yellowing of veins	Oldest leaves most sensitive	Epidermis and mesophyll cells	<1	<8200	1–2 days	
Hydrogen sulfide	Basal and marginal scorching	Youngest leaves most affected		20	28,000	5 h	
2,4-Dichlorophenoxyacetic acid (2-4D)	Scalloped margins, swollen stems, yellow-green mottling or stippling, suture red spot (2,4,5-T); epinasty	Youngest leaves most affected	Epidermis	<1	<9050	2 h	
Sulfuric acid	Necrotic spots on upper surface similar to those caused by caustic or acidic compounds; high humidity needed	All	All	—	—	—	

part of the year. These are more open woodlands, yet they two are highly productive. Tropical rain forests are the most threatened of all the forests due to human activities, e.g. clearing trees for agricultural products, harvesting whole trees for timber and urbanization, and roads that traverse habitats. These not only supplant habitats, but they truncate migration, foraging, predation, and breeding, i.e. the problem is greater than the areal extent of habitats displaced. The changes interrupt ecosystem dynamics and species activities, such as predator-prey relationships (Figure 14.4).

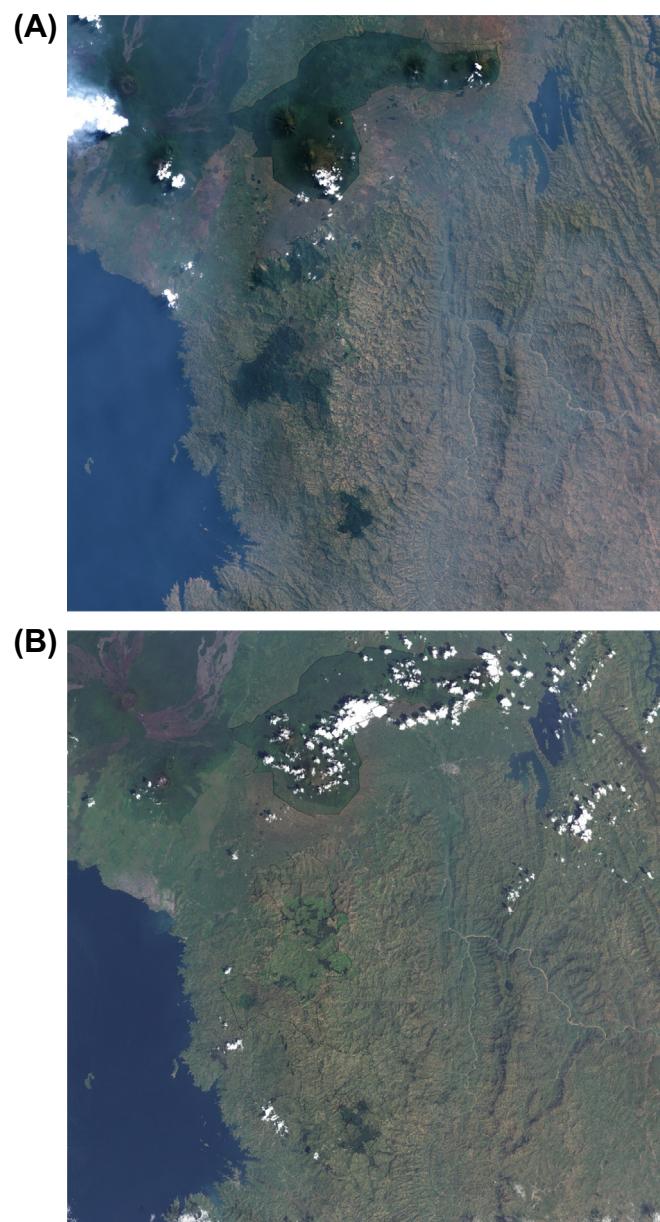
Ambient concentrations of air pollutants are not usually thought of as major contributors to rain forest destruction compared to physical destruction. However, acid rain, biome shifts due to global climate change and stratospheric ozone depletion can substantially stress trees and other vegetation.

Rain forests lose species to extinction at an alarming rate. Scientists estimate that about half of the world's species exist in rain forests, even though they cover but 7% of the earth's land surface. Rain forest species are particularly vulnerable because they adapted to microhabitats that only exist in the unique conditions under ambient moisture and temperature regimes. Other species are lost to habitat destruction and deforestation. Ecosystems' edges are particularly important to species survival. When they change due to climatic and anthropogenic stresses, canopy species (larger trees) can no longer survive. This leads to more destruction further within the ecosystem, with rapid decreases in species abundance and biodiversity.<sup>3</sup>

Rain forest destruction is indeed a societal problem. Local cultures have depended on the bounty for centuries. In fact, many of the primitive practices have been highly destructive, notably slash and burn. Farmers have completely deforested areas and other vegetation to make arable land. However, the remaining layer of ash is an indication that many of the soil nutrients have chemically altered and leached from the soil. This exacerbates erosion rates. In a short time, the crops are no longer productive. This is often worsened when the cropped field is converted to pasture, with resulting soil compaction and overgrazing.

In addition to the localized effects, deforestation increases the emissions of carbon dioxide ( $\text{CO}_2$ ) and other greenhouse gases to the atmosphere. Soil and plants in tropical forests sequester  $4.6 \times 10^9 - 5.8 \times 10^9$  metric tonnes of carbon worldwide with each square kilometer of tropical forest holding 45,000 tonnes of carbon. From 1850 to 1990, deforestation released 122 billion tonnes of carbon into the atmosphere. Currently, the deforestation carbon emission rate is 1.6 billion tonnes per year.<sup>13</sup>

A secondary air pollution impact of such deforestation is the increased emissions of fugitive dust. This is



**FIGURE 14.4** Decrease in extent and abundance of rain forests in Rwanda, Africa, from 1986 (photo (A)) and 2001 (photo (B)). The Gishwati Forest, Rwanda, has been threatened by environmental and societal influences. The genocide and refugee influxes increased the need for subsistence farming. About 99% of the rain forest vegetation was lost during this 15-year period. (For color version of this figure, the reader is referred to the online version of this book.) National Aeronautics and Space Administration. Earth Observatory. <http://earthobservatory.nasa.gov/IOTD/view.php?id=38644>; 2012 [accessed 10.03.12].

another example of the complexity of ecosystem-human interactions that adversely affect health. In addition, since the damage to humans from particulate matter is well documented, similar problems are likely to occur in other air-breathing animals. Thus, wildlife populations would be expected to be weakened, which

may show up in reduced species abundance, decreased diversity and changes to predator–prey relationships (e.g. loss of food species for top predators and reduced populations of animal species).

Rain forests, in particular, are being destroyed by varied and complex factors, so stopping the destruction is equally complicated. Without aggressive interventions, the disaster will only worsen.

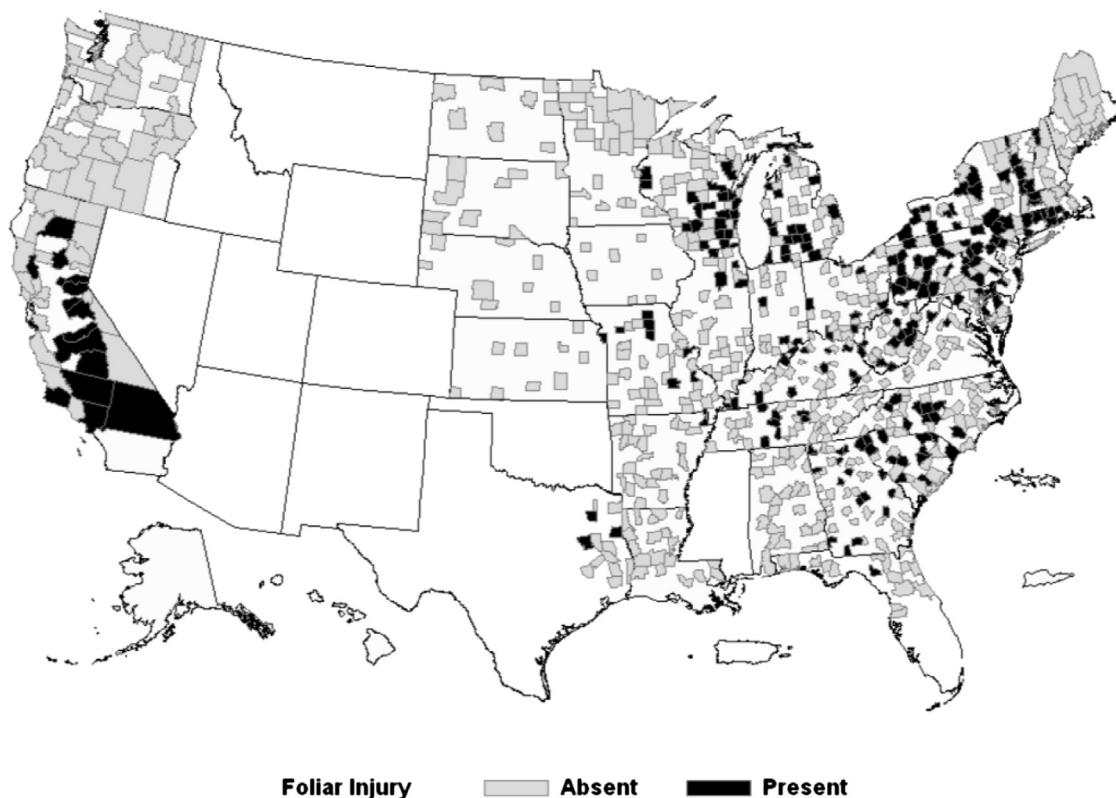
The damage can be acute or chronic, i.e. changes in a single season or changes in the entire ecosystem. Plant injury from O<sub>3</sub> exposure is widespread. In the United States, trees in forests, at least those that are sources of timber, are considered to be “crops”. The U.S. Forest Service is part of the U.S. Department of Agriculture. Forests across the country have experienced O<sub>3</sub> injury (Figure 14.5).

Approximately  $1.95 \times 10^{10}$  km<sup>2</sup> of the earth's surface has at least 20% or more crown tree cover, representing about one-third of the total land area.<sup>14</sup> The crown cover is the canopy cover plus the amount of skylight obstructed by tree canopies. Several different types of forest ecosystems can be defined based on their location and the species present. The largest in area are tropical forest systems, followed by temperate forests, rain

forests, and tidal zone systems. The temperate forest systems are located in the latitudes where the greatest industrialization is occurring and have the most opportunity to interact with pollutants in the atmosphere. The impact of air pollution on forest ecosystems ranges from beneficial to detrimental. The relationship of air pollutants with forests can be classified into three categories<sup>15</sup>: low dose (I), intermediate dose (II), and high dose (III). With this classification scheme, seemingly contradictory statements on the impact of air pollution on forests can be understood.

#### 14.4.1.1.1 LOW-DOSE LEVELS

Under low-dose conditions, forest ecosystems act as sinks for atmospheric pollutants and in some instances as sources. The atmosphere, lithosphere, and oceans are involved in large-scale cycling carbon, nitrogen, oxygen, sulfur, and other elements through each subsystem with different timescales. Under low-dose conditions, forest and other biomass systems have been utilizing chemical compounds present in the atmosphere and releasing others to the atmosphere for thousands of years. Industrialization has increased the concentrations of NO<sub>2</sub>, SO<sub>2</sub>, and CO<sub>2</sub> in the “clean



**FIGURE 14.5** County-level data regarding the presence or absence of ozone-related visible foliar injury to forests in the United States. U.S. Environmental Protection Agency. Review of the National Ambient Air Quality Standards for Ozone: Policy assessment of scientific and technical information. Staff Paper. Office of Air Quality Planning and Standards. Report No. EPA-452/R-07-007a. [http://www.epa.gov/ttn/naaqs/standards/ozone/data/2007\\_07\\_ozone\\_staff\\_paper.pdf](http://www.epa.gov/ttn/naaqs/standards/ozone/data/2007_07_ozone_staff_paper.pdf); 2007 [accessed 28.10.13].

background" atmosphere, and certain types of interactions with forest systems can be defined.

Forests can act as sources of some of the trace gases in the atmosphere, such as hydrocarbons, hydrogen sulfide,  $\text{NO}_x$ , and  $\text{NH}_3$ . Forests have been identified as emitters of terpene hydrocarbons, which are a component of the photochemistry that leads to the formation of ozone.<sup>c</sup> In 1960, emissions of terpenes from forest systems are approximately  $2 \times 10^8$  tonnes of reactive materials per year on a global basis.<sup>16</sup> This is several times the anthropogenic input. Yet, it is important to remember that forest emissions are much more widely dispersed and less concentrated than anthropogenic emissions. Table 14.4 shows terpene emissions from different types of forest systems in the United States.

Forest systems also act as sources of  $\text{CO}_2$  when controlled or uncontrolled burning and oxidation of organic compounds in detritus and litter occur. In addition, release of ethylene occurs during the flowering of various species. Thus, although trees are an important part of strategies to control global warming by storing (sequestering) carbon, especially in large root systems, they are also sources of  $\text{CO}_2$ . One additional form of emission to the atmosphere is the release of pollen grains. Pollen is essential to the reproductive cycle of most forest systems but becomes a human health hazard for individuals susceptible to hay fever. The contribution of sulfur from forests in the form of dimethyl sulfide is considered to be about 10–25% of the total amount released by soils and vegetation.<sup>17</sup>

Trees and soils of forests act as sources of  $\text{NH}_3$  and oxides of nitrogen. Ammonia is formed in the soil by several types of bacteria and fungi. The volatilization of ammonia and its subsequent release to the atmosphere is dependent on temperature and the pH of the soil. Commercial fertilizers are used as a tool in forest management. The volatilization of applied fertilizers may become a source of ammonia to the atmosphere, especially from the use of urea.

Nitrogen oxides are formed at various stages of the biological denitrification process. This process starts with nitrate; as the nitrate is reduced through various steps,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ , and  $\text{N}_2$  can be formed and, depending on the conditions, released to the atmosphere.

The interactions of air pollutants with forests at low-dose concentrations result in imperceptible effects on the natural biological cycles of these species. In some

instances, these interactions may be beneficial to the forest ecosystem. Forests, as well as other natural systems, act as sinks for the removal of trace gases from the atmosphere.

#### 14.4.1.1.2 INTERMEDIATE-DOSE LEVELS

The second level of interaction, the intermediate-dose level, can result in measurable effects on forest ecosystems. These effects consist of a reduction in forest growth, change in forest species, and susceptibility to forest pests. Both laboratory investigations and field studies show  $\text{SO}_2$  to be an inhibitor of forest growth. When various saplings have been exposed to  $\text{SO}_2$  in the laboratory, they show reduction in growth compared with unexposed saplings.<sup>18</sup> Various field investigations of forest systems in the vicinity of large point sources show the effects of elevated  $\text{SO}_2$  levels on the trees closer to the source. For example,  $\text{SO}_2$  from the Sudbury, Ontario (Canada) smelter caused a reduction in forest growth over a very large area, with the proximate trees severely defoliated, damaged, and killed.<sup>19</sup>

The effect of photochemical oxidants, mainly  $\text{O}_3$  and PAN, on the forests located in the San Bernardino Mountains northeast of Los Angeles, California, has been to change the forest composition and to alter the susceptibility of forest species to pests. This area has been subjected to increasing levels of oxidant since the 1950s (Figure 14.6). During the late 1960s and early 1970s, changes in the composition and esthetic quality of the forest were observed.<sup>20</sup>

During this period, the photochemical problem was expanding to a wider geographical region; and photochemical oxidant was transported to the San Bernardino Mountains with increasing frequency and at higher concentrations. The receptor forest system has been described as a mixed conifer system containing ponderosa pine, Jeffrey pine, white fir, and cedar, along with deciduous black oak. The damage to the ponderosa pine ranged from no visible injury to death. As the trees came under increased stress due to exposure to oxidant, they became more susceptible to pine beetle, which ultimately caused their death. The ponderosa pine appears to be more susceptible than the other members of this forest system, and continued exposure to photochemical oxidant may very well shift it from the dominant species to a minor one.

<sup>c</sup>This harkens back to the 1980s when President Reagan postulated that trees accounted for much pollution, which spawned the phrase, "killer trees". This led to some hilarious running gags and skits on the show, Saturday Night Live, where such a tree (played by the late John Belushi) would attempt entry into homes with obvious malicious intent. What made the skits so funny was, like most humor, they were based on some element of truth. For example, coniferous trees do emit large amounts of organic compounds to the troposphere, some of which are ozone precursors.

TABLE 14.4 Composition of U.S. Forest Service-type Groups by Foliar Terpene Emissions

	Percent of Total U.S. Forest Area	Percent of $\alpha$ Pinene Emitters	Percent of Isoprene Emitters
<b>Eastern type groups</b>			
<i>Softwood types</i>			
Loblolly-shortleaf pine	11	~100	Some from oak and sweet gum associates
Longleaf-slash pine	5	~100	Some from oak and sweet gum associates
Spruce-fir	4	~75	25% from spruce, which also emits $\alpha$ pinene
White-red-jack pine	2	~90	10% from aspen trees
<b>Subtotal</b>	<b>22%</b>	<b>~91%</b>	<b>~9%</b>
<i>Hardwood types</i>			
Oak-hickory	23	~10	70%, diluted by hickory, maple and black walnut
Oak-gum cypress	7	~50	50% from plurality of oak, cottonwood and willow
Oak-pine	5	~30	60%, diluted by black gum and hickory associates
Maple-beech-birch	6	~15	Terpene foliates are hemlock and white pine
Aspen-birch	5	~20	60%, diluted by birch, $\alpha$ pinene source balsam fir and balsam poplar
Elm-ash-cottonwood	4	—	30% from cottonwood, sycamore, and willow
<b>Subtotal</b>	<b>50%</b>	<b>~21%</b>	<b>~45%</b>
<b>Total</b>	<b>72%</b>	<b>—</b>	<b>—</b>
<b>Western type groups</b>			
<i>Softwoods types</i>			
Douglas fir	7	~100	—
Ponderosa pine	7	~100	5% from aspen associates
Lodgepole pine	3	~90	10% from Engelmann spruce and aspen
Fir-spruce	3	~100	40% from spruce trees
Hemlock-Sitka spruce	2	~100	25% from Sitka spruce
White pine	1	~100	5% from Engelmann spruce
Larch	1	~100	—
Redwood	0.5	~100	—
<b>Subtotal</b>	<b>24.5%</b>	<b>~98%</b>	<b>~12%</b>
<i>Hardwoods types</i>			
<b>Total</b>	<b>26.5%</b>		

Source: Ref. 16.

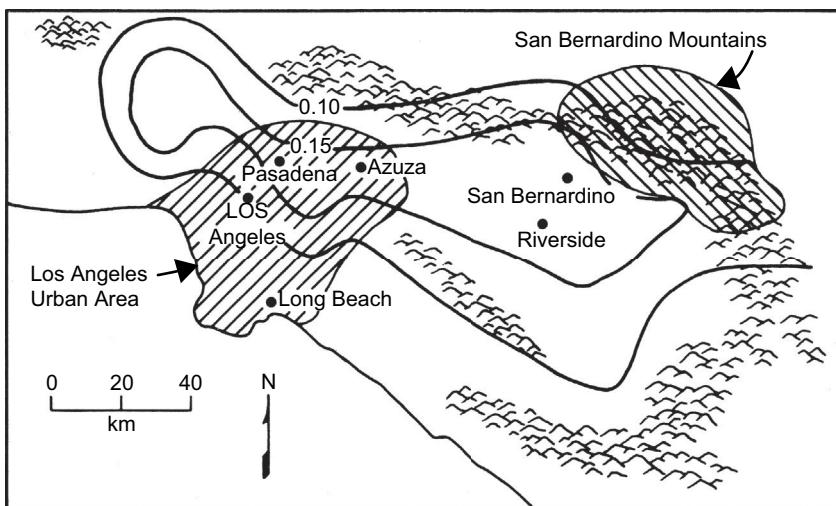
The interactions in the intermediate-dose category may result in effects on the reproduction cycle of species, the utilization of nutrients, the production of biomass, and the susceptibility to disease.

#### 14.4.1.3 HIGH-DOSE LEVELS

The third category for interactions is high dose (III). The effects produced by this level of interaction can be seen by the casual observer. The result of high-dose

exposure is destruction or severe injury of the forest system. High-dose conditions are almost always associated with point source emissions. The pollutants most often involved are  $\text{SO}_2$  and hydrogen fluoride. Historically, the most harmful sources of pollution for surrounding forest ecosystems have been smelters and aluminum reduction plants.

One example of high-dose interaction is the impact of a smelter on the surrounding area in Wawa, Ontario,



**FIGURE 14.6** Relationship between Los Angeles Basin's urban sources of photochemical smog and the San Bernardino Mountains, where ozone damage has occurred to the ponderosa pines. The solid lines are the average daily 1-h maximum does of ozone (ppm), July–September 1975–1977. Adapted from Davidson A. Ozone trends in the south coast air basin of California. In: Ozone/oxidants: interaction with the total environment. Pittsburgh (Pennsylvania): Air Pollution Control Association; 1979. p. 433–50.

Canada. This smelter began operating about 1940. Damage occurred in the prevailing downwind northeast sector for a distance of 60 km.<sup>21</sup> They analyzed vegetative plots and established four zones of impact in the downwind direction: within 8 km of the plant, damage was classified as “very severe” where no trees or shrubs survived; “severe damage” occurred at ~17 km, where no tree canopy existed; “considerable damage” existed at ~25 km, where some tree canopy remained, but with high tree mortality; and “moderate damage” was found at ~35 km, where a tree canopy existed but was put under stress and where the number of ground flora species was still reduced.

This type of severe air pollution damage has occurred several times in the past. If care is not taken, additional examples will be documented in the future.

#### 14.4.1.2 Crops and Food Supply

Food supply is a crucial part of civilization. Agriculture exists in various forms and takes advantage of numerous types of ecosystems that range from monocultures (e.g. large grain fields) to highly diverse systems from which crops of a few species are harvested (e.g. perennial polyculture forests). Air pollutants are a threat to any agricultural ecosystem (sometimes called “agroecosystems”), whether it has one dominant species or is highly biodiverse.

##### 14.4.1.2.1 VEGETATIVE INJURY AND DAMAGE

The U.S. Department of Agriculture makes a distinction between air pollution damage and air pollution injury. *Injury* is considered to be any observable alteration in the plant when exposed to air pollution. *Damage* is defined as an economic or esthetic loss due to interference with the intended use of a plant. This distinction indicates that injury by air pollution does not necessarily result in damage because any given injury may not

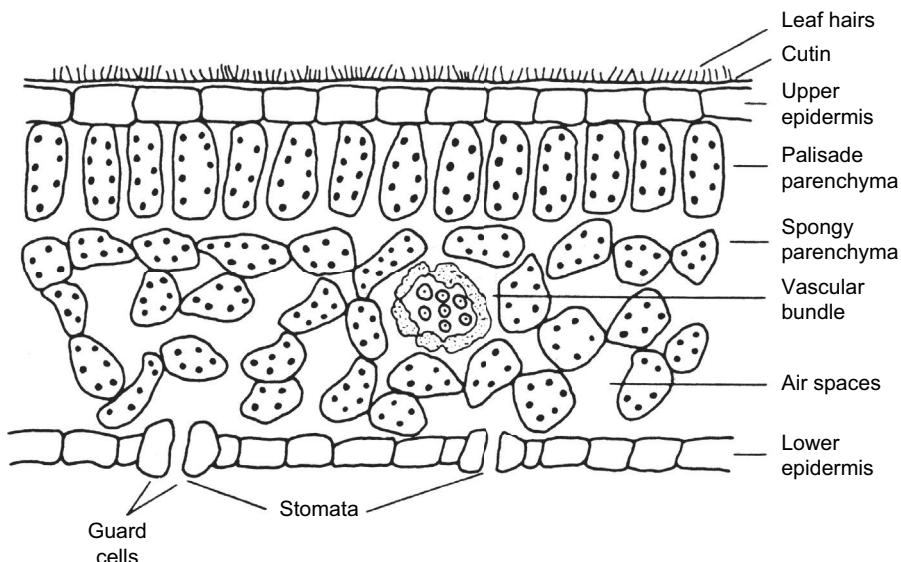
prevent the plant from being used as intended, e.g. marketed. Thus, damage is a value-laden concept.

Vegetation reacts with air pollution over a wide range of pollutant concentrations and environmental conditions. Many factors influence the outcome, including plant species, age, nutrient balance, soil conditions, temperature, humidity, and sunlight.<sup>22</sup> Any type of observable effect due to exposure can be termed plant injury. A schematic diagram in Figure 14.3 indicates the potential levels of injury with increasing exposure to air pollution. At low levels of exposure for a given species and pollutant, no significant effects may be observed. However, as the exposure level increases, a series of potential injuries may occur, including biochemical alterations, physiological response, visible symptoms, and eventual death.

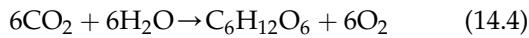
Air pollutants may enter plant systems by either a primary or a secondary pathway. The primary pathway is analogous to human inhalation described in Chapter 9. Figure 14.7 shows the cross section of a leaf, with both of the outer surfaces covered by a layer of epidermal cells, which help in moisture retention. Between the epidermal layers are the mesophyll cells—the spongy and palisade parenchyma. The leaf has a vascular bundle which carries water, minerals, and carbohydrates throughout the plant. Two important features shown in Figure 14.7 are the openings in the epidermal layers called *stomata*, which are controlled by guard cells which can open and close, and air spaces in the interior of the leaf. Similar to the selectivity of chemical exchanges by cells in the alveoli in the lung, the *stomata* selectively allow certain molecules to enter (e.g. nutrients). However, this same system also allows entry of xenobiotics and other air pollutants.

The leaf structure has several important functions, three of which are photosynthesis, transpiration, and

FIGURE 14.7 Cross section of leaf showing various components.



respiration.<sup>11</sup> Photosynthesis is accomplished by chloroplasts in the leaf, which combine water and CO<sub>2</sub> in the presence of sunlight to form sugars and release O<sub>2</sub>. A simplification of this process is:



Transpiration is the physical movement of water from the root system up to the leaves and its subsequent evaporation to the atmosphere. This process moves nutrients throughout the plant and cools the plant.

Respiration is a heat-producing process resulting from the oxidation of carbohydrates by O<sub>2</sub> to form CO<sub>2</sub> and H<sub>2</sub>O:



These three functions involve the movement of O<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O through the epidermal layers of the leaf. The analogy to human inhalation is obvious. With the diffusion of gases into and out of the leaf, pollutant gases have a direct pathway to the cellular system of the leaf structure. Direct deposition of particulate matter also occurs on the outer surfaces of the leaves.

The indirect pathway by which air pollutants interact with plants is through the root system. Deposition of air pollutants on soils and surface waters can cause alteration of the nutrient content of the soil in the vicinity of the plant. This change in soil condition can lead to indirect or secondary effects of air pollutants on vegetation and plants.

Injury to plants and vegetation is caused by a variety of factors of which air pollution is only one. Drought, too much water, heat and cold, hail, insects, animals, disease, and poor soil conditions are some of the other causes of plant injury and possible plant damage.<sup>23</sup> Estimates suggest that less than 5% of total crop losses are related to air pollution. Air pollution has a much greater

impact on some geographic areas and crops than others. Crop failure can be caused by fumigation from a local air pollution source or by more widespread and more frequent exposure to adverse levels of pollution.

The subtle interaction of air pollutants with these other stressors to plants and vegetation is the subject of ongoing research. For some plant systems, exposure to air pollutants may induce biochemical modifications which interfere with the water balance in plants, thereby reducing their ability to tolerate drought conditions.

#### 14.4.1.2.2 VEGETATIVE IMPACTS FROM ACID DEPOSITION

Acidic deposition refers to the transport of acid constituents from the atmosphere to the earth's surface. This process includes dry deposition of SO<sub>2</sub>, NO<sub>2</sub>, HNO<sub>3</sub>, and particulate sulfate matter and wet deposition ("acid rain") to surfaces. This process is widespread and alters distribution of plant and aquatic species, soil composition, pH of water, and nutrient content, depending on the circumstances.

The impact of acidic deposition on forests depends on the quantity of acidic components received by the forest system, the species present, and the soil composition (notably ionic strength and depth). Numerous studies have shown that widespread areas in the eastern portion of North America and parts of Europe are being altered by acidic deposition. Decreased pH in some lakes and streams in the affected areas was observed<sup>24</sup> in the 1960s and the trend continued for decades.

When a forest system is subjected to acidic deposition, the foliar canopy can initially provide some neutralizing capacity. If the quantity of acid components is too high, this limited neutralizing capacity is

overcome. As the acid components reach the forest floor, the soil composition determines their impact. The soil composition may have sufficient buffering capacity to neutralize the acid components. However, alteration of soil pH can result in mobilization or leaching of important minerals in the soil. In some instances, trace metals such as calcium or magnesium may be removed from the soil, altering the aluminum tolerance for trees.

This interaction between airborne acid components and the tree-soil system may alter the ability of the trees to tolerate other environmental stressors such as drought, insects, and other air pollutants like ozone. In Germany, considerable attention is focused on the role of ozone and acidic deposition as a cause of forest damage. Forest damage is a complex problem involving the interaction of exposures to acids and other air pollutants, forestry practices, and naturally occurring soil conditions. As in all ecosystems, forests must always be understood as complex, integrated systems with myriad interrelationships that can be affected by air pollutants.

#### 14.4.2 Effects on Fauna

Acidic deposition and the alteration of the pH of aquatic systems have led to the acidification of lakes and ponds in various locations in the world. Low-pH conditions result in lakes which contain no fish species.

Heavy metals on or in vegetation and water have been and continue to be toxic to animals and fish. Arsenic and lead from smelters, molybdenum from steel plants, and mercury from chlorine-caustic plants are major offenders. Poisoning of aquatic life by mercury is relatively new, whereas the toxic effects of the other metals have been largely eliminated by proper control of industrial emissions. Gaseous (and particulate) fluorides have caused injury and damage to a wide variety of animals—domestic and wild—as well as to fish. Accidental effects resulting from insecticides and nerve gas have been reported.

Autopsies of animals in the Meuse Valley, Donora, and London episodes described in Chapter 10, revealed evidence of pulmonary edema. Breathing toxic pollutants is not, however, the major form of pollutant intake for cattle; ingestion of pollution-contaminated feeds is the primary mode.

Air pollution's impact on fauna follows a two-step process: accumulation of airborne contaminants on or in vegetation or forage that serves as their feed and subsequent effects of the ingested herbage on animals. In addition to pollution-affected vegetation, carnivores (humans included) consume small animals that may have ingested exotic chemicals including pesticides, herbicides, fungicides, and antibiotics. As in humans, the principal route of exposure to air pollutants can be

indirect. After deposition, the animal ingests the contaminant. This reminds us that not every exposure to air pollution is by inhalation. Increasing environmental concern has pointed out the importance of the complete food chain for the physical and mental well-being of human beings.

##### **14.4.2.1 Effects of Metals and Metalloids**

The problems with metals in human populations discussed in previous chapters, especially Chapter 13, also affect other fauna. One of the earliest cattle problems involved widespread poisoning of cattle by arsenic at the turn of the century. Abnormal intake of arsenic results in severe colic (salivation, thirst, and vomiting), diarrhea, bloody feces, and a garlic-like odor on the breath; cirrhosis of the liver and spleen as well as reproductive effects may be noted. Arsenic trioxide in the feed must be approximately  $10 \text{ mg kg}^{-1}$  body weight for these effects to occur.

Cattle feeding on herbage containing  $25\text{--}50 \text{ mg kg}^{-1}$  ppm by weight lead (Pb) develop excitable jerking of muscles, frothing at the mouth, grinding of teeth, and paralysis of the larynx muscles; a “roaring” noise is caused by the paralysis of the muscles in the throat and neck.

Symptoms of molybdenum poisoning in cattle include emaciation, diarrhea, anemia, stiffness, and fading of hair color. Vegetation containing  $230 \text{ mg kg}^{-1}$  of this substance affects cattle.

Mercury in fish has been found in waters in the United States and Canada. Mercury in the waters is converted into methyl mercury by aquatic vegetation and other processes. Small fish consume such vegetation and in turn are eaten by larger fish and eventually by humans; food with more than  $0.5 \text{ ppm}$  of mercury ( $0.5 \text{ mg kg}^{-1}$ ) cannot be sold in the United States for human consumption. The U.S. Food and Drug Administration recommends that pregnant women and women of childbearing age should not exceed consuming 14 ounces of fish with  $0.5 \text{ ppm}$  mercury per week.

Mercury has a very complicated chemistry. It forms numerous chemical species with very different properties and behaviors in the environment. Three major types of mercury are important in air pollution: elemental mercury [ $\text{Hg}(0)$ ], which is the uncombined chemical element; divalent mercury [ $\text{Hg}(\text{II})$ ], which is chemically reactive and under most environmental conditions is found to be combined with other substances into mercury salts (e.g.  $\text{HgCl}_2$ ); and particulate-phase mercury [ $\text{Hg}(\text{p})$ ], most of which is actually the chemical species  $\text{Hg}(\text{II})$  but is only slightly reactive because it is mixed with solid-phase material in the atmosphere. These three species have very different affinities for compartments and organisms (Figure 14.8). Thus, the mercury that is

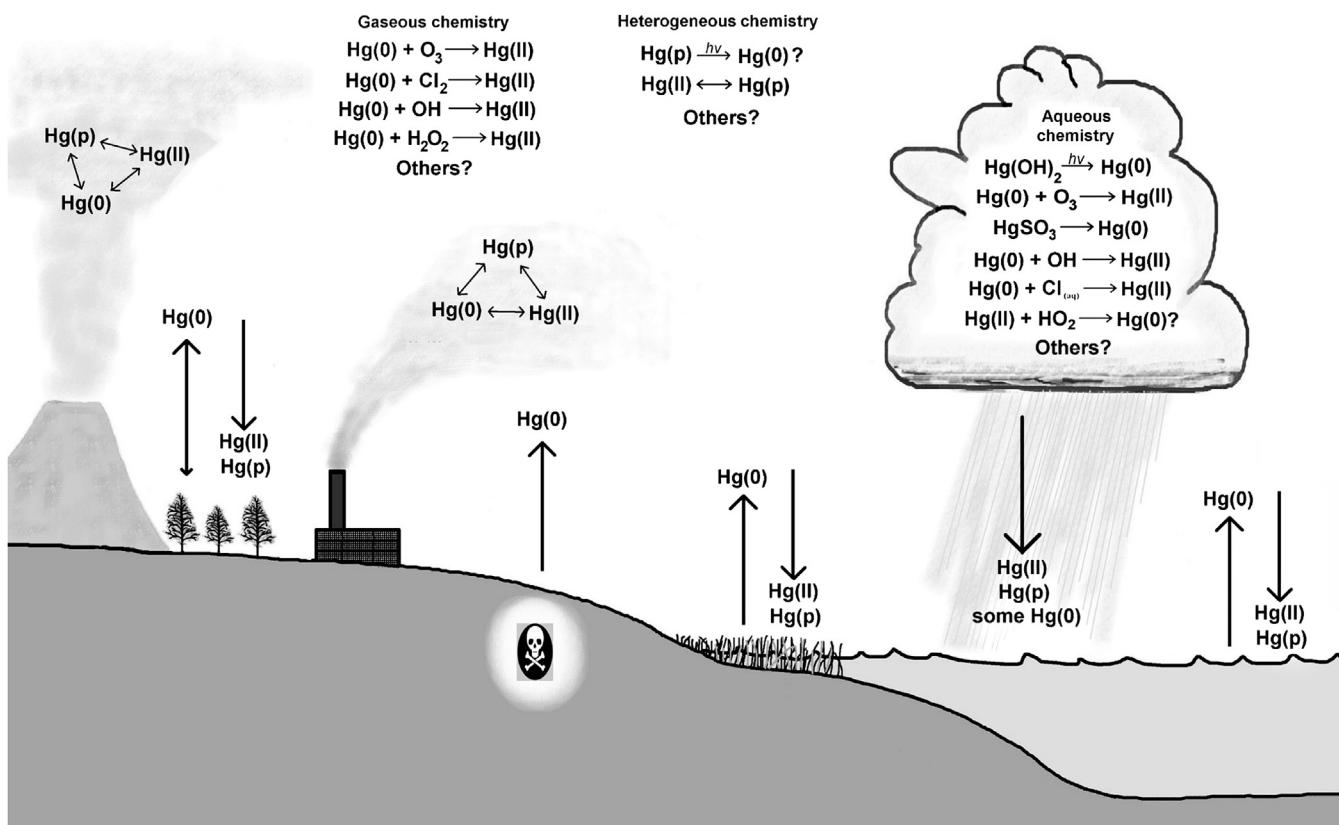


FIGURE 14.8 Chemical speciation of mercury (Hg) after it is released into the environment. Hg(0) is elemental, zero valence mercury; Hg(II) is divalent mercury (also known as reactive Hg); and Hg(p) is particulate-bound mercury. Drawing by Russell Bullock, National Oceanic and Atmospheric Administration, Research Triangle Park (North Carolina). Used with permission.

released from a stack can have a tortuous journey to and through the food chain.

#### 14.4.2.2 Gaseous and Particulate Effects

Periodically, accidental emissions of a dangerous chemical affect animal well-being. During nerve gas experimentation in a desolate area in Utah, a high-speed airplane accidentally dropped several 100 gallons of nerve gas. As a result of the discharge, 6200 sheep were killed. Considering the large number of exotic chemicals being manufactured, such unfortunate accidents may be anticipated in the future.

Fluoride emissions from industries producing phosphate fertilizers or phosphate derivatives have caused damage to cattle throughout the world; phosphate rock, the raw material, can contain up to 4% fluoride, part of which is discharged to air (and waters) during processing. In Polk and Hillsborough counties of Florida, the cattle population decreased by 30,000 between 1953 and 1960 as a result of fluoride emissions. Since 1950, research has greatly increased our knowledge of the effect of fluorides on animals; standards and guides for diagnosing and evaluating fluorosis in cattle have been compiled.

Chronic fluoride toxicity (fluorosis) is the type most frequently observed in cattle. The primary effects of fluorides in cattle are seen in the teeth and bones. Excessive intake weakens the enamel of developing teeth; the initially dulled erupted teeth can develop into soft teeth, with uneven wearing of molar teeth. Characteristic osteofluorotic bone lesions develop, causing intermittent lameness and stiffness in the animal. Fluoride content of the bone increases with dosage despite excretion in urine and feces. Secondary symptoms include reduced lactation, nonpliable skin, and dry, rough hair coat. As shown in Figure 14.9, the fluoride ingestion level correlates with the fluoride content of bones and urine as well as incisor teeth classification.<sup>25</sup>

Tolerance of animals for fluorides varies, dairy cattle being the most sensitive and poultry the least (Table 14.5). Fluorosis of animals in contaminated areas can be avoided by keeping the intake levels below those listed by incorporating clean feeds with those high in fluorides. It has also been determined that increased consumption of aluminum and calcium salts can reduce the toxicity of fluorides in animals. In addition, high-dose exposures can completely alter an

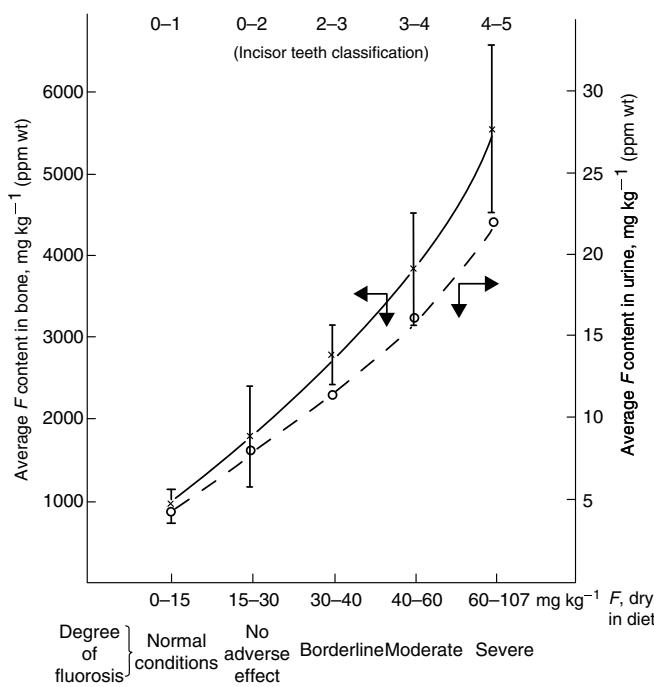


FIGURE 14.9 Effects of fluoride on 4-year-old dairy cattle.

TABLE 14.5 Fluoride Tolerance of Animals (ppm wt in Ration, Dry)\*

Species	Breeding or Lactating Animals (ppm) <sup>§</sup>	Finishing Animals to Be Sold for Slaughter with Average Feeding Period (ppm) <sup>§</sup>
Dairy, beef heifers	30	100
Dairy cows	30	100
Beef cows	40	100
Steers	—	100
Sheep	50	160
Horse	60	—
Swine	70	—
Turkeys	—	100
Chickens	—	150

<sup>§</sup>1 ppm wt = 1 mg kg<sup>-1</sup>.

\* Data based on soluble fluoride; increased values for insoluble fluoride compounds.

ecosystem. For example, if the population of a species of animals or plants that is sensitive to an air pollutant falls dramatically, then the entire predator–prey interactions can change. Thus, nonhuman species are indicators of environmental quality.

### 14.4.3 Effects on Abiotic Components of Ecosystems

#### 14.4.3.1 The Physics of Visibility

Impairment of visibility involves degradation of the ability to perceive the environment. Several factors are involved in determining visibility in the atmosphere (Figure 14.10): the optical characteristics of the illumination source; the viewed targets; the intervening atmosphere; and the characteristics of the observer's eyesight.<sup>26</sup>

To see an object, an observer must be able to detect the contrast between the object and its surroundings. If this contrast decreases, it is more difficult to observe the object. In the atmosphere, visibility can decrease for a number of reasons. For example, we may be farther away from the object (e.g. an airplane can move away from us); the sun's angle may change with the time of day; and if air pollution increases, the contrast may decrease, reducing our ability to see the object.

Objects close to us are easily perceived, but this diminishes as a function of distance. The lowest limit of contrast for human observers is called the *threshold contrast* and is important because this value influences the maximum distance at which we can see various objects. Thus, it is closely related to our understanding of good *versus* bad visibility for a particular set of environmental conditions.

Threshold contrast is illustrated in Figure 14.11.  $I$  is the intensity of light received by the eye from the object, and  $I + \Delta I$  represents the intensity coming from the surroundings. The threshold contrast can be as low as 0.018–0.03 and the object can still be perceptible. Other factors, such as the physical size of the visual image on the retina of the eye and the brain's response to the color of the object, influence the perception of contrast.

Let us consider the influence of gases and particles on the optical properties of the atmosphere. Reduction in visibility is caused by the following interactions in the atmosphere: light scattering by gaseous molecules and particles, and light absorption by gases and particles.<sup>27</sup>

Light-scattering processes involve the interaction of light with gases or particles in such a manner that the direction or frequency of the light is altered. Absorption processes occur when the electromagnetic radiation interacts with gases or particles and is transferred internally to the gas or particle.

Light scattering by gaseous molecules is wavelength dependent and is the reason why the sky is blue. This process is dominant in atmospheres that are relatively free of aerosols or light-absorbing gases. Light scattering by particles is the most important cause of visibility reduction. This phenomenon is dependent on the size of the particles suspended in the atmosphere.

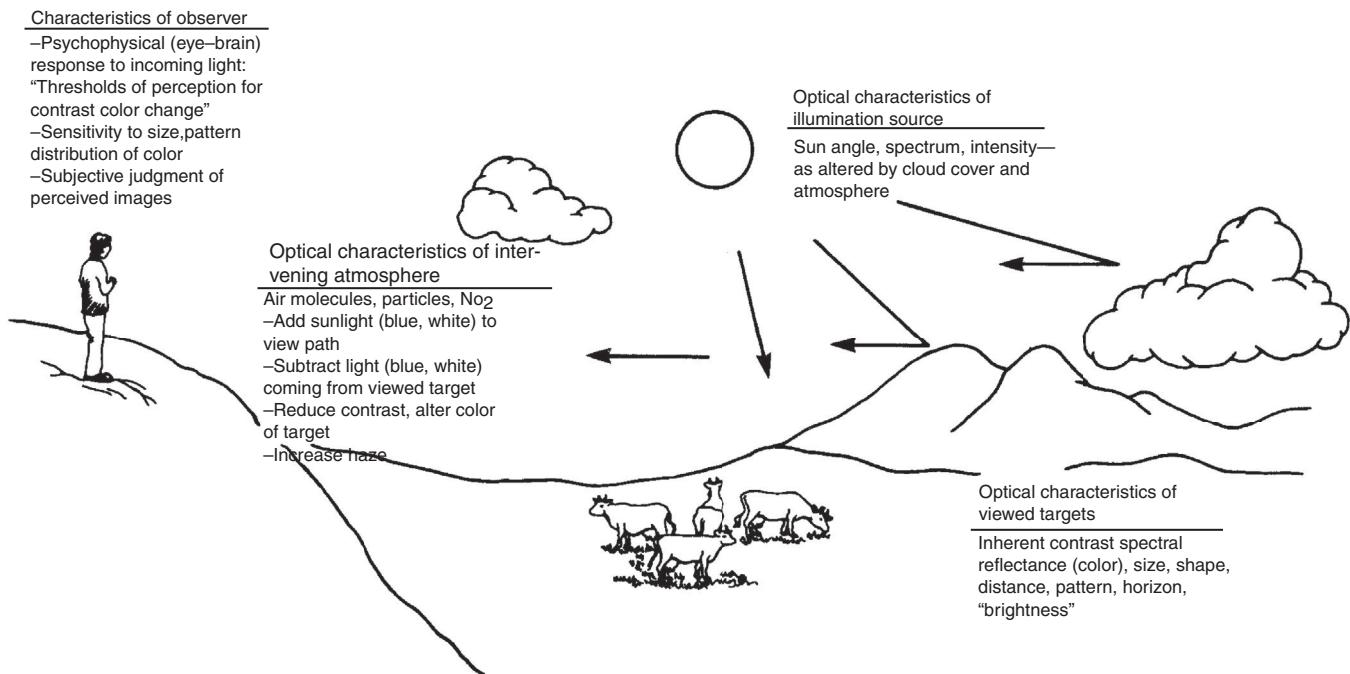


FIGURE 14.10 Factors determining visibility in the atmosphere. Ref. 26.

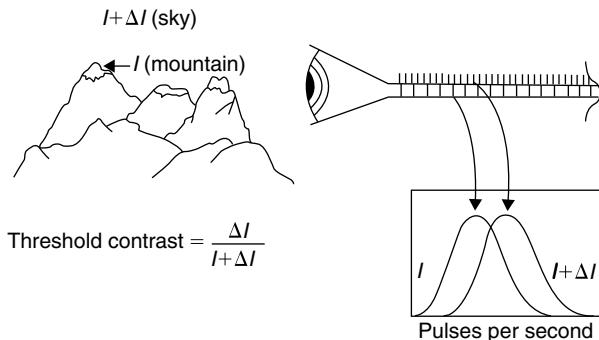


FIGURE 14.11 Threshold contrast in distinguishing an object from its surroundings. The eye responds to an increment in light intensity by increasing the number of signals (pulses) sent to the brain. The detection of threshold contrast involves the ability to discriminate between the target ( $I$ ) and the brighter background ( $I + \Delta I$ ). *Gregory RL., Eye and brain: the psychology of seeing. London: Weidenfeld and Nicolson; 1977.*

Light absorption by gases in the lower troposphere is limited to the absorption characteristics of nitrogen dioxide. This compound absorbs the shorter, or blue, wavelengths of visible light, causing us to observe the red wavelengths. We therefore perceive a yellow to reddish-brown tint in atmospheres containing quantities of NO<sub>2</sub>. Light absorption by particles is related principally to carbonaceous or black soot in the atmosphere. Other types of fine particles such as sulfates, although not good light absorbers, are very efficient at scattering light.

#### 14.4.3.1.1 LIGHT EXTINCTION IN THE ATMOSPHERE

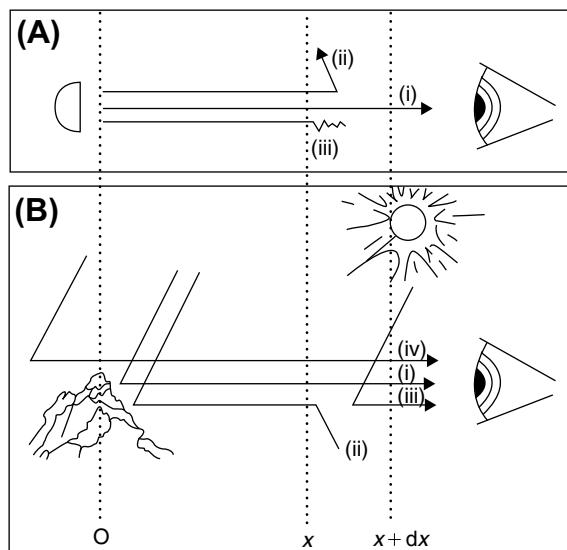
The interaction of light in the atmosphere is described mathematically in Eqn (14.7):

$$-dI = b_{\text{ext}} I dx \quad (14.6)$$

where  $-dI$  is the decrease in intensity,  $b_{\text{ext}}$  is the extinction coefficient,  $I$  is the original intensity of the beam of light, and  $dx$  is the length of the path traveled by the beam of light.

Figure 14.12(A) shows a beam of light transmitted through the atmosphere. The intensity of the beam  $I(x)$  decreases with the distance from the illumination source as the light is absorbed or scattered out of the beam. For a short period, this decrease is proportional to the intensity of the beam and the length of the interval at that point. Here  $b_{\text{ext}}$  is the extinction or attenuation coefficient and is a function of the degree of scattering and absorption of the particles and gases which are present in the beam path.

Figure 14.12(B) illustrates a slightly more complicated case, but one more applicable to atmospheric visibility. In this example, the observer still depends on the ability to perceive light rays emanating from the target object and on the scattering and absorption of those rays out of the beam. In addition, however, the observer must contend with additional light scattered into the line of sight from other angles. This extraneous light is sometimes called *air light*. Equation (14.7) is modified to account for this phenomenon by adding a term to represent this background intensity.



**FIGURE 14.12** (A) A diagram of extinction of light from a source such as an electric light in a reflector, illustrating (i) transmitted, (ii) scattered, and (iii) absorbed light. (B) A diagram of daylight visibility, illustrating (i) residual light from a target reaching an observer, (ii) light from a target scattered out of an observer's line of sight, (iii) air light from the intervening atmosphere, and (iv) air light constituting horizon sky. Ref. 26.

$$-dI = -dI(\text{extinction}) + dI(\text{air light}) \quad (14.7)$$

This air light term contributes to the reduced visibility we call *atmospheric haze*.

A simplified relationship developed by Koschmieder which relates the visual range and the extinction coefficient is given by

$$L_v = 3.92/b_{\text{ext}} \quad (14.8)$$

where  $L_v$  is the distance at which a black object is just barely visible.<sup>28</sup> Equation (14.9) is based on the following assumptions:

1. The background behind the target is uniform.
2. The object is black.
3. An observer can detect a contrast of 0.02.
4. The ratio of air light to extinction is constant over the path of sight.

While the Koschmieder relationship is useful as a first approximation for determining visual range, many situations exist in which the results are only qualitative.

The extinction coefficient  $b_{\text{ext}}$  is dependent on the presence of gases and molecules that scatter and absorb light in the atmosphere. The extinction coefficient may be considered as the sum of the air and pollutant scattering and absorption interactions, as shown in the following equation:

$$b_{\text{ext}} = b_{\text{rg}} + b_{\text{ag}} + b_{\text{scat}} + b_{\text{ap}} \quad (14.9)$$

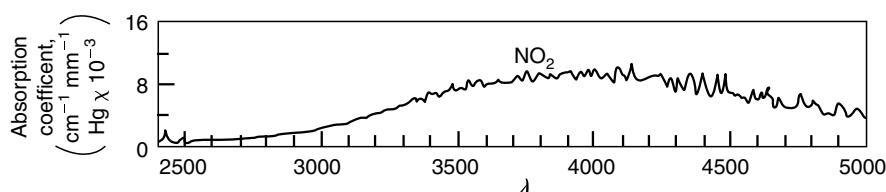
where  $b_{\text{rg}}$  is scattering by gaseous molecules (Rayleigh scattering),  $b_{\text{ag}}$  is absorption by  $\text{NO}_2$  gas,  $b_{\text{scat}}$  is scattering by particles, and  $b_{\text{ap}}$  is absorption by particles. These various extinction components are a function of wavelength. As extinction increases, visibility decreases.

The Rayleigh scattering extinction coefficient for particle-free air is  $0.012 \text{ km}^{-1}$  for “green” light ( $\gamma = 0.05 \mu\text{m}$ ) at sea level.<sup>29</sup> This permits a visual range of  $\sim 320 \text{ km}$ . The particle-free, or Rayleigh scattering, case represents the best visibility possible with the current atmosphere on earth.

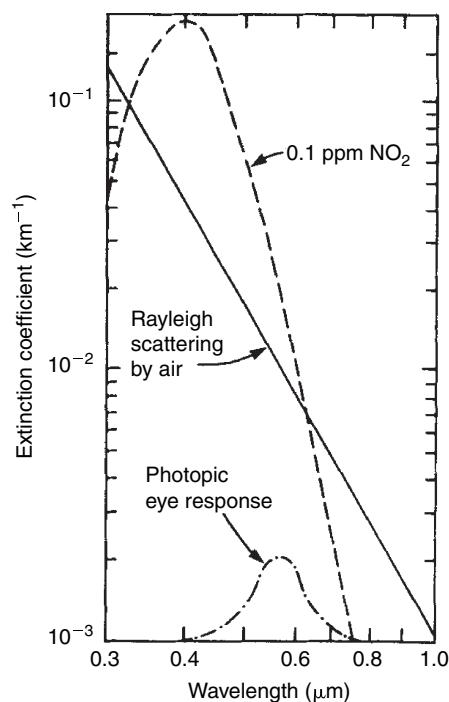
The absorption spectrum of  $\text{NO}_2$  shows significant absorption in the visible region (Figure 14.13).<sup>30</sup> As a strong absorber in the blue region,  $\text{NO}_2$  can color plumes red, brown, or yellow. Figure 14.14 shows a comparison of extinction coefficients of  $0.1 \text{ ppm } \text{NO}_2$  and Rayleigh scattering by air.<sup>31</sup> In urban areas, some discoloration can be due to area-wide  $\text{NO}_2$  pollution. In rural areas, the biggest problem with  $\text{NO}_2$  is that in coherent plumes from power plants, it contributes to the discoloration of the plume.

Suspended particles are the most important factor in visibility reduction. In most instances, the visual quality of air is controlled by particle scattering and is characterized by the extinction coefficient  $b_{\text{scat}}$ . The size of particles plays a crucial role in their interaction with light. Other factors are the refractive index and shape of the particles, although their effect is harder to measure and is less well understood. If we could establish these properties, we could calculate the amount of light scattering and absorption. Alternatively, the extinction coefficient associated with an aerosol can be measured directly.

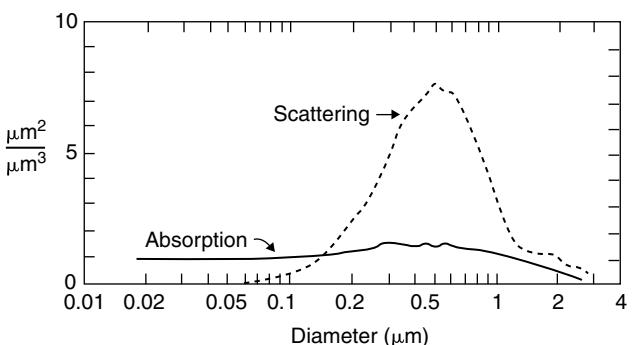
Light and suspended particles interact in the four basic ways shown in Figure 14.15: refraction, diffraction, phase shift, and absorption. For particles with a diameter of  $0.1\text{--}1.0 \mu\text{m}$ , scattering and absorption can be calculated by using the Mie equations.<sup>32</sup> Figure 14.16 shows the relative scattering and absorption efficiency



**FIGURE 14.13** Absorption spectrum of  $\text{NO}_2$ . Ref. 31.



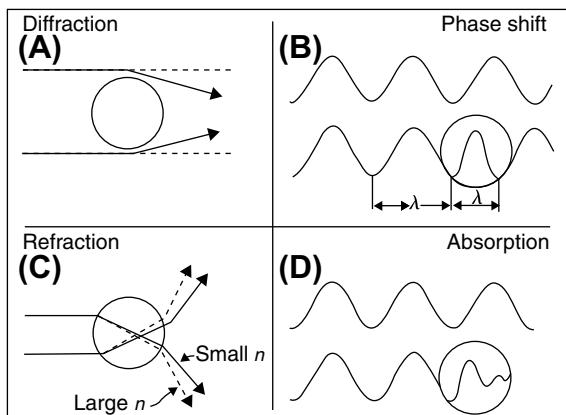
**FIGURE 14.14** Comparison of  $b_{\text{ext}}$  for 0.1 ppm NO<sub>2</sub> and Rayleigh scattering by air. The photopic eye response represents the range of wavelengths over which the eye detects light. Husar R, White WH, Paterson DE, Trijonis J. Visibility impairment in the atmosphere. Draft report prepared for the US Environmental Protection Agency under Contract No. 68022515, Task Order No. 28.



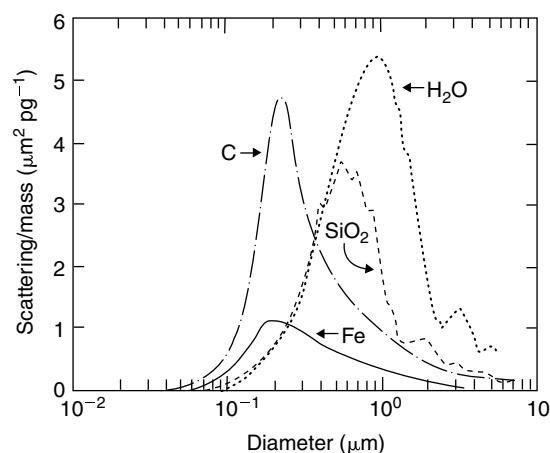
**FIGURE 14.16** Scattering and absorption cross section per unit volume as a function of particle diameter. Ref. 33.

per unit volume of particle for a typical aerosol containing some light-absorbing soot.<sup>33</sup> This clearly shows the importance of atmospheric particles in the diameter range 0.1–1.0  $\mu\text{m}$  as efficient light-scattering centers. With particles of larger and smaller diameters, scattering decreases. Absorption generally contributes less to the extinction coefficient than does the scattering processes. Atmospheric particles of different chemical composition have different refractive indices, resulting in different scattering efficiencies. Figure 14.17 shows the scattering-to-mass ratio for four different materials.<sup>34</sup> Clearly, carbon or soot aerosols, and aerosols of the same diameter with water content, scatter with different efficiencies at the same diameter.

Visibility is also affected by alteration of particle size due to hydroscopic particle growth, which is a function of relative humidity. In Los Angeles, California, the air, principally of marine origin, has numerous sea salt particles. Visibility is noticeably reduced when humidity exceeds about 67%. In a study of visibility related to both relative humidity and origin of air (maritime or



**FIGURE 14.15** Four forms of particle light interaction. Light scattering by coarse particles ( $0.2 \mu\text{m}$ ) is the combined effect of diffraction and refraction. (A) Diffraction is an edge effect whereby the light is bent to fill in the shadow behind the particle. (B) The speed of a wave front entering a particle with refractive index  $n > 1$  (for water,  $n = 1.33$ ) is reduced. (C) Refraction produces a lens effect. The angular dispersion resulting from bending incoming rays increases with  $n$ . (D) For absorbing media, the refracted wave intensity decays within the particle. When the particle size is comparable to the wavelength of light (0.1–1.0  $\mu\text{m}$ ), these interactions (A)–(D) are complex and enhanced. Ref. 26.



**FIGURE 14.17** Single particle scattering to mass ratio for particles of four different compositions. Carbon particles are also very efficient absorbers of light. Ref. 26.

continental), Buma<sup>35</sup> found that at a set relative humidity, continental air reduced visibility below 7 km more often than did air of maritime origin. This effect is presumably due to numerous hygroscopic aerosols from air pollution sources. Some materials, such as sulfuric acid mist, exhibit hygroscopic growth at humidity as low as 30%.

#### 14.4.3.1.2 TURBIDITY

The attenuation of solar radiation has been studied by McCormick and his associates<sup>36,37</sup> using the Voltz sun photometer, which makes measurements at a wavelength of 0.5 μm. The ratio of the incident solar transmissivity to the extraterrestrial solar intensity can be as high as 0.5 in clean atmospheres but can drop to 0.2–0.3 in polluted areas, indicating a decrease of 50% in ground-level solar intensity. The turbidity coefficient can also be derived from these measurements and used to approximate the aerosol loading of the atmosphere. By assuming a particle size distribution in the size range 0.1–10.0 μm and a particle density, the total number of particles can be estimated. The mass loading per cubic meter can also be approximated. Because of the reasonable cost and simplicity of the sun photometer, it is useful for making comparative measurements around the world.

#### 14.4.3.1.3 PRECIPITATION

Pollution can cause opposite effects in relation to precipitation. Addition of a few particles that act as ice nuclei can cause ice particles to grow at the expense of supercooled water droplets, producing particles large enough to fall as precipitation. An example of this is commercial cloud seeding with silver iodide particles released from aircraft to induce rain. If too many particles are added, none of them grow sufficiently to cause precipitation. Therefore, the effects of pollution on precipitation are complex.

#### 14.4.3.2 Formation of Atmospheric Haze

Atmospheric haze is the condition of reduced visibility caused by the presence of fine particles or NO<sub>2</sub> in the atmosphere. The particles must be 0.1–1.0 μm in diameter, the size range in which light scattering occurs. The source of these particles may be natural or anthropogenic.

Atmospheric haze has been observed in both the western and eastern portions of the United States. Typical visual ranges in the East are <15 mi and in the Southwest >50 mi. The desire to protect visual air quality in the United States is focused on the national parks in the West. The ability to see vistas over

Fifty to hundred kilometers in these locations are particularly vulnerable to atmospheric haze. This phenomenon is generally associated with diffuse or

widespread atmospheric degradation as opposed to individual plumes.

The major component of atmospheric haze is sulfate particulate matter (particularly ammonium sulfate), along with varying amounts of nitrate particulate matter, which in some areas can equal the sulfate. Other components include graphitic material, fine fly ash, and organic aerosols.

The sources of particulate matter in the atmosphere can be primary, directly injected into the atmosphere, or secondary, formed in the atmosphere by gas-to-particle conversion processes.<sup>38</sup> The primary sources of fine particles are combustion processes, e.g. power plants and diesel engines. Power plants with advanced control technology still emit substantial numbers and masses of fine particles with diameters <1.0 μm. The composition of these particles includes soot or carbonaceous material, trace metals, V<sub>2</sub>O<sub>5</sub>, and sulfates. In addition, large quantities of NO<sub>2</sub> and SO<sub>2</sub> are released to the atmosphere.

#### 14.4.3.2.1 PARTICLE FORMATION IN THE ATMOSPHERE

The secondary source of fine particles in the atmosphere is gas-to-particle conversion processes, considered to be the more important source of particles contributing to atmospheric haze. In gas-to-particle conversion, gaseous molecules become transformed to liquid or solid particles. This phase transformation can occur by three processes: absorption, nucleation, and condensation. *Absorption* is the process by which a gas goes into solution in a liquid phase. Absorption of a specific gas is dependent on the solubility of the gas in a particular liquid, e.g. SO<sub>2</sub> in liquid H<sub>2</sub>O droplets. *Nucleation* and *condensation* are terms associated with aerosol dynamics.

*Nucleation* is the growth of clusters of molecules that become a thermodynamically stable nucleus. This process is dependent on the vapor pressure of the condensable species. The molecular clusters undergo growth when the saturation ratio, *S*, is greater than 1, where *saturation ratio* is defined as the actual pressure of the gas divided by its equilibrium vapor pressure. *S* > 1 is referred to as a *supersaturated condition*.<sup>39</sup>

The size at which a cluster may be thermodynamically stable is influenced by the Kelvin effect. The equilibrium vapor pressure of a component increases as the droplet size decreases. Vapor pressure is determined by the energy necessary to separate a single molecule from the surrounding molecules in the liquid. As the curvature of the droplet's surface increases, fewer neighboring molecules will be able to bind a particular molecule to the liquid phase, thus increasing the probability of a molecule escaping the liquid's surface. Thus, smaller droplets will have a higher equilibrium vapor pressure. This would affect the minimum size necessary

for a thermodynamically stable cluster, suggesting that components with lower equilibrium saturation vapor pressures will form stable clusters at smaller diameters.

*Condensation* is the result of collisions between a gaseous molecule and an existing aerosol droplet when supersaturation exists. Condensation occurs at much lower values of supersaturation than nucleation. Thus, when particles already exist in sufficient quantities, condensation will be the dominant process occurring to relieve the supersaturated condition of the vapor-phase material.

A simple model for the formation and growth of an aerosol at ambient conditions involves the formation of a gas product by the appropriate chemical oxidation reactions in the gas phase. This product must have a sufficiently low vapor pressure for the gas-phase concentration of the oxidized product to exceed its saturation vapor pressure. When this condition occurs, nucleation and condensation may proceed, relieving supersaturation. These processes result in the transfer of mass to the condensed phase. Aerosol growth in size occurs while condensation is proceeding.

*Coagulation*, i.e. the process by which discrete particles come into contact with each other in the air and remain joined together by surface forces, represents another way in which aerosol diameter will increase. However, it does not alter the mass of material in the coagulated particle.

The clearest example of this working model of homogeneous gas-to-particle conversion is sulfuric acid aerosol formation. Sulfuric acid ( $H_2SO_4$ ) has an extremely low saturation vapor pressure. Oxidation of relatively small amounts of sulfur dioxide ( $SO_2$ ) can result in a gas-phase concentration of  $H_2SO_4$  that exceeds its

equilibrium vapor pressure in the ambient atmosphere, with the subsequent formation of sulfuric acid aerosol. In contrast, nitric acid ( $HNO_3$ ) has a much higher saturation vapor pressure. Therefore, the gas-phase concentration of  $HNO_3$  is not high enough to permit nucleation of nitric acid aerosol in typical atmospheric systems.

Atmospheric haze can occur over regions of several thousand square kilometers, caused by the oxidation of widespread  $SO_2$  and  $NO_2$  to sulfate and nitrate in relatively slow-moving air masses. In the eastern United States, large air masses associated with slow-moving or stagnating anticyclones have become sufficiently contaminated to be called *hazy blobs*. These blobs have been tracked by satellites as they develop and move across the country.<sup>40</sup>

The evolution of regional hazy air masses has been documented in several case studies. The development of one such system is shown in Figure 14.18. During a 10-day period in the summer of 1975, a large region of the eastern United States had decreased visibility associated with the presence of fine particles in the atmosphere. The phenomenon occurred in association with a slow-moving high-pressure system. Because it seldom rains during the passage of these systems, the fine particles may have stayed airborne for a longer period of time than usual.

#### 14.4.3.3 Effects of Atmospheric Haze

The United States Clean Air Act of 1977 set as a national goal the prevention of any future degradation and the reduction of any existing impairment of visibility in mandatory class I federal areas caused by anthropogenic air pollution. The Clean Air Act Amendments of 1990 reinforce the support of these goals (see Chapter 28

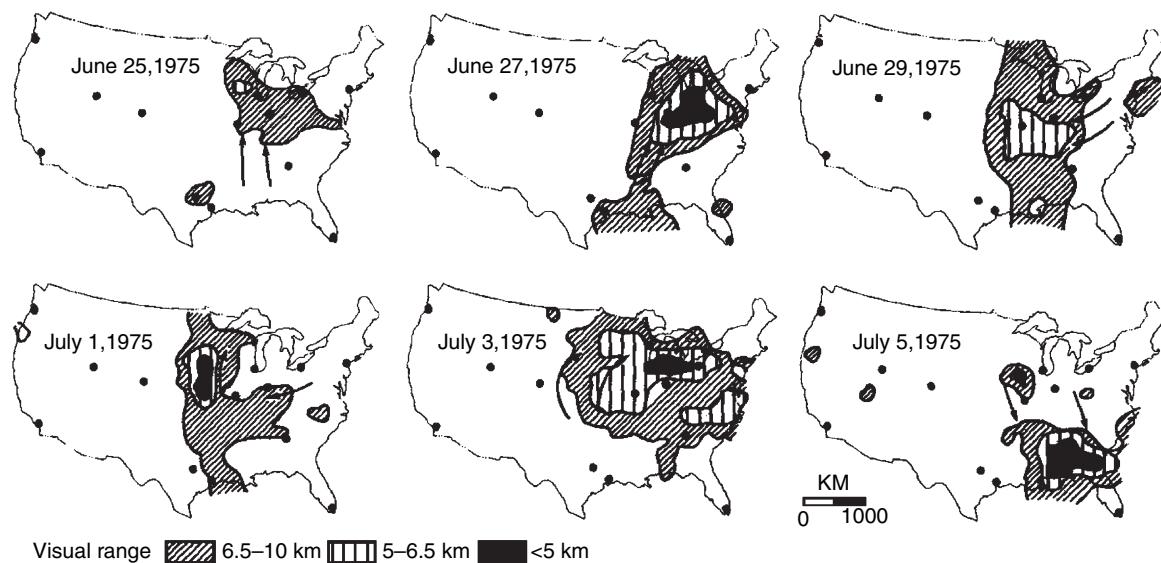


FIGURE 14.18 The evolution and transport of a large hazy air mass. Contour maps of noon visibility for June 25–July 5, 1975. Ref. 40.

for a discussion of federal classes of areas). These areas include most of the major national parks, such as the Grand Canyon, Yosemite, and Zion Park. This portion of the Clean Air Act addresses the problem of visibility degradation by atmospheric haze of anthropogenic origin. This legislation recognizes atmospheric haze as a cause of degradation in visual air quality.

All nations contain areas of exceptional scenic beauty. The value of these areas is largely determined by society. Many nations, determined to protect these areas, have established parks or preserves where only limited development can occur, in many instances limited to facilities such as food and lodging for visitors to the area.

The Grand Canyon National Park in the southwestern United States is a prime example of an area of natural beauty. This park is  $\sim 250$  km long, varying in width up to  $\sim 45$  km. The actual canyon is  $\sim 10$  km at its widest point, with the Colorado River running in the bottom of the canyon, 1600 m below the edge of the outer rim. Visitors go to parks for many reasons, such as hiking, camping, wildlife, and the enjoyment of solitude, but the overwhelming majority visit the Grand Canyon to enjoy the magnificent views from its rim. These views have detail in the foreground (0–5 km), with colored layers of rock strata on canyon walls perhaps 5–25 km distant and in the far background (25–50 km) additional geologic features which contribute to the viewers' appreciation of the scene. To enjoy these views, one must have good visibility over the entire path length from the details in the foreground to the objects in the distant background.

A survey by national park personnel indicates that large areas of the United States are subject to varying degrees of visibility degradation.<sup>26</sup> The middle portion of the eastern half of the country and the Florida Gulf Coast are subject to widespread hazy air masses associated with stagnation conditions. Large portions of the western half of the country are subject to atmospheric haze problems associated with power plants, urban plumes, and agricultural activities.

Average airport visibilities over the eastern half of the United States have been determined over a period of approximately 25 years (1948–1974).<sup>30</sup> Although seasonal variations occur, the long-term trend has been decreased visual air quality over the time period.

#### 14.4.3.4 Visibility

Holzworth and Maga<sup>41</sup> developed a technique for examining the trend in visibility and analyzed data for several California airports. Bakersfield's visibility deteriorated over the period 1948–1957 and Sacramento's visibility decreased over the period 1935–1958. Los Angeles had decreasing visibility from 1932 to 1947, with little change over the period 1948–1959.

Holzworth<sup>42</sup> reported on the frequency of visibility of less than 7 mi for 28 cities. Two periods of records were compared for each city. There were increases in low visibility in only 26% of the comparisons from the early period (around 1930–1940) to a later period (around the mid-1950s).

Miller et al.<sup>43</sup> using analyses for Akron, Ohio, Lexington, Kentucky, and Memphis, Tennessee, concluded that "summer daytime visibilities were significantly lower during the period 1966–1969 than visibilities for the preceding 4-year period".

Faulkenberry and Craig,<sup>44</sup> in examining the trends at three Oregon cities, utilized a modification of the Holzworth–Maga technique by which a single statistic can be calculated for each year, indicating the probability of observing better visibility at Salem, Oregon, with no trends at Portland and Eugene, Oregon, over the period 1950–1971.

Arizona has traditionally been a large copper-producing state. SO<sub>x</sub> emissions from copper smelters near Phoenix and Tucson are shown in Figure 14.19.<sup>27</sup> Phoenix is located 100 km from the nearest smelter, and Tucson is 60 km from the nearest smelter. The improvement in visibility in the 1967–1968 period was due to a decrease in SO<sub>x</sub> emissions when there was a 9-month shutdown caused by a strike. Improvement in

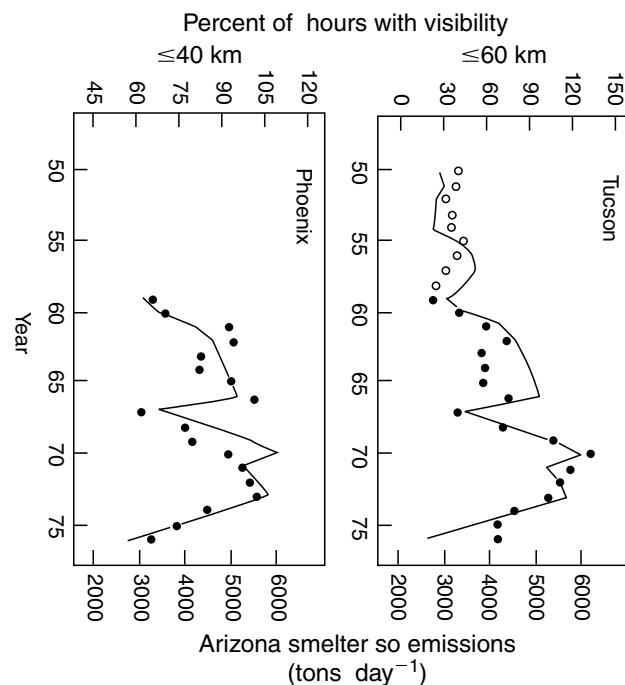


FIGURE 14.19 Historic trends in hours of reduced visibility at Phoenix and Tucson, Arizona, compared to trends in SO<sub>x</sub> emissions from Arizona smelters. The solid lines (—) represent yearly SO<sub>x</sub> emissions. The dots (...) represent yearly percentages of hours of reduced visibility. Note the open dots used to represent different locations in Tucson before 1958. Ref. 26.

visibility in the mid-1970 was the result of better control technology and process changes.

Zannetti et al.<sup>45</sup> did an analysis of visual range in the eastern United States again showing the importance of humidity but also showing the importance of air mass type, which is usually related to its direction of origin.

Mathai<sup>46</sup> summarized the specialty conference on atmospheric visibility. With the exception of water content of particles and the measurement of organic species, analytical laboratory techniques are readily available for particle analysis. Regulatory approaches to mitigate existing visibility impairment and to prevent further impairment are being formulated. A significant problem for regulation is the lack of proven techniques to quantify the contributions due to various sources.

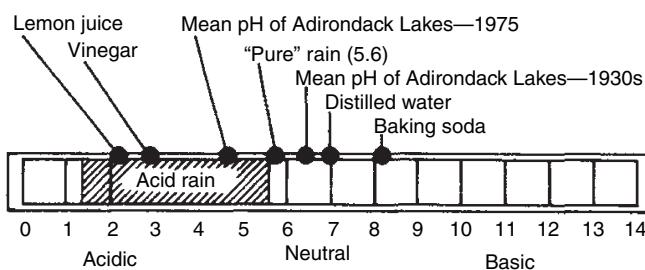
#### 14.4.3.5 Acidic Deposition

Over the past 25 years, evidence has been accumulated on changes in aquatic life and soil pH in Scandinavia, Canada, and the northeastern United States. Many believe that these changes are caused by acidic deposition traceable to pollutant acid precursors that result from the burning of fossil fuels. Acid rain is only one component of *acidic deposition*, a more appropriate description of this phenomenon. Acidic deposition is the combined total of wet and dry deposition, with wet acidic deposition being commonly referred to as acid rain.

Acidity is defined in terms of the pH scale, where pH is the negative logarithm of the hydrogen ion  $[H^+]$  concentration:

$$pH = -\log[H^+] \quad (14.10)$$

In the simplest case,  $CO_2$  dissolves in raindrops, forming carbonic acid. At a temperature of  $20^\circ C$ , the raindrops have a pH of 5.6, the value often labeled as that of clean or natural rainwater. It represents the baseline for comparing the pH of rainwater which may be altered by  $SO_2$  or  $NO_x$  oxidation products. Figure 14.20



**FIGURE 14.20** The pH scale is a measure of hydrogen ion concentration. The pH of common substances is shown with various values along the scale. The Adirondack Lakes are located in the state of New York and are considered to be receptors of acidic deposition. US Environmental Protection Agency. Acid rain—research summary. EPA-600/8-79-028. Cincinnati (OH); 1979.

illustrates the pH scale with the pH of common items and the pH range observed in rainwater. The pH of rainwater can vary from 5.6 due to the presence of  $H_2SO_4$  and  $HNO_3$  dissolved or formed in the droplets. These strong acids dissociate and release hydrogen ions, resulting in more acidic droplets. Basic compounds can also influence the pH. Calcium ( $Ca^{2+}$ ), magnesium ( $Mg^{2+}$ ), and ammonium ( $NH_4^+$ ) ions help to neutralize the rain droplet and shift the overall  $H^+$  toward the basic end of the scale. The overall pH of any given droplet is a combination of the effects of carbonic acid, sulfuric and nitric acids, and any neutralizers such as ammonia.

The principal elements of acidic deposition are shown in Figure 14.21. Dry deposition occurs when it is not raining. Gaseous  $SO_2$ ,  $NO_2$ , and  $HNO_3$  and acid aerosols are deposited when they come into contact with and stick to the surfaces of water bodies, vegetation, soil, and other materials. If the surfaces are moist or liquid, the gases can go directly into solution; the acids formed are identical to those that fall in the form of acid rain.  $SO_2$  and  $NO_2$  can undergo oxidation, forming acids in the liquid surfaces if oxidizers are present. During cloud formation, when rain droplets are created, fine particles or acid droplets can act as seed nuclei for water to condense. This is one process by which sulfuric acid is incorporated in the droplets. While the droplets are in the cloud, additional gaseous  $SO_2$  and  $NO_2$  impinge on them and are absorbed. These absorbed gases can be oxidized by dissolved  $H_2O_2$  or other oxidizers, lowering the pH of the raindrop. As the raindrop falls beneath the cloud, additional acidic gases and aerosol particles may be incorporated in it, also affecting its pH.

The United States has established a National Atmospheric Deposition Program, and Canada has established Canadian Air and Precipitation Monitoring Network (CAPMoN),<sup>47</sup> which consists of sampling networks and organizational and support structures to obtain quantitative information on the spatial and temporal distribution patterns of acidic deposition. CAPMoN is operated by Environment Canada, is designed to study the regional patterns and trends of atmospheric pollutants such as acid rain, smog, particulate matter and mercury, in both air and precipitation.<sup>48,49</sup> The lowest rainwater pH isopleths are associated with the regions of highest  $SO_2$  emissions. Although there is considerable controversy over the quality and strength of the link between  $SO_2$  and  $NO_x$  emissions from stationary sources and subsequent deposition of low-pH water hundreds of kilometers downwind, the National Research Council has concluded that a 50% reduction in the emissions of sulfur and nitrogen gases will produce about a 50% reduction in the acids deposited on the land and water downwind of the emission source. They also state that current meteorological models of atmospheric transport cannot identify

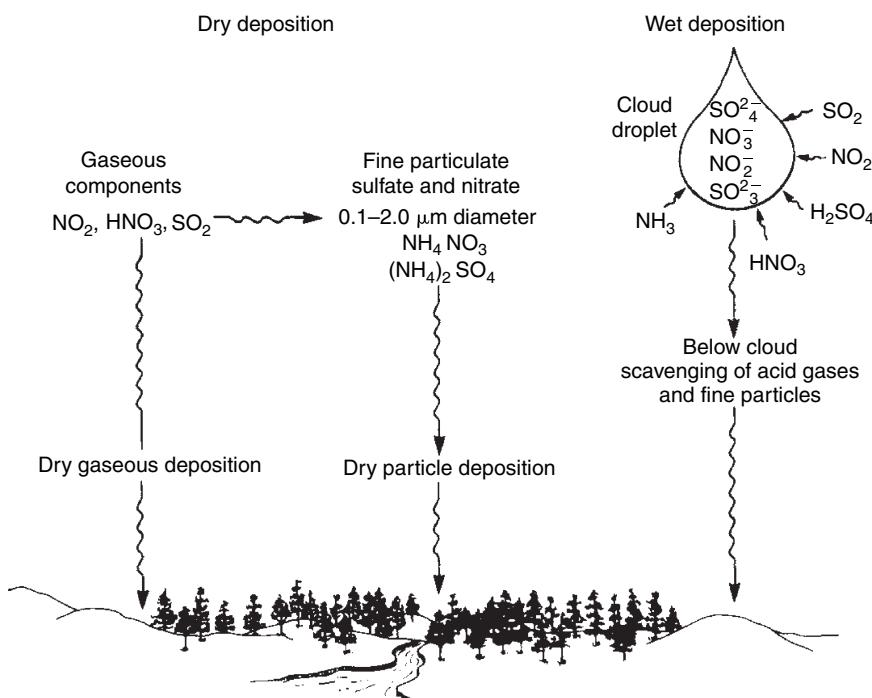


FIGURE 14.21 Atmospheric processes involved in acidic deposition. The two principal deposition pathways are dry deposition (nonrain events) and wet deposition (rain events).

specific sources with acidic deposition at a particular downwind location.<sup>50</sup>

A field study, the Eulerian Model Evaluation Field Study,<sup>51</sup> evaluated the performance of two models: the acidic deposition and oxidant model (ADOM)<sup>52</sup> and the regional acidic deposition model (RADM).<sup>53</sup> For both models the calculated values, such as air concentrations, are volume averages over grid cells which are 127 km on a side for the ADOM and 80 km for the RADM. These are compared with point measurements at a possible 97 locations. The ADOM tended to overestimate ground-level SO<sub>2</sub> and underestimate ground-level sulfate. Two factors not included in the model that may contribute to these results are consideration of conversion during surface fog and conversion in non-precipitating clouds. The RADM also overestimated SO<sub>2</sub> and underestimated aerosol sulfate.

In the eastern United States, acid rain consists of ~65% sulfuric acid, ~30% nitric acid, and ~5% other acids. In the West, windblown alkaline dusts buffer the acidity in rains occurring over many rural areas, whereas in urban areas 80% of the acidity is due to nitric acid.<sup>54</sup> Average pH in rainfall over the eastern United States for the period April 1979–March 1980 was less than 5.0, with some areas less than 4.2.<sup>55</sup> The lowest annual pH recorded was 3.78 at De Bilt, The Netherlands, in 1967, and the lowest in an individual rainfall was 2.4 at Pitlochry, Scotland, on April 10, 1974.<sup>56</sup>

One of the major effects of acidic deposition is felt by aquatic ecosystems in mountainous terrain, where considerable precipitation occurs due to orographic

lifting. The maximum effect is felt where there is little buffering of the acid by soil or rock structures and where steep lakeshore slopes allow little time for precipitation to remain on the ground surface before entering the lake. Maximum fish kills occur in the early spring due to the “acid shock” of the first meltwater, which releases the pollution accumulated in the winter snowpack. This first melt may be 5–10 times more acidic than rainfall.

Although the same measurement techniques for rainfall acidity have not been used over a long period of time and sampling has been carried out at relatively few locations, the trend between 1955–1956 and 1975–1976 was for the area with a pH of less than 4.6 to expand greatly over the eastern United States. The largest increases occurred over the southeastern United States, where industrialization grew rapidly during the period. The last several decades have also seen an increased area of lower pH over northern Europe.

#### 14.4.3.6 Effects of Acidic Deposition

Land, vegetation, and bodies of water are the surfaces on which acidic deposition accumulates. Bodies of freshwater represent the smallest proportion of the earth’s surface area available for acidic deposition. Yet, the best-known effect is acidification of freshwater aquatic systems.

Consider a lake with a small watershed in a forest ecosystem. The forest and vegetation can be considered as an acid concentrator. SO<sub>2</sub>, NO<sub>2</sub>, and acid aerosol are deposited on vegetation surfaces during dry

periods and rainfalls; they are washed to the soil floor by low-pH rainwater. Much of the acidity is neutralized by dissolving and mobilizing minerals in the soil. Aluminum, calcium, magnesium, sodium, and potassium are leached from the soil into surface waters. The ability of soils to tolerate acidic deposition is very dependent on the alkalinity of the soil. The soil structure in the northeastern United States and eastern Canada is quite varied, but much of the area is covered with thin soils with a relatively limited neutralizing capacity. In watersheds with this type of soil, lakes and streams are susceptible to low pH and elevated levels of aluminum. This combination has been found to be very toxic to some species of fish. When the pH drops to ~5, many species of fish are no longer able to reproduce and survive. In Sweden, thousands of lakes are no longer able to support fish. In the United States the number of polluted lakes is much smaller, but many more may be pushed into that condition by continued acidic deposition. In Canada, damage to aquatic systems and forest ecosystems is a matter of considerable concern.

Aquatic systems in areas of large snowfall accumulation are subjected to a pH surge during the spring thaw. Acidic deposition is immobilized in the snowpack, and when warm springtime temperatures cause melting, the melted snow flows into streams and lakes, potentially overloading the buffering capacity of the aquatic system.

A second area of concern is reduced tree growth in forests, discussed earlier. As acidic deposition moves through forest soil, the leaching process removes nutrients. If the soil base is thin or contains barely adequate amounts of nutrients to support a particular mix of species, the continued loss of a portion of the soil minerals may cause a reduction in future tree growth rates or a change in the types of trees able to survive in a given location.

## QUESTIONS

- What two aspects of risk are considered during the problem formulation step in the ecological risk assessment process? How does this differ from human risk assessment?
- Describe the structure of a temperate forest and how emissions of SO<sub>2</sub> can lead to changes in this structure.
- Give two examples of how an air pollutant can affect the biodiversity of an ecosystem.
- A wastewater treatment plant changed from applying sludge to the land to building an incinerator to burn the sludge. Before the incinerator began operation, the city required that insect species in a nearby wetland be counted as an indicator of changes in diversity that may result from the incinerator's

emissions. The local university recommended that 12 insect species be counted. The annual counts of these species beginning the year before the incinerator began operations (Year 0) are shown in the table. How has diversity changed with time?

Insect ID	Number counted, Year 0	Number counted, Year 1	Number counted, Year 2	Number counted, Year 3	Number counted, Year 4	Number counted, Year 5
A	11,007	21,000	23,090	29,005	33,090	35,090
B	5011	590	540	340	310	240
C	10,075	750	840	456	450	440
D	505	770	990	1100	1290	1250
E	200	21	0	35	0	0
F	1350	500	0	0	0	0
G	2717	453	578	345	123	78
H	1580	1231	1123	789	879	2123
J	5011	3200	2341	1344	1241	989
K	10,075	20,078	23,900	25,880	30,900	35,000
L	505	100	88	76	25	0
M	200	0	0	0	0	0

- The same insect counts were measured at a wetland 5 km upwind from the facility (the city recommended this as a background site). The results are shown in the table. What can be concluded about the role of the incinerator regarding changes in diversity? What uncertainties are there in your conclusions?

Insect ID	Number counted, Year 0	Number counted, Year 1	Number counted, Year 2	Number counted, Year 3	Number counted, Year 4	Number counted, Year 5
A	900	800	950	875	900	890
B	1000	1800	1550	1330	1235	1010
C	11,000	12,085	12,975	14,560	12,450	11,040
D	400	470	590	500	690	450
E	300	450	340	350	460	310
F	850	700	670	530	750	700
G	3017	3450	3780	4345	4125	3075
H	1800	1731	1823	1789	2079	1765
J	1200	1345	1470	1340	1205	1280
K	11,000	10,000	13,000	11,500	12,000	11,400
L	400	300	400	350	425	400
M	200	210	290	300	400	450

- What makes coral reefs sensitive to air pollution, either directly or indirectly?

7. What functions do the stomata serve in gas exchange with the atmosphere?
8. Explain how exposure to O<sub>3</sub> can damage a lettuce crop. Compare and contrast these mechanisms to the damage to it causes to a rain forest.
9. Explain how emissions of SO<sub>2</sub> can result in damage to plant life.
10. Distinguish between air pollution damage and injury.
11. Why is it difficult to prove that effects on plants in the field observed visually were caused by exposure to air pollution?
12. Why is air pollution damage important when estimates suggest that it accounts for less than 5% of total crop losses in the United States?
13. List examples of air pollution effects on plants that cannot be detected by visual symptoms.
14. Explain how acidic deposition stresses flora and fauna in ecosystems.
15. What types of trace gases are released to the atmosphere by forest ecosystems?
16. How can ozone and insects interact to damage trees in forests?
17. Calculate the daily fluoride intake of a dairy animal from (a) air and (b) food and water, based on the conditions below and assuming 100% retention of the fluoride:
  - a. Animal breathing rate: 30 kg air per day containing 6 µg fluoride per cubic meter of air (STP).
  - b. Animal food and water intake: Herbage 10 kg containing 200 mg kg<sup>-1</sup> of fluoride; Water 5 kg containing 1 mg kg<sup>-1</sup> of fluoride.
18. If you were a forest manager for a woody grove in Atlanta, Georgia, how might you use the information in **Table 14.4**? What if you were doing the same in Los Angeles, California? What differences, if any, would come into play?
19. Using heavy metals as an example, explain where humans reside in the food chain and how human health and ecosystem wellbeing are inextricably linked.
20. Compare **Table 14.3** and **Figure 14.7** to Figure 8.2 in Chapter 8. What can be said about the similarities and difference between faunal and floral interfaces with respect to exposure to air pollutants?

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# Air Pollution's Impact on Materials and Structures

## 15.1 ABIOTIC RECEPTORS

Chapter 1 introduced the connections between stressors and receptors. The previous chapters in Part II address human and ecological receptors. These dominate concerns about receptor impacts, but air pollution's damage to the things built by civilizations are also an important concern for society.

Chapter 14 considered the direct ecological injury brought by exposures to air pollutants, as well as the indirect impacts from even slight decreases in the pH of rainfall and other environmental conditions attributable to air pollution. These include abiotic features of ecosystems. However, many of these same processes also have substantial impact on materials important to humans.

Air pollution's impacts on materials and structures follow the same type of pathways as those that affect human health and ecosystems. The pathway may be by a direct release of a damaging agent (e.g. acidic aerosols or oxidizers, e.g. ozone [ $O_3$ ]):

Source → Air pollutant → Transport → Receptor (15.1)

The pathway may also involve atmospheric transformation of a less corrosive substance into a damaging agent (e.g. reactions to form acids):

Source → Precursor → Transformation  
→ Corrosive agent → Transport → Receptor  
(15.2)

Damage to materials increases societal costs, both financially and culturally. For example, in addition to the chemical reactions with material matrices within the structures, dry deposition of acidic compounds can coat buildings and other structures, which can lead to very high cleaning and maintenance costs. Coatings and paints are also vulnerable to air pollution, especially

sulfur dioxide ( $SO_2$ ), which reacts in the atmosphere to become sulfuric acid ( $H_2SO_4$ ). As evidence, the use of acid-resistant coatings has led to an average increase in the cost of \$5.00 per vehicle manufactured in the U.S., which translates into \$61 million per year.<sup>1</sup> The costs are much greater given this estimate applies to merely one sector of a vast global marketplace.

Material damage results from a wide range of air pollutants in all physical phases. Gases and vapors may be corrosive inherently, or they may be transformed chemically in the atmosphere into highly reactive substances, such as the formation of acids from oxides of sulfur and nitrogen. Material damage may also result from exposure to chemicals in aerosols that are deposited on materials and subsequently react to surfaces and crevices as acid aerosols and the dissolution of many types of materials by acid-forming gases. Exposure to acidic gases decreases the optimal life of paints, as well as reacts with minerals in stone and cement structures and products, compared to ordinary weathering processes, e.g. wind, moisture, temperature fluctuations, sunlight, and other meteorological factors. Building materials are expected to undergo weathering, but the rate increases dramatically with increasing exposure to air pollutants. In some cases, the first stages of weathering are actually protective, as when rust, verdigris, and other oxides form on metals. The oxidized layer acts as a protective film against subsequent corrosive attacks on the materials. However, the film can be rendered less effective in the presence of air pollutants, e.g. when  $SO_2$  that is converted to sulfates during deposition reacts with calcite (made up of calcium carbonate,  $CaCO_3$ ) in limestone and marble,<sup>a</sup> and with gypsum (calcium sulfate dihydrate).<sup>2</sup>

Similarly, the natural process of metal corrosion from exposure to natural environmental elements is hastened by exposure to anthropogenic pollutants, in particular  $SO_2$  or other acidic substances, which render

<sup>a</sup> Marble is metamorphosed limestone.

the protective film less effective. The rate of deterioration is determined by the pollutant concentration, the deposition rate, and the structural material's permeability and moisture content. These factors lead to increased exposed surface areas and contact with aqueous phase contaminants. However, the extent of the damage to materials produced by the pollutant species above and beyond that from the natural weathering processes is uncertain.

As with many elements of social welfare, monetized value represents a fraction of the real worth of materials that make up culturally and historically important objects, such as works of art and monuments. From an engineering standpoint, corrosion can also translate into diminished optimal lives of products and structures. For example, air pollutants can contribute to the dilapidation of infrastructures, including bridges, roads, power grids, and communication systems. As such, material damage translates into threats to public safety.

## 15.2 EFFECTS ON METALS

The principal effects of air pollutants on metals are corrosion of the surface, with eventual loss of material mass from the surface, and alteration in the electrical properties of the metals. Metals are divided into two categories: ferrous and nonferrous. Ferrous metals contain iron and include various types of steel. Nonferrous metals, such as zinc, aluminum, copper, and silver, do not contain iron.

Three factors influence the rate of corrosion of metals: moisture, type of pollutant, and temperature. In general, dry or cold locations tend to have the lowest rate of corrosion, the tropics and marine environments intermediate, and polluted industrial locations the highest rate of corrosion.

The role of moisture in corrosion of metals and other surfaces is twofold: surface wetness acts as a solvent for containments and is a medium for electrolysis. The presence of sulfate and chloride ions accelerates the corrosion of metals. Metal surfaces can come into contact with liquid water repeatedly over a period of time as the humidity fluctuates.

Several studies have been conducted in urban areas to relate air pollution exposure and metal corrosion. In Tulsa, Oklahoma, wrought iron disks were exposed in various locations.<sup>4</sup> Using weight change as a measure of air pollution corrosion, the results indicated higher corrosion rates near industrial sectors containing an oil refinery and fertilizer and  $H_2SO_4$  manufacturing facilities. Steel plates at 20 sites in Chicago, Illinois, were exposed at 20 locations, at which  $SO_2$  concentrations were also measured.<sup>5</sup> Figure 15.1 shows the

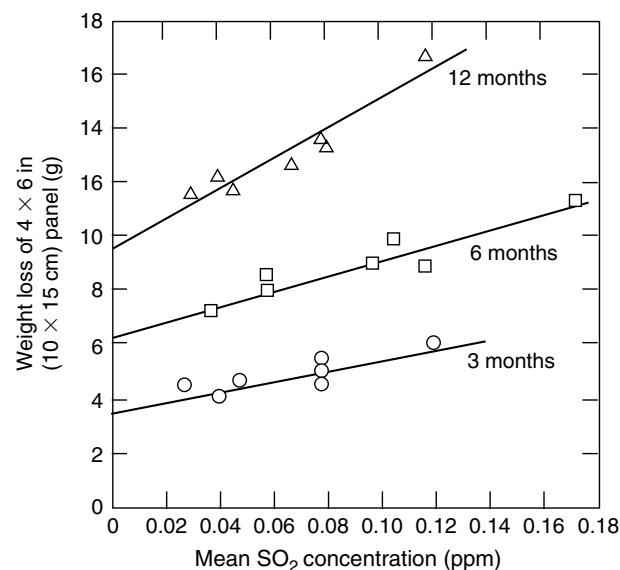


FIGURE 15.1 Relationship between corrosion of mild steel and corresponding mean sulfur dioxide concentration at seven Chicago, Illinois, sites. *Upham JB. J Air Pollut Control Assoc 1967;17:400.*

relationship between weight loss during 3-, 6-, and 12-month exposure periods and the mean  $SO_2$  concentration. Corrosion was also found to be higher in downtown locations than in suburban areas. Nonferrous metals are also subject to corrosion, but to a lesser degree than ferrous metals. Table 15.1 compares the weight loss of several nonferrous metals over a 20-year period.<sup>6</sup> The results vary depending on the type of exposure present. For example, corrosion values at an industrial site in England were 100 times higher than those found in an arid African location.<sup>3</sup>

Zinc is often used as a protective coating over iron to form galvanized iron. In industrial settings exposed to  $SO_2$  and humidity, this zinc coating is subject to sufficient corrosion to destroy its protective capacity. The useful life of a zinc-coated galvanized sheet has been studied in different environmental settings.<sup>7</sup> Table 15.2 shows the predicted useful life as a function of  $SO_2$  concentration.

Aluminum appears to be resistant to corrosion from  $SO_2$  at ambient air concentrations. Aluminum alloys tend to form a protective surface film that limits further corrosion upon exposure to  $SO_2$ . Laboratory studies at higher concentrations (280 ppm) show corrosion of aluminum at higher humidities (>70%), with the formation of a white powder of aluminum sulfate.

Copper and silver are used extensively in the electronics industry because of their excellent electrical conductivity. These metals tend to form a protective surface coating which inhibits further corrosion. When exposed to  $H_2S$ , a sulfide coating forms, increasing the resistance across contacts on electrical switches.<sup>8</sup>

TABLE 15.1 Weight Loss of Metal Panels\* after 20 years' Exposure in Various Atmospheres (c.1930–1954)<sup>§</sup>

City	Exposure Classification	Average Loss in Weight (%)					
		Commercial Copper (99.9% + Cu)	Commercial Aluminum (99% + Al)	Brass (85% Cu, 15% Zn)	Nickel (99% + Ni)	Commercial lead (99.92% Pb, 0.06% Cu)	Commercial zinc (99% Zn, 0.85% Pb)
Altoona, PA	Industrial	6.1	—	8.5	25.2	1.8	30.7
New York, NY	Industrial	6.4	3.4	8.7	16.6	—	25.1
La Jolla, CA	Seacoast	5.4	2.6	1.3	0.6	2.1	6.9
Key West, FL	Seacoast	2.4	—	2.5	0.5	—	2.9
State College, PA	Rural	1.9	0.4	2.0	1.0	1.4	5.0
Phoenix, AZ	Rural	0.6	0.3	0.5	0.2	0.4	0.8

\* Panels: 9 × 12 × 0.035 in (22.86 × 30.48 × 0.089 cm).

§ Data from Copson HR. Report of ASTM Subcommittee VI, of Committee B-3 on Atmospheric Corrosion, Am Soc Test Mater Special Technical Publication No. 175, 1955. Used by permission of the American Society for Testing and Materials, Philadelphia.

Source: Yocom JE, Upham JB. Effects of economic materials and structures. In: Stern AC, editor. Air pollution, 3rd ed., vol. I. New York: Academic Press; 1977. p. 80.

TABLE 15.2 Predicted Useful Life of Galvanized Sheet Steel with a 53-μm Coating at an Average Relative Humidity of 65%\*

SO <sub>2</sub> Concentration (μg m <sup>-2</sup> )	Type of Environment	Useful Life (years)		
		Predicted Best Estimate	Predicted Range	Observed Range
13	Rural	244	41.0	30–35
130	Urban	24	16.0–49.0	
260	Semi-industrial	12	10.0–16.0	15–20
520	Industrial	6	5.5–7.0	
1040	Heavy industrial	3	2.9–3.5	3–5

\* Yocom JE, Upham JB. Effects of economic materials and structures. In: Stern AC, editor. Air pollution, 3rd ed., vol. I. New York: Academic Press; 1977. p. 80.

It should be noted that metal damage research has been focused on a rather small subset of air pollutants' corrosion of metals and metal compounds, notably SO<sub>2</sub>, O<sub>3</sub>, and particulate matter.

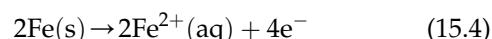
Metallic materials can also be damaged following deposition of acid aerosols and the dissolution of acid-forming gases on surfaces, increasing the corrosion of metals.<sup>9</sup>

Actually, the heterogeneous oxidation of metals is protective by forming an oxide coating, e.g. tarnish and rust. Copper tarnish, e.g., is a solid-gaseous reaction, producing a resistant coating of copper oxide:

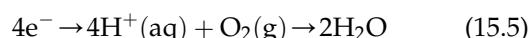


Corrosive action of metals often includes a galvanic process. That is, the liquid water reaching the metal surface either from precipitation or from condensation becomes an electrolyte solution with two dissimilar metals. The positive ions (cations) are attracted to

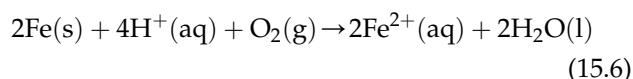
the negatively charged cathode and the negative ions (anions) are attracted to the positively charged anode. Thus, rust is a redox reaction that begins with the formation of iron cations via half-reactions:



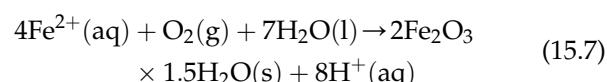
and,



Leading to the full reaction:



The divalent iron cation can then move toward the metal surface and precipitate as a hydrated form of ferric oxide [iron(III)oxide] which coats the metal:



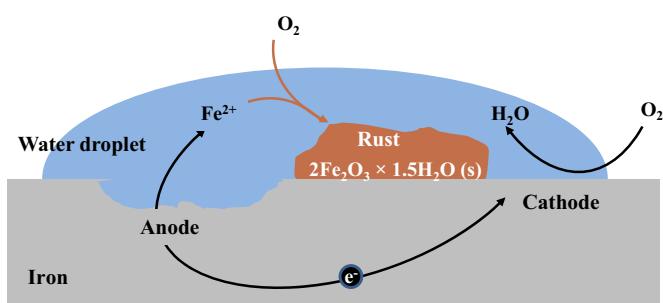


FIGURE 15.2 Galvanic corrosion of iron. (For color version of this figure, the reader is referred to the online version of this book.)

These reactions emphasize the importance of the physical phase of the contaminant, as well as the physical phase of the medium or substrate. Notably, the liquid phase of the water not only allows for the contact between the contaminants and the corroding surface, but also serves as the vehicle in which the ions form, undergo galvanic change, and are transported to the surface (Figure 15.2).

### 15.3 EFFECTS ON STONE

The primary concern in regard to air pollution damage to stone structures is the soiling and deterioration of limestone, which is widely used as a building material, and for its metamorphosed form, i.e. marble, in statuary.<sup>1</sup> Figure 15.3 shows the long-term effects of urban air pollution on the appearance of stone masonry. Many buildings in older cities have been exposed to urban smoke,  $SO_2$ , and  $CO_2$  for decades or centuries. The surfaces have become soiled and are subjected to chemical attack by acid gases. Exterior building surfaces are also subjected to a wet-dry cycle induced by changes in rain and humidity.  $SO_2$  and water react with limestone ( $CaCO_3$ ) to form calcium sulfate ( $CaSO_4$ ) and gypsum ( $CaSO_4 \times 2H_2O$ ). These two sulfates are fairly soluble in water, causing deterioration in blocks and in the mortar used to join the blocks. The soluble calcium sulfates can penetrate into the pores of the limestone and then recrystallize and expand, causing further deterioration of the stone.  $CO_2$  in the presence of moisture forms carbonic acid. This acid converts the limestone into bicarbonate, which is also water soluble and can be leached away by rain. This mechanism is present in the deterioration of marble statues.

The solid layer protection for metals discussed in the previous section also occurs on stone. For example, the calcium carbonate in limestone materials does not appear to react with sulfuric

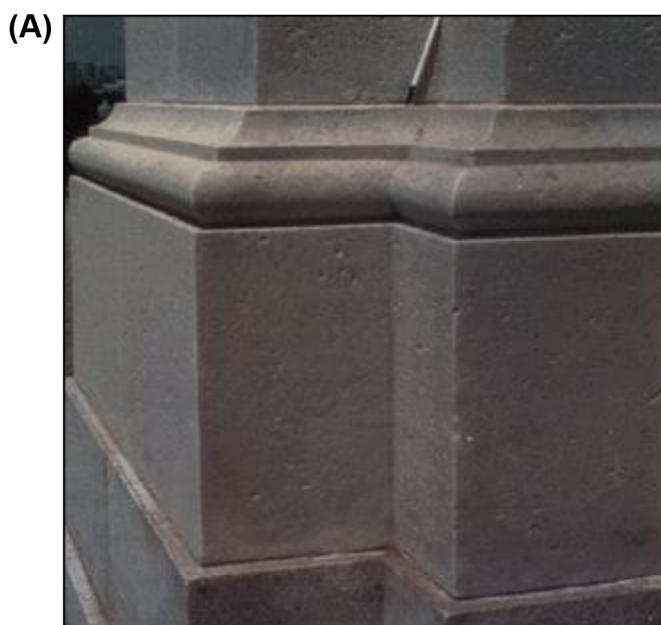


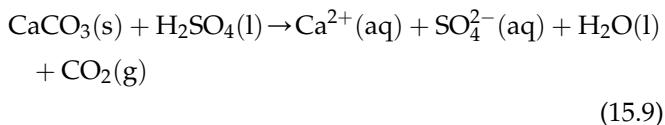
FIGURE 15.3 Effects of urban air pollution on materials. (A) Pock marks in marble column on the south side of the U.S. Capitol building. Silicate mineral inclusions in the marble loosen and fall out when the calcite around them is dissolved by precipitation with pH that has been lowered (i.e. higher acidity) by urban air pollution. (B) Marble block that forms the northeast corner of the Capitol balustrade shows preferential erosion of the calcite around a silicate mineral inclusion. (For color version of this figure, the reader is referred to the online version of this book.) Photos: U.S. Geological Survey. <http://pubs.usgs.gov/gip/acidrain/site1.html>; [accessed 29.10.13].

acid. The heterogeneous reaction (three phases) does indeed occur:



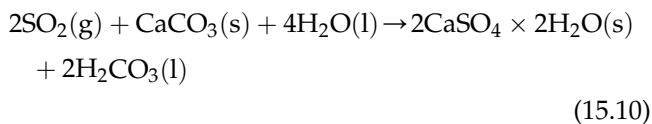
Similar to the tarnish and rust of metals, the calcium sulfate ( $CaSO_4$ ) is a resistant solid layer that protects the stone. These coatings on both the minerals and the metals begin to become less effective as acidic air

pollution increases the rates of oxidation and other corrosive reactions to the point that the natural processes cause deeper and more extensive damage into metals and stone due to increased ionic strength in the water to which they are exposed. Thus, [reaction \(15.8\)](#) must be reformulated when water is present, allowing the  $\text{CaCO}_3$  to become dissolved and aqueous (aq) ions to be released:



This ionic reaction is the corrosive one. Thus, comparing the two reactions, the solid phase  $\text{CaSO}_4$  is protective, but the cation ( $\text{Ca}^{2+}$ ) and anion ( $\text{SO}_4^{2-}$ ) increase corrosivity. This is the same type of process as when the ions in the half-reactions involved in rust, including the increase in  $\text{H}^+$  (i.e. decreasing pH), overcome the protective layer on metals. The increased ionic strength at least partially explains the difference in corrosion of buildings and structures that are protected from direct rainfall *versus* those that are sheltered under the same atmospheric conditions. That is, with identical  $\text{SO}_2$  concentrations, the protective layer is overridden in the unsheltered area due to increased moisture (i.e. water is needed for the ions).

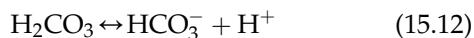
As evidence of surface destruction from air pollution, the dry deposition of  $\text{SO}_2$  enhances the effects of environmental elements on calcareous (limestone, marble, and cement) materials by converting calcium carbonate (calcite) to calcium sulfate dihydrate (gypsum):



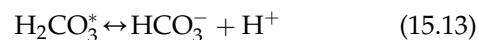
The rate of deterioration is determined by the  $\text{SO}_2$  concentration, the deposition rate, and the stone's permeability and moisture content; however, the extent of the damage to stones produced by the pollutant species above and beyond that from the natural weathering processes is uncertain. Note also that this reaction produces carbonic acid ( $\text{H}_2\text{CO}_3$ ), which is a naturally occurring component of many surface waters and is itself corrosive. In addition,  $\text{H}_2\text{CO}_3$  exists in equilibrium with carbon dioxide and water:



However, it also dissociates into the bicarbonate ions:



This increasing pH (release of  $\text{H}^+$ ) and ionic concentrations can lead to additional material damage. For many environmental situations,  $\text{H}_2\text{CO}_3$  includes dissolved  $\text{CO}_2$  (i.e.  $\text{CO}_2(\text{aq})$ ). An asterisk is added, i.e.  $\text{H}_2\text{CO}_3^*$ , to indicate the presence of both chemical species in equilibrium:



The bicarbonate ion then can dissociate into carbonate ions and additional hydrogen ions:



Again, the ionic strength and pH are major factors in the destruction of stone and cement structures. Most of the damage is the result of the gas–solid heterogeneous reaction of  $\text{SO}_2$  and  $\text{CaCO}_3$ . However, the ancillary effect of adding  $\text{H}_2\text{CO}_3^*$ ,  $\text{H}^+$ , and other ions in the aqueous phase exacerbates and increases the rate of degradation. Instead of attack by ions and acids in normal rain ( $\text{H}_2\text{CO}_3^*$  is the main reason that normal rain has a  $\text{pH} < 6$ ), the sequential additional acidity from [reaction \(15.8\)](#) adds to the damage and increases the rate of damage. Thus, the continuously increasing  $\text{CO}_2$  concentrations in the troposphere in recent decades would be expected to be accompanied by increased corrosion of stone structures.

## 15.4 EFFECTS ON FABRICS AND DYES

The major effects of air pollution on fabrics are soiling and loss of tensile strength. Oxides of sulfur are considered to cause the greatest loss of tensile strength. The mechanism is not understood, but it is likely that fine droplets of  $\text{H}_2\text{SO}_4$  aerosol deposit on the very thin nylon fibers, causing them to fail under tension. The reactions in the previous sections may apply as well. Cellulose fibers are also weakened by  $\text{SO}_2$ , possibly due to reactions similar to [reaction \(15.8\)](#), i.e. gas–solid heterogeneous reactions. Cotton, linen, hemp, and rayon are subject to damage from  $\text{SO}_2$  exposure.

A study in St Louis, Missouri, found that urban air pollution affects the tensile strength of cotton duck material.<sup>10</sup> Samples were exposed at seven locations for up to 1 year. [Figure 15.4](#) shows the relationship between tensile strength and pollutant exposure. Substantial loss of fabric strength was observed following exposures to sulfur trioxide at two levels of ambient air exposure. At high exposure (5.5 mg  $\text{SO}_3$  per square decimeter per day, i.e.  $5.5 \text{ mg dm}^{-2} \text{ day}^{-1}$ ) the material lost almost all of its strength after 1 year; and even the lower exposed (0.6 mg  $\text{SO}_3 \text{ dm}^{-2}$

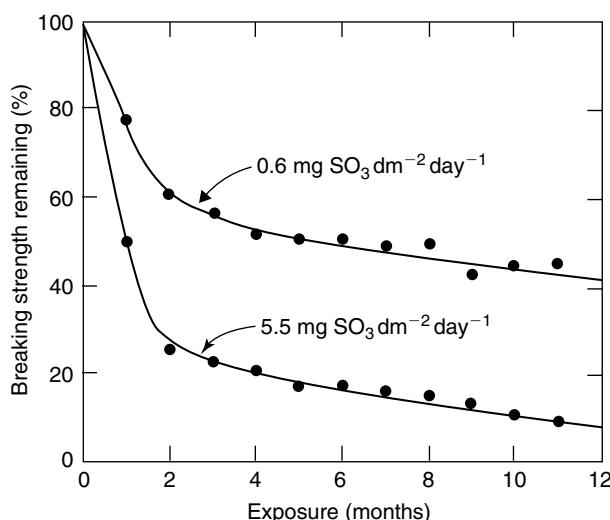


FIGURE 15.4 Effects of sulfation and time on tensile strength of cotton duck. Ref. 10.

day<sup>-1</sup>) materials exhibited less than one-half its initial tensile strength when exposed to air pollution for 1 year.

Particulate matter contributes to the soiling of fabrics. The increased frequency of washing to remove dirt results in more wear on the fabric, causing it to deteriorate in the cleaning process. This also means that any pollutants in detergents and other products needed for these additional washings will be released into sewers or septic systems, with a potential for surface and ground water contamination, including the addition of nutrients which can lead to eutrophication of lakes and other surface waters.

In addition to air pollution damage to fabrics, the dyes used to color fabrics have been subject to fading caused by exposure to air pollutants. Since the early 1900s, fading of textile dyes has been a continuing problem. The composition of dyes has been altered several times to meet demands of new fabrics and to "solve" the fading problem. Before World War I, dyes used on wool contained free or substituted amino acid groups, which were found to be susceptible to exposure to nitrogen dioxide (NO<sub>2</sub>).

When cellulose acetate rayon was introduced in the mid-1920s, previous dye technologies were replaced with new chemicals called dispersive dyes. Not long after their initial use, fading of blue, green, and violet shades began to be observed in material exposed to nitrogen oxides. The fabric was marked by a reddening discoloration. Laboratory studies duplicating ambient air levels of NO<sub>2</sub> and humidity reproduced these effects.<sup>11</sup>

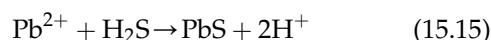
Ozone has also been found to cause fading of material. This was discovered when white fabrics developed a yellow discoloration.<sup>12a,12b</sup> This finding has led researchers to investigate the effects of O<sub>3</sub> on other chemicals added to the material, including optical brighteners, antistatic and soil-release finishes, and softeners. A very complex process occurred in which the dyes were migrating to the permanent-press-finish materials (e.g. softeners). Softeners have been found to be good absorbers of gases. Fading results from the combination of dye and absorbed NO<sub>2</sub> and O<sub>3</sub>. This combination with high relative humidities has caused color fading in numerous types of material and dye combinations. However, dyes and pigments have improved in recent decades, so that fading from airborne pollutants has become less of a problem.

## 15.5 EFFECTS ON LEATHER, PAPER, PAINT, AND GLASS

Sulfur dioxide affects the composition of leather and paper, causing significant deterioration. The major concern is the destruction of leather-bound books in the libraries of the world. SO<sub>2</sub> is absorbed by leather and converted to H<sub>2</sub>SO<sub>4</sub> which attacks the structure of the leather. Initially, the edges of the exposed back of the book begin to crack at the hinges. As the cracks expand, more leather is exposed and the cracks widen, with the back eventually falling off the book. Preventive measures now include storage in SO<sub>2</sub> free air.

The cellulose fiber in paper is attacked and weakened by SO<sub>2</sub>. Paper made before about 1750 is not significantly affected by SO<sub>2</sub>.<sup>13</sup> At about that time, the manufacture of paper changed to a chemical treatment process that broke down the wood fiber more rapidly. The process seems to introduce trace quantities of metals, which catalyze the conversion of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>. Sulfuric acid causes the paper to become brittle and more subject to cracking and tearing. New papers are available to minimize the interaction with SO<sub>2</sub>.

A hardened paint surface resists sorption by gases, although the presence of relatively high concentrations of 2620–5240 µg m<sup>-3</sup> SO<sub>2</sub> (1–2 ppm) increases the drying time of newly painted surfaces. Hydrogen sulfide (H<sub>2</sub>S) reacts with lead-based pigments:



This process blackens white and light-tinted paints. Although most paints no longer contain Pb-based

pigments, the reaction would be expected to be similar for other metal pigments, so a general metal (Me) reaction can be written for other divalent metals reacting with H<sub>2</sub>S:



If they indeed do behave like lead, other metal-based paints can discolor surfaces in several hours at a concentration of 70 µg m<sup>-3</sup> H<sub>2</sub>S (0.05 ppm).<sup>14</sup> In time the metal sulfide would be expected to oxidize to the original color. However, paints pigmented with titanium or zinc do not form a black precipitate in the first place, so the lead-based paint chemistry may not readily be generalizable to other metal pigments. Alkyd or vinyl vehicles and pigments contain no heavy metal salts for reaction with H<sub>2</sub>S.

Painted surfaces are also dirtied by particulate matter. Contaminating dirt can readily become attached to wet or tacky paint, where it is held tenaciously and forms focal points for gaseous sorption for further attack. Dirt that collects on roofs or in gutters, blinds, screens, windowsills, or other protuberances is eventually washed over external surfaces to mar decorative effects.

Automobile finishes can be damaged from scarring by calcium sulfate crystals formed when H<sub>2</sub>SO<sub>4</sub> in rain or dew react with dry deposited calcium.<sup>15</sup> As a result of air pollution regulations and advances in materials science, new coatings are being applied to metal and other surfaces. These coatings are also vulnerable to air pollution. For example, a study of chemical damage to melamine-acrylic base coat/clear-coat enamel paint systems by H<sub>2</sub>SO<sub>4</sub>, a simulated acid rain and sodium sulfate indicates that air pollutants in aqueous solution can damage surfaces coated with these enamels. In fact, these solutions penetrated the coating in a short time. Upon entry, chemical reactions occur which result in degradation of the polymer network. This alters the thermal properties and the appearance of the coating materials. The steps in degradation begin with hydrolysis of the melamine network, followed by either destruction or leaching of the melamine-acrylic composite.<sup>16</sup>

Glass is normally considered to be a very stable material. However, there is growing evidence that SO<sub>2</sub> air pollution may be accelerating the deterioration of medieval glass. A corrosion surface forms on these glass surfaces and the sulfate present helps prolong surface wetness. This condition is conducive to further attack and degradation of the glass surface.<sup>17</sup>

Inks and paints in paintings and other works of art are particularly vulnerable to O<sub>3</sub>. Because of the potential of O<sub>3</sub> to damage works of art, recommended O<sub>3</sub>

concentrations in museums, libraries, and archives are quite low, e.g. <0.013 ppm. Fading of art work has also been observed due to exposure to NO<sub>2</sub> and peroxyacetyl nitrate.<sup>18</sup>

## 15.6 EFFECTS ON RUBBER

Although it was known for some time that ozone cracks rubber products under tension, the problem was not related to air pollution. During the early 1940s, it was discovered that rubber tires stored in warehouses in Los Angeles, California, developed serious cracks. Intensified research soon identified the causative agent as O<sub>3</sub> that resulted from atmospheric reaction between sunlight (3000–4600 Å), oxides of nitrogen, and specific types of organic compounds, i.e. photochemical air pollution.

Natural rubber is composed of polymerized isoprene units. When rubber is under tension, O<sub>3</sub> attacks the carbon–carbon double bond, breaking the bond. The broken bond leaves adjacent C=C bonds under additional stress, eventually breaking and placing still more stress on surrounding C=C bonds. This “domino” effect can be discerned from the structural formulas in **Figure 15.5**. The number of cracks and the depth of the cracks in rubber under tension increase directly with increasing O<sub>3</sub> exposure.

Rubber products may be protected against ozone attack by the use of a highly saturated rubber molecule, the use of a wax inhibitor which will “bloom” to the surface, and the use of paper or plastic wrappings to protect the surface. Despite these efforts, rubber products generally still crack more on the west coast than on the east coast of the United States.

The elastomeric compounds, i.e. natural rubber and synthetic polymers and copolymers of butadiene, isoprene, and styrene, are especially susceptible to top degradation at even low concentrations of O<sub>3</sub>. These compounds are long-chain unsaturated organic molecules. Ozone is able to break the molecular chain at the carbon=carbon double bond; a chain of three oxygen atoms is added directly across the double bond, forming a five-membered ring structure.<sup>19</sup> The change in structure promotes the characteristic cracking of stressed/stretched rubber. Tensile strain of 5% generates surficial cracks in the rubber, which become more numerous with increased stress/stretching. The rate of crack growth depends on the degree of stress, the type of rubber compound, concentration, duration of contaminant exposure, velocity, and temperature.<sup>20a–20c</sup>

In one study, vulcanized natural rubber compounds were exposed for 24 h to varying O<sub>3</sub> concentrations under stressed conditions. Ozone concentrations were 60,

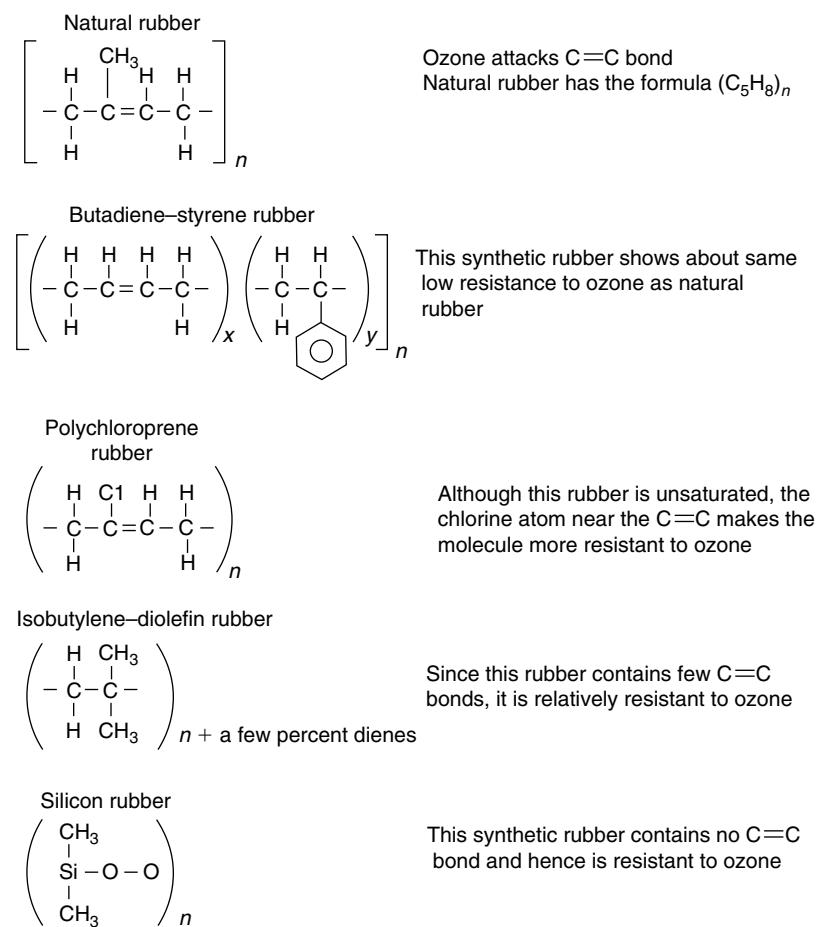


FIGURE 15.5 Susceptibility of natural and synthetic rubbers to attack by ozone.

80, 90, 100, and 120 ppb for durations of 2, 4, or 6 h. The 24 h mean O<sub>3</sub> concentrations ranged from 31 to 57.5 ppb. There was a clear relationship between the 24-h average O<sub>3</sub> concentration and the crack length frequencies on the

rubber surface.<sup>21</sup> Table 15.3 provides the mean 24-h O<sub>3</sub> concentration and lengths for two vulcanized natural rubber strips.

TABLE 15.3 Mean 24-h Ozone Concentrations Producing the Highest Frequency of Cracks of a Certain Length in the Middle and Central Zones of the Rubber Test Strips

Crack Length (mm)	1% Antiozonant 4010NA #		0.5% Antiozonant 4010NA	
	Middle Zones	Central Zones	Middle Zones	Central Zones
0.05–0.10	37.5	37.5	40.0	42.5
0.10–0.15	45.0	48.0	48.0	53.0
0.15–0.20	48.0	≥57.5	≥57.5	≥57.5
0.20–0.40	≥57.5	≥57.5	≥57.5	≥57.5

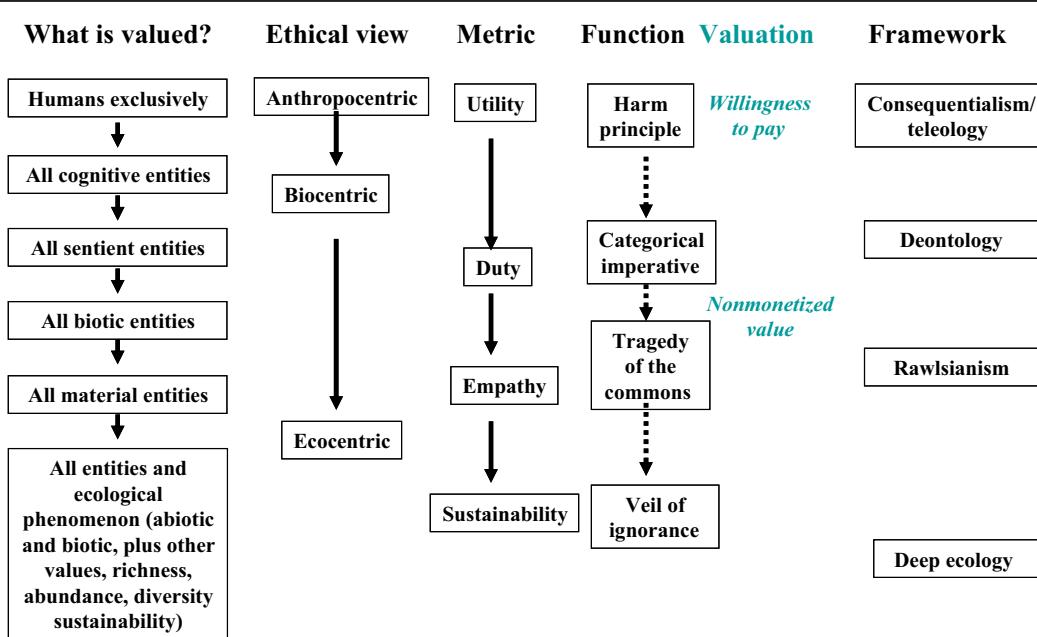
Ozone concentrations given in ppb.  
U.S. Environmental Protection Agency.

## 15.7 MATERIAL VALUE

The damage to materials is less important than human health and ecosystem effects, but the costs certainly affect society's welfare, threaten public safety, and lead to financial costs. Air pollution also destroys irreplaceable materials, including monuments, historically important structures and buildings, as well as works of art and cultural artifacts.

Materials generally have instrumental value, i.e. anthropocentric value based on somewhat arbitrary criteria. Material damage follows the prototypical stressor–receptor paradigm, but the value placed on the receptor is less intrinsic than health and ecological values. An example of intrinsic and instrumental values is shown in Table 15.4.

TABLE 15.4 Various Value Systems Related to Air Pollution.



Material damage is almost exclusively at the top of the diagram (human utility). The harm principle, categorical imperative, tragedy of the commons, and veil of ignorance are important ethical maxims recommended by John Stuart Mill, Immanuel Kant, Garrett Hardin, and John Rawls, respectively.

Adapted from: Vallero DA. Biomedical ethics for engineers: ethics and decision making in biomedical and biosystem engineering. Burlington (MA): Elsevier Academic Press; 2007; some information from: Meyers RB. Environmental values, ethics and support for environmental policy: a heuristic, and psychometric instruments to measure their prevalence and relationships. International conference on civic education research. 16–18 November, 2003 New Orleans, Louisiana; 2003.

## QUESTIONS

- Assuming that a relationship exists among corrosion, population, and sulfur dioxide, why might one expect this interdependence?
- Compare the solubilities in water of calcium carbonate, calcium sulfite, calcium sulfate, magnesium sulfate, and dolomite.
- Describe possible mechanisms for the deterioration of marble statuary.
- Explain why soiling and corrosion are hidden costs of air pollution.
- Describe possible preventive actions to limit deterioration of books and other print material in libraries.
- Explain the role of moisture in corrosion of materials.
- In your location, determine whether sulfur dioxide, ozone, or particulate matter contributes to soiling or corrosion problems.
- Describe why some types of synthetic rubber are less susceptible to ozone attack than natural rubber.
- Many people prefer cotton to synthetic fibers. What processes are available to increase cotton fabrics' resistance to the effects of air pollutants?

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## P A R T   I   I   I

# TROPOSPHERIC POLLUTION

The four chapters that comprise Part III describe the physical, chemical, and biological characteristics of air pollutants. Any description of air pollution processes and mechanisms must consider the inherent properties of the substance and how the substance behaves in the troposphere. From this perspective, the troposphere is not only the atmospheric layer where receptors are exposed to pollution, but the “reactor” and thermodynamic control volume where myriad transformations occur. It is also the layer that connects the biosphere, hydrosphere and the other layers of the atmosphere. Thus, most transport, as well as the biochemical and abiotic processes that determine the fate and harm caused by air pollution, take place in the troposphere.

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# Scale and Complexity of Air Pollution

Air pollution exists at all scales, from personal to global. Ambient air pollution scales may be further subdivided into local, urban, regional, continental, and global. The spheres of influence of the air pollutants themselves range from molecular (e.g. gases and nanoparticles) to planetary (e.g. dispersion of greenhouse gases throughout the troposphere). The spatial extent of the local scale is a radius of up to about 5 km on the earth's surface. The urban scale extends the radius to about 50 km. The regional scale radius is from 50 to 500 km. Continental scales are from 500 to several 1000 km in any direction, but is often the direction of the winds aloft, since this is the route traversed by the pollutant. Of course, the global scale extends worldwide.

## 16.1 MECHANICAL SCALE AND COMPLEXITY

Atmospheric physics is discussed in detail in Chapters 2 and 28. Respiratory physics, i.e. fluid mechanics of the respiratory system, is discussed in Chapter 9. Cellular transport is discussed throughout this text. The same laws of motion apply to every scale. Since physics and chemistry both play prominent roles in chemical transformation, the dynamics must be understood at each scale. Indeed, some of the terms used by chemists are the same as those used by physicists, but their meanings are somewhat nuanced, e.g. kinetics, equilibrium, and dynamics.

Numerous air terms have different connotations within the contexts of scale and complexity. For example, the term particle at the atomic scale usually means an atom, molecule, ion, or even an electron; whereas particle in most air pollution discussions means a single aerosol. Even among air pollution modelers and other air pollution experts, particle has a somewhat different meaning. Models often use the particle concept to represent a part of the atmosphere, analogous to a geometric point as a theoretical component of an air mass. Similarly, the term diffusion to most physicists and chemists means molecular movement due to

concentration gradients, but for others working in air pollution, the term is nearly synonymous with the spread and dilution of substances in a plume.<sup>a</sup> The term pathway also has scale and complexity dependence, such as the pathways representing modes of action leading to an effect from a dose at the cellular scale, as used in Chapter 7, *versus* the pathways of exposure that are larger scale (e.g. air that is inhaled, water that is consumed, soil that is contacted by skin), as used in Chapter 8. Ambiguity is always problematic in the life sciences, especially the biomedical and environmental sciences, and engineering. Therefore, this chapter seeks to clarify and differentiate the meanings of key terms within the context of time and space.

Mechanics is the field of physics concerned with the motion and the equilibrium of bodies within particular frames of reference. Air pollution scientists make use of the mechanical principles in practically every aspect of pollution, from the movement of fluids that carry contaminants to the forces within substances that affect their properties to the relationships between matter and energy within organisms and ecosystems. Engineering mechanics is important, for example, the design of pollution control equipment must properly account for statics and dynamics. Fluid mechanics is a particularly important branch of the mechanics of air pollution.

Statics is the branch of mechanics that is concerned with bodies at rest with relation to some frame of reference, with the forces between the bodies, and with the equilibrium of the system. It addresses rigid bodies that are at rest or moving with constant velocity. Hydrostatics is a branch of statics that is essential to environmental science and engineering in that it is concerned with the equilibrium of fluids (liquids and gases) and their stationary interactions with solid bodies, such as pressure. While many fluids are considered by environmental assessments, the principal fluids are water and air.

Dynamics is the branch of mechanics that deals with forces that change or move bodies. It is concerned with accelerated motion of bodies. It is an especially important

<sup>a</sup> This text's preferred term for the spread of plume is "dispersion".

science and engineering discipline because it is fundamental to understanding the movement of contaminants through the environment. Dynamics is sometimes used synonymously with kinetics. However, this text prefers the engineering approach to treat kinetics as one of the two branches of dynamics, with the other being kinematics. Dynamics combines the properties of the fluid and the means by which it moves. This means that the continuum fluid mechanics vary by whether the fluid is viscous or inviscid, compressible or incompressible, and whether flow is laminar or turbulent. For example, the properties of the two principal environmental fluids, i.e. water in an aquifer and an air mass in the troposphere, are shown in [Table 16.1](#). Thus, in air pollution mechanics, turbulent systems are quite common. However, within smaller systems, such as control technologies, laminar conditions can be prominent.

Kinematics is concerned with the study of a body in motion independent of forces acting on the body. That is, kinematics is the branch of mechanics concerned with motion of bodies with reference to force or mass. This is accomplished by studying the geometry of motion irrespective of what is causing the motion. Therefore, kinematics relates position, velocity, acceleration, and time. Chapters 24, 25, 29, 30, and 31 extensively apply kinematic principles. Aerodynamics and hydrodynamics are the important branches of environmental mechanics. Both are concerned with deformable bodies and with the motion of fluids. Therefore, they provide an important underlying aspect of contaminant transport and movements of fluids, and consider fluid properties such as compressibility and viscosity. These are crucial properties in explaining the movement of contaminants within plumes, flows in vents and pipes, and design of air pollution control systems.

Kinetics is the study of motion and the forces that cause motion. This includes analyzing force and mass as they relate to translational motion. Kinetics also considers the relationship between torque and moment of inertia for rotational motion. Note that chemists often refer to kinetics as those reactions that have yet to reach equilibrium, i.e. equality between both sides of the reaction. Indeed, this is the connotation used in Chapters 17 and 18. Thus,

**TABLE 16.1** Contrasts between Plume in Ground Water and Atmosphere

	Ground Water Plume	Air Mass Plume
General flow type	Laminar	Turbulent
Compressibility	Incompressible	Compressible
Viscosity	Low viscous $(1 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ at 288 K)	Very low viscosity $(1.781 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ at 288 K)

kinetic reactions employ a one-direction arrow ( $\rightarrow$ ), whereas equilibria show a two-direction arrow ( $\leftrightarrow$ ).

A key concept for environmental dynamics within the context of physical motion is that of linear momentum, the product of mass and velocity. A body's momentum is conserved unless an external force acts upon a body. Kinetics is based on Newton's first law of motion, which states that a body will remain in a state of rest or will continue to move with constant velocity unless an unbalanced external force acts on it. Stated as the law of conservation of momentum, linear momentum is unchanged if no unbalanced forces act on a body. Or, if the resultant external force acting on a body is zero, the linear momentum of the body is constant.

Kinetics is also based upon Newton's *second law of motion*, which states that the acceleration of a body is directly proportional to the force acting upon that body, and inversely proportional to the body's mass. The direction of acceleration is the same as the force of direction. The equation for the second law is:

$$F = \frac{dp}{dt} \quad (16.1)$$

where,  $p$  = momentum.

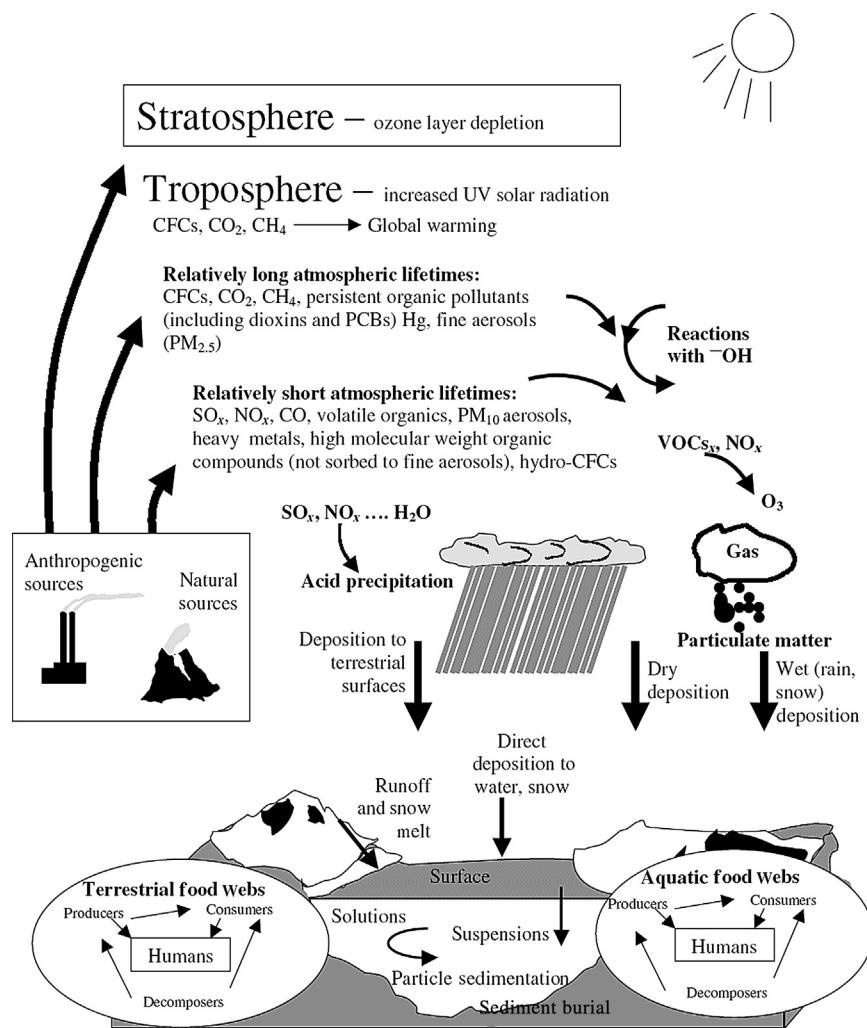
Newton's third law of motion states that for every acting force between two bodies, there is an equal but opposite reacting force on the same line of action:

$$F_{\text{reacting}} = -F_{\text{acting}} \quad (16.2)$$

Another force that is important in air pollution is friction, which is a force that always resists motion or an impending motion. Friction acts parallel to the contacting surfaces. When bodies come into contact with one another, friction acts in the direction opposite to that which is bringing the objects into contact. Forces are an important part of air pollution control systems. As such, forces are discussed in detail in Chapters 30 and 31.

Air pollutants may move within one environmental compartment, such as a source within a home. Most often, however, pollutants move among numerous compartments, such as when a contaminant moves from the source to the atmosphere, until it is deposited to the soil and surface waters, where it is taken up by plants, and eaten by animals. Science is by necessity compartmentalized among physics, chemistry, and biology. However, complex topics like pollutant transport require that all three of the sciences be considered. Thus, while the focus and language of this chapter is predominantly on physical transport, discussing chemical and biological phenomena at the same time can help to explain the concepts as they may be expected to occur in the real world.

The general behavior of contaminants after they are released is shown in [Figure 16.1](#). The movement of pollutants is known as transport. This is half of the often cited duo of environmental "fate and transport". Fate is an



**FIGURE 16.1 The physical movement and accumulation of contaminants after release.** Commission for Environmental Cooperation of North America. The sound management of chemicals (SMOC) Initiative of the Commission for Environmental Cooperation of North America: overview and update. Montreal (Canada); 2002; Adapted in Vallero DA. Environmental contaminants: assessment and control. Burlington (MA): Elsevier Academic Press; 2004. Notes: CFC = chlorofluorocarbon; PM = particulate matter; VOC = volatile organic compound.

expression of what contaminant becomes after all the physical, chemical, and biological processes of the environment have acted. It is the ultimate site of a pollutant after its release. The pollutant will undergo numerous changes in location and form before reaching its fate. Throughout the contaminant's journey, it will be physically transported and undergo coincidental chemical processes, known as transformations, such as photochemical and biochemical reactions (see Chapters 17 and 18). Certainly, fate implies more than physical transport. The fate of an air pollutant depends on abiotic chemical reactions, such as photolysis, endothermic, and exothermic reactions, and mechanical separation processes, as well as biotic transformation, e.g. microbial degradation.<sup>b</sup>

Usually, in the discussions of fate and transport, the reactions are those that occur in the ambient environment. The intentional treatment and control processes usually fall under the category of environmental engineering. For example, if a chlorinated solvent is released from a factory's vents and stacks, it may undergo transformations in the atmosphere before it reaches the soil. In the soil, the microbially mediated transformations may change the chemical structure to a simpler molecule, e.g. by mineralization. This lighter molecule may have a sufficiently high vapor pressure, which allows it to again move into the atmosphere, where it undergoes additional photochemical transformation, increasing its aqueous solubility. This new compound

<sup>b</sup> Of course, biotic processes employ the same principles as abiotic, e.g. electron transfer and redox, but they take place in different substrates (i.e. cells), at different rates, and use different substances (e.g. enzymes as catalysts).

is deposited onto the surface of the lake, where it is taken up by algae. The algae are food for fish, so this transformation product is bioaccumulated and further transformed in the fish. If the fish is eaten by humans, the ultimate fate of the original air pollutant released from the stacks and vents is in human tissue. Thus, the fate is a consequence of physics, chemistry, and biology.

Environmental engineering has a slightly different perspective of fate. Engineers seek control and design systems to accomplish outcomes. For example, engineers employ remediation reactions, such as thermal and mechanical separation processes, as well as abiotic chemical reactions, such as precipitation and hydrolysis, as well as biological processes, such as microbial metabolic biochemical reactions, to break down toxic substances into simpler, less toxic compounds. The same processes and reactions that occur in the ambient environment mentioned in the previous paragraph are used by engineers for the treatment and control processes that usually fall under the category of environmental engineering. Engineers have simply changed the scale from large environmental compartments like air masses and lakes to smaller reactors, such as pollutant collection and treatment devices.

Physical transport is influenced by the kinematics and mechanics of fluids. In addition, it is important to identify when these processes reach equilibrium, such as when a chemical is sequestered and stored. Fate is often described according to environmental media or compartments (see Chapter 18).

Understanding air pollutant transport begins with the characteristics of environmental fluids. Recall from Chapter 1 that a fluid is a collective term that includes all liquids and gases. A liquid is matter that is composed of molecules that move freely among themselves without separating from each other. A gas is matter composed of molecules that move freely and are infinitely able to occupy the space with which they are contained at a constant temperature. A fluid is a substance that will deform continuously upon the application of a shear stress; i.e. a stress in which the material on one side of a surface pushes on the material on the other side of the surface with a force parallel to the surface.

Fluids are generally divided into two types: *ideal* and *real*. The former has zero viscosity and, thus, no resistance to shear (explained below). An ideal fluid is incompressible and flows with uniform velocity distributions. It also has no friction between moving layers and no turbulence (i.e. eddy currents). On the contrary, a real fluid has finite viscosity, has nonuniform velocity distributions, is compressible, and experiences friction and turbulence. Real fluids are further subdivided according to their viscosities. A *Newtonian fluid* is one that has a constant viscosity at all shear rates at a constant temperature and pressure. Water and most solvents are Newtonian fluids. However, environmental

engineers are confronted with non-Newtonian fluids, i.e. those with viscosities not constant at all shear rates. Sites contaminated with drilling fluids and oils have large quantities of non-Newtonian fluids onsite.

As mentioned, one of the concepts of the particle is a theoretical point that has mass and location, but no geometric extension. We can observe this particle as it moves within the fluid as a representation of where that portion of the fluid is going and at what velocity. Another spatial and thermodynamic concept is the control volume, which is an arbitrary region in space that is defined by boundaries. The control volume's boundaries may be either stationary or moving. The control volume is a means of applying the first law of thermodynamics, i.e. conservation of mass and energy. The amount of mass or energy entering a control volume must equal the amount exiting the control volume minus what remains in the control volume. Thus, the control volume is useful in measuring and modeling the amount of an air pollutant entering, remaining, and exiting a parcel of air, water, soil, or even a cell or parcel of tissue in an organism (e.g. pharmacokinetics).

Contaminant transport requires motion. This highlights the need of understanding the spatial context and complexity of not only the air pollutant, but of the fluid behavior. The forces acting on a fluid may be body forces or surface forces. The former are forces that act on every particle within the fluid, occurring without actually making physical contact, such as gravitational force. The latter are forces that are applied directly to the fluid's surface by physical contact.

As mentioned in Chapter 2, in physics, stress represents the total force per unit area acting on a fluid at any point within the fluid volume. So, stress at any point  $P$  is:

$$\sigma(P) = \lim_{\delta A \rightarrow 0} \frac{\delta F}{\delta A} \quad (16.3)$$

where,  $\sigma(P)$  = vector stress at point  $P$ .

$\delta A$  = infinitesimal area at point  $P$ .

$\delta F$  = force acting on  $\delta A$ .

Fluid properties are characteristics of the fluid that are used to predict how the fluid will react when subjected to applied forces. If a fluid is considered to be infinitely divisible, that is, it is made up of many molecules that are constantly in motion and colliding with one another, this fluid is in continuum. That is, a fluid acts as though it has no holes or voids, meaning its properties are continuous (i.e. temperature, volume, and pressure fields are continuous). Assuming that a fluid is a continuum allows for the fluid's properties to be functions of position and time.

Fluid properties are important at every scale of air pollution. For example, fluid properties must be considered at the cellular scale, e.g. flow through cell membranes. Recall the discussion in Chapter 9 of the importance of Newtonian and non-Newtonian fluids in the cascade of

bronchial tubules in the lung, as well as the difference in flow from turbulent at the entry of air by inhalation to laminar flow at the blood–air exchange sites.

Such fluid properties can be represented by two fields. The density field is represented by:

$$\rho = \rho(x, y, z, t) \quad (16.4)$$

where,  $\rho$  = density of the fluid.

$x, y, z$  = coordinates in space.

$t$  = time.

The other fluid field is the velocity field:

$$\vec{v} = \vec{v}(x, y, z, t) \quad (16.5)$$

When a rate of change equals zero, the system is said to be in steady state. Thus, if the fluid properties and the flow characteristics at each position do not vary with time, the fluid is at steady flow:

$$\rho = \rho(x, y, z) \quad \text{or} \quad \frac{\partial \rho}{\partial t} = 0 \quad (16.6)$$

and

$$\vec{v} = \vec{v}(x, y, z) \quad \text{or} \quad \frac{\partial \vec{v}}{\partial t} = 0 \quad (16.7)$$

Conversely, a time-dependent flow is considered to be an unsteady flow. Any flow with unchanging magnitude and direction of the velocity vector  $\vec{v}$  is considered to be a uniform flow.

Fluids, then, can be classified according to observable physical characteristics of flow fields. A continuum fluids mechanics classification is shown in Figure 1.9. Laminar flow is in layers, whereas turbulent flow has random movements of fluid particles in all directions. In incompressible flow, the variations in density are assumed to be constant, while the compressible flow has density variations, which must be included in flow calculations. Viscous flows must account for viscosity while inviscid flows assume viscosity is zero.

The velocity field is very important in environmental modeling, especially in modeling plumes in the atmosphere and in groundwater, since the velocity field is a way to characterize the motion of fluid particles and provides the means for computing these motions. The velocity field may be described mathematically using Eqn (16.5). This is known as the Eulerian viewpoint.

Another way to characterize the fluid movement (i.e. flow) is to follow the particle (sometimes referred to as a “parcel”) as it moves, using time functions that correspond to each particle as shown in Figure 16.2. Recall from Chapters 6 and 9 that molecular diffusion is important at very small distances and for very small particles ( $\leq 0.1 \mu\text{m}$  diameter) given that Brownian motion allows

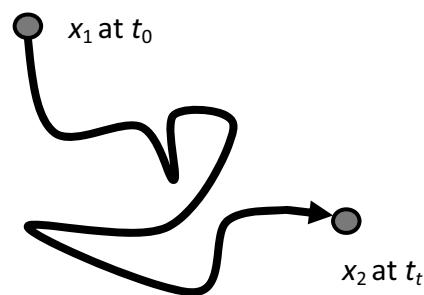


FIGURE 16.2 Random walk representing the movement of a particle; i.e. a hypothetical point that is moving in a random path during time interval  $(t_0 - t_1)$ . This is the theoretical basis for Lagrangian air plume models.

them to move in a “random walk” away from the air stream. Interception works mainly for particles with diameters between 0.1 and 1  $\mu\text{m}$ . The particle does not leave the air stream but comes into contact with the filter medium (e.g. a strand of fiberglass). Inertial impaction collects particles that are sufficiently large to leave the air stream by inertia (diameters  $\geq 1 \mu\text{m}$ ). This random walk of the particle provides what is known as the Lagrangian viewpoint, which is expressed mathematically as:

$$\vec{v} = [x(t), y(t), z(t)] \quad (16.8)$$

A Lagrangian plume model characterizes the plume by calculating the air dispersion from statistics of the trajectories of a large number of the particles (enough to represent the whole plume).

The major means by which air pollutants move in the atmosphere is advection, i.e. they move with the flow of the fluid where they reside, i.e. the air. This change in position in space is the fluid velocity ( $V$ ). This is a vector field quantity. Speed ( $V$ ) is the magnitude of the vector velocity  $V$  at some given point in the fluid, and average speed ( $\bar{V}$ ) is the mean fluid speed through a control volume’s surface. Therefore, velocity is a vector quantity (magnitude and direction), while speed is a scalar quantity (magnitude only). The standard units of velocity and speed are meter per second ( $\text{m s}^{-1}$ ).

Obviously, velocity is important in air pollution, especially with regard to complexity. For example, velocity<sup>c</sup> informs mixing rates after a pollutant is emitted into a plume. If an air pollutant is released into a well-mixed chamber, calculations of concentration would be simpler than an unmixed chamber. Unfortunately, this assumption translates into average concentrations within the entire chamber or plume. This is an example of the difficulty in stepping up laboratory or mesoscale findings to the real world. For example, an air pollutant plume is never homogeneous. It is certainly likely to have higher concentrations near the source, but it will also

<sup>c</sup>The distinction between velocity and speed is seldom made in air pollution.

have pockets of higher and lower concentrations given the variability of terrain, structures, albedo, clouds, temperature, and moisture. Even a small compartment, e.g. a room in a house, is never completely mixed, with regions of varying pollutant concentrations.

Pressure ( $p$ ) is also important at all scales. Recall that  $p$  is a force per unit area:

$$p = \frac{F}{A} \quad (16.9)$$

Thus,  $p$  is a type of stress that is exerted uniformly in all directions. This is arguably the most important type of stress in air pollution engineering, where it is common to use the term pressure instead of force to describe the factors that influence the behavior of fluids. The standard unit of  $p$  is the Pascal (Pa), which is equal to  $1 \text{ N m}^{-2}$ . For vapor pressure, partial pressures, and partitioning coefficients discussed in the next chapters, the most common units are the kilopascal (kPa) and millimeters of mercury (mm Hg). Pressure varies with area, as shown in Figure 16.3. In this example, the same weight (force) over different areas leads to different pressures, much higher pressure when the same force is distributed over a smaller area.

For a liquid at rest, the medium is considered to be a continuous distribution of matter. However, when considering  $p$  for a gas, the pressure is an average of the forces against the vessel walls; i.e. gas pressure. Fluid pressure is a measure of energy per unit volume per the Bernoulli equation, which states that the static pressure in the flow plus one half of the density times the velocity squared is equal to a constant throughout the flow, referred to as the total pressure of the flow:

$$p + \frac{1}{2}pV^2 + pgh = \text{constant} \quad (16.10)$$

where,

$p$  = pressure

$V$  = fluid velocity

$h$  = elevation

$g$  = gravitational acceleration

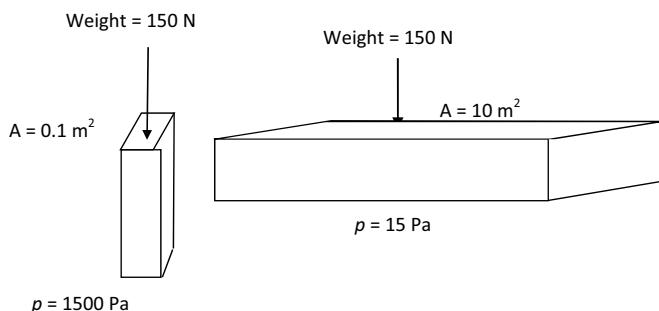


FIGURE 16.3 Difference in pressure with same weight over different areas.

To adhere to the conservation of energy principle, a flowing fluid will maintain the energy, but velocity and pressure can change. In fact, velocity and pressure will compensate for each other to adhere to the conservation principle, as stated in the Bernoulli equation:

$$p_1 + \frac{1}{2}pV_1^2 + pgh_1 = p_2 + \frac{1}{2}pV_2^2 + pgh_2 \quad (16.11)$$

This is shown graphically in Figure 16.4. The so-called "Bernoulli effect" occurs when increased fluid speed leads to decreased internal pressure.

In many air pollution scenarios, fluid pressure is measured against two references: zero pressure and atmospheric pressure. Absolute pressure is compared to true zero pressure and gage pressure is reported in reference to atmospheric pressure. To be able to tell which type of pressure is reported, the letter "a" and the letter "g" are added to units to designate whether the pressure is absolute or gage, respectively. So, it is common to see pounds per square inch designated as "psia" or inches of water as "in wg". If no letter is designated, the pressure is likely absolute pressure.

When a gage measurement is taken, and the actual atmospheric pressure is known, absolute and gage pressures are related:

$$p_{\text{absolute}} = p_{\text{gage}} + p_{\text{atmospheric}} \quad (16.12)$$

Barometric and atmospheric pressures are synonymous. A negative gage pressure implies a *vacuum* measurement. A reported vacuum quantity is to be subtracted from the atmospheric pressure. For example, when a piece of equipment is operating with 20 kPa vacuum, the absolute pressure is  $101.3 \text{ kPa} - 20 \text{ kPa} = 81.3 \text{ kPa}$ . (Note: The standard atmospheric pressure =  $101.3 \text{ kPa} = 1.013 \text{ bars}$ ). Thus, the relationship between vacuums, which are always given as positive numbers, and absolute pressure is:

$$p_{\text{absolute}} = p_{\text{atmospheric}} - p_{\text{vacuum}} \quad (16.13)$$

Pressure concepts are used throughout this text, as in most discussion of physics, chemistry, and biology. As

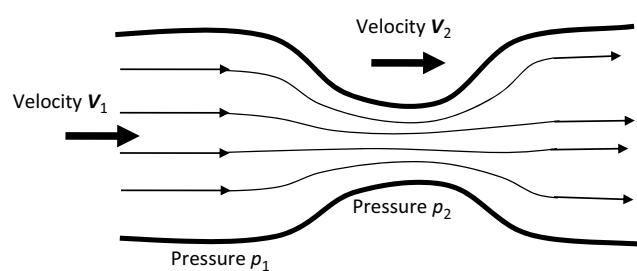
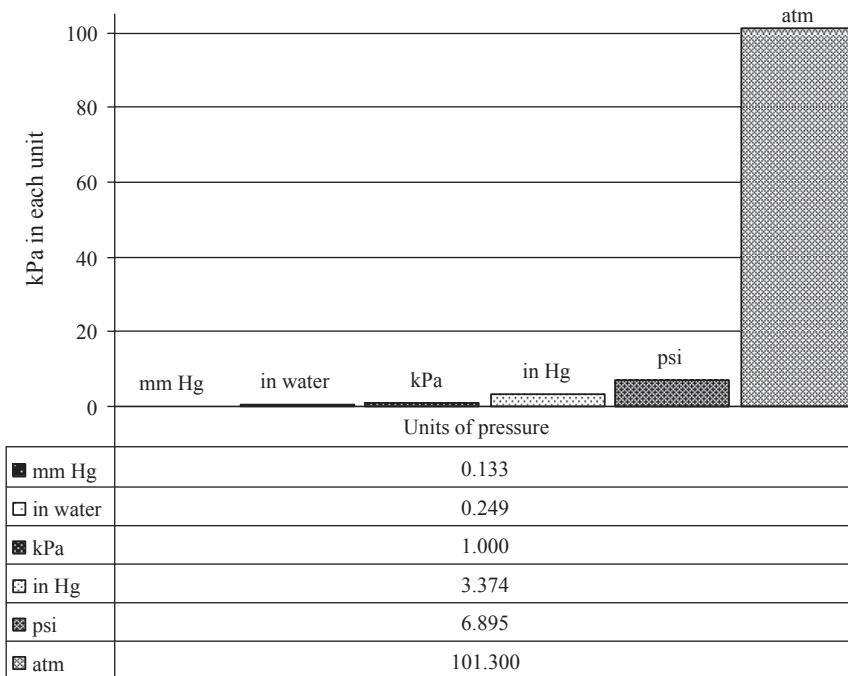


FIGURE 16.4 Bernoulli principle and the effect of relationship between pressure energy, area, and velocity. As the cross-sectional area of flow decreases, the velocity increases and the pressure decreases.



**FIGURE 16.5 Comparison of the size of pressure units.** Notes: mm Hg = millimeters of mercury; in water = inches of water; kPa = kilopascal; in Hg = inches of mercury; psi = pounds per square inch; and atm = atmospheres.

mentioned, the standard metric unit of pressure is the Pascal, which is quite small for most air pollution applications. Thus, the kPa is used most often. See Figure 16.5 for a comparison of relative size of pressure units commonly used in environmental assessments, research studies, and textbooks.

Acceleration is the time rate of change in the velocity of a fluid particle. In terms of calculus,<sup>d</sup> it is a second

derivative. That is, it is the derivative of the velocity function. Since the derivative of a function is itself a function, this indicates a fluid's rate of change. This explains why the second derivative must be a function showing the rate of change of the rate of change. This is obvious when one looks at the units of acceleration: length per time per time ( $\text{m s}^{-2}$ ) (See Example Box: Fluid Acceleration).

### EXAMPLE BOX: FLUID ACCELERATION

Consider a fluid is moving at the constant velocity of  $4 \text{ m s}^{-1}$ . What is the rate of change of the velocity? What is the second derivative of the fluid's movement?

#### Solution and Discussion

The function  $s = f(t)$  shows the distance the fluid has moved ( $s$ ) after  $t$  seconds. If the fluid is traveling at  $4 \text{ m s}^{-1}$ , then it must travel 4 m for each second, or  $4t$  meters after  $t$  seconds. The rate of change of distance (how fast the distance is changing) is the speed. We know that this is  $4 \text{ m s}^{-1}$ . So:

$$s = f(t) = 4t \text{ and,}$$

$$\frac{ds}{dt} = f'(t) = 4$$

In acceleration, we are interested in the rate of change of the rate of change. This is the rate of change of the fluid velocity. Since the fluid is moving at constant velocity, it is not accelerating.

Therefore, acceleration = 0.

This is also a way of saying that when one differentiates for a second time (i.e. finds the second derivative), the result = zero.

<sup>d</sup> Newton simultaneously invented the calculus with Gottfried Wilhelm Leibnitz (1646–1716) in the seventeenth century. Both are credited with devising the symbolism and the system of rules for computing derivatives and integrals, but their notation and emphases differed. A debate rages on who did what first, but both of these giants had good reason to revise the language of science; i.e. mathematics, to explain motion.

In the complexities of any air mass or other fluid bodies in the environment, the fluid concepts must be combined to describe fluid movement. If given the function  $f(t)$  as the displacement of a particle in the fluid at time  $t$ , the derivative of this function  $f'(t)$  represents the velocity. The second derivative  $f''(t)$  represents the acceleration of the particle at time  $t$ :

$$s = f(t) \quad (16.14)$$

$$v = \frac{ds}{dt} = f'(t) \quad (16.15)$$

$$a = \frac{d^2s}{dt^2} = f''(t) \quad (16.16)$$

If the derivative is zero, the function is flat and must therefore reside where the graph is turning. We are able to identify the turning points of a function by differentiating and setting the derivative equal to zero. Turning points may be of three types: minima (Figure 16.6A), maxima (Figure 16.6B), and points of inflection (Figure 16.6C). The graph shows how the derivatives are changing around each of these stationary points:

Near the point where the derivative is changing from negative to positive, it is increasing. In other words the rate of change in velocity is positive. So, the derivative of the derivative, i.e. second derivative, must be positive. When the second derivative is positive at a given

turning point, this is the minimum point. Likewise, at the maximum negative to positive means that the derivative is decreasing, i.e. the rate of change is negative. This means when the second derivative is negative at a given turning point, this must be a maximum point. At the inflection points, the rate of change is neither positive nor negative, i.e. the rate of change is zero.

As discussed in Chapter 2, the relationship between mass and volume is also important in air pollution physics and chemistry. For both the pollutant and the fluid in which it resides, air pollution estimates and assessments depend on reliable applications of density, specific weight, specific volume, mole fractions, viscosity, and other fluid properties.

Standardization is important in air pollution science and engineering, but information is reported in many different formats. In fact, engineers often resist the use of SI units more than their colleagues in the basic sciences. This may, at least in part, be due to the historic inertia of engineering, where many equations were derived from English units. When an equation is based on one set of units and is only reported in those units, it can take much effort to convert them to SI units. Exponents in many environmental equations have been empirically derived from studies wherein English units were applied (See Discussion Box: Units in Handbooks and Reference Manuals).

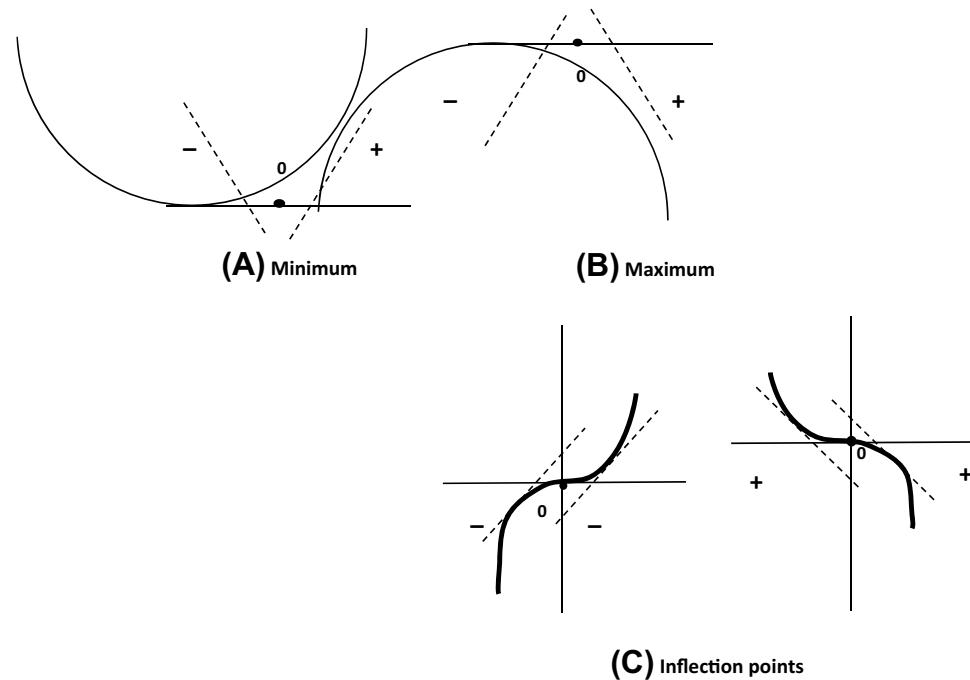


FIGURE 16.6 Turning points important to displacement, velocity, and acceleration of particles in a fluid.

## UNITS IN HANDBOOKS AND REFERENCE MANUALS

Standardization is important in air pollution science and engineering, but in the “real world”, information is reported in many different formats. In fact, engineers seem to resist the use of SI units more than their colleagues in the basic sciences. This may, at least in part, be due to the historic inertia of engineering, where many equations were derived from English units. When an equation is based on one set of units and is only reported in those units, it can take much effort to convert them to SI units. Exponents in many water quality, water supply, and sludge equations have been empirically derived from studies that applied English units.

Some equations may use either English or SI units, such as the commonly used Hazen–Williams formula for mean velocity flow ( $v$ ) in pressure pipes is:

$$v = 1.318C \cdot r^{0.63} \cdot s^{0.54} \quad (16.17)$$

where  $r$  is the hydraulic radius in feet or meters,  $s$  is the slope of the hydraulic grade line (head divided by length), and  $C$  is the friction coefficient (a function of pipe roughness).

The exponents apply without regard to units. Other formulae, however, require that a specific set of units be used. An example is the fundamental equation for kinetic energy. Two different equations are needed when using either the SI system or the English system, which requires the gravitation conversion constant ( $g_c$ ) in the denominator. These are, respectively:

$$E_{\text{kinetic}} = \frac{mv^2}{2} \quad (16.18)$$

$$E_{\text{kinetic}} = \frac{mv^2}{2g_c} \text{ (in ft – lbf)} \quad (16.19)$$

where  $m$  is mass and ft-lbf is foot-pound-force.

Two other important physical equations, potential energy and pressure require the insertion of their denominators:

$$E_{\text{potential}} = \frac{mgz}{g_c} \text{ (in ft – lbf)} \quad (16.20)$$

**Specific volume** The reciprocal of a substance’s density is known as its specific volume ( $v$ ). This is the volume occupied by a unit mass of a fluid. The units of  $v$  are reciprocal density units ( $\text{m}^3 \text{ kg}^{-1}$ ). Stated mathematically, this is:

$$v = \rho^{-1} \quad (16.22)$$

**Specific weight** As discussed in Chapter 1, the weight of a fluid per its volume is known as specific weight ( $\gamma$ ). Civil engineers sometimes use the term interchangeably with

$$p = \frac{\rho gh}{g_c} \text{ (in ft – lbf ft}^{-2}\text{)} \quad (16.21)$$

where  $g$  is the gravitational acceleration,  $\rho$  is density, and  $h$  is the height.

With this in mind, it is sometimes better to simply apply the formulae using English units and convert to metric or SI units following the calculation. In other words, rather than try to change the exponent or coefficient to address the difference in feet and meters, just use the units called for in the empirically derived equation. After completing the calculation, convert the answer to the correct units. This may seem contrary to the need to standardize units, but it may save time and effort in the long run. Either way, it is mathematically acceptable dimension analysis.

Another variation in units is how coefficients and constants are reported. For example, the octanol–water coefficient seems to be reported more often as  $\log K_{\text{ow}}$  than simply as  $K_{\text{ow}}$ . This is usually because the ranges of  $K_{\text{ow}}$  values can be so large. One compound may have a coefficient of 0.001, while another has one of 1000. Thus, it may be more manageable to report the  $\log K_{\text{ow}}$  values as  $-3$  and  $3$ , respectively.

Further, chemists and engineers are comfortable with the “ $p$ ” notation as a representative of the negative log. This could be because pH and pOH are common parameters. So, one may see the negative logarithm used with units in handbooks. For example, vapor pressure is sometimes reported as a negative log.

Therefore, examples and problems in handbooks and reference manuals make use of several different units as they are encountered in the environmental literature.

**density.** A substance’s  $\gamma$  is not an absolute fluid property because it depends on the fluid itself and the local gravitational force:

$$\gamma = g\rho \quad (16.23)$$

The units are the same as those for density; e.g.  $\text{kg m}^{-3}$ .

**Mole Fraction** In a composition of a fluid made up of two or more substances ( $A, B, C, \dots$ ), the mole fraction

$(x_A, x_B, x_C, \dots)$  is the number of moles of each substance divided by the total number of moles for the whole fluid:

$$x_A = \frac{n_A}{n_A + n_B + n_C + \dots} \quad (16.24)$$

The mole fraction value is always between 0 and 1. The mole fraction may be converted to mole percent as:

$$x_{A\%} = x_A \times 100 \quad (16.25)$$

For gases, the mole fraction is the same as the volumetric fraction of each gas in a mixture of more than one gas.

in the liquid surface normal to a line of unit length drawn in the surface. Surface tension decreases with temperature and depends on the contact fluid. Surface tension is involved in capillary rise and drop. Water has a very high  $\sigma$  value (approximately  $0.07 \text{ N m}^{-2}$  at  $200^\circ\text{C}$ ). Of the environmental fluids, only mercury has a higher  $\sigma$  (Table 16.2).

The high surface tension creates a type of skin on a free surface, which is how an object more dense than water (e.g. a steel needle) can “float” on a still water surface. It is the reason insects can sit comfortably on water surfaces. Surface tension is somewhat dependent on the

### MOLE FRACTION EXAMPLE

A total of 112 g of  $\text{MgCl}_2$  is dissolved in 1 l of water. The density of this solution is  $1.089 \text{ g cm}^{-3}$ . What is the mole fraction of  $\text{MgCl}_2$  in the solution at standard temperature and pressure.

#### Solution

The number of moles of  $\text{MgCl}_2$  is determined from its molecular weight:

$$\frac{112 \text{ g}}{95.22 \text{ g}} = 1.18 \text{ mol}$$

Next, we calculate the number of moles of water:

$$\text{Mass of water} = 1.00 \text{ l} \times (1000 \text{ cm}^{-3} \text{ l}^{-1}) \times (1.00 \text{ g cm}^{-3}) = 1000 \text{ g water and}$$

$$\text{Moles of water} = \frac{1000 \text{ g}}{18.02 \text{ g mol}^{-1}} = 55.49 \text{ mol}$$

$$\text{Thus, } x_{\text{MgCl}_2} = \frac{1.18 \text{ mol}}{55.49 + 1.18} = 0.021.$$

The mol% of  $\text{MgCl}_2$  is 2.1%.

**Compressibility** The fractional change in a fluid’s volume per unit change in pressure at constant temperature is the fluid’s coefficient of compressibility. Gases, like air are quite compressible. That is, gases have large variations in density ( $\rho$ ), much larger than in liquids. However, any fluid can be compressed in response to the application of pressure ( $p$ ). For example, water’s compressibility at 1 atm is  $4.9 \times 10^{-5} \text{ atm}^{-1}$ . This compares to the lesser compressibility of mercury ( $3.9 \times 10^{-6} \text{ atm}^{-1}$ ) and the much greater compressibility of hydrogen ( $1.6 \times 10^{-3} \text{ atm}^{-1}$ ).

A fluid’s bulk modulus,  $E$  (analogous to the modulus of elasticity in solids) is a function of stress and strain on the fluid (Figure 16.7), and is a description of its compressibility. It is defined according to the fluid volume ( $V$ ):

$$E = \frac{\text{stress}}{\text{strain}} = -\frac{dp}{dV/V_1} \quad (16.26)$$

$E$  is expressed in units of pressure (e.g. kPa). Water’s  $E = 2.2 \times 10^6 \text{ kPa}$  at  $20^\circ\text{C}$ .

**Surface Tension and Capillarity** Surface tension effects occur at liquid surfaces (interfaces of liquid–liquid, liquid–gas, liquid–solid). Surface tension,  $\sigma$ , is the force

gas that is contacting the free surface. If not indicated, it is usually safe to assume that the gas is the air in the troposphere.

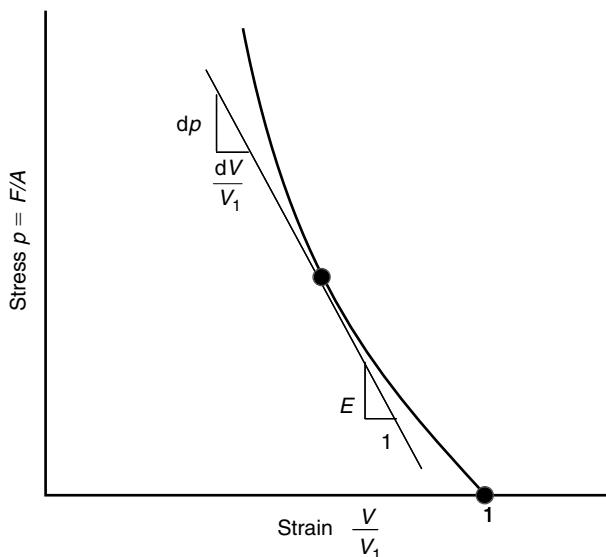


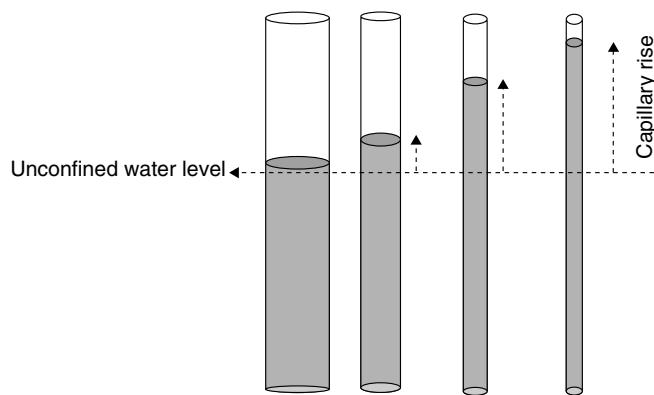
FIGURE 16.7 Stress and strain on a fluid, and the bulk modulus of fluids.

**TABLE 16.2** Surface Tension (Contact with Air) of Selected Fluids Important to Air Pollution

Fluid	Surface Tension, $\sigma$ ( $\text{N m}^{-1}$ at $20^\circ\text{C}$ )
Acetone	0.0236
Benzene	0.0289
Ethanol	0.0236
Glycerin	0.0631
Kerosene	0.0260
Mercury	0.519
<i>n</i> -Octane	0.0270
Tetrachloromethane	0.0236
Toluene	0.0285
Water	0.0728

Capillarity is a particularly important fluid property in the design of air pollutant sampling and analytical equipment, such as capillary action in filters and sorption traps used to collect gases and in capillary tubes used in chromatography. Capillarity is also an important factor in physiological response to air pollutants. For example, morphological changes have been observed in lung tissue exposed to ozone. These changes, in part, are due to ozone's effect on the alveolar capillaries and the degradation of capillary endothelia. This leads to less efficient oxygen exchange between the inhaled air and blood, which in turn leads to respiratory and cardiovascular stress.

Capillary rise occurs for two reasons, its adhesion to a surface, plus the cohesion of water molecules to one another. Higher relative surface tension causes a fluid to rise in a tube (or a pore) that is indirectly



**FIGURE 16.8** Capillary rise of water with respect to diameter of conduit.

proportional to the diameter of the tube. In other words, capillarity is greater the smaller the inside diameter of the tube (Figure 16.8). The rise is limited by the weight of the fluid in the tube. The rise ( $h_{\text{capillary}}$ ) of the fluid in a capillary is expressed as (Figure 16.9 displays the variables):

$$h_{\text{capillary}} = \frac{2\sigma \cos \lambda}{\rho_w g R} \quad (16.27)$$

where  $\sigma$  is the fluid surface tension ( $\text{g s}^{-2}$ ),  $\lambda$  is the angle of meniscus (concavity of fluid) in capillary (degrees),  $\rho_w$  is the fluid density ( $\text{g cm}^{-3}$ ),  $g$  is the gravitational acceleration ( $\text{cm s}^{-1}$ ), and  $R$  is the radius of capillary (cm).

The contact angle indicates whether cohesive or adhesive forces are dominant in the capillarity. When  $\lambda$  values are greater than  $90^\circ$ , cohesive forces are dominant; when  $\lambda < 90^\circ$ , adhesive forces dominate. Thus,  $\lambda$  is dependent on both the type of fluid and the surface to which it comes into contact. For example, water–glass  $\lambda = 0$ , ethanol–glass  $\lambda = 0$ , glycerin–glass  $\lambda = 19$ , kerosene–glass  $\lambda = 26$ , water–paraffin  $\lambda = 107$ , and mercury–glass  $\lambda = 140$ .

### CAPILLARITY EXAMPLE

What is the rise of contaminated water (i.e. a solution of water and soluble and insoluble contaminants) in a sorption material used to collect gaseous air pollutants that has an average pore space diameter of  $0.1\text{ cm}$ , at  $18^\circ\text{C}$  and a density of  $0.999\text{ g cm}^{-3}$ , under surface tension of  $50\text{ g s}^{-1}$  if the angle of contact of the meniscus is  $30^\circ$ ?

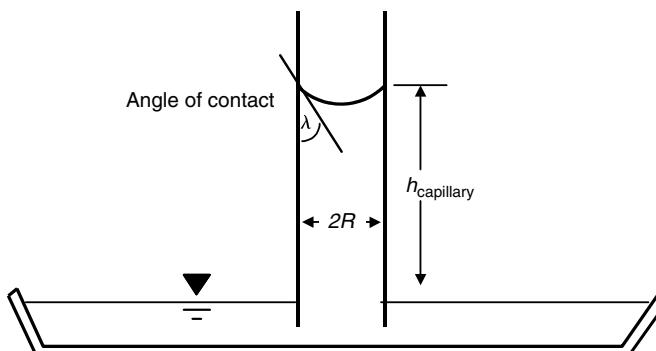
What would happen if the average pore space were  $0.01\text{ cm}$ , with all other variables remaining as stated?

#### Answer

$$h_{\text{capillary}} = \frac{2\sigma \cos \lambda}{\rho_w g R} = \frac{2 \times 80 \times \cos 30}{0.999 \times 980 \times 0.05} \text{ cm} \approx 0.25 \text{ cm}$$

If the pore space were  $0.01\text{ cm}$  in diameter, the rise would be  $2.5\text{ cm}$ . However, it is likely that the angle of contact would have also decreased since the angle is influenced by the diameter of the column (approaching zero with decreasing diameter).

Also note that since the solution is not 100% water, the curvature of the meniscus will be different, so the contact angle  $\lambda$  will likely be greater (i.e. less curvature) than the meniscus of water alone. The lower surface tension of the mixture also means that the capillary rise will be less.



**FIGURE 16.9 Rise of a fluid in a capillary.** In this example, adhesive forces within the fluid are dominant, so the meniscus is concave (i.e. a valley). This is the case for most fluids. However, if cohesive forces dominate, such as the extremely cohesive liquid mercury, the meniscus will be convex (i.e. a hill).

**Viscosity** How much a fluid resists flow when it is acted on by an external force, especially a pressure differential or gravity, is the fluid's viscosity. This is a crucial fluid property used in numerous environmental applications, including air pollution plume characterization.

Recall from Bernoulli's Eqn (16.10) and Figure 16.4 that if a fluid is flowing in a long, horizontal conduit with constant cross-sectional area, the pressure along the pipe must be constant. But why if we measure the pressure as the fluid moves in the conduit, would there be a *pressure drop*? A pressure difference is needed to push the fluid through the conduit to overcome the drag force exerted by the conduit walls on the layer of fluid that is making contact with the walls. Since the drag force exerted by each successive layer of the fluid on each adjacent layer that is moving at its own velocity, then a pressure difference is needed (Figure 16.10). The drag forces are known as *viscous forces*. Thus, the fluid velocity is not constant across the conduit's diameter,

owing to the viscous forces. The greatest velocity is at the center (furthest away from the walls), and the lowest velocity is found at the walls. In fact, at the point of contact with walls, the fluid velocity is zero.

So, if  $P_1$  is the pressure at point 1, and  $P_2$  is the pressure at point 2, with the two points separated by distance  $L$ , the pressure drop ( $\Delta P$ ) is proportional to the flow rate:

$$\Delta P = P_1 - P_2 \quad (16.28)$$

and

$$\Delta P = P_1 - P_2 = I_v R \quad (16.29)$$

where  $I_v$  is the volume flow rate, and  $R$  is the proportionality constant representing the resistance to the flow. This resistance  $R$  depends on the length ( $L$ ) of pipe section, the pipe's radius, and the fluid's viscosity.

Two types of viscosity are important in air pollution: absolute viscosity and kinematic viscosity.

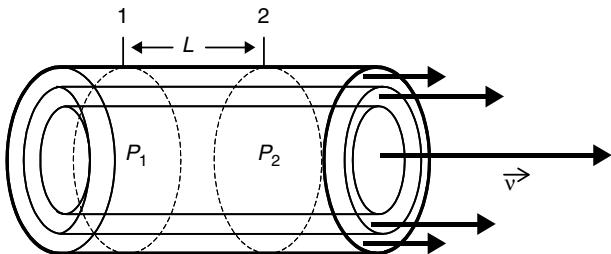
### VISCOSITY EXAMPLE 1

#### Answer

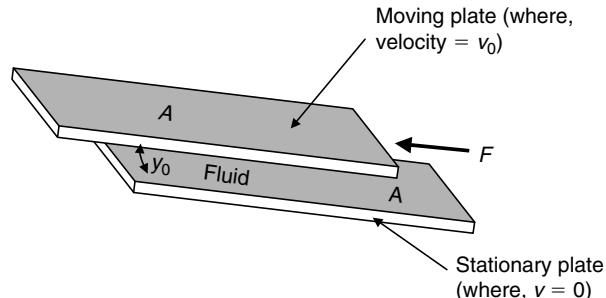
Solving for  $R$  from Eqn (16.29), and converting to SI units gives us:

$$\begin{aligned} R &= \Delta P(I_v)^{-1} \\ &= (100 \text{ torr})(0.71 \text{ s}^{-1})^{-1}(133.3 \text{ Pa})(1 \text{ torr})^{-1}(1 \text{ l}) \\ &\quad \times (10^3 \text{ cm}^{-3})^{-1}(1 \text{ cm}^{-3})(10^{-6} \text{ m}^{-3}) \\ &= 1.45 \times 10^7 \text{ Pa s m}^{-3} \\ &= 1.45 \times 10^7 \text{ N s m}^{-5} \end{aligned}$$

Workers are being exposed to an air pollutant known to decrease blood pressure in the capillaries, small arteries, and major arteries and veins after the blood is pumped from the aorta. If high-dose studies show an acute drop in the gage pressure of the circulatory system from 100 to 0 torr at a volume flow of  $0.71 \text{ s}^{-1}$ , given the total resistance of the circulatory system.



**FIGURE 16.10** Viscous flow through a horizontal conduit. The highest velocity is at the center of the conduit. As the fluid approaches the wall, the velocity declines and approaches zero.



**FIGURE 16.11** The sliding plate viscometer. A fluid of thickness  $y_0$  is placed between two plates of area  $A$ . The top plate moves at the constant velocity  $v_0$  by the exertion of force  $F$ . Lindeberg M. Civil engineering reference manual for the PE exam. 8th ed. Belmont (CA): Professional Publications, Inc.; 2001.

**Absolute viscosity** Physicists define the fluid's coefficient of viscosity by assuming that the fluid is confined between two parallel, rigid plates with equal area. The absolute viscosity of a fluid can be measured by a number of ways, but engineers commonly use the *sliding plate viscometer test*. The test applies two plates separated by the fluid to be measured (Figure 16.11).

For Newtonian fluids, the force applied in the viscometer test has been found to be in direct proportion to the velocity of the moving plate and inversely proportional to the length of separation of the two plates:

$$\frac{F}{A} \propto \frac{dv}{dy} \quad (16.30)$$

Using a constant this proportionality can become an equality:

$$\frac{F}{A} = \mu \frac{dv}{dy} \quad (16.31)$$

This equation is known as *Newton's law of viscosity*. Fluids that conform to this law are referred to as Newtonian fluids.<sup>e</sup> The constant,  $\mu$ , is the fluid's *absolute viscosity*. The  $\mu$  is also known as the *coefficient of viscosity*, but environmental texts often refer to  $\mu$  as *dynamic viscosity*. The term *fluidity* is the reciprocal of dynamic viscosity.

The inverse relationship between viscosity and fluidity should make sense after some thought. Since the definition of viscosity is the resistance to flow when an external force is applied, then it makes sense that if a substance does a poor job resisting the flow,

the substance must have a lot of fluidity. An electrical analogy might be that of conductivity and resistance. If copper wire has much less resistance to electrical flow than does latex rubber, we say that copper must be a good conductor. Likewise, if water at 35 °C is less effective at resisting flow downhill (i.e. gravity is applying our force) than is motor oil at the same temperature, we say that the water has less dynamic viscosity than the motor oil. And, we also say that the water has more fluidity than the oil. Before the modern blends of multiviscosity motor oils, the temperature–viscosity relationship was part of the seasonal rituals of the oil change. Less viscous motor oil (e.g. 10 W) had to be used in a car's engine to prepare for the lower temperatures in winter, so that the starter could "turn over" the engine (less viscous oil = less resistance the force of the starter moving the pistons). Conversely, in preparing for summer, a higher viscosity motor oil (commonly 40 W)<sup>f</sup> would be used because the high temperatures in the engine would allow the oil to "blow out" through the piston rings or elsewhere (because the oil was not doing a good job of resisting the force applied by the pistons and shot out of the engine). The newer oil formulations (e.g. 10–40 W) maintain a smaller range of viscosities, so automobile owners worry less about the viscosity.

The  $F/A$  term is known as the *shear stress*,  $\tau$ , of the fluid. The  $dv/dy$  term is known as the *velocity gradient* or the *rate of shear formation*.<sup>g</sup> So, the shear stress is linear;

<sup>e</sup>See discussion of Newtonian and non-Newtonian fluids earlier in this chapter.

<sup>f</sup>In the 1960s, many of us went further. We used 50 W or even higher viscosity racing formulas even if we never really allowed our cars to ever reach racing temperatures! We often applied the same logic for slicks, glass packs, four-barrel carburetors, and other racing equipment that was really never needed, but looked and sounded awesome!

<sup>g</sup>The  $dv dy^{-1}$  term is also known as the *rate of strain* and the *shear rate*.

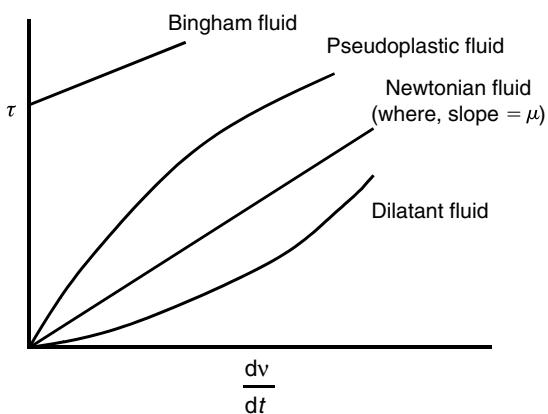


FIGURE 16.12 Hypothetical fluid types according to shear stress ( $\tau$ ) behavior relative to velocity gradient. Lindeberg M. Civil engineering reference manual for the PE exam. 8th ed. Belmont (CA): Professional Publications, Inc.; 2001.

i.e. it can be expressed as a straight line (in the form  $y = mx + b$ ):

$$\tau = \mu \frac{dv}{dy} \quad (16.32)$$

The relationship between the two sides of this equality determines the types of fluids, as shown in Figure 16.12. Most fluids encountered in environmental studies are Newtonian, including water, all gases, alcohols, and most solvents. Most solutions also behave as Newtonian fluids. Slurries, muds, motor grease and oils, and many polymers behave as *pseudoplastic fluids*; i.e. viscosities decrease with increasing velocity gradient. They are easily pumped, since higher pumping rates lead to a less viscous fluid. Some slurries behave as *Bingham fluids* (e.g. behave like toothpaste or bread dough), where the shear formation is resisted up to a point. For example, depending on their chemical composition, slurries used in wet scrubbers to collect gases (e.g. sulfur dioxide) may behave as Bingham fluids. The rare *dilatant fluids* are sometimes encountered in environmental engineering applications, such as clay slurries used as landfill liners and when starches and certain paints and coatings are spilled. These can be difficult fluids to remove and clean up, since their viscosities increase with increasing velocity gradient, so pumping these fluids at higher rates can lead to their becoming almost solid with a sufficiently high shear rate. *Plastic fluids* (Figure 16.13) require the application of a finite force before any fluid movement.

Categorizing and characterizing fluids according to their behavior under shear stress and velocity gradient is not absolute. For example, a Bingham fluid can resist shear stresses indefinitely so long as they are small, but these fluids will become pseudoplastic at higher

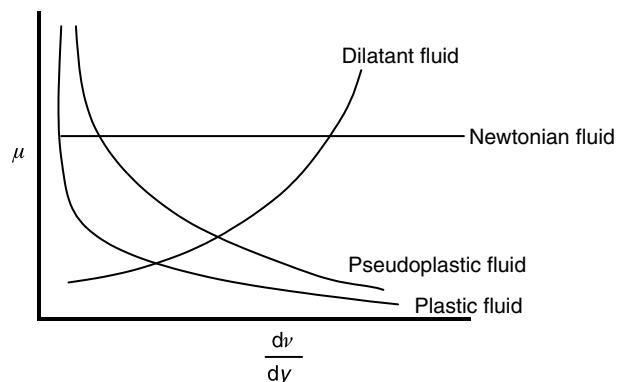


FIGURE 16.13 Hypothetical fluid types according to viscosity ( $\mu$ ) and shear rate (velocity). Lindeberg M. Civil engineering reference manual for the PE exam. 8th ed. Belmont (CA): Professional Publications, Inc.; 2001.

stresses. Even if all conditions remain constant, viscosity can also change with time. A *rheopectic fluid* is one where viscosity increases with time, and a *thixotropic fluid* is one that has decreasing viscosity with time. Those fluids that do not change with time are referred to as *time-independent fluids*. Colloidal materials, like certain components of sludges, sediments, and soils, act like thixotropic fluids. That is, they experience a decrease in viscosity when the shear is increased. However, there is no *hysteresis*, meaning that the viscosity does not return to the original state with the ceasing of the agitation.

There is a seeming paradox between viscosity and temperature. As a general rule, temperature is inversely proportional to viscosity of liquids, but temperature is directly proportional to the viscosity of gases. Viscosity of liquids is predominantly caused by molecular cohesion. These cohesive forces decrease with increasing temperature, which is why viscosity decreases with increasing temperature. Gas viscosity is mainly kinetic molecular in its origin, so increasing temperature means that more collisions will occur between molecules. The more the gas is agitated, the greater the viscosity, so gas velocity increases with increasing temperatures.

The viscosity of liquids increases only slightly with increasing pressure. Under environmental conditions, absolute viscosity can be considered to be independent of pressure.

Absolute viscosity units are mass per length per time (e.g.  $\text{g cm}^{-1} \text{s}^{-1}$ ). The coefficients for some common fluids are provided in Table 16.3. Note the importance of temperature in a substance's absolute viscosity, e.g. the several orders of magnitude decrease with only a  $20^\circ\text{C}$  increase in glycerin.

The units of  $\nu$  are area per second (e.g.  $\text{cm}^2 \text{s}^{-1}$  = stoke). Because kinematic viscosity is inversely

## VISCOSITY EXAMPLE 2

A liquid with the absolute viscosity of  $3 \times 10^{-5} \text{ g s cm}^{-1}$  flows through rectangular tube in an air sampling device. The velocity gradient is  $0.5 \text{ m s}^{-1} \text{ cm}^{-1}$ . What is the shear stress in the fluid at this velocity gradient?

### Answer

$$\begin{aligned}\tau &= \mu \frac{dv}{dy} \\ &= (3 \times 10^{-5} \text{ g s cm}^{-1})(0.5 \text{ m s}^{-1} \text{ cm}^{-1})(100 \text{ cm m}^{-1}) \\ &= 1.5 \times 10^{-3} \text{ g cm}^{-2}\end{aligned}$$

**TABLE 16.3** Absolute Viscosity of Fluids Important to Health and Environmental Studies

Fluid	Temperature (°C)	Absolute Viscosity, $\mu$ (Pa)
Water	0	$1.8 \times 10^{-3}$
	20	$1 \times 10^{-3}$
	60	$6.5 \times 10^{-2}$
Whole human blood	37	$4 \times 10^{-3}$
SAE 10 motor oil	30	$2 \times 10^{-1}$
Glycerin	0	10
	20	1.4
	60	$8.1 \times 10^{-2}$
Air	20	$1.8 \times 10^{-5}$

Source: Tipler P. Physics for scientists and engineers, vol. 1. New York: W.H. Freeman and Co.; 1999.

proportional to a fluid's density,  $\nu$  is highly dependent on temperature and pressure. Recall that absolute viscosity is only slightly affected by pressure. Table 16.4 can be used to convert most of the units of  $\mu$  and  $\nu$ .

*Laminar versus Turbulent Flow: The Reynolds Number* At a sufficiently high velocity, a fluid's flow ceases to be laminar and becomes turbulent. A dimensionless Reynolds number ( $N_R$ ) is used to differentiate types of

*Kinematic viscosity* The ratio of absolute viscosity to mass density is known as *kinematic viscosity* ( $\nu$ ):

$$\nu = \mu \rho^{-1} \quad (16.33)$$

flow. The  $N_R$  is expressed as the ratio of inertial to viscous forces in a fluid:

$$N_R = \frac{\text{Inertial forces}}{\text{Viscous forces}} \quad (16.34)$$

The inertial forces are proportional to the velocity and density of the fluid, as well as to the diameter of the conduit in which the fluid is moving. An increase in any of these factors will lead to a proportional increase in the momentum of the flowing fluid. We know from our previous discussion that the coefficient of viscosity or absolute viscosity ( $\mu$ ) represents the total viscous force of the fluid, so,  $N_R$  can be calculated as:

$$N_R = \frac{D_e v \rho}{\mu} \quad (16.35)$$

where  $D_e$  is the conduit's equivalent diameter, which is a so-called "characteristic dimension"<sup>h</sup> which evaluates the fluid flow as a physical length.

It is actually the inside diameter (i.d.) of the conduit, vent, or pipe. Recall that  $\mu \rho^{-1}$  is the kinematic viscosity  $\nu$ , so the Reynolds number can be stated as the relationship between the size of the conduit, the average fluid velocity  $v$ , and  $\nu$ :

$$N_R = \frac{D_e \nu}{v} \quad (16.36)$$

When fluids move at very low velocities, the bulk material moves in discrete layers parallel to one another. The only movement across the fluid layers is molecular

<sup>h</sup> Other equivalent diameters for fully flowing conduits are the annulus, square, and rectangle. Equivalent diameters for partial flows in conduits are the half-filled circle, rectangle, wide and shallow stream, and trapezoid. For calculations of these diameters, see Lindeberg, M., Civil Engineering Reference Manual for the PE Exam, 8th ed. Professional Publications, Inc., Belmont, CA, 2001.

TABLE 16.4 Viscosity Units and Conversions

Multiply	By	To Obtain
<b>ABSOLUTE VISCOSITY (<math>\mu</math>)</b>		
Centipoise (cP)	$1.0197 \times 10^{-4}$	$\text{kgf s m}^{-2}$
cP	$2.0885 \times 10^{-5}$	$\text{lbf-s ft}^{-2}$
cP	$1 \times 10^{-3}$	Pa
Pa	$2.0885 \times 10^{-3}$	$\text{lbf-s ft}^{-2}$
Pa	1000	cP
Dynes $\text{cm}^{-2}$	0.10	Pa
$\text{lbf-s ft}^{-2}$	478.8	Poise (P)
$\text{slug ft}^{-1} \text{s}^{-1}$	47.88	Pa
<b>KINEMATIC VISCOSITY (<math>\nu</math>)</b>		
$\text{ft}^2 \text{s}^{-1}$	$9.2903 \times 10^4$	Centistoke (cSt)
$\text{ft}^2 \text{s}^{-1}$	$9.2903 \times 10^{-2}$	$\text{m}^2 \text{s}^{-1}$
$\text{m}^2 \text{s}^{-1}$	10.7639	$\text{ft}^2 \text{s}^{-1}$
$\text{m}^2 \text{s}^{-1}$	$1 \times 10^6$	cSt
cSt	$1 \times 10^{-6}$	$\text{m}^2 \text{s}^{-1}$
cSt	$1.0764 \times 10^{-5}$	$\text{ft}^2 \text{s}^{-1}$
<b><math>\mu</math> TO <math>\nu</math></b>		
cP	$1/\rho (\text{g cm}^{-3})$	cSt
cP	$6.7195 \times 10^{-4}/\rho \text{ in lbm ft}^{-3}$	cSt
$\text{lbf-s ft}^{-2}$	$32.174/\rho \text{ in lbm ft}^{-3}$	$\text{ft}^2 \text{s}^{-1}$
$\text{kgf s m}^{-2}$	$9.807/\rho \text{ in kg m}^{-3}$	$\text{m}^2 \text{s}^{-1}$
Pa	$1000/\rho \text{ in g cm}^{-3}$	cSt
<b><math>\nu</math> TO <math>\mu</math></b>		
cSt	$\rho \text{ in g cm}^{-3}$	cP
cSt	$1.6 \times 10^{-5}$	Pa
$\text{m}^2 \text{s}^{-1}$	$0.10197 \times \rho \text{ in kg m}^{-3}$	$\text{kgf s m}^{-2}$
$\text{m}^2 \text{s}^{-1}$	$1000 \times \rho \text{ in g cm}^{-3}$	Pa
$\text{ft}^2 \text{s}^{-1}$	$3.1081 \times 10^{-2} \times \rho \text{ in lbm ft}^{-3}$	$\text{lbf-s ft}^{-2}$
$\text{ft}^2 \text{s}^{-1}$		$1.4882 \times 10^3 \times \rho \text{ in lbm ft}^{-3}$

motion, which creates viscosity. Such a flow is *laminar* (Figure 16.14). Laminar flow is more common in water than in air, especially in low velocity systems like groundwater.

With increasing fluid velocity, the bulk movement changes, forming eddy currents that create three-

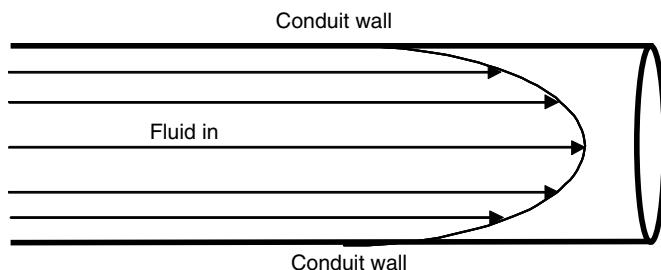


FIGURE 16.14 Laminar flow in closed conduit.

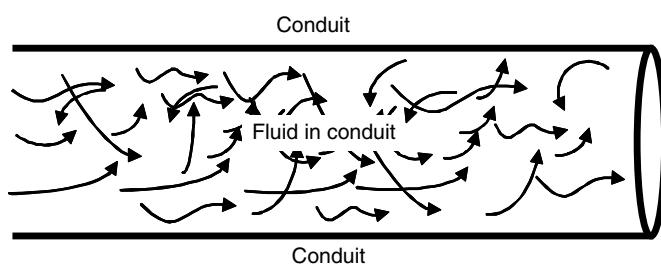


FIGURE 16.15 Turbulent flow in a closed conduit.

dimensional mixing across the flow stream. This is known as *turbulent* flow. Most pollution control equipment and atmospheric plumes are subjected to turbulent flow (Figure 16.15).

Flows in closed conduits with Reynolds numbers under 2100 are usually laminar.<sup>i</sup> Due to the relatively low velocities associated with this type of flow, they are mainly encountered with liquids such as water moving through underground strata and blood flowing in arteries. In open atmospheric conditions, such as a plume of an air pollutant, laminar flow is quite rare. Flows with Reynolds numbers greater than 4000 are usually turbulent. The range of  $N_R$  values between these thresholds are considered “critical flows” or “transitional flows”, that show properties of both laminar and turbulent flow in the flow streams. Usually, if the flow is in the transition region, engineers will design equipment as if the flow were turbulent, as this is the most conservative design assumption.

Under laminar conditions, the fluid particles adhere to the conduit wall. The closer to the wall that a particle gets, the more likely it will adhere to the wall. Laminar flow is, therefore, parabolic and its velocity at the conduit wall is zero (Figure 16.14). Laminar flow velocity is greatest at the pipe’s center ( $v_{\max}$  in the Figure 16.16), and is twice the value of the average velocity,  $v_{\text{average}}$ :

$$v_{\text{average}} = \frac{\dot{V}}{A} = \frac{v_{\max}}{2} \text{ (laminar)} \quad (16.37)$$

<sup>i</sup>The literature is not consistent on the exact Reynolds numbers as thresholds for laminar *versus* turbulent flow. Another value used by engineers is 2300.

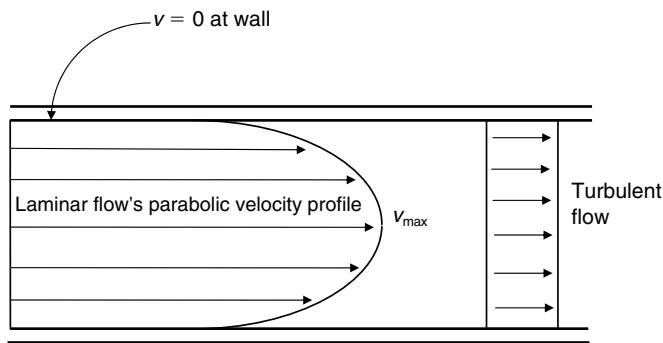


FIGURE 16.16 Velocity distributions of laminar and turbulent flows.

where  $\dot{V}$  is the volumetric fluid velocity and  $A$  is the cross-sectional area of the pipe. Turbulent flow velocity, on the other hand, has no relationship with the proximity to the wall due to the mixing (Figure 16.15). So, all fluid particles in a turbulent system are assumed to share the same velocity (as depicted in Figure 16.16), known as the average velocity or bulk velocity:

$$v_{\text{average}} = \frac{\dot{V}}{A} \quad (16.38)$$

There is a thin layer of turbulent flow near the wall of the conduit where the velocity increases from zero to  $v_{\text{average}}$ , known as the *boundary layer*. In fact, no flow is entirely turbulent and there is some difference between the centerline velocity and  $v_{\text{average}}$ . However, for many environmental applications the assumption of consistently mixed flow is acceptable.

### REYNOLDS NUMBER EXAMPLE 1

Find the Reynolds number of water flowing in a 0.2 m interior diameter (i.d.) pipe at  $0.1 \text{ m s}^{-1}$ . Assume that the water's coefficient of viscosity is  $8 \times 10^{-3} \text{ N s m}^{-3}$  and density is  $1000 \text{ kg m}^{-3}$ .

#### Solution

Use Eqn (16.36).

$$\begin{aligned} N_R &= \frac{D_e v \rho}{\mu} \\ &= \frac{(1000 \text{ kg m}^3)(0.1 \text{ m s}^{-1})(0.2 \text{ m})}{8 \times 10^{-3} \text{ N s m}^{-2}} \\ &= 2500 \end{aligned}$$

### REYNOLDS NUMBER EXAMPLE 2

How is the flow in Example 1 characterized? Assuming this flow is representative of a cooling tower in a power plant, what kind of flow should be assumed in selecting pumps and other equipment? Describe the difference in flow if, rather than a cooling tower, the flow would be from a wet scrubber system.

#### Solution

Since the  $N_R$  is greater than 2100, but less than 4000, the flow is considered transitional or critical. Therefore, the conservative design calls for an assumption that the flow is turbulent. If the flow were from a scrubber, this would likely have much higher suspended solids and may in some cases

become non-Newtonian. So, not only would the Reynolds number likely greatly decrease (i.e. laminar flow more likely with low velocity and high viscosity), but the characteristics of the fluid would also change if the flow were non-Newtonian. This is because the viscosities are not constant at all shear rates in non-Newtonian fluids.

The fundamental fluid properties and physical principles discussed in this chapter are important in all environmental sciences. In Chapters 30 and 31, we will extend these and other physical concepts specifically to carrier gases and removal of pollutants before they reach the atmosphere.

## 16.2 AIR POLLUTION VARIABILITY AND UNCERTAINTY

Air pollution occurs at every scale, from the cell to the planet. Cellular processes have been described in Part II. This section briefly considers the various types of variability and uncertainty of air pollution from the individual person to globe.

Variability describes the inherent heterogeneity across space, in time, or among individuals, which cannot be reduced with additional investigation, but only better understood or characterized.<sup>1</sup> In air pollution, variability exists at every scale regarding the amount and type of pollutant released, the transport, transformation and fate of the pollutant, the potential exposures to the pollutant, and possible outcomes resulting from contact with the pollutant for numerous receptors and their specific characteristics (e.g. demographic and socioeconomic status for human populations; biological organization and trophic status for ecosystems) or activities (e.g. the amount of water or fish consumed on a daily basis, residence in geographic areas). Variability affects the precision of estimates of air pollution quantities and location, as well as the degree to which results may be generalized. Examples of the kinds of air pollution variability include human (intra- and interindividual), ecosystem (predator-prey, productivity and diversity), which includes both spatial and temporal variabilities.

Human variability describes person-to-person differences in biological susceptibility, exposure, and effects from contact with air pollutants. Also, species and subspecies (e.g. polymorphisms) of organisms vary in their response to pollutants. This makes for difficulties in extrapolating results from animal studies to humans (both cancer and noncancer), as well as extrapolating the condition of an ecosystem from the condition of just a few species in that system. Thus, variability may be both intraspecies and interspecies.

Human populations have intra- and interindividual variability. Intra-individual variability refers to the changes that occur in one person over time. These changes can be physiological (e.g. body weight, age, and cognitive function) or behavioral (e.g. ingestion rates and activity patterns). The distinction between physiological and behavioral is somewhat arbitrary. For example, breathing rate may change physiological with aging or disease status, or because a person has changed activities (e.g. a less active job). Interindividual variability refers to the differences among individuals within a population; whereas intraindividual variability can arise from differences in physiological or behavioral characteristics.

Accuracy is an expression of the agreement between a measured or modeled value and the true value. Error is the difference between a measured or modeled quantity

and the true value. Thus, accuracy decreases with error, which is mainly comprised of systematic and random error. These and other sources of error are described in Table 16.5.

## 16.3 AIR POLLUTION SCALES IN SPACE AND TIME

Air pollution varies spatially and temporally, i.e. in space and time, respectively. Spatial variability can occur at regional, local, neighborhood, microenvironmental, and personal scales. For example, inhalation rates vary somewhat from one city to the next and certainly vary with latitude (e.g. different outdoor activities in Northern latitudes than in the Tropics). Temporal variability occurs over large time horizons, from very long or to very short periods. For example, a change in outdoor exercise can occur seasonally or even daily, depending on weather conditions. Such season variability is known as intra-annual variability.

Air pollution studies address the pollutant source, exposed population (e.g. infants and pregnant women), time frame of exposure, routes and pathways of exposure, microenvironment, and activities.

A person is exposed to pollutants continuously, with exposures varying according to activities and locations. The phenomenon known as “personal cloud” suggests a unique atmosphere surrounding the individual. The cloud indicates an increased personal exposure to air pollutants compared to indoor concentrations, or compared to the time-weighted indoor and outdoor concentrations (Figure 16.17). Results from several recent studies suggest that a number of factors, such as relative humidity and ventilation, may lead to very different exposures based on personal measurements *versus* ambient concentrations of air pollutants.

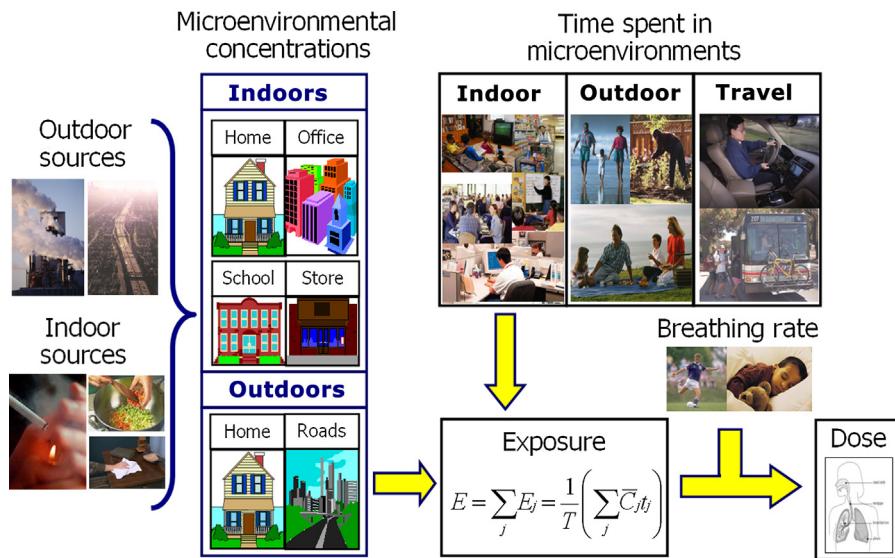
### 16.3.1 Personal Scale

With personal monitoring, the monitoring device is worn by individuals as they proceed through their normal activities. This approach is most common in workplaces. The radioactivity sensors worn by nuclear power plant workers are one example. Personal monitoring is increasingly being used, however, to estimate total human exposures, including exposures from the air people breathe, the water they drink, and the food they eat.<sup>1</sup> One advantage of personal monitoring is that the data provide valuable insights into the sources of the pollutants to which people are actually exposed. A challenge with personal monitoring is ensuring that sufficient sampling is done to be representative of the population being studied.

**TABLE 16.5** Types of Uncertainty and Contributing Errors in Air Pollution Science and Engineering

Type of Uncertainty	Type of Error Causing Uncertainty	Description or Example
Emissions	Misclassification and miscalculation	Reliance on third-party and other sources of information with little or no metadata regarding quality. Confusing actual emission measurements with reported estimates.
Transport and transformation	Incorrect model application	Applying a model for the wrong chemistry, atmospheric, terrain, and other conditions, e.g. using a simple dispersion model in a complex terrain. Applying a quantitative structural activity relationship (QSAR) to inappropriate compounds, e.g. for metals when the QSAR is only for organic compounds, or for semivolatile compounds when the QSAR is only for volatile organic species.
Exposure scenario	Misclassification	Failure to adequately identify exposure routes, exposure media, and exposed population
Sampling or measurement (parameter uncertainty)	Measurement: random	Random errors in analytical devices (e.g. imprecision of continuous monitors that measure stack emissions)
	Measurement: systemic	Systemic bias (e.g. estimating inhalation from indoor ambient air without considering the effect of volatilization of contaminants from hot water during showers)
	Surrogate data	Use of alternate data for a parameter instead of direct analysis of exposure (e.g. use of population figures as a surrogate for population exposure)
	Misclassification	Incorrect assignment of exposures of subjects in historical epidemiologic studies resulting from faulty or ambiguous information
	Random sampling error	Use of a small sample of individuals to estimate risk to exposed workers
	Nonrepresentativeness	Developing exposure estimates for a population in a rural area based on exposure estimates for a population in a city
Observational or modeling	Relationship errors	Incorrectly inferring the basis of correlations between environmental concentrations and urinary output
	Oversimplification	Misrepresentations of reality (e.g. representing a three-dimensional aquifer with a two-dimensional mathematical model)
	Incompleteness	Exclusion of one or more relevant variables (e.g. relating a biomarker of exposure measured in a biological matrix without considering the presence of the metabolite in the environment)
	Surrogate variables	Use of alternate variables for ones that cannot be measured (e.g. using wind speed at the nearest airport as a proxy for wind speed at the facility site)
	Failure to account for correlations	Not accounting for correlations that cause seemingly unrelated events to occur more frequently than expected by chance (e.g. two separate components of a nuclear plant are missing a particular washer because the same newly hired assembler put them together)
	Model disaggregation	Extent of (dis)aggregation used in the model (e.g. separately considering subcutaneous and abdominal fat in the fat compartment of a physiologically based pharmacokinetic (PBPK) model)
	Biological plausibility	Applying a PBPK model to chemicals for which it has not been coded, e.g. a one-compartment model for a compound with known metabolites.

Source of some of the information: U.S. Environmental Protection Agency. An examination of EPA risk assessment principles and practices. Report No. EPA/100/B-04/001. Washington (DC). <http://www.epa.gov/OSA/pdfs/ratf/final.pdf>; 2004 [accessed 30.10.13].



**FIGURE 16.17** Various scales of air pollution that contribute to personal exposures. A person spends varying amounts of time indoors and outdoors in numerous locations. Each has its own unique exposure profile due to varying airborne concentrations of pollutants and time spent in each microenvironment. In addition, unique characteristics of the person and activity, e.g. breathing rate, also change the amount of pollutant absorbed, which leads to a unique dose of the pollutant. (For color version of this figure, the reader is referred to the online version of this book.) Ozkaynak H. Case study applications of human exposure models. Eurotox 2009 conference, WHO/IPCS CEC6 exposure assessment course. Dresden, Germany; September 13, 2009.

Sampling the amount of pollutant near or within a person, e.g. using personal monitors and biomarkers, is known as a direct measurement. Use of models, microenvironmental measurements, and questionnaires, where measurements do not actually involve personal measurements, are examples of indirect methods of determining personal exposures to air pollutants. The direct/indirect nomenclature focuses on the type of measurements being made; the scenario evaluation/point-of-contact/reconstruction nomenclature focuses on how the data are used to develop the dose estimate. The three-term nomenclature is used in these guidelines to highlight the point that three independent estimates of dose can be developed.

As discussed in Chapter 8, there is seldom a sufficient amount of direct information from measurements to estimate and to predict exposures for a population. Thus, indirect methods must be used. Personal exposure<sup>2a,b</sup> can be expressed mathematically as a composite of the time in a microenvironment (e.g. in a garage, indoors at home, or in a car) and the concentration of the pollutant in that microenvironment:

$$E_i = \sum_{j=1}^m T_{ij} C_{ij} \quad (16.39)$$

where  $T_{ij}$  is the time spent in microenvironment  $j$  by person  $i$  with typical units of minutes,  $C_{ij}$  is the air pollutant concentration person  $i$  experiences in microenvironment  $j$  with typical units of  $\mu\text{g m}^{-3}$ ,  $E_i$  represents the exposure for person  $i$  integrated  $T_{ij}$ , and  $m$  is the number of

different microenvironments. Thus, the units of exposure are mass per volume-time  $\mu\text{g m}^{-3} \text{ min}^{-1}$ . Note, then, that exposure is the concentration per unit time. The calculation amounts to a weighted sum of concentrations with the weights being equal to the time spent experiencing a given concentration.

What people are doing is crucial to modeling their exposure to air pollutants. To support exposure, intake dose, and risk assessments, the EPA developed the Consolidated Human Activity Database (CHAD). CHAD is a relational database with a graphical user interface that facilitates queries and report generation.<sup>3</sup> It contains databases from previously existing human activity pattern studies, which were incorporated in two forms: (1) as the original raw data and (2) as data modified according to predefined format requirements. CHAD contains data obtained from pre-existing human activity studies that were collected at city, state, and national levels. People's diary information is input to CHAD. Figure 16.18 and Tables 16.6 and 16.7 provide the structure and data elements of CHAD. Most of the fields are answers from the questionnaire. Some fields vary from day to day for an individual and fields based on the diary entries will most likely be different for each day. The CHAD\_Diary table contains one record for each activity during a 24-h period. No record represents more than an hour or crosses the hour boundary. The minimal information in the diary data is the CHADID which links to the CHAD\_DATA, a sequence number, which indicates the order of the records in a day, start, end, and duration times, and an activity and location.

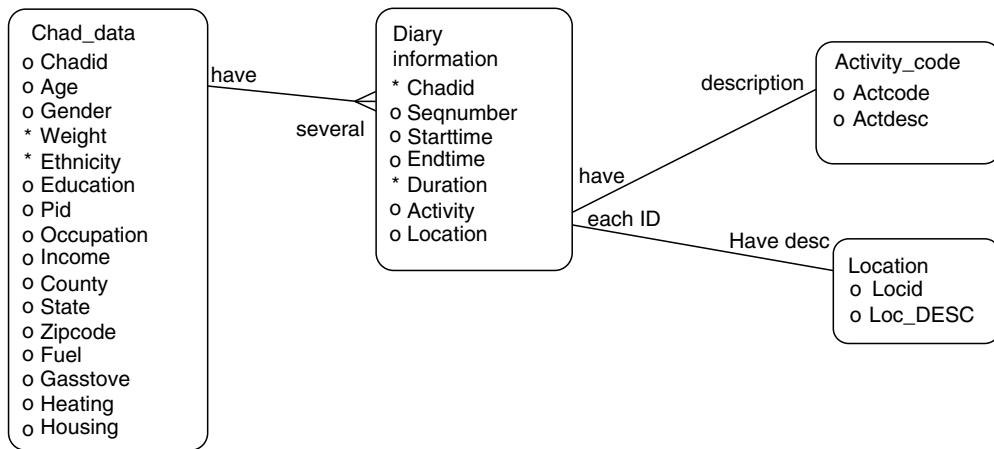


FIGURE 16.18 Schematic of the tables and relationships among the tables in the combined CHAD. Ref. 3.

TABLE 16.6 CHAD Diary Activity Code Descriptions

30000 Residence, general	31300 Waiting
30010 Your residence	31310 Wait for bus, train, ride (at stop)
30020 Other's residence	31320 Wait for travel, indoors
30100 Residence, indoor	31900 Other travel
30120 Your residence, indoor	31910 Travel by other vehicle
30121 Kitchen	32000 Other, indoor general
30122 Living room/family room	32100 Office building/bank/post office
30123 Dining room	32200 Industrial plant/factory/warehouse
30124 Bathroom	32300 Grocery store/convenience store
30125 Bedroom	32400 Shopping mall/non-grocery store
30126 Study/office	32500 Bar/night club/bowling alley
30127 Basement	32510 Bar/night club
30128 Utility room/laundry room	32520 Bowling alley
30129 Other indoor	32600 Repair shop
30130 Other's residence, indoor	32610 Auto repair shop/gas station
30131 Other's kitchen	32620 Other repair shop
30132 Other's living room/family room	32700 Indoor gym/sports or health club
30133 Other's dining room	32800 Child care facility
30134 Other's bathroom	32810 Child care facility, house
30135 Other's bedroom	32820 Child care facility, commercial
30136 Other's study/office	32900 Public building/library/museum/theater
30137 Other's basement	32910 Auditorium, sport's arena/concert hall
30138 Other's utility room/laundry room	32920 Library/courtroom/museum/theater
30139 Other indoor	33100 Laundromat
30200 Residence, outdoor	33200 Hospital/health care facility/doctor's office
30210 Your residence, outdoor	33300 Beauty parlor/barber shop/hairdresser's

(Continued)

TABLE 16.6 CHAD Diary Activity Code Descriptions—cont'd

30211 Your residence—pool, spa	33400 At work: no specific location, moving among locations
30219 Your residence—other outdoor	33500 At school
30220 Other's residence, outdoor	33600 At restaurant
30221 Other's residence—pool, spa	33700 At church
30229 Other's residence—other outdoor	33800 At hotel/motel
30300 Garage	33900 At dry cleaners
30310 Indoor garage	34100 Parking garage
30320 Outdoor garage	34200 Laboratory
30330 Your garage	34300 Other, indoor
30331 Your indoor garage	35000 Other outdoor, general
30332 Your outdoor garage	35100 Sidewalk/street/neighborhood
30340 Other's garage	35110 Within 10 yards of street
30341 Other's indoor garage	35200 Public garage/parking lot
30342 Other's outdoor garage	35210 Public garage
30400 Other, residence	35220 Parking lot
31000 Travel, general	35300 Service station/gas station
31100 Motorized travel	35400 Construction site
31110 Travel by car	35500 Amusement park
31120 Travel by truck	35600 School grounds/playgrounds
31121 Travel by truck (pick-up van)	35610 School grounds
31122 Travel by truck (other than pick-up or van)	35620 Playground
31130 Travel by motorcycle/moped/	35700 Sports stadium and amphitheater motorized scooter
31140 Travel by bus	35800 Park/golf course
31150 Travel by train/subway/rapid transit	35810 Park
31160 Travel by airplane	35820 Golf course
31170 Travel by boat	35900 Pool, river, lake
31171 Travel by motorized boat	36100 Restaurant, picnic
31172 Travel by unmotorized boat	36200 Farm
31200 Non-motorized travel	36300 Other outdoor
31210 Travel by walk	U uncertain
31220 Travel by bicycle/skateboard/roller-skates	X missing
31230 Travel in a stroller or carried by an adult	

Source: Ref. 3.

Thus, if we measure concentrations with personal and indoor air pollution monitors and we apply activity patterns, such as those in CHAD, we can estimate and predict personal exposures to numerous pollutants.

Obviously the mean personal exposure can be expressed in concentration units ( $\mu\text{g m}^{-3}$ ) by dividing  $E_i$  by the total time spent in each microenvironment

and summing these exposures. Further, this can also be seen as a continuum in which the personal exposure is assumed to be constant during each time comprising  $T_{ij}$ :

$$E_i = \int_1^2 C_{ij}(t; x; y; z) dt \quad (16.40)$$

**TABLE 16.7** CHAD Diary Activity Code Descriptions

10000 Work and other income-producing activities, general	15200 Attend other classes
10100 Work, general	15300 Do homework
10110 Work, general, for organizational activities	15400 Use library
10111 Work for professional/union organizations	15500 Other education
10112 Work for special interest identity organizations	16000 General entertainment/social activities
10113 Work for political party and civic participation	16100 Attend sports events
10114 Work for volunteer/helping organizations	16200 Participate in social, political, or religious activities
10115 Work of/for religious groups	16210 Practice religion
10116 Work for fraternal organizations	16300 Watch movie
10117 Work for child/youth/family organizations	16400 Attend theater
10118 Work for other organizations	16500 Visit museums
10120 Work, income-related only	16600 Visit
10130 Work, secondary (income-related)	16700 Attend a party
10200 Unemployment	16800 Go to bar/lounge
10300 Breaks	16900 Other entertainment/social events
11000 General household activities	17000 Leisure, general
11100 Prepare food	17100 Participate in sports and active leisure
11110 Prepare and clean-up food	17110 Participate in sports
11200 Indoor chores	17111 Hunting, fishing, hiking
11210 Clean-up food	17112 Golf
11220 Clean house	17113 Bowling/pool/ping pong/pinball
11300 Outdoor chores	17114 Yoga
11310 Clean outdoors	17120 Participate in outdoor leisure
11400 Care of clothes	17121 Play, unspecified
11410 Wash clothes	17122 Passive, sitting
11500 Build a fire	17130 Exercise
11600 Repair, general	17131 Walk, bike, or jog (not in transit)
11610 Repair of boat	17140 Create art, music, participate in hobbies
11620 Paint home/room	17141 Participate in hobbies
11630 Repair/maintain car	17142 Create domestic crafts
11640 Home repairs	17143 Create art
11650 Other repairs	17144 Perform music/drama/dance
11700 Care of plants	17150 Play games
11800 Care for pets/animals	17160 Use of computers
11900 Other household	17170 Participate in recess and physical education
12000 Child care, general	17180 Other sports and active leisure
12100 Care of baby	17200 Participate in passive leisure
12200 Care of child	17210 Watch
12300 Help/teach	17211 Watch adult at work

(Continued)

TABLE 16.7 CHAD Diary Activity Code Descriptions—cont'd

12400 Talk/read	17212 Watch someone provide child care
12500 Play indoors	17213 Watch personal care
12600 Play outdoors	17214 Watch education
12700 Medical care—child	17215 Watch organizational activities
12800 Other child care	17216 Watch recreation
13000 Obtain goods and services, general	17220 Listen to radio/listen to recorded music/watch TV
13100 Dry clean	17221 Listen to radio
13200 Shop/run errands	17222 Listen to recorded music
13210 Shop for food	17223 Watch TV
13220 Shop for clothes or household goods	17230 Read, general
13230 Run errands	17231 Read books
13300 Obtain personal care service	17232 Read magazines/not ascertained
13400 Obtain medical service	17233 Read newspaper
13500 Obtain government/financial services	17240 Converse/write
13600 Obtain car services	17241 Converse
13700 Other repairs	17242 Write for leisure/pleasure/paperwork
13800 Other services	17250 Think and relax
14000 Personal needs and care, general	17260 Other passive leisure
14100 Shower, bathe, personal hygiene	17300 Other leisure
14110 Shower, bathe	18000 Travel, general
14120 Personal hygiene	18100 Travel during work
14200 Medical care	18200 Travel to/from work
14300 Help and care	18300 Travel for child care
14400 Eat	18400 Travel for goods and services
14500 Sleep or nap	18500 Travel for personal care
14600 Dress, groom	18600 Travel for education
14700 Other personal needs	18700 Travel for organizational activity
15000 General education and professional training	18800 Travel for event/social activity
15100 Attend full-time school	18900 Travel for leisure
15110 Attend day-care	18910 Travel for active leisure
15120 Attend K-12	18920 Travel for passive leisure
15130 Attend college or trade school	U unknown
15140 Attend adult education and special training	X missing

Source: Ref. 3.

where  $C_i(t, x, y, z)$  is the concentration occurring at a specific point occupied by person  $i$  at time  $t$  and spatial coordinates  $(x, y, z)$ , and  $t_1$  and  $t_2$  are the respective starting and ending times of a given exposure episode. The concentrations can be measured using a real-time personal

monitoring device. These data are not actually continuous, but can be quite frequent (e.g. every few seconds).

Other times, fully continuous space is not assumed, which means that discrete microenvironments are used. If this is the case the equation appears as

$$E_i = \left( \sum_{j=1}^m \int_{t_{j1}}^{t_{j2}} C_{ij}(t) dt \right) \quad (16.41)$$

where  $C_{ij}(t)$  is the concentration to which the person is exposed in the discrete microenvironment  $j$  at a specific point in time  $t$  over the time interval defined by  $(t_{j1}, t_{j2})$ , where  $t_{j1}$  is the starting time for the microenvironment and  $t_{j2}$  is the ending time. If we assume that every person in a population is exposed to the same microenvironment concentrations, a simplified population exposure can be derived to show the total time spent by all receptors in each microenvironment:

$$\tilde{E} = \sum_{j=1}^m C_j \tilde{T}_j \quad (16.42)$$

where  $m$  is the number of microenvironments encountered,  $C_j$  is the average pollutant concentration in microenvironment  $j$  assigned to every person  $i$ ,  $\tilde{E}$  is the integrated exposure over all members of the population. The total time spent by all persons in microenvironment  $j$  is

$$\tilde{T}_i = \sum_{i=1}^n T_{ij} \quad (16.43)$$

where  $n$  is the total number of people in the population being modeled. This can be further simplified if we assume that each person spends the same total amount of time across all microenvironments:

$$T = T_i = \sum_{j=1}^m T_{ij} \quad (16.44)$$

Further, if the time spent by certain individuals in particular microenvironments is zero, then the average personal exposure ( $\bar{E}$ ) for the population would be

$$\bar{E}_c = \frac{1}{nT} \sum_{j=1}^m C_j \tilde{T}_j \quad (16.45)$$

Therefore, time–activity relationships and concentrations can be used to model expected exposures to air pollutants. Indoor and personal exposures can dominate exposures to many pollutants. For example, Figure 16.19 shows the modeled results of expected exposures to particulates ( $PM_{2.5}$ ) for a simulated population based on available measurements of ambient, indoor, and personal measurements, combined with information about microenvironments (e.g. types and time in each) and activities. Note that ambient contribution is quite small compared to personal and indoor exposures.<sup>4</sup>

### 16.3.2 Microenvironmental Scale

The next most important scale of exposure after personal scale is the microenvironment. For air pollutants, the microenvironment can be any air volume (e.g. home, office or vehicle) that is assumed to be sufficiently homogeneous and characterized in the concentrations of an air pollutant.

Persons can be exposed to harmful substances in the air that they breathe, the food that ingest and products that they use (Figure 16.20). Indeed, at the microenvironmental scale, inhalation is not the only pathway of exposure, since air pollutants may settle on surfaces (e.g. floors, furniture, and food). Thus, even for a pollutant that enters the microenvironment via the air, in addition to the inhalation and nasal routes, the route of exposure may be dermal or ingestion.

The source of microenvironmental exposures may be at a distance (e.g. the home is in the plume of pollutants released upwind). However, many microenvironmental exposures are generated with the microenvironment (e.g. smoking, use of personal care products, and applying pesticides). Some of the possible microenvironmental exposure scenarios are shown in Figure 16.18, the source emanates from leaking chemical drums. A less complicated scenario would be a stack release from an air pollutant that penetrates the microenvironment. A more complicated scenario would involve numerous steps following release from the source that include transport and transformation in the various compartments before finally arriving in the microenvironment.

Actual measurements within microenvironments are much more frequently conducted in occupational settings than in residential and other environmental settings. Thus, many microenvironmental pollution exposure estimates are based on indirect information, such as biomarkers. For example, in an occupational setting the amount of lead (Pb) in the air may well be measured using sampling equipment. However, in a residential setting, Pb exposures may have to be reconstructed from biomarker data and epidemiology, e.g. blood Pb from health clinics. The estimates would be based on assumptions about breathing rates and activities (e.g. the amount of time spent in each microenvironment), combined with pharmacokinetics (e.g. how much of the Pb is expected to be in a child's blood given assumptions about intake, uptake, adsorption, distribution, metabolism, and elimination). For example, if a child's blood concentration of contaminant A is  $10 \mu\text{g dl}^{-1}$ , the model may include average diary or the CHAD database mentioned previously to make assumptions about the respective time spent in each microenvironment.

If the pharmacokinetics model indicates that  $1 \mu\text{g dl}^{-1}$  of contaminant A in the blood relates to a concentration of  $0.3 \mu\text{g m}^{-3}$  of contaminant A in the air, then

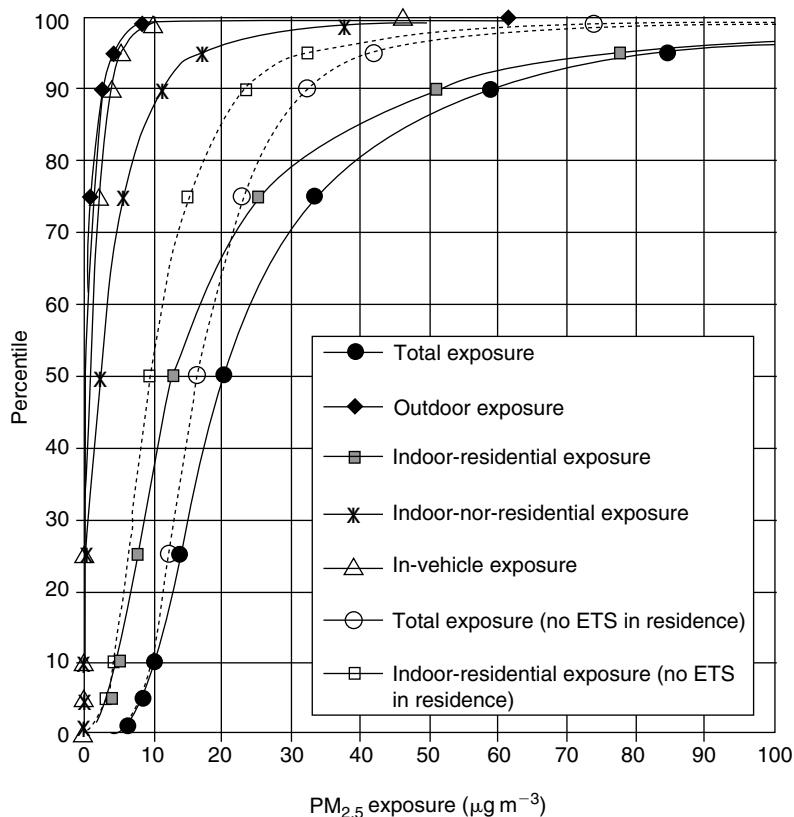


FIGURE 16.19 Cumulative frequency distributions of daily total and microenvironmental PM<sub>2.5</sub> exposures (µg m<sup>-3</sup>) for the simulated population of Philadelphia (solid lines). Distributions of total and indoor residential PM<sub>2.5</sub> exposures for the population without environmental tobacco smoke (ETS) exposure in the residence (dashed lines) are also shown. Ref. 4.

the estimate of average exposure concentration in all microenvironments would be  $10 \times 0.3 = 3 \mu\text{g m}^{-3}$ . Next, each microenvironment would have to be considered. For example, if the child spent 2 h each day outdoors, but there appears to be no outdoor source of contaminant A nearby, those 2 h may be dropped from the daily exposure, i.e. the other 22 h in other microenvironments must account the blood levels. Other microenvironments may be eliminated in the same way. Those that are left must account for the exposures. For example, if the likely microenvironments represent only 8 h per day, the extrapolated concentration in contaminated microenvironments would be  $3 \mu\text{g m}^{-3} \times 3 = 9 \mu\text{g m}^{-3}$ .

Note that the uncertainties are built into these models, e.g. blood and urine may be reliable biomarkers for less persistent compounds, since they may be sequestered and better represented in fatty tissue, hair or nails. However, the choice of biomarkers is complicated, so rules of thumb are not very useful. Each biomarker must be selected based on characteristics of the parent pollutant, the pharmacokinetics specific to each stratum of the population to which it will be

applied, e.g. children will have very different pharmacokinetics than adults, and the reliability of the algorithms and assumptions of the model being used.

When they are taken, actual microenvironmental measurements must be taken from specific zones expected to be relatively homogeneous and amenable to characterizing the conditions in that zone. Microenvironments may be further divided into time segments (e.g. kitchen-day, kitchen-night). This can produce measurements closely linked to the point of human contact in both location and time. Such studies represent a very limited environment, however, so care must be applied when attempting to use these measurements to represent a population of interest beyond the individuals spending time in the specific microenvironment in which air pollution measurements have been taken.

### 16.3.3 Ambient Scale

Most environmental air quality regulations apply to ambient air concentrations of pollutants. Although much of the exposures occur in microenvironments,

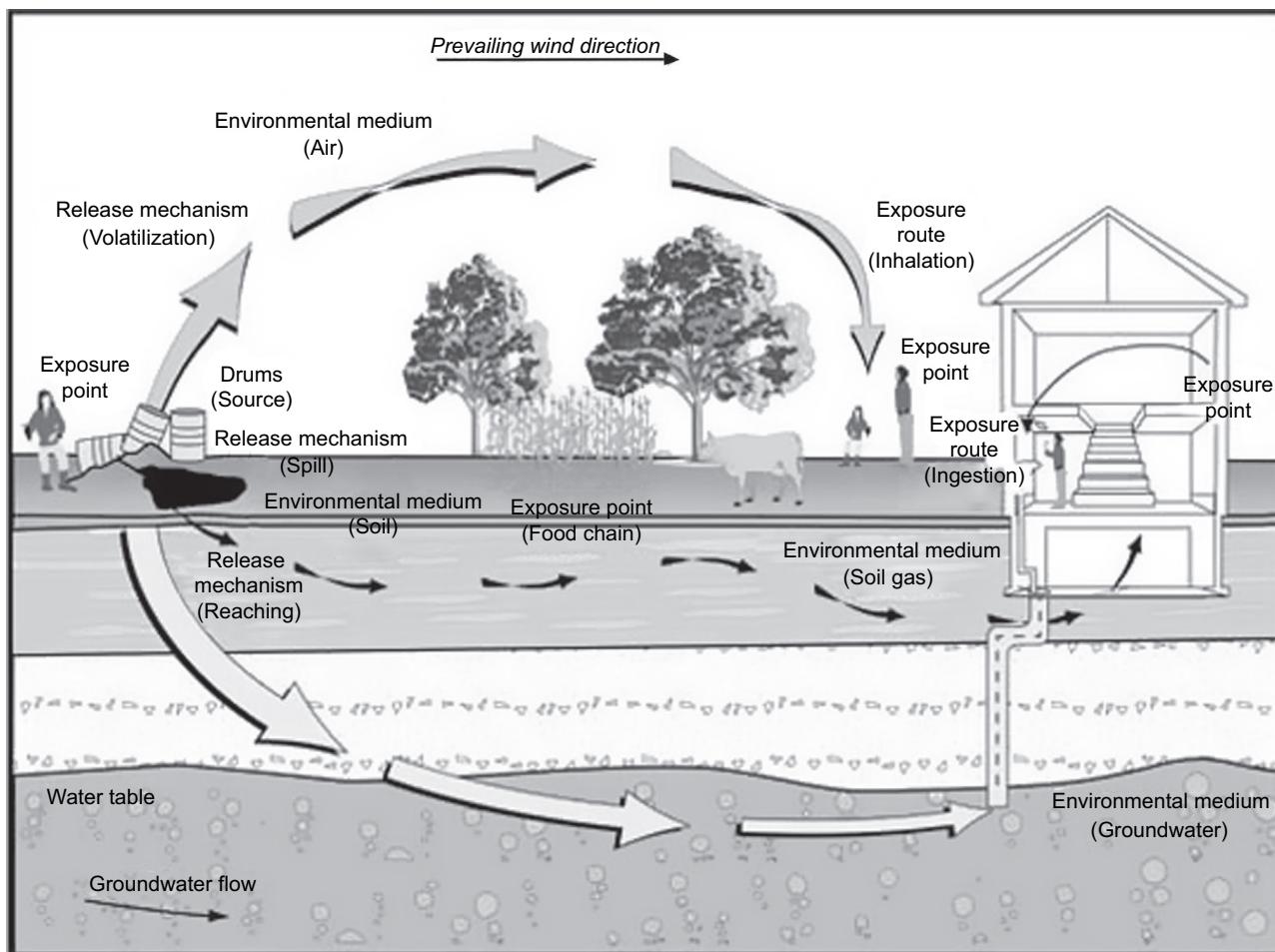


FIGURE 16.20 Schematic of an exposure entering a microenvironment from a distant source (i.e. waste drums). The schematic indicates numerous ways that contaminants can move from the source through media compartments to points of exposure. Agency for Toxic Substances and Disease Registry. Public health assessment guidance manual (2005 update). Atlanta: ATSDR. <http://www.atsdr.cdc.gov/HAC/PHAmanual/index.html>; 2005 [accessed 29.10.13].

most environmental legislation only addresses outdoor air. The divisions within ambient air are arbitrary and pollutant dependent. For example, carbon monoxide is more localized in extent than is ozone and photochemical oxidant smog.

#### 16.3.3.1 Local

Local air pollution problems are usually characterized by one or several large emitters or a large number of relatively small emitters. The potential impact on nearby receptors increases with decreasing height of release. Carbon monoxide, benzene, and 1,3-butadiene emitted from motor vehicles lead to high concentrations near roadway, for example. Any ground-level source, such as evaporation of volatile organic compounds from a waste treatment pond, will produce the highest concentrations near the source, with concentrations generally diminishing with distance. This is a local example of a concentration gradient.

Large sources that emit high above the ground through stacks, such as those in power plants or industrial sources, can also cause local problems, especially under unstable meteorological conditions that cause portions of the plume to reach the ground in high concentrations. In urban setting around the world, pollutants are frequently and continuously emitted from relatively short stacks or vents on the top of one- or two-story buildings. Under most conditions such releases are caught within the turbulent downwash downwind of the building. This allows high concentrations to be brought to the ground surface. Many different pollutants can be released in this manner, including compounds and mixtures that can cause odors. The modeling of the transport and dispersion of pollutants on this scale is discussed in Chapter 27.

Usually, the most acute effects of accidental releases are at the local scale. For example, a fire, derailed rail car leak, or an industrial accident usually requires

evacuation from within a local area. Indeed, guidelines are given for first responders on the recommended distances for such evacuations. Even for a highly toxic substance, the areas are generally at the neighborhood scale. For example, in the United States, the initial isolation and protective distances following a chlorine gas ( $\text{Cl}_2$ ) leak are<sup>5</sup>:

- If a tank, rail car, or tank truck is involved in a fire, isolate it for 0.5 mi (800 m) in all directions; also consider initial evacuation for 0.5 mi (800 m) in all directions.
- Small spills (involving the release of approximately 52.83 gallons (200 l) or less)
- First isolate in all directions: 100 ft (30 m).
- Then protect persons downwind during the day: 0.2 mi (0.2 km).
- Then protect persons downwind during the night: 0.8 mi (1.2 km).
- Large spills (involving quantities greater than 52.83 gallons (200 l))
- First isolate in all directions: 800 ft (240 m).
- Then protect persons downwind during the day: 1.5 mi (2.4 km).
- Then protect persons downwind during the night: 4.6 mi (7.4 km).

### 16.3.3.2 Urban

Air pollution problems in urban areas generally are of two types. One is the release of primary pollutants (those released directly from sources). The other is the formation of secondary pollutants (those that are formed through chemical reactions of the primary pollutants).

Air pollution problems can be caused by individual sources on the urban scale as well as the local scale. For pollutants that are relatively nonreactive, such as carbon monoxide and particulate matter,<sup>j</sup> or relatively slowly reactive, such as sulfur dioxide, the contributions from individual sources combine to yield high concentrations. Since a major source of carbon monoxide is motor vehicles, "hot spots" of high concentration can occur especially near multilane intersections. The emissions are especially high from idling vehicles. The hot spots are exacerbated if high buildings surround the intersection, since the volume of air in which the pollution is contained is severely restricted. The combination of these factors results in high concentrations.

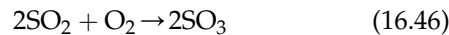
Tropospheric ozone is the dominant urban problem resulting from the formation of secondary pollutants. Many large metropolitan areas experience the formation of ozone from photochemical reactions of oxides

of nitrogen and various species of hydrocarbons. These reactions are catalyzed by the ultraviolet light in sunlight and are therefore called photochemical reactions. Many metropolitan areas are in nonattainment for ozone; that is, they are not meeting the air quality standards. The Clean Air Act Amendments (CAAAs) of 1990 recognized this as a major problem and have classified the various metropolitan areas to be in nonattainment according to the severity of the problem for that area. The CAAAs sets timetables for the various classifications for reaching attainment with the National Ambient Air Quality Standards. Oxides of nitrogen, principally nitric oxide (NO) but also nitrogen dioxide ( $\text{NO}_2$ ), are emitted from automobiles and from combustion processes. Hydrocarbons are emitted from many different sources. The various species have widely varying reactivities. Determining the emissions of these chemical species from myriad sources as a basis for pollution control programs can be difficult, but methods continue to improve. These and other aspects of atmospheric chemistry are discussed in Chapters 17 and 18.

#### 16.3.3.3 Regional

At least three types of problems contribute to air pollution problems on the regional scale. The first is the blend of urban oxidant problems at the regional scale. Many major metropolitan areas are in close proximity to one another and continue to grow. Urban geographers refer to some of the larger urban aggregations as "megapolises". As a result, the air from one metropolitan area, containing both secondary pollutants formed through reactions and primary pollutants, flows on to the adjacent metropolitan area. The pollutants from the second area are then added on top of the "background" from the first.

A second type of problem is the release of relatively slow-reacting primary air pollutants that undergo reactions and transformations during lengthy transport times. A common occurrence in environmental engineering is the direct relationship between time, spatial coverage, and chemical transformation. Thus, these protracted transport times result in transport distances over regional scales not only of the parent compounds but of numerous transformation byproducts. The gas, sulfur dioxide ( $\text{SO}_2$ ), released primarily through combustion of fossil fuels (especially from coal and oil) is oxidized during long-distance transport to sulfur trioxide ( $\text{SO}_3$ ):



<sup>j</sup>Fate may also include some remediation reactions, such as thermal and mechanical separation processes, but in discussions of fate and transport, the reactions are usually those that occur in the ambient environment. The treatment and control processes usually fall under the category of environmental engineering.

Although  $\text{SO}_2$  is a gas, both gas phase and liquid phase oxidation of  $\text{SO}_2$  occurs in the troposphere. The  $\text{SO}_3$  in turn reacts with water vapor to form sulfuric acid:



Sulfuric acid in turn reacts with numerous compounds to form sulfates. These are fine (submicrometer) particulates.

Nitric oxide ( $\text{NO}$ ) results from high-temperature combustion, both in stationary sources such as power plants or industrial plants in the production of process heat and in internal combustion engines in vehicles. The  $\text{NO}$  is oxidized in the atmosphere, usually rather slowly, or more rapidly if there is ozone present, to nitrogen dioxide ( $\text{NO}_2$ ).  $\text{NO}_2$  also reacts further with other constituents, forming nitrates, which is also in fine particulate form.

The sulfates and nitrates existing in the atmosphere as fine particulates, generally in the size range less than  $1 \mu\text{m}$ , can be removed from the atmosphere by several processes. "Rain out" occurs when the particles serve as condensation nuclei that lead to the formation of clouds. The particles are then precipitated if the droplets grow to sufficient size to fall as raindrops. Another mechanism, known as "washout", also involves rain, but the particles in air are captured by raindrops falling through the air. Both mechanisms contribute to "acid rain", which results in the sulfate and nitrate particles reaching lakes and streams, and increasing their acidity. As such, acid rain is both a regional and continental problem (see discussion in the next section).

A third type of regional problem is visibility, which may be reduced by specific plumes or by the regional levels of particulate matter that produce various intensities of haze. The fine sulfate and nitrate particulates just discussed are largely responsible for reduction of visibility (see Chapter 14). This problem is of concern in locations of natural beauty, where it is desirable to keep scenic vistas as free of obstructions to the view as possible. Regional haze is a type of visibility impairment that is caused by the emissions of air pollutants from numerous sources across a broad region. The CAAA provides special protections for such areas; the most restrictive denoted as mandatory Federal Class I areas that cover 156 national parks and wilderness areas. Decreased visibility can also impair safety, especially in aviation.

### 16.3.3.3 Continental

In a relatively small continental area such as Europe, there is little difference between what would be considered regional scale and continental scale. However, on larger continents there would be a substantial difference.

Perhaps of greatest concern on the continental scale is that the air pollution policies of a nation are likely to create impacts on neighboring nations. Acid rain in Scandinavia has been considered to have had impacts from Great Britain and Western Europe. Japan has considered that part of their air pollution problem, especially in the western part of the country, has origins in China and Korea. For decades, Canada and the United States have cooperated in studying and addressing the North American acid rain problem.

Acid rain is a continental and regional air pollution concern, affecting surface waters in large parts of North America and Europe. Actually, precipitation in North America was acidic even before industrialization. This is primarily due to the natural acidity rendered to water by carbon dioxide ( $\text{CO}_2$ ). The  $\text{CO}_2$  gas is dissolved into water droplets in the atmosphere, resulting in carbonic acid ( $\text{H}_2\text{CO}_3$ ), which is ionized. These ions increase the hydrogen ion ( $\text{H}^+$ ) concentration of the water vapor. Since pH is the negative log of the  $[\text{H}^+]$  concentration,<sup>k</sup> the pH of the water droplets must fall below neutral, i.e.  $\text{pH} = 7$ .

Acidic deposition may be wet or dry. Wet deposition refers to acidic rain, fog, and snow. The dry deposition fraction consists of acidic gases or particulates. The severity of ecological effects stemming from acid deposition depends on many factors, especially the strength of the acids and the buffering capacity of the soils and water.

Much of the pH reduction occurs as the result of interactions with a few specific air contaminants. For example, sulfur oxides produced in the burning of fossil fuels (especially coal) is a major contributor to low pH in rain. In fact,  $\text{CO}_2$  is not the principal concern of acid rain. Other processes have led to dramatic increases in droplet acidity, especially sulfuric and nitric acid formation from the ionization of the oxides of sulfur and nitrogen, which further decreases this pH level to those harmful to aquatic organisms. Acid precipitation can result from the emissions of plumes of strong acids, such as sulfuric acid ( $\text{H}_2\text{SO}_4$ ) or hydrochloric acid ( $\text{HCl}$ ) in the forms of acid mists, but most commonly the pH drop is the result of secondary reactions of the acid gases  $\text{SO}_2$  and  $\text{NO}_2$ . The dominant source of  $\text{SO}_2$  is emissions from the combustion of fuels containing sulfur. The precipitation from air containing high concentrations of sulfur oxides is poorly buffered and its pH readily drops.

Nitric oxide ( $\text{NO}$ ), nitrogen dioxide ( $\text{NO}_2$ ), and other oxidized forms of nitrogen are emitted from automobile exhaust, and any other high-temperature combustion. These reactions in the atmosphere also contribute to the acid mix in the atmosphere, with the major acid being nitric acid,  $\text{HNO}_3$ .

<sup>k</sup> More accurately, pH is the negative log of the hydronium ion,  $[\text{H}_3\text{O}^2]$ , concentration.

The continental impacts include numerous surface water bodies in North America and Scandinavia that have become so acidic that they no longer support fish life that was once abundant. In a recent study of Norwegian lakes, more than 70% of the lakes having a pH of less than 4.5 contained no fish, and nearly all lakes with a pH of 5.5 and above contained fish. The low pH not only affects fish directly, but also contributes to the release of potentially toxic metals such as aluminum, thus magnifying the problem.

In North America, acidic rain has already decimated the populations of numerous fish and many plants in 50% of the high mountain lakes in the Adirondacks. The pH in certain lakes has reached such levels of acidity as to replace the trout and native plants with acid-tolerant rough fish species and mats of algae.

The United States' recommended a deposition limit has ranged from 10 to 20 kg  $\text{SO}_4^{2-}$  per hectare per year. Putting this limit into the context of emissions, toward the end of the 20th century the state of Ohio's total annual emissions were  $2.4 \times 10^6$  metric tons of gaseous sulfur dioxide ( $\text{SO}_2$ ) per year. If these total emissions are converted to  $\text{SO}_4^{2-}$  and deposited on the State of Ohio, the total would be 360 kg per hectare per year.<sup>1</sup> Similar calculations for the sulfur emissions for northeastern United States indicate that the rate of sulfur emission is four to five times greater than the rate of deposition. As the reactions above indicate, much of the sulfur is oxidized into acidic chemical species.

Acidic deposition is an example of a continental pollution. The source can be coal burned in the U.S. West, Midwest, and Ohio River valley, but the effects are manifested thousands of miles away in the Canadian Shield. Similarly, acidic fjords and lakes in Scandinavia can be traced to the use of tall stacks in Great Britain and the lowland countries of continental Europe. British industries for some years simply built increasingly tall stacks as a method of air pollution control, reducing the immediate ground-level concentration, but emitting the same pollutants into the higher atmosphere. The air quality in the United Kingdom improved, but at the expense of acid rain at other parts of Europe. One of the difficulties in dealing with continental and intercontinental air pollution is that society must change its dependence of fossil fuels, at least those that emit chemical compounds that lead to damage to ecosystems long distances from those who benefit from the industrial output and energy production. To many nations, combustion is perceived to be tantamount to progress and development. Limitations of combustion are viewed as threats to economic development. Another perplexing aspect of acid rain is that the beneficiaries of the combustion do not suffer the direct, negative impacts of these benefits, e.g. energy production. This is akin to the water

pollution scenario where the communities downstream suffer for the benefits received by upstream polluters.

#### 16.3.3.4 Global

The release of radioactivity from the accidents at Chernobyl and more recently in Japan would be considered primarily a regional or continental problem. However, higher than usual levels of radioactivity were detected in Western North America soon after both accidents. The more recent meltdown of the Fukushima nuclear power plant in Japan is a warning that we have not learned the lessons of the interconnectedness and long-range vulnerabilities presented by air pollutants like radioisotopes. Similarly, persistent organic pollutants, such as polychlorinated biphenyls, have been observed in Arctic mammals, thousands of miles from their sources. These observations demonstrate the effects of long-range transport.

A particularly noteworthy air pollution problem of a global nature is the release of chlorofluorocarbons used as propellants in spray cans and in air conditioners, and their effect on the ozone layer high in the atmosphere (see Chapter 11).

Some knowledge of the exchange processes between the stratosphere and the troposphere and between the Northern and Southern Hemispheres was gained in the late 1950s and early 1960s as a result of the injection of radioactive debris into the stratosphere from atomic bomb tests in the Pacific. The debris was injected primarily into the Northern Hemisphere in the stratosphere. The stratosphere is usually quite stable and resists vertical air exchange between layers. It was found that the exchange processes in the stratosphere between the Northern and Southern Hemispheres is quite slow. However, radioactivity did show up in the Southern Hemisphere within 3 years of the onset of the tests, although the levels remained much lower than those in the Northern Hemisphere. Similarly, the exchange processes between the troposphere into the stratosphere are quite slow. The main transfer from the troposphere into the stratosphere is injection through the tops of thunderstorms that occasionally penetrate the tropopause, the boundary between the troposphere and the stratosphere. Some transfer of stratospheric air downward also occurs through occasional gaps in the tropopause. Since the ozone layer is considerably above the troposphere, the transfer of chlorofluorocarbons upward to the ozone layer is expected to take place very slowly. Thus, there was a lag from the first release of these gases until an effect was seen. Similarly, with the cessation of use of these materials worldwide, there has been a commensurate lag between in restoration of the ozone concentrations in the stratospheric layer (see Chapter 11).

Another global problem is climate change that is generated by excessive amounts of radiant gases (commonly known as greenhouse gases), especially methane ( $\text{CH}_4$ ) and  $\text{CO}_2$ .  $\text{CO}_2$  is not normally considered an air pollutant since it is the product of respiration and a reactant of photosynthesis. However, like other substances, it becomes a pollutant when its concentrations reach levels leading to adverse impacts. In the case of climate change, a portion of infrared radiation from the earth's surface is intercepted by the  $\text{CO}_2$  in the air and is reradiated both upward and downward. That which is radiated downward keeps the ground from cooling rapidly. As the carbon dioxide concentration continues to increase, the earth's temperature is expected to increase. It is not a question of eliminating  $\text{CO}_2$  from the atmosphere, which would be catastrophic in many ways, e.g. elimination of plant life, dramatic swings in diurnal temperatures, etc. It is a question of optimal ranges of  $\text{CO}_2$  in the troposphere and identifying when human activities add sufficient amounts to push the concentrations outside of the optimal  $\text{CO}_2$  concentration range.

The combine contributions from anthropogenic and natural sources of pollutants complicate the optimal range, since even the natural sources are highly variable. A natural air pollution problem that can cause global effects is the injection into the atmosphere of fine particulate debris by volcanoes. The addition of this particulate matter has caused some spectacular sunsets throughout the earth. If sufficient material is released, it can change the radiation balance. Blocking of the incoming solar radiation will reduce the normal degree of daytime warming of the earth's surface. A "mini-ice age" was caused in the mid-1800s, when a volcanic mountain in the Pacific erupted. The summer of that year was much cooler than usual and snow occurred in July in New England.

Global phenomena like climate can be sensitive to the effects of air pollutants. Like most environmental systems climate varies in its response to different pollutants. In fact, some pollutants lead to cooling whereas others lead to heating of the troposphere. Currently, the major concern of much of the scientific community is with warming. For example, the International Panel of Climate Change (IPCC) reports that between 1970 and 2004, global greenhouse gas emissions increased by 70%. Models vary in predicting how this increase will affect mean global temperatures and other climatic variables, but many scientists and policy makers fear that delays in curbing the trend could lead to a substantial environmental and societal catastrophe. Disasters can be direct, such as drought and biome shifting due to increased temperature. They may also be indirect, such as the economic and social costs of migrating populations due to sea level rise, or increased vector-borne

diseases due to changes in biodiversity brought on by alterations of the water cycle.

The atmosphere is a highly complex system, consisting of many interconnected and diverse systems at numerous scales. This chapter has introduced the scales of air pollution. The next chapters explain the air pollution processes that occur at various temporal and spatial scales.

## QUESTIONS

1. Air toxics are often studied at the urban scale. What is the approximate length of this scale?
2. How does flow generally differ for plumes in the troposphere compared to plumes in unconsolidated materials, e.g. ground water flow?
3. Give examples of air pollutants that have long tropospheric lifetimes and those that have short lifetimes.
4. How do ideal and real fluids differ?
5. Why is the concept of the control volume important to air pollution?
6. What is the major means of air pollutant movement in the troposphere?
7. If a PM monitor is operating at 19 kPa vacuum, what is absolute pressure of this system?
8. Over a 25-year period, the concentration of  $\text{SO}_2$  in a town is higher in the winter than in the summer every year on record. What type of variability is this?
9. A study is measuring occupational exposure to vapors of an organic solvent in the workplace. Concentrations of the compound are measured in the room where the solvent is used and compared to the concentration of the compound in the workers' urine. The study assumes that the only exposure to that solvent is occupational. However, two people also use the solvent at home in their hobbies. What type of error is being made here? Recommend at least two ways to decrease this error.
10. About 50% of the above solvent is changed physiologically after inhalation to a metabolite and the rest remains as the parent compound. However, 80% of the metabolite is eliminated into the urine within 24 h and 90% of the parent compound makes it to the urine in 24 h. The remaining part is stored in fats for a longer time period. If a worker takes up  $1 \text{ mg m}^{-3}$  of this compound, how much would be expected to be in the urine collected over a 24-h period, assuming that the company just started using the solvent today? What would need to be known if the solvent has been used for a longer time?
11. If the investigators in the two previous questions simply assume 100% of the solvent is in the urine

- sample after 24 h, what type of error would they be committing?
12. Based on your previous answers, what are the advantages and disadvantages of using urine versus blood as the medium for an exposure biomarker?
13. Consider how Eqn (16.39) is an improvement compared to assuming that a personal exposure is merely the integral of concentration with respect to time.
14. How does personal exposure to an air pollutant differ from the concentration of that pollutant in a microenvironment?
15. Why are blood and urine samples more reliable for reactive compounds than for very persistent and lipophilic compounds?
16. Are most of the neighborhood scale actions of first responder to maintain initial isolation and protective distances aimed at decreasing the hazard or decreasing the exposure to the air pollutant? Explain.
17. At what scale(s) does air pollution impair visibility? Explain.
18. Rank order the scale and complexity of problems caused by acid rain, nuclear meltdowns, stratospheric ozone depletion, and climate change. Discuss the physics, chemistry, and biology in your rationales.

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# Air Pollutant Kinetics and Transformation

## 17.1 CHEMICAL TRANSFORMATION

The extent and severity of air pollution begins with an understanding of the inherent properties of the agent, i.e. the air pollutant. The agent's properties are key to the conditions under which it will be transformed chemically as it forms within sources, moves to the atmosphere, and reaches its fate in the environment.

For this reason, chemical transformation of an air pollutant considers more than atmospheric transformation. Indeed, the most obvious stage of the air pollutant's life cycle is its residence in the atmosphere. That is what makes it an air pollutant. However, the stages before and after its atmospheric presence must also be understood, for example, to prevent air pollution before it happens. As evidence, sulfur dioxide ( $\text{SO}_2$ ) is an air pollutant that can be produced in a number of ways. If the source is combustion, the best means of preventing its formation occurs in the combustion process (using fuel with lower concentrations of sulfur). If it occurs as a result of the release of hydrogen sulfide ( $\text{H}_2\text{S}$ ) produced by anaerobic bacteria in sediment, which is subsequently transformed to  $\text{SO}_2$  in surface waters and the atmosphere, the prevention and controls would be different (e.g. increasing the oxygen content of the sediment to eliminate the anaerobes).

The atmospheric and microbial transformation results are the same, i.e. does the  $\text{SO}_2$  become transformed to other oxidized sulfur species and how much and where will this chemical compound be deposited? Although the resulting atmospheric concentrations of  $\text{SO}_2$  might be equal in both scenarios described in the previous paragraph (Figure 17.1), the transformations leading to these concentrations are quite different. In the first, the oxidation by combustion leads to the production of  $\text{SO}_2$  that is emitted directly to the atmosphere. In the second, sulfur compounds are formed in a low oxygen, reduced environment that releases a reduced form of sulfur, which is then oxidized abiotically in the atmosphere. The  $\text{SO}_2$  that is directly released to the atmosphere was already in an oxidized state, so it may remain in that form or be further oxidized.

If the fate is the human body or that of another organism, transformations continue in what is known as toxicokinetics, i.e. biochemical reactions or biotransformations that occur as a result of absorption, distribution, metabolism, and excretion of a substance. If the fate is an ecosystem or a habitat within the ecosystem, both abiotic and biotic transformations occur, depending on the conditions. Even if the fate is a material, such as part of a building or other structure, kinetics continue, e.g. a deposited sulfate compound may react with the calcium carbonate or metal in a bridge, causing corrosion and ultimately placing the driving public at risk.

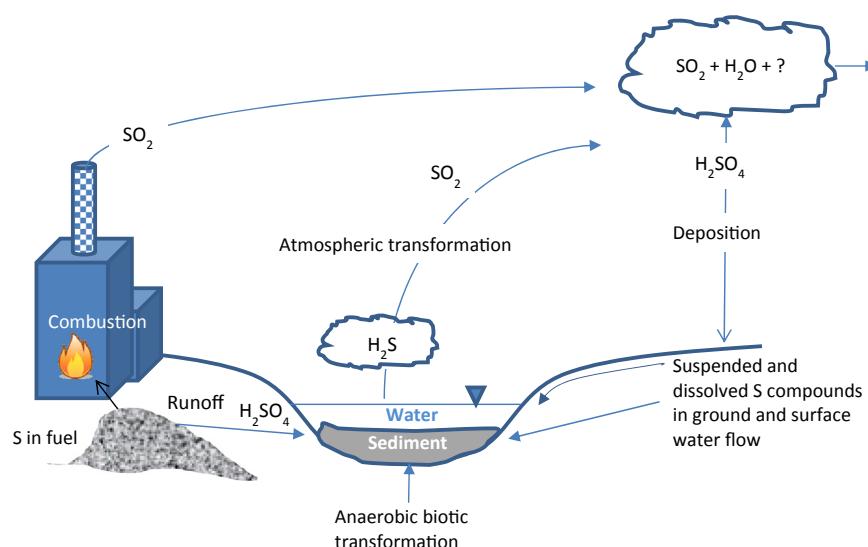
As discussed in Chapter 6, the inherent physical and chemical properties dictate some of these transformations, which can often be characterized using analytical tools, such as the quantitative structure activity relationship. These tools apply inherent properties of chemicals to estimate the damage these compounds will cause when released.

The inherent properties discussed in this chapter affect chemical transformations in the atmosphere and in other environmental compartments. Molecular weight, polarity, and molar volume are fundamental properties that are directly ascertained from the chemical structure. These drive other inherencies important to air pollution, especially aqueous solubility, vapor pressure, and dissociation constant.

The two properties that are always important in environmental and atmospheric transformation are solubility and vapor pressure, which have been described as saturation properties.<sup>1</sup> That is, they are expressions of the maximum amount of the chemical that can be held in the liquid (solubility) and gas (vapor pressure) phases. These inherent properties combine with others to make a chemical compound comparatively susceptible to environmental transformation or degradation, especially decomposition by photons (photochemical decomposition), water (hydrolysis), and energy transfer in organisms (biotic decomposition).

The inherent properties provide only part of the factors that explain the chemical transformation of a substance. The interconnectedness between physical, chemical, and

**FIGURE 17.1** Two possible transformation pathways leading to atmospheric sulfur dioxide: direct release from combustion and biotic transformation followed by oxidation in the atmosphere. (For color version of this figure, the reader is referred to the online version of this book.)



biological transformation must also account for the characteristics and processes of the environmental compartment (e.g. source substrates, air, water, biota) where the substances reside. Each chemical compound has a unique residence time or half-life ( $t_{1/2}$ ) within each compartment.

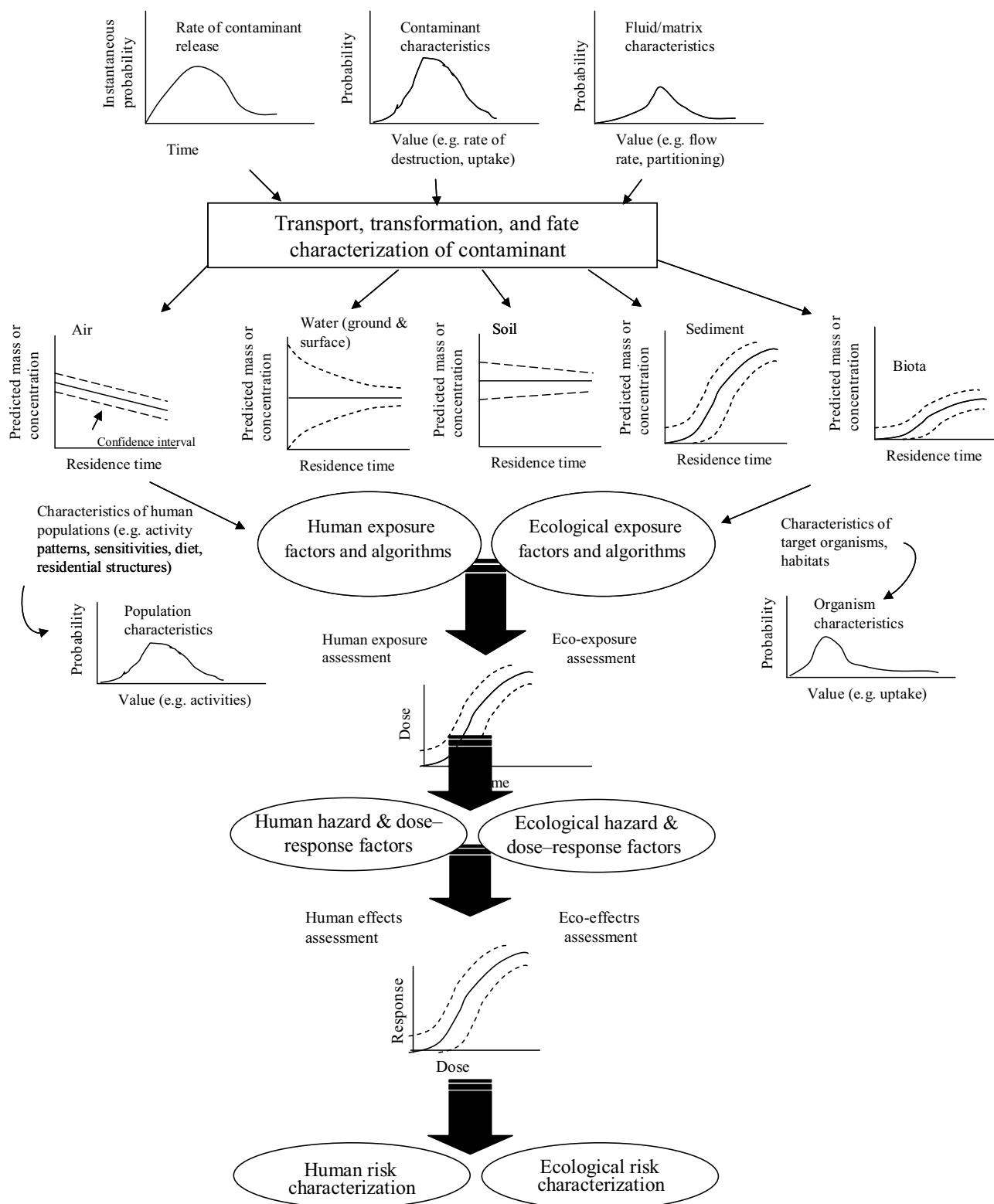
It should be noted that  $t_{1/2}$ , which is commonly used to indicate chemical and environmental persistence, is merely analogous, but not equal to the constant half-life of a radioisotope. The latter is so fixed that one can literally set an atomic clock by it. The  $t_{1/2}$  for chemicals in the environment is a function of inherent properties and environmental conditions.<sup>1</sup> All chemical transformations depend on temperature, atmospheric pressure, humidity, radical concentrations (especially hydroxyl), substrate (including water content and porosity), oxidation and reduction states, oxygen content, and microbial abundance and diversity. Thus, the  $t_{1/2}$  is highly variable by compartment and by season of the year.

Within each compartment, there are differences in factors and properties that trigger and maintain chemical reactions. For example, aromatic compounds with several halogen substitutions are highly lipophilic, so these compounds are likely to become dissolved in any organic solvents present in the soil or in a storage tank, rendering them more mobile. Conversely, these same compounds are less likely to come into contact with reactive substances in the absence of these organic solvents. Likewise, if oxygen molecules or radicals are present in abundance, oxidation reactions are likely; whereas, if oxygen is scarce, reduction reactions are expected. Thus, the inherent properties of the substance are influenced by and changed by the extrinsic properties of the media in which the pollutant resides in the environment. How molecules are sorbed to and desorbed from substrate and matrix surfaces also affects the extent of chemical transformation, i.e. tetrachlorodibenzo-*para*-dioxin is almost nonreactive in certain soils since the molecules are tightly bound to

abundant sorption site (one reason dioxin-contaminated soils are so difficult to treat; requiring large amounts of heat energy for desorption from soil surfaces). Type and amount of energy also dictates the kinds and rates of chemical transformation. If sunlight is abundant, photochemical reactions may occur. Oxidation and reduction (i.e. redox) reactions may occur if aerobic and anaerobic microbes are present, respectively, as these organisms accept and donate electrons for energy transfer.

Although this chapter specifically addresses chemical kinetics, it is difficult to disentangle transport and fate. This is because both air pollutant transport and fate are driven by thermodynamics. Energy is often described as a system's capacity to do work, so getting things done in the environment is really an expression of how efficiently energy is transformed from one form to another. Indeed, energy and matter relationships determine transport and transformation of substances in the environment. After a contaminant is released, transport mechanism begins. Physical processes determine the extent to which receptors (like people and ecosystems) will be exposed to the released substance and to any new chemical compounds it has become as it has been transported. Thus, transport and transformation determine a contaminant's fate in the environment.

Figure 17.2 shows how a chemical compound's transport, transformation, and fate lead to air pollution risk to human populations and ecosystems. Chemical transformation is crucial to these processes. If the compound is transformed into less toxic chemical species, the risks decline. Conversely, if the compound is released as a highly toxic compound that is not transformed during this journey, the risks remain high. The worst case scenario is that a toxic compound can become even more toxic and harmful after release, leading to increased risks.



**FIGURE 17.2** Importance of transport, transformation, and fate processes to human and ecological exposure and risk assessments. *Source for ecological exposure components: Suter G. Predictive risk assessment of chemicals. In: Suter G, editor. Ecological Risk Assessment. Chelsea (Michigan): Lewis Publishers; 1993.*

## 17.2 KINETICS

Chemical kinetics is the description of the rate of a chemical reaction. This is the rate at which the reactants are transformed into products. This may take place by abiotic or by biological systems, such as microbial metabolism. Since a rate is a change in quantity that occurs with time, the change we are most concerned with is the change in the concentration of our contaminants into new chemical compounds:

$$\text{Reaction rate} = \frac{\text{change in product concentration}}{\text{corresponding change in time}} \quad (17.1)$$

and,

$$\text{Reaction rate} = \frac{\text{change in reactant concentration}}{\text{corresponding change in time}} \quad (17.2)$$

When a compound breaks down, i.e. degrades, the change in product concentration will be decreasing proportionately with the reactant concentration. Thus, for substance A the kinetics is:

$$\text{Rate} = -\frac{\Delta(A)}{\Delta t} \quad (17.3)$$

The negative sign denotes that the reactant concentration (the parent contaminant) is decreasing. It stands to reason then that the degradation product C resulting from the concentration will be increasing in proportion to the decreasing concentration of the contaminant A, and the reaction rate for Y is:

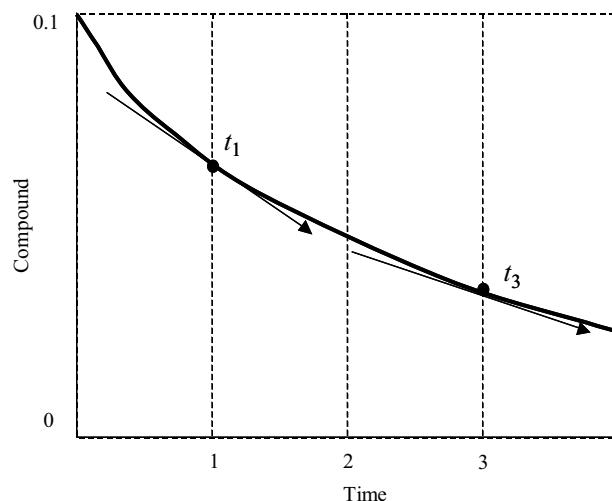
$$\text{Rate} = \frac{\Delta(C)}{\Delta t} \quad (17.4)$$

By convention, the concentration of the chemical is shown in parentheses to indicate that the system is not at equilibrium.  $\Delta(X)$  is calculated as the difference between an initial concentration and a final concentration:

$$\Delta(X) = \Delta(X)_{\text{final}} - \Delta(X)_{\text{initial}} \quad (17.5)$$

Thus, the rate of reaction at any time is the negative of the slope of the tangent to the concentration curve at that specific time (Figure 17.3).

For a reaction to occur, the molecules of the reactants must collide. High concentrations of a substance are more likely to collide than low concentrations. Thus, the reaction rate must be a function of the concentrations of the reacting substances. The mathematical expression of this function is known as the "rate law". The rate law can be determined experimentally for any contaminant. Varying the concentration of each reactant independently and then measuring the result will give a



**FIGURE 17.3** Kinetics of the transformation of a compound. The rate of reaction at any time is the negative of the slope of the tangent to the concentration curve at that time. The rate is higher at  $t_1$  than at  $t_3$ . This rate is concentration-dependent (first-order). *Spencer J, Bodner G, Rickard L. Chemistry: Structure and Dynamics. 2nd ed. New York (NY): John Wiley & Sons; 2003.*

concentration curve. Each reactant has a unique rate law (this is one of a contaminant's physicochemical properties).

In a reaction of reactants A and B to yield product C (i.e.  $A + B \rightarrow C$ ), the reaction rate increases in accordance with the increasing concentration of either A or B. If the amount of A is tripled, then the rate of this whole reaction triples. Thus, the rate law for such a reaction is:

$$\text{Rate} = k[A][B] \quad (17.6)$$

The rate law for the different reaction  $X + Y \rightarrow Z$ , in which the rate is only increased if the concentration of X is increased (changing the Y concentration has no effect on the rate law), must be:

$$\text{Rate} = k[X] \quad (17.7)$$

Equations (17.6) and (17.7) indicate that the concentrations in the rate law are the concentrations of reacting chemical species at any specific point in time during the reaction. The rate is the velocity of the reaction at that time. The constant  $k$  in the equations is the rate constant, which is unique for every chemical reaction and is a fundamental physical constant for a reaction, as defined by environmental conditions (e.g. pH, temperature, pressure, type of solvent).

The rate constant is the rate of the reaction when all reactants are present in a 1 molar (M) concentration. Accordingly, the rate constant  $k$  is the rate of reaction under conditions standardized by a unit concentration. By drawing a concentration curve for a contaminant that consists of an infinite number of points at each instant

of time, an instantaneous rate can be calculated along the concentration curve. At each point on the curve the rate of reaction is directly proportional to the concentration of the compound at that moment in time. This is a physical demonstration of kinetic order. The overall kinetic order is the sum of the exponents (powers) of all the concentrations in the rate law. So for the rate  $k[A][B]$ , the overall kinetic order is 2. Such a rate describes a second-order reaction because the rate depends on the concentration of the reactant raised to the second power. Other decomposition rates are like  $k[X]$ , and are first-order reactions because the rate depends on the concentration of the reactant raised to the first power.

The kinetic order of each reactant is the power that its concentration is raised in the rate law. So,  $k[A][B]$  is first-order for each reactant and  $k[X]$  is first-order X and zero-order for Y. In a zero-order reaction, compounds degrade at a constant rate and are independent of reactant concentration.

A “parent compound” is transformed into degradation products, sometimes called “chemical daughters” or “progeny”. For example, pesticide kinetics often concerns itself with the change of the active ingredient in the pesticide to its degradation products.

The degradation products themselves often undergo transformations, depending on environmental conditions. For example, as shown in Figure 17.4, a parent compound that is highly reactive may degrade within a few minutes after exiting a stack, producing a less reactive degradation product (DP1). Within the plume downwind of the stack, water vapor, and other compounds react with the degradation product, degrading 99% of it within a few hours. These newly transformed compound (DP2) may be less reactive and do not undergo further transformation. At distance A in Figure 17.4, the measurements would indicate about equal mass of the parent and DP1. However, at distance B, none of the parent compound is detected, and about the same amount of DP1 is measured as at distance A

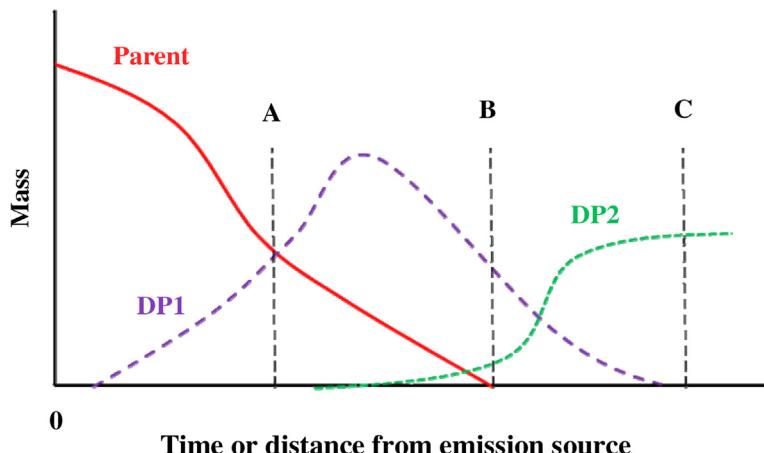
because there has been sufficient time for this transformation since the peak concentration. Very little of the DP2 is present at distance B since it only began to be produced since DP1’s degradation. At distance C, sufficient time has lapsed to allow all of mass of DP1 to be degraded into the less reactive DP2. Note that DP2 is not showing signs of decreasing even though all of DP1 is degraded, indicating it is not nearly as reactive as DP1. Indeed, it may travel a long distance before deposition. Persistent compounds can travel hundreds, even thousands of miles, before being deposited. This is known as long-range transport.

Incidentally, a compound dissolved in water vapor or sorbed to particulate matter can be washed out during a precipitation event. If this were the case for the three compounds in Figure 17.4, the atmospheric concentrations would decrease to nearly zero during the precipitation events. That is, if the washout occurred at time A, the atmospheric concentrations of the three chemicals would be about zero, but the wet deposition measurements (e.g. in sampling equipment on the earth’s surface) would be about the same of as those shown at time A: parent = DP1 and DP2 = 0; at time B, parent = 0 and DP1 > DP2; and at time C, parent = 0, DP1 = 0 and DP2 is at its maximum concentration.

That points out one of the values of taking deposition measurements, i.e. to see what was in the atmosphere at the time of the rain event. The other value is to see what is reaching the earth’s surface, since the air pollutants can become water and soil pollutants and can harm biota, e.g. sulfate compounds that stress vegetation. The combination of deposition and transformation is an example of how physics and chemistry must be considered in concert to determine the severity of air pollution.

### 17.2.1 Air Pollution Physics and Chemistry

Air pollution physics must be considered mutually with air pollution chemistry. Any complete discussion



**FIGURE 17.4** Hypothetical transformation of a reactive compound (parent), followed by the transformation of its first degradation product (DP1) in a plume moving downwind from the point of release to the atmosphere. DP1 is further degraded into a less reactive chemical species (DP2), indicated by its steady state after all of DP2 has been transformed. DP2 will remain in the atmosphere until it is either washed out and deposited or until it is completely degraded. (For color version of this figure, the reader is referred to the online version of this book.)

of the physical process of solubility, for example, must include a discussion of polarity. Further, any discussion of polarity must include a discussion of electronegativity. Likewise, discussions of sorption and air–water exchanges must consider both chemical and physical processes. Such is the nature of environmental science; all concepts are interrelated.

The interconnectedness between physical and chemical processes is evident in [Table 17.1](#), which lists some of the most important processes involved in the fate of environmental contaminants. This chapter highlights basic chemical processes that affect air pollution.

It is important to bear in mind that the air pollution processes are a function of both the chemical characteristics of the compartment (e.g. air) and those of the contaminant. The inherent properties of the air pollutant are influenced and changed by the extrinsic properties of the air and other media in which the pollutant resides in the environment. Thus, [Table 17.1](#) describes both sets of properties.<sup>a</sup>

Air pollution involves five categories of chemical reactions. Various types of reaction occur within boilers and other industrial operations; in stacks; in the plume; in the microenvironments and ecosystems; and within organisms.

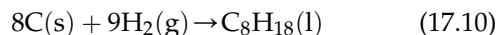
### 17.2.1.1 Synthesis or Combination

In combination reactions, two or more substances react to form a single substance:

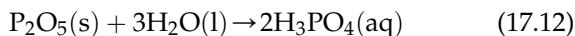
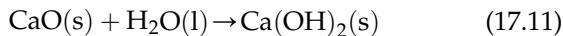


Two types of combination reactions are important in environmental systems, i.e. formation and hydration.

Formation reactions are those where elements combine to form a compound. Examples include the formation of ferric oxide and the formation of octane:



Hydration reactions involve the addition of water to synthesize a new compound, for example, when calcium oxide is hydrated to form calcium hydroxide, and when phosphate is hydrated to form phosphoric acid:



### 17.2.1.2 Decomposition



In decomposition, one substance breaks down into two or more new substances, such as in the decomposition of carbonates. For example, calcium carbonate breaks down into calcium oxide and carbon dioxide:

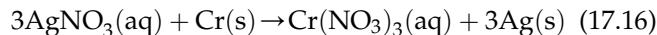


Most decomposition reactions need energy added to the reaction. When electricity provides the energy, it is known as electrolysis. When photons provide the energy, it is known as photolysis. When microbes decompose an organic compound into simpler compounds, the process is known as biodegradation.

### 17.2.1.3 Single Replacement



Single replacement (or single displacement) commonly occurs when one metal ion in a compound is replaced with another metal ion, such as when trivalent chromium replaces monovalent silver:

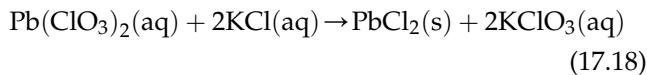


### 17.2.1.4 Double Replacement

Double replacement is also known as metathesis or double displacement:

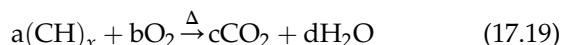


In these reactions, metals are exchanged between the salts. These newly formed salts have different chemical and physical characteristics from those of the reagents and are commonly encountered in metal precipitation reactions, such as when lead is precipitated (indicated by the "(s)" following PbCl<sub>2</sub>), as in the reaction of a lead salt with an acid like potassium chloride:



### 17.2.1.5 Complete Combustion

Complete or efficient combustion (thermal oxidation) occurs when an organic compound is oxidized in the presence of heat (indicated by Δ):



Combustion is the combination of O<sub>2</sub> in the presence of heat (as in burning fuel) producing CO<sub>2</sub> and H<sub>2</sub>O during complete combustion of organic compounds, such as the combustion of octane:



<sup>a</sup> This table is a useful reference for several chapters, especially Chapters 5, 6, 7, 16, 17, and 26.

TABLE 17.1 Processes Important to the Fate and Transport of Contaminants in the Environment

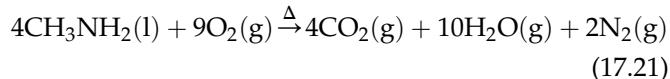
Process	Description	Physical Phases Involved	Major Mechanisms at Work	Outcome of Process	Factors Included in Process
Advection	Transport by turbulent flow; mass transfer	Aqueous, gas	Mechanical	Transport due to mass transfer	Concentration gradients, porosity, permeability, hydraulic conductivity, circuitousness, or tortuosity of flow paths
Dispersion	Transport from source	Aqueous, gas	Mechanical	Concentration gradient and dilution driven	Concentration gradients, porosity, permeability, hydraulic conductivity, circuitousness, or tortuosity of flow paths
Diffusion	Fick's law (concentration gradient)	Aqueous, gas, solid	Mechanical	Concentration gradient-driven transport	Concentration gradients
Liquid separation	Various fluids of different densities and viscosities are separated within a system	Aqueous	Mechanical	Recalcitrance due to formation of separate gas and liquid phases (e.g. gasoline in water separates among benzene, toluene, and xylene)	Polarity, solubility, $K_d$ , $K_{ow}$ , $K_{oc}$ , coefficient of viscosity, density
Density stratification	Distinct layers of differing densities and viscosities	Aqueous	Physical/chemical	Recalcitrance or increased mobility in transport of lighter fluids (e.g. light nonaqueous phase liquids, LNAPLs) that float at water table in groundwater, or at atmospheric pressure in surface water	Density (specific gravity)
Migration along flow paths	Faster through large holes and conduits, e.g. path between interstices of sorbant packing in air stripping towers	Aqueous, gas	Mechanical	Increased mobility through fractures	Porosity, flow path diameters
Sedimentation	Heavier compounds settle first	Solid	Chemical, physical, mechanical, varying amount of biological	Recalcitrance due to deposition of denser compounds	Mass, density, viscosity, fluid velocity, turbulence ( $R_N$ )
Filtration	Retention in mesh	Solid	Chemical, physical, mechanical, varying amount of biological	Recalcitrance due to sequestration, destruction, and mechanical trapping of particles	Surface charge, soil, particle size, sorption, polarity
Volatilization	Phase partitioning to vapor	Aqueous, gas	Physical	Increased mobility as vapor phase of contaminant migrates to soil-gas phase and atmosphere	Vapor pressure ( $P^0$ ), concentration of contaminant, solubility, temperature
Dissolution	Cosolvation, attraction of water molecule shell	Aqueous	Chemical	Various outcomes due to formation of hydrated compounds (with varying solubilities, depending on the species)	Solubility, pH, temperature, ionic strength, activity
Absorption	Retention on solid surface	Solid	Chemical, physical, varying amount of biological	Partitioning of lipophilic compounds into soil organic matter, and penetration into an aerosol	Polarity, surface charge, Van der Waals attraction, electrostatics, ion exchange, solubility, $K_d$ , $K_{ow}$ , $K_{oc}$ , coefficient of viscosity, density

(Continued)

TABLE 17.1 Processes Important to the Fate and Transport of Contaminants in the Environment—cont'd

Process	Description	Physical Phases Involved	Major Mechanisms at Work	Outcome of Process	Factors Included in Process
Adsorption	Retention on solid surface	Solid	Chemical, physical, varying amount of biological	Recalcitrance due to ion exchanges and charge separations on a particle's surface	Polarity, surface charge, Van der Waals attraction, electrostatics, ion exchange, solubility, $K_d$ , $K_{ow}$ , $K_{oc}$ , coefficient of viscosity, density
Complexation	Reactions with matrix (e.g. soil compounds like humic acid) that form covalent bonds	Solid	Chemical, varying amount of biological	Recalcitrance and transformation due to reactions with soil organic compounds to form residues (bound complexes)	Available oxidants/reductants, soil organic matter content, pH, chemical interfaces, available $O_2$ , electrical interfaces, temperature
Oxidation/ Reduction	Electron loss and gain	All	Chemical, physical, varying amount of biological	Destruction or transformation due to mineralization of simple carbohydrates to $CO_2$ and water from respiration of organisms	Available oxidants/reductants, soil organic matter content, pH, chemical interfaces, available $O_2$ , electrical interfaces, temperature
Ionization	Complete cosolvation leading to separation of compound into cations and anions	Aqueous	Chemical	Dissolution of salts into ions	Solubility, pH, temperature, ionic strength, activity
Hydrolysis	Reaction of water molecules with contaminants	Aqueous	Chemical	Various outcomes due to formation of hydroxides (e.g. aluminum hydroxide) with varying solubilities, depending on the species	Solubility, pH, temperature, ionic strength, activity
Photolysis	Reaction catalyzed by electromagnetic (EM) energy (sunlight)	Gas (major phase)	Chemical, physical	Photooxidation of compounds with hydroxyl radical upon release to the atmosphere	Free radical concentration, wavelength, and intensity of EM radiation
Biodegradation	Microbially mediated, enzymatically catalyzed reactions	Aqueous, solid	Chemical, biological	Various outcomes, including destruction and formation of daughter compounds (degradation products) intracellularly and extracellularly	Microbial population (count and diversity), pH, temperature, moisture, biofilm, acclimation potential of available microbes, nutrients, appropriate enzymes in microbes, available and correct electron acceptors (i.e. oxygen for aerobes, others for anaerobes)
Activation	Metabolic, detoxification process that renders a compound more toxic	Aqueous, gas, solid, tissue	Biochemical	Phase I or II metabolism, e.g. oxidation for epoxides on aromatics	Available detoxification and enzymatic processes in cells
Metal catalysis	Reactions sped up in the presence of certain metallic compounds (e.g. noble metal oxides in the degradation of nitric acid).	Aqueous, gas, solid, and biotic	Chemical (especially reduction and oxidation)	Same reaction, but faster	Species and oxidation state of metal

Complete combustion may also result in the production of molecular nitrogen ( $N_2$ ) when nitrogen-containing organics are burned, such as in the combustion of methylamine:



Incomplete combustion can produce a variety of compounds. Some are more toxic than the original compounds being oxidized, such as polycyclic aromatic hydrocarbons (PAHs), dioxins, furans, and CO. The alert reader will note at least two observations about these categories. First, all are kinetic, as denoted by the one-directional arrow ( $\rightarrow$ ). Second, in the environment, many processes are incomplete, such as the common problem of incomplete combustion and the generation of new compounds in addition to carbon dioxide and water.

With respect to the first observation, indeed, many equilibrium reactions take place. However, as mentioned in previous discussions, getting to equilibrium requires a kinetic phase. So, upon reaching equilibrium, the kinetic reactions (one-way arrows) would be replaced by two-way arrows ( $\leftrightarrow$ ). Changes in the environment or in the quantities of reactants and products can invoke a change back to kinetics.

Incomplete reactions are very important sources of environmental contaminants. For example, these reactions generate products of incomplete combustion (PICs), such as CO, PAHs, dioxins, furans, and hexachlorobenzene. However, even the products of complete combustion are not completely environmentally acceptable. Both carbon dioxide and water are greenhouse gases. Both are essential to life on earth, but excessive amounts of  $\text{CO}_2$  are strongly suspected of altering climate, especially increasing mean surface temperatures on earth. Thus,  $\text{CO}_2$  is considered by many to be an “air pollutant”.<sup>b</sup>

## 17.3 RATE LAWS AND AIR POLLUTION THERMODYNAMICS

Reaction rates give clues as to whether a reaction will occur within the atmosphere or any other environmental

compartments. For example, if an air pollutant is highly reactive (i.e. fast reaction rate) in water vapor that is dispersed and remains in a plume for days, it is quite likely that much if not all of the original compound will not be measured after that time. Instead, the compound’s transformation products would be present. However, if a compound has a very slow reaction rate, most of it is likely to be found in the plume. This is known as the atmospheric residence time, which is often expressed as its atmospheric half-life, i.e. the time it takes for half of the mass of the substance to be degraded. Thus, reaction rates also give clues as to how a pollutant will behave in the environment. This is the concern of equilibrium and partitioning in the environment (see Chapter 18).

Elemental mercury vapor ( $\text{Hg}^0$ ), for example, does not readily react with other atmospheric constituents. In addition,  $\text{Hg}^0$  has a very low aqueous solubility. These properties make for long atmospheric residence time (approximately one year).<sup>2,3</sup> However,  $\text{Hg}^0$  can be transformed to more reactive species that have much higher aqueous solubility than the zero-valence form.

Chemical transformation is explained by air pollution thermodynamics. Ecosystems and individual organisms and their components are systems.<sup>c</sup> Within the context of thermodynamics, a system is a sector or region in space or some parcel of a sector that has at least one substance that is ordered into phases. Reactors, stack gases, plumes, the open atmosphere, microenvironments, organisms and cells have qualities of both closed and open systems. A closed system does not allow material to enter or leave the system (engineers refer to a closed system as a “control mass”). The open system allows material to enter and leave the systems (such a system is known as a control volume).

In reality, air pollution results from complex interactions of substances in various states not only in the atmosphere, but in the many environmental media where substances are transformed. These transformations may render a compound that was previously not very toxic into a very toxic substance. Conversely, what may have been a precursor to an air pollutant may have been changed into a less toxic compound or compounds. During airborne transport, an air pollutant may also

<sup>b</sup> At the time this section was written, various governmental and nongovernmental groups in the United States were debating whether  $\text{CO}_2$  should become the seventh criteria air pollutant under the National Ambient Air Quality Standards of the Clean Air Act Amendments. One major question is whether indirect health effects, e.g. heat-related cardiovascular disease, should be considered strong enough rationale for this designation.

<sup>c</sup> Unfortunately, the English language has numerous connotations of “systems”. Even scientists have various definitions. For example, a more general understanding of scientists and technicians is that a “system” is a method of organization, e.g. from smaller to larger aggregations. The “ecosystem” and the “organism” are examples of both types of systems. They consist of physical phases and order (e.g. producer-consumer-decomposer; predator-prey; individual-association-community; or cell-tissue-organ-system). They are also examples of another concept of systems, i.e. a means for understanding how matter and energy move and change within a parcel of matter.

undergo chemical changes. These changes may form toxic compounds or other types of problems, e.g. they may become stronger greenhouse gases. After deposition, chemical reactions occur in the soil, water, and biota.

Thus, air pollutants are a mix of chemical reactions occurring at myriad rates. Air pollution seldom occurs in a single system. Indeed, a better way to consider these mixed systems is pseudo orders in the rate laws, i.e. “pseudo-open” and “pseudo-closed” systems. Applying the qualifier “pseudo” to absolute terms is a good way to describe the actual rates that occur in the environment, as opposed to well-controlled laboratory experiments.

The rate law for a chemical reaction is an equation that links the rate of the reaction with concentrations of reactants and rate constants (commonly, partial order reactions and rate coefficients). The rate is expressed as:

$$r = k[A]^x \times [B]^y \quad (17.22)$$

where  $k$  is the rate coefficient, the concentration of each chemical species are in brackets and the exponents are derived experimentally. A first-order reaction occurs at a linear rate:

$$r = -\frac{d[A]}{dt} = -k[A]^1 = -k[A] \quad (17.23)$$

Similarly, a second-order reaction rate is:

$$r = -\frac{d[B]}{dt} = -k[B]^2 \quad (17.24)$$

or,

$$r = -\frac{d[B]}{[B]^2} = -kdt \quad (17.25)$$

The rate equations for third and next orders would follow the same format. In air pollution, numerous reactants are involved in reactions. Thus, mixed second order rate reactions can be expressed as:

$$r = -\frac{d[B]}{dt} = -k[B][A] \quad (17.26)$$

When reaction rates exceed first-order, the chemical concentrations can be adjusted so that the kinetics appears to be first-order. So, for the simple reaction  $2A + B \rightarrow C$ , the rate law would be:

$$-\frac{1}{2} \frac{d[A]}{dt} = k[A][B] \quad (17.27)$$

Since the right side is a product of two reactants, the overall rate law is second order, but with excess concentrations of B, then [B] is almost completely changed in the reaction, i.e. [B] changes extremely more slowly than the change in [A]. In this instance, Eqn (17.27) can be better written as:

$$-\frac{1}{2} \frac{d[A]}{dt} \approx k'[A][B] \quad (17.28)$$

where  $k'$  is a pseudo-first-order rate coefficient (units are inverse time,  $s^{-1}$ ).

### 17.3.1 Examples of Reaction Rate Order

Extending the logic of the pseudo rate law to pseudo-open and pseudo-closed systems, the environment will be a mix of systems, none of which are completely open, closed, or isolated. Unlike a completely closed system, a microenvironment (e.g. room in a home) that allows a small amount of energy and mass to flow in and out may be treated as a pseudo closed system, since like the pseudo-first-order rate law, the inflows and outflows may virtually not limit reaction rates when compared to other factors. Even though the atmosphere is an open system, at certain scales and for defined conditions, it can be treated as a set of closed systems (e.g. layers that in fact allow heat exchange may be so different that each layer may be treated as a closed system).

Another thermodynamic concept that is important to air pollution is the thermodynamic property, i.e. a trait or attribute that can be used to describe a system and to differentiate that system from others. A property must be able to be stated at a specific time independently of its value at any other time and unconstrained by the process that induced the condition (state). An intensive property is independent of the system's mass (such as pressure and temperature). An extensive property is proportionality to the mass of the system (such as density or volume). Dividing the value of an extensive property by the system's mass gives a “specific property”, such as specific heat, specific volume, or specific gravity.

The thermodynamics term for the description of the change of a system from one state (e.g. equilibrium) to another is known as a process. Processes may be reversible or irreversible; they may be adiabatic (no gain or loss of heat, so all energy transfers occur through work interactions). Other processes include isometric (constant volume), isothermal (constant temperature), isobaric (constant pressure), isentropic (constant entropy), and isenthalpic (constant enthalpy).

### 17.3.2 Free Energy

Free energy is the measure of a system's ability to do work. If reactants in a reaction have greater free energy than the products, energy is released from the reaction; which means the reaction is exergonic. Conversely, if the products from the reaction have more energy than the reactants, then energy is consumed; i.e. it is an endergonic reaction. Equilibrium constants can be ascertained thermodynamically by employing the Gibbs free energy ( $G$ ) change for the complete reaction. This is expressed as:

$$G = H - TS \quad (17.29)$$

where  $G$  is the energy liberated or absorbed in the equilibrium by the reaction at constant  $T$ .  $H$  is the system's enthalpy and  $S$  is its entropy. Enthalpy is the thermodynamic property expressed as:

$$H = U + pV \quad (17.30)$$

where  $U$  is the system's internal energy.

The relationship between a change in free energy and equilibria can be expressed by:

$$\Delta G^* = \Delta G_f^{*0} + RT \ln K_{\text{eq}} \quad (17.31)$$

where  $\Delta G_f^{*0}$  = free energy of formation at steady state ( $\text{kJ g mol}^{-1}$ ).

In summary, the total energy in systems is known as enthalpy ( $H$ ) and the usable energy is known as free energy ( $G$ ). Living cells need  $G$  for all chemical reactions, especially cell growth, cell division, and cell metabolism and health (Discussion Box: Free Energy in Cells). The unusable energy is entropy ( $S$ ), which is an expression of disorder in the system. Disorder tends to increase as a result of the many conversion steps outside and inside of a system.

### FREE ENERGY IN CELLS

Thermodynamics is key to air pollution science and engineering. Heat exchange, partitioning, and other thermodynamic concepts are employed to determine the amount of air pollution generated, how an air pollutant moves after being emitted and the dynamics and size of air pollutant plumes. Another key area in need of thermodynamic understanding is the cell, whether a single-cell microbe or part of an organism, especially human cells.

Since disorder tends to increase as a result of the many conversion steps outside and inside of the cell, the cells have adapted ways of improving efficiencies. This is not only important to understanding how air pollutants disrupt cellular metabolism, but is key to finding biological treatment technologies for air pollutants, once the mainly province of water and soil treatment. Bioengineers seek ways to improve these efficiencies beyond natural

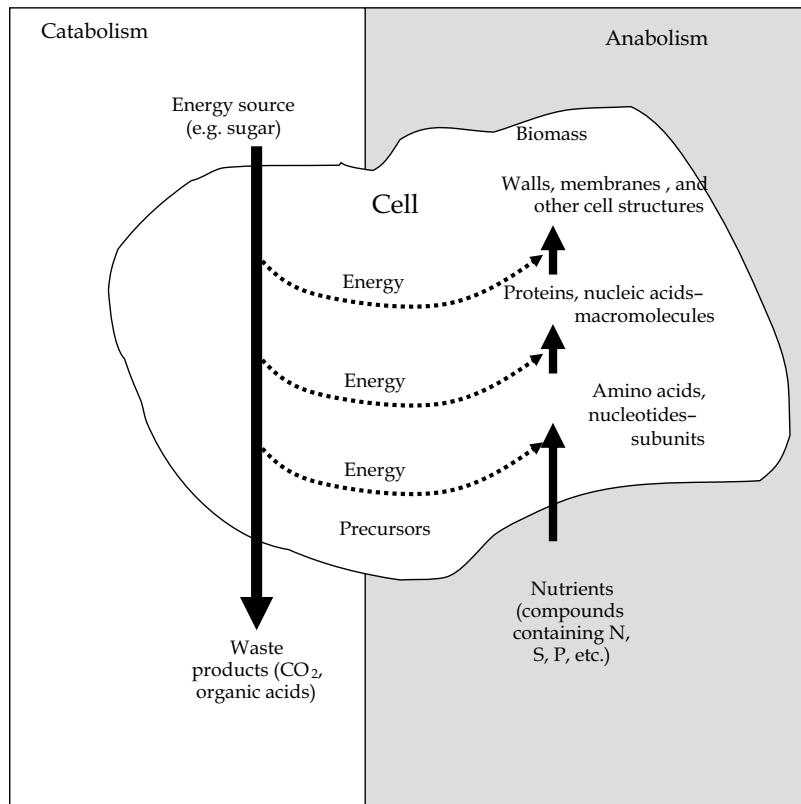


FIGURE 17.5 Cellular metabolism results from catabolic reactions that break down compounds to gain energy that is used to build biomolecules (anabolic metabolism) from nutrients that are taken up by the cell, beginning with simple precursors, then subunits, macromolecules. From these biomolecules, the cellular structures are built.

(Continued)

## FREE ENERGY IN CELLS (cont'd)

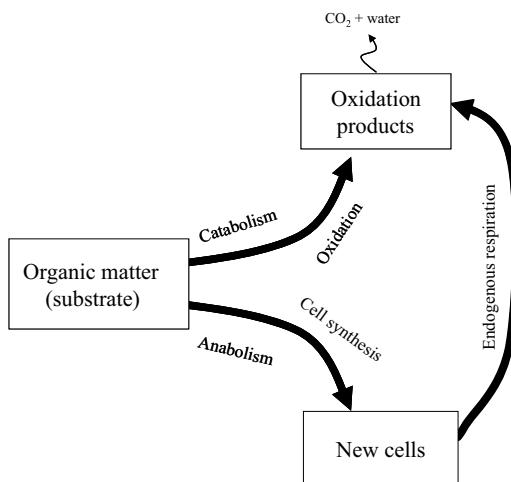
acclimation. Thus, to understand both air pollution toxicity and air pollution control biotechnologies, the processes that underlie microbial metabolism must be characterized.

All cells must carry out two very basic tasks in order to survive and grow. They must undergo biosynthesis, i.e. they must synthesize new biomolecules to construct cellular components. They must also harvest energy. Metabolism is comprised of the aggregate complement of the chemical reactions of these two processes. Thus, metabolism is the cellular process that derives energy from a cell's surroundings and uses this energy to operate and to construct even more cellular material.

Energy that does chemical work is exemplified by cellular processes (Figure 17.5). Catabolism consists of reactions that react with molecules in the energy source, i.e. incoming food, such as carbohydrates. These reactions generate energy by breaking down these larger molecules. Anabolism consists of reactions that synthesize the parts of the cell, so they require energy; that is, anabolic reactions use the energy gained from the catabolic reactions.

Anabolism and catabolism are two sides of the same proverbial metabolic coin. Anabolism is synthesizing, whereas catabolism is destroying. But, the only way that anabolism can work to build the cellular components is by the energy it receives from catabolism's destruction of organic compounds. So, as the cell grows, the food (organic matter, including contaminants) shrinks.

Air pollution biotechnology takes advantage of these two metabolic functions, depending on the microbial biodegradability of various organic substrates. The microbes



**FIGURE 17.6** Microbial oxidation that occurs during the degradation of organic compounds. Both the catabolic and anabolic processes generate oxidation products.

in a biofilter, for example, use the organic compounds as their exclusive source of energy (catabolism) and their sole source of carbon (anabolism). These life processes degrade the pollutants (Figure 17.6).

**TABLE 17.2** Genera of Microbes Shown to be Able to Degrade a Persistent Organic Contaminant, i.e. Crude Oil

Bacteria	Fungi
<i>Achromobacter</i>	<i>Allescheria</i>
<i>Acinetobacter</i>	<i>Aspergillus</i>
<i>Actinomyces</i>	<i>Aureobasidium</i>
<i>Aeromonas</i>	<i>Botrytis</i>
<i>Alcaligenes</i>	<i>Candida</i>
<i>Arthrobacter</i>	<i>Cephaiosporium</i>
<i>Bacillus</i>	<i>Cladosporium</i>
<i>Benekea</i>	<i>Cunninghamella</i>
<i>Brevibacterium</i>	<i>Debaromyces</i>
<i>Coryneforms</i>	<i>Fusarium</i>
<i>Erwinia</i>	<i>Gonytrichum</i>
<i>Flavobacterium</i>	<i>Hansenula</i>
<i>Klebsiella</i>	<i>Helminthosporium</i>
<i>Lactobacillus</i>	<i>Mucor</i>
<i>Leucothrix</i>	<i>Oidiodendrum</i>
<i>Moraxella</i>	<i>Paecylomyces</i>
<i>Nocardia</i>	<i>Phialophora</i>
<i>Peptococcus</i>	<i>Penicillium</i>
<i>Pseudomonas</i>	<i>Rhodosporidium</i>
<i>Sarcina</i>	<i>Rhodotorula</i>
<i>Sphaerotilus</i>	<i>Saccharomyces</i>
<i>Spirillum</i>	<i>Saccharomycopsis</i>
<i>Streptomyces</i>	<i>Scopulariopsis</i>
<i>Vibrio</i>	<i>Sporobolomyces</i>
<i>Xanthomyces</i>	<i>Torulopsis</i>
	<i>Trichoderma</i>
	<i>Trichosporon</i>

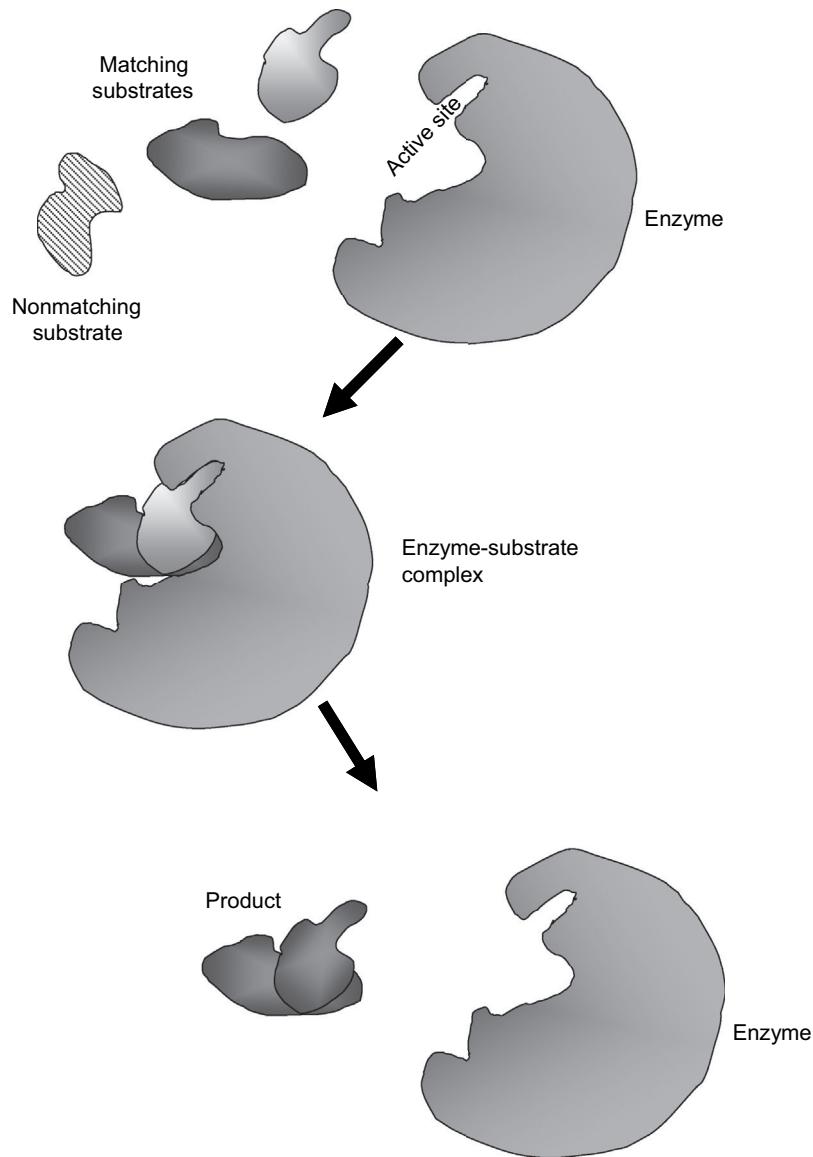
US Congress, Office of Technology Assessment. Bioremediation for marine oil spills—background paper, OTA-RP-O-70. Washington (DC): US Government Printing Office; 1991.

## FREE ENERGY IN CELLS (cont'd)

Microbes, e.g. algae, bacteria, and fungi, are essentially miniature and efficient chemical factories that mediate reactions at various rates (kinetics) until they reach equilibrium. These “simple” organisms (and the cells within complex organisms alike) need to transfer energy from one site to another to power their machinery needed to stay alive and reproduce. Microbes play a large role in degrading pollutants, whether in natural attenuation, where the available microbial populations adapt to the hazardous wastes as an energy source, or in engineered systems that do the same in a more highly concentrated substrate (Table 17.2). Some of the biotechnological

manipulation of microbes is aimed at enhancing their energy use, or targeting the catabolic reactions toward specific groups of food, i.e. organic compounds.

Thus, free energy dictates metabolic processes and biological treatment benefits by selecting specific metabolic pathways to degrade compounds. This occurs in a step-wise progression after the cell comes into contact with the compound. The initial compound, i.e. the parent, is converted into intermediate molecules by the chemical reactions and energy exchanges shown in Figures 17.4 and 17.5. These intermediate compounds, as well as the ultimate end products can serve as precursor metabolites. The reactions



**FIGURE 17.7 Substrates specific to the enzyme.** The breakdown of the enzyme–substrate complex yields a product and the enzyme becomes available for another catalytic reaction. The nonmatching substrate cannot enter into a complex, so it is not affected by the presence of this particular enzyme. However, another enzyme may have the “lock” to match this substrate’s “key”.

(Continued)

### FREE ENERGY IN CELLS (cont'd)

along the pathway depend on these precursors, electron carriers, the chemical energy, adenosine triphosphate (ATP), and organic catalysts (enzymes).

The reactant and product concentrations and environmental conditions, especially pH of the substrate, affect the observed  $\Delta G^*$  values. If a reaction's  $\Delta G^*$  is a negative value, the free energy is released and the reaction will occur spontaneously, and the reaction is exergonic. If a reaction's  $\Delta G^*$  is positive, the reaction will not occur spontaneously. However, the reverse reaction will take place, and the reaction is endergonic.

Time and energy are limiting factors that determine whether a microbe can efficiently mediate a chemical reaction, so catalytic processes are usually needed. Since an *enzyme* is a biological *catalyst*, these compounds (proteins) speed up the chemical reactions of degradation without themselves being used up. They do so by helping to break chemical bonds in the reactant molecules (Figure 17.7). By decreasing the activation energy needed, a biochemical reaction can be initiated sooner and more easily than if the enzymes were not present. Indeed, enzymes play a very large part in microbial metabolism. They facilitate each

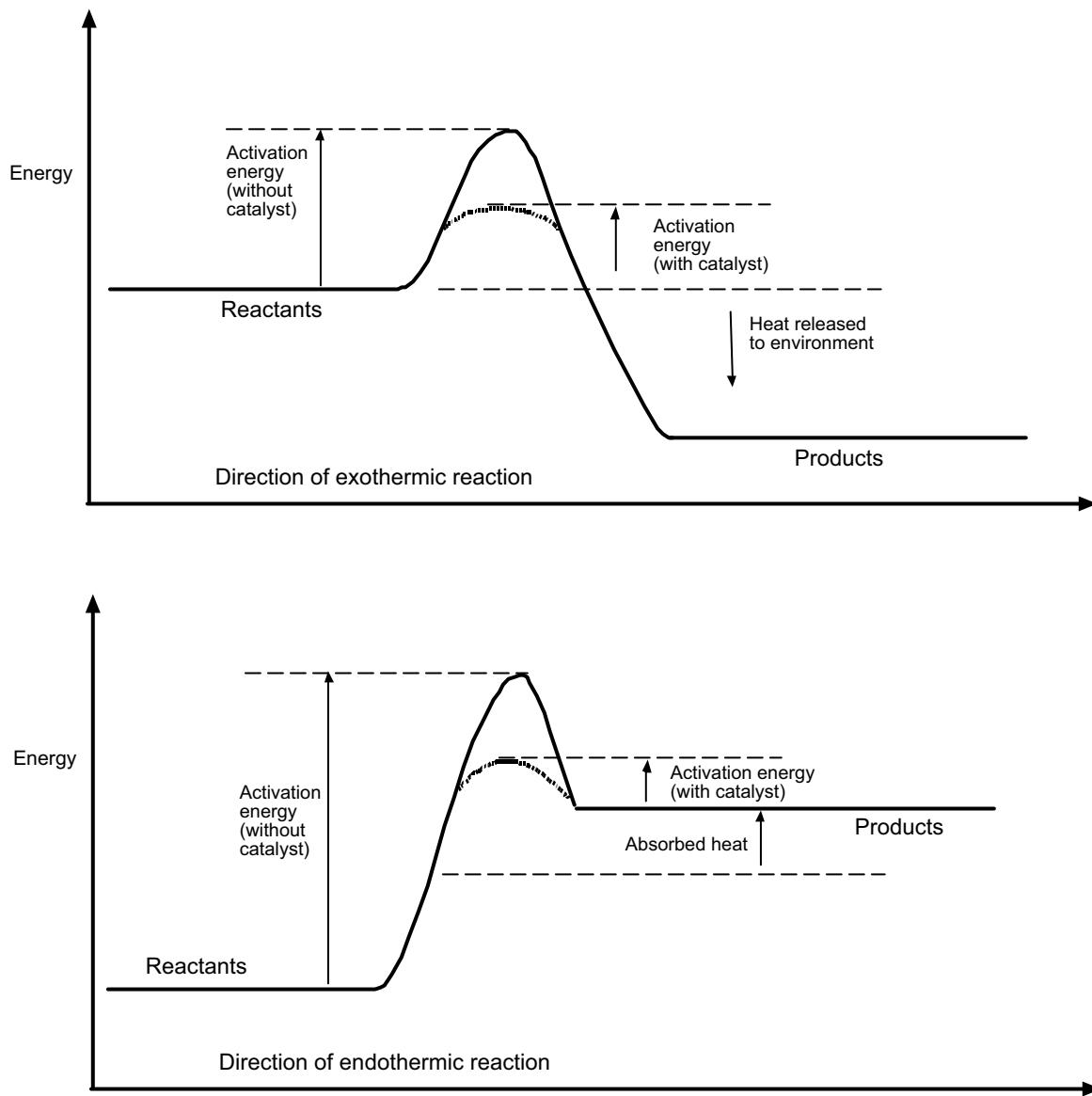


FIGURE 17.8 Effect of a catalyst on an exothermic reaction (top) and on an endothermic reaction (bottom).

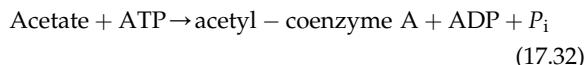
## FREE ENERGY IN CELLS (cont'd)

step along the metabolic pathway. As catalysts, enzymes reduce the reaction's *activation energy*, which is the minimum free energy required for a molecule to undergo a specific reaction. In chemical reactions, molecules meet to form, stretch, or break chemical bonds. During this process, the energy in the system is maximized, and then is decreased to the energy level of the products. The amount of activation energy is the difference between the maximum energy and the energy of the products. This difference represents the energy barrier that must be overcome for a chemical reaction to take place. Catalysts (in this case, microbial enzymes) speed up and increase the likelihood of a reaction by reducing the amount of energy, i.e. the activation energy, needed for the reaction.

Enzymes are usually quite specific. An enzyme is limited in the kinds of substrate that it will catalyze. Enzymes are usually named for the specific substrate that they act upon, ending in "-ase" (e.g. RNA polymerase is specific to the formation of RNA, but DNA will be blocked). Thus, the enzyme is a protein catalyst that has an active site at which the catalysis occurs. The enzyme can bind a limited number of substrate molecules. The binding site is specific, i.e. other compounds do not fit the specific three-dimensional shape and structure of the

active site (analogous to a specific key fitting a specific lock). The complex that results, i.e. the enzyme–substrate complex, yields a product and a free enzyme.

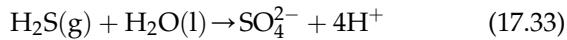
The most common microbial coupling of exergonic and endergonic reactions (Figure 17.8) by means of high-energy molecules to yield a net negative free energy is that of the nucleotide, ATP with  $\Delta G^* = -12$  to  $-15$  kcal mol $^{-1}$ . A number of other high-energy compounds also provide energy for reactions, including guanosine triphosphate (GTP), uridine triphosphate (UTP), cytosine triphosphate (CTP), and phosphoenolpyruvic acid (PEP). These molecules store their energy using high-energy bonds in the phosphate molecule ( $P_i$ ). An example of free energy in microbial degradation is the possible first step in acetate metabolism by bacteria:



In this case, the  $P_i$  represents a release of energy available to the cell. Conversely, to add the phosphate to the two- $P_i$  structure ADP to form the three- $P_i$  ATP requires energy (i.e. it is an *endothermic process*). Thus, the microbe stores energy for later use when it adds the  $P_i$  to the ATP.

## 17.4 ATMOSPHERIC TRANSFORMATION

During their time in the atmosphere, chemical compounds generally become oxidized. Gases in reduced states undergo step reactions to form ionic substances, which are in turn washed out by rain and other precipitation, known in the atmospheric sciences as deposition. For example, hydrogen sulfide ( $\text{H}_2\text{S}$ ) is a reduced species of sulfur. After emission to the atmosphere, it is dissolved in water vapor and is oxidized to form sulfate compounds or anions. For example, sulfate ions are formed when hydrogen sulfide is hydrolyzed:



As mentioned, mercury can undergo chemical transformations in the atmosphere which change its properties, including its likelihood to accumulate in organisms. Mercury will react in gas, liquid and solid phases. Reactions with ozone<sup>4</sup> ( $\text{O}_3$ ) and OH radicals<sup>5</sup> are the most important gas phase oxidation pathways. The  $\text{Hg}^0$  is oxidized to divalent ( $\text{Hg}^{2+}$ ), which is less volatile and more likely to condense on surfaces,

including particulate matter and biota. When Hg is dissolved in water, it can be oxidized, e.g. by  $\text{O}_3$  and OH radicals.<sup>6,7</sup>

The Hg aqueous phase reaction rates are much faster than those in the gas phase. However, the low aqueous solubility of  $\text{Hg}^0$  and the low water concentrations in the atmosphere make for about equal amounts of transformations for gas and liquid phases.

Incidentally, reduction also occurs in the atmosphere. For example, divalent mercury will be reduced to  $\text{Hg}^0$  if certain molecules, ions or radicals are present. For example  $\text{Hg}^{2+}$  can be reduced to  $\text{Hg}^0$  if sulfur dioxide ( $\text{SO}_2$ ) is dissolved in water vapor or hydroperoxyl ( $\text{HO}_2$ ) radicals are present.

Numerous types of reactions occur in air pollution chemical transformations. Atmospheric chemical reactions are often differentiated as either photochemical or thermal (or dark). Photochemical reactions are the interactions of photons with chemical species to form products, which may undergo further chemical reactions. These subsequent chemical reactions are called thermal reactions.

Atmospheric transformations are also differentiated as either homogeneous or heterogeneous. If the reaction only occurs in the gas phase, the reaction is homogeneous. If the reaction involves an interface with a surface of an aerosol or within a liquid droplet, it is heterogeneous. Another primary differentiation of reaction types is whether they are inorganic or organic reactions.

### 17.4.1 Inorganic Reactions

The inorganic chemical species most important to atmospheric kinetics and transformation reactions can be grouped into five classifications<sup>8</sup>:

1. Odd oxygen species
2. Odd hydrogen species
3. Reactive nitrogen species
4. Reactive sulfur species
5. Reactive halogen species

Odd oxygen species include O<sub>3</sub>, atomic O and O(1D), which is an O atom in an excited singlet state. Odd hydrogen species include OH, HO<sub>2</sub>, and atomic H. Reactive nitrogen species include NO, NO<sub>2</sub>, NO<sub>3</sub>, HNO<sub>2</sub>, HNO<sub>3</sub>, and NH<sub>3</sub>. Reactive sulfur species include SO<sub>2</sub>, SO<sub>3</sub>, H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and H<sub>2</sub>S. Reactive halogen species include F, FO, Cl, ClO, Br, BrO, I, IO, HCl, and Cl<sub>2</sub>.

Solar radiation initiates the formation of free radicals. The internal energy of molecules is composed of electronic energy states. Molecules interact with solar radiation by absorbing photons, causing the molecule to undergo a transition from the ground electronic state to an excited state. The change in energy between the two states corresponds to a quantum or photon of solar radiation. The frequencies ( $\nu$ ) of absorption are expressed by Planck's law:

$$E = h\nu = hc/\lambda \quad (17.34)$$

where  $h$  is Planck's constant,  $c$  is the speed of light, and  $\nu$  and  $\lambda$  are the frequency and wavelength of the light of the photon, respectively. The photon is represented as  $h\nu$ . Molecules and atoms interact with photons of solar radiation under certain conditions to absorb photons of light of various wavelengths. Each molecule absorbs solar radiation at its own range of wavelengths (Table 17.3). An excited molecule can follow several pathways, including fluorescence, collisional deactivation, direct reaction, and photodissociation.<sup>d</sup>

Transformations occur by rate order. The photolytic reactions discussed in the next section include

**TABLE 17.3** Bond Energy and Wavelengths for Important Bonds in Air Pollutant Molecules. The Likelihood of a Photolytic Reaction Depends on the Probability that a Compound Will Absorb a Specific Wavelength of Light or on the Probability that the Excited Molecular Species Will Undergo a Particular Reaction

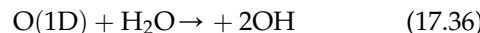
Bond	Bond Energy (kJ mol <sup>-1</sup> )	Wavelength (nm)
O–H	465	257
H–H	436	274
C–H	415	288
N–H	390	307
C–O	360	332
C–C	348	344
C–Cl	339	353
Cl–Cl	243	492
Br–Br	193	630
O–O	146	820

Felsot A. *Abiotic/biotic degradation & transformation (environmental attenuation of contaminants)* ES/RP 531—Fundamentals of environmental toxicology. Richland (Washington): Washington State University; 2005.

first-order reactions in the troposphere. For example, ozone is photolyzed to O(1D) and molecular oxygen:



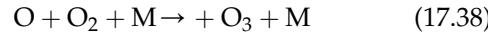
This is an extremely important first-order transformation because the O(1D) is hydrolyzed in a second-order reaction to form OH, which is the most important oxidizing agent in the atmosphere:



Another first-order photolytic reaction occurs when nitrogen dioxide is converted to atomic oxygen and NO:



The atomic O leads to the production of ozone in the atmosphere when it combines with molecular oxygen and a relatively nonreactive molecule (M):



In the stratosphere, first-order reactions include photolysis of molecular oxygen and nitrous oxide, which yield the atomic O needed to form the ozone layer:

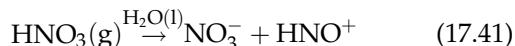


<sup>d</sup> Chapter 22 provides the reactions for each of these pathways for NO<sub>2</sub>. For example, for each photon absorbed below 400 nm, photodissociation occurs. For other photoabsorbers, HNO<sub>2</sub> and aldehydes, the photodissociation process leads to the formation of free radicals.

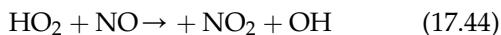
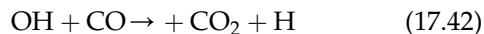
Another important first-order reaction in the stratosphere is the photolytic transformation of greenhouse gas, nitrous oxide, which slows its accumulation:



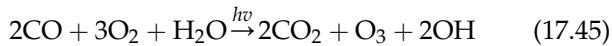
Other first-order reactions include those associated with chemical transfer across interfaces between physical phases (e.g. gas–liquid), such as those associated with acid rain. Heterogeneous reactions in a rain drop can break down nitric acid in the gas phase during washout, producing nitrate and hydronium ions in the rainwater:



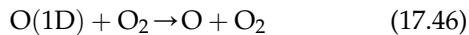
Second-order reactions are actually the most common type of atmospheric inorganic reaction, including the reactions of radicals, such as Eqn (17.35). Others include the transformation of carbon monoxide to carbon dioxide, the formation of HO<sub>2</sub> and formation of nitrogen dioxide from nitric oxide:



Carbon monoxide is a quite conservative (i.e. nonreactive) air pollutant. One pathway for breaking down CO is by oxidation by molecular oxygen in water and sunlight.<sup>8</sup> This can be ascertained by combining a number of the reactions discussed in this section:



Second-order reactions also occur in the stratosphere, including the reactions involving O(1D):



These reactions are involved in what is known as a null cycle, i.e. the net result of the reactions is that no products are formed or degraded, but light energy is absorbed and molecules are heated. However, when reactions 6.16 and 6.17 occur in the null cycle, that is how much of the ozone layer is formed<sup>8</sup>:

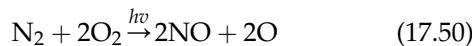


Other second-order stratospheric reactions include the transformation of compounds involved in the destruction of the ozone layer, including halocarbons such as the chlorofluorocarbons. When these relatively stable compounds find their way to the stratosphere, the molecules and fragments of their molecules photodissociate to form radicals, including F, FO, Cl, and ClO.

Second order reactions occur at extremely short wavelength ultraviolet radiation, such as:



Including other reactions discussed in this section, a pathway explains how reactive NO and O are formed from relatively nonreactive molecular nitrogen and oxygen via ultraviolet radiation:



These radicals in turn react with ozone.

Third and fourth-order reactions occur in the atmosphere. However, transition state and collision theories dictate that they are much less common than first and second-order reactions.

## 17.4.2 Organic Reactions

Rate reaction calculations for organic compounds are similar to those for inorganic reactions, but elementary reactions are not often applied to transformations of organic compounds in the atmosphere. More often, transformation pathways are described, such as oxidation–reduction and degradation pathways. These are discussed under “Biotic Degradation” below.

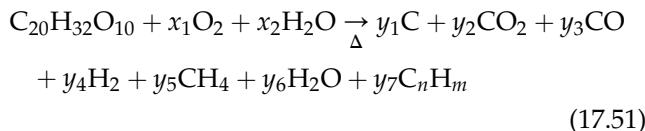
## 17.4.3 Hydrolysis

Compounds are degraded when they react with water. Hydrolysis is the potential of the chemical to be transformed into a byproduct and water. It has units of time for a pH of 7. A long hydrolysis time is of the order of many years. It contains the same root as photolysis, i.e. “lysis” meaning to break down. Hydrolysis occurs in every environmental compartment and is a key part of metabolism by organisms.

Molecules react with water vapor in the atmosphere. Hydrolysis is also important before and after the atmospheric residence of a pollutant. For example, complex molecules may be hydrolyzed by biotic and abiotic mechanisms, forming smaller, lighter molecules that have higher vapor pressures or that are more soluble in water. This increases the likelihood that they will reach the atmosphere. Following deposition, air pollutants may become hydrolyzed, making them more bioavailable and more likely to be taken up by organisms. Within organisms, hydrolysis is a key process in metabolism, making substances more polar (i.e. adding hydroxyl ions [OH<sup>-</sup>]), and increasing the aqueous solubility; thus, the compounds are more easily eliminated.

Hydrolysis often occurs simultaneously with other chemical transformation mechanisms. For example, in thermal processes to break down large organic

molecules, hydrolysis occurs along with gasification, pyrolysis, and combustion<sup>9</sup>:



The coefficients  $x$  and  $y$  balance the compounds on either side of the reaction. The delta under the arrow indicates heating. In many thermal reactions,  $\text{C}_n\text{H}_m$  includes the alkanes,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ ,  $\text{C}_5\text{H}_{12}$ , and benzene,  $\text{C}_6\text{H}_6$ .

Certain classes of chemicals hydrolyze extremely rapidly (e.g. a few hours), such as acid chlorides, epoxides and siloxanes. For these, knowledge of rate constant is not important since the reactions are considered to be immediate; meaning that the hydrolyzed products will comprise almost all of the mass reaching the troposphere.

Hydrolysis is highly dependent on temperature, with slight changes dramatically affecting the rate of the reaction e.g. some reaction rates will more than double with a 10 °F increase.<sup>10</sup>

#### 17.4.4 Multicompartmental Photochemical Transformation

Within the atmosphere, photochemical reactions account for a substantial amount of transformation of air pollutants. As mentioned, solar radiation influences the chemical processes in the atmosphere by interacting with molecules that act as photoacceptors. Free radicals are formed by the photodissociation of certain types of molecules. These free radicals are highly reactive neutral fragments of stable reactive molecules. Examples include atomic oxygen ( $\text{O}$ ), atomic hydrogen ( $\text{H}$ ), the hydroxyl radical ( $\text{OH}$ ), and the hydroperoxy radical ( $\text{HO}_2$ ). Aldehydes are the principal photoacceptors in photochemical oxidant smog,  $\text{NO}_2$ , nitrous acid ( $\text{HNO}_2$ ), and  $\text{O}_3$ . Photodissociation depends on the energy provided by photons.

Photochemical transformation was discussed in detail above under “Inorganic Reactions” within the context of atmospheric transformation. However, photochemical degradation occurs in all compartments where sunlight is present. Indeed, a compound will often undergo several types of transformation, including abiotic, e.g. photolysis and biotic degradation (Figure 17.9).

Photons ( $h\nu$ ) interact with and transform the molecules directly:



Photons also form many highly reactive atmospheric free radicals. Radicals are chemical species with an unpaired electron in the outermost shell. This unpaired electron imparts very high free energies to a radical, making it much more reactive than its nonradical counterparts (i.e. those with completely paired electrons). A chemical species with an odd number of electrons is a radical, whereas one with an even number of electrons is a nonradical.<sup>e</sup>  $\text{NO}$  is a radical since  $\text{N}$  has seven electrons and  $\text{O}$  has eight, for a sum of 15 electrons. However,  $\text{HNO}_3$  is a nonradical since  $\text{H}$  has one electron,  $\text{N}$  has seven and three  $\text{O}$  atoms ( $3 \times 8$ ) has 24 electrons, for a sum of 32 electrons.<sup>11</sup>

Given their reactivity, free radical concentrations are quite small in the atmosphere, usually  $<1$  ppb. These relatively small numbers are crucial to most atmospheric transformations, given that free radicals actually transform most chemical species in the atmosphere. Thus, free radical kinetics plays a large role in air pollution kinetics.<sup>12</sup>

The very low atmospheric concentrations of radicals translate into very few collisions between molecules. However, reactions between molecules almost always involve at least one radical species. Given a radical’s high free energy, they are generally formed endothermically from nonradical species, i.e. an external source of energy is needed. This energy is supplied by sunlight in the atmosphere:



Equation (17.53) provides the first step in the propagation of radical reaction chains, i.e. subsequent reactions of radicals with nonradical species:



To conserve the total odd number of electrons, the reaction of a radical with a nonradical must always yield a radical. The radical produced then reacts with another nonradical, and so on. This propagation processes large numbers of nonradicals through the chain. A nonradical species produced in this manner may photolyze so that additional radicals are generated according to Eqn (17.54). This photolysis is known as a branching reaction because it accelerates (i.e. “branches”) the chain by augmenting the reservoir of radicals.

Truncating the chain requires reactions between radicals; that is, a radical plus a radical that produces a nonradical and a nonradical. The termination may also involve a third body ( $\text{M}$ ), which is any relatively

<sup>e</sup>The major exception is atomic oxygen, which has eight electrons but two unpaired valence shell electrons in its “triplet”  $\text{O}(3\text{P})$  ground state ( $2s22\text{px}22\text{py}12\text{pz}1$ ). Thus, it is a radical; actually known as a biradical. Atomic oxygen has an even higher energy state given that all of its electrons are paired ( $2s22\text{px}22\text{py}2$ ), yielding a “singlet”  $\text{O}(1\text{D})$  state that is even more reactive than  $\text{O}(3\text{P})$ .

## Degradation in air

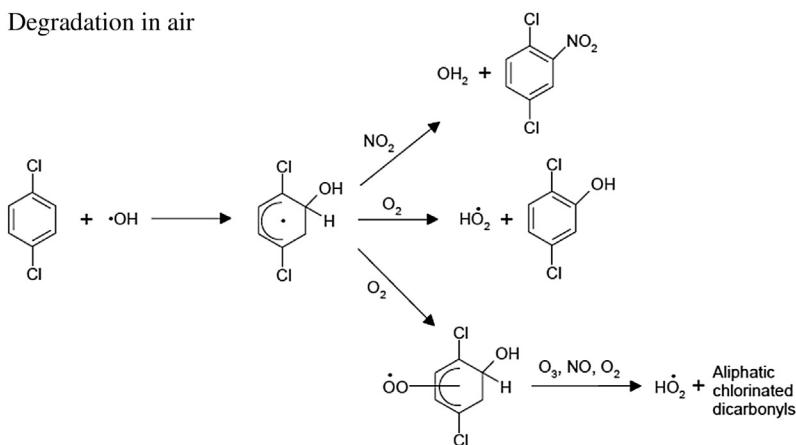
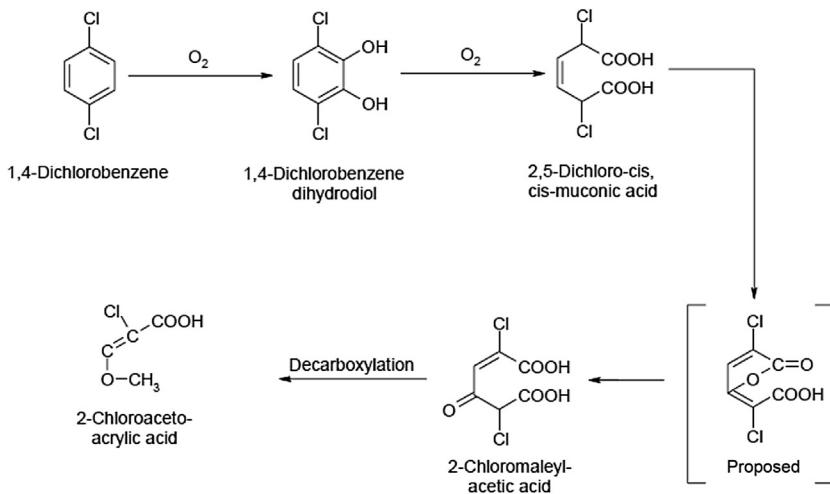
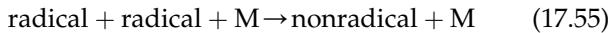


FIGURE 17.9 Degradation pathways of 1,4-dichlorobenzene reactions by a physicochemical process (photochemical) and biochemical process (biodegradation).

## Degradation in soil and water



nonreactive molecule (often  $\text{N}_2$  and  $\text{O}_2$ ) that removes excess energy, dissipating it as heat:



Such termination reactions generally occur more slowly than propagation reactions because radicals are present at low concentrations and collisions between radicals are therefore relatively infrequent.

### 17.4.5 Biotic Transformation

Organisms degrade compounds. Most biotic degradation occurs in water, soil, sediment, and biota. However, these processes determine the types of compounds that are emitted to the atmosphere. Basically, biotic transformations can be a combination of biological and nonbiologically mediated processes, including hydrolysis, oxidation, and reduction. There are also completely biologically mediated processes, especially conjugation. Conjugation reactions chemically link products of

hydrolysis, oxidation, and reduction (i.e. phase I metabolites) to glutathione, sugars, or amino acids, so that the subsequent metabolites (i.e. phase II metabolites) have increased aqueous solubility and, hopefully, less toxicity than the parent compound.

Certain molecules resist biodegradation in the environment. Their structure makes them unattractive as electron acceptors and donors to microbes. This recalcitrance is a function of both the chemical structure and the microorganisms' preferences for electron acceptance and carbon.

Actually, recalcitrance is not limited to microorganisms but is also applied to plants. Plants have the inherent capacity to degrade xenobiotic pollutants, but they generally lack the catabolic pathway to provide complete degradation, i.e. mineralization, relative to microbes. In fact, current research is being directed toward the transfer of genes involved in xenobiotic degradation from microbes to plants to enhance specific plant taxon's potential for remediating more

recalcitrant compounds, e.g. trichloroethylene, pentachlorophenol, trinitrotoluene (TNT), glycerol trinitrate, atrazine, ethylene dibromide, metolachlor, and hexahydro-1,3,5-trinitro-1,3,5-triazine.<sup>13</sup>

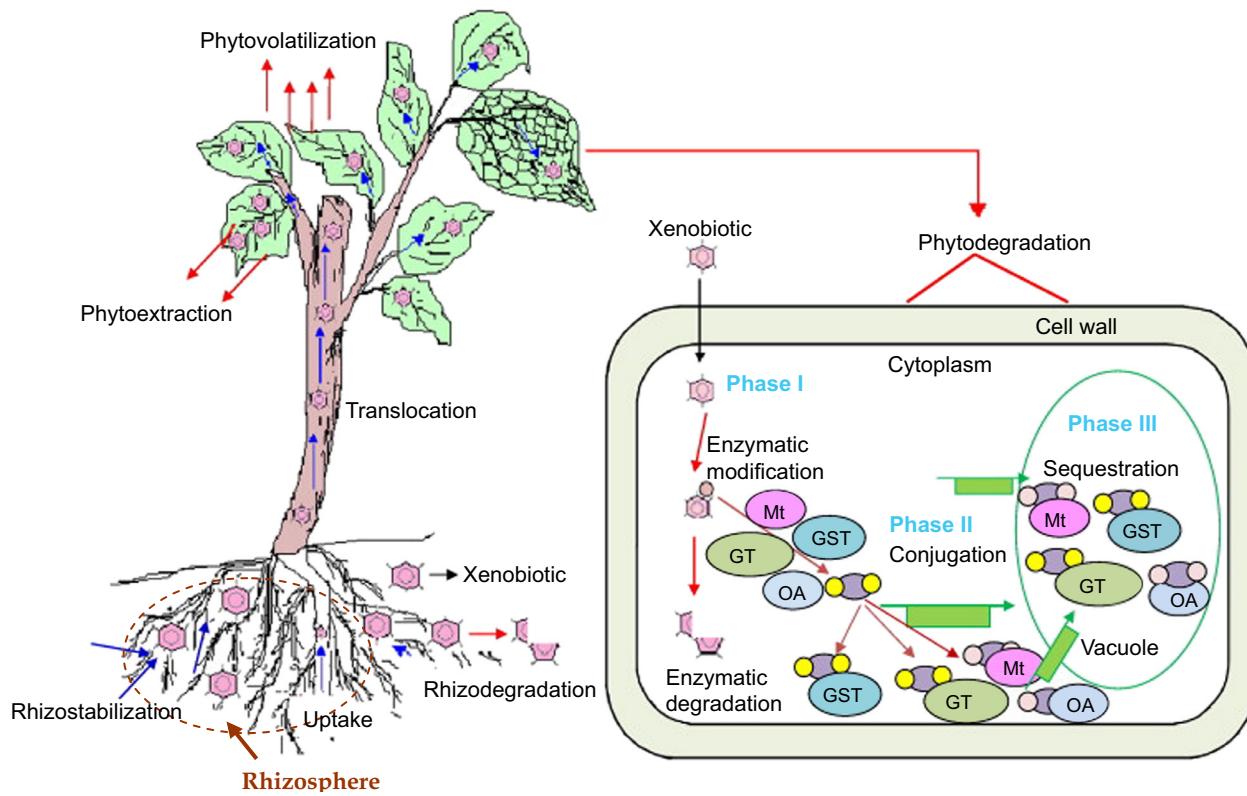
In fact, phytodegradation and microbial biodegradation are interrelated and mutual. Plant evapotranspiration, plant–microbe rhizosphere degradation, and microbial metabolic processes are combined. For example *in situ* natural and engineered remediation projects take advantage of both plant life and microbial populations, with much of the degradation at the root–microbe interface (i.e. in the rhizosphere) in the soil (Figure 17.10). Biotic transformation is enhanced in plants through numerous processes. During phytoextraction, recalcitrant compounds are removed and stored. In fact, recalcitrant compounds may be stored without metabolism for protracted periods. Phytodegradation, on the other hand, occurs when plants can metabolize a compound. The metabolism during phytodegradation may resemble that of animal degradation of toxic substances.<sup>14</sup>

The microbial-macrophytic rhizosphere stabilization and degradation are enhanced by the plant roots' release of cometabolites and by the roots' facilitating soil aeration (Figure 17.10). Thus, the physical contact and the

biochemistry needed for degradation is improved when roots and microbes are both available in the right environment.

The chemical–organism–environmental systematics inevitably leads to the question, then, as to what are the properties of molecules that render them recalcitrant? Why do some compounds that *should* be broken down, in fact persist in the environment for so long? Indeed, certain small, low molecular weight molecules can be recalcitrant. Some relatively low molecular weight compounds can last for years in the environment. This can result from the types of bonds, substitutions, stereochemistry and chemical conformation (e.g. when substituted halogens are arranged so that the molecule is smaller than other enantiomers).

In addition, certain environmental conditions add to the likelihood of biotic transformation. Therefore, the time it takes to break down molecules is a function of the structure of the molecule, the carbon preference of the organism and the environmental conditions. Pharmacologists use some standard screening approaches to characterize chemicals with respect to their likely biological activity based on chemical structures. For example, certain general molecular properties will drive



**FIGURE 17.10 Attenuation and degradation mechanisms in macrophytic plants.** A compound (xenobiotic) is stabilized or degraded in the rhizosphere, adsorbed or accumulated in the roots and transported to the aerial parts, volatilized or degraded inside the plant tissue. Degradation generally involves enzymatic mediated metabolism (Phase I); conjugation (Phase II); and active sequestration (Phase III). Note: Active transporters are marked in the green box (GST = glutathione S-transferases; GT = glucosyltransferases; Mt = malonyltransferases; OA = organic acids). Abhilash P.C., Jamil S, and Singh N. Transgenic plants for enhanced biodegradation and phytoremediation of organic xenobiotics. Biotechnology Advances 2009; 27(4):474–88. (For color version of this figure, the reader is referred to the online version of this book.)

the pharmacokinetics, i.e. the extent to which a chemical will be absorbed, distributed, metabolized, and eliminated after uptake into an organism. One model is the so-called “rule of five”, proposed by C.A. Lipinski,<sup>15</sup> which predicts that a compound is less likely to be absorbed and to permeate cellular membranes if:

1. The structure includes more than 5H-bond donors, expressed as the sum of hydroxyl and amine groups, i.e. OHs + NHs;
2. The molecular weight is greater than 500;
3. The log of the octanol–water coefficient ( $\text{Log } K_{\text{ow}}$ ) is greater than 5;
4. There are more than 10 H-bond acceptors (expressed as the sum of Ns and Os); and,
5. Compound classes that are substrates for biological transporters are exceptions to the rule.

Thus, large, lipophilic molecules that promote electron acceptance will resist biological activity. This rule can be instructive for understanding recalcitrance. Both chemical detoxification and chemical metabolism in cells of unicellular and multicellular organisms are biological processes. The degradation of a compound is a product of these biological processes. Therefore, the breakdown pathways may be predicted to some extent based on a substance’s inherent chemical and physical properties. In fact, personal care products and pharmaceuticals usually have to be somewhat recalcitrant to be used in the marketplace; otherwise their shelf life would be very short. For example, drugs must resist the effects of oxidation, heat, photolysis, and pH. Environmental fate of air pollutants and their degradation products can also be predicted to some extent using similar, general rules.

The insecticide DDT [1,1,1-trichloro-bis-(parachlorophenyl)-ethane] is structurally quite similar to another insecticide, methoxychlor [1,1,1-trichloro-2,2-bis(4-methoxyphenyl)ethane], except for the substitution at the outside (para) positions of the molecules (Figure 17.11). The DDT molecule is more recalcitrant because its para-substitutions are with chlorines i.e. para-chloro substitution, whereas the methoxychlor molecule is vulnerable to dealkylation of the para-methoxy ( $\text{H}_3\text{CO}$ ) groups. Most methoxychlor is likely removed from the air by

wet and dry deposition processes within weeks. Although methoxychlor binds tightly to soil particles, it usually does not persist since it is readily biodegraded. However soil-binding can increase persistence, especially when oxidation is suppressed. As evidence, methoxychlor has been found to have a soil half-life as high as 120 days in some low oxygen soil conditions.<sup>16</sup>

Methoxychlor’s degradation products are generally detected in lower levels of soil, probably because these compounds are more mobile than the parent methoxychlor. Methoxychlor has an affinity for sediment, so coupled with its biodegradability potential is seldom protected above detection levels in ground and surface waters, except near sources of release, likely to a large extent due to its low aqueous solubility (about  $1 \text{ mg l}^{-1}$ ). These factors mean that the less recalcitrant methoxychlor is much less likely to bioconcentrate in organisms compared to DDT, which has a range of bioaccumulation in fish, insects, and mammals.<sup>17</sup>

Likewise, the herbicides 2,4-D [2,4-dichlorophenoxyacetic acid] and 2,4,5-T [2,4,5-trichlorophenoxyacetic acid] are quite similar, but 2,4,5-T is much more recalcitrant due to the additional halogen (Cl) substitution (Figure 17.12). 2,4-D’s half-life in soil is less than 7 days, predominantly due to microbial degradation.<sup>18</sup> In water, biodegradation rates increase with increased concentrations of nutrients, sediment load, and dissolved organic carbon. Under oxygenated conditions the sediment half-life is 1 week to several weeks. Despite its short half-life in soil and in aquatic environments, it has been detected in ground and surface water in the United States and ground water in Canada.<sup>19</sup> The biodegradation rates for 2,4,5-T would be lower in most environments, due to the interference and added recalcitrance from the additional Cl atom.

Biotic and other transformations do not exclusively apply to an entire molecule. In fact, larger molecules are likely to contain different components with varied reactivity. One part of a compound may be susceptible to degradation while other parts are recalcitrant. For example, microbial enzymes can enhance the cleavage of one of a molecule’s moieties (e.g. an aliphatic group) which may be readily mineralized. However, other moieties will be recalcitrant to the enzymatic attack. In fact,

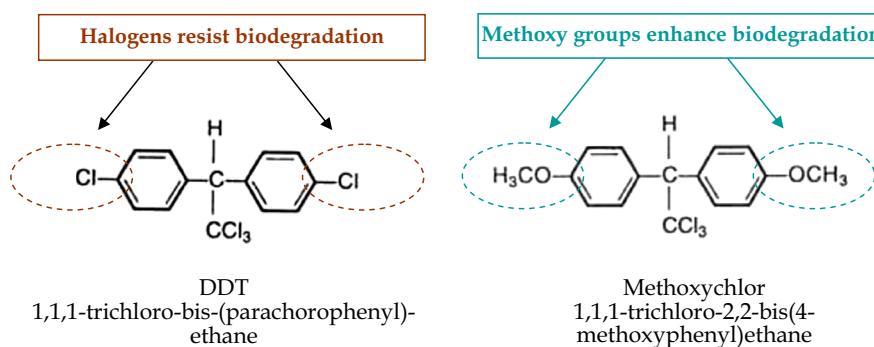
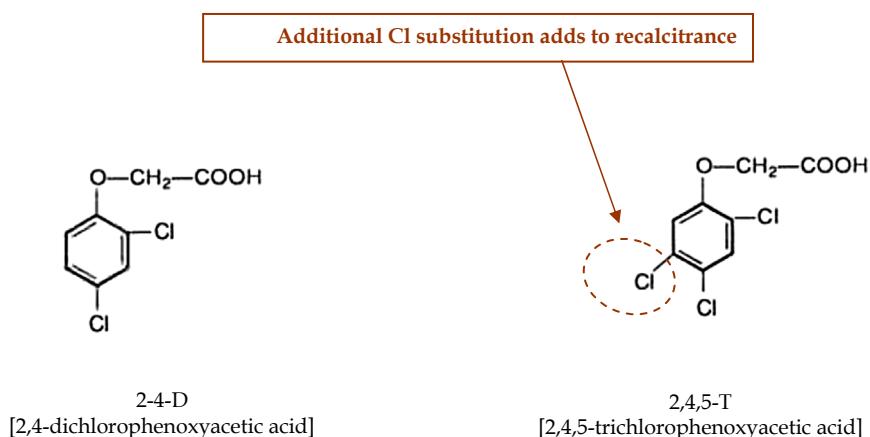


FIGURE 17.11 Structures of the insecticides and methoxychlor, showing the primary sites of attack. DDT is more recalcitrant than methoxychlor due to the chlorine substitutions, rather than the more easily degradable methoxy groups. (For color version of this figure, the reader is referred to the online version of this book.)

**FIGURE 17.12** Increased chlorine substitution of 2,4,5-T[2,4,5-trichlorophenoxyacetic acid] makes it more recalcitrant than the similarly structured 2-4-D [2,4-dichlorophenoxyacetic acid].(For color version of this figure, the reader is referred to the online version of this book.)



the remaining molecule could become even more recalcitrant and more toxic (i.e. a process known as biological activation).

Therefore, the expected kinetics of an environmental system depends on the characteristics of the air pollutant, the environmental compartment, and the atmospheric conditions. The next chapter introduces ways to predict the partitioning of the pollutant to and from the atmosphere.

## QUESTIONS

- What conditions are needed to transform elemental mercury ( $\text{Hg}^0$ ) to methylmercury?
- How can sorption affect the potential for degrading persistent compounds like tetrachlorodibenzo-p-dioxin?
- If a compound reacts in water vapor so that its concentration changes from 10 to 3 ppm in 1 h, what is its reaction rate?
- What is the activation energy? What role do catalysts play in this?
- This chapter mentions how reaction rates are temperature dependent. Indeed, the rate constant  $k$  reflects this in the Arrhenius equation:

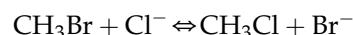
$$k = A \cdot e^{\frac{E_a}{RT}},$$

where  $A$  is the pre-exponential factor (constant);  $E_a$  is the Arrhenius activation energy,  $R$  is the universal gas constant, and  $T$  is the absolute temperature.

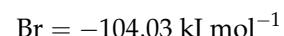
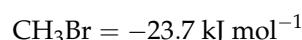
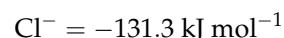
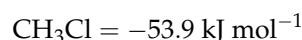
Using this equation, if a compound degrades to its metabolite at a rate of  $4.6 \times 10^{-2} \text{ day}^{-1}$  at  $20^\circ\text{C}$  and at  $1.1 \times 10^{-2} \text{ day}^{-1}$  at  $0^\circ\text{C}$ , determine its reaction rate at  $15^\circ\text{C}$ .

- A compound in air is inhaled and becomes more polar during Phase I metabolism. List the processes in Table 17.1 that are or could be occurring.

- Draw a curve with potential energy on the  $y$ -axis and the progression of the reaction of oxidation of carbon monoxide to carbon dioxide on the  $x$ -axis for a reaction. Draw another curve on the same graph for the same reaction, but which is catalyzed. How does activation energy differ for the two curves?
- Consider two stages in a catalytic converter in a car's exhaust system, the first contains platinum and the next contains a transition metal. Show the chemical reactions in both. Describe the rates and activation energy with and without the catalysis and how the chemical constituency of the exhaust would differ without the first, the second, and both the stages.
- What is the difference between catabolism and anabolism?
- Which order reactions are the most common type of inorganic reactions in the atmosphere?
- Describe the mechanisms important to air pollution that involve hydrolysis.
- Explain why each of the statements in the "rule of five", which were postulated for drugs can be valuable when considering air pollutants.
- In general, what happens to an organic compound's persistence when halogens are substituted on the molecule?
- Methyl bromide is transformed to methyl chloride at  $25^\circ\text{C}$  as follows:



The  $\Delta G_f^0(aq)$  values are:



In which direction will this reaction occur in an aqueous substrate containing 50 millimolar (mM)  $\text{Cl}^-$ , 2 mM  $\text{Br}^-$  and 50 times more  $\text{CH}_3\text{Cl}$  than  $\text{CH}_3\text{Br}$ ?

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# Air Pollutant Kinetics and Equilibrium

## 18.1 KINETICS VS EQUILIBRIUM

Chapter 17 applies chemical kinetics to the inherent properties of chemical compounds within the context of air pollutant transformation. The processes in Table 17.1 indicate that physics, chemistry, and biology are intertwined. Also introduced in Chapters 6 and 17 is the relationship between intrinsic properties of the pollutants and the environmental compartments where they reside. That is, the physicochemical properties must always be considered simultaneously with environmental conditions to understand fully the types and orders of the reactions introduced in Chapter 17.

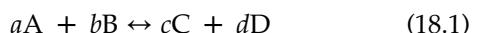
This chapter applies a number of the processes that occur among environmental compartments to estimate the affinities that a chemical compound has for the atmosphere, water, organic tissue, and other substrates at equilibrium.<sup>a</sup> Air pollution physics and chemistry are always considered together. The pollution processes are a function of both the chemical characteristics of the compartment (e.g. air) and those of the contaminant, because the inherent properties of the air pollutant are influenced and changed by the extrinsic properties of the air and other media.

### 18.1.1 Equilibrium and Partitioning

The kinetics discussion in Chapter 17 provides the first step in understanding an air pollutant's affinity for an environmental compartment and, conversely, its propensity to exit that compartment. This is known as environmental partitioning.

After kinetics, the chemistry of the air pollutant reaches equilibrium. This explains how a pollutant will behave in the environment, including the extent to

which it will reach the atmosphere and how long it will remain there. Consider the reversible reaction:



Equation (18.1) is depicted in Figure 18.1. Initially ( $t_0$ ), the rate of the forward reaction is high and the rate of the reverse reaction is low. As the reaction proceeds, the rate of the forward reaction decreases while the rate of the reverse reaction increases. This changes when the reaction rates become equal, i.e. at  $t_{\text{equil}}$  the rate of the forward reaction equals the rate of the reverse reaction, i.e. system has reached equilibrium.

Actually, the forward and reverse reactions continue at a microscopic scale, so it is more properly stated that the system has reached dynamic equilibrium. Recall from Chapter 17 that the reaction has a forward rate:



The reaction also has a backward rate:

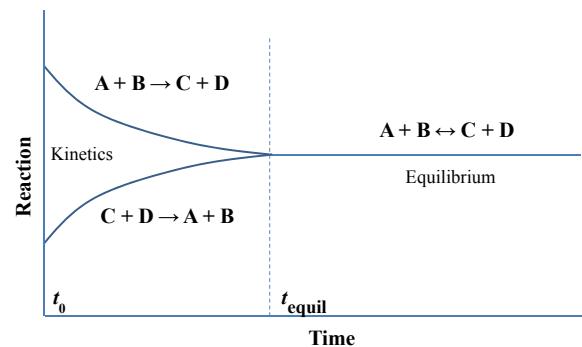


FIGURE 18.1 The change in rate of forward and reverse chemical reactions leading to equilibrium in a closed thermodynamic system. (For color version of this figure, the reader is referred to the online version of this book.)

<sup>a</sup> Partitioning is commonly considered to be an equilibrium phenomenon. However, it certainly occurs under nonequilibrium conditions. The equilibrium assumption makes the mathematics easier, but partitioning occurs before equilibrium is reached. For example, an octanol–water coefficient applies to equilibrium conditions where molecules moving between the octanol and water compartment are equal. Of course, before equilibrium occurred, molecules were already moving between the compartments.

As mentioned, at equilibrium the forward equals the backward rate:

$$k_f[A]^a[B]^b = k_b[C]^c[D]^d \quad (18.4)$$

Thus, an equilibrium constant,  $K_{eq}$ , can be found for this reaction:

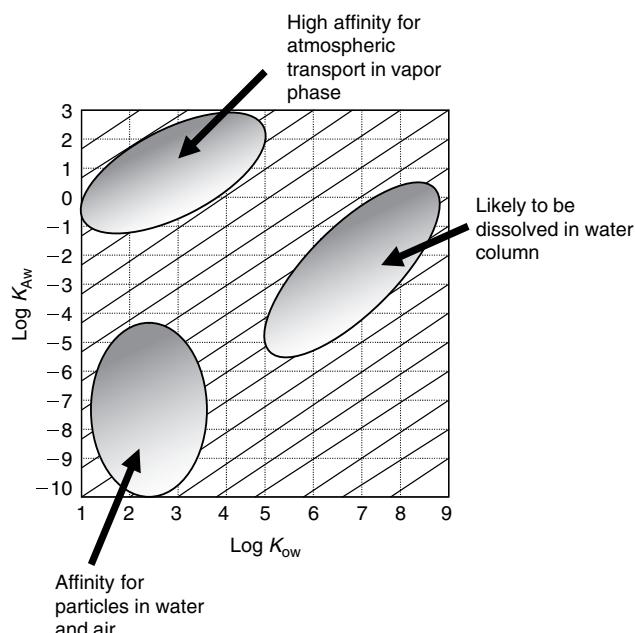
$$K_{eq} = \frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (18.5)$$

## 18.2 AIR POLLUTION CHEMODYNAMICS

Environmental chemodynamics is concerned with how chemicals move and change in the environment. Fluid properties have a great bearing on the movement and distribution of contaminants to, from, and within the atmosphere. Environmental partitioning relationships govern the "leaving" and "gaining" of pollutants among compartments, especially air, particles, surfaces, and organic tissues. These concepts may be applied to estimating and modeling where a contaminant will go after it is released. This movement is affected by sorption, solubility, volatilization, organic carbon–water partitioning, organic carbon–air partitioning, and bioaccumulation.

In chemodynamics, the environment is subdivided into finite compartments. Thermodynamically, the mass of the contaminant entering and the mass leaving a control volume must be balanced by what remains within the control volume (a requirement of all the conservation laws). Likewise, within that control volume, each compartment may be a gainer or loser of the contaminant mass, but the overall mass must balance. The generally inclusive term for these compartmental changes is known as fugacity or the "fleeing potential" of a substance. It is the propensity of a chemical to escape from one environmental compartment to another. Combining the relationships between and among all of the partitioning terms is one means of modeling chemical transport in the environment.<sup>1</sup> This is accomplished by using thermodynamic principles and, hence, fugacity is a thermodynamic term.

The simplest chemodynamic approach addresses each compartment where a contaminant is found in discrete phases of air, water, soil, sediment, and biota. This can be seen graphically in Figure 18.2. However, a complicating factor in environmental chemodynamics is that even within a single compartment, a contaminant may exist in various phases (e.g. dissolved in water and sorbed to a particle in the solid phase). The physical



**FIGURE 18.2** Relationship between air–water partitioning and octanol–water partitioning and affinity of classes of contaminants for certain environmental compartments. A source of this information and format is: van de Meent D, McKone T, Parkerton T, Matthies M, Scheringer M, Wania F, et al. Persistence and transport potential of chemicals in a multimedia environment. In: Proceedings of the SETAC Pellston workshop on criteria for persistence and long-range transport of chemicals in the environment, Fairmont Hot Springs, British Columbia, Canada, July 14–19, 1998. Pensacola (FL): Society of Environmental Toxicology and Chemistry; 1999.

interactions of the contaminant at the interface between each compartment are a determining factor in the fate of the pollutant. During a designated time period within a compartment, a contaminant may remain unchanged or it may move physically, or it may be transformed chemically into another substance. Actually, in many cases all three mechanisms will take place. One mass fraction will remain unmoved and unchanged. Another fraction remains unchanged but is transported to a different compartment. Another fraction becomes chemically transformed with all remaining products staying in the compartment where they were generated. And, a fraction of the original contaminant is transformed and then moved to another compartment. So, upon release from a source, the contaminant moves as a result of thermodynamics.

Fugacity requires that at least two phases be in contact with the contaminant. For example, the octanol–water coefficient ( $K_{ow}$ ) value is an indication of a compound's likelihood to exist in the organic vs aqueous phase.<sup>b</sup>

<sup>b</sup> Because of the large range in values,  $K_{ow}$  is reported as its logarithm, i.e.  $\log K_{ow}$ . In many texts, especially those of the biomedical and pharmacological sciences, as well as certain environmental and air pollution texts, the log octanol–water coefficient is designated as  $\log P_{ow}$  but most commonly as simply  $\log P$ . The terms are synonymous.

This means that if a substance is dissolved in water and the water comes into contact with another substance, e.g. octanol, the substance will have a tendency to move from the water to the octanol. Its octanol–water partitioning coefficient reflects just how much of the substance will move until the aqueous and organic solvents (phases) reach equilibrium. So, for example, in a spill of equal amounts of the polychlorinated biphenyl (PCB), dechlorobiphenyl ( $\log K_{ow}$  of 8.23), and the pesticide chlordane ( $\log K_{ow}$  of 2.78), the PCB has greater than five orders of magnitude affinity for the organic phases than does the chlordane. This does not mean that a great amount of either of the compounds is likely to stay in the water column, since they are both hydrophobic, but it does mean that they will vary in the time and mass of each contaminant moving between phases. The rate (kinetics) is different, so the time it takes for the PCB and chlordane to reach equilibrium will be different. This can be visualized by plotting the concentration of each compound with time (Figure 18.3). When the concentrations plateau, the compounds are at equilibrium with their phase.

When phases contact one another, a contaminant will escape from one to another until the contaminant reaches equilibrium among the phases contacting one another. Kinetics takes place until equilibrium is achieved.

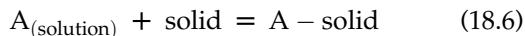
We can now consider the key partitioning factors needed for a simple chemodynamic model.

### 18.2.1 Partitioning to Solids: Sorption

The fate of an air pollutant can be estimated in part by differentiating the various ways that a contaminant will attach to or permeate into surfaces of solid phase particles. The mechanisms underpinning the affinity for the solid phase can be combined into a general phenomenon called *sorption*, which is the process in which a

contaminant or other solute becomes associated, physically or chemically, with a solid sorbent.

The physicochemical transfer<sup>2</sup> of a chemical, A, from liquid to solid phase is expressed as



The interaction of the solute (i.e. the chemical being sorbed) with the surface of a solid surface can be complex and dependent on the properties of the chemical and the solvent, which is usually water in air pollution applications. Other fluids are often of such small concentrations that they do not determine the ultimate solid–liquid partitioning. While, it is often acceptable to consider “net” sorption, there are four basic types or mechanisms of sorption:

- Adsorption** is the process wherein the chemical in solution attaches to a solid surface, which is a common sorption process in clay and organic constituents in soils. This simple adsorption mechanism can occur on clay particles where little carbon is available, such as in groundwater.
- Absorption** is the process that often occurs in porous materials so that the solute can diffuse into the particle and be sorbed onto the inside surfaces of the particle. This commonly results from short-range electrostatic interactions between the surface and the contaminant.
- Chemisorption** is the process of integrating a chemical into porous materials surface via chemical reaction. In an airborne particle, this can be the result of a covalent reaction between a mineral surface and the contaminant.
- Ion exchange** is the process by which positively charged ions (cations) are attracted to negatively charged particle surfaces and negatively charged ions (anions) are attracted to positively charged particle surfaces, causing ions on the particle surfaces to be displaced. Particles undergoing ion exchange can include soils, sediment, airborne particulate matter, or even biota, such as pollen particles. Cation exchange has been characterized as being the second most important chemical process on earth, after photosynthesis. This is because the cation exchange capacity (CEC), and to a lesser degree anion exchange capacity (AEC) in tropical soils, is the means by which nutrients are made available to plant roots. Without this process, the atmospheric nutrients and the minerals in the soil would not come together to provide for the abundant plant life on planet earth.<sup>3</sup>

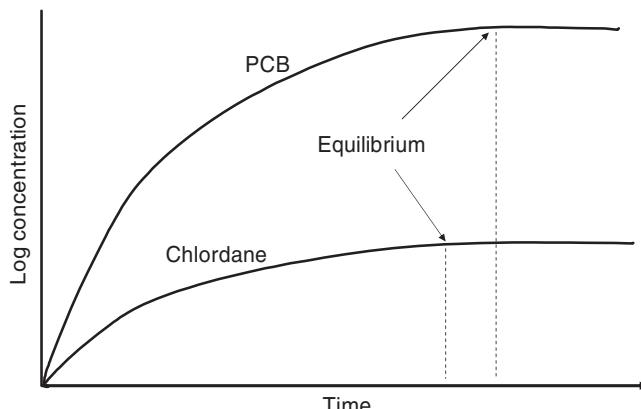


FIGURE 18.3 Relative concentrations of a PCB and chlordane in octanol with time.

These four types of sorption are a mix of physics and chemistry. The first two are predominantly controlled by physical factors, and the second two are combinations of chemical reactions and physical processes. Generally,

sorption reactions affect the following three processes<sup>4</sup> that affect the fate of an air pollutant:

1. The chemical contaminant's transport in water due to distributions between the aqueous phase and particles.
2. The aggregation and transport of the contaminant as a result of electrostatic properties of suspended solids.
3. Surface reactions such as dissociation, surface catalysis, and precipitation of the chemical contaminant.

Therefore, the types of sorption can be applied in specific ways to collect pollutants in air pollution control technologies. For example, collecting a contaminant on the surface of a sorbent depends solely on adsorption, while applying a control technology that traps the pollutant within the sorbent makes uses of absorption. Thus, adsorption is often a very effective means of collecting air pollutants in the vapor phase (See Section 30.9 in Chapter 30). Many technologies make use of both, as well as cation and anion exchange and chemisorption (see discussion below and in Chapters 30 and 31). Researchers attempt to parcel out which of the mechanisms are prominent in a given situation, since they vary according to the contaminant and the substrate.

When a contaminant enters the air, some of the chemical remains in the air, some in water droplets, and some of the chemicals are adsorbed onto the surfaces of the particles. Sometimes this sorption is strong due to cations adsorbing to the negatively charged particles. In other cases the attraction is weak. Sorption of chemicals on solid surfaces needs to be understood because they hold onto contaminants, not allowing them to move freely with the surrounding fluid, whether it be in the air, in a suspended droplet, or after deposition, in the soil solution. Indeed, sorption slows the rate at which deposited contaminants move downwardly through the soil profile.

Contaminants will eventually establish a balance between the mass on the solid surfaces and the mass that is in solution. Recall that molecules will migrate from one phase to another to maintain this balance. The properties of both the contaminant and the matrix will determine how and at what rates the molecules partition into the solid and liquid phases. These physicochemical relationships, known as *sorption isotherms*, are found experimentally. Figure 18.4 shows three isotherms for the polycyclic aromatic hydrocarbon, pyrene, from experiments using different matrices, i.e. soils and sediments.

The *x*-axis shows the concentration of pyrene dissolved in water, and the *y*-axis shows the concentration in the solid phase. Each line represents the relationship between these concentrations for a single type of matrix material. A straight-line segment through the origin represents the data well for the range of concentrations shown. Not all portions of an isotherm are linear,

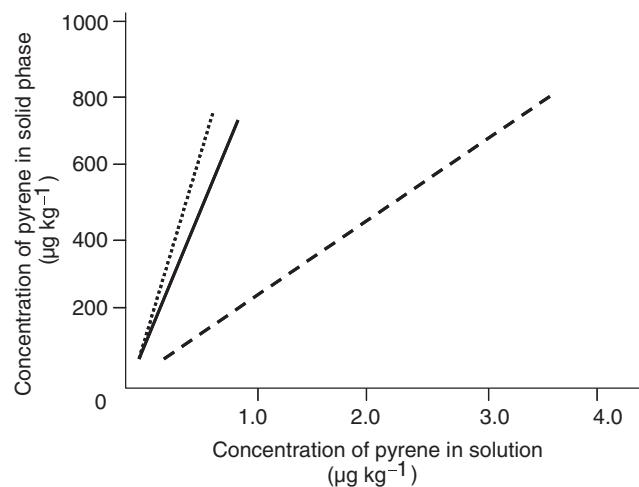


FIGURE 18.4 Three experimentally determined sorption isotherms for the polycyclic aromatic hydrocarbon, pyrene. Hassett J, Banwart W. The sorption of nonpolar organics by soils and sediments. In: Sawhney B, Brown K, editors. Reactions and movement of organic chemicals in soils. Soil Science Society of America. Special Publication 22; 1989. p. 35.

particularly at high concentrations of the contaminant. Linear chemical partitioning can be expressed as

$$S = K_D C_W \quad (18.7)$$

where *S* is the concentration of contaminant in the solid phase (mass of solute per mass of soil or sediment); *C<sub>W</sub>* is the concentration of contaminant in the liquid phase (mass of solute per volume of pore water); and *K<sub>D</sub>* is the partition coefficient (volume of pore water per mass of soil or sediment) for this contaminant in this soil or sediment.

For many soils and chemicals, the partition coefficient can be estimated using

$$K_D = K_{OC} C_{org} \quad (18.8)$$

where *K<sub>OC</sub>* is the organic carbon partition coefficient (volume of pore water per mass of organic carbon) and *C<sub>org</sub>* is the soil organic matter (mass of organic carbon per mass of soil).

This relationship is a very useful tool for estimating *K<sub>D</sub>* from the known *K<sub>OC</sub>* of the contaminant and the organic carbon content of the soil horizon of interest. The actual derivation of *K<sub>D</sub>* is

$$K_D = C_S(C_W)^{-1} \quad (18.9)$$

where *C<sub>S</sub>* is the equilibrium concentration of the solute in the solid phase and *C<sub>W</sub>* is the equilibrium concentration of the solute in the water.

Therefore, *K<sub>D</sub>* is a direct expression of the partitioning between the aqueous and solid (e.g. particle) phases. A strongly sorbed chemical like dioxin or the banned pesticide dichlorodiphenyltrichloroethane (DDT) can have a *K<sub>D</sub>* value exceeding 10<sup>6</sup>. Conversely, a highly

hydrophilic, miscible substance like ethanol, acetone, or vinyl chloride, will have  $K_D$  values less than 1. This relationship between the two phases demonstrated by Eqn (18.9) and shown in Figure 18.5 is roughly what environmental scientists call the Freundlich sorption isotherm:

$$C_{\text{sorb}} = K_F C^n \quad (18.10)$$

where  $C_{\text{sorb}}$  is the concentration of the sorbed contaminant, i.e. the mass sorbed at equilibrium per mass of sorbent, and  $K_F$  is the Freundlich isotherm constant. The exponent determines the linearity or order of the reaction. Thus, if  $n = 1$ , then the isotherm is linear; meaning the more of the contaminant in solution, the more would be expected to be sorbed to surfaces. For values of  $n < 1$ , the amount of sorption is in smaller proportion to the amount of solution and, conversely, for values of  $n > 1$ , a greater proportion of sorption occurs with less contaminant in solution. These three isotherms are shown in Figure 18.5. Also note that if  $n = 1$ , then Eqn (18.11) and the Freundlich sorption isotherm are identical.

Research has shown that when organic matter content is elevated in the particle, the amount of a contaminant that is sorbed is directly proportional to the particle's organic matter content. This allows for the conversion of the  $K_D$  values from those that depend on specific substrates, e.g. soil or sediment, and site-specific conditions to those that are substrate-independent and more generally applicable sorption constants,  $K_{\text{OC}}$ :

$$K_{\text{OC}} = K_D (f_{\text{OC}})^{-1} \quad (18.11)$$

where  $f_{\text{OC}}$  is the dimensionless weight fraction of organic carbon in the particle.  $K_{\text{OC}}$  and  $K_D$  have units of mass per

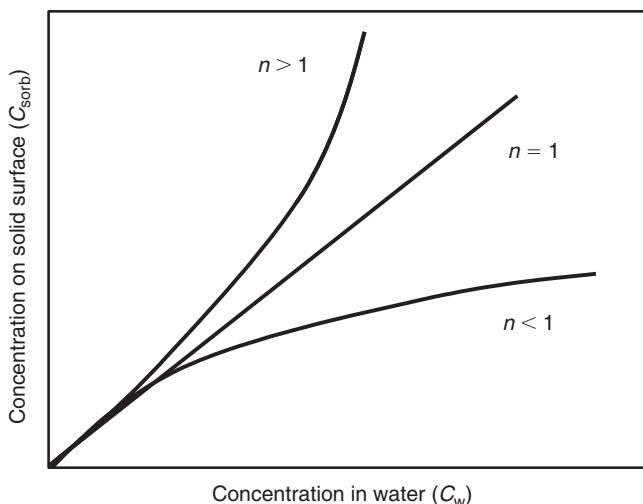


FIGURE 18.5 Hypothetical Freundlich isotherms with exponents ( $n$ ) less than, equal to, and greater than 1, as applied to the equation  $C_{\text{sorb}} = K_F C^n$ . Schwarzenbach R, Gschwend P, Imboden D. Environmental organic chemistry. New York (NY): John Wiley & Sons Inc.; 1993; and Hemond HF, Fechner-Levy EJ. Chemical fate and transport in the environment. San Diego (CA): Academic Press; 2000.

volume. Table 18.1 provides the log  $K_{\text{OC}}$  values that are calculated from chemical structure and those measured empirically for several organic compounds, and compares them to the respective  $K_{\text{ow}}$  values.

Sorption is arguably the most important transfer process that determines how bioavailable or toxic a compound will be in surface waters, but it is also very important for atmospheric transport. Surface water-atmosphere exchanges are a means by which large quantities of air pollutants reach the atmosphere. Also, sorption occurs at the microscopic scale in water droplets. In addition, chemical transport can occur to and from a solid particle via any fluid, including air as well as water.

### 18.2.2 Partitioning to the Liquid Phase: Dissolution

Unless otherwise stated, one can usually assume that when a compound is described as insoluble, such a statement means that the compound is *hydrophobic*. However, in environmental matters, it can be dangerous to make such assumptions, since such wide range of scientific and engineering disciplines are involved. A good resource for contaminant solubilities for water, dimethylsulfoxide (DMSO), ethanol, acetone, methanol, and toluene is the National Toxicology Program's *Chemical Solubility Compendium*<sup>5</sup> and the program's Health and Safety reports.<sup>6</sup> The latter are updated frequently and provide useful data on properties of toxic chemicals.

Most characterizations of contaminants will describe solubility in water and provide values for aqueous solubility, as well as a substance's solubility in other organic solvents, such as methanol or acetone.

The process of *cosolvation* is a very important mechanism by which a highly lipophilic and hydrophobic compound enters water. If a compound is hydrophobic and nonpolar, but is easily dissolved in acetone or methanol, it may well end up in the water because these organic solvents are highly miscible with water. The organic solvent and water mix easily, and a hydrophobic compound will remain in the water column because it is dissolved in the organic solvent, which in turn has mixed with the water. Compounds like PCBs and dioxins may be transported as cosolutes in water by this means. So, the combination of hydrophobic compounds being sorbed to suspended materials and cosolvated in organic cosolvents that are miscible in water can mean that they are able to move in water and receptors can be exposed through the water pathways.

Solubility is determined from saturation studies. In other words, in the laboratory at a certain temperature, as much of the solute is added to a solvent until the solvent can no longer dissolve the substance being added. So, if compound A has a published solubility of  $10 \text{ mg l}^{-1}$  in water at  $20^\circ\text{C}$ , this means that the 1 l of water could only dissolve 10 mg of that substance. If, under identical

TABLE 18.1 Calculated and Experimental Organic Carbon Coefficients ( $K_{OC}$ ) for Selected Contaminants Found at Hazardous Waste Sites Compared to Octanol–Water Coefficients ( $K_{ow}$ ). Conditions assumed to be 25° C and 1 atmos.

Chemical	$\log K_{ow}$	Calculated		Measured	
		$\log K_{OC}$	$K_{OC}$	$\log K_{OC}$	$K_{OC}$ (geomean)
Benzene	2.13	1.77	59	1.79	61.7
Bromoform	2.35	1.94	87	2.10	126
Carbon tetrachloride	2.73	2.24	174	2.18	152
Chlorobenzene	2.86	2.34	219	2.35	224
Chloroform	1.92	1.60	40	1.72	52.5
Dichlorobenzene, 1,2- ( <i>o</i> )	3.43	2.79	617	2.58	379
Dichlorobenzene, 1,4- ( <i>p</i> )	3.42	2.79	617	2.79	616
Dichloroethane, 1,1-	1.79	1.50	32	1.73	53.4
Dichloroethane, 1,2-	1.47	1.24	17	1.58	38.0
Dichloroethylene, 1,1-	2.13	1.77	59	1.81	65
Dichloroethylene, <i>trans</i> -1,2-	2.07	1.72	52	1.58	38
Dichloropropane, 1,2-	1.97	1.64	44	1.67	47.0
Dieldrin	5.37	4.33	21,380	4.41	25,546
Endosulfan	4.10	3.33	2138	3.31	2040
Endrin	5.06	4.09	12,303	4.03	10,811
Ethylbenzene	3.14	2.56	363	2.31	204
Hexachlorobenzene	5.89	4.74	54,954	4.90	80,000
Methyl bromide	1.19	1.02	10	0.95	9.0
Methyl chloride	0.91	0.80	6	0.78	6.0
Methylene chloride	1.25	1.07	12	1.00	10
Pentachlorobenzene	5.26	4.24	17,378	4.51	32,148
Tetrachloroethane, 1,1,2,2-	2.39	1.97	93	1.90	79.0
Tetrachloroethylene	2.67	2.19	155	2.42	265
Toluene	2.75	2.26	182	2.15	140
Trichlorobenzene, 1,2,4-	4.01	3.25	1778	3.22	1659
Trichloroethane, 1,1,1-	2.48	2.04	110	2.13	135
Trichloroethane, 1,1,2-	2.05	1.70	50	1.88	75.0
Trichloroethylene	2.71	2.22	166	1.97	94.3
Xylene, <i>o</i> -	3.13	2.56	363	2.38	241
Xylene, <i>m</i> -	3.20	2.61	407	2.29	196
Xylene, <i>p</i> -	3.17	2.59	389	2.49	311

Source: US Environmental Protection Agency; 1996. Soil Screening Program.

conditions, compound B has a published aqueous solubility of  $20 \text{ mg l}^{-1}$ , this means that 1 l of water could dissolve 20 mg of compound B, and that compound B has twice the aqueous solubility of compound A.

Actually, solutions are in “dynamic equilibrium” because the solute is leaving and entering the solution

at all times, but the average amount of solute in solution is the same. The functional groups on a molecule determine whether it will be more or less polar. So, compounds with hydroxyl groups are more likely to form H-bonds with water. Thus, methane is less soluble in water than methanol. Also, since water interacts strongly with ions,

salts are usually quite hydrophilic. The less the charge of the ion, the greater the solubility in water.

### 18.2.3 Partitioning to the Gas Phase: Volatilization

In its simplest connotation, volatilization is a function of the concentration of a contaminant in solution and the contaminant's partial pressure.

Henry's law states that the concentration of a dissolved gas is directly proportional to the partial pressure of that gas above the solution:

$$p_a = K_H [c] \quad (18.12)$$

where,  $K_H$  is the Henry's law constant,  $p_a$  is the partial pressure of the gas, and  $[c]$  is the molar concentration of the gas or,

$$p_a = K_H C_W \quad (18.13)$$

where  $C_W$  is the concentration of gas in water.

So, for any chemical contaminant we can establish a proportionality between the solubility and vapor pressure. Henry's law is an expression of this proportionality between the concentration of a dissolved

contaminant and its partial pressure in the headspace (including the open atmosphere) at equilibrium. A dimensionless version of the partitioning is similar to that of sorption, except that instead of the partitioning between solid and water phases, it is between the air and water phases ( $K_{AW}$ ):

$$K_{AW} = \frac{C_A}{C_W} \quad (18.14)$$

where  $C_A$  is the concentration of gas A in the air.

The relationship between the air–water partition coefficient and Henry's law constant for a substance is:

$$K_{AW} = \frac{K_H}{RT} \quad (18.15)$$

where  $R$  is the gas constant ( $8.21 \times 10^{-2} \text{ J atm mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the temperature (K).

Henry's law relationships work well for most environmental conditions. It represents a limiting factor for systems where a substance's partial pressure is approaching zero. At very high partial pressures (e.g. 30 Pa) or at very high contaminant concentrations (e.g. >1000 ppm), Henry's law assumptions cannot be met. Such vapor pressures and concentrations are seldom seen in ambient environmental situations, but may be seen in industrial and other source situations. Thus, in

### HENRY'S LAW EXAMPLE

At 25 °C, the log Henry's law constant ( $\log K_H$ ) for 1,2-dimethylbenzene ( $C_8H_{10}$ ) is 0.71  $\text{J atm mol}^{-1}$  and the log octanol–water coefficient ( $\log K_{ow}$ ) is 3.12. The log  $K_H$  for the pesticide parathion ( $C_{10}H_{14}NO_5PS$ ) is  $-3.42 \text{ J atm mol}^{-1}$ , but its log  $K_{ow}$  is 3.81. Explain how these substances can have similar values for octanol–water partitioning yet so different Henry's law constants. What principle physicochemical properties account for much of this difference?

#### Answer

Both dimethylbenzene and parathion have an affinity for the organic phase compared to the aqueous phase. Since Henry's law constants are a function of both vapor pressure ( $P^0$ ) and water solubility, and both compounds have similar octanol–water coefficients, the difference in the Henry's law characteristics must be mainly attributable to the compounds' respective water solubilities, their vapor pressures, or both.

Parathion is considered "semivolatile" because its vapor pressure at 20 °C is only  $1.3 \times 10^{-3} \text{ kPa}$ . Parathion's solubility<sup>7</sup> in water is  $12.4 \text{ mg l}^{-1}$  at 25 °C.

1,2-Dimethylbenzene is also known as *ortho*-xylene (*o*-xylene). The xylenes are simply benzenes with two more methyl groups. The xylenes have very high vapor pressures of  $4.5 \times 10^2 \text{ kPa}$ , and water solubilities<sup>8</sup> of about 200  $\text{mg l}^{-1}$  at 25 °C.

Thus, since both the solubilities are relatively low, it appears that the difference in vapor pressures is responsible for the large difference in the Henry's law constants, i.e. the much larger tendency of the xylene to leave the water and enter the atmosphere. Some of this tendency may result from the higher molecular weight of the parathion, but is also attributable to the additional functional groups on the parathion benzene than the two methyl groups on the xylene (Figure 18.6).

Another way to look at the chemical structures is to see them as the result of adding increasing complex functional groups, i.e. moving from the unsubstituted benzene to the single methylated benzene (toluene) to *o*-xylene to parathion. The substitutions result in respective progressively decreasing vapor pressures:

Benzene's  $P^0$  at 20 °C = 12.7 kPa

Toluene's  $P^0$  at 20 °C = 3.7 kPa

(Continued)

### HENRY'S LAW EXAMPLE (cont'd)

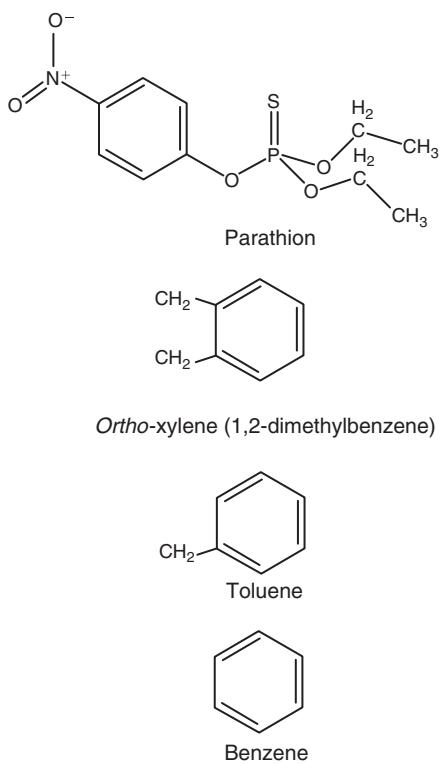


FIGURE 18.6 Molecular structure of the pesticide parathion and the solvents *ortho*-xylene, toluene, and benzene.

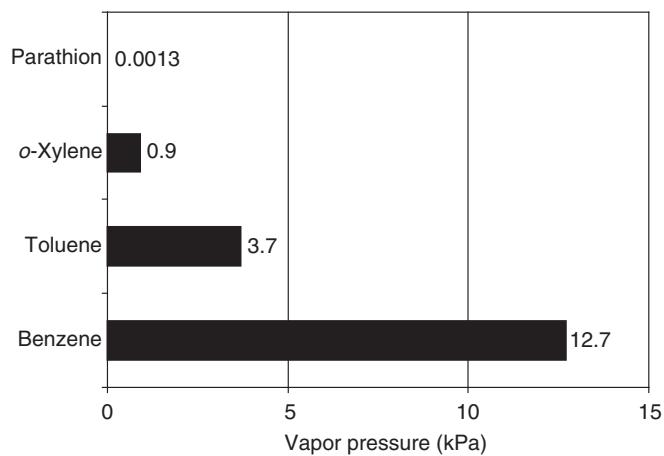


FIGURE 18.7 Effect of functional group substitutions on vapor pressure of four organic aromatic compounds.

*o*-Xylene's  $P^0$  at 20 °C = 0.9 kPa  
Parathion's  $P^0$  at 20 °C =  $1.3 \times 10^{-3}$  kPa

The effect of these functional group additions on vapor pressure is even more obvious when seen graphically (Figure 18.7).

modeling and estimating the tendency for a substance's release in vapor form, Henry's law is a good metric and is often used in compartmental transport models to indicate the fugacity from the water to the atmosphere.

It is important to keep in mind that Henry's law constants are highly dependent on temperature, since both vapor pressure and solubility are also temperature dependent. So, when using published  $K_H$  values, one must compare them isothermally. Also, when combining different partitioning coefficients in a model or study, it is important to either use only values derived at the same temperature (e.g. sorption, solubility, and volatilization all at 20 °C), or to adjust them accordingly. A general adjustment is an increase of a factor of 2 in  $K_H$  for each 8 °C temperature increase.

Also, any sorbed or otherwise bound fraction of the contaminant will not exert a partial pressure; so this fraction should not be included in calculations of partitioning from water to air. For example, it is important to differentiate between the mass of the contaminant in solution (available for the  $K_{AW}$  calculation) and that in the suspended solids (unavailable for  $K_{AW}$  calculation). This

is crucial for many hydrophobic organic contaminants, where they are most likely not to be dissolved in the water column (except as cosolutes), with the largest mass fraction in the water column being sorbed to particles.

The relationship between  $K_H$  and  $K_{ow}$  is also important. It is often used to estimate the *environmental persistence*, as reflected in the chemical *half-life* ( $t_{1/2}$ ) of a contaminant. However, many other variables determine the actual persistence of a compound after its release. Note in the table, for example, that benzene and chloroform have nearly identical values of  $K_H$  and  $K_{ow}$  yet benzene is far less persistent in the environment. Persistence is also an important factor in removing and treating the pollutant, including the choice between abiotic chemical destruction *versus* biodegradation.

With these caveats in mind, however, relative affinity for a substance to reside in air and water can be used to estimate the potential for the substance to partition not only between water and air, but more generally between the atmosphere and biosphere, especially when considering the long-range transport of contaminants (e.g. across continents and oceans).<sup>9</sup>

Such long-range transport estimates make use of both atmospheric  $t_{1/2}$  and  $K_H$ . The relationship between octanol–water and air–water coefficients can also be an important part of predicting a contaminant's transport. For example, Figure 18.2 provides some general classifications according to various substances'  $K_H$  and  $K_{ow}$  relationships. In general, chemicals in the upper left-hand group have a great affinity for the atmosphere, so unless there are contravening factors, this is where to look for them. Conversely, substances with relatively low  $K_H$  and  $K_{ow}$  values are less likely to be transported long distance in the air.

**Partitioning to Organic Tissue:** Relatively hydrophobic substances frequently have a strong affinity for fatty tissues (i.e. those containing high  $K_{ow}$  compounds). Therefore, such contaminants can be sequestered and can accumulate in organisms. In other words, certain chemicals are very *bioavailable* to organisms that may readily take them up from the other compartments. Bioavailability is an expression of the fraction of the total mass of a compound present in a compartment that has the potential of being absorbed by the organism. *Bioaccumulation* is the process of uptake into an organism from the abiotic compartments. *Bioconcentration* is the concentration of the pollutant within an organism above levels found in the compartment in which the organism lives. So, for a fish to bioaccumulate DDT, the levels found in the total fish or in certain organs (e.g. the liver) will be elevated above the levels measured in the ambient environment. In fact, DDT is known to bioconcentrate many orders of magnitude in fish. A surface water DDT concentration of 100 ppt in water has been associated with 10 ppm in certain fish species (a concentration of 10,000 times!). Thus, the straightforward equation for the *bioconcentration factor* (BCF) is the quotient of the concentration of the contaminant in the organism and the concentration of the contaminant in the host compartment. So, for a fish living in water, the BCF is

$$\text{BCF} = \frac{C_{\text{organism}}}{C_W} \quad (18.16)$$

The BCF is applied to an individual organism that represents a genus or some other taxonomical group. However, considering the whole food chain and trophic transfer processes, in which a compound builds up as a result of predator–prey relationships, the term *biomagnification* is used. Some compounds that may not appreciably bioconcentrate within lower trophic state organisms may still become highly concentrated. For example, even though plankton have a small BCF (e.g. 10), if subsequently higher-order organisms sequester the contaminant at a higher rate, by the time top predators (e.g. alligators, sharks, panthers, and humans) may

suffer from the continuum of biomagnification, with levels many orders of magnitude higher than what is found in the abiotic compartments.

For a substance to bioaccumulate, bioconcentrate, and biomagnify, it must be at least somewhat persistent. If an organism's metabolic and detoxification processes are able to degrade the compound readily, it will not be present (at least in high concentrations) in the organism's tissues. However, if an organism's endogenous processes degrade a compound into a chemical species that is itself persistent, the metabolite or degradation product will bioaccumulate, and may bioconcentrate, and biomagnify. Finally, cleansing or depuration will occur if the organism that has accumulated a contaminant enters an abiotic environment that no longer contains the contaminant. However, some tissues have such strong affinities for certain contaminants that the persistence within the organism will remain long after the source of the contaminant is removed. For example, the piscivorous birds, such as the common loon (*Gavia immer*), decrease the concentrations of the metal mercury (Hg) in their bodies by translocating the metal to feathers and eggs. So, every time the birds molt or lay eggs they undergo Hg depuration. Unfortunately, when the birds continue to ingest mercury that has bioaccumulated in their prey (fish), they often have a net increase in tissue Hg concentrations because the bioaccumulation rate exceeds the depuration rate.<sup>10</sup>

Bioconcentration can vary considerably in the environment. The degree to which a contaminant builds up in an ecosystem, especially in biota and sediments, is related to the compound's persistence. For example, a highly persistent compound often possesses chemical structures that are also conducive to sequestration by fauna. Such compounds are generally quite often lipophilic, have high  $K_{ow}$  values, and usually low vapor pressures. This means that they may bind to the organic molecules in living tissues and may resist elimination and metabolic process, so that they build up over time. However, the bioaccumulation and bioconcentration can vary considerably, both among biota and within the same species of biota. For example, the pesticide mirex has been shown to exhibit BCFs of 2600 and 51,400 in pink shrimp and fathead minnows, respectively. The pesticide endrin has shown an even larger interspecies variability in BCF values, with factors ranging from 14 to 18,000 recorded in fish after continuous exposure. Intraspecies BCF ranges may also be high, e.g. oysters exposed to very low concentrations of the organometallic compound, tributyl tin, exhibit BCF values ranging from 1000 to 6000.<sup>11</sup>

Even the same compound in a single medium, e.g. a lake's water column or sediment, will show large BCF

variability among species of fauna in that compartment. An example is the so-called “dirty dozen” compounds. This is a group of *persistent organic pollutants* that have been largely banned, some for decades, but that are still found in environmental samples throughout the world. As might be expected from their partitioning coefficients, they have concentrated in sediment and biota.

The worst combination of factors is when a compound is persistent in the environment, builds up in organic tissues, and is toxic. Such compounds are referred to as *persistent bioaccumulating toxic* substances (PBTs). Recently, the United Nations Environmental Program reported on the concentrations of the persistent and toxic compounds. Each region of the world was evaluated for the presence of these compounds. For example, the North American report<sup>12</sup> includes scientific assessments of the nature and scale of environmental threats posed by persistent toxic compounds. The results of these assessments are summarized in [Table 18.2](#) (organic compounds) and [Table 18.3](#) (organometallic compounds). In the United States, mining and mineral extraction activities contribute the large quantity of PBTs, with energy production the second largest source category ([Figure 18.8](#)). Organometallic compounds, especially lead and its compounds comprise the lion’s share of PBTs in the United States. And, the second largest quantity is represented by another metal, mercury, and its compounds ([Figure 18.9](#)).

The sources of PBTs are widely varied. Many are intentionally manufactured to serve some public need, such as the control of pests that destroy food and spread disease. Other PBTs are generated as unintended byproducts, such as the PICs. In either case, there are often measures and engineering controls available that can prevent PBT releases, rather than having to deal with them after they have found their way into the various environmental compartments.

#### 18.2.4 Concentration-Based and Fugacity-Based Transport Models

Let us now combine these phase and compartmental distributions into a simple fugacity-based, chemodynamic transport model. Such models are classified into three types:

- *Level 1 model:* This model is based on an equilibrium distribution of fixed quantities of contaminants in a closed environment (i.e. conservation of contaminant mass). No chemical or biological degradation, advection (discussed in detail later), and no transport among compartments (such as sediment loading or atmospheric deposition to surface waters).

A Level 1 calculation describes how a given quantity of a contaminant will partition among the water, air,

soil, sediment, suspended particles, and fauna, but does not take into account chemical reactions. Early Level 1 models considered an area of 1 km<sup>2</sup> with 70% of the area covered in surface water. Larger areas are now being modeled (e.g. about the size of the state of Ohio).

- *Level 2 model:* This model relaxes the conservation restrictions of Level 1 by introducing direct inputs (e.g. emissions) and advective sources from air and water. It assumes that a contaminant is being continuously loaded at a constant rate into the control volume, allowing the contaminant loading to reach steady state and equilibrium between contaminant input and output rates. Degradation and bulk movement of contaminants (advection) is treated as a loss term. Exchanges between and among media are not quantified.

Since the Level 2 approach is a simulation of a contaminant being continuously discharged into numerous compartments and which achieves a steady-state equilibrium, the challenge is to deduce the losses of the contaminant due to chemical reactions and advective (nondiffusive) mechanisms.

Reaction rates are unique to each compound and are published according to reactivity class (e.g. fast, moderate, or slow reactions), which allows modelers to select a class of reactivity for the respective contaminant to insert into transport models. The reactions are often assumed to be first order, so the model will employ a first-order rate constant for each compartment in the environmental system (e.g.  $x \text{ mol h}^{-1}$  in water,  $y \text{ mol h}^{-1}$  in air,  $z \text{ mol h}^{-1}$  in soil). Much uncertainty is associated with the reactivity class and rate constants, so it is best to use rates published in the literature based on experimental and empirical studies, wherever possible.

Advection flow rates in Level 2 models are usually reflected by residence times in the compartments. These residence times are commonly set to 1 h in each medium, so the advection rate ( $G_i$ ) is volume of the compartment divided by the residence time ( $t$ ):

$$G_i = Vt^{-1} \quad (18.17)$$

- *Level 3 model:* Same as Level 2, but does not assume equilibrium between compartments, so each compartment has its own fugacity. Mass balance applies to whole system and each compartment within the system. It includes mass transfer coefficients, rates of deposition, and resuspension of contaminant, rates of diffusion (discussed later), soil runoff, and area covered. All of these factors are aggregated into an intermedia transport term ( $D$ ) for each compartment.

TABLE 18.2 Summary of Persistent and Toxic Organic Compounds in North America, Identified by the United Nations as Highest Priorities for Regional Actions

Compound	Properties	Persistence/Fate	Toxicity*
<i>Aldrin</i> 1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo,exo-5,8-dimethanonaphthalene ( $C_{12}H_8Cl_6$ ).	Solubility in water: $27 \mu\text{g l}^{-1}$ at $25^\circ\text{C}$ ; vapor pressure: $2.31 \times 10^{-5} \text{ mmHg}$ at $20^\circ\text{C}$ ; $\log K_{ow}$ : 5.17–7.4.	Readily metabolized to dieldrin by both plants and animals. Biodegradation is expected to be slow and it binds strongly to soil particles, and is resistant to leaching into groundwater. Classified as moderately persistent with $t_{1/2}$ in soil ranging from 20 to 100 days.	Toxic to humans. Lethal dose for an adult estimated to be about $80 \text{ mg kg}^{-1}$ body weight. Acute oral $LD_{50}$ in laboratory animals is in the range of $33 \text{ mg kg}^{-1}$ body weight for guinea pigs to $320 \text{ mg kg}^{-1}$ body weight for hamsters. The toxicity of aldrin to aquatic organisms is quite variable, with aquatic insects being the most sensitive group of invertebrates. The 96-h $LC_{50}$ values range from 1 to $200 \mu\text{g l}^{-1}$ for insects, and from 2.2 to $53 \mu\text{g l}^{-1}$ for fish. The maximum residue limits in food recommended by the World Health Organization (WHO) varies from $0.006 \text{ mg kg}^{-1}$ milk fat to $0.2 \text{ mg kg}^{-1}$ meat fat. Water quality criteria between 0.1 and $180 \mu\text{g l}^{-1}$ have been published.
<i>Dieldrin</i> 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydroexo-1,4-endo-5,8-dimethanonaphthalene ( $C_{12}H_8Cl_6O$ ).	Solubility in water: $140 \mu\text{g l}^{-1}$ at $20^\circ\text{C}$ ; vapor pressure: $1.78 \times 10^{-7} \text{ mmHg}$ at $20^\circ\text{C}$ ; $\log K_{ow}$ : 3.69–6.2.	Highly persistent in soils, with a $t_{1/2}$ of 3–4 years in temperate climates, and bioconcentrates in organisms.	Acute toxicity for fish is high ( $LC_{50}$ between 1.1 and $41 \mu\text{g l}^{-1}$ ) and moderate for mammals ( $LD_{50}$ in mouse and rat ranging from $40$ – $70 \text{ mg kg}^{-1}$ body weight). Aldrin and dieldrin mainly affect the central nervous system but there is no direct evidence that they cause cancer in humans. The maximum residue limits in food recommended by WHO varies from $0.006 \text{ mg kg}^{-1}$ milk fat and $0.2 \text{ mg kg}^{-1}$ poultry fat. Water quality criteria between 0.1 and $18 \mu\text{g l}^{-1}$ have been published.
<i>Endrin</i> 3,4,5,6,9,9-Hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7;3,6-dimethanonaphth[2,3-b]oxirene ( $C_{12}H_8Cl_6O$ ).	Solubility in water: $220$ – $260 \mu\text{g l}^{-1}$ at $25^\circ\text{C}$ ; vapor pressure: $7 \times 10^{-7} \text{ mmHg}$ at $25^\circ\text{C}$ ; $\log K_{ow}$ : 3.21–5.34.	Highly persistent in soils ( $t_{1/2}$ of up to 12 years have been reported in some cases). BCFs of 14 to 18,000 have been recorded in fish, after continuous exposure.	Very toxic to fish, aquatic invertebrates, and phytoplankton; the $LC_{50}$ values are mostly less than $1 \mu\text{g l}^{-1}$ . The acute toxicity is high in laboratory animals, with $LD_{50}$ values of $3$ – $43 \text{ mg kg}^{-1}$ , and a dermal $LD_{50}$ of $6$ – $20 \text{ mg kg}^{-1}$ in rats. Long-term toxicity in the rat has been studied over 2 years and a NOEL of $0.05 \text{ mg kg}^{-1}$ bw day $^{-1}$ was found.
<i>Chlordane</i> 1,2,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene ( $C_{10}H_6Cl_8$ ).	Solubility in water: $180 \mu\text{g l}^{-1}$ at $25^\circ\text{C}$ ; vapor pressure: $0.3 \times 10^{-5} \text{ mmHg}$ at $20^\circ\text{C}$ ; $\log K_{ow}$ : 4.4–5.5.	Metabolized in soils, plants, and animals to heptachlor epoxide, which is more stable in biological systems and is carcinogenic. The $t_{1/2}$ of heptachlor in soil in temperate regions is 0.75–2 years. Its high partition coefficient provides the necessary conditions for bioconcentrating in organisms.	Acute toxicity to mammals is moderate ( $LD_{50}$ values between $40$ and $119 \text{ mg kg}^{-1}$ have been published). The toxicity to aquatic organisms is higher and $LC_{50}$ values down to $0.11 \mu\text{g l}^{-1}$ have been found for pink shrimp. Limited information is available on the effects in humans and studies are inconclusive regarding heptachlor and cancer. The maximum residue levels recommended by FAO/WHO are between $0.006 \text{ mg kg}^{-1}$ milk fat and $0.2 \text{ mg kg}^{-1}$ meat or poultry fat.
<i>Dichlorodiphenyltrichloroethane (DDT)</i> 1,1,1-Trichloro-2,2-bis-(4-chlorophenyl)-ethane ( $C_{14}H_9Cl_5$ ).	Solubility in water: $1.2$ – $5.5 \mu\text{g l}^{-1}$ at $25^\circ\text{C}$ ; vapor pressure: $0.02 \times 10^{-5} \text{ mmHg}$ at $20^\circ\text{C}$ ; $\log K_{ow}$ : 6.19 for pp-DDT, 5.5 for pp-DDD and 5.7 for pp-DDE.	Highly persistent in soils with a $t_{1/2}$ of about 1.1–3.4 years. It also exhibits high BCFs (in the order of 50,000 for fish and 500,000 for bivalves). In the environment,	Lowest dietary concentration of DDT reported to cause egg shell thinning was $0.6 \text{ mg kg}^{-1}$ for the black duck. $LC_{50}$ of $1.5 \text{ mg l}^{-1}$ for largemouth bass and $56 \text{ mg l}^{-1}$ for guppy have been reported. The acute toxicity of DDT for mammals is moderate with an $LD_{50}$ in rat of $113$ – $118 \text{ mg kg}^{-1}$ body

(Continued)

TABLE 18.2 Summary of Persistent and Toxic Organic Compounds in North America, Identified by the United Nations as Highest Priorities for Regional Actions—cont'd

Compound	Properties	Persistence/Fate	Toxicity*
<i>Toxaphene</i> Polychlorinated bornanes and camphenes ( $C_{10}H_{10}Cl_8$ ).	Solubility in water: $550 \mu\text{g l}^{-1}$ at $20^\circ\text{C}$ ; vapor pressure: $0.2\text{--}0.4 \text{ mmHg}$ at $25^\circ\text{C}$ ; $\log K_{ow}$ : $3.23\text{--}5.50$ .	the parent DDT is metabolized mainly to DDD and DDE.	weight. DDT has been shown to have an estrogen-like activity and possible carcinogenic activity in humans. The maximum residue level in food recommended by WHO/FAO, ranges from $0.02 \text{ mg kg}^{-1}$ milk fat to $5 \text{ mg kg}^{-1}$ meat fat. Maximum permissible DDT residue levels in drinking water (WHO) is $1.0 \mu\text{g l}^{-1}$ . Highly toxic in fish, with 96-h $LC_{50}$ values in the range of $1.8 \mu\text{g l}^{-1}$ in rainbow trout to $22 \mu\text{g l}^{-1}$ in bluegill. Long-term exposure to $0.5 \mu\text{g l}^{-1}$ reduced egg viability to zero. The acute oral toxicity is in the range of $49 \text{ mg kg}^{-1}$ body weight in dogs to $365 \text{ mg kg}^{-1}$ in guinea pigs. In long-term studies NOEL in rats was $0.35 \text{ mg kg}^{-1} \text{ bw day}^{-1}$ , $LD_{50}$ ranging from 60 to $293 \text{ mg kg}^{-1}$ bw. For toxaphene, there exists strong evidence of the potential for endocrine disruption. Toxaphene is carcinogenic in mice and rats and is of carcinogenic risk to humans, with a cancer potency factor of $1.1 \text{ mg kg}^{-1} \text{ day}^{-1}$ for oral exposure.
<i>Mirex</i> 1,a,2,2,3,3a,4,5,5a,5b,6-Dodecachloroacta-hydro-1,3,4-metheno-1H-cyclobuta[cd] pentalene ( $C_{10}Cl_{12}$ ).	Solubility in water: $0.07 \mu\text{g l}^{-1}$ at $25^\circ\text{C}$ ; vapor pressure: $3 \times 10^{-7} \text{ mmHg}$ at $25^\circ\text{C}$ ; $\log K_{ow}$ : 5.28.	Half-life in soil from 100 days up to 12 years. It has been shown to bioconcentrate in aquatic organisms (BCF of 4247 in mosquito fish and 76,000 in brook trout).	Acute toxicity for mammals is moderate with an $LD_{50}$ in rat of $235 \text{ mg kg}^{-1}$ and dermal toxicity in rabbits of $80 \text{ mg kg}^{-1}$ . Mirex is also toxic to fish and can affect their behavior ( $LC_{50}$ (96 h) from 0.2 to $30 \mu\text{g l}^{-1}$ for rainbow trout and bluegill, respectively). Delayed mortality of crustaceans occurred at $1 \mu\text{g l}^{-1}$ exposure levels. There is evidence of its potential for endocrine disruption and possibly carcinogenic risk to humans.
<i>Hexachlorobenzene (HCB)</i> ( $C_6H_6$ ).	Solubility in water: $50 \mu\text{g l}^{-1}$ at $20^\circ\text{C}$ ; vapor pressure: $1.09 \times 10^{25} \text{ mmHg}$ at $20^\circ\text{C}$ ; $\log K_{ow}$ : $3.93\text{--}6.42$ .	Estimated “field half-life” of 2.7–5.7 years. HCB has a relatively high bioaccumulation potential and long $t_{1/2}$ in biota.	$LC_{50}$ for fish varies between 50 and $200 \mu\text{g l}^{-1}$ . The acute toxicity of HCB is low with $LD_{50}$ values of $3.5 \text{ mg g}^{-1}$ for rats. Mild effects of the (rat) liver have been observed at a daily dose of $0.25 \text{ mg HCB kg}^{-1}$ bw. HCB is known to cause liver disease in humans (porphyria cutanea tarda) and has been classified as a possible carcinogen to humans by IARC.
<i>Polychlorinated biphenyls (PCBs)</i> ( $C_{12}H_{(10-n)}Cl_n$ , where $n$ is within the range of 1–10).	Water solubility decreases with increasing chlorination: $0.01\text{--}0.0001 \mu\text{g l}^{-1}$ at $25^\circ\text{C}$ ; vapor pressure: $1.6\text{--}0.003 \times 10^{-6} \text{ mmHg}$ at $20^\circ\text{C}$ ; $\log K_{ow}$ : $4.3\text{--}8.26$ .	Most PCB congeners, particularly those lacking adjacent unsubstituted positions on the biphenyl rings (e.g. 2,4,6-, 2,3,6- or 2,3,6-substituted on both rings) are extremely persistent in the environment. They are estimated to have $t_{1/2}$ ranging from 3 weeks to 2 years in air and, with the exception of mono- and dichlorodiphenyl, more than 6 years in aerobic soils and sediments. PCBs also have extremely long $t_{1/2}$ in adult fish, for example, an 8-year study of eels found that the $t_{1/2}$ of CB153 was more than 10 years.	$LC_{50}$ for the larval stages of rainbow trout is $0.32 \mu\text{g l}^{-1}$ with a NOEL of $0.01 \mu\text{g l}^{-1}$ . The acute toxicity of PCB in mammals is generally low and $LD_{50}$ values in rat of $1 \text{ g kg}^{-1}$ bw. IARC has concluded that PCBs are carcinogenic to laboratory animals and probably also for humans. They have also been classified as substances for which there is evidence of endocrine disruption in an intact organism.

*Polychlorinated dibenz-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) ( $C_{12}H_{(8-n)}Cl_nO_2$ ) and PCDFs ( $C_{12}H_{(8-n)}Cl_nO$ ) may contain between 1 and 8 chlorine atoms. Dioxins and furans have 75 and 135 possible positional isomers, respectively.*

Solubility in water: in the range 550–0.07 ng l<sup>-1</sup> at 25 °C; vapor pressure:  $2\text{--}0.007 \times 10^{-6}$  mmHg at 20 °C; log  $K_{ow}$ : in the range 6.60–8.20 for tetra- to octa-substituted congeners.

PCDD/Fs are characterized by their lipophilicity, semivolatility, and resistance to degradation ( $t_{1/2}$  of TCDD in soil of 10–12 years) and to long-range transport. They are also known for their ability to bioconcentrate and biomagnify under typical environmental conditions.

Toxicological effects reported refers to the 2,3,7,8-substituted compounds (17 congeners) that are agonist for the AhR. All the 2,3,7,8-substituted PCDDs and PCDFs plus dioxin-like PCBs (DLPCBs) (with no chlorine substitution at the *ortho* positions) show the same type of biological and toxic response. Possible effects include dermal toxicity, immunotoxicity, reproductive effects and teratogenicity, endocrine disruption, and carcinogenicity. At the present time, the only persistent effect associated with dioxin exposure in humans is chloracne. The most sensitive groups are fetus and neonatal infants. Effects on the immune systems in the mouse have been found at doses of 10 ng kg<sup>-1</sup> bw day<sup>-1</sup>, while reproductive effects were seen in rhesus monkeys at 1–2 ng kg<sup>-1</sup> bw day<sup>-1</sup>. Biochemical effects have been seen in rats down to 0.1 ng kg<sup>-1</sup> bw day<sup>-1</sup>. In a reevaluation of the TDI for dioxins, furans (and planar PCB), the WHO decided to recommend a range of 1–4 TEQ pg kg<sup>-1</sup> bw, although more recently the acceptable intake value has been set monthly at 1–70 TEQ pg kg<sup>-1</sup> bw.

Oral LD<sub>50</sub> is 3090 mg kg<sup>-1</sup> in rats, 1750 mg kg<sup>-1</sup> in mice, 750 mg kg<sup>-1</sup> in rabbits, and 1000 mg kg<sup>-1</sup> in hamsters. The dermal LD<sub>50</sub> in rabbits is 7500 mg kg<sup>-1</sup> and greater than 3000 mg kg<sup>-1</sup> in rats. Atrazine is practically nontoxic to birds. The LD<sub>50</sub> is greater than 2000 mg kg<sup>-1</sup> in mallard ducks. Atrazine is slightly toxic to fish and other aquatic life. Atrazine has a low level of bioaccumulation in fish. Available data regarding atrazine's carcinogenic potential are inconclusive.

Lindane is moderately toxic for invertebrates and fish, with LC<sub>50</sub> values of 20–90 µg l<sup>-1</sup>. The acute toxicity for mice and rats is moderate with LD<sub>50</sub> values in the range of 60–250 mg kg<sup>-1</sup>. In a number of studies, lindane resulted to have no mutagenic potential but an endocrine disrupting activity.

*Atrazine 2-Chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine ( $C_{10}H_6Cl_8$ ).*

Solubility in water: 28 mg l<sup>-1</sup> at 20 °C; vapor pressure:  $3.0 \times 10^{-7}$  mmHg at 20 °C; log  $K_{ow}$ : 2.34.

Does not adsorb strongly to soil particles and has a lengthy  $t_{1/2}$  (60–100 days). Atrazine has a high potential for groundwater contamination despite its moderate solubility in water.

*Hexachlorocyclohexane (HCH) 1,2,3,4,5,6-Hexachlorocyclohexane (mixed isomers) ( $C_6H_6Cl_6$ ).*

$\gamma$ -HCH (lindane): solubility in water: 7 mg l<sup>-1</sup> at 20 °C; vapor pressure:  $3.3 \times 10^{-5}$  mmHg at 20 °C; log  $K_{ow}$ : 3.8.

Lindane and other HCH isomers are relatively persistent in soils and water, with half-lives generally greater than 1 and 2 years, respectively. HCHs are much less bioaccumulative than other organochlorines of concern because of their relatively low lipophilicity. On the contrary, their relatively high vapor pressures, particularly of the  $\alpha$ -HCH isomer, determine their long-range transport in the atmosphere.

Properties largely dependent on the chlorine content. Solubility in water: 1.7–236 µg l<sup>-1</sup> at 25 °C; vapor pressure: very low, highest for short chains—those with 50% chlorine:  $1.6 \times 10^2$  mmHg at 40 °C; log  $K_{ow}$  in the range from 5.06 to 8.12.

May be released into the environment from improperly disposed metal-working fluids or polymers containing CPs. Loss of CPs by leaching from paints and coatings may also contribute to environmental contamination. Short-chain CPs with less than 50% chlorine content seem to be degraded under

Acute toxicity of CPs in mammals is low with reported oral LD<sub>50</sub> values ranging from 4 to 50 g kg<sup>-1</sup> bw, although in repeated dose experiments, effects on the liver have been seen at doses of 10–100 mg kg<sup>-1</sup> bw day<sup>-1</sup>. Short-chain and mid-chain grades have been shown, in laboratory tests, to show toxic effects on fish and other forms of aquatic life after long-term exposure. The NOEL appears to be in the

(Continued)

TABLE 18.2 Summary of Persistent and Toxic Organic Compounds in North America, Identified by the United Nations as Highest Priorities for Regional Actions—cont'd

Compound	Properties	Persistence/Fate	Toxicity*
depending on chain length: short (C10–C13), medium (C14–C17), and long (C18–C30) chain lengths.		aerobic conditions. The medium- and long-chain products are degraded more slowly. CPs are bioaccumulated and both uptake and elimination are faster for the substances with low chlorine content.	range of 2–5 $\mu\text{g l}^{-1}$ for the most sensitive aquatic species tested.
<i>Chlordecone or Kepone</i> Chemical name: 1,2,3,4,5,6,7,9,10,10-dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta(cd) pentalen-2-one ( $\text{C}_{10}\text{Cl}_{10}\text{O}$ ).	Solubility in water: 7.6 $\text{mg l}^{-1}$ at 25 °C; vapor pressure: less than $3 \times 10^{-5}$ mmHg at 25 °C; $\log K_{\text{ow}}$ : 4.50.	Estimated $t_{1/2}$ in soils is between 1 and 2 years, whereas in air is much higher, up to 50 years. Not expected to hydrolyze, biodegrade in the environment. Also direct photodegradation and vaporization from what not significant. General population exposure to chlordecone mainly through the consumption of contaminated fish and seafood.	Workers exposed to high levels of chlordecone over a long period (more than 1 year) have displayed harmful effects on the nervous system, skin, liver, and male reproductive system (likely through dermal exposure to chlordecone, although they may have inhaled or ingested some as well). Animal studies with chlordecone have shown effects similar to those seen in people, as well as harmful kidney effects, developmental effects, and effects on the ability of females to reproduce. There are no studies available on whether chlordecone is carcinogenic in people. However, studies in mice and rats have shown that ingesting chlordecone can cause liver, adrenal gland, and kidney tumors. Very highly toxic for some species such as Atlantic menhaden, sheepshead minnow, or Donaldson trout with $\text{LC}_{50}$ between 21.4 and 56.9 $\text{mg l}^{-1}$ .
<i>Endosulfan</i> 6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide ( $\text{C}_9\text{H}_6\text{Cl}_6\text{O}_3\text{S}$ ).	Solubility in water: 320 $\mu\text{g l}^{-1}$ at 25 °C; vapor pressure: $0.17 \times 10^{-4}$ mmHg at 25 °C; $\log K_{\text{ow}}$ : 2.23–3.62.	Moderately persistent in soil, with a reported average field $t_{1/2}$ of 50 days. The two isomers have different degradation times in soil ( $t_{1/2}$ of 35 and 150 days for $\alpha$ - and $\beta$ -isomers, respectively, in neutral conditions). It has a moderate capacity to adsorb to soils and it is not likely to leach to groundwater. In plants, endosulfan is rapidly broken down to the corresponding sulfate, on most fruits and vegetables, 50% of the parent residue is lost within 3–7 days.	Moderately to highly toxic to bird species (Mallards: oral $\text{LD}_{50}$ 31–243 $\text{mg kg}^{-1}$ ) and it is very toxic to aquatic organisms (96-h $\text{LC}_{50}$ rainbow trout 1.5 $\mu\text{g l}^{-1}$ ). It has also shown high toxicity in rats (oral $\text{LD}_{50}$ : 18–160 $\text{mg kg}^{-1}$ , and dermal: 78–359 $\text{mg kg}^{-1}$ ). Female rats appear to be 4–5 times more sensitive to the lethal effects of technical-grade endosulfan than male rats. The $\alpha$ -isomer is considered to be more toxic than the $\beta$ -isomer. There is a strong evidence of its potential for endocrine disruption.
<i>Pentachlorophenol (PCP)</i> ( $\text{C}_6\text{Cl}_5\text{OH}$ ).	Solubility in water: 14 $\text{mg l}^{-1}$ at 20 °C; vapor pressure: $16 \times 10^{-5}$ mmHg at 20 °C; $\log K_{\text{ow}}$ : 3.32–5.86.	Photodecomposition rate increases with pH ( $t_{1/2}$ 100 h at pH 3.3 and 3.5 h at pH 7.3). Complete decomposition in soil suspensions takes >72 days; other authors report $t_{1/2}$ in soils of about 45 days. Although enriched through the food chain, it is rapidly eliminated after discontinuing the exposure ( $t_{1/2}$ 10–24 h for fish).	Acutely toxic to aquatic organisms. Certain effects on human health. 24 h $\text{LC}_{50}$ values for trout were reported as 0.2 $\text{mg l}^{-1}$ , and chronic toxicity effects were observed at concentrations down to 3.2 $\mu\text{g l}^{-1}$ . Mammalian acute toxicity of PCP is moderate–high. $\text{LD}_{50}$ oral in rat ranging from 50 to 210 $\text{mg kg}^{-1}$ bw have been reported. $\text{LC}_{50}$ ranged from 0.093 $\text{mg l}^{-1}$ in rainbow trout (48 h) to 0.77–0.97 $\text{mg l}^{-1}$ for guppy (96 h) and 0.47 $\text{mg l}^{-1}$ for fathead minnow (48 h).
<i>Hexabromobiphenyl (HxBB)</i> ( $\text{C}_{12}\text{H}_4\text{Br}_6$ ). A congener of the	Solubility in water: 11 $\mu\text{g l}^{-1}$ at 25 °C; vapor pressure: mmHg at 20 °C; $\log K_{\text{ow}}$ : 6.39.	Strongly adsorbed to soil and sediments and usually persist in the environment. Resists chemical and biological	Few toxicity data are available from short-term tests on aquatic organisms. The $\text{LD}_{50}$ values of commercial mixtures show a relatively low order of acute toxicity ( $\text{LD}_{50}$ range

class polybrominated biphenyls (PBBs).

*Polybrominated diphenyl ethers (PBDEs)* ( $C_{12}H_{(10-n)}Br_nO$ , where  $n = 1-10$ ). As in the case of PCBs the total number of congeners is 209, with a predominance in commercial mixtures of the tetra-, penta- and octa-substituted isomers.

*Polycyclic aromatic hydrocarbons (PAHs)* A group of compounds consisting of two or more fused aromatic rings.

*Phthalates* Includes a wide family of compounds. Among the most common contaminants are: dimethylphthalate (DMP), diethylphthalate (DEP), dibutylphthalate (DBP), benzylbutylphthalate (BBP), di(2-ethylhexyl)phthalate (DEHP) ( $C_{24}H_{38}O_4$ ) and dioctylphthalate (DOP).

Solubility in water:  $\text{mg l}^{-1}$  at  $25^\circ\text{C}$ ; vapor pressure: 3.85 up to  $13.3 \times 10^{-3}$  mmHg at  $20-25^\circ\text{C}$ ;  $\log K_{ow}$ : 4.28–9.9.

Solubility in water:  $0.00014-2.1 \text{ mg l}^{-1}$  at  $25^\circ\text{C}$ ; vapor pressure: ranges from relatively volatile (e.g. naphthalene,  $9 \times 10^{-2}$  mmHg at  $20^\circ\text{C}$ ) to semivolatile (e.g. benzo(a)pyrene,  $5 \times 10^{-9}$  mmHg at  $25^\circ\text{C}$ ) to nearly nonvolatile (e.g. Indeno(1,2,3-cd)pyrene,  $1 \times 10^{-10}$  mmHg at  $25^\circ$ );  $\log K_{ow}$ : 4.79–8.20.

Properties of phthalic acid esters vary greatly depending on the alcohol moieties.  $\log K_{ow}$  1.5–7.1.

degradation. Found in sediment samples from the estuaries of large rivers and has been identified in edible fish.

Biodegradation does not seem to be an important degradation pathway, but the photodegradation may play a significant role. Have been found in high concentrations in marine birds and mammals from remote areas. The half-lives of PBDE components in rat adipose tissue vary between 19 and 119 days, the higher values being for the more highly brominated congeners.

from  $>1$  to  $21.5 \text{ g kg}^{-1}$  body weight in laboratory rodents). Oral exposure of laboratory animals to PBBs produced body weight loss, skin disorders, and nervous system effects, and birth defects. Humans exposed through contaminated food developed skin disorders, such as acne and hair loss. PBBs exhibit endocrine disrupting activity and possible carcinogenicity to humans.

Lower (tetra- to hexa-) PBDE congeners are likely to be carcinogens, endocrine disruptors, and/or neurodevelopmental toxicants. Studies in rats with commercial penta-BDE indicate a low acute toxicity via oral and dermal routes of exposure, with  $LD_{50}$  values  $>2000 \text{ mg kg}^{-1}$  bw. In a 30-day study with rats, effects on the liver could be seen at a dose of  $2 \text{ mg kg}^{-1}$  bw day $^{-1}$ , with a NOEL at  $1 \text{ mg kg}^{-1}$  bw day $^{-1}$ . The toxicity to *Daphnia magna* has also been investigated and  $LC_{50}$  was found to be  $14 \text{ }\mu\text{g l}^{-1}$  with a NOEC of  $4.9 \text{ }\mu\text{g l}^{-1}$ . Although data on toxicology is limited, they have potential endocrine disrupting properties, and there are concerns over the health effects of exposure.

Acute toxicity of low PAHs is moderate with an  $LD_{50}$  of naphthalene and anthracene in rat of 490 and  $18,000 \text{ mg kg}^{-1}$  body weight respectively, whereas the higher PAHs exhibit higher toxicity and  $LD_{50}$  of benzo(a)anthracene in mice is  $10 \text{ mg kg}^{-1}$  body weight. In *Daphnia pulex*,  $LC_{50}$  for naphthalene is  $1.0 \text{ mg l}^{-1}$ , for phenanthrene  $0.1 \text{ mg l}^{-1}$  and for benzo(a)pyrene is  $0.005 \text{ mg l}^{-1}$ . The critical effect of many PAHs in mammals is their carcinogenic potential. The metabolic actions of these substances produce intermediates that bind covalently with cellular DNA. IARC has classified benz[a]anthracene, benzo[a]pyrene, and dibenzo[a, h]anthracene as probable carcinogenic to humans. Benzo[b]fluoranthene and indeno[1,2,3-c,d]pyrene were classified as possible carcinogens to humans.

Acute toxicity of phthalates is usually low: the oral  $LD_{50}$  for DEHP is about  $26-34 \text{ g kg}^{-1}$ , depending on the species; for DBP reported  $LD_{50}$  values following oral administration to rats range from  $8-20 \text{ g kg}^{-1}$  body weight; in mice, values are approximately  $5-16 \text{ g kg}^{-1}$  body weight. In general, DEHP is not toxic for aquatic communities at the low levels usually present. In animals, high levels of DEHP damaged the liver and kidney and affected the ability to reproduce. There is no evidence that DEHP causes cancer in humans but they have been reported as endocrine disrupting chemicals. The Environmental Protection Agency (EPA) proposed a maximum admissible concentration (MAC) of  $6 \text{ }\mu\text{g l}^{-1}$  of DEHP in drinking water.

(Continued)

TABLE 18.2 Summary of Persistent and Toxic Organic Compounds in North America, Identified by the United Nations as Highest Priorities for Regional Actions—cont'd

Compound	Properties	Persistence/Fate	Toxicity*
<i>Nonyl- and octyl-phenols</i> NP: C <sub>15</sub> H <sub>24</sub> O; OP: C <sub>14</sub> H <sub>22</sub> O.	Log K <sub>ow</sub> : 4.5 (NP) and 5.92 (OP).	NP and OP are the end degradation products of APEs under both aerobic and anaerobic conditions. Therefore, the major part is released to water and concentrated in sewage sludges. NPs and t-OP are persistent in the environment with <i>t</i> <sub>1/2</sub> of 30–60 years in marine sediments, 1–3 weeks in estuarine waters, and 10–48 h in the atmosphere. Due to their persistence they can bioaccumulate to a significant extent in aquatic species. However, excretion and metabolism are rapid.	Acute toxicity values for fish, invertebrates, and algae range from 17 to 3000 µg l <sup>-1</sup> . In chronic toxicity tests the lowest NOEC are 6 µg l <sup>-1</sup> in fish and 3.7 µg l <sup>-1</sup> in invertebrates. The threshold for vitellogenin induction in fish is 10 µg l <sup>-1</sup> for NP and 3 µg l <sup>-1</sup> for OP (similar to the lowest NOEC). Alkylphenols are endocrine disrupting chemicals also in mammals.
<i>Perfluorooctane sulfonate (PFOS)</i> (C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> )	Solubility in water: 550 mg l <sup>-1</sup> in pure water at 24–25 °C; the potassium salt of PFOS has a low vapor pressure, 3.31 × 10 <sup>-4</sup> Pa at 20 °C. Due to the surface-active properties of PFOS, the log K <sub>ow</sub> cannot be measured.	Does not hydrolyze, photolyze, or biodegrade under environmental conditions. It is persistent in the environment and has been shown to bioconcentrate in fish. It has been detected in a number of species of wildlife, including marine mammals. Animal studies show that PFOS is well absorbed orally and distributes mainly in the serum and the liver. The half-life in serum is 7.5 days in adult rats and 200 days in cynomolgus monkeys. The half-life in humans is, on average, 8.67 years (range 2.29–21.3 years, SD = 6.12).	Moderate acute toxicity to aquatic organisms, the lowest LC <sub>50</sub> for fish is a 96-h LC <sub>50</sub> of 4.7 mg l <sup>-1</sup> to the fathead minnow ( <i>Pimephales promelas</i> ) for the lithium salt. For aquatic invertebrates, the lowest EC <sub>50</sub> for freshwater species is a 48-h EC <sub>50</sub> of 27 mg l <sup>-1</sup> for <i>Daphnia magna</i> and for saltwater species, a 96-h LC <sub>50</sub> value of 3.6 mg l <sup>-1</sup> for the Mysid shrimp ( <i>Mysidopsis bahia</i> ). Both tests were conducted on the potassium salt. The toxicity profile of PFOS is similar among rats and monkeys. Repeated exposure results in hepatotoxicity and mortality; the dose-response curve is very steep for mortality. PFOS has shown moderate acute toxicity by the oral route with a rat LD <sub>50</sub> of 251 mg kg <sup>-1</sup> . Developmental effects were also reported in prenatal developmental toxicity studies in the rat and rabbit, although at slightly higher dose levels. Signs of developmental toxicity in the offspring were evident at doses of 5 mg kg <sup>-1</sup> day <sup>-1</sup> and above in rats administered PFOS during gestation. Significant decreases in fetal body weight and significant increases in external and visceral anomalies, delayed ossification, and skeletal variations were observed. An NOAEL of 1 mg kg <sup>-1</sup> day <sup>-1</sup> and an LOAEL of 5 mg kg <sup>-1</sup> day <sup>-1</sup> for developmental toxicity were indicated. Studies on employees conducted at PFOS manufacturing plants in the United States and Belgium showed an increase in mortality resulting from bladder cancer and an increased risk of neoplasms of the male reproductive system, the overall category of cancers and benign growths, and neoplasms of the gastrointestinal tract.

\* Toxicity values include both acute and chronic endpoints, but are not exhaustive nor necessarily current, since additional studies have been conducted since 2002.

*t*<sub>1/2</sub>, chemical half-life; LD<sub>50</sub>, lethal dose to 50% of tested organism; LC<sub>50</sub>, lethal concentration to 50% of tested organism; BCF, bioconcentration factor; NOEL, no observable effect level; NOEC, no observable effect concentration; DDD, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; DDE, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene; VPL, vapor pressure lowering; IARC, International Agency for Research on Cancer; TCDD, tetrachlorodibenzo-*p*-dioxin; AhR, aryl hydrocarbon receptor; TDI, tolerable daily intake; TEQ, toxic equivalent; APEs, alkylphenol ethoxylates; NOAEL, no observed adverse effect level; LOAEL, lowest observed adverse effect level.

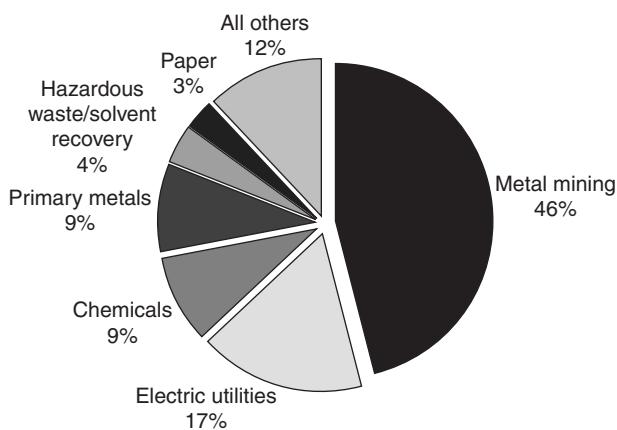
Source: United Nations Environmental Program; 2002, Chemicals: North American Regional Report, Regionally Based Assessment of Persistent Toxic Substances, Global Environment Facility.

TABLE 18.3 Summary of Persistent and Metallic Compounds in North America, Identified by the United Nations as Highest Priorities for Regional Actions

Compound	Properties	Persistence/Fate	Toxicity*
<i>Compounds of tin (Sn)</i> Organic tin compounds comprise mono-, di-, tri-, and tetra-butyl and triphenylene tin compounds. They conform to the following general formula ( $n\text{C}_4\text{H}_9)_n\text{Sn-X}$ and $(\text{C}_6\text{H}_5)_3\text{Sn-X}$ , where X is an anion or a group linked covalently through a heteroatom.	Log $K_{ow}$ : 3.19–3.84. In sea water and under normal conditions, tributyl tin exists as three species (hydroxide, chloride, and carbonate).	Under aerobic conditions, tributyl tin takes 30–90 days to degrade, but in anaerobic soils may persist for more than 2 years. Due to low water solubility it binds strongly to suspended material and sediments. Tributyl tin is lipophilic and accumulates in aquatic organisms. Oysters exposed to very low concentrations exhibit BCF values ranging from 1000 to 6000.	Tributyl tin is moderately toxic and all breakdown products are even less toxic. Its impact on the environment was discovered in the early 1980s in France with harmful effects in aquatic organisms, such as shell malformations of oysters, imposex in marine snails, and reduced resistance to infection (e.g. in flounder). Gastropods react adversely to very low levels of tributyl tin (0.06–2.3 $\mu\text{g l}^{-1}$ ). Lobster larvae show a nearly complete cessation of growth at just 1.0 $\mu\text{g l}^{-1}$ tributyl tin. In laboratory tests, reproduction was inhibited when female snails exposed to 0.06–0.003 $\mu\text{g l}^{-1}$ tributyl tin developed male characteristics. Large doses of tributyl tin have been shown to damage the reproductive and central nervous systems, bone structure, and the liver bile duct of mammals.
<i>Compounds of mercury (Hg)</i> The main compound of concern is methyl mercury ( $\text{HgCH}_3$ ).		Mercury released into the environment can either stay close to its source for long periods, or be widely dispersed on a regional or even worldwide basis. Not only are methylated mercury compounds toxic, but highly bioaccumulative as well. The increase in mercury as it rises in the aquatic food chain results in relatively high levels of mercury in fish consumed by humans. Ingested elemental mercury is only 0.01% absorbed, but methyl mercury is nearly 100% absorbed from the gastrointestinal tract. The biological $t_{1/2}$ of Hg is 60 days.	Long-term exposure to either inorganic or organic mercury can permanently damage the brain, kidneys, and developing fetus. The most sensitive target of low-level exposure to metallic and organic mercury from short- or long-term exposures is likely the nervous system.
<i>Compounds of lead (Pb)</i> Alkyl lead compounds may be confined to tetramethyl lead (TML, $\text{Pb}(\text{CH}_3)_4$ ) and tetraethyl lead (TEL, $\text{Pb}(\text{C}_2\text{H}_5)_4$ ).	Solubility in water: 17.9 $\text{mg l}^{-1}$ (TML) and 0.29 $\text{mg l}^{-1}$ (TEL) at 25 °C; vapor pressure: 22.5 and 0.15 mmHg at 20 °C for TML and TEL, respectively.	Under environmental conditions, dealkylation produces less alkylated forms and finally inorganic Pb. However, there is limited evidence that under some circumstances, natural methylation of Pb salts may occur. Minimal bioaccumulations have been observed for TEL in shrimps (650), mussels (120), and plaice (130) and for TML in shrimps (20), mussels (170), and plaice (60).	Exposure to Pb and its compounds have been associated with cancer in the respiratory and digestive systems of workers in lead battery and smelter plants. However, tetra-alkyl lead compounds have not been sufficiently tested for the evidence of carcinogenicity. Acute toxicity of TEL and TML are moderate in mammals and high for aquatic biota. LD <sub>50</sub> (rat, oral) for TEL is 35 $\text{mg Pb kg}^{-1}$ and 108 $\text{mg Pb kg}^{-1}$ for TML. LC <sub>50</sub> (fish, 96 h) for TEL is 0.02 $\text{mg kg}^{-1}$ and for TML is 0.11 $\text{mg kg}^{-1}$ .

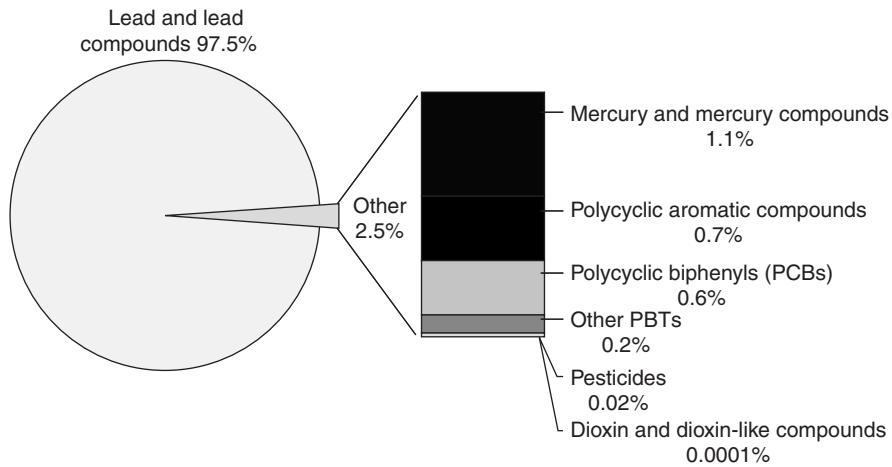
\* Toxicity values include both acute and chronic endpoints, but are not exhaustive nor necessarily current, since additional studies have been conducted since 2002.

 $t_{1/2}$ , chemical half-life; LD<sub>50</sub>, lethal dose to 50% of tested organism; LC<sub>50</sub>, lethal concentration to 50% of tested organism; BCF, bioconcentration factor; NOEL, no observable effect level; NOEC, no observable effect concentration.



**FIGURE 18.8** Total US releases of contaminants in 2001, as reported to the Toxic Release Inventory (TRI). Total releases = 2.8 billion kg. Note: Off-site releases include metals and metal compounds transferred off-site for solidification/stabilization and for wastewater treatment, including publicly owned treatment works. Off-site releases do not include transfers to disposal sent to other TRI facilities that reported the amount as an on-site release. *US Environmental Protection Agency*.

The assumption of equilibrium in Levels 1 and 2 models is a simplification, and often a gross oversimplification of what actually occurs in environmental systems. When, the simplification is not acceptable, kinetics must be included in the model. Numerous diffusive and nondiffusive transport mechanisms are included in Level 3 modeling. For example, values for the various compartments' unique intermedia transport velocity parameters (in length per time dimensions) are applied to all contaminants being modeled (these are used to calculate the *D* values mentioned above).



**FIGURE 18.9** Total US releases of PBTs in 2001, as reported in the Toxic Release Inventory (TRI). Total releases = 206 million kg. Note: Off-site releases include metals and metal compounds transferred off-site for solidification/stabilization and for wastewater treatment, including publicly owned treatment works. Off-site releases do not include transfers for disposal sent to other TRI facilities that reported the amount as an on-site release. *US Environmental Protection Agency*.

### 18.3 FUGACITY

As mentioned, the affinities of a compound for each phase foretells the amount and rate of transformation, transport, and fate of a chemical compound. This means that an air pollutant behaves in the environment in ways that can be expressed by the partition coefficients. These coefficients can be viewed as a potential. That is, at the time when equilibrium is achieved among all phases and compartments, the chemical potential in each compartment has been reached. Chemical concentration and fugacity are directly related to one another via the fugacity capacity constant, known as the *Z* value<sup>1</sup>:

$$C_i = Z_i \cdot f \quad (18.18)$$

where:

$C_i$  = Concentration of substance in compartment *i*  
(mass per volume)

$Z_i$  = Fugacity capacity (time<sup>2</sup> per length<sup>2</sup>)

$f$  = Fugacity (mass per length per time<sup>2</sup>)

Thus, at equilibrium, the fugacity of the system of all environmental compartments is:

$$f = \frac{M_{\text{total}}}{\sum_i (Z_i \cdot V_i)} \quad (18.19)$$

where:  $M_{\text{total}}$  = total number of moles of a substance in all of the environmental system's compartments; and  $V_i$  = volume of compartment *i* where the substance resides.

Assuming that a chemical substance obeys the ideal gas law (which is usually acceptable for ambient environmental pressures), then fugacity capacity is the

reciprocal of the gas constant ( $R$ ) and absolute temperature ( $T$ ). Recall that the ideal gas law states:

$$\frac{n}{V} = \frac{P}{RT} \quad (18.20)$$

where:

$n$  = Number of moles of a substance

$P^\circ$  = Substance's vapor pressure

Then,

$$P^\circ = \frac{n}{V} \cdot RT = f \quad (18.21)$$

And,

$$C_i = \frac{n}{V} \quad (18.22)$$

Therefore,

$$Z_{\text{air}} = \frac{1}{RT} \quad (18.23)$$

This relationship allows for predicting the behavior of the substance in the gas phase. The substance's affinity for other environmental media can be predicted by relating the respective partition coefficients to the Henry's law constants. For water, the fugacity capacity ( $Z_{\text{water}}$ ) can be found as the reciprocal of  $K_H$ :

$$Z_{\text{water}} = \frac{1}{K_H} \quad (18.24)$$

This is the dimensioned version of the Henry's law constant (length<sup>2</sup> per time<sup>2</sup>).

Fugacity can be calculated for every environmental compartment. This is important for air pollutants that have sources throughout the environment. For example, many persistent organic compounds spend part of their life cycles in sediment reservoirs beneath surface waters. As evidence, substances like polychlorinated aromatic compounds (e.g. PCBs) that have been banned and not used for decades continue to be emitted to the atmosphere. In sediment, the fugacity capacity is directly proportional to the contaminant's sorption potential, expressed as the solid–water partition coefficient ( $K_d$ ), and the average sediment density ( $\rho_{\text{sediment}}$ ). Sediment fugacity capacity is indirectly proportional to the chemical substance's Henry's law constant:

$$Z_{\text{sediment}} = \frac{\rho_{\text{sediment}} \cdot K_d}{K_H} \quad (18.25)$$

As discussed in Chapter 8, exposure assessment of an air pollutant focuses on ultimate fate in a human or other organism. Fugacity explains the partitioning that allows that to happen, but it also explains how the pollutant enters and exits biota in ecosystems. For biota, particularly fauna and especially fish and other aquatic vertebrates, the fugacity capacity is directly proportional to the

density of the fauna tissue ( $\rho_{\text{fauna}}$ ), and the chemical substance's BCF, and inversely proportional to the contaminant's Henry's law constant:

$$Z_{\text{fauna}} = \frac{\rho_{\text{fauna}} \cdot \text{BCF}}{K_H} \quad (18.26)$$

As in the case of the sediment fugacity capacity, a higher BCF means that the fauna's fugacity capacity increases and the actual fugacity decreases. Again, this is logical, since the organism is sequestering the contaminant and keeping it from leaving if the organism has a large BCF. This is a function of both the species of organism and the characteristics of the contaminant and the environment where the organism resides. So, factors like temperature, pH, and ionic strength of the water and metabolic conditions of the organism will affect BCF and  $Z_{\text{fauna}}$ . This also helps to explain why published BCF values may have large ranges.

The total biochemodynamic partitioning of the environmental system is merely the aggregation of all of the individual compartmental partitioning. So, the moles of the contaminant in each environmental compartment ( $M_i$ ) are found to be the product of the fugacity, volume, and fugacity capacity for each compartment:

$$M_i = Z_i \cdot V_i \cdot f \quad (18.27)$$

Comparing the respective fugacity capacities for each phase or compartment in an environmental system is useful for a number of reasons. First, if one compartment has a very high fugacity (thus, a low fugacity capacity) for a contaminant, and the source of the contaminant no longer exists, then one would expect the concentrations in that compartment to decrease rather precipitously with time under certain environmental conditions. Conversely, if a compartment has a very low fugacity, the contaminant would have a strong affinity for that compartment and only after much energy is added would it move away (the PCB example above illustrates this problem) and decrease the chemical concentration of the contaminant in that compartment. Second, if a continuous source of the contaminant exists, and a compartment has a high fugacity capacity (and low fugacity), this compartment may serve as a conduit for delivering the contaminant to other compartments with relatively low fugacity capacities. Third, by definition, the higher relative fugacities of one set of compartments compared to another set in the same ecosystem allow for comparative analyses and estimates of sources and sinks (or "hot spots") of the contaminant, which is an important part of fate, transport, exposure, and risk assessments.

Fugacity-based, multicompartamental environmental models take these relationships into account. The movement of a contaminant through the environment can be expressed with regard to how equilibrium is achieved in each compartment. The processes driving this movement

can be summarized into transfer coefficients or compartmental rate constants, known as  $D$  values.<sup>2</sup> So, by first calculating the  $Z$  values, as we did for toluene in the previous examples, and then equating inputs and outputs of the contaminant to each compartment, we can derive  $D$  value rate constants. The actual transport process rate ( $N$ ) is the product of fugacity and the  $D$  value:

$$N = D \cdot f \quad (18.28)$$

And, since the contaminant concentration is  $Z \cdot f$ , we can substitute and add a first-order rate constant  $k$  to give us a first-order rate  $D$  value ( $D_R$ ):

$$N = V[c]k = (V \cdot Z \cdot k) \cdot f = D_R \cdot f \quad (18.29)$$

Although the concentrations are shown as molar concentrations (i.e. in brackets), they may also be represented as mass per volume concentrations.<sup>b</sup>

Diffusive and nondiffusive transport processes follow Fick's laws, i.e. diffusive processes. They can also be expressed with their own  $D$  values ( $D_D$ ), which is related to the mass transfer coefficient ( $K$ ) applied to area  $A$ :

$$N = KA[c] = (K \cdot A \cdot Z) \cdot f = D_D \cdot f \quad (18.30)$$

Nondiffusive transport (bulk flow or advection) within a compartment with a flow rate ( $G$ ) has a  $D$  value ( $D_A$ ) and is expressed as:

$$N = G[c] = (G \cdot Z) \cdot f = D_A \cdot f \quad (18.31)$$

This means that a substance is moving through the environment, during its residence time in each phase, is affected by numerous physical transport and chemical degradation and transformation processes. The processes are addressed by models with the respective  $D$  values, so that the total rate of transport and transformation is expressed as:

$$f(D_1 + D_2 + \dots + D_n) \quad (18.32)$$

Very fast processes have large  $D$  values, and these are usually the most important when considering the contaminant's behavior and change in the environment.

Models, though imperfect, are important tools for estimating the movement of contaminants in the environment. They do not obviate the need for sound measurements. In fact measurements and models are highly complementary. Compartmental model assumptions must be verified in the field. Likewise, measurements at a limited number of points depend on models to extend their meaningfulness. Having an understanding of the basic concepts of a contaminant transport model, we are better able to explore the

principle mechanism for the movement of contaminants throughout the environment.

### 18.3.1 Fugacity Applied to Air Pollutant Exposure and Risk

Fugacity models are an important part of ecological and human risk assessments and will be discussed in Chapter 27 with other air quality models. However, the explanation of fugacity is well-explained within the context of models; fugacity models are discussed here. Fugacity estimates calculated using models can be inserted into exposure and risk models. For example, the  $f$  and  $Z$  values ascertained above can be used in exposure models to estimate the amount of a contaminant a person may expect to contact in the various environmental media.

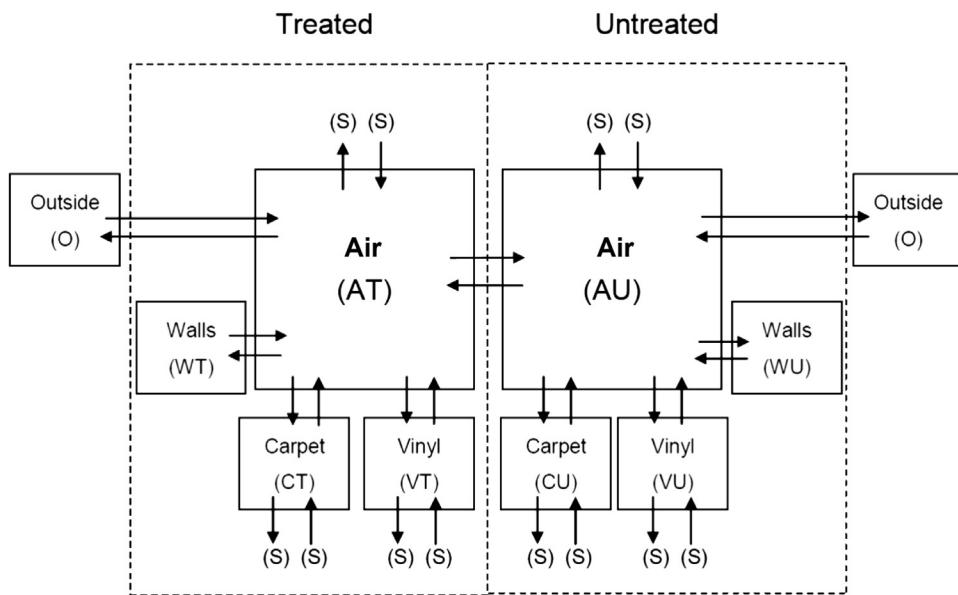
Exposure models like the Stochastic Human Exposure and Dose Simulation (SHEDS) model now include fugacity modules. The model predicts chemical concentrations as functions of time, in various potential contact media (e.g. textured surfaces, smooth surfaces, and air) based on: a simple decay/dispersion model; time-specific distributions (<1 day, 1–7 days, 8–30 days, >31 days); or user-specified time series from measurement studies or an external model.

The SHEDS fugacity module divides a microenvironment (e.g. rooms within a house), e.g. rooms with vinyl flooring, carpet, air, and wall compartments (Figure 18.10). Based on fugacity-based model inputs (Table 18.4), the module provides output concentrations of chemicals in time series for the different compartments and will be used as contacted concentrations for simulated persons in the microenvironments.<sup>3</sup>

## 18.4 INTEGRATING INHERENT PROPERTIES AND SUBSTRATE CHARACTERISTICS

As discussed in Chapter 6, the measure of the amount of chemical that can dissolve in a liquid is called solubility. It is usually expressed in units of mass of solute (that which is dissolved) in the volume of solvent (that which dissolves). Solubility may also be expressed in mass per mass or mass per volume, represented as parts per million (ppm), parts per billion (ppb), or parts per trillion (ppt). Occasionally, solubility is expressed as a percent or in parts per thousand; however, this is uncommon for contaminants, and is usually reserved for nutrients and essential gases (e.g. percent carbon dioxide in water or ppt water vapor in the air).

<sup>b</sup> Throughout this text, bracketed values indicate molar concentrations, but these may always be converted to mass per volume concentration values.



**FIGURE 18.10** Schematic of a microenvironment treated with a pesticide showing fugacity compartments. Each area is divided into four compartments: "air", "walls", "carpet", and "vinyl". The symbols in parentheses are the abbreviations given to each compartment in the fugacity module. The symbol "S" represents sources and/or sinks. The arrows in this diagram represent flows, either of the chemical itself (diffusive flows) or flows of particles which may carry the chemical (advection flows). *Graham G, Smith L, Zartarian V, Stallings C, Isaacs K, Xue J. Planned methodologies for extending SHEDS-Multimedia version 3 (aggregate) to SHEDS-Multimedia version 4 (cumulative or aggregate). Draft Report. U.S. Environmental Protection Agency. Research Triangle Park (North Carolina); 2007.*

The solubility of a compound is very important to environmental transport, including atmospheric transport. The diversity of solubilities in various solvents is a fairly reliable indication of where one is likely to find the compound in the environment. For example, the various solubilities of the most toxic form of dioxin, tetrachlorodibenzo-*para*-dioxin (TCDD), are provided in Table 18.5. Based on these solubility differences, if a combustor has been operating and releasing dioxins,

**TABLE 18.4** Chemical-Specific Inputs for the Stochastic Human Exposure and Dose Simulation (SHEDS) Fugacity Module

Variable Description	Units
Chemical decay rate in air	day <sup>-1</sup>
Chemical decay rate in carpet	day <sup>-1</sup>
Chemical decay rate in vinyl	day <sup>-1</sup>
Chemical decay rate in walls	day <sup>-1</sup>
Diffusion coefficient in air	m <sup>2</sup> day <sup>-1</sup>
Octanol–water partitioning coefficient ( $K_{ow}$ )	Unitless
Vapor pressure	Pa
Solubility	mol m <sup>-3</sup>
Molecular weight	g mol <sup>-1</sup>

*Source: Graham G, Smith L, Zartarian V, Stallings C, Isaacs K, Xue J. Planned methodologies for extending SHEDS-Multimedia version 3 (aggregate) to SHEDS-Multimedia version 4 (cumulative or aggregate). Draft Report. U.S. Environmental Protection Agency. Research Triangle Park (North Carolina); 2007.*

one would expect TCDD to have a much greater affinity for sediment, organic particles, and the organic fraction of soils. The low water solubilities indicate that dissolved TCDD in the water column should be at only extremely low concentrations. But, as will be seen in the discussion regarding cosolvation, for example, other processes may override any single process, e.g. dissolution, in an environmental system.

Polarity is an important physicochemical characteristic of a substance that determines its solubility. The polarity of a molecule is its unevenness in charge. Since the water molecule's oxygen and two hydrogen atoms are aligned so that there is a slightly negative charge at the oxygen end and a slightly positive charge at the hydrogen ends, and since "like dissolves like", polar substances have an affinity to become dissolved in water, and nonpolar substances resist being dissolved in water.

Increasing temperature, i.e. increasing kinetic energy, in a system increases the velocity of the molecules, so that intermolecular forces are weakened. With increasing temperature, the molecular velocity becomes sufficiently large so as to overcome all intermolecular forces, so that the liquid boils (vaporizes). Intermolecular forces may be relatively weak or strong. The weak forces in liquids and gases are often called van der Waals forces.

If a compound has high aqueous solubility, i.e. it is easily dissolved in water under normal environmental conditions of temperature and pressure, it is hydrophilic. If, conversely, a substance is not easily dissolved in water under these conditions, it is said to be hydrophobic. Since

**TABLE 18.5** Solubility of Tetrachlorodibenzo-*para*-dioxin in Water (25° C) and Organic Solvents (22° C).

Solvent	Solubility (ppm)
Water <sup>a</sup>	$2 \times 10^{-5}$ (mg l <sup>-1</sup> )
Water <sup>b</sup>	$6.90 \times 10^{-4}$ (mg l <sup>-1</sup> )
Methanol	10
Lard oil	40
<i>n</i> -Octanol	50
Acetone	110
Chloroform	370
Benzene	570
Chlorobenzene	720
<i>o</i> -dichlorobenzene	1400

<sup>a</sup>Shiu, WY, Doucette, W, Gobas, FAPC, Andren, A, Mackay, D. Physical-chemical properties of chlorinated dibenzo-*p*-dioxins. *Environmental Science & Technology*, 22, 651–658; 1988.

<sup>b</sup>Fiedler, H, Schramm, KW. QSAR generated octanol-water partition coefficients of selected mixed halogenated dibenzodioxins and dibenzofurans. *Chemosphere* (20): 1597–1602; 1990.

Note: temperature for solvents other than water not reported in source literature, assumed to be (22° C).

Source: Crummett, WB, Stehl, RH. Determination of chlorinated dibenzo-*p*-dioxins and dibenzofurans in various materials. *Environmental Health Perspectives*, 5, 15–25; 1973. (for all solvents except water).

many contaminants are organic (i.e. consist of molecules containing carbon-to-carbon bonds and/or carbon-to-hydrogen bonds), the solubility can be further differentiated as to whether under normal environmental conditions of temperature and pressure the substance is easily dissolved in organic solvents. If so the substance is said to be lipophilic (i.e. readily dissolved in lipids). If, conversely, a substance is not easily dissolved in organic solvents under these conditions, it is said to be lipophobic.

Although many possible outcomes can occur after a substance is released into the environment, the possibilities can fall into three basic categories:

1. the chemical may remain where it is released and retain its physicochemical characteristics (at least within a specified time);
2. the substance may be transported to another location; or
3. the substance may be changed chemically, known as the transformation of the chemical.

This is a restatement of the conservation law. Every molecule of mass moving into and out of the control volume must be accounted for, as well as any chemical changes to the contaminant that take place within the control volume. A control volume may be a simple cube ([Figure 18.11\(A\)](#)) through which contaminant fluxes are calculated. However, a control volume can also be a

cell within an organism, the organism itself (e.g. taking in substances, which it absorbs, metabolizes, distributes, and eliminates) or an entire ecosystem ([Figure 18.11\(B\)](#)).

The first law of thermodynamics requires that any change in storage of a substance's mass in a control volume must equal the difference between the mass of the chemical transported into the system less the mass of the chemical transported out of the system. Given the transformations discussed in Chapter 17, the actual chemical species transported in may be different from what is transported. Thus, the mass balance equation may be written as:

Accumulation or loss of contaminant A

$$\begin{aligned} &= \text{mass of A transported in} \\ &\quad - \text{mass of A transported out} \pm \text{reactions} \end{aligned} \quad (18.33)$$

The reactions may be either those that generate chemical A (i.e. sources), or those that destroy chemical A (i.e. sinks).

The entering mass transported equals the inflow to the system that includes pollutant discharges, transfer from other control volumes and other media (for example, if the control volume is soil, the water and air may contribute mass of chemical A), and formation of chemical A by abiotic chemistry and biological transformation. Conversely, the outflow is the mass transported out of the control volume, which includes uptake by biota, transfer to other compartments (e.g. volatilization to the atmosphere) and abiotic and biological degradation of chemical A.

The rate of change of mass in a control volume is equal to the rate of chemical A transported in less the rate of chemical A transported out, plus the rate of production from sources, and minus the rate of elimination by sinks. Stated as a differential equation, the rate of change contaminant A is

$$\frac{d[A]}{dt} = -v \cdot \frac{d[A]}{dx} + \frac{d}{dx} \left( D \cdot \frac{d[A]}{dx} \right) + r \quad (18.34)$$

where:

$v$  = fluid velocity,

$\frac{d[A]}{dx}$  = concentration gradient of chemical A, and

$r$  = internal sinks and sources within the control volume.

These rates operate at various scales. For example, [Eqn \(18.34\)](#) can be applied from the cell to the planet. It is even the basis for pharmacokinetic and pharmacodynamic modeling. Note that variable  $r$  is the focus of Chapter 17.

A basic concept of air pollution is that substances tend to have affinity for certain compartments in abiotic and biotic systems. Indeed, a symphony of mechanisms occurs.

As mentioned, compound that is released into the atmosphere will remain there for some time. Thereafter, it

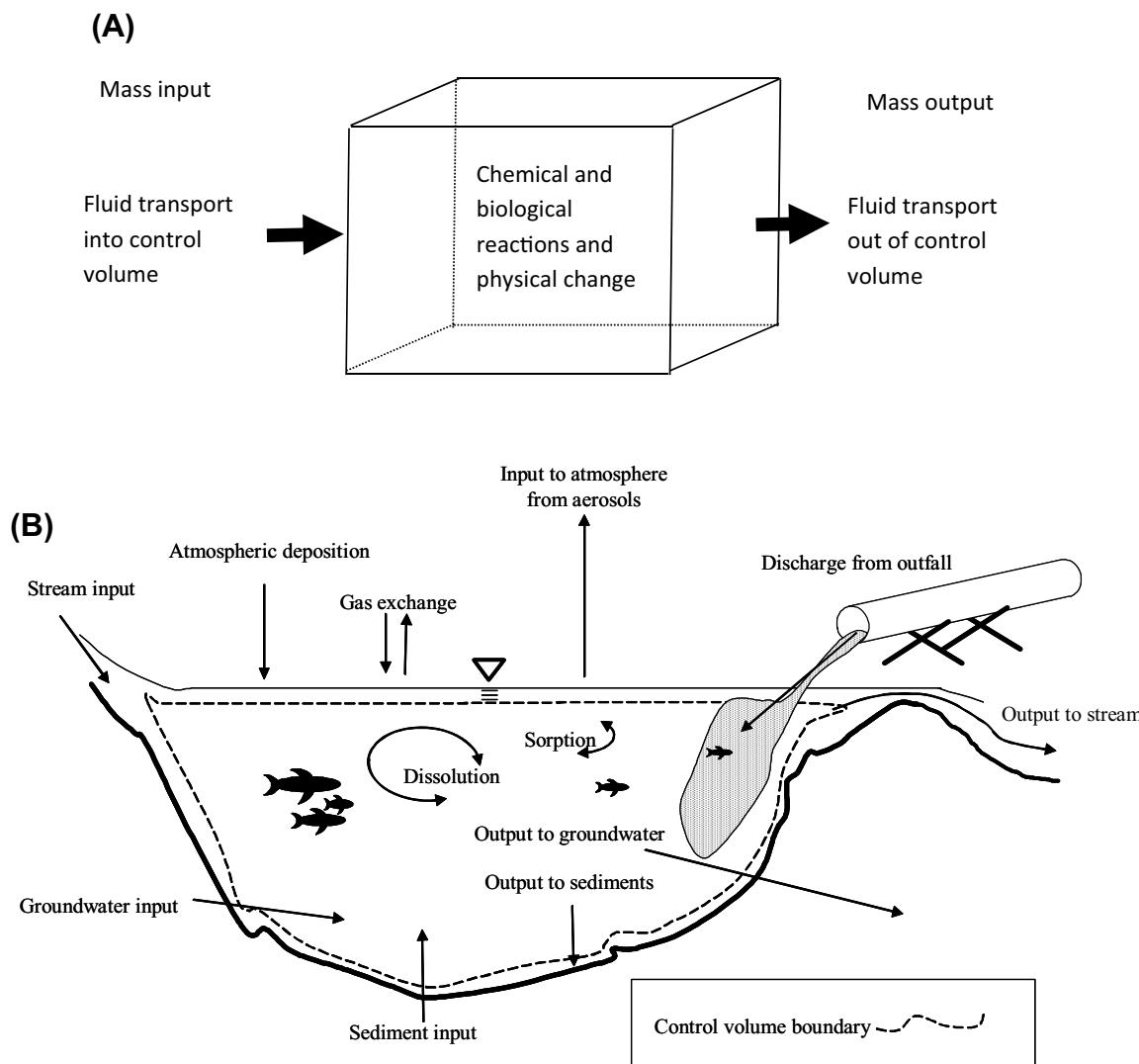


FIGURE 18.11 (A) Control volume of an environmental matrix (e.g. soil, sediment, or other unconsolidated material) or fluid (e.g. water, air, or blood). (B) A pond. Both volumes have equal masses entering and exiting, with transformations and physical changes taking place within the control volume.

may move to another compartment, remain unchanged for a designated time period, or it may move physically, or it may be transformed chemically into another substance.

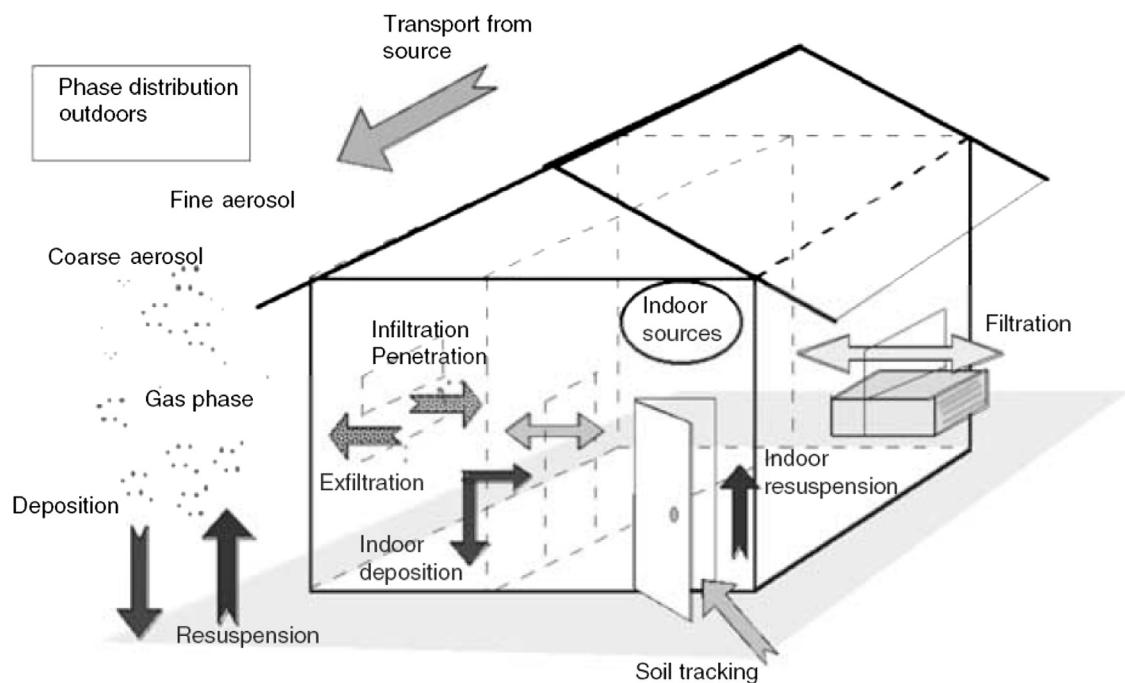
Partitioning occurs not only between an organism and the environmental compartments, but also within the organism. Air pollution and other health studies increasingly rely on biomarkers as indicators of concentrations that occur in control volumes where humans and organisms live. Physicians have used markers for decades, e.g. cholesterol, fat, and blood sugar. However, environmental toxicologists have adopted numerous chemicals to indicate pollution and its effect. Some of these chemicals are the parent substances to which the organism, including a person, has been exposed. A good example of this is the metal lead (Pb). The amount of lead in a child's blood or hair indicates the extent to

which the child has been exposed to Pb. In this case, total mass of Pb is a reliable indicator of the time and activities of the child within various control volumes, e.g. microenvironments in the home (Figure 18.12).

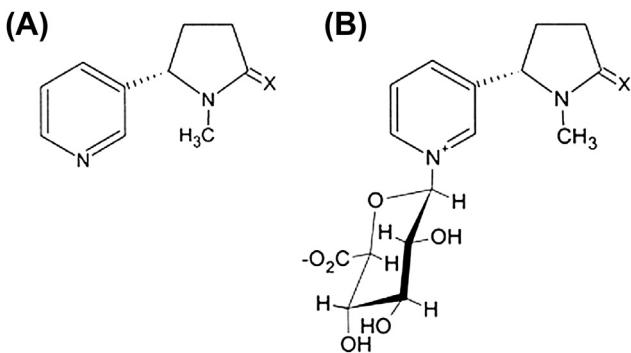
Given the  $r$  term in Eqn (18.34), however, the biomarkers are compounds other than the parent. Thus, biomarkers are often metabolites of the compounds. For example, smokers inhale nicotine, much of which is metabolized to cotinine (Figure 18.13). Thus, cotinine biomarkers can be measures of exposure to tobacco smoke.

The four types of sorption take place at surfaces and are crucial to film and molecular exchanges.

Biomolecules and xenobiotic compounds eventually establish a balance between the mass on the solid surfaces and the mass that is in solution. Molecules will migrate from one phase to another to maintain this



**FIGURE 18.12** The home as a microenvironmental control volume. See Figure 18.10 for an example of air pollutant partitioning within this microenvironment. U.S. Department of Energy, Lawrence Berkeley Laboratory. <http://etd.lbl.gov/ied/ERA/CalEx/partmatter.html>; 2003 [accessed 2004]; and Vallero DA. Environmental contaminants: assessment and control. Burlington (MA): Elsevier Academic Press; 2004.



**FIGURE 18.13** Chemical structures of: (A) S(-)-nicotine (when X = H<sub>2</sub>) or S(-)-cotinine (when X = O); and (B) S(-)-nicotine N1-glucuronide (when X = H<sub>2</sub>), or S(-)-cotinine N1-glucuronide (when X = O). Ghosheh O, Hawes EM. N-Glucuronidation of nicotine and cotinine in human: formation of cotinine glucuronide in liver microsomes and lack of catalysis by 10 examined UDP-glucuronosyltransferases. *Drug Metab Distrib* 2002;30(9):991-6.

balance. The properties of both the chemical and the soil (or other matrix) will determine how and at what rates the molecules partition into the solid and liquid phases. These physicochemical relationships, known as sorption isotherms, are found experimentally.

Of principal interest in air pollution, after a chemical has moved through water, soil, sediment, or biota, it must move into the atmosphere. As discussed in Chapter 6, volatilization is a function of the concentration of a contaminant in solution and the contaminant's partial pressure.

## 18.5 MOVEMENT INTO THE ATMOSPHERE

Vapor pressure is the pressure exerted by a vapor in a confined space. Similarly vaporization is the change of a liquid or solid to the vapor phase. So, if a substance vaporizes it can enter a plume. Thus, a principal means of a substance being released as a plume is volatilization, which is a function of the concentration of a contaminant in solution and the contaminant's partial pressure. That is, proportionality between solubility and vapor pressure can be established for any chemical.

Such a proportionality is Henry's law, which states that the concentration of a dissolved gas is directly proportional to the partial pressure of that gas above the solution:

$$p_a = K_H[c] \quad (18.35)$$

where,

$K_H$  = Henry's law constant,

$p_a$  = Partial pressure of the gas, and

$[c]$  = Molar concentration of the gas.

or,

$$p_a = K_H C_W \quad (18.36)$$

where,  $C_W$  is the concentration of gas in water.

Combining the concentration of a dissolved contaminant and its partial pressure in the headspace (including

the open atmosphere) at equilibrium is a reliable means of estimating the likelihood that a chemical will move into the atmosphere. A dimensionless version of  $K_H$  partitioning is similar to that of sorption, except that instead of the partitioning between solid and water phases, it is between the air and water phases ( $K_{AW}$ ):

$$K_{AW} = \frac{C_A}{C_W} \quad (18.37)$$

where  $C_A$  is the concentration of gas A in the air.

The relationship between the air–water partition coefficient and Henry's law constant for a substance is:

$$K_{AW} = \frac{K_H}{RT} \quad (18.38)$$

where,  $R$  is the gas constant ( $8.21 \times 10^{-2} \text{ J atm mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the temperature ( $^{\circ}\text{K}$ ).

Henry's law relationships work well for most environmental conditions, representing a limiting factor for systems where a substance's partial pressure is approaching zero. At very high partial pressures (e.g. 30 Pa) or at very high contaminant concentrations (e.g. >1000 ppm), Henry's law assumptions cannot be met. Such vapor pressures and concentrations are seldom seen in ambient environmental situations, but may be seen in industrial and other source situations. Thus, in modeling and estimating the tendency for a substance's release in vapor form, Henry's law is a good metric and is often used in compartmental transport models to indicate the fugacity from the water to the atmosphere.

Henry's law constants are highly dependent upon temperature, since both vapor pressure and solubility are also temperature dependent. So, when using published  $K_H$  values, one must compare them isothermally. Also, when combining different partitioning coefficients in a model or study, it is important either to use only values derived at the same temperature (e.g. sorption, solubility, and volatilization all at 20 °C), or to adjust them accordingly. A general adjustment is an increase of a factor of 2 in  $K_H$  for each 8 °C temperature increase.

Any sorbed or otherwise bound fraction of the contaminant will not exert a partial pressure, so this fraction should not be included in calculations of partitioning from water to air. For example, it is important to differentiate between the mass of the contaminant in solution (available for the  $K_{AW}$  calculation) and that in the suspended solids (unavailable for  $K_{AW}$  calculation). This is crucial for many hydrophobic organic contaminants, where they are most likely not to be dissolved in the water column (except as cosolutes), with the largest mass fraction in the water column being sorbed to particles.

The relationship between  $K_H$  and  $K_{ow}$  is also important. It is often used to estimate the environmental

persistence, as reflected by the chemical half-life ( $t_{1/2}$ ) of a contaminant. However, many other variables determine the actual persistence of a compound after its release. Note in the table, for example, that benzene and chloroform have nearly identical values of  $K_H$  and  $K_{ow}$ , yet benzene is far less persistent in the environment.

With these caveats in mind, however, relative affinity for a substance to reside in air and water can be used to estimate the potential for the substance to partition not only between water and air, but more generally between the atmosphere and biosphere, especially when considering the long-range transport of contaminants (e.g. across continents and oceans). Such long-range transport estimates make use of both atmospheric  $t_{1/2}$  and  $K_H$ . Also, the relationship between octanol–water and air–water coefficients can be an important part of predicting a contaminant's transport. As mentioned, Figure 18.2 provides some general classifications according various substances'  $K_{AW}$  and  $K_{ow}$  relationships. In general, chemicals in the upper left hand group have a great affinity for the atmosphere, so unless there are contravening factors, this is where to look for them. Conversely, substances with relatively low  $K_{AW}$  and  $K_{ow}$  values are less likely to be transported long distance in the air. Since  $K_{AW}$  is proportional to  $K_H$ , these grouping also apply to Henry's law constants.

In addition to the inherent properties of the compounds being degraded, the bioreactor processes take advantage of aerobic-heterotrophic-microbes' ability to use these substances as carbon and energy sources. Before this can happen, however, the contaminants and  $O_2$  must first move from the vapor phase to the aqueous phase where they can be metabolized by the microorganisms. Thus, even though these are volatile compounds they are actually exclusively treated in the aqueous phase. The volumetric mass transfer rate ( $\text{mol m}^{-3} \text{ s}^{-1}$ ) of gaseous substrates (e.g. compounds to be treated, oxygen, and nutrients) to the aqueous phase is:

$$K_{1a_{G/A}} \left( \frac{S_G}{K_{G/A}} - S_A \right) \quad (18.39)$$

where,  $K_{1a_{G/A}}$  is the global volumetric mass transfer coefficient ( $\text{h}^{-1}$ ),  $S_G$  and  $S_A$  are the substrate (e.g. benzene) concentrations ( $\text{mol m}^{-3}$ ) in the bulk gas and aqueous phases, respectively, and  $K_{G/A}$  is the substrate partition coefficient (dimensionless) between the gaseous and aqueous phases.  $K_{G/A}$  is calculated as follows:

$$K_{G/A} = \frac{S_G}{S_A^*} \quad (18.40)$$

where,  $S_A^*$  is the substrate concentration at the gas–aqueous interface ( $\text{mol m}^{-3}$ ).

In addition to the vapor phase and aqueous phase, there is also a nonaqueous (e.g. lipids) phase in the substrate (Figure 18.14). Reactions can only occur when reagents come into contact, which in air pollution often

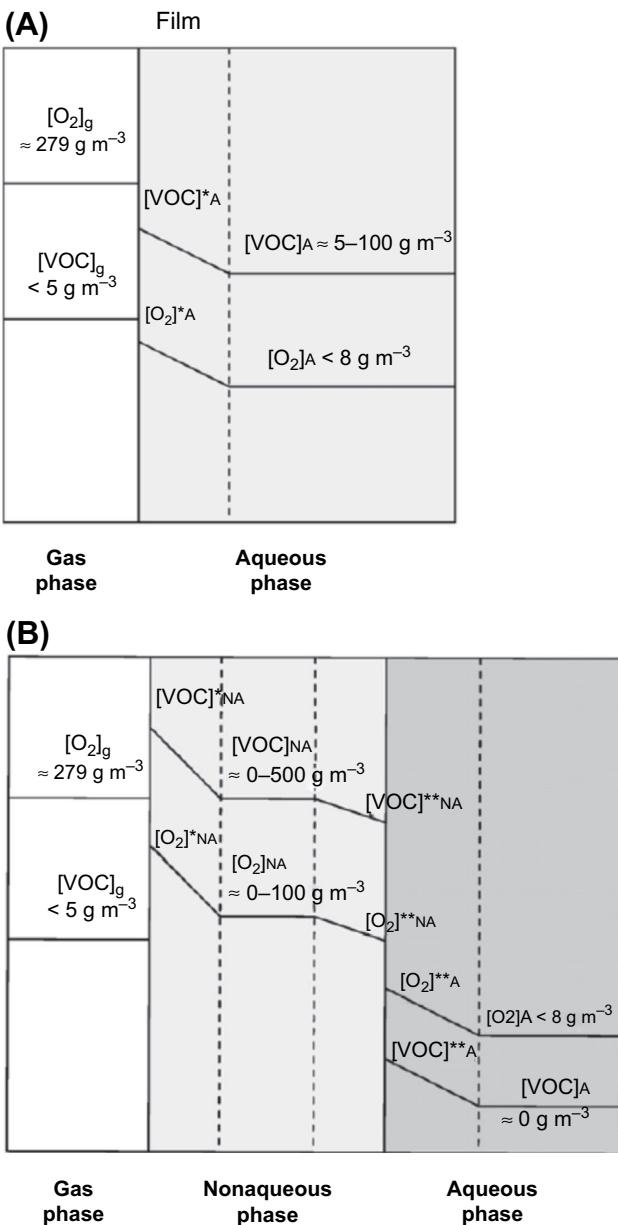


FIGURE 18.14 Concentration profiles of lipophilic substrates (volatile organic compounds—VOCs—and  $O_2$ ) in a single-phase system (A) and in a two-phase partitioning bioreactor (B).  $[VOC]$  and  $[O_2]$  = concentrations of volatile organic compounds and  $O_2$ , respectively, in the treated gas phase ( $[ ]_g$ ), aqueous phase ( $[ ]_A$ ), nonaqueous phase ( $[ ]_{NA}$ ),  $[ ]^*$  and  $[ ]^{**}$  represent the equilibrium concentrations at the gaseous/nonaqueous and nonaqueous/aqueous interfaces, respectively. Note: All concentrations based on air contaminated with  $5 \text{ g VOC m}^{-3}$ . Muñoz R, Villaverde S, Guiyssse B, Revah S. Two-phase partitioning bioreactors for treatment of volatile organic compounds. Biotechnol Adv 2007;25(4):410–22.

requires that an agent moves at least two phases (Figure 18.14(B)). This translates into a film profile, with sectors based on the octanol–water coefficient ( $K_{ow}$ ) and  $K_{G/A}$ . This partitioning can also occur between organisms and substrate, e.g. microbes, as depicted in Figure 18.15.

The inherent properties of air pollutants discussed in Chapter 6 do not fully explain pollution. The vapor pressure and molecular weight, for example, will give clues to the behavior of an air pollutant, but are not definitive. The physicochemical properties must be combined with environmental conditions to characterize and estimate the fate of the pollutant. After entering the air, water, soil, and biota, a chemical compound will either remain in a compartment or move to another. Indeed, this is seldom an exclusive residence, as some of the chemicals remain and the rest will move to one or more other compartments. The propensity for this distribution is known as partitioning.

Phase partitioning is also sometimes called “phase distribution”. Partitioning certainly is influenced by inherency. If a compound has high aqueous solubility, i.e. it is easily dissolved in water under normal environmental conditions of temperature and pressure, it is hydrophilic. That is, it is very likely to remain dissolved in water. If, conversely, a substance is not easily dissolved in water under these conditions, it is said to be hydrophobic, and many of its molecules will exit

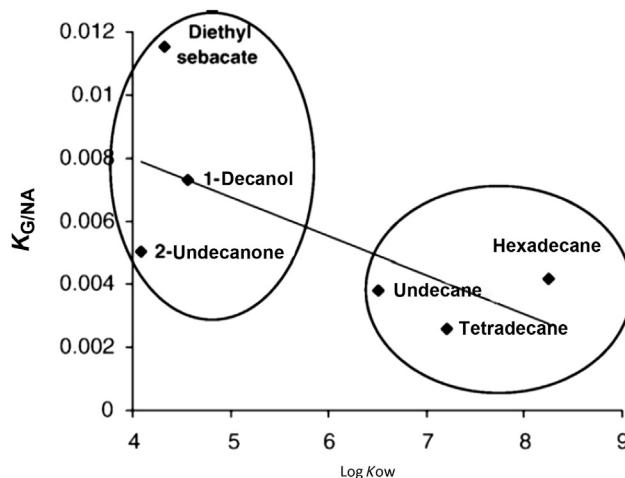


FIGURE 18.15 Gaseous–nonaqueous hexane partition coefficient ( $K_{G/NA}$ ) in organic solvents. The left cluster represents solvents toxic to the fungus, *Fusarium solani*. The right cluster shows biocompatible solvents that were biodegraded by *F. solani*. Note: Silicone oil ( $K_{G/NA} = 0.0034$ ; unknown  $\log K_{ow}$ ) was the only nonaqueous phase substance tested showing both biocompatible and nonbiodegradable characteristics. Muñoz R, Villaverde S, Guiyssse B, Revah S. Two-phase partitioning bioreactors for treatment of volatile organic compounds. Biotechnol Adv 2007;25(4):410–22; and Arriaga S, Muñoz R, Hernandez S, Guiyssse B, Revah S. Gaseous hexane biodegradation by *Fusarium solani* in two liquid phase packed-bed and stirred tank bioreactors. Environ Sci Technol 2007;40:2390–5.

the water and enter compartments with substances of which the chemical has more affinity, e.g. hydrophobic compounds in sediment or tissues in organisms. Thus, an inherent property, aqueous solubility is a factor of partitioning, yet does not fully predict the amount of a chemical that will be in each compartment. Such prediction is afforded by partitioning coefficients.

## 18.6 APPLICATION OF THE OCTANOL-WATER COEFFICIENT

The octanol–water partition coefficient ( $K_{ow}$ ) is arguably the most commonly applied partitioning coefficient for water systems, but it also has major applications in air and other media. Since many air toxics are organic compounds (i.e. consist of molecules containing carbon-to-carbon bonds and/or carbon-to-hydrogen bonds), the solubility can be further differentiated as to whether under normal environmental conditions of temperature and pressure the substance is easily dissolved in organic solvents. If so the substance is said to be lipophilic (i.e. readily dissolved in lipids). If, conversely, a substance is not easily dissolved in organic solvents under these conditions, it is said to be lipophobic.

This affinity for either water or lipids underpins an important indicator of environmental partitioning; i.e. the octanol–water partition coefficient ( $K_{ow}$ ). The  $K_{ow}$  is the ratio of a substance's concentration in octanol ( $C_7H_{13}CH_2OH$ ) to the substance's concentration in water at equilibrium (i.e. the reactions have all reached their final expected chemical composition in a control volume of the fluid). Octanol is a surrogate for lipophilic solvents in general because it has degrees of affinity for both water and organic compounds, that is, octanol is amphiphilic. Since the ratio forming the  $K_{ow}$  is  $[C_7H_{13}CH_2OH]:[H_2O]$ , then the larger the  $K_{ow}$  value, the more lipophilic the substance. Values for solubility in water and  $K_{ow}$  values of some important environmental compounds, along with their densities, are shown in Table 18.6.

Table 18.6 elucidates some additional aspects of solubility and organic/aqueous phase distribution. Water solubility is somewhat inversely related to  $K_{ow}$ , but the relationship is uneven. This results from the fact that various organic compounds are likely to have affinities for neither, either, or both the organic and the aqueous phases. Most compounds are not completely associated with either phase; i.e. they have some amount of amphiphilicity.

The relationship between density and organic/aqueous phase partitioning is very important to pollutant transport. For example a nonaqueous-phase liquid will partition at different rates in groundwater through the vadose (unsaturated) zone, depending on its density. A lighter compound may stay near the

TABLE 18.6 Solubility, Octanol–Water Partitioning Coefficient, and Density Values for Some Environmental Pollutants (at 22° C)

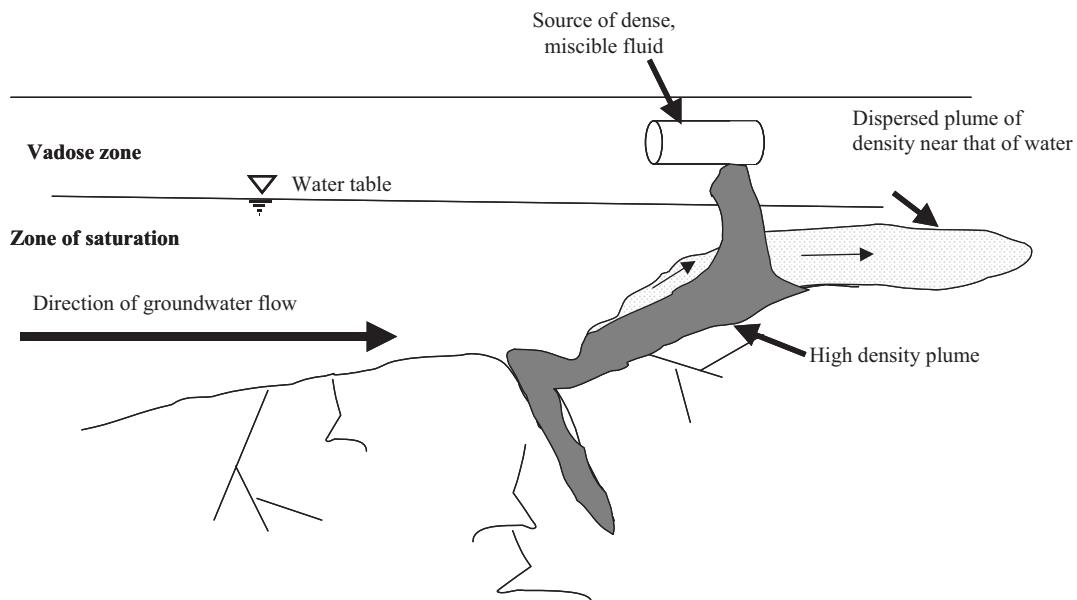
Chemical	Water Solubility (mg l <sup>-1</sup> )	$K_{ow}$	Density (kg m <sup>-3</sup> )
Atrazine	33	724	
Benzene	1780	135	879
Chlorobenzene	472	832	1110
Cyclohexane	60	2754	780
1,1-Dichloroethane	4960	62	1180
1,2-Dichloroethane	8426	30	1240
Ethanol	Completely miscible	0.49	790
Toluene	515	490	870
Vinyl chloride	2790	4	910
Tetrachlorodibenzo- <i>para</i> -dioxin (TCDD)	$1.9 \times 10^{-4}$	$6.3 \times 10^6$	

Source: Hemond HF, Fechner-Levy EJ. Chemical fate and transport in the environment. San Diego, CA: Academic Press; 2000; TCDD data from the NTP Chemical Repository, National Environmental Health Sciences Institute; 2003; and US Environmental Protection Agency; 2003. Technical Fact Sheet on Dioxin (2,3,7,8-TCDD).

surface and be more likely to volatilize into the atmosphere than a denser compound, even if they have equal high  $K_{ow}$  values and water solubility.

Also, what seem to be minor structural changes to a molecule can make quite a difference in phase partitioning and in density. Even the isomers (i.e. same chemical composition with a different arrangement) vary in their  $K_{ow}$  values and densities (note the "1,1" vs "1,2" arrangements of chlorine atoms on 1,1-dichloroethane, and 1,2-dichloroethane, causes the former to have a slightly decreased density but twice the  $K_{ow}$  value than the latter). The location of the chlorine atoms alone accounts for a significant difference in water solubility in the two compounds.

Movement in other environmental media often occurs prior to being released to the atmosphere. Most air pollution is emitted from stacks, vents, or ruptured containers above ground, but there are also sources that have their beginnings below ground. Leaking pipelines, underground tanks and contaminated soil, porous media, and water can be surreptitious sources of air pollutants. As mentioned, the relationship between density and organic/aqueous phase partitioning is very important to this type of pollutant transport, as shown in Figure 18.16. The transport of the lipophilic compounds through the vadose zone assumes that the compounds have extremely high  $K_{ow}$  values and extremely low water solubility. That is, they have a greater affinity for lipids than for water. As the aqueous solubility of a substance increases, its flow will increasingly follow the water flow lines.



**FIGURE 18.16 Hypothetical plume of a mixture of dense and light fluids.** Based on information provided by: Sara MN. Groundwater monitoring system design. In: Nielsen DM, editor. Practical handbook of ground-water monitoring. Chelsea (MI): Lewis Publishers; 1991.

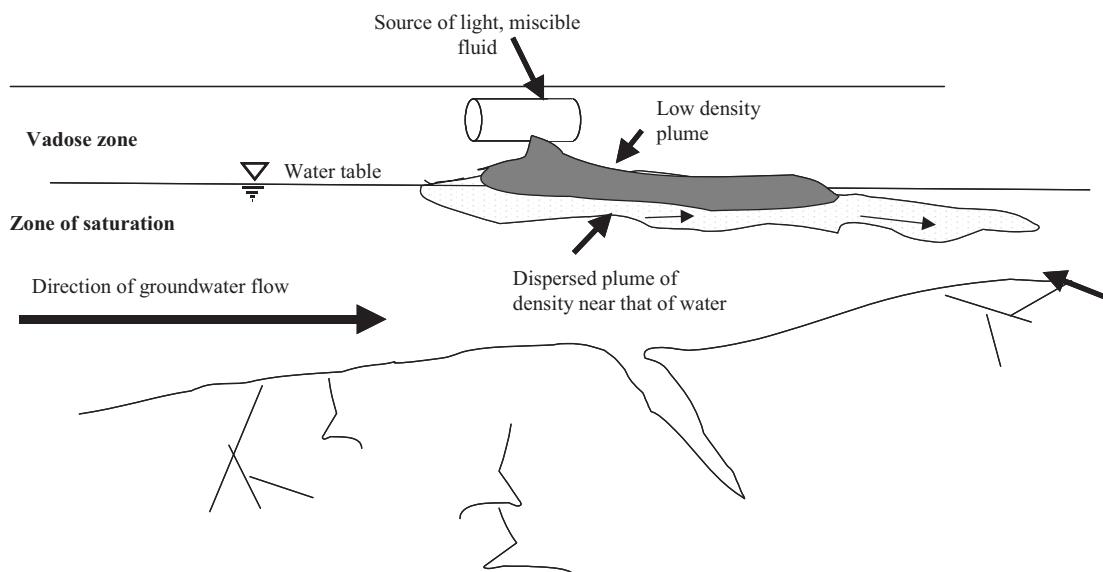
When a dense, miscible fluid seeps into the zone of saturation, the dense contaminants move downward. When these contaminants reach the bottom of the aquifer, the shape and slope of the underlying bedrock or relatively impervious layer dictates their continued movement of the contaminant plume, which will likely be in a direction other than the flow of the groundwater in the aquifer. Solution and dispersion near the boundaries of the plume will induce the formation of a secondary plume that will generally follow the direction of groundwater flow. The physics of this system points how predicting where the plume is heading will entail more than the fluid densities, and the need to know the characteristics of the contaminants in the plume, including their solubility and phase partitioning. So, monitoring wells will need to be installed upstream and downstream from the source.

Another possibility is that the water may contain an amphiphilic compound (e.g. an alcohol) or a surfactant, which dissolves both hydrophilic and lipophilic compounds. As such, even a highly lipophilic compound may be dissolved by this solvent or surfactant which is carried with the water and ultimately is volatilized into the atmosphere.

If a source consists entirely of a light, hydrophilic fluid, the plume may be characterized as shown in [Figure 18.17](#). Low-density organic fluids, however, often are highly volatile; i.e. their vapor pressures are sufficiently high to change phases from liquid to gas. So, another physicochemical property of environmental fluids, vapor pressure, must be considered along with density and solubility.

An important process in plume migration is that of cosolvation, the process where a substance is first dissolved in one solvent and then the new solution is mixed with another solvent. As mentioned, with increasing aqueous solubility, a pollutant will travel along the flow lines of the ground or surface water. Nonaqueous phase liquids (NAPLs) are an important class of chemicals that contaminate aquifers. If heavier than water they are known as dense nonaqueous phase liquids (DNAPs). By definition, such chemicals resist being dissolved in water. However, even a substance with low aqueous solubility can follow the flow under certain conditions. As evidence, a hydrophobic compound like a chlorinated benzene (DNAPL), which has very low solubility in pure water, can migrate into and within water bodies if it is first dissolved in an alcohol or an organic solvent (e.g. toluene). So, a DNAPL will migrate downward because its density is less than that of water. Likewise, the ordinarily lipophilic and low density compound can be transported in the vadose zone or upper part of the zone of saturation if it has undergone cosolvation with a DNAPL. Thus, the cosolvation of a light nonaqueous phase liquid (LNAPL), e.g. toluene, with a DNAPL in water could explain at least in part why a LNAPL is found in the lower part of an aquifer, as well as why a DNAPL is found in the upper part of the aquifer.

Contaminants are often mixtures. The constituents in these mixtures will partition within an environmental compartment at different rates. For example, the dense substance that moves toward the bottom of the aquifer in [Figure 18.17](#) with time may partition between lighter and denser constituents. The lighter constituents will be more likely to migrate upward and could become air



**FIGURE 18.17 Hypothetical plume of light fluid.** Based on information provided by: Sara MN. Groundwater monitoring system design. In: Nielsen DM, editor. Practical handbook of ground-water monitoring. Chelsea (MI): Lewis Publishers; 1991.

pollutants via volatilization than the denser constituents of the mixture, which will likely remain below the surface. However, this should be considered along with other inherent properties and environmental conditions. For example, even the denser constituents may migrate if they become sorbed to particles that migrate. In addition, some of the constituents may differentially migrate as a result of cosolvation. Others may resist dissolution and continue to migrate downwardly. The bottom line is that  $K_{ow}$  must be applied to each constituent and that partitioning is highly specific to environmental conditions.

## 18.7 PARTITIONING BETWEEN AIR AND TISSUE

The principal interest in partitioning between an organic substrate and water, i.e. the  $K_{ow}$ , was mainly the need of water pollution. Air pollution also needs a means of characterizing this partitioning for organic air pollutants in terms of sources likely to release the organic air pollutants. However, organic solvent and water partitioning is not completely useful for understanding the movement of substances among organic substrates and the air, especially within the lungs. Although both systems derive O<sub>2</sub> that is dissolved in a substrate (water or air),  $K_{ow}$  is very useful for gills, but much less useful for lungs. Thus, the octanol-air partitioning coefficient ( $K_{oa}$ ) was established.

Models have been developed to combine  $K_{ow}$  and the Henry's law constant ( $K_H$ ) to estimate the equilibrium

between air and organic tissues. Henry's law constant and the  $K_{oa}$  are physical-chemical properties that are often not measured but are needed to understand the environmental fate and transport of chemicals.

As mentioned, Henry's law constant is the air–water partition coefficient, which is the ratio of vapor pressure to solubility in water, corrected for molecular weight. It is commonly reported with units of atm m<sup>3</sup> mol<sup>-1</sup> or, if it is a unitless value, it is reported as the air–water partitioning coefficient ( $K_{AW}$ ). The conventional Henry's law constant is calculated as:

$$K_H = \frac{P^\circ \times MW}{760 \times C_{sol}} \quad (18.41)$$

where,  $P^\circ$  = vapor pressure (torr); MW = molecular weight (g mol<sup>-1</sup>); 760 = conversion factor (1 atm = 760 torr), and  $C_{sol}$  = water solubility (mg l<sup>-1</sup>). The resulting units for  $K_H$  are atm m<sup>3</sup> mol<sup>-1</sup>. The units of mg and liter (l) cancel since there are 1000 mg in 1 g and 0.001 m<sup>3</sup> in 1 l.

Thus, if two compounds have the same vapor pressure and aqueous solubility, the heavier compound will have a greater resistance to movement, i.e. less fugacity, than the lighter compound. Similarly, if two compounds have the same vapor pressure, the one that is more soluble in water will have less fugacity.

The unitless Henry's law constant ( $K_{AW}$ ) is calculated as:

$$K_{AW} = \frac{C_{air}}{C_{water}} = \frac{K_H}{R \cdot T} \quad (18.42)$$

where  $R$  is the ideal gas constant of 8.205746 × 10<sup>-5</sup> atm m<sup>3</sup> °K<sup>-1</sup> mol<sup>-1</sup>;  $T$  is absolute temperature

expressed in kelvin ( $^{\circ}\text{K}$ ); and  $K_{\text{H}}$  is expressed in  $\text{atm m}^3 \text{ mol}^{-1}$ . Use parameters measured or calculated for the same temperature (e.g.  $25^{\circ}\text{C}$ ).

### 18.7.1 Calculating the Octanol–Air Partition Coefficient

For air pollutants, partitioning between organic compounds and water, i.e.  $K_{\text{ow}}$ , is often insufficient to estimate transport and fate. Air is another fluid from which compounds partition. Thus, the potential air pollutant transport and bioaccumulation calls for another partitioning between air and the organic phase, analogous to the partitioning between the water and organic phase. This is the octanol–air coefficient ( $K_{\text{oa}}$ ) for a chemical compound.<sup>7</sup> The  $K_{\text{oa}}$  is the ratio of the concentration of a compound in an organic phase (*n*-octanol) and air at equilibrium  $\left( \frac{C_{\text{air}}}{C_{\text{water}}} = \frac{C_{\text{octanol}}}{C_{\text{air}}} \right)$ , where  $C_{\text{octanol}}$  and  $C_{\text{air}}$  represent equilibrium concentrations in air and *n*-octanol with the same units. The  $K_{\text{oa}}$  has been used to describe partitioning between air and aerosol particles, air and foliage, and air and soil.<sup>8,9</sup> Handbook values are available, but measured  $K_{\text{oa}}$  values may be substantially different than calculated values, so measured values are preferred.<sup>8</sup> In the absence of data,  $K_{\text{oa}}$  values calculated using a quantitative structural activity relationship (QSAR) calculator, such as EPI Suite<sup>TM,9</sup> and the following equations:

$$K_{\text{oa}} = \frac{K_{\text{ow}} \cdot R \cdot T}{K_{\text{H}}} \quad (18.43)$$

where,  $K_{\text{ow}}$  is the *n*-octanol–water partition coefficient (unitless)<sup>10</sup>;  $R$  is the ideal gas constant =  $8.205746 \times 10^{-5} \text{ atm m}^3 \text{ K}^{-1} \text{ mol}^{-1}$ ;  $T$  is absolute temperature expressed in kelvin (K); and  $K_{\text{H}}$  is the Henry's law constant expressed in  $\text{atm m}^3 \text{ mol}^{-1}$ .

The ideal gas law assumptions can simplify the equation to a relationship between water and air partitioning, i.e.  $K_{\text{ow}}$  and  $K_{\text{oa}}$ :

$$K_{\text{oa}} = \frac{K_{\text{ow}}}{K_{\text{AW}}} \quad (18.44)$$

$K_{\text{AW}}$  is the air–water partition coefficient (unitless).

When a measured  $K_{\text{oa}}$  is not available and long-range transport or terrestrial bioaccumulation may be a concern, the  $K_{\text{oa}}$  can be calculated by using Eqn (18.35) when measured  $K_{\text{ow}}$  and vapor pressure or Henry's law constant are available. If these are not available, a QSAR approach is recommended (e.g. EPI Suite<sup>TM</sup>). The published values for these key partitioning coefficients are given in Table 18.7.

Note that partitioning coefficients in Table 18.7 are reported as log values. This is because the ranges are so

large that log–log relationships are commonly used, including for comparing chemicals' affinities. Thus, Eqn (18.44) can be restated as:

$$\log K_{\text{oa}} = \log K_{\text{ow}} - \log K_{\text{AW}} \quad (18.45)$$

The values in Table 18.7 demonstrate the variability of estimates depending on the method used. For example, the published  $\log K_{\text{oa}}$  for methyl isocyanate (MIC) is 2.112; so taking its antilog gives a  $K_{\text{oa}} = 129$ . However, calculating  $K_{\text{oa}}$  from Eqn (18.44) gives an estimated value:

$$\log K_{\text{oa}} = \log K_{\text{ow}} - \log K_{\text{AW}} = 0.79 - (-1.4222) \approx 1.5.$$

The calculated value is 0.7 less than the measured or published value. The difference means that the calculated  $K_{\text{oa}}$  is underreported by about one-third. Thus, if the calculated value is used, the affinity for tissue is understated. That is, the MIC is less likely to exit from tissue into air than the calculated value indicates.

The published  $\log K_{\text{oa}}$  for formaldehyde is 2.77. Calculating an estimate for  $K_{\text{oa}}$  from Eqn (18.44) gives:

$$\log K_{\text{oa}} = \log K_{\text{ow}} - \log K_{\text{AW}} = 0.35 - (-4.861) \approx 4.81.$$

This difference is a large discrepancy, i.e. two orders of magnitude between the two methods. As for MIC, the calculated method underestimates formaldehyde's affinity for tissue and overestimates its likelihood to move into the air.

These differences may be explained somewhat by the fact that the calculation is actually a rule of thumb. Each partitioning coefficient is measured differently. For example,  $K_{\text{ow}}$  is actually not usually calculated as partitioning between pure octanol and pure water; rather the measurement reflects octanol saturated with water and water saturated with octanol.<sup>11</sup> Whenever the inherent properties like solubility and vapor pressure are incorrect, derived properties like  $K_{\text{ow}}$ ,  $K_{\text{AW}}$ , and  $K_{\text{oa}}$  will propagate and amplify such error.

These differences also appear in the organic carbon partitioning coefficients ( $K_{\text{OC}}$ ), i.e. the two right columns in Table 18.7, with large discrepancies between QSAR and  $K_{\text{ow}}$ -based  $K_{\text{OC}}$  values. This is a reminder that octanol is merely a surrogate or indicator of the organic phase. This problem emphasizes that an actual, published  $K_{\text{oa}}$  based on credible methods is preferred whenever possible.

## 18.8 DYNAMICS WITHIN AN ORGANISM

Air pollutant transport and fate focus on the kinetics and equilibria of the processes leading to the

**TABLE 18.7** Key Air, Water, and Organic Tissue Partitioning Coefficients for Hazardous Air Pollutants Calculated from Quantitative Structural Activity Relationships (QSAR) and from Published Estimates. Note: Table shows organic compounds only. The hazardous air pollutants also include metals and their compounds and asbestos. Conditions assumed to be 25° C and 1 atmos.

Chemical Name	Log $K_{ow}$ from QSAR	Log $K_{oa}$ from QSAR	Log $K_{AW}$	Log $K_{OC}$ from QSAR	Log $K_{OC}$ Estimated from $K_{ow}$
Acetaldehyde	-0.17	2.387	-2.564	-0.2676	0.5078
Acetamide	-1.16	5.179	-6.339	0.475	0.2244
Acetonitrile	-0.15	2.753	-2.851	0.6693	1.1292
Acetophenone	1.67	5.067	-3.371	1.7147	1.9946
2-Acetylaminofluorene	3.12	11.225	-8.105	3.3436	2.6255
Acrolein	0.19	3.025	-2.302	-0.007	0.6903
Acrylamide	-0.81	5.808	-7.158	0.755	0.5507
Acrylic acid	0.44	5.368	-4.82	0.1583	0.3493
Acrylonitrile	0.21	2.459	-2.249	0.93	1.4556
Allyl chloride	1.93	1.786	-0.347	1.5977	1.6746
4-Aminobiphenyl	2.84	8.064	-5.224	3.3928	2.4854
Aniline	1.08	5.19	-4.083	1.8465	1.4013
<i>o</i> -Anisidine	1.16	6.495	-4.422	1.662	1.6121
Benzene (including benzene from gasoline)	1.99	2.647	-0.644	2.1637	1.8482
Benzidine	1.92	10.595	-8.675	3.0757	1.6231
Benzotrichloride	3.9	5.873	-1.973	3.0005	3.3844
Benzyl chloride	2.79	3.858	-1.774	2.6495	1.9958
Biphenyl	3.76	5.531	-1.9	3.71	3.4799
Bis(2-ethylhexyl)phthalate (DEHP)	8.39	11.707	-4.957	5.0776	4.9977
Bis(chloromethyl)ether	0.57	2.929	-0.749	0.9867	1.1498
Bromoform	1.79	4.125	-1.66	1.5027	2.0826
1,3-Butadiene	2.03	1.527	0.478	1.5977	1.7267
Calcium cyanamide	-0.81	2.057	-7.975	0.6693	0.8637
Caprolactam (see modification)	0.66	6.645	-5.985	1.3892	1.2646
Captan	2.74	9.467	-6.543	2.4018	2.4663
Carbaryl	2.35	9.242	-6.874	2.55	2.1344
Carbon disulfide	1.94	1.848	-0.23	1.337	1.6833
Carbon tetrachloride	2.44	2.424	0.052	1.6424	2.4558
Carbonyl sulfide	-1.33	-1.634	1.397	-0.2676	-0.0398
Catechol	1.03	9.653	-7.309	2.3899	1.7455
Chloramben	1.9	10.966	-8.801	1.3299	1.1851
Chlordane	6.26	8.802	-2.702	4.8296	5.3979
Chlorine	0.85	None	None	1.1211	0.7373
Chloroacetic acid	0.34	5.443	-6.422	0.1583	0.2774
2-Chloroacetophenone	1.93	5.779	-3.849	1.9952	2.1882
Chlorobenzene	2.64	3.427	-0.896	2.369	2.4644

(Continued)

**TABLE 18.7** Key Air, Water, and Organic Tissue Partitioning Coefficients for Hazardous Air Pollutants Calculated from Quantitative Structural Activity Relationships (QSAR) and from Published Estimates. Note: Table shows organic compounds only. The hazardous air pollutants also include metals and their compounds and asbestos. Conditions assumed to be 25° C and 1 atmos.—cont'd

Chemical Name	Log $K_{ow}$ from QSAR	Log $K_{oa}$ from QSAR	Log $K_{AW}$	Log $K_{OC}$ from QSAR	Log $K_{OC}$ Estimated from $K_{ow}$
Chlorobenzilate	3.99	9.265	-5.529	3.1872	3.0699
Chloroform	1.52	2.401	-0.824	1.5027	1.7094
Chloromethyl methyl ether	0.32	2.226	-1.906	0.7261	1.0115
Chloroprene	2.53	2.169	0.361	1.7832	2.1954
Cresols/cresylic acid (isomers and mixture)	2.06	6.657	-4.388	2.4777	2.165
<i>o</i> -Cresol	2.06	6.657	-4.309	2.4865	2.1706
<i>m</i> -Cresol	2.06	6.657	-4.456	2.4777	2.1761
<i>p</i> -Cresol	2.06	6.657	-4.388	2.4777	2.165
Cumene	3.45	3.817	-0.328	2.8438	3.1761
2,4-D, salts and esters	2.62	9.044	-5.839	1.4717	1.7659
DDE	6	8.842	-2.769	5.0701	5.6496
Diazomethane	2	1.861	0.139	1.1211	1.7354
Dibenzofurans	4.05	6.825	-2.775	3.9619	3.5146
1,2-Dibromo-3-chloropropane	2.68	4.285	-2.221	2.0636	2.5686
Dibutylphthalate	4.61	8.912	-4.131	3.0635	3.283
1,4-Dichlorobenzene( <i>p</i> )	3.28	4.197	-1.006	2.5743	2.9852
3,3-Dichlorobenzidene	3.21	12.145	-8.935	3.5038	2.8234
Dichloroethyl ether (Bis(2-chloroethyl)ether)	1.56	3.672	-3.158	1.508	1.548
1,3-Dichloropropene	2.29	2.289	-0.838	1.8583	1.7614
Dichlorvos	0.6	5.055	-4.63	1.7321	1.8194
Diethanolamine	-1.71	7.085	-8.801	-0.6817	-0.7323
<i>N,N</i> -Diethyl aniline ( <i>N,N</i> -dimethylaniline)	2.17	4.625	-2.634	1.8958	2.1377
Diethyl sulfate	1.14	4.867	-3.6	1.4502	1.7171
3,3-Dimethoxybenzidine	2.08	13.211	-11.131	2.7066	1.9949
Dimethyl aminoazobenzene	4.29	9.309	-5.019	3.3071	3.8243
3,3'-Dimethyl benzidine	3.02	11.61	-8.59	3.5038	2.1762
Dimethyl carbamoyl chloride	-0.72	3.809	-4.529	-0.0527	0.254
Dimethyl formamide	-0.93	4.59	-5.52	-0.247	0.0936
1,1-Dimethyl hydrazine	-1.19	4.356	-5.546	1.0773	0.2233
Dimethyl phthalate	1.66	6.698	-5.094	1.4996	1.6789
Dimethyl sulfate	0.16	4.133	-3.786	0.9289	1.175
4,6-Dinitro- <i>o</i> -cresol, and salts	2.27	8.174	-4.242	2.8776	2.7083
2,4-Dinitrophenol	1.73	7.678	-5.454	2.6635	2.4538
2,4-Dinitrotoluene	2.18	7.602	-5.656	2.7601	2.4585
1,4-Dioxane (1,4-diethyleneoxide)	-0.32	3.297	-3.707	0.4205	0.5946

**TABLE 18.7** Key Air, Water, and Organic Tissue Partitioning Coefficients for Hazardous Air Pollutants Calculated from Quantitative Structural Activity Relationships (QSAR) and from Published Estimates. Note: Table shows organic compounds only. The hazardous air pollutants also include metals and their compounds and asbestos. Conditions assumed to be 25° C and 1 atm.—cont'd

Chemical Name	Log $K_{ow}$ from QSAR	Log $K_{oa}$ from QSAR	Log $K_{AW}$	Log $K_{OC}$ from QSAR	Log $K_{OC}$ Estimated from $K_{ow}$
1,2-Diphenylhydrazine	3.06	9.806	-4.709	3.1775	2.5081
Epichlorohydrin (l-chloro-2,3-epoxypropane)	0.63	3.269	-2.906	0.9959	1.0834
1,2-Epoxybutane	0.86	2.922	-2.133	0.9959	1.3102
Ethyl acrylate	1.22	3.519	-1.858	1.0273	1.5896
Ethyl benzene	3.03	3.521	-0.492	2.6495	2.7335
Ethyl carbamate (urethane)	-0.02	5.648	-5.58	1.0837	0.7596
Ethyl chloride (chloroethane)	1.58	1.931	-0.343	1.337	1.2407
Ethylene dibromide (dibromoethane)	2.01	3.285	-1.576	1.5977	1.7007
Ethylene dichloride (1,2-dichloroethane)	1.83	2.136	-1.317	1.5977	1.2841
Ethylene glycol	-1.2	4.071	-5.61	-1.0381	-0.65
Ethylene imine (aziridine)	-0.28	3.243	-3.306	0.9563	0.7266
Ethylene oxide	-0.05	2.259	-2.218	0.5102	0.6686
Ethylene thiourea	-0.49	4.372	-4.862	1.1128	0.8169
Ethyldene dichloride (1,1-dichloroethane)	1.76	2.066	-0.639	1.5027	1.5531
Formaldehyde	0.35	2.77	-4.861	-0.4836	0.8894
Heptachlor	5.86	8.003	-1.92	4.6155	4.747
Hexachlorobenzene	5.86	7.298	-1.158	3.792	4.2389
Hexachlorobutadiene	4.72	5.075	-0.376	2.9269	4.1482
Hexachlorocyclopentadiene	4.63	5.694	0.043	3.1473	4.3738
Hexachloroethane	4.03	4.797	-0.799	2.294	3.5927
Hexamethylene-1,6-diisocyanate	3.2	5.907	-2.707	3.6829	2.7769
Hexamethylphosphoramide	-0.22	9.315	-6.087	0.3474	1.0526
Hexane	3.29	1.445	1.867	2.119	3.3844
Hydrazine	-1.47	4.76	-6.23	1.1211	-1.797
Hydrochloric acid	0.54	1.04	-0.5	1.1211	0.4683
Hydrogen fluoride (hydrofluoric acid)	0.23	1.181	-0.951	1.1211	0.1992
Hydrogen sulfide (see modification)	0.23	0.679	-0.449	1.1211	-1.1981
Hydroquinone	1.03	9.653	-8.714	2.3811	1.5851
Isophorone	2.62	5.188	-3.566	1.8139	2.061
Lindane (all isomers)	4.26	None	None	3.4482	3.5927
Maleic anhydride	1.62	5.414	-3.794	-0.8957	1.3626
Methanol	-0.63	3.128	-3.73	-0.1968	0.0877
Methoxychlor	5.67	11.069	-5.081	4.4296	3.8468
Methyl bromide (bromomethane)	1.18	1.64	-0.523	1.1211	1.0324
Methyl chloride (chloromethane)	1.09	1.565	-0.443	1.1211	0.7894

(Continued)

**TABLE 18.7** Key Air, Water, and Organic Tissue Partitioning Coefficients for Hazardous Air Pollutants Calculated from Quantitative Structural Activity Relationships (QSAR) and from Published Estimates. Note: Table shows organic compounds only. The hazardous air pollutants also include metals and their compounds and asbestos. Conditions assumed to be 25° C and 1 atmos.—cont'd

Chemical Name	Log $K_{ow}$ from QSAR	Log $K_{oa}$ from QSAR	Log $K_{AW}$	Log $K_{OC}$ from QSAR	Log $K_{OC}$ Estimated from $K_{ow}$
Methyl chloroform (1,1,1-trichloroethane)	2.68	3.438	-0.153	1.6424	2.1607
Methyl ethyl ketone (2-butanone) (see modification)	0.26	2.83	-2.633	0.6542	1.2811
Methyl hydrazine	-1	4.889	-5.889	1.1243	0.3225
Methyl iodide (iodomethane)	1.59	2.238	-0.667	1.1211	1.3101
Methyl isobutyl ketone (hexone)	1.16	3.484	-2.249	1.1003	1.8453
Methyl isocyanate	0.79	2.212	-1.422	1.5977	0.6852
Methyl methacrylate	1.28	3.507	-1.885	0.961	1.6228
Methyl tert butyl ether	1.43	2.513	-1.62	1.0631	1.3544
4,4-Methylene bis(2-chloroaniline)	3.47	12.341	-8.871	3.7557	3.0446
Methylene chloride (dichloromethane)	1.34	1.768	-0.877	1.337	1.0845
Methylene diphenyl diisocyanate (MDI)	5.22	9.657	-4.437	5.4548	4.53
4,4'-Methylenedianiline	2.18	10.791	-8.611	3.3275	1.7614
Naphthalene	3.17	4.837	-1.745	3.1887	2.8637
Nitrobenzene	1.81	4.87	-3.008	2.3549	2.1675
4-Nitrobiphenyl	3.57	7.746	-4.176	3.9012	3.2571
4-Nitrophenol	1.91	8.954	-7.77	2.4636	2.3675
2-Nitropropane	0.87	3.388	-2.313	1.4886	1.6586
<i>N</i> -Nitroso- <i>N</i> -methylurea	-0.52	7.872	-8.392	1.0414	0.8765
<i>N</i> -Nitrosodimethylamine	-0.64	3.435	-4.128	1.3577	0.5662
<i>N</i> -Nitrosomorpholine	-0.43	5.809	-5.999	1.3524	0.5475
Parathion	3.73	8.647	-4.914	3.3842	3.1709
Pentachloronitrobenzene (quintobenzene)	5.03	8.742	-2.743	3.7779	3.8551
Pentachlorophenol	4.74	10.032	-5.999	3.6954	4.0684
Phenol	1.51	6.149	-4.866	2.2724	1.8995
<i>p</i> -Phenylenediamine	-0.39	7.17	-7.56	1.5293	0.7159
Phosgene	-0.71	-0.272	-0.166	-0.102	0.3031
Phosphine	-0.27	-0.269	-0.001	1.1211	-0.2347
Phosphorus	-0.27	-0.269	-0.001	1.1211	-0.2347
Phthalic anhydride	2.07	5.656	-6.176	0.1469	1.3515
Polychlorinated biphenyls (aroclors)	7.62	10.173	-2.553	5.3208	5.1682
1,3-Propane sultone	-0.28	3.736	-4.016	0.9737	-0.9317
Beta-propiolactone	-0.8	1.7	-2.5	0.5508	0.417
Propionaldehyde	0.33	2.764	-2.523	-0.007	1.0222
Propoxur (baygon)	1.9	8.763	-7.233	1.7778	1.7256
Propylene dichloride (1,2-dichloropropane)	2.25	2.432	-0.938	1.7832	1.718

**TABLE 18.7** Key Air, Water, and Organic Tissue Partitioning Coefficients for Hazardous Air Pollutants Calculated from Quantitative Structural Activity Relationships (QSAR) and from Published Estimates. Note: Table shows organic compounds only. The hazardous air pollutants also include metals and their compounds and asbestos. Conditions assumed to be 25° C and 1 atm.—cont'd

Chemical Name	Log $K_{ow}$ from QSAR	Log $K_{oa}$ from QSAR	Log $K_{AW}$	Log $K_{OC}$ from QSAR	Log $K_{OC}$ Estimated from $K_{ow}$
Propylene oxide	0.37	2.554	-2.546	0.7155	0.8511
1,2-Propylenimine (2-Methyl aziridine)	0.13	3.53	-3.388	1.1616	0.9534
Quinoline	2.14	6.691	-4.166	3.1887	1.7614
Quinone	0.25	7.552	-1.708	1.6148	1.9355
Styrene	2.89	3.838	-0.949	2.6495	2.5599
Styrene oxide	1.59	4.992	-3.19	2.0565	1.725
2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin	6.92	10.761	-2.689	5.3964	4.8308
1,1,2,2-Tetrachloroethane	2.19	3.399	-1.824	1.9775	2.0739
Tetrachloroethylene (perchloroethylene)	2.97	3.141	-0.14	1.9775	2.9505
Titanium tetrachloride	1.47	None	None	1.6424	1.2754
Toluene	2.54	3.154	-0.566	2.369	2.369
2,4-Toluene diamine	0.16	7.677	-7.517	1.7434	0.9593
2,4-Toluene diisocyanate	3.74	7.083	-3.343	3.8706	3.2455
<i>o</i> -Toluidine	1.62	5.686	-4.092	2.0606	1.6336
Toxaphene (chlorinated camphene)	6.75	9.556	-2.806	4.8178	5.8579
1,2,4-Trichlorobenzene	3.93	4.978	-1.236	3.1322	3.2931
1,1,2-Trichloroethane	2.01	2.768	-1.473	1.7832	1.6399
Trichloroethylene	2.47	2.497	-0.395	1.7832	2.0999
2,4,5-Trichlorophenol	3.45	8.481	-4.179	3.2497	3.294
2,4,6-Trichlorophenol	3.45	8.481	-3.973	3.2497	3.2774
Triethylamine	1.51	3.967	-2.215	1.7059	1.6618
Trifluralin	5.31	7.372	-2.376	4.2147	4.2518
2,2,4-Trimethylpentane	4.09	2	2.094	2.3808	3.5493
Vinyl acetate	0.73	2.05	-1.68	0.7469	1.2633
Vinyl bromide	1.52	1.819	-0.299	1.337	1.3622
Vinyl chloride	1.62	1.361	0.056	1.337	1.4056
Vinylidene chloride (1,1-dichloroethylene)	2.12	2.005	0.028	1.5027	1.8482
Xylenes (isomers and mixture)	3.09	3.662	-0.532	2.5743	2.7769
<i>o</i> -Xylenes	3.09	3.662	-0.674	2.5831	3.7422
<i>m</i> -Xylenes	3.09	3.662	-0.532	2.5743	2.7769
<i>p</i> -Xylenes	3.09	3.662	-0.55	2.5743	2.7335

release, behavior in environmental compartments, and movement among compartments. These same physical and chemical processes take place within an organism after uptake. The importance of the factors can be very different within the organism. For

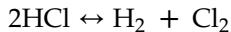
example, the degradation or activation of a pollutant may be much faster in the presence of organic catalysts, i.e. enzymes.

The reaction rates and equilibria differ, as do residence times and half-lives of chemical processes.

However, the laws of thermodynamics and motion apply at every level of interest to air pollution, from cells to the planet.

## QUESTIONS

- Describe two conditions that would shift the following reaction to the kinetics region:



- Why is it more appropriate to refer to equilibrium conditions in the atmosphere as being in "dynamic equilibrium" rather than simply in "equilibrium"?
- Give an example of an air pollution scenario for each of the four sorption mechanisms.
- Identify a chemical compound that has an affinity for particle in both air and water. Support your choice.
- Identify a chemical compound that has a high affinity for atmospheric transport in its vapor phase. Support your choice.
- Identify a chemical compound that is likely to be dissolved in water, so is more likely to be transported as an aerosol in the atmosphere than in its vapor phase. Support your choice.
- Why are log values used so often for partitioning coefficients?
- Consider the choice of octanol to represent the lipophilic component of  $K_{ow}$ . Why, for example, would it be used rather than a more hydrophobic halogenated organic compound, like hexachlorobenzene?
- What happens to a compound's  $K_{ow}$  value with increasing temperature?
- At pH = 7 and 25 °C, the concentration of compound A is found to be 15 µg l<sup>-1</sup> sorbed by the solid phase and 0.015 µg l<sup>-1</sup> and the concentration of compound B is found to be 150 µg kg<sup>-1</sup> sorbed by the solid phase and 250 µg kg<sup>-1</sup>. What can you say about the sorption partitioning of these two compounds? What would help this statement to become more generalized?
- An aerosol sample is analyzed and detects two organic compounds, one with  $\log K_D = -1.71 \text{ kg}^{-1}$  and one with  $\log K_D = 2.51 \text{ kg}^{-1}$ . The aerosol has a weight fraction of organic carbon equal to 0.014. What are the expected  $\log K_{OC}$  values for these two compounds? Which chemical has a stronger affinity for the organic fraction of a particle? Explain.
- Compare Henry's law to Raoult's law. How do they differ?
- A laboratory synthesizes air for an experiment in a 750 torr hood. It consists of 78 mol N<sub>2</sub>, 20 mol O<sub>2</sub> and 2 mol CO<sub>2</sub>. What is the partial pressure of the molecular oxygen?

- The above experiment requires 2500 l of the synthesized air need to be produced and the hood temperature is 30 °C, how many moles of molecular oxygen are needed?
  - Why does the calculation of  $K_{AW}$  exclude the sorbed and bound fraction of a pollutant?
  - Explain the difference between A and B in Figure 18.14. Which is more likely to apply to hydrophobic compound? Which is more likely to apply to a short-chain alcohol? Which is more likely to apply to a long-chain alcohol, like octanol? What is the difference between this partitioning and that for  $K_{AW}$ ?
  - The Henry's law constant is often used as an indicator of fugacity. Consider the definition of fugacity and under which conditions  $K_H$  may not be a good indicator.
  - The atmospheric concentration of atrazine is measured at 76 ng m<sup>-3</sup>. Find the partial pressure ( $p_a$ ) of atrazine in air at 27 °C? Is this concentration at equilibrium? (Molar mass of atrazine ≈ 216 g mol<sup>-1</sup>). Assume  $p_a = RT(n_{zA}/V_A) = RT(M_{zA}/m_z/V_A) = RTC_{zA}/MW_z$ .
- Where,
- $p_a$  = partial pressure of organic compound z (atm),  
 $R$  = gas constant (0.0821 l atm mol<sup>-1</sup> K<sup>-1</sup>),  
 $n_{zA}$  = number of moles of compound z in air,  
 $T$  = ambient temperature (K),  
 $M_{zA}$  = mass of compound z in given volume of air (g),  
 $m_z$  = molar mass of compound z (g mol<sup>-1</sup>),  
 $V_A$  = volume of air (l), and  
 $C_{zA}$  = concentration of compound z in air (g l<sup>-1</sup>).
- DDT and atrazine have very low vapor pressures ( $P^0 = 1.3 \times 10^{-10}$  atm and  $1.3 \times 10^{-10}$  atm, respectively, at 25 °C). However, atrazine's  $K_H$  is nearly three orders of magnitude lower than DDT's  $K_H$ . Explain why.
  - Download the Canadian Centre for Environmental Modelling and Chemistry's AirWater Model at: <http://www.trentu.ca/academic/aminss/envmodel/models/AW2D.html>. Using the default settings for the test chemical, set the total concentrations of the test chemical at 250 ng l<sup>-1</sup> in water and 33 ng m<sup>-3</sup> in air. Select the diagram. What percentage of the chemical would be sorbed to aerosols in the atmosphere? Which compartment has the highest fugacity?
  - Using the same model as above, at the same air and water concentrations, change the chemical properties from the default setting to 25 °C and to those of DDT: MW = 354.49, melting point = 109 °C,  $\log K_{ow} = 6.91$ , vapor pressure =  $2.5 \times 10^{-5}$  Pa, and aqueous solubility = 0.025 mg l<sup>-1</sup>. How does the diagram change? What would happen if the PM

- concentration were increased 10-fold from the default setting (raised to  $1000 \mu\text{g m}^{-3}$ )? What happens if the density of the airborne particles decreases from the default setting by 10-fold (from 2000 to  $200 \text{ kg m}^{-3}$ )?
22. Using the same model and concentrations as above, change the chemical properties from the default setting to  $20^\circ\text{C}$  and to those of the solvent trichloroethylene: MW = 131.38, melting point =  $-84.8^\circ\text{C}$ ,  $\log K_{\text{ow}} = 2.53$ , vapor pressure = 7706 Pa, and aqueous solubility =  $1100 \text{ mg l}^{-1}$ . How does the diagram change?
23. From these model runs, what seem to be the most important drivers of fugacity? What other variables and parameters would help increase the usefulness of fate and transport models?
24. Find a chemical compound that you know has been emitted in the atmosphere recently. Find published physical and chemical properties of this compound and run the AirWater Model for this compound at  $250 \text{ ng l}^{-1}$  in water and  $33 \text{ ng m}^{-3}$  in air. Change these ratios, as well as the environmental conditions to represent realistic scenarios. Describe your findings.
25. The fugacity capacity varies for different substrates. Explain why, assuming ideal gas conditions, that the fugacity capacity for a compound in air is the inverse of  $RT$ .
26. The published  $K_H$  for atrazine is  $6.2 \times 10^{-6} \text{ atm l mol}^{-1}$  at  $25^\circ\text{C}$ . Estimate its  $K_{\text{AW}}$  at  $25^\circ\text{C}$ .
27. Using the information above, will DDT be more or less likely to be transported atmospherically than atrazine? Which will be more likely to be transported in water? What other factors besides this partitioning need to be considered to give a more complete answer?
28. Bioconcentration and bioaccumulation tend to increase with increasing  $K_{\text{ow}}$  but the rates drop with very high values, e.g.  $\log K_{\text{ow}} > 7$ . Explain the reason(s) for this.
29. Mixtures are more representative of actual conditions than individual substances. What are some of the difficulties of calculating partitioning coefficients for substances in mixtures?
30. Give reasons that the atmospheric half-life of many organic compounds is proportional to  $\log K_{\text{oa}}$  and  $\log K_{\text{ow}}$ . What factors could make for variance from this proportionality?
31. Why might the  $\log K_{\text{OC}}$  values in a QSAR be different from those estimated from the  $K_{\text{ow}}$  values (e.g. 4,4'-methylenedianiline, *p*-phenylenediamine, phosphorus, propionaldehyde, and quinoline)?
32. Review the equations in Chapter 8 to estimate exposures to chemical compounds by inhaling vapors and aerosols. Compare these to the equations in this chapter. How can partitioning be incorporated into exposure estimates?
33. Give reasons why QSARs are often limited in partitioning information for metals.

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# Temporal Aspects of Air Pollution

## 19.1 TIME AND AIR POLLUTION

Time is a key aspect of air pollution. The focus of Part II is the harm that air pollutants can cause in human populations, in ecosystems, and to public welfare. This aspect of harm has to do with the severity and spatial extent of injury. Time certainly is a part of this harm. The longer the exposure, the greater will be the injury.

Indeed, many equations important to air pollution include a time factor, beginning with the first law of thermodynamics; i.e. the rate of change of mass of an air pollutant (i.e. change in mass with respect to time) within a control volume must equal the rate of the mass transported into the control volume minus the rate of mass transported out of the control volume:

$$\frac{d[A]}{dt} = -v \cdot \frac{d[A]}{dx} + \frac{d}{dx} \left( \Gamma \cdot \frac{d[A]}{dx} \right) \pm r \quad (19.1)$$

where,  $v$  = fluid velocity;  $\Gamma$  = a rate constant specific to the environmental medium;  $d[A]/dx$  = the concentration gradient of chemical  $A$ ; and  $r$  = internal sinks and sources within the control volume. The  $r$  term is usually considered to be a loss term, i.e. the mass of the compound exiting the control volume is decreased by the amount of reactivity. Thus, even the loss term includes a time function, i.e. the reaction rate (recall that this is shown graphically in Figure 8.4 in Chapter 8).

The hazardous aspects of an air pollutant include temporal factors. For example, animal studies are part of the process to construct and interpret the dose-response curves discussed in Chapter 7. A compound that causes cancer or noncancer outcomes in mammals, such as laboratory rats, would be suspected of doing the same in humans. However, models must be employed to extrapolate the rat-to-human relationship. Put simplistically, the process must compensate for the time difference (e.g. 6-month exposure to an animal *versus* lifetime exposure to a human); the animal dose must usually be much higher than the daily dose of the human for a chronic disease. That is, time is compensated mathematically by using dose.

The most basic way to express exposure to an air pollutant must account for time. Chapter 8 introduced the simplest quantitative expression of exposure:

$$E = Dt^{-1} \quad (19.2)$$

where,  $E$  = human exposure during the time period,  $D$  = mass of pollutant per body mass (dose), and  $t$  = exposure time.

In other words, dose is meaningless without factoring in time, demonstrated by the average daily dose (ADD), which averages exposures and doses during exposure duration periods. The ADD is ascertained by averaging an intake dose according to body weight and an averaging time:

$$ADD = \frac{I}{W \times t_{\text{averaging}}} \quad (19.3)$$

where,  $I$  is the intake dose;  $W$  is the body weight (kilograms); and  $t_{\text{averaging}}$  is the averaging time (days). For inhalation,  $I$  equals the concentration of the air pollutant times the inhalation rate times the exposure duration.

Thus, the temporal aspects of air pollution include exposure time and duration, reaction rates, and even partitioning within the environment, such as the time over which pollutants remain in the atmosphere, water, soil, sediment, and biota. These times are usually expressed as burdens and residence times, for which the most common metric is the half-life ( $t_{1/2}$ ), e.g. atmospheric  $t_{1/2}$ , soil  $t_{1/2}$ , or tissue  $t_{1/2}$ .

Another temporal aspect of air pollution is the resilience of the receptor or the reversibility of an impact (see Figures 4.2 and 4.3 in Chapter 4). The ability of receptors to withstand insults from air pollution drives decisions about how to address the pollution. For example, if the habitat of an endangered species is particularly vulnerable to deposition of acid aerosols leading to irreversible damage, the proper response would be to find ways to prevent the acidic deposition. However, if the habitat is vulnerable, but the system is able to recover in a few days, the response would likely be less aggressive. This is part of the thinking behind applying

“precaution” rather than “risk-based evidence” for potentially irreversible problems. If data indicate that an air pollutant’s damage will require years or decades to recover, then the precautionary approach would be to eliminate the source of the problem, even with lower thresholds of certainty that would be required under an evidence-based decision (e.g. for problems in the upper right-hand quadrant of Figure 4.2 in Chapter 4).

## 19.2 PERSISTENCE

The main concern about air pollution is its potential to cause harm to living things and their environments. The principal type of harm in organisms is toxicity. The pollutant is the toxic agent and the organism is the receptor of the toxicity. For the harm to result, then, the agent must be toxic when it reaches the receptor, or at least become toxic after it is taken up by the receptor. Thus, three of the most important characteristics of an air pollutant are its persistence, its potential to accumulate in organisms, and its toxicity. Indeed, the most worrisome pollutants are known as persistent, bioaccumulative, and toxic (PBT) substances.

Persistence is related to the partitioning coefficients discussed in Chapter 18. As mentioned, the environmental half-life ( $t_{1/2}$ ) is a common way to express a chemical substance’s persistence, i.e. the amount of time it takes to degrade one-half of the mass of a compound. The relationship between two partitioning coefficients and persistence is demonstrated in Table 19.1.

TABLE 19.1 Atmospheric Persistence Compared to Octanol–Water and Henry’s Law Coefficient

Compound	Half-Life (Days)	$\log K_{ow}$	$\log K_H$
Benzene	7.7	2.1	-0.6
Chloroform	360	1.97	-0.7
DDT	50	6.5	-2.8
Ethyl benzene	1.4	3.14	0.37
Formaldehyde	1.6	0.35	-5.0
Hexachlorobenzene	708	5.5	-3.5
Methyl chloride	470	0.94	-0.44
Methylene chloride	150	1.26	-0.9
PCBs	40	6.4	-1.8
1,1,1 Trichloroethane	718	2.47	0.77

PCBs, polychlorinated biphenyls.

Source: Toro D, Hellweger F. Long-range transport and deposition: the role of Henry’s law constant. Final report, International Council of Chemical Associations. 1999.

Thus,  $t_{1/2}$  is a metric of persistence, i.e. the larger the  $t_{1/2}$ , the more persistent the compound. Persistence is both an intrinsic and extrinsic property of a substance. It is dependent upon the molecular structure of the compound, such as the presence of aromatic rings, certain functional groups, isomeric structures, and especially the number and types of substitutions of hydrogen atoms with halogens (specifically chlorines and bromines).

Persistence is directly related to bioconcentration. Generally, the larger the  $t_{1/2}$  of a substance in a compartment, the larger the bioconcentration factor (BCF). For example, the lower  $t_{1/2}$  unsubstituted aliphatic compounds also often have lower BCFs, e.g. acrolein’s BCF is half that of the chlorinated aliphatic compound chloroform; and is four orders of magnitude lower than the BCF of the chlorinated aromatic compound, 2,3,7,8-tetrachlorodibenzo-*para*-dioxin.

Persistence potential also depends upon the contaminant’s relationship to its media. Compound  $t_{1/2}$  values are commonly reported for each compartment, so it is possible for a compound to be highly persistent in one medium, yet relatively reactive in another. Persistence varies within each compartment and depends on many factors, such as temperature, pH, intensity of sunlight, presence and diversity of microbes, and chemistry (e.g. reactivity of the pollutant, as well as the concentrations of oxidizing agents, free radicals, and catalysts).

The half-lives and rate constants ( $k$ ) discussed in Chapter 17 represent identically ordered decay processes, and are inversely related to one another. For example, first-order decay can be expressed in terms of concentration *versus* time, concentration *versus* distance, and as abiotic (e.g. photochemical) and biotic (e.g. microbial) degradation rates. The relationships between  $t_{1/2}$  and  $k$  can be stated mathematically. The first-order rates are

$$k = \frac{0.693}{t_{1/2}} \quad (19.4)$$

and

$$t_{1/2} = \frac{0.693}{k} \quad (19.5)$$

Thus, a half-life of 2 years is the same as a first-order rate constant of 0.35 per year, and a half-life of 10 years is the same as a first-order rate constant of 0.0693 (i.e. a slower rate constant is inversely related to a longer half-life). This is an important consideration in estimating the rate at which a contaminant plume will be attenuated, and is commonly used in groundwater studies. Atmospheric plumes move at rates orders of magnitude faster

than groundwater plumes, so any appreciable degradation in air requires much shorter half-lives (i.e. much less persistence).

Note that Table 19.1 contains no metals or metalloids, but only organic compounds. Obviously, outside of nuclear fission or fusion, elements do not undergo degradation. For example, the degradation of the listed organic compounds does not involve destruction of any element. The carbon, hydrogen, oxygen, and other atoms remain intact. However, in degradation, bonds are broken or added, elements are substituted and new compounds produced. This always involves changes in oxidation states. Thus, even though a metal is an element that will not be changed by degradation (i.e. its elemental half-life is theoretically infinite), particular metallic compounds will indeed change, just as the particular carbon compounds change in the organic degradation. Thus, even for inherently toxic compounds like mercury,  $t_{1/2}$  is a useful concept (e.g. to state the atmospheric conditions under which the methylmercury compounds degrade to elemental Hg<sup>0</sup> and simpler inorganic compounds).

The  $t_{1/2}$  is also an important part of endogenous kinetics within an organism, including adsorption, distribution, metabolism, and excretion of substances. The  $t_{1/2}$  of a compound is indirectly proportional to that compound's body burden. A large  $t_{1/2}$  increases the likelihood of accumulation over time. Thus, if substance A's  $t_{1/2} = 1$  day, and substance B's  $t_{1/2} = 100$  days, substance B would be expected to show a much larger body burden than substance A. A substance's  $t_{1/2}$  also indicates which aspects of the toxicokinetics are most important. For example, <15% of inorganic Hg is absorbed by the human gastrointestinal (GI) tract,<sup>1</sup> whereas about 95% of methylated forms of Hg are absorbed.<sup>2</sup> Thus, at the same intake rate, the actual uptake is more than six times larger for methylmercury than for inorganic Hg compounds.

Concentration *versus* time constants are known as point decay rates ( $k_{\text{point}}$ ), which are derived from a single concentration value *versus* time plot, and can be used to estimate the length of time that a plume will persist. Bulk attenuation rates ( $k$ ) are derived from concentration *versus* distance plots, and are used to see if the contaminant plume is expanding. Thus, they are most useful for groundwater contamination, but can be applied to other environmental media.

Substances that remain in the environment long after their release and deposition are more likely to continue to cause problems or to be a threat to environmental quality. The US Environmental Protection Agency considers a compound to be persistent if it has a  $t_{1/2}$  in water, soil, or sediment of greater than 60 days, and very persistent if the  $t_{1/2}$  is greater than 180 days. In air, the compound is considered persistent

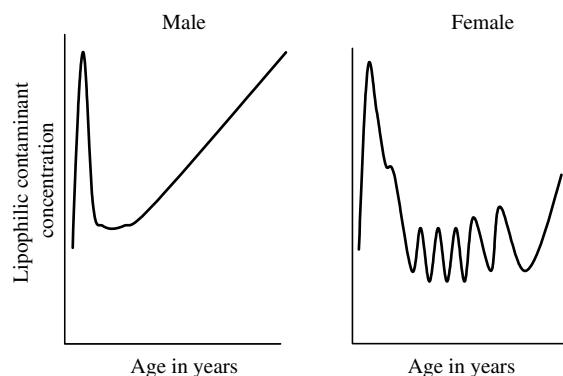
if its  $t_{1/2}$  is greater than two days. Some of the most notoriously toxic chemicals are also very persistent, including polychlorinated biphenyls (PCBs) and halogenated dioxins.

### 19.2.1 Persistent, Bioaccumulative, and Toxic Substances

The worst combination of factors occurs when a compound is persistent in the environment, builds up in organic tissues, and is toxic. As mentioned, these compounds are referred to as PBTs. Each of these factors, i.e. the "P", the "B", and the "T", is actually a function of both the contaminating agent (e.g. air pollutant) and the conditions of the environment wherein the agent resides. Recently, the United Nations Environmental Programme (UNEP) reported the concentrations of the persistent and toxic compounds. Each region of the world was evaluated for the presence of these compounds.

The sources of PBTs are widely varied. Many are intentionally manufactured to serve some public need, such as the control of pests that destroy food and spread disease. Other PBTs are generated as unintended by-products, such as the products of incomplete combustion. In either case, measures and engineering controls to prevent PBT releases are preferable to having to deal with them after they have found their way into the various environmental compartments. One of the principal reasons for the concern about the plethora of organic chemicals and heavy metals in the environment has been the connection between exposures to these substances and the occurrence of cancer and other chronic diseases. Intrinsic properties of compounds render them more or less toxic. In addition, physical and chemical properties determine whether the compounds will resist degradation and persist for long time periods and build up in organisms. PBTs are composed of myriad compounds (see Discussion Box: Long-range Atmospheric Transport and the Inuit in Chapter 12).

The concept of persistence elucidates the notion of trade-offs that frequently must be made when responding to environmental insults. It also underscores the importance of sound science and reliable data. For example, the pesticide DDT [1,1,1-trichloro-2,2-bis-(4-chlorophenyl)-ethane (C<sub>14</sub>H<sub>9</sub>Cl<sub>5</sub>)] is relatively insoluble in water (1.2–5.5 mg l<sup>-1</sup> at 25 °C) and is not very volatile (vapor pressure: 0.02 × 10<sup>-5</sup> mmHg at 25 °C).<sup>3</sup> The water solubility and vapor pressures alone may erroneously indicate that people and wildlife are not likely to be exposed in the air or water. However, the compound is highly persistent in soils, with a  $t_{1/2}$  of about 1.1–3.4 years, so it may still end up in drinking water in the form of suspended particles or in the air



**FIGURE 19.1** Prototypical body burdens of male and female blue whales (*Balaenoptera musculus*). Whalenet. Wheelock College. Contaminant analysis of organochlorines in blubber biopsies in the St. Lawrence. <http://whale.wheelock.edu/bwcontaminants/welcome.html>; 2004 [accessed 31.10.13].

sorbed to fine particles. DDT also exhibits high BCFs, i.e. approximately 50,000 for fish and 500,000 for bivalves. This indicates that once organisms become exposed, they tend to increase body burdens of DDT over their lifetimes. In the environment, the parent DDT is metabolized mainly to DDD and DDE.<sup>a</sup> Each has its own PBT characteristics. Thus, the half-lives of the parent compound and all its degradation products must be known.

There is a noteworthy exception to the continuous increase in body burden of highly persistent compounds over an organism's lifetime. During gestation, there can be *in utero*, cross-placental transfer of lipophilic compounds from the fat reserves of the mother to the baby (see Figure 19.1). The initial peaks in both the male and the female whale represent contaminant off-loading via the mother's milk. Since PCBs and pesticides are typically found in fat (i.e. they are highly lipophilic) and because milk is the means by which the baby receives the necessary fat for nutrition, the neonate receives large doses of these contaminants during the weaning stage of development. When the rate of weaning diminishes, uptake by the calf declines. This is a detoxification or depuration stage during which more mass of the contaminant is excreted than is absorbed. After this, for the rest of the male's life, the persistent compound body burden increases, whereas during the birthing stages of the female, there is an oscillation

between contaminant off-loading to the calves and accumulation periods.

The physicochemical properties of a substance determine how readily it will move among the environmental compartments, i.e. to and from sediment, surface water, soil, groundwater, air, and in the food web to be taken up by biota, including humans. So, if a substance is likely to leave the water, it is not persistent in water. However, if the compound moves from water to the sediment, where it persists for long periods of time, it must be considered environmentally persistent. This is an example of the difference in "chemical persistence" and "environmental persistence".

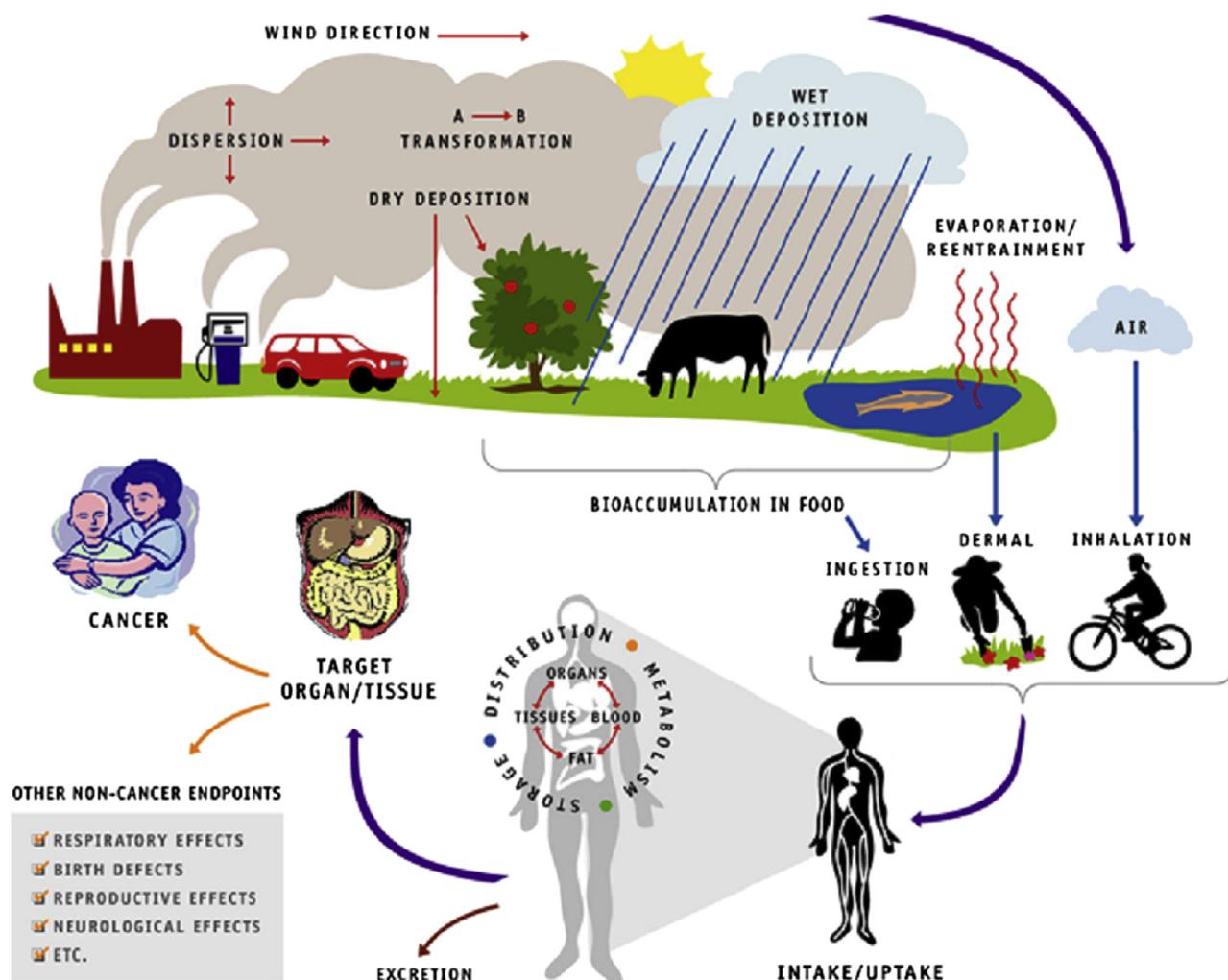
Persistence is indeed an intrinsic chemical property of a compound.<sup>b</sup> However, most environmental and biomedical scientists and engineers consider persistence to be both intrinsic and extrinsic (i.e. a function of the media, energy and mass balances, and equilibria). So, the environmental behavior of a compound must not only account for the molecular weight, functional groups, and ionic form of the compound, but also whether it is found in the air or water, and the condition of the media (e.g. pH, soil moisture, sorption potential, and microbial populations). The movement among phases and environmental compartments is known as partitioning. Many toxic compounds are semivolatile (i.e. at 20 °C and 101 kPa atmospheric pressure, vapor pressures =  $10^{-5}$  to  $10^{-2}$  kPa), under typical environmental conditions. As discussed in Chapter 18, these low vapor pressures and low aqueous solubilities translate into low fugacities, i.e. they lack a strong propensity to flee a compartment, e.g. to move from water to air.

Thus, a multipathway perspective must be employed for air pollution, with a time aspect to each pathway. After release into the environment, the deposition of air pollutants onto soil, plants, and water is followed by the uptake of the chemicals by biota, and potential exposures by organisms via contact with the contaminated soils, waters, and foods. Such a human health multipathway is shown in Figure 19.2. A multipathway analysis goes beyond the expected inhalation pathway to include other exposure pathways.

Even low  $K_H$  and  $K_{AW}$  compounds, however, can be transported long distances in the atmosphere when sorbed to particles. Fine particles can behave as colloids and stay suspended for extended periods of time,

<sup>a</sup> The two principal isomers of DDD are *p,p'*-2,2-bis(4-chlorophenyl)-1,1-dichloroethane and *o,p'*-1-(2-chlorophenyl)-1-(4-chlorophenyl)-2,2-dichloroethane. The principal isomer of DDE is *p,p'*-1,1'-(2,2-dichloroethenylidene)-bis[4-chlorobenzene].

<sup>b</sup> However, in a recent conversation, Daniel Chang, a computational chemist with the US Environmental Protection Agency, mentioned that the term "inherent" is seldom an accurate depiction of a substance. Certainly, atomic mass is an inherent property, but solubility and vapor pressure, in the strictest terms are not inherent, but highly dependent on environmental conditions. Thus, computational chemists like Dr Chang, who seek to parameterize based on first principles, are challenged to find those that are actually inherent to a substance.



**FIGURE 19.2** General overview of multisource, multipathway exposure pathways. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Chapter 9: overview of multisource multipathway risk assessment. Technical resource manual. Volume 3 – community scale assessment. Research Triangle Park (NC); 2006.

explaining in part why low  $K_H$  compounds can be found in the most remote locations relative to their sources, such as in the Arctic regions. This explains in part exposures to contaminants in the absence of a nearby source.

If the substrate has sufficient sorption sites, such as soil particles or carpet twill (see Figure 19.3), even a substance not expected to be persistent may become tightly bound and persistent. For example, once an air pollutant is transported and deposited on to highly sorbent clays and organic matter or onto carpet and other sorbent indoor surfaces, even a relatively reactive substance may become tightly bound and persistent.

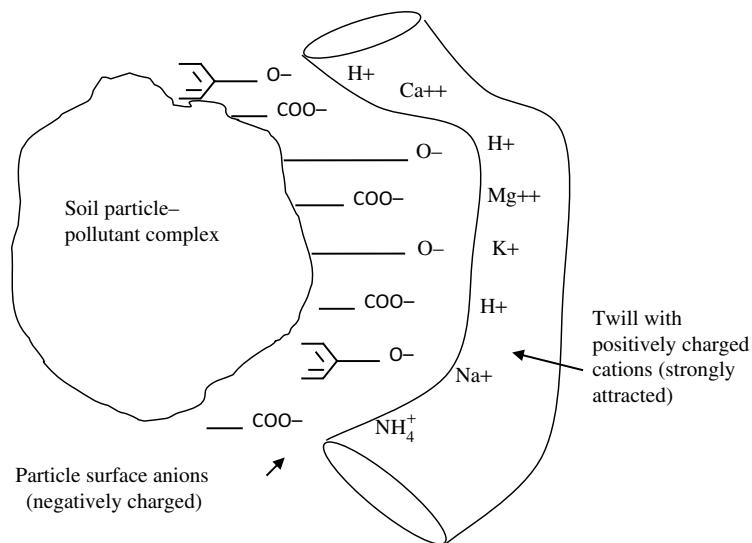
This type of substrate dependence is common in the environment and complicates  $t_{1/2}$  estimates. The properties of the compound and those of the water, soil, sediment, and other substrates determine the rate of sorption and other partitioning. Thus, care must be taken when considering the conditions under which

published atmospheric  $t_{1/2}$  values were calculated. For example, if a substance has much affinity for particulate matter in the atmosphere, its half-life may be diminished under conditions that lead to increased particle deposition. Conversely, the half-life may be increased if the compound sorbs to ultrafine particles that remain suspended longer than the compound's gas-phase  $t_{1/2}$ .

Thus, air pollution involves both chemical persistence and environmental persistence. Henry's law, solubility, vapor pressure, and sorption and other properties of a compound may provide *prima facie* indications that the compound is not persistent. However, in real-world scenarios, this may not be the case.

Indoor environments often lack conditions conducive to degradation, including less sunlight (i.e. lower photochemical degradation rates), microbial populations (i.e. lower biotic transformation rates), and moisture regimes (i.e. lower hydrolysis rates). Thus, an indoor air

**FIGURE 19.3** Negatively charged, pesticide-laden soil particle sorbed to carpet twill that contains numerous sorption sites (positively charged).

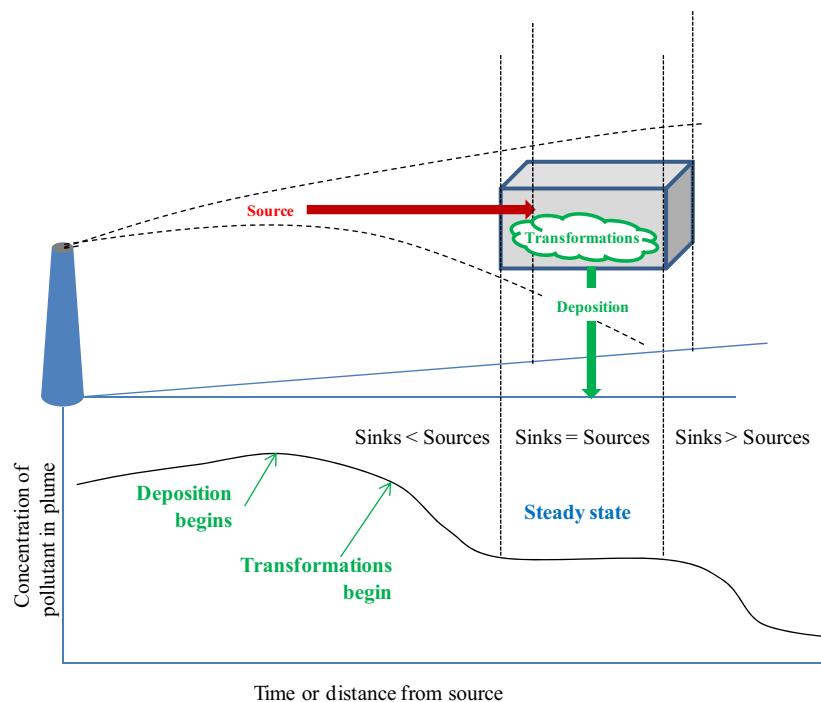


pollutant, e.g. a pesticide, which is not very persistent outdoors (e.g. in the garden) may become persistent indoors, e.g. a reactive pesticide that is tracked into a home and becomes entrapped in carpet fibers. This is important if the pesticide label's expected half-life was calculated with the assumption the product would be applied outdoors, but the product was used (or misused) indoors.

Another example of environmental *versus* inherent persistence is that of a steady state condition. For example, there may be a repository of a source of a

nonpersistent compound that leads to a continuous, persistent exposure of a neighborhood population. That is, loading of the compound into the parcel of atmosphere is equal to the deposition and degradation of the pollutant within the parcel for a specific time period. A parcel of the air mass may be viewed as a thermodynamic control volume. Once a steady state is reached, so long as the specific contaminant input (e.g. total stack releases) equals the rate of deposition and rate of transformation, then even an inherently reactive, nonpersistent compound is environmentally persistent (see Figure 19.4).

**FIGURE 19.4** Steady state period during which emissions equal rates of deposition and degradation. Sources dominate near the origin, and then steady state is reached and maintained so long as the sources and sinks are equal. Once deposition and transformation rates exceed source loading into the control volume, sinks begin to dominate, with a commensurate decline in pollutant concentration following the steady state conditions. (For color version of this figure, the reader is referred to the online version of this book.)



The situation depicted in [Figure 19.4](#) is also known as a source–sink scenario. In this case the source is the amount of contaminant exiting the stack and the sinks are the deposition and transformation processes. The steady state region exemplifies the spatiotemporal aspects of a plume.

Note that distance from the source can be determined by the rate of movement of the plume. For example, if the contaminant in the plume is moving advectively, i.e. being carried along with the air mass, at a velocity at  $1 \text{ m s}^{-1}$ , then a measurement 600 m downwind from the stack is the same as a measurement taken 600 s (10 min) after the contaminant is released. Of course, spatial measurements are constant and time-related measurements are relative, i.e. 600 m is always the same distance, whereas the plume velocity is changing continuously. However, it is often important to average time of flight for the contaminant, since the direction of wind will also change. Thus, the control volume in [Figure 19.4](#) will move with the movement of the air mass, so measurements may have to track with this movement (e.g. a stationary monitor will miss the conditions in the control volume, but a mobile monitor can be adjusted to move with the control volume if plume velocity is known). Thus, on a day with a rapidly moving air mass, the measurement would be taken farther from the source (e.g. 1200 m at  $2 \text{ m s}^{-1}$ ); and on days of a slower moving air mass the measurement would be taken nearer the source (e.g. 300 m at  $0.5 \text{ m s}^{-1}$ ).

Steady state concentration within a control volume can be expressed as

$$C_{ss} = \frac{S \times \tau}{V} \quad (19.6)$$

where,  $C_{ss}$  = steady state concentration in the control volume;  $S$  = source or sink rate (in steady state they are equal, so only one factor is needed);  $\tau$  = residence time; and  $V$  = control volume.

For example, if  $S = 1000 \mu\text{g h}^{-1}$  of benzene;  $\tau = 10 \text{ h}$ ; and  $V = 100 \text{ m}^3$ , then  $C_{ss} = (1000 \times 10)/100 = 100 \mu\text{g m}^{-3}$  in the control volume. The concentration increases with increasing  $\tau$ , i.e. the longer the time in the control volume, the greater the concentration of the air pollutant. Thus, if the residence time doubles to 20 h, the steady state concentration also doubles to  $200 \mu\text{g m}^{-3}$ . This illustrates the problem of temporal uncertainty. Overestimating the residence time can result in larger concentrations than would really occur, but underestimating the residence time would also give an incorrect estimate, e.g. that a control volume such as an urban airshed is meeting an air quality standard when it is not.

The processes within the ambient plume shown in [Figure 19.4](#) also occur in microenvironments. That is, there is infiltration into the microenvironment, as well

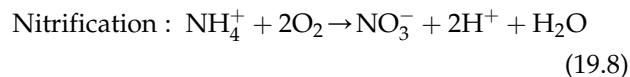
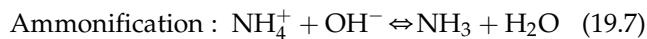
as deposition to surfaces and transformation within the microenvironment. Certainly, however, deposition does not mean the contaminant is gone. It has merely moved to another environmental compartment (e.g. atmosphere to soil in the ambient setting; air to walls and floors in the indoor microenvironment). In some cases, this either is met with new transformations (e.g. soil bacteria degrading the pollutant), or merely different routes of exposure (settled particulate matter that is ingested or contacted dermally). The lower rate of photolysis (degradation by light energy) indoors *versus* outdoors and the sorptive characteristics of the carpet twill, as well as if the pesticide molecule is sorbed to a soil particle embedded in the twill, can lead to dramatically increased environmental half-lives of certain substances. For example, ionic charge can affect the sorption, e.g. even a neutral compound can be held tightly to a substrate if it is part of an aerosol that has an abundance of negatively charged sites that increases its sorption to a substrate with positively charged sites (see [Figure 19.3](#)).

### 19.3 TEMPORAL ASPECTS OF TRANSFORMATION

The amount and form of any substance that is released into a system determines its pollution potential. Total emission data are not nearly as useful as speciation data. The total mass of nitrogen, for example, can be further quantified, not only by the gross mass of the substance entering the atmosphere, but also by the response within compartment of the atmosphere and hydrosphere. Hence the relationship between a substance's entry and its impact begin even before release.

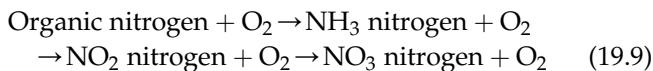
The first major division of loading of pollutants into the environment is between point sources and nonpoint sources. This is actually a distinction of convenience, used often in water, wastewater, and ecosystem discussions. For air pollutants, the distinction is often between a stationary source and a mobile source.

After and during an emission, an air pollutant or a precursor of an air pollutant will undergo change. The change depends on physical, chemical, and biological factors. For example, a nitrogen load of an ammonium compound may either be reduced (ammonification) or oxidized (nitrification).



Either of these reactions can occur abiotically, can be mediated by biota (e.g. microbes), and/or take place

within an organism. Other conditions in the stack and receiving atmosphere that affect loading include temperature, aerosols on which and in which sorption can occur, humidity, pH, and ionic strength. For example, under acidic conditions, most of the ammonia nitrogen will ionize to ammonium and under basic conditions the nonionized ammonia concentrations will increase in proportion to the ammonium. This is important since nonionized ammonia is very toxic to aquatic fauna, whereas ionized species are nutrients needed for flora and algae. After deposition, the decomposition of organic matter makes for very complex and heterogeneous reactions:



Even this is a gross oversimplification, since the oxidation and reduction depends on the types of bacteria present. For example, the  $\text{O}_2$  required for nitrification is theoretically  $4.56 \text{ mg O}_2 \text{ mg}^{-1} \text{ NH}_4^+$ , but this is an autotrophic reaction. Thus,  $\text{O}_2$  is being produced by the nitrifying bacteria, decreasing the amount needed. However, the growth rate of nitrifying microbes is far less than that of heterotrophic microbes decomposing organic wastes. Therefore, when large amounts of organic matter are being degraded, the nitrifiers' growth rate will be sharply limited by the heterotrophs, which means the rate of nitrification will commensurately be decreased.<sup>4</sup> Furthermore, these same responses to conditions exist for all other nutrients in the system, e.g. organic phosphorus will be oxidized and oxidized phosphorous species reduced, etc. Thus, the kinetics of contaminant loading into a control volume and the transformations within that control volume are quite complex.

## 19.4 BIOACCUMULATION

Another factor that affects the time that a contaminant exists is the extent to which it can be sequestered within biotic tissue. This is directly related to body burden, i.e. bioaccumulation is a type of biochemical residence time. If a substance enters an organism, its concentration may increase or decrease as a result of its inherent properties, e.g. persistence, and the biochemical processes that take place within an organism. Like other partitioning coefficients discussed in Chapter 18, such as Henry's law constants and  $K_{ow}$ , the partitioning that leads to bioaccumulation is often expressed as an equilibrium relationship between media. The two major partitioning coefficients are the BCF and bioaccumulation factor (BAF).

The BCF is an expression of the accumulation of a chemical into an organism's tissues entirely as a result of contact with the media (usually water):

$$\text{BCF} = \frac{C_{\text{organism}}}{C_{\text{media}}} \quad (19.10)$$

For example, after an air pollutant is deposited into surface waters, organisms will take up the pollutant directly from the water. If the  $\text{BCF} > 1$ , then the concentration in the organism is greater than the concentration in the medium, i.e. there is bioconcentration of the chemical.

Generally, the BCF is derived from laboratory measurements based on partition coefficients (e.g. between lipids in tissue and water), whereas BAF is based on field studies in the environment. The BAF is more comprehensive and consistent with biological organization and trophic status. Like BCF, the BAF calculation includes the uptake from the media (in this case, water), but BAF also accounts for the uptake of the chemical from the organism's food. Thus, BAF is a ratio of net uptake of a chemical from the environment by all possible routes (e.g. inhalation, ingestion, and dermal) from all sources (water, sediment, soil, air, and other organisms). The calculation is the same as that for BCF.

$$\text{BAF} = \frac{C_{\text{organism}}}{C_{\text{media}}} \quad (19.11)$$

Although the calculations for BCF and BAF are the same, more factors go into  $C_{\text{organism}}$  for BAF. Thus, a published BAF for a chemical should be based on direct contact with water, plus the accumulation up the food chain to the organism. So, if a predator species receives 0.1 mg toluene directly from the medium, and has one food that includes increases of the toluene through three successive trophic levels that provide 1 mg toluene, and another food species in a lower trophic level that provides 0.15 mg, the BAF would consider all three sources of toluene:  $0.1 + 1 + 0.15 = 1.25 \text{ mg toluene from media and food}$ .

Bioaccumulation can only occur after an exposure. Obviously, if there is no contact with the pollutant, it will not accumulate within an organism. Conversely, with increasing amounts of a pollutant in an environmental medium, the likelihood of bioaccumulation increases. However, this is not necessarily a linear relationship. Different genera of organisms readily accumulate certain compounds, but not others. Although a persistent compound often has a high potential for bioaccumulation, this is not always the case. For example, a compound that persists in the soil or water may not be easily taken up or may be efficiently metabolized and eliminated from the organism. A persistent compound, e.g. cyanide ( $\text{CN}^-$ ), may be so toxic that it destroys

animal cells to the extent that accumulation is offset. Also, trophic status and bioenergetics drive the extent of bioaccumulation. In food webs and food chains, even if an organism does bioaccumulate a chemical, but is not attractive as food for organisms in higher trophic states, these organisms will not bioaccumulate it. However, if it is attractive as a food source for another organism that happens to be a food source for that organism, then the chemical will likely accumulate. For example, a predator may not consume a first-level consumer that has accumulated a contaminant, but it may consume the predator of that first-level consumer. This is an important reason why top predators often have the highest concentrations of persistent contaminants.

Upon entering an organism a chemical compound moves and changes as a result of several processes, especially accumulation, metabolism, and excretion. All organisms share the pharmacokinetic processes of absorption, distribution, metabolism, and elimination or excretion. Bioaccumulation is a function of these processes. However, the type of chemicals able to be processed, the time that each mechanism takes, and the ultimate change to the compound after uptake vary significantly among species, or even strains of the same species. Thus bioaccumulation is a “species-dependent” factor.

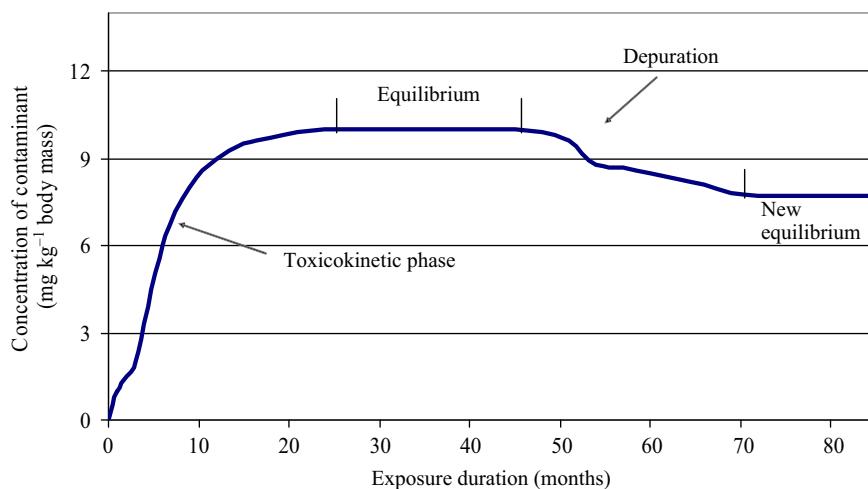
As mentioned, the mass of the chemical substance that ultimately is accumulated by an organism is known as the organism’s body burden. As shown in Figure 19.5, the pollutant uptake of a chemical can begin *in utero*, continuing throughout the toxicokinetic phase. If the rate of uptake is greater than the rate of elimination, then bioaccumulation occurs. Eventually, the accumulation reaches equilibrium with its surrounding environment. Thus, the body burden remains constant. If the concentration of the pollutant declines (e.g. treatment or with the elimination of the source) the pollutant will begin to be released from fatty tissues or other storage

sites (e.g. the liver). This process, known as depuration, will result in a reduced body burden.

Once a substance has been taken up by an organism, for an adverse effect, or any effect for that matter, to occur the substance must interact with its cells. The interaction sites may be on the cell’s surface or within a cell, such as when carcinogenic contaminant enters a cell’s nucleus and interferes with normal DNA sequencing. The contaminant may also interact within an organism’s extracellular spaces. In flora, for example, a chemical substance may interact with root cells, stomata, vascular tissue, and cuticle tissues. Animal interactive sites include skin and stomach tissue. The lung for land animals and the gills for fish are also sites that interact with contaminants that have been taken up.

If the dose-response and biological gradient relationships hold, and they usually do, the intensity of an adverse effect from exposure to an environmental contaminant must depend on the concentration of the contaminant. If a contaminant persists in an organism, it is more likely to elicit toxicity, particularly if the contaminant stays at the ultimate site of action. For example, if a neurotoxic contaminant is stored in fat reserves, but does not find its way to the central nervous system or any other nerve site, the organism will not exhibit neural dysfunction. However, once the neurotoxin is released and distributed to a nerve site, the neurotoxicity will be manifested. Thus, there may be a significant lag after initial exposure before a chemical reaches tissue that will be adversely affected. Once the contaminant finds its way to the site, e.g. a neurotoxic lead (Pb) or mercury (Hg) compound reaching a nerve cell, damage will likely increase the longer the compound remains at the vulnerable site.

Often, adverse effects are the result of cellular responses and interaction with the pollutant and/or its metabolite. Since the endogenous target molecule in the cell is the site of action, a contaminant’s potential to undergo chemical reactions with that molecule



**FIGURE 19.5 Bioaccumulation in an organism.** During the toxicokinetic stage, uptake of the chemical substance is greater than elimination. At equilibrium, the uptake and elimination processes are equal. During detoxification or depuration, elimination is greater than uptake, so the body burden of the organism will decrease until a new equilibrium is established. (For color version of this figure, the reader is referred to the online version of this book.)

represents the initiation of toxicity in the organism. For example, a dioxin molecule may react with a receptor molecule on the cell's surface. As discussed in Chapter 12, this reaction may signal the feminine or masculine responses (e.g. hair growth, testis or ova development) much like a hormone would do. In other words, the endocrine-disrupting compound and the natural hormone both bind to the cell's receptor. They are both ligands, i.e. molecules that travel through the bloodstream as chemical messengers that will bind to a target cell's receptor. Or, the new polypeptide that is formed from this receptor-contaminant interaction may react with DNA in the nucleus. The former reaction is an example of an endocrine response, while the latter may lead to mutagenicity or cancer.

The same chemical substance can elicit different responses. For example, halogenated dioxins have been shown to be endocrine disruptors by binding with or interfering with cellular receptors, and they are carcinogenic and mutagenic because of the reactions that they or their metabolites have with the DNA molecule. Contaminants may also react with a wide range of molecules besides receptors and DNA, including lipids and microfilament proteins. Contaminants may also enter into catalytic reactions, where enzymes are involved. Enzymes are important in the metabolism of cells, whether in a unicellular bacterium or a multicellular human being.

## 19.5 TEMPORAL ASPECTS OF TOXICOKINETICS

After absorption, the pollutant moves from the site of exposure (e.g. the skin, lung tissue, or stomach) via the circulatory system. The principal mechanism for transferring the compound is diffusion, i.e. movement of the substance from high to low concentrations. Most substances travel across epithelial barriers to find their way to blood capillaries via diffusion.<sup>c</sup> So, if a chemical mass is high enough (i.e. sufficient rate of exposure) and the chemical can be readily dissolved into the bloodstream, then absorption will occur. Absorption also depends on area of exposure, the type of epithelial layers, microcirculation intensity in the subepithelial regions, and the properties of the substance.<sup>6</sup>

As discussed in Part II, it is possible for some substances to be eliminated before being absorbed. This process is known as "presystemic elimination" and can take

place while the substance is being transferred from the exposure site (e.g. the outer layer of the skin or the GI tract). As a substance moves through the GI mucosal cells, lungs, or liver, much of the substance may be eliminated. The heavy metal manganese (Mn) can be eliminated during uptake by the liver, even before it is absorbed into the bloodstream. Presystemic elimination, however, does not necessarily mean that an organism experiences no adverse effect. In fact, in the example above, Mn exposure can damage the liver without ever being absorbed into the bloodstream. This is also one of the complications of biomarkers (to be discussed later), since the body is protected against Mn toxicity by low rates of absorption or by the liver's presystemic Mn elimination.<sup>7</sup>

Distribution is the step where substances move from the point of entry and/or absorption to other locations in an organism.<sup>8</sup> The principal mechanism for distribution is circulation of fluids. The absorbed substance first moves through cell linings of the absorbing organ, e.g. the skin or GI tract. After this, the substance enters that organ's interstitial fluid, i.e. the fluid that surrounds cells. About 15% of the human body mass is interstitial fluids. The substance may continue to be distributed into intracellular fluids, which account for about 40% of body mass. The substance can move to more remote locations in blood plasma (about 8% of body mass). Interstitial and intracellular fluids are stationary, i.e. they remain in place, so while the substance resides in these fluids they are not mechanically transported. Only after entering the bloodstream does distribution become rapid. A substance can leave the interstitial fluids by entering cells of local tissue, by flowing into blood capillaries and the blood circulatory system, and by moving into the lymphatic system.

A substance's distribution is largely influenced by its affinity for binding to proteins, e.g. albumin, in the blood plasma. When a substance binds to these proteins it is no longer available for potential cell interactions. In the bloodstream, only the bound fraction of the substance is in equilibrium with the free substance. Only the free (unbound) fraction may pass through the capillary membranes. The portion of the substance that is bound to proteins, therefore, determines the substance's biological half-life and toxicity. Passive diffusion of the toxicant to and from fluids is the result of the chemical substance's concentration gradient. The processes follow Fick's laws of diffusion. Fick's first law states

<sup>c</sup>This is an example of how the same mechanism, e.g. diffusion, differs in abiotic and biotic systems. Diffusion is not nearly as important in larger air pollution scenarios (plume leaving a stack), but is a major means by which the same pollutant may move within an organism. Larger scales depend principally on advective processes, whereas smaller, cellular scales depend very much on molecular diffusion.

that in a steady state, chemical flux moves from regions of high concentration to low concentration:

$$J_i = -\frac{Dc_i}{RT} \frac{\partial \mu_i}{\partial x} \quad (19.12)$$

where,  $J$  is the diffusion flux;  $i$  is the  $i$ th chemical species;  $D$  is the diffusion coefficient;  $\mu$  is the chemical potential;  $x$  is the position (i.e. distance);  $R$  is the universal gas constant; and  $T$  is the absolute temperature.

Diffusion is also a temporal concept, as expressed in Fick's second law:

$$\frac{\partial C}{\partial t} = -\frac{D\partial^2 C_i}{\partial x^2} \quad (19.13)$$

where,  $C$  is the concentration and  $t$  is time. Again, as in Figure 19.4, time and distance are correlated in contaminant transport (whether advective or, in this case, diffusive).

The apparent volume of distribution ( $V_D$ ) is the total volume of fluids (liters) in the body to which the chemical substance has been distributed:

$$V_D = \frac{m}{[C]_{\text{plasma}}} \quad (19.14)$$

where,  $m$  is the mass or toxicological dose (milligrams) of the chemical substance and  $[C]_{\text{plasma}}$  is the concentration of the chemical substance in the plasma (milligrams per liter).

Chemical substances distributed exclusively in the blood will have higher values of  $V_D$ , while those distributed to several fluid types (blood and the interstitial and intracellular fluids) will be more diluted and would have lower  $V_D$  values. These values can be influenced by a chemical substance's rates of sequestration, biotransformation, and elimination. The value is a good indication of just how widely a chemical substance is distributed within an organism. It is also a key factor in calculating the chemical substance's body burden (milligrams):

$$\text{Body burden} = [C]_{\text{plasma}} \cdot V_D \quad (19.15)$$

For example, if a person is exposed to 30 mg contaminant A and has a blood plasma concentration of  $3 \text{ mg l}^{-1}$ , the volume of distribution is the quotient of the dose and the concentration in the plasma. That person's  $V_D = 30/3 = 10 \text{ l}$  of contaminant A. If another person is exposed to 9 mg of contaminant B, but has a plasma concentration of  $3 \text{ mg l}^{-1}$ , then that person's  $V_D = 9/3 = 3 \text{ l}$  of contaminant B.

The body burden is the product of the plasma concentration and the volume of distribution, so the first person's body burden =  $3 \times 10 = 30 \text{ mg}$  of contaminant A, and the second person's body burden =  $3 \times 3 = 9 \text{ mg}$  of contaminant B.

Therefore, in this example, contaminant B is distributed to a lesser extent than A (only 30%). Also, this has caused

the first person to have a greater body burden of A than the second person does of B. It is important to keep in mind, however, that numerous factors can affect distribution and body burden. For example, the sex and age of a person can influence how rapidly a chemical substance is distributed. In fact, if men on average distribute these chemical substances 17.3 times more rapidly than women, then A and B could be the same chemical substance (all other factors, such as age, being equal).

The route of exposure is an important factor that can affect the concentration of the parent chemical substance or its metabolites within the blood or lymph regions. This can be important since the time and path taken by the chemical substance within the body can greatly increase the degree of biotransformation, storage, elimination, and, ultimately, toxicity. For example, if the contaminant goes directly to the liver before it travels to other parts of the body, most of the contaminant mass can be biotransformed rapidly. This means that "downstream" blood concentrations will be muted or entirely eliminated, which obviates any toxic effects. This occurs when chemical substances become absorbed through the GI tract. The absorbed chemical substance mass that enters the vascular system of the GI tract is carried by the blood directly to the liver via the portal system. Blood from the liver subsequently travels to the heart and then on to the lung, before being distributed to other organs. Thus, contaminants that enter from the GI tract are immediately available to be biotransformed or excreted by the liver and eliminated by the lungs. This is known as the "first-pass effect". For example, if the first-pass biotransformation of a contaminant is 75% via the oral exposure route, the contaminant-blood concentration is only about 25% of that of a comparable dose administered intravenously.

The routes of exposure follow the same principles discussed in earlier discussions. For example, respiratory exposures to contaminant gases are a function of gas diffusion. Fick's first law can be written as a concentration gradient:

$$J_{\text{Diffusion}} = -D \frac{dC}{dx} \quad (19.16)$$

This may be reordered for respiration, with values added for the contaminant and the lung:

$$J_{\text{Diffusion}} = -D \times \frac{S}{\text{M.W.}^{1/2}} \times \frac{A}{d} \times (p_a \times p_b) \quad (19.17)$$

where,  $J_{\text{Diffusion}}$  = diffusion rate (mass per length<sup>2</sup> per time)

$D$  = diffusion coefficient for the chemical substance (area per time)

$S$  = solubility of the chemical substance gas in the blood (mass per volume)

M.W. = molecular weight of the chemical substance (dimensionless)

$A$  = surface area of membrane in contact with the chemical substance (length<sup>2</sup>)

$d$  = membrane thickness (length)

$p_a$  = partial pressure of chemical substance gas in inhaled air (pressure units)

$p_b$  = partial pressure of chemical substance gas in blood (pressure units)

This Fickian relationship shows that so long as  $p_a$  is larger than  $p_b$ , the diffusion rate is positive and the chemical substance is taken up (i.e. is more likely to reach the target organ). As the partial pressure in the blood increases and becomes greater than that in the air, the gradient reverses and the chemical substance moves out of the lung. Also, note that for a highly soluble compound, the rate of diffusion is rapid. Obviously, the slowest processes (smallest variable in the numerators, largest variable in the denominators) will be rate limiting. Aerosols (particles) will effectively diffuse if the chemical substance is lipophilic. Particle size is a major limiting factor, and is inversely proportional to dose. Currently, particles with diameters  $\leq 2.5 \mu\text{m}$  are considered to be most effective in passing by the nasopharyngeal region and penetrating to the tracheobronchial region and being deposited in alveoli. Larger particles are filtered physically and are considered to be less problematic.

Fundamental chemical principles apply to other routes besides inhalation. For example, the pH varies among the fluids found in different organs, lowest in the stomach (pH near 1.0) and highest in some urines (pH about 7.8). Blood is also basic, with a pH of 7.4, while the small intestines are slightly acidic (pH about 6.5). This means that the acidity/basicity is very important to toxicokinetics. For example, lipophilic organic acids and bases will be absorbed by passive diffusion only when they are not in an ionized form, so the Henderson–Hasselbalch equation is a determinant in the amount of organic acids absorbed:

$$\text{pK}_a = \text{pH} + \log \frac{[\text{HA}]}{[\text{A}^-]} \quad (19.18)$$

Where,  $[\text{HA}]$  is the molar concentration of an undissociated weak acid and  $[\text{A}^-]$  is the molar concentration of its conjugate base. This is a very important part of the blood's buffering, especially via the bicarbonate buffering system. This buffering allows for an optimal range of acid-base homeostasis.

Chemical substances absorbed through the inhalation or dermal routes will enter the blood and go directly to the heart and systemic circulation. Therefore, the chemical substance is distributed to other organs of the body before it finds its way to the liver, and is not subject to

this first-pass effect. Also, a chemical substance entering the lymph of the intestinal tract will not first travel to the liver. Rather, the chemical substance will slowly enter the circulatory system. The proportion of a chemical substance that moves via lymph is much smaller than the amount carried in the blood. The chemical substance blood concentration also depends on the rate of biotransformation and excretion. Some chemical substances are rapidly biotransformed and excreted while others are slowly biotransformed and excreted.

Disposition is the temporal mechanism that integrates the processes of distribution, biotransformation, and elimination. Disposition (kinetic) models describe how a chemical substance moves within the body with time. The disposition models are named for the number of compartments of the body where a chemical substance may be transported. Important compartments include blood, fat (adipose) tissue, bone, liver, kidneys, and brain.

Kinetic models may be a one-compartment open model, a two-compartment open model, or a multiple-compartment model. The one-compartment open model describes the disposition of a substance that is introduced and distributed instantaneously and evenly in the body, and eliminated at a rate and amount that is proportional to the amount left in the body (see Figure 19.6). This is known as a "first-order" rate, and represented as the logarithm of concentration in blood as a linear function of time.

The  $t_{1/2}$  of a chemical that follows a one-compartment model is simply the time required for half the chemical to no longer be found in the plasma. Only a few contaminants adhere to simple, first-order conditions of the one-compartment model.

For most chemicals, it is necessary to describe the kinetics in terms of at least a two-compartment model (see Figure 19.7). This model assumes that the chemical substance enters and distributes in the first compartment, usually the blood. From there, the chemical substance

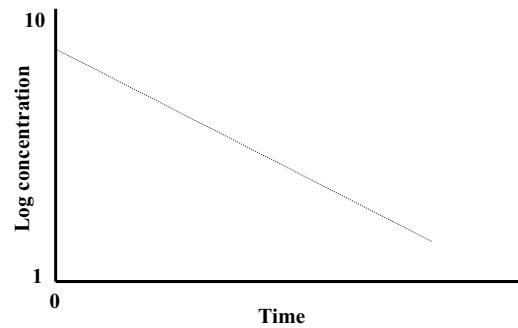
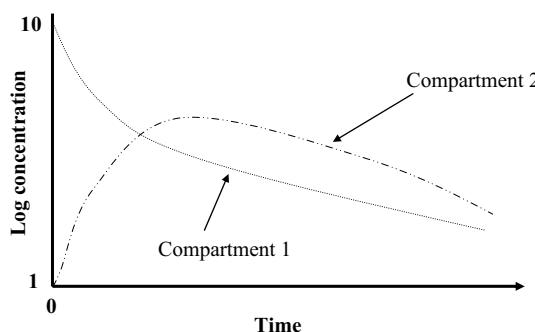


FIGURE 19.6 One-compartment toxicokinetic model. The decline of the chemical substance concentration ( $-\frac{dC}{dt}$ ) is determined by a single first-order process, e.g. elimination. Thus,  $\log C$  declines as a straight line on semilog paper.



**FIGURE 19.7 Two-compartment toxicokinetic model.** A multi-compartmental model involves more than one endogenous process, e.g. elimination plus distribution. These multiple processes change the concentrations by moving the chemical substance away from the vascular space. Thus,  $-\frac{dc}{dt}$  depends upon more than one of the processes, so the sum of more than one straight line, and is curvilinear when expressed semilogarithmically.

is distributed to another compartment from which it can be eliminated or it may return to the first compartment. Concentration in the first compartment declines continuously over time. Concentration in the second compartment increases, peaks, and subsequently declines as the chemical substance is eliminated from the body.

A  $t_{1/2}$  for a chemical whose kinetics fits a two-compartment model is often referred to as the “biological half-life”. This is the most commonly used measure of the kinetic behavior of a trace chemical substance.

Frequently the kinetics of a chemical within the body cannot be adequately described by either of these models since there may be several peripheral body compartments to which the chemical may be transported, including long-term storage. In addition, biotransformation and elimination of a chemical may not be simple processes but subject to different rates as the blood levels change.

## 19.6 TEMPORAL ASPECTS OF AIR QUALITY MODELS

Air quality models are used to estimate ambient concentrations and/or deposition rates for one or more substances in the atmosphere. These substances can be emitted from one or more sources. All air quality modeling systems have three major components, which used together, help in characterizing and predicting the environmental fate of air pollutants after emission. These components are (1) emissions; (2) meteorology; and (3) air quality.<sup>5</sup>

All three air modeling components are affected by time. Emissions are often expressed as rates (mass or volume per time). Meteorological parameters are time-dependent (e.g. wind speed, daily temperatures and

changes in humidity). Air quality is also time-dependent, e.g. concentrations of pollutants are constantly changing.

Time is truly of the essence in air pollution. It is a factor in every aspect, from the production and release of an air pollutant to residence times in the atmosphere and other environmental media to exposure in organisms to the kinetics and partitioning within the organism.

## QUESTIONS

- What properties tend to increase a chemical compound's atmospheric half-life?
- What environmental conditions tend to increase a chemical compound's half-life?
- Why are halogenated dioxins so persistent?
- A chemical undergoes first-order degradation. Its half-life is 2 days in the atmosphere. What is its  $k$  value?
- Why are half-life values not available for arsenic and cadmium?
- Why do the curves relating age and PCB concentration in lipids differ for males and females of the same genus of marine mammal?
- Give one scenario that includes the atmosphere, whereby beef at a grocery store is found to contain 15 ppt chlorinated dioxins.
- If PCBs have very low vapor pressures than Henry's Law constants, why are they found in elevated concentrations in the Arctic in areas where they have been used?
- How does environmental persistence differ from chemical persistence?
- If the air is moving to the north at  $5 \text{ m sec}^{-1}$ , and a plume from a stack reaches the earth's surface in 2 hours, where is the theoretical point that will receive this pollution? Why is it unlikely that this will indeed be the actual point? Give at least three reasons.
- Assume the reaction rate of para-dichlorobenzene with the  $\text{OH}\cdot$  radical is  $4.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ . If this is only emitted from a single manufacturing facility at a rate of  $\text{mg sec}^{-1}$ . What is the clear sky, daytime first-order reaction rate if the only photodegradation is the result of oxidation by an average of  $3.0 \times 10^6 \text{ OH}\cdot \text{ molecules cm}^{-3} \text{ air}$ ? How much of the compound will remain 8 km downwind, assuming an average wind speed is  $2 \text{ km hr}^{-1}$ ?
- Toluene has been measured in a warehouse for a month, with daily concentrations consistently ranging from  $15$  to  $25 \text{ mg m}^{-3}$ . The volume of the warehouse is  $4000 \text{ m}^3$ . The source rate from the various drums containing the toluene is estimated to be  $50 \text{ mg hr}^{-1}$ . Estimate the residence time of the

- toluene in the warehouse. What would happen to the toluene concentration if the source rate increased to  $100 \text{ mg hr}^{-1}$ ?
13. What is the difference between BCF and BAF? What are the four processes that affect BAF that can make the two values differ?
14. What is body burden? How is it likely to differ between hydrophilic and lipophilic compounds?
15. When using a BAF or BCF, what do you need to know about the value that has been reported before making general statements its meaning?
16. How are food webs and food chains influenced by the atmosphere? Draw a food web for a chemical compound. Where are humans in this web?
17. An organism has a single exposure to ethylbenzene. The body burden before the exposure was  $0 \text{ mg kg}^{-1}$  body mass and peaked after 2 days at  $5 \text{ mg kg}^{-1}$  body mass, before immediately beginning depuration. If a chemical compound's depuration and toxicokinetic phases are equal in duration and rate, what would you expect the body burden to be after 10 days?
18. If instead of a single dose of ethylbenzene, the body burden prior to day 0 was  $0 \text{ mg kg}^{-1}$  body mass and after 2 days reached equilibrium at  $5 \text{ mg kg}^{-1}$  body mass. Equilibrium lasted for 3 days, which was followed by the depuration phase that lasted for 2 days. If a chemical compound's depuration rate is half that of the accumulation during the toxicokinetic phase, what would you expect the body burden to be after 10 days?
19. The BAF for  $17\alpha$ -ethinylestradiol was found to range from 33 to 332 in surface waters. What types of organisms are likely to be near the lower BAF values and what types near the upper values?
20. BAF and BCF values are often estimated from a compound's  $K_{ow}$ . What can cause this estimation to be inaccurate?
21. A person breathes in  $10 \mu\text{g}$  of formaldehyde after opening a drum. Her blood plasma is found to be  $800 \text{ ng L}^{-1}$  formaldehyde. What is the apparent volume of distribution of formaldehyde in this person, assuming a one-compartment model?
22. If an airborne toxicant has  $\log K_{ow}$  of 5 and another has a  $\log K_{ow}$  of 1.5, what can you say about the expected volume of distribution? What can you say about expected body burden after 10 years of exposure?
23. You find the following information about two chemicals. Based on this information, which will have the longer atmospheric  $t_{1/2}$ ? Why? Which will have the larger BCF? Why? Explain the differences in the expected fugacity of the two compounds.

### Chemical A:

Molecular weight	485.8
Vapor pressure (Pa) at $25^\circ\text{C}$	$2.5 \times 10^{-4}$
Melting point ( $^\circ\text{C}$ )	79–82
Solubility in water ( $\mu\text{g/L}$ )	11
Henry's law constant ( $\text{Pa m}^3 \text{ mol}^{-1}$ ) at $25^\circ\text{C}$	0.85
Log octanol/water partition coefficient ( $K_{ow}$ ) at $25^\circ\text{C}$	6.81
Log octanol/air partition coefficient ( $K_{OA}$ ) at $25^\circ\text{C}$	10.5

### Chemical B:

Molecular weight	94.12
Vapor pressure (Pa) at $25^\circ\text{C}$	$3.5 \times 10^{-1}$
Melting point ( $^\circ\text{C}$ )	40.5
Solubility in water ( $\mu\text{g L}^{-1}$ )	$8.3 \times 10^7$
Henry's law constant ( $\text{Pa m}^3 \text{ mol}^{-1}$ ) at $25^\circ\text{C}$	0.04
Log octanol/water partition coefficient ( $K_{ow}$ ) at $25^\circ\text{C}$	1.48
Log octanol/air partition coefficient ( $K_{OA}$ ) at $25^\circ\text{C}$	Not reported

24. Physiologically, after exposure to these air pollutants, which is more likely to be distributed to and be accumulated in lipid-rich tissues? How do these factors affect the potential risk from these air pollutants if the toxicity is the same for both?
25. For the first responder, which is more likely to require a larger immediate evacuation zone in the event of a spill or leak? Explain.

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## P A R T I V

# BIOGEOCHEMISTRY OF AIR POLLUTANTS

For environmental scientists and engineers, one of the best ways to consider any constituent in the environment is by means of cycles. To this point in the book, the atmosphere has been the primary environmental compartment of concern, as it should be when considering air pollutants. However, the chapters in Part IV consider the atmosphere merely as one of several compartments within biogeochemical cycles.

Nitrogen, for example, is an essential nutrient for plants that is bioavailable only in certain forms in soil. These and other chemical forms can become air, water, and soil pollutants. The atmosphere connects pollutants and receptors by means of several biogeochemical cycles.

Each chapter in Part IV includes a discussion of the factors that influence a substance's fate in the environment, beginning with the water cycle. The troposphere is a large part of the water cycle, but certainly not the only layer. Thus, a complete understanding of air pollution must include the exchanges among the hydrosphere, atmosphere, and biosphere.

The chapters in Part IV consider the physical mechanisms by which air pollutants are transported and transformed. These cycling mechanisms can be combined with the inherent properties to estimate the extent to which a chemical will be more or less likely to move and where it may move in the environment. The physical and chemical mechanisms and properties will also determine how a chemical may be transformed into more or less toxic and more or less mobile and bioavailable substances.

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# The Hydrologic Cycle

## 20.1 THE WATER PLANET

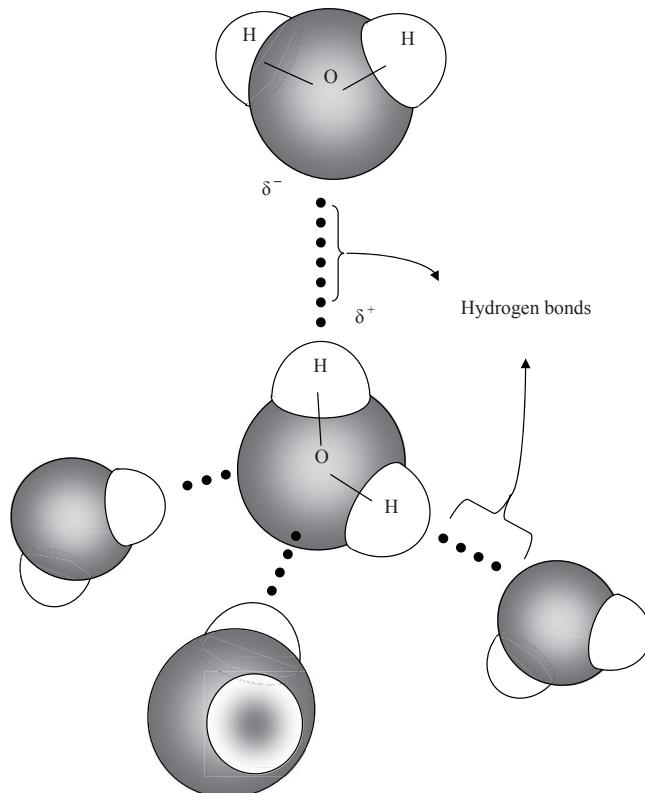
In Chapters 1, 2, and 9, several fluid properties are introduced. These apply to all fluids at all macroscopic scales, including those important for air pollution, especially air and water. In Chapter 27, these and other physical properties are applied to the processes and mechanisms in the atmosphere to employ models to predict how air pollutants will move in the troposphere, i.e. the lowest layer in which humans and other biota live.

## 20.2 THE WATER MOLECULE

Water is an amazing molecule (see [Figure 20.1](#)). Its features shape the earth's surface, e.g. the fact that due to its configuration it expands substantially as it freezes or sublimates (i.e. change of state from gas to solid). This molecular configuration also makes for the solvent characteristics of water. The water molecule's oxygen and two hydrogen atoms are aligned so that there is a slightly negative charge at the oxygen end and a slightly positive charge at the hydrogen end. Since in chemistry "like dissolves like", polar substances have an affinity to become dissolved in water, and nonpolar substances resist being dissolved in water. The hydrogen atoms form an angle of 105° with the oxygen atom. The asymmetry of the water molecule leads to a dipole moment (see the discussion in the next session) in the symmetry plane pointed toward the more positive hydrogen atoms. Thus, the highly polar H<sub>2</sub>O readily dissolves other polar compounds.

The interactions of air and water occur throughout the hydrosphere, i.e. the discontinuous stratum that holds the earth's water, including groundwater beneath the surface, surface water, water in soil and biota, and moisture in the atmosphere. The fluid properties of air and water combine in the hydrosphere, not only to make weather, but also to move and transform air

pollutants. The atmosphere holds about the same amount of water as the relatively small quantity of water in living organisms (0.0055% of total; 0.04% of freshwater) compared to the 96.5% in the oceans (see [Table 20.1](#)). However, the atmosphere accounts for much of water's activity on earth, from weather systems to nutrient cycling (see Chapter 22) to pollutant transformation (e.g. hydrolysis) and pollutant transport (e.g. wet and dry deposition).



**FIGURE 20.1** Configuration of the water molecule, showing the electronegativity ( $\delta$ ) at each end. The hydrogen atoms form an angle of 105° with the oxygen atom.

TABLE 20.1 Estimation of Water Volume in the Hydrosphere

Water Source	Water Volume ( $\times 1000 \text{ km}^3$ )	Percentage of Freshwater	Percentage of Total Water
Oceans, seas, & bays	1,338,000	—	96.5
Ice caps, glaciers, & permanent snow	24,064	68.6	1.74
Groundwater	23,400	—	1.7
Fresh	10,530	30.1	0.76
Saline	12,870	—	0.93
Ground ice & permafrost	300	0.86	0.022
Lakes	176.4	—	0.013
Fresh	91	0.26	0.007
Saline	85.4	—	0.007
Soil moisture	16.5	0.05	0.001
Atmosphere	12.9	0.04	0.001
Swamp water	11.5	0.03	0.0008
Rivers	2.1	0.006	0.0002
Biological water	1.1	0.003	0.0001

Source: U.S. Geological Survey. *The world's water*. <http://ga.water.usgs.gov/edu/earthwherewater.html>; 2013 [accessed 01.11.13].

## 20.3 THE HYDROSPHERE

The entire hydrosphere is involved in air pollution, whether it is exchange of pollutants between ground and surface waters and the atmosphere, the storage of

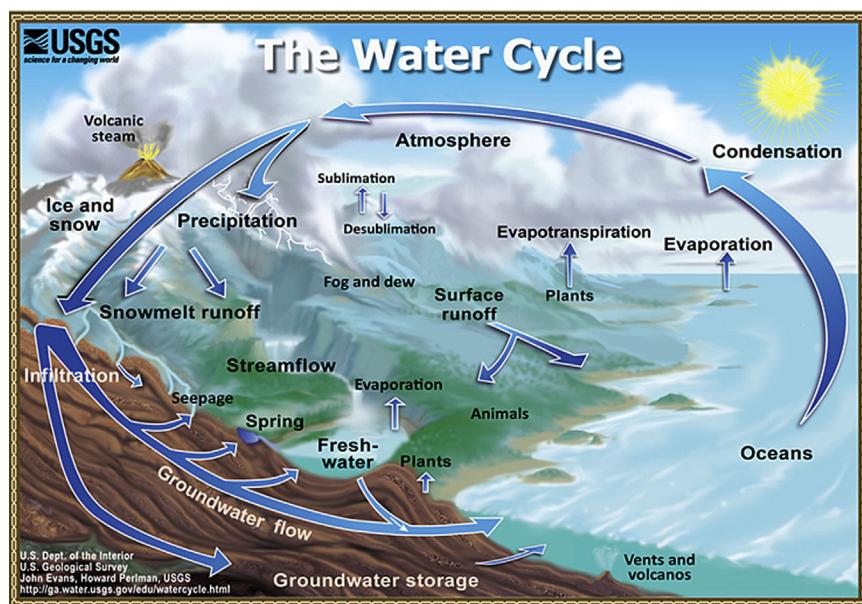
potential air pollutants in clouds and soil water, or the release and the biota's uptake of water from the atmosphere (see Figure 20.2).

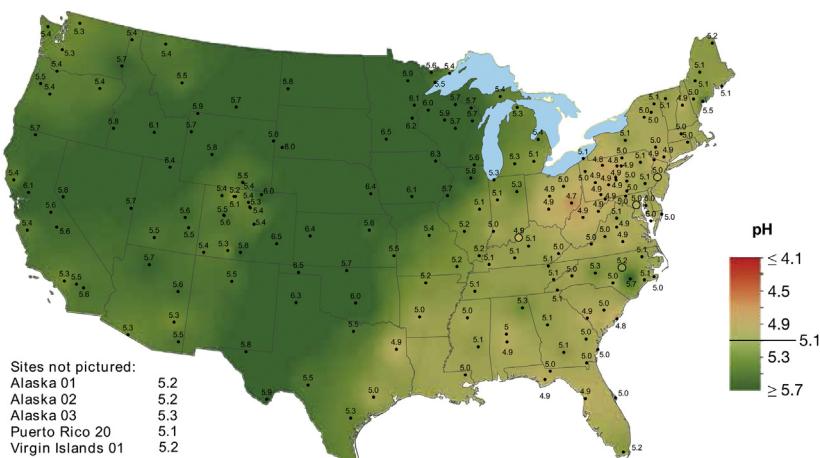
Air pollution is impacted by and affects the water cycle. For example, air pollution is directly affected when hydrolysis occurs in water droplets suspended in the atmosphere, which is an important type of reaction that degrades air pollutants. In addition, air pollution changes the water cycle by adding particulate matter (PM) on which water condenses. The water droplet is the site for much of the physical and chemical activities in the atmosphere, given that the PM in the atmosphere can have cores of sulfates and nitrates, with aerodynamic diameters  $<1 \mu\text{m}$ .

These aerosols can be removed from the atmosphere by several processes. "Rain out" occurs when the particles serve as condensation nuclei that lead to the formation of clouds. The particles are then precipitated if the droplets grow to sufficient size to fall as raindrops. Another mechanism, known as "washout", also involves rain, but the particles in air are captured by raindrops falling through the air. Both mechanisms contribute to "acid rain", which results in the sulfate and nitrate particles reaching lakes and streams, and increasing their acidity.

Both homogeneous and heterogeneous reactions occur in the atmosphere. If the reaction only occurs in the gas phase, the reaction is homogeneous. If the reaction involves an interface with a surface of an aerosol or within a liquid droplet, it is heterogeneous. Certain chemical species of S and N have sufficient aqueous solubility to be dissolved by the droplet. These liquid-phase compounds are already acidic (e.g. including concentrations of sulfuric acid [ $\text{H}_2\text{SO}_4$ ], nitric acid [ $\text{H}_2\text{NO}_3$ ], and

FIGURE 20.2 The hydrological (water) cycle. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Geological Survey. *Summary of the water cycle*. <http://ga.water.usgs.gov/edu/watercyclesummary.html>; 2013 [accessed 01.11.13].





carbonic acid ( $\text{H}_2\text{CO}_3^*$ )<sup>a</sup> before washout. Thus, the water droplet plays a key role in both dry and wet deposition of pollutants that lead to acidic conditions in soils and surface waters (see Figure 20.3).

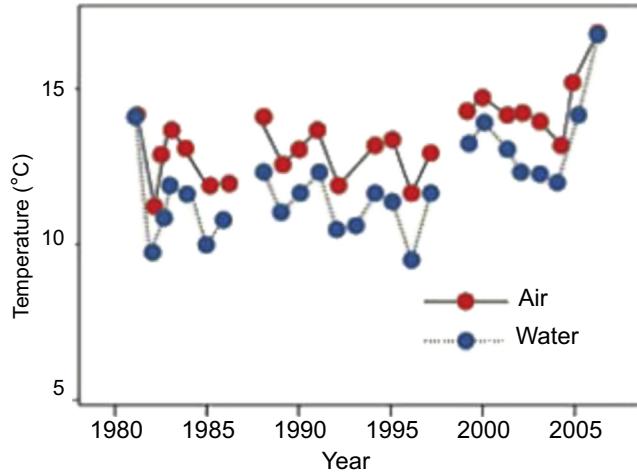
The ultimate change in pH in the hydrosphere brought on by acid rain is buffered to varying degrees by soils and surface waters, depending on the ionic strength of the soil water and surface water. These buffering processes are discussed in Chapter 21.

Air pollution also indirectly affects the hydrosphere when it changes climate. Humans and other creatures live in a very small optimal range of water, which is a balance of precipitation, evaporation, and other sources and sinks of water (see Figure 20.4). Increases in ambient

**FIGURE 20.3** Precipitation-weighted mean pH in wet deposition for the year 2012. (For color version of this figure, the reader is referred to the online version of this book.) National Atmospheric Deposition Program. National Atmospheric Deposition Program 2012 Annual Summary. NADP Data Report 2013-01. Illinois State Water Survey: University of Illinois at Urbana-Champaign; 2013.

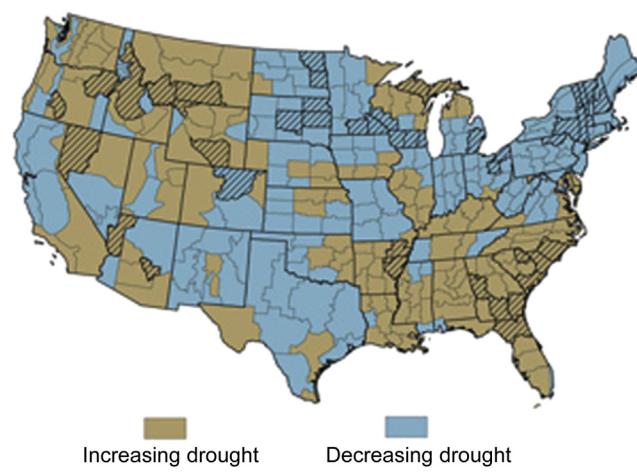
temperatures increase evaporation rates into the atmosphere. Warmer air holds more water than cooler air, so some areas will gain water, sometimes in excess (e.g. experience regional increases in flooding). The increased evaporation rates can also increase desiccation of soils and biota in the water loss areas (see Figure 20.5). These and other changes threaten the delicate balances within the optimal ranges of the water regimes.

The total amount of water in the hydrosphere will remain relatively the same, but the relative locations of the water could change substantially with changes in climate. For example, water may move from impounded surface waters to the atmosphere, which will change rain and other precipitation patterns, including hurricanes and other storm systems.



**FIGURE 20.4** Lake Superior water temperatures (1979–2006): the recent large jump in summer water temperature could be associated with the recent reduction in ice cover. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Ref. 1.

<sup>a</sup> The asterisk (\*) in  $\text{H}_2\text{CO}_3$  indicates that this actually occurs as an equilibrium among the acid and ions, especially carbonate and bicarbonate. See Chapter 21.



**FIGURE 20.5** Drought trends in the United States. Hatching indicating a significant trend. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Ref. 2.

### 20.3.1 Air Pollution's Indirect Effects on the Hydrosphere

A reasonable hypothesis is that any average global temperature increases due to increased atmospheric concentrations of global greenhouse gases will lead to some increase in the rate and amount of melting of polar ice and glaciers.<sup>2</sup> The net effect of this change of state of water would be a rise in sea level, as well as other large water bodies, e.g. the Great Lakes in North America (see Figure 20.4). If the rise is substantial it could be associated with displacing human populations (e.g. islanders and coastal dwellers). It could also greatly impact coastal ecosystems with biota that is not completely submerged for at least part of the year. Another indirect result would be the contamination of many coastal and near-coastal water supplies by salt water (e.g. ground water recharged by tidal rivers and estuaries).

The density difference between fresh and salt water is presenting a slowly unfolding public health problem for people living in coastal communities, as well as an environmental problem for marine and estuarine ecosystems. Salt water contains a significantly greater mass of ions than does freshwater (see Table 20.2). The denser saline water can wedge beneath freshwaters and pollute surface waters and groundwater (see Figure 20.6). This phenomenon, known as saltwater intrusion, can significantly alter an ecosystem's structure and function, and threaten freshwater organisms. It can also pose a huge challenge to coastal communities which depend on aquifers for their water supply. The freshwater Everglades, e.g. recharge the Biscayne aquifer, a natural underground layer that collects water.

TABLE 20.2 Important General Ionic Composition Classifications of Freshwaters and Marine Waters

Composition	River Water	Salt Water
pH	6–8	8
$\text{Ca}^{2+}$	$4 \times 10^{-5} \text{ M}$	$1 \times 10^{-2} \text{ M}$
$\text{Cl}^-$	$2 \times 10^{-4} \text{ M}$	$6 \times 10^{-1} \text{ M}$
$\text{HCO}_3^-$	$1 \times 10^{-4} \text{ M}$	$2 \times 10^{-3} \text{ M}$
$\text{K}^+$	$6 \times 10^{-5} \text{ M}$	$1 \times 10^{-2} \text{ M}$
$\text{Mg}^{2+}$	$2 \times 10^{-4} \text{ M}$	$5 \times 10^{-2} \text{ M}$
$\text{Na}^+$	$4 \times 10^{-4} \text{ M}$	$5 \times 10^{-1} \text{ M}$
$\text{SO}_4^{2-}$	$1 \times 10^{-4} \text{ M}$	$3 \times 10^{-2} \text{ M}$

M = molarity (moles per liter solution).

Sources: Hunter KA, Kim JP, Reid MR. Factors influencing the inorganic speciation of trace metal cations in freshwaters. *Mar Freshwater Res* 1999;50:367–72; and Schwarzenbach RR, Gschwend PM, Imboden DM. *Environmental organic chemistry*. New York (NY): Wiley Interscience; 1993.

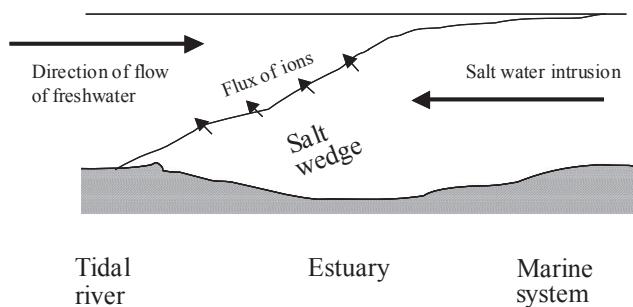


FIGURE 20.6 Saltwater intrusion into a freshwater system. This denser salt water submerges under the lighter freshwater system. The same phenomenon can occur in coastal aquifers.

The Biscayne aquifer is the primary water supply to the Florida Keys.

The effect in South Florida could be doubly troublesome. In addition to the type of saltwater intrusion shown in Figure 20.6, the rising sea level could submerge low-lying areas of the Everglades (see Figure 20.7), increasing the salinity in portions of the aquifer. In addition, the rising sea water could force salty waters upstream into coastal areas, thus threatening surface water supplies. Similar problems could also occur in Northeastern US aquifers that are recharged by fresh portions of streams that are vulnerable to increased salinity during severe droughts.<sup>3</sup> Indeed, similar groundwater–surface water–sea water interactions could be affected across the globe.

Salinity of water is a relative term. The values in Table 20.2 are at best averages and target concentrations. Actually, salinity is the concentration of total dissolved solids (TDS). Indeed, in the United States, the drinking water standard for TDS is a “secondary” or nuisance standard, which is  $500 \text{ mg l}^{-1}$ . Note that the classifications using two dominant ions,  $\text{Na}^+$  and  $\text{Cl}^-$ , differ by three orders of magnitude between “fresh” and “saline” waters. Consider the hypothetical example in Figure 20.8 of these ionic strengths (indicated by TDS) before and after saltwater intrusion. Although the water near the water supply is not “salt water”, nor does it currently violate the secondary drinking water standard, the ionic concentrations are cause for concern and serve as a warning that the trend is likely to be toward even higher salinity.

The foregoing discussion illustrates how an indirect air pollution effect (atmospheric warming from emissions of greenhouse gases) can have hydrologic impacts (warming and sea level rise) that lead to another form of pollution (freshwater contamination). The interconnectedness of the atmosphere, hydrosphere, and biosphere are complex and extensive (see Figure 20.9). A small change in one small part of the spheres can lead to unanticipated outcomes. Put within a chaos perspective, the hydrosphere has many features that are sensitive to initial conditions.

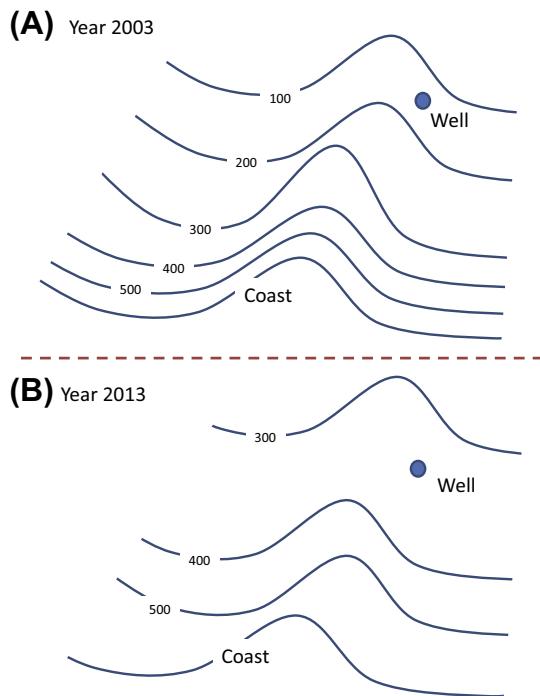
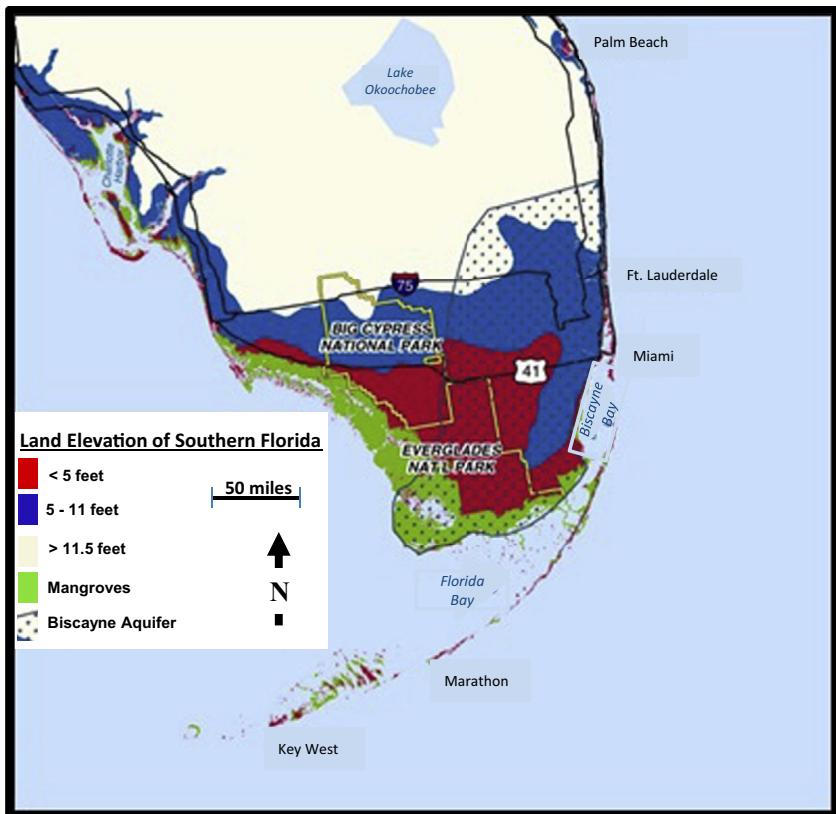


FIGURE 20.8 Hypothetical isopleths of total dissolved solid (TDS) concentration (milligrams per liter) in groundwater (e.g. 30 m depth). Note that the isopleths in A are widened compared to B. The increases in TDS concentrations over the decade indicate saltwater intrusion and potential contamination at the drinking water well site. (For color version of this figure, the reader is referred to the online version of this book.)

**FIGURE 20.7 Elevation and aquifer locations in southern Florida.** Although a small part of the aquifer is beneath salty mangrove area, most of it is recharged by the freshwater Everglades, rendering the area vulnerable to saltwater intrusion and increased salinity of both surface and groundwater sources of drinking water. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. *Saving Florida's vanishing shores*. [http://www.epa.gov/climatechange/Downloads/impacts-adaptation/saving\\_FL.pdf](http://www.epa.gov/climatechange/Downloads/impacts-adaptation/saving_FL.pdf); 2002 [accessed 01.11.13].

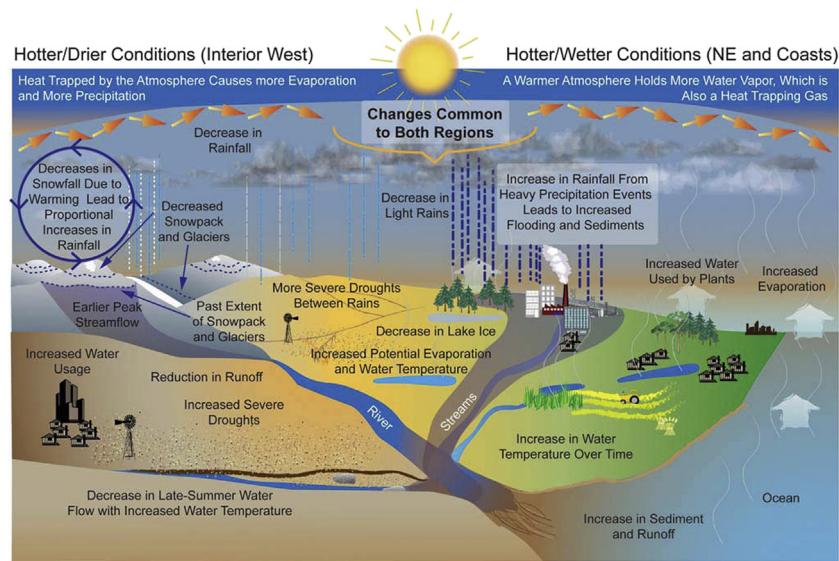
### 20.3.2 Extremes

Water quality can be adversely affected by either extreme of water availability. For example, water quality may suffer as a result of climate change in areas experiencing increases in rainfall as a result of heavier and more frequent precipitation events. In addition to the damage and safety hazards of a flood, more intensive precipitation events harm water infrastructures, e.g. sewer systems and wastewater treatment plants are not designed to handle the increased volumes of water, leading to greater numbers of pass-through of untreated sewage, and the concomitant health effects this brings. These events also overwhelm storm water sewers, increasing nutrient loadings to surface waters (see Chapter 22). This causes problems, such as eutrophication and fish kills due to the oxygen demand of the organic material and nutrients.<sup>1</sup>

## 20.4 SCALE AND COMPLEXITY OF WATER CYCLES

Myriad processes are involved in environmental systems, with water playing vital roles in most of them. The previous discussion has focused on the planetary

**FIGURE 20.9** Potential impacts of climate change of the hydrologic cycle. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 2.

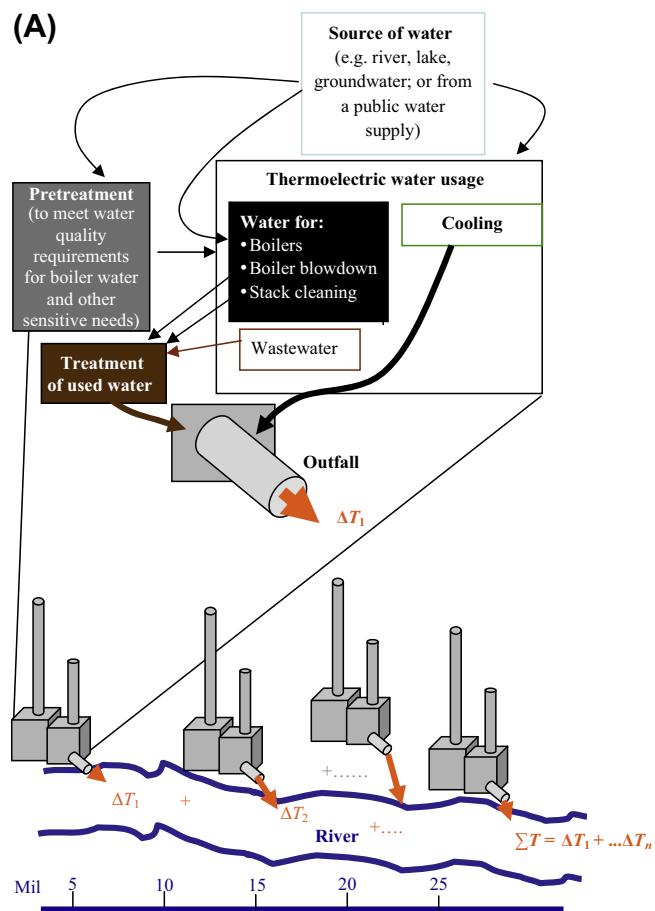


cycling of water, i.e. throughout the hydrosphere. However, water cycling takes place at all levels, each of which is important to air pollution.

Water plays a large role in climate. Microclimatological changes can occur due to the release of heated plumes from combustion facilities and vehicles. Exchanges between the atmosphere and other media, e.g. soil and sediment, create sinks and sources of energy. Heat reservoirs in terrestrial and aquatic systems receive added heat, which is released in ways that can alter habitats (e.g. changes to freeze-thaw cycles, seasonal variations, and selectivity of certain soil bacteria genera).

Water cycling is closely tied to energy cycling and balances. Some of these water-energy relationships are obvious and direct, e.g. the thermal inversions that lead to urban air pollution are the result of differences in heat energy in water vapor at various layers in the troposphere. Some of the water-energy relationships are more subtle and indirect, such as the transfer of energy between trophic states in an ecosystem, which relies in part on energy and water exchanges among biotic tissue and abiotic substrates (e.g. photosynthesis using aqueous-phase phosphorous compounds to transfer energy).

Water-energy cycling is also important in anthropogenic systems and is part of a design of pollution control equipment selection and application. For example, at the facility scale, water and energy are often addressed together, such as the management of water and energy at a factory or power plant. Managing water is a simultaneous process with managing energy. Indeed, mismanagement of water systems at the facility level can involve trade-offs between types of pollution. The first law of thermodynamics requires, e.g. that allowing



**FIGURE 20.10** Difference in cumulative heat contribution to a river from electric generating plants using a once-through cooling system (A) versus the same plants using a cooling water return system (B). The cumulatively added heat is greatly reduced with the closed water return systems compared to the once-through cooling systems (hypothetical scenario). (For color version of this figure, the reader is referred to the online version of this book.) Ref. 4a.

(B)

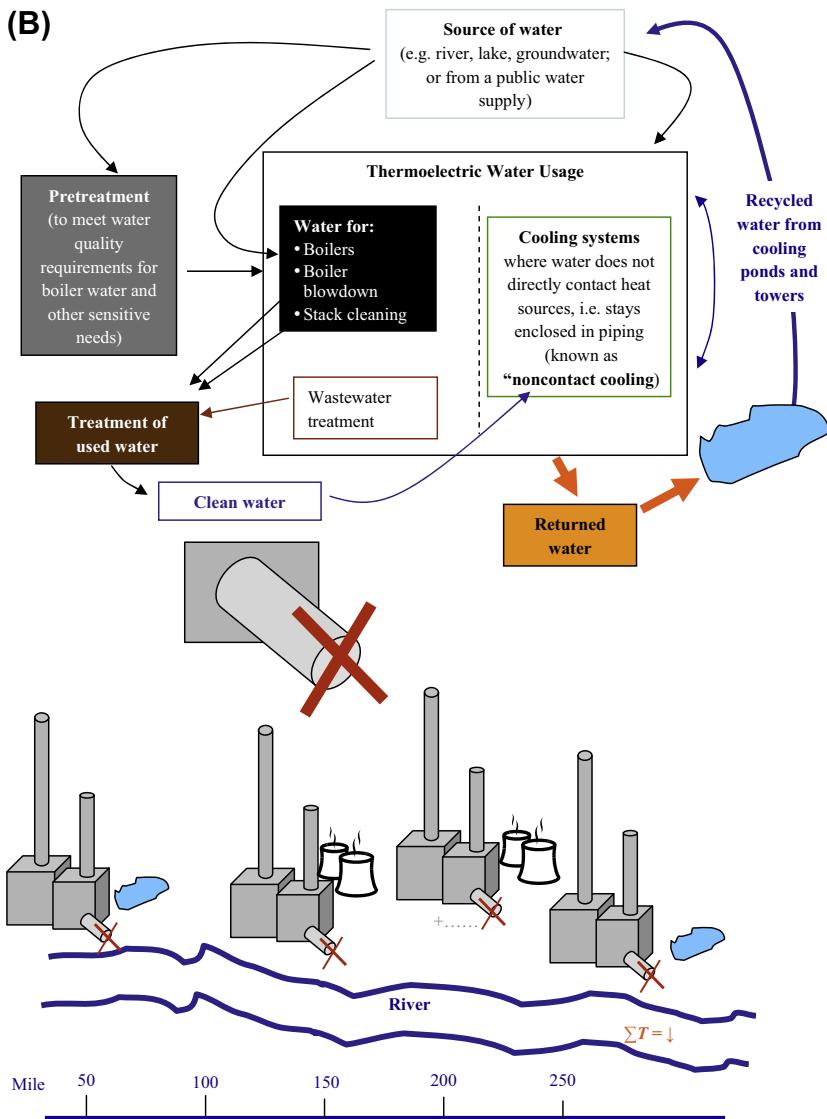


FIGURE 20.10 (Continued)

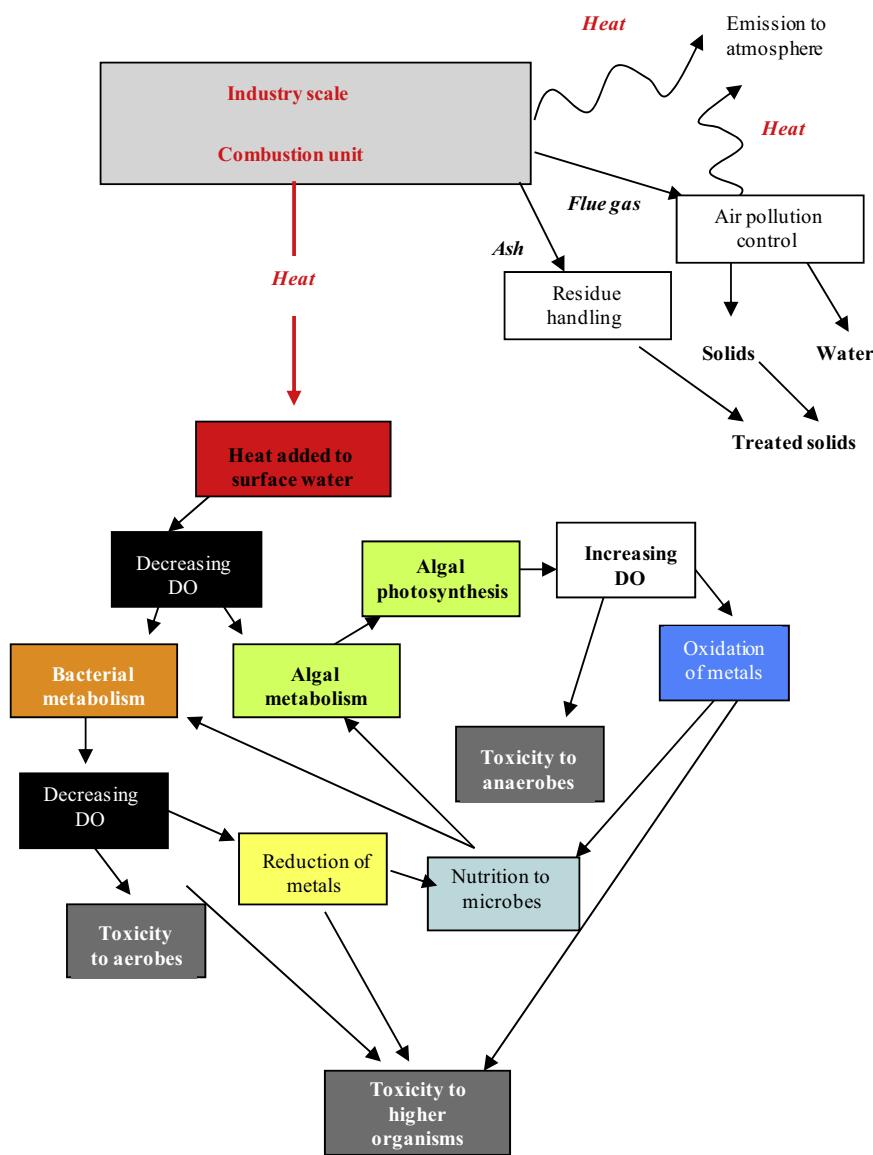
heated water to be released in any amount, even the permitted level, would increase the overall temperature of the receiving stream.

The water–energy exchanges will also scale upwardly. That is, heat can initiate cumulative environmental impacts, such as the heat exchange and balances were changing conditions of receiving water bodies.<sup>4a,4b</sup> Up to the 1970s, every power plant along the major rivers of the United States was releasing heated water to a stream (see Figure 20.10). This meant that the incremental effect of all the permitted releases led to a cumulative increase in the temperature. In the late 1970s, once-through cooling, i.e. letting water pass through turbines and then discharging to adjacent streams, was no longer allowed in US waters (Figure 20.10(A)). Other cooling systems, e.g. cooling towers and cooling lakes, had to be installed and operated, which meant power plant water systems became

more closed, both from a fluid dynamics and thermodynamic perspective (Figure 20.10(B)).

The heat from boilers and other industry-scale operations is going to be exchanged. This is a consideration in both air pollution and water pollution control decisions. Facility design determines in large part where the energy goes (see Figure 20.11). In fact, an air pollution control and heat control design can directly affect dissolved oxygen (DO) content of the receiving water since temperature is directly proportional to DO content. The DO is a limiting factor of the type of fish communities that can be supported by a water body (see Tables 20.3 and 20.4). The resulting net increase in heat may directly stress the biotic integrity of a surface water ecosystem, e.g. fish species vary in their ability to tolerate higher temperatures, meaning that the less tolerant, higher value fish will be inordinately threatened.

**FIGURE 20.11 Adverse effects in the real world usually result from a combination of conditions.** In this example, both energy and matter must be considered in the control of air pollution. The control of matter leaving the combustion unit (upper left-hand side) must be optimized with the transfer of energy (middle). The added heat results in an abiotic response (i.e. decreased dissolved oxygen (DO) concentrations in the water), which leads to biotic processes that either increase or decrease DO and increase the toxic responses (e.g. low DO and increase in metal bioavailability). (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Ref. 4a.



The increased temperature can also increase the aqueous solubility of substances that are toxic to organisms. For example, greater concentrations of mercury and other toxic metals will occur with elevated temperatures (see Chapter 23). The lower DO concentrations will lead to a reduced environment where the metals and compounds will form sulfides and other compounds that can be toxic to aquatic life. Thus, the change in temperature, the resulting decrease in DO and increasing metal concentrations, and the synergistic impact of combining the hypoxic water and reduced metal compounds are a cascade of harm to the stream's ecosystems (see Figure 20.3).

Biota also plays a role in the heat-initiated effect. Combined abiotic and biotic responses occur. Notably, the growth and metabolism of the bacteria results in even more rapidly decreasing DO levels. Algae both

consume DO for metabolism and produce DO by photosynthesis. The increase in temperature increases their aqueous solubility and the decrease in DO is accompanied by redox changes, e.g. formation of reduced metal species, such as metal sulfides. This is also being mediated by the bacteria, some of which will begin reducing the metals as the oxygen levels drop (reduced conditions in the water and sediment). However, the opposite is true in the more oxidized regions, i.e. the metals are forming oxides. The increase in the metal compounds combined with the reduced DO, combined with the increased temperatures can act synergistically to make the conditions toxic for higher animals, e.g. a fish kill.

The initiating abiotic effect (i.e. increased temperature) results in an increased microbial population. The associated decline in DO, however, is a net decline between photosynthetic and nonphotosynthetic microbes.

The growth and metabolism of the bacteria result in decreasing the DO levels, but the growth of the algae both consume DO for metabolism and produce DO by photosynthesis.

Meanwhile a combined abiotic and biotic response occurs with the metals. The increase in temperature increases their aqueous solubility and the decrease in DO is accompanied by redox changes, e.g. formation of reduced metal species, such as metal sulfides. These changes can increase the exposure of human populations to toxic substances. The increase in temperature in Figure 20.11, e.g. leads to increased solubility of metals. This is also being mediated by the bacteria, some of which will begin reducing the metals as the oxygen levels drop (reduced conditions in the water and sediment). However, the opposite is true in the

more oxidized regions, i.e. the metals are forming oxides. The increase in the metal compounds combined with the reduced DO, combined with the increased temperatures can act synergistically to make the conditions toxic for higher animals, e.g. a fish kill.<sup>5</sup> Predicting the likelihood of ecosystem change and adverse events like fish kills can be quite complicated, with many factors that either mitigate or exacerbate the outcome (see Figure 20.12). The increase in metal concentrations in water not only increases the potential exposure to total metal mass, but may also transform the metals into chemical species with much higher bioavailability, which increases the dose and body burden of the metals (e.g. methyl mercury in fish ingested by humans).

At the cellular scale, numerous processes and exchanges occur among and within the environmental compartments (see Figure 20.13); as well as those at the interface between the organism and the environment. The gill-water exchanges by fish, e.g. are analogous to the lung-air exchanges in air-breathing animals.

Transfer of matter via fluids is a key part of the bioaccumulation process in a multiphase system (water, sediment, particles, and biota), as represented by the gill<sup>6</sup> and the lung. The mechanisms include (1) water

TABLE 20.3 Relationship between Water Temperature and Maximum Dissolved Oxygen (DO) Concentration in Water (at 1 atm)

Temperature (°C)	Dissolved Oxygen (mg l <sup>-1</sup> )	Temperature (°C)	Dissolved Oxygen (mg l <sup>-1</sup> )
0	14.60	23	8.56
1	14.19	24	8.40
2	13.81	25	8.24
3	13.44	26	8.09
4	13.09	27	7.95
5	12.75	28	7.81
6	12.43	29	7.67
7	12.12	30	7.54
8	11.83	31	7.41
9	11.55	32	7.28
10	11.27	33	7.16
11	11.01	34	7.16
12	10.76	35	6.93
13	10.52	36	6.82
14	10.29	37	6.71
15	10.07	38	6.61
16	9.85	39	6.51
17	9.65	40	6.41
18	9.45	41	6.41
19	9.26	42	6.22
20	9.07	43	6.13
21	8.90	44	6.04
22	8.72	45	5.95

Sources: Ref. 4a; 4b.

TABLE 20.4 Normal Temperature Tolerances of Aquatic Organisms

Organism	Taxonomy	Range in Temperature Tolerance (°C)	Minimum Dissolved Oxygen (mg l <sup>-1</sup> )
Trout	<i>Salmo, Oncorhynchus, and Salvelinus</i> spp.	5–20	6.5
Smallmouth bass	<i>Micropterus dolomieu</i>	5–28	6.5
Caddisfly larvae	<i>Brachycentrus</i> spp.	10–25	4.0
Mayfly larvae	<i>Ephemerella invaria</i>	10–25	4.0
Stonefly larvae	<i>Pteronarcys</i> spp.	10–25	4.0
Catfish	Order Siluriformes	20–25	2.5
Carp	<i>Cyprinus</i> spp.	10–25	2.0
Water boatmen	<i>Notonecta</i> spp.	10–25	2.0
Mosquito larvae	Family Culicidae	10–25	1.0

Source: Ref. 4a; and Vernier Corporation. Computer 19: dissolved oxygen in water. [http://www2.vernier.com/sample\\_labs/BWV-19-COMP-dissolved\\_oxygen.pdf](http://www2.vernier.com/sample_labs/BWV-19-COMP-dissolved_oxygen.pdf); 2009 [accessed 19.10.09].

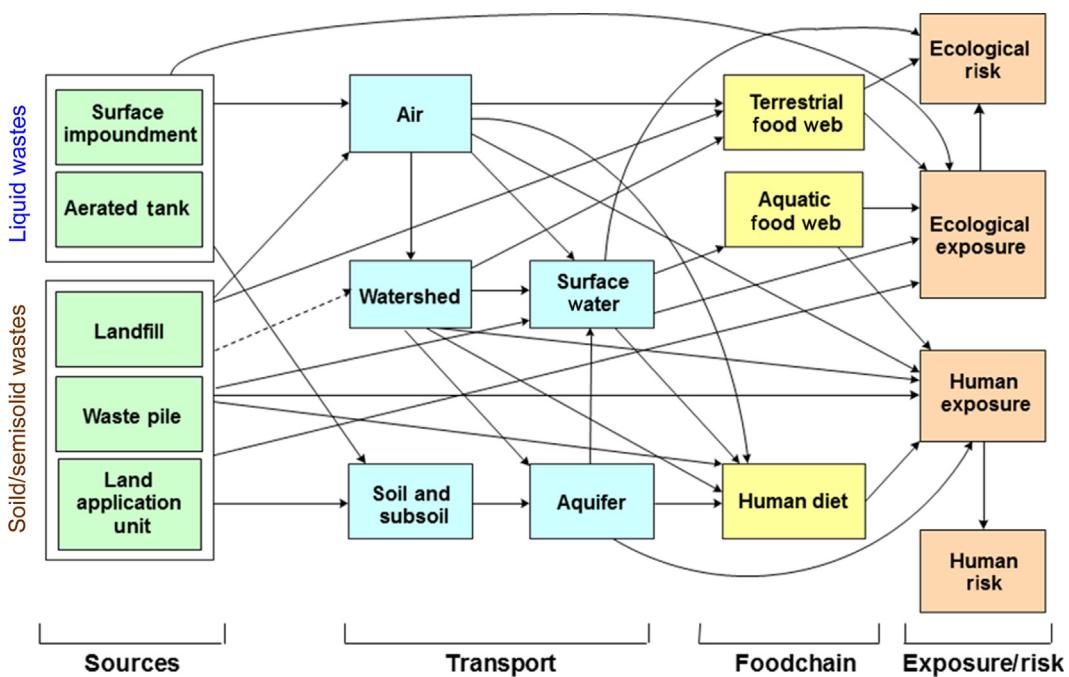
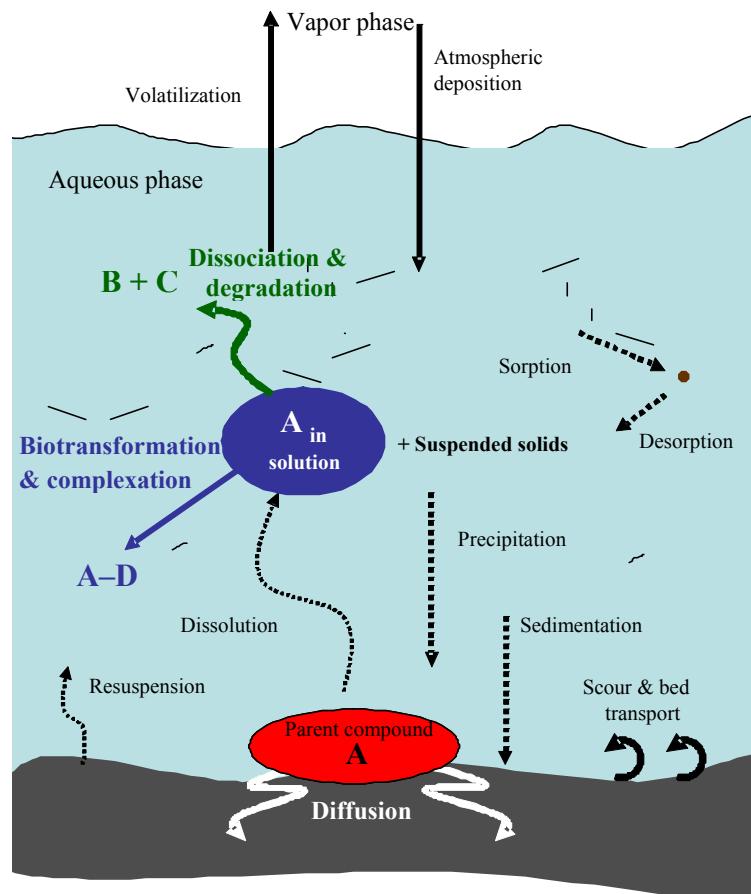


FIGURE 20.12 Environmental transport pathways can be affected by net heat gain. Compounds (nutrients, contaminants), microbes, and energy (e.g. heat) follow the path through the environment indicated by arrows. The residence time within any of the boxes is affected by conditions, including temperature. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Vallero DA, Reckhow KH, Gronewold AD. Application of multimedia models for human and ecological exposure analysis. International conference on environmental epidemiology and exposure. Durham (NC); October 17, 2007. Graphic adapted from U.S. Environmental Protection Agency.

FIGURE 20.13 Transport and transformation phenomena in a water system. The transformation processes, including dissociation and degradation to form metabolites and degradation products (B, C, and D), simultaneously consist of both abiotic (e.g. hydrolysis and photolysis) and biotic (i.e. biodegradation). The parent compound A and its reaction products include molecular diffusion (usually only important in quiescent systems, e.g. sediment layers) and advective processes. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Lyman WJ. Transport and transformation processes – chapter 15. In: Rand G, editor. Fundamentals of aquatic toxicology: effects, environmental fate, and risk assessment. 2nd ed. Washington (DC): Taylor & Francis; 1995.



flow across membrane; (2) blood flow within organism; (3) chemical flux across membrane; (4) binding and release from serum proteins; (5) sorption/desorption to blood cells; (6) chemical mass transfer from blood to tissues by perfusion; (7) complexation to and decomplexation from organic carbon in a particulate phase; (8) sorption to and desorption from coarse particulate solids, in addition to internal diffusion within the particles.

Water is integral and essential to biomass growth, which can be expressed as energy content and flow (e.g. kilocalories per fish and kilocalories per day).<sup>7a–7c</sup> Factors that lead to healthy human and ecological communities must account for atmospheric exchanges of mass and energy. The direct and indirect impacts can be dramatic.

The next chapters consider the cycling of important elements from a biogeochemical perspective. The cycling of these substances occurs predominantly via two fluids, water and air, at most scales, but predominately by three fluids at the organism scale, i.e. air, water, and blood. Organisms may be seen as microcosms of mass and energy cycling, regardless of scale. Indeed, cycling depends on the dynamics of water, air, and other fluids, whether among biomes or at the cellular level.

## QUESTIONS

1. How does particulate matter affect the earth's hydrological cycle?
2. Explain the atmosphere-hydrosphere interfaces and interactions in the formation and distribution of acidic deposition.
3. Explain the atmosphere-hydrosphere interfaces and interactions in the formation and distribution of ozone-depleting substances.
4. How does the water cycle affect the formation of tropospheric ozone and smog?
5. What is a biome shift? How might the hydrological cycle change and be changed by such shifts from climate change? Describe these changes in terms of physics, chemistry and biology.
6. DDT is found in a people's blood in the Arctic. Explain the role of the water cycle in this finding.
7. In spring 1999, scientists discovered a brownish pollution haze layer of aerosol over the Indian Ocean.

The formation of the haze layer is a seasonal phenomenon facilitated by an extended dry season, which prevents the removal of pollution from the atmosphere through rainfall. What is the role of the water cycle in this phenomenon and how might the water cycle be affected by such events?

8. From the perspective of pollutant transport and uptake by organisms, compare the physics and biology of the gill versus the lung. Why would this be important in a book about air pollution?

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# The Carbon Cycle

## 21.1 CARBON CHEMISTRY

Carbon (C) is arguably one of the most important elements in air pollution. All living systems on earth consist of molecular arrangements of the elements: carbon, oxygen, hydrogen, and most contain nitrogen. These four so-called biophile elements have an affinity for each other so as to form complex organic compounds.<sup>a</sup>

All of the earth's creatures are carbon-based. Biological processes, especially photosynthesis and respiration, by which energy is stored and used by organisms requires the C cycle. Much of this has to do with atomic structure of C. The atomic number of C is six, with four electrons in its outermost shell. This electron configuration is a tetrahedron and its oxidation state is often tetravalent. The C atom's theoretical tetrahedral shape minimizes the repulsion between pairs of electrons. For example, methane ( $\text{CH}_4$ ) assumes the molecular configuration of four equidistant H atoms surrounding the C atom (i.e. four C–H bonds).

This tetrivalence means that C can bond as  $\text{C}^{4+}$  or as  $\text{C}^{4-}$ , i.e. it can either give four away or gain four electrons. However, the electronegativity of C is 2.55, which is too low for C to gain electrons from most elements to form  $\text{C}^{4-}$ , but too high for C to lose electrons to form  $\text{C}^{4+}$ . Thus, C seldom forms ionic bonds, readily forms covalent bonds, i.e. most of the molecules formed with C are covalently bonded. This is the main reason that so many organic compounds are possible, and are the vast majority of compounds important in the environmental and medical sciences.

The negative and positive tetrivalence are prevalent, but certainly are not C's only oxidation states. Indeed, C may have any oxidation state from +4 to –4 (see Discussion Box: Finding Carbon's Oxidation States in Organic Compounds).

<sup>a</sup> In fact, until less than two centuries ago, such organic compounds were thought only to be able to be produced within natural biological systems. Friedrich Wöhler is credited with being the first to synthesize an organic compound outside of an organism when he reacted two inorganic compounds, i.e. silver isocyanate and ammonium chloride, to form the organic compound urea  $(\text{NH}_2)_2\text{CO}$  and silver chloride:  $\text{AgNCO} + \text{NH}_4\text{Cl} \rightarrow (\text{NH}_2)_2\text{CO} + \text{AgCl}$ .

Since most biochemicals and tissues consist of organic compounds, the carbon cycle plays numerous roles in air pollution, no matter the scale of the receptor. At the cellular scale, airborne organic toxicants interfere with cellular and genetic material, which leads to cancer and other diseases. At the personal scale, people inhale carbon monoxide, volatile organic compounds (VOCs), organometallic compounds, and carbon-containing aerosols. At the regional scale, mobile sources and vegetation (e.g. coniferous forests) emit VOCs that are part of mix needed to generate photochemical oxidant smog and ground-level ozone. At the planetary scale, chlorofluorocarbons (CFCs) and other halogenated compounds contribute to stratospheric ozone degradation; and CFCs, methane, and carbon dioxide are greenhouse gases.

The four electrons in the outer shell means that living systems can both oxidize and reduce C. Oxidation is the act of losing electrons from the outermost shell; reduction is the act of gaining electrons. Carbon redox occurs abiotically, e.g. by photochemical and thermal processes and biotically.

Biotic reduction often takes place in the absence of molecular oxygen ( $\text{O}_2$ ), such as in the rumen of cattle, in sludge at the bottom of a lagoon, or in buried detritus on the forest floor. Anaerobic bacteria obtain energy by reduction, breaking down organic compounds into methane ( $\text{CH}_4$ ) and water.

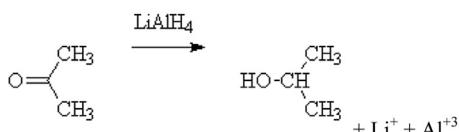
Conversely, aerobic microbes get their energy from oxidation, forming carbon dioxide ( $\text{CO}_2$ ) and water. Plants absorb  $\text{CO}_2$  for photosynthesis, the process whereby plants convert solar energy into biomass and release  $\text{O}_2$  as a by-product. Thus, the essential oxygen is actually the waste product of photosynthesis and is derived from carbon-based compounds. Respiration generates carbon dioxide as a waste product of oxidation that takes place in organisms, so there is a balance between

## FINDING CARBON'S OXIDATION STATES IN ORGANIC COMPOUNDS

The sum of all oxidation states of inorganic compounds is zero; otherwise it is an ion. For  $\text{KMnO}_4$  the potassium oxidation state must be +1 and the oxidation state of each oxygen is -2 (i.e. total oxidation number of -8 for the four O atoms). Thus, the oxidation state of manganese must be +7. This is also the case for inorganic carbon compounds. For example, for  $\text{CO}_2$ , carbon must have an oxidation state of +4, since the two O atoms have an oxidation state sum of -4.

Conversely, since C atoms in organic compounds can have any oxidation state from -4 to +4, when the C atoms exist in more than one location in a molecule, the oxidation state of each C must be calculated, and these may differ within the same molecule. For example, one C may have an oxidation state of -4 and another C may have an oxidation state of +1. That is, organic compounds may include several more unknown oxidation states than known oxidation states.

Thus, for organic compounds, even though an absolute value for the oxidation state cannot be determined, identifying the amount and location of changes in oxidation state during a reaction is crucial. When a ketone is converted to an alcohol, the only change in oxidation state occurs at the carbon with the oxygen; the method is outlined and shows that the carbon's oxidation state is reduced from +2 to 0, equivalent to addition of two electrons.



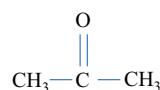
The C oxidation state changes may be found consistently by applying the following rules<sup>1</sup>:

1. Each element other than the carbons is assigned an expected oxidation state: H: +1; O: -2; halogens: -1; and as a consequence OH: -1. When these are not those expected from the outer shell, they follow general rules for various chemical classes, e.g. H has an oxidation state of -1 in hydrides such as  $\text{LiAlH}_4$ ; O has an oxidation state of -1 in peroxides such as  $\text{H}_2\text{O}_2$ , and the molecules consisting of a single elements, e.g. molecular nitrogen, chlorine, hydrogen, and oxygen ( $\text{N}_2$ ,  $\text{Cl}_2$ ,  $\text{H}_2$ , and  $\text{O}_2$ , respectively). This also applies to zero-valence or "elemental" metals, e.g. elemental mercury ( $\text{Hg}^0$  and  $\text{Pb}^0$ ).
2. The algebraic sum of oxidation states of all atoms in a neutral molecule must be zero (however, for ions the algebraic sum of the oxidation states of the constituent atoms must be equal to the charge on the ion).

3. All C atoms except the C that changes during the reaction are temporarily assigned an oxidation state of 0 to solve for each change. The oxidation state of this designated unknown C can then be calculated by the normal method for an inorganic (e.g. solving for Mn in  $\text{KMnO}_4$  above).

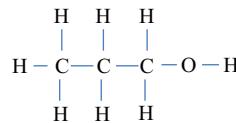
### Examples:

#### Acetone:



Carbon Position	Attached Atoms	Sum of Oxidation Numbers of Attached Atoms	C Oxidation State
1	3H; 1C	$3(+1) + 1(0) = +3$	-3
2	2C; 1O	$2(0) + 1(-2) = -2$	+2
3	3H; 1C	$3(+1) + 1(0) = +3$	-3

#### 2-Propanol:



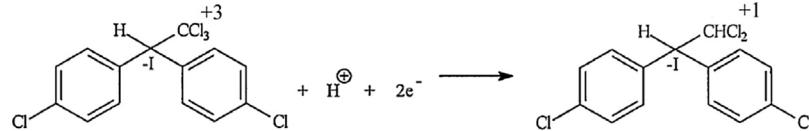
Carbon Position	Attached Atoms	Sum of Oxidation Numbers of Attached Atoms	C Oxidation State
1	3H; 1C	$3(+1) + 1(0) = +3$	-3
2	2C; 1H; 1OH	$2(0) + 1(+1) + 1(-1) = 0$	0
3	3H; 1C	$3(+1) + 1(0) = +3$	-3

Incidentally, this procedure can be used for other multi-valent elements, e.g. finding the valence of N in organic and inorganic compounds, which varies from -3 ( $\text{NH}_3$ ) to +5 ( $\text{HNO}_3$ ). Like C, N exists in numerous oxidation states in organic compounds and undergoes reduction and oxidation.

The oxidation state of an ionic compound can differ from the general rules. For example, for an ionic compound having a common element, e.g. ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), the oxidation states for each ion should be determined separately. If the formula of ammonium nitrate is considered as a combination of the two N atoms, it would be  $\text{N}_2\text{H}_4\text{O}_3$ . Using the general rules would give

## FINDING CARBON'S OXIDATION STATES IN ORGANIC COMPOUNDS (cont'd)

an average nitrogen oxidation state of +1. This is inappropriate, since this is an ionic compound. Thus, it is best to determine the oxidation state of each ion. The oxidation state of N in  $\text{NH}_4^+$  must be -3 since the ammonium cation



has a charge of +1: (-3 for N) + (+4 for the H atoms) = +1. The oxidation for N in  $\text{NO}_3^-$  must then be +5 since the nitrate anion has a charge of -1: (+5 for N) + (+6 for the O atoms).

Often for reduction–oxidation reactions involving large organic molecules, such as organochlorine pesticides, the net charge of the C, as well as N and sulfur, are often used rather than the individual charges. The electronegativity is used to determine oxidation states. For each atom in the organic molecule, the oxidation state can be calculated as +1 for each bond with an atom having greater electronegativity (or for each positive charge), -1 for each bond with an atom having less electronegativity (or for each negative charge), and 0 for each bond with an atom having the same electronegativity.

The pesticide DDT ( $1,1,1\text{-trichloro-2,2-bis-(4-chlorophenyl)-ethane}$  ( $\text{C}_{14}\text{H}_9\text{Cl}_5$ )) is reduced during metabolism to DDD ( $p,p'\text{-2,2-bis(4-chlorophenyl)-1,1-dichloroethane}$  or  $o,p'\text{-1-(2-chlorophenyl)-1-(4-chlorophenyl)-2,2-dichloroethane}$ ).

The reduction of DDT to DDD involves no change in any of the atoms in the molecule other than the C atom where the reaction occurs. At this attack site, the C is reduced from +3 to +1, so the half-reactions are



green plants' uptake of  $\text{CO}_2$  and release of  $\text{O}_2$  in photosynthesis and the uptake of  $\text{O}_2$  and release of  $\text{CO}_2$  in respiration by animals, microbes, and other organisms.

Hydrocarbons are formed when C reacts with hydrogen. In the strictest definition of organic chemistry, a hydrocarbon contains only C and H. A hydrocarbon molecule that contains the maximum number of H atoms is said to be saturated.

This is obviously reduction since one  $\text{H}^+$  is gained and a total of two electrons are transferred from an electron donor. This is known as reductive dechlorination, i.e. the loss of the Cl atom reduces the oxidation state of the C atom. All the rules of half-reaction apply and the reactions balance.<sup>2</sup>

It is important to keep in mind that reactions other than redox are involved in air pollution. For example, the DDT molecule as a whole is degraded without being reduced, when it is metabolized to DDE [ $p,p'\text{-1,1'-(2,2-dichloroethenylidene)-bis(4-chlorobenzene)}$  or dichlorodiphenyl-dichloroethylene]. As in the examples for the simpler molecules of acetone and 2-propanol, the C atoms undergo oxidation state changes, but the net change for the entire molecule is 0. That is, one of the C atoms changes from +3 to +2, but another C changes from -1 to 0. This reaction requires no electron transfer, as was needed for DDD. The DDT molecule is simply hydrolyzed to produce DDE plus water, releasing a chlorine ion ( $\text{Cl}^-$ ):

Hydrocarbons can be direct air pollutants (e.g. VOCs), as well as indirect air pollutants when they contribute to the formation of other pollution (e.g. photochemical reactions to form ozone and smog).

Combined with oxygen and hydrogen, carbon forms the biochemicals, including sugars, cellulose, lignin, chitins, alcohols, fats, and esters. Combined with nitrogen, carbon forms alkaloids—naturally occurring amines

TABLE 21.1 Approximate Mass of Carbon in the Earth's Major Sinks in 1999

Carbon Sink	Carbon Mass (US Billions of Metric Tons)
Atmosphere	766
Soil organic matter	1500–1600
Ocean	38,000–40,000
Marine sediments and sedimentary rocks	66,000,000–100,000,000
Terrestrial plants	540–610
Fossil fuel deposits	4000

Source: Schieber J. The importance of carbon for climate regulation. *Earth: our habitable planet*. <http://www.indiana.edu/~geol105b/1425chap8.htm>; 2007 [accessed 05.11.13].

produced by plants and animals, which combine to form proteins. Combined with sulfur, carbon is the source of antibiotics, proteins, and amino acids. Combined with phosphorus and a few other elements, carbon forms ribonucleic acid and deoxyribonucleic acid, the chemical codes of life.

From a mass balance perspective, C-based compounds that are considered to be air pollutants comprise a very small fraction of the carbon cycle (see Table 21.1).

Carbon compounds are at the center of technological, materials science, medical, and environmental breakthroughs. For example, many nanomaterials are carbon-based, such as carbon-60 ( $C_{60}$ ). Also, the functional groups attached to the outside of these nanospheres and tubes determine their usefulness (e.g. ways to keep them from aggregating into larger particles that do not possess the electromagnetic properties needed

for medicinal and engineering purposes) and the potential hazards (e.g. increased toxicity and mobility in bio-systems, such as the human body or ecosystems).

## 21.2 CARBON SINKS AND SOURCES

Carbon in its many inorganic and organic species is cycled continuously through the environment (see Figure 21.1).

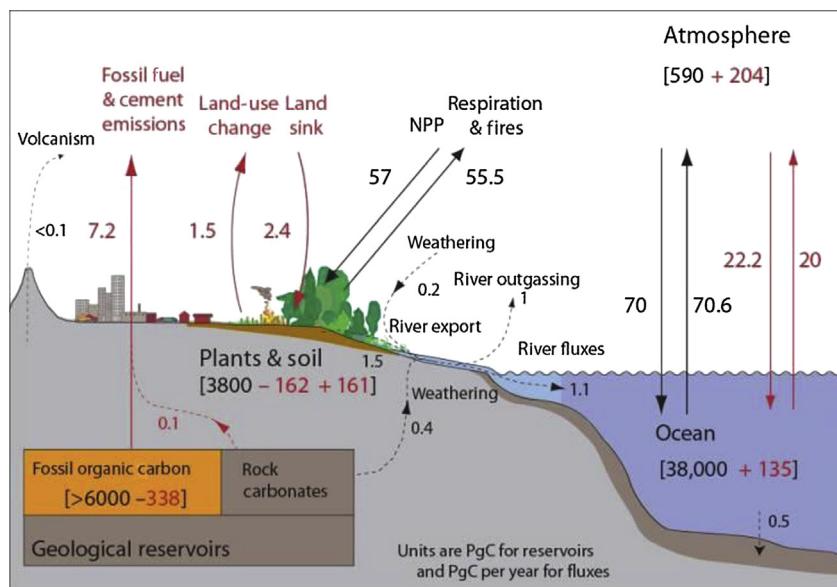
Figure 21.2 demonstrates the diversity of C sinks and sources. For example, if C can remain sequestered in the soil, roots, sediment, and other compartments, it is not released to the atmosphere. Thus, sequestering C is a means of ameliorating climate change by decreasing the amount of greenhouse gases released. Even relatively small amounts of methane and carbon dioxide can profoundly increase the atmosphere's greenhouse potential.

As mentioned, an organic compound is a compound that includes at least one carbon-to-carbon or carbon-to-hydrogen bond. C bonds to itself and to other elements in a myriad of ways, forming single, double, and triple bonds with itself. This makes for millions of possible organic compounds.

Even seemingly subtle changes to an organic molecule can profoundly affect its behavior in the atmosphere and the environment. For example, there are large ranges of solubility for organic compounds, depending upon the presence of polar groups in their structure. The addition of an alcohol group to the gas ethane to produce ethanol, e.g. by fermentation and other types of anaerobic digestion, changes the phase and increases aqueous solubility. This means that

FIGURE 21.1 Global carbon cycle from 2000 to 2005. Mean carbon storage (in square brackets) and exchanges of  $CO_2$  between different pools of carbon for the time period between 2000 and 2005. The black arrows indicate natural  $CO_2$  exchanges. The red arrows and numbers indicate additional exchanges and storage of carbon resulting from human activity. The exchanges are in petagrams (i.e.  $10^{15} g$ ) of carbon per year (PgC per year). NPP = net primary production, which is an indication of biotic activity and photosynthesis. (For interpretation of the references to color in this figure legend, the reader is referred to the online version of this book.)

Ref. 3



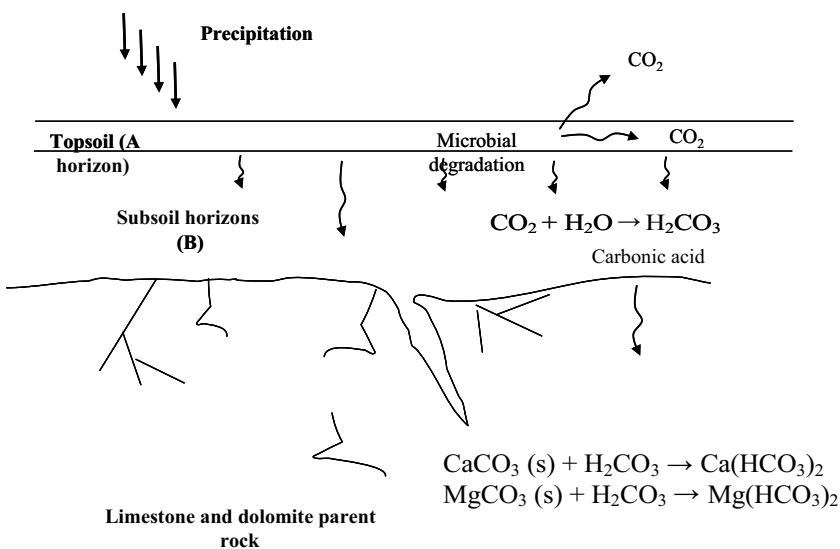


FIGURE 21.2 Biogeochemistry of carbon equilibrium. The processes that release carbonates are responsible for much of the buffering capacity of natural soils against the effects of acid rain.

considerations for siting a factory that makes use of organic compounds must take into account the physical, chemical, and biological affinities of all the substances, from the raw materials to intermediate compounds to the intended product. It also determines any pollution control devices. For example, if intermediate products have lower vapor pressures than raw materials, they will have to be addressed as air pollutants, whereas all the liquid phase compounds may be multiphase pollutants. Some may be released through leaks and conduits as liquids, but a portion will also partition to the gas phase (e.g. in the reactor headspace).

Alkanes are hydrocarbons that form chains with each link comprising the carbon. A single link is CH<sub>4</sub>, methane. The carbon chain length increases with the addition of carbon atoms which not only increases molecular weight but many other physicochemical characteristics, such as decreasing aqueous solubility and vapor pressure. The aromatics are based upon the six-carbon configuration of benzene (C<sub>6</sub>H<sub>6</sub>). The carbon-to-carbon bond in this configuration shares more than one electron, so that the benzene molecule has alternating double and single bonds between the carbon atoms. The double and single bonds flip; i.e. they resonate.

The organic compounds can undergo substitutions of the hydrogen atoms. These substitutions render new properties to the compounds, including changes in solubility, vapor pressure, and toxicity. For example, halogenation often renders the substitution molecule less reactive, more lipophilic, and increase bioavailability and toxicity.

By a vast majority, most carbon-based compounds are organic, but a number of inorganic compounds are also important to air pollution. Notably, CO<sub>2</sub> is an inorganic compound given that its C is bonded with O atoms and

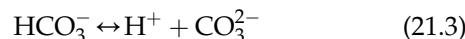
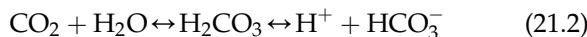
not with other C or H atoms. Cyanide compounds (CN<sup>-</sup>) and carbon monoxide (CO) are also inorganic compounds. Others include inorganic acids, e.g. carbonic acid (H<sub>2</sub>CO<sub>3</sub>) and cyanic acid (HCNO) and compounds derived from reactions with the anions carbonate (CO<sub>3</sub><sup>2-</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>).

## 21.3 CARBON EQUILIBRIUM AND CYCLING

Many carbon-based molecules exist in equilibrium with one another. For example, Figure 21.2 demonstrates the equilibrium among carbonates, bicarbonates, organic compounds, carbonic acid, and carbon dioxide. On a global scale, uncontaminated rain's mean pH is about 5.6, owing to its dissolution of carbon dioxide, CO<sub>2</sub>. As the water droplets fall through the air, the CO<sub>2</sub> in the atmosphere becomes dissolved in the water, setting up an equilibrium condition:



The CO<sub>2</sub> in the water reacts to produce hydrogen ions, as



Assuming the mean partial pressure CO<sub>2</sub> in the air to be  $3.0 \times 10^{-4}$  atm, it is possible to calculate the pH of water in equilibrium. Such chemistry is always temperature dependent, so let us assume that the air is 25 °C. The current mean concentration of CO<sub>2</sub> in the troposphere is approximately 370 ppm, but this concentration is rising by some estimates at a rate of 1 ppm per year.

Henry's law provides a way to explain C equilibrium. The law states that the concentration of a dissolved gas is directly proportional to the partial pressure of that gas above the solution:

$$p_a = K_H[c] \quad (21.4)$$

where,  $K_H$  = Henry's law constant;  $p_a$  = partial pressure of the gas; and  $[c]$  = molar concentration of the gas.

Or,

$$p_a = K_H C_W \quad (21.5)$$

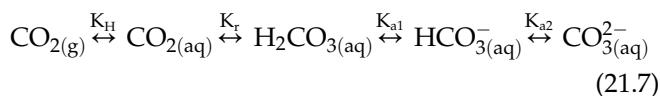
where,  $C_W$  is the concentration of gas in water.

Henry's law, as discussed in Chapter 18, is a function of a substance's solubility in water and its vapor pressure and expresses the proportionality between the concentration of a dissolved contaminant and its partial pressure in the open atmosphere at equilibrium. That is, the Henry's law constant is an example of an equilibrium constant, which is the ratio of concentrations when chemical equilibrium is reached in a reversible reaction, the time when the rate of the forward reaction is the same as the rate of the reverse reaction.

The  $\text{CO}_2$  concentration of the water droplet at equilibrium with air is obtained from the partial pressure of Henry's law constant:

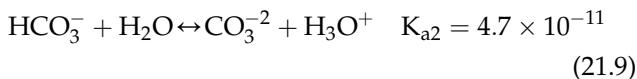
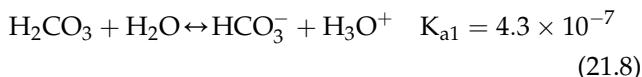
$$p_{\text{CO}_2} = K_H [\text{CO}_2]_{\text{aq}} \quad (21.6)$$

The change from carbon dioxide in the atmosphere to carbonate ions in water droplets follows a sequence of equilibrium reactions:



The processes that release carbonates increase the buffering capacity of natural soils against the effects of acidic water ( $\text{pH} < 5$ ). As discussed in Chapter 20, the ionic strength of the receiving soil or surface waters determines the actual change in pH. For example, the carbonate-rich soils like those central North America are able to withstand even elevated acid deposition compared to the thin soil areas, such as those in the Canadian Shield, the New York Finger Lakes region, and much of Scandinavia.

The concentration of carbon dioxide ( $\text{CO}_2$ ) is constant, since the  $\text{CO}_2$  in solution is in equilibrium with the air that has a constant partial pressure of  $\text{CO}_2$ . The two reactions and ionization constants for carbonic acid are:



$K_{a1}$  is four orders of magnitude greater than  $K_{a2}$ , so the second reaction can be ignored for the purposes of

C equilibrium. The solubility of gases in liquids can be described quantitatively by Henry's law. Thus,  $\text{CO}_2$  in the atmosphere at 25 °C, the Henry's law constant, and the partial pressure can be applied to find the equilibrium. The  $K_H$  for  $\text{CO}_2 = 3.4 \times 10^{-2} \text{ mol l}^{-1} \text{ atm}^{-1}$ . The partial pressure of  $\text{CO}_2$  is found by calculating the fraction of  $\text{CO}_2$  in the atmosphere. Assuming a mean concentration of  $\text{CO}_2$  in the earth's troposphere to be 370 ppm by volume in the atmosphere, the fraction of  $\text{CO}_2$  must be 370 divided by 1,000,000 or  $3.7 \times 10^{-4}$  atm.

Thus, the carbon dioxide and carbonic acid molar concentration can now be found:

$$\begin{aligned} [\text{CO}_2] &= [\text{H}_2\text{CO}_3] \\ &= 3.4 \times 10^{-2} \text{ mol l}^{-1} \text{ atm}^{-1} \times 0.000370 \text{ atm} \\ &= 1.3 \times 10^{-5} \text{ M} \end{aligned}$$

The equilibrium is  $[\text{H}_3\text{O}^+] = [\text{HCO}_3^-]$ . Taking this and the previously calculated  $\text{CO}_2$  molar concentration gives

$$\begin{aligned} K_{a1} &= 4.3 \times 10^{-7} = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{\text{CO}_2} = \frac{[\text{H}_3\text{O}^+]^2}{1.3 \times 10^{-5}} \\ [\text{H}_3\text{O}^+]^2 &= 5.6 \times 10^{-12} \\ [\text{H}_3\text{O}^+] &= 2.4 \times 10^{-6} \text{ M} \end{aligned}$$

The log of  $2.4 \times 10^{-6}$  is  $-5.63$ , so the negative log is about 5.63. Or, the droplet pH is about 5.63.

Carbon dioxide, with water, is the ultimate product of aerobic microbial respiration, but it is also an important greenhouse gas. From the preceding discussion, a global increase in  $\text{CO}_2$  concentrations must also change the mean acidity of precipitation. If the current trend continues, a rather constant increase in tropospheric  $\text{CO}_2$  concentrations is expected. For example, the increase from the present 370 to 400 ppm tropospheric  $\text{CO}_2$  concentrations would be accompanied by a proportional decrease in precipitation pH. The molar concentration can be adjusted using the previous equations:

$$\begin{aligned} 3.4 \times 10^{-2} \text{ mol l}^{-1} \text{ atm}^{-1} \times 0.000400 \text{ atm} \\ &= 1.4 \times 10^{-5} \text{ M}, \text{ so } 4.3 \times 10^{-7} \\ &= \frac{[\text{H}_3\text{O}^+]^2}{1.4 \times 10^{-5}} \text{ and } [\text{H}_3\text{O}^+]^2 \\ &= 6.0 \times 10^{-12} \text{ and } [\text{H}_3\text{O}^+] = 2.4 \times 10^{-6} \text{ M}. \end{aligned}$$

This is about  $-5.61$ , so the negative log is about 5.61. Or, the droplet pH is about 5.61. Thus, the worldwide average water droplet pH would be decreased only slightly, i.e. about 0.02. This means that the increase in atmospheric carbon dioxide can be expected to contribute to greater acidity in natural rainfall. The precipitation rates, i.e. the total amount of water released from the atmosphere and reaching the earth's surface, would also be affected if

greenhouse gas concentrations continue to increase, so any changes in atmospheric precipitation rates would also, on average, be expected to be more acidic. This is an interesting example of how the earth is actually a very large reactor. Changing one variable can profoundly change the entire system; in this instance the release of one gas changes numerous physical (e.g. temperature) and chemical (e.g. precipitation pH) factors, which in turn evoke a biological response (biome and ecosystem diversity).

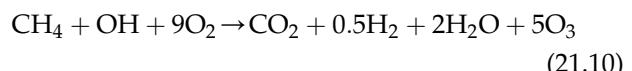
## 21.4 CARBON CYCLING AND CLIMATE

The discussion in the previous section indicates that there are many drivers and constraints involved in climate (see Figure 21.3). The increased amounts of CO<sub>2</sub> will likely affect global temperature, which affects biomes and the kinetics within individual ecosystems. Ecological structure, such as tree associations, canopies, and forest floors, as well as wetland structures may change, so that conditions may become reduced, with an attendant increase in anaerobic microbial decomposition, meaning greater releases of CH<sub>4</sub>, which would mean increasing global temperatures, all other factors being held constant. However, if greater biological activity and increased photosynthesis is triggered by the increase in CO<sub>2</sub>, and wetland depth is decreased, CH<sub>4</sub> global concentrations would fall, leading to less global temperature rise. Conversely, if this increased biological activity and photosynthesis leads to a decrease in forest

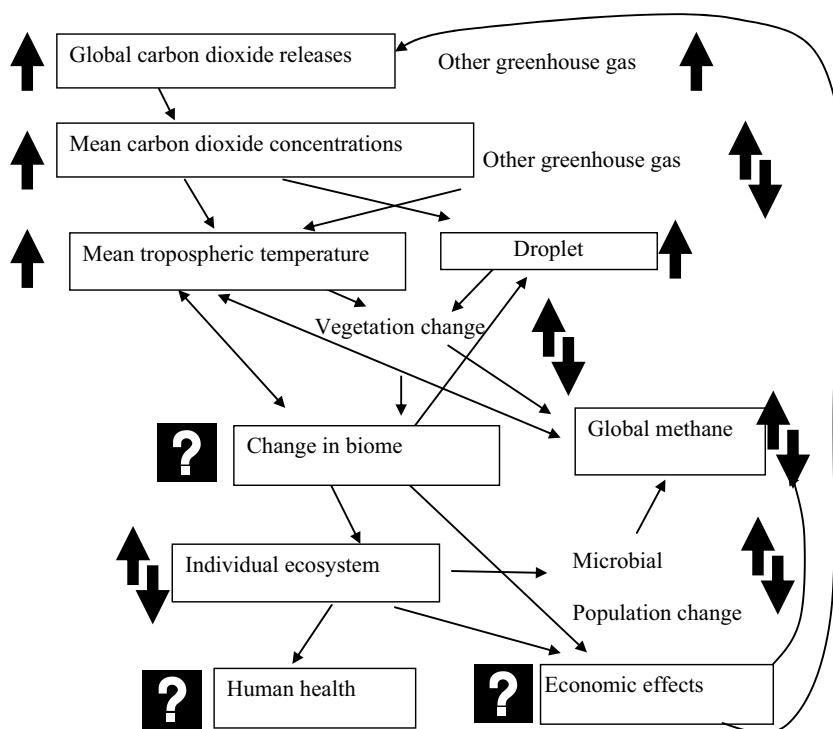
floor detritus mass, then less anaerobic activity may lead to lower releases of CH<sub>4</sub>. In actuality, there will be increases and decreases at various scales, so the net effects on a complex, planetary system is highly uncertain.

It is important to note that much of the concern for acid rain has been rightly concerned about compounds other than CO<sub>2</sub>, notably oxides of two other biophile elements, sulfur and nitrogen, which are discussed in the next chapter. These compounds can dramatically decrease the pH of rain. However, the increase in CO<sub>2</sub> means that the pH of rainfall, which is not neutral to begin with, can further adversely affect the fish and wildlife in and around surface waters as a consequence of C-based acidic compounds being added to the concentrations of sulfur and nitrogen compounds.

As mentioned, CH<sub>4</sub> is the product of anaerobic decomposition and human food production. Methane also is emitted during the combustion of fossil fuels and cutting and clearing of forests. The concentration of CH<sub>4</sub> in the atmosphere has been steady at about 0.75 for over a thousand years, and then increased to 0.85 ppm in 1900. Since then, in the span of only a hundred years, it has skyrocketed to 1.7 ppm. Methane is removed from the atmosphere by reaction with the hydroxyl radical (OH) as



This indicates that the reaction creates carbon dioxide, water vapor, and ozone, all which are greenhouse



**FIGURE 21.3** Systematic view of changes in tropospheric carbon dioxide. Thick arrows indicate whether this factor will increase (up arrow), decrease (down arrow), or vary depending on the specifics (e.g. some greenhouse gas releases have decreased, e.g. the chlorofluorocarbons, and some gases can cool the atmosphere, e.g. sulfate aerosols). Question mark indicates that the type and/or direction of change are unknown or mixed. Thin arrows connect the factors as drivers toward downstream effects.

gases; so the effect of one molecule of methane is devastating to the production of the greenhouse effect.

The difference in gas concentrations and the exchange coefficients between the atmosphere and surface waters determines how quickly a molecule of gas can move across the ocean–atmosphere boundary. It takes about 1 year to equilibrate CO<sub>2</sub> in the surface ocean with atmospheric CO<sub>2</sub>, thus large atmosphere–ocean differences in CO<sub>2</sub> concentrations are common. Biota and ocean circulation account for the majority of the difference. The oceans contain vast C reservoirs. The atmosphere exchanges CO<sub>2</sub> with these reservoirs, wherein CO<sub>2</sub> reacts with water to form carbonic acid and its dissociation products. With the increased atmospheric CO<sub>2</sub> concentrations, the interaction with the ocean surface alters the chemistry of the seawater resulting in ocean acidification.<sup>3</sup>

Ocean uptake of anthropogenic CO<sub>2</sub> is primarily a physical response to increasing atmospheric CO<sub>2</sub> concentrations. Increasing the partial pressure of a gas in the atmosphere directly above the body of water causes the gas to diffuse into that water until the partial pressures across the air–water interface are equilibrated. The effects are complex, e.g. increasing CO<sub>2</sub> also modifies the climate, which in turn may change ocean circulation, which changes the rate of ocean CO<sub>2</sub> uptake. Marine ecosystem changes also alter the uptake.<sup>3</sup>

The earth acts as a reflector to the sun's rays, receiving the radiation from the sun, reflecting some of it into space (i.e. albedo), and adsorbing the rest, only to reradiate this into space as heat. Carbon cycling directly affects albedo by affecting the vegetative cover. In effect the earth acts as a wave converter, receiving the high-energy high-frequency radiation from the sun and converting most of it into low-energy low-frequency heat to be radiated back into space. In this manner, the earth maintains a balance of temperature. Green plants ameliorate the effects of these light–heat exchanges.

The light energy and the heat energy have to be defined in terms of their radiation patterns, as shown in Figure 21.4. The incoming radiation (light) wavelength has a maximum at around 0.5 nm and almost all of it is less than 3 nm. The heat energy spectrum, or that energy reflected back into space, has a maximum at about 10 nm and almost all of it at a wavelength higher than 3 nm.

As both light and heat energy pass through the earth's atmosphere they encounter the aerosols and gases surrounding the earth. These can either allow the energy to pass through, or they can interrupt it by scattering or absorption. If the atoms in the gas molecules vibrate at the same frequency as the light energy, they will absorb the energy and not allow it to pass through. Aerosols will scatter the light and provide a “shade” for the earth. The incoming radiation is impeded by water vapor and oxygen and ozone, as discussed in the preceding section. Most of the light energy comes through unimpeded.

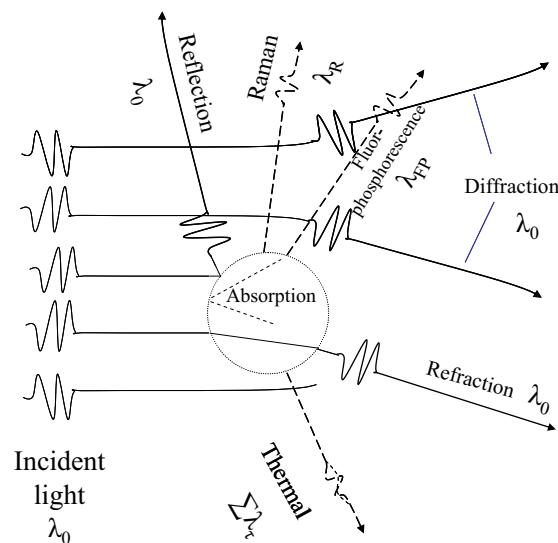


FIGURE 21.4 Patterns for heat and light energy. (For color version of this figure, the reader is referred to the online version of this book.)

The heat energy, however, encounters several potential impediments. As it is trying to reach outer space, it finds that water vapor, CO<sub>2</sub>, CH<sub>4</sub>, O<sub>3</sub>, and N<sub>2</sub>O. These compounds all have absorptive wavelengths in the middle of the heat spectrum. Quite obviously, an increase in the concentration of any of these will greatly limit the amount of heat transmitted into space. These gases are appropriately called greenhouse gases because their presence will limit the heat escaping into space, much like the glass of a greenhouse or even the glass in your car limits the amount of heat that can escape, thus building up the temperature under the glass cover.

The effectiveness of a particular gas to promote global warming (or cooling, as is the case with aerosols) is known as forcing. The gases of most importance in forcing are listed in Table 21.2.

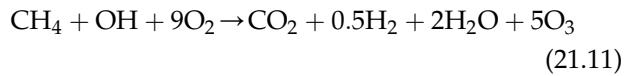
The effectiveness of CO<sub>2</sub> as a global warming gas has been known for over 100 years, but the first useful measurements of atmospheric CO<sub>2</sub> were not taken until 1957. The data from Mauna Loa in Hawaii are exceptionally useful since they show that even in the 1950s the

TABLE 21.2 Relative Forcing of Increased Global Temperature (Excluding Water Vapor)

Greenhouse Gas	Percentage of Relative Radiative Forcing
Carbon dioxide, CO <sub>2</sub>	64
Methane, CH <sub>4</sub>	19
Halocarbons (mostly CFCs)	11
Nitrous oxide, N <sub>2</sub> O	6

$\text{CO}_2$  concentration had increased from the baseline 280 ppm to 315 ppm, and this has continued to climb over the last 50 years at a constant rate of about 1.6 ppm per year. Arguably, the most serious problem with  $\text{CO}_2$  is that the effects on global temperature due to its greenhouse effect are delayed. The  $\text{CO}_2$  that is already in the troposphere will, even if combustion sources stopped emitting any new  $\text{CO}_2$  into the atmosphere, increase concentrations of  $\text{CO}_2$  from our present 370 ppm to possibly higher than 600 ppm. That is, if every combustion source immediately stopped emitting  $\text{CO}_2$  today, we have already contaminated the global atmosphere to where we will have doubled the  $\text{CO}_2$  concentration. The effect of this is discussed below.

Methane is the product of anaerobic decomposition and human food production. One of the highest producers of methane in the world is New Zealand, which boasts 80 million sheep. Methane also is emitted during the combustion of fossil fuels and cutting and clearing of forests. The concentration of  $\text{CH}_4$  in the atmosphere has been steady at about 0.75 ppm for over a thousand years, and then increased to 0.85 ppm in 1900. Since then, in the space of only a hundred years, it has skyrocketed to 1.7 ppm. Methane is removed from the atmosphere by reaction with the hydroxyl radical ( $\text{OH}$ ) as



But in so doing, it creates carbon dioxide, water vapor, and ozone, all of which are greenhouse gases, so the effect of one molecule of methane is devastating to the production of the greenhouse effect.

Halocarbons are the same classes of compounds involved in the destruction of atmospheric ozone, and are also at work in promoting global warming. The most effective global warming gases are CFC-11 and CFC-12, both of which are no longer manufactured, and the banning of these substances has shown a leveling off in the stratosphere.

Certainly, not all greenhouse gases are C-based. Nitrous oxide is emitted to the atmosphere predominantly as a result of human activities, especially the cutting and clearing of tropical forests (which, as mentioned, also has deleterious albedo consequences). The greatest problem with nitrous oxide is that there appear to be no natural removal processes for this gas and so its residence time in the stratosphere is quite long. This is another example of the interrelationships and interdependencies between the C and N cycles.

The net effect of these global pollutants is still being debated. Various atmospheric models used to predict temperature change over the next 100 years vary widely. They nevertheless agree that some positive change will occur. By the year 2100, even if we do not increase our

production of greenhouse gases and international agreements are reached and subsequently followed, the global temperature is likely to be between 0.5 and 1.5 °C warmer than at present. This effect of this on natural systems and dynamics in the oceans and atmosphere could be devastating.

The cycling of C indicates the numerous complexities in addressing air pollution science and engineering. For example, pollution control efficiency and success have often been based on  $\text{CO}_2$  production rates, i.e. the greater the amount of  $\text{CO}_2$  leaving a stack, the better air pollution control equipment is operating. This is because complete combustion results in the production of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Likewise, the production of  $\text{CH}_4$  has been an indication of complete anaerobic digestion of organic compounds. Both these indicators of pollution control success are greenhouse gases.

Air pollution decisions are often made among competing interests and perspectives. These involve trade-offs. For example, remediating a contaminated site may call for excavation of soil, which is then incinerated. The complete incineration will result in generating and emitting greenhouse gases. Determining whether this approach is successful and appropriate depends on the extent and quality of options from which these emissions occur. For example, if dioxin-laden soil is incinerated, this may have been the only viable approach to detoxify a very toxic and persistent compound. Releasing  $\text{CO}_2$  in this case is truly a measure of success.

Another lesson that can be drawn from C cycling is that of feedback systems. For example, scientific principles can be put to work at various points in the event cascade in Figure 21.3 to weight the factors in terms of their contribution to climate change and to begin to address these factors with engineering and other interventions. As evidence, several steps in the causal chain occur before a biome is adversely affected. Therefore, preventing the impact will require the elimination of an action that leads to other actions that ultimately affect the biome. This is preferable to allowing the biome impact to occur and then to remediate the problems that it brings.

One of the biggest engineering challenges is how to select and operate control technologies in a manner fully cognizant and deferential of the biogeochemical cycles. This view would likely bring valuable information to the current debates on the projected impact of global climate change; especially, in light of the seeming paucity of ways to deal with the problem. The National Academy of Engineering has identified the most important challenges to the future of engineering. Both the nitrogen and carbon biogeochemical cycles are explicitly identified among the most pressing engineering needs.

The biogeochemical cycle that extracts nitrogen from the air for its incorporation into plants—and hence

food—has become altered by human activity. With widespread use of fertilizers and high-temperature industrial combustion, humans have doubled the rate at which nitrogen is removed from the air relative to preindustrial times, contributing to smog and acid rain, polluting drinking water, and even worsening global warming. Engineers must design countermeasures for the nitrogen cycle problems discussed in the next chapter, while maintaining the ability of agriculture to produce adequate food supplies.<sup>4</sup> The C cycle and nutrient cycles are inextricably linked. Like C, chemical species of N and the other nutrient elements are essential and toxic, depending on its dose and form. The Academy articulates this challenge:

The biogeochemical cycle that extracts nitrogen from the air for its incorporation into plants—and hence food—has become altered by human activity. With widespread use of fertilizers and high-temperature industrial combustion, humans have doubled the rate at which nitrogen is removed from the air relative to preindustrial times, contributing to smog and acid rain, polluting drinking water, and even worsening global warming. Engineers must design countermeasures for nitrogen cycle problems, while maintaining the ability of agriculture to produce adequate food supplies.<sup>4</sup>

Engineers can expect to be increasingly asked to recommend improvements to the biogeochemical cycling of C, such as enhancements to the food life cycles (e.g. animal feeding operations, farmlands, rangelands, and groceries). How can engineering innovation improve the efficiency of various human activities related to nitrogen, from making fertilizer to recycling food wastes? Currently, less than half of the fixed nitrogen generated by farming practices actually ends up in harvested crops. And less than half of the nitrogen in those crops actually ends up in the foods that humans consume. In other words, fixed nitrogen leaks out of the system at various stages in the process—from the farm field to the feedlot to the sewage treatment plant. Engineers not only need to identify the leakage points and to devise systems to plug them, i.e. the structural and mechanical solutions, but also must engage biological solutions, such as understanding the processes that lead to increased C and nutrient emissions, and applying this understanding to modify the processes accordingly.<sup>5</sup>

## **21.5 CARBON GEOENGINEERING**

Recently, some engineers and scientists have suggested that it would be prudent to consider engaging

in planetary-scale interventions, so-called geoengineering, to mitigate global climate change and global warming in particular. Geoengineering differs from other methods for mitigating global warming because it involves a deliberate effort to affect the climate at a global scale. Although geoengineering is not a new idea, it has taken on added significance as a result of difficulties with implementing other proposals to mitigate climate change. While proponents of geoengineering admit that these measures can be associated with significant risks to the environment and public health, they maintain that they are well worth pursuing, given the failure to date of means of mitigating global warming. Conversely, some environmental groups have voiced strong opposition to all forms of geoengineering.

Carbon sequestration is one type of geoengineering that has received considerable attention. Actually, sequestration is an ongoing, geophysical process. Carbon compounds, especially CO<sub>2</sub> and CH<sub>4</sub>, find their way to the ocean, forests, and other carbon sinks.<sup>b</sup> Like many geobiochemical processes, sequestration is one that can be influenced by human activity. Thus, there is a conservation aspect to protecting these mechanisms that are working to our benefit.

The second approach is one that is most familiar to the engineer, that is, application of scientific principles to enhance sequestration. These sequestration technologies include new ways either to sequester carbon or to enhance or expedite processes that already exist.

Conservation is an example of a more “passive” approach. There are currently enormous releases of carbon that, if eliminated, would greatly reduce the loading to the troposphere. For example, anything we can do to protect the loss of forest, woodlands, wetlands, and other ecosystems is a way of preventing future problems. In fact, much of the terrestrial fluxes and sinks of carbon involves the soil. Keeping the soil in place must be part of the overall global strategy to reduce greenhouse gases.

Anticipating the continued use of fossil fuels, engineers have explored technological methods of capturing the carbon dioxide produced from fuel burning and sequestering it underground.<sup>6</sup> Sequestration is a biosystematic solution since it is an ongoing process on planet earth, with myriad interactions between biotic and abiotic factors. The arrows in [Figure 21.1](#) show that carbon compounds, especially CO<sub>2</sub> and CH<sub>4</sub>, find their way to the ocean, forests, and other carbon sinks. Like many biogeochemical processes, sequestration can be influenced by human action.

<sup>b</sup> This is a common theme of environmental engineering, i.e. to borrow a naturally occurring process, but to speed it up and otherwise enhance it to address pollution. Wastewater treatment, and biological (e.g. biofilters) air pollution control systems, for example, mimic soil and water microbial systems.

### 21.5.1 Carbon Sequestration in Soil

The soil is home to *Pseudomonas* and numerous other species that have been used to treat wastes for decades. The very essence of a soil's "value" has been its capacity to support plant life, especially crops. At a minimum, air pollution prevention strategies must include an understanding of soil properties such as their texture or grain size (see Table 21.3), ion exchange capacities, ionic strength, pH, microbial populations, and soil organic matter content.

Soil is a matrix made up of various components, including organic matter and unconsolidated material. The matrix contains liquids (i.e. "substrate" to the chemist and bioengineer) within its interstices. Much of the substrate in this matrix is water with varying amounts of solutes. Under most environmental conditions, air and water are solutions of very dilute amounts of compounds. For example, air's solutes represent small percentages of the solution at the highest (e.g. water vapor) and most other solutes represent parts per million (recall that there is about 370 ppm carbon dioxide). Soil is a conglomeration of all states of matter. Soil is predominantly solid, but frequently has large fractions of liquid (soil water) and gas (soil air, methane, and carbon dioxide) that make up the matrix. The composition of each fraction is highly variable. For example, soil gas concentrations are different from those in the atmosphere and change profoundly with depth from the surface. Table 21.4 illustrates the inverse relationship between carbon dioxide and molecular oxygen. Sediment can be envisioned as an underwater soil. It is a collection of particles that have settled on the bottom of water bodies.

Ecosystems are combinations of these media. For example, a wetland system consists of plants that grow in soil, sediment, and water. The water flows through

TABLE 21.3 Commonly Used Soil Texture Classifications

Name	Size Range (mm)
Gravel	>2.0
Very coarse sand	1.0–1.999
Coarse sand	0.500–0.999
Medium sand	0.250–0.499
Fine sand	0.100–0.249
Very fine sand	0.050–0.099
Silt	0.002–0.049
Clay	<0.002

Source: Lochnachar T, Brown K, Cooper T, Milford M. Sustaining our soils and society. Washington (DC): American Geological Institute, Soil Science Society of America, USDA Natural Resource Conservation Service; 1999.

TABLE 21.4 Composition of Two Important Gases in Soil Air

Depth from Surface (cm)	Silty Clay		Silty Clay Loam		Sandy Loam	
	O <sub>2</sub> (% Volume of Air)	CO <sub>2</sub> (% Volume of Air)	O <sub>2</sub> (% Volume of Air)	CO <sub>2</sub> (% Volume of Air)	O <sub>2</sub> (% Volume of Air)	CO <sub>2</sub> (% Volume of Air)
30	18.2	1.7	19.8	1.0	19.9	0.8
61	16.7	2.8	17.9	3.2	19.4	1.3
91	15.6	3.7	16.8	4.6	19.1	1.5
122	12.3	7.9	16.0	6.2	18.3	2.1
152	8.8	10.6	15.3	7.1	17.9	2.7
183	4.6	10.3	14.8	7.0	17.5	3.0

Source: Evangelou VP. Environmental soil and water chemistry: principles and applications. New York: John Wiley and Sons, Inc.; 1998.

living and nonliving materials. Microbial populations live in the surface water, with aerobic species congregating near the water surface and anaerobic microbes increasing with depth due to the decrease in oxygen levels, due to the reduced conditions. Air is not only important at the water and soil interfaces, but it is a vehicle for nutrients and contaminants delivered to the wetland. The groundwater is fed by the surface water during high water conditions, and feeds the wetland during low water conditions.

These environmental media are compartments, each with boundary conditions, kinetics, and partitioning relationships within a compartment or among other compartments. Chemicals, whether nutrients or contaminants, change as a result of the time spent in each compartment. The bioengineering challenge is to describe, characterize, and predict the behaviors of various chemical species as they move through the media. When something is amiss, the cause and cure lie within the physics, chemistry, and biology of the system.

Soil conservation is an important part of sustainable agriculture and food production, since it entails keeping soil from becoming a pollutant in the surface waters, and its ability to sieve and filter pollutants that would otherwise end up in drinking water. Another perhaps less obvious benefit is that soil is a vast sink for carbon. Soil is lost when land is degraded by deforestation and as a result of inadequate land use and management in sensitive soil systems, especially those in the tropics and subtropics, such as slash and burn and other aggressive practices. As is often the case in ecosystems, some of the most valuable ecosystems in terms of the amount of carbon sequestered and oxygen generated are also the most sensitive. Tropical systems, e.g., often have some of the thinnest soils due to the rapid oxidation processes that take place in humid, oxidized environments.

Sensitive systems are given value by society for a single purpose. Bauxite, e.g., is present in tropical soils due to the physical and chemical conditions of the tropics (aluminum in parent rock material, oxidation, humidity, and ion exchange processes). However, from a life cycle and resource planning perspective, such single-mindedness is folly. The decision to extract bauxite, iron, or other materials from sensitive tropical rain forests must be seen in terms of local, regional, and global impacts. With this in mind, international organizations are promoting improved land use systems and land management practices, which give both economic and environmental benefits.

Keeping soil intact protects biological diversity, improves ecosystem conditions, and increases carbon sequestration. This last-mentioned benefit includes numerous forms of carbon in all physical phases. Soil gases include CO<sub>2</sub> and CH<sub>4</sub>. Plant root systems, fungi, and other organisms that are composed of amino acids, proteins, carbohydrates, and other organic compounds live in the soil. Even inorganic forms of carbon are held in soil, such as the carbonate, bicarbonate, and carbonic acid chemical species that are in soils as a result of chemical reactions with parent rock material, especially limestone and dolomite. When the soils are lost, all these carbon compounds become available to be released to the atmosphere. Thus, soil conservation is a passive process that can be enhanced to sequester carbon.

### 21.5.2 Active Carbon Sequestration

Active sequestration is the application of technologies to send carbon to the sinks, including deep rock formations and the oceans. Such technology can be applied directly to sources. Such technology can be applied directly to sources. For example, fires from China's coal mines presently release about 1 billion metric tons of CO<sub>2</sub> into the atmosphere every year. Estimates put

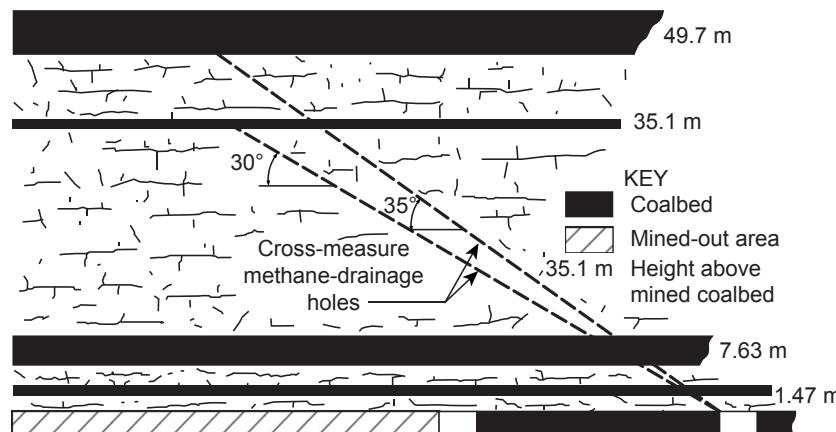
India's coal mine fire releases to be about 50 million tons. This accounts for as much as 1% of all carbon greenhouse releases. This is about the same as the CO<sub>2</sub> released by all of the gasoline-fuel automobiles in the United States. Engineering solutions that reduce these emissions would actively improve the net greenhouse gas global flux.

The United States has a checkered history when it comes to coal mine fires. Some underground mines have burned for more than a century. Intuitively, putting out such fires may seem straightforward. For example, we know that combustion depends on three components: a fuel, a heat source, and oxygen. All three are needed, so a coal fire can be eliminated if just one of these essential ingredients is removed. Unfortunately, since the fire is in an underground vein, fuel is plentiful. Actually, the solid-phase coal is less of a factor than the available CH<sub>4</sub>, which is ubiquitous in coal mines. And like the "whack-a-mole" game, the avenues of access to the fire mean that the heat source is available in different channels. When one is closed off, another appears.

So, the only remaining option is to deprive the fire of O<sub>2</sub>. In fact, most attempts have been outright failures in this regard. Flooding the mines has been ineffective, since the fire simply finds alternative pathways in the leaky underground strata. Excavation has to almost be 100% to be effective. Flushing with slurries has the same problems. In fact, miner safety and postignition fire suppression can be seen as competing factors in mining. To ensure sufficient oxygen levels and low toxic gas concentrations the mine's ventilation systems require methane-drainage holes to control methane at the face. In many abandoned mines, cross-measure holes (see Figure 21.5) were the most common types. These systems are one reason that oxygen remains available to the fire.<sup>7</sup>

Recent studies have shown that certain foams can deprive fires of O<sub>2</sub> over extensive areas. For example, a

**FIGURE 21.5** Section view of cross-measure methane-drainage holes in a coal mine ventilation system. Ref. 7; and McKensey BR, Longwell JWR. Ventilation with methane and spontaneous combustion-Pacific Colliery. Paper in fourth international mine ventilation congress (Brisbane, Australia, July 3–6, 1988). Melbourne (Australia): Australian Institute of Mining and Metallurgy; 1988. p. 617–24.



study sanctioned by the US National Institute of Occupational Safety and Health (NIOSH) showed preliminary success in sealing a coal mine from oxygen inflow, and suppression of the fire with liquid nitrogen and gas-enhanced foam.<sup>8</sup> The technology needs to be advanced to address the very large fires. The fire studied by NIOSH (see Figure 21.6) was caught in the early stages and suppressed within 2 weeks. But, like many engineering prototypes, showing that it can work is only the first step to ensure it will work.

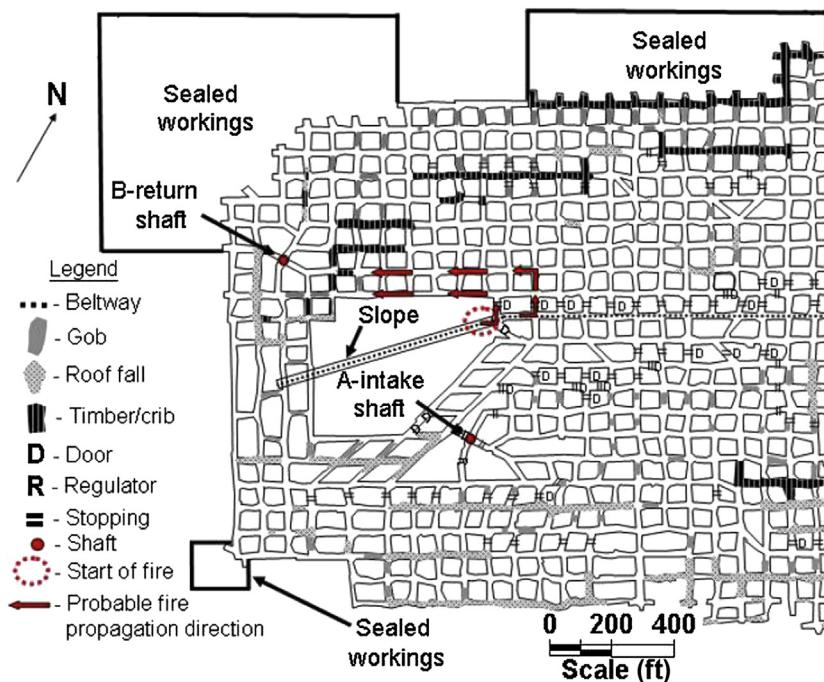
Another active geoengineering approach is an enhancement of existing processes. For example, in addition to conserving present levels of carbon sequestration, technologies can be adapted to increase the rates of sequestration. The scale of such technology can range from an individual source, such as a fossil fuel burning electricity generation station that returns its stack gases to an underground rock stratum, to an extensive system of collection and injection systems that include a whole network of facilities. The combination of disincentives, like carbon taxes, and application of emerging technologies can decrease the carbon flux to the atmosphere. Thus, green engineering is part of the overall, comprehensive geopolitical strategy.

Even a system as large as the ocean has its limits in greenhouse gas sequestration. For starters, most of the CO<sub>2</sub> generated by human activities (i.e. anthropogenic) resides in the upper layers of the ocean (see Figure 21.7). Carbon compounds move into and out of oceans predominantly as a function of the solubility of the compound and water temperature. For CO<sub>2</sub>, this means that more of the compound will remain in the ocean

water with decreasing temperature. Ocean mixing is very slow. Thus, the anthropogenic CO<sub>2</sub> from the atmosphere is predominantly confined to the very top layers. Virtually half of the anthropogenic CO<sub>2</sub> taken up by the ocean for the previous two centuries has stayed in the upper 10% of the ocean. The ocean has removed 48% of the CO<sub>2</sub> released to the troposphere from burning fossil fuels and cement manufacturing.<sup>9</sup>

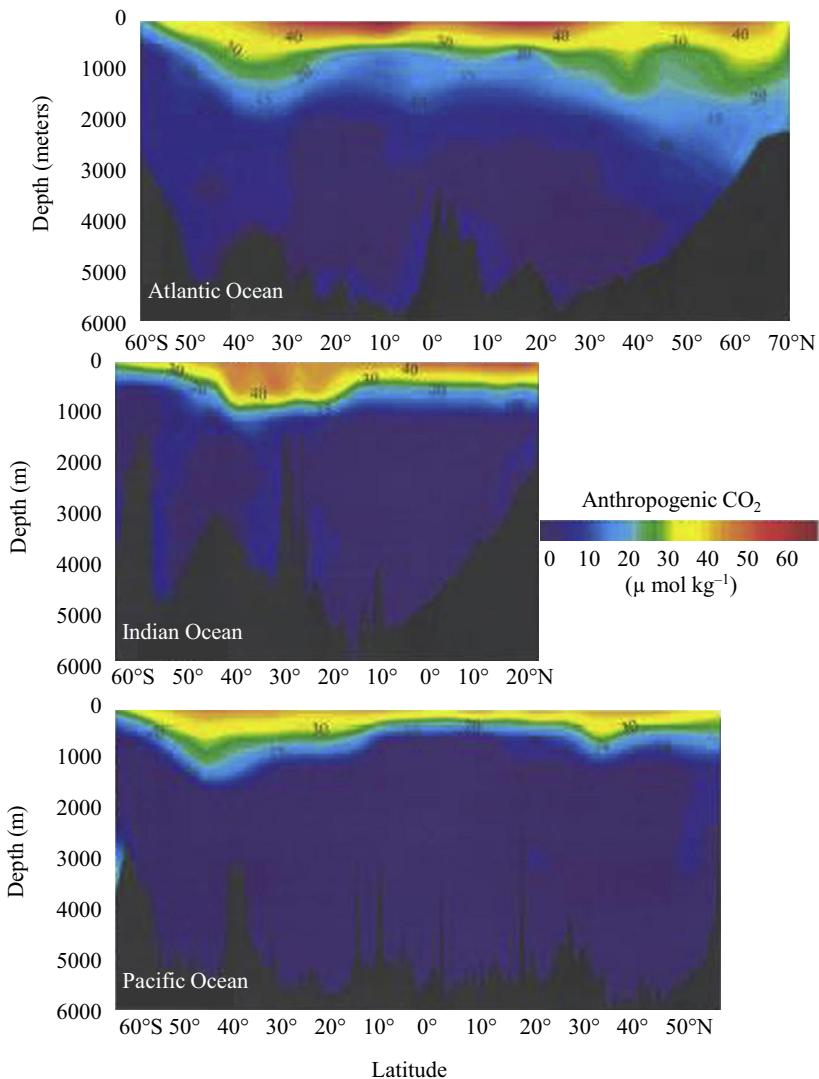
Sequestration not only requires moving C to a sink, but also holding the C for long time periods. Thus, to keep CO<sub>2</sub> sequestered, it must move to the cooler, deeper parts of the ocean. Otherwise, when CO<sub>2</sub> resides near the warmer surface, it is more likely to be released to the atmosphere. The actual mass of C can be increased by management. For example, certain species of plankton are often limited in growth by metals, especially iron. Thus, increasing the iron concentrations in certain ocean layers could dramatically increase the ability of these organisms to take up and store C. In addition, even if the technological means of moving C to the ocean reservoirs is workable, the sequestration may lead to large-scale and virtually irreversible consequences. In particular, there is already troubling evidence of ocean acidification due to increases in atmospheric CO<sub>2</sub> concentrations, notwithstanding the effects of intentional sequestration (see Discussion Box in Chapter 5: Ocean Acidification).

Obviously, any large-scale endeavor like geoengineering must be approached with an appropriate amount of caution. The best decisions are ones that account for all possible outcomes, certainly not exclusively the ones hoped for. Such an approach would likely include

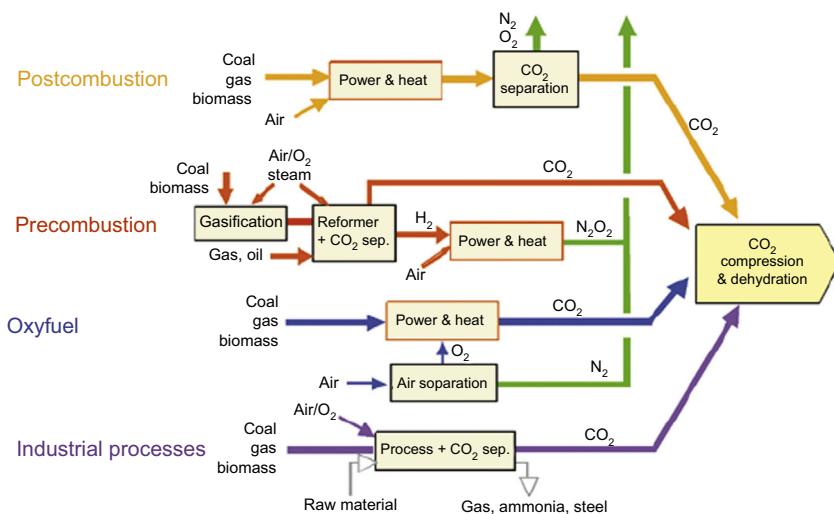


**FIGURE 21.6** Map of fire zone in Excel #3 coal mine in eastern Kentucky. (For color version of this figure, the reader is referred to the online version of this book.)

**FIGURE 21.7 Anthropogenic carbon concentrations in three ocean systems.** Note that most of the CO<sub>2</sub> resides above the 1000 m depth. (For color version of this figure, the reader is referred to the online version of this book.) *Adapted from an original illustration by Northern Arizona University. Used with permission.*



**FIGURE 21.8 Schematic diagram of potential means of capturing carbon dioxide.** (For color version of this figure, the reader is referred to the online version of this book.) *Intergovernmental Panel on Climate Change. Special report on carbon dioxide capture and storage. [www.ipcc.ch/pdf/special-reports/srccs\\_chapter3.pdf](http://www.ipcc.ch/pdf/special-reports/srccs_chapter3.pdf); 2005 [accessed 09.03.12].*



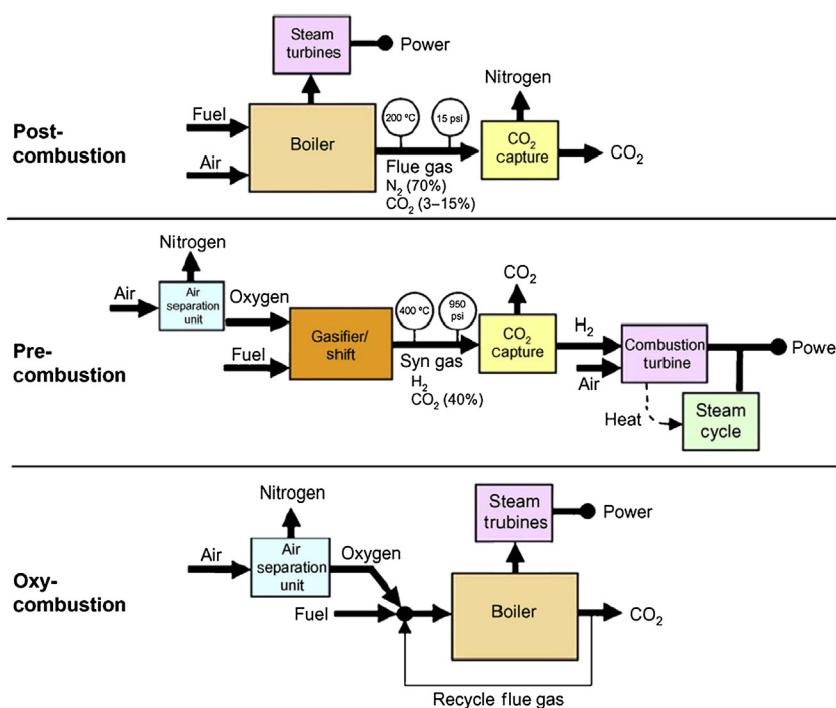


FIGURE 21.9 Block diagrams illustrating postcombustion, precombustion, and oxy-combustion systems. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 11.

tests in laboratories, stepped up to prototypes on as many possible scenarios and species possible, before actual implementation.

With these caveats, C sequestration is promising. The Intergovernmental Panel on Climate Change has identified four basic systems for capturing CO<sub>2</sub> from use of fossil fuels and/or biomass processes:

1. Capture from industrial process streams
2. Postcombustion capture
3. Oxyfuel combustion capture
4. Precombustion capture<sup>10</sup>

The likely critical paths of these technologies are shown in Figure 21.8 and general configurations of the technologies are depicted in Figure 21.9. Thus, at numerous points in the C biogeochemical cycle, there are numerous ways of conserving and adding to natural sequestration processes that could significantly decrease the net greenhouse gas concentrations in the atmosphere.

The sequestration can take place at numerous locations in the C cycles. For example, a promising approach is to deploy the biotic portion of the C cycle. Organisms have very effective means of sequestering CO<sub>2</sub> during respiration. Technologies can be developed to take advantage of metabolic reactions involving CO<sub>2</sub> in living organisms, particularly enzymatic processes. In one enzyme-based system,<sup>11</sup> CO<sub>2</sub> is captured and released by emulating the mammalian respiratory system (see Figure 21.10). The process employs carbonic anhydrase (CA) contained in a hollow fiber liquid membrane. The

CA developing membrane is used to separate CO<sub>2</sub> from the flue gas. Modifying the membrane allows for enhanced diffusion of CO<sub>2</sub> due to the strong interactions between the permeating CO<sub>2</sub> molecules and the amine functional membrane pores should enhance selective diffusion of CO<sub>2</sub>. Movement of other gases, such as O<sub>2</sub>, N<sub>2</sub>, and SO<sub>2</sub> is blocked, which increases selective sequestration of CO<sub>2</sub>.

Carbon cycling must be considered along with the biogeochemical cycling of other substances. The cycling

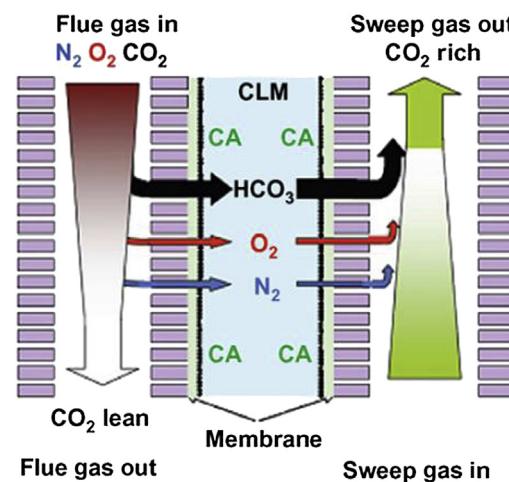


FIGURE 21.10 Schematic of carbozyme permeation process for carbon dioxide sequestration. CLM = contained liquid membrane; CA = carbonic anhydrase. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 11.

of C is affected by and affects the types and rates of cycling of many other elements, especially N and S, which are discussed in the next chapter.

## QUESTIONS

1. Identify and briefly describe the four major biophile molecules in terms of their role in living systems.
2. What inherent characteristics make for carbon-based organisms on earth?
3. What inherent characteristics make for the large number of carbon-based air pollutants?
4. Find the oxidation states of the each carbon position in octanol.
5. Find the oxidation states of the each carbon position in acetaldehyde.
6. Describe the difference in the metabolism or degradation of DDT to DDD *versus* DDT to DDE.
7. What are the largest and smallest oxidation numbers that carbon can attain? Give two examples of molecules for C having these valences.
8. Can a mole of glucose be degraded to two molecules of lactic acid?
9. Give an example of a direct hydrocarbon air pollutant and an indirect hydrocarbon air pollutant.
10. What is the largest source of carbon emitted into the atmosphere? What is the largest C sink? Given these numbers, is the anthropogenic fraction important?
11. Assuming that other sources of acidity remain constant, e.g., concentrations of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{NO}_3$  do not change, what would happen to the average pH in rainfall if the global  $\text{CO}_2$  average concentration increases to 550 ppm?
12. Describe two scenarios of each item in Figure 21.3 showing question marks, where there would be benefits from increased concentrations of  $\text{CO}_2$ . Describe two scenarios in which they would worsen as a result of increased  $\text{CO}_2$ .
13. Describe the pros and cons of geoengineering solutions to global climate change.
14. Explain the reasons for the  $\text{O}_2$  and  $\text{CO}_2$  concentration profiles in soil. How do these profiles change soil chemistry? How does this affect the atmosphere?

15. Describe two physical differences between terrestrial and ocean C sequestration.
16. Describe two chemical differences between terrestrial and ocean C sequestration.
17. Give examples of two biotechnologies that can be employed to enhance C sequestration.

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# The Nitrogen and Sulfur Cycles

In many texts, nitrogen (N) and sulfur (S) are addressed together, along with phosphorous (P) and potassium (K). These are considered to be macronutrients since plant life depends on them for survival and growth. Thus, ecologists and other environmental scientists may argue that this chapter be correctly entitled "Nutrient Cycling". However, from an air pollution perspective, N and S compounds deserve special attention.

Many N and S compounds are air pollutants. Two of the six National Ambient Air Quality Standards (NAAQS) pollutants are oxides of these elements, i.e. sulfur dioxide ( $\text{SO}_4$ ) and nitrogen dioxide ( $\text{NO}_2$ ). In addition, the oxides of nitrogen ( $\text{NO}_x$ ), made up of  $\text{NO}_2$  and nitric oxide (NO), are major precursors of another NAAQS pollutant, i.e. ozone. Even more N and S compounds are constituents in the cells of the living receptors affected by pollutants, including amines, proteins, and genetic molecules. The good news is that, in the Western hemisphere, the tropospheric concentrations of N and S pollutants have generally fallen in recent decades (Figure 22.1). The bad news is that these improvements are not being experienced in many parts of the world.

## 22.1 THE NITROGEN CYCLE

Nitrogen is part of the abiotic (nonliving) and biotic (living) parts of earth. The element exists in myriad chemical forms that move at varying rates in the nitrogen cycle. Like carbon discussed in the previous chapter, N is stored in reservoirs such as the atmosphere, living organisms, soils, and oceans.<sup>4</sup> From these sinks, N cycles between the biosphere and the atmosphere. The N cycles among ecosystems and the organisms, including humans, within these ecosystems.

Most of the earth's mass of N resides in the atmosphere. Approximately 79% of the molecules in Earth's atmosphere are molecular nitrogen ( $\text{N}_2$ ). All organisms must metabolize N into larger molecules; notably amino acids, proteins, and deoxyribonucleic acid (DNA).

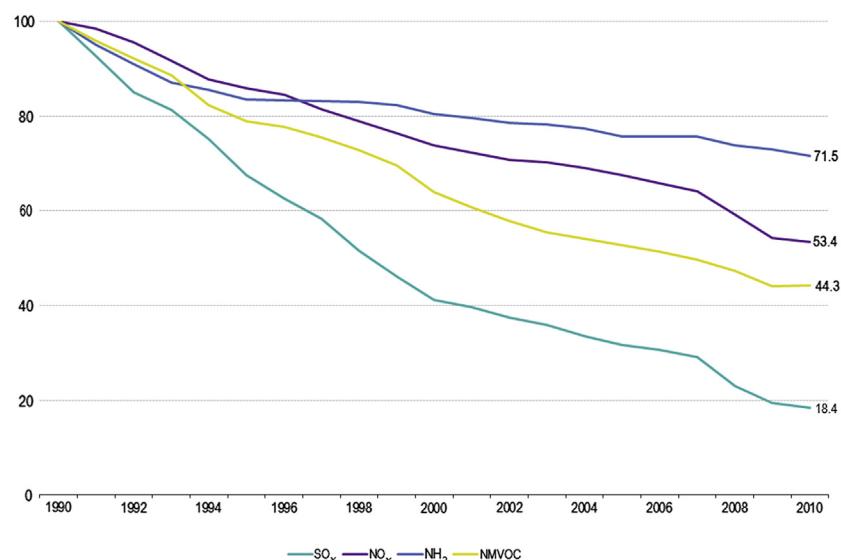
Amino acids contain the functional group amine ( $\text{NH}_2$ ) and are the building blocks of proteins. DNA consists of adenine, cytosine, guanine, and thymine, which consist of rings of carbon and nitrogen atoms, with various side chains.

The  $\text{N}_2$  is not directly available to most organisms (a major exception being the N-fixing bacteria found in legume roots). The atmospheric  $\text{N}_2$  is converted to bioavailable N species (e.g. nitrates;  $\text{NO}_3^-$ ) abiotically (e.g. lightning strikes or fires) and biotically (e.g. by the N-fixing bacteria known as diazotrophs).

Energy exchange in many ecosystems is largely controlled by available N as a result of N-limits of the flora and microorganisms living within these systems. Indeed, along with P, the amount of N is the major limiting factor on the rate of net primary production of biomass in most ecosystems. That is, an increase in bioavailable N is associated with an increase in production of biomass of these organisms in an ecosystem. For example, increasing the amount of carbon in a lake system will have little effect on the production of biomass since most systems have ample mass of bioavailable C. Conversely, increasing bioavailable N in most lake systems increases total biomass. Similar limits are placed on terrestrial biota. Thus, N is a limiting factor for plant growth.

The N-cycle mirrors the trophic state and energy cycles in ecosystems. Producers convert mineral forms of N to N-containing molecules, e.g. amino acids and DNA. Consumers then receive N by consuming producers and forming even larger N-containing molecules, e.g. proteins (built from amino acids). Higher trophic state consumers receive N from consuming lower level organisms, i.e. both consumers and producers. Decomposers convert N in the opposite direction, i.e. mineralization, converting the N-containing, organic molecules of dead organisms to inorganic compounds, e.g. ammonium ( $\text{NH}_4^+$ ) salts. The  $\text{NH}_4^+$  salts have high aqueous solubility and readily absorb to soil particles. At these sites, bacteria and other microbes can oxidize the  $\text{NH}_4^+$  into nitrite ( $\text{NO}_2^-$ ) compounds and in turn to nitrate ( $\text{NO}_3^-$ ) compounds. This oxidation process is known as *nitrification*. The  $\text{NO}_3^-$

**FIGURE 22.1 Index of emission trends for air pollutants in Europe.** 1990 emissions = 100.  $\text{SO}_x$ , oxides of sulfur;  $\text{NO}_x$ , oxides of nitrogen;  $\text{NH}_3$ , ammonia; NMVOC, nonmethane volatile organic compounds. (For color version of this figure, the reader is referred to the online version of this book.) European Environmental Agency. Air pollution statistics. European Commission Eurostat. [http://epp.eurostat.ec.europa.eu/statistics\\_explained/index.php/Air\\_pollution\\_statistics](http://epp.eurostat.ec.europa.eu/statistics_explained/index.php/Air_pollution_statistics); 2013 [accessed 12.11.13].



compounds are quite bioavailable to most plant life (i.e. macrophytes). These dissolved oxidized forms of N are reduced (i.e. denitrified) by bacteria known as *denitrifiers*. This is a major process by which N is returned to the atmosphere.

Ionization is an important part of N and S cycling, as it is for all nutrient cycling. This is due to the configuration of electrons in an atom. The arrangement of the electrons in the atom's outermost shell, i.e. valence, determines the ultimate chemical behavior of the atom. The outer electrons become involved in the transfer to and the sharing with shells in other atoms, i.e. forming new compounds and ions. An atom will gain or lose valence electrons to form a stable ion that has the same number of electrons as the noble gas nearest the atom's atomic number. As mentioned, the N cycle includes three principal forms that are soluble in water under environmental conditions: the cation (positively charged ion) ammonium ( $\text{NH}_4^+$ ) and the anions (negatively charged ions) nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ). Nitrates and nitrites combine with various organic and inorganic compounds. Following entry into the body,  $\text{NO}_3^-$  is converted to  $\text{NO}_2^-$ . Since  $\text{NO}_3^-$  is soluble and readily available as a nitrogen source for plants (e.g. to form plant tissue such as amino acids and proteins), farmers are the biggest users of  $\text{NO}_3^-$  compounds in commercial fertilizers (although even manure can contain high levels of  $\text{NO}_3^-$ ).

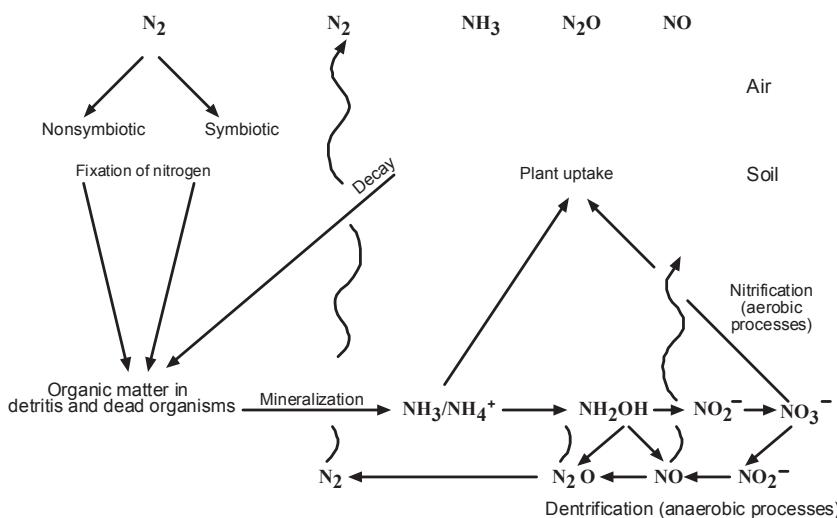
Nitrogen in several forms finds its way from the atmosphere to the soil through abiotic and biotic processes. As mentioned,  $\text{NO}_3^-$  compounds are formed from lightning and by nitrogen-fixing bacteria in legumes' root nodules. The Rhizobia (genera *Rhizobium*, *Sinorhizobium*, and *Bradyrhizobium*) are Gram-negative motile, rod-shaped, aerobic soil bacteria that infect legume roots (Figure 22.2) in a symbiotic relationship



**FIGURE 22.2 The root nodules of a 4-week-old *Medicago italicica* inoculated with *Sinorhizobium meliloti*.** (For color version of this figure, the reader is referred to the online version of this book.) Wikipedia photo; [http://upload.wikimedia.org/wikipedia/commons/b/b3/Medicago\\_italica\\_root\\_nodules\\_2.JPG](http://upload.wikimedia.org/wikipedia/commons/b/b3/Medicago_italica_root_nodules_2.JPG); [accessed 03.10.09].

with legumes, e.g. *Medicago*, *Melilotus*, and *Trigonella*. The symbiotic relationship results from the bacteria fixing atmospheric nitrogen, providing ammonium for protein production in the plant. In exchange, the bacteria obtain energy from the plant.<sup>5</sup>

Nitrate compounds are also formed by microbial (fungal and bacterial) degradation of detritus by aerobes and anaerobes on the forest floor. With moisture, numerous simultaneous chemical reactions occur, making for a balance among various chemical forms of N (as well as those of S, P, K, C, and other nutrients). The chemical reactions in the N cycle, as in any nutrient cycle, require various energy sources, especially light, heat, and metabolic energy. Some biochemical processes within an organism fix molecular nitrogen ( $\text{N}_2$ ) from the atmosphere to form simple N-compounds (e.g. diazotrophs in root nodules), which in turn form amino acids in the tissues of plants and animals.



**FIGURE 22.3** Nitrogen cycling in the troposphere. Vallero DA. *Environmental contaminants: assessment and control*. Burlington (MA): Elsevier Academic Press; 2004.

The mineralization and denitrification occurs by numerous processes, in addition to microbial degradation, including photolysis, hydrolysis, and reduction or oxidation. The result is a wide array of conversions of nitrogen-containing organic compounds (e.g., proteins and amino acids) to inorganic (mineral) forms, such as ammonia, ammonium hydroxide, nitrite, and nitrate. Note that the gases at the top of Figure 22.3 include those that are important in air pollution. For example, NO is one of the compounds involved in the photochemistry that leads to the formation of the pollutant ozone ( $O_3$ ) in the troposphere. Note also that the relationship between microbes and macrophytes is central in the figure. Much of the chemistry occurs on the floor in the detritus where microbes degrade complex molecules. Nutrients in the soil are transported by the roots capillary action to plant cells. Gases are transpired through leaves back to the atmosphere.

The atmospheric speciation at the top of Figure 22.3 is an oversimplification, with many competing processes. For example,  $NO_2^-$  compounds in the soil can release nitrous acid (HONO) directly to the atmosphere. When soil contains elevated amounts of nitrates due to fertilization, HONO is released to the atmosphere. The more acidic the soil, the greater will be the release of HONO. In the troposphere, HONO leads to the formation of hydroxyl radicals, which both degrade and increase the deposition of air pollutants. Large volumes of acids are released from soil continuously to the atmosphere. Soils with high N concentrations form the acids from  $NO_2^-$  ions. These anions are first released into the soil by microbes that have transformed ammonium

and nitrate ions into nitrite ions. Increasing soil acidity produces high nitrite concentrations, leading to greater concentrations of HONO emitted to the troposphere.<sup>6</sup> About 30% of the primary OH radical production is attributed to the photolysis of HONO.

Thus, what may at first appear as a soil–water interaction (fertilizer added to increase crop yield) is indeed a soil–water–biota (microbial) process, followed by an air–water interaction (chemical transformation of air pollutants, followed by precipitation). In this instance, the air pollutants are decreased by increasing concentrations of water pollutants (nitrates and ammonium).

Figure 22.3 also shows that when organic compounds are degraded by microbes, especially nitrifying bacteria, oxides of nitrogen ( $NO_x$ ) are released to the atmosphere. Thus, the flux of nitric oxide (NO) and nitrogen dioxide ( $NO_2$ ) from the soil to the lower troposphere is inversely related to the rate of degradation of organic compounds in the soil.

Ion exchange is actually an example of sorption; i.e., movement of a chemical species from the liquid or gas phase to the solid phase.<sup>a</sup> Plants grow as a function of available nutrients that they are able to sorb, which is affected by available N and other cycles within the forest ecosystem.<sup>7</sup> With this growth, compounds of N and other nutrients find their way to the atmosphere.

Nitrogen has three common oxidation states, +3, +4, and +5. Thus, like carbon, the multiple oxidation states mean that N can form many compounds, even with a single, other element. For example, it can combine

<sup>a</sup> Movement of a chemical species from solid to liquid phase is dissolution. Movement from the solid phase to gas phase is volatilization.

with oxygen to form  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ , or  $\text{N}_2\text{O}_5$ , all important air pollutants or precursors to air pollutants.

Nitrite is an intermediate compound in both nitrification and denitrification. The N in the nitrate anion ( $\text{NO}_3^-$ ) has an oxidation state of +5 (i.e. three O atoms each with -2 charge plus 5 yields the nitrate charge of -1). The nitrite anion has a trivalent N, i.e.  $\text{N}^{3+}$  (i.e. two O atoms each with -2 charge plus 3 yields the nitrite charge of -1). The major mechanism for producing  $\text{N}^{3+}$  in soil is by biological nitrification and denitrification processes. Nitrifying microbes produce nitrite ions from ammonium. Denitrifying microbes produce nitrite from nitrate.<sup>6</sup>

The N compounds enter the troposphere by several mechanisms. In addition to the ordinary concentrations of molecular N, various nitrogen compounds are formed from reactions ranging from very fast (especially combustion) to quite slow, multistage (microbial) reaction rates. The two principal air pollutants regulated throughout the world are nitric oxide and nitrogen dioxide. Nitric oxide (NO) is a colorless, odorless gas and is essentially insoluble in water. Nitrogen dioxide ( $\text{NO}_2$ ) has a pungent acid odor and is somewhat soluble in water.

Air pollution experts now refer to NO and  $\text{NO}_2$  collectively as  $\text{NO}_x$ . This is in part because the NO lifetime after emission is quite short (>minute <hour).<sup>8</sup> The simple oxidation of molecular N at high temperature is



The emitted NO rapidly undergoes photochemical transformation to  $\text{NO}_2$ :

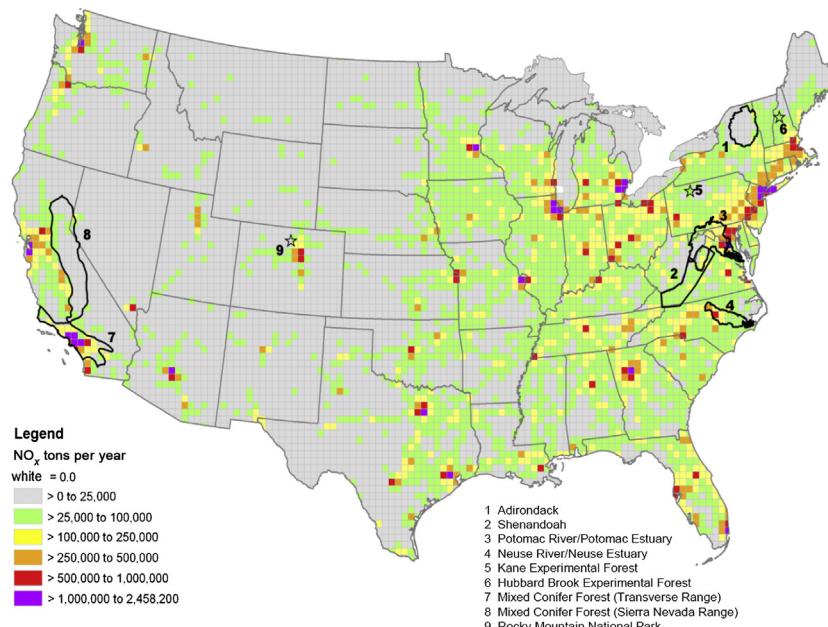


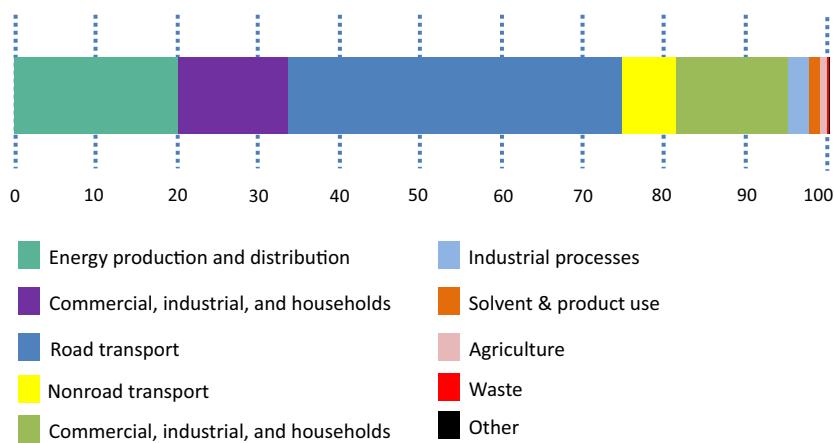
Indeed, NO and  $\text{NO}_2$  can interconvert, depending on redox and photochemical conditions in the troposphere and stratosphere. For example, in sunlight, ultraviolet radiation splits  $\text{NO}_2$  into NO and O. So, it is often preferred to consider the dynamic relationship of the two molecules rather than to ascribe a single speciation, especially for characterizing the atmosphere. However, the two compounds must be distinguished in risk assessments given their very different health effects.

Mobile sources (i.e. cars, trucks, trains, boats, and aircraft) comprise the largest contributor to  $\text{NO}_x$  emissions in the United States (59%; 12.7 Mt in 2002). The US's largest contributing stationary source category is electric generation (22%; 4.6 Mt in 2002), followed by industrial factories (11%; 2.4 Mt in 2002). The eastern and midwestern US regions had the highest emissions (Figure 22.4). Europe has similar emission profiles for  $\text{NO}_x$  (Figure 22.5), with the largest percentage coming from mobile sources (road and nonroad transport), and the largest stationary source being energy production and distribution.

Although both NO and  $\text{NO}_2$  can be harmful to humans and ecosystems, NO is also actually essential to metabolism, so is harmful at much higher concentrations than that of  $\text{NO}_2$ . On the other hand,  $\text{NO}_2$  is inherently toxic, causing respiratory problems. Both compounds are precursors to tropospheric ozone

**FIGURE 22.4** Total oxides of nitrogen ( $\text{NO}_x$ ) emissions (tons per year) in 2002. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Ref. 9.

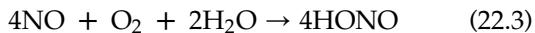




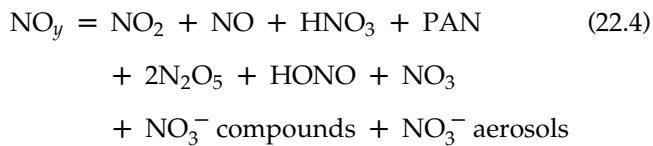
**FIGURE 22.5** European Union nations' percentage contribution to nitrogen ( $\text{NO}_x$ ) emissions by industrial sector in 2010. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: European Environmental Agency. Air pollution statistics. European Commission Eurostat. [http://epp.eurostat.ec.europa.eu/statistics\\_explained/index.php/Air\\_pollution\\_statistics](http://epp.eurostat.ec.europa.eu/statistics_explained/index.php/Air_pollution_statistics); 2013 [accessed 12.11.13].

formation, so present indirect health problems when the smog and  $\text{O}_3$  are inhaled.

Nitrogen species important to air quality include many compounds in addition to  $\text{NO}_x$ . Atmospheric N reactions can be more complicated than may be inferred from Reactions (22.1) and (22.2). For example, the  $\text{NO}_x$  reaction from NO to  $\text{NO}_2$  likely involves water and an intermediate, i.e. nitrous acid (HONO):



The larger suite of N air pollution compounds is known as *total reactive nitrogen*, which is denoted as  $\text{NO}_y$ . This suite includes NO and  $\text{NO}_2$ , plus their oxidation products.<sup>10</sup> The major vapor phase and particulate constituents of  $\text{NO}_y$  include NO,  $\text{NO}_2$ , nitric acid ( $\text{HNO}_3$ ), peroxyacetyl nitrate (PAN), HONO, organic nitrates, and particulate nitrates:



Every  $\text{NO}_y$  compound is derived directly from  $\text{NO}_x$  emissions or through transformations in the troposphere.<sup>9</sup> Most of the compounds originate from combustion processes. As noted, the atmosphere itself is the source of much of the nitrogen leading to the formation of nitrogen compounds. Molecular nitrogen ( $\text{N}_2$ ) makes up the largest share of gaseous content of the earth's atmosphere (79% by volume). Because  $\text{N}_2$  is relatively nonreactive under most atmospheric conditions, it seldom enters into chemical reactions, but under pressure and at very high temperatures, such as in an internal combustion engine or industrial boiler, the molecular N will react with  $\text{O}_2$ , i.e. Reaction (22.1).

This  $\text{N}_2$  precursor is known as "thermal  $\text{NO}_x$ " since the oxides form at high temperatures, such as near burner flames in combustion chambers. Approximately 90–95% of the nitrogen oxides generated in combustion processes are in the form of NO. Other nitrogen oxides can also form at high heat and pressure, especially  $\text{NO}_2$ . Most motor vehicles around the world still employ temperature/high-pressure internal combustion engines. Thus, such mobile sources contribute largely to the tropospheric concentrations of  $\text{NO}_x$ , making it a major mobile source air pollutant in terms of human health directly (e.g. respiratory toxicity of  $\text{NO}_2$ ) and indirectly (i.e.  $\text{NO}_x$  as the key components in tropospheric ozone production). These conditions of high temperature and pressure can also exist in boilers such as those in power plants, so  $\text{NO}_x$  is also commonly found in high concentrations leaving fossil fuel power generating stations.

In addition to the atmospheric molecular nitrogen as a precursor of nitrogen air pollutants of combustion, fossil fuels themselves contain varying concentrations of N. Nitrogen oxides that form from the fuel or feedstock are called "fuel  $\text{NO}_x$ ". Unlike the sulfur compounds, which mainly exit stationary source stacks as vapor phase compounds (e.g.  $\text{SO}_2$  and other oxides of sulfur), a significant fraction of the fuel nitrogen burned in power plants and other stationary sources remains in the bottom ash or in unburned aerosols in the gases leaving the combustion chamber, i.e. the fly ash. Nitrogen oxides can also be released from nitric acid plants and other types of industrial processes involving the generation and/or use of nitric acid ( $\text{HNO}_3$ ).

At temperatures far below combustion, such as those often present in the ambient atmosphere,  $\text{NO}_2$  can form the molecule  $\text{NO}_2-\text{O}_2\text{N}$  or simply  $\text{N}_2\text{O}_4$  that consists of two identical simpler  $\text{NO}_2$  molecules. This molecular configuration is known as a *dimer*. The dimer  $\text{N}_2\text{O}_4$  is distinctly reddish brown and contributes to the brown

haze that is often associated with photochemical smog incidents.

In addition to the health effects associated with  $\text{NO}_2$  exposure, much of the concern for regulating emissions of nitrogen compounds is to suppress the reactions in the atmosphere that generate the highly reactive molecule ozone ( $\text{O}_3$ ). Nitrogen oxides play key roles in  $\text{O}_3$  formation. Ozone forms photochemically (i.e. the reaction is caused or accelerated by light energy) in the lowest level of the atmosphere, known as the *troposphere*, where people and other biota live. Nitrogen dioxide is the principal gas responsible for absorbing sunlight needed for these photochemical reactions. So, in the presence of sunlight, the  $\text{NO}_2$  that forms from the  $\text{NO}$  incrementally stimulates the photochemical smog-forming reactions because nitrogen dioxide is very efficient at absorbing sunlight in the ultraviolet portion of its spectrum. This is why ozone episodes are more common in the summer and in areas with ample sunlight. Other chemical ingredients, i.e. ozone precursors, in  $\text{O}_3$  formation include volatile organic compounds, and carbon monoxide ( $\text{CO}$ ). Governments regulate the emissions of precursor compounds to diminish the rate at which  $\text{O}_3$  forms.

Cyanide ( $\text{CN}^-$ ) is another N anion that is important to air pollution. Cyanide in the bloodstream impairs oxidative phosphorylation, a process by which oxygen is taken up for the production of essential cellular energy in the form of adenosine triphosphate (ATP). This process transfers electrons from nicotinamide adenine dinucleotide to form water from  $\text{H}^+$  and  $\text{O}_2$ , through a series of reactions catalyzed by enzymes. With less  $\text{O}_2$  available to react with the cytochrome C and hence complete the electron transport process, ATP production is diminished. The high binding affinity of  $\text{CN}^-$  to the ferric ion in hemoglobin is responsible for the decrease in  $\text{O}_2$  carried in the blood. Thus,  $\text{CN}^-$  binds preferentially to hemoglobin and prohibits oxygen binding.

Methemoglobinemia is a particularly troublesome outcome resulting from endogenous production of the  $\text{CN}^-$  anion, such as from the exposure of infants to nitrates in drinking water. Ingesting high concentrations of nitrates can cause serious short-term illness and even death in infants of 6 months or younger. The serious illness in infants is due to the conversion of microbial  $\text{NO}_3^-$  to  $\text{NO}_2^-$  in the gastrointestinal tract. Small children's lower stomach acidity (greater pH) allows for more prolific bacterial growth than do adult stomachs. Also,  $\text{NO}_3^-$  is more easily converted to  $\text{NO}_2^-$  than in adult hemoglobin and circulatory system, which are too immature in small children to return to normal hemoglobin. As a result, the increased  $\text{NO}_2^-$  concentrations interfere with the oxygen-carrying capacity of the blood. Especially in small children, when nitrates compete successfully against molecular oxygen, the blood carries methemoglobin (as opposed to healthy hemoglobin),

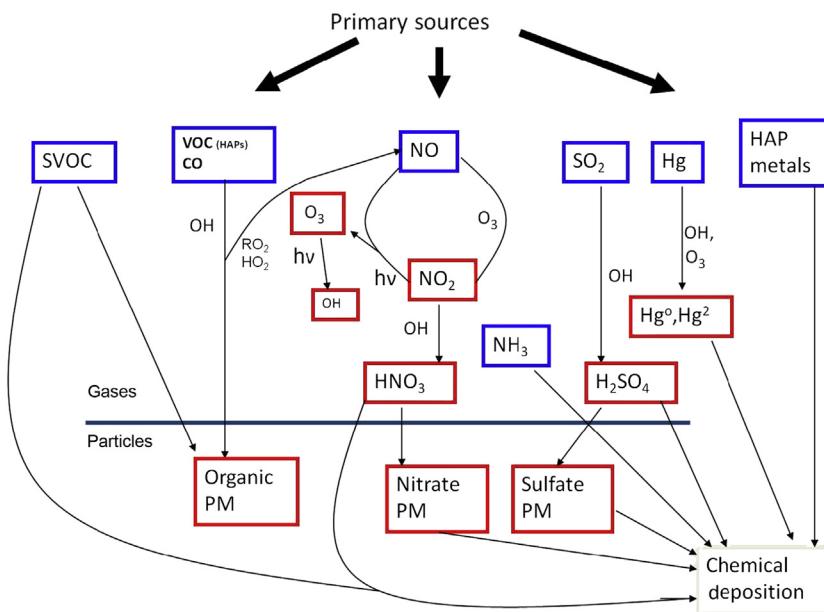
giving rise to clinical symptoms. At 15–20% methemoglobin, children can experience shortness of breath and blueness of the skin (i.e. clinical cyanosis). At 20–40% methemoglobin, hypoxia will result. This acute condition can deteriorate a child's health rapidly over a period of days, especially if the water source continues to be used. Long-term, elevated exposures of nitrates and nitrites can cause an increase in the kidneys' production of urine (diuresis), increased starchy deposits, and hemorrhaging of the spleen.<sup>11</sup>

A few animal studies suggest that elevated  $\text{NO}_3^-$  and  $\text{NO}_2^-$  in exposures may also elicit other effects, e.g. increased miscarriage rates and anencephaly. Nitrate exposure may also cause hypothyroidism (i.e. by mimicking and blocking iodide compounds from reaching the thyroid).<sup>12</sup>

## 22.2 INTERACTIONS BETWEEN SULFUR AND NITROGEN

From the standpoint of air pollution, the biogeochemical cycles must not be limited to single elements. As shown in Figure 22.6, after a compound is emitted, it reacts with numerous other compounds and changes physically and chemically. It is transported advectively, is dispersed, and finally deposited to the earth's surface, where it continues to undergo physical, chemical, and biological changes. This is demonstrated by the interactions of N and S in acid deposition, as well as by the integration of myriad atmospheric chemical species that influence and are influenced by N and S.<sup>9</sup> This includes both the formation of conventional NAAQS pollutants, like ozone and particulate matter (PM), as well as the transformation and changes in bioavailability of toxic air pollutants, e.g. mercury ( $\text{Hg}$ ) and semivolatile organic compounds like dioxins and organochlorine pesticides.

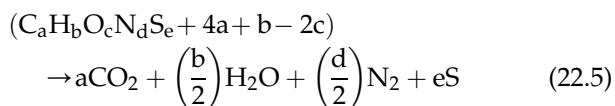
The atmospheric movement of N and S compounds and other pollutants from sources to receptors is only one form of translocation. The second one involves the attempt to control air pollutants at the source. For example, the control of  $\text{SO}_2$  and PM by wet or dry scrubbing techniques yields large quantities of waste materials—often toxic—which are subsequently stored onsite at the facility or taken to landfills and other long-term disposal sites. If these wastes are not properly stored, they can be released to soil or water systems, e.g. from runoff of acids or spills into nearby surface water, resulting in acidic, as well as heavy metal and metalloid contamination. The prime examples involve the disposal of toxic materials in dump sites or landfills. The Resource Conservation and Recovery Act of 1976 and subsequent revisions are examples of legislation to ensure proper management of solid waste



**FIGURE 22.6** Interactions between nitrogen and sulfur compounds, and among S and N compounds and other air pollutants. SVOC, semi-volatile organic compound; VOC, volatile organic compound; RO<sub>2</sub>, radical consisting of a chain of organic compounds with H substituted with O<sub>2</sub> (e.g. propane, C<sub>3</sub>H<sub>8</sub>, reacts with OH to form the radical, C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>); Hg, mercury. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Ref. 9.

disposal and to minimize damage to areas near landfills.<sup>13</sup> However, given the massive volume of wastes generated by energy production, especially ash from coal-fired power plants, such solid waste laws are limited in their ability to ensure proper storage in ash piles and pits, putting adjacent surface water and groundwater at risk.

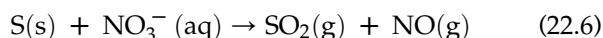
The oxidized chemical species of sulfur and nitrogen, e.g. sulfur dioxide (SO<sub>2</sub>) and nitrogen dioxide (NO<sub>2</sub>), form acids when they react with water. This can occur in any media, e.g. the atmosphere (i.e. acid deposition), and in mining waste and ash runoff to surface waters and groundwater. The lowered pH is responsible for numerous environmental problems. Many compounds contain both N and S along with the typical organic elements (C, H, and O). The reaction for the combustion of such compounds, in general form, is



Reaction (22.5) demonstrates the incremental complexity as additional elements enter the reaction. In the real world, pure reactions are rare. The environment is filled with mixtures and heterogeneous reactions. Reactions can occur in sequence, parallel, or both. For example, a feedstock to a municipal incinerator contains myriad types of wastes, from garbage to household chemicals to commercial wastes, and even small

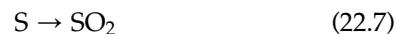
(and sometimes) large industrial wastes that may be illegally dumped. The N-content of typical cow manure is about 5 kg (metric ton)<sup>-1</sup> (about 0.5%). If the fuel used to burn the waste also contains S along with the organic matter, then the five elements will react according to the stoichiometry of Reaction (22.5).

Certainly, combustion specifically and oxidation generally are very important processes that lead to N and S pollutants. But they are certainly not the only ones. As mentioned, oxidation and reduction of N and S occur in ecosystems as represented by trophic state and energy levels. The formation of sulfur dioxide (SO<sub>2</sub>) and nitric oxide (NO) by acidifying molecular sulfur is a redox reaction:



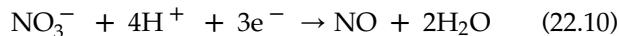
The designations in parentheses give the physical phase of each reactant and product: "s" for solid; "aq" for aqueous; and "g" for gas.

The oxidation half-reactions for this reaction are the following:

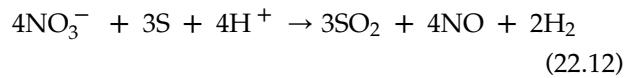
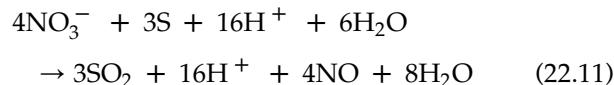


The reduction half-reactions for this reaction are as follows:





Therefore, the balanced oxidation-reduction reactions are



### 22.3 THE SULFUR CYCLE

Compounds of sulfur (S), as those of N, exist at atmospheric concentrations well in excess of what would be expected from equilibrium geochemistry in an atmosphere with 21% O<sub>2</sub>.<sup>14</sup> Sulfur is released to the atmosphere as either reduced forms, e.g. hydrogen sulfide, or oxidized forms, e.g. sulfur dioxide (Figure 22.7). Both forms include air pollutants. Hydrogen sulfide is oxidized to sulfur dioxide in a three-step process. Note that the hydroxyl radical initiates the transformation from hydrogen sulfide to sulfur dioxide:

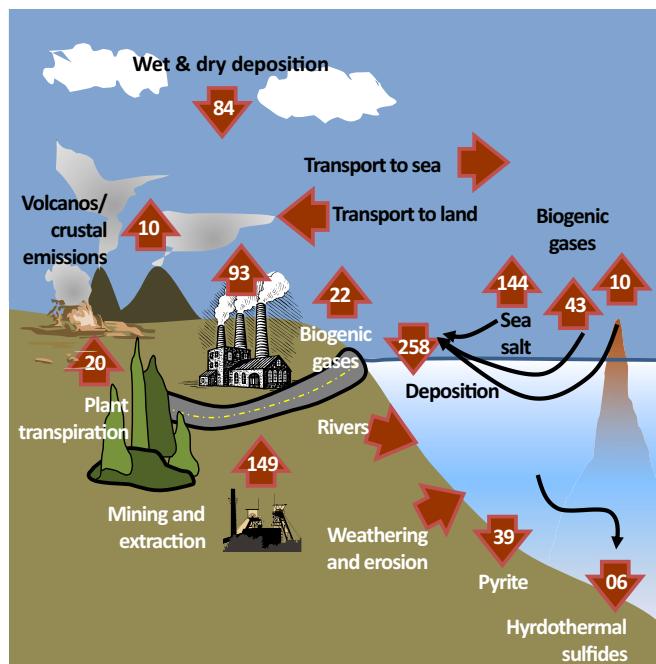
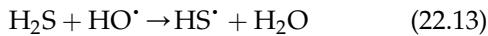
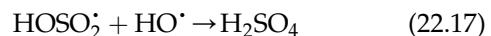


FIGURE 22.7 Fluxes of sulfur to and from the atmosphere (teragrams of S in arrows). (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Ref. 15.



The atmospheric reactions of SO<sub>2</sub> are very complex, and proceed through at least three different pathways to the sulfate ion (SO<sub>4</sub><sup>2-</sup>). Sulfur dioxide can react with the hydroxyl radical to form the HSO<sub>3</sub> radical, which then can react with another hydroxyl radical to form water and SO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>. Sulfur dioxide has sufficient aqueous solubility to dissolve in water droplets where it can react with oxygen gas to form SO<sub>4</sub><sup>2-</sup>. The third pathway to sulfate occurs when sulfur dioxide reacts with hydrogen peroxide to form sulfuric acid:



With sufficient residence time in the atmosphere, S will be oxidized to the sulfate ion, usually forming sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). Ammonia (NH<sub>3</sub>), the most common base in the atmosphere, reacts with H<sub>2</sub>SO<sub>4</sub> to form ammonium bisulfate (NH<sub>4</sub>HSO<sub>4</sub>) and ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). The compounds H<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>HSO<sub>4</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> all are hydroscopic substances, i.e. readily dissolved in water. Thus, they wash out of the atmosphere during precipitation events.<sup>15</sup>

Arguably, the most common reduced form of sulfur that is the highly toxic and important pollutant, hydrogen sulfide (H<sub>2</sub>S). Certain microbes, especially bacteria, reduce nitrogen and sulfur, using the N or S as energy sources through the acceptance of electrons. For example, sulfur-reducing bacteria can produce H<sub>2</sub>S by chemically changing oxidized forms of sulfur, especially sulfates (compounds containing the ion, SO<sub>4</sub><sup>2-</sup>). To do so, the bacteria must have access to the sulfur, i.e. it must be in the water, which can be in surface or groundwater, or the water in soil and sediment. These sulfur-reducers are often anaerobes, i.e. bacteria that live in water where concentrations of molecular oxygen (O<sub>2</sub>) are deficient. The bacteria remove the O<sub>2</sub> molecule from the sulfate leaving only the S, which in turn combines with hydrogen (H) to form gaseous H<sub>2</sub>S.

In groundwater, sediment water, and soil water, H<sub>2</sub>S is formed from the anaerobic or nearly anaerobic decomposition of deposits of organic matter, e.g. plant residues. Thus, redox principles can be used to treat H<sub>2</sub>S contamination, i.e. the compound can be oxidized using a number of different oxidants (Table 22.1). Strong oxidizers, like molecular oxygen and hydrogen peroxide,

TABLE 22.1 Theoretical Amounts of Various Agents Required to Oxidize 1 mg l<sup>-1</sup> of Sulfide Ion

Oxidizing Agent	Amount (mg l <sup>-1</sup> ) Needed to Oxidize 1 mg l <sup>-1</sup> of S <sup>2-</sup> Based on Practical Observations	Theoretical Stoichiometry (mg l <sup>-1</sup> )
Chlorine (Cl <sub>2</sub> )	2.0–3.0	2.2
Chlorine dioxide (ClO <sub>2</sub> )	7.2–10.8	4.2
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	1.0–1.5	1.1
Potassium permanganate (KMnO <sub>4</sub> )	4.0–6.0	3.3
Oxygen (O <sub>2</sub> )	2.8–3.6	0.5
Ozone (O <sub>3</sub> )	2.2–3.6	1.5

Source: Water Quality Association. Ozone task force report "Ozone for POU, POE & small water system applications". Lisle (IL); 1999.

TABLE 22.2 Typical Chemical Composition (Percent) of Fine Particulate Matter (PM<sub>2.5</sub>)

	Eastern US	Western US	Diesel PM <sub>2.5</sub>
Elemental carbon	4	15	75
Organic carbon	21	39	19
Sulfate, nitrate, ammonium	48	35	1
Minerals	4	15	2
Unknown	23	—	3

Source: U.S. Environmental Protection Agency. Air quality criteria for particulate matter. External review draft. October 1999.

most effectively oxidize the reduced forms of S, N, or any reduced compound.

Sulfur is also an important component of PM (Table 22.2). For example, diesel PM is formed by a number of simultaneous physical processes during cooling and dilution of exhaust, i.e. nucleation, coagulation, condensation, and adsorption. The core of the particles is formed by nucleation and coagulation from primary spherical particles consisting of solid carbonaceous matter, known as elemental carbon (EC) and ash (metals and other elements). By coagulation, adsorption, and condensation, various organic and S compounds (e.g. sulfates) are added and combined with other condensed material (Figure 22.8).<sup>16</sup>

The small diameter of diesel PM (<0.5 μm) makes for very large surface areas. Less than 0.5 mm, these particles have a very large surface area per gram of mass, which allows them to adsorb large quantities of ash, organic compounds, and sulfate. The specific surface area of the EC core is approximately 30–50 m<sup>2</sup> g<sup>-1</sup>. The organic constituents originate from unburned fuel,

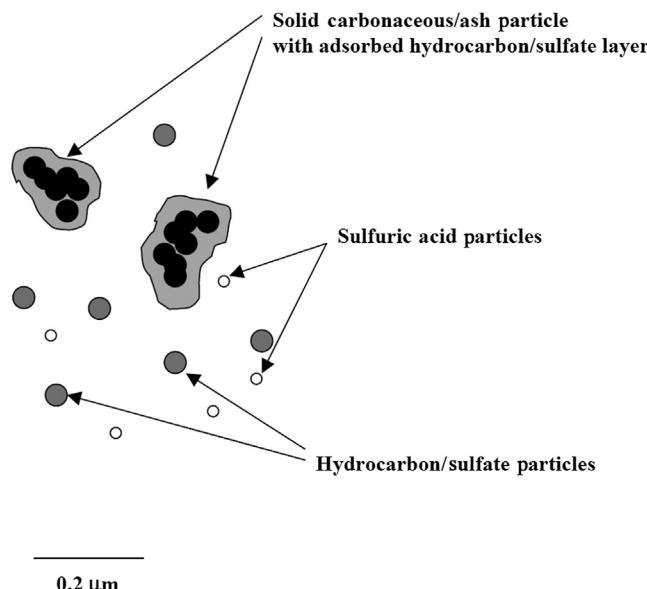


FIGURE 22.8 Diesel particulate matter of three different chemical compositions. Ref. 16.

engine lubrication oil, and small quantities of partial combustion and pyrolysis products. During combustion, S compounds in the fuel are oxidized to sulfur dioxide (SO<sub>2</sub>). From 1% to 4% of fuel S is oxidized to form H<sub>2</sub>SO<sub>4</sub>. Upon cooling, this sulfuric acid and water condense into an aerosol that is nonvolatile under ambient conditions.<sup>16</sup>

Thus, N and S compounds are ubiquitous in the atmosphere and the environment. They are constituents of both essential and detrimental compounds. As such, their complete biogeochemical cycles must be understood to explain the formation and fate of air pollutants.

## 22.4 OTHER NUTRIENT CYCLES

Numerous other nutrients besides N and S also form compounds that are air pollutants or are otherwise important to air quality. Indeed, the cycling of other nonmetals is crucial to complete understanding of most air pollutants. In fact, P molecules are essential parts of energy transfer during photosynthesis. Phosphorous fertilizer manufacturing and the application of P-containing compounds in agriculture, on the other hand, are major sources of air and water pollution. When P compounds deposit onto surface waters, the increased P concentrations accelerate eutrophication and, along with increasing N concentrations, contribute to the so-called dead zones in large water bodies, such as the Chesapeake Bay.

Actually, P and K are intricately woven into the N and S cycles. P is a component of atmospheric deposition, along with N and S compounds. The P component is

usually higher when the amount of wet deposition exceeds dry deposition, since P is usually bound to aerosols. Thus, in areas where large amounts of P are applied as a fertilizer to land or in arid regions with strong winds to transport soils, airborne P concentrations can be substantial, albeit still less than airborne N concentrations.<sup>1</sup> Most of the total P in the atmosphere exists in mineral form as aerosols, but there are also large global sources of P from biomass burning, and a lesser amount from energy and industrial combustion sources.<sup>2</sup>

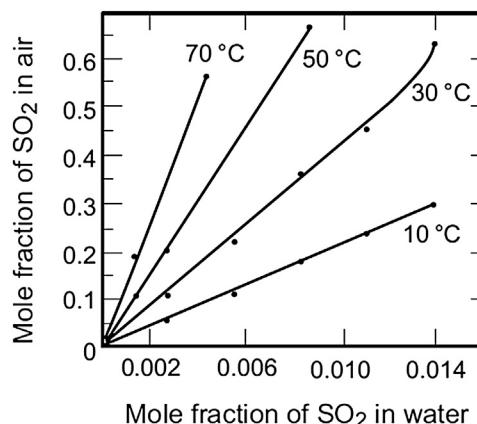
Phosphate fertilizer production is an important source of fluoride compounds. The movement of fluoride through the atmosphere and into a food chain illustrates an air–water interaction at the local scale (<100 km).<sup>3</sup> Other industrial sources of fluoride include aluminum processing and glass manufacturing plants. Domestic livestock in the vicinity of substantial fluoride sources are exposed to fluoride by ingestion of forage crops. Fluoride released into the air by industry is deposited and accumulated in vegetation. Its concentration has been found in some areas to be sufficient to cause damage to the teeth and bone structure of the animals that consume the crops.

Potassium is also a part of the biogeochemistry of N and S. For example, when base cations like K deposited on soil and other surfaces, they increase the surface's pH. This alkalinity buffers the acidity generated by N and S acidic compounds (e.g.  $\text{H}_2\text{NO}_3$  and  $\text{H}_2\text{SO}_4$ , respectively).

## QUESTIONS

- List three similarities between sulfur and nitrogen regarding air pollution.
- What are the major differences between nitrogen in abiotic systems and biotic systems?
- Most of the abundant gas in the atmosphere is not bioavailable to plants. How does this become bioavailable?
- How does nitrogen's oxidation number change as molecular nitrogen is chemically transformed to nitrate? What types of reactions are involved in this transformation?
- What is  $\text{NO}_x$ ? What is  $\text{NO}_y$ ?
- When oxides of N are emitted from combustions, where did the N come from?
- What is the source of most of the sulfur in the atmosphere?
- Describe the conditions whereby nitrogen is reduced in the environment. Describe the conditions whereby it is oxidized in the environment.
- Identify a nitrogen-containing dimer important to air pollution. How can it form?

- Describe the conditions whereby nitrogen is reduced in the environment. Describe the conditions whereby it is oxidized in the environment.
- What is the role of HONO in air pollution formation?
- Describe the etiology of methemoglobinemia.
- During the combustion of sulfur-containing fuels, approximately 94 to 95% of the sulfur is converted to sulfur dioxide. Generally 0.5 to 2% of the fuel sulfur is converted to sulfur trioxide,  $\text{SO}_3$ . Sulfur trioxide remains in the vapor state until temperatures decrease below approximately 300°C, at which the sulfur trioxide reacts with water. Show this reaction.
- Review this figure. Describe how the state of  $\text{SO}_2$  at the point of emission from the stack will differ from that 100 m downwind.



- Based on the following data for the solubility of  $\text{SO}_2$  in pure water at 30°C and 101.3 kPa, plot the equilibrium diagram and determine if Henry's law applies.

Concentration $\text{SO}_2$ (gm $\text{SO}_2$ per 100 gm $\text{H}_2\text{O}$ )	$p^*\text{SO}_2$ ( $\text{SO}_2$ partial pressure)
0.5	6 kPa (42 mm Hg)
1.0	11.6 kPa (85 mm Hg)
1.5	18.3 kPa (129 mm Hg)
2.0	24.3 kPa (176 mm Hg)
2.5	30.0 kPa (224 mm Hg)
3.0	36.4 kPa (273 mm Hg)

- Give reasons for the regional variations of nitrogen and sulfur composition of ambient fine particulate matter in the U.S.
- Explain how PM emitted from diesel engines is able to sorb sulfates.

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## Metal and Metalloid Cycles

The atmosphere is an important compartment in the cycling of toxic metals and metalloids and their compounds. A number of metals have received much attention as air pollutants. For example, the list of 187 hazardous air pollutants (see Table 7.2) subject to US regulations under Section 112 of the Clean Air Act Amendments includes a number of metals and two metalloids:

- Beryllium
- Cadmium
- Chromium
- Cobalt
- Lead
- Manganese
- Mercury
- Nickel
- Selenium
- Antimony (metalloid)
- Arsenic (metalloid)

As discussed in Chapter 13, one of the key adverse outcomes of certain metals is damage to the central nervous systems (CNS) and peripheral nervous systems (PNS), especially lead (Pb) and mercury (Hg). Other metals, such as manganese (Mn), have also been associated with chronic, neurological disorders. Metals and their inorganic and organometallic compounds are well known for major contamination events and exposures to large numbers of susceptible populations, such as small children. The chemical species of metals and metalloids vary considerably depending on their oxidation states and the elements with which they combine. For example, mercury's mobility in the environment and its toxicity to humans and animals is determined by its chemical form. Dimethylmercury is highly toxic, accumulates in the food chain, and has high affinity for organic tissues, but elemental (zero valence) mercury is much less toxic and is slower to bioaccumulate.

With the exception of the noble gases, all elements exist in the environment in a number of oxidation or valence states. Unlike organic compounds, which can be treated by destruction (actually conversion to simpler

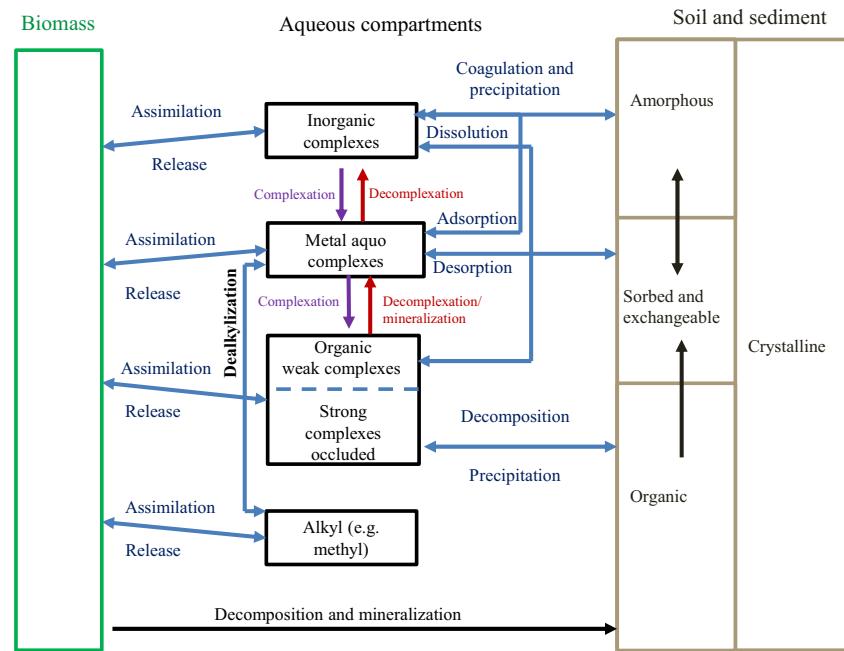
compounds, and finally to carbon dioxide and water), metals are not treated by destruction, but by changing valence, i.e. oxidation states. As mentioned for mercury, each form of any metal has its own toxicity and dictates its fate in the environment. Chromium, e.g. in its trivalent state ( $\text{Cr}^{+3}$ ) is an essential form of the metal. Although toxic at sufficiently high concentrations,  $\text{Cr}^{+3}$  is less inherently hazardous than the hexavalent form  $\text{Cr}^{+6}$ , which is highly toxic to aquatic fauna and is a suspected human carcinogen. Toxicity, persistence, and fate are also determined by the metal's equilibrium chemistry, especially the amount in ionic forms and the amount that forms salts with nonmetals.

Atmospheric deposition is an important source of many metals, including cadmium, copper, lead, and zinc, but less important for other metals (e.g. iron, aluminum, and manganese).<sup>1</sup> Dust is a major source of metal-laden particles that can be transferred to the atmosphere, as well as to numerous compartments in the biosphere and hydrosphere. The actual metal loads vary seasonally, depending on rainfall and prevailing winds, as well as spatially. For example, particulate matter transport to oceans is highest in waters downwind of deserts.<sup>2</sup> Other metal sinks include melt from glaciers and icebergs, seasonal sea ice melting, island wakes, volcanism, and hydrothermal activity.<sup>3</sup>

Metal cycling is influenced by other cycles. For example, acidification of the oceans and acid deposition onto terrestrial systems will change the rates and types of metal cycling.

Metal cycling is intricately linked to organisms in the biosphere. The concentrations, transformation, and cycling are driven by the growth rates, biomass sequestration, species diversity, and trophic interactions of biota. Indeed, many metals are micronutrients, without which plants and microbes suffer deficiencies. Above these levels, organisms suffer toxic effects. In forests, metals may become stable and immobile on the floor due to adsorption onto detritus. On the other hand, organic acids in the vegetation (e.g. leaf leachate) and bacterial decomposition in soil organic matter (i.e. mineralization) may increase solubility and otherwise mobilize the metals.<sup>1</sup>

**FIGURE 23.1 Sources, sinks, and mobilization of metals in the biosphere.** Individual behavior and pathways vary for each metal. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 1.



Metal mobility in the biosphere and bioavailability vary among genera of organisms and their affinities for the various metals. Generally, metals can be assimilated into environmental compartments by two processes (Figure 23.1). One mechanism depends on ionic species forming surface complexes with carrier proteins during active transport, allowing metal cations to be transported across cellular membranes. The second mechanism is nonionic. Metal species may be transported across biological membranes by concentration gradients, i.e. molecular or passive diffusion.<sup>1</sup>

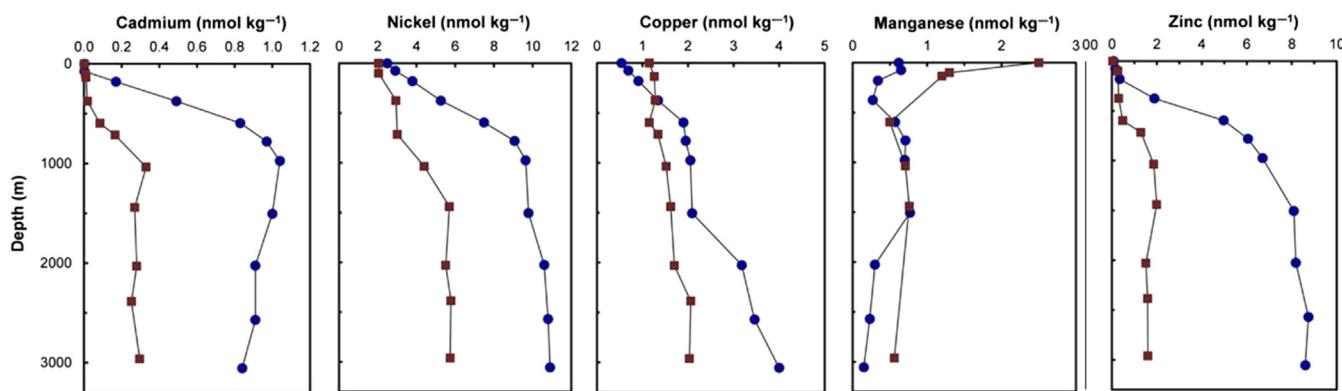
A ligand<sup>a</sup> is a functional group (either a molecule or ion) that binds to a central metal atom to form a coordination complex. The bonding between the metal and ligand generally involves formal donation of one or more of the ligand's electron pairs. The metal–ligand bonding can be covalent or ionic. Metals associate with a range of ligands to form the complexes shown in the center of Figure 23.1. These include metal aquo complexes, i.e. coordination compounds containing metal (Me) ions with water serving as the only ligand; general stoichiometry is  $[Me(H_2O)_n]^{z+}$ . The aquo complexes are the predominant metal species in aqueous solutions of many metal salts, e.g. metal nitrates, sulfates, and perchlorates. Metal complexes also include those with the  $OH^-$  functional group (i.e. hydroxo complexes), other inorganic ligands (e.g.  $Cl^-$ ,  $SO_4^{2-}$ , and  $HCO_3^-$ ), and organic ligands.<sup>1</sup>

Trace metals can be mobilized and immobilized from the solid phase (i.e. following the behavior of sorption and desorption, as discussed in Chapter 18). The solid phase may include suspended particles, soil, and sediments. Solid–solution interactions of trace metals occur through adsorption/desorption reactions on organic and inorganic functional groups. They may also occur directly as precipitation/dissolution reactions. In the solid phase, metals associate with surface functional groups, hydroxide, carbonate, sulphide minerals (in amorphous or crystalline forms), or organic matter. Finally, biota may alter the cycling of trace metals through uptake by assimilation or surface interactions.<sup>1</sup>

The ocean is a vast sink for metals. For example, zinc (Zn), cadmium (Cd), nickel (Ni), and copper (Cu) have residence times ranging from 3000 to 100,000 years, given mean deep ocean ventilation time of about 1000 years. Generally, metal concentrations increase with depth (Figure 23.2).

Concentrations of most heavy metals exist at low concentrations in the ocean (ranging from 0.002 nanomolar (nM) for cadmium (Cd) and manganese (Mn) to 0.1 nM for iron (Fe) and zinc (Zn)). In the ocean, as well as other environmental compartments, metals can be taken up incidentally with essential metals. For example, Cd is a nutrient analog for Zn in surface waters.<sup>4</sup> Surficial metal concentrations often increase by orders of magnitude moving from open ocean water to coastal and estuarine

<sup>a</sup> The term ligand has at least two different environmental and biomedical meanings. In addition to the one defined here, a ligand is also a molecule that travels through the bloodstream, serving as a chemical messenger that will bind to a target cell's receptor (see Chapter 12).



**FIGURE 23.2** Depth profiles of five metals in the central North Pacific (■, 32.7°N, 145.0°W, September 1977) and North Atlantic (●, 34.1°N, 66.1°W, July 1979). Manganese concentrations in the Pacific were analyzed in acidified, unfiltered seawater samples. Ref. 1; and Sunda WG. Feedback interactions between trace metals and phytoplankton in the ocean. *Front Microbiol* 2012;3:204. <http://dx.doi.org/10.3389/fmicb.2012.00204>.

systems, as a result of loading of metals from inland streams, groundwater, dust, and sediments.<sup>5</sup>

The heavy metal concentration gradients between coastal and open water are fairly consistent.<sup>6</sup> Iron concentrations, e.g. may reach 20 micromolar ( $\mu\text{M}$ ) in high humic rivers, which is 4–6 orders of magnitude higher than Fe concentrations in surface ocean waters. Most iron in freshwater streams exists as colloidal suspensions (0.02–0.4  $\mu\text{m}$  diameter). These colloids degrade rapidly when they contact high salinity, which induces coagulation and settling. Reported gradient concentrations for cobalt (Co) in the coastal waters of Baja California ranged from 0.93 to as much as 3.6 nM.<sup>7</sup> That is about 4 times more concentrated at the coast, near the source than in more oceanic waters. In other parts of the world, a similar pattern has been identified. Therefore, the freshwater–saltwater boundary effectively serves to precipitate many metals to the sediment.<sup>8</sup>

On the other hand, anoxic and reduced environments, such as in high-organic content sediments, may remobilize a portion of the metals that have settled, via reduction of particulate metals to more soluble species.<sup>9</sup> Chemical and physical processes work together to link metals found in sedimentary materials to the atmosphere and other environmental compartments. Weathering breaks down the rocks into smaller materials such as clays and silts. With the increase in the surface area as the particle size decreases, the materials becoming capable of trapping larger loads of charged molecules and ions, as well as incorporating lipophilic organic molecules. Due to their characteristic hydrophobicity and their tendency to be excluded from the water phase (i.e. decreased polarity), these organic molecules sorb to these particles as well. Thus, the receiving areas will often contain larger quantities of fine sediments, and with attendant, higher metal concentrations, and higher organic content.<sup>10</sup>

Another important factor in the metal cycle is temperature. Increasing concentrations of metals will occur in

water with increasing temperatures. Temperature change also alters biomass and metal exchanges with organisms. Increasing temperature decreases dissolved molecular oxygen (DO) concentrations, which in turn leads to a reduced environment where the metals and compounds will form sulfides and other compounds that can be toxic to the fish and other higher order aquatic organisms, but advantageous to anaerobes, including metal-reducing bacteria. Thus, the change in temperature, the resulting decrease in DO and increasing metal concentrations, and the synergistic impact of the combining the hypoxic water and reduced metal compounds is a cascade of harm to the stream's ecosystems.

Combined abiotic and biotic processes are affected by and affect metal geochemical cycling. Notably, the growth and metabolism of the bacteria results in even more rapidly decreasing DO levels. Algae both consume DO for metabolism and produce DO by photosynthesis. The increase in temperature concomitantly increases the aqueous solubility of metals, and the decrease in DO is accompanied by redox changes, e.g. formation of reduced metal species, such as metal sulfides. This is also being mediated by the bacteria, some of which will begin to reduce the metals as the molecular oxygen levels decline, leading to overall reduced conditions in the water and sediment. The opposite process occurs with increasing oxidation. In the more oxidized regions, the metals form metal oxides. The increase in the metal compounds combines with the changing concentrations of DO, and with the increased temperatures to act synergistically to change the metal cycles toward a more aerobic system.<sup>11</sup>

The biota–metal cycling relationship is not entirely linear and continuous in space and time. For example, the initiating abiotic effect discussed above, i.e. increased temperature, results in an increased microbial population. As mentioned, the growth and metabolism of the bacteria decrease DO levels, but the

growth of the algae both consume DO for metabolism and produce DO by photosynthesis. Meanwhile a combined abiotic and biotic response occurs with the metals. At higher temperatures, the aqueous solubility of metals increases. As mentioned, the decrease in DO concentrations is accompanied by redox changes, e.g. formation of reduced metal species, such as metal sulfides; but in the environment this is also being mediated by the bacteria, some of which will begin reducing the metals as the oxygen levels drop (reduced conditions in the water and sediment). However, the opposite is true in the more oxidized regions, i.e. the metals are forming oxides. The net increase or decrease in the metal concentrations, the speciation of metal compounds, and the changes in redox, combined with the increased temperatures may or may not act synergistically to make the conditions toxic for higher animals, e.g. a fish kill.<sup>12</sup>

The extent and severity of metal-induced or metal-mediated ecosystem damage depends on species diversity, e.g. the balance of algae and bacteria, as well as on the types of metallic compounds formed and any catalysts that may increase metal chemistry. Of course, metals are not the only, nor usually the most prominent cause of fish kills and other ecosystem effects. Indeed, they are usually merely contributing causes unless the metal concentrations are extremely high. Conversely, some damage can be mediated by increasing the concentrations of certain metals. Given that a number of metals are micronutrients, if metal concentrations are decreased or the chemical forms are completely not bioavailable, this could be a contributing factor in ecosystem damage (i.e. a metal-deficient species could adversely affect predator-prey, biomass production, etc.).

Human activities change the geochemistry of metals. After extraction, the processes used to refine and manufacture products from the ores exposes human populations and ecosystems to metal concentrations well above natural norms. In addition, metal compounds end up in products or otherwise come into contact with people and the environment.

Extraction of metals is an example of how humans have changed the biogeochemical cycling throughout the hydrosphere, atmosphere, and biosphere. Human activities can greatly accelerate the mobilization of metals, several-fold over natural releases from weathering and natural fluxes, i.e. degassing from the earth's crust and mantle, which is the sum of volcanic emissions to the atmosphere and net hydrothermal flux to the sea (Table 23.1).<sup>13</sup>

For both metals and nonmetals, the activities by humans greatly increase the amount of potentially toxic substances released to the environment. For example, the human-to-natural weathering ratio for copper (Cu) is 14.2, meaning that all of the weathering processes around the globe account for 14 times less than the extraction and processing of Cu by humans. Put another way, mercury's (Hg) ratio of 3.3 means that without human extractions and manufacturing, only one-third of the Hg would be released into the environment. Thus, since the total Hg loading to the environment drives the amount of toxic forms (e.g. methylmercury) reaching and accumulating in the food chain, this means that human activities are substantially increasing the amount of toxic Hg in the food being ingested and air being inhaled by humans.

Considering that weathering takes place over most of the earth's surface, including land and water, this indicates the extent of anthropogenic activities in mobilizing

TABLE 23.1 Estimates of the Global Flux in the Biogeochemical Cycles of Certain Elements (10<sup>12</sup> g per year)

Element	Juvenile Flux <sup>1</sup> (1)	Chemical Weathering (2)	Natural Cycle <sup>2</sup> (3)	Biospheric Recycling Ratio 3/(1 + 2)	Human Mobilization <sup>3</sup> (4)	Human-to-Natural Ratio 4/(1 + 2)
Boron	0.02	0.19	8.8	42	0.58	2.8
Carbon	30	210	107,000	446	8700	36.3
Nitrogen	5	20	9200	368	221	8.8
Phosphorous	~0	2	1000	500	25	12.5
Sulfur	10	70	450	5.6	130	1.6
Chlorine	2	260	120	0.46	170	0.65
Calcium	120	500	2300	3.7	65	0.10
Iron	6	1.5	40	5.3	1.1	0.14
Copper	0.05	0.056	2.5	23.6	1.5	14.2
Mercury	0.0005	0.0002	0.003	4.3	0.0023	3.3

<sup>1</sup>Emission from the earth's crust and mantle; i.e. sum of volcanic emissions to the atmosphere and net hydrothermal flux to the sea.

<sup>2</sup>Annual biogeochemical cycle to/from the earth's biota on land and in the oceans, in the absence of humans.

<sup>3</sup>Direct and indirect mobilization by extraction and mining from the earth's crust or (for N) industrial fixation.

Source: Ref. 13.

potential air pollutants. As such, the composition of the atmosphere has been changing substantially and relatively rapidly in recent centuries and decades compared to the previous millennia.

## 23.1 HEAVY METAL CYCLING

So-called “heavy metals” dominate the list of “toxic metals”. The designation of “heavy” is any metal with the atomic mass greater than or equal to that of iron. These include the transition metals, lanthanides, and actinides.<sup>14</sup> This chapter addresses the metals often associated with air pollution and environmental damage, as well the most notorious metalloid, arsenic.

Most toxic metals exist naturally in very small concentrations but for some, the toxic levels can be just above the background concentration. In many cases small amounts are essential. The dose–response curve for these metals would be U-shaped, with deficiencies at low doses, toxicity at high doses, and an optimal dose range between deficiency and toxicity (see Chapter 7).

Many texts refer to this group of metals and metalloids as trace metals. However, “trace” is not so much a descriptive term as an adjective for low concentrations. In most parts of the world, metal toxicity is a relatively uncommon medical condition. Poisonings, e.g. lead and arsenic poisoning, are often meant to be acute effects, including death, at high doses. Such doses are unusual in general air pollution scenarios, except in and near specialized industrial environments. Generally, atmospheric concentrations are much lower than those that induce acute effects, so the principal air pollution concern about metals is longer-term, low concentration exposures.

Following are brief discussions of mercury, cadmium, and lead. These metals are discussed throughout this book, but are highlighted here given their importance to air pollution.

### 23.1.1 Mercury

The metal mercury (Hg) has been of interest to scientists and the general public of late. For example, there has been much concern as to whether a preservative used in vaccines might be part of the cause for the apparent increase in autism in recent decades. The metal has also been central to the debate about the safety of seafood and tradeoffs of hazards to unborn and nursing babies and the benefits of breast feeding. Actually, mercury is a natural component of the earth, with an average abundance of approximately  $0.05 \text{ mg kg}^{-1}$  in the earth’s crust, with significant local variations.

It is an unusual metal in that it is a liquid at room temperature (it melts at  $38.9^\circ\text{C}$  and boils at  $303^\circ\text{C}$ ) and is

heavy, with a density of  $13.5 \text{ g cm}^{-3}$  at  $25^\circ\text{C}$ . Studies have indicated that Hg can be a toxic substance and that one of its compounds, methylmercury chloride is a highly toxic substance. Mercury persists in the environment, but is also readily transformed. When reduced and alkylated, Hg becomes more toxic, e.g. methylmercury biomagnifies up the food chain, and reaches a wide variety of species and ecosystems. Thus both human and ecosystems may be exposed to excessive levels of mercury in the environment.<sup>15</sup> Not only is the exposure to total Hg problematic, the conditions of many systems make for the most toxic forms of Hg, e.g. reduced and low oxygen environments and metabolic processes within organisms.

Mercury ores that are mined generally contain about 1% mercury but at the Almaden mine in Spain, they are mining an ore which contains about 12% mercury. Although about 25 mercury minerals are known, virtually the only deposits that are being mined contain cinnabar ( $\text{HgS}$ ), a bright red substance which is also used to produce the color vermillion. Despite a decline in global mercury consumption, competing sources of mercury and low prices, the mining of mercury continues in a number of countries. Spain, China, Kyrgyzstan, and Algeria have dominated this activity in recent years. The last US mine was closed in 1982. There are reports of small mines in China, Russia (Siberia), Outer Mongolia, Peru, and Mexico. In the early 1980s, the annual production from mining  $\text{HgS}$  was 7000 tons, today it is less than half of that and is about 2000 tons.<sup>16</sup>

Mercury is also obtained: as a by-product of mining or refining of other metals (such as zinc, gold, and silver) or minerals and even from natural gas; from recycling spent products; and reprocessing mine tailings containing Hg. In the United States, this recovery of mercury as a by-product of other metal mining (primarily gold) from recycling and from the decommissioning of chlor-alkali plants amounts to about 250 tons per year.<sup>16</sup>

Concentrations of total mercury in the atmosphere of the northern hemisphere have recently been estimated at  $2 \text{ ng m}^{-3}$ , whereas those in the southern hemisphere being half this value. Values in urban areas are usually higher (e.g.  $10 \text{ ng m}^{-3}$ ). Mercury has an appreciable vapor pressure ( $2 \times 10^{-3} \text{ mm Hg}$  or  $0.3 \text{ Pa}$  at  $25^\circ\text{C}$ ) which is the reason for it being in the atmosphere.<sup>17,18</sup> It has been estimated that each year 2000–3000 tons<sup>19</sup> enter the atmosphere from natural and anthropogenic sources. Natural sources, such as volcanoes, are responsible for approximately half of atmospheric mercury emissions. The anthropogenic half can be divided into the following estimated percentages which excludes biomass burning, an important source in some regions.<sup>20,21</sup> (See Discussion Box: Metal Contamination Cases in Japan).

## METAL CONTAMINATION CASES IN JAPAN

Minamata, a small factory town on Japan's Shiranui Sea, was the site of chronic Hg exposure. Minamata is "nitrogen" in Japanese, owing to the town's production of commercial fertilizer by the Chisso Corporation for decades, beginning in 1907.<sup>22</sup> Beginning in 1932, the company produced pharmaceutical products, perfumes, and plastics and processed petrochemicals. Chisso became highly profitable, notably because it became the only Japanese source of a high-demand primary chemical, diethyl phthalate, a plasticizing agent. These processes needed the reactive organic compound, acetaldehyde, which is produced using mercury. The residents of Minamata played a huge price for this industrial heritage. Records indicate that from 1932 to 1968, the company released approximately 27 tons of mercury compounds into the adjacent Minamata Bay. This directly affected the dietary intake of the toxic mercury of fisherman, farmers and their families in Kumamoto, a small village about 900 km from Tokyo. The consumed fish contained extremely elevated concentrations of a number of mercury compounds, including the highly toxic methylated forms (i.e. monomethylmercury and dimethylmercury), leading to classic symptoms of methyl mercury poisoning. In fact, the symptoms were so pronounced the syndrome of these effects came to be known as the "Minamata Disease".

In mid-1950s, residents began to report what they called the "strange disease", including the classic form of mercury toxicity, i.e. disorders of the PNS and CNS, respectively. Diagnoses included numbness in lips and limbs, slurred speech, and constrict vision. The physician from the Chisso Corporation Hospital, reported in 1956 that "an unclarified disease of the central nervous system has broken out". The physician correctly associated the fish dietary exposure to the health effects. Soon after this initial public health declaration, government investigators linked the dietary exposures to the bay water. The company continued the chemical production, but within 2 years, moved their chemical releases upstream from Minamata Bay to the Minamata River. The Hg pollution became more widespread, leading to a partial ban by the Kumamoto Prefecture government responded allowing fisherman to catch, but not to sell, fish from Minamata Bay. However, the ban did not reduce the local people's primary exposure since they depended on the bay's fish for sustenance. The ban did acquit the government from further liability.

In 1959, Kumamoto University researchers determined that the organic forms of mercury were the cause of the "Minamata Disease".<sup>a</sup> In 1968, the Chisso Corporation stopped releasing mercury compounds into the Minamata River and Bay since the mercury production method had

become antiquated. About 4000 people have either been officially recognized as having "Minamata Disease" or are in the queue for verification from the board of physicians in Kumamoto Prefecture. Fish consumption from the bay has never stopped, but Hg concentrations in fish appear to have decreased.

Elsewhere, the mines of central Japan located near the Toyama Prefecture have been removing metals from the surrounding mountains as early as 710. Gold was the first metal to be mined from the area, followed by silver in 1589, and shortly thereafter, lead, copper, and zinc. At the start of the twentieth century, the Mitsui Mining and Smelting Co., Ltd controlled the production of these mines. As a result of the Russo-Japanese War, World War I, and World War II, a surge in the demand for metals in the use of weapons caused mass increases in the mines' production aided with the advent of new European technologies in mining.<sup>23</sup>

Along with the huge increase in mining production, came a significant increase in pollution produced from the mines. Liquid and solid wastes were dumped into the surrounding waters, including the Jinzu River which flows into the Sea of Japan, and the five major tributaries that flow into the Jinzu River. The Jinzu River water system supplies the water to the surrounding city of Toyama, 30 km downstream from the main mining operations. This water was primarily used by the surrounding areas in irrigation for the rice paddies. In addition, the water provided a source of water used for drinking, washing, and fishing.

In addition, large amounts of cadmium were released into the Jinzu River Basin from 1910 until 1945. Cadmium was extracted from the earth's crust during the production of other metals like zinc, lead, and copper that were being mined near the Toyama area. Cadmium is a naturally occurring element that does not corrode easily, enters the air during mining, can travel long distances, and then falls into the ground or water only to be taken up by fish, plants, animals, or humans from the environment.<sup>24</sup> The cadmium from the mines deposited in the river and land of the Jinzu River Basin were absorbed by surrounding plants and animals causing fish to die and the rice to grow poorly. Furthermore, humans living in the area consumed the poisoned water and rice.

As a result of the ingestion of cadmium, a new disease specific to the Toyama Prefecture appeared in 1912. Initially, the disease was not well understood and was suspected to be either a regional or bacterial disease or the result of lead poisoning. However, in 1955, Ogino and his colleagues suspected cadmium as the cause of the disease and named the disease *Itai Itai*. In 1961, the Kamioka

## METAL CONTAMINATION CASES IN JAPAN (cont'd)

Mining Station of Mitsui Mining and Smelting company was linked as the direct source of the cadmium poisoning, and the Toyama Prefecture, 30 km downstream, was designated the worst cadmium contaminated area (Figure 23.3). The concentrations of cadmium in this prefecture were orders of magnitude higher than that found in background levels and were well above even other industrialized locations (Table 23.2).

Cadmium exposure results in two major health-related problems of *Itai Itai* disease, irreversible kidney damage and bone disease (*Itai Itai* is Japanese for "Ouch Ouch"). After exposure to high levels of cadmium, the kidneys have decreased ability to remove acids from the blood due to proximal tubular dysfunction resulting in hypophosphatemia (low phosphate blood levels); gout

(arthritic disease); hyperuricemia (elevated uric acid levels in the blood); hyperchloremia (elevated chloride blood levels); and kidney atrophy (as much as 30%). Following kidney dysfunction, victims of the disease develop osteomalacia (soft bones), loss of bone mass, and osteoporosis leading to severe joint and back pains and increase risk of fractures.

<sup>a</sup>This is an all too common professional ethics problem, i.e. lack of full disclosure. It is often, in retrospect, a very costly decision to withhold information about a product, even if the consequences of releasing the information would adversely affect the "bottom line". Ultimately, as has been seen in numerous environmental and other damage cases, the costs of not disclosing are severe, such as bankruptcy and massive class action lawsuits, let alone the fact that a company's decision may have led to the death and disease of the very people they claim to be serving, i.e. their customers and workers.

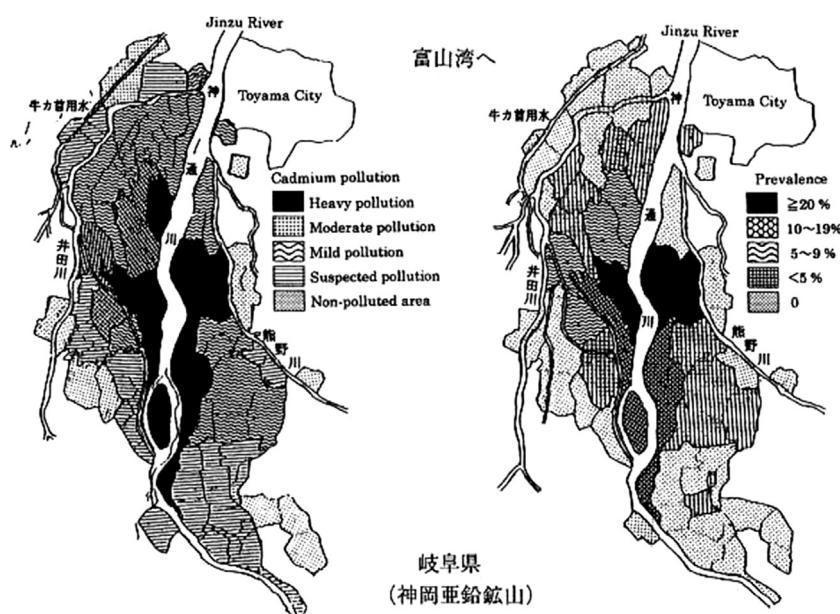


FIGURE 23.3 The co-occurrence of cadmium contamination with the prevalence of *Itai Itai* disease in women over age 50 in Toyama Prefecture (c. 1961). Kanazawa Medicine, 1998.

The concerns about Hg now largely include the atmosphere. As mentioned in Chapters 13 and 14, Hg in stack emissions from coal-fired power plants is the major source of Hg deposition in North America. Thus, atmospheric transport and deposition of Hg contributes to the buildup of Hg in the food chain. As a result, airborne Hg is a substantial source of Hg exposure, not only by inhalation but also by ingestion.

The cycling of all chemical species of Hg is shown in Figure 23.4. The exchanges with the atmosphere occur

between both land and surface waters. Indeed, most of the exchanges occur between water and air, with sediments as a large global Hg sink. The natural sources include volcanoes and biogenic (especially flora) emissions.

The mercury cycle depicted in Figure 14.8 and discussed in Chapter 14 includes numerous compartments and cycling at various scales. The chemical speciation of Hg is quite complex, consisting of numerous chemical and physical forms with very different properties.

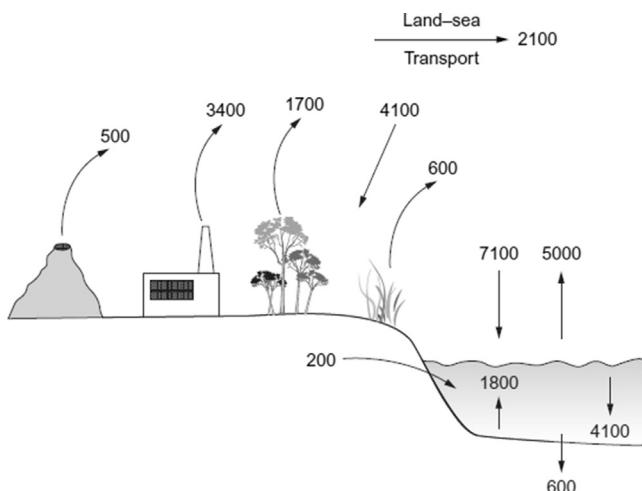
**TABLE 23.2** Estimates of Average Daily Dietary Intake of Cadmium Based on Food Analysis in Various Countries

Country	Estimates ( $\mu\text{g Cd per day}$ )	Reference
<b>AREAS OF NORMAL EXPOSURE</b>		
Belgium	15	Buchet et al. (1983)
Finland	13	Koivistoinen (1980)
Japan	31	Yamagata & Iwashima (1975)
Japan	48	Suzuki & Lu (1976)
Japan	49	Ushio & Doguchi (1977)
Japan	35	Iwao (1977)
Japan	49	Ohmomo & Sumiya (1981)
Japan 5	9	Iwao et al. (1981a)
Japan	43.9 (Males) 37.0 (Females)	Watanabe et al. (1985)
New Zealand	21	Guthrie & Robinson (1977)
Sweden	10	Wester (1974)
Sweden	17	Kjellström (1977)
United Kingdom	10–20	Walters & Sherlock (1981)
USA	41	Mahaffey et al. (1975)
<b>AREAS OF ELEVATED EXPOSURE</b>		
Japan	211–245	Japan Public Health Association (1970)
Japan	180–391	
Japan	136	Iwao et al. (1981a)
United Kingdom	36	Sherlock et al. (1983)
United Kingdom	29	Sherlock et al. (1983)
USA	33	Spencer et al. (1979)

Source: International Programme on Chemical Safety. Environmental health criteria: 134 (Cadmium). Geneva (Switzerland): World Health Organization; 1992.

However, airborne Hg mercury takes three fundamental physicochemical forms:

1. Elemental or zero-valence mercury ( $\text{Hg}^0$ ), which is the uncombined chemical element.
2. Divalent mercury ( $\text{Hg}^{2+}$ ), which is chemically reactive and under most environmental conditions is found to be combined with other substances into mercury salts (e.g.  $\text{HgCl}_2$ ).
3. Particulate-phase mercury [ $\text{Hg(p)}$ ], most of which is actually the chemical species  $\text{Hg(II)}$  but is only



**FIGURE 23.4** Total mercury cycling of mercury ( $10^6 \text{ g Hg year}^{-1}$ ). Ref. 13.

slightly reactive because it is mixed with solid-phase material in the atmosphere.

These three forms of Hg vary in their affinities for tissue, their persistence, and their bioavailability. Mercury compounds may remain in the atmosphere for extended periods depending on the oxidation state. For example,  $\text{Hg}^0$  has an atmospheric residence time of about 1 year, but  $\text{Hg}^{2+}$  for just a few weeks.<sup>25</sup> This is in part because the  $\text{Hg}^0$  is oxidized to  $\text{Hg}^{2+}$ , which is the major chemical species in both wet and dry Hg deposition to the earth's surface.<sup>26</sup>

Extraction activities, not just of Hg but also of other ores and by combustion of fossil fuels (especially coal), adds Hg to the atmosphere. During biogeochemical cycling, Hg is readily interconverted among  $\text{Hg}^0$ ,  $\text{Hg}^{2+}$ , and  $\text{Hg(p)}$ . When the Hg is deposited, especially in detritus in forest and other ecosystems, it is reduced. The  $\text{Hg}^0$  is then reemitted in the vapor phase.<sup>27</sup> The remaining nonvolatilized Hg fraction accumulates in soil organic matter<sup>28</sup> or binds to organic compounds suspended in surface waters.<sup>29</sup>

In oceans, part of the  $\text{Hg}^{2+}$  that is deposited onto the surface is reduced photochemically to  $\text{Hg}^0$ . This  $\text{Hg}^0$  fraction is then reemitted to the atmosphere advectively by winds and by partitioning as a dissolved gas to the atmosphere<sup>30</sup> (see discussion of Henry's Law and air–water equilibrium constants in Chapter 18). Mercury accumulates with increasing latitude. In polar regions, oxidation to  $\text{Hg}^{2+}$  is likely mediated by bromine (Br) in the atmosphere.<sup>13</sup>

The transformation chemistry of Hg, therefore, determines not only how Hg will speciate in the atmosphere and other parts of the environment, but also the likely exposure scenarios that will result. The food chain characteristics of Hg are very important.

For example, Hg increases in bioavailability when it resides in sediment, i.e. decreased dissolved O<sub>2</sub> allows for reduction and methylation of other forms of Hg. Thus, the form of Hg in atmospheric deposition is likely to be changed as it moves among compartments and as it is taken up and metabolized by organisms. For example, sulfate-reducing bacteria convert oxidized forms of Hg to methylmercury (CH<sub>3</sub>Hg), which is much more bioavailable and toxic than the oxidized precursors.

Indeed, the same amount of atmospheric deposition onto a surface water body may yield dramatically different tissue concentrations in fish than in another water body nearby if the two systems have varying depths of organic sediment. The system with deeper organic sediments is likely to have fish with higher CH<sub>3</sub>Hg concentrations due to the bacterial sulfate reduction. There also appears to be a direct relationship between acid deposition and methylation of Hg if the acid is H<sub>2</sub>SO<sub>4</sub>.<sup>13</sup>

### 23.1.2 Cadmium

Cadmium (Cd) occurs in the earth's crust at a concentration of 0.1–0.5 ppm and is commonly associated with other metal ores (e.g. zinc, lead, and copper). Ocean water Cd concentrations range between <5 and 110 ng l<sup>-1</sup>, with higher levels reported near coastal areas and in marine phosphates and phosphorites. Surface waters and groundwater generally contain <1 µg l<sup>-1</sup> Cd. Soil Cd concentrations are dependent on several factors, e.g. the specific Cd compound's mobility, natural geochemistry, and Cd loading from agricultural chemicals and atmospheric deposition. Volcanoes, forest fires, sea salt aerosols, and other natural phenomena also load Cd into the atmosphere.<sup>31</sup>

In recent years, cadmium (Cd) is most prominent as an element in nickel–cadmium (NiCd) batteries, but Cd has been used extensively in metal plating and other industries (see Discussion Box: Metal Contamination Cases in Japan). Exposure to Cd has been associated with kidney damage (proteinuria) and respiratory effects, e.g. reduction in forced vital capacity and reduction in peak expiratory flow rate.<sup>32</sup>

The molecular weight of Cd is 112.41 g mol<sup>-1</sup>. Other physicochemical properties are density = 8.642 g cm<sup>-3</sup> at 20 °C; boiling point = 765 °C; melting point = 320.9 °C; and vapor pressure = 0.13 kPa at 394 °C. Thus, under most environmental conditions, Cd<sup>0</sup> is nonvolatile and would likely need to be sorbed to aerosols to reach the atmosphere. However, Cd exists in various chemical species. Two chemicals that are particularly toxic are cadmium chloride (CdCl<sub>2</sub>) and cadmium oxide (CdO). The aqueous solubility of CdCl<sub>2</sub> is rather high (about 100 mg ml<sup>-1</sup> at 20 °C). Its

vapor pressure is higher than Cd<sup>0</sup>, although it is nonvolatile under environmental conditions (0 kPa at 20 °C). The aqueous solubility of CdO is low (<1 mg ml<sup>-1</sup>). CdO is nonvolatile under environmental conditions (0 kPa at 20 °C). Cadmium carbonate (CdCO<sub>3</sub>) is also insoluble in water. Cadmium sulfate (CdSO<sub>4</sub>) and cadmium sulfide (CdS) are soluble in water (e.g. CdS aqueous solubility = 1.3 mg l<sup>-1</sup> at 18 °C).

Given the low solubilities and vapor pressures of most Cd compounds, dissolution and volatilization must be assisted by other mechanisms to mobilize Cd. For example, when Cd is ground to powder it burns and vaporizes. Thus, a major mechanism for entry into the atmosphere is combustion. Concentrations of Cd in fossil fuels, e.g. coal and crude oil, and incineration of municipal wastes (e.g. batteries in the waste stream) are the largest sources of airborne Cd.

The oxidation state of Cd is most often +2, but also occurs as +1. The +1 state is reached in a manner similar to that of Hg. That is, Cd must first exist as a divalent cation, before conversion to Cd<sup>+</sup>. For example, dissolving elemental Cd in a mixture of cadmium chloride and aluminum chloride (wherein Al has a +3 oxidation state) yields a compound wherein Cd has +1 oxidation state:



This reaction is unlikely to occur often in nature, so the +1 oxidation state is more likely to be found in industrial and laboratory settings.

### 23.1.3 Lead

The US Agency for Toxic Substances and Disease Registry (ATSDR) in 1999 ranked lead (Pb) second in the list of prioritized hazardous substances. The noxious effects of lead have been known for a long time—we are aware of the Romans inadvertently poisoning themselves by drinking and eating out of lead vessels. The World Health Organization has guidelines for lead in the air and in water of 0.5 µg m<sup>-3</sup> and 0.1 mg l<sup>-1</sup>, respectively. The Centers for Disease Control and Prevention in the US state that a blood level of 10 µg dl<sup>-1</sup> (100 µg l<sup>-1</sup> or 0.48 µmol l<sup>-1</sup>) in children is a cause for concern. Lead poisoning occurs through ingestion, inhalation, and dermal contact, with inhalation perhaps, the most common exposure route. Factory workers dealing with lead and lead products and people living near such factories are the most likely to be affected. In countries where lead tetraethyl is still added to gasoline, the general public is exposed to significant lead levels through vehicles exhausts, and even lead containing dust in the air.<sup>33</sup>

The toxicity of Pb is discussed in Chapter 13. Generally, exposures to lead can result in anemia;

nervous system dysfunction; impaired cognitive, motor, and language skills; learning difficulties; nervousness and emotional instability; insomnia; nausea; lethargy; weakness, hypertension, kidney problems, decreased fertility, and increased level of miscarriages, and low birth weight and premature deliveries. Children are at particular risk to Pb toxicity, including neurological impairment, growth retardation, delayed sexual maturation, and impaired vitamin D metabolism. Children are very much more susceptible to damage from lead than adults, and neurological impairment can occur in children with blood lead levels  $<10 \mu\text{g dl}^{-1}$ .<sup>34</sup>

The biogeochemical cycling of Pb appears to be similar to that of other divalent metals. As evidence, uptake by plant life increases with increasing concentrations in soil and water. For example, studies have shown the most influential factor in biotic Pb concentrations (also Zn, Cu, and Ni) is the distance from the ocean shore. For example, in arctic willow growing a few meters from the tide line, the Pb content was higher than that of the same plant species growing about 1 km from the coast line and sheltered from the sea.<sup>35</sup>

A major transport mechanism for Pb is by aerosols. In continental climates with dry and hot summer and severe winter, strong winds can transport particulates for short and long distance, depending on the consistency of wind speed and inversely proportional to aerosol size. The sources are often anthropogenic. For example, the atmospheric transport of soil particles with sorbed organic compounds, heavy metals, and metalloids (e.g. Ni, Cd, Co, Zn, Pb, As) have origins from both industrial emissions into the atmosphere and waste landfill sites.<sup>35</sup>

Lead and other metals vary by ecosystem type, depending on deposition rates, uptake by organisms and sequestration within abiotic and biotic sinks. For example, averaged Pb fluxes in biological cycling of boreal and subboreal forest ecosystems vary considerably among types. The flux in subboreal northern taiga coniferous forests had a turnover flux of  $1.9 \text{ g Pb per hectare per year}$  ( $\text{g Pb ha}^{-1}$  per year); subboreal coniferous and small-leaved forests had  $4.2 \text{ g Pb ha}^{-1}$  per year; subboreal broad-leaved forests had  $7.9 \text{ Pb ha}^{-1}$  per year; and sphagnum forest swamps had  $12.0 \text{ Pb ha}^{-1}$  per year.<sup>35</sup>

## 23.2 METALLOID CYCLING

Arsenic (As) and antimony (Sb) are the two metalloids of principal concern in air pollution. Both As and Sb belong to Group 15 of the period table.

### 23.2.1 Arsenic

Arsenic has been known for centuries and its compounds have been used in all sorts of preparations, including cosmetics; paints; artist's colors and dyes; alloys of lead, copper, and brass; pesticides; wood preservatives; tonics; glass production (it removes the green tint from the iron impurities); and even medicines. There is a theory that the once-popular arsenic-based wallpaper pigment, Paris green [copper (II) acetoarsenite], was the cause of Napoleon's mysterious death in 1821. In the late nineteenth century, arsenic compounds were linked to the deaths of more than 1000 children through inhaling arsenic vapors from moldy green wallpaper—probably the Paris green type. About the same time, arsenic-based medications for syphilis, asthma, and psoriasis were considered the cause of skin cancer. Paris green [copper (II) acetoarsenite] is a highly toxic emerald-green crystalline powder that has been used as a rodenticide and insecticide, and also as a pigment, despite its toxicity. It is also used as a blue colorant in fireworks. The color is apparently vivid, blue green when very finely ground, and a deeper true green when coarsely ground.<sup>36–38</sup>

Today, in the US, the main use of arsenic is wood preservatives for outdoor and industrial environments. The use of arsenic compounds have dropped dramatically over the past 10 years. In 2001, the US imported 25,000 tons of arsenic compounds but in 2009 only 3600 tons was imported.<sup>39</sup> Almost 90% of the imports are being used in chromated copper arsenate (CCA) wood preservative for "pressure-treated" decking, landscaping, walkways, and industrial usage. The rest is used in semiconductors, specialized metal, a few remaining pesticides and treatments for acute leukemia and other cancers.

Arsenic ores (arsenic sulfides, orpiment, and realgar) have been mined and used since ancient times. It is very probable that its toxic nature has been known for a very long time.<sup>40</sup> Arsenic and many As compounds are very toxic to humans. Arsenic disrupts the adenosine triphosphate (ATP) reactions in the body and is very toxic to all animal life. Arsenic and its compounds, notably  $\text{As}^{3+}$ , have in the past been used in the production of pesticides (e.g. in treated wood products), herbicides, and insecticides. In 1980, the US National Toxicology Program listed inorganic arsenic compounds as known human carcinogen. Subsequently, in 1981, inorganic arsenic-based pesticides were banned, and by 1985 the US had stopped producing arsenic. The applications of arsenic have declined considerably since that time but in many parts of the world arsenic compounds are used in wood preservatives for industrial applications. Developed

nations and the US continue to import As for this and other specialized purposes.

The main route for human poisoning by arsenic is from drinking groundwater that contained high concentrations of arsenic. This has been the cause of a number of tragic disasters around the world (see later). A 2007 study found that over 137 million people in more than 70 countries are probably affected by arsenic poisoning of drinking water.<sup>41</sup> Arsenic is toxic to aquatic life, birds, and land animals and in soils, where arsenic content is high, plant growth and crop yields may be poor. Aquatic life is particularly sensitive to arsenic compounds and moderately toxic to birds and land animals. Arsenic is very persistent in the environment and is expected to bioaccumulate in fish and shellfish. In spite of this, there are some microorganisms that have evolved to tolerate relatively high concentrations of As and some even thrive on it, using As for an energy source. The energy generation is based on the redox chemistry of arsenic. Arsenic has four main oxidation states: -3, 0, +3, and +5 with the predominant inorganic forms being arsenates (+5) and arsenites (+3). Under aerobic conditions, some microorganisms obtain energy by the oxidation of  $\text{As}^{3+}$  to  $\text{As}^{5+}$ , with the resultant electrons being transferred to electron acceptors such as nitrate ions or oxygen and the ATP pump. Under anaerobic conditions, energy for growth is obtained by the microbial reduction of  $\text{As}^{5+}$  to  $\text{As}^{3+}$  coupled to the oxidation of organic matter or inorganic electron donors such as hydrogen or sulphide ions. These microbial processes together with inorganic and physical processes make up the global arsenic cycle.<sup>42,43</sup>

Because arsenic is in the same column of the periodic table as is phosphorus, its compounds resemble those of phosphorus. The trivalent form is the most common; and is the basis for the arsenates and most organoarsenic compounds. Both  $\text{As}_2\text{S}_3$  (orpiment) and  $\text{As}_4\text{S}_4$  (realgar) are composed of trivalent arsenic. The  $\text{As}_4\text{S}_4$  species is made possible by As–As bonds in the molecule.

An advocacy nongovernmental organization in 2001 in the US, wanting to ban arsenic in all consumer products, found that pressure treated wood leached more than 1 mg of arsenic onto a moistened hand wipe the size of a 4-year-old's hand. This is 100 times the US Environmental Protection Agency's  $10 \mu\text{g l}^{-1}$  "allowable daily exposure level" for drinking water, assuming the child has a liter a day. Likely due in part to these findings, the wood processing industry agreed to stop using arsenic-based wood preservatives for household use as of December 2003.

However, organic arsenic herbicides (not as toxic as their inorganic compounds) are still in use on cotton and turf, including golf courses, lawns, school yards, athletic fields, and rights-of-way.

In Europe, the Directive 2003/2/EC<sup>44</sup> restricts the marketing and use of arsenic, including CCA wood treatment. Treated CCA wood is not permitted to be used in residential or domestic constructions but is permitted for use in various industrial and public works, such as bridges, highway safety fencing, electric power transmission, and telecommunications poles. This directive is not unlike the ruling in the US.

In many other parts of the world, the same type of ruling exists: in Australia, the use of CCA preservative for treatment of timber was restricted to certain applications from March 2006 and CCA may no longer be used to treat wood used in "intimate human contact" applications and that includes children's play equipment, furniture, residential decking, and hand railing. Use for low contact residential, commercial, and industrial applications remains unrestricted, as does its use in all other situations. Similarly to the US Environmental Protection Agency (EPA) regulations, the Australian authorities did not recommend dismantling or the removal of existing CCA treated wood structures.

In many parts of the world (parts of SE Asia, Chile, Argentine, parts of Western USA, Taiwan, Thailand, Mainland China, Bangladesh, and West Bengal), the arsenic concentration in groundwater is high enough to cause serious arsenic poisoning to people drinking the water. However, nowhere in the world is the problem greater than in the Ganges delta (Bangladesh and to a lesser extent West Bengal).<sup>45,46</sup>

Bangladesh, in the 1970s, had one of the highest infant mortality rates in the world. This was largely due to ineffective water purification and sewage systems. Most drinking water used to be collected from open dug wells and ponds with little or no arsenic, but contaminated with water transmitting diseases such as diarrhea, dysentery, typhoid, cholera, and hepatitis. At that time, the UNICEF and the World Bank aided workers worked out a solution; they decided to drill tube wells (boreholes) deep underground to tap into the groundwater.<sup>47</sup>

As a result, 8 million tube wells were constructed to provide "safe" drinking water and in a short time, the infant mortality and diarrheal illness were reduced by 50%. Most of the wells were augured to depths between 20 and 100 m. Unfortunately one in five of these wells was contaminated with arsenic which was above the government's drinking water standard set at  $0.05 \text{ mg l}^{-1}$ ; this being five times the World Health Organization's acceptable maximum concentrations of arsenic in safe drinking water which was  $0.01 \text{ mg l}^{-1}$ . The crisis came to the attention of international organizations in 1995 and the resultant study involved the analysis of thousands of water samples as well as hair, nail, and urine samples.<sup>48–50</sup> Indeed, 61 out of 64 provinces in Bangladesh (900 villages) and in West

Bengal 17 provinces, were found with arsenic water levels above the government limit. Results showed that many of the wells which had been dug more than 20 m and less than 100 m were contaminated, whereas groundwater and well water from depths greater than 100 m were free of arsenic. The explanation was that groundwater closer to the surface had spent a shorter time in the ground, therefore had not dissolved significant amounts of arsenic from the soil, and furthermore, the water from the wells deeper than 100 m was exposed to older sediments which have already been depleted of arsenic.<sup>51</sup> The total number of people using arsenic-rich water (levels  $>0.1 \text{ mg l}^{-1}$ ) was 1.4 million in West Bengal and a staggering 46–57 million in Bangladesh.<sup>52,53</sup>

The biogeochemistry of As is similar to that of the heavy metals. Microbes play a key role in As cycling and toxicity. Anaerobic bacteria can reduce As<sup>5+</sup> during cometabolism.<sup>b</sup> When an As undergoes cometabolism, the reactions are catalyzed by an enzyme that is fortuitously produced by the organisms for other purposes. The microbe does not directly benefit from the degradation of the compound. The biotransformation of the As compound could actually be harmful or can inhibit growth and metabolism a microbe. In addition, aerobic microorganisms can oxidize As<sup>3+</sup>. Thus, both aerobic and anaerobic microorganisms can cycle and transform As in the environment.

Microbes degrade soil-borne contaminants, but these microbial mechanisms are enhanced by the biochemodynamics of the root zone (the *rhizosphere* – see Figure 17.10 in Chapter 17). This process is slower usually than phytodegradation. This process can enhance As cometabolism because plant roots release natural substances, e.g. sugars, alcohols, and acid, that are food for soil microorganisms. The fixation and release of nutrients are also a natural type of bio-stimulation for the microbes. In addition, the roots provide conduits and physical loosening of soil, improving microbial contact with oxygen and nutrients.

### 23.2.2 Antimony

Antimony (Sb) exists in fossil fuels, especially in coal. Fossil fuel combustion is likely the largest source of anthropogenic Sb emissions to the atmosphere. Abundant in sulfide minerals and co-occurring with heavy metals, Sb emissions likely result from the mining and

metallurgy of nonferrous metals, especially Pb, Cu, and Zn.

Their identical outer orbital electron configuration means that Sb and As have the same range of oxidation states in environmental systems (i.e. –3 to +5). The major chemical forms of both are the oxides, hydroxides, or oxoanions, in the +5 state in oxidized environments (i.e. antimonates and arsenates) or in the +3 state in more reduced environments (i.e. antimoniates and arsenites). Like As, the toxicity of Sb depends upon speciation. The organoantimonials (e.g. methylated Sb species) are less toxic than the antimonates (Sb<sup>5+</sup>), which are less toxic than the antimoniates (Sb<sup>3+</sup>).<sup>54</sup>

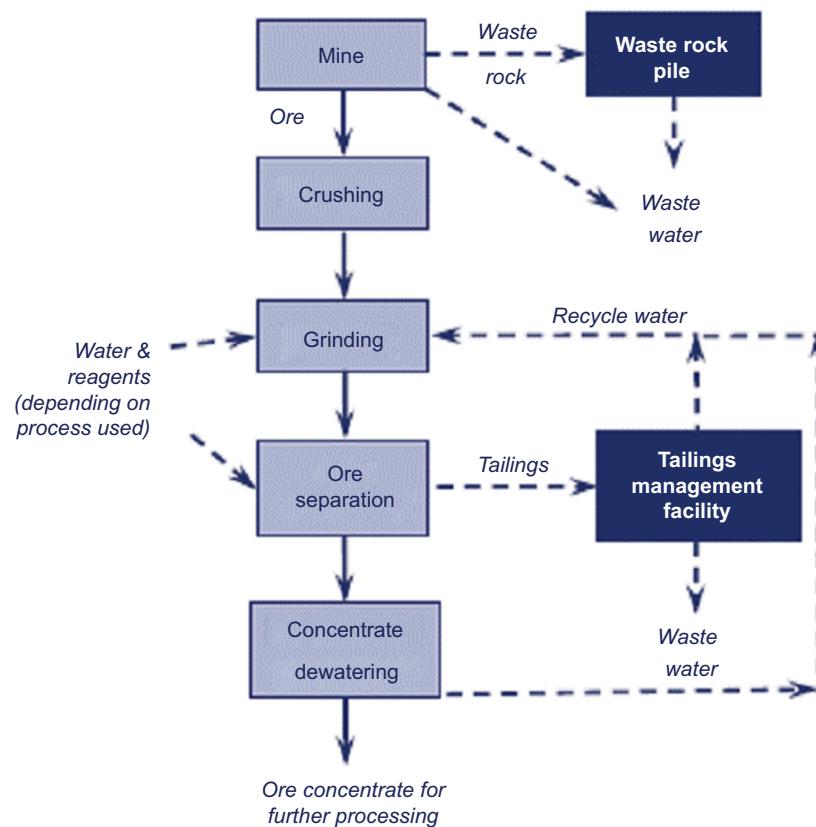
Metalloids seem to behave similarly to heavy metals regarding biogeochemistry. However, this cannot be assumed in all environments, given the lack of relevant and specific data. These data are particularly lacking for Sb.<sup>54</sup>

## QUESTIONS

- Consider the metals listed as air toxics. Why is each designated as the metal and its compounds?
- What are the major ways that metals find their way to the atmosphere?
- Numerous genera of bacteria reduce metals during metabolism. Consider how this process may be used to treat metallic air pollutants and to prevent their entry into the atmosphere.
- Numerous genera of flora translocate metals during photosynthesis, transpiration, and respiration. Consider how these processes may be used to treat metallic air pollutants and to prevent their entry into the atmosphere.
- Review the following table of the chemical composition of an ore deposit. If a company is planning to extract ores from this deposit, from the standpoint air pollution, which site poses the greatest potential problems during extraction? What information is missing from this table that is needed to make this determination?

Constituent	Percent (Mass) by Location					
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
FeO	0.26	0.82	0.26	0.10	0.33	0.46
Fe <sub>2</sub> O <sub>3</sub>	97.8	97.2	98.3	98.7	96.6	86.7
SiO <sub>2</sub>	0.96	0.80	0.41	0.62	1.20	5.10

<sup>b</sup> Cometabolism is the fortuitous degradation of a compound because it exists along with another compound that is an energy source for the microbe. For example, engineers have used soil bacteria (e.g. *Pseudomonas spp.*) to degrade persistent compounds like tetrachloroethylene (PERC). Most microbes would not be able to attack the PERC molecule, but producing an enzyme (e.g. methane monooxygenase) in the process of degrading short chain alkanes or sugar compounds, some of the PERC is also degraded.



**FIGURE 23.5. Ore processing flow.** Source: Environment Canada (2009). *Environmental Code of Practice for Metal Mines. Report No. TD195 M5 E58 2009.*

Percent (Mass) by Location						
Constituent	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
Al <sub>2</sub> O <sub>3</sub>	0.58	0.65	0.35	0.43	1.00	6.00
S	<0.001	0.002	0.006	0.001	<0.001	0.003
P <sub>2</sub> O <sub>5</sub>	<0.02	0.02	0.02	<0.02	0.05	0.02
MnO	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ZnO	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PbO	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
CuO	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MgO	<0.01	<0.01	<0.01	<0.01	0.02	0.02
TiO <sub>2</sub>	<0.02	<0.02	<0.02	<0.02	0.03	0.17
C	0.013	0.020	0.020	0.010	0.019	0.083

6. When refined, which type of air pollutants would you expect from the above ores?
7. Identify the locations on Figure 23.5 where air pollutants may be emitted by type and relative amounts.

8. Cyanide compounds are used in a gold leaching operation to extract gold from ore. Cyanide freed from the gold-cyanide complexes can be recovered from the tailings and reused to leach more gold from the ore pile. What potential problems could result from these operations? Show at least one chemical reaction that could lead to air pollution.
9. How can smelting a metal ore produce both sulfur dioxide and metallic aerosols? Show illustrative reactions and explain the emissions.
10. The following table shows the elemental total mass contents (mass of element/total mass expressed in %) of particulate matter (PM) emitted by a lead (Pb) recycling facility (Uzu G, Sobanska S, Sarret G, Pradère P, Dumat C. Characterization of lead-recycling facility emissions at various workplaces: major insights for sanitary risks assessment. *J Hazard Mat* 2011;186: 1018–1027). Explain the differences in the metal content by PM size for the metals. For example, why do the Cd fractions increase so much in the emissions? What are the sources of lead? Why is the content so high? Why does arsenic percent decrease in the furnace

	Al	As	Cd	Cu	Fe	Na	Ni	Pb	Sb	Zn	S	Cl	C	O
<b>REFINING</b>														
PM <sub>tot</sub>	0.07	0.3	0.2	0.6	1.3	2.2	0.5	41	1.9	0.2	2.9	n.d.	2.2	20.5
PM <sub>10–2.5</sub>	0.08	0.6	0.2	0.7	1.4	5.9	0.3	32	2.3	0.4	7.2	0.35	4.1	19.2
PM <sub>2.5–1</sub>	0.09	0.5	0.2	0.7	1.4	8.9	0.2	32.3	2.1	0.4	7.4	n.d.	4.3	20
<b>FURNACE</b>														
PM <sub>tot</sub>	0.1	0.06	0.2	0.2	5.7	6.8	0.08	25.7	0.55	0.2	2.8	n.d.	4.6	20.1
PM <sub>10–2.5</sub>	0.07	0.08	0.4	0.2	4.5	10.3	0.05	45.2	0.6	0.3	7.6	0.54	6.5	21
PM <sub>2.5–1</sub>	0.05	0.08	0.7	0.1	2.1	8.3	0.02	38	0.49	0.4	8.2	n.d.	5.1	20.1
<b>EMISSIONS</b>														
PM <sub>tot</sub>	0.02	0.09	2.7	0.09	1.2	5	0.02	33.4	0.18	0.7	3.3	n.d.	1	15
PM <sub>10–2.5</sub>	0.005	0.08	2.3	0.06	0.4	4	0.009	26.7	0.14	0.5	7.4	1.93	1.2	15.1
PM <sub>2.5–1</sub>	0.001	0.09	2.5	0.05	0.1	3.2	0.004	27.3	0.13	0.5	7.8	n.d.	1.2	14.9

Notes: n.d. = not determined. Results are averaged upon three replicates, standard deviations not exceeding 0.1%.

compared to the refining process, while iron's increases?

11. If the emission standard for Pb is 200 µg m<sup>-3</sup> for the above facility, how much of the PM would be removed to achieve this standard, assuming that all of the Pb is in particulate form? How easy will this be?
12. Show a reaction that could occur from mercury deposited onto surface waters that leads to monomethylmercury.

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## P A R T V

# ADDRESSING AIR POLLUTION

Parts I through IV primarily focus on the ways to describe air pollution and to estimate its impacts on human health and the environment. The fate of air pollutants is the result of physical, chemical, and biological processes beginning even before the air pollutant's existence and the myriad mechanisms and events that ultimately lead to exposure and risk. Along the way, indicators of these processes can be measured and predicted from models. At various points in space and time, interventions and preventive steps can be taken to interrupt this source-to-effect paradigm.

The major objective of Part V is to provide an introduction to the ways to measure the type and extent of the pollution and the means for preventing, controlling, and treating emissions and reducing risks. Scientifically credible and sound information is needed to address any environmental problem. Air pollution varies in type and scale. Its extent and characteristics must be documented to begin to ameliorate the problems that it causes. The progress made by control and prevention actions must be evaluated by comparing changes in air quality over time and space. Ultimately, these air quality changes must be compared to improvements in human health, ecosystem condition, and public welfare, e.g. less material destruction from air pollutants.

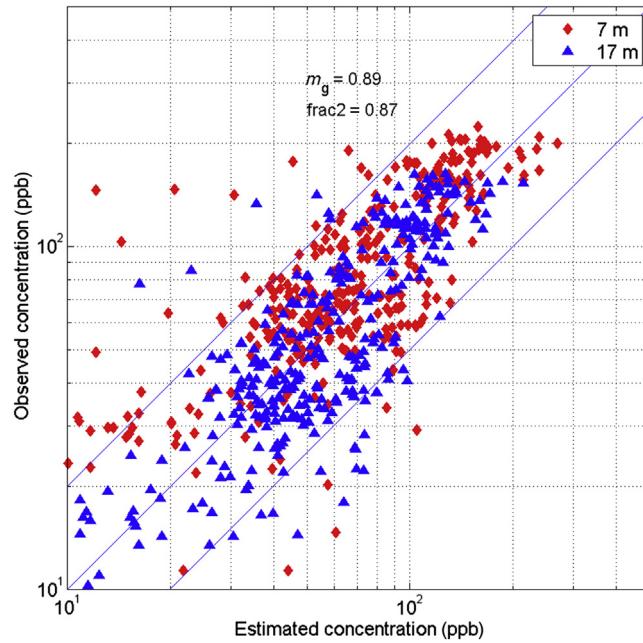
A reliable measurement of air pollution is the first step in providing data to support decisions needed to decrease and eliminate exposures and risks. The measurements themselves are seldom sufficient since they are limited in time and space. Also, individual measurements usually only provide information about one or a few substances in the atmosphere. The actual measurements are often not available for the entire geographic area of interest, or the measurements that are available may have been taken for reasons other than the particular air pollution problem at hand.

Since measurements are only relevant to the time and place where they are taken, air pollution models are needed to interpolate between measurements and extrapolate from samples to characterize the extent and severity of air pollution and to predict future air pollution scenarios. The models can be as simple as averaging concentrations from measurements, or they may consist of very complex algorithms and numerous parameters. Air pollution modeling was introduced in Chapter 19, but is discussed in detail in Chapter 27.

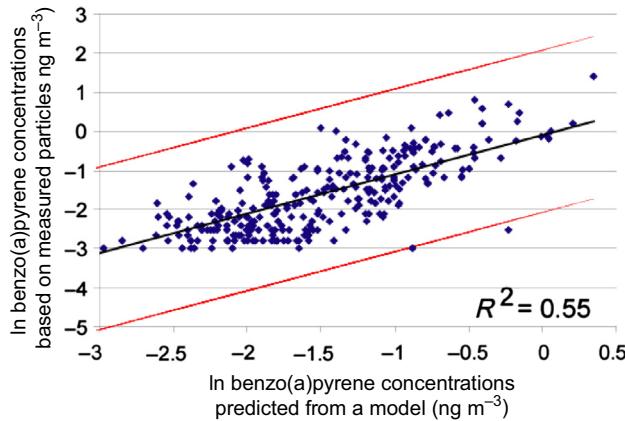
Measurements are not only important in their own right, but also needed to evaluate models and to ground truth models, i.e. evaluating the model's predictions against a well-designed and controlled set of predictions. Such measurement results are often called "knowns" to which modeled ("predicted") results are compared (see [Figure V.1](#)).

Another example of the value of measurements is when they are used to extend existing knowledge about one air pollutant for which much is known to learn about another pollutant or class of pollutants for which there is scant information. For example, there is a wealth of measured and modeled data regarding particulate matter (PM), but relatively little about toxic chemicals. [Figure V.2](#) uses a multiple linear regression model to fit measurements of the carcinogenic compound benzo(a)pyrene, a polycyclic aromatic hydrocarbon (PAH), concentrations to predict concentrations of PAH concentrations in ambient air.

The comparison of measured to modeled results is often quantified using a coefficient of determinations, denoted  $R^2$ . The  $R^2$  ranges from 0 to 1, with 1 meaning that all the points fit on a single line. The  $R^2$  of 0.55 in [Figure V.2](#) is actually rather high for this type of comparison. It is worth noting here the fallacy known as "*cum hoc ergo propter hoc*", Latin meaning "with this, therefore because of this" (also "*post hoc ergo propter hoc*"—Latin for "after this, because of this"). This is a warning to those who employ statistics that even a strong correlation between two variables, does not necessarily imply that one caused the other. For example, a recent study reported that the contribution from diesel emissions to the formation of secondary organic aerosols (SOA) was nearly zero in the Los



**FIGURE V.1** Model estimates compared with the nitric oxide (NO) measurements collected at 7 and 17 m from a roadway shoulder at a height of 2 m. The observed concentrations are consistent with model estimates: 87% of the model estimates are within a factor of two of the observations, and the underprediction bias is about 10%. (For color version of this figure, the reader is referred to the online version of this book.) Venkatram A, Snyder M, Isakov V, Kimbrough S. Impact of wind direction on near-road pollutant concentrations. *Atmos Environ* 2013;80:248–58.



**FIGURE V.2** Example of comparing observed air pollutant concentrations to known, measured results. Measured benzo(a)pyrene, a polycyclic aromatic hydrocarbon (PAH), concentrations are compared to predicted concentrations, using a multiple linear regression model compared to measurements of PAH concentrations in ambient air particulate matter (dots). The inner line represents the mean prediction. The outer lines represent the 95% confidence levels. Such a model would be very useful since particulate matter data are more readily and reliably available than data for polycyclic aromatic hydrocarbons and other hazardous air pollutants. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Lobscheid AB, McKone TE, Vallero DA. Exploring relationships between outdoor air particulate-associated polycyclic aromatic hydrocarbon and PM<sub>2.5</sub>: a case study of benzo(a)pyrene in California metropolitan regions. *Atmos Environ* 2007;41: 5659–72.

Angeles Basin. Thus, the study concluded that substantial reductions in SOA from the local to global scales must be achieved through gasoline vehicle emissions.<sup>1</sup> The study correlated two different ratios of toluene and benzene concentrations to represent SOA with carbon monoxide (CO) concentrations (most CO comes from gasoline vehicles), and comparing weekdays to weekends (w on weekdays, finding  $R^2$  ranging from 0.40 to 0.50).

The correlation could indeed mean that gasoline vehicles do emit substantially all the SOA. The authors concluded that the correlations were observed independently. The  $R^2$  may indeed support the conclusion. However, inferences about possible sources must be considered that the correlation may not solely be caused by gasoline vs diesel engines. For example, a reviewer of the study cited reasons for the need to search for other “third variables”:

1. Trucks are powered by both gasoline and diesel engines.
2. Almost all long-haul trucks use diesel engines.
3. The reduction in truck traffic on weekends could be due to a reduction in short-haul, local deliveries by gasoline-powered vehicles.<sup>2</sup>

Certainly, finding an association between two variables is important and necessary to find a cause. Measurements of each variable provide the first step toward a causal link between the two variables, if indeed one exists. Methods exist for applying associations and correlations of measurements to search for causes. Statisticians use tests to quantify the extent to which an outcome can be attributed to chance *versus* the relationship between an independent and dependent variable (e.g. *p*-values). This is known as statistical significance. A *p*-value states the probability of getting a test statistic that is at least as much as what has been observed. That is, the *p*-value determines how consistent the observed results are with the variable being studied *versus* pure chance. Thus, a *p*-value of 0.05 would mean that there is a 5% chance that the finding is due to chance.

Such statistical tools are useful, but air pollution scientists need more clarity in assigning causality, especially when trying to link a disease or mortality to exposures to pollutants. Furthermore, engineers need to know as much as possible about causes in order to recommend appropriate steps for removing and treating pollutants, as well as preventing the formation of pollutants. Planners need to know the concentrations of pollutants at which harm is observed so that standards can be set. The biomedical research community has made great strides in recent decades in bridging associations and causality, such as whether a substance is toxic based on existing data from animal studies (“comparative biology”) and human studies (“epidemiology”).

Often, science must rely on enough weight-of-evidence to support or reject a suspicion that a substance causes a disease. The medical research and epidemiological communities use a number of criteria to determine the strength of an argument for causality, but the first well-articulated criteria are what have come to be known as Hill’s causal criteria<sup>3</sup> (see Table V.1).

As mentioned, correlations are often the beginning of data reduction, but several steps are needed to reduce and to interpret measurements, including fitting the data to new models or simply applying a point measurement to a larger spatial area.

Once a model has been evaluated, the choice of whether to monitor or model (or both) must be based on the objective of the study, where the study is being conducted, and how measurements and modeling results will be applied (e.g. to change road patterns, to add a control device, and to declare that an area is not meeting standards). For example, if the study is to determine how much a person is exposed to benzene as that person goes about daily activities, then personal monitoring is the best option since it reflects the pattern that the person follows during these activities. If the objective is to determine whether a company is meeting its air pollution permit requirements, a stack test for the pollutants listed in the permit may be needed. If the objective is to estimate how much a particular community is exposed to an air pollutant, then ambient monitoring and models may be needed to characterize the plume moving away from the source.

## V.1 Measured vs Modeled Results

The decision on whether to use measurements directly or modeled results, or both, depends on how the information will be used. Each has pros and cons.<sup>5</sup>

Reliable measurements require ample time to acquire data. Setup can take several months from the development of the study design and quality assurance plan to obtaining access to setting up monitors to actual sample collection. Field data must adhere to approved methods, quality assurance, and equipment limitations. Logistics and feasibility issues may call for changes deviating from the desired number and locations of sites from ideal to acceptable (e.g. pump failures, operator training and retaining qualified labor, funding, confidentiality, service connection outages, and

TABLE V.1 Hill's Criteria for Causality

**Factors to Be Considered in Determining whether Exposure to a Chemical Elicits an Effect**

*Criterion 1: Strength of association.* For a chemical exposure to cause an effect, the exposure must be associated with that effect. Strong associations provide more certain evidence of causality than is provided by weak associations. Common epidemiological metrics used in association include risk ratio, odds ratio, and standardized mortality ratio.

*Criterion 2: Consistency.* If the chemical exposure is associated with an effect consistently under different studies using diverse methods of study of assorted populations under varying circumstances by different investigators, the link to causality is stronger. For example, if the carcinogenic effects of chemical X is found in mutagenicity studies, mouse and Rhesus monkey experiments, and human epidemiological studies, there is greater consistency between chemical X and cancer than if only one of these studies showed the effect.

*Criterion 3: Specificity.* The specificity criterion holds that the cause should lead to only one disease and that the disease should result from only this single cause. This criterion appears to be based in the germ theory of microbiology, where a specific strain of bacteria and viruses elicits a specific disease. This is rarely the case in studying most chronic diseases, since a chemical can be associated with cancers in numerous organs, and the same chemical may elicit cancer, hormonal, immunological, and neural dysfunctions.

*Criterion 4: Temporality.* Timing of exposure is critical to causality. This criterion requires that exposure to the chemical must precede the effect. For example, in a retrospective study, the researcher must be certain that the manifestation of a disease was not already present before the exposure to the chemical. If the disease were present prior to the exposure, it may not mean that the chemical in question is not a cause, but it does mean that it is not the sole cause of the disease (see "Specificity" above).

*Criterion 5: Biologic gradient.* This is another essential criterion for chemical risks. In fact, this is known as the "dose-response" step in risk assessment. If the level, intensity, duration, or total level of chemical exposure is increased a concomitant, progressive increase should occur in the toxic effect.

*Criterion 6: Plausibility.* Generally, an association needs to follow a well-defined explanation based on a known biological system. However, "paradigm shifts" in the understanding of key scientific concepts do change.<sup>4</sup> A noteworthy example is the change in the latter part of the twentieth century of the understanding of how the endocrine, immune, neural systems function, from the view that these are exclusive systems to today's perspective that in many ways they constitute an integrated chemical and electrical set of signals in an organism.<sup>a</sup>

*Criterion 7: Coherence.* The criterion of coherence suggests that all available evidence concerning the natural history and biology of the disease should "stick together" (cohere) to form a cohesive whole. By that, the proposed causal relationship should not conflict or contradict information from experimental, laboratory, epidemiologic, theory, or other knowledge sources.

*Criterion 8: Experimentation.* Experimental evidence in support of a causal hypothesis may come in the form of community and clinical trials, *in vitro* laboratory experiments, animal models, and natural experiments.

*Criterion 9: Analogy.* The term analogy implies a similarity in some respects among things that are otherwise different. It is thus considered one of the weaker forms of evidence.

<sup>a</sup>For example, Candace Pert, a pioneer in endorphin research, has espoused the concept of mind/body, with all the systems interconnected, rather than separate and independent systems.

access to sites). Often, however, existing sampling networks with trained operators and equipment may already be available that can be used "as is" or modified to meet the measurement needs. Operation costs and feasibility continue to improve for many air pollutants. For example, increasingly reliable passive samplers obviate the need for pumps and electricity.

After an air pollution model has been developed, as the expanse in space and time grows, the model will provide information faster and for much less cost than will monitoring. Models generally are subdivided into tiers, ranging from high-level, large-scale models used for screening down to very specific models of a particular room or even within the human body. Many screening-level models can be run in spreadsheet formats and require relatively simple input parameters. Many dispersion models, along with technical reference manuals and other support documents, are available (e.g. see <http://www.epa.gov/ttn/scram/>). Resources normally need to be expended to enhance emission inventories to improve precision and representativeness of the modeled results.

Measurements and models are employed to estimate the movement of air pollutants after being released from specific sources to general ambient concentrations of pollutants at various scales. Dispersion models are useful in deciding where to site monitors to determine whether air quality standards are being met (see Figure V.3).

The major advantage of monitoring is that it will provide actual measured concentrations at a specific place and time. A valuable tool for siting air pollution monitors is the wind rose. Wind roses can be obtained from the National Oceanic and Atmospheric Administration, which are average directions of decades of wind data each hour of each day. The “spokes” show the frequency of winds by direction. Each spoke’s length indicates the percentage of time when the wind blows from that direction. Each concentric dotted-line circle represents increasing frequencies moving out from the center. Each spoke is broken into discrete frequency categories that are color coded to indicate the percentage of time that wind speeds are within that category. For example, [Figure V.4](#) shows a wind rose for April for Fresno, California, which indicates that the predominant wind direction is from the northwest.<sup>6</sup> The wind dominance can be calculated by summing up the frequencies of the longest spokes. In this case, WNW, W, and NNW = 16 + 25 + 9, respectively, or 50%. The NW quadrant of the wind rose for Fresno in April comprises 50% of all hourly wind directions. The rose also indicates that the winds from the northeast or the southwest are rare. Wind roses also indicate wind speed. These wind roses also provide details on speeds from different directions. Fresno’s wind rose indicates that 8% of the time in April the wind blows from the northwest at relatively low speeds from 1.8 to 3.34 m s<sup>-1</sup>. Similarly, on this spoke it can be calculated that winds blow from the northwest at speeds between 3.34 and 5.4 m s<sup>-1</sup> about 10% of the time (18 – 8%), 6% of the time from 5.4 to 8.49 m s<sup>-1</sup> (24–18), between 8.49 and 11.06 m s<sup>-1</sup> about 1% of the time (25 – 24), and less than 0.5% of the time at high speeds greater than 11.06 m s<sup>-1</sup>.

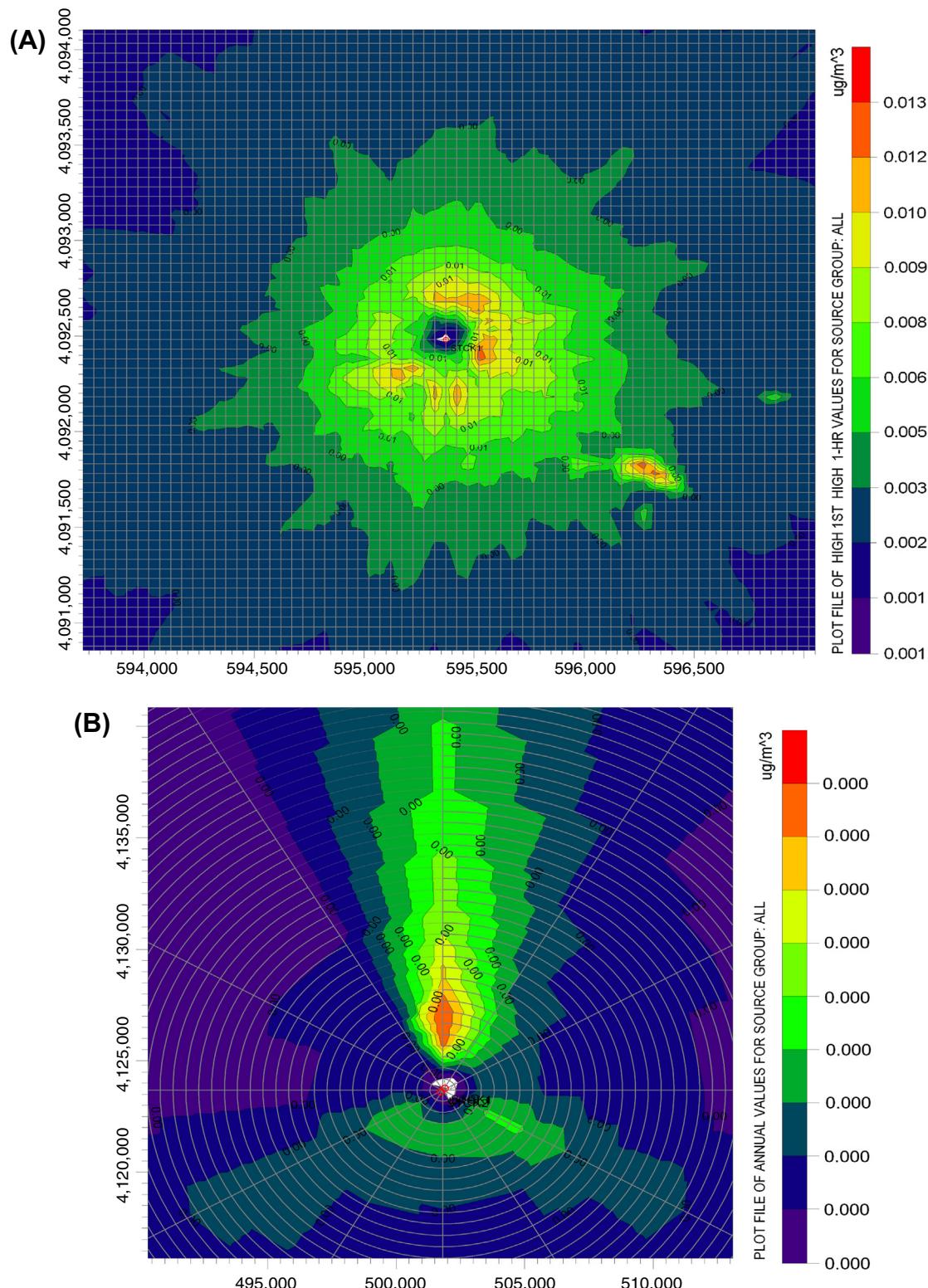
Such information is useful in siting monitors to gain information about specific pollutants. For example, this wind rose would be useful if an air pollutant is only released in the spring (e.g. pollen) or a short-term change in traffic due to repairs. In this case, the site could be located northwest of the source. However, this is seldom the case, since wind direction and speed varies intra-annually and sources are seldom limited to a single month. Indeed, for Fresno, the wind direction changes dramatically in the winter (see [Figure V.5](#)). Thus, for most air pollution monitoring, the annual wind rose ([Figure V.6](#)) is preferred to monthly. The disadvantage of an annual wind rose is that it may wash out an important extreme condition, e.g. very high winds for a short time period that could transport pollutants in different directions and longer distances than would be expected based on an average direction and speed. In this case, quarterly wind roses may be preferable (see [Figure V.7](#)).

It is also important to note that the Fresno wind rose is based on an airport monitor. This is very common, since airports need immediate and accurate information about wind direction and speed to determine shear and other safety considerations. Terrain and meteorological conditions change rapidly with distance from the airport. For example, meteorological data from the three major airports in the New York area did not reflect conditions near the World Trade Center following the attacks on September 11, 2001. In addition, an air pollution plume from a source seldom directly follows the path of the wind rose due to obstructions, air masses, and other physical phenomena.

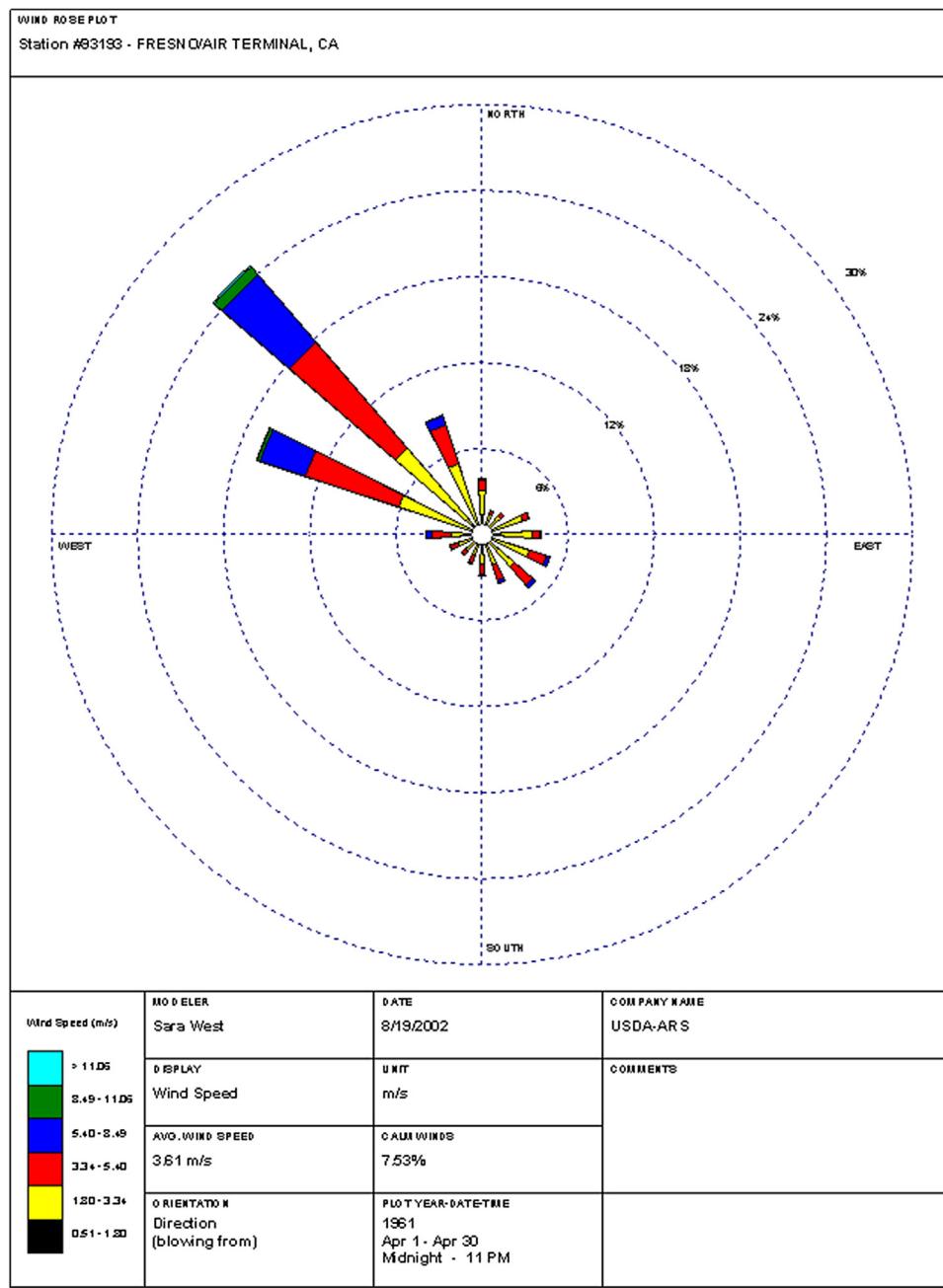
Monitoring pollution from extreme events, such as a wildfire, will need much more precise wind information than what is provided by the wind rose. Meteorological models can be used to support wind rose information. For example, the Hybrid Single Particle Lagrangian Integrated Trajectory model can provide daily meteorological information (see [Figure V.8](#)).

Numerous monitoring sites may be required to characterize concentrations over an area. The density of sampling is driven by the amount of uncertainty that can be tolerated and still meet the study objectives. The required sampling density may be less if reliable geographic information systems and other spatial support methods are available to facilitate interpolation between locations. The downside is that the monitoring may not be representative of a large geographic area. That is, sampling density may need to be quite high to provide meaningful interpolation of a large region for air pollutants that change rapidly, e.g. highly reactive compounds, and for highly variable meteorology.

Monitoring can be used to identify and measure exposures for specific individuals at a specific location of concern (e.g. near a roadway, a school, or a vulnerable population). These data can provide a quick screen to determine whether more extensive monitoring is needed. Monitoring can also identify areas and actual levels of exposure occurring if a person were present at the monitoring site. Monitoring may indicate the point of maximal exposure, e.g. an expected



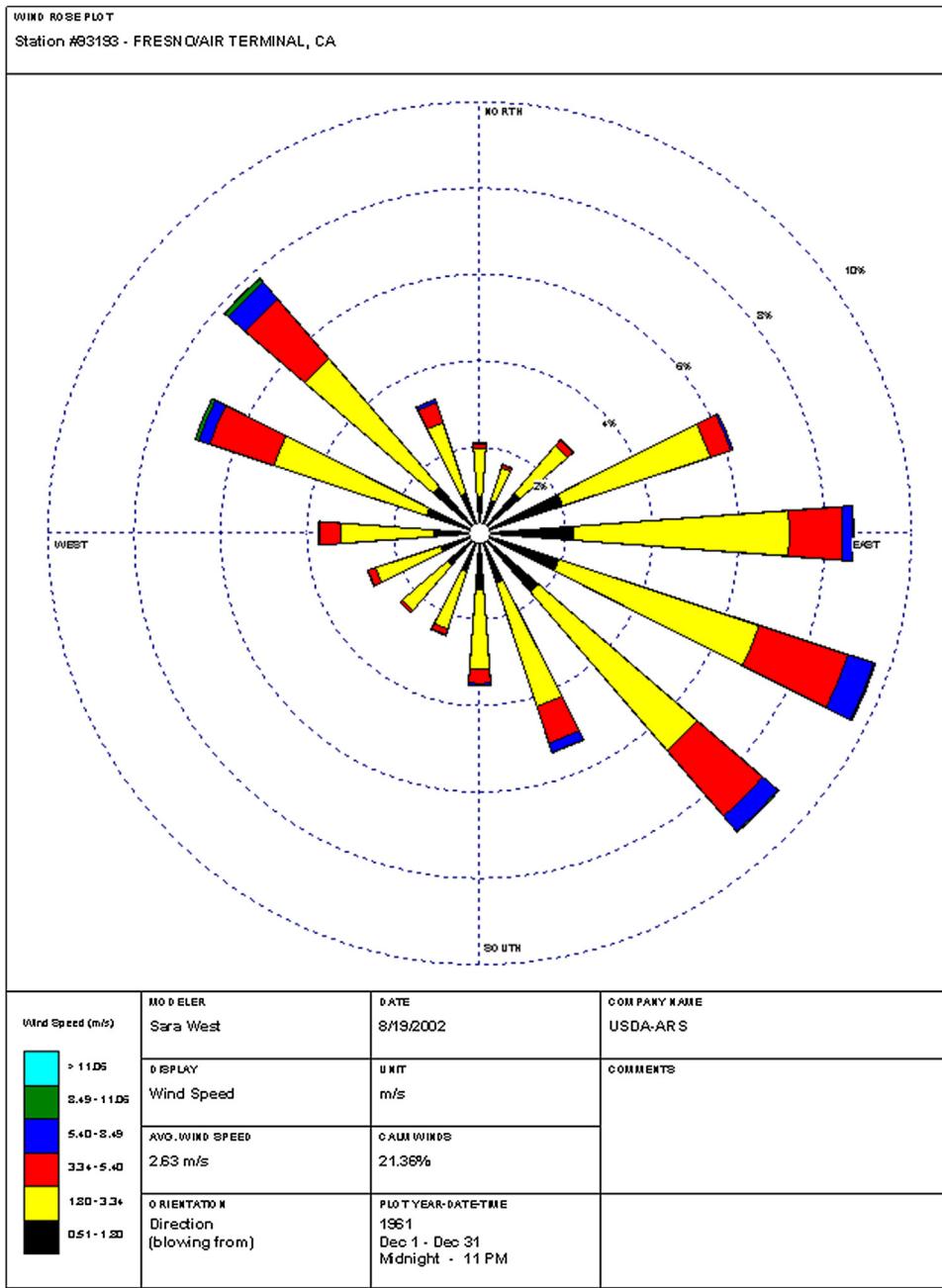
**FIGURE V.3** Example of modeling to estimate the dispersion of dioxins and furans (legend units in micrograms per cubic meter) after release from a secondary aluminum smelter to determine whether the source is meeting US emission requirements of the National Emission Standards for Hazardous Air Pollutants established under Section 112 of the Clean Air Act Amendments of 1990. The sampling results varied by frequency: (A) 1 h average, and (B) annual average. (For color version of this figure, the reader is referred to the online version of this book.) Shaikh T. Air toxics and modeling. 2009 Region 4 regulatory modelers workshop. <http://www.epa.gov/region4/air/modeling/09workshop.html>; 2009 [accessed 28.08.13].



**FIGURE V.4** April wind rose for Fresno, California. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Department of Agriculture. Natural resources and conservation service. Wind rose data. <http://www.wcc.nrcs.usda.gov/climate/windrose.html>; 2013 [accessed 28.08.13].

worst case scenario (such as a person living at the property line of a source). The selection of the monitoring locations is critical. For example, if the intent is to provide a snapshot of an average concentration in a community, the worst case scenario would show a positive bias, i.e. mean ambient air pollutant concentrations would actually be less than measurements at the property line.

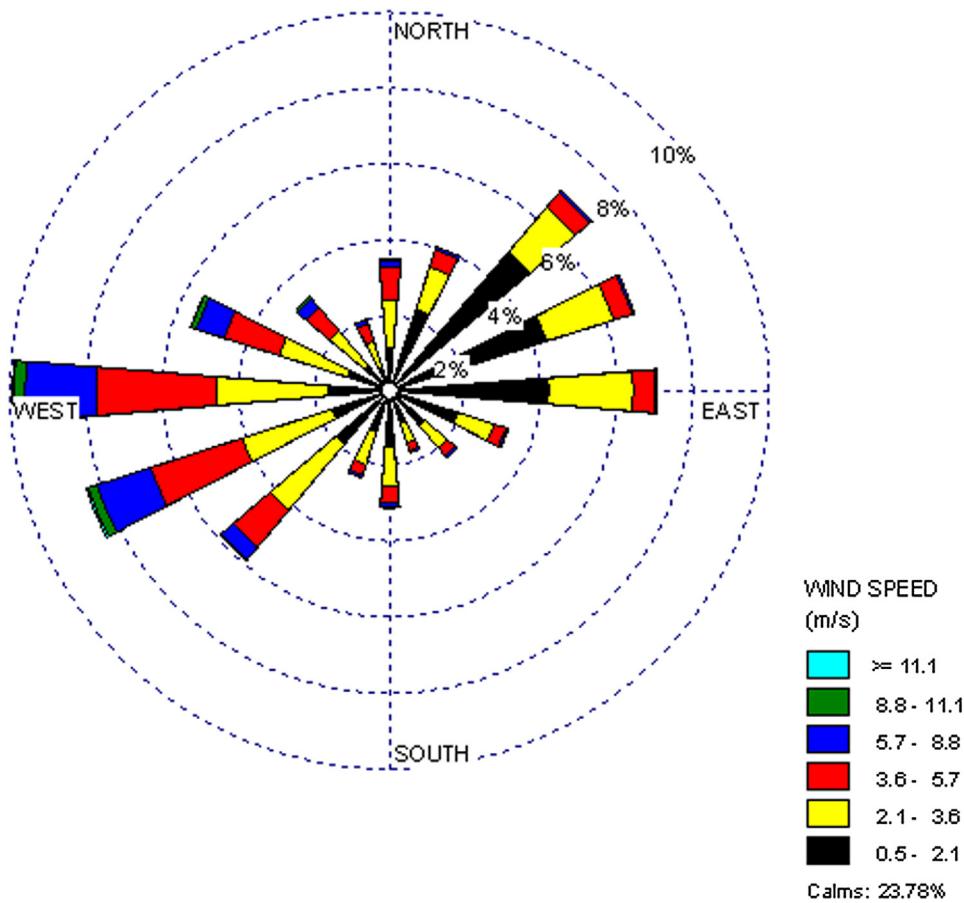
Modeling results can estimate concentrations over a large spatial area (e.g. a 50 km radius from a source) and can provide a snapshot view of the assessment area. Screening-level models can provide a predicted estimate of whether significant concentrations are likely. A simple screening analysis may be sufficient for a "yes or no" decision, e.g. whether or not a particular risk management or



**FIGURE V.5 December wind rose for Fresno, California.** (For color version of this figure, the reader is referred to the online version of this book.) U.S. Department of Agriculture. Natural resources and conservation service. Wind rose data. [http://www.wcc.nrcs.usda.gov/ftref/downloads/climate/windrose/california/fresno/fresno\\_dec.gif](http://www.wcc.nrcs.usda.gov/ftref/downloads/climate/windrose/california/fresno/fresno_dec.gif); 2013 [accessed 28.08.13].

engineering control technology is needed. If the answer is yes, a higher tier model would be employed to ascertain the appropriate risk management and engineering controls. Thus, models are useful in identifying the areas where maximum concentrations are likely to occur, and thus where to focus on ways to prevent and reduce air pollutant concentration. However, intrinsic uncertainties and limitations, e.g. discrete divisions of the wind field used in models (wind roses often have only eight wind directions), can lead to incorrect predictions of the locations of maximum air pollutant concentrations.

Monitoring may confirm significant exposure pathways and routes, by comparing measured concentrations to risk-based thresholds and screening levels, e.g. reference concentrations and cleanup

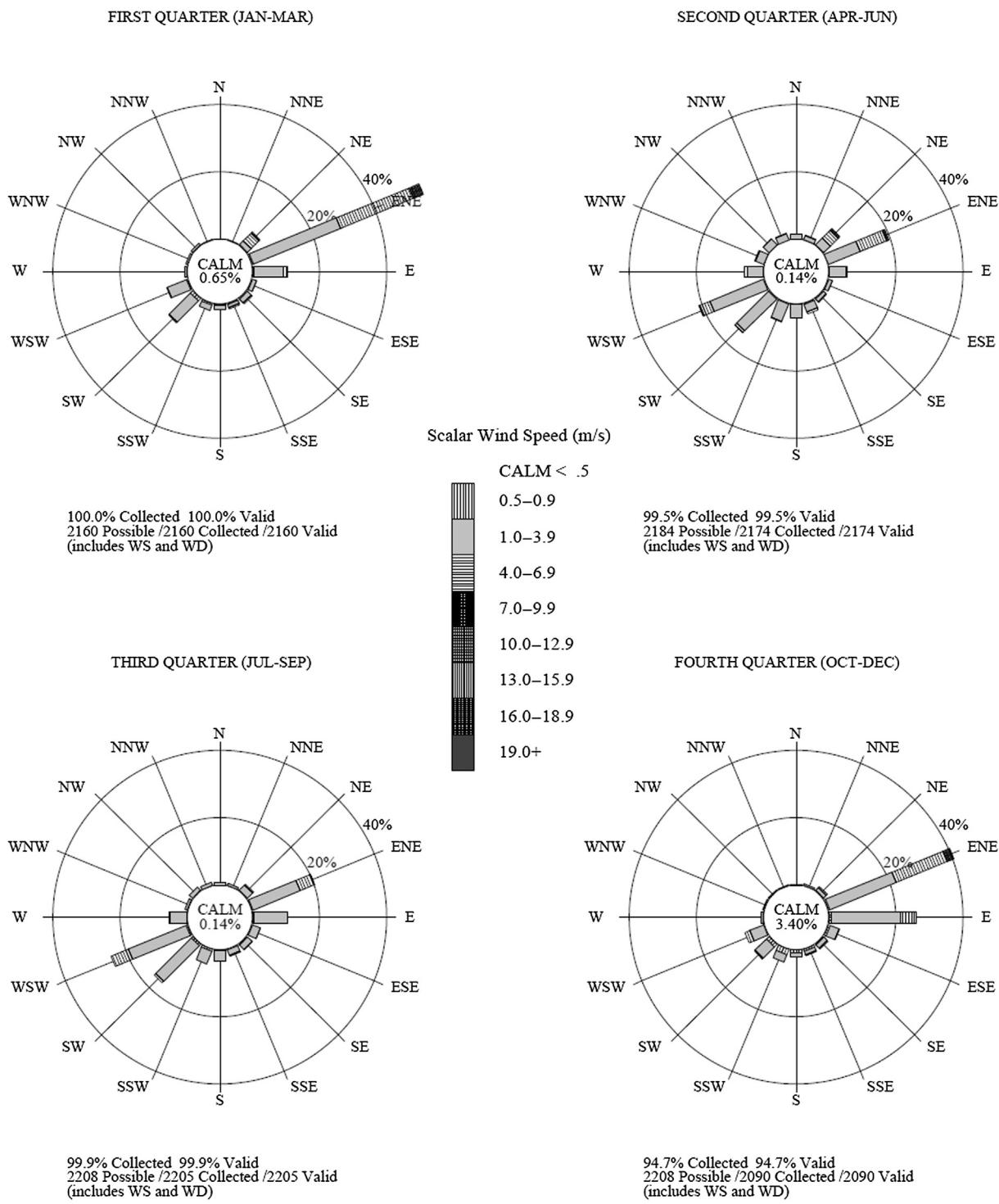


**FIGURE V.6 Example of annual wind rose.** This wind rose was generated from 30 years (1961–1990) of wind speed and wind direction data collected at the National Weather Service meteorological monitoring station located at Bristol, Tennessee, at the Tri-City Airport (NWS Station #13877). (For color version of this figure, the reader is referred to the online version of this book.)

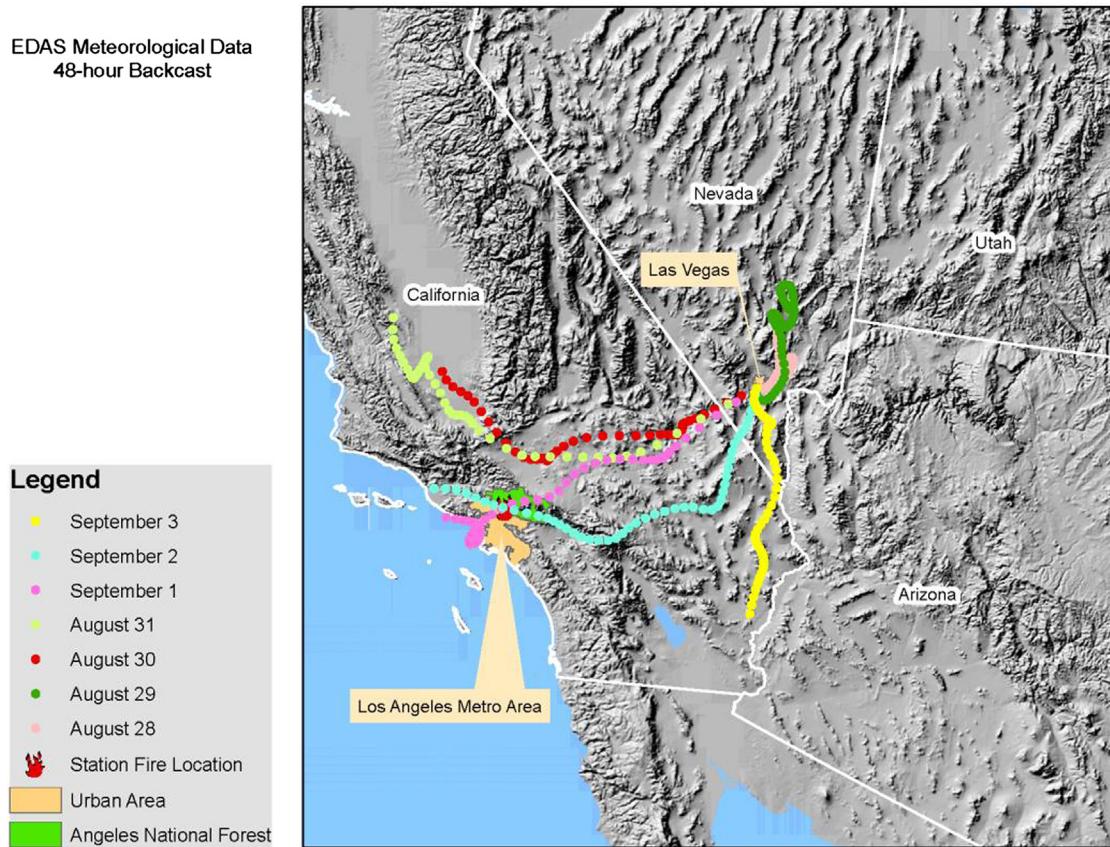
standards. Air pollutant measurements also can be used to identify compounds that may not have been suspected and, hence, were not included in models, such as identifying gaps in emissions inventories. Models can also be used to identify the specific chemicals of concern and tie them to exposure pathways and routes that are expected to be the largest contributors to air pollution risk. This helps to identify enhancements to air pollution data and to choose appropriate risk management actions.

Monitoring can only evaluate current conditions, whereas models support options for pollution control and prevention, as well as to predict contingencies, e.g. evaluating “what if” scenario. For example, a model may be used to predict the expected ambient concentrations of benzene in the air if emission could be lowered by 10%, 25%, or not at all. Indeed, not only may complex modeling allow explicit predictions and estimates of variability beyond concentrations, but also of potential exposures (i.e. exposure models). Monitoring provides direct and reliable means to characterize variability, but this often is prohibitively expensive given the large number of samples that are needed for even relatively small geographic areas and populations.

The bottom line is that models must use simplifying assumptions and data inputs that may or may not be representative of the specific assessment area. This introduces uncertainty into model predictions. Monitoring can be used to confirm actual exposure levels, to investigate assumptions or calibrate models to site-specific conditions, and to close gaps in data, which would result in reducing uncertainties. The next two chapters address the measurements and modeling methods and results separately, but it is important to recognize that they are complementary assets in assessing and addressing air pollution, which are the focus of the remaining chapters in Part V.



**FIGURE V.7 Quarterly wind roses for Yukon Flats National Wildlife Refuge, Alaska.** Based on the differences in direction, to properly measure the plume from a source, monitors would likely have to be located in each of the quadrants. If portable, the monitors could be moved monthly or quarterly to an ideal location. However, a single stationary site may be appropriate if, as in this case, the purpose is not to determine the effect of a source or sources, but to be part of an extensive network that measures air pollution levels in national parks to establish current air quality conditions and to assess long-term trends of air pollutants that affect park resources. The data are also used to determine compliance with the National Ambient Air Quality Standards and to assess national and regional air pollution control policies. U.S. Department of the Interior. National Park Service. Gaseous Air Pollutant Monitoring Network. Annual Data Summary: Yukon Flats National Wildlife Refuge; 2001. <http://www.nature.nps.gov/air-monitoring/ads/docs/2002/YUFL-PF.pdf>; [accessed 28.08.13].



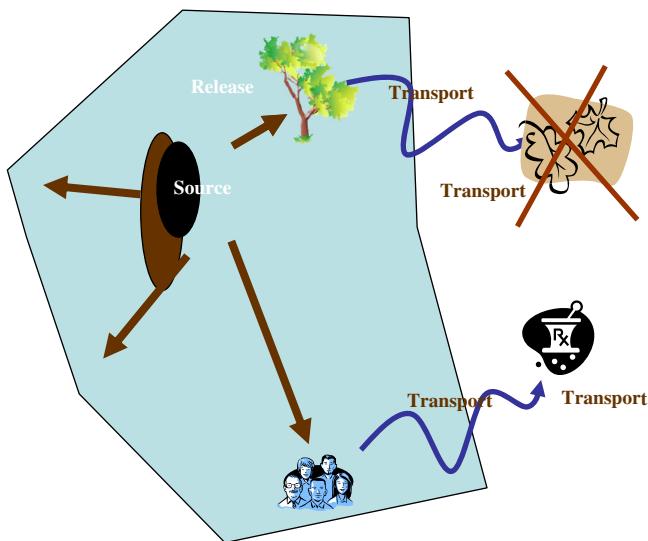
**FIGURE V.8 HYSPLIT model results from backward trajectory calculations for 48 h for the period of August 28 through September 3, 2009.** The meteorological input for the model was from the Eta Data Assimilation System (Draxler RR, Rolph GD. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory). NOAA Air Resources Laboratory: Silver Spring (Maryland); 2012). The results were plotted using ESRI's ArcMAP application (Environmental Systems Research Institute, Inc. 2006. Redlands, Washington). The model indicates highly variable meteorological conditions, but is generally conducive to the movement of air masses from southern California, area of the Station Fire, to the Las Vegas, Nevada, urban area. (For color version of this figure, the reader is referred to the online version of this book.) Kimbrough S. Personal communication; 2013.

Both direct measurements from monitors and estimates from models based on these measurements are used to decide on the optimal actions that are needed. These include the installation of air pollution control technologies, air pollution prevention and green engineering programs, and risk reduction measures at various scales. Such risk reduction actions include improvements in transportation, siting of industrial and other air pollution sources, improvements to buildings to reduce exposures to indoor air pollution, and changes in personal habits and activities.

## V.2 Air Pollution from Source to Dose to Effects

Air pollutants must be known throughout their life cycles (see Figure V.9). Thus, they must be measured or at least estimated at their sources, after being emitted, during their time in the atmosphere and hydrosphere, after humans and ecosystems are exposed, and following uptake by humans and organisms.

The flow of the chapters in Part V follows the paths in Figure V.9; beginning with the measurements of sources of air pollution in Chapter 24, followed by ambient air measurements in Chapter 25. Chapter 26 addresses measurement technologies used indoors and in and around individual persons. Chapter 27 addresses modeling approaches at various scales. Chapters 30 and 31 provide engineering and control technologies needed to address the improvements in the air quality discussed in Chapter 28 that is affected by the emissions described in Chapter 29. These



**FIGURE V.9 Sites of interaction with air pollutants.** (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Letcher T, Vallero D. Waste: a managers handbook. Amsterdam (NV): Elsevier Academic Press; 2011.

improvements depend on the soundness of characterizing the pollution identified by the measurement and modeling approaches discussed in Chapters 24 through 28.

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# Source Sampling and Emission Measurement

## 24.1 SOURCES OF POLLUTION

The sources of air pollution are nearly as numerous as the grains of sand. In fact, the grains of sand themselves are air pollutants when the wind entrains them and they become airborne. We would class them as a natural air pollutant, which implies that such pollution has always been with us. Natural sources of air pollution are defined as sources not caused by people in their activities.

Consider the case in which someone has removed the ground cover and left a layer of exposed soil. Later the wind picks up some of this soil and transports it a considerable distance to deposit it at another point, where it affects other people. Would this be classed as a natural pollutant or an anthropogenic pollutant? We might call it natural pollution if the time span between when the ground cover was removed and when the material became airborne was long enough. But, how long would be long enough? The answers to such questions are not as simple as they may first appear. One question leads to another, each answered within its own context and adding uncertainty. This is one of the reasons why pollution problems require careful study and analysis before a decision to control them at a certain level can be made.

If the amount of a pollutant emitted can be decreased, then the atmospheric concentrations can also be decreased. If these concentrations decrease in the breathing zone, then the exposure to the contaminant also lessens. If the exposure declines, the adverse effects become ameliorated or eliminated. So, addressing air pollution starts at the source.

### 24.1.1 Natural Sources

An erupting volcano emits particulate matter. Pollutant gases such as  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and methane are also emitted. The emission from an eruption may be of such a magnitude as to harm the environment for a considerable distance from the volcanic source. Clouds of volcanic particulate matter and gases have remained airborne for very long periods

of time. The 1980 eruption of Mt. St. Helens in the state of Washington is a classic example of volcanic activity that can release many tons of pollutants into the winds aloft; allowing for widespread and long-range pollutant transport. This included not only the ash from the volcano, but the emission of organic pollutants from the burning of vegetation that ensued.

Accidental fires in forests and on the prairies are usually classified as natural sources even though they may have been originally ignited by human activities. In many cases foresters intentionally set fires in forestlands to burn off the residue, but lightning setting off a fire in a large section of forestland could only be classed as natural. A large uncontrolled forest fire is a frightening thing to behold. Such a fire emits large quantities of pollutants in the form of smoke, unburned hydrocarbons, carbon monoxide, carbon dioxide, oxides of nitrogen, and ash. Forest fires in the Pacific Northwest of the United States have been observed to emit a plume which caused reduction in visibility and sunlight as far away as 350 km from the actual fire.

Dust storms that entrain large amounts of particulate matter are a common natural source of air pollution in many parts of the world. Even a relatively small dust storm can result in suspended particulate matter readings one or two orders of magnitude above ambient air quality standards. Visibility reduction during major dust storms is frequently the cause of severe highway accidents and can even affect air travel. The particulate matter transferred by dust storms from the desert to urban areas causes problems to householders, industry, and automobiles. The materials removed by the air cleaner of an automobile are primarily natural pollutants such as road dust and similar entrained material.

The oceans of the world are an important natural source of pollutant material. The ocean is continually emitting aerosols to the atmosphere, in the form of salt particles, which are corrosive to metals and paints. The action of waves on rocks reduces them to sand, which may eventually become airborne. Even the shells

washed up on the beach are eroded by wave and tidal action until they are reduced to such a small size that they too may become airborne.

An extensive source of natural pollutants is the trees and other plant life of the earth. Even though these green plants play a large part in the conversion of carbon dioxide to oxygen through photosynthesis, they are still the major sources of hydrocarbons on the planet. The familiar blue haze over forested areas, including urban areas with large amounts of tree cover, is nearly all from the atmospheric reactions of the volatile organics given off by the trees of the forest.<sup>1</sup>

This section's objective is not to "blame" nature for pollution, but to ensure that natural sources are properly considered. For example, the anthropogenic sources of a pollutant may be relatively small, but it may be sufficient to cause damage when added to the biogenic or other natural sources of that same pollutant in a particular area during a specific period of time. Indeed, the Clean Air Act has provisions to account for exceptional events that may include fires and other natural and/or extraordinary sources. An area that may otherwise have to take actions (e.g. traffic pattern changes, reductions in stationary source emissions, etc.), may not have to do so if the contribution from natural sources were found to be the cause of not attaining the air quality standards.

### 24.1.2 Bioaerosols

Another air pollutant problem, which can be attributed to plant life, is the pollens which cause respiratory distress and allergic reactions in humans. Pollen is a type of bioaerosol, which can be a living or formerly living organism (e.g. mold and other fungi), a release of part of an organism (e.g. a spore, cyst, or pollen) or residue from an organism (feces from insects or dander

from animals).<sup>2</sup> These particles are increasingly associated with diseases, such as asthma, especially when exposures are combined with other air pollutants and genetic factors (see Figure 24.1).<sup>3</sup>

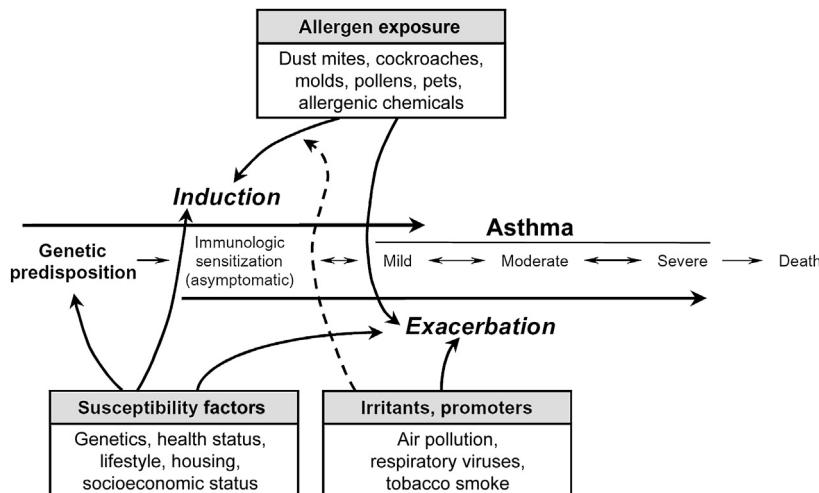
Particularly troublesome products of bioaerosols are aflatoxins, the toxic metabolites of mold (*Aspergillus flavus* and *Aspergillus parasiticus*). Engineering and food supply controls have greatly reduced potential exposures,<sup>4</sup> but aflatoxins remain an important class of biogenic air pollutants. The general population is exposed through food ingestion, but aflatoxins are also air pollutants, especially from inhalation of dust emitted when workers handle crops and feeds on which *Aspergillus* has been growing. Agricultural workers and farmers are obviously at highest risk of airborne aflatoxins. For example, aflatoxins have been measured at concentrations of 0.02–0.8 ng m<sup>-3</sup> in respirable dust samples collected at rice and corn processing plants in India<sup>5</sup> and 0.04–4800 ng m<sup>-3</sup> during U.S. bin cleaning and other operations.<sup>6</sup>

Other natural sources, such as alkaline and saltwater lakes, are usually quite local in their effect on the environment. Sulfurous gases from hot springs also fall into this category in that the odor is extremely strong when close to the source but disappears a few kilometers away.

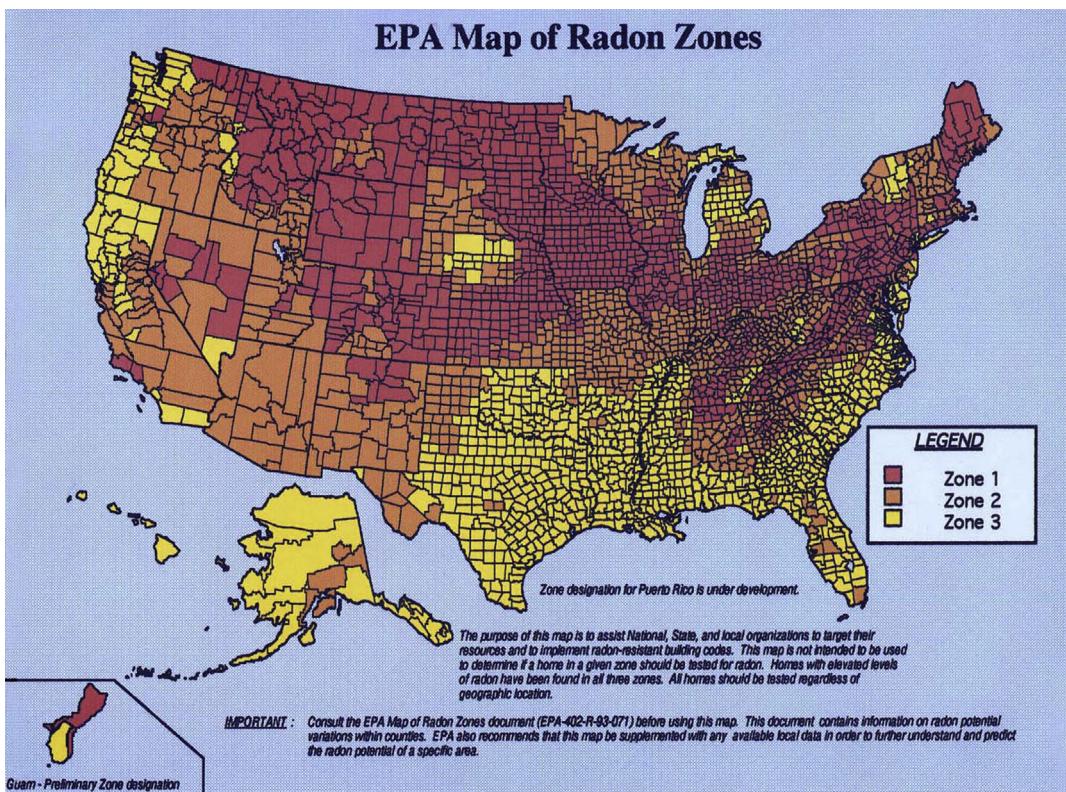
In terms of human health effects from natural air pollutants, radon (Rn), asbestos, ozone (O<sub>3</sub>) emissions by vegetation and particulate and products of incomplete combustion emissions from wildfires can be substantial.

### 24.1.3 Radon

When radium decays, it releases radon. Since it is in Group 18 (noble gases), like helium and argon, it is chemically inert, i.e. its outermost electron shell is filled



**FIGURE 24.1** Natural sources of air pollution can induce diseases. For example, asthma may be induced by a series of factors, sometimes beginning with genetically susceptible persons who are exposed to bioaerosols. The bioaerosol exposure may be exacerbated by other anthropogenic and natural pollutants (dashed arrow). The severity of the disease varies (double-headed arrows) according to environmental influences and susceptibility. Ref. 3.



**FIGURE 24.2** Zones of potential exposure to radon in the U.S. Zone 1 has the highest and Zone 3 has the lowest potential, based on the Radon Index Matrix, a quantitative assessment of radon potential derived from five factors to determine radon potential—indoor radon measurements; geology; aerial radioactivity; soil permeability; and foundation type. Zone 1 counties have a predicted average indoor radon screening level greater than  $4 \text{ pCi l}^{-1}$ . Zone 2 counties have a predicted average indoor radon screening level between 2 and  $4 \text{ pCi l}^{-1}$ . Zone 3 counties have a predicted average indoor radon screening level less than  $2 \text{ pCi l}^{-1}$ . The radon potential assessment is based on geologic provinces. It should be noted that these are very broad geographic provinces and that high radon readings have been found in all zones, including Zone 3. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. EPA map of radon zones. <http://www.epa.gov/radon/zonemap.html>; 2013 [accessed 29.08.13].

so that it does not react with other chemicals. Ordinarily, this is a desirable property in terms of toxicity and hazard, since the substance does not react biochemically and, thus, does not damage cells. However, the radioactivity of Rn does indeed damage tissues.

With an atomic weight of 222, radon is the heaviest mononuclear gas. Thus, when it migrates into buildings, it tends to accumulate in lower levels, especially crawl spaces and basements. It is odorless, colorless, and tasteless, so it can only be detected with a sensitive equipment.

The amount of radon in rock and soil is highly variable, but even at low concentrations, the gas will move from interstices in porous media and through fissures between particles into the ambient air. Ambient radon concentrations are about  $0.4 \text{ picocuries per liter of air}$  ( $\text{pCi l}^{-1}$ ). More importantly, radon may seep through foundations, floors, and walls of buildings and increase indoor concentrations. The mean U.S. indoor radon concentration is higher than ambient, i.e. about  $1.3 \text{ pCi l}^{-1}$  of air. However, it is not uncommon to measure indoor

radon in the range of  $5\text{--}50 \text{ pCi l}^{-1}$ , with maximums of  $2.0 \times 10^3 \text{ pCi l}^{-1}$  (see Figure 24.2). Local geological, soil, and weather conditions affect the migration rate of radon into buildings. In addition, since radon's decay products are metals, they may be sorbed by aerosols, increasing the likelihood of inhalation exposure.<sup>7</sup>

#### 24.1.4 Naturally Occurring Asbestos

Asbestos is a unique type of air pollutant. It is a particle with a large aspect ratio (length:width), i.e. a fiber. Asbestos comprises a group of highly fibrous minerals with separable, long, and thin fibers. It is known to be highly toxic and, when inhaled, can cause asbestosis, mesothelioma, and lung cancer. Exposures in schools, industry, mechanical operations, mining, and other human enterprises are the most notorious. However, so-called “naturally occurring asbestos” (NOA) also presents threats to public health. The term is in quotes because all asbestos occurs naturally. It is not manufactured as such, as the fibers are separated from ore and

used in products and building materials. NOA may have nothing to do with mining or manufacturing. For example, people may be exposed to asbestos fibers when foundations are dug for homes and other buildings, overburden is removed in building roads, rock is weathered naturally, and from other seemingly innocuous activities that usually do not involve hazardous substances.

Globally, collected samples from Antarctic ice indicate chrysotile asbestos has been a ubiquitous contaminant of the environment for at least 10,000 years. Snow samples in Japan have shown ambient background levels are one to two orders of magnitude higher in urban than in rural areas. Higher concentrations of airborne asbestos fibers are reported in urban areas where there are more asbestos containing materials and mechanisms of release (vehicles braking and weathering of asbestos cement materials); concentrations in the range of  $1\text{--}20 \text{ ng m}^{-3}$  have been reported. Fibers longer than  $5 \mu\text{m}$  are rarely found in rural areas.<sup>8</sup>

The size and shape of any aerosol, including a fiber, greatly influences its toxicity. As discussed in Chapter 7, smaller particles (diameter  $< 2.5 \mu\text{m}$ ) can infiltrate the lungs more deeply and deposit with greater efficiency than larger particles. Fibers are defined by regulatory agencies like the U.S. Environmental Protection Agency<sup>9</sup> and Occupational Safety and Health Administration<sup>10</sup> to have aspect ratios equal to or greater than 3:1.

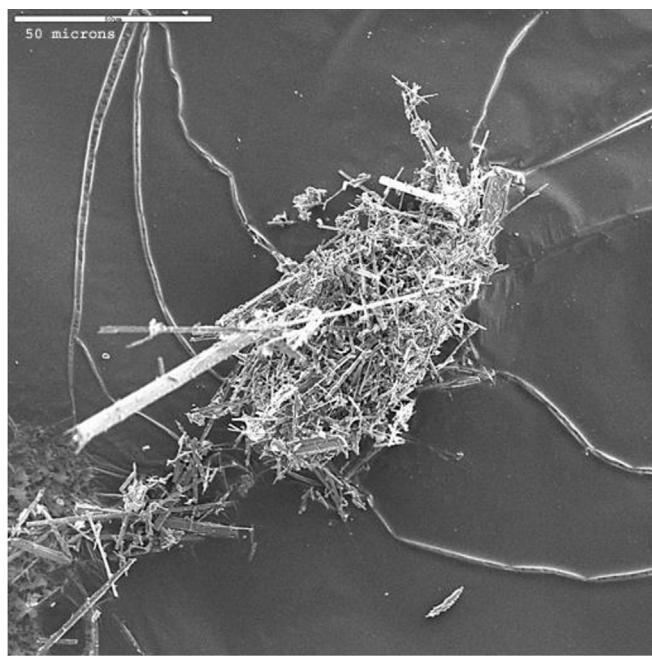
Asbestos exists in nature in two mineral forms, amphibole (Figure 24.3) and serpentine. Chrysotile (Figure 24.4) is the only asbestos member of serpentine group. Some studies<sup>11</sup> show that amphibole fibers stay in the lungs longer than chrysotile, and this tendency may account for their increased toxicity. Chrysotile fibers are long and flexible, which explains their wide use in commercial products. Amphiboles are brittle, rod or needle-shaped fibers. Exposure to either type can lead to respiratory diseases, but amphibole fibers are more persistent after deposition in the lung.<sup>12</sup>

#### 24.1.5 Biogenic Emissions

Natural sources such as volcanic eruptions and forest fires can combine with anthropogenic sources to worsen air pollution episodes, such as inversions and ground-level ozone episodes.<sup>13</sup>

Natural emissions can be from abiotic or biotic origin. The NOA is an example of an abiotic source. A person's lifetime exposure to asbestos must add all sources, including NOA.

Biotic sources that release substances as part of their life cycle are known as biogenic emissions. These emissions can be by any type of organism during its life cycle, i.e. animal, plant, and microbe. For example, an animal



**FIGURE 24.3 Reflectance spectrograph of a cluster of amphibole asbestos fibers.** The bundles adhere due to static electricity. Clark RN, Hoefen TM, Swayze GA, Livo KE, Meeker GP, Sutley SJ, et al. Reflectance spectroscopy as a rapid assessment tool for the detection of amphiboles from the Libby, Montana region. *U.S. Geological Survey Open-File Report 03-128*; 2005.



**FIGURE 24.4 Road-cut adjacent to an interstate highway near New York City exposed serpentinite (about 50% chrysotile asbestos).** Powell W. Core 8.2. Geology in the modern world. Asbestos in NYC: it's not just in the buildings. (For color version of this figure, the reader is referred to the online version of this book.) *New York (NY): City University of New York*; 2002.

may release  $\text{CO}_2$  and methane during its life stages as it respires. After its death, microbes will release  $\text{CH}_4$  and  $\text{H}_2\text{S}$  as they respire anaerobically. Later, plants will release  $\text{O}_2$  as they photosynthesize the mineralized nutrients left behind in the detritus and soil by the microbes. This oversimplification of the respiration and photosynthesis processes illustrates the biogenic emission of three air pollutants,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{S}$ .

Indeed the contributions can be large in certain areas. As mentioned in Chapter 7, a recent study in South Queensland, Australia, found that 61.2% of the emissions of volatile organic compounds (VOCs) in that region came from biogenic sources (e.g. vegetative transpiration) and another 5.7% from bush fires and biomass burning.<sup>14</sup>

Such emissions need to be accounted for, even if the sources are not controllable. For example, biogenic source measurements may be used to decide about any additional controls that are needed during times of large VOC contributions to an ozone event. The logical decision sequence is:

1. What is the air quality standard for a specific pollutant?
2. What is the biogenic contribution to the ambient air (ambient measurement or model)?
3. What is the anthropogenic contribution by category (ambient measurement, source-apportionment, and receptor models)?
4. What quantity (flux) of the pollutant is combining from a particular biogenic source (e.g. forest emission measurement)?
5. How can this addition be compensated for with reductions of anthropogenic sources of this pollutant?
6. How long will these biogenic sources continue (continuous biogenic source measurements and modeling)?
7. What is a feasible and effective way to compensate for these biogenic emissions in the future (e.g. is this a very rare and extreme event, or is it likely to continue or recur given biological and meteorological conditions)?

The bottom line for public health agencies is to keep exposures to hazardous substances below an adverse effect concentration. For example, if sound science has shown that children should not breathe air containing more than 10 ppm of a compound, and the uncontrollable emissions contribute concentrations that would be 5 ppm in the ambient air, the controllable sources would have to be controlled so that they would lead to less than 5 ppm concentrations in the ambient air (and with uncertainty, possibly much less to provide an ample margin of safety). If the biogenic emissions contribute enough of the pollutant to translate into 7 ppm, the controllable emissions from stationary and mobile sources would have contribute concentrations that would lead to ambient concentrations less than 3 ppm (again with an ample margin of safety, even less than 3 ppm). The latter case of higher natural emission rates is known as an exceptional and/or extreme event. Air pollution regulatory agencies often take into consideration of such extreme events. In the United States, a request

exceptional event flag<sup>15</sup> must be accompanied by a demonstration that:

1. The event satisfies all of the criteria set forth in 40 CFR §50.1(j). It affects air quality; is not reasonably controllable or preventable; and is caused by human activity that is unlikely to recur at a particular location, or is a natural event.
2. There is a clear causal relationship between the measurement under consideration and the event that is claimed to have affected the air quality in the area.
3. The event is associated with a measured concentration in excess of normal historical fluctuations, including background.
4. There would have been no exceedance or violation but for the event.

## 24.2 ANTHROPOGENIC SOURCES

Most of the emphasis of air pollution regulations is associated with human-induced pollution. This is for a number of reasons. If humans cause pollution, then they understand the events that lead to the pollution, which is the first step to reverse-engineer the pollution process. Thus, if they are willing, humans may stop the pollution by either preventing the activities that contribute to the formation, release, and exposure of the pollutants; and/or they may design interventions to reduce or eliminate the pollution or prevent exposure.

Thus, emissions at various points along the pollution-generation pathway need to be measured to recommend appropriate prevention (e.g. substitution of pollution-generating substances with more innocuous substances) and control technologies (e.g. removing gases and aerosols from the waste stream before emissions). Without accurate and representative measurements, such prevention and intervention may well be incorrect or poorly designed.

To comply with emission standards often requires source measurements. For example, an incinerator may not only be required to measure pollutants that are exiting the stack but also demonstrate removal efficiencies. Other source measurements are indicators of contribution to overall ambient air quality (see Chapters 26 and 28). That is, source measurements can help to demonstrate the individual's contribution to the ambient concentrations of a particular pollutant as designated in an air quality plan, such as a State Implementation Plan in the United States.

Measurements of anthropogenic sources are also necessary to support modeling (see Chapter 27). Measurements are needed to provide ground truth or to evaluate pollutant dispersion models. They are also



FIGURE 24.5 Source test.

needed for receptor and source-apportionment models, e.g. to determine the amount of a tracer that exits a stack compared to measurements at various points downwind. From these measurements, the model can be constructed to estimate back-trajectories from ambient measurements to potential sources.

#### 24.2.1 Source Sampling and Monitoring

Air pollutants released to the atmosphere may be characterized by qualitative descriptions or quantitative analysis. For example, a plume may be characterized as brown, dense smoke, or 60% opacity. The first two descriptors are qualitative; the third quantitative. It may also be described as containing certain concentration of particulate matter (e.g.  $100 \text{ mg m}^{-3}$  PM<sub>2.5</sub>). These are quantitative descriptions made by observing the effluent as it entered the atmosphere.<sup>a</sup> Arguably, quantitative data are the best way to characterize the emission and air quality, and the best way to answer the following questions. How many parts per million of a criteria or toxic pollutant are being released from all sources in Toledo, Torino, and Toronto today? How many kilograms per hour are being emitted by this power plant? How many kilograms per year are emitted by this same plant? To obtain these numbers, it becomes necessary to sample or to monitor the emission. Sampling and monitoring, therefore, are necessary for air pollution evaluation and control. In any situation concerning atmospheric emission of pollutants, source sampling or monitoring is necessary to

obtain accurate data. Figure 24.5 shows a simple source test being conducted.

#### 24.2.2 Source Sampling

The purpose of source sampling is to obtain as representative, precise, and accurate a sample as possible of the material entering the atmosphere at a minimum cost. This statement needs to be examined in light of each source test conducted. The following questions should continually be answered during the sampling period: (1) The sample must be representative of the emission. Is the sampling and collecting of the material representative of what is actually being released? Is this the material entering the atmosphere? Sampling at the base of a tall stack may be much easier than sampling at the top, but the fact that a pollutant exists in the breeching does not mean that it will eventually be emitted to the atmosphere. Molecules can also undergo both physical and chemical changes before leaving the stack. (2) Maximum accuracy in sampling is desirable. Is maximum accuracy attainable? Decisions regarding the total effluent will be based on what was found from a relatively small sample. Only if the sample accurately represents the total will the extrapolation to the entire effluent be valid. (3) Collecting a sample is a costly and time-consuming process. Are financial considerations being properly factored into the decision-making process and are the costs being minimized consistent with other objectives? It makes little sense to spend \$5000 on an extensive stack testing analysis to decide whether to purchase a \$10,000 scrubber of 95% efficiency or to try to get by with a \$7000 scrubber of 90% efficiency. The test results would be of little value, since they can only be compared to scrubber specifications for the higher efficiency system. And, the difference in costs is nominal compared to the test costs.

The reasons for performing a source test differ. The test might be necessary for one or more reasons: (1) To obtain data concerning the emissions for an emission inventory or to identify a predominant source in the area. An example of this would be determination of the hydrocarbon release from a new type of organic solvent used in a degreasing tank. (2) To determine compliance with regulations. If authorization is obtained to construct an incinerator and the permit states that the maximum allowable particulate emission is 230 mg per standard cubic meter corrected to 12% CO<sub>2</sub>, a source

<sup>a</sup> Another characterization often applied in air pollution is “semi-quantitative”. The meaning is less clear than qualitative or quantitative; only that it has elements of both. An example may be that a concentration is increasing or decreasing over a time period, but the amount of the increase or decrease is not known (only that the problem is worsening or improving). This is also an example of different types of values; if the data include ratio and interval values, the description is likely to be quantitative. If the values are ordinal (i.e. the rank is known, but not the absolute value), this can be considered semiquantitative. If the values are nominal, the description is, at best, qualitative (e.g. brown smoke, white smoke, no smoke).

test must be made to determine compliance with the permit. (3) To gather information that will enable selection of appropriate control equipment. If a source test determines that the emission is 3000 mg of particulate per cubic meter and that it has a weight mean size of 5  $\mu\text{m}$ , a control device must be chosen which will collect enough particulate to meet some required standard, such as 200 mg per cubic meter. (4) To determine the efficiency of control equipment installed to reduce emissions. If a manufacturer supplies a device guaranteed to be 95% efficient for removal of particulate with a weight mean size of 5  $\mu\text{m}$ , the effluent stream must be sampled at the inlet and outlet of the device to determine if the guarantee has been met (see Chapter 32 for a discussion of how to calculate efficiency).

### 24.2.3 Statistics of Sampling

Recall that most statistics are inferential. That is, we must infer the conditions of a larger population from a much smaller sample. Thus, we must be careful in how we interpret the meaning of a sample. A sample collected at the rate of  $0.3 \text{ l min}^{-1}$  from a stack discharging  $2000 \text{ m}^3 \text{ min}^{-1}$  to the atmosphere is likely to include substantially large error. Another term for bias is systematic error. If the sample is truly representative, it is said to be both accurate and unbiased. If the sample is not representative, it may be biased because of some consistent phenomenon (some of the hydrocarbons condense in the tubing ahead of the trap) or in error because of some uncontrolled variation (only 1.23 g of sample was collected, and the analytical technique is accurate to  $\pm 0.5 \text{ g}$ ).<sup>16</sup>

For practical purposes, source testing can be considered as simple random sampling.<sup>17</sup> The source may be considered to be composed of such a large population of samples that the population  $N$  is infinite. From this population,  $n$  units are selected in such a manner that each unit of the population has an equal chance of being chosen. For the sample, we can determine the sample mean,  $\bar{y}$ :

$$\bar{y} = \frac{y_1 + y_2 + \dots + y_n}{n} \quad (24.1)$$

If the sample is unbiased we can estimate the source mean ( $\bar{Y}$ ), so that:

$$\bar{Y} = \bar{y} \quad (24.2)$$

For example, if we were to take six samples of carbon monoxide from the exhaust of an idling automobile and obtain the CO percentages as shown in Table 24.1. The sample mean is:

$$\bar{y} = \frac{1.8 + 1.6 + 1.8 + 1.9 + 1.7 + 1.8}{6} = 1.767$$

TABLE 24.1 Idling Internal Combustion Engine, CO Percentages

Test Number	CO (%)
1	1.8
2	1.6
3	1.8
4	1.9
5	1.7
6	1.8

The source mean is assumed to be the same if the sample is unbiased, as seen by:

$$\bar{Y} = \bar{y} = 1.767 \quad (24.3)$$

The variance of the sample and the population (source) may also be assumed equal if the sample is unbiased. The variance is  $S^2$ , defined as:

$$S^2 = \frac{\sum_1^n (y_i - \bar{y})^2}{n-1} \quad (24.4)$$

The variance of the source is usually calculated by the formula:

$$s^2 = \frac{1}{n-1} \left[ \sum y_i^2 - \frac{(\sum y)^2}{n} \right] \quad (24.5)$$

For the preceding example, this is found as follows:

$$\sum y_i^2 = 18.78, \quad \sum y_i = 10.6, \quad n = 6$$

$$s^2 = \frac{1}{6-1} \left[ 18.78 - \frac{(10.6)^2}{6} \right] = 0.01067$$

The standard deviation of the sample is defined as the square root of the variance. For the example, the standard deviation is:

$$s = (s^2)^{1/2} = (0.01067)^{1/2} = 0.103$$

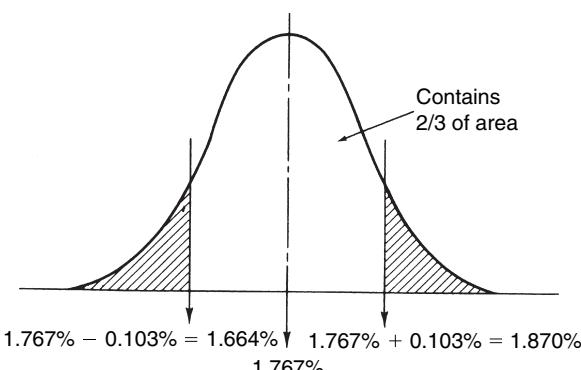


FIGURE 24.6 Distribution of carbon monoxide from an automotive source.

The sample represents a population (source) which, if normally distributed, has a mean of 1.767% and a standard deviation of 0.103%. This can be illustrated as shown in [Figure 24.6](#). If there is reason to believe that the distribution is not normal, other nonparametric statistical methods may be used.

The inference from the statistical calculations is that the true mean value of the carbon monoxide from the idling automobile has a 66.7% chance of being between 1.664% and 1.870%. The best single number for the carbon monoxide emission would be 1.767% (the mean value).

Further statistical procedures can be applied to determine the confidence limits of the results. Generally, only the values for the mean and standard deviation would be reported. The reader is referred to any good statistical text to expand on the brief analysis presented here.

## 24.2.4 The Source Test

### 24.2.4.1 Test Preliminaries

The first thing that must be done for a successful source test is a complete review of all relevant background material. The test request may come in either verbal or written form. If it is verbal, it should be put into writing for the permanent record. The request may contain much or little information, but it is important to verify that it is complete and understood. Questions to ask are: (1) Why should the test be made? Is it to measure a specific pollutant such as  $\text{SO}_2$ , or is it to determine less specific goal, such as identifying where a loss of a compound is occurring (e.g. between a reactor and stack) or what is causing the odor problem in the new residential area? (2) What will the test results be used for? Will it be necessary to go to court, or are the results for general information only? This may make a difference regarding the test method selected or of the necessary precision and accuracy of a given test. (3) What equipment or process is to be tested? (4) What are its operational requirements? (5) What methods would be preferred by the analytical group? (6) Are the analytical methods standard or unique? (7) Can all contaminants be sampled in a single test or will a series of test be needed (or separate tests for different target analytes)?

A literature search regarding the process and test should be conducted unless the test crew is thoroughly familiar with the source and all possible test methods. It is important to check the regulations regarding the process and specific test procedures as a part of the search.<sup>18</sup>

When all the background material has been reviewed, it is time to inspect the source to be tested. The inspector should be accompanied by the plant manager, engineer, or someone who knows the process in detail. It is also important that any technicians or mechanics be contacted at this time regarding necessary test holes, platforms,

scaffolding, power requirements, and other logistical and facilities-related information. During this inspection, checks should be made for environmental conditions and space requirements at the sampling site. Every visitor to the site, whether an employee of the organization or a third-party inspector, should be thoroughly familiar with all safety requirements and possible hazards. In fact, safety materials should be obtained and reviewed before setting foot on the premises. A number of companies require any visitor to complete safety training for certain installations. Even if the company or other site does not require this training, anyone visiting should contact the appropriate health and safety agency (e.g. city, county, state, or federal) to ensure they are properly prepared, including any personal protective equipment needed. All appropriate safety training should be completed prior to entry. Testing in a noisy or dusty place at elevated temperatures is certainly uncomfortable and possibly hazardous. In particular, hazardous situations must be avoided, such as entry into enclosed and confined areas and handling of hazardous materials. Evacuation and warning systems must be known, e.g. what to do in the event of a steam leak. Rough estimates of several important factors should be made at this time. These estimates can be noted in writing during the inspection. A simple check sheet, such as the one shown in [Figure 24.7](#), should be a great aid.

The information obtained during the background search and from the source inspection will enable selection of the test procedure to be used. The choice will be based on the answers to several questions: (1) What are the legal requirements? For specific sources there may be only one acceptable method. (2) What range of accuracy is desirable? Should the sample be collected by a procedure that is  $\pm 5\%$  accurate, or should a statistical technique be used on data from eight tests at  $\pm 10\%$  accuracy? The same is true for acceptable precision. Costs of different test methods will certainly be a consideration here. (3) Which sampling and analytical methods are available that will give the required accuracy for the estimated concentration? An Orsat gas analyzer with a sensitivity limit of  $\pm 0.02\%$  would not be chosen to sample carbon monoxide at 50–100 ppm. Conversely, an infrared gas analyzer with a full-scale deflection of 1000 ppm would not be chosen to sample  $\text{CO}_2$  from a power boiler. (4) Is a continuous record required over many cycles of source operation, or will one or more grab samples suffice? If a source emits for only a short period of time, a method would not be selected which requires hours to gather the required sample.

The test must be scheduled well in advance for the benefit of all concerned. The plant personnel, as well as the test crew, should be given the intended date and time of the test. It is also a good idea to let the chemist or analytical service know when the testing will be

Source test preliminary visit check list	
Plant _____	
Location _____	
By _____	Date _____
1. Gas flow at test point, m/min _____	, m <sup>3</sup> /min _____
2. Gas temperature, °C _____	
3. Gas pressure, mm of water (±) _____	
4. Gas humidity, R. H., % _____	
5. Pollutants of concern _____	
6. Estimate of concentration _____	
7. Any toxic materials? _____	
8. Test crew needed _____	
9. Site check:	
Electric power _____	Test holes _____
Ambient temperature _____	Illumination _____
Platform _____	Scaffolding _____
Hoist _____	Ladders _____
Test date _____	
10. Environmental or safety gear _____	
11. Personnel involved (names)	
Plant manager or foreman _____	
Mechanic or electrician _____	

FIGURE 24.7 Source test checklist.

conducted so that they can be ready to do their portion of the work. It may be necessary to schedule or rent equipment in advance, such as boom trucks or scaffolding. When scheduling the test, make sure that the source will be operating in its normal manner. A boiler may be operating at only one-third load on weekends because the plant steam load is off the line and only a small heating load is being carried.

#### 24.2.4.2 Gas Flow Measurement

The volume of gaseous effluent from a source must be determined to obtain the mass loading to the atmosphere. Flow measurement through the sampling train is necessary to determine the volume of gas containing the pollutant of interest. Many of the sampling devices used for source testing have associated gas flow indicators which must be continually checked and calibrated.

Gas flows are often determined by measuring the associated pressures. Figure 24.8 illustrates several different pressure measurements commonly made on systems carrying gases. Static pressure measurements are made to adjust the absolute pressure to standard conditions specified in the test procedure.

The quantity of gaseous effluent leaving a process is usually calculated from the continuity equation, which for this use is written as

$$Q = AV \quad (24.6)$$

where  $Q$  is the flow at the specified conditions of temperature, pressure, and humidity;  $A$  is the area through

which the gas flows; and  $V$  is the velocity of the effluent gas averaged over the area.

$A$  is commonly measured, and  $V$  determined, to calculate  $Q$ . The velocity  $V$  is determined at several points, in the center of equal duct areas, and averaged. Table 24.2 shows one commonly accepted method of dividing stacks or ducts into equal areas for velocity determinations.

For rectangular ducts, the area is evenly divided into the necessary number of measurement points. For circular ducts, Table 24.3 can be used to determine the location of the traverse points. In using this table, realize that traverses are made along two diameters at right angles to each other, as shown in Figure 24.9.

In most source tests, the measurement of velocity is made with a pitot-static tube, usually referred to simply as a *pitot tube*. Figure 24.10 illustrates the two types of pitot tubes in common use.

The standard type of pitot tube shown in this figure does not need to be calibrated, but it may be easily plugged in some high-effluent loading streams. The type S pitot tube shown in Figure 24.10 does not plug as easily, but it does need calibration to assure its accuracy. The type S pitot tube is also more sensitive to alignment with the gas flow to obtain the correct reading. The velocity pressure of the flowing gas is read at each point of the traverse, and the associated gas velocity is calculated from the formula:

$$V = 420.5 \left[ (P_v / \rho)^{1/2} \right] \quad (24.7)$$

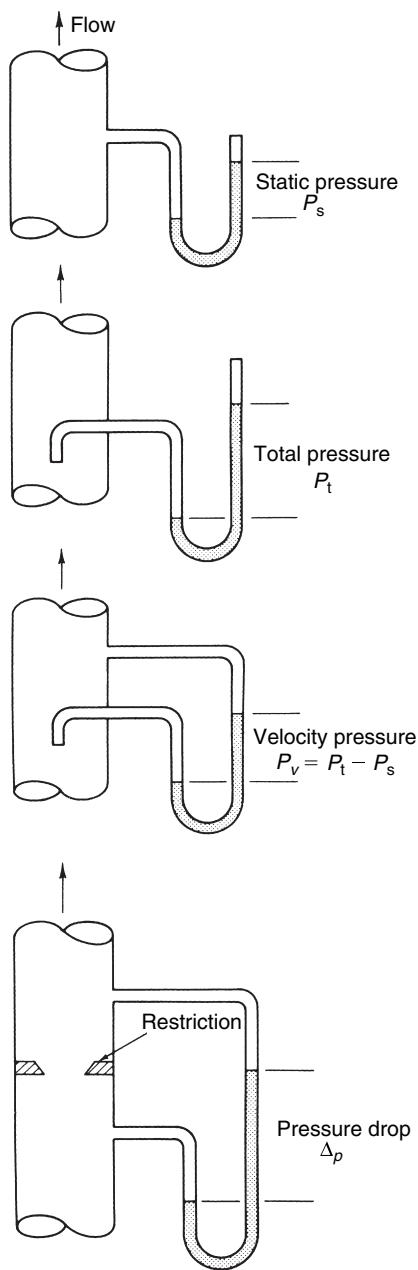


FIGURE 24.8 Pressures commonly measured in flow systems.

TABLE 24.2 Number of Velocity Measurement Points

Stack Diameter or (Length + Width)/2 (m)	Number of Velocity Measurement Points
0.0–0.3	8
0.3–0.6	12
0.6–1.3	16
1.3–2.0	20
2.0→	24

TABLE 24.3 Velocity Sampling Locations, Diameters from Inside Wall to Traverse Point

Point Number	Number of Equal Areas to be Sampled				
	2	3	4	5	6
1	0.067	0.044	0.033	0.025	0.021
2	0.250	0.147	0.105	0.082	0.067
3	0.750	0.295	0.194	0.146	0.118
4	0.933	0.705	0.323	0.226	0.177
5		0.853	0.677	0.342	0.250
6		0.956	0.806	0.658	0.355
7			0.895	0.774	0.645
8			0.967	0.854	0.750
9				0.918	0.823
10				0.975	0.882
11					0.933
12					0.979

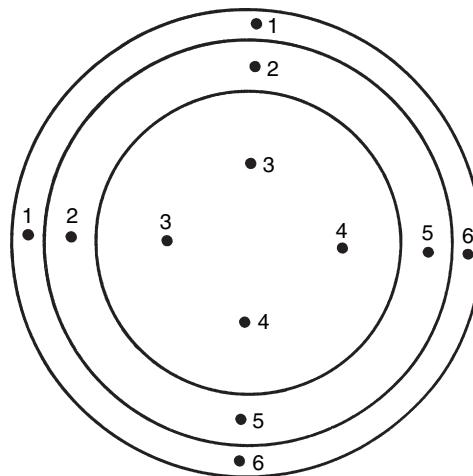
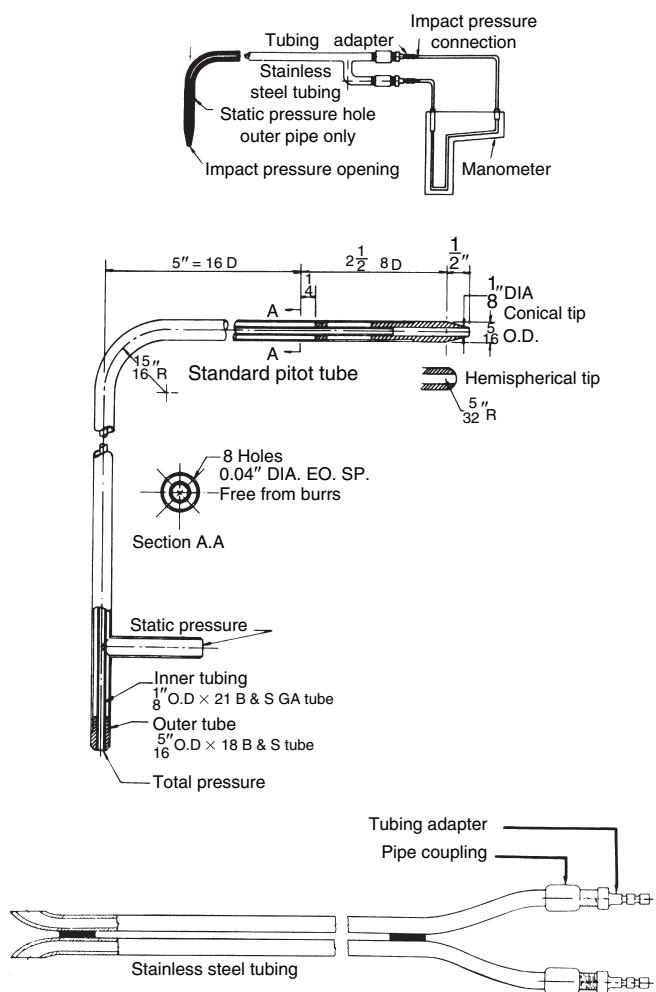


FIGURE 24.9 Circular duct divided into three equal areas, as described in Table 24.3. Numbers refer to sampling points.

where  $V$  is the velocity in meters per minute,  $P_v$  is the velocity pressure in millimeters of water, and  $\rho$  is the gas density in kilograms per cubic meter. The velocities are averaged for all points of the traverse to determine the gas velocity in the duct. Velocity pressures should not be averaged, as a serious error results.

Gas velocities can also be measured with anemometers (rotating vane, hot wire, etc.), from visual observations such as the velocity of smoke puffs, or from mass balance data (knowing the fuel consumption rate, air/fuel ratio, and stack diameter).

In the sampling train itself, the gas flow must be measured to determine the sample volume. Particulates



**FIGURE 24.10 Pitot tubes for velocity determination.** Annual Book of Standards.<sup>18</sup> Note: English units were used by the American Society for Testing and Materials.

and gases are measured as micrograms per cubic meter. In either case, determination of the fraction requires that the gas volume be measured for the term in the denominator. Some sample trains contain built-in flow-indicating devices such as orifice meters, rotometers, or gas meters. These devices require calibration to assure that they read accurately at the time of the test and under test conditions.

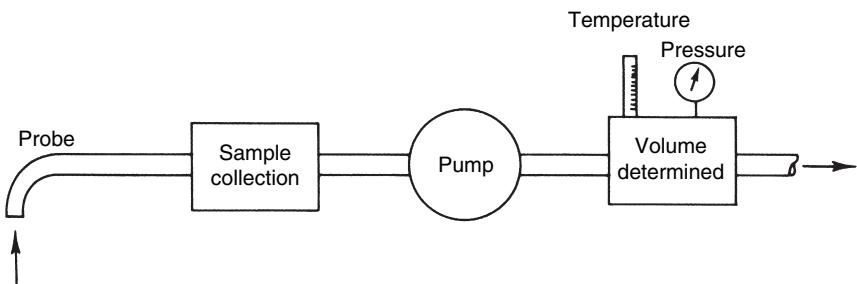
To determine the volume through the sampling train, a positive displacement system can be used. A known volume of water is displaced by gas containing the sample. Another inexpensive procedure that works well consists of measuring the time needed for the gas to fill a plastic bag to a certain static pressure. The volume of the bag can be accurately measured under the same conditions and hence the flow determined by dividing the bag volume by the time required to fill it.

#### 24.2.4.3 Collection of the Source Sample

A typical sample train is shown in [Figure 24.11](#). This shows the minimum number of components, but in some systems the components may be combined. Extreme care must be exercised to assure that no leaks occur in the train and that the components of the train are identical for both calibration and sampling. The pump shown in [Figure 24.11](#) must be both oil-less and leakproof. If the pump and volume measurement devices are interchanged, the pump no longer needs to be oil-less and leakproof, but the volume measurement will be in error unless it is adjusted for the change in static pressure. Some sampling trains become very complex as additional stages with controls and instruments are added. Many times the addition of components to a sampling train makes it so bulky and complicated that it becomes nearly impossible to use. A sampling train developed in an air-conditioned laboratory can be useless on a shaky platform in a snowstorm.

Standard sampling trains are specified for some tests. One of these standards is the system specified for large, stationary combustion sources.<sup>19</sup> This train was designed for sampling combustion sources and should not be selected over a simpler sampling train when sampling noncombustion sources such as low-temperature effluents from cyclones, baghouses, filters, etc.<sup>20</sup>

Before taking the sample train to the test site, it is wise to prepare the operating curves for the particular job. With most factory-assembled trains, these curves are a part of the package. If a sampling train is assembled from components, the curves must be developed. The type of curves will vary from source to source and



**FIGURE 24.11 Sampling train.**

from train to train. Examples of useful operating curves include (1) velocity vs velocity pressure at various temperatures,<sup>21</sup> (2) probe tip velocity vs flowmeter readings at various temperatures, and (3) flowmeter calibration curves of flow vs pressure drop. It is much easier to take an operating point from a previously prepared curve than to take out a calculator and pad to make the calculations at the moment of the test. Remember, too, that time may be a factor and that settings must be made as rapidly as possible to obtain the necessary samples.

For sampling particulate matter, one is dealing with pollutants that have very different inertial and other characteristics from the carrying gas stream. It becomes important, therefore, to sample so that the same velocity is maintained in the probe tip as exists in the adjacent gas stream. Such sampling is called *isokinetic*. Isokinetic sampling, as well as anisokinetic sampling, is illustrated in Figure 25.26 in Chapter 25.

If the probe velocity is less than the stack velocity, particles will be picked up by the probe, which should have been carried past it by the gas streamlines. The inertia of the particles allows them to continue on their path and be intercepted. If the probe velocity exceeds the stack velocity, the inertia of the particles carries them around the probe tip even though the carrying gases are collected. Adjustment of particulate samples taken anisokinetically to the correct stack values is possible if all of the variables of the stack gas and particulate can be accounted for in the appropriate mathematical equations.

Modern transducers and microprocessors have been used successfully to automate particulate sampling trains in order to eliminate the operating curves and manual adjustments.<sup>22</sup> The automated samplers adjust continuously to maintain isokinetic conditions. In addition, the microprocessor continuously calculates and displays both instantaneous sampling conditions and the total sample volume collected at any given moment. The use of the automated system with the microprocessor, therefore, eliminates both operator and calculation errors.

Several separating systems are used for particulate sampling. All rely on some principle of separating the aerosol from the gas stream. Many of the actual systems use more than one type of particulate collection device in series. If a size analysis is to be made on the collected material, it must be remembered that multiple collection devices in series will collect different size fractions. Therefore, size analyses must be made at each device and mathematically combined to obtain the size of the actual particulate in the effluent stream. In any system the probe itself removes some particulate before the carrying gas reaches the first separating device, so the probe must be cleaned and the weight of material added to that collected in the remainder of the train.

Care should be exercised when sampling for aerosols that are condensable. Some separating systems, such as wet impingers, may remove the condensables from the gas stream, whereas others, such as electrostatic precipitators, will not. Of equal concern should be possible reactions in the sampling system to form precipitates or aerosols which are not normally found when the stack gases are exhausted directly to the atmosphere. SO<sub>3</sub> plus other gaseous products may react in a water-filled impinger to form particulate matter not truly representative of normal SO<sub>3</sub> release.

When sampling particulate matter from combustion processes, it is necessary to take corresponding CO<sub>2</sub> readings of the effluent. Emission standards usually require combustion stack gases to be reported relative to either 12% CO<sub>2</sub> or 50% excess air. Adjusting to a standard CO<sub>2</sub> or excess air value normalizes the emission base. Also, emission standards require that the loadings be based on weight per standard cubic volume of air (usually at 20 °C and 760 mmHg). In most regulations, the agency requires that the standard volume be dry, but this is not always specified.

For sampling of gases, the sample can be collected by any of several devices. Some commonly used manual methods include Orsat analyzers, absorption systems, adsorption systems, bubblers, reagent tubes, condensers, and traps. Continuous analyzers are now more widely used than manual methods. Some types of continuous analyzers include infrared and ultraviolet instruments; flame ionization detectors; mass spectrometers; calorimetric systems; gas, liquid, and solid chromatography; coulometric and potentiometric systems; chemiluminescence; and solid-state electronic systems. Since gases undergoing analysis do not need to be sampled isokinetically, it is only necessary to insert a probe and withdraw the sample. Usually, the gas sample should be filtered to remove any accompanying particulate matter which could damage the analytical instrumentation.

For the detection and intensity of odorous substances, the nose is still the instrument usually relied upon. Since odors are gaseous, they may be sampled by simply collecting a known volume of effluent and performing some manipulation to dilute the odorous gas with known volumes of "pure" air. The odor is detected by an observer or a panel of observers. The odor-free air for dilution can be obtained by passing air through activated carbon or any other substance that removes all odors while not affecting the other gases that constitute normal air. The odor-free air is then treated by adding more and more of the odorous gas until the observer just detects the odor. The concentration is then recorded as the odor threshold as noted by that observer. The test is not truly quantitative, as much variation between observers and samples is common.

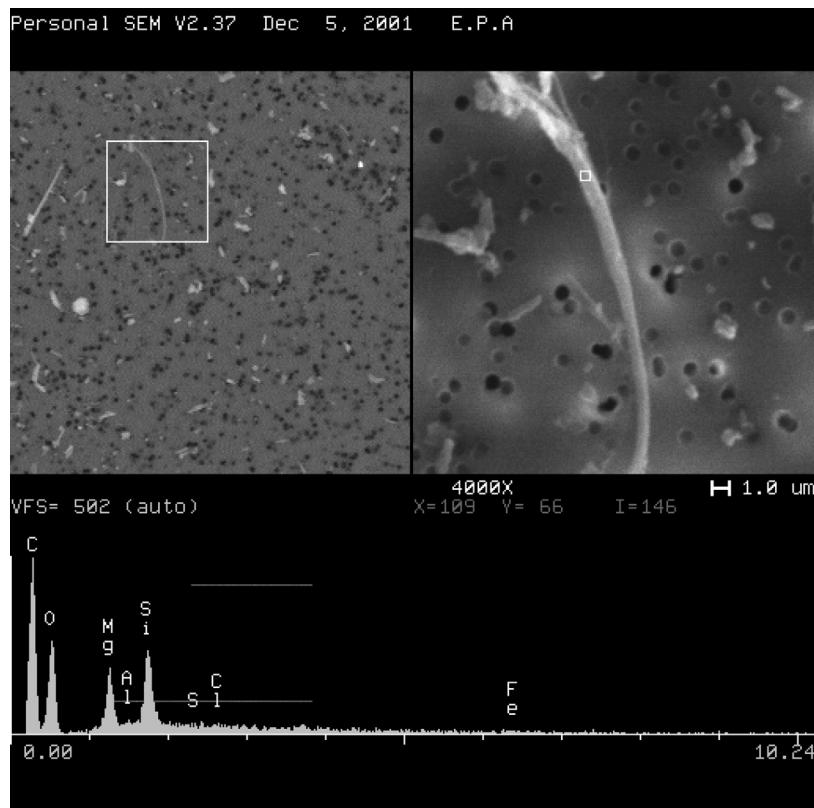
If the compound causing the odor is known and can be chemically analyzed, it may be possible to get valid quantitative data by direct gas sampling. An example would be a plant producing formaldehyde. If the effluent were sampled for formaldehyde vapor, this could be related, through proper dispersion formulas, to indicate whether the odor would cause any problems in residential neighborhoods adjacent to the plant.

Extreme care should be taken in transporting and storing the samples between the time of collection and the time of analysis. Some condensable hydrocarbon samples have been lost because the collection device was subjected to elevated temperatures during shipment. Equally disastrous is placing the sample in an oven at 105 °C to drive off the moisture, only to discover that the particles of interest had a very low vapor pressure and also departed the sample. At such times, source sampling can be very frustrating.

A very important analytical tool that is overlooked by many source-testing personnel is the microscope. Microscopic analysis of a particulate sample can tell a great deal about the type of material collected as well as its

size distribution. This analysis is necessary if the sample was collected to aid in the selection of a piece of control equipment. All of the efficiency curves for particulate control devices are based on fractional sizes. One would not try to remove a submicron-size aerosol with a cyclone collector, but unless a size analysis is made on the sampled material, one is merely guessing at the actual size range.

Scanning electron microscopy (SEM) may be used for the analysis of particles in air (see Figure 1.4 in Chapter 1 and Figure 24.12). Air samples are collected on filters and prepared for analysis. Filters are carbon or gold-coated and mounted so that an electron beam is directed at the sample, and emissions are measured by a detector at an angle to the electron beam. An image of the surface features on the filter can then be observed at magnifications commonly up to 20,000 $\times$  and higher, when needed. Many SEM systems also include energy dispersive spectroscopy (EDS) to complement the morphology from SEM with the elemental composition of the particle. However, EDS will not provide individual chemical species. For example, the EDS spectrum may show that the particle consists of 20% iron and



**FIGURE 24.12** Scanning electron microscopy (SEM) of fibers in dust collected near the World Trade Center, Manhattan, NY, in September 2001. Acquired using an Aspex Instruments, Ltd, SEM. The bottom of the micrograph represents the elemental composition of the highlighted 15-μm long fiber by energy dispersive spectroscopy (EDS). This composition (i.e. O, Si, Al, and Mg) and the morphology of the fibers indicate they are probably asbestos. The EDS carbon peak results from the dust being scanned on a polycarbonate filter. U.S. Environmental Protection Agency; 2004. Photo courtesy of Conner T, used with permission.

30% zinc, but the actual compounds (e.g. iron sulfide, iron oxide, or organic iron and zinc compounds) are not known. In such cases, scientific judgment may be needed. For example, if the sample is collected near a smelter and the stack is known to generate oxidized species, metal oxides are more likely to dominate. In a reduced environment, conversely, the sulfides are likely to account for a larger part of the particle's composition.

#### **24.2.4.4 Calculations and Report**

The measurement data must be reduced. For sampling a relatively small number of sources, a simplified calculation form may be used. Such forms enable the office personnel to perform the arithmetic necessary to arrive at the answers, freeing the technical staff for proposals, tests, and reports. However, with the growing use of smart phones and other devices in the field, calculations can now be conducted in the field. Many of the manufacturers of source-testing equipment include example calculation forms as part of their operating manuals. Some standard sampling methods include calculation forms as a part of the method.<sup>23</sup> Air pollution control agencies often have standard forms and spreadsheets for their own use and will supply copies on request.

The source test report is the end result of a large amount of work. It should be thorough, accurate, and written in a manner understandable to the person who intends to use it. It should state the purpose of the test, what was tested, how it was tested, the results obtained, and the conclusions reached. The actual data and calculations should be included in the appendix of the source test report so that they are available to substantiate the report if questioned.

#### **24.2.5 Source Monitoring**

The monitoring of pollutant concentration or mass flow of pollutants is of interest to both plant owners and regulatory agencies. Industry uses such measurements to keep a record of process operations and emissions for its own use and to meet regulatory requirements. Agency officials use the information for compiling emission inventories, modeling of air sheds, and in some cases for enforcement.

A monitoring system is selected to meet specific needs and is tailored to the unique properties of the emissions from a particular process. It is necessary to take into account the specific process, the nature of the control devices, the peculiarities of the source, and the use of the data obtained.<sup>23</sup>

Source monitoring can best be treated as a system concept ideally consisting of six unit operations, as shown in Table 24.4. In the United States, installation

**TABLE 24.4** System Concept of Stationary Source Measurements

Operation	Objective
Sampling site selection	Representative sampling consistent with intended interpretation of measurement
Sample transport (when applicable)	Spatial and temporal transfer of sample extract with minimum and/or known effects on sample integrity
Sample treatment (when applicable)	Physical and/or chemical conditioning of sample consistent with analytical operation, with controlled and/or known effects on sample integrity
Sample analysis	Generation of qualitative and quantitative data on pollutant or parameter of interest
Data reduction and display	Calibration and processing of analog data and display of final data in a format consistent with measurement objectives
Data interpretation	Validly relating the measurement data to the source environment within the limitations of the sampling and analytical operations

Source: Nader.<sup>24</sup>

and operation of monitoring systems have been prescribed for a number of industries, as shown in Table 24.5.

##### **24.2.5.1 Types of Monitors**

Continuous emission monitors (CEMs) for plume opacity have been required on all utility, fossil fuel-fired, steam generators (over 264 MJ) constructed in the United States since December 1971. These monitors are *in situ* opacity meters which measure the attenuation of a light beam projected across the stack (see Figure 25.8 in Chapter 25). Remote-sensing monitors have been developed, but these have not yet been approved as equivalent to the *in situ* opacity monitors. CEMs for gaseous emissions are also available and required for certain facilities. Figure 24.13 illustrates various approaches to monitoring particulate opacity and gaseous emissions.

##### **24.2.5.2 Quality Assurance in Monitoring**

In order to assure that the source is being accurately monitored, several requirements must be met.<sup>16</sup> Some of these requirements, which assure representative, uncontaminated samples, are shown in Table 24.6.

##### **24.2.5.3 Monitoring of Particulate Emissions**

The most common monitoring of particulate matter is for light attenuation (opacity). Less frequently used

TABLE 24.5 Source Emissions Requiring Continuous Monitoring by United States New Source Performance Standards

Source	Pollutant						Scrubber Pressure Loss and Water Pressure	Flow Rate
	SO <sub>2</sub>	NO <sub>x</sub>	CO	Opacity	H <sub>2</sub> S	Total Reduced Sulfur		
Electric power plants	x	x		x				
Sulfuric acid plants	x							
Onshore natural gas processing	x							
SO <sub>2</sub> emissions								
Nitric acid plants		x						
Petroleum refineries	x		x	x	x	x		
Iron and steel mills (BOF)*							x	
Steel mills (electric arc)				x				x
Ferroalloy production				x				
Glass manufacturing plants				x				
Portland cement plants				x				x
Primary copper smelters	x			x				
Primary zinc smelters	x			x				
Primary lead smelters	x			x				
Coal preparation plants							x	
Wet process phosphoric acid plants							x	
Superphosphoric acid plants							x	
Diammonium phosphate plants							x	
Triple superphosphate plants							x	
Granular triple superphosphate plants							x	
Phosphate rock plants			x				x	
Metallic mineral processing plants							x	
Nonmetallic mineral processing plants							x	
Kraft pulp mills			x		x		x	x
Gas turbines <sup>§</sup>							x	
Lime kilns <sup>¶</sup>			x		x		x	
Ammonium sulfate plants							x	
Lead-acid battery manufacture							x	

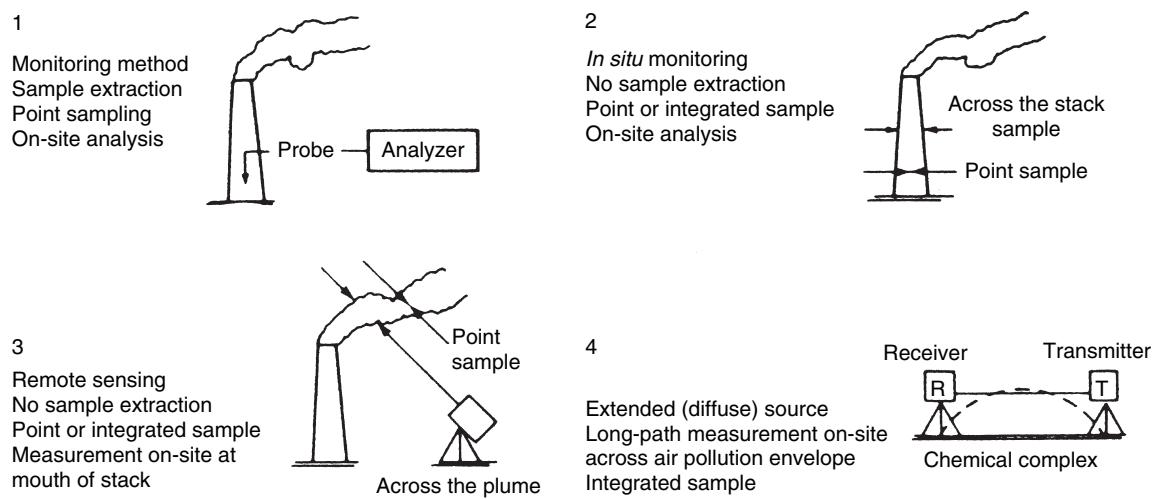
x = continuous monitoring required

\* BOF, basic oxygen furnace.

<sup>§</sup>Monitor sulfur and nitrogen content of fuel and water/fuel ratio.

<sup>¶</sup>Also monitor scrubber liquid flow rate.

Source: Code of Federal Regulations.<sup>23</sup>

FIGURE 24.13 Sampling approaches to monitoring source emissions. Nader.<sup>24</sup>

methods exist for monitoring mass concentration, size distribution, and chemical composition.

Opacity is a function of light transmission through the plume. Opacity is defined as follows:

$$\text{Opacity} = (1 - I/I_0) \times 100 \quad (24.8)$$

where  $I_0$  is the incident light flux and  $I$  is the light flux leaving the plume. Techniques for monitoring visible emissions (opacity) are listed in Table 24.7.

#### 24.2.5.4 Monitoring of Gaseous Emissions

Gas-monitoring systems are more widely used than particulate monitoring systems. They can also be used

TABLE 24.6 Stationary Source Monitoring Requirements

Requirement	Method of Attainment
Maintain gas temperature above the water or acid dew point	Heat lines or dilute with dry air
Remove water before sample enters instrument	Refrigerate or desiccate sample
Remove particulate matter before sample enters instrument	Use cyclone or filter in sample line
Dilute sample to lower the temperature to an acceptable level for the instrument	Air dilute with necessary blowers, flow measurement, and control systems
Maintain integrity of particulate sample (mass, size, and chemical composition)	Use isokinetic sampling, refrigerated sample transport, and careful handling to minimize physical or chemical changes

for both emission compliance monitors and process control systems. Gas monitors may be of either the *in situ* or the extractive type and use the approaches illustrated in Figure 24.13. Table 24.8 lists the various types of gas-monitoring systems.

#### 24.2.5.5 Data Reduction and Presentation

Continuous monitors usually indicate the pollutant concentration on both an indicator and a chart recording. This provides a visual indication of the instantaneous emissions, along with a permanent record of the quantitative emissions over a period of time. The monitoring system may also be equipped with an alarm device to signal the operator if the allowable emission level is being exceeded. Data-logging systems coupled with microprocessors are popular. These systems can give instantaneous values of the variables and pollutants of interest, along with the averages or totals for the period of concern.

TABLE 24.7 Opacity Monitoring Techniques

Method of Analysis	Measurement System
In-stock opacity	Optical transmissometer
Plume opacity	Lidar (light detection and ranging)
Selective opacity (for fine particles)	Extractive with light-scattering determination

TABLE 24.8 Gas Emission Monitoring Systems

Analytical Scheme	Sampling Approach*	Pollutant Capability <sup>§</sup>
<b>CHEMIELECTROMAGNETIC</b>		
Colorimetry	E	SO <sub>2</sub> , NO <sub>x</sub> , H <sub>2</sub> S, TS
CHEMILUMINESCENT	E	NO <sub>x</sub>
<b>ELECTROMAGNETIC/ELECTROOPTICAL</b>		
Flame photometry	E	SO <sub>2</sub> , H <sub>2</sub> S, TRS, TS
Nondispersive infrared	E	SO <sub>2</sub> , NO, CO, HC, CO <sub>2</sub>
Nondispersive, ultraviolet, and visible	E	SO <sub>2</sub> , NO <sub>x</sub> , NH <sub>3</sub> , H <sub>2</sub> S
Dispersive, infrared, and ultraviolet	I	SO <sub>2</sub> , NO, CO, CO <sub>2</sub> , HC, H <sub>2</sub> S
Dispersive, infrared, and ultraviolet	E	SO <sub>2</sub> , CO, CO <sub>2</sub> , HC, NO
Correlation, ultraviolet	I	SO <sub>2</sub>
Correlation, ultraviolet and visible	R	SO <sub>2</sub> , NO <sub>x</sub>
Derivative, ultraviolet	I	SO <sub>2</sub> , NO <sub>2</sub> , NO, O <sub>2</sub> , NH <sub>3</sub> , CO
Fluorescence, ultraviolet	E	SO <sub>2</sub>
<b>ELECTRICAL</b>		
Conductivity	E	SO <sub>2</sub> , NH <sub>3</sub> , HCl
Coulometry	E	SO <sub>2</sub> , H <sub>2</sub> S, TRS
Electrochemical	E, I	SO <sub>2</sub> , NO <sub>x</sub> , CO, H <sub>2</sub> S, O <sub>2</sub>
Flame ionization	E	HC
<b>THERMAL</b>		
Oxidation	E	CO
Conductivity	E	SO <sub>2</sub> , NH <sub>3</sub> , CO <sub>2</sub>
<b>HYBRID</b>		
Gas chromatography, flame ionization	E	CO, HC
Gas chromatography, flame photometry	E	Sulfur compounds

\* E, extractive; I, in situ; R, remote.

<sup>§</sup>HC, hydrocarbons; TRS, total reduced sulfur; TS, total sulfur; NO<sub>x</sub>, total oxides of nitrogen, but system may be specific for NO, NO<sub>2</sub>, or both.

Source: Nader.<sup>24</sup>

## QUESTIONS

- Describe three ways that measurements support air quality models.
- Describe three ways that models support air pollutant measurements.
- What is the major difference between an air pollution dispersion model and an air pollution receptor model?
- Give an example of the “*cum hoc ergo propter hoc*” fallacy related to air pollution measurements, in addition to the one given in the introduction to Part V.

- Give an example of a very strong association in air pollution that is not causal.
- Give an example of using an air pollution model to interpolate results and an example of using a model to extrapolate results.
- Propose two reasons for the temporal differences in A and B in Figure V.3.
- Would the wind rose in Figure V.4 be useful in predicting the effects of the Santa Ana winds on ground-level ozone? Why or why not?
- Give an example of an extreme event that would lead to not attaining an ambient air standard.

10. What are the problems associated with using airport meteorological data for air pollution predictions and assessments?
11. Name a natural source of reduced sulfur compounds in the atmosphere and a natural source of oxidized sulfur compounds in the atmosphere. Show the reactions that lead to these products.
12. For several decades, opposition to applying sludge (i.e. biosolids) to the land has met with criticism, including the potential to release bioaerosols into the air. What are two ways that the bioaerosols reach the troposphere?
13. Select a source to support your position as to whether the above concerns are reasonable.
14. What are the problems with [Figure 24.2](#) in terms of representativeness and scale?
15. Arguably, all asbestos is "naturally occurring". What do air pollution experts mean when they use this term?
16. Give an example of the importance of being able to differentiate a biogenic emission from an emission.
17. During a pitot traverse of a duct, the following velocity pressures, in millimeters of water, were measured at the center of equal areas: 13.2, 29.1, 29.7, 20.6, 17.8, 30.4, 28.4, and 15.2. If the flowing fluid was air at 760 mmHg absolute and 85 °C, what was the average gas velocity?
18. Would you expect errors of the same magnitude when sampling anisokinetically at 80% of stack velocity as when sampling anisokinetically at 120% of stack velocity? Explain.
19. Suppose a particulate sample from a stack is separated into two fractions by the sampling device. Both are sized microscopically and found to be lognormally distributed. One has a count mean size of 5.0 µm and a geometric deviation of 2.0. The other has a count mean size of 10.0 µm and a geometric deviation of 2.2. Two grams of the smaller-sized material were collected for each 10 g of the larger. What would be reported for the weight mean size and geometric deviation of the stack effluent?
20. A particulate sample was found to weigh 0.0216 g. The sample volume from which it was collected was 0.60 m<sup>3</sup> at 60 °C, 760 mmHg absolute, and 90% relative humidity. What was the stack loading in milligrams per standard cubic meter?
21. PM is collected on a filter to determine size by mass, as well as chemical composition of the PM. If sulfates and anions of volatile acids are present, how may they bias the PM<sub>2.5</sub> by chemical reactions that could occur on the filter after collection?
22. A particulate sample was found to contain 350 mg m<sup>-3</sup>. The CO<sub>2</sub> during the sampling period averaged 7.2%. If the exhaust gas flow was 2000 m<sup>3</sup> min<sup>-1</sup>, what would be the particulate loading in both milligrams per cubic meter and kilograms per hour, corrected to 12% CO<sub>2</sub>?
23. Give an example of how opacity monitoring of a coal-fired boiler could be used to improve combustion efficiency.
24. Use Boyle's law to explain how to collect a sample of air which will be analyzed for benzene.
25. Use Fick's law to explain the difference between active monitoring and passive monitoring of benzene in the air.
26. Use the Beer–Lambert law to explain how a gas chromatograph is used to analyze benzene in the air.
27. Use Stoke's law to explain how to collect aerosols.
28. An opacity monitor is set so that the incident light is 100 units. Prepare a graph of the percentage of opacity vs the light flux leaving the plume (opacity, 0–100%; exiting light flux, 0–100 units).
29. List the advantages and disadvantages of both *in situ* and extractive gas monitors.
30. Discuss the advantages and disadvantages of one-time source testing for a specific emission vs continuous monitoring of the same emission.

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# Methods for Measuring Air Pollutants

## 25.1 INTRODUCTION

Air pollution results from myriad sources and impacts very complex systems ranging in scale from the cell to the planet. Chapter 24 begins with a distinction between natural and anthropogenic sources of air pollution. This chapter describes approaches for measuring air pollutants and other characteristics of the ambient atmosphere or, more precisely, the ambient troposphere. These measurements give general information about the quality of air, not a particular source, whether natural or human-induced.

The primary focus of ambient monitoring is to identify and to quantify pollutants at various scales in the atmosphere, ranging from planetary (e.g. greenhouse gases) to neighborhood. Chapter 24 applies the methods and approaches to air monitoring at various scales. Between neighborhood and global scales are various size air pollution compartments, from regional to urban to community to indoor. Within these environmental compartments are matrices of nonliving (i.e. abiotic) and living (biotic) components. To determine the condition of such systems, various means of measurement are needed. The measurements may be direct or indirect. Direct physical and chemical measurements include the concentrations and sizes of particles captured on filters, concentrations of gases and vapors collected in traps, temperature, humidity, and pH of water droplets. Others are indirect, such as light scattering as indication of the number of aerosols in the atmosphere. This chapter provides an overview of some of the most important measurement methods in use today. In addition, the chapter introduces some of the techniques available for sampling, analysis, and extrapolation and interpolation (e.g. models) of measured results, although air quality modeling is treated in much greater detail in Chapter 27.

Air pollutants must be known throughout their life cycles (Figure V.7). Thus, they must be measured or at least estimated at their sources, after being emitted, during their time in the atmosphere and hydrosphere, after

humans and ecosystems are exposed and following uptake by humans and organisms.

The representativeness and usefulness of air quality monitoring depend on the quality of each step from sample collection to sample preparation to analysis. Sampling is a statistical term, i.e. a sample is a subset of a population or domain from which information can be inferred about the entire population or domain. Thus, care must be taken to ensure the quality of every interdependent step in air quality measurements.

Since a sample represents a very small fraction of the larger population or airshed from which the sample was drawn, it requires a model to provide an estimate of the air quality. The model may be represented mathematically or spatially. For example, a sample of air may consist of a canister or bag that holds a defined quantity of air collected during a particular time period at a specific location. The air must be subsequently analyzed and these analytic results can be used to extrapolate air quality from that location and time to larger spatial areas and longer time frames. The sample is representative of a portion of an air mass or, more likely, a part of an air mass, such as zones around a source with isopleths of the concentration of an air pollutant. All of the samples must be collected and their results aggregated to ascertain with defined certainty the quality of an air mass. More samples will be needed for a large urban airshed than for that of a small town. Intensive sampling is often needed for highly toxic contaminants and for sites that may be particularly critical, e.g. near a hazardous waste site or in an "at risk" neighborhood (such as one near a manufacturing facility that uses large quantities of potentially toxic materials). Similar to other statistical measures, environmental samples allow for statistical inference. In case, inferences are made regarding the condition of an ecosystem and the extent and severity of exposure of a human population.

Sampling regimes follow the life cycle of an air pollutant. Chapter 24 addresses the pollutant at its source. The measurements at the point of a pollutant's

release into the environment usually represent the highest concentrations of an air pollutant during its life cycle, excluding measurements within the reactor. A reactor may be specifically designed to produce a compound, e.g. a pesticide or household chemical, with releases to the environment through stacks and vents. The next steps in the chemical's life cycle involve dilution of concentrations until the substance is again concentrated by organisms (Figure 25.1).

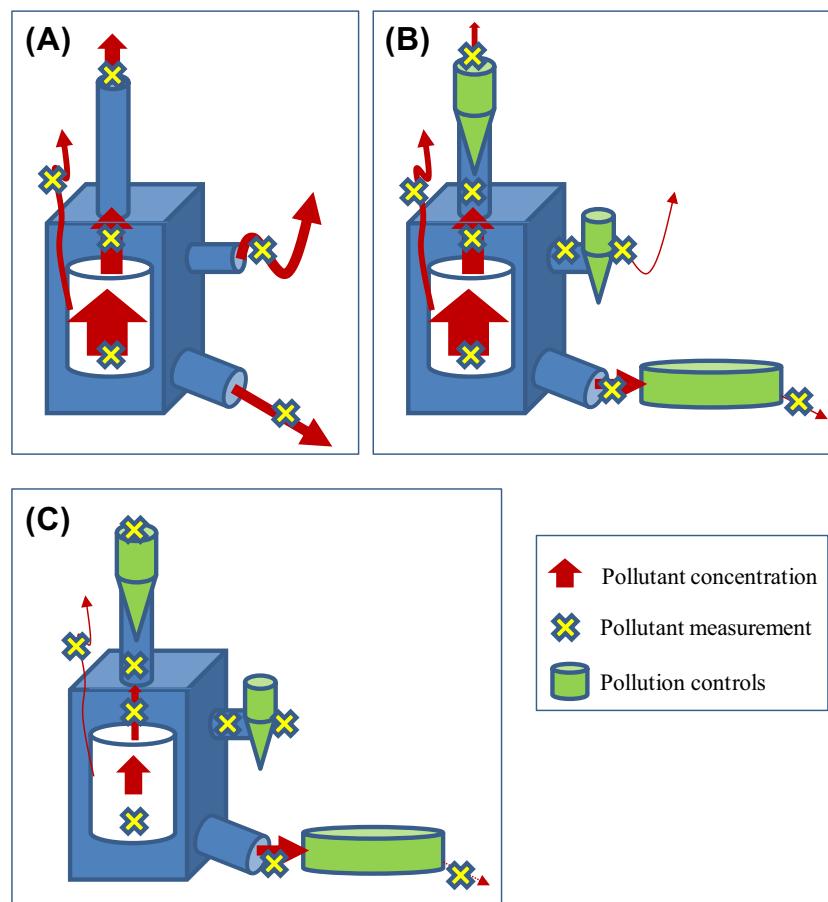
The measurement locations shown in Figure 25.1 are at the emission level for a particular facility. Ambient concentrations of these same pollutants are the result of all facilities and other sources. Thus, ambient measurements need to represent a type of mixed average for a region or for a particular population. An example of the former is ground-level ozone for the entire region (e.g. the airshed for St. Louis would include several counties in Missouri and Illinois, and the airshed of London, England would include the city and suburbs). An example of the latter would be the concentrations of benzene or carbon monoxide for several city blocks in downtown St. Louis and London. Thus, the type of measurement depends on the mixing and dispersion of a pollutant *and* the population expected to be exposed to

that pollutant. The method, then, varies according to the accuracy, precision, and representativeness needed.

"Grab" samples provide straightforward and quick means of measuring air pollution. A grab sample is a single sample taken to represent an entire system. Such a sample is limited in location vertically and horizontally, so there is much uncertainty. However, the representativeness is improved with greater sampling density. For example, if 10 samples are taken at 10 spatially distributed sites, the inferences are improved. Furthermore, if the samples were taken in each season, then there would be some improvement to understanding of intra-annual variability. If the sampling is continued for several years, the interannual variability is better characterized.

Grab samples of particulate matter and gases can be taken at any location in Figure 25.1. They may be taken in a stack or vent for an emissions snapshot. They are often taken to estimate concentrations in the ambient air impacted by a particular source, such as a high-traffic roadway and an industrial facility. For example, to estimate the amount of a toxic chemical compound in the atmosphere surrounding a chemical plant, an engineer collects air samples in canisters downwind from

**FIGURE 25.1** Change in concentrations of a hypothetical chemical compound during its life cycle. The width of arrows represents pollutant concentration. (A) Sampling locations prior to installation of pollution control equipment. (B) Sampling locations to determine effectiveness of pollution control equipment. Ideally, sampling is needed at the entrance and exit of each pollution control device to determine pollution control efficiency. (C) Sampling locations to determine effectiveness of changes to reactor, e.g. green chemistry and substitution of reagents to decrease or eliminate pollution, such as the substitution of a chlorinated compound with a nonchlorinated solvent, thereby eliminating organochlorine emissions. The scenario shown in (C) has completed eliminated stack and vent emissions, and decreased fugitive emissions from the reactor (Figure 25.2), as well as decreased the pollutant concentrations in the effluent being released into surface and groundwater. (For color version of this figure, the reader is referred to the online version of this book.)



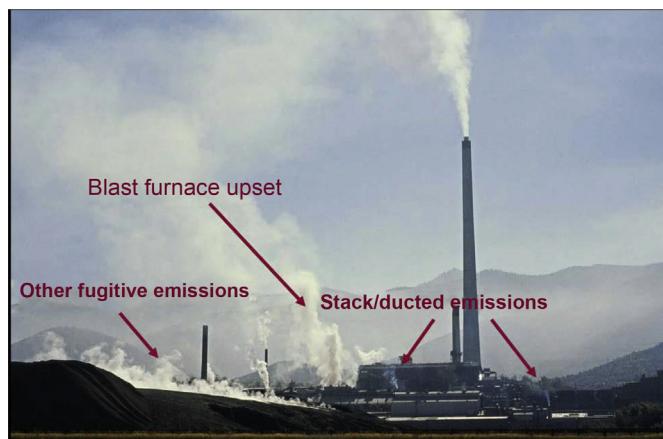


FIGURE 25.2 Types of fugitive emissions. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 1.

the plant (see Discussion Box: Sampling Gases and Vapors). Sampling at only one point, i.e. filling one canister, may not reveal much about the presence of the compound. If the sample is taken at the stack outlet, this is a grab sample of emission. If the sample is taken properly, it may accurately represent a snapshot of the emission, but it will not represent the actual emission. For example, if it is taken during a short period of time when the chemical plant is operating near capacity, the compound concentrations will overestimate longer time periods. That is, it cannot be used to estimate weekly, daily, or even an hourly emission. It is mere an instantaneous measurement of the compound being emitted. Likewise, if the sample is taken when the plant is idle or at very low operating conditions, the instantaneous measurement will underestimate the emission.

In addition to grab samples, numerous other means of collecting samples are routinely used to assess ambient air quality, including continuous sampling with stationary measurement apparatus and periodic sampling with portable devices (e.g. canisters and bags). The sampling can be active, i.e. with pumps to deliver air at a constant rate, or passive, taking advantage of diffusion characteristics of the pollutants and other compounds. These and other methods differ as to whether the pollutant is a gas or an aerosol. Air pollutant concentrations can be ascertained through various other types of sampling, depending on the pollutant of concern. The sampling may be real-time, where measurements including simultaneous sampling and analysis, or more typically for most pollutants, may follow a protocol for a series of various steps between the sampling site and the laboratory:

1. Sampling preparation (e.g. canister cleaning, filter weighing, on-site setup, and chain-of-custody);
2. Sample collection in the field;
3. Sample transportation to laboratory;

4. Extraction of collection media (e.g. removal of analyte from foam traps and sorbent using solvents, pressurization, etc. such as Soxhlet, supercritical fluid, and other extraction technologies);
5. Collection of extract in solvent;
6. Concentration of solvent (if concentrations are extremely low, to raise concentrations above detection limits of equipment);
7. Separation (e.g. gas or liquid chromatography); and
8. Laboratory analysis (e.g. mass spectroscopy).

These steps are described in detail in Chapter 26.

Once the decision has been made as to the type of sampling and analysis, the representativeness of the samples needs to be considered. Thus, all sampling of ambient air quality needs to follow a sampling protocol. Following are some of the most common approaches to ascertain pollution concentrations for a designated airshed or its subdivisions:

*Random sampling:* The major value of random sampling is statistical representativeness, with a sufficient number of samples for the defined confidence levels (e.g. X samples needed for 95% confidence, random sampling may lead to large areas missed for sampling because due to chance distribution of results). It also neglects prior knowledge of the site. Consider a search for possible sources of benzene and toluene in the air of a neighborhood in which old maps show that a gasoline station was previously located in the study area. A purely random sample of a large area does not employ prior knowledge regarding the possible source if samples near the station, even though there may be a buried tank releasing benzene–toluene–ethylbenzene–xylanes (BTEX) into the groundwater which may migrate through the vadose zone and reach the atmosphere.

*Stratified random sampling:* Dividing an area into sub-areas and randomly sampling within each subarea could avoid the omission problems of random sampling alone.

*Stratified sampling:* In this design, specific air pollutants or other parameters are targeted. The areas are subdivided and sampling patterns and densities varied in different areas. Stratified sampling can be used for complex and large sources, such as mining and agriculture fugitive emissions.

*Grid or systematic sampling:* In this design, the entire area is covered. Sampling locations are readily identifiable, which is valuable for follow-on sampling, if necessary.

*Judgmental sampling:* Samples are collected based upon knowledge of the site. This overcomes the problem of ignoring sources or sensitive areas, but is vulnerable to bias of both inclusion and exclusion. Obviously, this would not be used for spatial representation, but for pollutant transport, plume characterization, or monitoring near a sensitive site (e.g. a day care center).

At every stage of monitoring from sample collection through analysis and archiving, only qualified and authorized persons should be in possession of the samples. This is usually assured by requiring chain-of-custody manifests. Sample handling includes specifications on the temperature range needed to preserve the sample, the maximum amount of time the sample can be held before analysis, special storage provisions (e.g. some samples need to be stored in certain solvents), and chain-of-custody provisions (only certain, authorized persons should be in possession of samples after collection).

Each person in possession of the samples must require that recipient sign and date the chain-of-custody form before transferring the samples. This is because samples have evidentiary and forensic content, so any compromising of the sample integrity must be avoided.

Emission estimates are different from exposure estimates. Even a well-designed emission measurement cannot be representative of ambient conditions. Thus emission estimates are quite different from ambient measurements. Ambient samples do not accurately represent indoor concentrations. Indoor measurements do not necessarily represent concentrations near a person's breathing zone. Thus, grab samples are often taken, only give a crude estimate of concentrations at a specific place and time. They do not give a precise or accurate estimate of the actual or potential exposure to an air pollutant, but they may be a valuable first step.

In the United States, the Environmental Protection Agency (EPA) frequently updates the methods for measuring the criteria air pollutants (<http://www.epa.gov/ttnamti1/files/ambient/criteria/reference-equivalent-methods-list.pdf>). The methods for measuring ambient concentrations of specified air pollutants are referred to as "reference methods" or "equivalent methods".<sup>2</sup> Each method listed is considered to be an acceptable approach,

subject to limitations (e.g. operating range or temperature range) specified in the applicable designation to be used by state and local air quality surveillance systems, unless the applicable designation is subsequently canceled. Automated methods for pollutants other than PM<sub>10</sub> are acceptable only if sheltered at temperatures between 20 and 30 °C, with line voltages between 105 and 125 V unless otherwise specified in the method description. New analyzers or PM<sub>10</sub> samplers that are sold as reference or equivalent methods must carry a label or sticker identifying them as designated methods. For analyzers or PM<sub>10</sub> or samplers sold prior to the designation of a method with the same or similar model number, the model number does not necessarily identify an analyzer or sampler as a designated method.<sup>3</sup>

### 25.1.1 Ambient Sampling System Configuration

The principal requirement of an ambient air sampling system is to obtain a sample that is representative of the atmosphere at a particular place and time and that can be evaluated as a mass or volume concentration.<sup>4</sup> The sampling system must minimize its intrusiveness, i.e. the sampling process itself must avoid introducing error and sampling apparatus should not alter the chemical or physical characteristics of the sample in an undesirable manner. The major components of most sampling systems are an inlet manifold, an air mover, a collection medium, and a flow measurement device.

The inlet manifold transports material from the ambient atmosphere to the collection medium or analytical device, preferably in an unaltered condition. The inlet opening may be designed for a specific purpose. All inlets for ambient sampling must be rainproof. Inlet manifolds are made out of glass, Teflon, stainless steel, or other relatively unreactive materials and permit the remaining components of the system to be located at a distance from the sample manifold inlet. The air mover provides the force to create a vacuum or lower pressure at the end of the sampling system. In most instances, air movers are pumps. The collection medium for a sampling system may be a liquid or solid sorbent for dissolving gases, a filter surface for collecting particles, or a chamber to contain an aliquot of air for analysis. The flow device measures the volume of air associated with the sampling system. Examples of flow devices are mass flow meters, rotameters, and critical orifices.

Air sampling systems can take several forms and may not necessarily have all four components (Figure 25.3). Figure 25.3(A) is typical of many extractive sampling techniques in practice, e.g. SO<sub>2</sub> in liquid sorbents and polynuclear aromatic hydrocarbons on solid sorbents. Figure 25.3(B) is used for "open-face" filter collection,

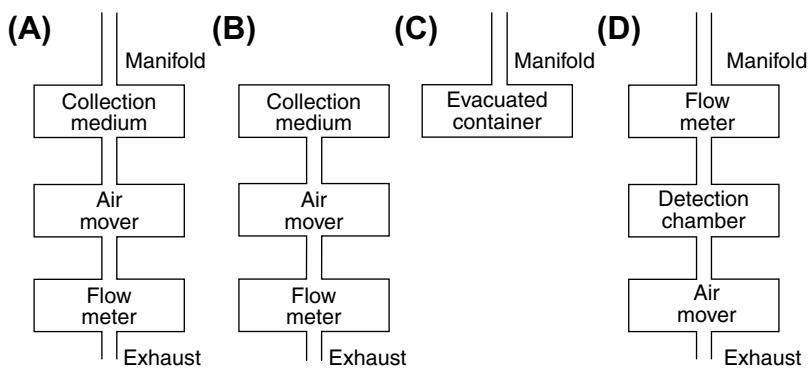


FIGURE 25.3 Schematic diagrams of four types of air sampling systems.

in which the filter is directly exposed to the atmosphere being sampled. Figure 25.3(C) is an evacuated container used to collect an aliquot of air or gas to be transported to the laboratory for chemical analysis; e.g. polished stainless steel canisters are used to collect ambient hydrocarbons for air toxic analysis. Figure 25.3(D) is the basis for many of the automated continuous analyzers, which combine the sampling and analytical processes in one piece of equipment, e.g. continuous ambient air monitors for SO<sub>2</sub>, O<sub>3</sub>, and NO<sub>x</sub>.

For any of any sampling system configuration or the specific material sampled, several characteristics are important for all ambient air sampling systems. These are collection efficiency, sample stability, recovery, minimal interference, and an understanding of the mechanism of collection. Ideally, the first three would be 100% and there would be no interference or change in the material when collected.

One example of these factors is demonstrated when sampling for sulfur dioxide (SO<sub>2</sub>). Liquid sorbents for SO<sub>2</sub> depend on the solubility of SO<sub>2</sub> in the liquid collection medium. Certain liquids at the correct pH are capable of removing ambient concentrations of SO<sub>2</sub>

with 100% efficiency until the characteristics of the solution are altered so that no more SO<sub>2</sub> may be dissolved in the volume of liquid provided. Under these circumstances, sampling is 100% efficient for a limited total mass of SO<sub>2</sub> transferred to the solution, and the technique is acceptable as long as sampling does not continue beyond the time that the sampling solution is saturated.<sup>4</sup> A second example is the use of solid sorbents such as Tenax for volatile hydrocarbons by the physical adsorption of the individual hydrocarbon molecules on active sites of the sorbent.<sup>5</sup> Collection efficiency drops drastically when the active sites become saturated.

Sample stability becomes increasingly important with increasing length of time between sampling and analysis (see Discussion Box: Air Quality Sampling in the Gulf of Mexico). Effects of temperature, trace contaminants, and chemical reactions can cause the collected species to be lost from the collection medium or to undergo a transformation that will prevent its recovery. Nearly 100% recovery is also required because a variable recovery rate will prevent quantification of the analysis. Interference should be minimal and, if present, well understood.

### AIR SAMPLING IN THE GULF OF MEXICO

The Deepwater Horizon incident oil spill occurred about 52 mi southeast of Venice, Plaquemines Parish, Louisiana (28.73667°N, -88.38722°W).<sup>6</sup> The source was a leaking production well and a release of diesel fuel caused by damage from the sinking of the Transocean Deepwater Horizon drill rig at British Petroleum (BP) Canyon 252. Oil leaked from the spill was transported by wind and wave action. Although most of the publicity and concern following the Deepwater Horizon Incident off the coast

of Louisiana had to do with water and beach contamination, the risks from airborne pollutants also had to be addressed. The Dallas Regional Office of the U.S. EPA conducted air sampling and air monitoring following the near Venice, Plaquemines Parish, Louisiana. The airborne spectral photometric environmental collection technology (ASPECT) airborne monitoring system be prepared to deploy to collect data regarding emissions and release tracking. The goal of this mission is to collect data over

(Continued)

## AIR SAMPLING IN THE GULF OF MEXICO (cont'd)

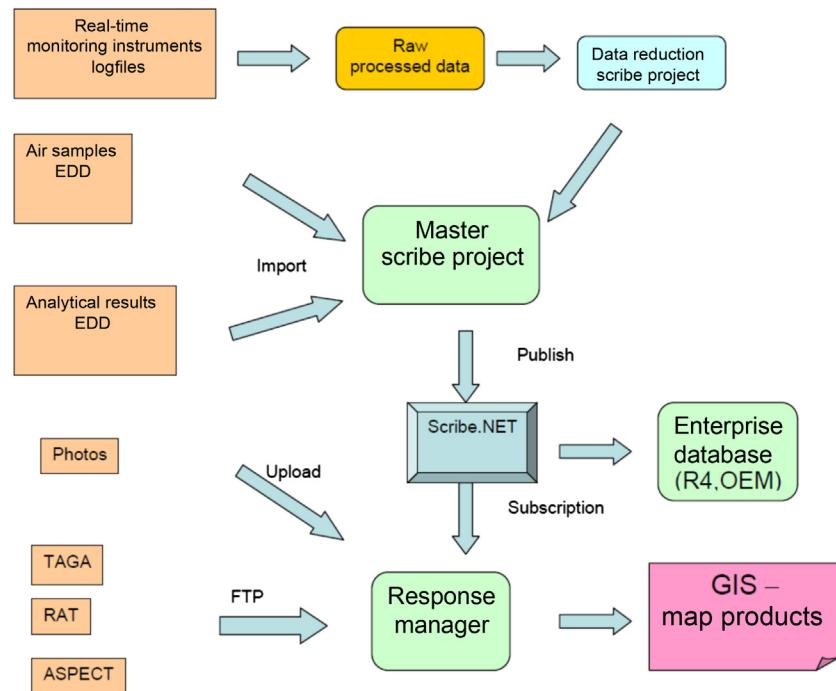
the source area (sunken rig) to establish a chemical fingerprint of the release source, collect data over the site of an in situ burn of contained oil to provide information on burn effectiveness, and a higher altitude photo reconnaissance to cover a broader area of the oil release.

The air monitoring and sampling were needed to confirm the presence of fine particulates (2.5 µm and smaller) and vapors, i.e. volatile organic compounds (VOCs), hydrogen sulfide ( $H_2S$ ) and carbon monoxide (CO) in air resulting from the off shore oil release and the in situ burning of the oil on the Gulf of Mexico. The data were needed to evaluate the potential impact from inhalation by people responding to the spill and citizens living in the area affected by air quality impacts from the spill.

Given the chemical makeup of crude oil, aromatic organic compounds would likely make up the chemical plume in the atmosphere. The plume can be represented by a simple substituted benzene, i.e. toluene, benzene with a single methyl group ( $C_7H_8$ ). The Agency for Toxic Substance and Disease Registry (ATSDR) recommended the Acute Exposure Guidance Level of 200 parts per

million (ppm) toluene for an 8-h average to be a conservative, public health action level. As a screening level for occupancy, the ATSDR recommended using EPA's Reference Concentration of (RFC) equivalent, i.e. 1 ppm toluene. The RFC is based on a subchronic human occupational study that matches the projected exposure duration.<sup>7</sup> Exposure duration is very difficult to predict in a disaster, especially one like the Gulf spill, where numerous efforts at capping the spill were unsuccessful and with each failure, the prospects of longer exposures increased.

Aromatic organic compounds are present as both aerosols and vapor phase. Given the characteristic of the crude oil (e.g. no polycyclic aromatic hydrocarbons and no paraffins), most of the constituents would be expected to be alkanes. Thus, ATSDR recommended using the Department of Energy's Temporary Emergency Exposure Limit (TEEL-0) of 50 ppm for a 1-h average as an action level for considering protective measures for VOCs in air. As a screening level for occupancy, ATSDR recommended the chronic inhalation minimum risk level (MRL) of 0.6 ppm for *n*-hexane. The MRL is based on human occupational studies with an uncertainty factor of 100. The actual plume was likely a



**FIGURE 25.4 Workflow of data collected in atmosphere about the Gulf of Mexico during the Deepwater Horizon incident.** ASPECT = airborne spectral photometric environmental collection technology; EDD = electronic data delivery; GIS = geographic information system; RAT = rapid assessment tool; TAGA = trace atmospheric gas analyzer. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 7.

## AIR SAMPLING IN THE GULF OF MEXICO (*cont'd*)

mixture, so the most representative sampling method could be considered to be a broad spectrum real-time air monitoring device for total organic compounds. A reading above 50 ppm was deemed to indicate the need for protective measures.<sup>8</sup>

One of the options for handling spilled crude oil involved combustion in place, i.e. in situ burning. When burning, the ATSDR recommended using of the action levels of PM<sub>2.5</sub> and PM<sub>10</sub> under the National Ambient Air Quality Standards (NAAQS), i.e. 35 and 150 µg m<sup>-3</sup>, respectively, would be considered safe. Concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> approaching the Clean Air Act (CAA) Significant Harm Level of 350 and 600 µg m<sup>-3</sup>, respectively, warranted the potential needed for protective measures to reduce exposure.<sup>8</sup>



FIGURE 25.5 Air monitoring station near Grand Isle State Park, Grand Isle, Louisiana. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 10.

The U.S. EPA obtained atmospheric measurements using the ASPECT, which provides photographic and infrared imagery, along with chemical, geospatial and radiological data at nearly real-time.<sup>9</sup> The air pollutant suite of sensors is mounted in a twin engine aircraft and uses the principles of remote passive infrared detection to image, map, identify, and quantify chemical vapors and plumes. The one-half mile wide infrared imager coupled high-speed spectrometry allowed plume measurements to be taken at a rate of about two square miles per minute.<sup>9</sup>

The data gathered from the air pollutant sensor suite were processed according to the workflow in Figure 25.4. This consisted of real-time monitoring; sampling and analytical data gathering; trace atmospheric gas analyzer (TAGA) results; geographic information system (GIS) data; and aerial photography.

In addition to the aircraft sensors, atmospheric pollution from the spill was measured at stationary monitoring sites (Figure 25.5). Air quality samples were collected using portable high-level screening monitors and from portable particle pollution monitors for total VOCs, hydrogen sulfide (H<sub>2</sub>S), and PM<sub>10</sub>. In addition canisters and cartridges were used to collect air samples. These samples provided measurements of VOCs and polycyclic aromatic hydrocarbons.<sup>10</sup>

Near the spill site, the lower layer of the atmosphere (from the surface to about 600 m) effectively trapped most of the air pollutants emitted from the surface. Thus, organic compounds from the spill and the products of their atmospheric chemical processing were present in the atmosphere (Table 25.1). Directly downwind from the spill site, aromatic compounds increased compared to upwind readings (benzene and toluene) measurements were twice those for a polluted city (e.g. maximum observed concentrations in Los Angeles).

Most of the results for organic compounds were below 20 ppb (by volume). The chemical constituency of these particles was mainly organic compounds (similar to U.S. cities with large emissions from motor vehicles). These types of comparisons are common in environmental sciences and are known as benchmarks. The highest concentrations of PM<sub>10</sub> were approximately 25 µg m<sup>-3</sup>. The highest concentrations of ozone were about 80 ppb (by volume). Most of the organic contamination was confined to a relatively narrow plume (<20 km wide) emitted by the spill site.<sup>11</sup>

**TABLE 25.1** Air Quality Measurements Conducted during 10 June 2010 Flight Segments. For Comparison Purposes the Last Column Shows Maximum Values Observed during a Recent Research Flight by the Same Aircraft with the Same Set of Instruments over the Los Angeles Urban Area

Variable	Units	DWH Spill Region		Downwind DWH Plume		Near Shore		Background Gulf Air		Maximum Los Angeles
		Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	
Ozone	ppbv	57	83	45	60	54	69	30	35	75
Carbon monoxide	ppbv	145	152	140	163	156	168	90	97	540
Nitrogen dioxide	ppbv	0.1	0.5	0.1	1.3	0.1	2.1	0.1	1.6	29
PANs	ppbv	0.4	1.0	0.3	0.6	0.3	0.7	0.1	0.1	
Acetaldehyde	ppbv	2.02	3.38	1.05	2.69	0.50	0.71	0.26	0.52	3.9
Benzene	ppbv	0.20	0.53	0.06	0.17	0.05	0.10	<0.01	0.06	0.47
Toluene	ppbv	0.65	2.06	0.04	0.30	0.02	0.07	0.01	0.04	1.2
C8 aromatics	ppbv	1.58	5.96	0.05	0.65	0.01	0.02	<0.01	0.02	0.87
C9 aromatics	ppbv	1.88	9.21	0.06	0.77	<0.01	0.03	<0.01	0.02	0.34
C10 aromatics	ppbv	1.06	3.78	0.03	0.41	<0.01	0.02	<0.01	0.01	***
C11 aromatics	ppbv	0.62	1.67	0.02	0.21	<0.01	0.03	<0.01	0.02	***
Naphthalene	ppbv	0.28	0.50	0.02	0.16	<0.01	0.02	<0.01	0.03	***
Total AMS PM	$\mu\text{g m}^{-3}$	14.1	18.8	14.8	25.9	7.3	14.4	2.1	3.1	18
Organic AMS PM	$\mu\text{g m}^{-3}$	11.6	16.0	12.1	23.3	4.3	11.1	0.2	0.7	7.5
Sulfate AMS PM	$\mu\text{g m}^{-3}$	1.6	2.0	1.9	2.8	2.1	4.4	1.5	2.2	
Sampling transect	Kilometers	26		92		260		53		

The concentrations do not include nonvolatile material or particles larger than about  $0.6 \mu\text{m}$  diameter. AMS = aerosol mass spectrometer; DWH = deepwater horizon; PM = particulate matter; PAN = peroxyacetyl nitrates; maximum values are the maximum averages over 1 km of flight path. \*\*\*Not measured; generally the concentrations of these species are so low that they are not normally monitored.

Source: Ref. 11.

## 25.2 GASES AND VAPORS

Airborne contaminants may be found either in the gas phase or as components of a particle. The gas phase air pollutants include both the criteria pollutants and air toxics. The two major goals of testing for air pollutants are identification and quantification of a sample of ambient air. Air pollution measurement techniques generally pass through evolutionary stages. The first is the qualitative identification stage. This is followed by separate collection and quantification stages. The last stage is the concurrent collection and quantification of a given pollutant. For example, the early procedures detected the presence of  $\text{SO}_2$  in ambient air by exposing a lead peroxide candle for a period of time and then measuring the amount of lead sulfate formed. Because the volume of air in contact with the candle was not measured, the technique could not quantify the amount of  $\text{SO}_2$  per unit volume of air.

The next stage in the evolution of  $\text{SO}_2$  measurement was to pass a known volume of ambient air through an

absorbing solution in a container in the field and then returning this container to the laboratory for a quantitative determination of the amount of absorbed  $\text{SO}_2$ . The United Nations Environmental Program–World Health Organization's worldwide air sampling and analysis network used this method for  $\text{SO}_2$ , the only gaseous pollutant measured by the network. The final evolutionary step has been the concurrent collection and quantification of  $\text{SO}_2$ . An example of this is the flame photometric  $\text{SO}_2$  analyzer, in which  $\text{SO}_2$ -laden air is fed into an  $\text{H}_2$  flame, and light emissions from electronically excited combustion products are detected by a photomultiplier tube. Prior calibration of the analyzer permits the rapid determination of  $\text{SO}_2$ . This is but one of the many methods available for the measurement of  $\text{SO}_2$ . In the United States, the reference method for detecting  $\text{SO}_2$  in the ambient air is known as the pararosaniline method, which is described in detail in Section 25.2.1.6.4 of this chapter.

Hundreds of chemical species are present in urban atmospheres. The gas-phase air pollutants most

commonly monitored are CO, O<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub>, and nonmethane volatile organic compounds (NMVOCs). All of these are NAAQS criteria pollutants, although NMVOCs is not directly regulated, is measured as an indication of the hydrocarbons as a component of ground-level O<sub>3</sub>. Indeed, the measurement of specific hydrocarbon compounds has become routine in the United States for two reasons: (1) their potential role as air toxics and (2) the

need for detailed hydrocarbon data for control of urban ozone concentrations. Hydrochloric acid (HCl), ammonia (NH<sub>3</sub>), and hydrogen fluoride (HF) are measured less often, depending on the sources in an airshed. Calibration standards and procedures are available for all of these analytic techniques, ensuring the quality of the analytical results. See Table 25.2 for a summary of emission limits for one particular source class, incinerators.

**TABLE 25.2** Sampling Required to Demonstrate Compliance with Emission Limits for the New Source Performance Standards (NSPS) for Hospital/Medical/Infectious Waste Incinerators (HMIWI), Pursuant to the U.S. Court of Appeals for the District of Columbia Circuit Ruling of March 2, 1999, Remanding the Rule to the U.S. Environmental Protection Agency for Further Explanation of the Agency's Reasoning in Determining the Minimum Regulatory "Floors" for New and Existing HMIWI

Pollutant (Units)	Unit Size*	Proposed Demand Limit for Existing HMIWI <sup>§</sup>	Proposed Demand Limit for New HMIWI <sup>§</sup>
HCl (ppmv)	L, M, S	78 or 93% reduction <sup>¶</sup>	15 <sup>¶</sup> or 99% reduction <sup>¶</sup>
	SR	3100 <sup>¶</sup>	N/A <sup>  </sup>
CO (ppmv)	L, M, S	40 <sup>¶</sup>	32
	SR	40 <sup>¶</sup>	N/A <sup>  </sup>
Pb (mg/dscm)	L, M	0.78 or 71% reduction	0.060 or 98% reduction <sup>¶</sup>
	S	0.78 or 71% reduction	0.78 or 71% reduction
	SR	8.9	N/A <sup>  </sup>
Cd (mg/dscm)	L, M	0.11 or 66% reduction <sup>¶</sup>	0.030 or 93% reduction
	S	0.11 or 66% reduction <sup>¶</sup>	0.11 or 66% reduction <sup>¶</sup>
	SR	4 <sup>¶</sup>	N/A <sup>  </sup>
Hg (mg/dscm)	L, M	0.55 <sup>¶</sup> or 87% reduction	0.45 or 87% reduction
	S	0.55 <sup>¶</sup> or 87% reduction	0.47 or 87% reduction
	SR	6.6	N/A <sup>  </sup>
PM (gr/dscf)	L	0.015 <sup>¶</sup>	0.009
	M	0.030 <sup>¶</sup>	0.009
	S	0.050 <sup>¶</sup>	0.018
	SR	0.086 <sup>¶</sup>	N/A <sup>  </sup>
CDD/CDF, total (ng dscm <sup>-1</sup> )	L, M	115	20
	S	115	111
	SR	800 <sup>¶</sup>	N/A <sup>  </sup>
CDD/CDF, TEQ (ng dscm <sup>-1</sup> )	L, M	2.2	0.53
	S	2.2	2.1
	SR	15 <sup>¶</sup>	N/A <sup>  </sup>
NO <sub>x</sub> (ppmv)	L, M, S	250 <sup>¶</sup>	225
	SR	250 <sup>¶</sup>	N/A <sup>  </sup>
SO <sub>2</sub> (ppmv)	L, M, S	55 <sup>¶</sup>	46
	SR	55 <sup>¶</sup>	N/A <sup>  </sup>

\* L: large; M: medium; S: small; SR: small rural.

<sup>§</sup>All emission limits are measured at 7% oxygen.

<sup>¶</sup>No change proposed.

<sup>||</sup>Not applicable.

### 25.2.1 Gas and Vapor Phase Measurement Methods

Gaseous pollutants are generally collected by the sampling systems shown in [Figure 25.3](#). The sampling manifold's only function is to transport the gas from the manifold inlet to the collection medium in an unaltered state. The manifold must be made of nonreactive material. Tests of material for manifold construction can be made for specific gases to be sampled. In most cases, glass or Teflon will not adsorb or react with the gases. No condensation should be allowed to occur in the sampling manifold.

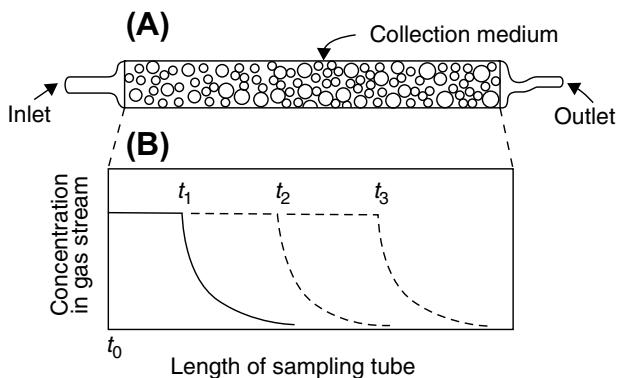
The volume of the manifold and the sampling flow rate determine the time required for the gas to move from the inlet to the collection medium. This residence time can be minimized to decrease the loss of reactive species in the manifold by keeping the manifold as short as possible.

The collection medium for gases can be liquid or solid sorbents, an evacuated flask, or a cryogenic trap. Liquid collection systems take the form of bubblers which are designed to maximize the gas–liquid interface. Each design is an attempt to optimize gas flow rate and collection efficiency. Higher flow rates permit shorter sampling times. However, excessive flow rates cause the collection efficiency to drop below 100%.

#### 25.2.1.1 Extractive Sampling

When bubbler systems are used for collection, the gaseous species generally undergoes hydration or reaction with water to form anions or cations. For example, when  $\text{SO}_2$  and  $\text{NH}_3$  are absorbed in bubblers they form  $\text{HSO}_3^-$  and  $\text{NHO}_4^+$ , and the analytical techniques for measurement actually detect these ions. [Table 25.3](#) gives examples of gases which may be sampled with bubbler systems.

Bubblers are more often utilized for sampling programs that do not require a large number of samples or frequent sampling. The advantages of these types of sampling systems are low cost and portability. The disadvantages are the high degree of skill and careful handling needed to ensure quality results. Solid sorbents such as Tenax, XAD, and activated carbon (charcoal) are used to sample hydrocarbon gases by trapping the species on the active sites of the surface of the sorbent. [Figure 25.6](#) illustrates the loading of active sites with increasing sample time. It is critical that the breakthrough sampling volume, the amount of air passing through the tube that saturates its absorptive capacity, not be exceeded. The breakthrough volume is dependent on the concentration of the gas being sampled and the absorptive capacity of the sorbent. This means that the user must have an estimate of the upper limit of concentration for the gas being sampled.



**FIGURE 25.6 Solid sorbent collection tube.** (A) The tube is packed with a granular medium. (B) As the hydrocarbon-containing air is passed through the collection tube at  $t_1$ ,  $t_2$ , and  $t_3$ , the collection medium becomes saturated at increasing lengths along the tube.

After the sample has been collected on the solid sorbent, the tube is sealed and transported to the analytical laboratory. To recover the sorbed gas, two techniques may be used. The tube may be heated while an inert gas is flowing through it. At a sufficiently high temperature, the absorbed molecules are desorbed and carried out of the tube with the inert gas stream. The gas stream may then be passed through a preconcentration trap for injection into a gas chromatograph for chemical analysis. The second technique is liquid extraction of the sorbent and subsequent liquid chromatography. Sometimes a derivatization step is necessary to convert the collected material chemically into compounds which will pass through the column more easily, e.g. conversion of carboxylic acids to methyl esters. Solid sorbents have increased our ability to measure hydrocarbon species under a variety of field conditions. However, this technique requires great skill and sophisticated equipment to obtain accurate results. Care must be taken to minimize problems of contamination of the collection medium, sample instability on the sorbent and incomplete recovery of the sorbed gases.

Special techniques are employed to sample for gases and particulate matter simultaneously.<sup>12</sup> Sampling systems have been developed which permit the removal of gas-phase molecules from a moving airstream by diffusion to a coated surface and permit the passage of particulate matter downstream for collection on a filter or other medium. These diffusion denuders are used to sample for  $\text{SO}_2$  or acid gases in the presence of particulate matter. This type of sampling has been developed to minimize the interference of gases in particulate sampling and vice versa.

The third technique, shown in [Figure 25.3\(C\)](#), involves collection of an aliquot of air in its gaseous state for transport back to the analytical laboratory. Use of a pre-evacuated flask permits the collection of a gas

TABLE 25.3 Collection of Gases by Absorption

Gas	Sampler	Sorption Medium	Airflow (l m <sup>-1</sup> )	Minimum Sample (l)	Collection Efficiency	Analysis	Interferences
Ammonia	Midget impinger	25 ml 0.1 N sulfuric acid	1–3	10		Nessler reagent	—
	Petri bubbler	10 ml of above	1–3	10	+95	Nessler reagent	—
Benzene	Glass bead column	5 ml Nitrating acid	0.25	3–5	+95	Butanone method	Other aromatic hydrocarbons
Carbon dioxide	Fritted bubbler	10 ml 0.1 N barium hydroxide	1	10–15	60–80	Titration with 0.05 N oxalic acid	Other acids
Ethyl benzene	Fritted bubbler or midget impinger	15 ml spectrograde isooctane	1	20	+90	Alcohol extraction, ultraviolet analysis	Other aromatic hydrocarbons
Formaldehyde	Fritted bubbler	10 ml 1% sodium bisulfite	1–3	25	+95	Liberated sulfite titrated, 0.01 N iodine	Methyl ketones
Hydrochloric acid	Fritted bubbler	0.005 N sodium hydroxide	10	100	+95	Titration with 0.01 N silver nitrate	Other chlorides
Hydrogen sulfide	Midget impinger	15 ml 5% cadmium sulfate	1–2	20	195	Add 0.05 N iodine, 6 N sulfuric acid, back-titrate 0.01 N sodium thiosulfate	Mercaptans, carbon disulfide, and organic sulfur compounds
Lead, tetraethyl, and tetramethyl	Dreschel-type scrubber	100 ml 0.1 M iodine monochloride in 0.3 N	1.8–2.9	50–75	100	Dithizone	Bismuth, thallium, and stannous tin
Mercury, diethyl, and dimethyl	Midget impinger	15 ml of above	1.9	50–75	91–95	Same as above	Same as above
	Midget impinger	10 ml 0.1 M iodine monochloride in 0.3 N hydrochloric acid	1–1.5	100	91–100	Dithizone	Copper

(Continued)

TABLE 25.3 Collection of Gases by Absorption—cont'd

Gas	Sampler	Sorption Medium	Airflow (l m <sup>-1</sup> )	Minimum Sample (l)	Collection Efficiency	Analysis	Interferences
Nickel carbonyl	Midget impinger	15 ml 3% hydrochloric acid	2.8	50–90	190	Complex with alpha-furil-dioxime	—
Nitrogen dioxide	Fritted bubbler (60–70 µm pore size)	20–30 ml Saltzman reagent*	0.4	Sample until color appears; probably 10 mL of air	94–99	Reacts with absorbing solution	Ozone in fivefold excess peroxyacetyl nitrate
Ozone	Midget impinger	1% Potassium iodide in 1 N potassium hydroxide	1	25	+95	Measures color of iodine liberated	Other oxidizing agents
Phosphine	Fritted bubbler	15 ml 0.5% silver diethyl dithiocarbamate in pyridine	0.5	5	86	Complexes with absorbing solution	Arsine, stibine, and hydrogen sulfide
Styrene	Fritted midget impinger	15 ml Spectrograde isoctane	1	20	+90	Ultraviolet analysis	Other aromatic hydrocarbons
Sulfur dioxide	Midget impinger, fritted rubber	10 ml Sodium tetrachloromercurate	2–3	2	99	Reaction of dichlorosulfito-mercurate and formaldehyde-depararosaniline	Nitrogen dioxide, <sup>§</sup> hydrogen sulfide <sup>¶</sup>
Toluene diisocyanate	Midget impinger	15 ml Marcali solution	1	25	95	Diazotization and coupling reaction	Materials containing reactive hydrogen attached to oxygen (phenol); certain other diamines
Vinyl acetate	Fritted midget impinger and simple midget impinger in series	Toluene	1.5	15	+99 (84 with fritted bubbler only)	Gas chromatography	Other substances with same retention time on column

\* 5 g sulfanilic; 140 ml glacial acetic acid; 20 ml 0.1% aqueous N-(1-naphthyl) ethylene diamine.

<sup>§</sup>Add sulfamic acid after sampling.

<sup>¶</sup>Filter or centrifuge any precipitate.

sample in a specially polished stainless steel container. By use of pressure–volume relationships, it is possible to remove a known volume from the tank for subsequent chemical analysis. Another means of collecting gaseous samples is the collapsible bag. Bags made of polymer films can be used for collection and transport of samples. The air may be pumped into the bag by an inert pump such as one using flexible metal bellows, or the air may be sucked into the bag by placing the bag in an airtight container which is then evacuated. This forces the bag to expand, drawing in the ambient air sample.

Most air pollutants are sampled by obtaining a known amount of air in a container. For vapor-phase compounds, the containers are either a canister or bag. Depending on how long it takes to fill the container, this technique provides a prolonged snapshot of an air pollutant's concentration. That is, the sample is not a point, but is a time interval. For example, if a valve allows air to enter on a 6-l canister at a rate of  $0.5 \text{ l min}^{-1}$ , the canister will be full in 12 min. Thus, if the sample begins at 5:00 p.m. on Monday, it will be full at 5:12 p.m. that day. If the concentration of 1,3-butadiene is found to be  $10 \text{ mg m}^{-3}$ , that is the concentration at that location integrated over that 12 min period during rush hour. If only a few cans are available, but a longer time is needed, e.g. 1 h during the highest traffic, the valve may be adjusted to a lower flow rate, so that the canister fills 5 times more slowly, i.e.  $0.1 \text{ l min}^{-1}$ , and the concentration is integrated over the entire hour.

If the concentrations in the 12-min canister are  $10 \text{ mg m}^{-3}$ , but the 1-h canister is found to be  $25 \text{ mg m}^{-3}$  for the same compound at the same location, this could indicate that traffic is higher after 5:12 p.m., or that a particular source (e.g. poorly maintained trucks) may appear later. Then again, this could be an anomalous event (one large source happened to pass by the sampler). For example, if three other similar sites find little difference between the 12-min and 1-h integration times, the site with the difference would probably need a few more comparisons. Finding the optimal sampling interval and the appropriate sampling locations depends on comparisons such as these.

Canisters and bags can be filled two ways. In the example above, the air in the canister had been removed and the empty canister's vacuum, pulled in the air, since fluids flow from higher to lower pressure. The canister or bag can then be returned to the laboratory whereupon the analyst removes small amounts of the contents into detectors.



**FIGURE 25.7 Six-liter summa canister.** (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. [http://www.epa.gov/region6/6pd/rcre\\_c/ca/canister.html](http://www.epa.gov/region6/6pd/rcre_c/ca/canister.html); 2013 [accessed 13.08.13].

Air pollution studies make wide use of evacuated stainless steel canisters with electropolished inner surfaces,<sup>13</sup> known as Summa canisters (Figure 25.7). The electropolishing and chemical deactivation yields an internal surface with very low chemical reactivity. These canisters are employed to sample for vapors, especially VOCs.<sup>14</sup> The VOCs sampled with Summa canisters consist of both aliphatic and aromatic hydrocarbons, including halogenated forms.<sup>15</sup> Several of these are shown in Table 25.4. This technique has also been applied to a variety of practical applications, such as indoor air quality problems. Canisters are cleaned and evacuated, so that the lower pressure inside the canister allows air to enter without the need for a sampling pump.

Many air pollutants are chemically reactive and may combine with chemicals on the surfaces inside of collection systems. Thus, stainless steel canisters are now often coated with relatively inert substances, especially fused silica, which allows them to be stored longer prior to chemical analysis.<sup>a</sup> When the canister is delivered to

<sup>a</sup> The same considerations need to be made for other air pollutant container, e.g. selecting a collection bag must consider the rate of degradation induced by the compounds that will be stored in the bag.

**TABLE 25.4** Select Organic Compounds That Can Be Collected Using Summa Canisters and Tedlar Bags

Analyte	CRQL (ppbv)
Acetone	5
Acetonitrile	5
Acetonitrile	5
Acrylonitrile	5
Benzene	2
Benzyl chloride	5
Bromodichloromethane	2
Bromomethane	5
1,3-Butadiene	5
2-Butanone	5
Chlorobenzene	2
Chlorodifluoromethane	2
Chloroethane	2
Chloroform	2
1,2-Dichlorobenzene	
<i>trans</i> -1,2-Dichloroethene	2
1,2-Dichloropropane	2
Dichlorofluoromethane	2
<i>t</i> -1,2-Dichloropropene	2
<i>cis</i> -1,2-Dichloropropene	5
1,2-Dichloro-1,1,2,2-tetrafluoroethane	2
<i>n</i> -Pentane	2
Propylene	5
Styrene	5
1,2,4-Trichlorobenzene	2
1,1,1-Trichloroethane	5
1,1,2-Trichloroethane	5
1,1,2,2-Tetrachloroethane	2
Tetrachloroethene	5
Tetrachloromethane (carbon tetrachloride)	2
Toluene	5
Trichloroethene	2
Trichlorofluoromethane	2
1,1,2-Trichloro-1,2,2-trifluoroethane	2
Xylenes ( <i>m</i> - and <i>p</i> -)	5
Xylene ( <i>o</i> -)	5

CRQL = contract required quantitation limit; ppbv = parts per US billion by volume. The CRQL is the lowest concentration that must be detected by an EPA Superfund contract laboratory.

Source: U.S. Environmental Protection Agency. <http://www.epa.gov/region9/qa/pdfs/aircrf.pdf>; 2013 [accessed 13.08.13].

the laboratory, it is pressurized with nitrogen, and the contents are analyzed by gas chromatography/mass spectrometry (GC/MS).

Several canisters can be used to provide a map of air pollution. The number of canisters per unit area is known as the sampling density. Highly reactive contaminants with short half-lives may require greater sampling density than less reactive pollutants, since the former may breakdown in relatively short distances from their sources.

The amount of time that a sample can be stored in a container varies by the type of compounds and the container. For example, the U.S. EPA recommends that VOCs not be held in a Summa canister for more than 14 days from collection and 12 days from the receipt at the laboratory. In tedlar bags, the holding times are much shorter, i.e. 40 h from collection and 36 h from receipt by the laboratory. Also, the conditions of storage are usually specified. For VOCs, both bags and canisters can be preserved at ambient temperatures and near atmospheric pressure. However, for some highly reactive compounds, refrigeration, and other preservation techniques will be required.

### 25.2.1.2 *In Situ Sampling and Analysis*

The fourth sampling technique involves a combination of sampling and analysis. The analytical technique is incorporated in a continuous monitoring instrument placed at the sampling location. Most often, the monitoring equipment is located inside a shelter such as a trailer or a small building, with the ambient air drawn to the monitor through a sampling manifold. The monitor then extracts a small fraction of air from the manifold for analysis by an automated technique, which may be continuous or discrete. Instrument manufacturers have developed automated *in situ* monitors for several air pollutants, including SO<sub>2</sub>, NO, NO<sub>2</sub>, O<sub>3</sub>, and CO. This approach is also being increasingly applied for organic pollutants. For example, real-time GC-MS are being used to monitoring a wide range of organic compounds, including air toxics.

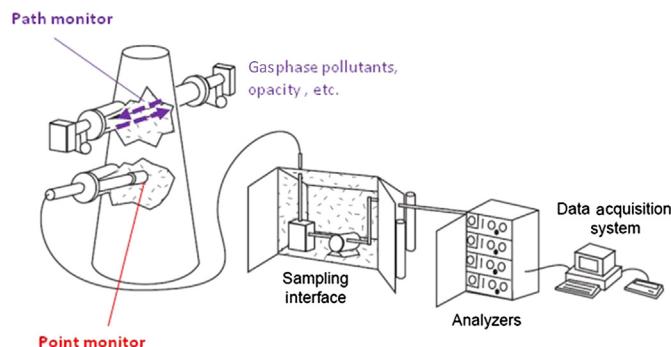
Continuous emission monitoring (CEM) is an important type of combined real-time sampling. Indeed, it is increasingly used in the source applications discussed in Chapter 24. Regulatory agencies are increasingly requiring enhanced and periodic measurements to ensure compliance with emission standards for specific pollutants. In the United States, these are known as the “compliance assurance monitoring (CAM) rule”. The rule is designed to ensure proper operation of air pollution control equipment. The CAM rule has two general means of compliance: direct and indirect. Direct compliance assurance can be accomplished using CEM. Indirect compliance assurance is based on measurements of key parameters related to how well the equipment

is operating (e.g. temperature, flow, pressure drop, voltage changes).<sup>16</sup> The CAA requires CEM for large sources and sources that must be monitoring under New Source Review (see Chapter 3).

The CEM is an integrated system that collects samples directly from the stack or other air pollutant conveyance to the atmosphere. The system consists of the equipment needed to determine a pollutant's concentration or emission rate. The system components shown in Figure 25.8 are: (1) the sampling and conditioning system; (2) chemical analyzers; (3) the data acquisition system (DAS); and (4) the controller system. In addition to measuring various gas and particulate phase pollutant, CEM also is used for opacity, and volumetric flow rates.

There are two basic types of CEMS: extractive and in situ. The monitor and analyzers of an in situ CEM are located within the stack. Extractive CEM systems capture a sample from within a stack, condition the sample (e.g. remove moisture and impurities) and move the sample to the analyzer. As shown in Figure 25.8, point measurements measure pollutant concentrations at a single precise point where the sampling cell is located, whereas path measurements are taken across a given path in the emissions stream. Path readings are often from a signal across the stack and reflecting it back to a detector near the source of the signal. The measured concentrations crossing that path are averaged over a given period of time.

Numerous gaseous compounds are being sampled with CEM, including  $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{O}_2$ , total hydrocarbons, and hydrochloric acid (HCl). This concept also applied outside of the stack. For example, several open-path, continuous monitoring methods are being used successfully for a wide range of pollutants in the ambient air. These are discussed later in this chapter.



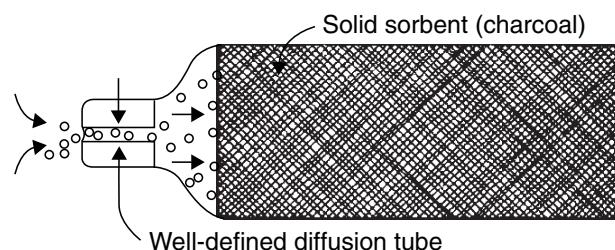
**FIGURE 25.8 Components and flow of a continuous emission monitoring (CEM) system for more than one gas-phase pollutant.** (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: U.S. Environmental Protection Agency. EPA air pollution control cost manual. 6th ed. EPA/452/B-02-001; 2002.

### 25.2.1.3 Passive Sampling Systems

Passive or static sampling systems are those that do not have an active air-moving component, such as the pump, to pull a sample to the collection medium. This type of sampling system has been used for over 100 years. Examples include the lead peroxide candle used to detect the presence of  $\text{SO}_2$  in the atmosphere and the dust fall bucket and trays or slides coated with a viscous material used to detect particulate matter. This type of system suffers from inability to quantify the amount of pollutant present over a short period of time, i.e. less than 1 week. The potentially desirable characteristics of a static sampling system have led to further developments in this type of technology to provide quantitative information on pollutant concentrations over a fixed period of time. Static sampling systems have been developed for use in the occupational environment and are also used to measure the exposure levels in the general community, e.g. radon gas in residences.

Generally, passive systems apply to gases and vapors, since particles are assumed not to diffuse. The advantages of static sampling systems are their portability, convenience, reliability, and low cost. The systems are lightweight and can be attached directly to individuals. Nonstatic sampling systems can, of course, also be attached to individuals, but are less convenient because the person must carry a battery-powered pump and its batteries. Static sampling systems are very reliable, and the materials used limit the costs to acceptable levels.

Two principles are utilized in the design of static samplers: diffusion and permeation.<sup>17,18</sup> Since most of the atmosphere consists of molecular nitrogen and oxygen, samplers applying the diffusion principle depend on the molecular interactions of  $\text{N}_2$ ,  $\text{O}_2$ , and the trace pollutant gases of interest. If a concentration gradient can be established for the trace pollutant gas, under certain conditions the movement of the gas will be proportional to the concentration gradient (Fick's law of diffusion), and a sampler can be designed to take advantage of this technique. Figure 25.9 illustrates this principle. The sampler has a well-defined inlet, generally with a cylindrical shape, through which the pollutant gas must diffuse. At the end of the tube, a collection medium



**FIGURE 25.9 Passive sampler based on the diffusion principle.**

removes the pollutant gas for subsequent analysis and maintains a concentration gradient between the inlet of the tube and the collection medium. The mathematical relationship (Fick's law) describing this type of passive sampler is given by:

$$R = -DA \left( \frac{dC}{dx} \right) \quad (25.1)$$

where,  $R$  is the rate of transport by diffusion in moles per second,  $D$  is the diffusion coefficient in square centimeters per second,  $A$  is the cross-sectional area of the diffusion path in square centimeters,  $C$  is the concentration of species in moles per cubic centimeter, and  $x$  is the path length in centimeters.

The ability of gases to permeate through various polymers at a fixed rate depending on a concentration gradient has been used to create static samplers. This principle was originally developed to provide a standard calibration source of trace gas by putting that gas in a polymer tube under pressure and letting the material diffuse or permeate through the wall to the open atmosphere. Permeation samplers operate in the reverse direction. Figure 25.10 illustrates this type of system. A thin film membrane is open to the atmosphere on one side and to a collection medium on the other. A pollutant gas in the atmosphere diffuses through the membrane and is collected in the medium. The mathematical relationship for a permeation sampler is given by:

$$k = \left( \frac{Ct}{m} \right) \quad (25.2)$$

where  $k$  is the permeation constant,  $C$  is the concentration of gas in parts per million,  $t$  is the time of exposure, and  $m$  is the amount of gas absorbed in micrograms.

Permeation systems (Figure 25.10) can be calibrated in the laboratory and then used in the field for sample

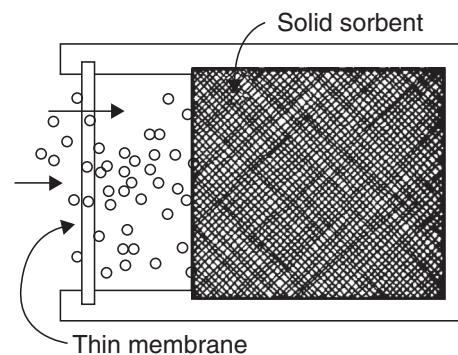


FIGURE 25.10 Passive sampler based on the permeation principle.

collection for a fixed period of time, e.g. 8 h or 7 days. The sampler is returned to the laboratory for analysis. These systems can be made for specific compounds by selecting the appropriate collection medium and the polymer membrane (Table 25.5).

#### 25.2.1.4 Open-Path Technologies for Gas-Phase Air Pollutants

A number of open-path technologies are being used to detect and quantify air pollution in the ambient air. These include tunable lasers, differential absorption techniques, and Fourier transform approaches.

The tunable diode laser (TDL) provides real-time concentration measurements for several air pollutants (Table 25.6). The TDL requires only minimal maintenance and no consumables, and is user friendly (e.g. not sensitive to common vibration levels, minimal drift, frequent calibration unnecessary, immune to ambient relative humidity and temperature changes and laser intensity fluctuations, no sample preconditioning or treatment required before analysis, simple field deployment

TABLE 25.5 Permeation Samplers for Selected Gases

Gas	Membrane	Sorber	Sensitivity
Chlorine	Dimethyl silicone (DMS) (single-backed)	Buffered (pH 7) fluorescein, 0.005% NaBr (0.31%)	0.013 ppm (8-h exposure)
Sulfur dioxide	DMS (single-backed)	Tetrachloromercurate (II)	0.01 ppm (8-h exposure)
Vinyl chloride	DMS (single-backed)	Activated charcoal (CS <sub>2</sub> desorption)	0.02 ppm (Linear to 50 ppm +)
Alkyl lead	DMS (unbacked)	Silica gel (ICl desorption)	0.2 µg
Benzene	Silicon polycarbonate	Activated charcoal (CS <sub>2</sub> desorption)	0.02 ppm (8-h exposure)
Ammonia	Vinyl silicone	0.6% Boric acid	0.4 ppm (8-h exposure)
Hydrogen sulfide	DMS (single-backed)	0.02 N NaOH, 0.003 M EDTA	0.01 ppm
Hydrogen cyanide	DMS (single-backed)	0.01 N NaOH	0.01 ppm (8-h exposure)

Source: Ref. 18.

**TABLE 25.6** Detection Limits for Airborne Compounds Quantified Using Tunable Diode Laser Technologies

Gaseous Compounds Measured by OP-TDL Systems	Approximate $\lambda$ (nm)	Reported Detection Limit (ppm-m)
Ammonia	760, 1500	0.5–5.0
Carbon monoxide	1570	40–1000
Carbon dioxide	1570	40–1000
Hydrogen chloride	1790	0.15–1
Hydrogen cyanide	1540	1.0
Hydrogen fluoride	1310	0.1–0.2
Hydrogen sulfide	1570	20
Methane	1650	0.5–1
Nitric oxide	1800	30
Nitrogen dioxide	680	0.2
Oxygen	760	50
Water	970, 1200, 1450	0.2–1.0
Acetylene	1520	*
Ethylene	1693	*
Formaldehyde	1930	*
Hydrogen bromide	1960	*
Hydrogen iodide	1540	*
Nitrous oxide	2260	*
Phosphine	2150	*
Propane	1400, 1500, 1700	*

Notes:  $\lambda$  = tuned wavelength; \* = no established detection limit since these are not commonly measured.

Source: Ref. 19.

and installation, and able to use low-power optical sources). The system can handle long open paths and provides high temporal resolution, and includes a stable multipass optical cell, which is highly sensitive. Temperature and pressure controls are internal. The drawbacks of TDL are that it can only detect a single compound per laser. It is limited in the number of detectable compounds. Indeed, sensitivity is limited to those compounds with overtone absorbencies in the near- to mid-infrared range. Particulate matter and airborne objects interfere with the path.<sup>19</sup>

Differential absorption lidar (DIAL) is used to detect concentrations of gases within a transect in the atmosphere. Lidar is an acronym for light detection and ranging, and the technique is used for measuring physical characteristics of the atmosphere.<sup>20</sup> DIAL measurements consist of probing the atmosphere with pulsed laser radiation at two wavelengths. One wavelength is

efficiently absorbed by the trace gas, and the other wavelength is less efficiently absorbed. The radiation source projects packets of energy through the atmosphere, which interact with the trace gas. The optical receiver collects radiation backscattered from the target. By controlling the timing of source pulses and processing of the optical receiver signal, one can determine the concentration of the trace gas over various distances from the analyzer. This capability permits three-dimensional mapping of pollutant concentrations. Applications are plume dispersion patterns and three-dimensional gaseous pollutant profiles in urban areas.

The DIAL system provides spatially resolved pollutant concentration in two dimensions, in a relatively short period of time. They are deployable in many different applications and configurations, and are quite portable. The path lengths are generally between 1 and 3 km, but can be of varying lengths. For example, near a facility's fence line, the paths may be shorter to determine differences in concentrations at various directions from the source and under different wind directions.

Numerous air pollutants are detected with DIAL. SO<sub>2</sub> and O<sub>3</sub> are detected by an ultraviolet DIAL system operating at wavelengths near 300 nm.<sup>21</sup> Tunable infrared CO<sub>2</sub> lasers are used in applications of IR-DIAL systems (Figure 25.11) which are capable of measuring a number of gases,<sup>22</sup> including SO<sub>2</sub>, CO, hydrochloric acid (HCl), methane (CH<sub>4</sub>), CO<sub>2</sub>, H<sub>2</sub>O, nitrous oxide (N<sub>2</sub>O), ammonia (NH<sub>3</sub>), and hydrogen sulfide (H<sub>2</sub>S). The number of air toxics measured by DIAL is increasing (see Table 25.7).<sup>19</sup> The components of this type of system are shown in Figure 25.12. The laser source is

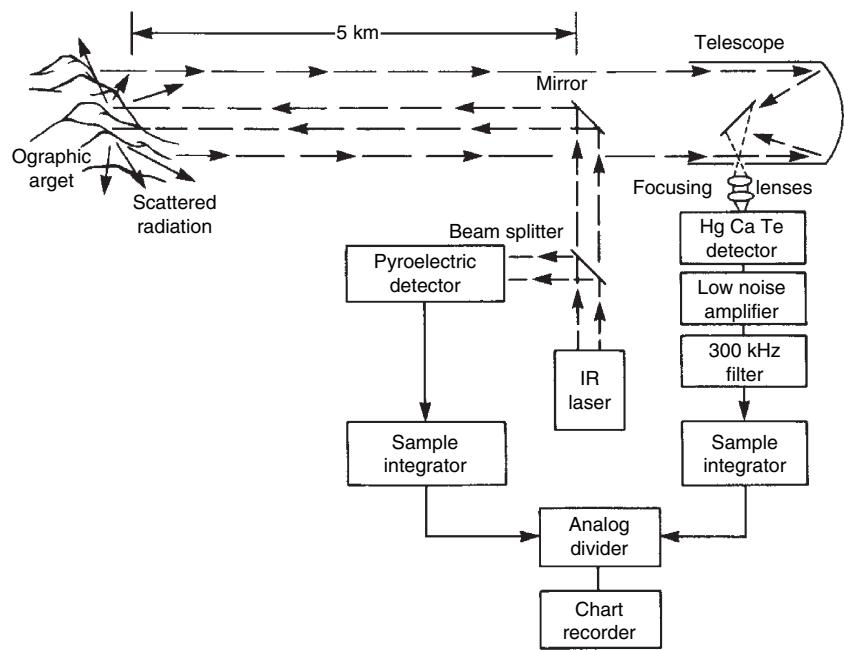
**TABLE 25.7** Air Toxics Detected Using Differential Absorption Lidar (DIAL)

Species Measured by DIAL	Concentration Sensitivity	Maximum Range
Benzene	10 ppb	800 m
Sulfur dioxide	10 ppb	3 km
Toluene	10 ppb	800 m
Ethane	20 ppb	800 m
Ethylene	10 ppb	800 m
Methane	50 ppb	1 km
General hydrocarbons	40 ppb	800 m
Hydrogen chloride	20 ppb	1 km
Methanol	200 ppb	500 m

Notes: Concentration sensitivities for measurements of a 50 m wide plume at a range of 200 m, under typical meteorological conditions (from National Physical Laboratory (NPL), Middlesex, UK). The range value represents the typical working maximum range for the NPL DIAL system.

Source: Ref. 19.

**FIGURE 25.11 An infrared-DIAL system.**  
Source: Murray, EA and Van der Laan, JE. *Appl. Opt.* 1978; 17: 81-817.



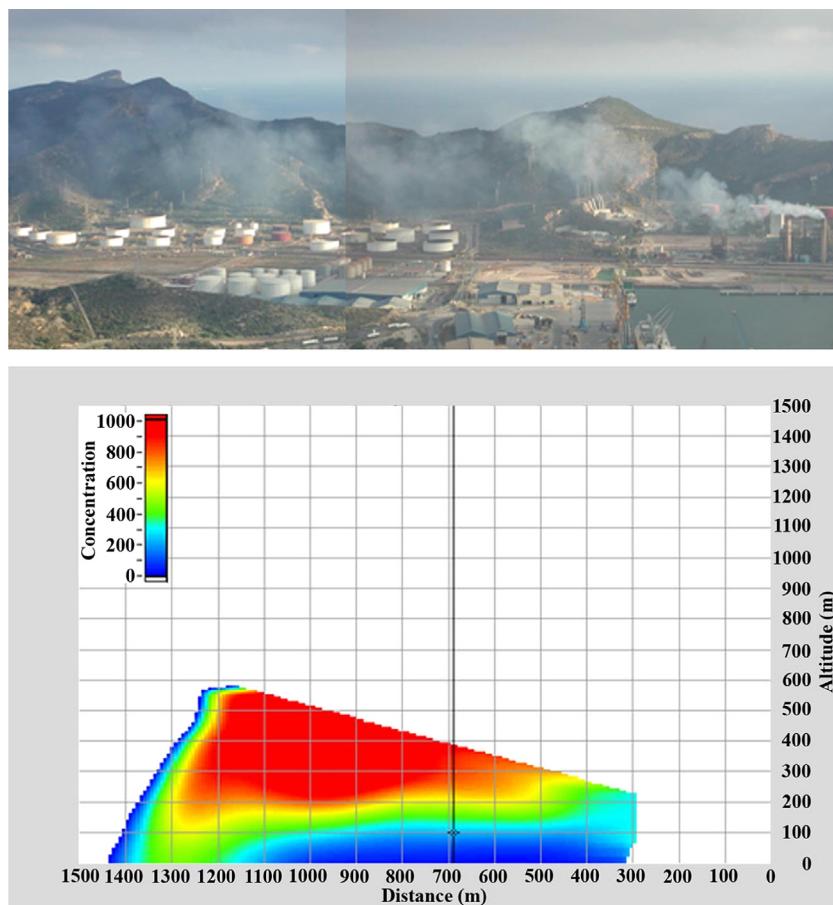
switched between the low-absorption and high-absorption frequencies for the trace gas to be detected.<sup>23</sup> The system is pointed toward a target, and focusing lenses are used to collect the returning signal. The beam splitter diverts a portion of the transmitted beam to a detector. The backscattered and transmitted pulses are integrated to yield direct current electrical signals. Examples of lidar readings for toluene and SO<sub>2</sub> are shown in Figures 25.12 and 25.13, respectively.

The DIAL system is limited to those chemical species with the unique chemical properties required to be detected. For example, only a few wavelengths are

measured. Often, spectral artifacts appear at the same energy spectrum as the pollutant of concern, but the specific chemical causing the interference cannot be identified.<sup>19</sup> This could lead to positive bias (i.e. the peak will be higher than the peak that would have been present if only the pollutant of concern were present). The reported concentration is the maximum concentration detected in a cell in the measurement plane. The path is one-dimensional, but the measurement plane is two dimensional. Thus, the resolution of the planes can be calculated from the DIAL system resolution. For example, if the path is 3.75 m, each cell is 3.75 m square.

**FIGURE 25.12 Screenshot from lidar system, showing the backscatter signal of a pair of wavelengths used to measure toluene.** A known amount of toluene was released in a chamber and measured 275 m from the lidar. The blue line represents the  $\lambda_{\text{on}}$ . The red line is  $\lambda_{\text{off}}$ , and, it is unaffected by the presence of toluene. (For color version of this figure, the reader is referred to the online version of this book.) Moreno J, Moreno-Grau S, García-Sánchez A. Lidar probes air pollution. SPIE Newsroom. February 21, 2008. doi: 10.1117/2.1200702.1096.

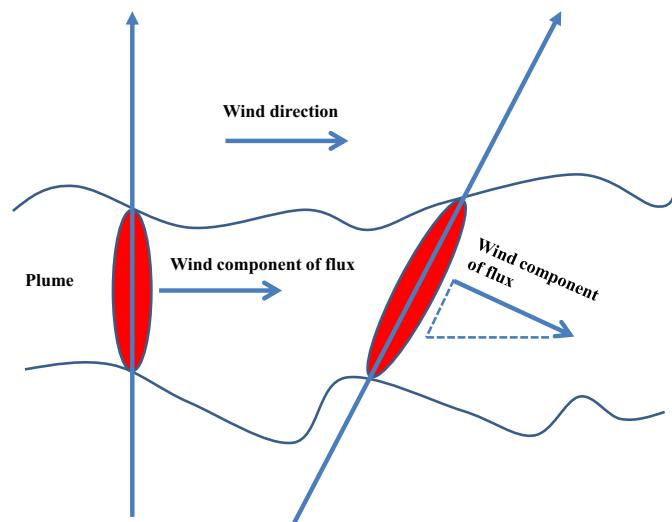




**FIGURE 25.13** Lidar measurement of concentrations of sulfur dioxide ( $\mu\text{g m}^{-3}$ ) downwind of an electric power generating facility. The lidar was located beside the chimneys. Photo was taken during the lidar measurement. (For color version of this figure, the reader is referred to the online version of this book.) Moreno J, Moreno-Grau S, García-Sánchez A. Lidar probes air pollution. SPIE Newsroom. February 21, 2008. doi: 10.1117/2.1200702.1096.

Figure 25.14 shows how the emission rate can be calculated from DIAL readings. The concentration assigned to each cell is multiplied by the perpendicular wind field determined for that cell. The individual emission rates are summed to give the total emission rate through the plane. This figure shows two hypothetical plume calculations, i.e. the one to the left has a small plume cross-section, and therefore a small integrated emission rate, and one to the right has a larger plume cross-section, and therefore represents a larger emissions rate. Note that the peak concentration in both is similar, and indeed may even be higher in the small plume than the large plume, but the angle of the path dilutes the concentration.

Other widely used open-path technologies are the open-path infrared (IR) and differential optical absorption spectroscopy (DOAS). Open-path technologies take advantage of energy–molecule relationships. For example, the vibrational frequencies of all the IR absorbing molecules in the IR beam path are captured in the IR spectrum. Likewise, vibrational frequencies



**FIGURE 25.14** Two hypothetical plume cross-sections used for concentration calculations, i.e. the one to the left has a small plume cross-section, and therefore a small integrated emission rate, and one to the right has a larger plume cross-section, and therefore represents a larger emissions rate. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Ref. 1.

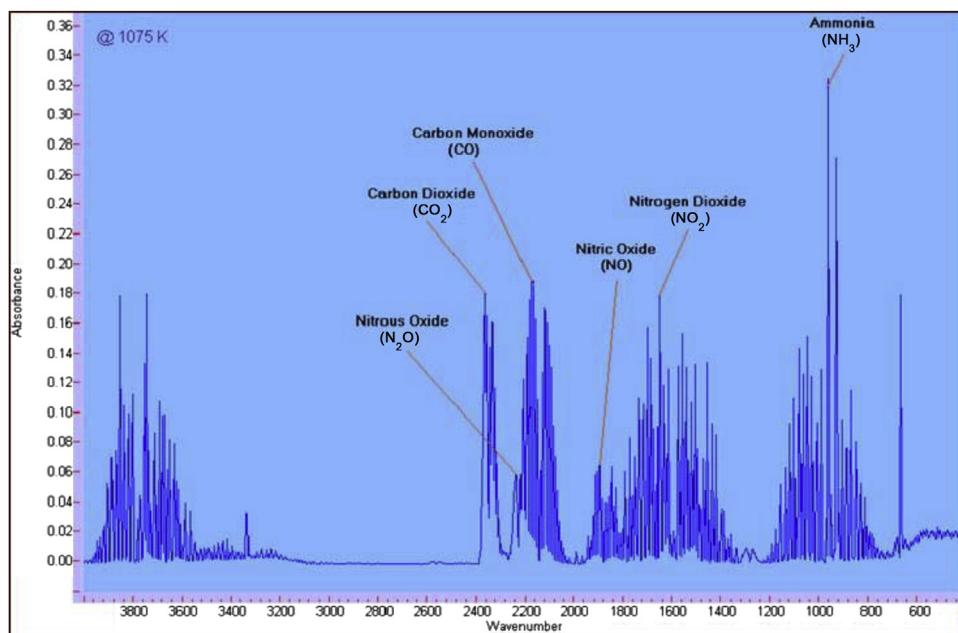


FIGURE 25.15 Fourier transform infrared absorption spectrum recorded at 1075 K. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 1.

of all the ultraviolet (UV) absorbing molecules in the UV beam path are captured in the UV spectrum, and so on. When a molecule absorbs light, the energy of the molecule is increased and the molecule is promoted from its lowest energy state (ground state) to an excited state. Light energy in a specific wavelength region of the electromagnetic spectrum stimulates molecular vibrations. Molecular species display their own characteristic vibrational structure when stimulated by that specific wavelength region of radiation. Figure 25.15 provides an example of the IR absorption spectra for nitrous oxide, CO<sub>2</sub>, CO, NO, NO<sub>2</sub>, and NH<sub>3</sub>. Vibrational frequency is represented by wave number, and the wave number and vibrational structure identify a particular molecule.

The open-path Fourier transform infrared (OP-FTIR) spectroscopy is quite versatile in that it is able to quantify many chemicals in air simultaneously, whereas most open-path systems must be tuned to a specific compound (Figure 25.16). OP-FTIR detects numerous compounds in the low ppb range. FTIR provides mean concentrations over designated path lengths. TDLs have similar detection limits as FTIR, but are an example of a compound-specific open-path approach, or at least are restricted to detecting chemicals that respond to the small frequency range they operate in. Like FTIR, open-path Raman spectroscopy can quantify many chemicals and may achieve low detection limits; however, its weak signal diminishes resolution. However, relative humidity is a major interference of FTIR but not for Raman, so Raman is likely preferred in high moisture conditions.<sup>24</sup>

The Beer–Lambert Law states that for a constant path length, the intensity of the incident, i.e. direct, light energy traversing an absorbing medium diminishes exponentially with concentration, i.e. energy absorption is proportional to chemical concentration:

$$A = eb[C] \quad (25.3)$$

where,  $A$  is the absorbency of the molecule,  $e$  is the molar absorptivity (proportionality constant for the molecule),  $b$  is the light's path length, and  $[C]$  is the chemical concentration of the molecule. Thus, the concentration of the chemical can be ascertained by measuring the light

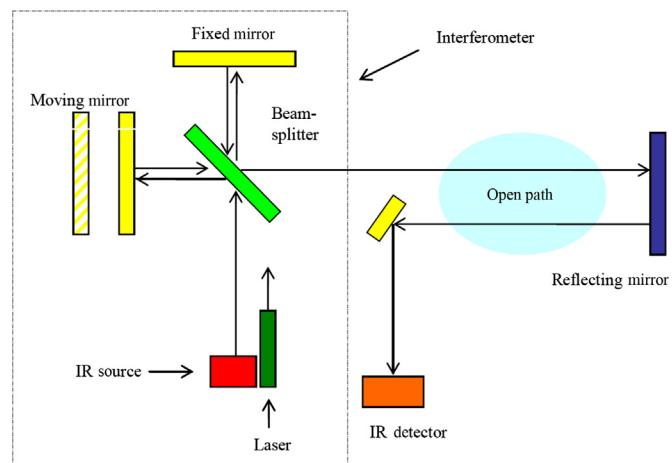
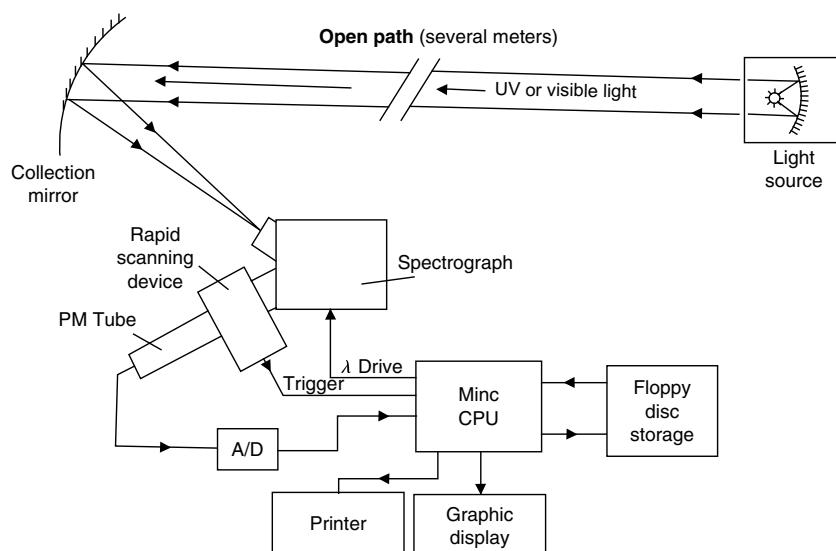


FIGURE 25.16 Schematic of open-path Fourier transform infrared (OP-FTIR) spectroscopy system. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 1.



**FIGURE 25.17** Schematic of an open-path air measurement device: differential optical adsorption spectrometer (DOAS), which measures the absorption through an atmospheric path (typically 0.5–1.5 km) of two closely spaced wavelengths of light from an artificial source. One wavelength is chosen to match an absorption line of the specific compound of interest, and the other is near that line to account for atmospheric effects (EPA/600/P-93/004 aF, pp. 3–98). The term absorption line is used to mean a wavelength that a given atom or molecule absorbs more than it does other wavelengths. For example, if ozone is the compound of interest, a wavelength would be identified which ozone absorbs more than other wavelengths. As in other open-path systems (e.g. FTIR) a beam of electromagnetic radiation (in this case, visible or ultraviolet light) containing this particular wavelength is directed at a segment (open path) of the atmosphere, and the amount of the wavelength absorbed would be measured and calibrated against a known concentration of the compound of interest. U.S. Environmental Protection Agency. Air quality criteria for ozone and photochemical oxidants. (EPA/600/P-93/004aF), July 1996.

absorbed. The FTIR instrument measures intensity in the IR spectrum; and applies the intensity signature of the returning incident spectrum, along with Beer's law, to identify and quantify compounds.

Like other open-path systems, FTIR measurements can be made actively or passively, i.e. respectively, providing its own energy or receiving it externally. In the active mode, an instrument focuses a light beam before passing it through an interferometer, which converts the light beam into a modulated signal as a function of optical path difference. When the beams are recombined, certain wavelengths recombine constructively and some destructively, which creates an interference pattern, which is called an interferogram.<sup>1</sup> The recombined IR beam then passes from the beam-splitter into the open path where a portion of the IR energy is absorbed by the gaseous compounds to be measured. The resulting IR beam reaches the IR detector where the interference pattern is detected, digitized, and transformed mathematically into a standard single beam infrared frequency spectrum using a mathematical algorithm known as a Fourier transform. The encoded light beam passes from the sending optics across the transect being measured for contaminants (i.e. the open path), then back to receiving optics and onto a detector. The detector then records the signal and mathematically derives the concentration using a Fourier transform technique. This produces a spectrum,

such as the one depicted in Figure 25.15, which can be used to identify specific contaminants and their concentrations.

The passive mode works in the same manner as the active mode, but uses no sending unit. Rather, the instrument uses an external energy source (e.g. the sun or combustion gases) to provide the infrared light. Receiving optics focus the light into the interferometer that encodes them into an interferogram format. This is then directed onto a detector for recording. As with the active approach, the detector then records the signal and mathematically derives the concentration using a Fourier transform technique to quantify the concentrations of the pollutants.

The DOAS system (Figure 25.17) quantifies concentrations of gaseous compounds by measuring the absorption of light by chemical compounds in the air, again, by applying the Beer–Lambert law. However, the wavelength is in the higher frequency wavelengths, i.e. the visible, and often in the ultraviolet (UV) range, i.e. UV-DOAS.

A positive attribute of the UV-DOAS is its extremely long path-length capability—typically 500 m with some research applications up to 10 km.<sup>25</sup> The UV-DOAS is most frequently used to measure or monitor criteria and smog-related air pollutants, and for pollutants that do not produce ideal IR absorption bands. However, because the absorption bands for

UV-DOAS are very wide, its specificity is limited, i.e. many compounds cannot be accurately quantified by UV-DOAS. In addition, N<sub>2</sub> and O<sub>2</sub> molecules in the air cause broad spectral scattering and interfere with many of the compounds that can be measured. The UV-DOAS has detection limits in the low (ppb) range, and has reached parts per trillion (ppt) in some research applications when used with optimum measurement path lengths.<sup>25</sup>

Generally at the UV, visible, and near-IR wavelengths (approximately 180–780 nm) changes occur in the energy between the bonding electrons in molecules that absorb the light. The wavelength ranges produced by UV-DOAS include the rotational and vibrational transitions caused by near-IR light, so the typical application of UV-DOAS restricts the UV light to a wavelength range of 245–380 nm. Due to the range of excitations measured, molecular absorption bands tend to be far broader than that of the FTIR systems. Compounds that can be accurately detected and measured with the UV-DOAS must have specific chemical structure characteristics that allow for unique absorption bands. This limits the number of compounds that can be monitored.<sup>25</sup>

#### 25.2.1.5 Remote-Portable Technologies for Gas-Phase Air Pollutants

Generally, the approaches discussed in this section have been and continue to be used effectively to measure numerous gas-phase pollutants. However, the state-of-the-science in measurement continues to grow. Sensors, open-path detectors and other real-time detection systems, e.g. transform infrared, DOAS and tuned lasers, are being used with much success. Also, new materials, particularly nanomaterials, are being applied to environmental sampling and analysis.

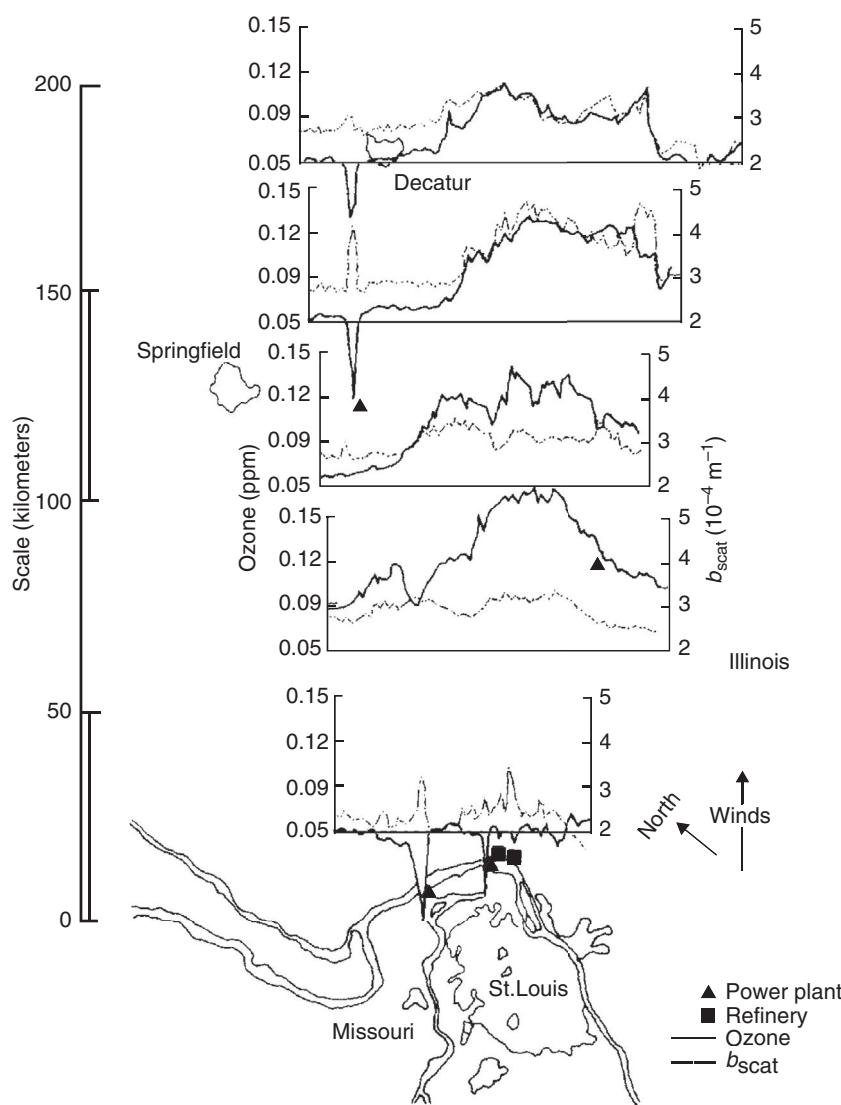
Remote sensing involves monitoring in which the analyzer is physically removed from the volume of air being analyzed. Satellites have been used to monitor light-scattering aerosol over large areas.<sup>26</sup> Large point sources such as volcanic activity and forest fires can be tracked by satellite. The development and movement of hazy air masses have been observed by satellite imagery. Remote sensing methods are available for determining the physical structure of the atmosphere with respect to turbulence and temperature profiles.

Mobile monitoring is accomplished from a movable platform, i.e. a motor vehicle or an aircraft (see Discussion Box: Air Quality Sampling in the Gulf of Mexico). Emissions are measured by source monitoring techniques (Chapter 24). Atmospheric transport and chemical transformation processes occur in the region between the source and the receptor, so mobile forms of air pollution measurement are needed to show variability of pollution concentrations in time and space.

By using mobile platforms containing air pollution instrumentation, one can obtain data to help understand the formation and transport of photochemical smog, acidic deposition, and the dispersion of air pollutants from sources. Mobile monitoring platforms may also be moved to “hot spots”, i.e. areas suspected of having high concentrations of specific air pollutants. These areas may be nearby locations downwind of a large source or a particular location that is an unfavorable receptor due to meteorological conditions. Vehicular and aircraft monitoring systems can also be moved to locations where hazardous chemical spills, nuclear and chemical plant accidents, or volcanoes or earthquakes have occurred.

The major advantage of a mobile monitoring system is its ability to obtain air quality information in the intermediate region between source monitors and stationary fixed monitors. The major disadvantage is the paucity of suitable instrumentation that operates properly in the mobile platform environment. Limitations of existing instrumentation for the use on movable platforms are inadequate temperature and pressure compensation; incompatible power, size, and weight requirements; and excessive response time. Most movable platforms are helicopters, airplanes, trucks, or vans. These platforms do not provide the relatively constant-temperature environment required by most air quality instrumentation. Equipment mounted in aircraft is subject to large pressure variations with changing altitude. Most instrumentation is designed to operate with alternating current electrical power, whereas relatively low amounts of direct current power are available in aircraft or vans. Space is at a premium, and response times are often too slow to permit observation of rapid changes in concentration as aircraft move in and out of a plume.

Despite these limitations, mobile monitoring systems have been used for decades to obtain useful information, such as the verification and tracking of the St. Louis, Missouri, urban plume. The measurement of a well-defined urban plume spreading northeastward from St. Louis<sup>30</sup> is shown in Figure 25.18. These data were collected by a combination of instrumented aircraft and mobile vans. Cross-sectional paths were flown by the aircraft at increasing distances downwind. Meteorological conditions of low wind speed in the same direction helped to maintain this urban plume in a well-defined condition for several hundred kilometers downwind. The presence of large point sources of NO and SO<sub>2</sub> was observed by the changes in the O<sub>3</sub> and  $b_{\text{scat}}$  profiles. Sharp decreases in ozone concentration occurred when large amounts of NO were present, and rapid increases in  $b_{\text{scat}}$  were caused by the primary and secondary particulate matter from power plant plumes embedded in the



**FIGURE 25.18** A St. Louis, Missouri, urban plume in the 1970s. Ozone and  $b_{\text{scat}}$  profiles at four distances downwind of St. Louis track a detectable urban plume for 150 km. Ref. 27.

larger urban plume. The overall increasing level of ozone and  $b_{\text{scat}}$  at greater downwind distances was caused by the photochemical reactions as the urban plume was transported farther away from St. Louis. This type of plume mapping can be accomplished only by mobile monitoring systems.

Recently, the mobile technologies have improved. For example, the trace ambient gas analyzer includes a portable gas chromatography system. The system has been used to measure various organic compounds in the air, e.g. chlorine dioxide ( $\text{ClO}_2$ ) in the ambient air near residences adjacent to a Congressional building in Washington, DC.<sup>28</sup> The  $\text{ClO}_2$  detection limits for this

system were 900 ppqv (parts per quadrillion by volume) in real time.<sup>b</sup>

#### 25.2.1.6 Specific Monitoring Methods for Gas-Phase Criteria Pollutants

Although the previous methods for measuring gaseous pollutants are many and varied, regulatory agencies require specific methods to ensure that ambient air quality standards are being met. As mentioned, in many countries there are legal rules designating the type of method. Thus, even if the scientific evidence strongly supports a method, it will not meet regulatory requirements unless it is considered to be a reference

<sup>b</sup> These low detection limits were needed since the action levels for  $\text{ClO}_2$  are also quite low, i.e. 25 ppbv for 15 min at a location. The action limits must be higher than detection limits to ensure safety, e.g. whether to evacuate a building.

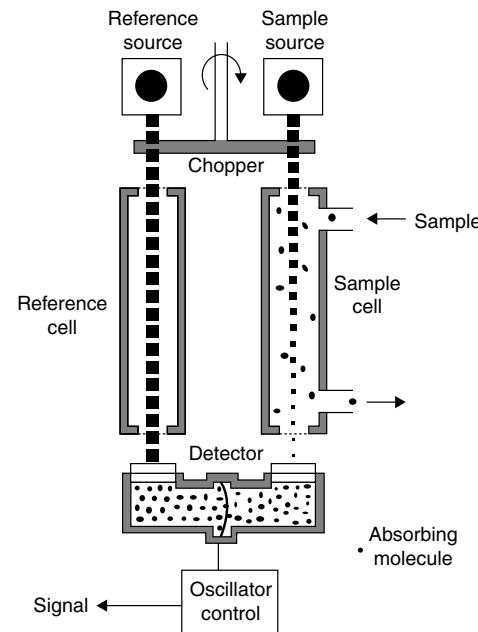
or equivalent method. Following is a discussion of these methods, but the reader is advised to refer to the regulatory agency rules in a specific jurisdiction prior to citing and using these methods to ensure the method is currently equivalent to the rules of that jurisdiction.

The methods listed below are merely the scientific explanation of how the systems under reference and equivalent methods work. The reference methods for countries change as the state of the science of measurement technologies change. However, the use of open path and other continuous systems are also useful for air pollutant detection for criteria pollutants and air toxics. For example, the 1-h SO<sub>2</sub> NAAQS was changed in 2010, with the intention of increased protection of public health by reducing exposure to high, short-term SO<sub>2</sub> concentrations. This will increase the need for exploratory monitoring conducted with highly time resolved data (i.e. frequency in minutes to hours). As mentioned, continuous methods can show short-term peak SO<sub>2</sub> concentrations because of the high time resolution. These peaks would be missed by longer time averaging. Unfortunately, continuous methods have not been very economically or logically feasible for many situations. However, like many other aspects of society, e.g. smart phones, recent technological advances in sensor and sampling technology are providing more compact and less costly continuous methods. These sensors are not reference or equivalent methods, but will likely be valuable in increasing sampling density in time and space, including exploratory monitoring. Most new sensors use proprietary methods, but are generally electrochemical devices. The accuracy and precision of these sensors will be evaluated, likely be colocation and comparison with reference and equivalent methods in the field.<sup>29</sup> In addition, passive methods commonly used in the past for saturation studies are commercially available, easy to use, and are relatively inexpensive. However, passive methods do not resolve the temporal need to see the peaks, since they are integrated samples collected over days to weeks. They can certainly improve the sampling spatial density, e.g. to determine long-term concentration trends, but they do not offer the same insight into where the short-term peak concentrations may be occurring in an area around or otherwise impacted by an air pollutant source. Thus, passive methods are not the recommended method of choice for conducting exploratory monitoring to aid in determining where to place source oriented monitors and should be considered as only a complementary or back-up strategy to other methods and approaches to identify criteria and air toxics monitoring sites.<sup>30</sup> The length of any exploratory monitoring is determined by the source (e.g. does the facility have peak operating periods, or does it change operations seasonally?), meteorology, and other intra-annual variability.

### 25.2.1.6.1 CARBON MONOXIDE

Like all other criteria pollutants, measurement apparatus to detect and quantify carbon monoxide (CO) concentrations consists of three basic systems: pneumatic, analytical, and electronic. The pneumatic system consists of pumps, valves, lines, conduits, filters, flow meter, and other components to bring the air to the analytical system, which detects physical response (e.g. IR absorbance). The electronic system converts this basic physical and chemical information, e.g. absorbance of light energy, to concentrations for a particular pollutant.

The primary reference method used for measuring carbon monoxide in the United States is based on nondispersive infrared (NDIR) photometry.<sup>31</sup> The principle involved is the preferential absorption of infrared radiation by carbon monoxide. Figure 25.19 is a schematic representation of an NDIR analyzer. Like the FTIR methods addressed previously, NDIR is based on IR absorption and concentration relationships according to the Beer–Lambert Law. The analyzer has a hot filament source of infrared radiation, a chopper, a sample cell, reference cell, and a detector. The reference cell is filled with a noninfrared-absorbing gas, and the sample cell is continuously flushed with ambient air containing an unknown amount of CO. The detector cell is divided into two compartments by a flexible membrane, with each compartment filled with CO. Movement of the membrane causes a change in electrical capacitance in a control circuit whose signal is processed and fed to a recorder.



**FIGURE 25.19** Nondispersive infrared (NDIR) analyzer. Bryan BJ. Ambient air quality surveillance. In: Stern AC, editor. Air Pollution, 3rd ed., vol. III. New York (NY) Academic Press; 1976. p. 375.

The chopper intermittently exposes the two cells to infrared radiation. The reference cell is exposed to a constant amount of infrared energy which is transmitted to one compartment of the detector cell. The sample cell, which contains varying amounts of infrared-absorbing CO, transmits to the detector cell a reduced amount of infrared energy that is inversely proportional to the CO concentration in the air sample. The unequal amounts of energy received by the two compartments in the detector cell cause the membrane to move, producing an alternating current (AC) electrical signal whose frequency is established by the chopper spacing and the speed of chopper rotation. The signal is sent to a DAS. The CO instrument needs to be calibrated often, i.e. injecting air with known concentrations of CO into the system and comparing readings.

Water vapor absorbs IR, so it is a serious interfering substance in this technique. A moisture trap such as a drying agent or a water vapor condenser is required to remove water vapor from the air to be analyzed. Instruments based on other techniques are available which meet the performance specifications, such as those listed in Table 25.2. Equivalent methods for CO and the other criteria pollutants are published online and updated as new methods are approved.<sup>3</sup>

#### 25.2.1.6.2 OZONE

The principal method used for measuring ozone is based on chemiluminescence.<sup>32</sup> When ozone and ethylene react chemically, products are formed which are in an excited electronic state. These products fluoresce, releasing light. The principal components are a constant source of ethylene, an inlet sample line for ambient air, a reaction chamber, a photomultiplier tube, and signal-processing circuitry. The rate at which light is received by the photomultiplier tube is dependent on the concentrations of O<sub>3</sub> and ethylene. If the concentration of ethylene is made much higher than the ozone concentration to be measured, the light emitted is proportional only to the ozone concentration.

Instruments based on this principle may be calibrated by a two-step process shown in Figure 25.20.<sup>33</sup> A test atmosphere with a known source of ozone is produced by an ozone generator, a device capable of generating stable levels of O<sub>3</sub>. Step 1 involves establishing the concentration of ozone in the test atmosphere by ultraviolet (UV) photometry. This is followed by step 2, calibration of the instrument's response to the known concentration of ozone in the test atmosphere.

The O<sub>3</sub> method is presently being investigated for possible improved detection, i.e. the nitric oxide (NO)-chemiluminescence ozone analyzer.<sup>34</sup> This method is

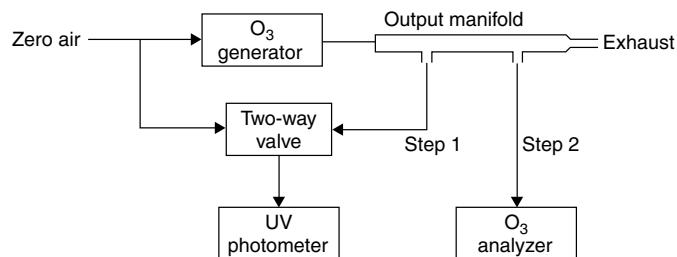
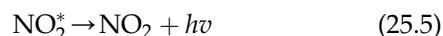


FIGURE 25.20 Two-step calibration apparatus for an ultraviolet (UV) ozone analyzer.

based on the dry, gas-phase reaction between NO and O<sub>3</sub> generates nitrogen dioxide in an activated state (NO<sub>2</sub><sup>\*</sup>), and molecular oxygen (O<sub>2</sub>). As the unstable, activated nitrogen dioxide (NO<sub>2</sub><sup>\*</sup>) returns to a lower energy state (NO<sub>2</sub>), it emits a photon (*hν*) while it luminesces in a broadband spectrum from visible light to infrared light (approximately 590–2800 nm). The two-step gas-phase reaction proceeds as follows:



Then, the activated nitrogen dioxide breaks down to nitrogen dioxide and a photon:



The number of photons emitted during the reaction is directly proportional to the O concentration in the sample. As the gas phase reaction proceeds in the analyzer mixing chamber/reaction cell, the emitted photons are counted by a photomultiplier tube (PMT). The electronics of the analyzer converts the *hν* count is converted to O concentration, using a mathematical algorithm.

In the United States, the NO-chemiluminescence method has been designated as a federal equivalent method (FEM) for ozone, i.e. it meets all of the same performance specifications as the existing federal reference method (FRM), and is comparable to the existing FRM from a measurement perspective. As of 2014, the NO-chemiluminescence devices are becoming increasingly available from vendors. The NO-chemiluminescence method behaves in the same manner as the ethylene (C<sub>2</sub>H<sub>4</sub>) chemiluminescence FRM when exposed to the same interferents<sup>c</sup> found in ambient air that may have an effect on the response of the widely used ultraviolet-spectrophotometric ozone methods. Also, care must be taken with this method in that NO is toxic in high concentrations, including the concentrations of NO found in an NO cylinder source (asphyxiant). For practical purposes, the US EPA recommends two FRMs for ozone measurement, i.e. both NO-chemiluminescence method and ethylene chemiluminescence.

<sup>c</sup>These interferents are listed in 40 CFR Part 53, Table B-3 (e.g. H<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>O).

This NO-chemiluminescence method is quite similar to the  $\text{NO}_2$  method discussed below.

#### 25.2.1.6.3 NITROGEN DIOXIDE

The principal method used for measuring  $\text{NO}_2$  is also based on chemiluminescence (Figure 25.21).<sup>35</sup>  $\text{NO}_2$  concentrations are determined indirectly from the difference between the NO and  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) concentrations in the atmosphere. These concentrations are determined by measuring the light emitted from the chemiluminescent reaction of NO with  $\text{O}_3$  (similar to the reaction of  $\text{O}_3$  with ethylene noted for the measurement of  $\text{O}_3$ ), except that  $\text{O}_3$  is supplied at a high constant concentration, and the light output is proportional to the concentration of NO present in the ambient airstream.

Figure 25.22 illustrates the analytical technique based on this principle. To determine the  $\text{NO}_2$  concentration, the NO and  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) concentrations are measured. The block diagram shows a dual pathway through the instrument, one to measure NO and the other to measure  $\text{NO}_x$ . The NO pathway has an ambient airstream containing NO (as well as  $\text{NO}_2$ ), an ozone stream from the ozone generator, a reaction chamber, a photomultiplier tube, and signal-processing circuitry. The  $\text{NO}_x$  pathway has the same components, plus a converter for quantitatively reducing  $\text{NO}_2$  to NO. The instrument can also electronically subtract the NO from  $\text{NO}_x$  and yield as output the resultant  $\text{NO}_2$ .

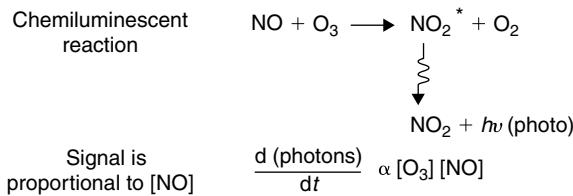


FIGURE 25.21  $\text{NO}_2$  chemiluminescent detection chemistry and physics based on the reaction of NO and  $\text{O}_2$ .

FIGURE 25.22 Schematic diagram of chemiluminescent detector for  $\text{NO}_2$  and NO. PMT: photomultiplier tube.

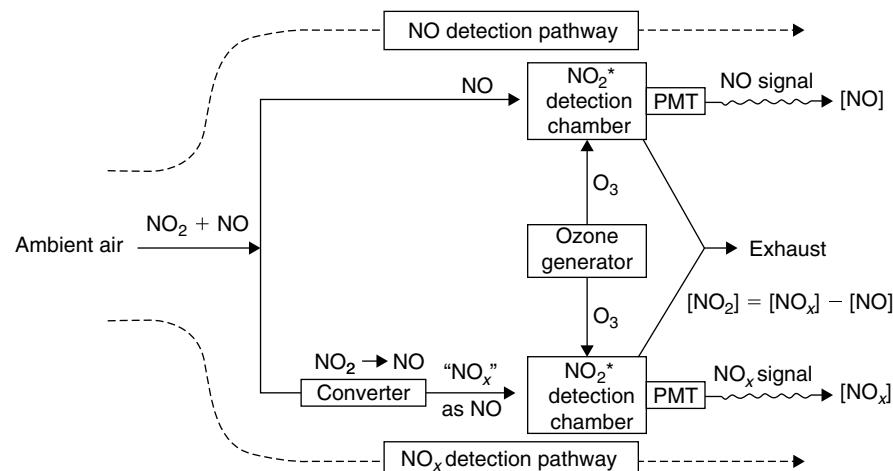
Air passing through the NO pathway enters the reaction chamber, where the NO present reacts with the  $\text{O}_3$ . The photons produced are measured by the photomultiplier tube and converted to an NO concentration. The  $\text{NO}_2$  in the airstream in this pathway is unchanged. In the  $\text{NO}_x$  pathway, the NO- and  $\text{NO}_2$ -laden air enters the converter, where the  $\text{NO}_2$  is reduced to form NO; all of the  $\text{NO}_x$  exits the converter as NO and enters the reaction chamber. The NO reacts with  $\text{O}_3$  and the output signal is the total  $\text{NO}_x$  concentration. The  $\text{NO}_2$  concentration in the original airstream is the difference between  $\text{NO}_x$  and NO. Calibration techniques use gas-phase titration of an NO standard with  $\text{O}_3$  or an  $\text{NO}_2$  permeation device.

#### 25.2.1.6.4 SULFUR DIOXIDE

Several manual and continuous analytical techniques are used to measure  $\text{SO}_2$  in the atmosphere. Methods for determining levels in the air include ion chromatography, titration, calorimetry, mass spectrometry, conductometry, amperometric detection, flame photometric detection, and turbidimetry. Of these methods, ion chromatography generally has the lowest detection limit for  $\text{SO}_2$ .<sup>36</sup>

The manual techniques involve two-stage sample collection and measurement. Samples are collected by bubbling a known volume of gas through a liquid collection medium. Collection efficiency is dependent on the gas–liquid contact time, bubble size,  $\text{SO}_2$  concentration, and  $\text{SO}_2$  solubility in the collection medium. The liquid medium contains chemicals which stabilize  $\text{SO}_2$  in solution by either complexation or oxidation to a more stable form. Field samples must be handled carefully to prevent losses from exposure to high temperatures. Samples are analyzed at a central laboratory by an appropriate method.

The West–Gaeke manual method, which has been modified since its inception, had been the basis for the



U.S. EPA reference method for measurement of  $\text{SO}_2$ .<sup>37</sup> The method uses the colorimetric principle; i.e. the amount of  $\text{SO}_2$  collected is proportional to the amount of light absorbed by a solution. The collection medium is an aqueous solution of sodium or potassium tetrachloromercurate (TCM). Absorbed  $\text{SO}_2$  forms a stable complex with TCM. This enhanced stability permits the collection, transport, and short-term storage of samples at a central laboratory. The analysis proceeds by adding bleached pararosaniline dye and formaldehyde to form red-purple pararosaniline methylsulfonic acid. Optical absorption at 548 nm is linearly proportional to the  $\text{SO}_2$  concentration. Procedures are followed to minimize interference by  $\text{O}_3$ , oxides of nitrogen, and heavy metals.

In the United States, the current  $\text{SO}_2$  reference method employs ultraviolet fluorescence (UVF). The UVF system depicted in Figure 25.23 includes a measurement cell, a UV light source of appropriate wavelength, a UV detector system with appropriate wavelength sensitivity, a pump and flow control system for sampling the ambient air and moving it into the measurement cell, as well as filters and other conditioning components needed to minimize measurement interferences, suitable control, and measurement processing capability. The  $\text{SO}_2$  concentrations are derived from an automated measurement of the intensity of fluorescence released by  $\text{SO}_2$  in an ambient air sample contained in a measurement cell of an analyzer when the air sample is irradiated by UV light passed through the cell. The fluorescent light released by the  $\text{SO}_2$  is

also in the ultraviolet region, but at longer wavelengths than the excitation light. Typically, optimum instrumental measurement of  $\text{SO}_2$  concentrations is obtained with an excitation wavelength in a band between approximately 190–230 nm, and measurement of the  $\text{SO}_2$  fluorescence in a broadband around 320 nm. Interferents include aromatic hydrocarbon species, and possibly other compounds.<sup>38</sup>

The continuous methods combine sample collection and the measurement technique in one automated process. The measurement methods used for continuous analyzers include conductometric, colorimetric, coulometric, and amperometric techniques for the determination of  $\text{SO}_2$  collected in a liquid medium.<sup>39</sup> Other continuous methods utilize physicochemical techniques for detection of  $\text{SO}_2$  in a gas stream. These include flame photometric detection (described earlier) and fluorescence spectroscopy.<sup>40</sup> Instruments based on all of these principles are available which meet standard performance specifications.

#### 25.2.1.6.5 NONMETHANE VOLATILE ORGANIC COMPOUNDS

The large number of individual hydrocarbons in the atmosphere and the many different hydrocarbon classes make ambient air monitoring a very difficult task. The ambient atmosphere contains a ubiquitous concentration of methane ( $\text{CH}_4$ ) at approximately 1.6 ppm worldwide [9]. The concentration of all other hydrocarbons in ambient air can range from 100 times less to 10 times

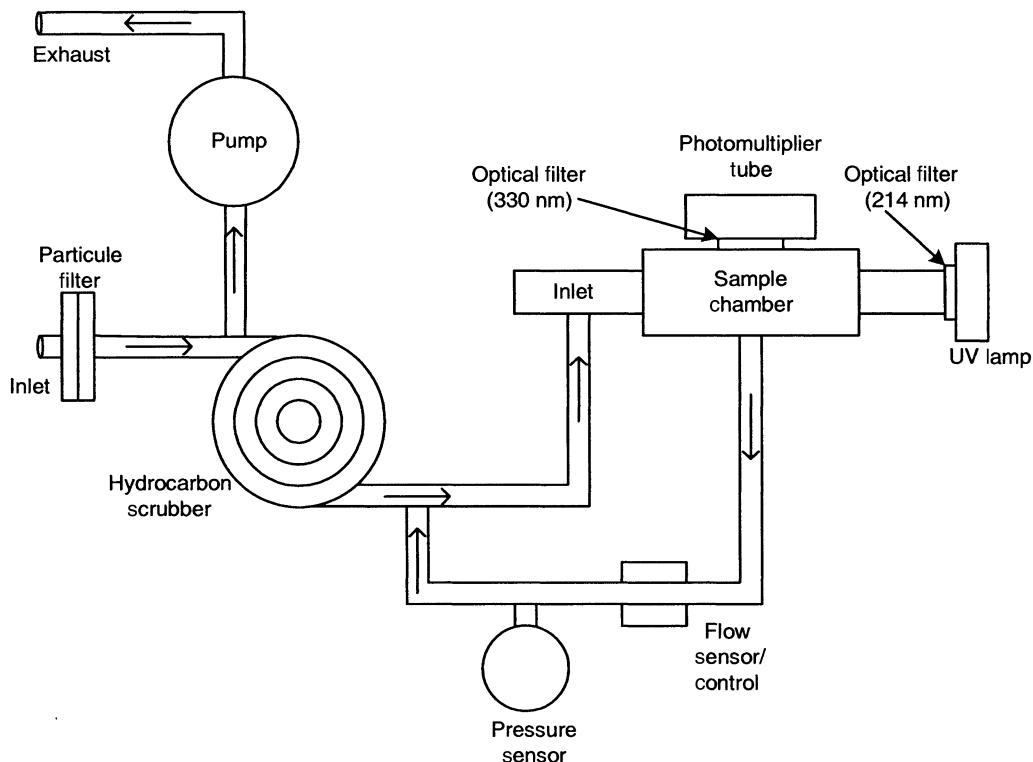


FIGURE 25.23 Schematic of ultraviolet fluorescence (UVF) federal reference method for analyzing sulfur dioxide in ambient air. Ref. 38.

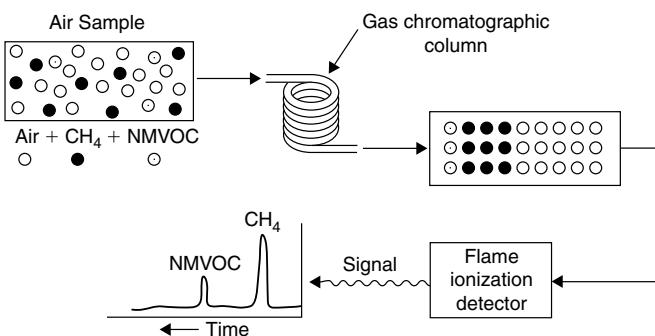
greater than the methane concentration for a rural versus an urban location. The terminology of the concentration of hydrocarbon compounds is potentially confusing. Hydrocarbon concentrations are referred to by two units—parts per million by volume (ppmv) and parts per million by carbon (ppmC). Thus, 1  $\mu\text{l}$  of gas in 1 l of air is 1 ppmv, so the following is true:

Mixing Ratio	ppmv	ppmC
$\frac{1 \mu\text{l} \text{ of O}_3}{1 \text{l of air}} =$	1 ppm ozone	—
$\frac{1 \mu\text{l} \text{ of SO}_2}{1 \text{l of air}} =$	1 ppmv SO <sub>2</sub>	—
$\frac{1 \mu\text{l} \text{ of CH}_4}{1 \text{l of air}} =$	1 ppmv CH <sub>4</sub>	1 ppmC CH <sub>4</sub>
$\frac{1 \mu\text{l} \text{ of C}_2\text{H}_6}{1 \text{l of air}} =$	1 ppmv C <sub>2</sub> H <sub>6</sub>	2 ppmC C <sub>2</sub> H <sub>6</sub>

The unit ppmC takes into account the number of carbon atoms contained in a specific hydrocarbon and is the generally accepted way to report ambient hydrocarbons. This unit is used for three reasons: (1) the number of carbon atoms is a very crude indicator of the total reactivity of a group of hydrocarbon compounds; (2) historically, analytical techniques have expressed results in this unit; and (3) considerable information has been developed on the role of hydrocarbons in the atmosphere in terms of concentrations determined as ppmC. With decreasing detection limits the units are also expressed as parts per billion by volume (ppbv) and ppbC.

Historically, measurements have classified ambient hydrocarbons into two classes: methane (CH<sub>4</sub>) and all other NMVOCS. Analyzing hydrocarbons in the atmosphere involves a three-step process: collection, separation, and quantification. Collection involves obtaining an aliquot of air, e.g. with an evacuated canister. The principal separation process is gas chromatography (GC), and the principal quantification technique is with a calibrated flame ionization detector (FID). Mass spectroscopy (MS) is used along with GC to identify individual hydrocarbon compounds. Since the NMVOCS are in the gas phase, they are evacuated from the container directly to the GC.

A simple schematic diagram of the GC/FID principle is shown in [Figure 25.24](#). Air containing CH<sub>4</sub> and other hydrocarbons classified as NMVOCS pass through a GC column and the air, CH<sub>4</sub>, and NMVOC molecules are clustered into groups because of different absorption/desorption rates. As CH<sub>4</sub> and NMVOC groups exit the column, they are “counted” by the FID. The signal output of the detector is proportional to the two groups and may be quantified when compared with standard concentrations of gases. This simplified procedure has been used extensively to collect hydrocarbon concentration data for the ambient atmosphere. A major



**FIGURE 25.24 Schematic diagram of hydrocarbon detection by gas chromatography. NMVOC = nonmethane volatile organic carbon.**

disadvantage of this technique is the grouping of all hydrocarbons other than CH<sub>4</sub> into one class. Hydrocarbon compounds with similar structures are detected by an FID in a proportional manner, but for compounds with significantly different structures the response may be different. This difference in sensitivity results in errors in measurements of NMVOC mixtures.

More sophisticated GC columns and techniques perform more detailed separations of mixtures of hydrocarbons into discrete groups. The equipment and supplies are constantly improving sensitivity and specificity to particular compounds. As such, some time is needed to explore the best columns and mobile phase mixtures to optimize the analysis.

Other types of detectors include the flame photometric detector (FPD) and the electron capture detector (ECD). The FID is composed of an H<sub>2</sub> flame through which the hydrocarbon gases are burned, forming charged carbon atoms, and an electrometer grid which generates a signal current proportional to the number of carbon atoms in the flame. The example of 1 ppmv methane (CH<sub>4</sub>) and 1 ppmv (but 2 ppmC) ethane (C<sub>2</sub>H<sub>6</sub>) is related to this detection principle. One ppmv of CH<sub>4</sub> and 1 ppmv of C<sub>2</sub>H<sub>6</sub> in air have the same number of molecules of hydrocarbon in a given volume of air, but if an aliquot of each mixture were run through an FID, the signal for ethane would be nearly twice the methane signal: 2 ppmC ethane compared to 1 ppmC methane.

The FPD is also used to measure sulfur-containing compounds and therefore is useful for measurement of sulfur-containing hydrocarbons such as dimethylsulfide or furan. The FPD has an H<sub>2</sub> flame in which sulfur-containing gases are burned. In the combustion process, electronically excited S<sub>2</sub><sup>\*</sup> is formed. A photomultiplier tube detects light emitted from the excited sulfur at ~395 nm. The ECD is preferred for measuring nitrogen-containing compounds such as peroxyacetyl nitrate and other oxidized species of nitrogen. The ECD contains a radioactive source which establishes a stable ion field. Nitrogen-containing compounds capture

electrons in passing through the field. Alterations in the electronic signal are related to the concentration of the nitrogen species.

### 25.3 PARTICULATE MATTER

Particulate matter (PM) includes any airborne substances that are not in the gas phase, either liquid or solid. They are generally classified according to the particle's diameter, e.g. total suspended particulates (TSP) includes all aerosols in the atmosphere, but smaller particles are of most concern because they remain suspended and they cause the most health effects. These are usually classified as the coarse fraction, i.e. aerodynamic diameter, i.e. 2.5–10  $\mu\text{m}$  diameters (PM<sub>10</sub>) and the fine fraction and  $\leq 2.5 \mu\text{m}$  diameters (PM<sub>2.5</sub>). The three major characteristics of particulate pollutants in the ambient atmosphere are total mass concentration, size distribution, and chemical composition. In the United States, the PM<sub>2.5</sub> concentration, particulate matter with an aerodynamic diameter  $< 2.5 \mu\text{m}$ , is the quantity measured for an air quality standard to protect human health from effects caused by inhalation of suspended particulate matter. However, there remains a strong interest in the coarse fraction (PM<sub>10</sub>) because it may be linked with certain diseases (e.g. asthma) and because it often has toxic components (e.g. sorbed metals and semivolatile organic compounds like dioxin). The size distribution of particulate pollutants is very important in understanding the transport and removal of particles in the atmosphere and their deposition behavior in the human respiratory system. Their chemical composition may determine the type of effects caused by particulate matter on humans, vegetation, and materials.

More recently, particles have been classified even further; with ultrafines have diameter of about 0.1  $\mu\text{m}$ , i.e. 100 nm. Interestingly, this is the same size as that of nanoparticles. However, a distinction between nanoparticles and ultrafines are that nanoparticles are considered to be made intentionally, whereas ultrafines are considered to be unintentional byproducts from other activities (e.g. diesel combustion). Another distinction is that the 100 nm length is a single dimension, i.e. a nanoparticle has at least one dimension that is  $\leq 100 \text{ nm}$ , whereas an ultrafine particle has an aerodynamic diameter of 100 nm. Thus, a long chain of carbon-60 spheres would still be considered a nanoparticle because its width is less than 100 nm, but an

aggregate of ultrafine particle may be considered larger than an ultrafine particle because its Stokes diameter is greater than 100 nm. Recall from Chapter 6 that the Stokes particle diameter ( $D_{ps}$ ) is the diameter of a sphere with the same density and settling velocity as the particle. The diameter is derived from the aerodynamic drag force caused by the difference in velocity of the particle and the surrounding fluid. For spherical particles,  $D_{ps}$  is identical to the physical or actual diameter, but for aggregates and other nonspherical aerosols they can differ. A hollow particle is obviously different from a solid particle, so density also comes into play. For example, for particles with dimensions  $> 500 \text{ nm}$ , the aerodynamic diameter is approximated<sup>d</sup> as the product of the  $D_{ps}$  and the square root of the particle density.

Particles can be directly emitted into the atmosphere (primary aerosols) or form from gas-phase constituents after emission (secondary aerosol). The secondary source of fine particles in the atmosphere is gas-to-particle conversion processes, considered to be the more important source of particles contributing to atmospheric haze. In gas-to-particle conversion, gaseous molecules become transformed to liquid or solid particles. This phase transformation can occur by three processes: absorption, nucleation, and condensation. Absorption is the process by which a gas goes into solution in a liquid phase. Absorption of a specific gas is dependent on the solubility of the gas in a particular liquid, e.g. SO<sub>2</sub> in liquid H<sub>2</sub>O droplets. Nucleation and condensation are terms associated with aerosol dynamics.

Nucleation is the growth of clusters of molecules that become a thermodynamically stable nucleus. This process is dependent on the vapor pressure of the condensable species. The molecular clusters undergo growth when the saturation ratio,  $S$ , is greater than 1, where saturation ratio is defined as the actual pressure of the gas divided by its equilibrium vapor pressure. The condition when  $S > 1$  is referred to as a supersaturated condition.

The size at which a cluster may be thermodynamically stable is influenced by the Kelvin effect. The equilibrium vapor pressure of a component increases as the droplet size decreases. Vapor pressure is determined by the energy necessary to separate a single molecule from the surrounding molecules in the liquid. As the curvature of the droplet's surface increases, fewer neighboring molecules will be able to bind a particular molecule to the liquid phase, thus increasing the probability of a molecule escaping the liquid's surface. Thus, smaller droplets will have a higher equilibrium vapor

<sup>d</sup> Aerosol textbooks provide methods to determine the aerodynamic diameter of particles less than 0.5 mm. For larger particles gravitational settling is often used for sizing that is expressed as mass of ranges of aerodynamic diameter, e.g. mass of PM2.5 and mass of PM10.

pressure. This would affect the minimum size necessary for a thermodynamically stable cluster, suggesting that components with lower equilibrium saturation vapor pressures will form stable clusters at smaller diameters.

Condensation is the result of collisions between a gaseous molecule and an existing aerosol droplet when supersaturation exists. Condensation occurs at much lower values of supersaturation than nucleation. Thus, when particles already exist in sufficient quantities, condensation will be the dominant process occurring to relieve the supersaturated condition of the vapor-phase material.

A simple model for the formation and growth of an aerosol at ambient conditions involves the formation of a gas product by the appropriate chemical oxidation reactions in the gas phase. This product must have a sufficiently low vapor pressure for the gas-phase concentration of the oxidized product to exceed its saturation vapor pressure. When this condition occurs, nucleation and condensation may proceed, relieving supersaturation. These processes result in the transfer of mass to the condensed phase. Aerosol growth in size occurs while condensation is proceeding.

Coagulation is the process by which discrete particles come into contact with each other in the air and remain joined together by surface forces. Coagulation represents another way in which aerosol diameter will increase. However, it does not alter the mass of material in the coagulated particle.

The clearest example of this working model of homogeneous gas-to-particle conversion is sulfuric acid aerosol formation. Sulfuric acid ( $H_2SO_4$ ) has an extremely low saturation vapor pressure. Oxidation of relatively small amounts of sulfur dioxide ( $SO_2$ ) can result in a gas-phase concentration of  $H_2SO_4$  that exceeds its equilibrium vapor pressure in the ambient atmosphere, with the subsequent formation of sulfuric acid aerosol. In contrast, nitric acid ( $HNO_3$ ) has a much higher saturation vapor pressure. Therefore, the gas-phase concentration of  $HNO_3$  is not high enough to permit nucleation of nitric acid aerosol in typical atmospheric systems.

### 25.3.1 Sampling Particulates

The complexity and diversity of particulate composition, size, mass and concentrations in the atmosphere dictate the need for accurate and representative PM monitoring. The major purpose of ambient particulate sampling is to obtain mass concentration and chemical composition data, preferably as a function of particle diameter. This information is valuable for a variety of problems: effects on human health, identification of particulate matter sources, understanding of atmospheric haze, and particle removal processes.

The primary approach is to separate the particles from a known volume of air and subject them to weight determination and chemical analysis. The principal methods for extracting particles from an airstream are filtration and impaction. All sampling techniques must be concerned with the behavior of particles in a moving airstream. The difference between sampling for gases and sampling for particles begins at the inlet of the sampling manifold and is due to the discrete mass associated with individual particles.

Particulate matter is collected using equipment that separates out the size fraction of concern. This separation predominantly occurs by four mechanical processes: (1) diffusion; (2) interception; (3) inertial impaction; and (4) electrostatics (Figure 6.33 in Chapter 6).

Diffusion applies exclusively to the extremely small particles ( $\leq 0.1 \mu m$  diameter), i.e. those that experience Brownian motion and undergo a "random walk" away from the airstream. Interception captures PM with diameters between 0.1 and 1  $\mu m$ . The particle remains in the airstream but contacts the filter medium. Inertial impaction collects PM with large enough diameters and mass to exit the airstream via inertia (diameters  $\geq 1 \mu m$ ). Electrostatics consist of electrical interactions between the atoms in the filter and those in the particle at the point of contact (van der Waal's forces), as well as electrostatic attraction (charge differences between particle and filter medium). Other important factors include the thickness and pore diameter of the filter, the uniformity of particle diameters and pore sizes, the solid volume fraction, the rate of particle loading onto the filter (e.g. affecting particle "bounce"), the particle phase (liquid or solid), capillarity and surface tension (if either the particle or the filter media are coated with a liquid), and atmospheric and stack conditions, e.g. velocity, temperature, pressure, and viscosity.

Commonly, the both PM and gaseous pollutant concentration units for ambient measurements are mass ( $\mu g$ ) per unit volume ( $m^3$ ). However, for PM, the concentration is reported according to the mass fraction for different PM size ranges. Size classification involves the use of specially designed inlet configurations, e.g.  $PM_{2.5}$  sampling. To determine mass concentration, all the particles are removed from a known volume of air and their total mass is measured. This removal is accomplished by two techniques, filtration and impaction. Mass measurements are made by pre- and post-weighing of filters or impaction surfaces. To account for the absorption of water vapor, the filters are generally equilibrated at standard or other conditions specified in the PM method (e.g.  $T = 20^\circ C$  and 50% relative humidity).

Filters vary in pore size, strand diameter, chemical composition and quality. Vendors document the important physical properties of the commonly used filter

materials and the expected filter efficiencies (Table 25.8). In airborne PM purposes, most fibrous filters consist of glass fibers, cellulose, quartz, polystyrene, and polycarbonate materials. Membrane filters are made of cellulose esters, polytetrafluoroethylene (PTFE), polyethylene, polycarbonate, silver and other materials. If physical properties dictate the filter choice, then glass fiber filters would be used. However, these inorganic silicate materials can become highly radioactive during certain analyzes and are therefore not useful during a nondestructive activation technique is applied. Similarly, carbon-based filters would not generally be used in a destructive technique, since the carbon in cellulose, PTFE, etc. would show up in the analysis and produce a positive C bias (e.g. for an organic C to elemental C ratio calculation). If the analysis will include fibers, especially asbestos, it mixed cellulose would be preferred for transmissive electron microscopy (TEM), since the filter material can be destroyed during etching (i.e. the cellulose is dissolved leaving the fibers more visible to TEM). However, the pore size would vary according to the type of investigation (e.g. if longer fibers are of major interest, an 8 µm pore size would be used, whereas if fibers of interest are shorter, the 4.5 µm pore size filter would be the best choice).<sup>42</sup> Thus, subsequent elemental analysis after collection is an important selection criterion for PM filters.<sup>41</sup>

Size distributions are determined by classifying airborne particles by aerodynamic diameter, electrical mobility, or light-scattering properties. The most common technique is the use of multistage impactors, each stage of which removes particles of progressively smaller diameter. Figure 25.25 shows a four-stage impactor. The particulate matter collected on each stage is weighed to yield a mass size distribution or is subjected to chemical analysis to obtain data on its chemical size distribution. Impactors are used to determine size distributions for particle diameters of 0.1 µm and larger.

Electrical mobility is utilized to obtain size distribution information in the 0.01–1.0 µm diameter range. This measurement method requires unipolar charging of particles and their separation by passage through an electrical field.<sup>43</sup> By incrementally increasing the electrical field strength progressively, larger charged particles may be removed from a flowing airstream. The change in the amount of charge collected by an electrometer grid is then related to the number of particles present in a particular size increment. Instruments based on this principle yield a number size distribution.

Light-scattering properties of particles are also utilized to determine a number-size distributions.<sup>44</sup> Individual particles interact with a light beam and scatter light at an angle to the original direction of the beam. The intensity of the scattered light is a function of the diameter and the refractive index of the particle. Inlet

TABLE 25.8 Published Impurities (ng cm<sup>-2</sup>) for Blank Values for Selected Fibrous and Membrane Filters

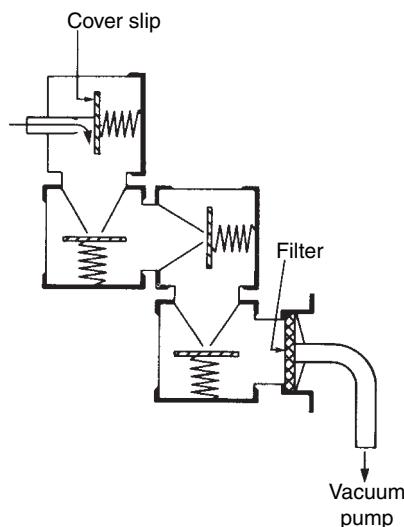
Element	W 41	W 541	MFHA + W 41	MFAA + W 41	Nucl.	QM-A
Na	150	100	800	740	45	58,000
Mg	<80	<60	<400	<370	<5	—
Al	12	11	30	17	4	—
Cl	100	400	1200	1400	—	2900
K	15	12	145	62	2	6700
Ca	140	35	810	560	3	—
Sc	<0.005	0.004	0.006	0.008	0.0003	0.12
Ti	10	2	25	<30	1.4	—
V	<0.03	0.03	<0.10	<0.21	0.01	—
Cr	3	2	25	36	1	24
Mn	0.5	0.5	8	2.1	<0.2	3.9
Fe	40	30	80	100	12	580
Co	0.1	0.04	0.3	0.25	0.01	9.3
Cu	<4	2	24	17	1.2	29
Zn	<25	3	50	<180	0.7	880
As	<0.1	0.04	<0.4	0.13	0.04	—
Se	<0.3	0.2	—	1.0	6.2	—
Br	5	2	9	7.7	2	—
Sb	0.15	0.07	0.8	0.23	0.006	4.1
La	<0.2	0.04	<0.6	<0.5	<0.003	—

W 41 = Whatman 41; cellulose fiber W 541 = Whatman 541, cellulose fiber; MFHA Millipore cellulose ester = membrane (0.45 µm pore size); MFAA: Millipore cellulose ester membrane (0.8 µm pore size); Nucl. = Nucleopore membrane (pore size 0.4 µm); QM-A = Whatman QM-A, quartz microfiber filter.

Source: Ref. 41.

systems are designed to dilute a particle-laden airstream sufficiently to permit only one particle in the beam at a time. The intensity of the scattered light, as measured by a photomultiplier tube, is proportional to particle size. The number of electrical pulses of each magnitude is accumulated in a multichannel analyzer. By sampling at a known flow rate, the number of particles of different diameters is counted with this type of instrument. This principle is also used in nephelometers, i.e. portable PM detectors.

The chemical composition of particulate pollutants is determined in two forms: specific elements, or specific compounds or ions. Knowledge of their chemical composition is useful in determining the sources of airborne particles and in understanding the fate of particles in the atmosphere. Elemental analysis yields results in terms of the individual elements present in a sample such as a given quantity of sulfur, S. From



**FIGURE 25.25 Schematic diagram of a four-stage cascade impactor.** Giever PM. Particulate matter sampling and sizing. In: Stern AC, editor. Air Pollution, 3rd ed., vol. III. New York (NY): Academic Press; 1976. p. 41.

elemental analysis techniques we do not obtain direct information about the chemical form of S in a sample such as sulfate ( $\text{SO}_4^{2-}$ ) or sulfide. Two nondestructive techniques used for direct elemental analysis of particulate samples are X-ray fluorescence (XRF) spectroscopy and neutron activation analysis (NAA).

XRF is a technique in which a sample is bombarded by X-rays.<sup>45</sup> Inner shell electrons are excited to higher energy levels. As these excited electrons return to their original state, energy with wavelengths characteristic of each element present in the sample is emitted. These high-energy photons are detected and analyzed to give the type and quantity of the elements present in the sample. The technique is applicable to all elements with an atomic number of 11 (sodium) or higher. In principle, complex mixtures may be analyzed with this technique. Difficulties arise from a matrix effect, so that care must be taken to use appropriate standards containing a similar matrix of elements. This technique requires relatively expensive equipment and highly trained personnel.

Neutron activation analysis (NAA) involves the bombardment of the sample with neutrons, which interact with the sample to form different isotopes of the elements in the air sample.<sup>46</sup> Many of these isotopes are radioactive and may be identified by comparing their radioactivity with standards. The NAA technique is not quite as versatile as XRF and requires a neutron source.

Pretreatment of the collected particulate matter may be required for chemical analysis. Pretreatment generally involves extraction of the particulate matter into a liquid. The solution may be further treated to transform the material into a form suitable for analysis. Trace metals may be determined by AA spectroscopy,

emission spectroscopy, polarography, and anodic stripping voltammetry. Analysis of anions is possible by colorimetric techniques and ion chromatography. Sulfate ( $\text{SO}_4^{2-}$ ), sulfite ( $\text{SO}_3^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), chloride ( $\text{Cl}^-$ ), and fluoride ( $\text{F}^-$ ) may be determined by ion chromatography.<sup>47</sup>

Analytical methods available to laboratories with only general-purpose analytical equipment may be found in the suggested reading materials and references at the end of this chapter.

### 25.3.2 Behavior of Particles at Sampling Inlets

Recall from Chapter 6 that the sampling inlet is very important for PM measurements. An inlet of the PM<sub>2.5</sub> sampler is often designed to extract ambient aerosols from the surrounding airstream, remove particles with aerodynamic diameters  $>10\ \mu\text{m}$ , and move the remaining smaller particles to the next stage. An impactor and filter assembly can remove particles with diameters  $<10\ \mu\text{m}$  and  $>2.5\ \mu\text{m}$  in diameter but will allow particles of  $2.5\ \mu\text{m}$  in diameter to pass and be collected on a filter surface. Particles  $<10\ \mu\text{m}$  but  $<2.5\ \mu\text{m}$  are removed downstream from the inlet by a single-stage, single-flow, single-jet impactor assembly. Aerosols are collected on filters which are weighed before and after sampling, e.g. 37 mm diameter glass filters immersed in low volatility, low viscosity diffusion oil. The oil is added to reduce the impact of “bounce”, i.e. particle hit the filter and are not reliably collected.

Sampling errors may occur at the inlet, and particles may be lost in the sampling manifold while being transported to the collection surface. Figure 25.26 illustrates the flow patterns around a sampling inlet in a uniform flow field. Figure 25.26(A) shows that when no air is permitted to flow into the inlet, the streamline flow moves around the edges of the inlet. As the flow rate through the inlet increases, more and more of the streamlines are attracted to the inlet. Figure 25.26(B) is known as the isokinetic condition, i.e. the sampling flow rate is equal to the flow field rate. An example of an isokinetic condition is an inlet with its opening into the wind pulling air at the wind speed. When one is sampling for gases, this is not a serious constraint because the composition of the gas will be the same under all inlet flow rates; i.e. there is no fractionation of the air sample by different gaseous molecules.<sup>48</sup>

Although the isokinetic condition may be assumed often for gas-phase pollutants, particle-containing airstreams present a different situation. Figure 25.26(B), the isokinetic case, is the ideal case. The ideal sample inlet would always face into the wind and sample at the same rate as the instantaneous wind velocity (extremely improbable). Under isokinetic sampling conditions, parallel airstreams flow into the sample inlet,

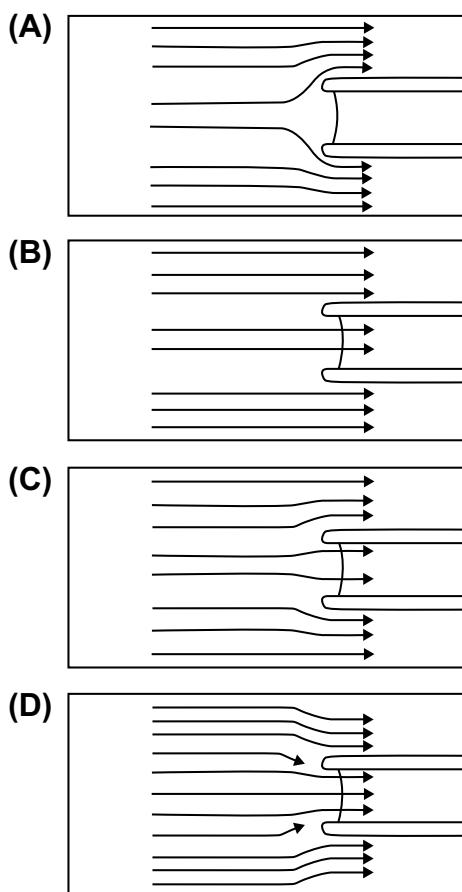


FIGURE 25.26 Four streamline flow patterns around a sampling inlet in a uniform flow field.

carrying with them particles of all diameters capable of being carried by the stream flow. When the sampling rate is lower than the flow field (Figure 25.26(C)), the streamlines start to diverge around the edges of the inlet and the larger particles with more inertia are unable to follow the streamlines and are captured by the sampling inlet. The opposite happens when the sampling rate is higher than the flow field. The inlet captures more streamlines, but the larger particles near the edges of the inlet may be unable to follow the streamline flow and escape collection by the inlet. The inlet may be designed for particle size fractionation; e.g. a PM<sub>2.5</sub> inlet will exclude particles larger than 2.5 µm aerodynamic diameter (Figures 3.2 and 3.3).

These inertial effects become less important for particles with diameters less than 5 µm and for low wind velocities, but for samplers attempting to collect particles above 5 µm, the inlet design and flow rates become important parameters. In addition, the wind speed has a much greater impact on sampling errors associated with particles more than 5 µm in diameter.

After the great effort taken to get a representative sample into the sampling manifold inlet, care must be taken to move the particles to the collection medium

in an unaltered form. Potential problems arise from too long or too twisted manifold systems. Gravitational settling in the manifold will remove a fraction of the very large particles. Larger particles are also subject to loss by impaction on walls at bends in a manifold. Particles may also be subject to electrostatic forces which will cause them to migrate to the walls of nonconducting manifolds. Other problems include condensation or agglomeration during transit time in the manifold. These constraints require sampling manifolds for particles to be as short and have as few bends as possible.

The collection technique involves the removal of particles from the airstream. The two principal methods are filtration and impaction. Filtration consists of collecting particles on a filter surface by three processes: direct interception, inertial impaction, and diffusion.<sup>49</sup> Filtration attempts to remove a very high percentage of the mass and number of particles by these three processes. Any size classification is done by a preclassifier, such as an impactor, before the particle stream reaches the surface of the filter.

### 25.3.3 Indirect PM Measurements

In addition to collecting, weighing and analyzing PM by mass and size, various indirect methods are employed. As discussed in Chapter 6, PM concentrations by size can be estimated by light scattering. The amount of scattering is calibrated against known PM concentrations, e.g. collocating one of the direct measurement instruments with the nephelometer and comparing results.

The concentration of particulates is directly proportionate to the amount of scattering detected, so an optical device can provide an indirect measure of PM<sub>2.5</sub> concentration can be determined by a ratio of scattering to PM<sub>2.5</sub> concentrations compared at several sites and over time. Of course, since this is an indirect method, interferences can be substantial, including changes in environmental conditions, especially relative humidity. Since nephelometers do not collect PM, no analysis of particles for chemical composition is possible. In addition, extremely small particles in the air may be missed by an optical microscope, individually weighing so little that their presence is masked in gravimetric analysis by the presence of a few large particles (see Discussion in Chapter 6).

The open-path technologies discussed earlier for gas-phase pollutants can sometimes be used for PM. Recent studies indicate a relationship between PM size and plume light extinction. Each plume has unique features in specific regions of the open-path extinction spectra. The extinction measurements a PM plume can be combined with algorithms to retrieve an estimate of mean mass distribution. Larger PM (1–20 mm diameter) has

interferences in IR extinction spectra, whereas smaller PM will affect the visible and UV wavelength region.<sup>50</sup>

The DIAL, OP-FTIR and other open-path systems are being evaluated to address aerosols. This is challenging in that aerosol cloud is much more complex than a gaseous cloud given the many physical properties of the specific material, meaning that radiation interactions between particles and the atmosphere add variability beyond that of gas-phase pollutants. This will include new algorithms for analyzing the open-path signals.<sup>51</sup>

## 25.4 MEASURING GAS AND PARTICULATE PHASES TOGETHER

Ambient air always contains particulate matter, which can interfere with the measurement of gases. For example, if one is trying to determine the amount of NO<sub>2</sub> in the air, but any solid-phase nitrate particles and nitric acid vapor will interfere with the results. Thus, there are two basic reasons to know the phase distribution of an air sample, i.e. to know and decrease interference and to account for the total amount of a contaminant in both phases.

### 25.4.1 Denuders

One way to ascertain both particulate and gas phases is the use of the diffusion denuders mentioned above. Actually, the term diffusion denuder tells only half of the denuder story. The denuder is also a particle-gas phase separation device.

In a denuder, air is pulled through a hollow tube that is coated with sorbing media. The flow is kept laminar by modulating the flow rate to the tube diameter. This increases diffusion several orders of magnitude greater than Brownian molecular diffusivity of the particulate matter, allowing the gas to move into the sorbing media in the interior walls of the tubes much faster than under normal, turbulent conditions. The tube length is chosen to ensure that all, or at least a known and consistent amount, of the gas moves into the walls before the air exits the tube. However, most of the particles remain suspended in the airflow and can be captured, e.g. with filters.

Annual denuders are a specific type that employs two concentric tubes, with inner surface of the outer tube and the outer surface of the inner tube coated with the sorbing media. This doubles the surface area into which the gas will move, thus improving collection efficiency, shortening overall tube length, shortening sampling time and/or allowing for higher flow rates. These and other denuders are often used in sampling airborne semivolatile organic compounds (SVOCs). These substances are often found in both vapor and particulate

phases, so the separation of the denuder is ideal (see Discussion Box: "Measuring SVOCs in the Air" in Chapter 11).

## 25.5 ANALYSIS AND MEASUREMENT OF ODORS

Odors are an important, yet not well understood, aspect of air pollution. Human smell is initiated by sniffing, which transports air with concentrations of odorant molecules past curved bony structures, i.e. turbinates, in the nose. The turbinates generate turbulent airflow that mixes volatile compounds and particles and carries them to thin mucus layer that coats the olfactory epithelium (Figure 25.27). Smell connects to other senses. For example, the smell from the burning plastics, oxidizing metal, semivolatile and VOCs, and particulate matter is physiologically linked to memory centers.

Odors have often been associated with air pollution episodes and disasters. In addition to the link between memory and olfactory centers. Indeed, the nasal pathway is a means by which air pollutants are taken up by humans. This goes beyond nuisance and is an indication of potential adverse health effects. For example, nitric oxide (NO) is a neurotoxic gas released from many sources, such as confined animal feeding operations, breakdown of fertilizers after they are applied to the soil and crops, and emissions from vehicles. Besides being inhaled into the lungs, NO can reach

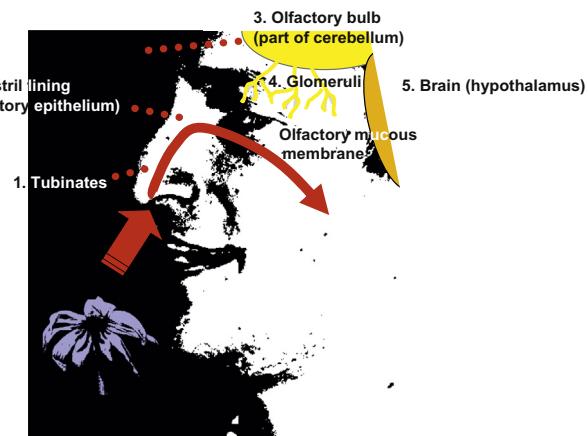


FIGURE 25.27 Human smell is initiated by sniffing, which transports air with concentrations of odorant molecules past curved bony structures, i.e. turbinates, in the nose. The turbinates generate turbulent airflow that mixes volatile compounds and particles and carries them to thin mucus layer that coats the olfactory epithelium. The olfactory epithelium contains odor sensing cells. (For color version of this figure, the reader is referred to the online version of this book.) Vallero DA, Vesilind PA. Socially responsible engineering: justice in risk management. Hoboken (New Jersey): John Wiley & Sons; 2007 ISBN: 9780471787075; Adapted from: Nagle HT, Schiffman SS, Gutierrez-Osuna R. The how and why of electronic noses. IEEE Spectrum. 35(9): 22–34.

the brain directly. The gas can pass through a thin membrane via the nose to the brain.

The nasal exposure is a different paradigm from that usually used to calculate exposure. In fact, most sources do not have a means for calculating exposures other than dermal, inhalation, and ingestion. Research has linked people's emotional states to odors, e.g. near confined animal feeding operations in North Carolina.<sup>52</sup> People who live near swine facilities are negatively affected when they smell odors from the facility. This is consistent with other research that has found that people experience adverse health symptoms more frequently when exposed to livestock odors. These symptoms include eye, nose, and throat irritation, headache, nausea, diarrhea, hoarseness, sore throat, cough, chest tightness, nasal congestion, palpitations, shortness of breath, stress, and drowsiness. There is quite a bit of diversity in response, with some people being highly sensitive to even low concentrations of odorant compounds while others are relatively unfazed even at much higher concentrations. Actually, response to odors can be triggered by three different mechanisms. In the first mechanism, symptoms can be induced by exposure to odorant compounds at sufficiently high concentrations to cause irritation or other toxicological effects. The irritation, not the odor, evokes the health symptoms. The odor sensation is merely as an exposure indicator. In the second mechanism, symptoms of adverse effects result from odorants concentrations lower than those eliciting irritation. This can be owing to genetic predisposition or conditioned aversion. In the third mechanism, symptoms can result from a coexisting pollutant, e.g. an endotoxin, which is a component of the odorant mixture. Technologies are advancing, including the development of "artificial noses".<sup>53</sup>

Odorants are chemical compounds such as H<sub>2</sub>S, which smells like rotten eggs, and may be measured by chemical or organoleptic methods. Organoleptic methods are those which rely on the response to odor of the human nose. Although chemical methods may be useful in identifying and quantifying specific odorants, human response is the only way to assess the degree of acceptability of odorants in the atmosphere. This is due to several factors: the nonlinear relationship between odorant concentration and human response, the variability of individual responses to a given odorant concentration, and the sensory attributes of odor.

Four characteristics of odor are subject to measurement by sensory techniques: intensity, detectability, character (quality), and hedonic tone (pleasantness–unpleasantness).<sup>54</sup> Odor intensity is the magnitude of the perceived sensation and is classified by a descriptive scale, e.g. faint–moderate–strong, or a 1–10 numerical scale. The detectability of an odor or

threshold limit is not an absolute level but depends on how the odorant is present, e.g. alone or in a mixture. Odor character or quality is the characteristic which permits its description or classification by comparison to other odors, i.e. sweet or sour, or like that of a skunk. The last characteristic is the hedonic type, which refers to the acceptability of an odorant. For the infrequent visitor, the smell of a large commercial bread bakery may be of high intensity but pleasant. For the nearby resident, the smell may be less acceptable.

The sensory technique used for assessing human perception of odors is called *olfactometry*. The basic technique is to present odorants at different concentrations to a panel of subjects and assess their response. The process favored by the U.S. National Academy of Sciences is dynamic olfactometry.<sup>55</sup> This technique involves a sample dilution method in which a flow of clean, nonodorous air is mixed with the odorant under dynamic or constant flow conditions. With this type of apparatus and standard operating conditions, it is possible to determine the detection threshold and the recognition threshold. At high dilution, the panel will be able to tell only whether an odorant is present or absent. Only at higher concentrations, typically by a factor of 2–10, will the subjects be able to identify the odorant.

The olfactometric procedure contains the following elements:

1. Dynamic dilution.
2. Delivery of diluted odorant for smelling through a mask or port.
3. Schedule of presentation of various dilutions and blanks.
4. Obtaining responses from the panelists.
5. Calculation of a panel threshold from experimental data.
6. Panelist selection criteria.

The first element, dynamic dilution, provides a reproducible sample for each panelist. The system must minimize the loss of the odorant to the walls of the delivery apparatus, provide clean dilution air of odor-free quality, maintain a constant dilution ratio for the duration of a given test, and have no memory effect when going from high to low concentrations or switching between odorants of different characters. The type of mask or port and the delivery flow rate have been found to influence the response of panelists in determining odor threshold and intensity.

The schedule of presentation may influence the results. The sensory effects are judgment criterion, anticipation, and adaptation. The judgment criterion determines how the panelist will respond when asked whether or not an odor is sensed. Individuals differ in

their readiness to be positive or negative. The anticipation effect is a tendency to expect an odor over a given series of trials. Subjects show some positive response when no odorant is present. The adaptation effect is the temporary desensitization after smelling an odorant. This is also called olfactory fatigue and often occurs in occupational settings. Because of olfactory fatigue, investigators evaluating odor concentration in the field must breathe air deodorized by passage through an activated carbon canister before and after sniffing the ambient air being evaluated.

Individuals differ in their sensitivity to odor. Figure 25.28 shows a typical distribution of sensitivities to ethylsulfide vapor. There are currently no guidelines on inclusion or exclusion of individuals with abnormally high or low sensitivity. This variability of response complicates the data treatment procedure. In many instances, the goal is to determine some mean value for the threshold representative of the panel as a whole. The small size of panels (generally fewer than 10 people) and the distribution of individual sensitivities require sophisticated statistical procedures to find the threshold from the responses.

Thresholds may also be determined by extrapolation of dose-response plots. In this approach, the perceived odor intensity is measured at several dilutions using some intensity rating method (Figure 25.28). The threshold value may be selected at some value (e.g. zero intensity) and the concentration determined with the dilution ratio.

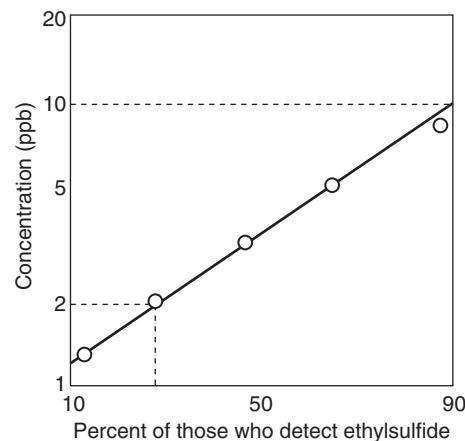


FIGURE 25.28 Distribution of sensitivity to ethylene sulfide odor (based on data from 33 human subjects). The abscissa is the percentage of the individuals who detected the presence of ethylene sulfide at various levels. Dravnick A, Jarke F. Odor threshold measurement by dynamic olfactometry: Significant operational variables. J Air Pollut Control Assoc. 30: 1284–1289.

## 25.6 ANALYSIS AND MEASUREMENT OF VISIBILITY

Impairment of visibility is a degradation of our ability to perceive objects through the atmosphere (Figure 25.29). Several factors influence our concept of visibility: the characteristics of the source, the human observer, the object, and the degree of pollution in the atmosphere. Our attempts to measure visibility at a given

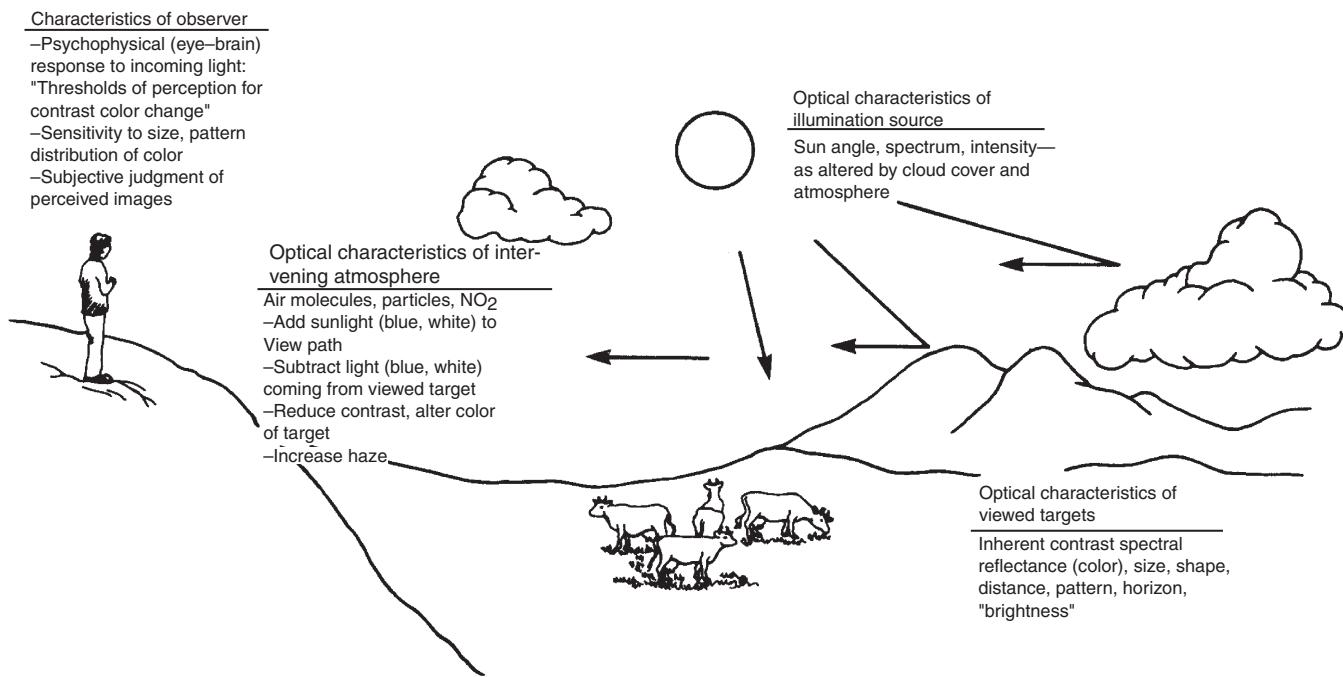


FIGURE 25.29 Factors determining visibility in the atmosphere. US Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park (North Carolina): Protecting Visibility; 1979. Report No. EPA-450/5-79-008.

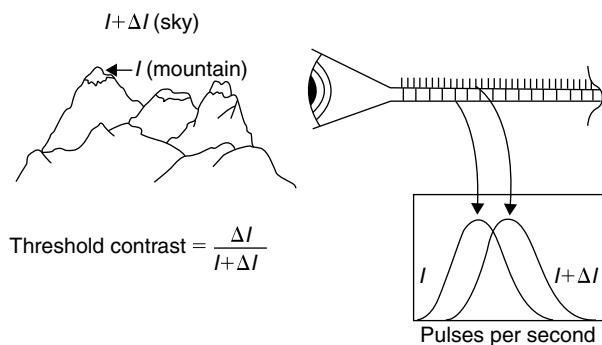
location can take two approaches: human observations and optical measurements. In pristine locations such as national parks, use of human observers has permitted us to gain an understanding of the public's concept of visibility impairment. Although it is difficult to quantify the elements of human observations, this type of research, when coupled with optical measurements, provides a better measure of visibility at a given location.<sup>56a–56c</sup>

To see an object, an observer must be able to detect the contrast between the object and its surroundings. If this contrast decreases, it is more difficult to observe the object. In the atmosphere, visibility can decrease for a number of reasons. For example, we may be farther away from the object (e.g. an airplane can move away from us); the sun's angle may change with the time of day; and if air pollution increases, the contrast may decrease, reducing our ability to see the object.

Objects close to us are easily perceived, but this diminishes as a function of distance. The lowest limit of contrast for human observers is called the *threshold contrast* and is important because this value influences the maximum distance at which we can see various objects. Thus, it is closely related to our understanding of good vs bad visibility for a particular set of environmental conditions.

Threshold contrast is illustrated in Figure 25.30.  $I$  is the intensity of light received by the eye from the object, and  $I + \Delta I$  represents the intensity coming from the surroundings. The threshold contrast can be as low as 0.018–0.03 and the object can still be perceptible. Other factors, such as the physical size of the visual image on the retina of the eye and the brain's response to the color of the object, influence the perception of contrast.

Reduction in visibility is caused by the following interactions in the atmosphere: light scattering by gaseous



**FIGURE 25.30 Threshold contrast in distinguishing an object from its surroundings.** The eye responds to an increment in light intensity by increasing the number of signals (pulses) sent to the brain. The detection of threshold contrast involves the ability to discriminate between the target ( $I$ ) and the brighter background ( $I + \Delta I$ ). *Gregory RL. Eye and brain: the psychology of seeing. London (UK): Weidenfeld and Nicolson; 1977.*

molecules and particles, and light absorption by gases and particles.<sup>57</sup> Light-scattering processes involve the interaction of light with gases or particles in such a manner that the direction or frequency of the light is altered. Absorption processes occur when the electromagnetic radiation interacts with gases or particles and is transferred internally to the gas or particle.

Light scattering by gaseous molecules is wavelength dependent and is the reason why the sky is blue. This process is dominant in atmospheres that are relatively free of aerosols or light-absorbing gases. Light scattering by particles is the most important cause of visibility reduction. This phenomenon is dependent on the size of the particles suspended in the atmosphere.

Light absorption by gases in the lower troposphere is limited to the absorption characteristics of nitrogen dioxide. This compound absorbs the shorter, or blue, wavelengths of visible light, causing us to observe the red wavelengths. We therefore perceive a yellow to reddish-brown tint in atmospheres containing quantities of NO<sub>2</sub>. Light absorption by particles is related principally to carbonaceous or black soot in the atmosphere. Other types of fine particles such as sulfates, although not good light absorbers, are very efficient at scattering light.

The interaction of light in the atmosphere is described mathematically as:

$$-dI = b_{\text{ext}} I \cdot dx \quad (25.6)$$

where  $-dI$  is the decrease in intensity,  $b_{\text{ext}}$  is the extinction coefficient,  $I$  is the original intensity of the beam of light, and  $dx$  is the length of the path traveled by the beam of light.

Figure 25.31(A) shows a beam of light transmitted through the atmosphere. The intensity of the beam  $I(x)$  decreases with the distance from the illumination source as the light is absorbed or scattered out of the beam. For a short period, this decrease is proportional to the intensity of the beam and the length of the interval at that point. Here  $b_{\text{ext}}$  is the extinction or attenuation coefficient and is a function of the degree of scattering and absorption of the particles and gases which are present in the beam path.

Figure 25.31(B) illustrates a slightly more complicated case, but one more applicable to atmospheric visibility. In this example, the observer still depends on the ability to perceive light rays emanating from the target object and on the scattering and absorption of those rays out of the beam. In addition, however, the observer must contend with additional light scattered into the line of sight from other angles. This extraneous light is sometimes called *air light*. Equation (23.7) is modified to account for this phenomenon by adding a term to represent this background intensity.

$$-dI = dI(\text{extinction}) + dI(\text{air light}) \quad (25.7)$$

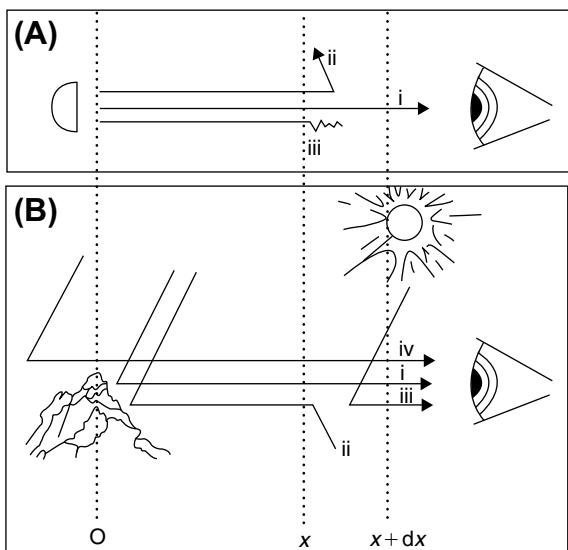


FIGURE 25.31 (A) A diagram of extinction of light from a source such as an electric light in a reflector, illustrating (i) transmitted, (ii) scattered, and (iii) absorbed light. (B) A diagram of daylight visibility, illustrating (i) residual light from a target reaching an observer, (ii) light from a target scattered out of an observer's line of sight, (iii) air light from the intervening atmosphere, and (iv) air light constituting horizon sky. US Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park (North Carolina): Protecting Visibility; 1979. Report No. EPA-450/5-79-008.

This air light term contributes to the reduced visibility we call *atmospheric haze*.

A simplified relationship developed by Koschmieder<sup>58</sup> which relates the visual range and the extinction coefficient is given by

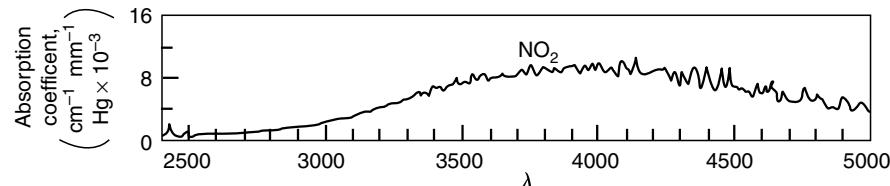
$$L_v = \frac{392}{b_{\text{ext}}} \quad (25.8)$$

where,  $L_v$  is the distance at which a black object is just barely visible.<sup>59</sup> Equation (23.8) is based on the following assumptions:

1. The background behind the target is uniform.
2. The object is black.
3. An observer can detect a contrast of 0.02.
4. The ratio of air light to extinction is constant over the path of sight.

While the Koschmieder relationship is useful as a first approximation for determining visual range, many situations exist in which the results are only qualitative.

FIGURE 25.32 Absorption spectrum of nitrogen dioxide. Ref. 61.



The extinction coefficient  $b_{\text{ext}}$  is dependent on the presence of gases and molecules that scatter and absorb light in the atmosphere. The extinction coefficient may be considered as the sum of the air and pollutant scattering and absorption interactions, as shown in the following equation:

$$b_{\text{ext}} = b_{\text{rg}} + b_{\text{ag}} + b_{\text{scat}} + b_{\text{ap}} \quad (25.9)$$

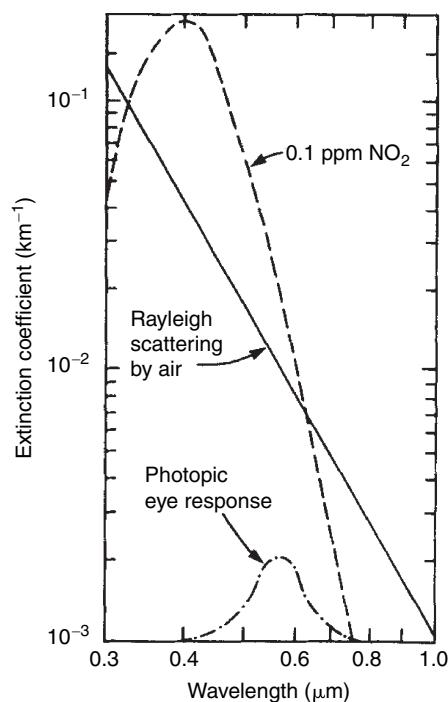
where,  $b_{\text{rg}}$  is scattering by gaseous molecules (Rayleigh scattering),  $b_{\text{ag}}$  is absorption by NO<sub>2</sub> gas,  $b_{\text{scat}}$  is scattering by particles, and  $b_{\text{ap}}$  is absorption by particles. These various extinction components are a function of wavelength. As extinction increases, visibility decreases.

The Rayleigh scattering extinction coefficient for particle-free air is  $0.012 \text{ km}^{-1}$  for "green" light ( $\gamma = 0.05 \mu\text{m}$ ) at sea level.<sup>60</sup> This permits a visual range of  $\sim 320 \text{ km}$ . The particle-free, or Rayleigh scattering, case represents the best visibility possible with the current atmosphere on earth.

The absorption spectrum of NO<sub>2</sub> shows significant absorption in the visible region (Figure 25.32).<sup>61</sup> As a strong absorber in the blue region, NO<sub>2</sub> can color plumes red, brown, or yellow. Figure 25.33 shows a comparison of extinction coefficients of 0.1 ppm NO<sub>2</sub> and Rayleigh scattering by air.<sup>62</sup> In urban areas, some discoloration can be due to area-wide NO<sub>2</sub> pollution. In rural areas, the biggest problem with NO<sub>2</sub> is that in coherent plumes from power plants, it contributes to the discoloration of the plume.

Suspended particles are the most important factor in visibility reduction. In most instances, the visual quality of air is controlled by particle scattering and is characterized by the extinction coefficient  $b_{\text{scat}}$ . The size of particles plays a crucial role in their interaction with light. Other factors are the refractive index and shape of the particles, although their effect is harder to measure and is less well understood. If we could establish these properties, we could calculate the amount of light scattering and absorption. Alternatively, the extinction coefficient associated with an aerosol can be measured directly.

Aerosol chemical composition determines the amount of light absorbed and scattered. For example, plumes will appear to be darker or lighter as a result of incoming light and the chemical makeup of the particles in the plume. In Figure 25.34, the two plumes on the left are contain large amounts of PM, whereas the two



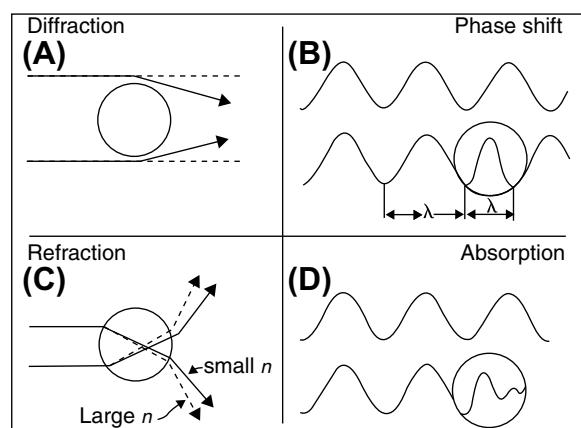
**FIGURE 25.33 Comparison of  $b_{\text{ext}}$  for 0.1 ppm  $\text{NO}_2$  and Rayleigh scattering by air.** The photopic eye response represents the range of wavelengths over which the eye detects light. Husar R, White WH, Patterson DE, Trijoniis J. (1979). *Visibility Impairment in the Atmosphere*. Draft report prepared for the US Environmental Protection Agency under Contract No. 68022515, Task Order No. 28.



**FIGURE 25.34 Effect of aerosol chemical composition on plume color.** (For color version of this figure, the reader is referred to the online version of this book.) Photo credit: Malm WC. Introduction to Visibility. U.S. National Park Service. <http://www.epa.gov/airquality/visibility/pdfs/introvis.pdf>; [accessed 22.11.13].

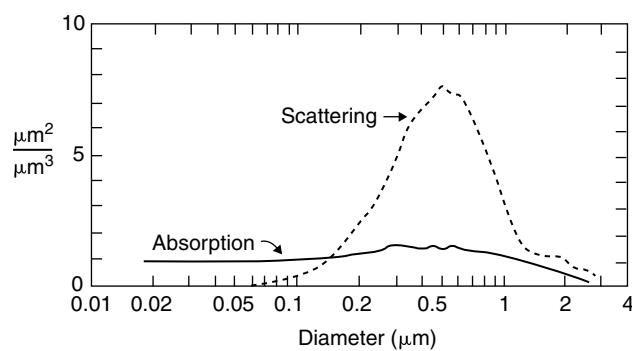
plumes on the right consist primarily of water droplets. The plume on the far right, which is illuminated by direct sunlight, appears to be white. The second identical water droplet plume, which is shaded, is much darker.

Light and suspended particles interact in the four basic ways: refraction, diffraction, phase shift, and absorption (Figure 25.35). For particles with a diameter of



**FIGURE 25.35 Four forms of particle light interaction.** Light scattering by coarse particles ( $>2 \mu\text{m}$ ) is the combined effect of diffraction and refraction. (A) Diffraction is an edge effect whereby the light is bent to fill in the shadow behind the particle. (B) The speed of a wavefront entering a particle with refractive index  $n > 1$  (for water,  $n = 1.33$ ) is reduced. (C) Refraction produces a lens effect. The angular dispersion resulting from bending incoming rays increases with  $n$ . (D) For absorbing media, the refracted wave intensity decays within the particle. When the particle size is comparable to the wavelength of light ( $0.1\text{--}1.0 \mu\text{m}$ ), these interactions (A)–(D) are complex and enhanced. US Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park (North Carolina): Protecting Visibility; 1979. Report No. EPA-450/5-79-008.

$0.1\text{--}1.0 \mu\text{m}$ , scattering and absorption can be calculated by using the Mie equations.<sup>63</sup> Figure 25.36 shows the relative scattering and absorption efficiency per unit volume of particle for a typical aerosol containing some light-absorbing soot.<sup>64</sup> This clearly shows the importance of atmospheric particles in the diameter range  $0.1\text{--}1.0 \mu\text{m}$  as efficient light-scattering centers. With particles of larger and smaller diameters, scattering decreases. Absorption generally contributes less to the extinction coefficient than does the scattering processes. Atmospheric particles of different chemical composition have different refractive indices, resulting in different scattering efficiencies. Figure 25.37 shows the scattering-to-mass ratio for four different materials.



**FIGURE 25.36 Scattering and absorption cross-section per unit volume as a function of particle diameter.** Ref. 66.

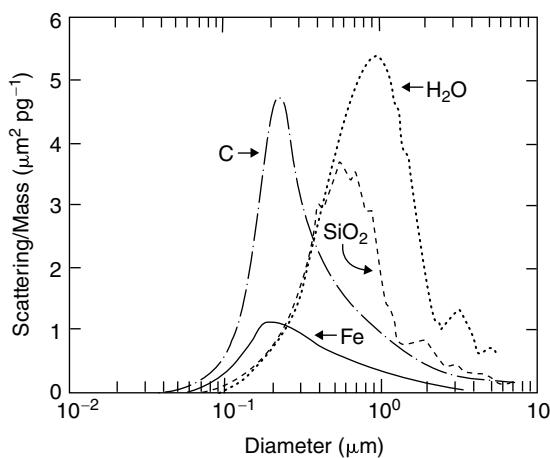


FIGURE 25.37 Single particle scattering to mass ratio for particles of four different compositions. Carbon particles are also very efficient absorbers of light. Ref. 64.

Clearly, carbon or soot aerosols, and aerosols of the same diameter with water content, scatter with different efficiencies at the same diameter.

Visibility is also affected by alteration of particle size due to hydroscopic particle growth, which is a function of relative humidity. In Los Angeles, California, the air, principally of marine origin, has numerous sea salt particles. Visibility is noticeably reduced when humidity exceeds about 67%. Relative humidity and origin of air (maritime or continental) also affect visibility; presumably due to numerous hygroscopic aerosols from

air pollution sources. Some materials, such as sulfuric acid mist, exhibit hygroscopic growth at humidity as low as 30%.

The ratio of the incident solar transmissivity to the extraterrestrial solar intensity can be as high as 0.5 in clean atmospheres but can drop to 0.2–0.3 in polluted areas, indicating a decrease of 50% in ground-level solar intensity. The turbidity coefficient can also be derived from these measurements and used to approximate the aerosol loading of the atmosphere. By assuming a particle size distribution in the size range 0.1–10.0  $\mu\text{m}$  and a particle density, the total number of particles can be estimated. The mass loading per cubic meter can also be approximated. Because of the reasonable cost and simplicity of the sun photometer, comparative measurements can now be made around the world.

Atmospheric haze is the condition of reduced visibility caused by the presence of fine particles or  $\text{NO}_2$  in the atmosphere, which can be uniform or layered (Figure 25.38). The particles must be 0.1–1.0  $\mu\text{m}$  in diameter, the size range in which light scattering occurs. The source of these particles may be natural or anthropogenic. Atmospheric haze has been observed in both the western and eastern portions of the United States. Typical visual ranges in the East are <15 mi and in the Southwest >50 mi. The desire to protect visual air quality in the United States is focused on the national parks in the West. The ability to see vistas over 50–100 km in these locations makes them particularly vulnerable to atmospheric haze. This phenomenon is generally

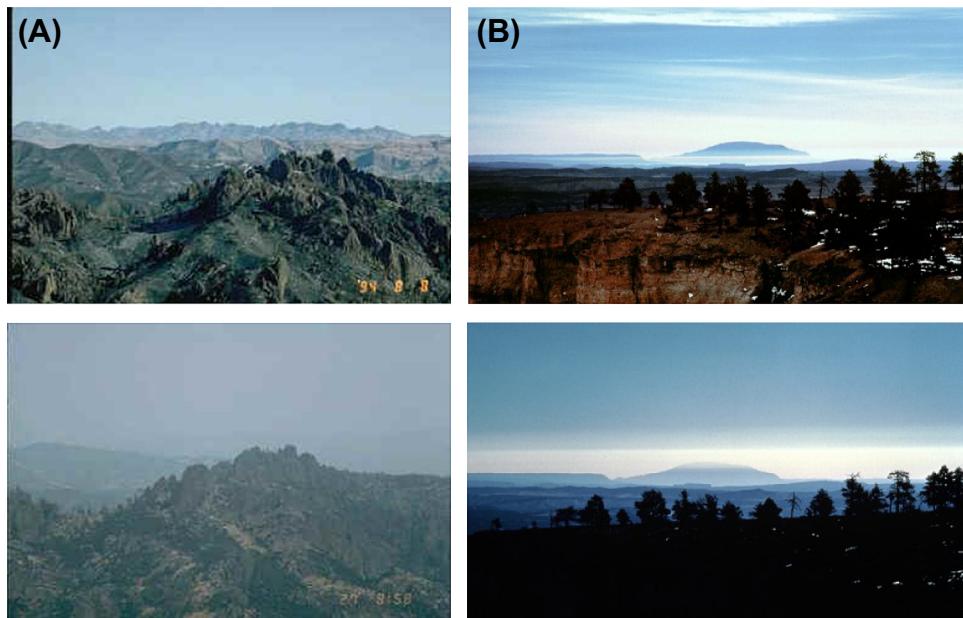
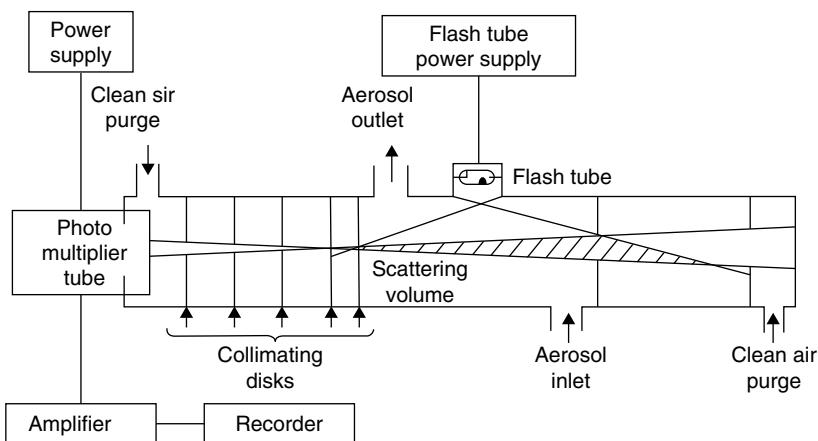


FIGURE 25.38 Example of uniform (A) and layered (B) haze. (A) Top photo has about 200 mi visibility and the bottom photo with uniform haze has about 15 mi. (B) Top photo, lower altitude layer of haze obscures bottom of Navajo Mountain; whereas higher altitude haze in the bottom photo obscures the top. (For color version of this figure, the reader is referred to the online version of this book.) Interagency Monitoring of Visual Environments. <http://vista.cira.colostate.edu/improve/Education/Glossary/Haze.htm>; 2013 [accessed 22.11.13].



**FIGURE 25.39 Schematic diagram of the integrating nephelometer.** Ref. 65; Waggoner AP, Ahliquist NC, Charlson RJ. Measurement of the aerosol total scatter-backscatter ratio. *Applied Optics* 1972;11(2): 2886–2889.

associated with diffuse or widespread atmospheric degradation as opposed to individual plumes.

The major component of atmospheric haze is sulfate particulate matter (particularly ammonium sulfate), along with varying amounts of nitrate particulate matter, which in some areas can equal the sulfate. Other components include graphitic material, fine fly ash, and organic aerosols. The haze-inducing PM can be primary, i.e. directly injected into the atmosphere, or secondary, formed in the atmosphere by gas-to-particle conversion processes.

Optical measurements permit the quantification of visibility degradation under different conditions. Several instruments are capable of measuring visual air quality, e.g. cameras, photometers, telephotometers, transmissometers, and scattering instruments.

Photography can provide a permanent record of visibility conditions at a particular place and time. This type of record can preserve a scene in a photograph in a form similar to the way it is seen. Photometers measure light intensity by converting brightness to representative electric signals with a photodetector. Different lenses and filters may be used to determine color and other optical properties. When used in combination with long-range lenses, photometers become telephotometers. This type of instrument may view distant objects with a much smaller viewing angle. The output of the photodetector is closely related to the perceived optical properties of distant targets. Telephotometers are often used to measure the contrast between a distant object and its surroundings, a measurement much closer to the human observer's perception of objects.

A transmissometer is similar to a telephotometer except that the target is a known light source. If we know the characteristics of the source, the average extinction coefficient over the path of the beam may be calculated. Transmissometers are not very portable in terms of looking at a scene from several directions. They are also very sensitive to atmospheric turbulence, which limits the length of the light beam.

Scattering instruments are also used to measure visibility degradation. The most common instrument is the integrating nephelometer, which measures the light scattered over a range of angles. The physical design of the instrument, as shown in Figure 25.39, permits a point determination of the scattering coefficient of extinction,  $b_{ext}$ .<sup>65</sup> In clean areas,  $b_{ext}$  is dominated by scattering, so that the integrating nephelometer yields a measure of the extinction coefficient. The  $b_{ext}$  can be related to visual range through the Koschmieder relationship, described above.

Other measurements important to visual air quality are pollutant related, i.e. the size distribution, mass concentration, and number concentration of airborne particles and their chemical composition. From the size distribution, the Mie theory of light scattering can be used to calculate the scattering coefficient. Table 25.9 summarizes the different types of visual monitoring methods.

## 25.7 ANALYSIS AND MEASUREMENT OF ACIDIC DEPOSITION

The two components of acidic deposition are wet deposition and dry deposition. The collection and subsequent analysis of wet deposition are intuitively straightforward. A sample collector opens to collect rainwater at the beginning of a rainstorm and closes when the rain stops. The water is then analyzed for pH, anions (negative ions), and cations (positive ions). The situation for dry deposition is much more difficult.<sup>66</sup> Collection of particles settling from the air is very dependent on the surface material and configuration. The surfaces of trees, plants, and grasses are considerably different from that of the round, open-top canister often used to collect dry deposited particles. After collection, the material must be suspended or dissolved in pure water for subsequent analysis.

TABLE 25.9 Visibility Monitoring Methods

Method	Parameters Measured	Advantages	Limitations	Preferred Use
Human observer	Perceived visual quality, atmospheric color, plume blight, visual range	Flexibility, judgment; large existing database (airport visual range)	Labor intensive; variability in observer perception; suitable targets for visual range not generally available	Complement to instrumental observations; areas with frequent plume blight, discoloration; visual ranges with available target distances
Integrating nephelometer	Scattering coefficient ( $b_{\text{scat}}$ ) at site	Continuous readings; unaffected by clouds, night; $b_{\text{scat}}$ directly relatable to fine aerosol concentration at a point; semiportable; used in a number of previous studies; sensitive models available; automated	Point measurement, requires assumption of homogeneous distribution of particles; neglects extinction from absorption, coarse particles ( $>3-10 \mu\text{m}$ ); must consider humidity effects at high relative humidity	Areas experiencing periodic, well-mixed general haze; medium to short viewing distances; small absorption coefficient ( $b_{\text{abs}}$ ); relating to point composition measurements
Multiwavelength telephotometer	Sky and/or target radiance, contrast at various wavelengths	Measurement over long view path (up to 100 km) with suitable illumination and target, contrast transmittance, total extinction, and chromaticity over sight path can be determined; includes scattering and absorption from all sources; can detect plume blight; automated	Sensitive to illumination conditions; useful only in daylight; relationship to extinction, aerosol relationship possible only under cloudless skies; requires large, uniform targets	Areas experiencing mixed or inhomogeneous haze, significant fugitive dust; medium to long viewing distances (one-fourth of visual range); areas with frequent discoloration; horizontal sight path
Transmissometer	Long path extinction coefficient ( $b_{\text{ext}}$ )	Measurement over medium view path (10–25 km); measures total extinction, scattering and absorption; unaffected by clouds, night	Calibration problems; single wavelength; equivalent to point measurement in areas with long view paths (50–100 km); limited applications to date still under development	Areas experiencing periodic mixed general haze, medium to short viewing distance areas with significant absorption ( $b_{\text{abs}}$ )
Photography	Visual quality, plume blight, color, contrast (limited)	Related to perception of visual quality; documentation of vista conditions	Sensitive to lighting conditions; degradation in storage; contrast measurement from film subject to significant errors	Complement to human observation, instrumental methods; areas with frequent plume blight, discoloration
Particle samplers	Particles	Permit evaluation of causes of impairment	Not always relatable to visual air quality; point measurement	Complement to visibility measurements
Hi vol.	TSP	Large database, amenable to chemical analysis; coarse particle analysis	Does not separate sizes; sampling artifacts for nitrate, sulfate; not automated	Not useful for visibility sites
Cascade impactor	Size-segregated particles (more than two stages)	Detailed chemical, size evaluation	Particle bounce, wall losses; labor intensive	Detailed studies of scattering by particles, $2 \mu\text{m}$
Dichotomous and fine particle samplers (several fundamentally different types)	Fine particles ( $2.5 \mu\text{m}$ ) coarse particles ( $2.5-15 \mu\text{m}$ ) inhalable particles ( $0-15 \mu\text{m}$ )	Size cut enhances resolution, optically important aerosol analysis, low artifact potential, particle bounce; amenable to automated compositional analysis; automated versions available; large networks under development	Some large-particle penetration; 24 h or longer sample required in clean areas for mass measurement; automated version relatively untested in remote locations	Complement to visibility measurement, source assessment for general haze, ground-level plumes

Source: US Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park (North Carolina): Protecting Visibility; 1979. Report No. EPA-450/5-79-008.

An overview of acid rain monitoring activities in North America shows several national and regional programs in operation in the United States, Canada, and Mexico.<sup>67</sup> The National Atmospheric Deposition Program has established the nationwide sampling network of ~100 stations in the United States. The sampler is shown in Figure 25.40, including a wet deposition collection container. The wet collection bucket is covered with a lid when it is not raining. A sensor for rain moves the lid to open the wet collector bucket and cover the dry bucket at the beginning of a rainstorm. This process is reversed when the precipitation ends.

The primary constituents to be measured are the pH of precipitation, sulfates, nitrates, ammonia, chloride ions, metal ions, phosphates, and specific conductivity. The pH measurements help to establish reliable long-term trends in patterns of acidic precipitation. The sulfate and nitrate information is related to anthropogenic sources where possible. The measurements of chloride ions, metal ions, and phosphates are related to sea spray and wind-blown dust sources. Specific conductivity is related to the level of dissolved salts in precipitation.

The flowchart for analysis of wet and dry precipitation shown in Figure 25.40 includes the weight

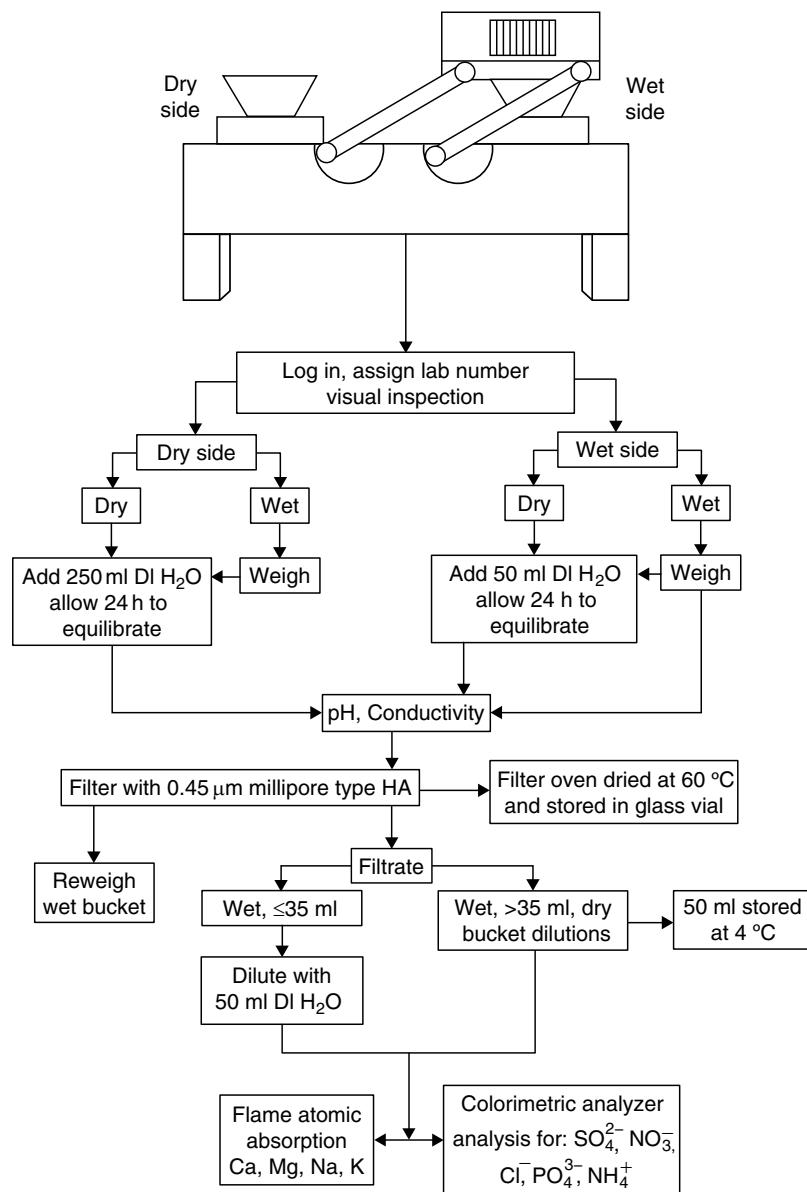


FIGURE 25.40 Schematic diagram of an integrated precipitation collector (top) and flowchart of the steps needed for sample analysis. DI H<sub>2</sub>O = distilled water. National Acidic Deposition Program. Quality Assurance Report, Central Analytical Laboratory, Illinois Institute of Natural Resources, Champaign, III, March 1980.

determinations, followed by pH and conductivity measurements and finally chemical analysis for anions and cations. The pH measurements are made with a well-calibrated pH meter, with extreme care taken to avoid contaminating the sample. The metal ions  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  are determined by flame photometry, which involves absorption of radiation by metal ions in a hot flame. Ammonia and the anions  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  are measured by automated colorimetric techniques.

## 25.8 MEASURING AIR TOXICS

In addition to the criteria pollutants, there are numerous hazardous air pollutants that must also be measured. The characteristics of these pollutants vary considerably in inherent properties, including vapor pressure, ranging from entirely gas-phase to highly volatile to semivolatile to nonvolatile (e.g. sorbed to aerosols). The methods for the gas-phase fraction mirror those of the gas phase pollutants if they possess the key physical and chemical similarities, e.g. absorbance and fluorescence by UV, visible, or IR wavelengths. The compounds bound to particles may be analyzed by PM chemical constituent determinations, such as X-ray fluorescence. However, such methods do not provide the actual chemical forms (i.e. speciation), but merely give elemental composition. To ascertain specific

compounds of concern will require wet chemistry and other more laborious approaches.

Given the diversity of air toxics, individual methods of collection, handling, storage, extraction, separation and detection must be tailored to the specific characteristics of these compounds. To this end, air quality regulation agencies have developed compendia of methods. For example, the U.S. EPA maintains a set of 17 methods in a standardized format with a variety of applicable sampling methods, as well as several analytical techniques, for specific classes of organic pollutants, as appropriate to the specific pollutant compound, its level, and potential interferences. Consequently, this treatment allows the user flexibility in selecting alternatives to complement his or her background and laboratory capability. These methods may be modified from time to time as advancements are made.<sup>68</sup>

The visual guide to the organization of the compendium for specific methods covering a variety of organic compounds is shown in Figure 25.41.

The methods assigned the "A" notation are methods which were published in the First Edition (Compendium Methods TO-1 through TO-14) of the Compendium and have now been updated due to technological advances in either the sampling or analysis methodology. In addition, three new methods (Compendium Methods TO-15 through TO-17) have been added to make the complete Second Edition of the Compendium. These methods were added due to

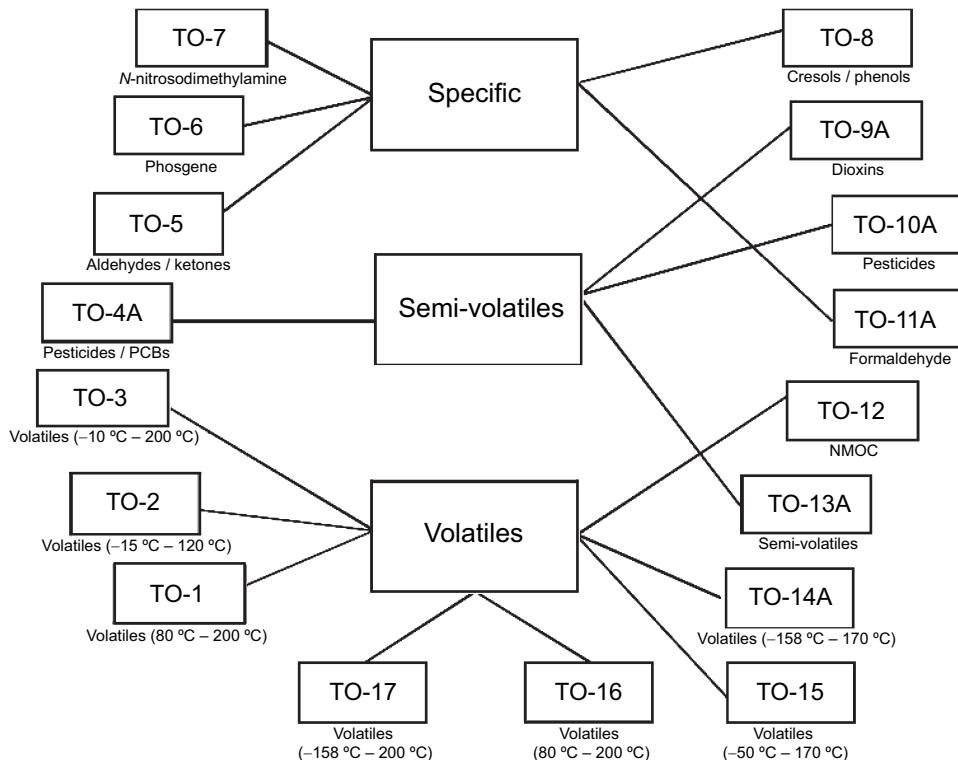


FIGURE 25.41 Visual guide to the air toxics methods compendium. Ref. 68.

TABLE 25.10 Listing of Compounds Classes in Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air – Second Edition

Compendium Method No.	Type of Compounds Determined	Sample Collection Device	Analytical Methodology*
TO-1§	Volatile organic compounds	Tenax® solid sorbent	GC/MS
TO-2§	Volatile organic compounds	Molecular sieve sorbent	GC/MS
TO-3§	Volatile organic compounds	Cryotrap	GC/FID
TO-4A	Pesticides/PCBs	Polyurethane foam	GC/MD
TO-5§	Aldehydes/ketones	Impinger	HPLC
TO-6§	Phosgene	Impinger	HPLC
TO-7§	Anilines	Adsorbent	GC/MS
TO-8§	Phenols	Impinger	HPLC
TO-9A	Dioxins	Polyurethane foam	HRGC/HRMS
TO-10A	Pesticides/PCBs	Polyurethane foam	GC/MD
TO-11A	Aldehydes/ketones	Adsorbent	HPLC
TO-12§	Nonmethane organic compounds (NMOC)	Canister or on-line	FID
TO-13A	Polycyclic aromatic hydrocarbons	Polyurethane foam	GC/MS
TO-14A	Volatile organic compounds (nonpolar)	Specially-treated canister	GC/MS and GC/MD
TO-15	Volatile organic compounds (polar/nonpolar)	Specially-treated canister	GC/MS
TO-16	Volatile organic compounds	Open-path monitoring	FTIR
TO-17	Volatile organic compounds	Single/multibed adsorbent	GC/MS, FID, etc.

\* GC/MS = Gas chromatography/mass spectrometry. GC/FID = Gas chromatography/flame ionization detector. HPLC = High performance liquid chromatography. GC/IT = Gas chromatography/ion trap detector. GC/MD = Gas Chromatography/Multi-detector. FTIR = Fourier transform infrared spectroscopy. HRGC/HRMS = High resolution gas chromatography/high resolution mass spectrometry.

§Methods denoted by “§” have not been changed since their publication in the First Edition of the Compendium, so the full content of these methods is not repeated in this Second Edition. Therefore, the full content of these methods must be obtained from the original Compendium (EPA 600/4-89-017).

Source: Ref. 70. <http://www.epa.gov/ttnamt1/files/ambient/airtox/tocomp99.pdf>; [accessed 21.11.13].

their advanced technology application involving specially treated canisters (Compendium Method TO-15), long path (open path) Fourier transform infrared spectroscopy (Compendium Method TO-16), and multibed sorbent techniques (Compendium Method TO-17).

Rather than attempt to describe these diverse methods here, the reader is advised to visit the compendium site (Link: <http://www.epa.gov/ttnamt1/airtox.html>) and browse for the most appropriate method for a given pollutant (Table 25.10). For example, if the compound of concern is a semivolatile compound, there are four possible methods, according to the visual guide. If the compound is a dioxin, then Method TO-9A should be used. However, if the compound is a polycyclic aromatic hydrocarbon, browsing the likely methods shows that TO-13A is most applicable. The method provides every step from sample selection through laboratory analyses, including quality control and assurance.<sup>69–71</sup>

## QUESTIONS

1. Give reasons why indene does not appear until 900°C in Figure 29.3. What does this indicate about PAHs?
2. What are the advantages and disadvantages of grab samples? Of random sampling?
3. If 6-l stainless steel canisters collect air samples every 12 h at 100 m downwind from a chemical plant and analyzed for VOCs, can these results be used to predict concentrations of VOCs that are precursors of a county's ground-level ozone concentrations? Why or why not?
4. A canister is properly logged and labeled by a field technician, who follows storage and transport protocols and gives it to the laboratory technician. The laboratory technician places the canister in the appropriate storage container. Later that afternoon, the laboratory technician evacuates the canister into a gas chromatograph-mass spectrometer and logs

- the procedure and readings in the laboratory notebook. What step, if any, is missing from this chain-of-custody so far?
5. List the advantages and disadvantages of remote sensing techniques by optical methods.
  6. If you know that benzene is being emitted by a factory and that a neighborhood 5 mi downwind has elevated benzene concentrations, which open-path method do you recommend to sample benzene at the fence line and why?
  7. What is the difference between a gas and a vapor? How is this important to measuring air pollutants?
  8. What are the physical differences between PM and gas phase pollutants?
  9. A source is known to generate benzo(*a*)pyrene and halogenated compounds with vapor pressures between  $10^{-3}$  and  $10^{-4}$  kPa. Which type of measurement methods do you recommend and why?
  10. What were the major air pollutants of concern following the Deepwater Horizon spill? What methods were used to detect these pollutants? List any possible weaknesses in this approach.
  11. What are the advantages and disadvantages of using a nephelometer to measure PM?
  12. How does the sampling inlet affect sample collection?
  13. What is the difference between uniform and layered haze?
  14. Describe how an aerosol consisting mainly of carbon would differ in haze formation than one consisting mainly of sulfates.
  15. How might measurement of acrolein be biased?
  16. What are the two main types of acidic deposition? How do these differences influence sampling and analysis?
  17. If you need to collect and analyze air samples of 1,3-butadiene, which air toxics method do you recommend? How about air samples of acrolein?
  18. Why is measuring dry deposition often more complicated and difficult than measuring wet deposition?
  19. In the United States, what is the purpose of the federal reference method (FRM)?
  20. Give a reason that the size of an ultrafine particle on a filter may be larger than when it was collected from the troposphere.
  21. Give a reason that the size of an aerosol on a filter may be smaller than when it was collected from the troposphere.

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### Suggested Readings in Addition to the References

Air pollution analytical methods continue to evolve and to improve. A good way to stay up-to-date on current methods is to visit the website for the US EPA's Ambient Monitoring Technology Information Center: <http://www.epa.gov/ttn/amtic>. Other sources include:

# Applying and Interpreting Air Quality Monitoring Data

## 26.1 INTRODUCTION

The methods described in Chapter 25 can be applied at various scales, from regional measurements of ozone to urban airsheds to neighborhoods to property adjacent to sources to microenvironments to personal. The representativeness and usefulness of air quality monitoring depend on the quality of each step from sample collection to sample preparation to analysis. Sampling is a statistical term, i.e. a sample is a subset of a population or domain from which information can be inferred about the entire population or domain. Thus, care must be taken to ensure the quality of every interdependent step in air quality measurements.

Since the sample taken represents a very small fraction of the larger population or airshed from which the sample was taken, it requires a model to provide an estimate of the air quality (see Chapter 27). The model may be represented mathematically or spatially. For example, a sample of air may consist of a canister or bag that holds a defined quantity of air that will be subsequently analyzed. The sample is representative of an air mass or, more likely, a part of an air mass, such as zones around a source with isopleths of the concentration of an air pollutant. A number of samples must be collected and their results aggregated to ascertain with defined certainty the quality of an air mass. More samples will be needed for a large urban air shed than for that of a small town. Intensive sampling is often needed for highly toxic contaminants and for sites that may be particularly critical, e.g. near a hazardous waste site or in an “at risk” neighborhood (such as one near a manufacturing facility that uses large quantities of potentially toxic materials and that has asthmatic children living there). Similar to other statistical measures, environmental samples allow for statistical inference. In this case, inferences are made regarding the condition of an ecosystem and the extent and severity to which a human population is exposed to air pollutants.

## 26.2 STATIONARY MONITORING NETWORKS

For most countries, the largest geographic scale of air quality monitoring is ambient monitoring with relatively low sampling density, e.g. one sampling site for every  $100 \text{ km}^{-1}$ , depending on the pollutant and on the resources available. For example, monitors are sited to indicate the extent and severity of pollution for a county or an urban area. The coverage is determined by the particular pollutant of interest, combined with meteorological and terrain conditions. Some pollutants, like ozone and greenhouse gases, cover large areas, whereas other more reactive or highly toxic pollutants may only be detectable within a few meters of their source.

In the United States, the Environmental Protection Agency (EPA) has established National Ambient Air Quality Standards (NAAQS) to protect human health and welfare.

Perhaps the best introduction to large-scale ambient monitoring is to discuss each stationary site network separately. The networks have increased in sampling density and in the number of the compounds being measured. They have also been continuously enhanced as new technologies have become more reliable.

The US standards are defined in terms of concentration and time span for a specific pollutant; for example, the National Ambient Air Quality Standards (NAAQS) for carbon monoxide is 9 parts per million by volume (ppmv) for 8 h, not to be exceeded more than once per year. For a state or local government to establish compliance with the NAAQS, measurements of the actual air quality must be made. To obtain these measurements, state and local governments have established stationary monitoring networks with instrumentation complying with federal specifications. From these measurements, regulating agencies determine whether a given location is attaining the air quality standard. If so, the area is said

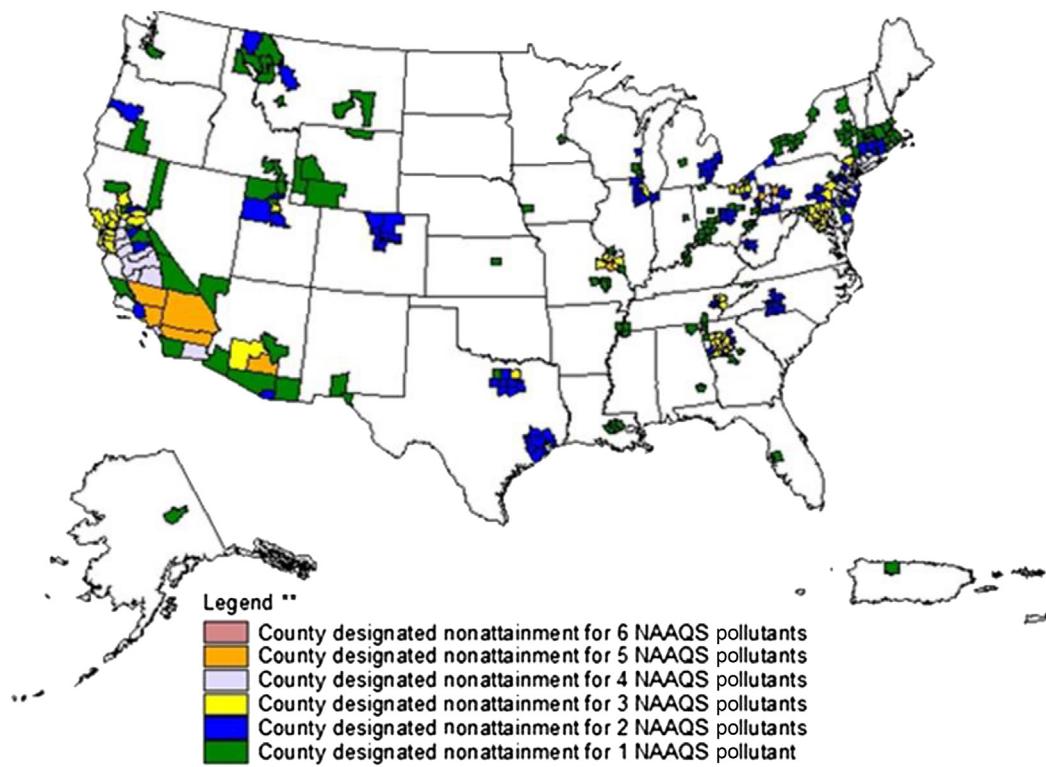


FIGURE 26.1 Counties that have been designated nonattainment for National Ambient Air Quality Standards (NAAQS) health standards, as of July 31, 2013. The largest areas are those not attaining one or two standards. The standards shown are for carbon monoxide, lead (both the original 1978 standard and the more stringent, revised standard of 2008), nitrogen dioxide, ozone (both the original 1997 8-h standard and the more stringent, revised 8-h standard of 2008), particulate matter ( $PM_{2.5}$  and  $PM_{10}$ —both the 1997 standards and the more stringent 2006 standard), and sulfur dioxide. U.S. Environmental Protection Agency. The green book nonattainment areas for criteria pollutants. (For color version of this figure, the reader is referred to the online version of this book.) <http://www.epa.gov/oaps001/greenbk/index.html>; [accessed 15.08.13].

to be in attainment for that pollutant. If not, the area is designated to be a nonattainment area. Figure 26.1 shows the US counties that are deemed to be nonattainment areas for any of the six of the NAAQS, i.e. particulates, carbon monoxide (CO), nitrogen dioxide ( $NO_2$ ), sulfur dioxide ( $SO_2$ ), ozone ( $O_3$ ), and lead (Pb).

The county designations in Figure 26.1 are based on data from stationary monitoring networks. The stationary monitoring sites in these areas also operated to determine the impact of new sources of emissions. As part of the environmental impact statement and prevention of significant deterioration processes, the projected impact of a new source on existing air quality must be assessed. Air quality monitoring is one means of making this type of assessment. A monitoring network is established at least 12 months before construction to determine prior air quality. Once the facility is completed and in operation, the network data determine the actual impact of the new source.

The trends in atmospheric pollutants, such as  $O_3$ ,  $SO_2$ , methane ( $CH_4$ ), nitric oxide (NO),  $NO_2$ , and CO are measured in rural as well as urban locations. Atmospheric budgets of various gases are developed to allow estimation of whether sources are anthropogenic or

natural. In addition, certain pollutants, such as Pb, are measured more intensively near known sources, such as smelters.

A stationary monitoring network should yield the following information: (1) background concentration levels, (2) highest concentration levels, (3) representative concentration levels in high-density areas, (4) the impact of local sources, (5) the impact of remote sources, and (6) the relative impact of natural and anthropogenic sources.

The spatial scale of an air quality monitoring network is determined by monitoring objectives. Spatial scales include personal (<1 m, one person), microscale (1–100 m), middle scale (100 m–0.5 km), neighborhood scale (0.5–4.0 km), urban scale (4–50 km), and regional scale (tens to hundreds of km). Table 26.1 shows the relationship between spatial scale and monitoring objectives.<sup>1</sup>

Sampler siting within a network must meet the limitations of any individual sampling site and the relationship of sampling sites with each other.<sup>2</sup> The overall approach for selection of sampling sites is (1) to define the purpose of the collected data, (2) to assemble site selection aids, (3) to define the general areas for samplers

TABLE 26.1 Relationship of the Scale of Representativeness and Monitoring Objectives

Siting Scales	Monitoring Objectives
Personal	Personal cloud
Personal, micro, middle, neighborhood (sometimes urban)	Highest concentration affecting people
Neighborhood, urban	High-density population exposure
Micro, middle, neighborhood	Source impact
Neighborhood, region	General/background concentration

based on chemical and meteorological constraints, and (4) to determine the final sites based on sampling requirements and surrounding objects.<sup>3</sup> Several purposes of air quality monitoring were mentioned earlier, such as air quality standard compliance, long-term trends, and new facility siting.

The tools available for site selection include climatological data, topography, population data, emission inventory data, and diffusion modeling. Climatological data are useful in relating meteorology to emission patterns. For example, elevated levels of photochemical oxidant are generally related to stagnant meteorological conditions and warm temperatures. Seasonal climatological patterns of prevailing winds and frequency of inversions will influence the location of sampling stations. Various types of maps are useful for establishing topography, population density, and location of sources of various pollutants. Wind roses overlaid with emission

sources and population densities help to locate the general areas for location of samplers.

Various types of dispersion models are available that can use as input emission patterns, climatological data, and population data to rank sampling locations by concentration threshold, resolution of peak concentrations, and frequency of exposure<sup>4</sup> or to rank sampling locations for maximum sensitivity to source emission changes, to provide coverage of as many sources or to cover as large a geographic area as possible.<sup>5</sup>

The last step in selecting specific sites is based on the following: availability of land and electrical power, security from vandalism, absence of nearby structures such as large buildings, probe height (inlet >3 m), and cost.

An example of matching scale and objective is the determination of CO exposure of pedestrians on sidewalks in urban street canyons. The location of a station to meet this objective would be an elevation about 3 m on a street with heavy vehicular traffic and large numbers of pedestrians.

In the United States, ambient air quality monitoring is conducted by state and local agencies. The network consists of four major categories of monitoring stations:

State and Local Air Monitoring Stations (SLAMS)

National Air Monitoring Stations (NAMS)

Special Purpose Monitoring Stations (SPMS)

Photochemical Assessment Monitoring Stations (PAMS).

By far the most ambient sites are in SLAMS (see Figure 26.2). The networks include a variety of monitoring sites in general categories to measure the highest concentrations expected to occur in the area covered by

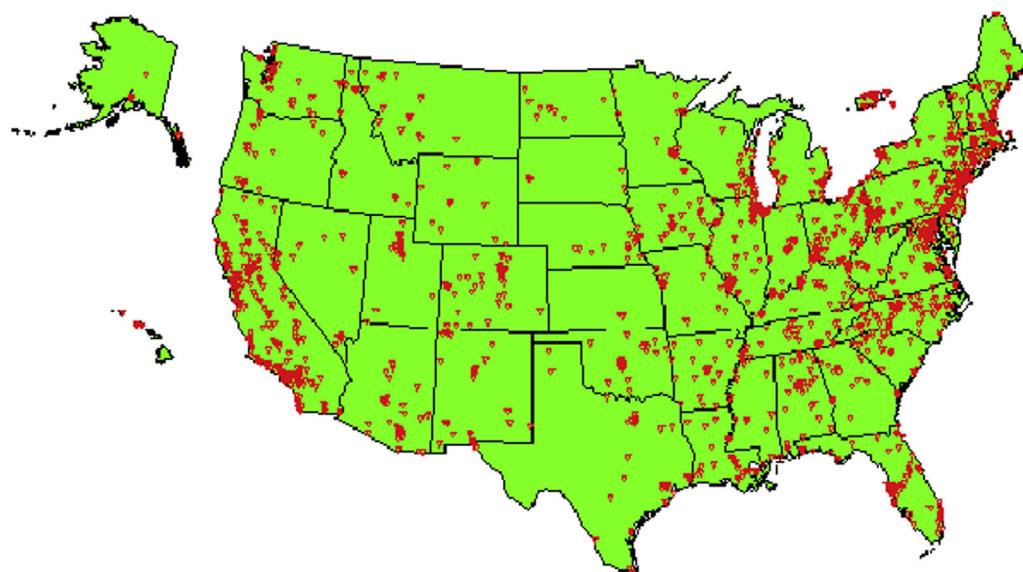


FIGURE 26.2 State and Local Air Monitoring Stations (SLAMS) network, consisting of about 4000 monitoring stations. The sampling density is highest near higher populated areas. The distribution of sites is mainly determined by the needs of state and local air pollution control agencies to meet state implementation plan (SIP) requirements. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 6.

the network, as well as typical concentrations in areas of high population density. The network should also indicate the impact of substantial sources and source categories on ambient pollution levels, provide data on general background concentration levels, and information regarding the extent of regional pollutant transport among populated areas, including support of secondary standards. Some sites are also designed to ascertain air pollution impacts on visibility, vegetation damage, or other welfare-based impacts, to judge compliance with and progress toward meeting ambient air quality standards, to activate emergency control procedures that prevent or alleviate air pollution episodes, to show air pollution trends throughout the region, including nonurban areas, and to provide reliable and representative data for air pollution research. This research includes the evaluation of health effects; options for urban planning, land use, and transportation planning; development and evaluation of abatement strategies; and development, evaluation, and ground truthing of air quality models.<sup>6</sup>

### **26.3 AIR POLLUTANT PHASES**

Chapter 25 introduced measurement approaches for both gas-phase and particulate-phase pollutants. The United States, under the Clean Air Act, lists six principal, i.e. “criteria”, pollutants for which EPA has established NAAQS. The four gas-phase criteria pollutants, i.e. carbon monoxide, sulfur dioxide, nitrogen dioxide, and ozone, are gases at standard temperature and

pressure. Monitoring programs need to interpret vapor measures as well, since many of the gas-phase pollutants are actually vapors, i.e. they are predominantly liquid under environmental conditions, but over time, partition to the atmosphere.

Vapor-phase compounds, many hydrocarbons and organic solvents, must be quantified to explain ground-level ozone. The smog results from a photochemical oxidation process involving hydrocarbons, oxides of nitrogen, and other compounds, leading to the production of ozone. In addition, many of the air toxics are vapors, rather than ideal gases. For most air pollution assessment and control purposes, however, many of these vapors can be considered to be ideal gases. Indeed, the gas-phase detection equipment described in Chapter 24 treats them as gases.

Particulate matter (PM) encompasses any particle, whether liquid or solid. For ambient air quality monitoring purposes, an aerosol is a liquid or solid particle that is suspended in the air. As discussed in Chapters 6 and 9, PM can be expressed as total suspended particulates (TSP); however, this is generally not reported for health purposes. More commonly, PM is differentiated by a particle’s aerodynamic diameter, i.e. 2.5–10 µm diameter for PM<sub>10</sub> and ≤2.5 µm diameter for PM<sub>2.5</sub>. The mass of PM in these size ranges per volume of air is usually reported.

Both size ranges are regulated in many countries (see Table 26.2). For example, in the United States, the NAAQS for PM<sub>10</sub> is a 24-h average of 150 µg m<sup>-3</sup> (not to exceed this concentration more than once per year), and an annual average of 50 µg m<sup>-3</sup> arithmetic mean.

**TABLE 26.2** Comparison of the WHO Guidelines and Standards from Different Countries. Modified From World Health Organization Air Quality Guidelines, Global Update, 2005, A Report on a Working Group Meeting, Bonn, Germany, 18–20 October 2005

Regulating/Advising Entity	PM <sub>10</sub> (µg m <sup>-3</sup> )		PM <sub>2.5</sub> (µg m <sup>-3</sup> )	
	1 year	24 h	1 year	24 h
World Health Organization	20	50	10	25
European Union	40	50	25	—
United States	50	150	12	35
California	20	50	15	65
Japan	—	100	12	65
Brazil	50	150	—	—
Mexico	50	120	15	65
South Africa	60	180	15	65
India (sensitive populations/residential/industrial)	50/60/120	—	—	—
China (classes I/II/III)	40/100/150	50/150/250	—	35

Source: Nemmar A, Holme JA, Rosas I, Schwarze PE, Alfaro-Moreno E. Recent advances in particulate matter and nanoparticle toxicology: a review of the *in vivo* and *in vitro* studies. Biomedical Research International. 2013; Published online 2013 June 20. doi: [10.1155/2013/279371](https://doi.org/10.1155/2013/279371); Gwinn MR, Vallyathan V. Nanoparticles: health effects—pros and cons. Environmental Health Perspectives. 2006;114(12):1818–1826.

The PM<sub>2.5</sub> standard is a bit more complicated. The standard protecting public health (i.e. primary standard) is 12 µg m<sup>-3</sup> for a 3-year annual mean (annual means averaged over 3 years). The standard protecting public welfare (i.e. secondary standard) is 15 µg m<sup>-3</sup> for an annual mean averaged over 3 years. The primary and secondary 24-h standard is 35 µg m<sup>-3</sup> (98th percentile, averaged over 3 years).<sup>7</sup>

Particles in the atmosphere come from myriad sources, e.g. combustion, windblown dust, and gas-to-particle conversion processes, as mentioned in Chapters 1 and 3. Figure 3.2 illustrates the wide range of particle diameters potentially present in the ambient atmosphere. A typical size distribution of ambient particles is shown in Figure 3.3. The distribution of number, surface, and mass can occur over different diameters for the same aerosol. Variation in chemical composition as a function of particle diameter has also been observed, as shown in Table 26.3. The percentages do not add up to 100% because they exclude oxygen (except for the nitrate and sulfate components), nitrogen (except for the nitrate component), hydrogen, and other components of the compounds of the listed elements in the form in which they actually exist in the atmosphere; for example, the most common form of particulate sulfur and sulfate in the atmosphere is (NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>). These mean chemical composition and atmospheric concentrations of suspended total, coarse, and fine PM (total, coarse, and fine) were measured over two decades ago. At that time, approximately 30% of the mass of PM is in the fine fraction (<2.5 µm), 30% is in the coarse fraction (>15 µm), and 40% is coarser still—between 15 and about 50 µm.

These atmospheric concentrations and compositions have changed substantially since 1980. For much of the developed world, total, coarse, and fine PM concentrations have fallen considerably (see Table 26.4). Note that the concentrations in Table 26.3 are in micrograms per cubic meter, but those in Table 26.4 are in nanograms per cubic meter. The tables are not exactly comparable, given that the 1980 data are for the United States generally, and the 2010 data are for a regional background site in Europe. However, the European site actually had higher mean PM<sub>2.5</sub> concentrations than several other background sites in Europe (e.g. across Spain, Portugal, Germany, and Scandinavia, but lower than those in Switzerland, Italy, and Austria).<sup>8</sup>

Indeed, the PM at the site was high in organic matter, sulfates, nitrates, ammonia, and crustal material, with only a small amount of elemental carbon, which likely means a lower contribution from combustion sources. The general downward trend can be tracked to increased pollution control and prevention efforts. In addition, the change in composition and amount of PM is in some manner affected by the economy.

During the latter part of sampling, i.e. 2008–2010, Europe and much of the world suffered from an economic recession. Another factor is the change in meteorology, e.g. higher precipitation due to the North Atlantic Oscillation (i.e. pressure differences between Icelandic low-pressure and Azores high-pressure systems) especially affected winter PM concentrations.<sup>8</sup>

### 24.3.1 Pollutant Characterization

Pollutants in the gas phase are usually characterized according to chemistry, i.e. oxidation state, fraction of specific compounds (i.e. chemical speciation), and half-life in the atmosphere. However, the gas-phase compounds can be expressed simply as atmospheric concentrations, e.g. 100 ng benzene per cubic meter of air, 500 µg of carbon monoxide in a room's air, or 3 ppb mercury in the ambient air.

This is not the case for aerosols, which must be characterized in numerous ways. The vast majority of PM efforts has addressed the mass of PM by size, with smaller diameter PM being the principal concern. However, other characterizations are necessary. For example, morphology can make for a more or less toxic particle. The notable example is asbestos and other fibers, wherein aspect ratio (i.e. width:length) plays a major role in the type and severity of lung disease. Also, chemical constituents are important, e.g. the presence of toxic compounds and metals.

Morphology is particularly important for the ultrafine particle size range (aerodynamic diameter <0.1 µm). Particles include primary and secondary components. The primary component, i.e. those directly emitted from sources, frequently include aggregates of smaller particles. The secondary component consists of PM formed in the atmosphere after the emission. These often include sulfuric acid, sulfates, and nonvolatile to semivolatile organic transformation products. The common means of characterizing PM morphology is by electron microscopy. Unfortunately, these secondary products often vaporize during electron microscopy, so they are likely to be missed.

Thus, current methods have at least two characterization weaknesses. First, the individual particle may be much smaller than what appears on the filter, which is actually an aggregate of many smaller particles. The smaller particles have much greater surface area, so they are much more likely to aggregate on filter media than larger particles. Second, the actual morphological measurement, e.g. scanning electron microscopy, is likely to alter the actual morphology and chemical constituency of the particle. While this is problematic for PM<sub>2.5</sub>, it is much worse for ultrafine particles.<sup>9</sup>

TABLE 26.3 Mean Chemical Composition and Atmospheric Concentrations of Suspended Particulate Matter Sampled by the United States Environmental Protection Agency's Inhalable Particle and National Air Surveillance Networks—Microgram per Cubic Meter and Percentage of Total Mass Sampled, 1980

Type of Sample	Urban				Rural			
	745		2255 <sup>§</sup>		133 <sup>#</sup>			
Particle Size	Coarse, 15–2.5 µm		Fine, Less than 2.5 µm		All Less than <i>ca.</i> 50 µm			
	Mean Value of 745 Values	Percentage	Mean Value of 745 Values	Percentage	Mean Value of 2255 Values	Percentage	Mean Value of 133 Values	%
All (total mass)	21.655	100.00	22.680	100.00	74.990	100.00	36.504 <sup>§</sup>	100.00
Aluminum	1.797	8.30	0.353	1.56	—	—	—	—
Antimony	0.051	0.24	0.050	0.22	—	—	—	—
Arsenic	0.003	0.01	0.004	0.02	0.005 <sup>  </sup>	0.01	0.003 <sup>#</sup>	0.01
Barium	0.060	0.28	0.060	0.26	0.273	0.36	0.281	0.77
Beryllium <sup>#</sup>	—	—	—	—	(0.095)	—	(0.084)	—
Bromine	0.019	0.09	0.077	0.34	—	—	—	—
Cadmium	0.006	0.03	0.007	0.03	0.002	0.01	0.001	0.01
Calcium	1.503	6.94	0.340	1.50	—	—	—	—
Chlorine	0.440	2.03	0.155	0.68	—	—	—	—
Chromium	0.008	0.04	0.006	0.03	0.013 <sup>  </sup>	0.02	0.015 <sup>#</sup>	0.05
Cobalt	—	—	—	—	0.001 <sup>  </sup>	0.01	0.001 <sup>#</sup>	0.01
Copper	0.019	0.09	0.026	0.12	0.143	0.19	0.136	0.37
Iron	0.743	3.43	0.205	0.90	0.923	1.23	0.254	0.70
Lead	0.083	0.38	0.314	1.38	0.353	0.47	0.066	0.18

Manganese	0.021	0.10	0.013	0.06	0.031	0.04	0.008	0.02
Mercury	0.003	0.01	0.003	0.01	—	—	—	—
Molybdenum	—	—	—	—	0.002	0.01	0.001	0.01
Nickel	0.004	0.02	0.007	0.03	0.007	0.01	0.002	0.01
Phosphorus	0.056	0.26	0.021	0.09	—	—	—	—
Potassium	0.222	1.03	0.156	0.69	—	—	—	—
Selenium	0.001	0.01	0.002	0.01	—	—	—	—
Silicon	2.561	11.83	0.360	1.59	—	—	—	—
Strontium	0.246	0.21	0.051	0.22	—	—	—	—
Sulfur	0.339	1.56	2.056	9.07	—	—	—	—
Tin	0.006	0.03	0.006	0.03	—	—	—	—
Titanium	0.042	0.19	0.015	0.07	—	—	—	—
Vanadium	0.008	0.04	0.010	0.04	0.015	0.02	0.004	0.01
Zinc	0.038	0.18	0.067	0.30	0.147	0.20	0.114	0.31
Nitrate	0.699	3.23	1.071	4.72	4.647	6.20	2.341	6.41
Sulfate	0.706	3.26	5.30	23.37	10.811	14.42	8.675	23.77
Sum of percentages	—	43.82**	—	47.34**	—	23.20	—	32.64

<sup>§</sup>Except for arsenic, chromium, and cobalt where the number of samples was 1245.

<sup>¶</sup>Except for arsenic, chromium, and cobalt where the number of samples was 30.

<sup>||</sup>Except for arsenic, chromium, and cobalt where the mean total mass was  $76.647 \mu\text{g m}^{-3}$ .

<sup>#</sup>Except for arsenic, chromium, and cobalt where the mean total mass was  $30.367 \mu\text{g m}^{-3}$ .

<sup>\*\*</sup>Sulfur is counted twice: as sulfur and as sulfate. Some of this sulfur exists as sulfides, sulfites, and forms other than sulfate.

\* nanogram per cubic meter.

**TABLE 26.4** Chemical Composition of Fine Particulates and Percentage Reductions of Various Trace Elements Measured at Montseny Monitoring Station in Northeast Spain. The Site is Part of the Europe-Wide Measurement Network EUSAAR (European Supersites for Atmospheric Aerosol Research)

Element	Measurement Time Period	Mean Concentration ( $\text{ng m}^{-3}$ )	Statistical Significance ( $\alpha$ )	Percentage Reduction
Pb	2002–2010	$3.82 \pm 1.41$	0.01	67
Cd	2002–2010	$0.13 \pm 0.06$	0.01	75
Cu	2004–2010	$2.52 \pm 0.69$	0.05	44
Sb	2004–2010	$0.29 \pm 0.13$	0.01	58
Sn	2004–2010	$0.76 \pm 0.32$	0.01	58
As	2002–2010	$0.22 \pm 0.06$	0.05	51
V	2002–2010	$2.11 \pm 0.57$	—	41
Cr	2002–2010	$0.82 \pm 0.20$	—	34
Ni	2002–2010	$1.22 \pm 0.34$	0.1	45
Co	2002–2010	$0.06 \pm 0.02$	0.05	53
Li	2002–2010	$0.06 \pm 0.02$	—	43
Ti	2002–2010	$3.51 \pm 1.19$	—	34
Mn	2002–2010	$1.94 \pm 0.49$	0.1	37
Ga	2002–2010	$0.04 \pm 0.02$	0.1	53
Rb	2002–2010	$0.14 \pm 0.03$	—	43
Sr	2002–2010	$0.47 \pm 0.26$	—	49
La	2002–2010	$0.07 \pm 0.01$	—	34
Ce	2002–2010	$0.13 \pm 0.02$	—	17
Pr	2002–2010	$0.02 \pm 0.01$	0.05	46
Nd	2002–2010	$0.06 \pm 0.02$	0.1	49

Source: Ref. 8.

## 26.4 AIR POLLUTION FROM HAZARDOUS WASTE SITES

Air contaminant releases from hazardous waste sites can occur from wastes placed above ground or below ground. The following are categories of air contaminant releases:

- Fugitive dust resulting from
  - Wind erosion of contaminated soils
  - Vehicle travel over contaminated roadways
- Volatilization release from
  - Covered landfills (with and without gas generation)
  - Spills, leaks, and landforming
  - Lagoons

The EPA has detailed procedures for conducting air pathway analysis for Superfund applications.<sup>10</sup> Decision network charts are given for all expected situations.

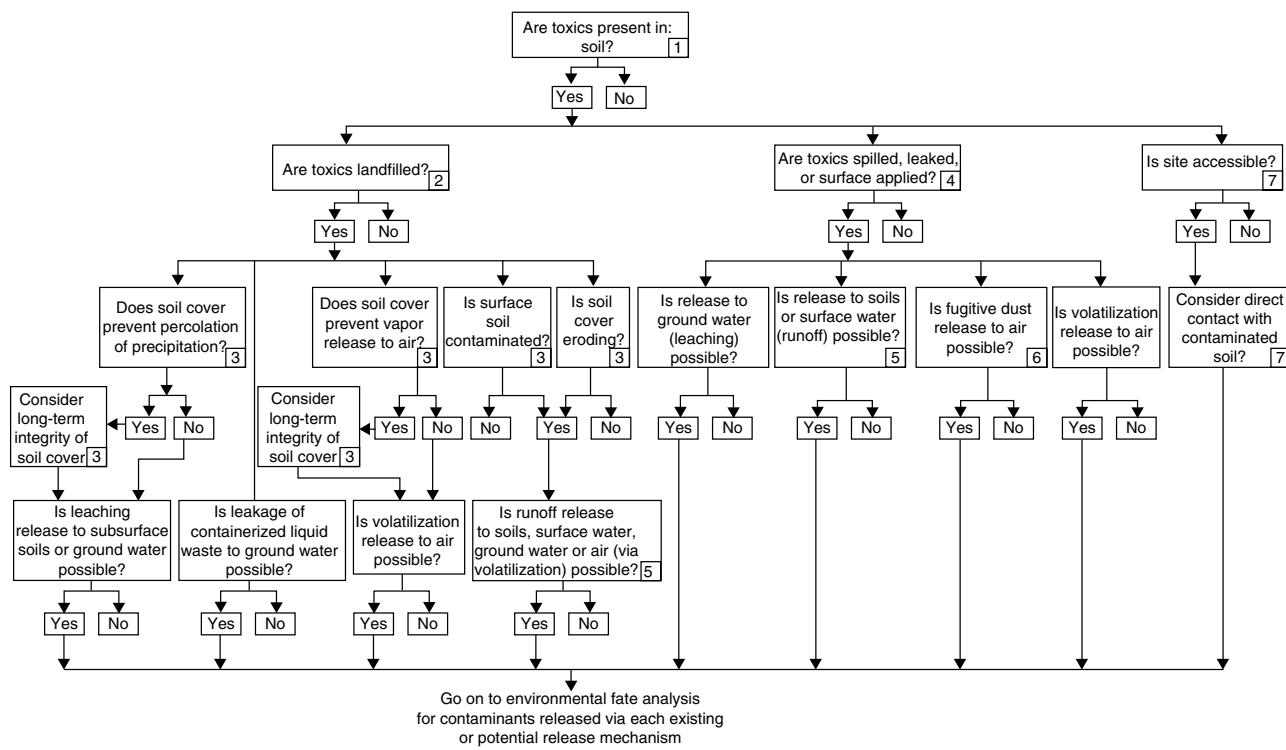
Figures 26.3 and 26.4 present the decision networks that guide contaminant release screening analysis.

Figure 26.3 deals with contaminants in or under the soil and Figure 26.4 addresses aboveground wastes. Any release mechanisms evident at the site will require a further screening evaluation to determine the likely environmental fate of the contaminants involved.

### 26.4.1 Contaminant Fate Analysis

Simplified environmental fate estimation procedures are based on the predominant mechanisms of transport within each medium, and they generally disregard intermedia transfer or transformation processes. In general, they produce conservative estimates (i.e. reasonable upper bounds) for final ambient concentrations and the extent of hazardous substance migration. However, caution should be taken to avoid using inappropriate analytical methods that underestimate or overlook significant pathways that affect human health.

When more in-depth analysis of environmental fate is required, the analyst must select the modeling procedure that is most appropriate to the circumstances. In



**FIGURE 26.3** Contaminant release decision network: contaminants in soil.

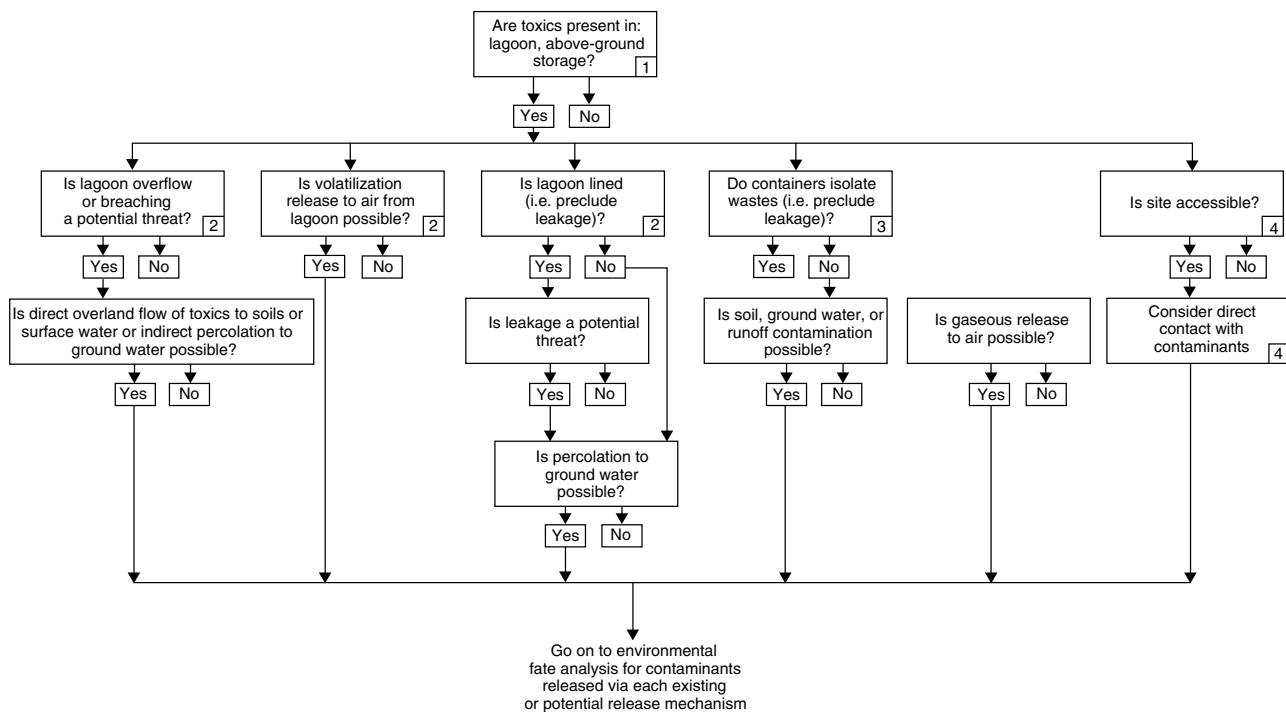


FIGURE 26.4 Contaminant release decision network: contaminants above ground.

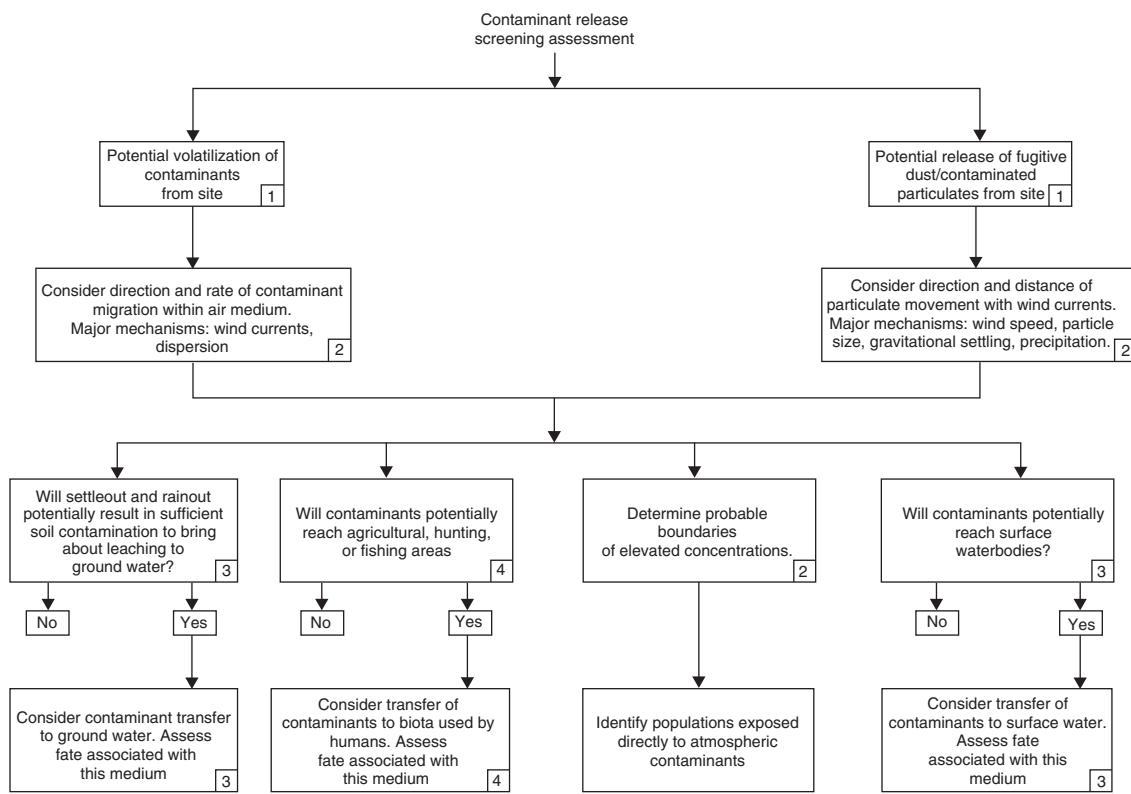


FIGURE 26.5 Environmental fate screening assessment decision network: atmosphere.

general, the more sophisticated models are more data, time, and resource intensive.

Figures 26.5–26.7 present the decision network for screening contaminant fate in air, surface water, groundwater, and biota. Pathways must be further evaluated to determine the likelihood of population exposure.

#### 26.4.1.1 Atmospheric Fate

The following numbered paragraphs refer to particular numbered boxes in Figure 26.5:

1. The atmospheric fate of contaminants must be assessed whenever it is determined that significant gaseous or airborne particulate contaminants are released from the site. The atmospheric fate of contaminants released originally to other media, but eventually partitioned to the atmosphere beyond site boundaries, must also be assessed whenever this intermedia transfer is likely to be significant.
2. The predominant directions of contaminant movement will be determined by relative directional frequencies of wind over the site (as reflected in area-specific wind rose data). Atmospheric stability and wind speeds determine off-site areas affected by

ambient concentrations of gaseous contaminants. Usually, high stability and low-wind speed conditions result in higher atmospheric concentrations of gaseous contaminants close to the site. High stability and moderate wind speeds result in moderate concentrations over a larger downwind area. Low stability or high-wind speed conditions cause greater dispersion and dilution of contaminants, resulting in lower concentrations over larger areas.

For particulate contaminants (including those adsorbed to dust or soil particles), ambient concentrations in the atmosphere and areas affected by airborne contaminants are determined by wind speed and stability and also by particle size distribution. High winds result in greater dispersion and cause particles to remain airborne longer (which may also increase release rates). Low winds and high stability result in rapid settling of particles and in a more concentrated contaminant plume closer to the site. Larger particles settle rapidly, decreasing the atmospheric concentrations with distance from the site. Finer particles remain airborne longer, and their behavior more closely approximates that of gaseous contaminants, as described.

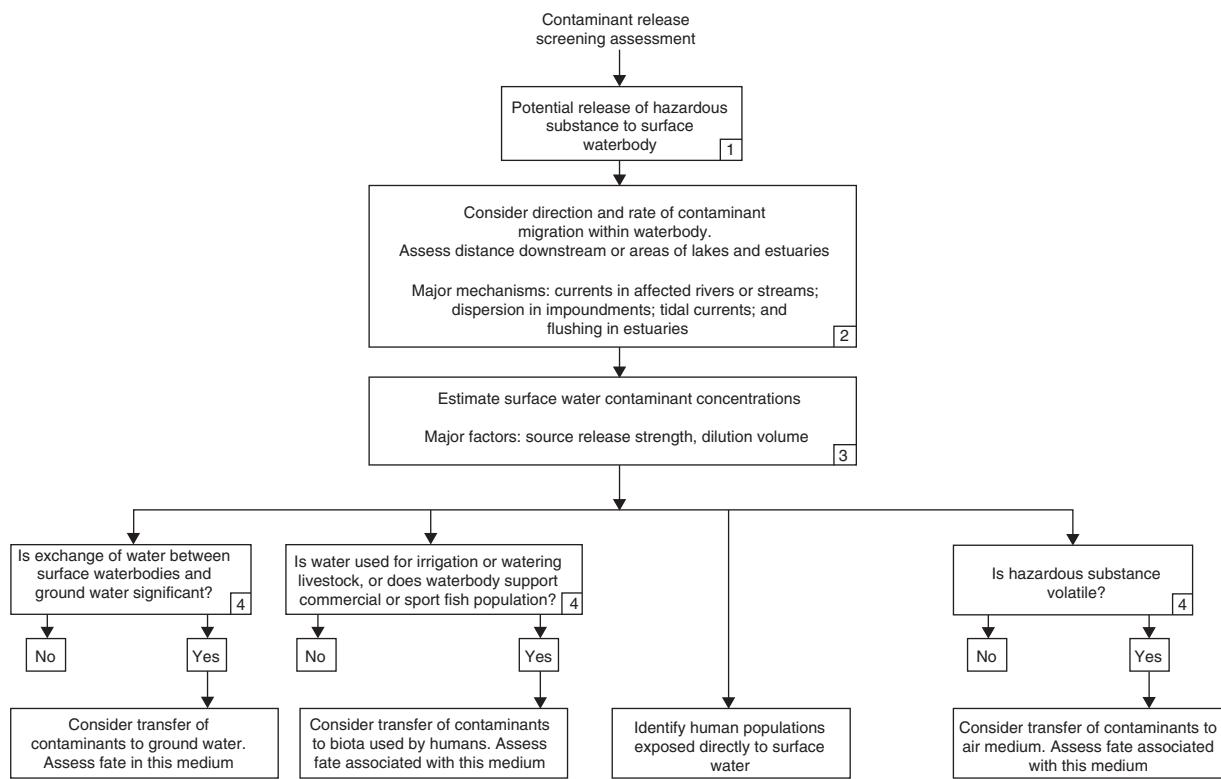


FIGURE 26.6 Environmental fate screening assessment decision network: surface water.

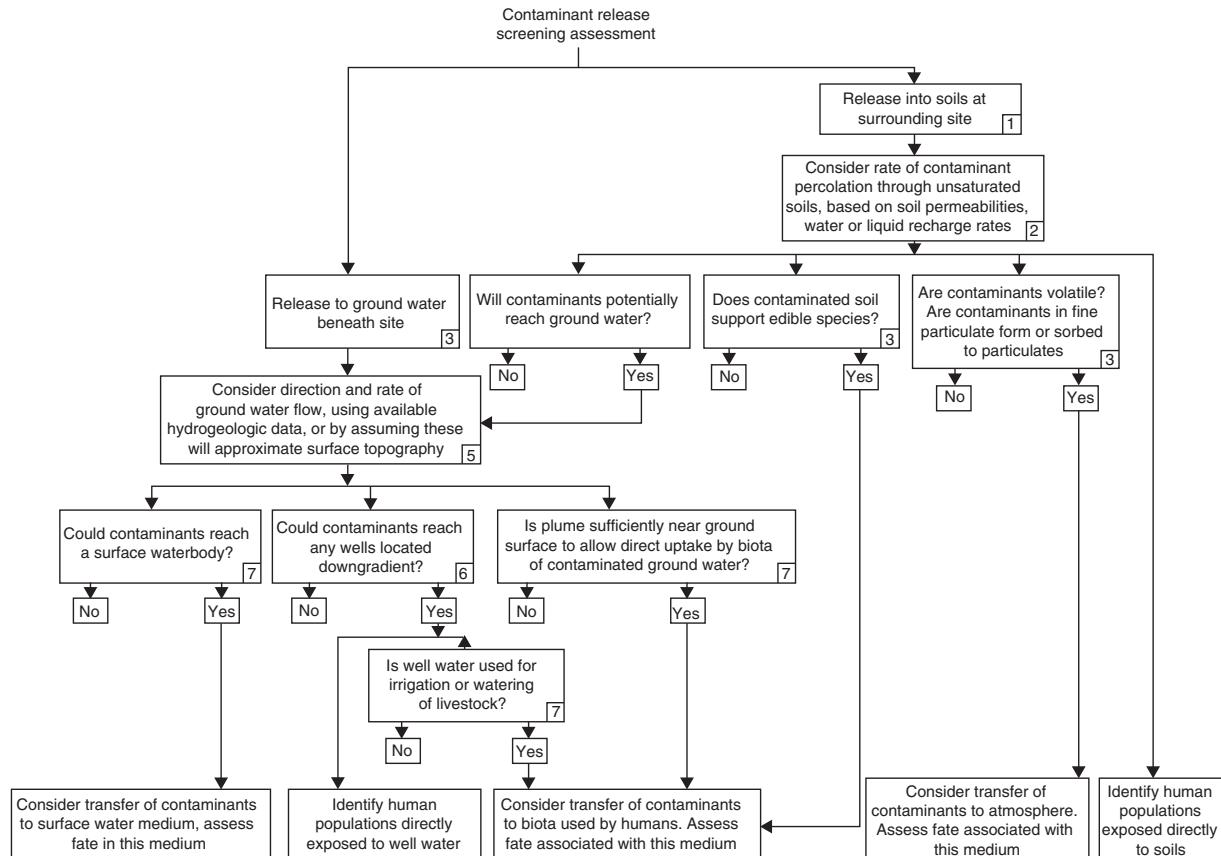


FIGURE 26.7 Environmental fate screening assessment decision network: soils and groundwater.

3. Settling and rainout are important mechanisms of contaminant transfer from the atmospheric media to both surface soils and surface waters. Rates of contaminant transfer caused by these mechanisms are difficult to assess qualitatively; however, they increase with increasing soil adsorption coefficients, solubility (for particulate contaminants or those adsorbed to particles), particle size, and precipitation frequency.

Areas affected by significant atmospheric concentrations of contaminants exhibiting the foregoing physical and chemical properties should also be considered as potentially affected by contaminant rainout and settling to surface media. Contaminants dissolved in rainwater may percolate to groundwater, run off or fall directly into surface waters, and adsorb to unsaturated soils. Contaminants settling to the surface through dry deposition may dissolve in or become suspended in surface waters or may be leached into unsaturated soils and groundwater by subsequent rainfall. Dry deposition may also result in formation of a layer of relatively high contamination at the soil surface. When such intermedia transfers are likely, one should assess the fate of contaminants in the receiving media.

4. If areas identified as likely to receive significant atmospheric contaminant concentrations include areas supporting edible biota, the biouptake of contaminants must be considered as a possible environmental fate pathway. Direct biouptake from the atmosphere is a potential fate mechanism for lipophilic contaminants. Biouptake from soil or water following transfer of contaminants to these media must also be considered as part of the screening assessments of these media.

#### **26.4.1.2 Surface Water Fate**

The following numbered paragraphs refer to particular numbered boxes in [Figure 26.6](#):

1. The aquatic fate of contaminants released from a site designated to be hazardous under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), as well as those transferred to surface water from other media beyond site boundaries must be considered.
2. Direction of contaminant movement is usually clear only for contaminants introduced into rivers and streams. Currents, thermal stratification or eddies, tidal pumping, and flushing in impoundments and estuaries render qualitative screening assessment of contaminant directional transport highly conjectural for these types of water bodies. In most cases, entire water bodies receiving contaminants must be

considered potentially significant human exposure points. More in-depth analyses or survey data may subsequently identify contaminated and unaffected regions of these water bodies.

3. Similarly, contaminant concentrations in rivers or streams can be roughly assessed based on rate of contaminant introduction and dilution volumes. Estuary or impoundment concentration regimes are highly dependent on the transport mechanisms enumerated. Contaminants may be localized and remain concentrated or may disperse rapidly and become diluted to insignificant levels. The conservative approach is to conduct a more in-depth assessment and use model results or survey data as a basis for determining contaminant concentration levels.
4. Important intermedia transfer mechanisms that must be considered where significant surface water contamination is expected include transfers to groundwater where hydrogeology of the area indicates significant surface water–groundwater exchange, transfers to biota where waters contaminated with lipophilic substances support edible biotic species, and transfer to the atmosphere where surface water is contaminated by volatile substances. High temperatures, high surface area/volume ratios, high wind conditions, and turbulent stream flow also enhance volatilization rates.

Contaminant transfer to bed sediments represents another significant transfer mechanism, especially in cases where contaminants are in the form of suspended solids or are dissolved hydrophobic substances that can become adsorbed by organic matter in bed sediments. For the purposes of this chapter, sediments and water are considered part of a single system because of their complex interassociation. Surface water–bed sediment transfer is reversible; bed sediments often act as temporary repositories for contaminants and gradually rerelease contaminants to surface waters. Sorbed or settled contaminants are frequently transported with bed sediment migration or flow. Transfer of sorbed contaminants to bottom-dwelling, edible biota represents a fate pathway potentially resulting in human exposure. Where this transfer mechanism appears likely, the biotic fate of contaminants should be assessed.

#### **26.4.1.3 Soil and Ground Water Fate**

The following numbered paragraphs refer to particular numbered boxes in [Figure 26.7](#):

1. The fate of contaminants in the soil medium is assessed whenever the contaminant release atmospheric, or fate screening, assessment results show that significant contamination of soils is likely.

2. The most significant contaminant movement in soils is a function of liquid movement. Dry, soluble contaminants dissolved in precipitation, run-on, or human applied water will migrate through percolation into the soil. Migration rates are a function of net water recharge rates and contaminant solubility.
3. Important intermedia transfer mechanisms affecting soil contaminants include volatilization or resuspension to the atmosphere and biouptake by plants and soil organisms. These, in turn, introduce contaminants into the food chain.

## 26.4.2 Modeling

An extremely difficult task is the estimation of emissions from hazardous waste sites. Frequently, both the amounts of materials existing within the site and the compounds and mixtures that are represented are not known. Even if both of these pieces of information are reasonably well known, the conditions of the containers holding these chemicals are not initially known.

Hazardous materials may enter the air pathway by evaporation from leaking containers and release of these gases through fissures and spaces between soil particles. Another pathway may release hazardous substances to the air if they are water soluble. Then groundwater passing leaking containers may carry substances to or near the surface, where they may be released to the air near the original source or at locations at significant distances.

### 26.4.2.1 Estimates of Long-Term Impact

If the foregoing problems of emissions estimation can be overcome, or if it is possible to make estimates of maximum possible and minimum possible emissions, then it is quite easy to make estimates of resulting long-term impact on the surrounding area. The representation of the emissions may be through consideration of an area source or area sources; or if vent pipes are releasing material or flaring the gases, point sources should be used.

A single finite line source method is used to simulate area sources in the long-term (seasons to years) Industrial Source Complex Long Term (ISCLT) model.<sup>11</sup> Although this method has been criticized as frequently underestimating concentrations for receptors that are quite close to the area source (within two or three side lengths away), this model is usually used for these estimates. In addition to the long-term estimate of emission rate for each constituent to be modeled, the ISCLT model requires meteorological data in the form of a joint frequency distribution of three parameters: wind direction (in 16 classes), wind speed (in 6 classes), and Pasquill stability class (in 6 classes). As long as the emissions

can be considered relatively constant over the period of simulation, the long-term estimates will represent mean concentrations over the period represented by the meteorological data.

### 26.4.2.2 Estimates of Short-Term Impact during Remediation

If it is necessary to consider short-term (hours or days) impact, the point, area, and line (PAL) air quality model<sup>12</sup> will do a superior simulation of the area sources and a similar simulation of any point sources as done by the ISCLT model. PAL also includes a version with deposition and settling algorithms.

In addition to short-term emission estimates, normally for hourly periods, the meteorological data include hourly wind direction, wind speed, and Pasquill stability class. Although of secondary importance, the hourly data also include temperature (only important if buoyant plume rise needs to be calculated from any sources) and mixing height.

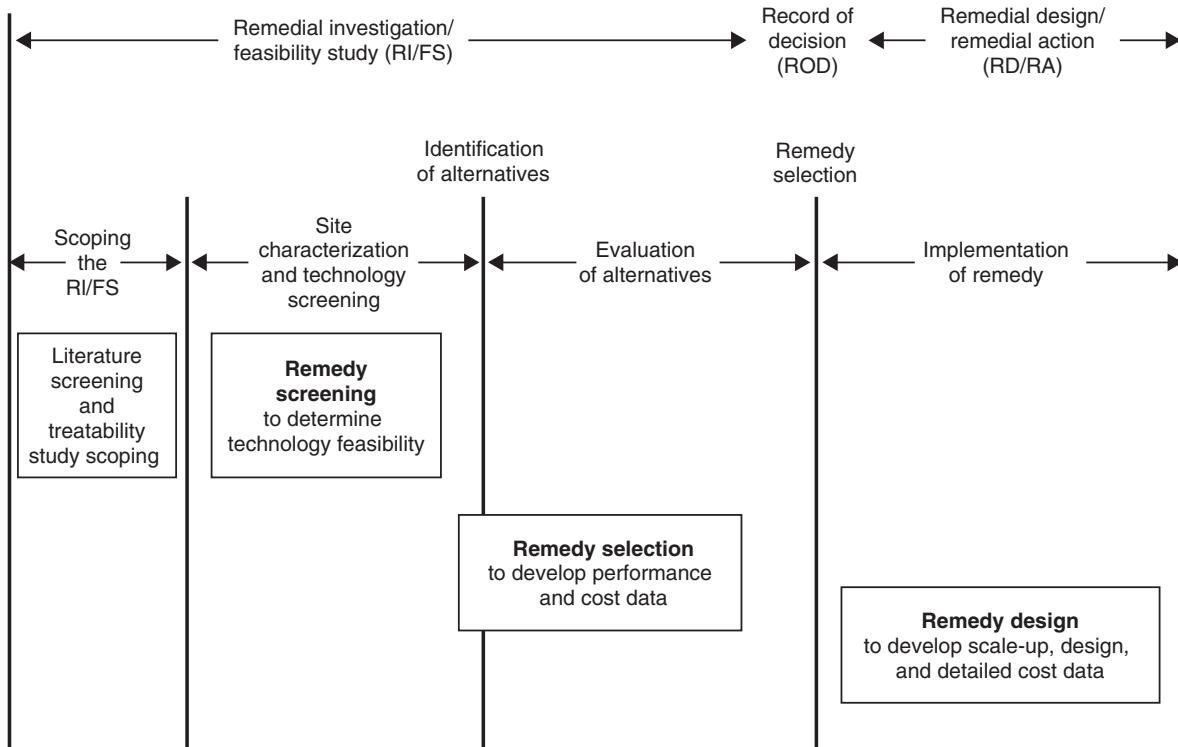
The short-term model can then be used to estimate resulting concentrations during specific periods or to estimate concentrations for suspected adverse meteorological conditions, so that changes can be incorporated in the remediation process if concentrations are expected to be higher than desirable.

## 26.4.3 Assessment of a Hazardous Waste Site

The contaminant cleanup process is shown in Figure 26.8. The first step of a contaminant cleanup is a preliminary assessment (PA). During the PA of a site, readily available information about a site and its surrounding area are collected to "distinguish between sites that pose little or no threat to human health and the environment and sites that may pose a threat and require further investigation".<sup>13</sup> Any possible emergency response actions may also be identified. A site inspection or site investigation (SI) is performed if the PA, based on limited data, calls for one (that is why this step is often referred to as the PA/SI).<sup>14</sup>

In the United States, certain hazardous waste sites are considered to be of sufficient concern to be "listed" on the National Priority List (NPL). The listing is actually a combination of the hazard (usually toxicity) of the contaminants found at the site and the likelihood that people or ecosystems will be exposed to these pollutants. Severely polluted sites and sites that contain very toxic compounds in measurable quantities are ranked higher than those with less toxic substances in lesser quantities.

A public disclosure of the condition following contaminant treatment must be made. This final record of decision (ROD) indicates that the specific engineering remedy has been selected for the site. Like any other



**FIGURE 26.8 Steps in a contaminated site cleanup, as mandated by Superfund.** US Environmental Protection Agency. Guide for conducting treatability studies under CERCLA: thermal desorption. EPA/540/R-92/074 B; 1992.

aspects of hazardous waste cleanup, this decision is subject to later contests (legal, scientific, or otherwise). Since public officials are not exempt from personal tort liabilities in their decisions, the ROD is usually made as a collective, agency decision based on past and ongoing contaminant measurements, and includes provisions for monitoring for years to come to ensure that the engineered systems continue to perform according to plan. The ROD must also ensure that a plan for operating and maintaining all systems is in place, including a plan for dealing with failures and other unexpected contingencies, such as improvements in measurement techniques that later identify previously undetected pollutants.

Scientists conduct exposure assessments to evaluate the kind and magnitude of exposure to contaminants. Such assessments are usually site specific for clearly identified contaminants of concern. For example, they may be conducted for an abandoned hazardous waste site or a planned industrial facility. For the former site, the list of contaminants of concern would be based on sampling and analysis of the various environmental compartments, while the latter would be based on the types of chemicals to be used or generated in the construction and operation of the industrial facility. Thus,

the assessment considers sources of contaminants, pathways through which contaminants are moving or will be moving, and routes of exposure where the contaminants find their way to receptors (usually people, but also receptors in ecosystems, such as fish and wildlife). **Table 26.5** includes some of the most important considerations in deciding on the quality of information needed to conduct an exposure assessment.

The necessary information to quantify is determined by both the characteristics of the contaminant and the route of exposure.

#### **26.4.3.1 The Hazard Quotient**

The hazard quotient (HQ) is the ratio of the potential exposure to a specific contaminant to the concentration at which no adverse effects are expected (known as the reference dose or RfD). The HQ is the ratio of a single contaminant exposure, over a specified time period, to a RfD for that contaminant, derived from a similar exposure period:

$$HQ = \frac{\text{Exposure}}{\text{RfD}} \quad (26.1)$$

If the calculated HQ is less than 1, no adverse health effects are expected to occur at these contaminant

TABLE 26.5 Questions to Be Asked When Determining the Adequacy of Information Needed to Conduct Exposure Assessments

Compartment	Question
Soil	<p>If humans have access to contaminated soils, can ranges of contamination be provided on the basis of land use (i.e. restricted access, road/driveway/parking lot access, garden use, agriculture and feedlot use, residential use, playground and park use, etc.)?</p> <p>Have the soil depths been specified? Do soil data represent surface soil data (&gt;3 in in depth) or subsurface soil data (0.3 in in depth)? If soil depth is known, but does not meet surface or subsurface soil definitions, designate the data as soil and specify the depth (e.g. 0–6 in). If the soil depth is unknown, the health assessor should designate the data as unspecified soil.</p> <p>Has soil been defined in the data? If not, the health assessor should assume soil includes any unconsolidated natural material or fill above bedrock that is not considered to be soil and excludes man-made materials such as slabs, pavements, or driveways of asphalt, concrete, brick, rock, ash, or gravel. A soil matrix may consist of pieces of each of these materials.</p> <p>Do soil data include uphill and downhill samples and upwind and downwind samples both on and off the site?</p>
Sediment	<p>Have the sediment samples been identified as grab samples or cores? Was the depth of the samples specified?</p> <p>Was the sampling program designed to collect sediment samples at regular intervals along a waterway or from depositional areas or both?</p> <p>Do the sediment data include results for upstream and downstream samples both on- and off-site?</p> <p>Has sediment been defined by the samplers? (To prevent confusion between sediment and soil, assume “sediment” is defined as any solid material, other than waste material or waste sludge that lies below a water surface, that has been naturally deposited in a waterway, water body, channel, ditch, wetland, or swale, or that lies on a bank, beach, or floodway land where solids are deposited.)</p> <p>Have any sediment removal activities (e.g. dredging, excavation) occurred that may have altered the degree of sediment contamination (leading to a false negative). This becomes important when the following occur:</p> <ol style="list-style-type: none"> <li>1. Sediment contamination in fishable waters is used to justify sampling and analyses of edible biota.</li> <li>2. Sediment data are used to justify additional downstream sampling, particularly at points of exposure and in areas not subject to past removal activities.</li> <li>3. The significance of past exposure is assessed.</li> </ol>
Surface water	<p>Do surface water data include results for samples both upstream and downstream of the site?</p> <p>Was information obtained on the number of surface water samples taken at each station, as well as the frequency, duration, and dates of sampling?</p>
Groundwater	<p>Were groundwater samples collected in the aquifer of concern?</p> <p>Did sampling occur both up-gradient and down-gradient of the site and the site’s groundwater contamination plume?</p>
All	Did the sampling design include selected hot spot locations and points of possible exposure?

Source: Agency for Toxic Substances and Disease Registry. ATSDR Public Health Assessment Guidance Manual; 2003.

concentrations. If the calculated HQ is greater than 1, there is a likelihood that adverse action can occur at these concentrations. For example, the chromic acid ( $\text{Cr}^{6+}$ ) mists dermal chronic RfD of  $6.00 \times 10^{-3} \text{ mg kg}^{-1} \text{ day}^{-1}$ . If the actual dermal exposure of people living near a plant is calculated (e.g. by intake or lifetime average daily dose) to be  $4.00 \times 10^{-3} \text{ mg kg}^{-1} \text{ day}^{-1}$ , the HQ is  $2/3$  or 0.67. Since this is less than 1, one would not expect people chronically exposed at this level to show adverse effects from skin contact. However, at this same chronic exposure, i.e.  $4.00 \times 10^{-3} \text{ mg kg}^{-1} \text{ day}^{-1}$ , to hexavalent chromic acid mists via oral route, the RfD is  $3.00 \times 10^{-3} \text{ mg kg}^{-1} \text{ day}^{-1}$ , meaning the  $\text{HQ} = 4/3$  or 1.3. The value is greater than 1, so we cannot rule out adverse noncancer effects.

The calculated HQ value cannot be translated into a probability that adverse health effects will occur (i.e. it is not actually a metric of risk). The HQ is merely a benchmark that can be used to estimate the likelihood of risk.<sup>15</sup> It is not even likely to be proportional to the risk. So, an HQ 0.1 does not necessarily mean that adverse effects will occur.

Noncancer hazard estimates often have substantial uncertainties from a variety of sources. Scientific estimates of contaminant concentrations, exposures, and risks always incorporate assumptions to the application of available information and resources. Uncertainty analysis is the process used by scientists to characterize just how good or bad the data are in making these estimates.

### 26.4.3.2 The Hazard Index

The HQ values are for individual contaminants. The hazard index (HI) is the sum of more than one HQ value to express the level of cumulative noncancer hazard associated with inhalation of multiple pollutants (e.g. certain classes of compounds, such as solvents, pesticides, dioxins, fuels):

$$HI = \sum_1^n HQ \quad (26.2)$$

An HI can be developed for all pollutants measured, such as the 32 compounds measured in New Jersey as part of the National Air Toxics Assessment (Figure 26.9). An HI can also be site specific. For example, if an environmental audit shows that only  $CCl_4$  and  $Cr^{6+}$  were detected by sampling of soil. Recall that the previously calculated  $Cr^{6+}$  dermal HQ was 0.67. The dermal chronic RfD of  $CCl_4$  is  $4.55 \times 10^{-4} \text{ mg kg}^{-1} \text{ day}^{-1}$ . If the exposure is  $1.00 \times 10^{-4} \text{ mg kg}^{-1} \text{ day}^{-1}$ , the HQ for chronic dermal exposure to tetrachloromethane is  $1.00/4.55 = 0.22$ .

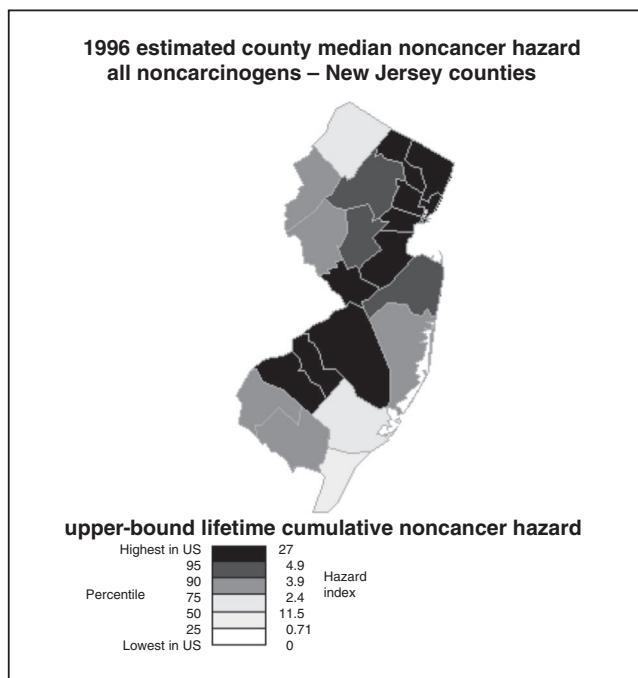
Thus, the HI for this site is  $0.67 + 0.22 = 0.89$ . Since the HI is under 1, the noncancer effect is not expected at these levels of exposure to the two compounds.

However, if the chronic dermal exposure to  $CCl_4$  had been  $2.00 \times 10^{-4} \text{ mg kg}^{-1} \text{ day}^{-1}$ , the HQ for  $CCl_4$  would have been 0.44, and the HI would have been calculated as  $0.67 + 0.44 = 1.11$ . This is a benchmark that indicates that the cumulative exposures to the two contaminants may lead to noncancer effects.

### 26.4.3.3 Comprehensive Risk Communication

The amount of data and information regarding contaminant concentrations, exposure, and effects can be overwhelming when presented to the public and clientele. Thus, these data must be reduced into meaningful formats. The Ohio Environmental Protection Agency's Urban Air Toxic Monitoring Program<sup>16</sup> provides an example of how to collect measurements to support actions aimed at reducing potential air pollution risks in large urban areas with many industrial sources. Air quality samples were collected between 1989 and 1997 near a large industrial area in Cuyahoga County. The contaminant concentrations are typical of urban areas, and the concentrations are expected to decrease in coming years. Samples were analyzed for volatile organic compounds (VOCs), heavy metals, and polycyclic aromatic hydrocarbons (PAHs). The state agency conducted a risk assessment based on both the cancer and noncancer health risks, assuming that an individual is exposed constantly to the same concentration of the pollutant for a lifetime (i.e. exposure duration = total lifetime). The results of the cancer health risk assessment are provided in Table 26.6. Heavy metals contributed the majority of the cancer risk (about 66%).

Each category in the table shows the cumulative risks from exposure to all compounds detected under a specific contaminant class. The US EPA has generally considered acceptable exposure risks for individual compounds to range from  $10^{-6}$  to  $10^{-4}$ . Commonly, only one or a few contaminants are contributing the lion's share of risk to each contaminant class. For example, a particularly carcinogenic PAH, like benzo(a)pyrene or dibenz(a,h)anthracene (each with a



**FIGURE 26.9 Noncancer hazard index for 32 air toxics included in the Clean Air Act, based on inhalation exposure data in New Jersey from political subdivisions.** Estimates do not include indoor emissions and are based on exposure estimates for the median individual within each census tract, which EPA considers to be a "typical" exposure, meaning that individuals may have substantially higher or lower exposures based on their activities. *US Environmental Protection Agency. National Air Toxics Assessment.*

**TABLE 26.6 Cumulative Cancer Risk Based on Air Sampling in Cuyahoga County, Ohio, 1989–1997**

Source of Cancer Risk	Total Estimated Risk
VOCs	$0.515 \times 10^{-4}$
Heavy metals	$1.21 \times 10^{-4}$
PAHs	$0.123 \times 10^{-4}$
Total carcinogenic risk	$1.85 \times 10^{-4}$

*Source: Ohio Environmental Protection Agency; 1999.*

TABLE 26.7 Individual Chemical Species Used to Calculate Cancer Risks Shown in Table 26.6

Compound	Carcinogenic Unit Risk ( $\mu\text{g m}^{-3}$ ) <sup>-1</sup>	Source	Average Concentration ( $\mu\text{g m}^{-3}$ )	Carcinogenic Risk
<b>VOCS</b>				
Methyl chloride	1.8 E-06	HEAST	0.68	1.22 E-06
Dichloromethane	4.7 E-07	IRIS	2.06	9.70 E-07
Trichloromethane	2.3 E-05	IRIS	0.27	6.29 E-06
Benzene	8.3 E-06	IRIS	3.91	3.25 E-05
Carbon tetrachloride	1.5 E-05	IRIS	0.55	8.30 E-06
Trichloroethene	1.7 E-06	HEAST	0.55	9.42 E-07
Tetrachloroethene	9.5 E-07	HEAST	1.07	1.02 E-06
Styrene	5.7 E-07	HEAST	0.49	2.81 E-07
<i>Sum</i>				5.15 E-05
<b>HEAVY METALS</b>				
Arsenic	4.30 E-03	IRIS	0.00271	1.17 E-05
Cadmium	1.80 E-03	IRIS	0.00765	1.38 E-05
Chromium(total)*	1.20 E-02	IRIS	0.00800	9.60 E-05
<i>Sum</i>				1.21 E-04
<b>PAHS</b>				
Benzo(a)pyrene <sup>§</sup>	2.10 E-03	1	0.006	1.26 E-06
Benzo(a)anthracene	2.10 E-04	0.1	0.0048	1.01 E-06
Benzo(b)fluoranthene	2.10 E-04	0.1	0.0023	4.83 E-07
Benzo(k)fluoranthene	2.10 E-04	0.1	0.0007	1.47 E-07
Chrysene	2.10 E-05	0.01	0.0047	9.87 E-08
Dibenz(a,h)anthracene	2.10 E-03	1	0.0041	8.61 E-06
Indeno[1,2,3-cd]pyrene	2.10 E-03	0.1	0.0031	6.51 E-07
<i>Sum</i>				1.23 E-05
<i>Total carcinogenic risk</i>				1.85 E-04

\* Estimation based on the slope factor of chromium (VI), i.e.  $\text{Cr}^{6+}$ .

§ Estimation based on the slope factor of oral route.

HEAST = Health Effects Assessment Summary Tables (U.S. EPA); IRIS = Integrated Risk Information System (U.S. EPA)

Source: Ohio Environmental Protection Agency. *Cleveland Air Toxics Study Report*; 1999.

inhalation cancer slope factor of 3.10), could account for most of the risk, even if its concentrations are about the same as other PAHs. In fact, this appears to be the case when looking at the individual chemical species listed in Table 26.7 that were used to derive the risks. Likewise, the VOC cancer risk was largely determined by the concentrations of benzene, while the heavy metals, although largely influenced by hexavalent chromium ( $\text{Cr}^{6+}$ ), were more evenly affected by arsenic and cadmium.

The cancer risk calculations are based on the unit risk estimate (URE), which is the upper bound excess lifetime cancer risk that may result from continuous exposure to an agent at a defined concentration. For

inhalation, this concentration is  $1 \mu\text{g m}^{-3}$  in air. For example, if the URE =  $1.5 \times 10^{-6}$  per  $\mu\text{g m}^{-3}$ , then 1.5 excess tumors are expected to develop per million population being exposed daily for a lifetime to  $1 \mu\text{g}$  of the contaminant per cubic meter of air.

The cancer risk reported for each individual contaminant is below the level designated by federal health agencies as acceptable, and falls with the range of risks expected for large cities, with their numerous sources of toxic air contaminants (i.e. the so-called “urban soup”).

The noncancer HI calculations are provided in Table 26.8. Noncarcinogenic health effects include developmental, reproductive, or cardiovascular health

TABLE 26.8 Cumulative Hazard Index Based on Air Sampling in Cuyahoga County, Ohio, 1989–1997

Source of Noncarcinogenic Risk	Hazard Index (HI)
VOCs	0.63
Heavy metals	0.008
PAHs	0.012
Total noncarcinogenic risk	0.65

Source: Ohio Environmental Protection Agency; 1999.

problems. Any total HI number below 1 is generally regarded as a safe level of exposure.<sup>a</sup>

As was the case for cancer risk, a few compounds can drive the noncancer HI. For example, the case above, 3-chloropropene and tetrachloromethane, accounts for an HI of 0.53, while all the other measured VOCs account for only 0.10. And, these two compounds account for almost 82% of the total noncarcinogenic risk estimates.

## 26.5 QUALITY ASSURANCE

Air quality monitoring for standards compliance, new facility siting, and long-term trend measurement has been going on for many years. Historically, a large number of federal, state, and local organizations, both governmental and nongovernmental, have been using a variety of technologies and approaches to obtain air quality data. This has resulted in multiple data sets of variable accuracy and precision. Questionable or conflicting air quality data are of little value in ascertaining compliance with air quality standards, determining whether air quality is improving or worsening in a given region over an extended period, or understanding the chemistry and physics of the atmosphere.

In order to minimize the collection of questionable air quality data, the US EPA has established and implemented stringent regulations requiring well-documented quality assurance programs for air quality monitoring activities.<sup>1</sup>

Quality assurance programs are designed to serve two functions: (1) assessment of collected air quality data and (2) improvement of the data collection process. These two functions form a loop; as air quality data are collected, procedures are implemented to determine whether the data are of acceptable precision and accuracy. If they are not, increased quality control procedures are implemented to improve the data collection process.

The components of a quality assurance program are designed to serve the two functions just mentioned—control and assessment. Quality control operations are defined by operational procedures, specifications, calibration procedures, and standards and contain the following components:

1. Description of the methods used for sampling and analysis
2. Sampling manifold and instrument configuration
3. Appropriate multipoint calibration procedures
4. Zero/span checks and record of adjustments
5. Control specification checks and their frequency
6. Control limits for zero, span, and other control limits
7. The corrective actions to be taken when control limits are exceeded
8. Preventative maintenance
9. Recording and validation of data
10. Documentation of quality assurance activities

Table 26.9 contains a specific example of these components for ambient monitoring for ozone.

In addition to fulfilling the in-house requirements for quality control, state and local air monitoring networks that are collecting data for compliance purposes are required to have an external performance audit on an annual basis. Under this program, an independent organization supplies externally calibrated sources of air pollutant gases to be measured by the instrumentation undergoing audit. An audit report summarizes the performance of the instruments. If necessary, further action must be taken to eliminate any major discrepancies between the internal and external calibration results.

Data quality assessment requirements are related to precision and accuracy. Precision control limits are established, i.e. 110% of span value:

$$d_i = [(y_i - x_i)/x_i] \times 100 \quad (26.3)$$

where,  $d_i$  is the percentage difference,  $y_i$  the analyzer's indicated concentration of the test gas for the  $i$ th precision check, and  $x_i$  the known concentration of the test gas for the  $i$ th precision check. The average percentage difference needs to be calculated for a given period, often for each quarterly reporting period to comply with air pollution regulations. This average difference is calculated as

$$d_{av} = \frac{1}{n} \sum_{i=1}^n d_i \quad (26.4)$$

<sup>a</sup> However, it should be noted that any quantitative or semi-quantitative expression like the HI includes uncertainty. Thus, the “safety” must include confidence intervals or other depictions of uncertainty. For example, if the confidence only allows an HI to be reported as 0.65 to 1.22, this would not be considered to be safe, since the interval could indeed be a noncancer risk above 1.

**TABLE 26.9** Quality Assurance Components for Ambient Ground-Level Ozone Monitoring

Component	Description
Method	Chemiluminescent O <sub>3</sub> monitor Calibration method by certified ozone UV transfer method
Manifold/instrument	Instrument connected to sampling manifold which configuration draws ambient air at 3 m into instrument shelter
Calibration	Multipoint calibration on 0.5-ppm scale at 0.0, 0.1, 0.2, and 0.4 ppm weekly
Zero/span check	Zero check $\pm 0.005$ ppm Span check 0.08–0.10 on a 1.0-ppm full-scale daily
Control specification checks	Ethylene flow Sample flow, daily
Corrective limits	$\pm 0.005$ ppm zero and span
Corrective action	Do multipoint calibration; invalidate data collection since last zero/span check within control limits
Preventive maintenance	Manufacturer's procedures to be followed
Recording and validating data	Data reported weekly to quality assurance coordinator, with invalid data flagged
Documentation	Data volume includes all quality control forms, e.g. zero/span control charts and multipoint calibration results

The standard deviation associated with this average (mean) is

$$S_j = \sqrt{\frac{1}{n-1} \left[ \sum_{i=1}^n d_i^2 - \frac{1}{n} \left( \sum_{i=1}^n d_i \right)^2 \right]} \quad (26.5)$$

The external audit results are used to determine the accuracy of the measurements. Accuracy is calculated from percentage differences,  $d_i$ , for the audit concentrations and the instrument response.

### 26.5.1 Data Quality Objectives

Data collected for the Ambient Air Quality Monitoring Program are used to make very specific decisions that can have an economic impact on the area represented by the data. Data quality objectives (DQOs) are qualitative and quantitative statements that clarify the purpose of the study, define the most appropriate type of information to collect, determine the most appropriate conditions from which to collect that information,

and specify tolerable levels of potential decision errors. The DQO must be based on the data requirements of the decision makers who need confidence that the data used to make environmental decisions are of adequate quality. The data used in these decisions are never completely free of error and always contain some level of uncertainty. Thus, for example, it is possible that decision makers may declare an area "nonattainment" when the area is actually in "attainment", i.e. a false rejection (Figure 26.10) or to declare an area to be in "attainment" when actually it is not meeting the ambient standard, i.e. a false acceptance (Figure 26.11).

Ambient air measurements require much coordination to ensure quality. In the United States, a primary quality assurance organization (PQAO) is a monitoring organization or a group of monitoring organizations that share a number of quality assurance factors.<sup>17</sup> The measurement uncertainty among all stations in the organization is expected to be reasonably homogeneous in light of common factors, including

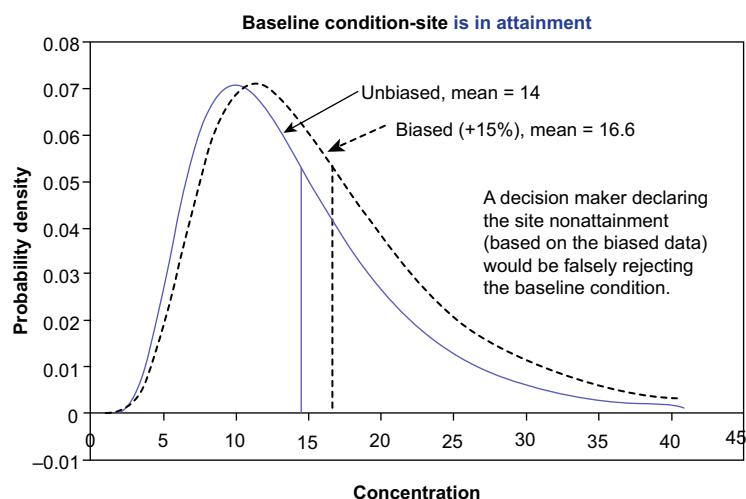
1. Operation by a common team of field operators according to a common set of procedures;
2. Use of a common QAPP or standard operating procedures;
3. Common calibration facilities and standards;
4. Oversight by a common quality assurance organization; and
5. Support by a common management, laboratory, or headquarters.

For some pollutants, the number of monitoring sites in a PQAO may be used to determine the number and frequency of quality control checks, including the number of collocated monitors and audit frequencies.

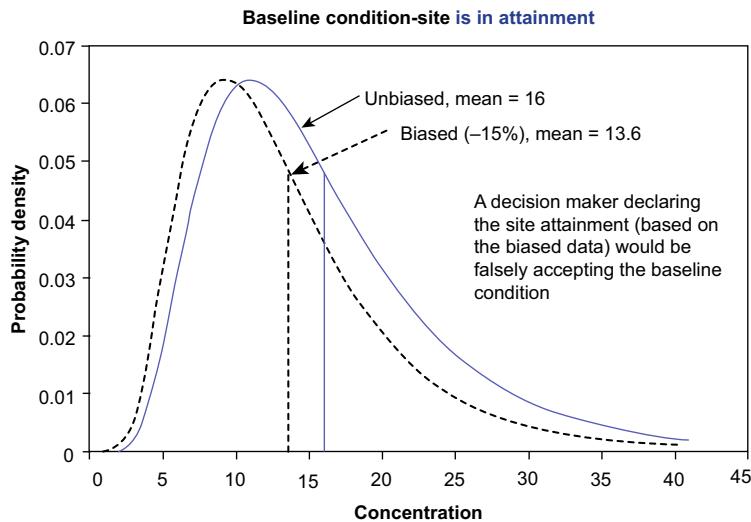
Data assessments for completeness, precision, and bias are aggregated at the PQAO level. The common factors are the key criteria to be used when an agency decides the sites to be considered for aggregation to a PQAO. There are cases where state, local, and tribal monitoring organizations have consolidated to one PQAO. All of the factors do not always have to be fulfilled, but common protocols and quality assurance plans are often needed to consolidate sites. Figure 26.12 shows the relationship of pollutants monitored at unique sites and how these unique sites can relate to monitoring organizations and PQAOs. In the case of PQAO #1, a tribal monitoring organization and local monitoring organization have common factors that allow for consolidation.<sup>18</sup>

An air monitoring plan must be in place before samples are collected and arrive at the laboratory. The plan includes quality assurance provisions and describes the procedures to be employed. These procedures must be strictly followed to investigate environmental conditions. The plan describes in detail the sampling

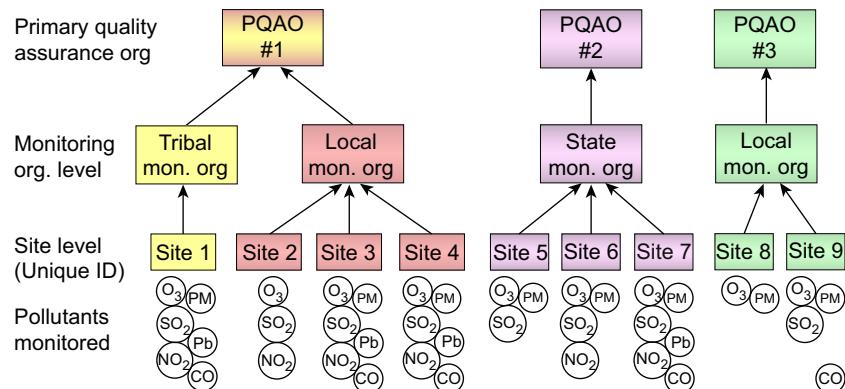
**FIGURE 26.10** Effect of positive bias on the annual average estimate of the concentration of an air pollutant, resulting in a false rejection error (area is actually meeting the standard, but bias leads to a “nonattainment” designation). (For color version of this figure, the reader is referred to the online version of this book.) Ref. 18.



**FIGURE 26.11** Effect of negative bias on the annual average resulting in a false acceptance error (area is actually not meeting the standard, but bias leads to an “attainment” designation). (For color version of this figure, the reader is referred to the online version of this book.) Ref. 18.



**FIGURE 26.12** Relationship between the primary quality assurance organization and monitoring organizations with respect to multiple pollutant monitoring of criteria air pollutants. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 18.



apparatus (e.g. real-time probes, sample bags, bottles, and soil cores), the number of samples needed, sample handling, and transportation. The quality and quantity of samples are determined by the DQOs, which are defined by the objectives of the overall contaminant assessment plan (together the assessment plan and quality assurance (QA) plan is a quality assurance project plan or QAPP). The DQOs can be either qualitative or quantitative statements that translate nontechnical project goals into scientific and engineering outputs needed to answer technical questions.<sup>19</sup>

Quantitative DQOs specify a required level of scientific and data certainty, while qualitative DQOs express decisions goals without specifying those goals in a quantitative manner. Even when expressed in technical terms, DQOs must specify the decision that the data will ultimately support, but not the manner that the data will be collected. DQOs guide the determination of the data quality that is needed in both the sampling and analytical efforts. The US EPA has listed three examples of the range of detail of quantitative and qualitative DQOs<sup>20</sup>:

*Example of a less detailed, quantitative DQO:* Determine with greater than 95% confidence that an emission does not pose a human exposure hazard.

*Example of a more detailed, quantitative DQO:* Determine to a 90% degree of statistical certainty whether or not the concentration of mercury released from a site is less than 1 ppbv.

*Example of a detailed, qualitative DQO:* Determine the proper disposition of each canister delivered in real

time using a dynamic work plan and a field method able to turnaround lead (Pb) results on the air samples within 2 h of sample collection.

Thus, if the condition in question is tightly defined, e.g. the hourly change in the emission of formaldehyde from a particular vent, a small number of samples or real-time probes would be defined as the DQO. Conversely, if the environmental assessment is more complex and larger in scale, e.g. the characterization of year-round outdoor and indoor air quality of an environmental justice neighborhood, the sampling plan's DQO may dictate that numerous samples at various points be continuously sampled for wide range of inorganic and organic contaminants. This is even more complicated when nonchemical stressors are of concern, e.g. pollen and other bioaerosols, nanoparticles, electromagnetic radiation, and odors.

The sampling plan may have to include media other than the air, e.g. soil, water, and biota, such as near a hazardous waste site. The sampling and analysis plan should explicitly point out which methods will be used. For example, if toxic chemicals are being monitored, the US EPA specifies specific sampling and analysis methods.<sup>21–23</sup>

The geographic area where data are to be collected is defined by distinctive physical features such as volume or area, e.g. metropolitan city limits, property boundaries down to a depth of 6 cm, a specific group of homes, the length along a shoreline, or the natural habitat range of a particular animal species. Care should be taken to define boundaries. For example, Figure 26.13 shows a

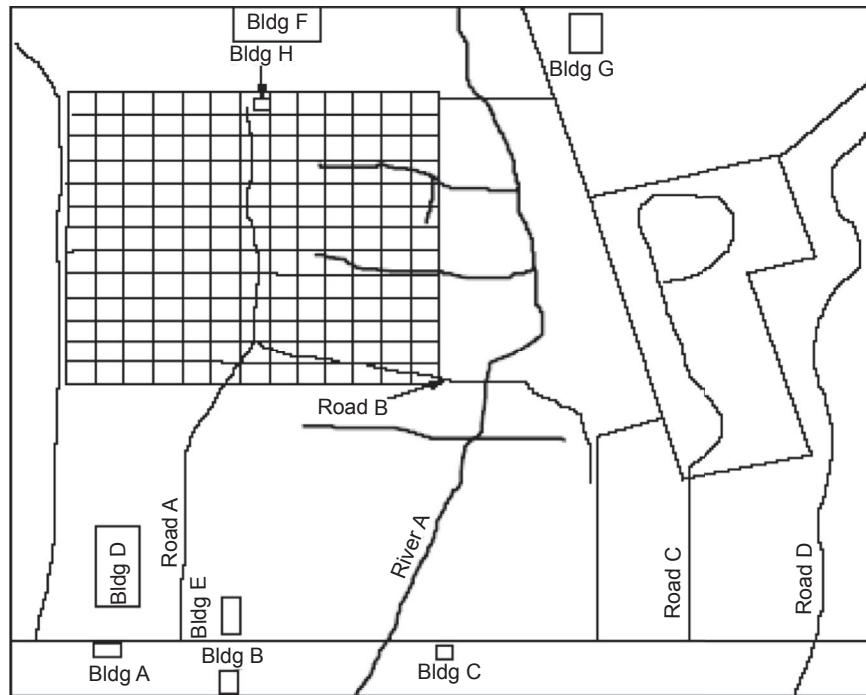


FIGURE 26.13 Environmental assessment area delineated by map boundaries. Ref. 24.

sampling grid, with a sample taken from each cell in the grid.<sup>22</sup> The target population may be divided into relatively homogeneous subpopulations within each area or subunit. This can reduce the number of samples needed to meet the tolerable limits on decision errors and to improve efficiency.

Time is another essential parameter that determines the type and extent of monitoring needed. Conditions vary over the course of a study due to changes in weather conditions, seasons, operation of equipment, and human activities. These include seasonal changes in ground-water levels, seasonal differences in farming practices, daily or hourly changes in airborne contaminant levels, and intermittent pollutant discharges from industrial sources. Such variations must be considered during data collection and in the interpretation of results. Some examples of environmental time-sensitivity are

- concentrations of lead in dust on windowsills may show higher concentrations during the summer when windows are raised and paint/dust accumulates on the windowsill;
- terrestrial background radiation levels may change due to shielding effects related to soil dampness;
- amount of pesticides on surfaces may show greater variations in the summer because of higher temperatures and volatilization;
- instruments that may not give accurate measurements when temperatures are colder; and
- airborne PM measurements that may not be accurate if the sampling is conducted in the wetter winter months rather than the drier summer months.

Feasibility should also be considered. This includes gaining legal and physical access to the properties, equipment acquisition and operation, and environmental conditions, times, and conditions when sampling is prohibited (e.g. freezing temperatures, high humidity, and noise).

Basically, the DQOs frame the amount and type of uncertainty that can be tolerated. This remains a challenge for air pollution. As mentioned, measurements of ambient air quality are typically made at one or a few sites in an airshed in order to determine the compliance of air quality data with ambient air quality standards. For example, sites vary considerably regarding emission densities and dispersion, meteorology, topography, street topography, and other conditions. Thus, the minimum numbers and locations of monitors need to be justified scientifically. The more heterogeneous the area, the greater the number of monitoring sites that will be needed.

Spatial variability informs this somewhat decision in part, e.g. known differences in ambient concentrations across the airshed. In a way, the monitor provides information about a relatively homogeneous parcel within

the heterogeneous airshed, so spatial representativeness of a monitoring site may be defined as the area within which pollutant concentrations are approximately constant.<sup>23</sup>

## 26.6 MONITORING PLAN EXAMPLE

Consider a plan to measure mobile source air toxic (MSAT) concentrations and variations in concentrations as a function of distance from the highway and to establish relationships between MSAT concentrations as related to highway traffic flows including traffic count, vehicle types and speeds, and meteorological conditions such as wind speed and wind direction. Specifically, the monitoring plan has the following goals<sup>24</sup>:

1. Identify the existence and extent of elevated air pollutants near roads.
2. Determine how vehicle operations and local meteorology influence near-road air quality for criteria and toxic air pollutants.
3. Collect data that will be useful in evaluating and refining, if necessary, models used to determine the emissions and dispersion of motor vehicle-related pollutants near roadways.

Such a complex monitoring effort requires management and technical staff with a diversity of skills that can be brought to bear on the implementation of this project. This diverse skill set includes program management, contracts administration, field monitoring experience, laboratory expertise, and QA oversight.

The purpose of any site selection process is to gather and analyze sufficient data that would lead one to draw informed conclusions regarding the selection of the most appropriate site for the monitoring at a specific location. Moreover, the site selection process needs to include programmatic issues to ensure an informed decision is reached. Selecting a monitoring site must be based on scientific and feasibility factors, as shown in [Table 26.10](#) and [Figure 26.14](#). Each step has varying degrees of complexity due to “real-world” issues. The first step was to determine site selection criteria (see [Table 26.11](#)). The follow-on steps include (1) develop list of candidate sites and supporting information; (2) apply site selection filter (“coarse” and “fine”), (3) site visit; (4) select candidate site(s) via team discussion; (5) obtain site access permission(s); and (6) implement site logistics.

A list of candidate sites based on these criteria can then be developed. Geographic information system (GIS) data, tools, and techniques and on-site visits would be used to compare various sites that meet these criteria. Quite commonly, even a well-designed monitoring plan will need to be adjusted during the

TABLE 26.10 Selective Steps in Selecting a Near-Road Air Quality Monitoring Site

Site Selection Steps	Method	Comment
Determine site selection criteria	Monitoring protocol	
Develop list of candidate sites	Geographic information system (GIS) data; on-site visit(s)	Additional sites added as information is developed.
Apply coarse site selection filter	Team discussions, management input	Eliminate sites below acceptable minimums
Site visit	Field trip	Application of fine site selection filter
Select candidate site(s)	Team discussions, management input	
Obtain site access permissions	Contact property owners	If property owners do not grant permission, then the site is dropped from further consideration
Site logistics (i.e. physical access, utilities—electrical and communications)	Site visit(s), direct contact with utility companies	

Source: Ref. 26.

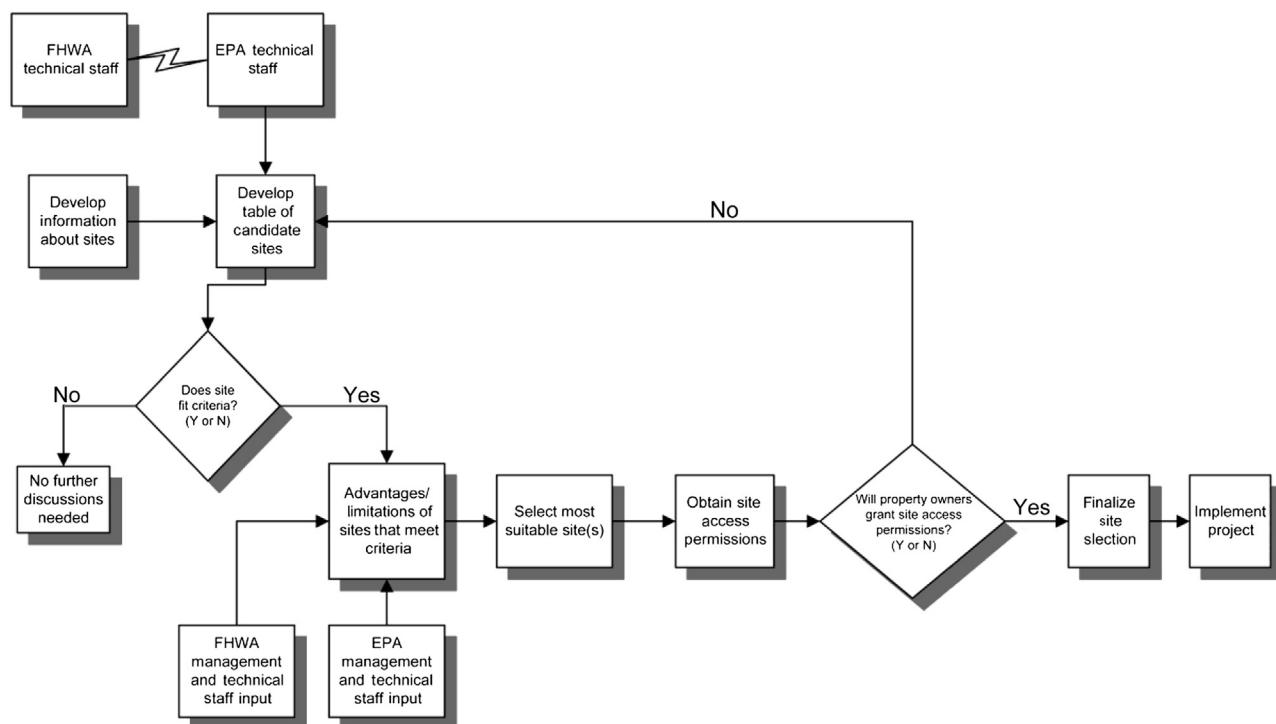


FIGURE 26.14 Monitoring location selection decision flow chart. Ref. 26

implementation phase. For example, investigators may discover barriers or differing conditions from what was observed in the planning phase (e.g. different daily traffic counts or new road construction).

After applying site selection criteria as a set of “filters”, candidate sites are incrementally eliminated. For example, the first filter would be sites with low traffic counts; the next filter, the presence of extensive sound

barriers, eliminates additional sites; and other filters, e.g. complex geometric design or lack of available traffic volume data, eliminates additional sites. Next, feasibility considerations would eliminate additional candidate sites.

An important component of “ground truthing” or site visit is to obtain information from local sources. Local businesses and residents can provide important

TABLE 26.11 Example Selection Considerations and Criteria

Selection Considerations	Monitoring Protocol Criteria
<b>ESSENTIAL CRITERIA</b>	
AADT >150,000	Only sites with more than 150,000 annual average daily traffic (AADT) are considered as candidates.
Geometric design	The geometric design of the facility, including the layout of ramps, interchanges and similar facilities, will be taken into account. Where geometric design impedes effective data collection on MSATs and PM <sub>2.5</sub> , those sites will be excluded from further consideration. All sites have a "clean" geometric design.
Topology (i.e. sound barriers, road elevation)	Sites located in terrain making measurement of MSAT concentrations difficult or that raise questions of interpretation of any results will not be considered. For example, sharply sloping terrain away from a roadway could result in underrepresentation of MSAT and PM <sub>2.5</sub> concentration levels on monitors in close proximity to the roadway simply because the plume misses the monitor as it disperses.
Geographic location	Criteria applicable to representing geographic diversity within the United States as opposed to within any given city.
Availability of data (traffic volume data)	Any location where data, including automated traffic monitoring data, meteorological or MSAT concentration data, are not readily available or instrumentation cannot be brought in to collect such data will not be considered for inclusion in the study.
Meteorology	Sites will be selected based on their local climates to assess the impact of climate on dispersion of emissions and atmospheric processes that affect chemical reactions and phase changes in the ambient air.
<b>DESIRABLE, BUT NOT ESSENTIAL CRITERIA</b>	
Downwind sampling	Any location where proper siting of downwind sampling sites is restricted due to topology, existing structures, meteorology, etc., may exclude otherwise suitable sites for consideration and inclusion in this study.
Potentially confounding air pollutant sources	The presence of confounding emission sources may exclude otherwise suitable sites for consideration and inclusion in this study.
Site access (admin/physical)	Any location where site access, is restricted or prohibited either due to administrative or physical issues, will not be considered for inclusion in the study.

Source: Ref. 26.

information needed in a decision process, such as types of chemicals stored previously at a site, changes in vegetation, or even ownership histories.

The use of spatial tools in decision processes is increasing.<sup>27a,27b</sup> Until recently, the use of GIS and other spatial tools in decision processes have required the acquisition of large amounts of the data. In addition, the software has not been user-friendly. GIS data have now become more readily available in both quantity and quality, and GIS exists in common operating system environments.

Typical data layers that are required are the location of suitable soils, wells, surface water sources, residential areas, schools, airports, roads, etc. From these data, layers queries are formulated to provide the most suitable sites (e.g. depth to water table may help identify sources of pollution). Typically, quantitative weighting criteria are associated with the siting criteria as well as elements of the data layers (e.g. certain types of soils

would be more suitable than others and thus would have applicable quantitative values).<sup>28</sup>

## 26.7 LABORATORY ANALYSIS

Although real-time analysis of air and other media is becoming more commonplace, many if not most air samples must continue to be brought to a laboratory analyzed after collection. The steps that must be taken to interpret the concentration of air pollutant in the sample are known as "wet chemistry".

### 26.7.1 Extraction

When an environmental sample arrives at the laboratory, the next step may be "extraction". Extraction is needed when the actual sample collection was by trapping the chemicals onto sorbents; meaning that the

chemicals must first be freed from the sorbant matrix. It would not be needed for air samples that can be carried into the chromatograph. However, numerous toxic chemicals have low vapor pressures and may not be readily dissolved in water. Thus, they may be found in various media, e.g. sorbed to particles, in the gas phase, or in the water column suspended to colloids (and very small amounts dissolved in the water itself). To collect such chemicals in the gas phase, a common method calls for trapping it on polyurethane foam (PUF) or other sorbants.

To analyze semivolatile organic compounds (SVOCs) in the air, the PUF or other sorbing media must be extracted. Since SVOCs partition between air and particles, to determine the amount of SVOC in PM requires extraction. Indeed, extraction is arguably one of most important and limiting steps in measuring some of the most toxic air pollutants, including the halogenated dioxins, persistent pesticides and products of incomplete combustion, e.g. PAHs (see Discussion Box: Laboratory Analysis of Semivolatile Organic Compounds).

## DISCUSSION BOX

### Laboratory Analysis of Semivolatile Organic Compounds

As mentioned in Chapter 25, the compendium of air toxic methods is a valuable resource. Thus, for sampling and analyzing SVOCs, a good place to start is the US EPA's "Method 1613", Tetra-through octa-chlorinated dioxins and furans by isotope dilution high resolution gas chromatograph/high resolution mass spectrometry (HRGC/HRMS) (Rev. B); as well as the USEPA's "RCRA SW846 Method 8290", Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by HRGC/HRMS. For air, the best method is the PS-1 high-volume sampler system described in US EPA "Method TO-9A" in Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, EPA/625/R-96/010b (1999).

The extraction can be by solvent extraction, by supercritical fluid extraction (SFE), or by other techniques depending on the compound and the sorbant used to collect it. The procedure to analyze SVOCs begins with preparation of the sample for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (e.g. EPA Method 3500) and, if necessary, sample cleanup procedures (i.e. EPA Method 3600). Next, the extract is introduced into the GC/MS by injecting the sample extract into a GC with a narrow-bore fused-silica capillary column. The GC column is temperature programmed to separate the analytes, which are then detected with a mass spectrometer connected to the gas chromatograph. This is usually preferred; however,

sometimes certain analytes cannot be detected directly with MS (e.g. highly polar compounds must first be derivatized). Thus, other detection systems, such as ultraviolet (UV) light, may need to be employed. The drawback is that the detection limits are often higher than that of MS.

Analytes eluted from the capillary column are introduced into the mass spectrometer using a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impactlike) spectra of authentic standards (i.e. by the mass to charge [m/z] ratios of the molecular fragments). The column is selected based on the retention time (RT) of the particular SVOC. However, the most commonly used column for SVOCs is 30 m × 0.25 mm or 0.32 mm interior diameter (ID) 1 μm film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve that has been prepared in a solvent of known concentrations of the target SVOC.

Interference is a problem, since SVOCs are ubiquitous in the environment (e.g. phthalates are used as plasticizers even in laboratory settings). Thus, GC/MS data from all blanks, samples, and spikes must be evaluated for such interferences.

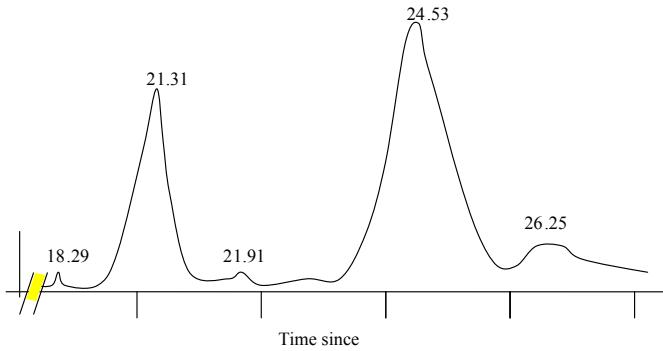
#### SVOC Chromatography Example

Consider the situation where an analytical laboratory has generated the following chromatogram and table

(Continued)

### DISCUSSION BOX (cont'd)

from high-performance liquid chromatography (HPLC)/UV at 254 nm using a 5  $\mu\text{m}$ , C<sub>18</sub>, 4.6  $\times$  250-mm column from a water sample you submitted:



concentration. Then you could calculate (actually the HPLC software will calculate) the calibration curve. So, for example, if a peak with an area of 200 is associated

Retention Time	Area	Type	Area/Height	Area %
18.29	NA	NA	NA	0.1
21.31	NA	NA	NA	31.4
21.91	NA	NA	NA	0.2
24.53	NA	NA	NA	67.2
26.25	NA	NA	NA	1.1

Even with the missing entries in the table, one can still ascertain certain information. What are the RTs of compound A and B? Which compound is present in a larger amount? Which compound has the higher boiling point? What would happen to the RTs of compounds A and B if the column temperature were raised? What if compound B were suspected to be benzo(a)pyrene based on company records and the type of industries nearby?

Thoughtful targeting of laboratory studies can answer these questions.

The RT of compound A is 21.31 min, shown above the peak and in the table's RT column. The RT of compound B is 24.53 min. You cannot tell from this table or chromatogram which compound is present in a larger amount, since the only way to do so is to have calibration curve from known concentrations of compound A and compound B (at least three, but preferably five). For example, you would run the HPLC successively with injections of pure solutions of 0.01, 0.1, 1, 10, and 100  $\mu\text{g l}^{-1}$  concentrations of compound A, and again with pure solutions of the same concentrations of compound B. These concentrations would give peak areas associated with each known

with 1  $\mu\text{g l}^{-1}$  of compound A and a peak with an area of 2000 is associated with 10  $\mu\text{g l}^{-1}$  of compound A (i.e. a linear calibration curve) at 21.31 min after the aliquot is injected into the HPLC, then when you run your unknown sample and a peak at 21.31 min with an area of 1000 would mean you have about 5  $\mu\text{g l}^{-1}$  concentration of compound A in your sample. The same procedure would be followed to draw a calibration curve for compound B at an RT of 24.53 min.

The reason it is not sufficient to look at the percent area is that each compound is physically and chemically different, and recall from the Beer–Lambert law (see Chapter 25) that the amount of energy absorbed (in this case, the UV light) is what gives us the peak. If a molecule of compound A absorbs UV at this wavelength (i.e. 254 nm) at only 25% as that of compound B, compound A's concentration would be higher than that of compound B (because even though compound B has twice the percent area, its absorbance is four times that of compound B).

Compound A has the lower boiling point since it comes off the column first. Of course, this is only true if other factors, especially polarity, are about the same. For example, if compound B has about the same polarity as the column being used, but compound A has a very different polarity, compound A will have a greater tendency to leave the column. Generally, however, RT is a good indicator of boiling point; i.e. lower RTs mean lower boiling points.

If the column temperature were raised, both compounds A and B would come off the column in a shorter time. Thus, the RTs of both compounds A and B would be shorter than before the temperature was raised.

## DISCUSSION BOX *(cont'd)*

To determine whether the peak at 24.53 min is benzo(a)pyrene, you must first obtain a true sample of pure benzo(a)pyrene to place in a standard solution. This is the same process as you used to develop the calibration curve above. That is, you would inject this standard of known benzo(a)pyrene into the same HPLC and the same volume of injection. If the standard gives a peak at an RT at about 25 min, there is a good chance it is benzo(a)pyrene. As it turns out, benzo(a)pyrene absorbs UV at 254 nm and does come off an HPLC column at about 25 min.

The column type also affects RT and peak area. The one used by the laboratory is commonly used for PAHs, including benzo(a)pyrene. However, numerous columns can be used for SVOCs, so both the RT and peak area will vary somewhat. Another concern is coelution, i.e. two distinct compounds that have nearly the same RTs.

One means of reducing the likelihood of coelution is to target the wavelength of the UV detector. For example, the recommended wavelength for benzo(a)pyrene is 254 nm, but 295 nm is preferred by environmental chromatographers because the interference peak in the benzo(a)pyrene window is decreased at 295 nm. Another way to improve detection is to use a diode array detection system with the UV detector. This gives a number of different chromatograms simultaneously at various wavelengths. Finally, there are times when certain detection systems are completely unable to detect a specific molecule. For example, if a molecule does not absorb UV light (i.e. it lacks a group of atoms in a molecule responsible for absorbing the UV radiation, known as chromophores), there is no way to use any UV detector. In this case another detector, e.g. MS, must be used.

Extraction makes use of physics and chemistry. For example, many compounds can be simply extracted with solvents, usually at elevated temperatures. A common solvent extraction is the Soxhlet extractor, named after the German food chemist, Franz Soxhlet (1848–1913). The Soxhlet extractor (the US EPA Method 3540) removes sorbed chemicals by passing a boiling solvent through the media. Cooling water condenses the heated solvent and the extract is collected over an extended period, usually several hours. Other automated techniques apply some of the same principals as solvent extraction, but allow for more precise and consistent extraction, especially when large volumes of samples are involved. For example, SFE brings a solvent, usually carbon dioxide, to the pressure and temperature near its critical point of the solvent, where the solvent's properties are rapidly altered with very slight variations of pressure.<sup>29</sup> Solid phase extraction, which uses a solid and a liquid phase to isolate a chemical from a solution, and is often used to clean up a sample before analysis. Combinations of various extraction methods can enhance the extraction efficiencies, depending upon the chemical and the media in which it is found. Ultrasonic and microwave extractions may be used alone or in combination with solvent extraction. For example, the US EPA Method 3546 provides a procedure for extracting hydrophobic (that is, not soluble in water) or slightly water-soluble organic compounds from particles such as soils, sediments, sludges, and solid wastes. In this method, microwave energy elevates the temperature and pressure conditions (i.e. 100–115 °C and

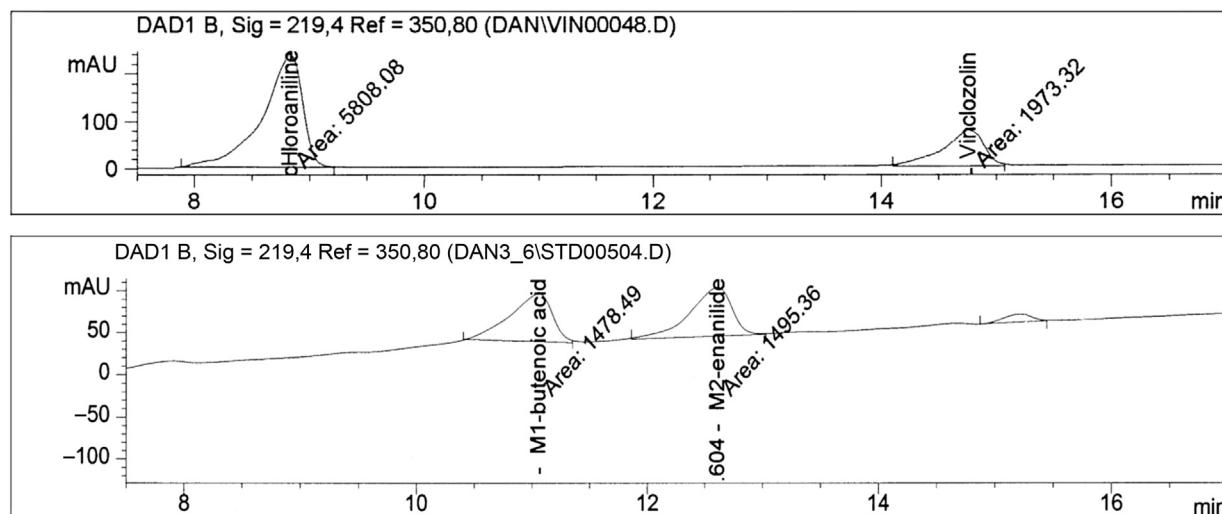
50–175 psi) in a closed extraction vessel containing the sample and solvent(s). This combination can improve recoveries of chemical analytes and can reduce the time needed compared with the Soxhlet procedure alone.

As mentioned, not every sample needs to be extracted. For example, air monitoring using canisters and bags allows the air to flow directly into the analyzer. Some air samples may also be directly injected into a detector on-site, such as a mobile gas chromatograph on a motor vehicle equipped with a chemical analysis system, such as the US EPA's Trace Atmospheric Gas Analyzer (TAGA).

### 26.7.2 Separation Science

After extraction, if needed, the chemical compound of interest (e.g. the air pollutant) in the sample must be separated from the column and move to the detector. Surface methods, such as fluorescence, sputtering, and atomic absorption (AA), require only that the sample be mounted on specific media (e.g. filters). Also, continuous monitors like the chemiluminescent system mentioned in the next section provide ongoing measurements.

Chromatography is often used synonymously with separation; however, chromatography often includes both separation and detection. So, to explain the process this discussion will treat separation as a distinct process. Separation makes use of the chemicals' different affinities for certain surfaces under various temperature and pressure conditions. The first step, injection, introduces the extract to a "column". The term column is



**FIGURE 26.15 Chromatogram of four compounds emitted from soil in a chamber and trapped on polyurethane foam, which was extracted using supercritical fluid extraction.** The extract was separated by gas chromatography and detected using high-performance liquid chromatography. *Vallero D.* Engineering the Risks of Hazardous Wastes. Boston (MA): Butterworth-Heinemann; 2003.

derived from the time when columns were packed with sorbents of varying characteristics, sometimes meters in length, and the extract was poured down the packed column to separate the various analytes. Today, columns are of two major types, gas and liquid. GC makes use of hollow tubes ("columns") coated inside with compounds that hold organic chemicals. The columns are in an oven, so that after the extract is injected into the column, the temperature is increased, as well as the pressure, and the various organic compounds in the extract are released from the column surface differentially, whereupon they are collected by a carrier gas (e.g. helium) and transported to the detector. Generally, the more volatile compounds are released first (they have the shortest RTs), followed by the semivolatile organic compounds. So, boiling point is often a very useful indicator as to when a compound will come off a column. This is not always the case, since other characteristics such as polarity can greatly influence a compound's resistance to be freed from the column surface. For this reason, numerous GC columns are available to the chromatographer (different coatings, interior diameters, and lengths). Rather than coated columns, liquid chromatography (LC) makes use of columns packed with different sorbing materials with differing affinities for compounds. Also, instead of a carrier gas, LC uses a solvent or blend of solvents to carry the compounds to the detector. In HPLC, pressures are also varied.

Detection is the final step for quantifying the chemicals in a sample. The type of detector needed depends upon the kinds of pollutants of interest. Detection gives the "peaks" that are used to identify compounds (Figure 26.15). For example, if hydrocarbons are of

concern, GC with flame ionization detection (FID) may be used. GC-FID gives a count of the number of carbon atoms, so, for example, long chains can be distinguished from short chains. The short chains come off the column first and have peaks that appear before the long-chain peaks. However, if pesticides or other halogenated compounds are of concern, electron capture detection is a better choice.

A number of detection approaches are also available for LC. Probably the most common is absorption. Chemical compounds absorb energy at various levels, depending upon their size, shape, bonds, and other structural characteristics. Chemicals also vary in whether they will absorb light or how much light they can absorb depending upon wavelength. Some absorb very well in the UV range, while others do not. Diode arrays help to identify compounds by giving a number of absorption ranges in the same scan. Some molecules can be excited and will fluoresce. As mentioned, the Beer–Lambert law states that energy absorption is proportional to chemical concentration. Thus, the concentration of the chemical can be ascertained by measuring the light absorbed. The peaks on the chromatograph are calibrated to concentration by a calibration curve generated from known concentrations of the pollutant. The calibration curve simply associates absorbance, fluorescence, or other response to concentration. A calibration plot can be derived from this information. Figure 26.16 provides data for the calibration plot for a response of an ion from the herbicide clofibric acid ( $2-(4\text{-chlorophenoxy})-2\text{-methylpropanoic acid}$  or  $\text{C}_{10}\text{H}_{11}\text{ClO}_3$ ) vs an ion of an internal standard. The data were derived by plotting the ratio of the response of the analyte to that of the internal standard vs the ratio of the amount of analyte to that

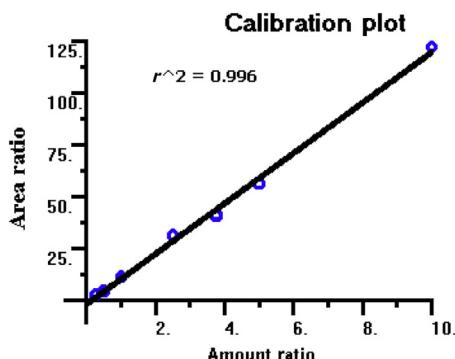


FIGURE 26.16 Calibration plot of 2-(4-chlorophenoxy)-2-methylpropanoic acid] vs an ion of an internal standard. U.S. Environmental Protection Agency. Trace organic analysis. (For color version of this figure, the reader is referred to the online version of this book.) <http://www.epa.gov/esd/chemistry/org-anal/faq.htm>; 2013 [accessed 20.11.13].

of the internal standard. A regression of some order (usually linear, quadratic, or cubic) is performed on the data to obtain a calibration line.<sup>30</sup>

The equation of the calibration plot can be used to calculate the amount of the target analyte (s) in a sample in the form of an extract that has been added at a known level with the internal standard. For example, the internal standard is added at 10 ng for a 1 g sample the level is 10 ppb for the internal standard. From this value the amount of target can be calculated from the equation of the calibration curve. Usually, these calculations are performed by data system based on the calibration curve.<sup>31</sup>

One of the most popular detection methods for environmental pollutants is MS, which can be used with either GC or LC separation. The MS detection is highly sensitive for organic compounds and works by using a stream of electrons to consistently break apart compounds into fragments. The positive ions resulting from the fragmentation are separated according to their masses. This is referred to as the "mass to charge ratio" or m/z. No matter which detection device is used, software is used to decipher the peaks and to perform the quantitation of the amount of each contaminant in the sample.

For inorganic substances and metals, the additional extraction step may not be necessary. The actual media (e.g. collected airborne particles) may be measured by surface techniques like AA, X-ray fluorescence (XRF), inductively coupled plasma (ICP), or sputtering. As for organic compounds, the detection approaches can vary. For example, ICP may be used with absorption or MS. If all one needs to know is elemental information, for example, to determine total lead or nickel in a sample, AA or XRF may be sufficient. However, if speciation (i.e. knowing the various compounds of a metal), then significant sample preparation is needed, including a process known as "derivatization". Derivatizing a

sample is performed by adding a chemical agent that transforms the compound in question into one that can be recognized by the detector. This is done for both organic and inorganic compounds, for example, when the compound in question is too polar to be recognized by MS.

The physical and chemical characteristics of the compounds being analyzed must be considered before visiting the field and throughout all the steps in the laboratory. Although it is beyond the scope of this book to go into detail, it is worth mentioning that the quality of results generated about contamination depends upon the sensitivity and selectivity of the analytical equipment. Table 26.12 defines some of the most important analytical chemistry threshold values.

## 26.8 STATISTICAL ANALYSIS AND DISPLAY

In general, air quality data are classified as a function of time, location, and magnitude. Several statistical parameters may be used to characterize a group of air pollution concentrations, including the arithmetic mean, the median, and the geometric mean. These parameters may be determined over averaging times of up to 1 year. In addition to these three parameters, a measure of the variability of a data set, such as the standard deviation or the geometric standard deviation, indicates the range of data around the value selected to represent the data set.

Raw data must be analyzed and transformed into a format useful for specific purposes. Summary tables, graphs, and geographic distributions are some of the formats used for data display. Air quality information often consists of a large body of data collected at a variety of locations and over different seasons. Table 26.13 shows the tabular format used by a local air pollution authority to report the status of compliance with air quality standards.<sup>32</sup> The format has location, maximum values, annual means, and number of occurrences of hourly values above a given concentration as a function of the month of the year. One can quickly determine which areas are violating a standard, at what time of the year elevated concentrations are occurring, and the number of good data points collected.

Pollutant concentration maps may be constructed as shown in Figure 26.17. In this example, elevated levels of ambient PM are associated with population centers.<sup>33</sup> For a given geographic area, isopleths, lines showing equal concentrations of a pollutant, are drawn on a map. Regions of high concentration are quickly identified. Further action may be taken to determine the cause, such as review of emission inventories of additional sampling.

TABLE 26.12 Expressions of Chemical Analytical Limits

Type of Limit	Description
Limit of detection (LOD)	Lowest concentration or mass that can be differentiated from a blank with statistical confidence. This is a function of sample handling and preparation, sample extraction efficiencies, chemical separation efficiencies, and capacity and specifications of all analytical equipment being used (see IDL below).
Instrument detection limit (IDL)	The minimum signal greater than noise detectable by an instrument. The IDL is an expression of the piece of equipment, not the chemical of concern. It is expressed as a signal to noise (S:N) ratio. This is mainly important to the analytical chemists, but the engineer should be aware of the different IDLs for various instruments measuring the same compounds, so as to provide professional judgment in contracting or selecting laboratories and deciding on procuring for appropriate instrumentation for all phases of remediation.
Limit of quantitation (LOQ)	The concentration or mass above which the amount can be quantified with statistical confidence. This is an important limit because it goes beyond the "presence-absence" of the LOD and allows for calculating chemical concentration or mass gradients in the environmental media (air, water, soil, sediment, and biota).
Practical quantitation limit (PQL)	The combination of LOQ and the precision and accuracy limits of a specific laboratory, as expressed in the laboratory's quality assurance/quality control (QA/QC) plans and standard operating procedures (SOPs) for routine runs. The PQL is the concentration or mass that the engineer can consistently expect to have reported reliably.

Source: Vallero D. Engineering the Risks of Hazardous Wastes. Boston (MA): Butterworth-Heinemann; 2003.

The methods described in Chapter 25 and the air quality results discussed in Chapter 28 are often for specific pollutants in particular spatial contexts, e.g. benzene concentrations indoors, CO concentrations at a roadway intersection, or O<sub>3</sub> concentrations for an entire metropolitan area. However, this is not how air pollution exists. It is usually a complex mixture of criteria pollutants and air toxics that include solid, liquid, and vapor phases, which are generated from myriad sources, transformed in the atmosphere and other environmental compartments, and transported to the places where people breathe.

Some pollutants are expected to be complex mixtures, (e.g. coke oven emission or diesel PM), but in the real world every air pollutant is a component of a complex mixture. For example, a person standing near a road is being simultaneously exposed to benzene, 1,3-butadiene, CO, NO<sub>2</sub>, O<sub>3</sub>, PM<sub>2.5</sub>, and numerous other chemicals. The respective totals will vary. For example, there is likely to have concentration gradients with distance downwind from the road. Also, if the person goes inside, the pollution mixture changes.

Consider a person moving in space, as depicted in Figure 26.18. Ozone is usually a regional pollutant, so the concentrations are stable until the person goes indoors, where the concentrations are much lower. Benzene and 1,3-butadiene are near-road pollutants, so they are highest near the roadway and decrease with distance downwind; however, benzene is also a common indoor pollutant, if a benzene source (e.g. gas stove) is indoors, benzene concentrations increase indoors. PM has numerous sources, including vehicle emissions and fugitive dust from roads. There must be

another source upwind (e.g. cement mixing operation). Like benzene, PM is also generated by numerous indoor sources. In addition, fine particulate (e.g. <2.5 μm diameter) also penetrate from outdoors to indoors. As a result, the net PM concentrations consist of indoor sources plus PM from penetration.

Concentrations of VOCs and PM indoors are often higher than outdoor concentrations, but contaminants generated by outdoor sources are transported to and penetrate into microenvironments. However, all pollutants have considerable variability in time and space. For example, diurnal spatial variations in O<sub>3</sub> concentrations are controlled by the relative importance of transport *versus* local photochemical production and loss rates, the timing for entrainment of air from the nocturnal residual boundary layer, and the diurnal variability in mixing layer height. Figure 26.19 indicates that the daily 1-h O<sub>3</sub> concentration maxima generally occur in midafternoon and daily 1-h minima tend to occur during the early morning. There is also considerable spread in these data, however, so caution is advised when extrapolating results from one region to another.<sup>34</sup> Indeed, this caution goes beyond O<sub>3</sub> and should be considered a general caution for most air pollutants.

## 26.9 CRITERIA AND STANDARDS

For any pollutant, air quality criteria may refer to different types of effects. For example, Tables 26.14–26.20 list effects on humans, animals, vegetation, materials, and the atmosphere caused by various

TABLE 26.13 Summary of Air Quality Statistics in the California's South Coast Air Basin and the Desert Area of Coachella Valley in the Salton Sea Air Basin for December 2002

Pollutant Averaging Time	State Standard	Federal Standard	Maximum Concentrations			
			ppm $\mu\text{g}^{-1} \text{ m}^{-3}$	% State Standard	% Federal Standard	Location
<b>OZONE</b>						
1 h	>0.09 ppm	>0.12 ppm	0.06	60	48	Several locations
8 h		>0.08 ppm	0.055		65	Banning airport
<b>CARBON MONOXIDE</b>						
8 h	>9.0 ppm	m	8.40	92	88	South central Los Angeles county
<b>NITROGEN DIOXIDE</b>						
1 h	>0.25 ppm		0.10	38		Southwest coastal Los Angeles county
24 h			0.069			South San Gabriel Valley
<b>SULFUR DIOXIDE</b>						
1 h	>0.25 ppm		0.02	8		South coastal Los Angeles county
24 h	>0.04 ppm	>0.14 ppm	0.010	24	7	North coastal Orange county
<b>PARTICULATE (<math>PM_{10}</math>)</b>						
24 h	>50 $\mu\text{m gm}^{-3}$	>150 $\mu\text{m gm}^{-3}$	95	186	63	Metropolitan Riverside county
<b>PARTICULATE (<math>PM_{2.5}</math>)</b>						
24 h		>65 $\mu\text{m gm}^{-3}$	55.4		85	South coastal Los Angeles county
<b>SULFATES</b>						
24 h	>25 $\mu\text{m gm}^{-3}$		4.7	19		South central Los Angeles county
<b>LEAD*</b>						
30 Days		>1.5 $\mu\text{m gm}^{-3}$		0.03	2	Central los Angeles
30 Days*				0.19	13	Several locations

\* Maximum monthly average concentration recorded at special monitoring sites in the immediate vicinity of major lead sources.

Source: South Coast Air Quality Management District (2002). Air Quality Standards Compliance Report, December 2002, and Summary Statistics for 2002, vol. 15, No. 12.

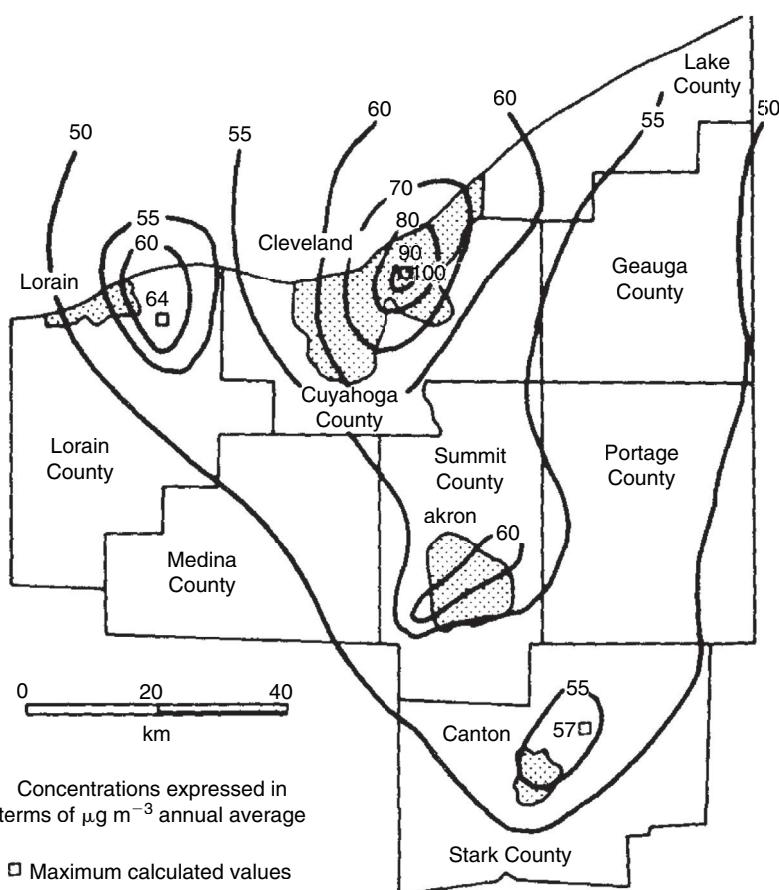


FIGURE 26.17 Concentration isopleth diagram of ambient particulate matter calculated by a computer model. Zimmer CE. In: Stern AC, editor. Air Pollution. 3rd ed. vol. 3. New York (NY): Academic Press; 1976.

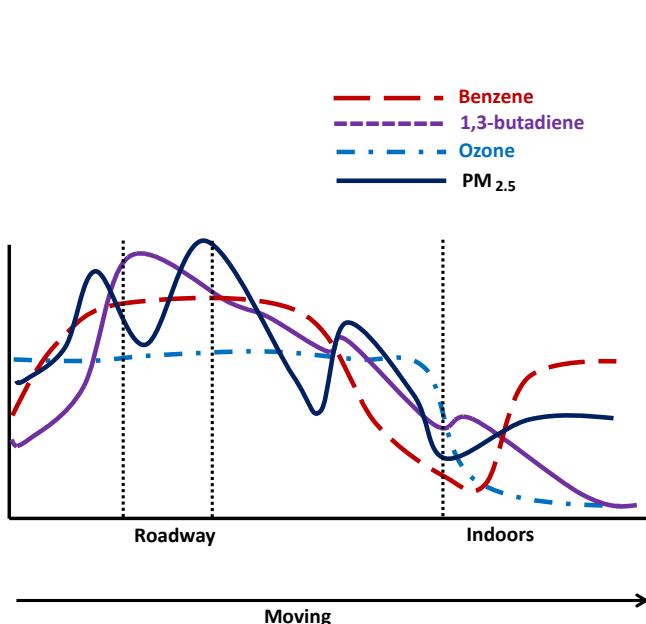
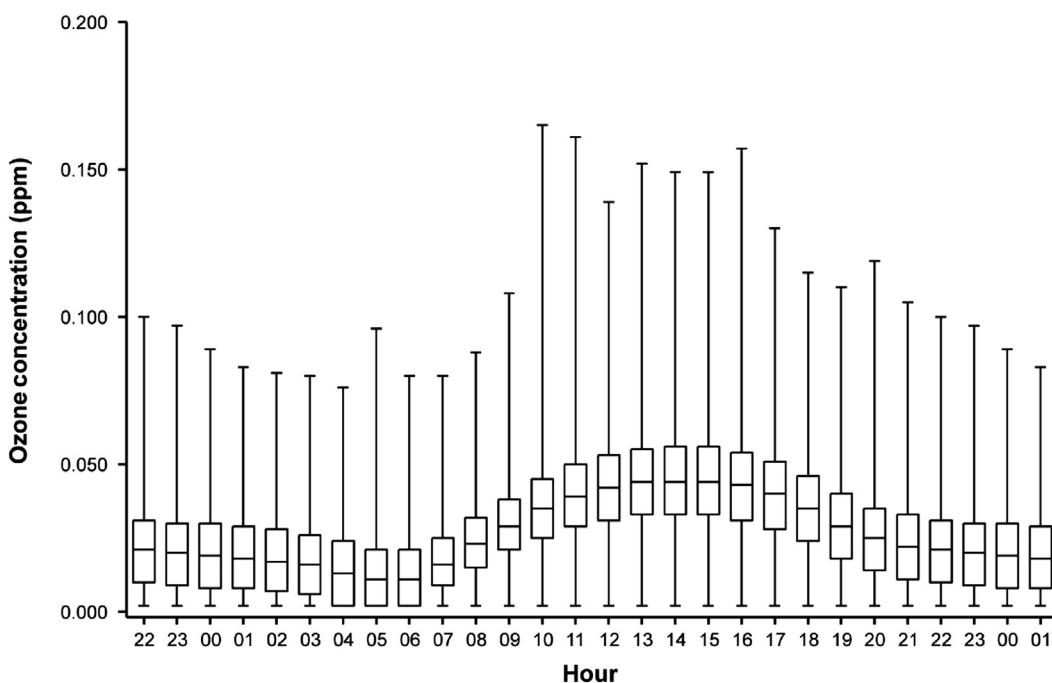


FIGURE 26.18 Hypothetical exposure to four pollutants as a person moves. (For color version of this figure, the reader is referred to the online version of this book.)

exposures to sulfur dioxide, PM, nitrogen dioxide, carbon monoxide, ozone, and lead. These data are from the Air Quality Criteria for these pollutants published by the US EPA.

Criteria stipulate conditions of exposure and may refer to sensitive population groups or to the joint effects of several pollutants. Air quality criteria are descriptive. They describe effects that can be expected to occur wherever the ambient air level of a pollutant reaches or exceeds a specific concentration for a particular time period. Criteria will change as new information becomes available.

In linking effects to particular pollutants, i.e. air pollution cause–effect relationships, information must be derived from (1) extrapolation from animal experimentation, (2) clinical observation of individual cases of persons exposed to the pollutant or toxicant, and (3) most important, epidemiological data relating population morbidity and mortality to air pollution. There are no human diseases uniquely caused by air pollution. In all air pollution-related diseases in which there is buildup of toxic material in the blood, tissue, bone, or teeth, part or all of the buildup could be from ingestion



**FIGURE 26.19** Composite, nationwide diurnal variability in hourly averaged ozone concentrations (parts per million) in urban areas. Values shown are averages from April to October, 2000–2004. Boxes define the interquartile range and the whiskers, the minima, and maxima. U.S. Environmental Protection Agency. Air Quality Criteria for Particulate Matter. Report No. EPA/600/P-99/002aF; 2006; and Fitz-Simons T, McCluney L Rizzo M. Analysis of 2004 ozone data for the ozone NAAQS review [memorandum to Dr. Joseph Pinto]. NC: U.S. Environmental Protection Agency, Research Triangle Park; August 22, 2005.

of food or water containing the material. Respiratory diseases can be caused by smoking or occupational exposure. They may be of a bacterial, viral, or fungal origin quite divorced from the inhalation of human-made pollutants in the ambient air. These causes in addition to the variety of congenital, degenerative, nutritional, and psychosomatic causes of disease must all be ruled out before a disease can be attributed to air pollution. However, air pollution commonly exacerbates preexisting disease states. In human health, air pollution can be the “straw that breaks the camel’s back”.

Air quality standards prescribe pollutant levels that cannot legally be exceeded during a specific time period in a specific geographic area. Air quality standards are based on air quality criteria, with added safety factors as desired. Periodically, the US government reviews the scientific basis for the standards for each criteria pollutant by preparing an Air Quality Criteria Document (AQCD).<sup>35a,35b</sup>

The Clean Air Act requires an update and revision of the AQCD for PM every 5 years. The most recent started in 1998, following July 1997 promulgation of a new PM NAAQS. The PM AQCD is the scientific basis for the additional technical and policy assessments that form the basis for EPA decisions on the adequacy of the current PM NAAQS and the appropriateness of new or revised

standards for PM. The original NAAQS for PM, issued in 1971 as TSP standards, were revised in 1987 to focus on protecting against human health effects associated with exposure to ambient particles with aerodynamic diameters less than or equal to 10 microns ( $<10 \mu\text{m}$ ). These are able to deposit in the thoracic (tracheobronchial and alveolar) portions of the lower respiratory tract. The  $\text{PM}_{10}$  NAAQS set in 1987 ( $150 \mu\text{g m}^{-3}$ , 24 h;  $50 \mu\text{g m}^{-3}$ , annual average) were retained in modified form and new standards ( $65 \mu\text{g m}^{-3}$ , 24 h;  $15 \mu\text{g m}^{-3}$ , annual average) for particles  $<2.5 \mu\text{m}$  ( $\text{PM}_{2.5}$ ) were promulgated in July 1997.

The current criteria document has pointed out a number of areas of uncertainty that need to be addressed. These are provided in Table 26.21. Although much has been learned about the hazards, exposure, effects, and risks of particulates, much still needs to be known. The main focus of the PM document is the evaluation and interpretation of pertinent atmospheric science information, air quality data, human exposure information, and health and welfare effects information published since what was assessed during the development of the 1996 PM AQCD. A number of draft versions of AQCD chapters have been evaluated via expert peer-review workshop discussions and peer reviews.

The document is a rich resource for information about PM and air pollution in general. It is divided into two

TABLE 26.14 Information Used for United States Air Quality Criteria for Carbon Monoxide

Individuals	Consumer and Health Professionals	Manufacturers	Building Owners and Managers	Builders and Architects	State and Local Governments	Federal Government
Find low-emission products in purchasing decisions	Be knowledgeable of symptoms, effects, and mitigation and advise clients	Adopt test procedures and standards to minimize product and material emissions	Adopt ventilation maintenance procedures to eliminate and prevent contamination and ensure and adequate supply of clean air to building occupants	Adopt indoor air quality as a design objective	Conduct studies of specific problems in state or local area and adopt mitigation strategies	Conduct research and technology transfer programs
Maintain and use products to minimize emissions	Develop information and education programs for constituent publics	Adequately label products as to emission level and proper use and maintenance of products	Use zone ventilation or local exhaust for indoor sources	Ensure compliance with indoor air quality ventilation standards	Establish building codes for design, construction, and ventilation requirements to ensure adequate indoor air quality	Coordinate actions of other sectors
Exercise discretionary control over ventilation to ensure clean air supply	Substitute materials to minimize emissions from products manufactured	Develop specific procedures for use of cleaning solvents, paints, herbicides, insecticides, and other contaminants to protect occupants	Adopt low emission requirements in procurement specifications for building materials from manufacturers	Enforce and monitor code compliance	Coordinate actions of other sectors, encourage, or require specific sectors to take actions toward mitigation	
Be knowledgeable of indoor air quality problems and take actions to avoid personal exposure	Develop training programs for commercial users to ensure low emissions  Conduct research to advance mitigation technology	Adopt investigatory protocols to respond to occupant complaints	Contain or ventilate known sources	Educate and inform building community, health community, and public about problems and solutions		

Source: US Environmental Protection Agency Report to Congress on Indoor Air Quality, EPA/400/1-89/001c; August 1989.

TABLE 26.15 Summary of Lowest Observed Effect Concentrations for Key Lead (Pb)-Induced Health Effects in Adults

Lowest Observed Effect Level (PbB)* ( $\mu\text{g dL}^{-1}$ )	Heme Synthesis and Hematological Effects	Neurological Effects	Effects on the Kidney	Reproductive Function Effects	Cardiovascular Effects
100–120		Encephalopathic signs and symptoms	Chronic nephropathy		
80	Frank anemia				
60				Female reproductive effects	
50	Reduced hemoglobin production	Overt subencephalopathic neurological symptoms		Altered testicular	
40	Increased urinary ALA and elevated coproporphyrins	Peripheral nerve dysfunction (slowed nerve conduction)			Elevated blood pressure (white males, aged 40–59 years)
30					
25–30	Erythrocyte protoporphyrin (EP) elevation in males				
15–20	EP elevation in females				
<10	ALA-d <sup>§</sup> inhibition				?s

The diagram illustrates the relationship between PbB levels and health effects. It shows a vertical column of PbB levels on the left, corresponding to specific health effects listed in the table. Arrows point downwards from each row, indicating that as PbB levels decrease, the range of health effects narrows and shifts from more general symptoms at higher levels to more specific, localized effects at lower levels.

\* PbB = blood lead concentrations. dL = deciliter = 0.1 L (a commonly used unit in medical literature).

§ALA, ALA-D: aminolevulinic acid dehydrase.

Source: US Environmental Protection Agency. Air quality criteria for lead, EPA-600-8-83/028aF; June 1986.

TABLE 26.16 Summary of Lowest Observed Effect Levels for Key Lead-Induced Health Effects in Children

Lowest Observed Effect Level (PbB)* ( $\mu\text{g dL}^{-1}$ )	Heme Synthesis and Hematological Effects	Neurological Effects	Renal System Effects	Gastrointestinal Effects
80–100		Encephalopathic signs and symptoms	Chronic nephropathy (aminoaciduria, etc.)	Colic, other overt gastrointestinal symptoms
70	Frank anemia			
60		Peripheral neuropathies		
50			?	
40	Reduced hemoglobin synthesis	Peripheral nerve dysfunction (slowed NCVs) <sup>  </sup>		
	Elevated coproporphyrin	CNS cognitive effects (IQ deficits, etc.)		
	Increased urinary ALA <sup>¶</sup>			
30		?	Vitamin D metabolism interference	
15	Erythrocyte protoporphyrin elevation	Altered CNS electrophysiological response		
10	ALA-D <sup>¶</sup> inhibition		?	
	Py-5-N activity inhibition <sup>§</sup>			
		?		
		?		

\* PbB: blood lead concentrations.

<sup>¶</sup>Py-5-N: pyrimidine-5*'*-nucleotidase.

<sup>¶</sup>ALA, ALA-D: aminolevulinic acid dehydrase.

<sup>||</sup>NCV: nerve conduction velocity.

CNS = central nervous system; IQ = intelligence quotient.

Source: US Environmental Protection Agency. Air quality criteria for lead, EPA-600, EPA-600-8-83/028 aF; June 1986.

TABLE 26.17 Information Used for United States Air Quality Criteria for Sulfur Dioxide

Point of Impact	Agency/Activity	Comments
Direct control of indoor concentrations and/or exposures	OSHA air standards BPA radon action level  NASA air standards	Limited to industrial environments  Limited to residents in BRA's weatherization program  Adopted OSHA standards
Control of emissions by restricting activities or product composition	EPA drinking water MCLs for radon and VOCs  EPA pesticide restrictions  CPSC consumer product bans  Smoking restrictions imposed by DOD, DOT, and GSA  VA restrictions on asbestos use	Indoor air exposures considered in determining drinking water levels  Restricts use and sales of pesticides that may cause indoor air pollution  Bans on use of some potential indoor pollutants in consumer products  Restricts smoking in specified indoor environments
Control through assessment and mitigation procedures	EPA asbestos rules  GSA building assessments  NIOSH building assessments  DOD/USAF chlordane assessments  NASA HVAC system maintenance	Provides for the assessment and mitigation of asbestos hazards in schools  Investigates GSA-controlled buildings for indoor air problems  Responds to air quality health complaints  Investigates USAF facilities for chlordane problems  Assesses and corrects HVAC operation to optimize indoor air quality
Effort to increase knowledge of indoor air quality problems and controls	Research efforts by EPA, CPSC, DOE, HHS, BPA, DOT, NASA, NIST, NSF, TVA, HUD, and GSA  Information dissemination by EPA, CPSC, DOE, HHS, BPA, HUD, TVA, FTC, NASA, NIST, and NIBS	

OSHA, Occupational Safety and Health Administration; BPA, Bonneville Power Administration; NASA, National Aeronautics and Space Administration; MCL, maximum contaminant levels; VOC, volatile organic compounds; CPSC, Consumer Products Safety Commission; DOD, Department of Defense; DOT, Department of Transportation; CSA, General Services Administration; VA, Veterans Administration; NIOSH, National Institute of Occupational Safety and Health; USAF, United States Air Force; HVAC, heating ventilation and air conditioning; DOE, Department of Energy; HHS, Health and Human Services; NIST, National Institute of Standards and Technology; NSF, National Science Foundation; TVA, Tennessee Valley Authority; HUD, Housing and Urban Development; FTC, Federal Trade Commission; NIBS, National Institute of Building Sciences.

Source: US Environmental Protection Agency Report to Congress on Indoor Air Quality, EPA/400/1-89/001c; August 1989.

volumes: Volume I (Chapters 1 through 5, EPA/600/P-99/002aD) and Volume II (Chapters 6 through 9, EPA/600/P-99/002bD). After the brief general introduction in Chapter 1, Chapters 3 and 4 provide background information on physical and chemical properties of PM and related compounds; sources and emissions; atmospheric transport; transformation and fate of PM; methods for the collection and measurement of PM; and ambient air concentrations; Chapter 5 describes PM environmental effects on vegetation and ecosystems, impacts on man-made materials and visibility, and relationships to global climate change processes; and Chapter 6 contains factors affecting exposure of the general population. Chapters 6 through 8 evaluate

information concerning the health effects of PM. Chapter 7 discusses dosimetry of inhaled particles in the respiratory tract; and Chapter 8 assesses information on the toxicology of specific types of PM constituents, including laboratory animal studies and controlled human exposure studies. Chapter 8 discusses epidemiologic studies. Chapter 10 integrates key information on exposure, dosimetry, and critical health risk issues derived from studies reviewed in other criteria document chapters.

As mentioned, tropospheric or "ground-level" ozone ( $O_3$ ) is also the subject of a high profile AQCD. Following the review of criteria as contained in the EPA document, *Air Quality Criteria for Ozone and Other*

TABLE 26.18 Information Used for United States Air Quality Criteria for Nitrogen Dioxide

Concentration of Nitrogen Dioxide in Air (ppm)	Exposure Time	Human Symptoms and Effects on Vegetation, Materials, and Visibility
300	—	Rapid death
150	—	Death after 2 or 3 weeks by bronchiolitis fibrosa obliterans
50	—	Reversible, nonfatal bronchiolitis
10	—	Impairment of ability to detect odor of nitrogen dioxide
5	15 min	Impairment of normal transport of gases between the blood and lungs in healthy adults
2.5	2 h	Increased airway resistance in healthy adults
2	4 h	Foliar injury to vegetation
1.0	15 min	Increased airway resistance in bronchitics
1.0	48 h	Slight leaf spotting of pinto bean, endive, and cotton
0.3	—	Brownish color of target 1 km distant
0.25	Growing season	Decrease of growth and yield of tomatoes and oranges
0.2	8 h	Yellowing of white fabrics
0.12	—	Odor perception threshold of nitrogen dioxide
0.1	12 weeks	Fading of dyes on nylon
0.1	20 weeks	Reduction in growth of Kentucky bluegrass
0.05	12 weeks	Fading of dyes on cotton and rayon
0.03	—	Brownish color of target 10 km distant
0.003	—	Brownish color of target 100 km distant

Source: US Environmental Protection Agency. Draft Air Quality Criteria for Oxides of Nitrogen. NC: Research Triangle Park; 1981; and Review of the National Ambient Air Quality Standard for Nitrogen Dioxide, Assessment of Scientific and Technical Information, EPA-450/5-82-002. NC: US Environmental Protection Agency, Research Triangle Park; March 1982.

TABLE 26.19 Information Used for United States Air Quality Criteria for Ozone

Concentration of Ozone in Air (ppm)*	Human Symptoms and Vegetation Injury Threshold
10.0	Severe pulmonary edema; possible acute bronchiolitis; decreased blood pressure; rapid weak pulse
1.0	Coughing; extreme fatigue; lack of coordination; increased airway resistance; decreased forced expiratory volume
0.5	Chest constriction; impaired carbon monoxide diffusion capacity; decrease in lung function without exercise
0.3	Headache; chest discomfort sufficient to prevent completion of exercise; decrease in lung function in exercising subjects
0.25	Increase in incidence and severity of asthma attacks; moderate eye irritation
0.15	For sensitive individuals, reduction in pulmonary lung function; chest discomfort; irritation of the respiratory tract, coughing, and wheezing
	Threshold for injury to vegetation
0.12	United States national primary and secondary ambient air quality standard, attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is equal to or less than 1, as determined in a specified manner

\* 1 ppm: 2140  $\mu\text{g m}^{-3}$  ozone.

40 CFR § 50, July 1992.

Source: Air Quality Criteria for Ozone and Other Photochemical Oxidants, EPA 600/8-78-004. NC: US Environmental Protection Agency, Research Triangle Park; April 1978 and Revisions to National Ambient Air Quality Standards for Photochemical Oxidants. Fed. Reg. Part V; February 9, 1979. p. 8202–8237.

TABLE 26.20 Information Used for United States Air Quality Criteria for Particulate Matter (PM)

Concentration of PM in Air ( $\mu\text{g m}^{-3}$ )					Human Symptoms and Effects on Visibility
Total Suspended Particulate (TSP); diameters $>25 \mu\text{m}$	Thoracic Particulate (TP); diameters $<10 \mu\text{m}$	Fine Particulate (FP), diameters $\leq 2.5 \mu\text{m}$	Exposure Time		
2000	—	—	2 h	Personal discomfort	
1000	—	—	10 min	Direct respiratory mechanical changes	
—	350	—		Aggravation of bronchitis	
	150	—	24 h	United States primary national ambient air quality standard as of September, 1987	
180	90	—		Increased respiratory disease symptoms	
	150	—	24 h	United States primary national ambient air quality standard as of September, 1987	
110	55	—	24 h	Increased respiratory disease risk	
	50	—	Annual geometric mean	United States primary national air quality standard as of September, 1987	
—	—	22	13 weeks	Usual summer visibility in eastern United States, nonurban sites	

40 CFR § 50, July 1992.

Source: *Air Quality Criteria for Particulate Matter and Sulfur Oxides, Draft Final*. NC: US Environmental Protection Agency, Research Triangle Park; December 1981 and *Review of the National Ambient Air Quality Standard for Particulate Matter: Assessment of Scientific and Technical Information*, EPA-450/5-82-001. NC: US Environmental Protection Agency, Research Triangle Park; January 1982.

*Photochemical Oxidants* published in 1978, the chemical designation of the standards was changed from photochemical oxidants to ozone ( $\text{O}_3$ ) in 1979 and a 1-h  $\text{O}_3$  NAAQS was set. The 1978 document focused mainly on the air quality criteria for  $\text{O}_3$  and, to a lesser extent, on those for other photochemical oxidants (e.g. hydrogen peroxide and the peroxy acetyl nitrates), as have subsequently revised versions of the document.

As is true for PM, to meet Clean Air Act requirements noted above for periodic review of criteria and NAAQS, the  $\text{O}_3$  criteria document, *Air Quality Criteria for Ozone and Other Photochemical Oxidants*, was next revised and released in August 1986; and a supplement, *Summary of Selected New Information on Effects of Ozone on Health and Vegetation*, was issued in January 1992. These documents were the basis for a March 1993 decision by EPA that revision of the existing 1-h NAAQS for  $\text{O}_3$  was not appropriate at that time. That decision, however, did not take into account newer scientific data that had become available after completion of the 1986 criteria document. Such literature was assessed in the next periodic revision of the  $\text{O}_3$  AQCD, which was completed in 1996 and provided scientific bases supporting the setting by EPA in 1997 of the current 8-h  $\text{O}_3$  NAAQS. The purpose of this revised AQCD for  $\text{O}_3$  and related photochemical oxidants is to evaluate and assess the latest scientific information published since that assessed in the 1996  $\text{O}_3$  AQCD, with the main focus being on pertinent new information useful in evaluating health and

environmental effects data associated with ambient air  $\text{O}_3$  exposures. However, other scientific data are also discussed in order to provide a better understanding of the nature, sources, distribution, measurement, and concentrations of  $\text{O}_3$  and related photochemical oxidants and their precursors in the environment.

Like the PM document, the ozone AQCD contains a wealth of information. The Executive Summary describes the key findings and conclusions as they pertain to background information on  $\text{O}_3$ -related atmospheric science and air quality, human exposure aspects, dosimetric considerations, health effect issues, and environmental effect issues. Chapter 1 provides a general introduction, including an overview of legal requirements, the chronology of past revisions of  $\text{O}_3$ -related NAAQS, and orientation to the structure of this document. Chapters 3 and 4 provide background information on atmospheric chemistry/physics of  $\text{O}_3$  formation, air quality, and exposure aspects to help to place ensuing discussions of  $\text{O}_3$  health and welfare effects into perspective. Chapters 5 through 8 then assess dosimetry aspects, experimental (controlled human exposure and laboratory animal) studies, and epidemiologic (field/panel; other observational) studies. Chapter 9 then provides an integrative synthesis of key findings and conclusions derived from the preceding chapters with regard to ambient  $\text{O}_3$  concentrations, human exposures, dosimetry, and health effects. Chapter 9 deals with effects of  $\text{O}_3$  on vegetation, crops, and natural ecosystems,

**TABLE 26.21** Key Areas of Uncertainty That Need to Be Addressed for Particulate Matter as an Air Pollutant

<b>Research Topic 1.</b>	<b>Outdoor Measures vs Actual Human Exposures</b>
<ul style="list-style-type: none"> <li>• What are the quantitative relationships between concentrations of particulate matter and gaseous copollutants measured at stationary outdoor air monitoring sites and the contributions of these concentrations to actual personal exposures, especially for subpopulations and individuals?</li> </ul>	
<b>Research Topic 2.</b>	<b>Exposures of Susceptible Subpopulations to Toxic Particulate Matter Components</b>
<ul style="list-style-type: none"> <li>• What are the biologically important constituents and specific characteristics of particulate matter whose exposure causes responses in potentially susceptible subpopulations and the general population?</li> </ul>	
<b>Research Topic 3.</b>	<b>Characterization of Emission Sources</b>
<ul style="list-style-type: none"> <li>• What are the size distributions, chemical composition, and mass-emission rates of particulate matter emitted from the collection of primary-particle sources in the United States, and what are the emissions of reactive gases that lead to secondary particle formation through atmospheric chemical reactions?</li> </ul>	
<b>Research Topic 4.</b>	<b>Air-Quality Model Development and Testing</b>
<ul style="list-style-type: none"> <li>• What are the linkages between emission sources and ambient concentrations of the biologically important components of particulate matter?</li> </ul>	
<b>Research Topic 5.</b>	<b>Assessment of Hazardous Particulate Matter Components</b>
<ul style="list-style-type: none"> <li>• What is the role of physicochemical characteristics of particulate matter in eliciting adverse health effects?</li> </ul>	
<b>Research Topic 6.</b>	<b>Dosimetry: Deposition and Fate of Particles in the Respiratory Tract</b>
<ul style="list-style-type: none"> <li>• What are the deposition patterns and fate of particles in the respiratory tract of individuals belonging to presumed susceptible subpopulations?</li> </ul>	
<b>Research Topic 7.</b>	<b>Combined Effects of Particulate Matter and Gaseous Pollutants</b>
<ul style="list-style-type: none"> <li>• How can the effects of particulate matter be disentangled from the effects of other pollutants? How can the effects of long-term exposure to particulate matter and other pollutants be better understood?</li> </ul>	
<b>Research Topic 8.</b>	<b>Susceptible Subpopulations</b>
<ul style="list-style-type: none"> <li>• What subpopulations are at increased risk of adverse health outcomes from particulate matter?</li> </ul>	
<b>Research Topic 9.</b>	<b>Mechanisms of Injury</b>
<ul style="list-style-type: none"> <li>• What are the underlying mechanisms (local pulmonary and systemic) that can explain the epidemiologic findings of mortality/morbidity associated with exposure to ambient particulate matter?</li> </ul>	
<b>Research Topic 10.</b>	<b>Analysis and Measurement</b>
<ul style="list-style-type: none"> <li>• To what extent does the choice of statistical methods in the analysis of data from epidemiologic studies influence estimates of health risks from exposures to particulate matter? Can existing methods be improved? What is the effect of measurement error and misclassification on estimates of the association between air pollution and health?</li> </ul>	

Source: National Research Council. Research Priorities for Airborne Particulate Matter. III. Early Research Progress. Washington (DC): National Academy Press; 2001.

whereas Chapter 10 evaluates tropospheric O<sub>3</sub> relationships to alterations in surface-level UVB<sup>b</sup> flux and climate change and Chapter 12 assesses materials damage (these all being key types of welfare effects of relevance to decisions regarding secondary O<sub>3</sub> NAAQS review).

Ozone illustrates the complexity of applying measurement data to assess air pollution. It is a secondary pollutant formed by atmospheric reactions involving

two classes of precursor compounds, i.e. VOCs and nitrogen oxides (NO<sub>x</sub>). Carbon monoxide also contributes to O<sub>3</sub> formation. The formation of O<sub>3</sub> and associated compounds is a complex, nonlinear function of the intensity and spectral distribution of sunlight; atmospheric mixing and numerous atmospheric reactions of varying concentrations of precursors in ambient air. The photochemical oxidation of most anthropogenically and naturally generated VOCs is initiated by reaction

<sup>b</sup> Electromagnetic radiation in the ultraviolet (UV) spectrum has wavelengths between 400 and 100 nanometers (nm), with energy between 3.1 and 12.4 electronvolts (eV) per photon. The UV radiation is divided into three compartments: UVA (400–315nm and 3.10–3.94 eV); UVB (315–280nm and 3.94–4.43 eV) and UVC (280–100nm and 4.43–12.4 eV). The UVA is not absorbed by the stratospheric ozone layer, but the medium wavelength UVB mostly is, and the short wavelength UVB is completely absorbed by the ozone layer and troposphere. Exposure to UVB causes sunburn and skin cancer. All three wavelengths, however, are considered to present carcinogenic risk. The World Health Organization has designated all UV to be a Group 1 carcinogen, i.e. "enough evidence to conclude that it can cause cancer" (<http://www.who.int/uv/health/en/>; accessed on May 14, 2014).

with hydroxyl (OH) radicals. At night, when they are most abundant, NO<sub>3</sub> radicals oxidize alkenes. In coastal and other select environments, Cl and Br radicals can also initiate the oxidation of VOCs. Virtually all classes of VOCs (e.g. alkanes, alkenes, aromatic hydrocarbons, and carbonyl compounds) and CO are in sufficient quantities in many urban areas to form ground-level ozone. Although knowledge of the oxidative mechanisms of VOCs has improved, there remain substantial gaps in scientific understanding of the role of many chemical classes, e.g. aromatic hydrocarbons. As evidence, only about half of the C that is initially present in aromatic hydrocarbons in smog chamber studies is speciated. Also, many heterogeneous reactions are involved. Gas phase reactions are joined by reactions on the aerosol surfaces or within cloud droplets. Most of the well-established multiphase reactions appear to decrease the rate of O<sub>3</sub> formation in polluted environments. With typical PM concentrations in ambient air, direct reactions of O<sub>3</sub> and atmospheric particles appear to be too slow to decrease O<sub>3</sub> formation. Oxidants other than O<sub>3</sub> are found in the gas phase and in particles. Much still needs to be learned about the chemistry occurring in particle bound-water and the mechanisms leading to the formation of reactive oxygen species in particles.<sup>36</sup>

Although air quality standards are based predominantly on biological criteria, e.g. to protect human health and ecosystem condition, certain physical criteria also deserve consideration. Most materials will deteriorate even when exposed to an unpolluted atmosphere. Iron will rust, metals will corrode, and wood will rot. To prevent deterioration, protective coatings are applied. Materials-related costs are part of the economic aspects of air pollution rule-making. Some materials, such as railroad rails, are used without protective coatings. There are costs associated with the decrease in their life in a polluted atmosphere as compared to an unpolluted one. One may argue that for materials on which protective coatings are used, only pollution levels that damage such coatings are of concern. One may further argue that some air pollution damage to protection coatings is tolerable, since by their very nature such coatings require periodic replenishment to maintain their protective integrity or appearance; therefore, only coatings that require more frequent replenishment than they would in an unpolluted atmosphere should enter into the establishment of deterioration costs and air quality standards. This argument certainly does hold with respect to the soiling of materials and structures. In fact, it is frequently the protective coatings themselves that require replacement because they become dirty long before their useful life as protectants has terminated. It can readily be shown that there are costs associated with soiling, including the cost of removing soil, the

cost of protective coatings to facilitate the removal of soil, the premature disposal of material when it is no longer economical or practicable to remove soil, and the growth inhibition of vegetation due to leaf soiling. However, decision making for air quality standards related to soiling is based less on economic evaluation than on esthetic considerations, i.e. on subjective evaluation of how much soiling the community will tolerate. This latter determination is judgmental and difficult to make. It may be facilitated by opinion surveys, but even when the limit of public tolerance for soiling is determined, it still has to be restated in terms of the pollution loading of the air that will result in this level of soiling.

An important effect from air pollution is change in spectral transmission within the atmosphere. The UV and visible spectral regions are of greatest concern. Changes in UV radiation have demonstrable adverse effects, e.g. a decrease in the stratospheric ozone layer permits harmful UV radiation to penetrate to the surface of the earth. Excessive exposure to UV radiation results in increases in skin cancer and cataracts. The worldwide effort to reduce the release of stratospheric ozone-depleting chemicals such as chlorofluorocarbons is directed toward reducing this increased risk of skin cancer and cataracts for future generations.

The fact that after a storm or the passage of a frontal system the air becomes crystal clear and one can see for many kilometers does not give a true measure of year-round visibility under unpolluted conditions. Between storms, even in unpolluted air, chemical compounds released from natural sources build up enough PM in the air so that on many days of the year there is less than ideal visibility. Throughout the world, mountains are called "Smoky" or "Blue" or some other name to designate the prevalence of a natural haze, which gives them a smoky or bluish color and impedes visibility. When the Spanish first explored the area that is now Los Angeles, California, they gave it the name "Bay of the Smokes". The Los Angeles definition of air quality before the advent of smog was that "You could see Catalina Island on a clear day". The part of the definition that is lacking is some indication of how many clear days there were before the advent of smog.

There are costs associated with loss of visibility and solar energy. These include increased need for artificial illumination and heating; delays, disruptions, and accidents involving air, water, and land traffic; vegetation growth reduction associated with reduced photosynthesis; and commercial losses associated with the decreased attractiveness of a dingy community or one with restricted scenic views. However, these costs are less likely to be involved in deciding, for air quality standard-setting purposes, how much of the attainable visibility improvement to aim for than are esthetic

considerations. Just as in the previously noted case of soiling, judgment on the limit of public tolerance for visibility reduction still has to be related to the pollutant loading of the atmosphere that will yield the desired visibility. Obviously, the pollutant level chosen for an air quality standard must be lower than the values required for soiling or visibility, otherwise one will be achieved without the other. Whether the level chosen will not be lower than the atmospheric pollutant level required for prevention of health effects will depend on the esthetic standards of the jurisdiction.

### 26.9.1 Conversion of Biological Data and Criteria to Standards

There is considerable variability among species with respect to damage to vegetation by any specific pollutant. In addition, the substantial geographic variability with respect to where these species grow naturally or are cultivated may mean that none of the species particularly susceptible to damage by low levels of pollution may be present during a pollution episode. As an example, the pollution level at which citrus trees are adversely affected, while meaningful in setting air quality standards in California and Florida, is meaningless for this purpose in Minnesota and Wisconsin. In like manner, a jurisdiction may take different viewpoints with respect to indigenous and imported species. Regulators might set air quality standards low enough to protect its indigenous vegetation even if this level is too high to allow satisfactory growth of imported species. Even if a particularly susceptible species is indigenous, it may be held in such low local esteem commercially or aesthetically that the jurisdiction may be unwilling to let the damage level of that species be the air quality standard discriminator. In other words, the people would rather have that species damaged than assume the cost of cleaning up the air to prevent the damage. This same line of reasoning applies to effects on wild and domestic animals.

A jurisdiction may base part of its decision making regarding vegetation and animal damage on aesthetics. Its citizens may wish to grow certain ornamentals or raise certain species of pet birds or animals and allow these wishes to override the agricultural, forestry, and husbandry economics of the situation. Usually, however, economic considerations predominate in decision making. Costs of air pollution effects on agriculture are the sum of the loss in income from the sale of crops or livestock and the added cost necessary to raise the crops or livestock for sale. To these costs must be added the loss in value of agricultural land as its income potential decreases and the loss suffered by the segments of local industry and commerce that are dependent on farm crops and the farmer for their existence. An interesting

sidelight is that when such damage occurs on the periphery of an urban area, it is frequently a precursor to the breakup of such farmland into residential development, with a financial gain rather than a loss to the landowner. When the crop that disappears is an orchard, grove, or vineyard that took years to establish, and when usable farm buildings are torn down, society as a whole suffers a loss to the extent that it will take much time and money to establish a replacement for them at new locations. To some industries, air pollution costs include purchase of farm and ranch land to prevent litigation to recover damages, annual subsidy payments to farmers and ranchers in lieu of such litigation, and maintenance of air quality monitoring systems to protect themselves against unwarranted litigation for this purpose.

There is a range of ambiguity in our human health effects criteria data. In this range there is disagreement among experts as to its validity and interpretation. Thus, from the same body of health effects data, one could adopt an air quality standard on the high side of the range of ambiguity or one on the low side. Much soul searching is required before one accepts the results of questionable human health effects research and is accused of imposing large costs on the public by so doing, or of rejecting these results and being accused of subjecting the public to potential damage of human health.

### 26.9.2 Air Quality Standards

Since air pollution is controlled by air quality and emission standards, the principal philosophical discussions in the field of air pollution control focus on their development and application.

The US Clean Air Amendments of 1977 defined two kinds of air quality standards: primary standards, levels that will protect health but not necessarily prevent the other adverse effects of air pollution, and secondary standards, levels that will prevent all the other adverse effects of air pollution (Table 24.8). The amendments also define air quality levels that cannot be exceeded in specified geographic areas for "prevention of significant deterioration" (PSD) of the air of those areas. Although they are called "increments" over "baseline air quality" in the law, they are in effect tertiary standards, which are set at lower ambient levels than either the primary or secondary standards (Table 26.22). The PSD program applies to any "major emitting facility" in attainment areas. For 28 named categories, a major emitting facility is one with a "potential to emit" 100 tons or more per year of any regulated air pollutant. However, any source is regulated under PSD if it has a potential to emit 250 or more tons per year. Emission potential assumes maximum design capacity (42 USC § 7479).

**TABLE 26.22** Prevention of Significant Deterioration (PSD) Increments in the United States

<b>US Federal Prevention of Significant Deterioration (PSD) Increments</b>	
<b>CLASS I PSD INCREMENTS*</b>	
Sulfur dioxide	Increment ( $\mu\text{g m}^{-3}$ )
Annual arithmetic mean	2
24-h Maximum	5
3-h Maximum	25
Nitrogen dioxide	Increment ( $\mu\text{g m}^{-3}$ )
Annual arithmetic mean	25
Particulate matter ( $\text{PM}_{10}$ )	Increment ( $\mu\text{g m}^{-3}$ )
Annual arithmetic mean	4
24-h Maximum	8
<b>CLASS II PSD INCREMENTS<sup>§</sup></b>	
Sulfur dioxide	Increment ( $\mu\text{g m}^{-3}$ )
Annual arithmetic mean	20
24-h Maximum	91
3-h Maximum	512
Nitrogen dioxide	Increment ( $\mu\text{g m}^{-3}$ )
Annual arithmetic mean	25
Particulate matter ( $\text{PM}_{10}$ )	Increment ( $\mu\text{g m}^{-3}$ )
Annual arithmetic mean	17
24-h Maximum	30
<b>CLASS III PSD INCREMENTS<sup>¶</sup></b>	
Sulfur dioxide	Increment ( $\mu\text{g m}^{-3}$ )
Annual arithmetic mean	40
24-h Maximum	182
3-h Maximum	700
Nitrogen dioxide	Increment ( $\mu\text{g m}^{-3}$ )
Annual arithmetic mean	50
Particulate matter ( $\text{PM}_{10}$ )	Increment ( $\mu\text{g m}^{-3}$ )
Annual arithmetic mean	34
24-h Maximum	60

\* Class I areas are pristine, such as national parks, national seashores, and natural wilderness areas.

§ Class II areas allow moderate deteriorations (unless otherwise designated, all areas are considered class II).

¶ Class III are specifically designated for heavy industrial uses.

40 CFR § 51.166 (c).

Increments are said to be “consumed” as new sources are given permits that allow pollution to be introduced into these areas. Jurisdictions with authority to issue permits may choose to “allocate” portions of a PSD increment (or the difference between actual air quality

and the primary or secondary standard) for future consumption, rather than to allow its consumption on a first-come, first-served basis.

The states are required to submit to the federal EPA plans, known as State Implementation Plans (SIP), showing how they will achieve the standards in their jurisdictions within a specified time period. If after that time period there are areas within the states where these standards have not been attained, the states are required to submit and obtain EPA approval of revised plans to achieve the standards in these “nonattainment” areas. EPA also designates certain areas where the standards are being met, but which have the potential for future nonattainment, as Air Quality Maintenance Areas. Such regions have stricter requirements than attainment areas for the granting of permits for new sources of the pollutant not in attainment status.

The Canadian Clean Air Act allows the provincial minister to formulate air quality objectives reflecting three ranges of ambient air quality for any contaminant. The *tolerable* range denotes a concentration that requires abatement without delay. The *acceptable* range provides adequate protection against adverse effects. The *desirable* range defines a long-term goal for air quality and provides the basis for a nondegradation policy for unpolluted parts of the country (Table 26.23). The Canadian ambient  $\text{PM}_{2.5}$  and ozone standards are shown in Table 26.24. As in the United States, these Canada-wide standards (CWSs) for PM are aimed at protecting human health, i.e. mainly  $\text{PM}_{2.5}$  fraction, but are expected to incorporate advancements in scientific, technical, and economic information and analysis. The Canadian standard focuses on the sources of PM and PM precursor emissions that provide the greatest health benefit, but acknowledges that health effects are also associated with the coarse fraction of PM with diameters between 10 and 2.5  $\mu\text{m}$ . Thus, actions to reduce the concentrations of these coarser fractions in the atmosphere are also needed. In addition, some Canadian jurisdictions currently have ambient air quality objectives, guidelines, or standards related to the coarser fraction of PM, and should continue to use them to design air quality management programs for  $\text{PM}_{10}$ . CWSs related to the coarser fraction may be a useful addition at a later date.

There are other aspects that should be considered in any future update of these PM and ozone CWSs. Species of the PM and  $\text{O}_3$  standards other than the relatively short-term exposure species established under these standards, e.g. seasonal or annual average targets, may be added in the future. In addition, secondary-type standards to protect vegetation, visibility, materials, or other adverse effects may need to be assessed, since the CWSs presently relate primarily to protection of human health.

TABLE 26.23 National Ambient Air Quality Standards for Canada

Pollutant	Averaging time			Published	Reviewed
	1 h	24 h	Annual		
Carbon monoxide ( $\text{mg m}^{-3}$ )	D	15	6 (8 h)	1974	1996
	A	35	15 (8 h)		1996
	T		20 (8 h)		1996
Hydrogen fluoride ( $\mu\text{g m}^{-3}$ )	RL		1.1	0.5(7d)	1997
Nitrogen dioxide ( $\mu\text{g m}^{-3}$ )	D			60	1975
	A	400	200	100	1975
	T	1000	300		1989
Ozone ( $\mu\text{g m}^{-3}$ )	D	100	30	1974	1989
	A	160	50		1989
	T	300			1989
	RL			*	
PM, 10 ( $\mu\text{g m}^{-3}$ )	RL		25		1998
PM, 2.5 ( $\mu\text{g m}^{-3}$ )	RL		15		1998
Sulfur dioxide ( $\mu\text{g m}^{-3}$ )	D	450	150	30	1974
	A	900	300	60	1974
	T		800		1989
Total reduced sulfur compounds	RL			*	
	AQO			*	
Total suspended particulates ( $\mu\text{g m}^{-3}$ )	D			60	1974
	A		120	70	1974
	T		400		1978

\*Reviews in progress.

Notes: D, desirable; A, acceptable; T, tolerable; RL, reference level; AQO, air quality objective.

Source: Canadian Council of Ministers of the Environment. Canadian national ambient air quality objectives: process and status. In: Canadian environmental quality guidelines. Winnipeg (Canada): Canadian Council of Ministers of the Environment; 1999.

TABLE 26.24 Canada-Wide Standards Have Been Established for Ozone and PM to Minimize the Risk to Human Health and the Environment

Ozone	65 ppb ( $130 \mu\text{g m}^{-3}$ ) averaged over an 8-h period. Achievement will be based on the 4th highest measurement annually as averaged over 3 consecutive years.
PM <sub>2.5</sub>	30 $\mu\text{g m}^{-3}$ averaged over a 24-h period. Achievement will be based on the 98th percentile ambient measurement annually, averaged over 3 consecutive years.

Source: Canadian Council of Ministers of the Environment. Canada-wide standards for particulate matter (PM) and ozone. [http://www.ccme.ca/assets/pdf/pmozone\\_standard\\_e.pdf](http://www.ccme.ca/assets/pdf/pmozone_standard_e.pdf); 2000 [accessed 23.11.13].

Other countries have developed similar standards for the same air pollutants addressed by Canada and the United States. Some examples of air quality standards for other countries are given in Table 26.25.

## 26.10 INDOOR AIR

As mentioned, indoor air pollution can be very different from outdoor pollution for many pollutants. In much of the world, people spend more time indoors than out. However, other than occupational exposures, most national regulations address emissions and ambient concentrations, but not indoor levels.

A combination of events is moving many countries to consider the quality of air in other locations where we

TABLE 26.25 Air Quality Standards for Selected Pollutants in Several Countries and for International Organizations Around the World in 1999

Country	Suspended particulate matter (SPM), $\mu\text{g m}^{-3}$		Sulfur dioxide ( $\text{SO}_2$ ), $\mu\text{g m}^{-3}$		Oxides of Nitrogen ( $\text{NO}_x$ ), $\mu\text{g m}^{-3}$	
	24 h	1 year	24 h	1 year	24 h	1 year
<b>INDIA</b>						
Industrial	500	360	120	80	120	80
Residential	200	140	80	60	80	60
Sensitive	100	70	30	15	30	15
<b>CHINA</b>						
Class III	500		250		150	
Class II	300		150		100	
Class I	150		50		50	
Australia		90		60		
Japan	100		100		100	
USA	260		365	80		100
EU	300	150	250	80		200
WHO	150–230	60–90	100–150	40–60	150	

Source: Conservation of Clean Air and Water in Europe (CONCAWE). Potential for exhaust after treatment and engine technologies to meet future emissions limit, Report No. 99/55. Brussels (Belgium); 1999.

live parts of our lives. Attention is now being refocused on “indoor” air quality.

In developing countries, priorities have often differed from those of wealthier nations. Industrialization, water and food supply, sanitation, infrastructure improvements, and basic health care are often the focus of the leaders of a country. In some areas, the availability of a job is much more problematic than some consideration about the quality of the air in the workplace or the home. Many dwellings in developing countries do not have closable windows and doors, so the outdoor and indoor air quality issues are different. In some houses where cooking is done by firewood or charcoal, the air quality outdoors may be considerably better than that inside the smoky residence. The evolution of our modern society and the concomitant changes in lifestyle, workplace, and housing improvements place concerns about indoor air quality in a different category than for developing countries and from the times of our ancestors.

For many industrialized countries, efforts to improve the outdoor air quality have been under way for the majority of this century. In many locations around the world, significant improvements have taken place. Air quality in many major cities such as London, New York, and Chicago has improved from the conditions present in the first half of the twentieth century. Mechanisms and control programs are in place in the developed countries to continue the improvement of

ambient air quality. Considerable effort and energy have been expended to characterize, evaluate, and control air pollution emissions to the atmosphere.

Buildings and their design have undergone major changes. Fifty years ago, central heating and windows that could be opened and closed depending on the season were the norm for commercial buildings. Now we have multistory buildings with central heating and air conditioning and sealed glass exterior walls. Residential housing has undergone similar design and structural changes, in some cases resulting in dwellings that may have poorer indoor air quality.

New residences and commercial buildings are designed and built with energy conservation as a major design criterion. New materials have been developed and are being used in construction. Although these modifications have helped to save energy, a consequence of some of these modifications is slower exchange of air with the outside. This helps considerably with the heating or cooling system because energy must condition this “new” air, which is introduced into the structure. However, the decreased air exchange rates usually translate into dirtier air.

A second consideration is the change in lifestyle for individuals in industrialized societies. We are no longer a society dependent on occupations that require us to be outdoors for a significant part of our day. Over the past two decades, studies of daily activities have consistently shown for urban populations that, on average, we spend

about 90% of our time indoors in our homes, cars, offices, factories, public buildings such as restaurants, malls, and others. Any given individual activity profile may differ significantly from this average.

Exposure assessment techniques now attempt to include as many as possible of the locations in which individuals now spend time. The concept involves identification of microenvironments that are important for potential exposure. For example, exposure to CO would include time spent in commuting, parking garages, in residences with gas stoves, as well as time spent outdoors. This approach classifies time spent in these microenvironments and the typical concentrations of CO in these locations.

### 26.10.1 Factors Influencing Indoor Air Quality

Several factors influence the quality of air indoors: the rate of exchange of air with air from outdoors, the concentration of pollutants in outdoor air, the rate of emissions from sources indoors, the rate of infiltration from soil gases, and the rate of removal in the indoor environment (Figure 26.20).

The source of indoor air pollutants may be inside the building, or they may be transported into the interior space from the outside. Sources located indoors include building materials, combustion sources, furnishings, and pets. Emissions of organic gases are higher with increased temperature and humidity but usually decrease with age of the structure or furnishings. Construction materials and the composition of furnishings inside the building may give off or out-gas pollutants into the interior airspace, e.g. glues or adhesives. Natural gas for cooking and kerosene space heaters release NO and CO<sub>2</sub> even when operating properly. Molds may grow in the ventilation ducts and be distributed throughout a building.<sup>37</sup>

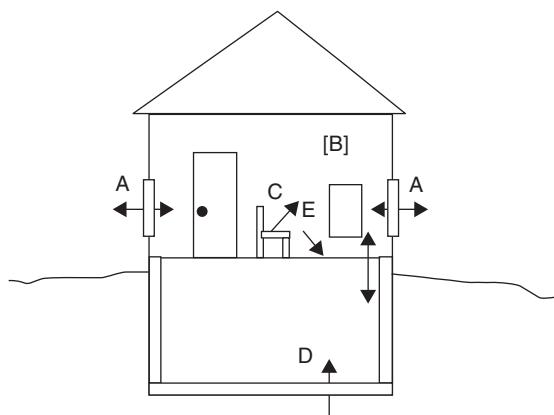


FIGURE 26.20 Representation of home with various sources and sinks for indoor air pollutants: A, exchange; B, indoor concentration; C, out-gassing of building and furniture materials; D, infiltration from soils; E, removal on interior surfaces.

Radon from the soil can enter buildings through cracks in the foundation when the pressure inside is lower than in the soil. The rate of infiltration depends on the soil type, the building structure, and the pressure differential between the soil and the building.

Air is exchanged between indoors and outdoors by several ways: natural ventilation, mechanical ventilation, and infiltration or exfiltration. Natural ventilation involves movement of air through building openings like doors, windows, and vents. Mechanical ventilation involves fans and heating and air-conditioning systems. Infiltration and exfiltration represents undesirable movement of air in and out of the structure. Buildings are characterized as “tight” when infiltration rates are low.

The air exchange rate influences the concentration of indoor pollutants in two ways. At higher air exchange rates, the pollutants inside a structure are removed from the interior. As long as the ambient outside air has lower pollutant concentrations, high exchange rates help lower indoor air pollutant levels. However, if the pollutant concentration outside is elevated, then an increase in the air exchange rate will bring these materials into the building; e.g. an idling vehicle adjacent to an air intake will transfer exhaust fumes into the building. At lower exchange rates, pollutants released from sources inside the building can contribute to higher levels of indoor pollutants.

The concentration of indoor pollutants is a function of removal processes such as dilution, filtration, and destruction. Dilution is a function of the air exchange rate and the ambient air quality. Gases and PM may also be removed from indoor air by deposition on surfaces. Filtration systems are part of many ventilation systems. As air is circulated by the air-conditioning system it passes through a filter that can remove some of the PM. The removal efficiency depends on particle properties; including size and surface characteristics, such as electrostatics. In addition, some reactive gases like NO<sub>2</sub> and SO<sub>2</sub> are readily adsorbed on interior surfaces of a building or home.

### 26.10.2 Indoor Air Pollutants

Table 26.26 shows the major categories of indoor air pollutants and sources. Table 26.27 shows a summary of reported indoor air pollutant concentrations compiled by the US EPA. Information in this table is not meant to be representative of typical indoor concentrations but only examples of measurements obtained by investigators and reported in the literature.

Airborne material affecting the quality of indoor air may be classified as gases or PM. Gases that may be potential problems are radon, CO, NO<sub>2</sub>, and hydrocarbons.

**TABLE 26.26** Commonly Measured Indoor Air Pollutants and Typical Sources

Pollutant	Source
Combustion gases—CO and NO	Combustion—furnace, cooking stove, space heater, etc.
VOCs	Out-gassing of building materials, coatings, wall and floor coverings, and furnishings
Formaldehyde and other aldehydes and carbonyls	Out-gassing of pressed wood and insulation foam
Pesticides	Household products
Particulate matter	Combustion
Biological agents—molds, spores, and dander	Contaminated ventilation systems, ceiling tile and wallboard, outdoor and indoor plant materials, and pets
Environmental tobacco smoke (ETS)	Smoking in building
Radon	Infiltration from soil beneath structure
Asbestos	Construction coatings, tile, and insulation

PM may come from tobacco smoke, mold spores, animal dander, plant spores, and others as shown in [Table 26.26](#). Other factors interact to influence our perception of indoor air quality, including humidity, temperature, lighting, and sound level.

### 26.10.3 Effects of Indoor Air Pollutants

Effects of indoor air pollutants on humans are essentially the same as those described in Chapter 7. However, there can be some additional pollutant exposures in the indoor environment that are not common in the ambient setting. From the list in [Table 26.26](#), radon exposure indoors presents a radiation hazard for the development of lung cancer. Environmental tobacco smoke (ETS) has been found to cause lung cancer and other respiratory diseases. Indeed, ETS consists of many organic and inorganic compounds and metals, which may act synergistically to cause disease. Biological agents such as molds and other toxins may also be a more likely exposure hazard indoors than outside. Certainly, any pollutant can be found indoors, often at much higher concentrations than in the ambient air. For example, semivolatile organic compounds, such as polycyclic aromatic hydrocarbons and perfluoride compounds, especially perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), are rather ubiquitous. For example, long-term uptake doses of PFOS

and PFOA in the range of 3 to 220 ng per kg body weight per day ( $\text{ng kg}^{-1}$ ) and 1 to 130 ng  $\text{kg}^{-1}$   $\text{d}^{-1}$ , respectively.<sup>38</sup>

Arguably the most prominent and the most hazardous indoor pollutant is asbestos. Chronic exposures are directly associated with mesothelioma, lung cancer, and asbestosis. That is why governments at all levels have aggressively implemented programs to protect children and others in schools and other indoor micro-environments from exposures to airborne asbestos fibers. Asbestos and other fibers are discussed in detail in Chapter 6.

Mold is ubiquitous, but indoor exposures need not be high. Mold's growth is usually increased with increasing temperature and humidity under environmental conditions, but this does not mean molds cannot grow in colder conditions. Species may be of wide range of colors and often elicit particles and gases that render odors, often referred to as "musty". Like other fungi, molds reproduce by producing spores that are emitted into the atmosphere. Living spores are disseminated to colonize growth wherever conditions allow. Most ambient air contains large amounts of so-called bio-aerosols, i.e. particles that are part of living or once living organisms. In the instance, the bioaerosols are live mold spores, meaning that inhalation is a major route of exposure.

Indoor sources of molds include leaking pipes and fixtures, damp spaces such as those in basements and crawl spaces, heating, air-conditioning and ventilation systems, especially those that allow for condensation from temperature differentials between surfaces and ambient air, kitchens, and showers.

Some molds produce toxic substances called mycotoxins. There is much uncertainty related to possible health effects associated with inhaling mycotoxins over a long time period. Extensive mold growth may cause nuisance odors and health problems for some people. It can damage building materials, finishes, and furnishings and, in some cases, cause structural damage to wood.

Sensitive persons may experience allergic reactions, similar to common pollen or animal allergies, flulike symptoms, and skin rash. Molds may also aggravate asthma. Rarely, fungal infections from building-associated molds may occur in people with serious immune disease. Most symptoms are temporary and eliminated by correcting the mold problem, although much variability exists on how people are affected by mold exposure. Particularly sensitive subpopulations include

- Infants and children
- Elderly people
- Pregnant women
- Individuals with respiratory conditions or allergies and asthma

TABLE 26.27 Summary of Reported Indoor Air Pollutant Concentrations in the United States

Pollutant	Measured Concentration			Types of Building	Reference
	Minimum	Maximum	Mean		
Radon			0.8 pCi l <sup>-1</sup>	Residences	EPA (1987d) <sup>39</sup>
	0.5 pCi l <sup>-1</sup>	2000 pCi l <sup>-1</sup>		Residences	EPA (1987b) <sup>40</sup>
	0.14 pCi l <sup>-1</sup>	4.11 pCi l <sup>-1</sup>		New public buildings	Sheldon et al. (1988) <sup>41</sup>
	0.3 pCi l <sup>-1</sup>	1.68 pCi l <sup>-1</sup>	—	Old public buildings	Sheldon et al. (1988) <sup>41</sup>
	—	—	1.7–2.4 pCi l <sup>-1</sup>	Three office buildings	Bayer and Black (1988a) <sup>42</sup>
ETS (as respirable suspended particulate or RSP) (as nicotine)	—	—	28 µg m <sup>-3</sup> (1)*	Residences	NRC (1986b) <sup>43</sup>
	—	—	74 µg m <sup>-3</sup> (2)	Residences	NRC (1986b) <sup>43</sup>
	—	—	32 µg m <sup>-3</sup> (3)	Residences	DHHS (1986) <sup>44</sup>
	—	—	50 µg m <sup>-3</sup> (4)	Residences	DHHS (1986) <sup>44</sup>
	—	—	0.7–3.2 ppb	Three office buildings	Bayer and Black (1988a) <sup>42</sup>
Biological contaminants	—	564–5360 CFU m <sup>-3</sup> <sup>§</sup>		Three office buildings	Bayer and Black (1988a) <sup>42</sup>
Formaldehyde	—	131–319 µg m <sup>-3</sup>	78–144 µg m <sup>-3</sup>	Residences	Hawthorne et al. (1987) <sup>37</sup>
	ND <sup>¶,¶</sup>	192 ppb	—	New public buildings	Sheldon et al. (1988) <sup>41</sup>
	ND	103 ppb	—	Old public buildings	Sheldon et al. (1988) <sup>41</sup>
	—	—	25–39 ppb	Three office buildings	Bayer and Black (1988a) <sup>42</sup>
Benzene	—	120 µg m <sup>-3</sup>	20 µg m <sup>-3</sup>	Various	Wallace et al. (1983) <sup>45</sup>
Carbon tetrachloride	—	14 µg m <sup>-3</sup>	2.5 µg m <sup>-3</sup>	Various	Wallace et al. (1983) <sup>45</sup>
Trichloroethylene	—	47 µg m <sup>-3</sup>	3.6 µg m <sup>-3</sup>	Various	Wallace et al. (1983) <sup>45</sup>
Tetrachloroethylene	—	250 µg m <sup>-3</sup>	10 µg m <sup>-3</sup>	Various	Wallace et al. (1983) <sup>45</sup>
Chloroform	—	200 µg m <sup>-3</sup>	8 µg m <sup>-3</sup>	Various	Wallace et al. (1983) <sup>45</sup>
Dichlorobenzenes	—	1200 µg m <sup>-3</sup>	41 µg m <sup>-3</sup>	Various	Wallace et al. (1983) <sup>45</sup>
<b>PESTICIDES</b>					
Diazionon	ND	8.9 µg m <sup>-3</sup>	1.4 µg m <sup>-3</sup>	Residences	Lewis et al. (1986) <sup>46</sup>
Chlordane	ND	1.7 µg m <sup>-3</sup>	0.51 µg m <sup>-3</sup>	Residences	Lewis et al. (1986) <sup>46</sup>

\* (1) 73 residences without smokers; (2) 73 residences with smokers; (3) nonsmokers not exposed to ETS; and (4) nonsmokers exposed to ETS.

<sup>§</sup>Summation of mesophilic bacteria, fungi, and thermophilic bacteria. CFU: colony-forming units.

<sup>¶</sup>ND: not detected.

Source: US Environmental Protection Agency Report to Congress on Indoor Air Quality, EPA/400/1-89/001c; August 1989.

- Persons with weakened immune systems (e.g. chemotherapy patients, organ or bone marrow transplant recipients, and people with human immunodeficiency virus infections or autoimmune diseases)

Persons cleaning mold should wear gloves, eye protection, and a dust mask or respirator to protect against breathing airborne spores (Figure 8.18). A professional experienced in mold evaluation and remediation, such as an industrial hygienist, may need to be consulted to address extensive mold growth in

structures. It is important to correct large mold problems as soon as possible by first eliminating the source of the moisture and removing contaminated materials, cleaning the surfaces, and finally drying the area completely.

If visible mold is present, then it should be remediated, regardless of what species are present and whether samples are taken. In specific instances, such as cases where health concerns are an issue, litigation is involved, or the source(s) of contamination is unclear, sampling may be considered as part of a building evaluation. Sampling is needed in situations where visible

mold is present and there is a need to have the mold identified. A listing of accredited laboratories can be found at [www.aiha.org/LaboratoryServices/html/lists.htm](http://www.aiha.org/LaboratoryServices/html/lists.htm).

Radon gas is formed in the process of radioactive decay of uranium. The distribution of naturally occurring radon follows the distribution of uranium in geological formations. Elevated levels have been observed in certain granite-type minerals. Residences built in these areas have the potential for elevated indoor concentrations of radon from radon gas entering through cracks and crevices and from out-gassing from well water.

Radon gas is radioactive and emits alpha particles in the decay process. The elements resulting from radon decay are called radon daughters or progeny. These radon daughters can attach to airborne particles, which can deposit in the lung. The evidence supporting the radon risk of lung cancer comes from studies of uranium mine workers, in whom elevated rates of lung cancer have been observed. When an analysis of the potential exposure to radon inside homes was conducted by the US EPA, an estimate of 5000–20,000 excess lung cancer deaths was projected annually.<sup>47</sup> The risk is associated directly with increased lifetime doses, i.e. the longer the time spent living in a residence with elevated levels of radon, the higher the risk. Indoor levels of radon range from less than  $1\text{--}200 \text{ pCi l}^{-1}$ . Levels as high as  $12\,000 \text{ pCi l}^{-1}$  have been observed but most levels are much lower. The US EPA has established an action level of  $4 \text{ pCi l}^{-1}$  for indoor radon, and if a home screening test shows concentrations below  $4 \text{ pCi l}^{-1}$ , no remedial action is suggested.

ETS, sometimes referred to as “second-hand smoke” or “passive smoking”, represents the exposure to tobacco smoke by individuals other than the smoker. For decades, the US Surgeon General has indicated that smoking is a cause of lung cancer and cardiovascular disease for individuals who smoke. The US EPA has also concluded that ETS is a lung carcinogen for others breathing it.

The presence of biological contaminants gained widespread recognition with the outbreak of Legionnaires’ disease in Philadelphia, Pennsylvania, in 1976. In that year, 221 persons attending a convention of Legionnaires developed pneumonia symptoms and 34 subsequently died. The agent, a bacterium later named *Legionella pneumophila*, was found in the cooling tower of the hotel’s air-conditioning system. This bacterium has subsequently been responsible for other outbreaks of Legionnaires’ disease. The bacteria in water supplies may be eliminated by suitable treatment procedures. *Legionella* represents one of many types of biological agents that can cause allergic reactions and illness in the indoor environment.

One of the more difficult challenges remaining is the characterization of “sick building” syndrome. On numerous occasions, some employees in certain office buildings or other workplaces have developed a combination of symptoms including respiratory problems, dryness of the eyes, nose, and throat, headaches, and other nonspecific complaints. In such situations a substantial portion of the workers may exhibit these symptoms, which decrease in severity or stop when the worker is away from the building over the weekend or for longer periods. Investigations into the cause of these symptoms sometimes provide explanations, uncover ventilation problems, or identify an irritant gas. But many of these problem buildings are very difficult to understand and additional research is necessary to understand the cause-and-effect relationships.

#### 26.10.4 Control of Indoor Air Pollutants

The control and regulation of indoor air quality are influenced by individual property rights and a complicated mosaic of federal, state, and local government jurisdiction with conflicts, overlaps, and gaps in addressing these issues. Table 26.28 shows a large number of U.S. agencies and departments involved in indoor air quality control efforts at the federal level.

Government can institute certain laws and regulations for the citizens’ well-being. Environmental and occupational examples abound, such as clean water and air legislation and workplace safety and health regulations. As the extension of this role into the home occurs, implementation and enforcement become more problematic. Examples of proactive regulatory approaches are building codes, zoning, consumer product standards, and safety requirements. Table 26.29 shows what various parties, from the individual to the federal government, can do to improve indoor air quality. Many of these efforts focus on education, improved materials, and better design of products and structures.

The technological control strategies are related back to Figure 26.20. If the hazard is the result of elevated concentrations, then the technological solution is to reduce or remove the sources or dilute or remove the agent.

Control techniques are discussed for agents mentioned earlier—radon, ETS, and biological agents—and also for VOCs. The sources of VOCs are highly variable, including chemicals that off-gas from articles and construction materials, and those released during cooking, heating and other indoor combustion activities. For most pollutants, it is preferable to prevent their entry into the indoor environment rather than treat and remove them after entry. For example, radon enters the residence by two principal routes: infiltration from soil beneath the structure and out-gassing from well water during showers. Elevated levels of radon are generally

TABLE 26.28 Indoor Air Responsibility of Federal Agencies

Point of Impact	Agency/Activity	Comments
Direct control of indoor concentrations and/or exposures	OSHA air standards BPA radon action level NASA air standards	Limited to industrial environments Limited to residents in BRA's weatherization program Adopted OSHA standards
Control of emissions by restricting activities or product composition	EPA drinking water MCLs for radon and VOCs EPA pesticide restrictions CPSC consumer product bans Smoking restrictions imposed by DOD, DOT, and GSA VA restrictions on asbestos use	Indoor air exposures considered in determining drinking water levels Restricts use and sales of pesticides that may cause indoor air pollution Bans on use of some potential indoor pollutants in consumer products Restricts smoking in specified indoor environments Restricts use of asbestos in VA buildings
Control through assessment and mitigation procedures	EPA asbestos rules GSA building assessments NIOSH building assessments DOD/USAF chlordane assessments NASA HVAC system maintenance	Provides for the assessment and mitigation of asbestos hazards in schools Investigates GSA-controlled buildings for indoor air problems Responds to air quality health complaints Investigates USAF facilities for chlordane problems Assesses and corrects HVAC operation to optimize indoor air quality
Effort to increase knowledge of indoor air quality problems and controls	Research efforts by EPA, CPSC, DOE, HHS, BPA, DOT, NASA, NIST, NSF, TVA, HUD, and GSA Information dissemination by EPA, CPSC, DOE, HHS, BPA, HUD, TVA, FTC, NASA, NIST, and NIBS	

OSHA, Occupational Safety and Health Administration; BPA, Bonneville Power Administration; NASA, National Aeronautics and Space Administration; MCL, maximum contaminant levels; VOC, volatile organic compounds; CPSC, Consumer Products Safety Commission; DOD, Department of Defense; DOT, Department of Transportation; CSA, General Services Administration; VA, Veterans Administration; NIOSH, National Institute of Occupational Safety and Health; USAF, United States Air Force; HVAC, heating, ventilation, and air conditioning; DOE, Department of Energy; HHS, Health and Human Services; NIST, National Institute of Standards and Technology; NSF, National Science Foundation; TVA, Tennessee Valley Authority; HUD, Housing and Urban Development; FTC, Federal Trade Commission; NIBS, National Institute of Building Sciences.

Source: US Environmental Protection Agency Report to Congress on Indoor Air Quality, EPA/400/1-89/001c; August 1989.

observed in basements or first-floor rooms. The mitigation techniques available include increased ventilation of the crawl space beneath the first floor, soil gas venting from beneath a basement floor, and sealing of all openings to the subsurface soil. These steps reduce the entry of radon into the home. Elevated levels of radon in well water can be removed by aeration or filtration by absorbent-filled columns.

Control of ETS is complicated because of the personal behavior of individuals. For public buildings and facilities like offices, restaurants, and malls, many governmental bodies are placing restrictions on smoking in these areas, which can range from complete bans to requiring a restaurant to have a portion of a

dining area for smokers and the remainder for nonsmokers. The difficulty for the restaurant owner is ensuring that the nonsmoking section is free of ETS. Education is the primary approach to "control" in the home. Information about the effects of ETS on family members, especially the health of pregnant women, unborn and young children, has modified the behavior of some smokers.

Control of biological agents is multifaceted. In the case of *Legionella*, cleaning and maintenance of heating and air-conditioning systems are generally sufficient to reduce the risk of this disease. In home heating and air-conditioning systems, mold and bacteria may be present and controlled with maintenance procedures and

TABLE 26.29 Stakeholder Interests in Improving Indoor Air Quality

<b>Individuals</b>	<b>Consumer And Health Professionals</b>	<b>Manufacturers</b>	<b>Building Owners And Managers</b>	<b>Builders And Architects</b>	<b>State And Local Governments</b>	<b>Federal Government</b>
Find low-emission products in purchasing decisions	Be knowledgeable of symptoms, effects, and mitigation and advise clients	Adopt test procedures and standards to minimize product and material emissions	Adopt ventilation maintenance procedures to eliminate and prevent contamination and ensure and adequate supply of clean air to building occupants	Adopt indoor air quality as a design objective	Conduct studies of specific problems in state or local area and adopt mitigation strategies	Conduct research and technology transfer programs
Maintain and use products to minimize emissions	Develop information and education programs for constituent publics	Adequately label products as to emission level and proper use and maintenance of products	Use zone ventilation or local exhaust for indoor sources	Ensure compliance with indoor air quality ventilation standards	Establish building codes for design, construction, and ventilation requirements to ensure adequate indoor air quality	Coordinate actions of other sectors
Exercise discretionary control over ventilation to ensure clean air supply	Substitute materials to minimize emissions from products manufactured	Develop specific procedures for use of cleaning solvents, paints, herbicides, insecticides, and other contaminants to protect occupants	Adopt low-emission requirements in procurement specifications for building materials from manufacturers	Enforce and monitor code compliance	Coordinate actions of other sectors, encourage, or require specific sectors to take actions toward mitigation	
Be knowledgeable of indoor air quality problems and take actions to avoid personal exposure	Develop training programs for commercial users to ensure low emissions	Adopt investigatory protocols to respond to occupant complaints	Contain or ventilate known sources	Educate and inform building community, health community, and public about problems and solutions		

Source: US Environmental Protection Agency Report to Congress on Indoor Air Quality, EPA/400/1-89/001c; August 1989.

increasingly available technologies (e.g. UV disinfection). Growth may be inhibited by lower humidity levels. Keeping a house clean lowers the presence of dust mites, pollen, dander, and other allergens.

For VOCs, control options are multiple. Source reduction or removal includes product substitution or reformulation. Particleboard or pressed wood has been developed and used extensively in building materials for cabinet bases and subflooring and in furniture manufacturing for frames. If the product is not properly manufactured and cured prior to use as a building material, VOCs can out-gas into the interior of the residence or building. Other sources of VOCs may be paints, cleaning solutions, fabrics, binders, and adhesives. Proper use of household products will lower volatile emissions.

In many of the industries associated with building or household products, efforts are under way to reduce the potential for subsequent VOC release to the interior of residences or commercial buildings. Modification of the manufacturing process, solvent substitution, product reformulation, and altering installation procedures are a few of the approaches available.

When VOCs are present indoors at elevated concentrations, modification of ventilation rates is a control option for diluting and reducing these concentrations. The American Society of Heating, Refrigerating and Air-Conditioning Engineers has established standards for ventilation rates for outside air per individual. The guideline is 15 cfm per person.<sup>48</sup> This guideline is designed to bring sufficient fresh air into a building to minimize the buildup of contaminants and odors.

## 26.11 PERSONAL MONITORING

No matter what the quality of ambient and even indoor measurements of air pollutants, these are not often a good indication of the levels of exposure to air pollutants that people actually receive. Their activities and locations often vary considerably from person to person. In fact, the phenomenon known as "personal cloud" has recently been characterized to help predict a person's exposures and risks to air pollutants. The cloud indicates an increased personal exposure to air pollutants compared to indoor concentrations, or compared to the time-weighted indoor and outdoor concentrations. Results from several recent studies suggest that a number of factors, such as relative humidity and ventilation may lead to very different exposures based on personal measurements vs ambient concentrations of air pollutants. For example, one recent study found that while ambient fine particle concentrations may somewhat represent exposures to fine particles, the ability of either ambient gases or ambient fine particles to represent exposure to gases is quite small (see Table 26.30).

With personal monitoring, the monitoring device is worn by individuals as they proceed through their normal activities. This approach is most common in workplaces. The radioactivity sensors worn by nuclear power plant workers are one example. Personal monitoring is increasingly being used, however, to estimate total human exposures, including exposures from the air people breathe, the water they drink, and the food they eat.

One advantage of personal monitoring is that the data provide valuable insights into the sources of the pollutants to which people are actually exposed. A challenge with personal monitoring is ensuring that sufficient sampling is done to be representative of the population being studied.

To make full use of the data discussed in Chapters 25 and 26, they must be extended in time and space beyond the measurements. This is possible with a variety of models, a number of which are discussed in Chapter 27.

## QUESTIONS

1. Give two differences in siting criteria for an ambient air quality monitoring site for CO vs ground-level O<sub>3</sub>.
2. A county is designated nonattainment for O<sub>3</sub>, NO<sub>2</sub>, and CO. What is the likelihood that the SIP will have to address mobile sources?
3. A county is designated nonattainment for SO<sub>2</sub> and PM<sub>2.5</sub>. What is the likelihood that the SIP will have to address mobile sources?
4. Give an example of an air pollutant that will likely need to be extracted prior to chemical analysis. Give an example of an air pollutant that will likely not need to be extracted. What physical properties are associated with the need for extraction?
5. What type of measurement equipment would you recommend to determine the PM<sub>2.5</sub> personal cloud?
6. What type of measurement equipment would you recommend to determine the CO levels at the off ramp of an interstate highway? At a toll booth on a turnpike?
7. List the two major functions of a quality assurance program and describe how they are interrelated.
8. In the county where you live, decide which month and location have the greatest number of hours with ozone concentrations >0.01 ppm. What are the major factors in this decision?
9. How would the release of a volatile gas from contaminated soil be affected by the soil temperature?
10. The US EPA Hazardous Ranking System computes a numerical score for hazardous waste. If the score exceeds a predetermined value, the waste site is placed on the NPL for Superfund cleanup. Discuss the pros and cons of such a ranking system.

TABLE 26.30 Comparison of Ambient Concentrations of Air Pollutants to Personal Exposures

Pollutant*	n	Summer				n	Fall				
		ND	LOD	Mean ? SD	Maximum		ND	LOD	Mean ? SD	Maximum	
<b>AMBIENT CONCENTRATIONS</b>											
<i>Particles</i>											
PM <sub>2.5</sub>	65	0	0	20.1 ± 9.3	46.6	72	0	0	19.3 ± 12.2	50.7	
SO <sub>4</sub> <sup>2-</sup>	61	0	0	7.7 ± 4.8	25.0	72	0	0	6.2 ± 4.7	22.4	
EC	56	0	1	1.1 ± 0.5	2.9	71	0	0	1.1 ± 0.7	3.6	
<i>Gases</i>											
O <sub>3</sub>	62	0	4	29.3 ± 13.4	74.8	72	0	21	16.0 ± 8.1	42.4	
NO <sub>2</sub>	62	1	44	9.5 ± 7.4	37.9	71	0	16	11.3 ± 6.0	27.9	
SO <sub>2</sub>	63	23	53	2.7 ± 3.9	21.9	71	24	43	5.4 ± 9.6	63.6	
<b>PERSONAL EXPOSURES</b>											
<i>Particles</i>											
PM <sub>2.5</sub>	169	0	0	19.9 ± 9.4	59.0	204	0	0	20.1 ± 11.6	66.0	
SO <sub>4</sub> <sup>2-</sup>	165	0	2	5.9 ± 4.2	25.6	188	0	0	4.4 ± 3.3	16.3	
EC	166	7	12	1.1 ± 0.6	4.6	197	1	1	1.2 ± 0.7	6.2	
<i>Gases</i>											
O <sub>3</sub>	183	2	168	5.3 ± 5.2	35.7	226	84	207	3.9 ± 4.4	21.3	
NO <sub>2</sub>	183	1	117	9.9 ± 6.0	38.9	228	1	32	12.1 ± 6.1	38.8	
NO <sub>2</sub> <sup>§</sup>	130	1	93	9.0 ± 5.2	38.9	139	1	28	9.9 ± 4.6	28.7	
NO <sub>2</sub> <sup>¶</sup>	53	0	24	12.3 ± 7.1	33.5	89	0	4	15.7 ± 6.4	38.8	
SO <sub>2</sub>	185	99	173	1.5 ± 3.3	30.4	228	72	217	0.7 ± 1.9	14.2	

\* PM<sub>2.5</sub>, SO<sub>4</sub><sup>2-</sup>, and EC in units of micrograms per cubic meter; O<sub>3</sub>, NO<sub>2</sub>, and SO<sub>2</sub> in units of parts per billion.

§ Samples from subjects without gas stoves in their homes.

¶ Samples from subjects with gas stoves in their homes.

ND: number of samples with values below the analytical LOD (i.e. not detected).

Source: Sarnat SE, Coull BA, Schwartz J, Gold DR, Suh HH. Factors affecting the association between ambient concentrations and personal exposures to particles and gases. Environ Health Perspect 2006;114(5):649–654.

11. Describe a possible situation in which an air contaminant is controlled but the control system used transfers the contaminant problem to another medium, such as water or soil.
12. Explain the differences between a hazard quotient, hazard index, and cumulative cancer risk.
13. What are appropriate uses of mobile platforms for monitoring?
14. List the reasons for establishing a stationary air monitoring network.
15. What factors can account for differences between ambient concentrations of a pollutant and actual, personal exposures to the same pollutant?
16. An adhesive is applied to the walls and is found to have a total VOC indoor emission rate of 271 mg m<sup>-3</sup>. How should these emissions be sampled?
17. The 90th percentile concentration of α-pinene is found to have 20 µg m<sup>-3</sup> indoor air concentration in a southeastern US state. The manufacturer of a furniture wax wants to know how much of this compound is being released during the application of its product in a volunteer's residence. What are the minimum number of sampling sites to begin to find the sources of this VOC and the frequency of sampling at those sites?
18. The company has another product that contains n-dodecane, which has a 90th percentile 20 µg m<sup>-3</sup> indoor air concentration in the same town. What are the minimum number of sampling sites to begin to find the sources of this compound and the frequency of sampling at those sites?
19. Total PCB daily air concentrations in a room in a home are found to be 1140 ng m<sup>-3</sup> on a summer day

- and  $495 \text{ ng m}^{-3}$  on a winter day. What do you require to know about these measurements before accepting these data?
20. Similar intra-annual variability was observed in 10 rooms in 10 different homes in Europe. What factors could lead to the seasonal variability?
21. What is the “sick building syndrome”? What types of data are needed to determine whether a building is “sick”?
22. People in a large skyscraper complain on adjacent floors about irritation of eyes, skin, and mucous membranes. What types of air pollutants could be causing this and how can they be quantified?
23. A month after the above incident, the health department takes blood samples of the people in the building to determine if air pollutants observed a month earlier are present. However, only 15% of the workers on the floors agree to give blood. If you compile these results, what type of error must you report? How can this be calculated?
24. What is the difference between LOD and LOQ? If one data set has an LOD only and another has LOQs, what can be done with the LOQ data than cannot be done with the LOD data?
25. Why do individual calibration curves have to be developed for each compound of interest? Why should a calibration curve be developed when an LC or GC column is replaced?
26. If you are trying to determine whether airborne Hg concentrations in a county are contributing to autism, what type of measurement data would you need?
27. You are the city engineer sitting in a discussion about a program to give kerosene space heaters to needy people. Recent inspections of target homes show that the air exchange rates ( $QV^{-1}$ ) at present to be an average four per hour. Before the heaters are given away, the city, with the help of a team of volunteers, will fix windows, caulk, and add insulation so that any home receiving the heater will be at most 1.5 air exchanges per hour. The manufacturer specs show that the heaters will produce 23 mg of carbon monoxide per second. If the average home will use one heater in the living room ( $500 \text{ m}^3$ ) and one in each of the three bedrooms (each  $400 \text{ m}^3$ ), do you foresee any problems with this plan? Would you want to live and sleep in a home with these CO concentrations (e.g. based on health standards)? Support your recommendation in a memo to the mayor and city council.
28. Later in the same meeting, you are asked to consider the use of building materials for the new library. The

architects call for library panel constructed of fiberboard. It is much more aesthetically appealing than the alternate material (drywall). The fiberboard emits formaldehyde at  $360 \mu\text{g m}^{-2} \text{ h}^{-1}$  and the library walls to be covered represent a surface area of  $20,000 \text{ m}^2$ . The emission rate is expected to drop by  $40 \mu\text{g m}^{-2} \text{ h}^{-1}$  each year as the product gives off gases and the formaldehyde decomposes. The drywall emits no HCHO, but in a few places the drywall will be reinforced with plywood, which emits  $4 \mu\text{g m}^{-2} \text{ h}^{-1}$  (but only from  $1500 \text{ m}^2$  of wall surface). However, the grout used if the drywall is selected emits radon at a rate of  $1 \times 10^{-5} \mu\text{g m}^{-2} \text{ h}^{-1}$ . (Remember that the volume being used here is liters, not cubic meters, and that the density of water is much higher than that of air.) The volume of the library will be  $250,000 \text{ m}^3$ . Assume that the library air will be well mixed. The library is designed to have 1.2 air exchanges per hour. Recent measurements in the area around the building site have detected  $5 \mu\text{g m}^{-3}$  HCHO in the ambient air. Write a memo to the library planning commission communicating your calculations and estimates, as well as your recommendations about the choice of wall materials. Also, make some recommendations on what corrective actions will need to be taken if they still wish to install the panel as the architects wish, or if they go with the alternative.

29. From the previous three problems, can you draw any conclusions about the relationship of indoor air quality and energy efficiency (e.g. the role that air exchange rates play in both)? Can you think of some approaches that could ameliorate both air quality and energy efficiency in the same building?

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# Modeling Applications

## 27.1 VALUE OF MODELS

Models provide a means for representing a complicated system in an understandable way. They take many forms, beginning with “conceptual models” that explain the way a system works, including all the factors and parameters of how a pollutant moves in the air after an emission. Conceptual models are a first and important step in identifying the major influences on where a chemical is likely to be found in the environment, and as such, need to be developed to help target sources of data needed to assess an environmental problem. In general, developing a model requires two main steps: First, a model of the domain and the processes being studied must be defined. Then, at the model boundaries, a model of the boundary conditions must represent the influencing environment surrounding the study domain. Scientists often develop “physical” or “dynamic” models to estimate the location where a chemical would be expected to move under controlled conditions, only on a much smaller scale. For example, the US Environmental Protection Agency (EPA) employs chambers or full-size test houses to model the fate of pollutants indoors. Like all models, the dynamic model’s accuracy is dictated by the degree to which the actual conditions can be simulated and the quality of the information that is used.<sup>1</sup>

Numerical models apply mathematical expressions to approximate a system. There are three thermodynamic systems:

1. Isolated systems, in which no matter or energy crosses the boundaries of the system (i.e. no work can be done on the system).
2. Closed systems, in which energy can exchange with surroundings, but no matter crosses the boundary.
3. Open systems, in which both matter and energy freely exchange across system boundaries.

Isolated systems are usually only encountered in highly controlled reactors, so are important in modeling pesticide formulation and manufacturing, but not directly pertinent to pesticide exposure modeling. In

fact, most microenvironmental systems are open, but with simplifying assumptions, some subsystems can be treated as closed.

Pesticide transport and fate models can be statistical and/or “deterministic”. Statistical models include the pollutant dispersion models, such as the Lagrangian models, which follow the movement of a control volume starting from the source to the receptor locations. These often assume idealized Gaussian distributions of pesticides from a point of release, i.e. the pollutant concentrations are normally distributed in both the vertical and horizontal directions from the source. The Lagrangian approach is common for atmospheric releases. However, recent models based on the Lagrangian approach have incorporated descriptions of complex turbulence. “Stochastic” models are statistical models that assume that the events affecting the behavior of a chemical in the environment are random, so such models are based on probabilities. These are being commonly adopted in the modeling of human exposures to air pollutants.

Deterministic models are used when the physical, chemical, and other processes are sufficiently understood so as to be incorporated to reflect the movement and fate of chemicals. These are very difficult models to develop because each process must be represented by a set of algorithms in the model. Also, the relationship between and among the systems, such as the kinetics and mass balances, must also be represented. Thus, the modeler must “parameterize” every important event following a pesticide’s release to the environment. Often, hybrid models using both statistical and deterministic approaches are used, for example, when one part of a system tends to be more random, while another has a very strong basis in physical principals. Numerous models are available to address the movement of chemicals through a single environmental media, but increasingly, environmental scientists and engineers have begun to develop “multimedia models”, such as compartmental models that help to predict the behavior and changes to chemicals as they move within and among reservoirs (e.g. carpet), in the air as dust and vapors, and in exchanges with surfaces.<sup>1</sup>

## 27.2 METEOROLOGICAL BASES OF ATMOSPHERIC POLLUTION

Air pollutants reach receptors by being transported and perhaps transformed in the atmosphere (Figure 27.1). The location of receptors relative to sources and atmospheric influences affect pollutant concentrations, and the sensitivity of receptors to these concentrations determines the effects. The location, height, and duration of release, as well as the amount of pollutant released, are also of importance. Some of the influences of the atmosphere on the behavior of pollutants, primarily the large-scale effects, are discussed here, as well as several effects of pollutants on the atmosphere.

### 27.2.1 Ventilation

If air movement past a continuous pollutant source is slow, pollutant concentrations in the plume moving downwind will be much higher than they would be if the air were moving rapidly past the source. If polluted air continues to have pollution added to it, the concentration will increase. Generally, a source emits into different volumes of air over time. However, there can be a buildup of concentration over time even with significant air motion if there are many sources.

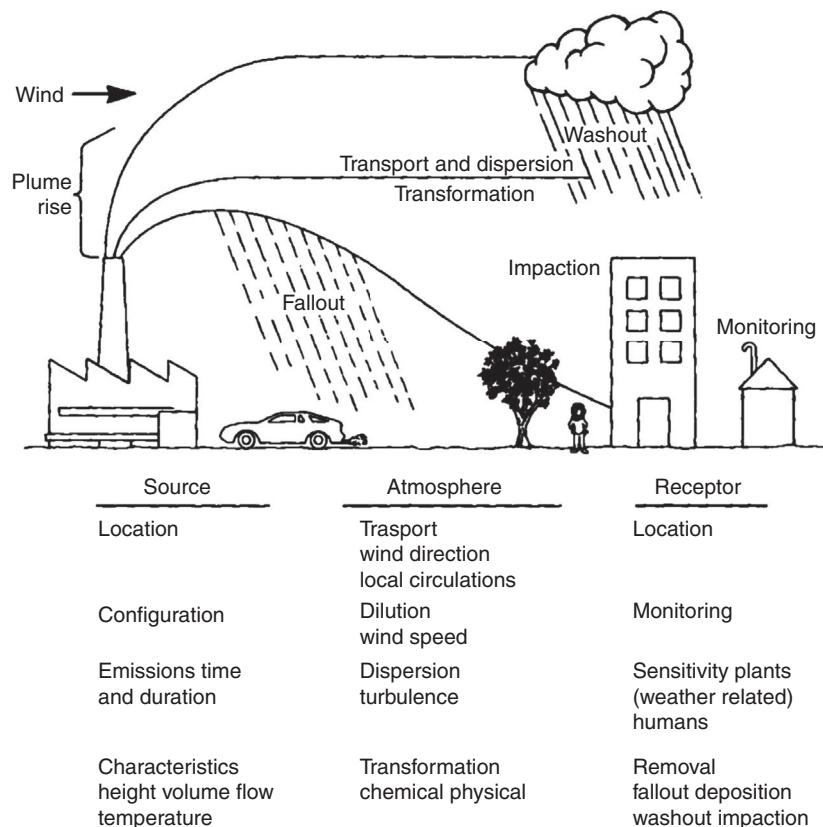
Low- and high-pressure systems have considerably different ventilation characteristics. Air generally moves

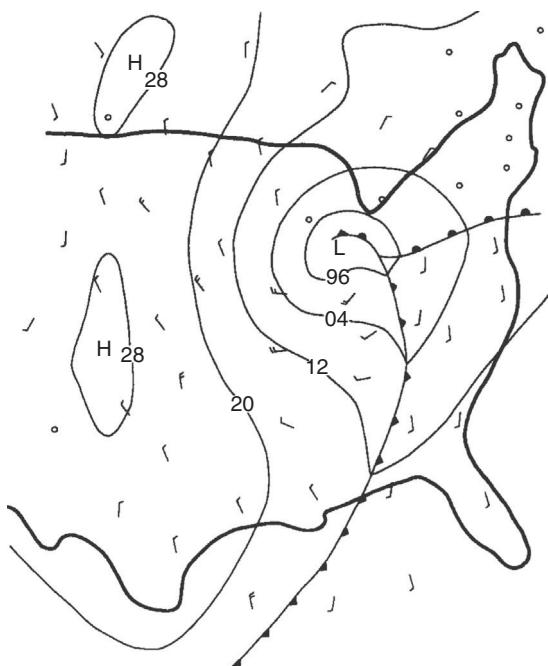
toward the center of a low (Figure 27.2) in the lower atmosphere, due in part to the frictional turning of the wind toward low pressure. This convergence causes upward vertical motion near the center of the low. Although the winds very near the center of the low are generally light, those away from the center are moderate, resulting in increased ventilation rates. Note the increased wind in the area to the west of the low in Figure 27.2. Low-pressure systems generally cover relatively small areas (although the low-pressure system shown in Figure 27.2 covers an extensive area) and are quite transient seldom remaining the same at a given area for a significant period of time. Lows are frequently accompanied by cloudy skies, which may cause precipitation. The cloudy skies minimize the variation in atmospheric stability from day to night. Primarily because of moderate horizontal wind speeds and upward vertical motion, ventilation (i.e. total air volume moving past a location) in the vicinity of low-pressure systems is quite good.

High-pressure systems are characteristically the opposite of lows. Since the winds flow outward from the high-pressure center, subsiding air from higher in the atmosphere compensates for the horizontal transport of mass.

This sinking air causes a subsidence inversion. Partially because of the subsiding vertical motion, the skies are usually clear, allowing maximum radiation—incoming during the day and outgoing at night—

FIGURE 27.1 The atmosphere's role in air pollution.





**FIGURE 27.2** Surface chart for the eastern United States on Friday, November 20, 1981. Contours are isobars of atmospheric pressure; 12 is 1012 mb. Line with triangles, cold front; line with semicircles, warm front; line with both triangles and semicircles, an occluded front (a cold front that has caught up with a warm front). Wind direction is with the arrow; wind speed is 10 knots for 1 barb, 5 knots for one-half barb. Small station circles indicate calm. H, center of high pressure; L, center of low pressure.

causing extremes of stability; there is instability during the day and stability at night, with frequent radiation inversions. Highs generally occupy large areas, and although they are transient, they are usually slow moving. Winds over large areas are generally light; note the winds to the south of the high in the lower left corner of Figure 27.2. Thus, the ventilation in the vicinity of high-pressure systems is generally much less than that of lows.

### 27.2.2 Stagnation

At times the ventilation rate becomes very low. Such a lack of air motion usually occurs in the weak pressure gradient near the center of an anticyclone (i.e. of a high). If the high has a warm core, there is likely to be very little air movement near the center, i.e. stagnation. Under such circumstances, winds are very light. Skies are usually cloudless, contributing to the formation of surface-based radiation inversions at night. Although the clear skies contribute to instability in the daytime, the depth of the unstable layer (i.e. mixing height) may be severely limited due to the subsidence inversion over the high.

The mixing height at a given time may be estimated by use of the morning radiosonde ascent plotted on a

thermodynamic chart. The surface temperature at the given time is plotted on the diagram. If a dry adiabat is drawn through this temperature, the height above ground at the point where this dry adiabat intersects the morning sounding is the mixing height for that time. The mixing height for the time of maximum temperature is the maximum mixing height. Use of this sounding procedure provides an approximation because it assumes that there has been no significant advection since the time of the sounding.

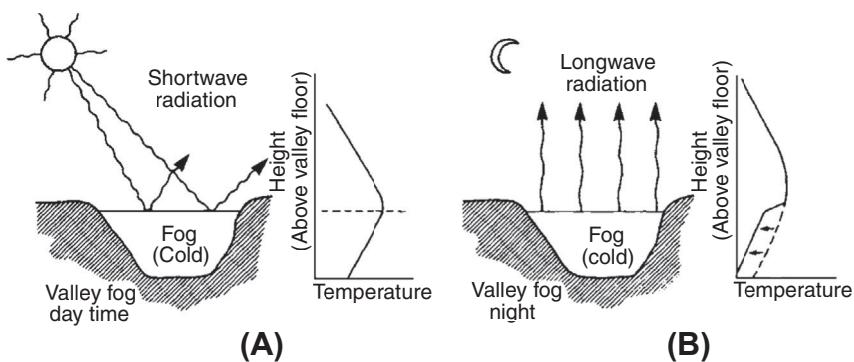
### 27.2.3 Meteorological Conditions during Historic Pollution Episodes

As discussed in Chapter 10, meteorological conditions can make the difference between a rather normal day and an air pollution episode. In the episode at Donora, Pennsylvania, during the period October 25–31, 1948,<sup>2</sup> a nearly stationary polar high-pressure system caused the regional winds to be extremely light. Cold air accumulated in the bottom of the river valley and fog formed, which persisted past midday for four consecutive days. The top of a fog layer has a high albedo that reflects solar radiation, so that only part of the incoming radiation is available to heat the fog layer and eliminate it (Figure 27.3(A)). During the night, longwave radiation leaves the top of the fog layer, further cooling and stabilizing the layer (Figure 27.3(B)). Wind speeds at Donora were less than  $3.1 \text{ m s}^{-1}$  ( $7 \text{ mi h}^{-1}$ ) from the surface up to 1524 m (5000 ft) altitude for three consecutive days, so that pollutants emitted into the air within the valley were not transported far from their point of emission. Maximum temperatures at Donora at an elevation of 232 m (760 ft) mean sea level were considerably lower than those at the Pittsburgh airport, elevation 381 m (1250 ft), indicating the extreme vertical stability of the atmosphere. In the vicinity of Donora there were sources of sulfur dioxide, PM, and carbon monoxide. Previous recorded periods of stagnation had occurred in Donora in October 5–13, 1923 and October 7–18, 1938. This indicates that certain locations are vulnerable to such episodes, given their topography, e.g. river valleys.

Similar meteorological conditions have led to other episodes, such as the anticyclonic conditions that formed a dense 4-day fog occurred in London and its surroundings during December 5–9, 1952.<sup>3,4</sup> This system became stationary, so that there was almost no wind until milder weather returned.

Measurements of PM less than approximately  $20 \mu\text{m}$  in diameter and of sulfur dioxide were made at 12 sites in the greater London area during the episode. Note that this was before modern air pollutant monitoring techniques were standardized as they are today. However, the measurements appear to be reliable, since their methods have been well documented. The measurements

**FIGURE 27.3 Dense fog maintaining stability in a valley.** It reflects short-wave radiation during the day (A) and radiates heat from the top of the fog at night (B). Adapted from Schrenk et al.<sup>2</sup>



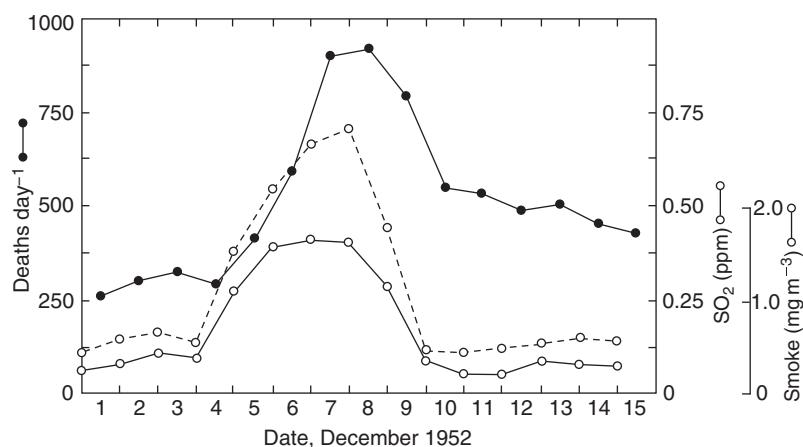
were made by pumping air through a filter paper and then through a hydrogen peroxide solution. The smoke deposit on the filter was analyzed by reflectometer; the sulfur dioxide was determined by titrating the hydrogen peroxide with standard alkali, eliminating interference by carbon dioxide. Using the sampling procedure, sulfur dioxide existing as a gas and dissolved in fine fog droplets was measured. Any sulfur dioxide associated with larger fog droplets or adsorbed on particles collected on the filter would not be measured.

Smoke concentrations ranged from 0.3 to more than  $4 \text{ mg m}^{-3}$ . Daily means of the sampling stations are shown in Figure 27.4. Sulfur dioxide measurements ranged from less than 0.1 ppm ( $260 \mu\text{g m}^{-3}$ ) to 1.34 ppm ( $3484 \mu\text{g m}^{-3}$ ). Also, 4 of the 11 stations had at least one daily value in excess of 1 ppm, and 9 of the 11 stations had at least one daily value in excess of 0.5 ppm. Compare these levels to the US primary standard for sulfur dioxide, which is a maximum 24-h concentration of  $365 \mu\text{g m}^{-3}$  (0.14 ppm), not to be exceeded more than once per year. Daily means are shown in Figure 27.4. The mean smoke and SO<sub>2</sub> values rose and later decreased in parallel. Daily concentrations of smoke averaged over all stations rose to about five times normal and sulfur dioxide to about six times normal, peaking on December 7 and 8, respectively. In

addition to the daily measurements at 12 sites, monthly measurements at 117 sites were made using lead peroxide candles. This allowed determination of the spatial pattern. The December 1952 concentrations were about 50% higher than those of December 1951.

From the commencement of the fog and low visibility, many people experienced difficulty breathing, the effects occurring more or less simultaneously over a large area of hundreds of square kilometers. The rise in the number of deaths (Figure 27.4) paralleled the mean daily smoke and sulfur dioxide concentrations; daily deaths reached a peak on December 8 and 9, with many of them related to respiratory troubles. Although the deaths decreased when the concentrations decreased, the deaths per day remained considerably above the preepisode level for some days. A vexing question is whether most of the persons who died have died soon afterward anyway. If this were the case, a below-normal death rate would have occurred following the episode. This situation did not seem to exist, but detailed analysis was complicated by increased deaths in January and February 1953, which were attributed primarily to an influenza outbreak. This is an example of the difficulty of attributing effects to elevated pollutant concentrations, given the complexity of estimating the amounts to which receptors are actually exposed, i.e. concentration is an important factor, but

**FIGURE 27.4 Daily air pollution (SO<sub>2</sub> and smoke) and deaths during the 1952 London episode.** Adapted from Wilkins.<sup>3</sup>



not the only factor in calculating air pollution exposure (see Chapter 8).

The excess deaths may be attributed to the synergistic effect of fine particles and sulfur dioxide.

Surface inversions cause the condensation of fog, which, once formed, can persist. Air pollution is exacerbated with the persistence of fog for days coupled with considerable emissions of pollutants into a volume with topography that confines air movement.

### 27.2.3.1 Air Pollution Emergencies

Government authorities increasingly are facing emergencies that may require lifesaving decisions to be made rapidly by those on the scene. Of increasing frequency are transportation accidents involving the movement of volatile hazardous materials. A railroad derailment accident of a tank car of liquefied chlorine on February 26, 1978, at Youngtown, Florida, in which seven people died, and an accident in Houston, Texas, involving a truck carrying anhydrous ammonia on May 11, 1976, which also claimed seven lives are examples. Two potentially dangerous situations involved barges with tanks of chlorine, one that sank in the lower Mississippi River and another that came adrift and came to rest on the Ohio River dam at Louisville, Kentucky; neither resulted in release of material.

Releases of radioactive materials from nuclear power plants have occurred, as during the worst US nuclear accident at Three-Mile Island, Pennsylvania in 1979, and much larger releases during the 1986 disaster at Chernobyl, Ukraine and the 2011 disaster at Fukushima, Japan. In such situations, releases may be sufficient to require evacuation of residents.

Although nuclear releases are highly troubling, air pollution episodes have most often involved chemical releases. Air pollution disasters at Bhopal, India (organic chemical compounds), Chernobyl (radioisotopes) and Manhattan, New York (particulates and vapors) were unprecedented at the time they occurred. Bhopal, India—On December 2, 1984, the contents of a methyl isocyanate (MIC) storage tank at the Union Carbide India plant in Bhopal became hot. Pressure in the tank became high. Nearly everything that could go wrong did. The refrigerator unit for the tank, which would have slowed the reactions, was turned off. After midnight, when the release valve blew, the vent gas scrubber that was to neutralize the gas with caustic soda failed to work. The flare tower, which would have burned the gas to harmless by-products, was down for repairs. As a result, many tons of MIC were released from the tank. The gas spread as a foglike cloud over a large, highly populated area to the south and east of the plant.<sup>5</sup> The number of fatalities was in excess of 2000 with thousands of others injured. Although little is available in the way of meteorological measurements,

it is assumed that winds were quite light and that the atmosphere at this time of day was relatively stable.

Chernobyl, USSR—On April 26, 1986, shortly after midnight local time, a serious accident occurred at a nuclear power plant in Chernobyl in the Ukraine. It is estimated that 4% of the core inventory was released between April 26 and May 6. Quantities of Cs-137 (cesium) and I-131 (iodine) were released and transported, resulting in contamination, primarily by wet deposition of cesium, in Finland, northern Sweden and Norway, the Alps, and the northern parts of Greece. Because of temperatures of several thousand kelvin during the explosion-like release, the resulting pollutant cloud is assumed to have reached heights of 2000 m or more. The estimated southeast winds at plume level initially moved the plume toward Finland, northern Sweden, and northern Norway. As winds at plume level gradually turned more easterly and finally north and northwesterly, contaminated air affected the region of the Alps and northern Greece. A number of investigators, including Hass et al.,<sup>6</sup> modeled the long-range transport including wet and dry removal processes. These attempts were considered quite successful, as radioactivity measurements provided some confirmation of the regions affected. Elevated levels of radioactivity were measured throughout the Northern Hemisphere. Because of the half-life of about 30 years for Cs-137, the contamination will endure.

World Trade Center (WTC), New York—On September 11, 2001, terrorists intentionally crashed fully fueled Boeing 767 jets into the twin towers of the heavily populated WTC. The burning fuel, building materials and building contents, as well as the fibers and particles released during the collapse were the source of dangerous gas and particle phase pollutants released throughout the city. In addition to the immediate threat, the fire smoldered for months following the attack, which was a source of a variety of pollutants (see Table 10.1 in Chapter 10).

In such emergencies, it is most important to know the local wind direction at the accident site, so that the area that should be immediately evacuated can be determined. The next important factor is the wind speed, so that the travel time to various areas can be determined, again primarily for evacuation purposes. Both of these can be estimated on-site by simple means such as watching the drift of bubbles released by a bubble machine. It should be borne in mind that wind speeds are higher above ground and that wind direction is usually different. In fact, the WTC episode dramatically demonstrated the importance of local meteorology. The wind directions at Ground Zero were almost always different than that measured at any of the three nearby, major airports. And, the three airports often have meteorological conditions different from one another.

As evacuation is taking place, it is important to determine whether meteorological events will cause a wind

direction shift later on, requiring a change in the evacuation scenario. Particularly in coastal areas, or areas of significant terrain, authorities should be alert to a possible change in wind direction in going from night to day or vice versa. Useful advice may be obtained from the nearest weather forecaster, although accurate forecasting of wind direction for specific locations is not easy. Accurate air movement measurements and predictions are a matter of safety, even life and death. Portable meteorological stations have become accurate, precise, and reasonably available. These should be deployed during any emergency involving airborne contaminants, or the potential for such.

If the situation is one of potential rather than current release, specific concentrations at various distances and localities may be estimated for various conditions.

#### 27.2.4 Pollution Processes the Atmosphere

Obvious effects of pollutants on the atmosphere include increased PM, which decreases visibility and inhibits incoming solar radiation, and increased gaseous pollutant concentrations, which absorb longwave radiation and increase surface temperatures. However, particulate and gaseous pollutants affect the atmosphere in many other ways.

##### 27.2.4.1 Turbidity

The attenuation of solar radiation has been studied by McCormick and his associates<sup>7,8</sup> utilizing the Voltz sun photometer, which uses measurements at a wavelength of  $0.5\text{ }\mu\text{m}$ . The ratio of ground-level solar intensity at  $0.5\text{ }\mu\text{m}$  to extraterrestrial solar intensity can be as high as 0.5 in clean atmospheres but can drop to 0.2–0.3 in polluted areas, indicating that ground-level solar intensity can be decreased as much as 50% by pollution in the air. By making measurements using aircraft at various heights, the vertical extent of the polluted air can be determined. The turbidity coefficient can also be derived from the measurements and used to estimate the aerosol loading of the atmosphere. By assuming a particle size distribution in the size range  $0.1\text{--}10\text{ }\mu\text{m}$  and a particle density, the total number of particles can be estimated. The mass loading per cubic meter can also be estimated. Because of the reasonable cost and simplicity of the sun photometer, it is useful for making comparative measurements around the world.

##### 27.2.4.2 Precipitation

Depending on its concentration, pollution can have opposite effects on the precipitation process. Addition of a few particles that act as ice nuclei can cause ice particles to grow at the expense of supercooled water droplets, resulting in particles large enough to fall as precipitation. An example of this is commercial cloud

seeding, with silver iodide particles released from aircraft to induce rain. If too many such particles are added, none of them will grow sufficiently to cause precipitation. Therefore, the effects of pollution on precipitation are not at all straightforward.

There have been some indications, although controversial, of increased precipitation downwind of major metropolitan areas. Urban addition of nuclei and moisture and urban enhancement of vertical motion due to increased roughness and the urban heat island effect have been suggested as possible causes.

##### 27.2.4.3 Fogs

As mentioned in the previous section, the increased number of nuclei in polluted urban atmospheres can cause dense persistent fogs due to the many small droplets formed. Fog formation is very dependent on humidity and, in some situations, humidity is increased by release of moisture from industrial processes. Low atmospheric moisture content can also occur, especially in urban areas; two causes are lack of vegetation and rapid runoff of rainwater through storm sewers. Also, slightly higher temperatures in urban areas lower the relative humidity.

##### 27.2.4.4 Solar Radiation

In the early part of this century, the loss of ultraviolet light in some metropolitan areas due to heavy coal smoke was of concern because of the resulting decrease in the production of natural vitamin D, which causes the disease rickets. Recently, measurements in Los Angeles smog have revealed much greater decreases in ultraviolet than visible light. This is due to both absorption by ozone of wavelengths less than  $0.32\text{ }\mu\text{m}$  and absorption by nitrogen dioxide in the  $0.36\text{--}0.4\text{ }\mu\text{m}$  range. Heavy smog has decreased ultraviolet radiation by as much as 90%.

#### 27.2.5 Removal Mechanisms

Except for fine PM ( $0.2\text{ }\mu\text{m}$  or less), which may remain airborne for long periods of time, and gases such as carbon monoxide, which do not react readily, most airborne pollutants are eventually removed from the atmosphere by sedimentation, reaction, or dry or wet deposition.

##### 27.2.5.1 Sedimentation (Settling by Gravity)

Particles less than about  $20\text{ }\mu\text{m}$  are treated as dispersing as gases, and effects due to their fall velocity are generally ignored. Particles greater than about  $20\text{ }\mu\text{m}$  have appreciable settling velocities. The fall velocity of smooth spheres as a function of particle size has been plotted (Figure 27.5) by Hanna et al.<sup>9</sup> Particles in the range  $20\text{--}100\text{ }\mu\text{m}$  are assumed to disperse approximately as gases, but with their centroid moving downward in the atmosphere according to the fall velocity.

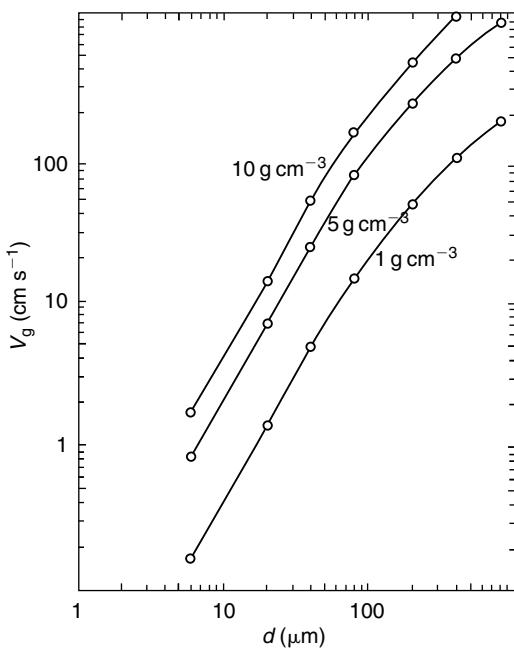


FIGURE 27.5 Fall velocity of spherical particles as a function of particle diameter and density. Adapted from Hanna et al.<sup>9</sup>

This can be accounted for by subtracting  $v_{gt}$  from the effective height of release, where  $v_g$  is the gravitational fall velocity of the particles and  $t$ , in seconds, is  $x/u$ , where  $x$  is downwind distance from the source in m and  $u$  is wind speed. This is called the *tilted plume model*. The model may be modified to decrease the strength of the source with distance from the source to account for the particles removed by deposition.

For 20–100 μm particles, the deposition  $w$  on the ground is

$$w = v_g C(x, y, z) \quad (27.1)$$

where the air concentration  $C$  is evaluated for a height above ground  $z$  of about 1 m.

Particles larger than 100 μm fall through the atmosphere so rapidly that turbulence has less chance to act upon and disperse them. The trajectories of such particles are treated by a ballistic approach.

### 27.2.5.2 Reaction (Transformation)

Transformations due to chemical reactions throughout the plume are frequently treated as exponential losses with time. The concentration  $C(t)$  at travel time  $t$  when pollutant loss is considered compared to the concentration  $\chi$  at the same position with no loss is

$$\frac{C(t)}{\chi} = \exp(-(0.693t/L)) \quad (27.2)$$

where  $L$  is the half-life of the pollutant in seconds. The half-life is the time required to lose 50% of the pollutant.

### 27.2.5.3 Dry Deposition

Although it does not physically explain the nature of the removal process, deposition velocity has been used to account for removal due to impaction with vegetation near the surface or for chemical reactions with the surface. McMahon and Denison<sup>10</sup> gave many deposition velocities in their review paper. Examples (in centimeters per second) are sulfur dioxide, 0.5–1.2; ozone, 0.1–2.0; iodine, 0.7–2.8; and carbon dioxide, negligible.

### 27.2.5.4 Wet Deposition

Scavenging of particles or gases may take place in clouds (rainout) by cloud droplets or below clouds (washout) by precipitation. A scavenging ratio or washout ratio  $W$  can be defined as

$$W = \frac{k\rho}{C} \quad (27.3)$$

where  $k$  is concentration of the contaminant in precipitation in micrograms per gram;  $\rho$  is the density of air, which is approximately  $1200 \text{ g m}^{-3}$ ; and  $C$  is the concentration in micrograms per cubic meter, of the pollutant in the air prior to scavenging. McMahon and Denison<sup>10</sup> gave a table of field observations of washout ratios. The values for various pollutants range from less than 100 to more than 4000. These values are a function of particle size and rainfall intensity, generally decreasing with the latter and increasing with the former.

Scavenging may also be considered as an exponential decay process:

$$C(t) = C(0)e^{-\Lambda t} \quad (27.4)$$

where  $C(t)$  is the concentration in micrograms per cubic meter at time  $t$  in seconds,  $C(0)$  is the concentration at time 0, and  $\Lambda$  is the scavenging or washout coefficient,

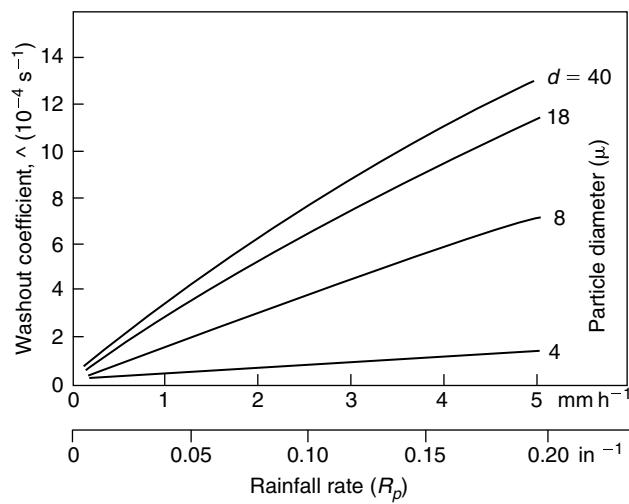


FIGURE 27.6 Typical values of the washout coefficient as a function of rainfall rate and particle diameter. After Engelmann.<sup>11</sup>

per second. Figure 27.6, after Engelmann,<sup>11</sup> gives the washout coefficient as a function of particle diameter and rainfall rate. McMahon and Denison<sup>10</sup> give a table of field measurements of scavenging coefficients. This same concept can be applied to gaseous pollutants. Fewer data are available for gases. Values ranging from  $0.4 \times 10^{-5}$  to  $6 \times 10^{-5}$  for SO<sub>2</sub> are given by McMahon and Denison<sup>10</sup> and compared reasonably well with an equation for SO<sub>2</sub> by Chamberlain<sup>12</sup>:

$$\Lambda = 10 \times 10^{-5} J^{0.53} \quad (27.5)$$

where  $J$  is rainfall intensity in millimeters per hour.

## 27.3 TRANSPORT AND DISPERSION OF AIR POLLUTANTS

### 27.3.1 Wind Velocity

#### 27.3.1.1 Wind Direction

The initial direction of transport of pollutants from their source is determined by the wind direction at the source. Air pollutant concentrations from point sources are probably more sensitive to wind direction than any other parameter. If the wind is blowing directly toward a receptor (a location receiving transported pollutants), a shift in direction of as little as 5° (the approximate accuracy of a wind direction measurement) causes concentrations at the receptor to drop about 10% under unstable conditions, about 50% under neutral conditions, and about 90% under stable conditions. The direction of plume transport is very important in source impact assessment where there are sensitive receptors or two or more sources and in trying to assess the performance of a model through comparison of measured air quality with model estimates.

There is normally considerable wind direction shear (change of direction) with height, especially near the ground. Although surface friction causes the wind to shift clockwise (veer) with height near the ground, the horizontal thermal structure of the atmosphere may exert a dominating influence at higher altitudes, such that the wind will shift counterclockwise (back) with additional height. Cold air advection in an air layer will cause the wind to back with height through that layer. Warm air advection will cause veering with height.

#### 27.3.1.2 Wind Speed

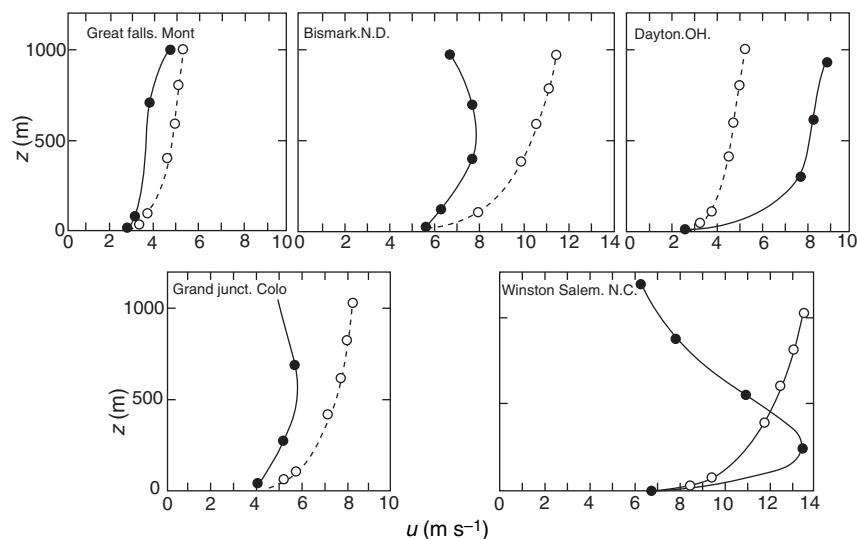
Wind speed generally increases with height. A number of expressions describe the variation of wind speed in the surface boundary layer. A power law profile has frequently been used in air pollution work:

$$u(z) = u(z_a)(z/z_a)^p \quad (27.6)$$

where  $u(z)$  is the wind speed at height  $z$ ,  $u(z_a)$  the wind speed at the anemometer measurement height  $z_a$ , and  $p$  an exponent varying from about 0.1 to 0.4. Figure 27.7 gives the measured wind speed variation with height for specific instances for five locations. The result of using the power law profile (Eqn 27.6) is also shown (open circles and dashed lines) using a value of  $p$  of 1/7. It should be noted that the power law wind profiles do not necessarily represent the data well. The exponent actually varies with atmospheric stability, surface roughness, and depth of the layer.<sup>13</sup>

One of the effects of wind speed is to dilute continuously released pollutants at the point of emission. Whether a source is at the surface or elevated, this dilution takes place in the direction of plume transport. Figure 27.8 shows this effect of wind speed for an elevated source with an emission of 6 mass units per second. For a wind speed of  $6 \text{ m s}^{-1}$ , there is 1 unit between

FIGURE 27.7 Wind variation with height—measured (solid lines) and one-seventh power law (dashed lines).



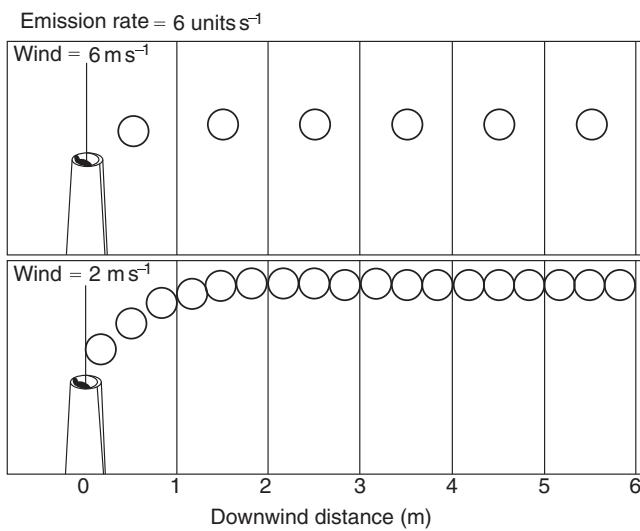


FIGURE 27.8 Dilution by wind speed.

the vertical parallel planes 1 m apart. When the wind is slowed to  $2 \text{ m s}^{-1}$ , there are 3 units between those same vertical parallel planes 1 m apart. Note that this dilution by the wind takes place at the point of emission. Because of this, wind speeds used in estimating plume dispersion are generally estimated at stack top.

Wind speed also affects the travel time from source to receptor; halving of the wind speed will double the travel time. For buoyant sources, plume rise is affected by wind speed; the stronger the wind, the lower the plume. Specific equations for estimating plume rise are presented in Chapter 2.

### 27.3.2 Turbulence

*Turbulence* is highly irregular motion of the wind. The atmosphere does not flow smoothly but has seemingly random, rapidly varying erratic motions. This uneven flow superimposed on the mean flow has swirls or eddies in a wide range of sizes. The energy cascades through the eddy sizes, which are described by L. F. Richardson in verse:

Big whirls have little whirls that feed on their velocity  
And little whirls have lesser whirls and so on to viscosity.

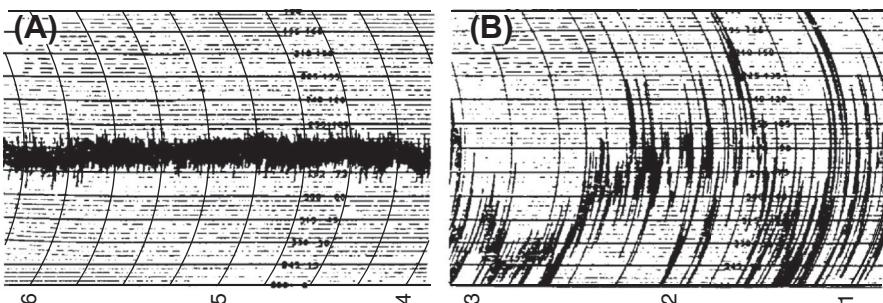
There are basically two different causes of turbulent eddies. Eddies set in motion by air moving past objects are the result of mechanical turbulence. Parcels of superheated air rising from the heated earth's surface, and the slower descent of a larger portion of the atmosphere surrounding these more rapidly rising parcels, result in thermal turbulence. The size and, hence, the scale of the eddies caused by thermal turbulence are larger than those of the eddies caused by mechanical turbulence.

The manifestation of turbulent eddies is gustiness and is displayed in the fluctuations seen on a continuous record of wind or temperature. Figure 27.9 displays wind direction traces during (A) mechanical and (B) thermal turbulence. Fluctuations due to mechanical turbulence tend to be quite regular, that is, eddies of nearly constant size are generated. The eddies generated by thermal turbulence are both larger and more variable in size than those due to mechanical turbulence.

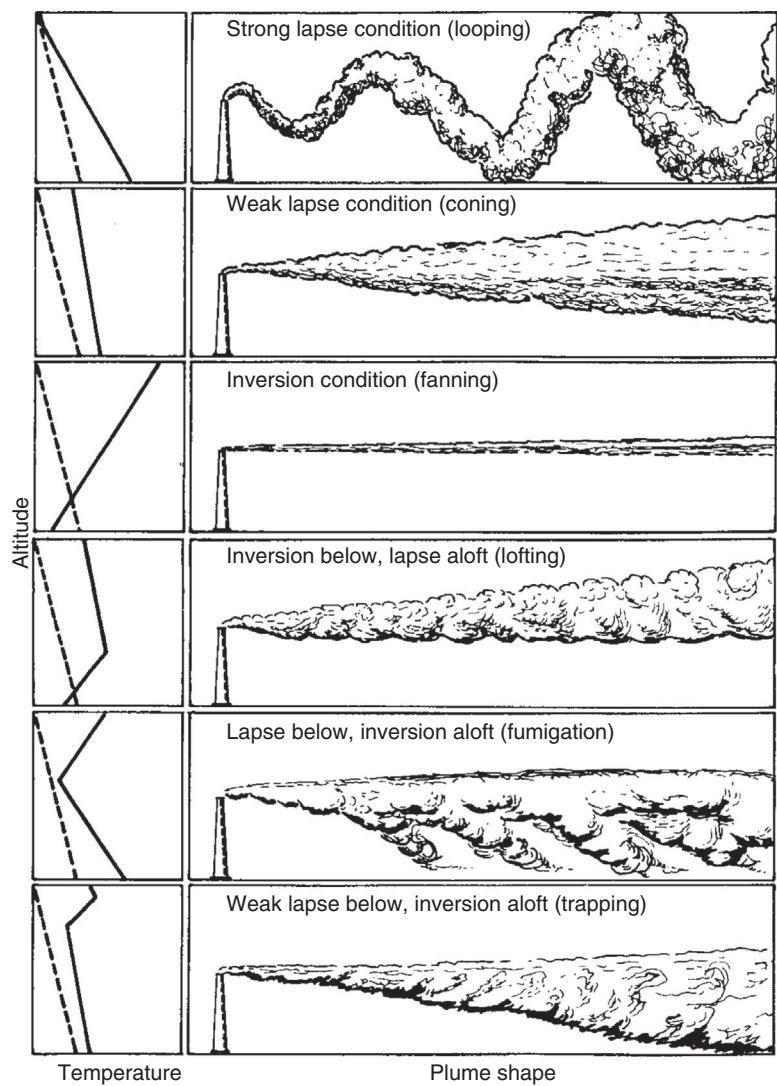
The most important mixing process in the atmosphere that causes the dispersion of air pollutants is called *eddy diffusion*. The atmospheric eddies cause a breaking apart of atmospheric parcels, which mixes polluted air with relatively unpolluted air, causing polluted air at lower and lower concentrations to occupy successively larger volumes of air. Eddy or turbulent dispersion is most efficient when the scale of the eddy is similar to that of the pollutant puff or plume being diluted. Smaller eddies are effective only at tearing at the edges of the pollutant mass. On the other hand, larger eddies will usually only transport the mass of polluted air as a whole.

The size and influence of eddies on the vertical expansion of continuous plumes have been related to vertical temperature structure.<sup>15</sup> Three appearances of instantaneous plumes related to specific lapse rates and three appearances of instantaneous plumes related to combinations of lapse rates are shown in Figure 27.10. Strong lapse is decrease in temperature with height in excess of the adiabatic lapse rate. Weak lapse is decrease in temperature with height at a rate between the dry adiabatic rate and the isothermal condition (no change of temperature with height).

A number of methods have been used to measure or estimate the level of turbulence in the atmosphere and,

FIGURE 27.9 Examples of turbulence on wind direction records: (A) mechanical and (B) thermal. From Smith.<sup>14</sup>

**FIGURE 27.10** Vertical expansion of continuous plumes related to vertical temperature structure. The dashed lines correspond to the dry adiabatic lapse rate for reference.



in turn, its dispersive ability. These methods vary from direct measurement of wind fluctuations by sensitive wind measurement systems; to classification based on the appearance of the chart record of the wind direction trace; to classification of atmospheric stability indirectly by wind speed and estimates of insolation (incoming solar radiation) or outgoing longwave radiation. Details of these methods are given in the next section.

### 27.3.3 Estimating Concentrations from Point Sources

The principal framework of empirical equations that form a basis for estimating concentrations from point sources is commonly referred to as the *Gaussian plume model*. Employing a three-dimensional axis system of downwind, crosswind, and vertical with the origin at

the ground, it assumes that concentrations from a continuously emitting plume are proportional to the emission rate, that these concentrations are diluted by the wind at the point of emission at a rate inversely proportional to the wind speed, and that the time-averaged (about 1 h) pollutant concentrations crosswind and vertically near the source are well described by Gaussian or normal (bell-shaped) distributions. The standard deviations of plume concentration in these two directions are empirically related to the levels of turbulence in the atmosphere and increase with distance from the source.

In its simplest form, the Gaussian model assumes that the pollutant does not undergo chemical reactions or other removal processes in traveling away from the source and that pollutant material reaching the ground or the top of the mixing height as the plume grows is eddy-reflected back toward the plume centerline.

### 27.3.3.1 The Gaussian Equations

All three of the Gaussian Eqns (27.7)–(27.9) are based on a coordinate scheme with the origin at the ground,  $x$  downwind from the source,  $y$  crosswind, and  $z$  vertical. The normal vertical distribution near the source is modified at greater downwind distances by eddy reflection at the ground and, when the mixing height is low, by eddy reflection at the mixing height. *Eddy reflection* refers to the movement away ("reflection") of circular eddies of air from the earth's surface, since they cannot penetrate that surface. Cross-sections in the horizontal and vertical at two downwind distances through a plume from a 20-m-high source with an additional 20 m of plume rise (to result in a 40-m effective height) are shown in Figure 27.11. The following symbols are used:

$C$  concentration, grams per cubic meter

$Q$  emission rate, grams per second

$u$  wind speed, meters per second

$\sigma_y$  standard deviation of horizontal distribution of plume concentration (evaluated at the downwind distance  $x$  and for the appropriate stability), meters

$\sigma_z$  standard deviation of vertical distribution of plume concentration (evaluated at the downwind distance  $x$  and for the appropriate stability), meters

$L$  mixing height, meters

$h$  physical stack height, meters

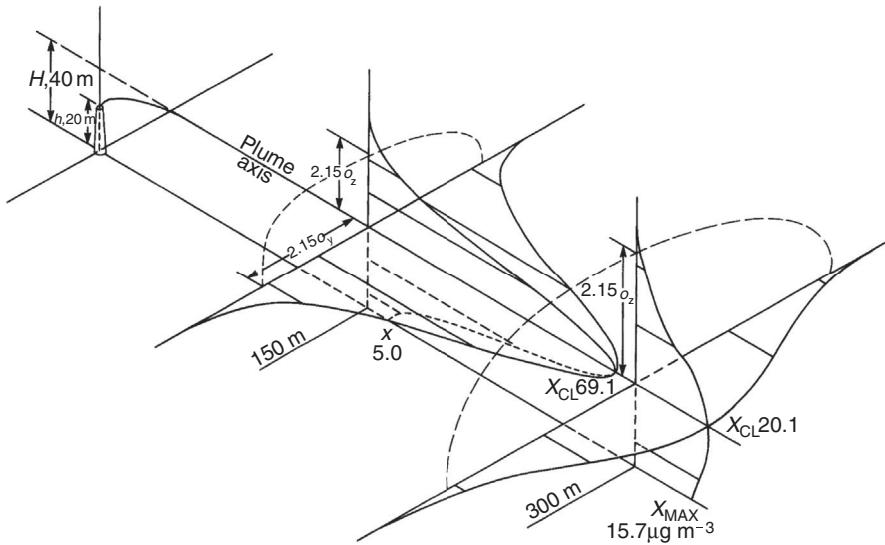
$H$  effective height of emission, meters

$x$  downwind distance, meters

$y$  crosswind distance, meters

$z$  receptor height above ground, meters

The concentration  $\chi$  resulting at a receptor at  $(x, y, z)$  from a point source located at  $(0, 0, H)$  is given by one of the three following equations. (Methods for obtaining values for the dispersion parameters  $\sigma_y$  and  $\sigma_z$  in the following equations are discussed later in this chapter.)



For stable conditions or unlimited vertical mixing (a very high mixing height), use

$$C = Q(1/u) \left\{ g_1 / [(2\pi)^{0.5} \sigma_y] \right\} \left\{ g_2 / [(2\pi)^{0.5} \sigma_z] \right\} \quad (27.7)$$

where

$$g_1 = \exp(-0.5y^2/\sigma_y^2)$$

$$g_2 = \exp[-0.5(H-z)^2/\sigma_z^2] + \exp[-0.5(H+z)^2/\sigma_z^2]$$

Note that if  $y = 0$ , or  $z = 0$ , or both  $z$  and  $H$  are 0, this equation is greatly simplified. For locations in the vertical plane containing the plume centerline,  $y = 0$  and  $g_1 = 1$ .

For unstable or neutral conditions, where  $\sigma_z$  is greater than  $1.6L$ , use the following equation to find the steady state concentration:

$$C = Q(1/u) \left\{ g_1 / [(2\pi)^{0.5} \sigma_y] \right\} (1/L) \quad (27.8)$$

For these large  $\sigma_z$  values, eddy reflection has occurred repeatedly both at the ground and at the mixing height, so that the vertical expanse of the plume has been uniformly mixed through the mixing height, i.e.  $1/L$ .

For unstable or neutral conditions, where  $\sigma_z$  is less than  $1.6L$ , use the following equation provided that both  $H$  and  $z$  are less than  $L$ :

$$C = Q(1/u) \left\{ g_1 / [(2\pi)^{0.5} \sigma_y] \right\} \left\{ g_3 / [(2\pi)^{0.5} \sigma_z] \right\} \quad (27.9)$$

where

$$g_3 = \sum_{N=-\infty}^{\infty} \left\{ \exp[-0.5(H-z+2NL)^2/\sigma_z^2] \right. \\ \left. + \exp[-0.5(H+z+2NL)^2/\sigma_z^2] \right\}$$

FIGURE 27.11 Example of two cross-sections through a Gaussian plume (total mass under curves conserved).  $H$  = effective height of emission;  $x_{MAX}$  = maximum reach of plume downwind;  $x_{CL}$  = centerline distance.

This infinite series converges rapidly, and evaluation with  $N$  varying from  $-4$  to  $+4$  is usually sufficient. These equations are used when evaluating by computer, as the series  $g_3$  can easily be evaluated.

When estimates are being made by hand calculations, Eqn (27.7) is frequently applied until  $\sigma_z = 0.8L$ . This will cause an inflection point in a plot of concentrations with distance.

By adding Eqn (27.9), which includes multiple eddy reflections, and changing the criteria for the use of Eqn (27.8) to situations in which  $\sigma_z$  is evaluated as being greater than  $1.6L$ , a smooth transition to uniform mixing, Eqn (27.8), is achieved regardless of source or receptor height. By differentiating Eqn (27.7) and setting it equal to zero, an equation for maximum concentration can be derived:

$$C_{\max} = \frac{2Q}{\pi ueH^2} \frac{\sigma_z}{\sigma_y} \quad (27.10)$$

and the distance to maximum concentration is at the distance where  $\sigma_z = H/(2)^{0.5}$ . This equation is strictly correct only if the  $\sigma_z/\sigma_y$  ratio is constant with distance.

### 27.3.3.2 Alternate Coordinate Systems for the Gaussian Equations

For estimating concentrations from more than one source, it is convenient to use map coordinates for locations. Gifford<sup>16</sup> has pointed out that the resulting calculated concentration is the same whether the preceding axis system is used or whether an origin is placed at the ground beneath the receptor, with the  $x$ -axis oriented upwind, the  $z$ -axis remaining vertical, and the  $y$ -axis crosswind.

This latter axis system is convenient in assessing the total concentration at a receptor from more than one source provided that the wind direction can be assumed to be the same over the area containing the receptor and the sources of interest.

Given an east–north coordinate system ( $R, S$ ) the upward distance  $x$  and the crosswind distance  $y$  of a point source from a receptor are given by

$$x = (S_p - S_r)\cos \theta + (R_p - R_r)\sin \theta \quad (27.11)$$

$$y = (S_p - S_r)\sin \theta - (R_p - R_r)\cos \theta \quad (27.12)$$

where  $R_p, S_p$  are the coordinates of the point source;  $R_r, S_r$  are the coordinates of the receptor; and  $\theta$  is the wind direction (the direction from which the wind blows). The units of  $x$  and  $y$  will be the same as those of the coordinate system  $R, S$ . In order to determine plume dispersion parameters, distances must be in kilometers or meters. A conversion may be

required to convert  $x$  and  $y$  above to the appropriate units.

### 27.3.3.3 Determination of Dispersion Parameters

#### 27.3.3.3.1 BY DIRECT MEASUREMENTS OF WIND FLUCTUATIONS

Hay and Pasquill<sup>17</sup> and Cramer<sup>18,19</sup> have suggested the use of fluctuation statistics from fixed wind systems to estimate the dispersion taking place within pollutant plumes over finite release times. The equation used for calculating the variance of the bearings (azimuth) from the point of release of the particles,  $\sigma_p^2$ , at a particular downwind location is

$$\sigma_p^2 = \sigma_a^2(\tau, s) \quad (27.13)$$

where  $\sigma_a^2$  is the variance of the azimuth angles of a wind vane over the sampling period  $\tau$  calculated from average wind directions averaged over averaging periods of duration  $s$ ;  $s$  equals  $T/\beta$ , where  $T$  is the travel time to the downwind location;  $T$  is equivalent to  $x/u$ , where  $x$  is the downwind distance from the source and  $u$  is the transport wind speed. Here  $\beta$  is the ratio of the timescale of the turbulence moving with the air stream (Lagrangian) to the timescale of the turbulence at a fixed point (Eulerian). Although  $\beta$  has considerable variation (from about 1 to 9), a reasonable fit to field data has been found using a value of 4 for  $\beta$ .

A similar equation can be written for vertical spread from an elevated source. The standard deviation of the vertical distribution of pollutants at the downwind distance  $x$  is given by

$$\sigma_z = \sigma_e(\tau, s)x \quad (27.14)$$

where  $\sigma_z$  is in meters and  $\sigma_e$  is the standard deviation of the elevation angle, in radians, over the sampling period  $\tau$  calculated from averaged elevation angles over averaging periods  $s$ . Here, as before,  $s$  equals  $T/\beta$  where  $T$  is travel time, and  $\beta$  can be approximated as equal to 4;  $x$  in Eqn (27.14) is in meters. In application,  $\sigma$  values can be calculated over several set averaging periods  $s$ . The distances to which each  $\sigma$  applies are then given by  $x = \beta us$ .

To calculate plume dispersion directly from fluctuation measurements, Draxler<sup>20</sup> used equations in the form

$$\sigma_y = x\sigma_a f_y \quad (27.15)$$

$$\sigma_z = x\sigma_e f_z \quad (27.16)$$

He analyzed dispersion data from 11 field experiments in order to determine the form of the functions  $f_y$  and  $f_z$ , including release height effects. Irwin<sup>21</sup> has

used simplified expressions for these functions where both  $f_y$  and  $f_z$  have the form

$$f = 1 / [1 + 0.9(T/T_0)^{0.5}] \quad (27.17)$$

where travel time  $T$  is  $x/u$ ;  $T_0$  is 1000 for  $f_y$ ;  $T_0$  is 500 for  $f_z$  for unstable (including daytime neutral) conditions; and  $T_0$  is 50 for  $f_z$  for stable (including nighttime neutral) conditions.

### 27.3.3.3.2 BY CLASSIFICATION OF WIND DIRECTION TRACES

Where specialized fluctuation data are not available, estimates of horizontal spreading can be approximated from conventional wind direction traces. A method suggested by Smith<sup>14</sup> and Singer and Smith<sup>22</sup> uses classification of the wind direction trace to determine the turbulence characteristics of the atmosphere, which are then used to infer the dispersion. Five turbulence classes are determined from inspection of the analog record of wind direction over a period of 1 h. These classes are defined in Table 27.1. The atmosphere is classified as A, B<sub>2</sub>, B<sub>1</sub>, C, or D. At Brookhaven National Laboratory, where the system was devised, the most unstable category, A, occurs infrequently enough that insufficient information is available to estimate its dispersion parameters. For the other four classes, the equations, coefficients, and exponents for the dispersion parameters are given in Table 27.2, where the source to receptor distance  $x$  is in meters.

### 27.3.3.3.3 BY CLASSIFICATION OF ATMOSPHERIC STABILITY

Pasquill<sup>24</sup> advocated the use of fluctuation measurements for dispersion estimates but provided a scheme "for use in the likely absence of special measurements of wind structure, there was clearly a need for broad

TABLE 27.1 Brookhaven Gustiness Classes

A	Fluctuations of wind direction exceeding 90°
B <sub>2</sub>	Fluctuations ranging from 45° to 90°
B <sub>1</sub>	Similar to A and B <sub>2</sub> , with fluctuations confined to a range of 15°–45°
C	Distinguished by the unbroken solid core of the trace, through which a straight line can be drawn for the entire hour without touching "open space". The fluctuations must be 15°, but no upper limit is imposed
D	The trace approximates a line. Short-term fluctuations do not exceed 15°

Based on variations of horizontal wind direction over 1 h at the height of release.  
Source: From Singer and Smith.<sup>22</sup>

TABLE 27.2 Coefficients and Exponents for Brookhaven Gustiness Classes

Type	a	b	c	d
B <sub>2</sub>	0.40	0.91	0.41	0.91
B <sub>1</sub>	0.36	0.86	0.33	0.86
C	0.32	0.78	0.22	0.78
D	0.31	0.71	0.06	0.71

Note:  $\sigma_y = ax^b$ ;  $\sigma_z = cx^d$  ( $x$  is in meters).

Source: Adapted from Gifford.<sup>23</sup>

estimates" of dispersion "in terms of routine meteorological data". The first element is a scheme that includes the important effects of thermal stratification to yield broad categories of stability. The necessary parameters for the scheme consist of wind speed, insolation, and cloudiness, which are basically obtainable from routine observations (Table 27.3).

Pasquill's dispersion parameters were restated in terms of  $\sigma_y$  and  $\sigma_z$  by Gifford<sup>26,27</sup> to allow their use in the Gaussian plume equations. The parameters  $\sigma_y$  and  $\sigma_z$  are found by estimation from the graphs (Figure 27.12), as a function of the distance between source and receptor, from the appropriate curve, one for each stability class.<sup>23</sup> Alternatively,  $\sigma_y$  and  $\sigma_z$  can be calculated using the equations given in Tables 27.4 and 27.5, which are used in the point source computer

TABLE 27.3 Pasquill Stability Categories

Surface Wind Speed (m s <sup>-1</sup> )	Isolation			Night	
	Strong	Moderate	Slight	Thinly Overcast or ≥4/8 Low Cloud	≤3/8 Cloud
<2	A	A–B	B	—	—
2–3	A–B	B	C	E	F
3–5	B	B–C	C	D	E
5–6	C	C–D	D	D	D
>6	C	D	D	D	D

(for A–B, take the average of values for A and B, etc.)

#### Notes

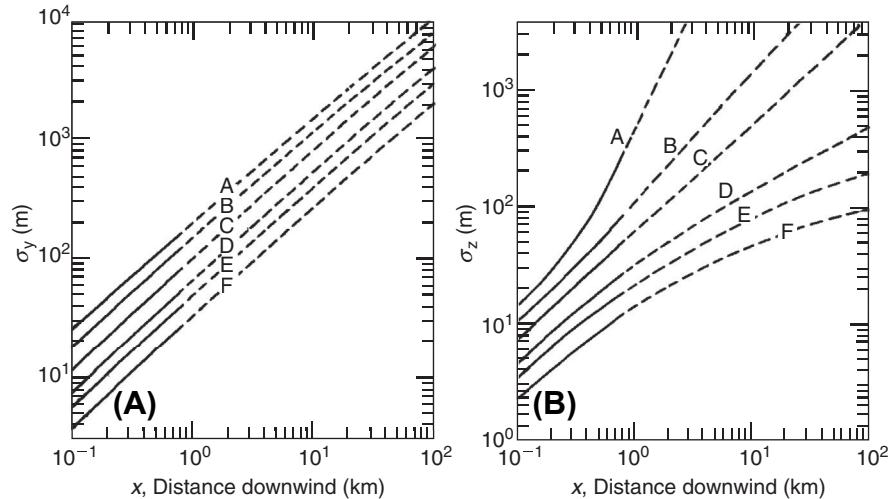
1. Strong insolation corresponds to sunny midday in midsummer in England; slight insolation to similar conditions in midwinter.

2. Night refers to the period from 1 h before sunset to 1 h after sunrise.

3. The neutral category D should also be used, regardless of wind speed, for overcast conditions during day or night and for any sky conditions during the hour preceding or following night as defined above.

Source: From Pasquill.<sup>25</sup>

FIGURE 27.12 Pasquill–Gifford: (A)  $\sigma_y$  and (B)  $\sigma_z$ . From Gifford.<sup>23</sup>



techniques PTDIS and PTMTP.<sup>28</sup> These parameter values are most applicable for releases near the ground (within about 50 m).

Other estimations of  $\sigma_y$  and  $\sigma_z$  by Briggs for two different situations, urban and rural, for each Pasquill stability class, as a function of distance between source and receptor, are given in Tables 27.6 and 27.7.<sup>23</sup>

#### 27.3.3.4 Example of a Dispersion Calculation

As an example of the use of the Gaussian plume equations using the Pasquill–Gifford dispersion parameters, assume that a source releases  $0.37 \text{ g s}^{-1}$  of a pollutant at an effective height of 40 m into the atmosphere with the wind blowing at  $2 \text{ m s}^{-1}$ . What is the approximate distance of the maximum concentration, and what is the concentration at this point if the atmosphere is appropriately represented by Pasquill stability class B?

*Solution:* The maximum occurs approximately when  $\sigma_z = H/(2)^{1/2} = 28.3 \text{ m}$ . Under B stability, this occurs at

$x = 0.28 \text{ km}$ . At this point,  $\sigma_y = 49.0 \text{ m}$  (from Table 27.4). First, the maximum can be estimated by Eqn (27.10):

$$C_{\max} = \frac{2Q}{\pi ueH^2} \frac{\sigma_z}{\sigma_y} = \frac{2(0.37)}{\pi 2e40^2} \frac{28.3}{49.0} = 1.56 \times 10^{-5} \text{ g m}^{-3}$$

To see if this is approximately the distance of the maximum, the equation

$$C = [Q/(\pi u \sigma_y \sigma_z)] \exp[-0.5(H/\sigma_z)^2] \quad (27.18)$$

which results from Eqn (27.7) with  $y$  and  $z$  equal to 0, is evaluated at three distances: 0.26, 0.28, and 0.30 km. The parameter values and the resulting concentrations are given in the following table:

$x$ (km)	$\sigma_z$ (m)	$\sigma_y$ (m)	$C$ ( $\text{g m}^{-3}$ )
0.26	26.2	45.9	$1.53 \times 10^{25}$
0.28	28.2	49.0	$1.56 \times 10^{25}$
0.30	30.1	52.2	$1.55 \times 10^{25}$

$\sigma_z$  is obtained from equations in Table 27.5.

$\sigma_y$  is obtained from equations in Table 27.4.

which verifies that, to the nearest 20 m, the maximum is at 0.28 km. Note that the concentration obtained from this equation is the same as that obtained from the approximation equation for the maximum.

Buoyancy-induced dispersion, which is caused near the source due to the rapid expansion of the plume during the rapid rise of the thermally buoyant plume after its release from the point of discharge, should also be included for buoyant releases.<sup>27</sup> The effective vertical dispersion  $\sigma_{ze}$  is found from

$$\sigma_{ze}^2 = (\Delta H/3.5)^2 + \sigma_z^2 \quad (27.19)$$

TABLE 27.4 Pasquill–Gifford Horizontal Dispersion Parameter

Stability	Parameter		
A	$T = 24.167$	$-2.5334$	$\ln x$
B	$T = 18.333$	$-1.8096$	$\ln x$
C	$T = 12.5$	$-1.0857$	$\ln x$
D	$T = 8.3333$	$-0.72382$	$\ln x$
E	$T = 6.25$	$-0.54287$	$\ln x$
F	$T = 4.1667$	$-0.36191$	$\ln x$

Note:  $\sigma_y$  (m) =  $465.116x \tan T$ ;  $x$  is downwind distance in kilometers;  $T$  is one-half Pasquill's  $\theta$  (degrees).

TABLE 27.5 Pasquill–Gifford Vertical Dispersion Parameter

Stability	Distance (km)	a	b	$\sigma_z^*$
A	>3.11			5000 m
	0.5–3.11	453.85	2.1166	
	0.4–0.5	346.75	1.7283	104.7
	0.3–0.4	258.89	1.4094	71.2
	0.25–0.3	217.41	1.2644	47.4
	0.2–0.25	179.52	1.1262	37.7
	0.15–0.2	170.22	1.0932	29.3
	0.1–0.15	158.08	1.0542	21.4
	<0.1	122.8	0.9447	14.0
	≥35			5000 m
B	0.4–35	109.30	1.0971	
	0.2–0.4	98.483	0.98332	40.0
	<0.2	90.673	0.93198	20.2
C	All x	61.141	0.91465	
D	>30	44.053	0.51179	
	10–30	36.650	0.56589	251.2
	3–10	33.504	0.60486	134.9
	1–3	32.093	0.64403	65.1
	0.3–1	32.093	0.81066	32.1
	<0.3	34.459	0.86974	12.1
E	>40	47.618	0.29592	
	20–40	35.420	0.37615	141.9
	10–20	26.970	0.46713	109.3
	4–10	24.703	0.50527	79.1
	2–4	22.534	0.57154	49.8
	1–2	21.628	0.63077	33.5
	0.3–1	21.628	0.75660	21.6
	0.1–0.3	23.331	0.81956	8.7
	<0.1	24.260	0.83660	3.5
	≥60	34.219	0.21716	
F	30–60	27.074	0.27436	83.3
	15–30	22.651	0.32681	68.8
	7–15	17.836	0.4150	54.9
	3–7	16.187	0.4649	40.0
	2–3	14.823	0.54503	27.0
	1–2	13.953	0.63227	21.6
	0.7–1.0	13.953	0.68465	14.0
	0.2–0.7	14.457	0.78407	10.9
	<0.2	15.209	0.81558	4.1

\*  $\sigma_z$  at boundary of distance range for all values except 5000 m.

Note:  $\sigma_z$  (m) =  $ax^b$ ; x is downwind distance in kilometers.

TABLE 27.6 Urban Dispersion Parameters by Briggs (for Distances between 100 and 10,000 m)

Pasquill Type	$\sigma_y$ (m)	$\sigma_z$ (m)
A–B	$0.32x(1 + 0.0004x)^{-0.5}$	$0.24x(1 + 0.001x)^{0.5}$
C	$0.22x(1 + 0.0004x)^{-0.5}$	$0.20x$
D	$0.16x(1 + 0.0004x)^{-0.5}$	$0.14x(1 + 0.0003x)^{-0.5}$
E–F	$0.11x(1 + 0.0004x)^{-0.5}$	$0.08x(1 + 0.0015x)^{-0.5}$

Source: From Gifford.<sup>23</sup>

where  $\Delta H$ , the plume rise, and  $\sigma_z$  are evaluated at the distance  $x$  from the source. Beyond the distance to the final rise,  $\Delta H$  is a constant. At shorter distances, it is evaluated for the gradually rising plume (see Chapter 2).

Since in the initial growth phases of a buoyant plume the plume is nearly symmetrical about its centerline, the buoyancy-induced dispersion in the crosswind (horizontal) direction is assumed to be equal to that in the vertical. Thus, the effective horizontal dispersion  $\sigma_{ye}$  is found from

$$\sigma_{ye}^2 = (\Delta H/3.5)^2 + \sigma_y^2 \quad (27.20)$$

The Gaussian plume equations are then used by substituting the value of  $\sigma_{ye}$  for  $\sigma_y$  and  $\sigma_{ze}$  for  $\sigma_z$ .

## 27.3.4 Dispersion Instrumentation

### 27.3.4.1 Measurements near the Surface

Near-surface (within 10 m of the ground) meteorological instrumentation always includes wind measurements and should include turbulence measurements as well. Such measurements can be made at 10 m above ground by using a guyed tower. A cup anemometer and wind vane (Figure 27.13), or a vane with a propeller speed sensor mounted in front (Figure 27.14), can be the basic wind system. The wind sensor should have a threshold starting speed of less than  $0.5 \text{ m s}^{-1}$ , an accuracy of  $0.2 \text{ m s}^{-1}$  or 5%, and a distance constant of less

TABLE 27.7 Rural Dispersion Parameters by Briggs (for Distances between 100 and 10,000 m)

Pasquill Type	$\sigma_y$ (m)	$\sigma_z$ (m)
A	$0.22x(1 + 0.0001x)^{-0.5}$	$0.20x$
B	$0.16x(1 + 0.0001x)^{-0.5}$	$0.12x$
C	$0.11x(1 + 0.0001x)^{-0.5}$	$0.08x(1 + 0.0002x)^{-0.5}$
D	$0.08x(1 + 0.0001x)^{-0.5}$	$0.06x(1 + 0.0015x)^{-0.5}$
E	$0.06x(1 + 0.0001x)^{-0.5}$	$0.03x(1 + 0.0003x)^{-1}$
F	$0.04x(1 + 0.0001x)^{-0.5}$	$0.016x(1 + 0.0003x)^{-1}$

Source: From Gifford.<sup>23</sup>



FIGURE 27.13 Microvane and three-cup anemometer. *Photo courtesy of R. M. Young Co.*

than 5 m for proper response. The primary quantity needed is the hourly average wind speed. A representative value may be obtained from values taken each minute, although values taken at intervals of 1–5 s are better.

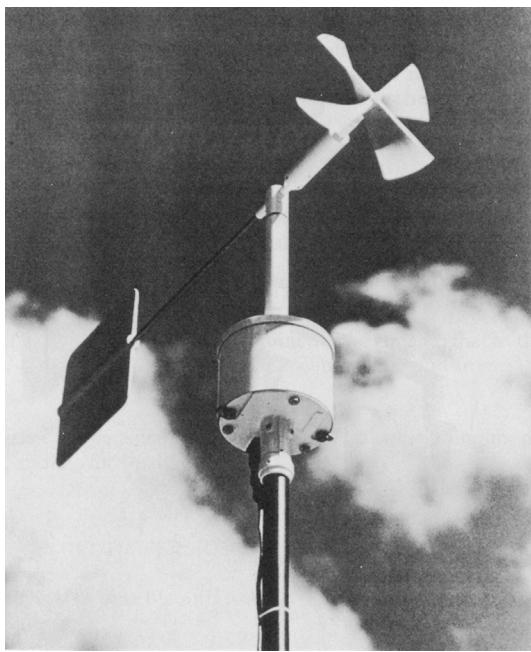


FIGURE 27.14 Propeller vane wind system. *Photo courtesy of R. M. Young Co.*

The vane can be used for both average wind direction and the fluctuation statistic  $\sigma_a$ , both determined over hourly intervals. The vane should have a distance constant of less than 5 m and a damping ratio greater than or equal to 0.4 to have a proper response. Relative accuracy should be 1° and absolute accuracy should be 5°. In order to estimate  $\sigma_a$  accurately, the direction should be sampled at intervals of 1–5 s. This can best be accomplished by microcircuitry (minicomputer) designed to sample properly the output from the vane and perform the calculations for both mean wind and  $\sigma_a$ , taking into account crossover shifts of the wind past the 360° and 0° point.

The elevation angle, and through appropriate data processing  $\sigma_e$ , can be measured with a bivane (a vane pivoted so as to move in the vertical as well as the horizontal). Bivanes require frequent maintenance and calibration and are affected by precipitation and formation of dew. A bivane is therefore more a research instrument than an operational one. Vertical fluctuations may be measured by sensing vertical velocity  $w$  and calculating  $\sigma_w$  from the output of a propeller anemometer mounted on a vertical shaft. The instrument should be placed away from other instrumentation and the propeller axis carefully aligned to be vertical. The specifications of this sensor are the same as those of the wind sensor. Because this instrument will frequently be operating near its lower threshold and because the elevation angle of the wind vector is small, such that the propeller will be operating at yaw angles where it has least accuracy, this method of measuring vertical velocity is not likely to be as accurate as the measurement of horizontal fluctuation.

Rather than using separate systems for horizontal and vertical wind measurements, a  $u-v-w$  anemometer system (Figure 27.15) sensing wind along three orthogonal axes, with proper processing to give average wind direction and  $\sigma_a$  from the combination of the  $u$  and  $v$  components and  $w$  and  $\sigma_w$  from the  $w$  component may be used.

Additional near-surface measurements may also be required to support calculated quantities such as the bulk Richardson number (a stability parameter):

$$Ri_B = \frac{gh}{T} \frac{\theta_h - \theta_z}{u_h^2}$$

which requires a temperature gradient, a temperature, and wind speed at the height of the boundary layer  $h$ . For this purpose, in addition to the wind speed at 10 m from the instrumentation, a vertical temperature difference measurement is needed. This can be obtained for the interval of 2–10 m above ground using two relatively slow response sensors wired to give the temperature difference directly. Again, hourly averages are of greatest interest. The specifications are response

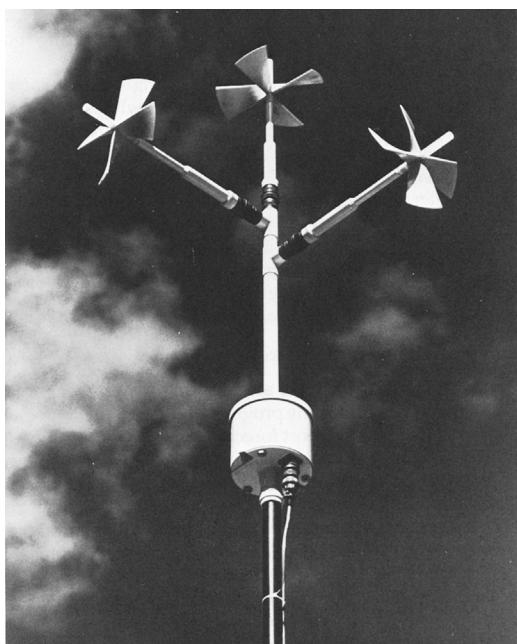


FIGURE 27.15  $U, V, W$  wind system. Photo courtesy of R. M. Young Co.

time of 1 min, accuracy of  $0.1^{\circ}\text{C}$ , and resolution of  $0.02^{\circ}\text{C}$ . Both sensors should use good-quality aspirated radiation shields to give representative values. Sensor sampling about every 30 s yields good hourly averages.

Radiation instruments are useful in determining stability such as F. B. Smith's<sup>29</sup> stability parameter  $P$ . Although somewhat similar to the Pasquill stability class (Table 27.3),  $P$  is continuous (rather than a discrete class) and is derived from wind speed and measurement of upward heat flux or, lacking this, incoming solar radiation (in daytime) and cloud amount at night. Pyranometers measure total sun and sky radiation. Net radiometers measure both incoming (mostly shortwave) radiation and outgoing (mostly longwave) radiation. Data from both are useful in turbulence characterization, and the values should be integrated over hourly periods. Care should be taken to avoid shadows on the sensors. The net radiometer is very sensitive to the condition of the ground surface over which it is exposed.

#### 27.3.4.2 Measurements above the Surface

Measurements above the surface are also important to support pollutant impact evaluation. The radiosonde program of the National Weather Service (Figure 27.16), established to support forecast and aviation weather activities, is a useful source of temperatures and data on winds aloft, although it has the disadvantage that measurements are made at 12-h intervals and the surface layer is inadequately sampled because of the fast rate of rise of the balloon. Mixing height, the height

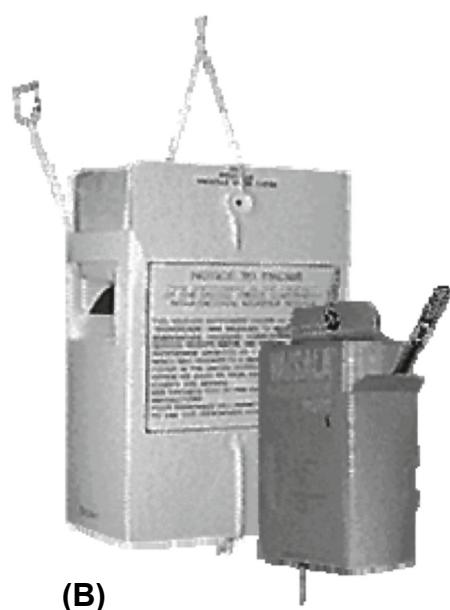
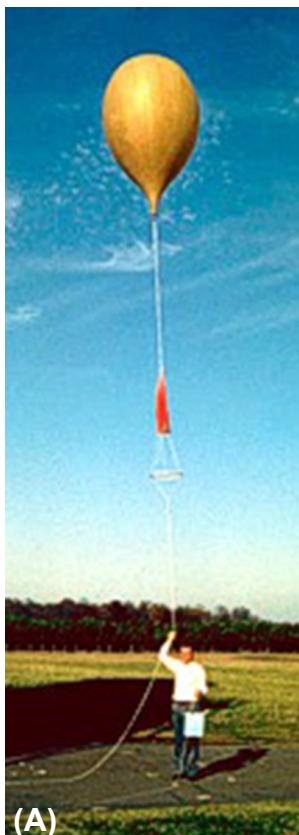


FIGURE 27.16 (A) Radiosonde launch and (B) sensor transmitter. Photos courtesy of National Oceanic and Atmospheric Administration.

above ground of the neutral or unstable layer, is calculated from the radiosonde information (see Chapter 2).

Measurements of wind, turbulence, and temperature aloft may also be made at various heights on meteorological towers taller than 10 m. Where possible, the sensors should be exposed on a boom at a distance from the tower equal to two times the diameter of the tower at that height.

Aircraft can take vertical temperature soundings and can measure air pollutant and tracer concentrations and turbulence intensity. Airborne lidar can measure plume heights, and integrating nephelometers can determine particle size distributions.

Since operating aircraft, building towers, and establishing instruments on towers are extremely expensive, considerable attention has focused on indirect upper air sounding from the ground. Mixing height within the range of measurement (approximately 500–600 m above ground) can be determined by either the Doppler or the monostatic version of sodar (sound direction and ranging) with a spatial resolution of about 30 m. Data on wind and turbulence can be determined by Doppler sodar, frequency modulated-continuous wave (FM-CW) radar, and lidar. Doppler sodar measurements of wind components are within approximately  $0.5 \text{ m s}^{-1}$  of tower measurements. Measurements represent 30-m volume averages in the vertical. A height of 500 m above ground, and sometimes over 1000 m, can be reached routinely.

Some measurements that are completely impractical for routine measurement programs are useful during periods of intensive field programs. Winds and temperatures can be measured through frequent releases of balloon-carried sensors. Lidar is useful for determining plume dimensions. The particle lidar measures backscatter of laser radiation from particles in the plume and particles in the free air. The differential absorption lidar uses two wavelengths, one with strong absorption by sulfur dioxide and the other for weak absorption. The difference determines the amount of sulfur dioxide in the plume. Positioning of the lidar and its scanning mode determines whether vertical or horizontal dimensions of the plume are measured.

#### 27.3.4.3 Data Reduction and Quality Assurance

A meteorological measurement program includes data reduction, calculation of quantities not directly measured, data logging, and archiving. Special-purpose minicomputers are used for sampling sensor output at frequent intervals (down to fractions of a second), calculating averages, and determining standard deviations. The output from the minicomputer should go to a data logger so that the appropriate information can be recorded on magnetic tape or disk or paper

tape. If only hourly values must be archived, a considerable period of record for all data from a site can be contained on a single tape, disk, or cassette. Hard copy from a printer is usually also obtained. Immediate availability of this copy can aid in detecting system or sensor malfunctions. Sometimes analog charts are maintained for each sensor to provide backup data recovery (in case of reduction error or data logger malfunction) and to detect sensor malfunction.

An extremely important part of a measurement program is an adequate quality assurance program. Cost cutting in this part of the program can result in useless measurements. A good-quality assurance program includes calibration of individual components and of the entire system in the laboratory; calibration of the system upon installation in the field; scheduled maintenance and servicing; recalibration (perhaps quarterly); and daily examination of data output for unusual or unlikely values. More frequent servicing than that recommended by manufacturers may be required when sensors are placed in polluted atmospheres that may cause relatively rapid corrosion of instrument parts.

### 27.3.5 Atmospheric Tracers

#### 27.3.5.1 Technique

Tracer studies are extremely important in furthering our knowledge of atmospheric dispersion. These studies consist of release of a known quantity of a unique substance (the tracer), with measurements of that substance at one or more downwind sampling locations. Early experiments released uranine dye as a liquid spray; the water evaporated, leaving fine fluorescent particles to be sampled. Later, dry fluorescent particles (e.g. zinc–cadmium sulfide) having a relatively narrow range of particle sizes were used. Since the early 1970s, the gas sulfur hexafluoride has been used for most tracer studies, with collection in bags at sampling locations for later laboratory analysis using electron-capture gas chromatography.

Most recently, the US Departments of Homeland Security, Energy, and Commerce, and the EPA have used perfluoride tracers (PFTs) in their Urban Dispersion Program. The PFTs have the advantage over sulfur hexafluoride in that there are a very few sources that may interfere with the measurements. In addition, the various chemical forms of PFTs can be readily identified at very low concentrations (circa parts per quadrillion). Having a number of different chemical forms allows the tracer measurements to be linked to different sources. In fact, this was accomplished in tracer studies conducted in New York City in 2005 (see Figures 27.17 and 27.18).<sup>30</sup>

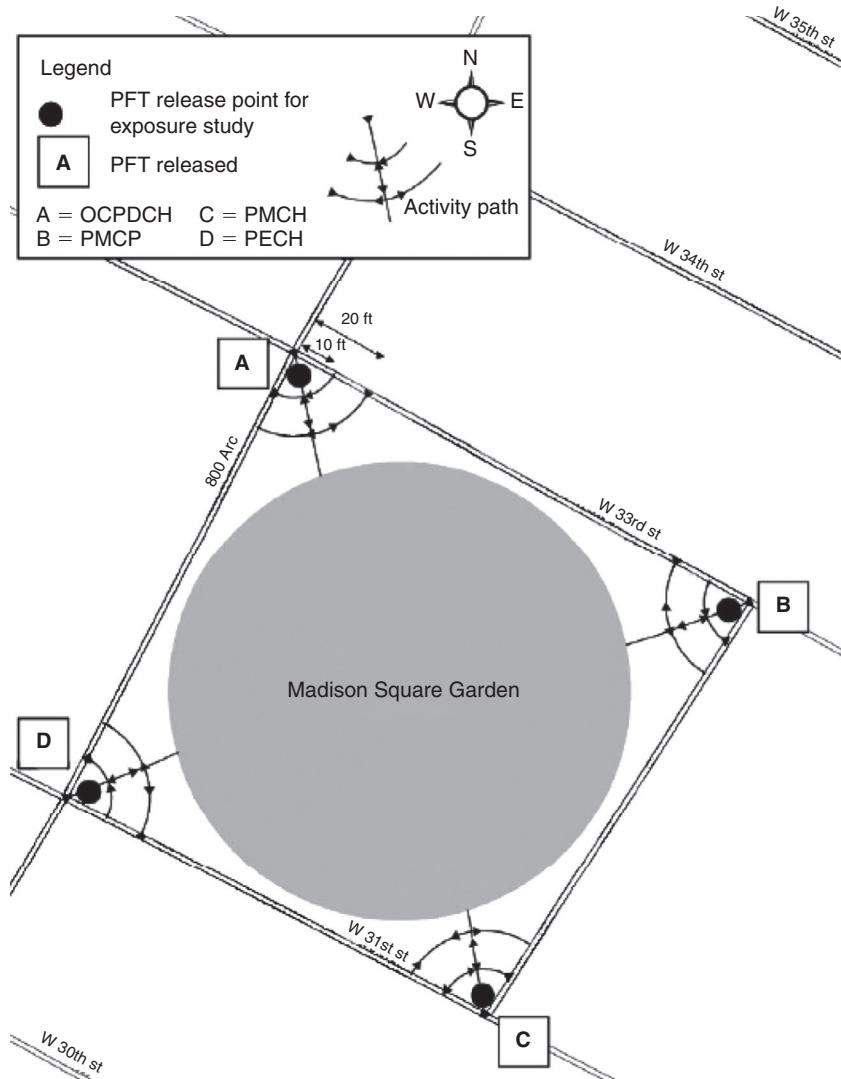


FIGURE 27.17 Location of perfluoride tracer (PFT) releases in March 2005 Urban Dispersion Program study around Madison Square Garden in New York City. The tracers are PMCP (perfluoromethylcyclopentane), oc-PDCH (perfluoro-1,2-dimethylcyclohexane), PMCH (perfluoromethyl-cyclohexane), and PECH (perfluoroethyl-cyclohexane). Ref. 30.

Tracer studies are generally conducted by going into the field for a 2-week to 1-month intensive study period. The tracer is released, generally from a constant height, continuously at a constant rate for a set period (perhaps 2–3 h) on a day selected for its meteorological conditions with the wind forecast to blow toward the sampling network. Sampling equipment is arranged at ground level on constant-distance arcs usually at three or four distances. The samplers begin at a set time as switched on by the field crew or by radio control. More sophisticated samplers allow the unattended collection sequentially of several samples. Sampling time varies from around 20 min to several hours. This procedure measures horizontal dispersion at the height of the samplers.

Although it is highly desirable to determine vertical dispersion as well by direct measurement, it is seldom practical. Sampling in the vertical can be done by sampling on fixed towers or arranging samplers along

the cables of captive balloons. Both of these methods are extremely expensive in terms of both equipment and personnel. Although it is possible to sample the tracer with aircraft, the pass through the pollutant plume occurs at such high speed that it is difficult to relate this instantaneous sample to what would occur over a longer sampling time of from 20 min to 1 h.

### 27.3.5.2 Computations

If the tracer concentration is  $\chi_i$  measured at each sampling position that has its position at  $y_i$  on a scale along the arc (either in degrees or in meters), estimates of the mean position of the plume at ground level and the variance of the ground-level concentration distribution are given by

$$y = \frac{\sum \chi_i y_i}{\sum \chi_i} \quad (27.21)$$

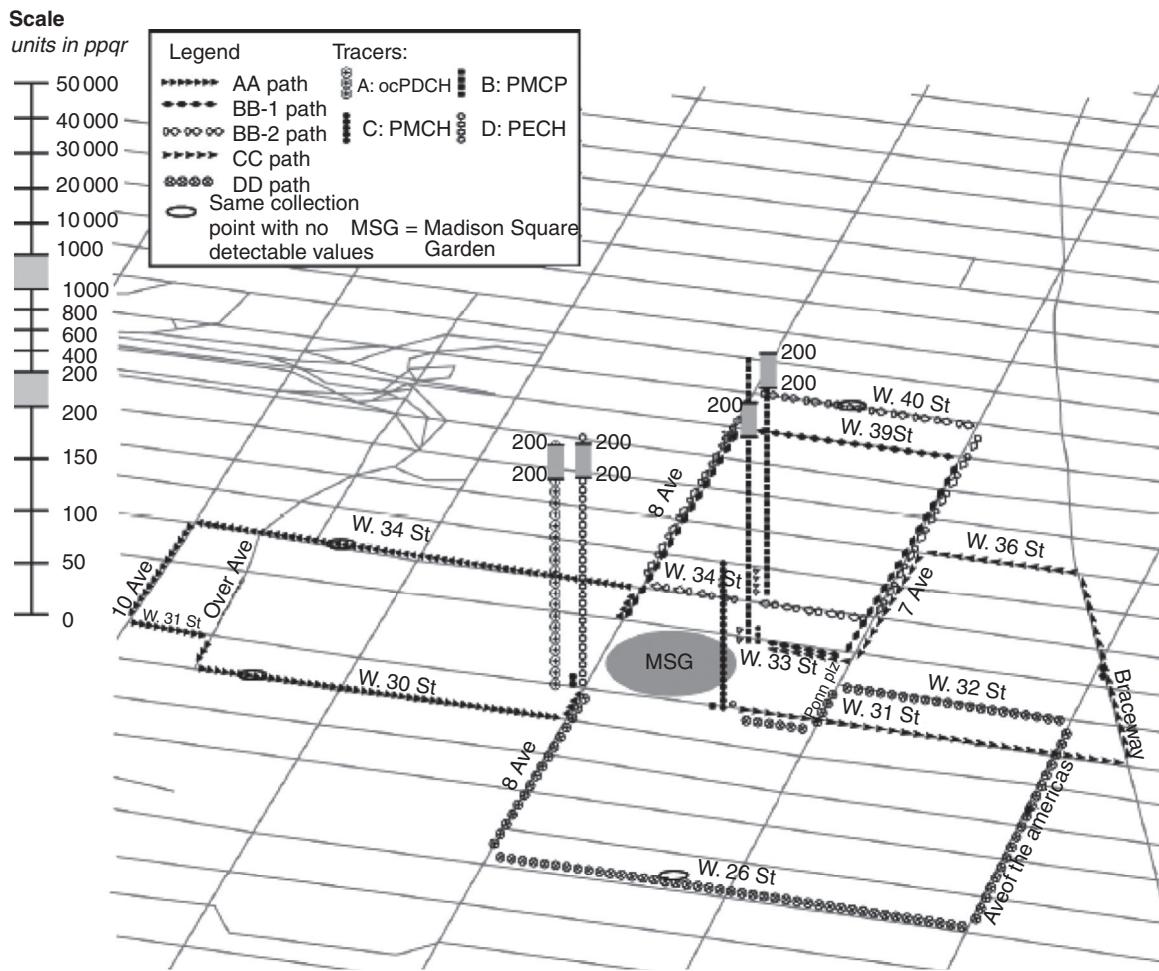


FIGURE 27.18 Neighborhood scale personal exposure monitoring, 9:00–9:30 a.m., during release of PFTs on March 10, 2005 releases in the Urban Dispersion Program study around Madison Square Garden in New York City. The tracers are PMCP (perfluoromethylcyclopentane), oc-PDCH (perfluoro-1,2-dimethylcyclohexane), PMCH (perfluoromethylcyclohexane), and PECH (perfluoroethylcyclohexane). Ref. 30.

$$\sigma_y^2 = \frac{\sum \chi_i \sum \chi_i y_i^2 - (\sum \chi_i y_i)^2}{(\sum \chi_i)^2} \quad (27.22)$$

In the example shown in Figure 27.19, measurements were made every  $2^\circ$  on an arc 5 km from the source. The mean position of the plume is at an azimuth of  $97.65^\circ$  and the standard deviation is  $4.806^\circ$ .

$$\sigma_y(m) = \sigma_y(\text{degrees}) \frac{\pi}{180} x(m) \quad (27.23)$$

In this case,  $\sigma_y$  is 419 m. The peak concentration can be found from the measurements or from the Gaussian distribution fitted to the data and the peak concentration obtained from the fitted distribution. Provided that the emission rate  $Q$ , the height of release  $H$ , and the mean wind speed  $u$  are known, the standard deviation of the vertical distribution of the pollutant can be approximated from either the peak concentration (actual or fitted) or the crosswind integrated

(CWI) concentration from one of the following equations:

$$\sigma_z \exp 0.5(H/\sigma_z)^2 = 2Q / [(2\pi)^{0.5} u \chi_{\text{CWI}}] \quad (27.24)$$

$$\sigma_z \exp 0.5(H/\sigma_z)^2 = Q / [(\pi) u \sigma_y C_{\text{peak}}] \quad (27.25)$$

The CWI concentration in grams per square meter may be approximated from the tracer measurements from

$$C_{\text{CWI}} = \text{sampler spacing (m)} \sum C_i \quad (27.26)$$

Using the data from Figure 27.20, the calculated  $\sigma_z$  from the CWI concentration is 239 m; from the observed peak concentration it is 232 m; and from the fitted peak concentration it is 235 m. Note that errors in any of the parameters  $H$ ,  $Q$ , or  $u$ , will cause errors in the estimated  $\sigma_z$ .

Although extremely useful, tracer experiments require considerable capital expenditures and personnel. In

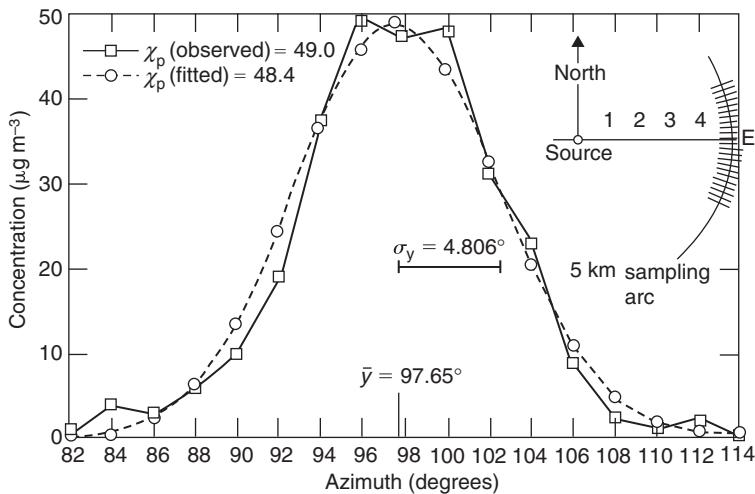


FIGURE 27.19 Example of tracer concentration measurements along a sampling arc.

addition to the difficulties and uncertainty in making estimates of various parameters, especially  $\sigma_z$ , one of the difficulties in interpreting tracer studies is relating the atmospheric conditions under which the study was conducted to the entire spectrum of atmospheric conditions. For example, trying to interpret a series of tracer experiments, even if conducted over a relatively large number of hours, in relation to the conditions that cause the second highest concentration once a year is extremely difficult, if not impossible.

### 27.3.6 Concentration Variation with Averaging Time

If emission and meteorological conditions remained unchanged hour after hour, concentrations at various locations downwind would remain the same. However, since such conditions are ever-changing, concentrations

vary with time. Even under fairly steady meteorological conditions, with the mean wind direction remaining nearly the same over a period of some hours, as the averaging time increases, greater departures in wind direction from the mean are experienced, thus spreading the time-averaging plume more and reducing the longer averaging time concentration compared with that experienced for shorter averaging times at the location of the highest concentrations. This effect is more pronounced for receptors influenced by single point sources than for those influenced by a number of point sources or by a combination of point and area sources, because there will be many hours when the wind is not blowing from the source to the receptor.

Figure 27.18 shows the maximum sulfur dioxide concentrations for eight averaging times over a 1-year period (1976) for two air monitoring stations in the Regional Air Monitoring (RAM) network in St. Louis. These two monitoring stations, 104 and 113, have the highest and lowest maximum 1-h concentrations of the 13 stations with sulfur dioxide measurements. These maximum concentrations deviate only slightly from a power law relation:

$$C_p = at_p^b \quad (27.27)$$

where  $\chi_p$  is the maximum concentration for the period  $p$ ,  $t_p$  is the averaging time in hours, and  $a$  and  $b$  are appropriate constants. The power  $b$  is  $-0.28$  for station 104 and  $0.33$  for station 113.

Larsen<sup>31–34</sup> has developed averaging time models for use in analysis and interpretation of air quality data. For urban areas where concentrations for a given averaging time tend to be lognormally distributed, that is, where a plot of the log of concentration versus the cumulative frequency of occurrence on a normal frequency distribution scale is nearly linear, the two-parameter averaging time model (Figure 27.21) is

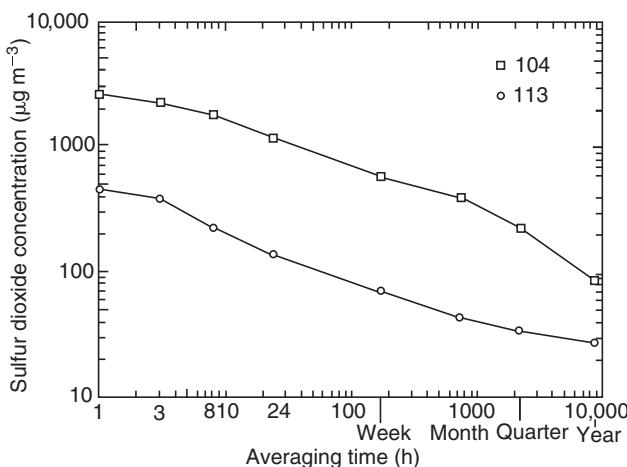
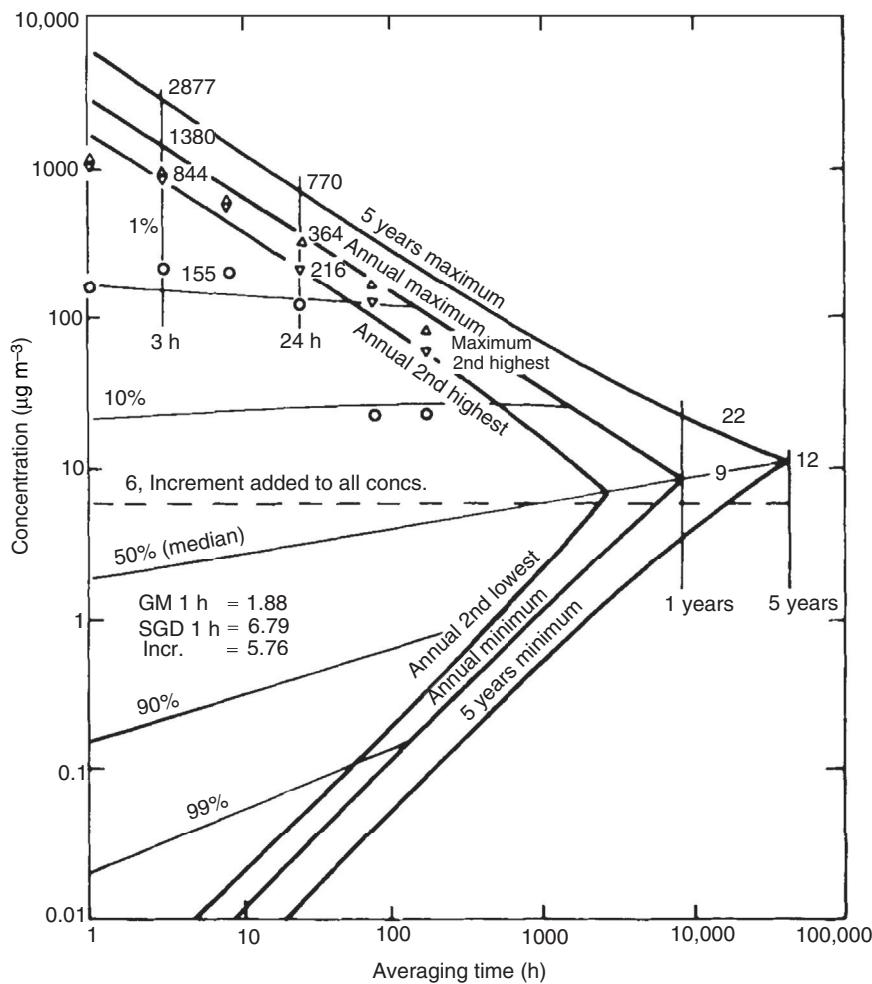


FIGURE 27.20 Variation of St. Louis SO<sub>2</sub> maximum concentrations with sampling time for locations with highest (station 104) and lowest (station 113) maximum 1-h concentrations.

FIGURE 27.21 Three-parameter averaging-time model fitted through the arithmetic mean and the second highest 3-h and 24-h SO<sub>2</sub> concentrations measured in 1972 a few miles from a coal-burning power plant. *From Larsen.*<sup>34</sup>



adequate. The two parameters are the geometric mean and the standard geometric deviation. If these two parameters for a pollutant at a site can be determined for an averaging time, the model can calculate them and the annual maximum concentration expected for any other averaging time. For receptors in the vicinity of point sources, where for a given averaging time many concentrations will be zero, a three-parameter averaging time model is required. The third parameter is an increment (positive or negative) that is added to every observed concentration. In Figure 27.21, the three-parameter model applied to data from the vicinity of a power plant, 6  $\mu\text{g m}^{-3}$  has been added to each observed concentration.

## 27.4 AIR POLLUTION MODELING AND PREDICTION

To build new facilities or to expand existing ones without harming the environment, it is desirable to

assess the air pollution impact of a facility prior to its construction, rather than construct and monitor to determine the impact and whether it is necessary to retrofit additional controls. Potential air pollution impact is usually estimated through the use of air quality simulation models. A wide variety of models is available. They are usually distinguished by type of source, pollutant, transformations and removal, distance of transport, and averaging time. No attempt has been made here to list all the models in existence at the time of this writing.

In its simplest form, a model requires two types of data inputs: information on the source or sources including pollutant emission rate and meteorological data such as wind velocity and turbulence. The model then simulates mathematically the pollutant's transport and dispersion, and perhaps its chemical and physical transformations and removal processes. The model output is air pollutant concentration for a particular time period, usually at specific receptor locations.

Impact estimates by specific models are required to meet some regulatory requirements.

### 27.4.1 Plume Rise

Gases leaving the tops of stacks rise higher than the stack top when they are either of lower density than the surrounding air (buoyancy rise) or ejected at a velocity high enough to give the exit gases upward kinetic energy (momentum rise). Buoyancy rise is sometimes called *thermal rise* because the most common cause of lower density is higher temperature. Exceptions are emissions of gases of higher density than the surrounding air and stack downwash, discussed next. To estimate effective plume height, the equations of Briggs<sup>35–39</sup> are used. The wind speed  $u$  in the following equations is the measured or estimated wind speed at the physical stack top.

#### 27.4.1.1 Stack Downwash

The lowering below the stack top of pieces of the plume by the vortices shed downwind of the stack is simulated by using a value  $h\epsilon$  in place of the physical stack height  $h$ . This is somewhat less than the physical height when the stack gas exit velocity  $v_s$  is less than 1.5 times the wind speed  $u$  (meters per second):

$$h' = h \text{ for } v_s > 1.5u \quad (27.28)$$

$$h' = h + 2d[(v_s/u) - 1.5] \text{ for } v_s < 1.5u \quad (27.29)$$

where  $d$  is the inside stack-top diameter,  $m$ . This  $h\epsilon$  value is used with the buoyancy or momentum plume rise equations that follow. If stack downwash is not considered,  $h$  is substituted for  $h\epsilon$  in the equations.

#### 27.4.1.2 Buoyancy Flux Parameter

For most plume rise estimates, the value of the buoyancy flux parameter  $F$  in  $\text{m}^4 \text{s}^{-3}$  is needed:

$$F = gv_s d^2 (T_s - T) / (4T_s) \quad (27.30)$$

$$F = 2.45v_s d^2 (T_s - T) / T_s$$

where  $g$  is the acceleration due to gravity, about  $9.806 \text{ m s}^{-2}$ ,  $T_s$  is the stack gas temperature in kelvin,  $T$  is ambient air temperature in kelvin, and the other parameters are as previously defined.

#### 27.4.1.3 Unstable–Neutral Buoyancy Plume Rise

The final effective plume height  $H$ , in meters, is stack height plus plume rise. Where buoyancy dominates, the horizontal distance  $x_f$  from the stack to where the final plume rise occurs is assumed to be at  $3x^*$ , where  $x^*$  is the horizontal distance, in kilometers, at

which atmospheric turbulence begins to dominate entrainment.

For unstable and neutral stability situations, and for  $F$  less than 55,  $H$ , in meters, and  $x_f$ , in kilometers, are

$$H = h' \times 21.425F^{3/4} / u \quad x_f = 0.049F^{5/8} \quad (27.31)$$

For  $F$  equal to or greater than 55,  $H$  and  $x_f$  are

$$H = h' \times 38.71F^{3/5} / u \quad x_f = 0.119F^{2/5} \quad (27.32)$$

#### 27.4.1.4 Stability Parameter

For stable situations, the stability parameter  $s$  is calculated by

$$s = g(\Delta\theta/\Delta z)/T$$

where  $\Delta\theta/\Delta z$  is the change in potential temperature with height.

#### 27.4.1.5 Stable Buoyancy Plume Rise

For stable conditions when there is wind,  $H$  and  $x_f$  are

$$H = h' \times 2.6[F/(us)]^{1/3} \quad x_f = 0.00207us^{-1/2} \quad (27.33)$$

For calm conditions (i.e. no wind) the stable buoyancy rise is

$$H = h' \times 4F^{1/4}S^{-3/8} \quad (27.34)$$

Under stable conditions, the lowest value of Eqn (27.33) or Eqn (27.35) is usually taken as the effective stack height.

The wind speed that yields the same rise from Eqn (27.33) as that from Eqn (27.35) for calm conditions is

$$u = 0.2746F^{1/4}S^{1/8} \quad (27.35)$$

#### 27.4.1.6 Gradual Rise: Buoyancy Conditions

Plume rise for distances closer to the source than the distance to the final rise can be estimated from

$$H = h' \times 160F^{1/3}x^{2/3} / u \quad (27.36)$$

where  $x$  is the source-to-receptor distance, kilometers. If this height exceeds the final effective plume height, that height should be substituted.

#### 27.4.1.7 Unstable–Neutral Momentum Plume Rise

If the stack gas temperature is below or only slightly above the ambient temperature, the plume rise due to momentum will be greater than that due to buoyancy. For unstable and neutral situations,

$$H = h' \times 3dv_s / u \quad (27.37)$$

This equation is most applicable when  $v_s/u$  exceeds 4. Since momentum plume rise occurs quite close to the source, the horizontal distance to the final plume rise is considered to be zero.

#### 27.4.1.8 Stable Momentum Plume Rise

For low-buoyancy plumes in stable conditions, plume height due to momentum is given by

$$H = h' \times 1.5 [(v_s^2 d^2 T) / (4T_s u)]^{1/3 - 1/6} \quad (27.38)$$

Equation (27.38) should also be evaluated and the lower value is used.

#### 27.4.1.9 Momentum–Buoyancy Crossover

There is a specific difference between stack gas temperature and ambient air temperature that gives the same result for buoyancy rise as for momentum rise. For unstable or neutral conditions this is as follows: For  $F$  less than 55,

$$(T_s - T)_c = 0.0297 T_s v_s^{1/3} / d^{2/3} \quad (27.39)$$

For  $F$  equal to or greater than 55,

$$(T_s - T)_c = 0.00575 T_s v_s^{2/3} / d^{1/3} \quad (27.40)$$

For stable conditions,

$$(T_s - T)_c = 0.01958 T_s v_s^{1/2} \quad (27.41)$$

#### 27.4.1.10 Maximum Concentrations as a Function of Wind Speed and Stability

Using an example source with  $Q = 0.37$ ,  $h = 20$ ,  $d = 0.537$ ,  $v_s = 20$ , and  $T_s = 350$ , with plume rise calculated using the above equations, maximum ground-level concentrations are shown (Figure 27.22) as functions of stability class and wind speed calculated using the Gaussian model with Pasquill–Gifford

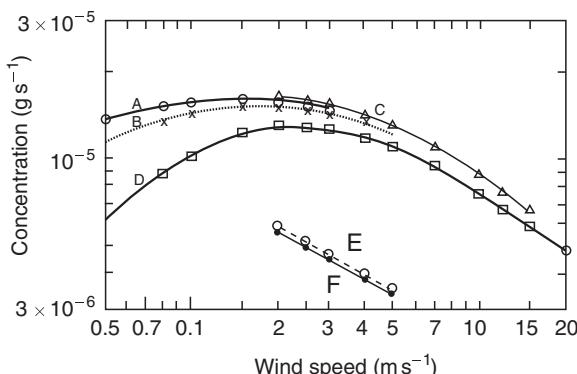


FIGURE 27.22 Concentration of an air pollutant at the point of maximum ground-level concentration as a function of wind speed and Pasquill stability category (A–F).

dispersion parameters. Maximum concentrations are nearly the same for stabilities A, B, and C and occur at wind speeds of 1.5–2.0 m s<sup>-1</sup>. The maximum for D stability occurs at around  $u = 2.5$  m s<sup>-1</sup>. Because of the competing effects of dilution by wind and lower effective stack heights with higher wind speeds, concentrations do not change rapidly with wind speed. For E and F stabilities the concentrations are nearly the same (assuming that  $\Delta\theta/\Delta z$  is 0.02 K m<sup>-1</sup> for E stability and 0.035 for F stability), but are considerably less than for the unstable and neutral cases.

#### 27.4.2 Modeling Techniques

Gaussian techniques are reasonable for estimates of concentrations of nonreactive pollutants within 20 km of point sources. It is preferable to utilize on-site wind fluctuation measurements to estimate the horizontal and vertical spreading of a pollutant plume released from a point source.

In addition to the Gaussian modeling techniques already discussed, four other methods will be considered.

##### 27.4.2.1 Box Model

Models that assume uniform mixing throughout the volume of a three-dimensional box are useful for estimating concentrations, especially for first approximations. For steady-state emission and atmospheric conditions, with no upwind background concentrations, the concentration is given by

$$\chi = \Delta x q_a / (z_i u) \quad (27.42)$$

where  $\chi$  is the steady state concentration,  $\Delta x$  is the distance over which the emissions take place,  $q_a$  is the area emission rate,  $z_i$  is the mixing height, and  $u$  is the mean wind speed through the vertical extent of the box.

When there is an upwind background concentration  $\chi_b$  and the mixing height is rising with time into a layer aloft having an average concentration of  $\chi_a$ , the equation of continuity is

$$\begin{aligned} \delta\chi/\delta t = & [\Delta x q_a + u z_i (\chi_b - \chi)] / \Delta x z_i \\ & + \Delta x (\Delta z_i / \Delta t) (\chi_a - \chi) \end{aligned} \quad (27.43)$$

This forms a basis for an urban photochemical box model (PBM)<sup>40</sup> discussed later in this chapter.

##### 27.4.2.2 Narrow Plume Hypothesis

By assuming that the principal contributors to the concentration at a receptor are the sources directly upwind, especially those nearby, the concentration due to area sources can be calculated using the vertical

growth rate rather than uniform vertical mixing and considering the specific area emission rate of each area upwind of the receptor. Area emission rate changes in the crosswind direction are neglected as being relatively unimportant. The expansion in the vertical is usually considered using the Gaussian vertical growth.<sup>41,42</sup>

#### 27.4.2.3 Gradient Transport Models

The mean turbulent flux of concentration in the vertical direction  $z$  is  $w'\chi'$ . Assuming that this turbulent flux is proportional to the gradient of concentration, and in the direction from higher to lower concentrations, an overall diffusivity  $K$  can be defined as

$$\overline{w'\chi'} = -K(\delta\chi/\delta z) \quad (27.44)$$

The change in concentration with respect to time can be written as

$$\begin{aligned} \frac{\delta\chi}{\delta t} + \left( \bar{u}\frac{\delta\chi}{\delta x} + \bar{v}\frac{\delta\chi}{\delta y} + \bar{w}\frac{\delta\chi}{\delta z} \right) &= \frac{\delta}{\delta x} K_x \frac{\delta\chi}{\delta x} + \frac{\delta}{\delta y} K_y \frac{\delta\chi}{\delta y} \\ &\quad + \frac{\delta}{\delta z} K_z \frac{\delta\chi}{\delta z} + S \end{aligned} \quad (27.45)$$

where the term in parentheses on the left accounts for advection. The terms on the right account for diffusivities in three directions,  $K_x$ ,  $K_y$  and  $K_z$  (where  $K_x$  is in the direction of the wind,  $K_y$  is horizontally crosswind, and  $K_z$  is vertically crosswind), and  $S$  represents emissions. This equation is the basis for the gradient transport model, which can handle varying wind and diffusivity fields. The vector speeds  $\bar{u}$ ,  $\bar{v}$ , and  $\bar{w}$  (where  $\bar{u}$  is in the direction of the wind,  $\bar{v}$  is horizontally crosswind, and  $\bar{w}$  is vertically crosswind) and concentrations imply both time and space scales. Fluctuations over times and distances less than these scales are considered as turbulence and are included in the diffusivities.

The gradient transport model is most appropriate when the turbulence is confined to scales that are small relative to the pollutant volume. It is therefore most applicable to continuous line and area sources at ground level, such as automobile pollutants in urban areas, and to continuous or instantaneous ground-level area sources. It is not appropriate for elevated point source diffusion until the plume has grown larger than the space scale. Numerical rather than analytical solutions of Eqn (27.45) are used.

Errors in advection may completely overshadow diffusion. The amplification of random errors with each succeeding step causes numerical instability (or distortion). Higher order differencing techniques are used to avoid this instability, but they may result in sharp gradients, which may cause negative concentrations to appear in the computations. Many of the numerical instability (distortion) problems can be overcome

with a second-moment scheme,<sup>43</sup> which advects the moments of the distributions instead of the pollutants alone. Six numerical techniques were investigated,<sup>44</sup> including the second-moment scheme; three were found that limited numerical distortion: the second-moment, the cubic spline, and the chapeau function.

In the application of gradient transfer methods, horizontal diffusion is frequently ignored, but the variation in vertical diffusivity must be approximated.<sup>9,29,45,46</sup>

#### 27.4.2.4 Trajectory Models

In its most common form, a trajectory model moves in a vertical column, with a square cross-section intersecting the ground, at the mean wind speed, with pollutants added to the bottom of the column as they are generated by each location over which the column passes. Treatment of vertical dispersion varies among models, from those that assume immediate vertical mixing throughout the column to those that assume vertical dispersion using a vertical coefficient  $K_z$  with a suitable profile.<sup>47</sup>

Modeling a single parcel of air as it is being moved along allows the chemical reactions in the parcel to be modeled. A further advantage of trajectory models is that only one trajectory is required to estimate the concentration at a given end point. This minimizes calculation because concentrations at only a limited number of points are required, such as at stations where air quality is routinely monitored. Since wind speed and direction at the top and the bottom of the column are different, the column is skewed from the vertical. However, for computational purposes, the column is usually assumed to remain vertical and to be moved at the wind speed and direction near the surface. This is acceptable for urban application in the daytime, when winds are relatively uniform throughout the lower atmosphere.

Trajectory models of a different sort are used for long-range transport, because it is necessary to simulate transport throughout a diurnal cycle in which the considerable wind shear at night transports pollutants in different directions. Expanding Gaussian puffs can be used, with the expanded puff breaking, at the time of maximum vertical mixing, into a series of puffs initially arranged vertically but subsequently moving with the appropriate wind speed and direction for each height.

#### 27.4.3 Modeling Nonreactive Pollutants

##### 27.4.3.1 Seasonal or Annual Concentrations

In estimating seasonal or annual concentrations from point or area sources, shortcuts can generally be taken rather than attempting to integrate over short intervals, such as hour-by-hour simulation. A frequent shortcut

consists of arranging the meteorological data by joint frequency of wind direction, wind speed, and atmospheric stability class, referred to as a STability ARray (STAR). The Industrial Source Complex Long Term (ISCLT)<sup>48</sup> is a model of this type and is frequently used to satisfy regulatory requirements where concentrations averaged over 1 year (but not shorter averaging times) or longer are required. Further simplification may be achieved by determining a single effective wind speed for each stability–wind direction sector combination by weighting  $1/u$  by the frequency of each wind speed class for each such wind direction–stability combination. Calculations for each sector are made, assuming that the frequency of wind direction is uniform across the sector.

#### **27.4.3.2 Single Sources: Short-term Impact**

Gaussian plume techniques have been quite useful for determining the maximum impact of single sources, which over flat terrain, occurs within 10–20 km of the source. The ISCST model<sup>48</sup> is usually used to satisfy regulatory requirements. Because the combination of conditions that produces multihour high concentrations cannot be readily identified over the large range of source sizes, it has been a common practice to calculate the impact of a source for each hour of the year for a large number of receptors at specific radial distances from the source for 36 directions from the source, e.g. every 10°. Averaging and analysis can proceed as the calculations are made to yield, upon completion of a year's simulation, the highest and second-highest concentrations over suitable averaging times, such as 3 and 24 h. Frequently, airport surface wind data have been utilized as input for such modeling, extrapolating the surface wind speed to stack top using a power law profile, with the exponent dependent on stability class, which is also determined from the surface data. Although the average hourly wind direction at stack top and plume level is likely to be different from that at the surface, this has been ignored because hourly variations in wind direction at plume level closely parallel surface directional variations. Although the true maximum concentration may occur in a somewhat different direction from that calculated, its magnitude will be closely approximated.

Several point source algorithms from the Hybrid Plume Dispersion Model<sup>49,50</sup> and a multiple source Gaussian dispersion algorithm using on-site turbulence data (TUPOS)<sup>51,52</sup> incorporate the use of fluctuation statistics (the standard deviations of horizontal and vertical wind directions) and non-Gaussian algorithms for strongly convective conditions. Because during strong convective

conditions, thermals with updrafts occupy about 30–35% of the area and slower descending downdrafts occupy 65–70% of the area, the resulting distribution of vertical motions are not Gaussian but have a smaller number of upward motions, but with higher velocity, and a larger number of downward motions, but with lower velocity. These skewed vertical motion distributions then cause non-Gaussian vertical distributions of pollutant concentrations.

#### **27.4.3.3 Multiple Sources and Area Sources**

The problem, already noted, of not having the appropriate plume transport direction takes on added importance when one is trying to determine the effects of two or more sources some distance apart, since an accurate estimate of plume transport direction is necessary to identify critical periods when plumes are superimposed, increasing concentrations.

In estimating concentrations from area sources, it is important to know whether there is one source surrounded by areas of no emissions or whether the source is just one element in an area of continuous but varying emissions.

To get an accurate estimate of the concentrations at all receptor positions from an isolated area source, an integration should be done over both the alongwind and crosswind dimensions of the source. This double integration is accomplished in the point, area, and line (PAL) source model<sup>53</sup> by approximating the area source using a number of finite crosswind line sources. The concentration due to the area source is determined using the calculated concentration from each line source and integrating numerically in the alongwind direction.

If the receptor is within an area source, or if emission rates do not vary markedly from one area source to another over most of the simulation area, the narrow plume hypothesis can be used to consider only the variation in emission rates from each area source in the alongwind direction. Calculations are made as if from a series of infinite crosswind line sources whose emission rate is assigned from the area source emission rate directly upwind of the receptor at the distance of the line source. The Atmospheric Turbulence and Diffusion Laboratory (ATDL) model<sup>54</sup> accomplishes this for ground-level area sources. The RAM model<sup>42</sup> does this for ground-level or elevated area sources.

Rather than examining the variation of emissions with distance upwind from the receptor as already described, one can simplify further by using the area emission rate of only the emission square in which the receptor resides.<sup>55</sup> The concentration  $\chi$  is then given by

$$C = Gq_a/u \quad (27.46)$$

where  $q_a$  is the area emission rate,  $u$  is the mean wind speed over the simulation period, and the constant  $G$  is dependent on the stability, the effective height of emission of the sources, and the characteristics of the pollutant. For estimation of annual concentrations with this method,  $G = 50$ , 200, and 600 for  $\text{SO}_2$ , PM, and CO, respectively.<sup>56</sup>

#### **27.4.3.4 Pollutants that Deposit**

The Fugitive Dust Model (FDM)<sup>57</sup> was formulated to estimate air concentrations as well as deposition from releases of airborne dust. It has a greatly improved deposition mechanism compared with that in previous models. It considers the mass removed from the plume through deposition as the plume is moved downwind. Up to 20 particle size fractions are available. The particle emissions caused as material is raised from the surface by stronger winds is built internally into this model. It has the capacity of making calculations for PAL sources. The area source algorithm has two options, simulation of the area source by five finite line sources perpendicular to wind flow or a converging algorithm that provides greater accuracy. Currently, the model should be used for releases at or below 20 m above ground level.

#### **27.4.3.5 Dispersion from Sources over Water**

The Offshore and Coastal Dispersion (OCD) model<sup>58</sup> was developed to simulate plume dispersion and transport from offshore point sources to receptors on land or water. The model estimates the overwater dispersion by use of wind fluctuation statistics in the horizontal and the vertical measured at the overwater point of release. Lacking these measurements, the model can make overwater estimates of dispersion using the temperature difference between water and air. Changes taking place in the dispersion are considered at the shoreline and at any point where elevated terrain is encountered.

#### **27.4.3.6 Dispersion over Complex Terrain**

Development efforts in complex terrain by US EPA researchers using physical modeling, both in the wind tunnel and in the towing tank, and field studies at three locations have resulted in the development of Complex Terrain Dispersion Model Plus Algorithms for Unstable Situations (CTDMPLUS) complex terrain dispersion model plus the calculation of concentrations for unstable conditions.<sup>59</sup> Complex terrain is the situation in which there are receptor locations above stack top. Using the meteorological conditions and the description of the

nearby terrain feature, the model calculates the height of a dividing streamline. Releases that take place below the height of this streamline tend to seek a path around the terrain feature; releases above the streamline tend to rise over the terrain feature. Because the dispersion is calculated from fluctuation statistics, the meteorological measurements to provide data input for the model are quite stringent, requiring the use of tall instrumented towers. Evaluations of both the model<sup>60</sup> and a screening technique derived from the model<sup>61</sup> indicate that the model does a better job of estimating concentrations than previous complex terrain models.

#### **27.4.4 Modeling Pollutant Transformations**

##### **27.4.4.1 Individual Plumes**

Most pollutants react after release. However, many pollutants have such long half-lives in the atmosphere, it is safe to assume for most modeling purposes that they are nonreactive. However, numerous other pollutants undergo degradation within the atmosphere to such an extent that the model needs to consider their transformation to properly predict concentrations of the parent compound. The transformation is affected by numerous factors, including cloud chemistry and other aspects of water vapor, aerosol concentrations, catalysis, and photochemistry. In fact, many of the processes described in Table 6.1 occur in the atmosphere.

An understanding of the transformation of  $\text{SO}_2$  and  $\text{NO}_x$  into other constituents no longer measurable as  $\text{SO}_2$  and  $\text{NO}_x$  is needed to explain mass balance changes from one plume cross-section to another. This loss of the primary pollutant  $\text{SO}_2$  has been described as being exponential, and rates up to 1% per hour have been measured.<sup>62</sup> The secondary pollutants generated by transformation are primarily sulfates and nitrates.

The horizontal dispersion of a plume has been modeled by the use of expanding cells well mixed vertically, with the chemistry calculated for each cell.<sup>63</sup> The resulting simulation of transformation of NO to  $\text{NO}_2$  in a power plant plume by infusion of atmospheric ozone is a peaked distribution of  $\text{NO}_2$  that resembles a plume of the primary pollutants,  $\text{SO}_2$  and NO. The ozone distribution shows depletion across the plume, with maximum depletion in the center at 20 min travel time from the source, but relatively uniform ozone concentrations back to initial levels at travel distances 1 h from the source.

##### **27.4.4.2 Urban-Scale Transformations**

Approaches used to model ozone formation include box, gradient transfer, and trajectory methods. Another method, the particle-in-cell method, advects centers of

mass (that have a specific mass assigned) with an effective velocity that includes both transport and dispersion over each time step. Chemistry is calculated using the total mass within each grid cell at the end of each time step. This method has the advantage of avoiding both the numerical diffusion of some gradient transfer methods and the distortion due to wind shear of some trajectory methods.

It is not feasible to model the reaction of each hydrocarbon species with oxides of nitrogen. Therefore, hydrocarbon species with similar reactivities are lumped together, e.g. into four groups of reactive hydrocarbons: olefins, paraffins, aldehydes, and aromatics.<sup>64</sup>

In addition to possible errors due to the steps in the kinetic mechanisms, there may be errors in the rate constants due to the smog chamber databases from which they were derived. A major shortcoming is the limited amount of quality smog chamber data available.

The emission inventory and the initial and boundary conditions of pollutant concentrations have a large impact on the ozone concentrations calculated by photochemical models.

To model a decrease in visibility, the chemical formation of aerosols from sulfur dioxide and oxidants must be simulated.

In a review of ozone air quality models, Seinfeld<sup>65</sup> indicates that the most uncertain part of the emission inventories is the hydrocarbons. The models are especially sensitive to the reactive organic gas levels, speciation, and the concentrations aloft of the various species. He points out the need for improvement in the three-dimensional wind fields and the need for hybrid models that can simulate subgrid-scale reaction processes to incorporate properly effects of concentrated plumes. Schere<sup>66</sup> points out that we need to improve the way vertical exchange processes are included in the model. Also, although the current models estimate ozone quite well, the atmospheric chemistry needs improvement to better estimate the concentrations of other photochemical components such as peroxyacetyl nitrate (PAN), the hydroxyl radical (OH), and volatile organic compounds (VOCs). In addition to the improvement of databases, including emissions, boundary concentrations, and meteorology, incorporation of the urban ozone with the levels at larger scales is needed.

#### **27.4.4.3 Regional-Scale Transformations**

In order to formulate appropriate control strategies for oxidants in urban areas, it is necessary to know the amount of oxidant already formed in the air reaching the upwind side of the urban area under various atmospheric conditions. Numerous physical and chemical processes are involved in modeling transformations<sup>67,68</sup> on the regional scale (several days, 1000 km): (1)

horizontal transport; (2) photochemistry, including very slow reactions; (3) nighttime chemistry of the products and precursors of photochemical reactions; (4) nighttime wind shear, stability stratification, and turbulence episodes associated with the nocturnal jet; (5) cumulus cloud effects—venting pollutants from the mixed layer, perturbing photochemical reaction rates in their shadows, providing sites for liquid-phase reactions, influencing changes in the mixed-layer depth, perturbing horizontal flow; (6) mesoscale vertical motion induced by terrain and horizontal divergence of the large-scale flow; (7) mesoscale eddy effects on urban plume trajectories and growth rates; (8) terrain effects on horizontal flows, removal, and diffusion; (9) subgrid-scale chemistry processes resulting from emissions from sources smaller than the model's grid can resolve; (10) natural sources of hydrocarbons, NO<sub>x</sub>, and stratospheric ozone; and (11) wet and dry removal processes, washout, and deposition.

Approaches to long-term (monthly, seasonal, annual) regional exchanges are EURMAP<sup>69</sup> for Europe and ENAMAP<sup>70</sup> for eastern North America. These two models can calculate SO<sub>2</sub> and sulfate air concentrations as well as dry and wet deposition rates for these constituents. The geographic region of interest (for Europe, about 2100 km N–S by 2250 km E–W) is divided into an emissions grid having approximately 50 by 50 km resolution. Calculations are performed by releasing a 12-h average emission increment or “puff” from each cell of the grid and tracking the trajectories of each puff by 3-h time steps according to the 850-mb winds interpolated objectively for the puff position from upper air data.

Uniform mixing in the vertical to 1000 m and uniform concentrations across each puff as it expands with the square root of travel time are assumed. A 0.01 h<sup>-1</sup> transformation rate from SO<sub>2</sub> to sulfate and 0.029 and 0.007 h<sup>-1</sup> dry deposition rates for SO<sub>2</sub> and sulfate, respectively, are used. Wet deposition is dependent on the rainfall rate determined from the surface observation network every 6 h, with the rate assumed to be uniform over each 6-h period. Concentrations for each cell are determined by averaging the concentrations of each time step for the cell, and deposition is determined by totaling all depositions over the period.

The EURMAP model has been useful in estimating the contribution to the concentrations and deposition on every European nation from every other European nation. Contributions of a nation to itself range as follows: SO<sub>2</sub> wet deposition, 25–91%; SO<sub>2</sub> dry deposition, 31–91%; sulfate wet deposition, 2–46%; sulfate dry deposition, 4–57%.

In the application of the model to eastern North America, the mixing height is varied seasonally, and hourly precipitation data are used.

## 27.4.5 Modeling Air Pollutants

### 27.4.5.1 The Need for Models

Models provide a means for representing a real system in an understandable way.<sup>a</sup> They take many forms, beginning with “conceptual models” that explain the way a system works, such as delineation of all the factors and parameters of how a particle moves in the atmosphere after its release from a power plant. Conceptual models help to identify the major influences on where a chemical is likely to be found in the environment, and as such, need to be developed to help target sources of data needed to assess an environmental problem.

In general, developing an air pollution model requires two main steps. First, a model of the domain and the processes being studied must be defined. Then, at the model boundaries, a model of the boundary conditions is especially needed to represent the influential environment surrounding the study domain. The quality of the model study is related to the accuracy and representativeness to the actual study.

### 27.4.5.2 Physical Models

Research scientists often develop “physical” or “dynamic” models to estimate the location where a contaminant would be expected to move under controlled conditions, only on a much smaller scale. For example, the US EPA’s wind tunnel facility in Research Triangle Park is sometimes used to support studies when local buildings and terrain have significant influences. For example, the wind tunnel housed a scaled model of the town of East Liverpool, Ohio and its surrounding terrain to estimate the movement of the plume from an incinerator. The plume could be observed under varying conditions, including wind direction and height of release. Like all models, the dynamic models’ accuracy is dictated by the degree to which the actual conditions can be simulated and the quality of the information that is used. More recently, the wind tunnel was used to simulate pollutant transport and dispersion in Lower Manhattan to simulate possible plumes of pollutants from the collapse of the WTC towers on September 11, 2001. The 1:600 scale model was constructed on a turn-table to test different wind directions (see Figure 27.23). In addition to the building of Lower Manhattan and the rubble pile as it appeared approximately 1 week after the collapse, smoke for visualization and tracer gas for measurement dispersion patterns were released from positions throughout the simulated 16-acre site.



**FIGURE 27.23** Example of neutrally buoyant smoke released from the WTC physical model, showing flow from left to right is displayed; natural light is illuminating the smoke and a vertical laser sheet is additionally illuminating the plume near the centerline of source. *US Environmental Protection Agency. Perry S, Heath D. Fluid modeling facility. Research Triangle Park (NC); 2006.*

The study design includes smoke visualization for a qualitative examination of dispersion in this very complex urban landscape, known as an “urban street canyon”. Detailed measurements were taken of flow velocities and turbulence, as well as concentration distribution, which suggested a number of flow phenomena that are not possible to consider using simple Gaussian dispersion algorithms given in the specific example of Figure 27.11. The Gaussian plume model can be generalized as depicted in Figure 27.24; however, these randomized models cannot represent deterministic aspects of the plume, such as vertical venting behind large/tall buildings, channeling down street canyons, and both horizontal and vertical recirculations associated with individual structures and groups of tall and tightly compacted buildings (such as the Wall Street area in the southeast edge of Manhattan, New York).

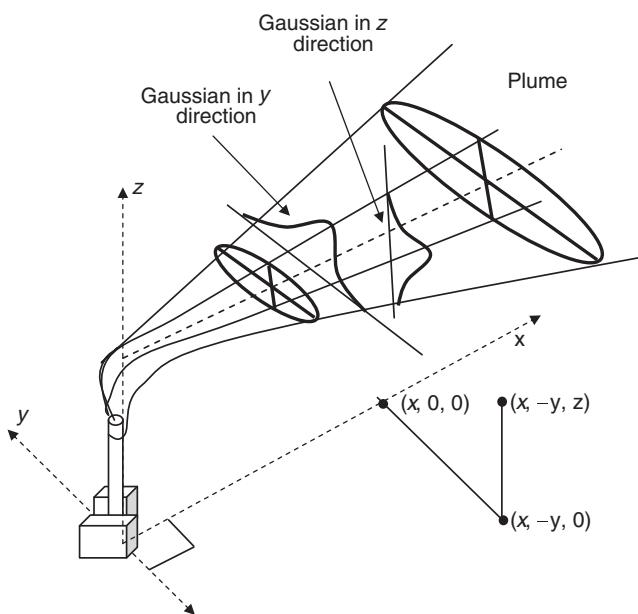
### 27.4.5.3 Numerical Simulation Models<sup>b</sup>

Numerical models apply mathematical expressions to approximate a system. System is a thermodynamic concept. Recall that we deal with three basic types of systems in air pollution sciences:

1. Isolated systems, in which no matter or energy crosses the boundaries of the system (i.e. no work can be done on the system).

<sup>a</sup>See Leete J. Groundwater modeling in health risk assessment. In: Benjamin S, Belluck D, editors. *A practical guide to understanding, managing and reviewing environmental risk assessment reports*, chapter 17. Boca Raton, FL: Lewis Publishers; 2001.

<sup>b</sup> Alan H. Huber contributed substantially to this discussion. The author appreciates these insights from one of the pioneers in the application of CFD to air pollutant transport phenomena.



**FIGURE 27.24** Generalized atmospheric plume model based on random distributions in the horizontal and vertical directions. Turner D. Workbook of atmospheric dispersion estimates. Office of Air Programs Publication No. AP-26 (NTIS PB 191 482). US Environmental Protection Agency, Research Triangle Park (NC); 1970.

2. Closed systems, in which energy can exchange with surroundings, but no matter crosses the boundary.
3. Open systems, in which both matter and energy freely exchange across system boundaries.

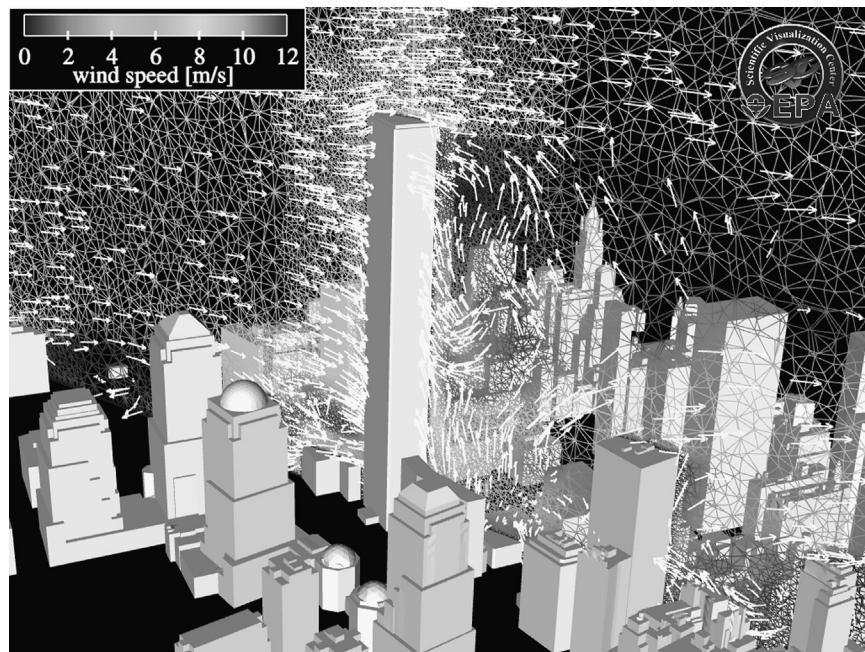
Isolated systems are usually only encountered in highly controlled reactors, so are not pertinent to this discussion. In fact, most air pollution systems are open, but with simplifying assumptions, some subsystems can be treated as closed.

Rapid advances in high performance computing hardware and software are leading to increasing applications of numerical simulation models that characterize an atmospheric plume as a system. These methods simulate spatially and temporally resolved details of the pathways of air pollutants from source emissions to pollutant concentrations within the local “virtual” microenvironment. This approach to air pollution modeling applies numerical representation of fluid flow in a fluid continuum. Such an approach is known as computational fluid dynamics (CFD), which determines a numerical solution to the governing equations of fluid flow while advancing the solution through space or time to obtain a numerical description of the complete flow field of interest. CFD models are based on the first principles of physics; in particular, they start with single-phase flow based on Navier–Stokes equations.

The Navier–Stokes equations are deterministic. They consider simultaneously the conservation of energy, momentum, and mass. Practical CFD solutions require a subgrid-scale model for turbulence. As computing capacities advance, the scale where turbulence is modeled can be reduced and the application of higher order numerical methods can support increasingly representative and accurate turbulence models. The transport and dispersion of air pollutants is part of the fluid flow solution. CFD methods have been developed and routinely applied to aerospace and automotive industrial applications and are now being extended to environmental applications.

High-fidelity fine-scale CFD simulation of pollutant concentrations within microenvironments (e.g. near roadways or around buildings) is feasible now that high-performance computing has become more accessible. Fine-scale CFD simulations have the added advantage of being able to account rigorously for topographical details such as terrain variations and building structures in urban areas as well as their local aerodynamics and turbulence. Thermal heat fluxes may be added to terrain and building surfaces to simulate the thermal atmospheric boundary layer, their influences on pollution transport and dispersion. The physics of particle flow and chemistry can be included in CFD simulations. The results of CFD simulations can be directly used to better understand specific case studies as well as to support the development of better simplified algorithms for adoption into other modeling systems. For example, CFD simulations with fine-scale physics and chemistry can enhance and complement photochemical modeling with Community Multiscale Air Quality (CMAQ). Also, detailed CFD simulation for a complex site study can be used to develop reliable parameterizations to support simplified and rapid application air pollution model.

A few examples illustrate the utility of CFD modeling. Currently the main features of CFD application are the inclusion of site-specific geometry and dynamic processes affecting air pollution transport and dispersion. The future will bring more refined spatial and temporal details, along with particle physics and chemistry. A vertical slice of the domain cells and a 10% sample of calculated wind vectors for these cells are shown in Figure 27.25. The figure demonstrates a tendency for downward airflow on the windward faces of buildings and upward airflow on the leeward building faces. Figure 27.25 shows two different looking plume depictions for ground-level point emissions. In one case, the emissions plume is caught in the leeward building updraft leading to significant vertical mixing, whereas the other case shows emissions remaining close to the ground as they move through the street canyons. Figure 27.26 shows vertical slices of concentration for roadway emissions



**FIGURE 27.25** A vertical slice of the resolved grid and sample (10%) of wind vectors in a CFD model of New York City. Courtesy: Huber AH. US Environmental Protection Agency, Research Triangle Park (NC) (unpublished work, used with permission).

represented as a box along the streets. There are significant differences for the case with a building on only one side of the roadway (A), relative to the street canyon (B), which induces a region of circulation (C).

CFD models have also found much use in estimating indoor and personal exposure to air pollutants. CFD modeling can also be used to simulate indoor air movement and pollution dispersion. For example, Furtaw<sup>c</sup> presents an example of this in a room where air movement vectors and pollutant concentration isopleths are around an emission source (represented by the small square in Figure 27.27). While CFD model simulation of every room in many buildings may not be a feasible, example case studies are possible for very critical situations or generic situations leading to the development of exposure factors for typical indoor room environments. Similarly, Settles<sup>d</sup> provides an excellent perspective on the increasing role for CFD model simulations for both ambient and indoor air concentrations as are critical to many homeland security issues involving potential human exposures. Figure 27.28 illustrates an application of CFD model simulations of trace concentrations behind a walking human. The computational solutions are obtained using Reynolds averaged numerical simulation (RANS). CFD model simulations at the human exposure

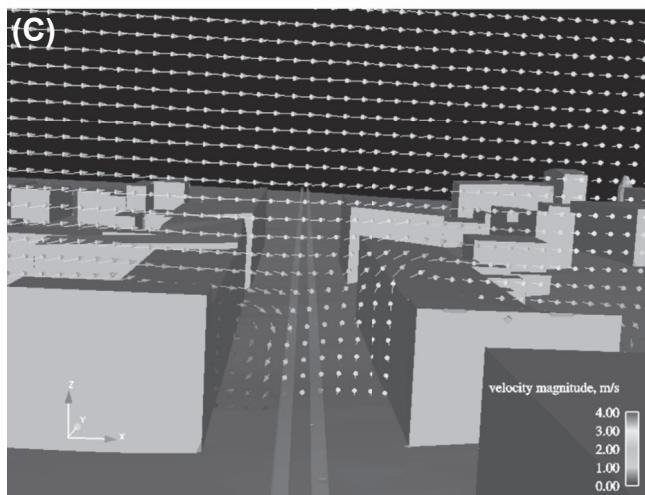
scales can be very detailed and particularly useful in developing human exposure factors applicable for more general population-based human exposure models.

Some of atmospheric concentrations of pollutants consist of a regional background concentration due to long-range transport and regional-scale mixing as well as specific local microenvironmental concentrations. Concentrations within the local microenvironment often dominate a profile of total human exposure to the pollutant. Regional air quality applications are normally applied at grid resolutions larger than 10 km. Urban applications are applied at smaller grid scales but there is a meaningful limit due to the subgrid-scale process models. In other words, there is no value in applying the model at fine scales without supporting details on the finer resolution. For example, the present framework of the CMAQ modeling system well supports environmental issues where large-sized grid-averaged concentrations are applicable. For example, regional emission control strategies are especially applicable while specific profiles of human exposure concentrations are not.

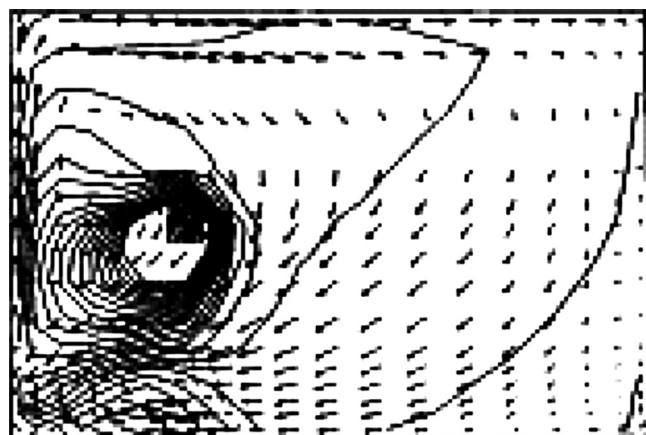
The large grid-sized modeling system may be used for estimating profiles of human exposure for pollutants having coarse temporal and spatial distributions. Human exposure concentrations on the subgrid scales

<sup>c</sup> Furtaw EJ. An overview of human exposure modeling activities at the USEPA's National Exposure Research Laboratory. *Toxicol Ind Health* 2001;17(5–10):302–14.

<sup>d</sup> Settles GS. Fluid mechanics and homeland security. *Annu Rev Fluid Mech* 2006;38:87–110.



**FIGURE 27.26** Vertical slice view of a CFD model of roadway emissions represented as a source box along the roadway: (A) concentrations for street bounded by building on one side; (B) concentrations for street canyon; and (C) wind vectors for street canyon. Courtesy: *Unpublished work by Huber AH. US Environmental Protection Agency, Research Triangle Park (NC)*.



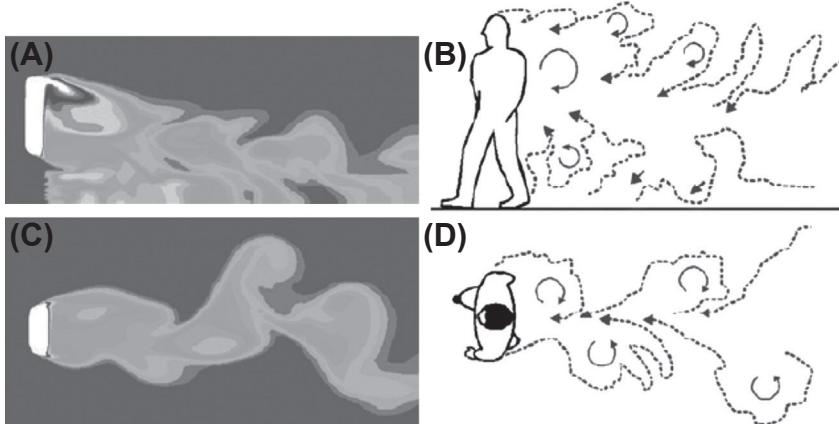
**FIGURE 27.27** CFD model simulation of indoor air in a room. Furtaw EJ. An overview of human exposure modeling activities at the US EPA's National Exposure Research Laboratory. *Toxicol Ind Health* 2001; 17(5–10):302–14.

need to apply a subgrid-scale model including human exposure factors to estimate exposed populations (such as that shown in Figure 27.29). Such constraints related to local-scale air pollution and human exposure will be further discussed in the modeling sections below. Advances in numerical simulations models will continue to supplement and to improve the more simplified models presented in the following sections, particularly for simulations where building environments and complex terrain are significant.

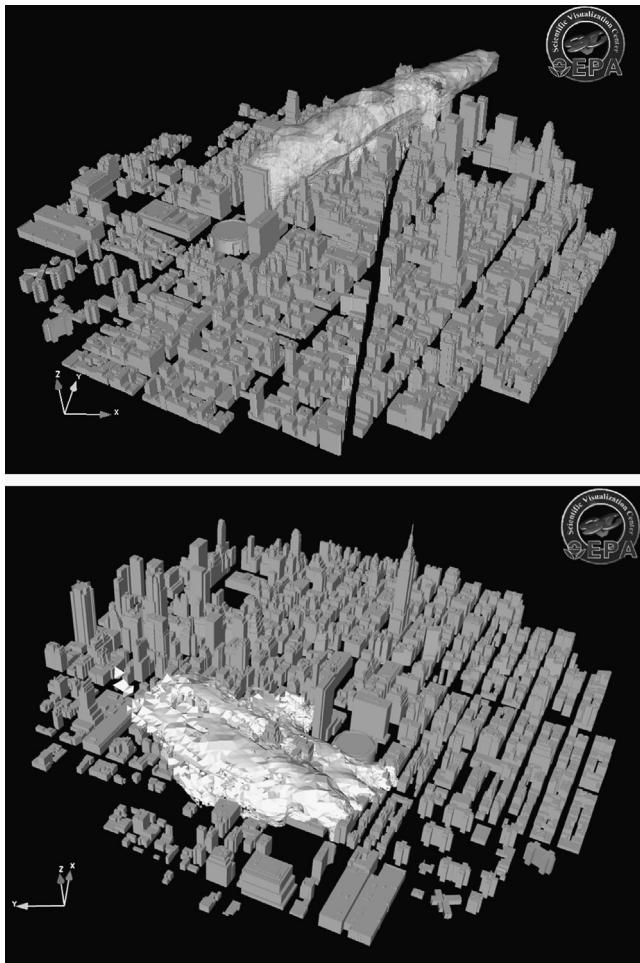
Transport and fate models can be statistical and/or “deterministic”. Statistical models include the pollutant dispersion models, such as the Lagrangian models, which assume Gaussian distributions of pollutants from a point of release (see Figure 27.24). That is, the pollutant concentrations are normally distributed in both the vertical and horizontal directions from the source. The Lagrangian approach is common for atmospheric releases. “Stochastic” models are statistical models that assume that the events affecting the behavior of a chemical in the environment are random, so such models are based on probabilities.

Deterministic models are used when the physical, chemical, and other processes are sufficiently understood so as to be incorporated to reflect the movement and fate of chemicals. These are very difficult models to develop because each process must be represented by a set of algorithms in the model. Also, the relationship between and among the systems, such as the kinetics and mass balances, must also be represented.

Thus, the modeler must “parameterize” every important event following a chemical’s release to the environment. Often, hybrid models using both statistical and deterministic approaches are used, for example, when one part of a system tends to be more random, while another has a very strong basis in physical principals. Numerous models are available to address the movement



**FIGURE 27.28** The instantaneous trace contaminant concentration in the wake of a walking person, from Edge et al. (2005). Frames (A) and (C) are Reynolds average numerical simulation (RANS) solutions using a blended  $k - \bar{w}$ / $k - \varepsilon$  2-equation turbulence model and a simplified representation of the human body. Frames (B) and (D) are drawn from flow visualization experiments of an actual walking person. A side view is depicted in frames (A) and (B); frames (C) and (D) show the top view. Settles GS. *Fluid mechanics and homeland security*. Annu Rev Fluid Mech 2006;38:87–110.



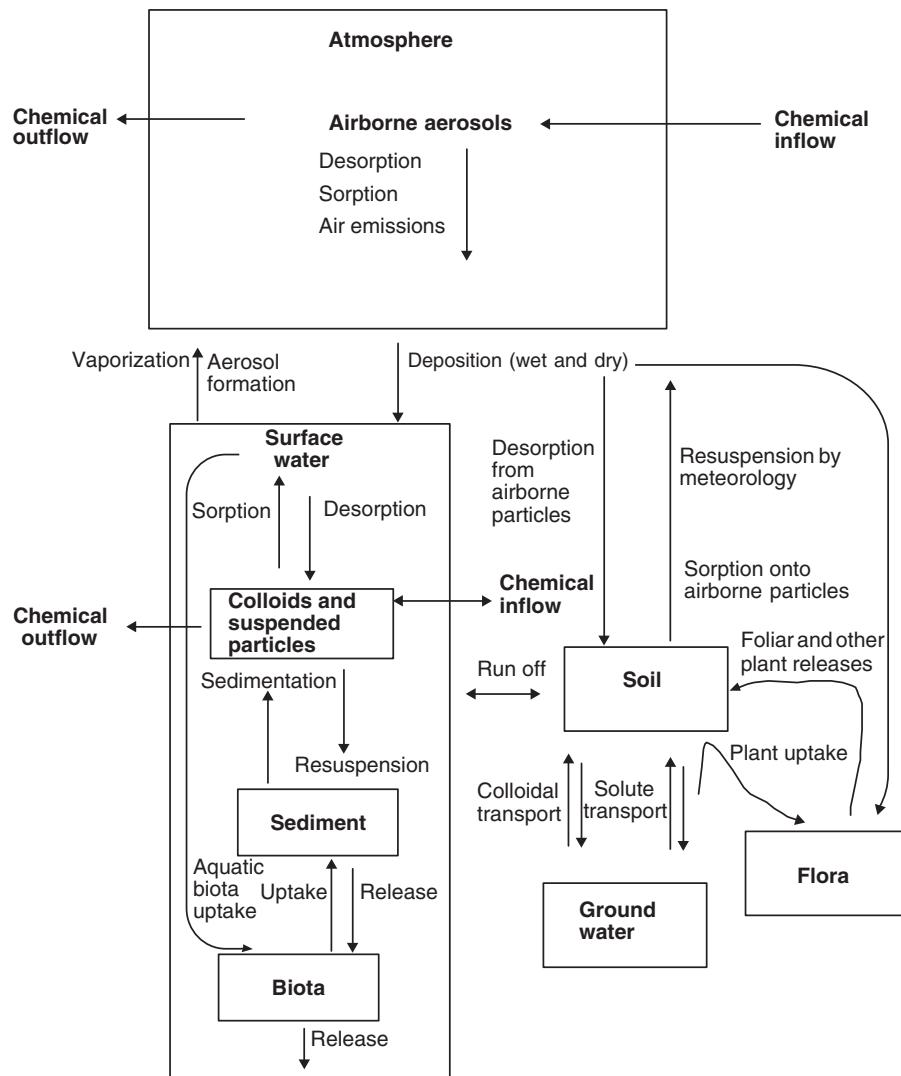
of chemicals through a single environmental media, but increasingly, environmental scientists and engineers have begun to develop “multimedia models”, such as compartmental models that help to predict the behavior and changes to chemicals as they move within and among the soil, water, air, sediment, and biota (see Figure 27.30).<sup>e</sup> Such models will likely see increased use in all environmental science and engineering.

Environmental chemodynamics describe the movement and change of chemicals in the environment (see Chapter 6). From an air pollution modeling perspective, the air is among one compartment among many. Most air pollution modeling is conducted as if the troposphere were the only compartment. This is usually a reasonable approach. However, influences shown in Figure 27.30 are always present. Air is a medium by which pollutants are transported. It is also the location of chemical reactions and physical changes, such as the agglomeration of smaller particles and the formation of particles from gas-phase pollutants. Fluid properties have a great bearing on the movement and distribution of contaminants. However, specific partitioning relationships that control the “leaving” and “gaining” of pollutants among particle, soil, and sediment surfaces, the atmosphere, organic tissues, and water can also be

**FIGURE 27.29** Plumes from ground-level point source emissions in a CFD model of New York City (midtown area). Huber AH. US Environmental Protection Agency, Research Triangle Park (NC) (unpublished work, used with permission).

<sup>e</sup>The compartmental or “box and arrow” models such as the one in Figure 27.30 are being enhanced by environmental scientists and chemical engineers. They depict of the first law of thermodynamics, with each box representing a control volume of a given substance, e.g. incoming air pollutant, changes due to reactions within the control volume, and exiting substances, i.e. the parent compound and its degradation products. Much of the information in this figure can be attributed to discussions with Yoram Cohen, a chemical engineering professor at UCLA, and Ellen Cooter, a National Oceanic and Atmospheric Administration modeler on assignment to the US EPA’s National Exposure Research Laboratory in Research Triangle Park, NC.

**FIGURE 27.30** Example framework and flow of a multimedia, compartmental chemical transport, and transformation model. Algorithms and quantities must be provided for each box. Equilibrium constants (e.g. partitioning coefficients) must be developed for each arrow and, steady state conditions may not be assumed, reaction rates and other chemical kinetics must be developed for each arrow and box.



applied to model where a chemical ends up and the chemical form it assumes. This is known as environmental fate. These relationships are sorption, solubility, volatilization, and organic carbon–water partitioning, which are, respectively, expressed by coefficients of sorption (distribution coefficient ( $K_D$ ) or solid–water partition coefficient ( $K_p$ )), dissolution or solubility coefficients, air–water partitioning (and the Henry's law ( $K_H$ ) constant), and organic carbon–water ( $K_{oc}$ ). These equilibrium coefficients are discussed in detail in Chapter 18.

#### 27.4.5.4 Using Models to Predict Air Pollution

Air quality models mathematically simulate the physical and chemical processes that affect air pollutants as they disperse and react in the atmosphere. Meteorological data and source information (e.g. emission rates and stack height) are put into models to

characterize pollutants that are emitted directly into the atmosphere. Air quality modelers generally refer to these as primary pollutants. Secondary pollutants, those that form as a result of complex chemical reactions within the atmosphere, can also be modeled. Models are a key component of air quality management at all scales. They are widely used by local, state, and federal agencies charged with addressing air pollution, especially to identify source contributions to air quality problems and to help to design effective strategies aimed at reducing air pollutants. Models can be used to verify that before issuing a permit, a new source will not exceed ambient air quality standards or, if appropriate, to agree on appropriate additional control requirements. Models are useful as prediction tools, for example, to estimate the future pollutant concentrations from multiple sources after a new regulatory program is in place. This gives a

measure of the expected effectiveness of various options in reducing harmful exposures to humans and the environment.

#### 27.4.5.5 Dispersion Modeling

Dispersion modeling is used to predict concentrations at selected downwind receptor locations. According to the EPA, these air quality models help to determine compliance with National Ambient Air Quality Standards (NAAQS), and other regulatory requirements such as New Source Review (NSR) and Prevention of Significant Deterioration (PSD) regulations.<sup>f</sup> These guidelines are periodically revised to ensure that new model developments or expanded regulatory requirements are incorporated. The EPA recommends the atmospheric modeling system (AERMOD) be used by states and local regulators to determine their progress in reducing criteria air pollutants under the Clean Air Act (CAA). AERMOD is a steady state plume model that incorporates air dispersion based on planetary boundary-layer turbulence structure and scaling concepts, including treatment of both surface and elevated sources, and both simple and complex terrain.

AERMOD is better able to characterize plume dispersion than the model it replaced, the Industrial Source Complex 3 (ISC3), which had been EPA's preferred model since 1980. In particular, AERMOD can simulate elevated air pollution sources as well as those at the surface, and can assimilate both simple and complex terrain (see Figure 27.31). A substantial advance is that AERMOD makes use of updated physics algorithms. Thus, since November 9, 2006, AERMOD replaced ISC3 as the EPA's preferred general-purpose model. Regulators now use it to estimate local levels of ozone, VOCs, carbon monoxide, NO<sub>2</sub>, SO<sub>2</sub>, PM, and lead. Areas that have been unable to attain CAA standards for these criteria pollutants are required to use AERMOD to revise their State Implementation Plans (SIPs) for existing air pollution sources. States must also use AERMOD for their NSR and PSD determinations.

AERMOD modeling can be used to extrapolate from a limited number of data points. For example, it was recently used by the EPA in its regulatory impact analysis of the new standard for particulates by comparing a number of regulatory scenarios in terms of the costs and human health and welfare

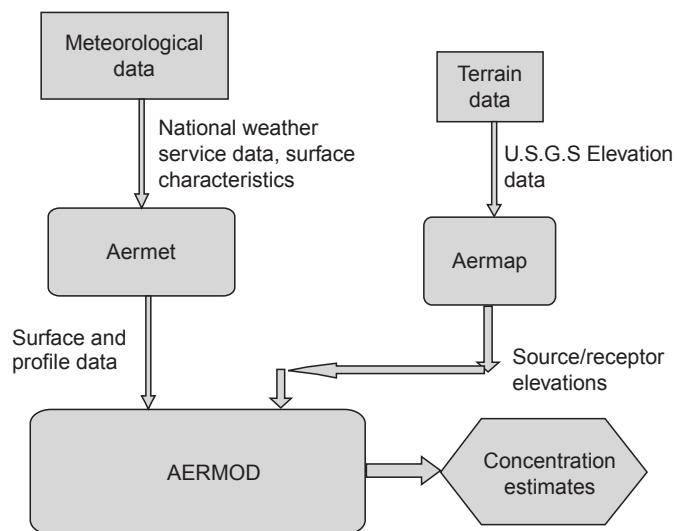


FIGURE 27.31 Flow and processing of the complete AERMOD modeling system, which consists of the AERMOD dispersion model and two preprocessors. US Environmental Protection Agency.

benefits. In this case, the comparison was among scenarios associated with attaining both the selected and one alternative standard for annual and daily PM<sub>2.5</sub> concentrations:

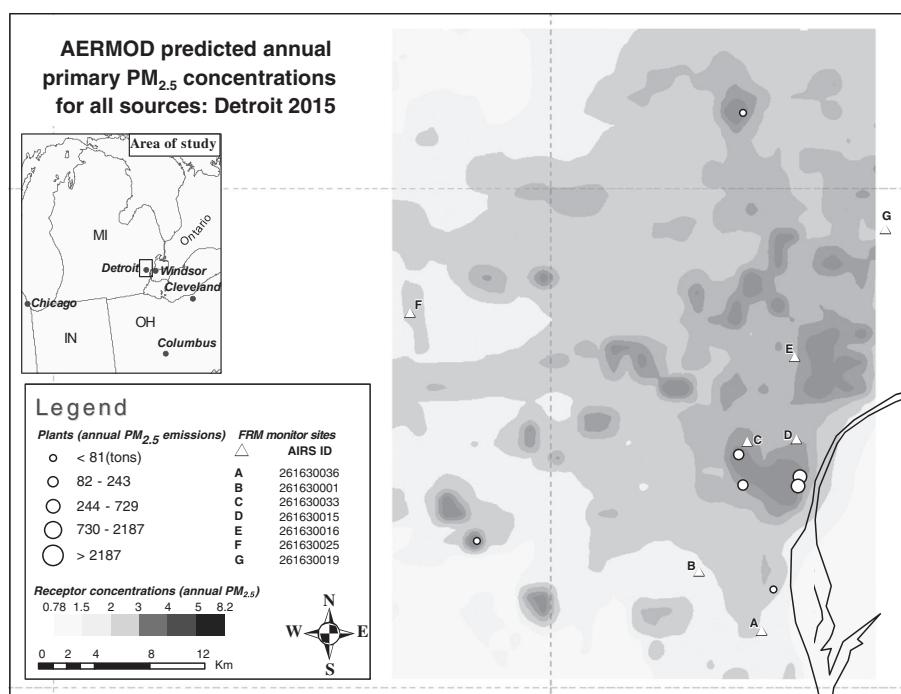
Combination of Annual and Daily Values (Annual/Daily in $\mu\text{g m}^{-3}$ )	Scenario
15/65	1997 Standards
15/35	New standard
14/35	Alternative

One of the urban areas compared in analysis was Detroit, Michigan. The primary PM<sub>2.5</sub> impacts at monitor locations in Wayne County, Michigan; the model shows locations where the annual (15  $\mu\text{g m}^{-3}$ ) and daily (35  $\mu\text{g m}^{-3}$ ) standards may well be exceeded.<sup>g</sup> Figure 27.32 provides the spatial gradient of primary PM<sub>2.5</sub> for the urban area associated with emissions from all sources. The model shows that this particular Wayne County monitor is expected to exceed 15  $\mu\text{g m}^{-3}$  by 2.4  $\mu\text{g m}^{-3}$  in the year 2015. This indicates that local sources of primary PM<sub>2.5</sub> contribute 3.3  $\mu\text{g m}^{-3}$ .

<sup>f</sup>These models are addressed in Appendix A of EPA's *Guideline on Air Quality Models* (also published as Appendix W of 40 CFR Part 51), which was originally published in April 1978 to provide consistency and equity in the use of modeling within the US air quality management system.

<sup>g</sup>US Environmental Protection Agency. *Regulatory impact analysis for the revised particulate matter*. National Ambient Air Quality Standards; 2006.

**FIGURE 27.32** Spatial gradient in Detroit, MI of AERMOD predicted annual primary PM<sub>2.5</sub> concentrations (micrograms per cubic meter) for all sources: 2015. Note: Dashed line reflects the 36-km grid cells from regional-scale modeling with CMAQ model.



to this monitor location and that the application of controls for the 15/65 scenario would yield a  $0.56 \mu\text{g m}^{-3}$  reduction in PM<sub>2.5</sub> concentrations. The modeling results indicate little additional reductions at this monitor for the 15/35 scenario but an additional  $0.46 \mu\text{g m}^{-3}$  reduction in PM<sub>2.5</sub> concentrations for the 14/35 scenario. The AERMOD simulations of annual and daily exceedances are shown in [Tables 27.8](#) and [27.9](#), respectively.

In 1991, the California Air Resources Board issued the first version of CALPUFF, an advanced, integrated Gaussian puff modeling system. The EPA recommends CALPUFF for nonsteady state conditions. Since CALPUFF is a multilayer, multispecies nonsteady state puff dispersion model, it can be used to simulate the effects of time- and space-varying meteorological conditions on pollution transport, transformation, and removal. It can be applied at scales of tens to hundreds of kilometers. It includes algorithms for subgrid-scale effects (such as terrain impingement), as well as longer range effects (such as pollutant removal due to wet scavenging and dry deposition, chemical transformation, and visibility effects of PM concentrations). Thus, CALPUFF is particularly useful for long-range pollutant transport and for complex terrain. The system actually consists of three parts. In addition to CALPUFF, it includes a diagnostic three-dimensional meteorological

model (CALMET), as well as postprocessing package (CALPOST).

CALPUFF is one of the models used to characterize the plume from Ground Zero at WTC in New York City. The predicted plumes provided general insights into the likely pathway for pollutant emissions released from the collapse and the fire at the WTC site, both temporally and spatially (see [Figure 27.33](#)). Huber et al.<sup>h</sup> give some perspective about the use of CALPUFF:

A CALMET–CALPUFF-type modeling system cannot provide as precise an estimate of pollution levels as fuller physics models might, is considered to be adequate for many applications. Even without the precise concentrations, knowing generally where the plume may have been can still help determine where to conduct more refined modeling of human exposures and where to study the population exposure in epidemiological studies. Having such results rapidly as a forecast or screening model could be very valuable to decision makers.

Other models used by regulatory agencies include

- **Buoyant Line and Point Source (BLM):** A Gaussian plume dispersion model designed to handle unique modeling problems associated with aluminum reduction plants and other industrial sources where plume rise and downwash effects from stationary line sources are important.

<sup>h</sup> Huber A, Georgopoulos P, Gilliam R, Stenchikov G, Wang S-W, Kelly B, et al. Modeling air pollution from the collapse of the World Trade Center and assessing the potential impacts on human exposures. *Environ Manage* February 2004;23–6.

TABLE 27.8 Summary of Modeled Source Contributions of Primary PM<sub>2.5</sub> to Monitors with Potential Annual Exceedances in Detroit, Michigan, for the Year 2015

Source Sectors	Model Predicted Annual Concentrations ( $\mu\text{g m}^{-3}$ )*				
	Primary PM <sub>2.5</sub> Emissions (ton year <sup>-1</sup> )	Primary PM <sub>2.5</sub> Contribution	15/65 Control Scenario	15/35 Control Scenario	14/35 Control Scenario
<b>WAYNE COUNTY MONITOR #261630033, ANNUAL DV = 17.4</b>					
Other industrial sources	1375	0.712	0.171	0.000	0.222
CMV, aircraft, locomotive	638	0.540	0.191	0.000	0.000
Metal processing	852	0.484	0.037	0.000	0.000
Onroad (gasoline and diesel)	1187	0.336	0.000	0.025	0.025
Commercial cooking	984	0.271	0.050	0.000	0.000
Area fugitive dust	10,270	0.237	0.000	0.000	0.000
Power sector	18,016	0.233	0.059	0.000	0.014
Other area	888	0.210	0.000	0.000	0.168
Nonroad (gasoline and diesel)	1603	0.197	0.033	0.019	0.019
Natural gas combustion	119	0.034	0.000	0.000	0.000
Residential wood burning	703	0.026	0.005	0.000	0.000
Residential waste burning	1741	0.015	0.000	0.000	0.007
Glass manufacturing	334	0.010	0.000	0.000	0.000
Cement manufacturing	700	0.009	0.009	0.000	0.000
Auto industry	413	0.005	0.000	0.000	0.000
Prescribed/open burning	444	0.004	0.000	0.000	0.003
Point fugitive dust	15	0.001	0.000	0.000	0.000
Wildfires	51	0.001	0.000	0.000	0.000
Total (all sources)	40,333	3.324	0.556	0.043	0.459
<b>WAYNE COUNTY MONITOR #261630015, ANNUAL DV = 15.69</b>					
CMV, aircraft, locomotive	638	0.727	0.257	0.000	0.000
Metal processing	852	0.399	0.031	0.000	0.000
Other industrial sources	1375	0.395	0.094	0.000	0.125
Commercial cooking	984	0.365	0.068	0.000	0.000
Power sector	18,016	0.311	0.064	0.000	0.031
Onroad (gasoline and diesel)	1187	0.214	0.000	0.016	0.016
Area fugitive dust	10,270	0.183	0.000	0.000	0.000
Other area	888	0.154	0.000	0.000	0.123
Nonroad (gasoline and diesel)	1603	0.147	0.025	0.014	0.014
Residential wood burning	703	0.024	0.005	0.000	0.000
Residential waste burning	1741	0.013	0.000	0.000	0.007
Glass manufacturing	334	0.009	0.000	0.000	0.000
Cement manufacturing	700	0.008	0.008	0.000	0.000
Auto industry	413	0.005	0.000	0.000	0.000
Prescribed/open burning	444	0.003	0.000	0.000	0.003

(Continued)

**TABLE 27.8** Summary of Modeled Source Contributions of Primary PM<sub>2.5</sub> to Monitors with Potential Annual Exceedances in Detroit, Michigan, for the Year 2015—cont'd

Source Sectors	Model Predicted Annual Concentrations ( $\mu\text{g m}^{-3}$ )*				
	Primary PM <sub>2.5</sub> Emissions (ton year <sup>-1</sup> )	Primary PM <sub>2.5</sub> Contribution	15/65 Control Scenario	15/35 Control Scenario	14/35 Control Scenario
Natural gas combustion	119	0.002	0.000	0.000	0.000
Point fugitive dust	15	0.001	0.000	0.000	0.000
Wildfires	51	0.000	0.000	0.000	0.000
Total (all sources)	40,333	2.962	0.550	0.030	0.319

\* Natural gas combustion source category results are adjusted to reflect new emissions factor (94% reduction).

CMV = commercial motor vehicle.

Source: US Environmental Protection Agency, Regulatory Impact Analysis for the Revised Particulate Matter National Ambient Air Quality Standards, 2006.

**TABLE 27.9** Summary of Modeled Source Contributions of Primary PM<sub>2.5</sub> to Monitors with Potential Daily Exceedances in Detroit, Michigan, for the Year 2015

Source Sectors	Model Predicted Annual Concentrations ( $\mu\text{g m}^{-3}$ )*				
	Primary PM <sub>2.5</sub> Emissions (ton year <sup>-1</sup> )	Primary PM <sub>2.5</sub> Contribution	15/65 Control Scenario	15/35 Control Scenario	14/35 Control Scenario
<b>WAYNE COUNTY MONITOR #261630033, DAILY DV = 39.06<sup>b</sup></b>					
Power sector	18,016	0.896	0.344	0.000	0.021
Metal processing	852	0.623	0.048	0.000	0.000
Cement manufacturing	700	0.024	0.024	0.000	0.000
Glass manufacturing	334	0.025	0.000	0.000	0.000
Auto industry	413	0.014	0.000	0.000	0.000
Other industrial sources	1375	1.691	0.378	0.000	0.579
CMV, aircraft, locomotive	638	0.833	0.297	0.000	0.000
Nonroad (gasoline and diesel)	1603	0.296	0.041	0.030	0.030
Onroad (gasoline and diesel)	1187	0.475	0.000	0.035	0.035
Residential waste burning	1741	0.022	0.000	0.000	0.011
Residential wood burning	703	0.038	0.008	0.000	0.000
Commercial cooking	984	0.587	0.109	0.000	0.000
Prescribed/open burning	444	0.006	0.000	0.000	0.005
Wildfires	51	0.000	0.000	0.000	0.000
Area fugitive dust	10,270	0.522	0.000	0.000	0.000
Point fugitive dust	15	0.002	0.000	0.000	0.000
Other area	888	0.362	0.000	0.000	0.289
Natural gas combustion	119	0.003	0.000	0.000	0.000
Total (all sources)	40,333	6.418	1.250	0.065	0.970
<b>WAYNE COUNTY MONITOR #261630015, DAILY DV = 38.6<sup>b</sup></b>					
Power sector	18,016	0.730	0.149	0.000	0.083
Metal processing	852	1.604	0.123	0.000	0.000
Cement manufacturing	700	0.003	0.003	0.000	0.000

**TABLE 27.9** Summary of Modeled Source Contributions of Primary PM<sub>2.5</sub> to Monitors with Potential Daily Exceedances in Detroit, Michigan, for the Year 2015—cont'd

Source Sectors	Model Predicted Annual Concentrations ( $\mu\text{g m}^{-3}$ )*				
	Primary PM <sub>2.5</sub> Emissions (ton year <sup>-1</sup> )	Primary PM <sub>2.5</sub> Contribution	15/65 Control Scenario	15/35 Control Scenario	15/35 Control Scenario
Glass manufacturing	334	0.008	0.000	0.000	0.000
Auto industry	413	0.003	0.000	0.000	0.000
Other industrial sources	1375	0.844	0.264	0.000	0.153
CMV, aircraft, locomotive	638	2.082	0.725	0.000	0.000
Nonroad (gasoline and diesel)	1603	0.118	0.017	0.012	0.012
Onroad (gasoline and diesel)	1187	0.189	0.000	0.014	0.014
Residential waste burning	1741	0.021	0.000	0.000	0.011
Commercial cooking	984	0.534	0.099	0.000	0.000
Prescribed/open burning	444	0.005	0.000	0.000	0.004
Wildfires	51	0.000	0.000	0.000	0.000
Area fugitive dust	10,270	0.159	0.000	0.000	0.000
Point fugitive dust	15	0.003	0.000	0.000	0.000
Other area	888	0.160	0.000	0.000	0.128
Natural gas combustion	119	0.024	0.000	0.000	0.000
Total (all sources)	40,333	6.502	1.383	0.026	0.406

\* Natural gas combustion source category results are adjusted to reflect new emissions factor (94% reduction).

† Each daily results reflects the 98th percentile day or the third highest day modeled with AERMOD so for monitor #261630015, that day is November 18 and for monitor #261630033, that day is January 1.

Source: US Environmental Protection Agency, Regulatory Impact Analysis for the Revised Particulate Matter National Ambient Air Quality Standards, 2006.

- *California Line Source Dispersion Model (CALINE3)*: A steady-state Gaussian dispersion model designed to determine air pollution concentrations at receptor locations downwind of roadways located in relatively uncomplicated terrain.
- *CAL3QHC*: A CALINE3-based CO model with queuing and hot spot calculations and with a traffic model to calculate delays and queues that occur at signalized intersections.
- *CAL3QHCR*: This is a more refined version based on CAL3QHC that requires local meteorological data.
- *CTDMPLUS*: A refined point source Gaussian air quality model for use in all stability conditions for complex terrain. The model contains, in its entirety, the technology of CTDM for stable and neutral conditions.
- *Offshore and Coastal Dispersion Model Version 5 (OCD)*: A straight line Gaussian model developed to determine the impact of offshore emissions from point, area, or line sources on the air quality of coastal regions. OCD incorporates overwater plume transport and dispersion as well as changes that occur as the plume crosses the shoreline. Hourly

meteorological data are needed from both offshore and onshore locations.

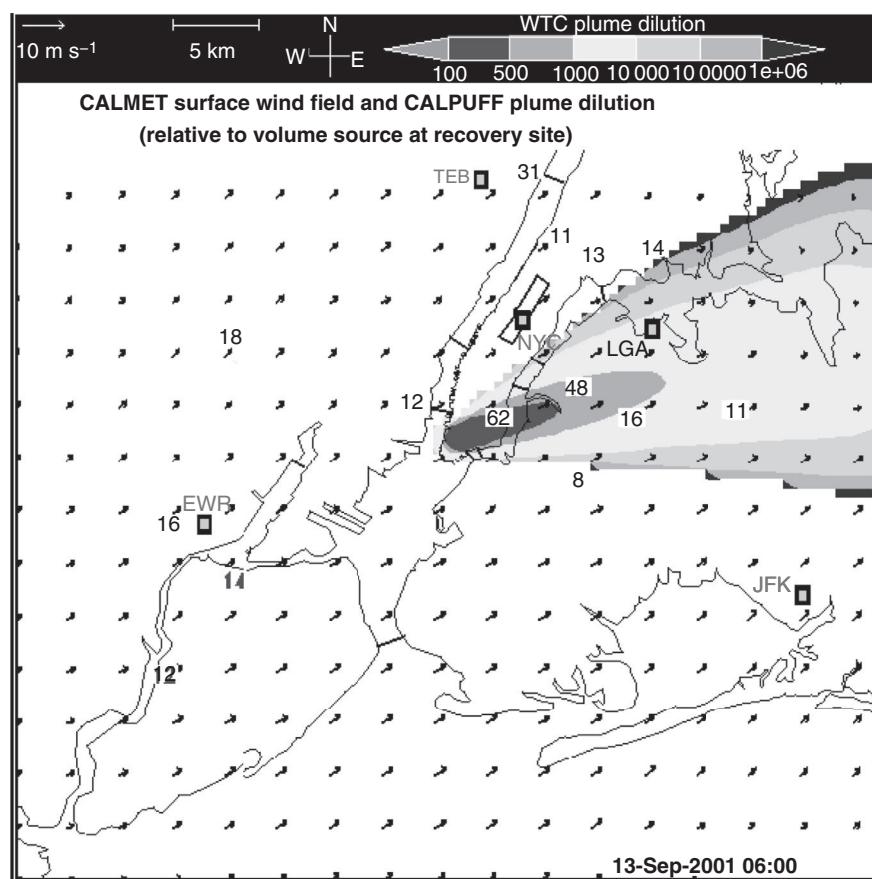
Documentation and access to these models are available at the EPA Technology Transfer Network Web site: [http://www.epa.gov/scram001/dispersion\\_prefrec.htm#blp](http://www.epa.gov/scram001/dispersion_prefrec.htm#blp).

#### 27.4.5.6 Photochemical Models

Photochemical air quality models have become widely recognized and routinely utilized tools for regulatory analysis and attainment demonstrations by assessing the effectiveness of control strategies. These models are large-scale air quality models that simulate the changes of pollutant concentrations in the atmosphere using a set of mathematical equations characterizing the chemical and physical processes in the atmosphere. They are applied at multiple spatial scales from local, regional, national, and global.

Photochemical models structure the atmosphere as a modeled volume with a three-dimensional grid with thousands of grid cells. Each grid cell can be envisioned as a box. The boxes are stacked one atop another and

FIGURE 27.33 Plume simulated with CALPUFF showing the averaged hourly PM<sub>2.5</sub> dilution of a volume source at the World Trade Center, New York City. Huber A. US Environmental Protection Agency.



differ in height. Shorter boxes represent the parcels of air nearest to the ground surface. The photochemical calculates concentrations of pollutants, such as ozone, in each cell by simulating the movement of air into and out of cells by advection and dispersion. The model also includes algorithms to simulate mixing of pollutants vertically among layers, introduction of emissions from sources into each cell, as well as sets of chemical reactions, equations of pollution precursors and meteorology, especially incoming solar radiation (i.e. insolation) in each cell.

Photochemical air quality models are of two basic mathematical types: the Lagrangian trajectory model that employs a moving frame of reference and the Eulerian grid model that uses a fixed coordinate system with respect to the ground. Early modeling efforts often used Lagrangian methods to simulate the formation of pollutants because of its computational simplicity. Describing physical processes, however, is incomplete, which is the major disadvantage of the Lagrangian method. Thus, most photochemical air quality models in operation today use three-dimensional Eulerian grid mathematics that allow for improved and more complete characterization of the physical processes in the atmosphere. This allows chemical-species concentrations to be predicted throughout the entire model domain.

Arguably, the principal photochemical model in use is the CMAQ modeling system, which has been developed to improve the environmental management community's ability to evaluate the impact of air quality management practices for multiple pollutants at multiple scales and enhance the scientist's ability to probe, to understand, and to simulate chemical and physical interactions in the atmosphere. The most recent CMAQ version is available for download from the Community Modeling and Analysis System Web site at <http://www.cmascenter.org/>.

Several other photochemical models have been developed and are applied to various pollutants. These include

- Comprehensive Air Quality Model with Extensions—simulates air quality over different geographic scales; treats a wide variety of inert and chemically active pollutants, including ozone, PM, inorganic and organic PM<sub>2.5</sub>/PM<sub>10</sub>, and mercury and other toxics; and has plume-in-grid and source apportionment capabilities.
- Regional Modeling System for Aerosols and Deposition—calculates the concentrations of both inert and chemically reactive pollutants by simulating the physical and chemical processes in the atmosphere that affect pollutant concentrations over

- regional scales; and includes processes relevant to regional haze, PM, and other airborne pollutants, including soluble acidic components and mercury.
- Urban Airshed Variable Grid (Urban Airshed Model (UAM)-V) Photochemical Modeling System—pioneering effort in photochemical air quality modeling in the early 1970s that has been used widely for air quality studies focusing on ozone. It is a three-dimensional photochemical grid model designed to calculate the concentrations of both inert and chemically reactive pollutants by simulating the physical and chemical processes in the atmosphere that affect pollutant concentrations. It is typically applied to model air quality episodes, i.e. periods during which adverse meteorological conditions result in elevated ozone pollutant concentrations.

#### **27.4.5.7 Receptor Models**

Receptor models are mathematical or statistical procedures for identifying and quantifying the sources of air pollutants at a receptor location. Unlike photochemical and dispersion air quality models, receptor models do not use pollutant emissions, meteorological data, and chemical transformation mechanisms to estimate the contribution of sources to receptor concentrations. Instead, receptor models use the chemical and physical characteristics of gases and particles measured at source and receptor to both identify the presence of and to quantify source contributions to receptor concentrations. These models are therefore a natural complement to other air quality models and are used as part of SIPs for identifying sources contributing to air quality problems. The EPA has developed the Chemical Mass Balance (CMB) and UNMIX models as well as the Positive Matrix Factorization (PMF) method for use in air quality management.

The CMB fully apportions receptor concentrations to chemically distinct source types depending on the source profile database, while UNMIX and PMF internally generate source profiles from the ambient data. UNMIX is multivariate receptor modeling package that uses observations of particulate composition and seeks to find the number, composition, and contributions of the contributing sources or source type. CMB is one of several receptor models that have been applied to air quality problems since the 1980s. Based on an effective-variance least-squares method, it has supported numerous SIPs, when they include a source apportionment component. CMB requires speciated profiles of potentially contributing sources and the corresponding ambient data from analyzed samples collected at a single receptor site. CMB is ideal for localized nonattainment problems and has proven to be a useful tool in applications where steady state Gaussian

plume models are inappropriate, as well as for confirming or adjusting emissions inventories.

The EPA UNMIX model, as the name implies, disaggregates (“unmixes”) the concentrations of chemical species measured in the ambient air to identify the contributing sources. Chemical profiles of the sources are not required, but instead are generated internally from the ambient data by UNMIX, using a mathematical formulation based on a form of factor analysis. For a given selection of chemical species, UNMIX estimates the number of sources, the source compositions, and source contributions to each sample.

The PMF technique is a form of factor analysis where the underlying covariability of many variables (e.g. sample to sample variation in PM species) is described by a smaller set of factors (e.g. PM sources) to which the original variables are related. The structure of PMF permits maximum use of available data and better treatment of missing and below-detection-limit values.

When the results of air pollution measurements are interpreted, one of the first questions asked by scientists, engineers, and policy makers is where did it come from? Sorting out the various sources of pollution is known as *source apportionment*. A number of tools are used to try to locate the sources of pollutants. A widely used approach is the “source–receptor model” or as it is more commonly known, the *receptor model*.

The distinction between receptor and dispersion models has to do with the direction of the prediction. Dispersion models start from the source and estimate where the plume and its contaminants are heading. Conversely, receptor models are based on measurements taken in the ambient environment and from these observations, make use of algorithms and functions to determine pollution sources. One common approach is the mathematical “back trajectory” model. Often, chemical co-occurrences are applied. So, it may be that a certain fuel is frequently contaminated with a conservative and, hopefully, unique element. Some fuel oils, for example, contain trace amounts of the element vanadium. Since there are few other sources of vanadium in most ambient atmospheric environments, its presence is a strong indication that the burning of fuel oil is a most likely source of the plume. The model, if constructed properly, can even quantify the contribution. So, if measurements show that sulfur dioxide ( $\text{SO}_2$ ) concentrations are found to be  $10 \mu\text{g m}^{-3}$  in an urban area, and vanadium is also found at sufficient levels to indicate that home heating systems are contributing a certain amount of the  $\text{SO}_2$  to the atmosphere, the model will correlate the amount of  $\text{SO}_2$  coming from home heating systems. If other combustion sources, e.g. cars and power plants, also have unique trace elements associated

with their SO<sub>2</sub> emissions, further SO<sub>2</sub> source apportionment can occur, so that the total may look something like Table 7.2.

For a discussion of source–receptor relationships and modeling, see Discussion Box: Source Apportionment, Receptor Models, and Carbon Dating in Chapter 6.

#### 27.4.5.8 Personal Exposure Models

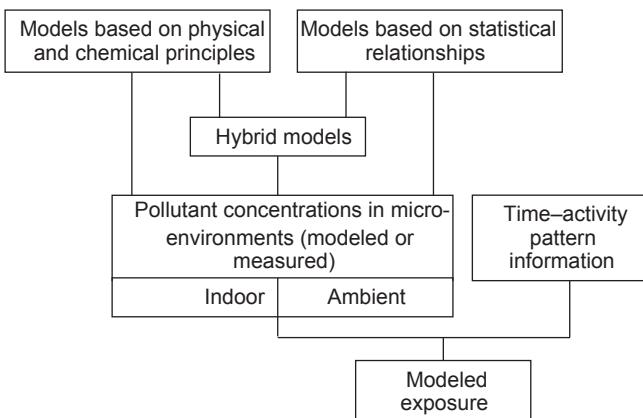
The actual exposures that people receive can also be modeled (see Figure 27.34). According to the EPA, there are three techniques to estimate pollutant exposures quantitatively:

Sometimes the approaches to assessing exposure are described in terms of “direct measures” and “indirect measures” of exposure (e.g. NRC, 1994). Measurements that actually involve sampling on or within a person, for example, use of personal monitors and biomarkers, are termed as “direct measures” of exposure. Use of models, microenvironmental measurements, and questionnaires, where measurements do not actually involve personal measurements, are termed as “indirect measures” of exposure. The direct/indirect nomenclature focuses on the type of measurements being made; the scenario evaluation/point-of-contact/reconstruction nomenclature focuses on how the data are used to develop the dose estimate. The three-term nomenclature is used in these guidelines to highlight the point that three independent estimates of dose can be developed.

There is seldom a sufficient amount of direct information from measurements to estimate and to predict exposures for a population. Thus, indirect methods must be used. Personal exposure<sup>i</sup> can be expressed mathematically as a composite of the time in a microenvironment (e.g. in a garage, indoors at home, or in a car) and the concentration of the pollutant in that microenvironment:

$$E_i = \sum_{j=1}^m T_{ij} C_{ij} \quad (27.47)$$

where  $T_{ij}$  is the time spent in microenvironment  $j$  by person  $i$  with typical units of minutes,  $C_{ij}$  is the air pollutant concentration person  $i$  experiences in microenvironment  $j$  with typical units of micrograms per cubic meter,  $E_i$  represents the exposure for person  $i$  integrated  $T_{ij}$ , and  $m$  is the number of different microenvironments. Thus, the units of exposure are mass per volume-time (micrograms per cubic meter per minute). Note, then, that



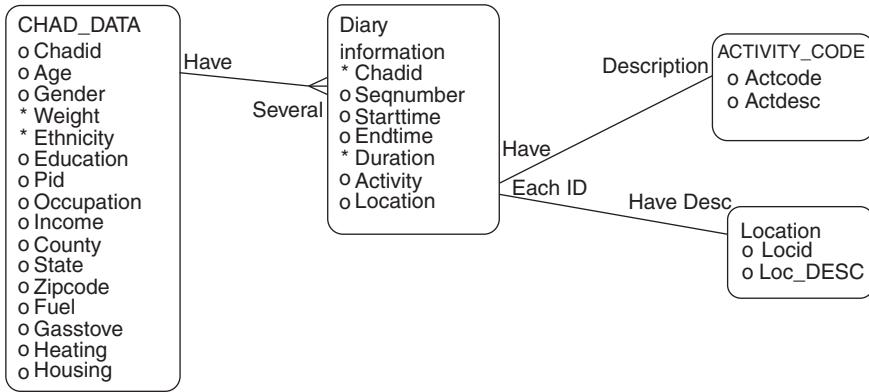
**FIGURE 27.34 Schematic of human exposure modeling.** Adapted from: US National Research Council, Chapter 6: Models, in *Human Exposure Assessment for Airborne Pollutants: Advances and Applications*. Committee on Advances in Assessing Human Exposure to Airborne Pollutants and Committee on Geosciences, Environment, and Resources. Washington (DC): National Academy Press; 1990.

exposure is the concentration per unit time. The calculation amounts to a weighted sum of concentrations with the weights being equal to the time spent experiencing a given concentration.

What people are doing is crucial to modeling their exposure to air pollutants. To support exposure, intake dose, and risk assessments, the EPA developed the Consolidated Human Activity Database (CHAD). CHAD is a relational database with a graphical user interface that facilitates queries and report generation.<sup>j</sup> It contains databases from previously existing human activity pattern studies, which were incorporated in two forms: (1) as the original raw data and (2) as data modified according to predefined format requirements. CHAD contains data obtained from preexisting human activity studies that were collected at city, state, and national levels. People’s diary information is input in CHAD. Figure 27.35 and Tables 27.10 and 27.11 provide the structure and data elements of CHAD. Most of the fields are answers from the questionnaire. Some fields vary from day to day for an individual and fields based on the diary entries will most likely be different for each day. The CHAD\_DIARY table contains one record for each activity during a 24-h period. No record

<sup>i</sup>The principal reference for this discussion is Klepeis NE. Modeling human exposure to air pollution. In: Ott WR, Wallace LA, Steinemann A, editors. *Exposure analysis*. Boca Raton: CRC Press; 2006; and Klepeis NE, Nazaroff WW. Modeling residential exposure to secondhand tobacco smoke. *Atmos Environ* 2006;40(23):4393–407. Other resources for all discussions about human exposure science have benefited from ongoing discussions with Wayne Ott and Lance Wallace, as well as the insights of Gerry Alkand, Larry Purdue, Judy Graham, Jerry Blancato, Paul Lioy, Tom McCurdy, Alan Huber, Alan Vette, Linda Sheldon, Dave Mage, Dale Pahl, Tom McKone, Edo Pellizzari, Ron Williams, and Curt Dary.

<sup>j</sup>The source of this discussion is Stallings C, Tippett JA, Glen G, Smith L. *CHAD users guide: extracting human activity information from CHAD on the PC*. ManTech Environmental Services, modified by Systems Development Center Science Applications International Corporation, Research Triangle Park, NC; 2002.



**FIGURE 27.35** Schematic of the tables and relationships among the tables in the combined CHAD. Stallings C, Tippett JA, Glen G, Smith L. CHAD users guide: extracting human activity information from CHAD on the PC. ManTech Environmental Services, modified by Systems Development Center Science Applications International Corporation, Research Triangle Park (NC); 2002.

represents more than an hour or crosses the hour boundary. The minimal information in the diary data is the CHADID, which links to the CHAD\_DATA, a sequence number, which indicates the order of the records in a day, start, end, and duration times, and an activity and location.

Thus, if we measure concentrations with personal and indoor air pollution monitors and we apply activity patterns, such as those in CHAD, we can estimate and predict personal exposures to numerous pollutants.

Obviously the mean personal exposure can be expressed in concentration units (micrograms per cubic meter) by dividing  $E_i$  by the total time spent in each microenvironment and summing these exposures. Further, this can also be seen as a continuum in which the personal exposure is assumed to be constant during each time comprising  $T_{ij}$ :

$$E_i = \int_1^2 C_{ij}(t; x; y; z) dt \quad (27.48)$$

where  $C_i(t, x, y, z)$  is the concentration occurring at a specific point occupied by person  $i$  at time  $t$  and spatial coordinates  $(x, y, z)$ , and  $t_1$  and  $t_2$  are the respective starting and ending times of a given exposure episode. The concentrations can be measured using a real-time personal monitoring device. These data are not actually continuous, but can be quite frequent (e.g. every few seconds).

Other times, fully continuous space is not assumed, which means that discrete microenvironments are used. If this is the case the equation appears as

$$E_i = \left( \sum_{j=1}^m \int_{j_1}^{j_2} C_{ij}(t) dt \right) \quad (27.49)$$

where  $C_{ij}(t)$  is the concentration to which the person is exposed in the discrete microenvironment  $j$  at a specific point in time  $t$  over the time interval defined by  $[t_{j_1}, t_{j_2}]$ ,

where  $t_{j_1}$  is the starting time for the microenvironment and  $t_{j_2}$  is the ending time. If we assume that every person in a population is exposed to the same microenvironment concentrations, a simplified population exposure can be derived to show the total time spent by all receptors in each microenvironment:

$$\tilde{E} = \sum_{j=1}^m C_j \tilde{T}_j \quad (27.50)$$

where  $m$  is the number of microenvironments encountered,  $C_j$  is the average pollutant concentration in microenvironment  $j$  assigned to every person  $i$ ,  $\tilde{E}$  is the integrated exposure over all members of the population. The total time spent by all persons in microenvironment  $j$  is

$$\tilde{T}_i = \sum_{i=1}^n T_{ij} \quad (27.51)$$

where  $n$  is the total number of people in the population being modeled. This can be further simplified if we assume that each person spends the same total amount of time across all microenvironments:

$$T = T_i = \sum_{j=1}^m T_{ij} \quad (27.52)$$

Further, if the time spent by certain individuals in particular microenvironments is zero, then the average personal exposure for the population would be

$$\bar{E}_c = \frac{1}{nT} \sum_{j=1}^m C_j \tilde{T}_j \quad (27.53)$$

Therefore, time–activity relationships and concentrations can be used to model expected exposures to air pollutants. Indoor and personal exposures can dominate exposures to many pollutants. For example, Figure 27.36 shows the modeled results of expected exposures to particulates ( $PM_{2.5}$ ) for a simulated population based on available measurements of ambient, indoor, and

**TABLE 27.10** CHAD Diary Location Codes

30000 Residence, general	31300 Waiting
30010 Your residence	31310 Wait for bus, train, ride (at stop)
30020 Other's residence	31320 Wait for travel, indoors
30100 Residence, indoor	31900 Other travel
30120 Your residence, indoor	31910 Travel by other vehicle
30121 Kitchen	32000 Other, indoor general
30122 Living room/family room	32100 Office building/ bank/post office
30123 Dining room	32200 Industrial plant/factory/ warehouse
30124 Bathroom	32300 Grocery store/ convenience store
30125 Bedroom	32400 Shopping mall/ nongrocery store
30126 Study/office	32500 Bar/night club/ bowling alley
30127 Basement	32510 Bar/night club
30128 Utility room/laundry room	32520 Bowling alley
30129 Other indoor	32600 Repair shop
30130 Other's residence, indoor	32610 Auto repair shop/ gas station
30131 Other's kitchen	32620 Other repair shop
30132 Other's living room/family room	32700 Indoor gym/sports or health club
30133 Other's dining room	32800 Child care facility
30134 Other's bathroom	32810 Child care facility, house
30135 Other's bedroom	32820 Child care facility, commercial
30136 Other's study/office	32900 Public building/library/ museum/theater
30137 Other's basement	32910 Auditorium, sports arena/concert hall
30138 Other's utility room/ laundry room	32920 Library/courtroom/ museum/theater
30139 Other indoor	33100 Laundromat
30200 Residence, outdoor	33200 Hospital/health care facility/doctor's office
30210 Your residence, outdoor	33300 Beauty parlor/barber shop/hairdresser's
30211 Your residence—pool, spa	33400 At work: no specific location, moving among locations
30219 Your residence—other outdoor	33500 At school

**TABLE 27.10** CHAD Diary Location Codes—cont'd

30220 Other's residence, outdoor	33600 At restaurant
30221 Other's residence—pool, spa	33700 At church
30229 Other's residence—other outdoor	33800 At hotel/motel
30300 Garage	33900 At dry cleaners
30310 Indoor garage	34100 Parking garage
30320 Outdoor garage	34200 Laboratory
30330 Your garage	34300 Other, indoor
30331 Your indoor garage	35000 Other outdoor, general
30332 Your outdoor garage	35100 Sidewalk/street/ neighborhood
30340 Other's garage	35110 Within 10 yards of street
30341 Other's indoor garage	35200 Public garage/parking lot
30342 Other's outdoor garage	35210 Public garage
30400 Other, residence	35220 Parking lot
31000 Travel, general	35300 Service station/gas station
31100 Motorized travel	35400 Construction site
31110 Travel by car	35500 Amusement park
31120 Travel by truck	35600 School grounds/ playgrounds
31121 Travel by truck (pickup van)	35610 School grounds
31122 Travel by truck (other than pickup or van)	35620 Playground
31130 Travel by motorcycle/ moped/motorized scooter	35700 Sports stadium and amphitheater
31140 Travel by bus	35800 Park/golf course
31150 Travel by train/subway/ rapid transit	35810 Park
31160 Travel by airplane	35820 Golf course
31170 Travel by boat	35900 Pool, river, lake
31171 Travel by motorized boat	36100 Restaurant, picnic
31172 Travel by unmotorized boat	36200 Farm
31200 Nonmotorized travel	36300 Other outdoor
31210 Travel by walk	U Uncertain
31220 Travel by bicycle/ skateboard/roller-skates	X Missing
31230 Travel in a stroller or carried by an adult	

Source: Stallings C, Tippett JA, Glen G, Smith L. CHAD users guide: extracting human activity information from CHAD on the PC. *ManTech Environmental Services, modified by Systems Development Center Science Applications International Corporation, Research Triangle Park (NC); 2002.*

**TABLE 27.11** CHAD Diary Activity Code Descriptions

10000 Work and other income-producing activities, general	15200 Attend other classes
10100 Work, general	15300 Do homework
10110 Work, general, for organizational activities	15400 Use library
10111 Work for professional/union organizations	15500 Other education
10112 Work for special interest identity organizations	16000 General entertainment/social activities
10113 Work for political party and civic participation	16100 Attend sports events
10114 Work for volunteer/helping organizations	16200 Participate in social, political, or religious activities
10115 Work of/for religious groups	16210 Practice religion
10116 Work for fraternal organizations	16300 Watch movie
10117 Work for child/youth/family organizations	16400 Attend theater
10118 Work for other organizations	16500 Visit museums
10120 Work, income-related only	16600 Visit
10130 Work, secondary (income-related)	16700 Attend a party
10200 Unemployment	16800 Go to bar/lounge
10300 Breaks	16900 Other entertainment/social events
11000 General household activities	17000 Leisure, general
11100 Prepare food	17100 Participate in sports and active leisure
11110 Prepare and clean up food	17110 Participate in sports
11200 Indoor chores	17111 Hunting, fishing, hiking
11210 Clean up food	17112 Golf
11220 Clean house	17113 Bowling/pool/ping pong/pinball
11300 Outdoor chores	17114 Yoga
11310 Clean outdoors	17120 Participate in outdoor leisure
11400 Care of clothes	17121 Play, unspecified
11410 Wash clothes	17122 Passive, sitting
11500 Build a fire	17130 Exercise
11600 Repair, general	17131 Walk, bike, or jog (not in transit)

**TABLE 27.11** CHAD Diary Activity Code Descriptions—cont'd

11610 Repair of boat	17140 Create art, music, participate in hobbies
11620 Paint home/room	17141 Participate in hobbies
11630 Repair/maintain car	17142 Create domestic crafts
11640 Home repairs	17143 Create art
11650 Other repairs	17144 Perform music/drama/dance
11700 Care of plants	17150 Play games
11800 Care for pets/animals	17160 Use of computers
11900 Other household	17170 Participate in recess and physical education
12000 Child care, general	17180 Other sports and active leisure
12100 Care of baby	17200 Participate in passive leisure
12200 Care of child	17210 Watch
12300 Help/teach	17211 Watch adult at work
12400 Talk/read	17212 Watch someone provide child care
12500 Play indoors	17213 Watch personal care
12600 Play outdoors	17214 Watch education
12700 Medical care—child	17215 Watch organizational activities
12800 Other child care	17216 Watch recreation
13000 Obtain goods and services, general	17220 Listen to radio/listen to recorded music/watch TV
13100 Dry clean	17221 Listen to radio
13200 Shop/run errands	17222 Listen to recorded music
13210 Shop for food	17223 Watch TV
13220 Shop for clothes or household goods	17230 Read, general
13230 Run errands	17231 Read books
13300 Obtain personal care service	17232 Read magazines/not ascertained
13400 Obtain medical service	17233 Read newspaper
13500 Obtain government/financial services	17240 Converse/write
13600 Obtain car services	17241 Converse
13700 Other repairs	17242 Write for leisure/pleasure/paperwork
13800 Other services	17250 Think and relax
14000 Personal needs and care, general	17260 Other passive leisure
14100 Shower, bathe, personal hygiene	17300 Other leisure

(Continued)

**TABLE 27.11** CHAD Diary Activity Code Descriptions—cont'd

14110 Shower, bathe	18000 Travel, general
14120 Personal hygiene	18100 Travel during work
14200 Medical care	18200 Travel to/from work
14300 Help and care	18300 Travel for child care
14400 Eat	18400 Travel for goods and services
14500 Sleep or nap	18500 Travel for personal care
14600 Dress, groom	18600 Travel for education
14700 Other personal needs	18700 Travel for organizational activity
15000 General education and professional	18800 Travel for event/social activity training
15100 Attend full-time school	18900 Travel for leisure
15110 Attend day care	18910 Travel for active leisure
15120 Attend K-12	18920 Travel for passive leisure
15130 Attend college or trade school	U Unknown
15140 Attend Adult education and special training	X Missing

Source: Stallings C, Tippett JA, Glen G, Smith L. CHAD users guide: extracting human activity information from CHAD on the PC. *ManTech Environmental Services, modified by Systems Development Center Science Applications International Corporation, Research Triangle Park (NC); 2002.*

personal measurements, combined with information about microenvironments (e.g. types and time in each) and activities. Note that ambient contribution is quite small compared to personal and indoor exposures.<sup>k</sup>

#### 27.4.5.9 Modeling Air Toxics

The Clean Air Act Amendments of 1990 (CAA90) included a specific health outcome provision related to toxic air pollutants. The law included 190 substances that need to be addressed because they have been known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or to cause adverse environmental effects. The 1990 amendments established a range of air toxics requirements for EPA to implement that generally fall into four categories:

- Establishing emission standards based on existing pollution control technologies, called Maximum Achievable Control Technology (MACT), for an estimated 84,000 major stationary sources within 158 industries.

- Examining the remaining health risk (called the “residual risk”) from these sources 8 years after implementing each MACT standard and, if warranted, issuing additional standards to protect public health or the environment.
- Regulating air toxics emissions from small stationary sources, such as dry cleaners.
- Evaluating the need for and feasibility of regulation of air toxics emissions from mobile sources, such as cars, and regulating these sources based on this evaluation.

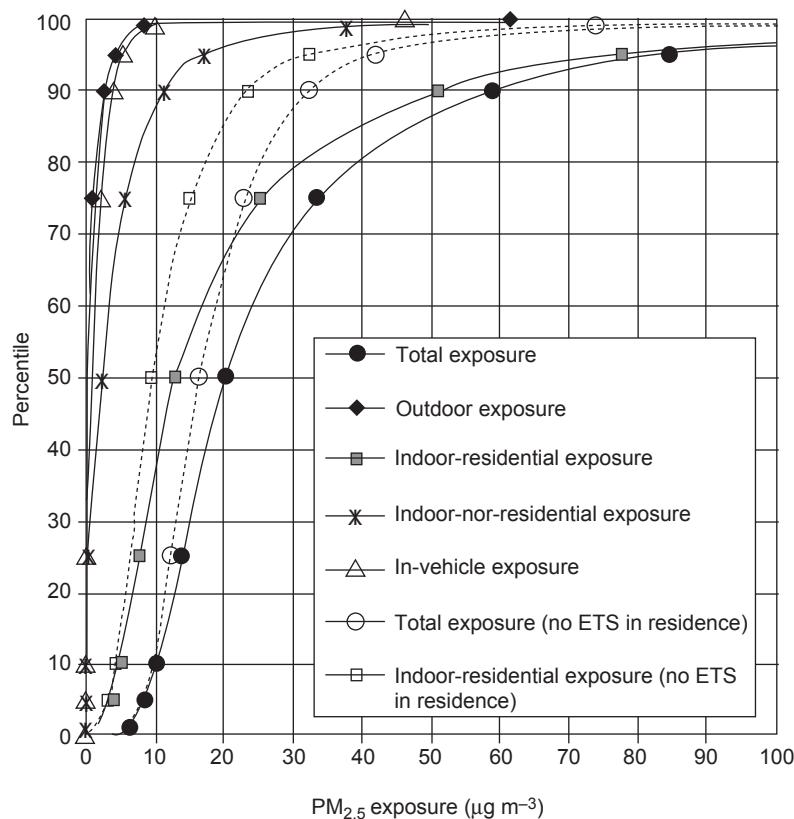
The amendments also required the EPA to periodically assess the costs and benefits of the entire CAA. This called for an assessment of the Act's costs and benefits prior to 1990 along with projections of future economic impacts resulting from the amendments (see the earlier discussion in this chapter regarding the regulatory impact analysis as it pertains to PM).

Air toxics originate from a variety of sources (see Figure 27.37). Of the numerous compounds that are classified as air toxics, however, about 60% are represented by just five pollutant classes (see Table 27.12). The EPA has completed MACT standards for major stationary sources. The EPA establishes the federal standard, but the state and local air pollution control agencies generally implement the EPA's emission standards. These agencies can choose to impose more stringent requirements than the federal standards, and some state and local agencies have developed innovative air toxics programs that go beyond the federal program, which is enabling them to address air toxics that would be insufficiently covered by EPA's standards.

The CAA residual risk program (i.e. the risk remaining after technology-based standards have been in place), must try to determine whether the most highly exposed individuals face excess cancer risk of more than one in 1 million ( $risk = 1 = 10^{-6}$ ). In cases where estimated risks exceed this threshold, the EPA must develop a new residual risk standard to provide an ample margin of safety for those potentially affected individuals. In fact, the EPA generally uses a lifetime cancer risk of one in 10,000 ( $risk = 1 = 10^{-4}$ ) as the upper boundary of acceptability. The ample margin of safety decision must also consider costs, technological feasibility, uncertainties, and other relevant factors. In this feasibility step, EPA must also assess whether to adopt more stringent standards to prevent adverse effects to wildlife, aquatic life, or natural resources considering cost, energy, and other pertinent details.

The residual risk process is dynamic and continuously updated (For updates, see: <http://www.epa.gov/ttn/atw/rrisk/rtrpg.html>). The reviews are intended to

<sup>k</sup>Burke JM, Zufall MJ, Ozkaynak AH. A population exposure model for particulate matter: case study results for PM<sub>2.5</sub> in Philadelphia, PA: <http://www.epa.gov/heasd/pm/pdf/exposure-model-for-pm.pdf>; [accessed 23.02.07].



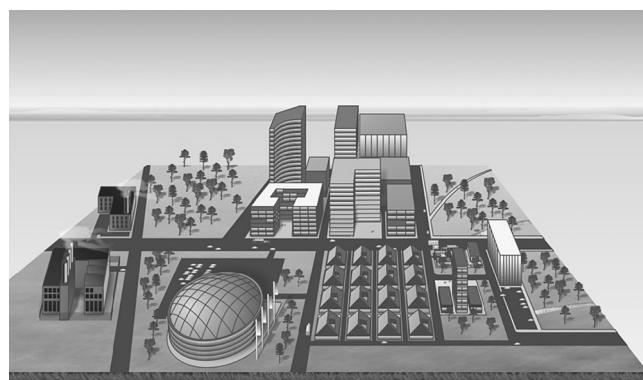
**FIGURE 27.36** Cumulative frequency distributions of daily total and microenvironmental PM<sub>2.5</sub> exposures (micrograms per cubic meter) for the simulated population of Philadelphia (solid lines). Distributions of total and indoor residential PM<sub>2.5</sub> exposures for the population without environmental tobacco smoke (ETS) exposure in the residence (dashed lines) are also shown. Burke JM, Zufall MJ, Ozkaynak AH. A population exposure model for particulate matter: case study results for PM<sub>2.5</sub> in Philadelphia (PA) <http://www.epa.gov/heasd/pm/pdf/exposure-model-for-pm.pdf>; [accessed 23.02.07].

provide information on any potential adverse health effects that may warrant further regulation. According to the US Government Accountability Office (GAO)<sup>1</sup>:

EPA does not have reliable data on the degree to which its programs have reduced risks. Furthermore, the data that are available suggest that the agency still has substantial opportunities to control emissions from mobile and small stationary sources.

EPA faces significant challenges in implementing the air toxics program, many of which stem from its relatively low priority within the agency. Importantly, the agency lacks a comprehensive strategy for managing its implementation of the remaining air toxics requirements. Senior EPA officials said that the program's agenda is largely set by external stakeholders who file litigation when the agency misses deadlines. For example, EPA currently faces a court order to issue emissions standards for small stationary sources. Previous reports by GAO identified inadequate funding for the air toxics program as a challenge, and key stakeholders—including senior EPA officials, environmental advocates, and state and local agency officials—said resource constraints continue to pose a major challenge. The percentage of funding for the air toxics program relative to all clean air programs ranged from 18% to 19% between 2000 and 2003 and declined to 15% in 2004

and 12% in 2005. EPA has not estimated the level of resources necessary to comply with the remaining requirements of the 1990 amendments, according to a senior program official. We believe that such estimates would help inform congressional oversight and appropriations decisions. Senior EPA officials and other stakeholders also cited a lack of information on the



**FIGURE 27.37** Common sources of air toxics emissions. US Government Accountability Office. Clean Air Act: EPA should improve the management of its air toxics program. Report No. GAO-06-669; June 2006.

<sup>1</sup>US Government Accountability Office, *Clean Air Act: EPA should improve the management of its air toxics program*. Report No. GAO-06-669, June 2006.

TABLE 27.12 The Five Most Commonly Emitted Air Toxics, 2002

Pollutant	Percentage of Total Air Toxics Emissions	Primary Sources of Emissions	Health Effects
Toluene	18	Mobile sources	Impairment of the nervous system with symptoms including tiredness, dizziness, sleepiness, confusion, weakness, memory loss, nausea, loss of appetite, and hearing and color vision loss; kidney problems; unconsciousness; and death.
Xylenes	13	Mobile sources, asphalt paving	Irritation of the skin, eyes, nose, and throat; headaches, dizziness, memory loss, and changes in sense of balance; lung problems; stomach discomfort; possible effects on the liver and kidneys; unconsciousness; and death.
Hydrochloric acid	12	Coal-fired utility and industrial boilers	Eye, nose, and respiratory tract irritation; corrosion of the skin, eyes, mucous membranes, esophagus, and stomach; severe burns; ulceration; scarring; inflammation of the stomach lining; chronic bronchitis; and inflammation of the skin.
Benzene	9	Mobile sources, open burning, pesticide application	Drowsiness, dizziness, vomiting, irritation of the stomach, sleepiness, convulsions, rapid heart rate, headaches, tremors, confusion, unconsciousness, anemia, excessive bleeding, weakened immune system, increased incidence of cancer (leukemia), and death.
Formaldehyde	7	Mobile sources, open burning	Irritation of the eyes, nose, throat, and skin; severe pain; vomiting; coma; limited evidence of cancer; and death.

US Environmental Protection Agency and Agency for Toxic Substances and Disease Registry.

benefits of regulating air toxics as a major challenge, which, in turn, reinforces the program's relative priority because the agency cannot demonstrate its effectiveness. The stakeholders identified a number of other challenges, but perceptions varied by stakeholder group. For example, EPA and industry stakeholders rated the large number of statutory requirements as a challenge, while environmental stakeholders rated a lack of reliable data on air toxics sources and their emissions as a challenge.

The EPA is required to conduct a National-Scale Air Toxics Assessment (NATA) as a part of the national air toxics program, which

- expands air toxics monitoring;
- develops emission inventories;
- conducts national and local-scale air quality analyses;
- characterizes risks associated with air toxics exposures;
- conducts research on health and environmental effects and exposures to both ambient and indoor sources; and
- conducts exposure modeling.

This helps EPA set program priorities, characterize risks, and track progress toward meeting goals, especially providing trends in air quality as the United States transitions from technology-based standards to a greater number of risk-based standards (see [Figure 27.38](#)).

As part of the NATA program, EPA conducted a national screening-level assessment using 1996 emissions

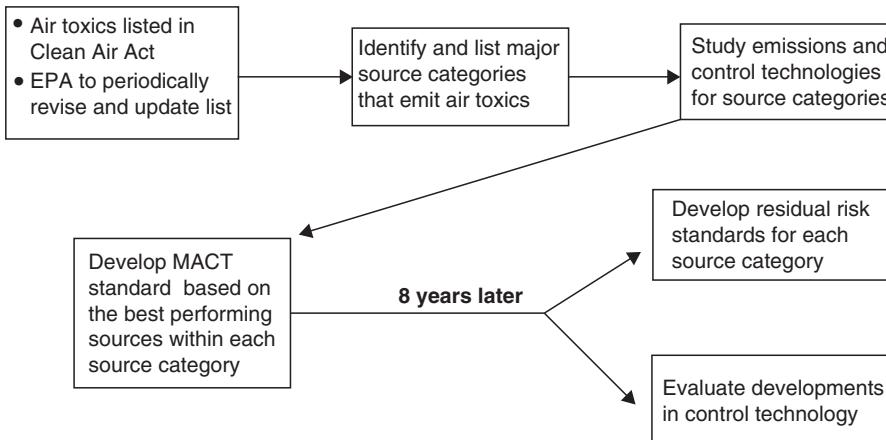
inventory data to characterize air toxics risks nationwide. This helped to characterize the potential health risks associated with inhalation exposures to 33 air toxics and diesel PM. These 34 air toxics were identified as priority pollutants in EPA's Integrated Urban Air Toxics Strategy.<sup>m</sup>

The Assessment System for Population Exposure Nationwide (ASPEN) is the model used to estimate toxic air pollutant concentrations. It is based on the EPA's ISCLT, which simulates the behavior of the pollutants once they are emitted into the atmosphere. ASPEN uses estimates of toxic air pollutant emissions and meteorological data from National Weather Service stations to estimate air toxics concentrations nationwide.

ASPEN incorporates a number of critical pollutant concentration variables, including

- rate of release;
- location of release;
- the height from which the pollutants are released;
- wind speeds and directions from the meteorological stations nearest to the release;
- breakdown of the pollutants in the atmosphere after being released (i.e. reactive decay);
- settling of pollutants out of the atmosphere (i.e. deposition); and
- transformation of one pollutant into another (i.e. secondary formation).

<sup>m</sup> A list of the 34 selected toxics can be found at <http://www.epa.gov/ttn/atw/nata/34poll.html>.



**FIGURE 27.38** Overview of the regulatory process for major stationary sources of air toxics, including MACT standards and 8-year technology and residual risk reviews. US Government Accountability Office. Clean Air Act: EPA should improve the management of its air toxics program. Report No. GAO-06-669; June 2006.

The model estimates toxic air pollutant concentrations for every census tract in contiguous United States, Puerto Rico, and the Virgin Islands. Census tracts are land areas defined by the US Bureau of the Census and typically contain about 4000 residents each. These census tracts are usually smaller than two square miles in size in cities, but much larger in rural areas.

NATA is intended to identify ambient concentrations of air toxics attributable to anthropogenic (human-generated) emissions, within 50 km of each source. However, for many pollutants, ambient concentrations have “background” components attributable to long-range transport, resuspension of previous emissions, and nonanthropogenic sources. To estimate ambient concentrations of air toxics accurately, these background concentrations must be addressed. In the 1996 assessment, with exception of diesel PM, background concentrations were based on measured values of 13 pollutants. The background concentrations used in the 1996 NATA are provided in Table 27.13.

The modeled estimates for most of the pollutants are generally lower than the measured ambient annual average concentrations when evaluated at the monitors. However, when the maximum modeled estimate for distances up to 10–20 km from the monitoring location are compared to the measured concentrations, the modeled estimates approach the monitored concentrations. This may be the result of spatial uncertainty of the underlying data (emissions and meteorological), as well as the tendency of existing air toxics monitoring networks to characterize the higher (if not maximum) air pollution impact areas in the ambient air. Also, the model estimates are more uncertain at the census tract scale, but are more reliable at more extensive geographic scales, such as a county or state. Further, ASPEN and underlying data are used to estimate exposures and risks (see Figure 27.39).

## 27.4.6 Model Performance, Accuracy, and Utilization

### 27.4.6.1 Methodology of Assessing Model Performance

A number of statistics have been suggested<sup>71,72</sup> as measures of model performance. Different types of models and the use of models for different purposes may require different statistics to measure performance.

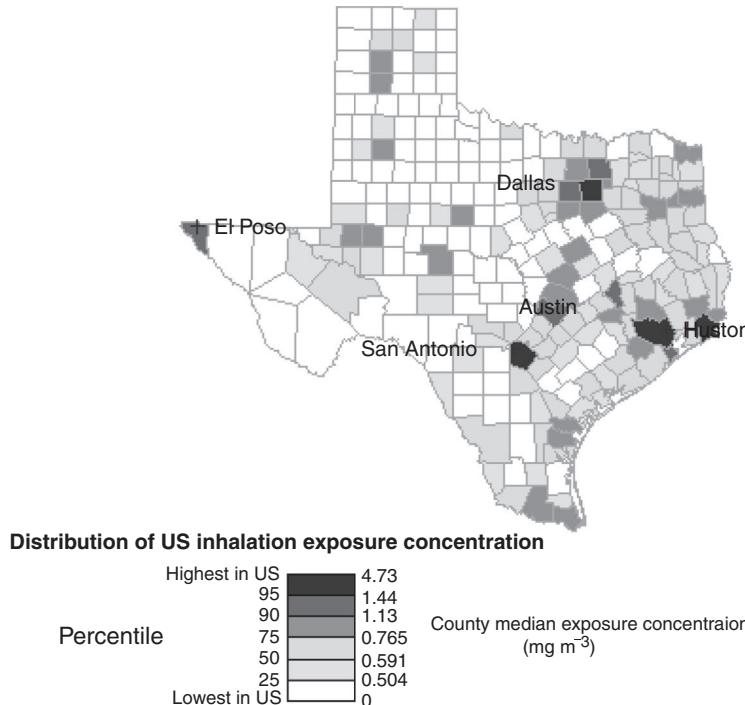
In time series of measurements of air quality and estimates of atmospheric concentration made by a model, residuals  $d$  can be computed for each location.

**TABLE 27.13** Background Concentration Estimates Used in the National-Scale Air Toxics Assessment

Pollutant	Background Concentration ( $\mu\text{g m}^{-3}$ )
Benzene	0.48
Carbon tetrachloride	0.88
Chloroform	0.083
Ethylene dibromide	0.0077
Ethylene dichloride	0.061
Formaldehyde	0.25
Hexachlorobenzene	0.000093
Mercury compounds	0.0015
Methylene chloride	0.15
Polychlorinated biphenyls	0.00038
Perchloroethylene (tetrachloroethylene)	0.14
Trichloroethylene	0.081

Source: US Environmental Protection Agency.

**FIGURE 27.39** Estimated county median exposure benzene concentrations in Texas in 1996. A county's shading indicates its exposure concentration compared with all other counties in the nation. The exposure concentration value displayed is the county median in micrograms of benzene per cubic meter of air (micrograms per cubic meter). Similar maps can be generated for other states and various air toxics at the US Environmental Protection Agency's National Air Toxics Assessment Web site: <http://www.epa.gov/ttn/atw/nata/mapexpo.html>.



The residual  $d$  is the difference between values paired timewise:

$$d = M - E \quad (27.54)$$

where  $M$  is the measured value and  $E$  is the value estimated by the model.

A measure of bias  $\bar{d}$  is the first moment of the distribution of these differences, or the average difference:

$$\bar{d} = \frac{1}{N} \sum d \quad (27.55)$$

A measure of the variability of the differences is the variance  $S^2$ , which is the second moment of the distribution of these differences:

$$S^2 = \sum (d - \bar{d})^2 / N = \frac{\sum d^2}{N} - \left( \frac{\sum d}{N} \right)^2 \quad (27.56)$$

The square root of the variance is the standard deviation.

The mean absolute error (MAE) is

$$MAE = \sum |d| / N \quad (27.57)$$

The mean square error (MSE) is

$$MSE = \sum d^2 / N \quad (27.58)$$

The root-mean-square error is the square root of the MSE. Note that since the root-mean-square error involves the square of the differences, outliers have more influence on this statistic than on the MAE.

The fractional error (FE)<sup>73</sup> is

$$FE = (M - E) / 0.5(M + E) \quad (27.59)$$

The mean fractional error (MFE) is

$$MFE = \sum FE / N \quad (27.60)$$

The FE is logarithmically unbiased, that is, an  $M$  which is  $k$  times  $E$  produces the same magnitude FE (but of opposite sign) as an  $M$  which is  $1/k$  times  $E$ .

In addition to analyzing the residuals, it may be desirable to determine the degree of agreement between sets of paired measurements and estimates. The linear correlation coefficient  $r_{EM}$  is

$$r_{EM} = \frac{N \sum E \cdot M - \sum E \sum M}{\sqrt{\left[ N \sum E^2 - (\sum E)^2 \right] \left[ N \sum M^2 - (\sum M)^2 \right]}} \quad (27.61)$$

The slope  $b$  and intercept  $a$  of the least-squares line of best fit of the relation  $M = a + bE$  are

$$\text{Intercept : } a = \frac{\sum E^2 \sum M - \sum E \sum E \cdot M}{N \sum E^2 - (\sum E)^2} \quad (27.62)$$

$$\text{Slope : } b = \frac{N \sum E \cdot M - \sum E \sum M}{N \sum E^2 - (\sum E)^2} \quad (27.63)$$

The temporal correlation coefficient at each monitoring location can be calculated by analysis of the paired values over a time period of record. The spatial

correlation coefficient at a given time can be calculated by analysis of the paired values from each station. For the spatial correlation coefficient to have much significance, there should be 20 or more monitoring locations.

Techniques to use for evaluations have been discussed by Cox and Tikvart,<sup>74</sup> Hanna,<sup>75</sup> and Weil et al.<sup>76</sup> Hanna<sup>77</sup>, which demonstrate how resampling of evaluation data will allow use of the bootstrap and jack-knife techniques so that error bounds can be placed about estimates.

The use of various statistical techniques has been discussed<sup>78</sup> for two situations. For standard air quality networks with an extensive period of record, analysis of residuals, visual inspection of scatter diagrams, and comparison of cumulative frequency distributions are quite useful techniques for assessing model performance. For tracer studies the spatial coverage is better, so that identification of maximum measured concentrations during each test is more feasible. However, temporal coverage is more limited with a specific number of tests not continuous in time.

The evaluations cited in the following sections are examples of the use of various measures of performance.

#### 27.4.6.2 Performance of Single-Source Models

Since wind direction changes with height above ground and plume rise will cause the height of the plume to vary in time, it is difficult to model accurately plume transport direction. Because of this transport wind direction error, analyses of residuals and correlations are not frequently utilized for assessment of single-source model performance. Instead, cumulative frequency distributions of estimated and measured concentrations for specific averaging times at each location are examined, as well as comparison of the highest concentrations such as the five highest for each averaging time of interest, e.g. 3 and 24 h.

The performance of one specific single source atmospheric dispersion model, CRSTER,<sup>78</sup> for the second-highest once-a-year 24-h concentrations, is summarized in Figure 27.40 in terms of ratios of estimates to measurements. Overestimates by more than a factor of 2 occur for all receptors whose elevations are near or exceed stack top. The value  $\Delta E$  is the elevation of the receptor minus the elevation of the stack base;  $h$  is the physical stack height. Over seven sites, having stacks varying from 81 to 335 m, for receptors having elevations above the stack base less than 0.7 of the stack height, the second-highest, once-a-year 24-h estimates were within a factor of 2 of the measurements for 25 of 35 monitoring stations.

Comparisons<sup>81</sup> of measured concentrations of SF<sub>6</sub> tracer released from a 36-m stack, and those estimated by the Point-to-Multipoint (PTMPT) model for 133 data

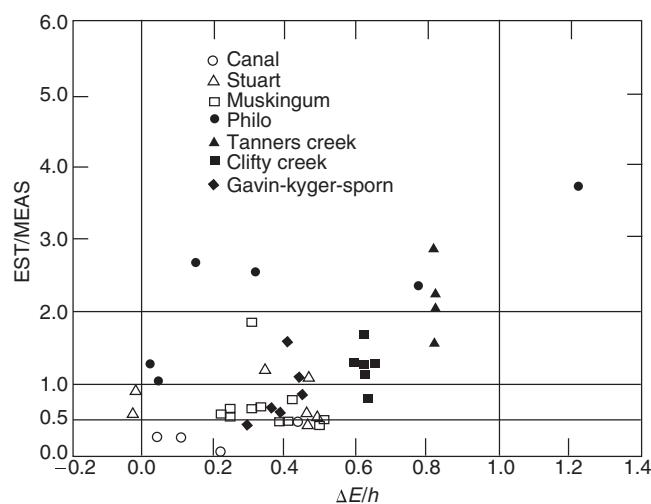


FIGURE 27.40 Ratio of second-highest 24 h estimated concentrations from the single source dispersion model (CRSTER)<sup>78</sup> to measured concentrations as a function of the excess of receptor elevation over stack base evaluation  $\Delta E$  relative to the stack height  $h$ . Names with each symbol are power plants. *From Turner and Irwin.<sup>80</sup>*

pairs over Pasquill stabilities varying from B through F, had a linear correlation coefficient of 0.81. Here 89% of the estimated values were within a factor of 3 of the measured concentrations. The calculations were most sensitive to the selection of stability class. Changing the stability classification by 1 varies the concentration by a factor of 2–4.

#### 27.4.6.3 Performance of Urban Models for Nonreactive Pollutants

Because there are multiple sources of most pollutants in urban areas, and because the meteorology of urban areas is modified so that the extremes of stability are avoided, concentrations tend to vary much less in urban than in rural areas.

For sources having a large component of emissions from low-level sources, the simple Gifford–Hanna model given previously as Eqn (27.46),  $C = Gq_a/u$ , works well, especially for long-term concentrations, such as annual ones. Using the derived coefficients of 225 for PM and 50 for SO<sub>2</sub>, an analysis of residuals (measured minus estimated) of the dependent data sets (those used to determine the values of the coefficient  $G$ ) of 29 cities for PM and 20 cities for SO<sub>2</sub> and an independent data set of 15 cities for PM is summarized in Table 27.14. For the dependent data sets, overestimates result. The standard deviations of the residuals and the MAE are about equal for particulates and sulfur dioxide. For the independent data set the mean residual shows only slight overestimation, and the standard deviation of residuals and MAE are considerably smaller.

TABLE 27.14 Residual Analysis for the Gifford–Hanna Model (Eqn (27.46))

Pollutant	<i>N</i>	$\bar{M}$	$S_M$	$\bar{E}$	$S_E$	$\bar{d}$	$S_d$	$ \bar{d} $
Particulate	29	110.7	27.8	171.9	111.5	-61.2	103.7	81.3
SO <sub>2</sub>	20	89.8	83.1	116.25	72.0	-26.5	101.2	82.5
Independent data set particulate	15	91.6	38.7	93.2	51.7	-1.6	24.9	21.3

Note: *N* is the number of cities, *M* is measured, *E* is estimated from the model, *d* is residual (measured—estimated) and *S* values are standard deviations.  
Data are from Gifford and Hanna.<sup>55</sup>

TABLE 27.15 Residual Analysis Using 1969 New York Data\*

Model	Pollutant	<i>N</i>	$\bar{M}$	$S_M$	$\bar{E}$	$S_d$	$ \bar{d} $
CDM	Particulate	113	82	23	74	22	16
6B	Particulate	113	82	23	67	25	19
CDM	SO <sub>2</sub>	75	135	72	138	52	37
6B	SO <sub>2</sub>	75	135	72	127	56	38

\* Adapted from Turner et al.<sup>82</sup>

Note: *N* is the number of monitoring stations, *M* is measured, *E* is estimated from the model, *d* is residual (measured—estimated), and *S* values are standard deviations.

A version of the Gifford–Hanna model was evaluated<sup>81</sup> using 1969 data for 113 monitoring stations for PM and 75 stations for SO<sub>2</sub> in the New York metropolitan area. This version differed from Eqn (27.46) in considering major point source contributions and the stack height of emission release. This model produced results (Table 27.15) comparable to those of the much more complicated Climatological Dispersion Model (CDM).<sup>82</sup>

The urban RAM model was evaluated<sup>83</sup> using 1976 sulfur dioxide data from 13 monitoring locations in St. Louis on the basis of their second-highest once-a-year concentrations. The ratio of estimated to measured 3-h average concentrations was from 0.28 to 2.07, with a median of 0.74. Half of the values were between 0.61 and 1.11. For the 24-h average concentrations the ratios ranged from 0.18 to 2.31, with a median of 0.70. Half of the values were between 0.66 and 1.21. Thus, the urban RAM model generally underestimates concentrations by about 25%.

#### 27.4.6.4 Performance of Photochemical Models

The performance of photochemical models is evaluated by their ability to estimate the magnitude, time, and location of occurrence of the secondary pollutant oxidant (ozone). Several photochemical models were evaluated using 10 days' data from St. Louis (Table 27.16). Among those evaluated were the PBM,<sup>40</sup> which features a single variable-volume reacting cell. This model is most appropriate for use with light winds, so that most of the emissions will remain

in the cell and react, rather than being rapidly transported through the downwind side of the cell. The maximum measured concentrations for the 10 days ranged from 0.08 to 0.18 ppm; the maximum model estimates ranged from 0.07 to 0.22 ppm.

The second model evaluated was the Lagrangian Photochemical Model,<sup>85</sup> a trajectory model. Backward trajectories were first determined so that starting positions could be used that would allow trajectories to reach station locations at the times of measurement. Measured concentrations ranged from 0.20 to 0.26 ppm and estimated concentrations from 0.05 to 0.53 ppm.

The third model evaluated was the UAM,<sup>86</sup> a three-dimensional grid-type model. The area modeled was 60 by 80 km, consisting of cells 4 km on a side. There are four layers of cells in the vertical, the bottom simulating the mixing layer. The model provides both spatially and temporally resolved estimates. Hour-averaged

TABLE 27.16 Residual Analyses of Three Photochemical Models

Model	Ozone (ppm)			
	<i>N</i>	$-d$	$S_d$	$  -d  $
Photochemical box model	10	-0.033	0.041	0.039
Lagrangian photochemical model	10	-0.004	0.110	0.080
Urban airshed model	10	0.074	0.033	0.074

Note: *N* is the number of days, *d* is residual (measured—estimated), and *S* is the standard deviation.

Adapted from Shreffler and Schere.<sup>85</sup>

estimates of each pollutant species at each monitoring site within the model domain are given. Measured concentrations ranged from 0.17 to 0.24 ppm and estimated concentrations ranged from 0.10 to 0.17 ppm. The model underestimates the concentration at the point of the observed maximum each day.

Seinfeld<sup>65</sup> indicates that photochemical models estimating peak ozone concentrations in urban areas are generally within 30% of measured peaks.

#### **27.4.6.5 Utilization of Models**

For the air quality manager to place model estimates in the proper perspective to aid in making decisions, it is becoming increasingly important to place error bounds about model estimates. In order to do this effectively, a history of model performance under circumstances similar to those of common model use must be established for the various models. It is anticipated that performance standards will eventually be set for models.

#### **27.4.6.5 Modeling to Meet Regulatory Requirements**

In the United States if the anticipated air pollution impact is sufficiently large, modeling has been a requirement for new sources in order to obtain a permit to construct. The modeling is conducted following guidance issued by the US EPA.<sup>87,88</sup> The meeting of all requirements is examined on a pollutant-by-pollutant basis. Using the assumptions of a design that will meet all emission requirements, the impact of the new source, which includes all new sources and changes to existing sources at this facility, is modeled to determine pollutant impact. This is usually done using a screening-type model such as SCREEN.<sup>89</sup> The impacts are compared to the modeling significance levels for this pollutant for various averaging times. These levels are generally about 20% of the National Ambient Air Quality Standards. If the impact is less than the significance level, the permit can usually be obtained without additional modeling. If the impact is larger than the significance level, a radius is defined, which is the greatest distance to the point at which the impact falls to the significance level. Using this radius, a circle is defined, which is the area of significance for this new facility. All sources (not only this facility, but all others) emitting this pollutant are modeled to compare anticipated impact with the NAAQS and with the PSD increments.

The implementation of CAAA90 not only requires permission for new sources but also permits for existing facilities. There is also a requirement for reexamination of these permits at intervals not longer than 5 years. The permit programs are set up and administered by the states under the review and guidance of EPA. These programs include the collection of permit fees sufficient to support the program. Implementation

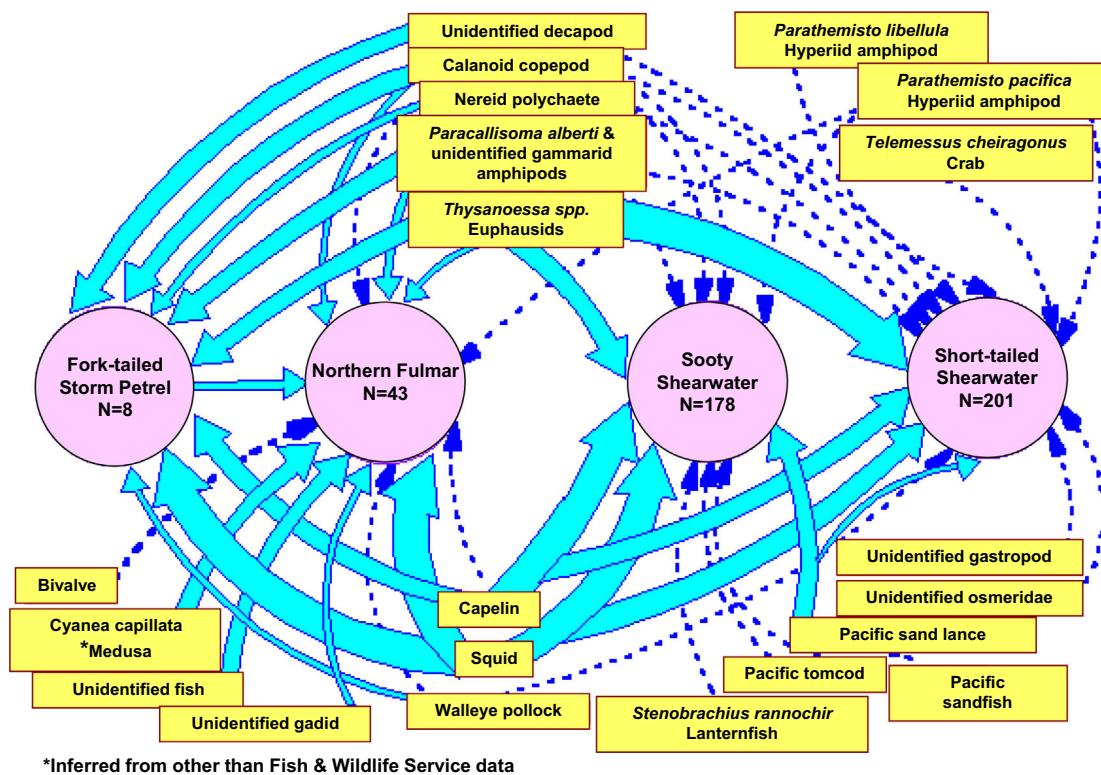
of CAAA90 will require the application of MACT on an industry-by-industry basis as specified by EPA. Following the use of MACT, a calculation will be made of the residual risk due to the remaining pollutant emissions. This is accomplished using air quality dispersion modeling that is interpreted using risk factors derived from health information with the inclusion of appropriate safety factors.

Because of their inclusion of the effects of building downwash, the ISC2 models,<sup>48</sup> ISCST and ISCLT (short-term performing calculations by hourly periods and long-term using the joint frequencies of wind direction, wind speed, and Pasquill stability, commonly referred to as STAR data) are recommended. The ISC2 models differ only slightly from the earlier ISC models (several small errors that make little difference in the resulting calculations were corrected). The recoding of the model to result in ISC2 was requested by EPA to overcome a difficult-to-understand code that had resulted from a number of changes that had been incorporated. The ISC models will make calculations for three types of sources: point, area, and volume. There are recognized deficiencies in the area source algorithm incorporated in the ISC models.

Models are continuing to improve, but many challenges remain. Combined with better measurements and analytical procedures, the new models are crucial to air pollution control and planning decisions.

## **27.5 MODELING AIR POLLUTION PARTITIONING**

Predicting the movement, transformation, and fate of an air pollutant must account not only for the initial contact with the pollutant, but also for what happens to the pollutant after contact with the receptor. Absorption, distribution, metabolism, and elimination of the pollutant and its metabolites within an organism after uptake is known as pharmacokinetics, or when specifically applied to pollutants, toxicokinetics. Air pollutant exposure can be modeled in a unidirectional and one-dimensional fashion, such as the flow within an ecosystem (mass and energy transfer between trophic levels, i.e. bioenergetics). In addition, risk and exposure assessments must consider multiple levels of biological organization that can describe the interrelationships within the biological system. Mechanisms can be derived by characterizing and perturbing these networks (e.g. behavioral and environmental factors).<sup>90</sup> This can apply to a food chain or food web model (Figure 7.2 in Chapter 7), surface exchanges (Figure 8.2 in Chapter 8) a multi-species kinetic model (Figure 27.41), or numerous other modeling platforms.



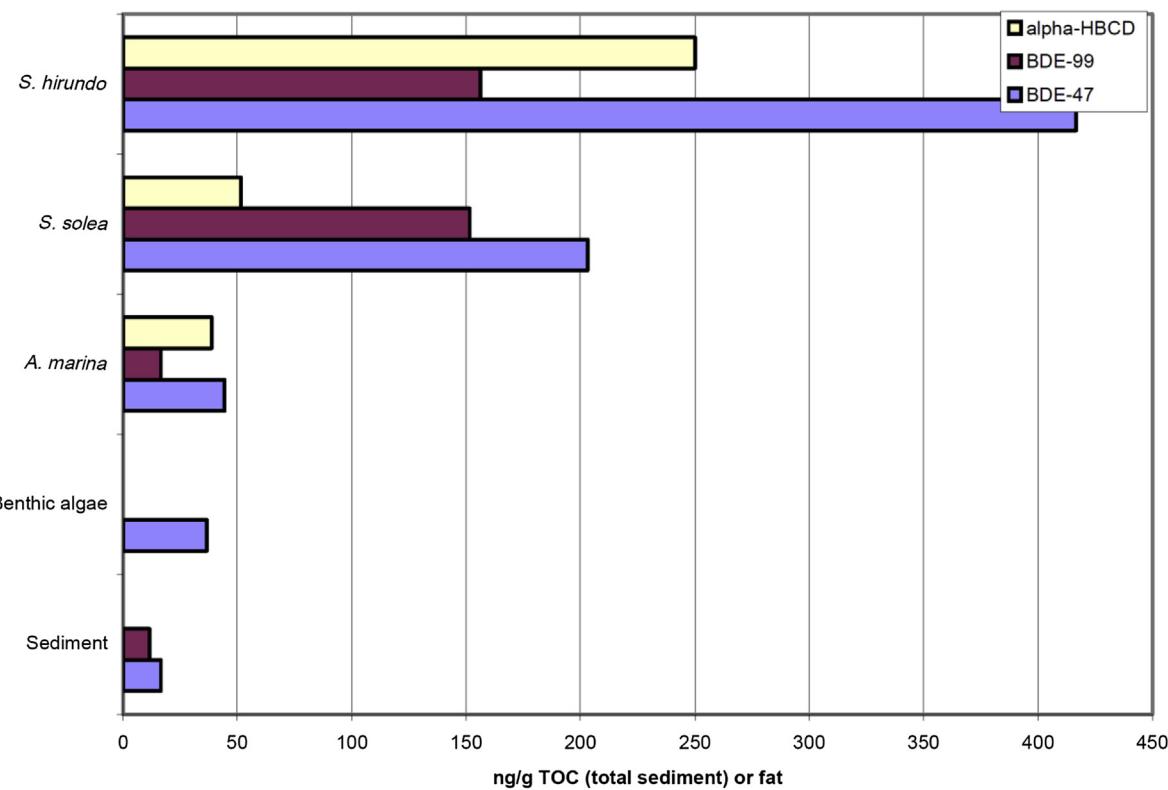
**FIGURE 27.41** Flow of energy and mass among invertebrates, fish and seabirds (*Procellariiform*) in the Gulf of Alaska. The larger the width of the arrow, the greater the relative flow. Note how some species prefer crustaceans (e.g. copepods and euphausiids), but other species consume larger forage species like squid. Sanger GA. Diets and food web relationships of seabirds in the Gulf of Alaska and adjacent marine areas. U.S. Department of Commerce, National Oceanic and Atmospheric Administration, OCSEAP Final Report # 45; 1983. p. 631–771.

The affinities and partitioning discussed in Chapter 18 can be modeled. Food web and food chain diagrams and models are often useful in estimating and predicting environmental insults after an air pollutant has been deposited. They can begin with estimates of soil-to-air and water-to-air exchanges, e.g. the long-range transport of persistent compounds followed by predator-prey and food linkages in the web (Figure 27.41), lead to dramatic differences in pollutant concentration in the tissue of different species in the system. The inherent properties and partitioning discussed in Chapter 6 and Chapter 18, respectively, greatly influence the rate of accumulation, e.g. bioaccumulation factors and octanol-air and octanol-water partitioning. Figure 27.42 illustrates that after the deposition of the persistent flame retardants, these semivolatile organic pollutants build up in the food chain. This is known as biomagnification, with the highest concentrations of the pollutants found in top predators. Food web and food chains are key modes by which humans and other organisms become exposed to contaminants, including air pollutants. Webs and chains account for the interrelationships among the abiotic (nonliving) and biotic (living) environments. Organisms, including humans, live within an interconnected network or web of life, with strands of energy and mass affecting the potential exposure.

The toxicokinetic model (Figure 27.43) begins to show the complexity of the processes and mechanisms at play after a pollutant's intake. In this case, several models must be consolidated to show the kinetics, beginning with a breathing lung model consisting of alveoli, lower dead space, lung tissue, pulmonary capillaries, and upper dead space compartments. Gastrointestinal (GI) models allow for multiple circulating compounds with multiple metabolites entering and leaving each compartment, i.e. the GI model consists of the wall and lumen for the stomach, duodenum, lower small intestine, and colon, with lymph pool and portal blood compartments included. Bile flow is treated as an output from the liver to the duodenum lumen. All uptaken substances are treated as circulating. Nonspecific ligand binding, e.g. plasma protein binding, is represented in arterial blood, pulmonary capillaries, portal blood, and venous blood.

### 27.5.1 Pollutant Transport

For an air pollutant to come into contact with human populations and ecosystems it must first be transported from the source. The distance may be quite small (e.g. less than a meter from a tailpipe to a person standing nearby) to very large (e.g. intercontinental transport of persistent compounds, greenhouse gases, and the



**FIGURE 27.42 Concentrations of selected brominated flame retardants in a simplified benthic food chain of the Western Scheldt Estuary, The Netherlands.** *Sterna hirundo* = common tern; *Solea solea* = sole; and *Arenicola marina* = lugworm. Note the increasing concentrations of the pollutants moving up the food chain, from the lowest concentration in the sediment to the benthic organisms living in and on the sediment to the highest concentrations in the fish-eating birds. *van den Heuvel-Greve MJ, Leonards PEG, Vethaak AD. Food web transfer of dioxins and other organic contaminants in the Western Scheldt: implications for human and environmental health. International Council for the Exploration of the Sea. Theme Session on Human Health Risks and Marine Environmental Quality; 2006.* (For color version of this figure, the reader is referred to the online version of this book.)

ingredients of acid rain). However, the physical processes are similar.

Molecular diffusion is the exception, since it dominates only when advection and dispersion are near zero. This is seldom the case for any extended time period, so molecular diffusion is usually negligible in the ambient atmosphere. However, it is a very important transport process in quiescent systems, such as wet soils and sediment, where concentration gradients serve as the major transport process. Thus, air pollution sources, such as movement of contaminants through porous media may have to occur first, before a contaminant can volatilize or aerosolize into the atmosphere.

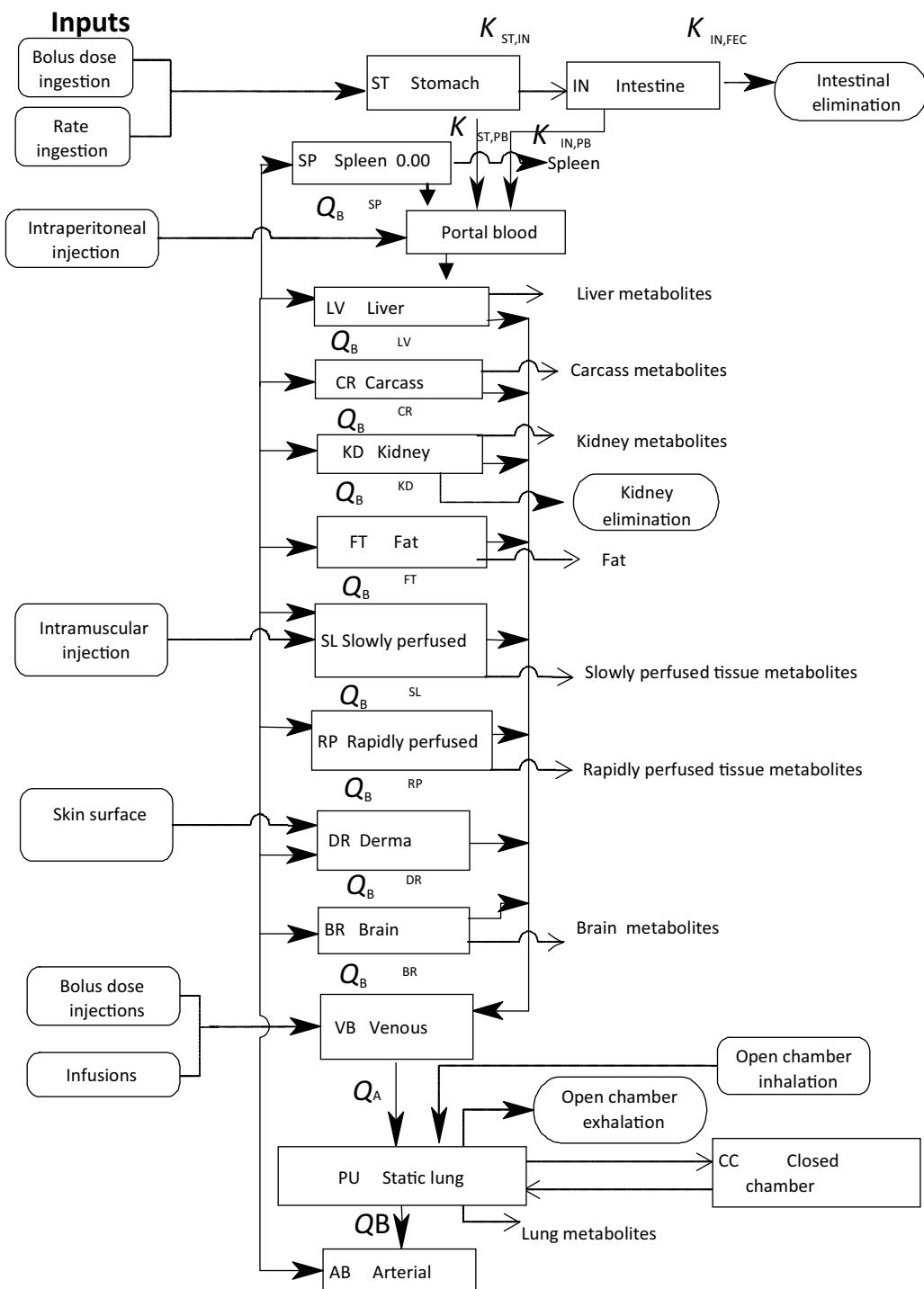
## 27.5.2 Advection

Air pollutants can be transported within the hydro-sphere and troposphere. In fact, this may be the dominant transport mechanism for pollen, cysts, and spores. From a purely physical motion perspective, the most straightforward pollutant transport process arguably is advection ( $J_{\text{Advection}}$ ). Advection is the transport of matter within the streamlines of a fluid, i.e. with the water or airflow.

In terms of total volume and mass of pollutants moved, advection accounts for the lion's share. In fact, another name for advection is bulk transport. During advection, a contaminant is moved along with the fluid or, in the language of environmental science, the environmental medium. The contaminant is merely "hitching a ride" on the fluid as it moves through the environment. Environmental fluids move within numerous matrices, such as the flow of air and water between soil particles, within sediment, in unconsolidated materials underground, and in the open atmosphere. Surface water is also an environmental medium in which advection occurs.

Advection is considered a passive form of transport because the contaminant moves along with the transporting fluid. That is, the contaminant moves only because it happens to reside in the medium. Advection occurs within a single medium and among media. The rate and direction of transport is completely determined by the rate and direction of the flow of the media.

The simplest bulk transport within one environmental medium or compartment is known as homogeneous advection, where only one fluid is carrying the contaminant. The three-dimensional rate of homogeneous,



**FIGURE 27.43 Toxicokinetic model used to estimate dose as part of an environmental exposure.** This diagram represents the static lung, with each of the compartments (brain, carcass, fat, kidney, liver, lung tissue, rapidly and slowly perfused tissues, spleen, and the static lung) having two forms of elimination, an equilibrium binding process, and numerous metabolites. Notes:  $K$  = kinetic rate;  $Q$  = mass flow; and  $Q_B$  = blood flow. Dary CC, Georgopoulos PJ, Vallero DA, Tornero-Velez R, Morgan M, Okino M, et al. (2007). Characterizing chemical exposure from biomonitoring data using the exposure related dose estimating model (ERDEM). 17th Annual conference of the international society of exposure analysis. Durham, NC. October 17, 2006; 2007. Adapted from: Blancato JN, Power FW, Brown RN, Dary CC. Exposure related dose estimating model (ERDEM): a physiologically-based pharmacokinetic and pharmacodynamic (PBPK/PD) model for assessing human exposure and risk. Report No. EPA/600/R-06/061. Las Vegas (Nevada): U.S. Environmental Protection Agency; 2006.

advective transport is simply the product of the fluid medium's flow rate and the concentration of the contaminant in the medium:

$$N = QC \quad (27.64)$$

where  $Q$  is the flow rate of the fluid medium (e.g. cubic meters per second) and  $C$  is the concentration of the chemical contaminant being transported in the medium (e.g. micrograms per cubic meter). Therefore, the units for three-dimensional advection are mass per time (e.g. micrograms per second). For example, the homogeneous advection of air containing  $100 \mu\text{g m}^{-3}$  vinyl chloride (gas phase) flowing at  $10 \text{ m}^3 \text{s}^{-1}$  is  $1000 \mu\text{g s}^{-1}$  or  $1 \text{ mg s}^{-1}$ . Thus, this plume of vinyl chloride can be characterized as a  $1 \text{ mg m}^{-3}$  plume until it is further diluted in the atmosphere.

Heterogeneous advection refers to those cases where there is a secondary phase present inside the main advective medium, e.g. the presence of PM (i.e. suspended solids) carried by wind. Heterogeneous advection involves more than one transport system within the compartment. In the vinyl chloride case above, if particle matter is also flowing in the plume and the PM has a concentration of  $100 \mu\text{g m}^{-3}$  and vinyl chloride makes up 0.05 of this PM concentration, then the aerosol phase of vinyl chloride in the plume is  $5 \mu\text{g m}^{-3}$  and the homogeneous particle phase advection is  $5 \mu\text{g m}^{-3} \times 10 \text{ m}^3 \text{s}^{-1} = 50 \mu\text{g s}^{-1}$ . This value must be added to the gas phase homogeneous calculation, so that the heterogeneous (gas and particle phases) vinyl chloride advection would be  $1000 \text{ s}^{-1}$  (gas) +  $50 \mu\text{g s}^{-1}$  (PM) =  $1050 \mu\text{g s}^{-1}$ . Thus, not only the concentration of the dissolved fraction of the contaminant must be known but also the concentration of chemical in and on the solid particles.

Heterogeneous advection is a common transport mechanism for highly lipophilic compounds or otherwise

insoluble matter that is often sorbed to particles as compared to dissolved in water. This may be similar to chemical transport, such as when metals form both lipophilic and hydrophilic species (e.g. ligands), depending upon their speciation. Many biomolecules and other complex organic compounds, such as the PAHs and PCBs, are relatively insoluble in water. Therefore, most of their advective transport is by attaching to particles. In fact, lipophilic organics are likely to have orders of magnitude greater concentrations in suspended matter than is dissolved in the water (recalling the discussion of  $K_{ow}$  in Chapters 17 and 18).

Another example of advective transport is atmospheric deposition of contaminants. The sorption of contaminants to the surface of atmospheric water droplets is known as wet deposition and sorption to solid particles is known as dry deposition. The process where these contaminants are delivered by precipitation to the earth is advection.

Rather than three-dimensional transport, many advective models are represented by the one-dimensional mass flux equation for advection, which can be stated as

$$J_{\text{Advection}} = \bar{v} \eta_e C \quad (27.65)$$

where

$\bar{v}$  = average linear velocity (meters per second)

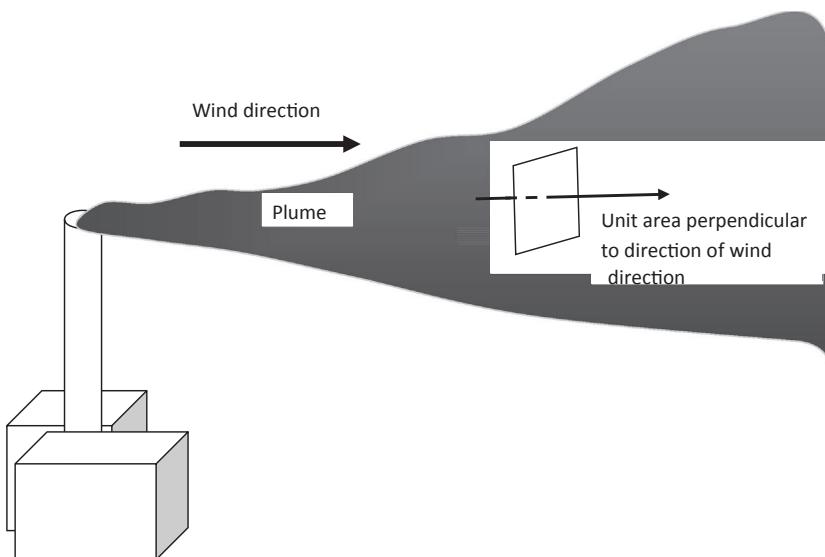
$\eta_e$  = effective porosity (percent, unitless)

$C$  = chemical concentration of the solute (kilogram per cubic meter)

Probably the most common application of the flux term is in two dimensions:

$$J_{\text{Advection}} = \bar{v} C \quad (27.66)$$

Two-dimensional fluxes are an expression of the transport of a contaminant across a unit area. This rate of this transport is the flux density (see [Figure 27.44](#)), which is



**FIGURE 27.44** Flux density of an imaginary cross-sectional area across which contaminant flux is calculated in the atmosphere.

the contaminant mass moving across a unit area per time. In most environmental applications, fluid velocities vary considerably in time and space (think about calm vs gusty wind conditions, for example). Thus, estimating flux density for advection in a turbulent fluid usually requires a time integration to determine average concentrations of the contaminant. For example, a piece of air monitoring equipment may collect samples every minute, but the model or calculation calls for an hourly value, so the 60 values are averaged to give one integrated concentration of the air pollutant.

For example, if the atmospheric concentration of pollutant A is  $15 \text{ ng m}^{-3}$  and it is moving at a velocity of  $0.1 \text{ m s}^{-1}$ , the average flux density of the pollutant A as it moves downwind can be calculated as

$$[A] = 15 \text{ ng m}^{-3}$$

$$J_{\text{Advection}} = \bar{v}C = (0.1 \text{ m s}^{-1})(15 \text{ ng m}^{-3}) = 1.5 \text{ ng m}^{-2}$$

### 27.5.3 Dispersion

Numerous dispersion processes are at work in environmental biochemodynamic systems. As is the case for diffusion, the type of dispersion can vary according to scale. Contaminant transport literature identifies two principal types, i.e. hydrodynamic dispersion and mechanical dispersion. However, these are actually not mutually exclusive terms. In fact, mechanical dispersion is a factor in dynamic dispersion.

Computational approximations are based on first principles of motion and thermodynamics and can be applied to any physical agent. For example, they may be applied to escaped or intentionally released genetically engineered microbe or its spores. They may also be useful in predicting the dispersion of agents in emergency situations.

The process of a contaminant plume's spread into multiple directions longitudinally is known dynamic dispersion. If in air, the spreading is known as *aerodynamic dispersion*, and if in water it is hydrodynamic dispersion. This spreading results from physical processes that affect the velocity of different molecules in an environmental medium. For example, in aquifers, the process is at work when the contaminant traverses the flow path of the moving groundwater. This is the

result of two physical mechanisms: molecular diffusion and mechanical dispersion. Molecular diffusion can occur under both freely flowing and stagnant fluid systems, while mechanical dispersion is of most importance in flowing systems. The units of dynamic dispersion  $d_d$  are area per time (e.g. square centimeters per second).

Since dispersion is the mixing of the pollutant within the fluid body (e.g. the atmosphere), the question arises as to whether it is better to calculate the dispersion from physical principles, using a deterministic approach, or to estimate the dispersion using statistics, actually probabilities. The Eulerian model bases the mass balance around a differential volume. A Lagrangian model applies statistical theory of turbulence, assuming that turbulent dispersion is a random process described by a distribution function. The Lagrangian model follows the individual random movements of molecules released into the plume, using statistical properties of random motions that are characterized mathematically. Thus, this mathematical approach estimates the movement of a volume of chemical (particle)<sup>n</sup> from one point in the plume to another distinct point during a unit time. Thus, the path each particle takes during this time is an ensemble mean field relates to the particle displacement probabilities:

$$\bar{C}(x, y, z, t) = M_{\text{Total}}P(Dx, t) \quad (27.67)$$

where

$Dx = x_2 - x_1$  = particle displacement

$P(Dx_2, t)$  = probability that the point  $x_2$  will be immersed in the dispersing media at time  $t$

$M_{\text{Total}}$  = total mass of particles released at  $x_1$

$\bar{C}$  = mean concentration of all released

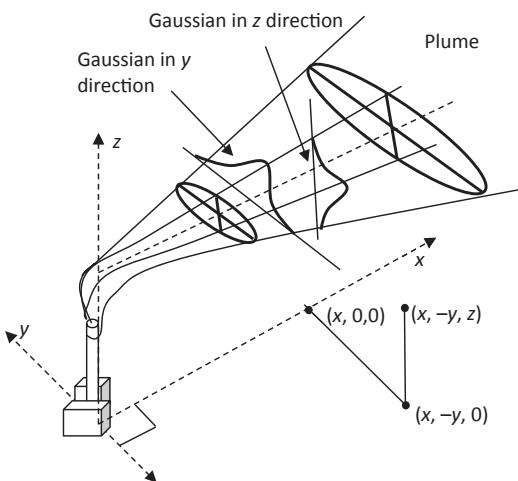
particles = mass of particles the plume  $dx \cdot dy \cdot dz$  around  $x_2$

Gaussian dispersion models assume a normal distribution of the plume (see Figure 27.45). This is a common but at best a first approximation of the actual dispersion within a biochemodynamic system.

In a deterministic approach, the dispersion includes mixing at all scales. At the larger scales, characteristics of strata and variability in the permeability of the layers must be described. So, a deterministic dispersion flux would be

$$J_{\text{Dispersion}} = D \cdot \underline{\text{grad}} C \quad (27.68)$$

<sup>n</sup> Science is not always consistent with its terminology. The term "particle" is used in many ways. In dispersion modeling, the term particle usually means a theoretical point that is followed in a fluid. The point represents the path that the pollutant is expected to take. Particle is also used to mean aerosol in atmospheric sciences. Particle is also commonly used to describe unconsolidated materials, such as soils and sediment. The present discussion, for example, accounts for the effects of these particles (e.g. frictional) as the fluid moves through unconsolidated material. The pollutant PM, particle matter, is commonly referred to as "particles". Even the physicist's particle-wave dichotomy comes into play in environmental analysis, as the behavior of light is important in environmental chromatography.



**FIGURE 27.45 Gaussian plume.** The pollutants are assumed to be distributed vertically and horizontally in a statistically normal manner about the plume centerline away from the point of release.

where

$J_{\text{Dispersion}}$  = mass flux of solute due to dispersion (kilograms per square meter per second)

$D$  = dispersion tensor (meters per second)

$C$  = concentration of chemical contaminant (kilogram per cubic meter)

The  $D$  includes coefficients for each direction of dispersion, i.e. longitudinally, horizontally, and vertically ( $D_{xx}$ ,  $D_{xy}$ ,  $D_{xz}$ ,  $D_{yy}$ ,  $D_{yz}$ ,  $D_{zz}$ ).

#### 27.5.4 Diffusion

In diffusion, contaminants and other solutes move from higher to lower concentrations in a solution. For example, if a wet soil contains methylmercury ( $\text{CH}_3\text{Hg}$ ) compounds in concentrations of  $100 \text{ ng l}^{-1}$  at a depth of 3 mm and at  $10 \text{ ng l}^{-1}$  depth of 2 mm, diffusion would account for the upward transport of the  $\text{CH}_3\text{Hg}$  through the soil. Diffusion is described by *Fick's laws*. The first law says that the flux of a solute under steady state conditions is a gradient of concentration with distance:

$$J_{\text{Diffusion}} = -D \frac{d[C]}{dx} \quad (27.69)$$

where  $D$  is a diffusion coefficient (units of area/time),  $[C]$  is the molar concentration of the contaminant, and  $x$  is distance between the points of contaminant concentration measurements (units of length). Note that the concentration can also be expressed as mass per fluid volume (e.g. milligram per liter), in which case, flux is expressed as

$$J_{\text{Diffusion}} = -D \frac{dC}{dx} \quad (27.70)$$

The concentration gradient can also appear in the form

$$J_{\text{Diffusion}} = -d_o i_c \quad (27.71)$$

where  $d_o$  is again the proportionality constant, and

$$i_c = \frac{\partial C}{\partial x} \quad (27.72)$$

The negative sign denotes that the transport is from greater to lesser contaminant concentrations. Fick's second law comes into play when the concentrations are changing with time. The change of concentrations with respect to time is proportional to the second derivative of the concentration gradient:

$$\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial x^2} \quad (27.73)$$

All of the diffusion expressed in these equations is one dimensional, but three-dimensional forms are available and used in models.

Two types of diffusion are important to transport of contaminants: molecular diffusion and turbulent or eddy diffusion. Each Fickian process operates at its own scale. At the molecular level, in surface waters and atmospheric systems, diffusion dominates as a transport mechanism only in a very thin boundary layer between the fluid media. However, in sediments, sludge, and groundwater, this can be an important transport mechanism. Since the concentration gradient ( $i_c$ ) is the change in concentration (e.g. in units of kilogram per cubic meter) with length (in meters), the units of  $i_c$  are  $\text{kg m}^{-4}$ . Diffusion is therefore analogous to the physical potential field theories (i.e. flow is from the direction of high potential to low potential, such as from high pressure to low pressure). This gradient is observed in all phases of matter, solid, liquid, or gas. So, molecular diffusion is really only a major factor of transport in porous media, such as soil or sediment, and can be ignored if other processes, such as advection, bring about a flow of  $2 \times 10^{-5} \text{ m s}^{-1}$  or higher.<sup>o</sup> However, it can be an important process for source characterization, since it may be the principal means by which a contaminant becomes mixed in a quiescent container (such as a drum, a buried sediment, or a covered pile) or at the boundaries near clay or artificial liners in landfill systems.

Turbulent motion in fluids is characterized by the formation of eddies of various sizes. These eddies can be modeled according to Fick's first law (concentration

<sup>o</sup>This value is taken from Tucker WA, Nelkson LH. Diffusion coefficients in air and water. *Handbook of chemical property estimation techniques*. New York, (NY): McGraw-Hill; 1982. Flows this low are not uncommon in some groundwater systems or at or in clay liners in landfills.

gradients), so that the same equations in this chapter applied to molecular diffusion may also be used to estimate the transport of contaminants by eddy diffusion. Like molecular diffusion, eddy diffusion can be modeled in one, two, or three dimensions. One-dimensional models assume that the diffusion coefficient ( $D$ ) does not change with respect to direction. However,  $D$  must be adjusted to the model. This must be done when  $D$  is expected to vary with spatial location and time (which it always does, but if the change is not significant, it may be ignored). The coefficient may also be anisotropic, that is, it may vary in different directions or vertically in the air or water.

Pollutants can diffuse from biotechnological operations. Assume, for example, that a composting system is operating in a building with a “footprint” of  $200 \text{ m}^2$  of untreated soil. The soil air  $3 \text{ m}$  beneath the compost has a concentration of  $2 \mu\text{g cm}^{-3}$  total hydrocarbons (THC). If the diffusion coefficient is  $0.01 \text{ cm}^2 \text{ s}^{-1}$  in this particular soil and assuming that the air is well mixed, the flux density of the vapor and the rate of vapor release by molecular diffusion can be calculated as a one-dimensional flux, the vertical concentration (upward on  $z$  axis)

$$\begin{aligned}\frac{dC}{dz} &= (2 \times 10^{-6} \text{ g cm}^{-3}) / (300 \text{ cm}) \\ &= 6.7 \times 10^{-9} \text{ g cm}^{-4}\end{aligned}$$

The flux density is

$$\begin{aligned}J_{\text{Diffusion}} &= -D \frac{dC}{dx} \\ &= (10^{-2} \text{ cm}^2 \text{ s}^{-1}) \times (6.7 \times 10^{-9} \text{ g cm}^{-4}) \\ &= 6.7 \times 10^{-11} \text{ g cm}^{-2} \text{ s}^{-1}\end{aligned}$$

Applying the flux density to the  $200 \text{ m}^2$  ( $2 \times 10^6 \text{ cm}^2$ ), the penetration of the vapor into the air

$$\begin{aligned}(6.7 \times 10^{-11} \text{ g cm}^{-2} \text{ s}^{-1}) \times (2 \times 10^6 \text{ cm}^2) \\ \times (3600 \text{ s h}^{-1}) \times (24 \text{ h day}^{-1}) = 11.5 \text{ g day}^{-1}\end{aligned}$$

## 27.5.5 Combined Effect of Fluxes, Sinks, and Sources

Numerous, interrelated biochemodynamic processes determine transport and environmental fate of contaminants. Recall that one of the laws dictating fluid dynamics mentioned at the beginning of this discussion included conservation of mass. This is true, of course, but the molecular structure of the chemical may very well change. The transport depends upon chemical characteristics of the compound (e.g. solubility, vapor pressure, reactivity, and oxidation state) and those of the environment (e.g. presences of microbes, redox potential, ionic strength, and pH). The chemical

degradation can be as simple as a first-order decay process (i.e. the degradation of the contaminant concentration  $C$ ):

$$\frac{\partial C}{\partial t} = -\lambda c \quad (27.74)$$

The degradation ( $\lambda$ ) terms are applied to each chemical. The new degradation products call for an iterative approach to the transport and fate of each degradation product can be described. As a new compound is formed, it must go through the same scrutiny for each transport step. This is even more critical if the degradates are toxic. Some are even more toxic than the parent compound.

A model of the expected total flux representing the fate ( $J_{\text{Fate}}$ ) of the contaminant can therefore be

$$\begin{aligned}J_{\text{Fate}} &= J_{\text{Desorption}} + J_{\text{Diffusion}} + J_{\text{Dilution}} + J_{\text{Dispersion}} \\ &\quad + J_{\text{Advection}} - J_{\text{Sorption}} - \lambda[c]\end{aligned} \quad (27.75)$$

### 27.5.5.1 Biochemodynamic Transport Models

The partitioning and transport mechanisms discussed in this chapter can be combined into fugacity-based, chemodynamic transport models. Such models are of three types:

*Level 1 model:* This model is based on an equilibrium distribution of fixed quantities of contaminants in a closed environment (i.e. conservation of contaminant mass). There is no chemical or biological degradation, advection, and no transport among compartments (such as sediment loading or atmospheric deposition to surface waters).

A level 1 calculation describes how a given quantity of a contaminant will partition among the water, air, soil, sediment, suspended particles, and fauna, but does not take into account chemical reactions. Early level 1 models considered an area of  $1 \text{ km}^2$  with 70% of the area covered in surface water. Larger areas are now being modeled (e.g. about the size of the state of Ohio).

*Level 2 model:* This model relaxes the conservation restrictions of level 1 by introducing direct inputs (e.g. emissions) and advective sources from air and water. It assumes that a contaminant is being continuously loaded at a constant rate into the control volume, allowing the contaminant loading to reach steady state and equilibrium between contaminant input and output rates. Degradation and bulk movement of contaminants (advection) is treated as a loss term. Exchanges between and among media are not quantified.

Since the level 2 approach is a simulation of a contaminant being continuously discharged into numerous compartments and that achieves a steady state equilibrium, the challenge is to deduce the losses of the contaminant due to chemical reactions and advective (nondiffusive) mechanisms.

Reaction rates are unique to each compound and are published according to reactivity class (e.g. fast, moderate, or slow reactions), which allows modelers to select a class of reactivity for the respective contaminant to insert into transport models. The reactions are often assumed to be first order, so the model will employ a first-order rate constant for each compartment in the environmental system (e.g.  $x \text{ mol h}^{-1}$  in water,  $y \text{ mol h}^{-1}$  in air,  $z \text{ mol hr}^{-1}$  in soil). Much uncertainty is associated with the reactivity class and rate constants, so it is best to use rates published in the literature based upon experimental and empirical studies, wherever possible.

Advection flow rates in level 2 models are usually reflected by residence times in the compartments. These residence times are commonly set at 1 h in each medium, so the advection rate ( $r_i$ ) is the volume of the compartment divided by the residence time ( $t$ ):

$$r_i = Vt^{-1} \quad (27.76)$$

*Level 3 model:* Same as level 2, but does not assume equilibrium between compartments, so each compartment has its own fugacity. Mass balance applies to the whole system and each compartment within the system. Includes mass transfer coefficients, rates of deposition and resuspension of contaminant, rates of diffusion, soil runoff, and area covered. All of these factors are aggregated into an intermedia transport term ( $D$ ) for each compartment.

The assumption of equilibrium in level 1 and 2 models is a simplification, and often a gross oversimplification of what actually occurs in environmental

systems. When the simplification is not acceptable, kinetics must be included in the model. Numerous diffusive and nondiffusive transport mechanisms are included in level 3 modeling. For example, values for the various compartments' unique intermedia transport velocity parameters (in length per time dimensions) are applied to all contaminants being modeled (these are used to calculate the  $D$  values).

It is important to note that models are only as good as the information and assumptions that go into them. For example, neighborhood-scale effects (see Figure 27.46) can modify estimates from transport models or from measurement interpolations (barriers, channeling, local flows, and trapping). This applies to all transport models, whether highly computational or simplified. Site-specific differences can greatly affect predicted outcomes, such as whether terrain is complex or simple, whether there are frequent inversions, whether sources emit the contaminant continuously or haphazardly, etc. This is true at all scales. For example, microenvironmental models must account for variability in room configurations, movements and activities of occupants, and seasonal changes.

Myriad physical, chemical, and biological processes are at work within the atmosphere and environmental systems and in the various receptor systems after products and organisms are released. Combinations of these processes into equations and models can increase uncertainty, which can be propagated and magnified as the factors and variables interact. Thus, air pollution

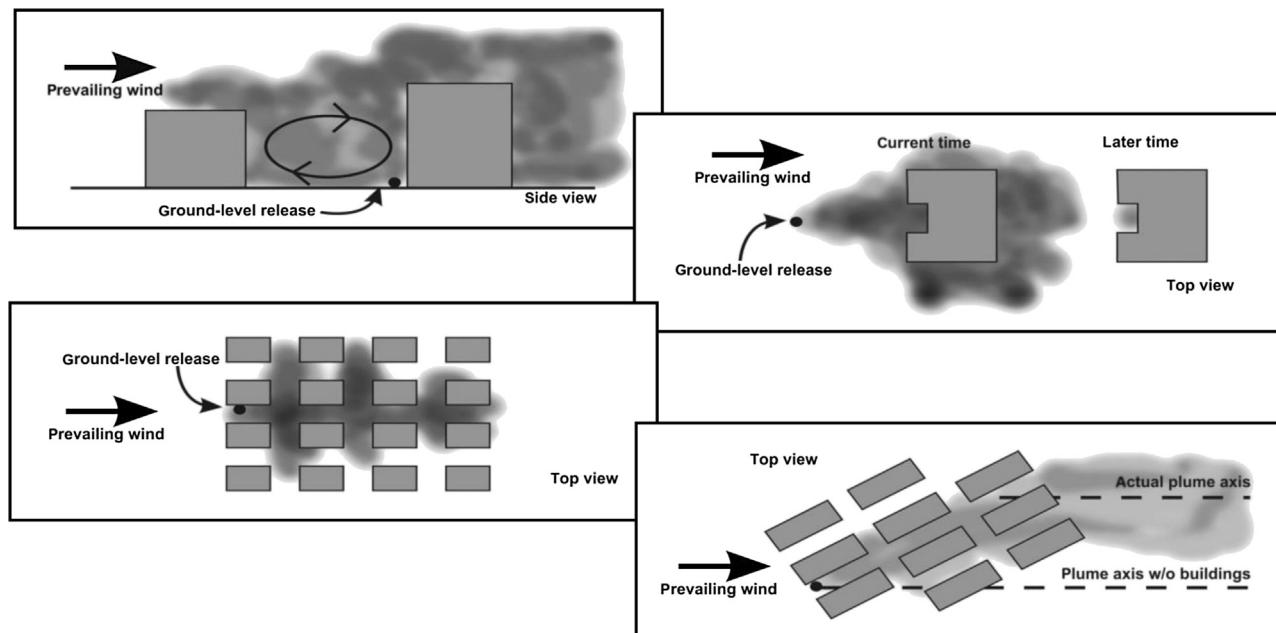


FIGURE 27.46 Scale effects can modify significantly estimates from atmospheric transport models or from monitor interpolations (barriers, channeling, local flows, and trapping); there is need for both computational and simplified models. Vallero DA, Isukapalli SS, Georgopoulos PG, Liou PJ. Improved assessment of risks from emergency events: application of human exposure measurements. 4th Annual interagency workshop: Using environmental information to prepare and respond to emergencies. New York (NY), July 17, 2009.

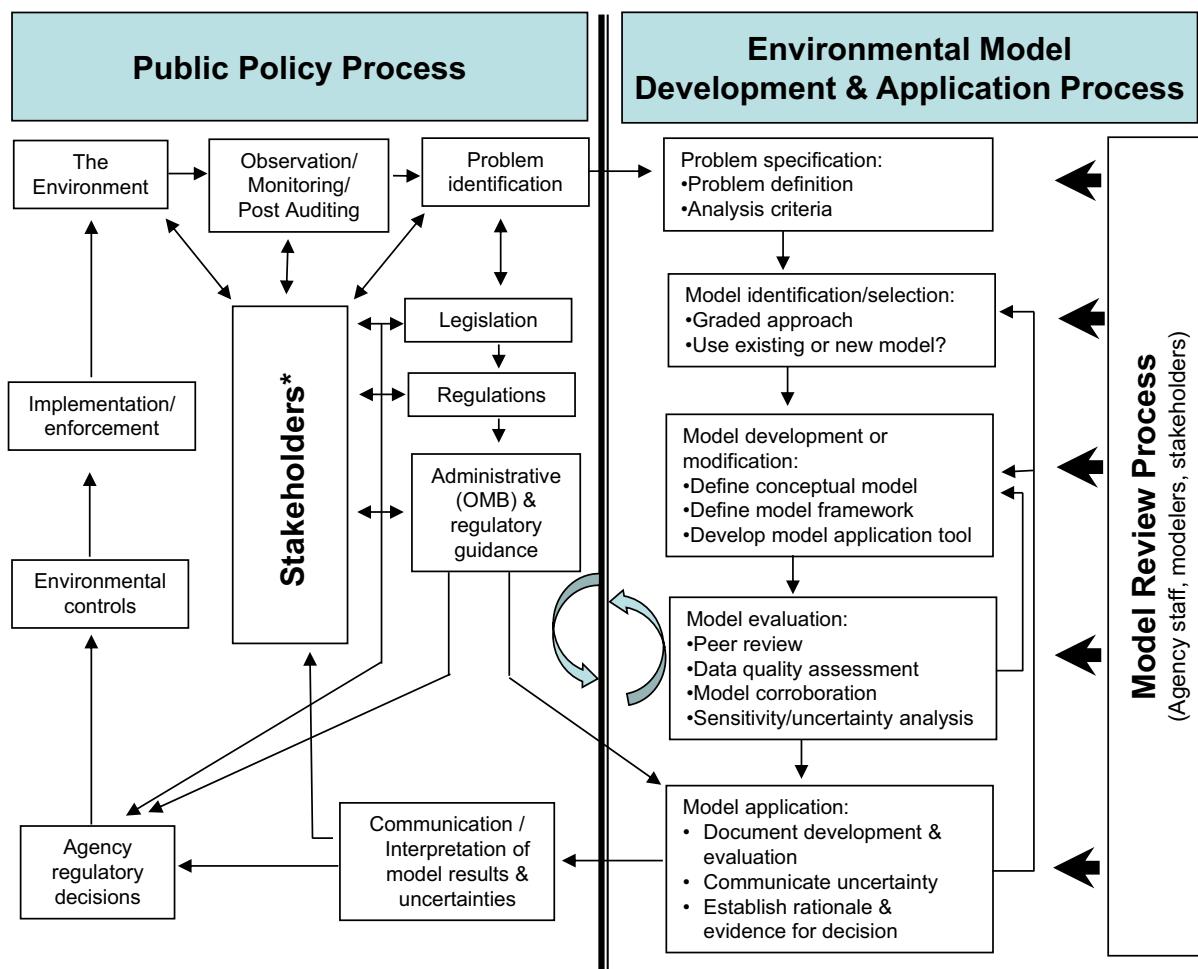
## ADDRESSING UNCERTAINTY

The processes that lead to the ultimate fate of air pollutants are complicated. Their relationships with one another are complex. These complexities must be captured in a model for at least two reasons. First, they must document what is going on during a given period of time. Almost always, actual measurement data are not available to characterize the movement and change of materials in the environment. Second, models provide a means of predicting outcomes based on currently available information. Therefore, the uncertainties stem from the model itself and the data being input. Figure 27.47 illustrates the steps

that should be taken to develop an air pollution or any environmental model.

The model generators are to the left and the users are to the right. This illustrates the connection between the biochemodynamic factors as applied to decision making. Each arrow indicates the connection between processes; each factor and process introduces information to the model, but simultaneously adds uncertainty.

Uncertainty lies in estimating the values to be assigned to each compartment of a model, including theoretical

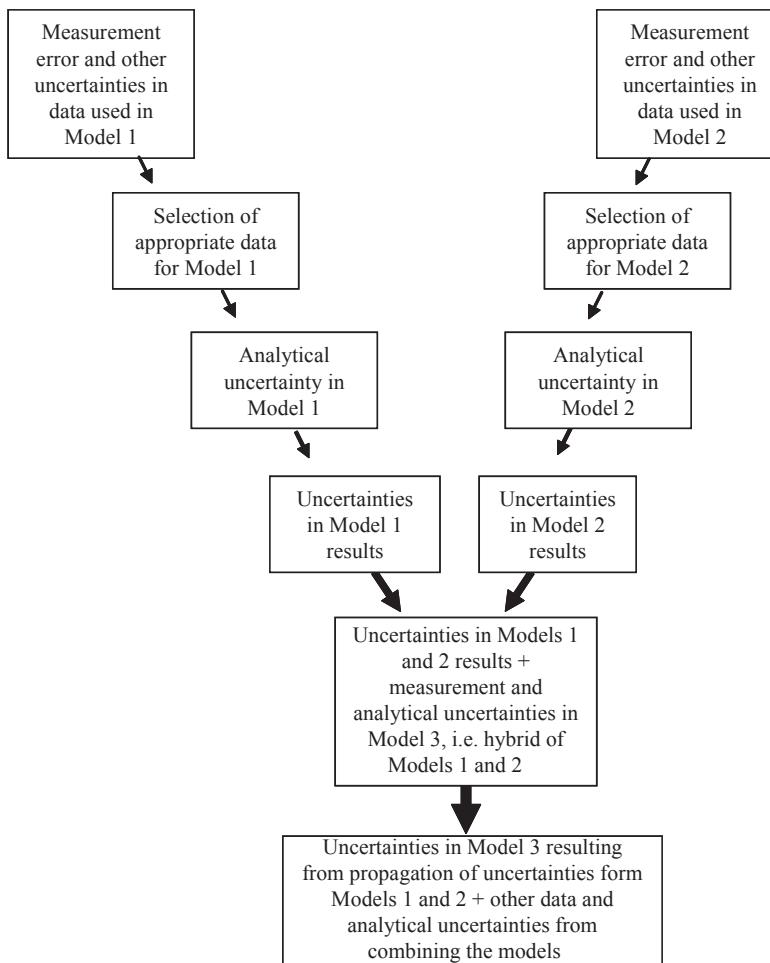


**\*Stakeholders include:**

- Source facility owners or responsible parties
- Directly affected neighboring property owners & public
- Courts and interested government entities (e.g. agencies)
- Advocacy groups (e.g. environmental, industry, and trade organizations)

**FIGURE 27.47 Steps needed to develop and implement an environmental decision model from inception to completion.** These include problem specification; model identification and selection (a site-specific model may be generated de novo or based on an existing model framework); model development (including problem- and site-specific model conceptualization, model formulation and design, and model calibration); model evaluation (e.g. based on peer review, data quality assessment, model code verification, model confirmation/corroboration, sensitivity analysis, and uncertainty analysis); model use (diagnostic analysis, solution, and application support for decision making); and review after use. (For color version of this figure, the reader is referred to the online version of this book.) US Environmental Protection Agency. Science Advisory Board, Regulatory Environmental Modeling, Guidance Review Panel. Review of Agency Draft guidance on the development, evaluation, and application of regulatory environmental models and models knowledge base. EPA-SAB-06-009; 2006. Letter to Administrator Stephen L. Johnson, August 22, 2006.

## ADDRESSING UNCERTAINTY (cont'd)



**FIGURE 27.48** Propagation of uncertainty in environmental models.

uncertainty (e.g. which of the published values of the partitioning coefficients discussed in Chapter 18 are relevant to a particular scenario) and measurement uncertainty (e.g. limitations in the ability to measure in the real world, such as the need for destructive methods or analytical problems, such as storing samples before they can be analyzed). However, models add another dimension to uncertainty (see Figure 27.48). Uncertainty increases with each addition of information, each algorithm, and each assumption. Combining models adds even more uncertainty.

Uncertainty can be classified as either aleatory or epistemic. Aleatory uncertainty is random uncertainty or stochastic uncertainty that is impossible to predict. All environmental systems have inherent, random uncertainty that cannot be reduced by additional observations.

On the other hand, epistemic uncertainty arises from insufficient knowledge about the system. Thus, as more reliable information becomes available regarding the processes described in this chapter, one would expect epistemic uncertainty to fall. Thus, from a scalar perspective, any model outcome ( $Y$ ) is affected by a function of the probability of these two types of uncertainty<sup>91</sup>:

$$Y = h(U, V) \quad (27.77)$$

where  $U$  = all epistemic uncertainties (uncertain parameters),  $V$  = aleatory uncertainties (stochastic variables), and  $h$  is the computational model considered as a deterministic function of both uncertainties.

An example of aleatory uncertainty would be a forecast of failure to contain a genetically engineered microbe within the physical confinement of a laboratory or a

(Continued)

## ADDRESSING UNCERTAINTY (cont'd)

cleanup site, e.g. where the occurrence of failure occurs randomly over time and the actual time of failure cannot be predicted, no matter the size of the data set. Conversely, epistemic uncertainty includes uncertainties inherent to a variable or parameter, as well as uncertainties in the model's algorithms. For example, a model may miss a possible route by which an air pollutant can be released because of wrong information about the molecule's affinity to a certain type of aerosol or soil particle. With increasing information about these relationships, the epistemic uncertainty should decrease and the predictive capability of the model would commensurately increase.

A means of predicting this type of uncertainty is by hierarchical holographic modeling (HHM), which addresses large system complexities by

Identifying the components and processes of all subsystems and suggests ways in which they might interact with each other based on established/supportive information. The technique decomposes the system by looking

at it from many different perspectives including, for example, the functions, activities, geo-political boundaries, or structures of the system. HHM can be used in one of two ways—as a hazard identification tool or as a comprehensive analytical modeling tool. The analyst constructs an HHM by first identifying the most appropriate perspectives for the problem in hand. These are used to define the sub-systems which in turn are further decomposed into components, processes, functions or activities, which may or may not overlap with other sub-systems. The analyst can investigate the quantitative properties of the system if the functions, activities, components or processes of the system can be described by a series of overlapping models, subject to overall system constraints. The analyst(s) can also identify hazards by comparing potential interactions between the sub-systems in a qualitative fashion. This is best achieved by a team, whose members are expert in one or more of the chosen perspectives.<sup>92a,92b</sup>

With reliable hazard and exposure calculations, risks can be characterized quantitatively.

transport, biochemodynamic, exposure and risk models, and applications must find ways to identify and minimize the effect of these uncertainties. (See discussion box, "Addressing Uncertainties".)

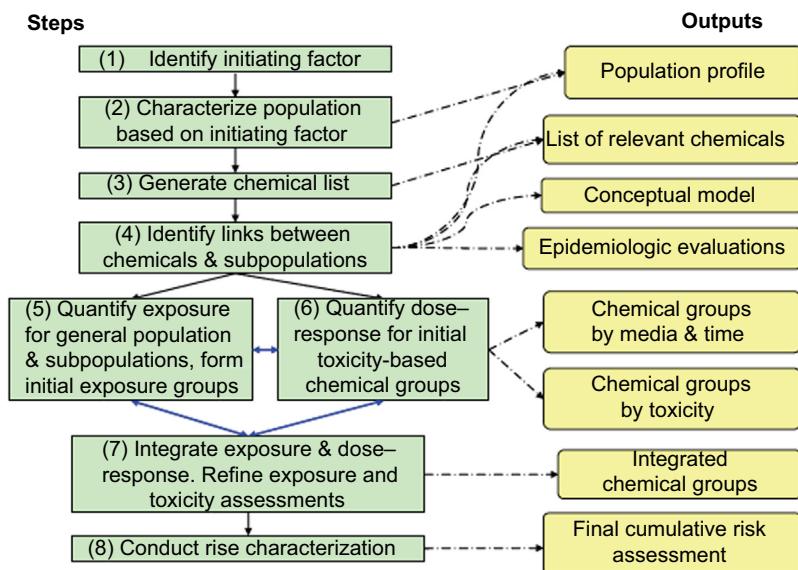
## 27.6 EXPOSURE AND DOSE MODELS

Exposure modeling begins with the initial collection and organization of information to focus on the cumulative factors that lead to the exposure (see Figure 27.49). These steps in Figure 27.50 are often not sequential and require iterations to parameterize and input data regarding population vulnerabilities, public health information, toxicological and epidemiologic data, completed exposure pathways, differential exposures, and contact the air pollutant.<sup>93</sup> This effort can provide population profiles, listing of relevant chemicals, chemical groups for use in risk analysis and characterization, and a conceptual model. The final step of interface exposure assessment results with the dose-response assessment.

Rather than employing single values to generate a discrete estimate of exposure as is done in deterministic approaches, a probabilistic approach can be used to better depict the uncertainty and variability in influential

input variables. Fundamental to a probabilistic approach is using statistical distributions for input variables, parameterizing these distributions, and characterizing the conditions or probabilities associated with the use of particular distributions. The complexity needed in these models depends on the variables that use statistical distributions, whether multiple variables correlate with one another (e.g. body mass, fat-free body mass, overall fitness) and the number of individuals to which the model will be applied. The probability model will provide a statistical distribution of the estimated exposure or doses for the receptors.

Models used to estimate and predict exposures to air pollutants have advanced in application and reliability in recent years. Although many of the physical and chemical factors, parameters, and algorithms are similar to those discussed in this chapter, the differences are substantial in terms of scale and weighting, as well as in the behavioral and biological features. Some of the kinetics within an organism, i.e. toxicokinetics, has been discussed in this chapter, but this is after intake and exposure, i.e. physiologically based pharmacokinetic models. Exposure models that lead to this contact and intake depend on the types, intensities, and extent of activities, as well as biological factors like breathing rates

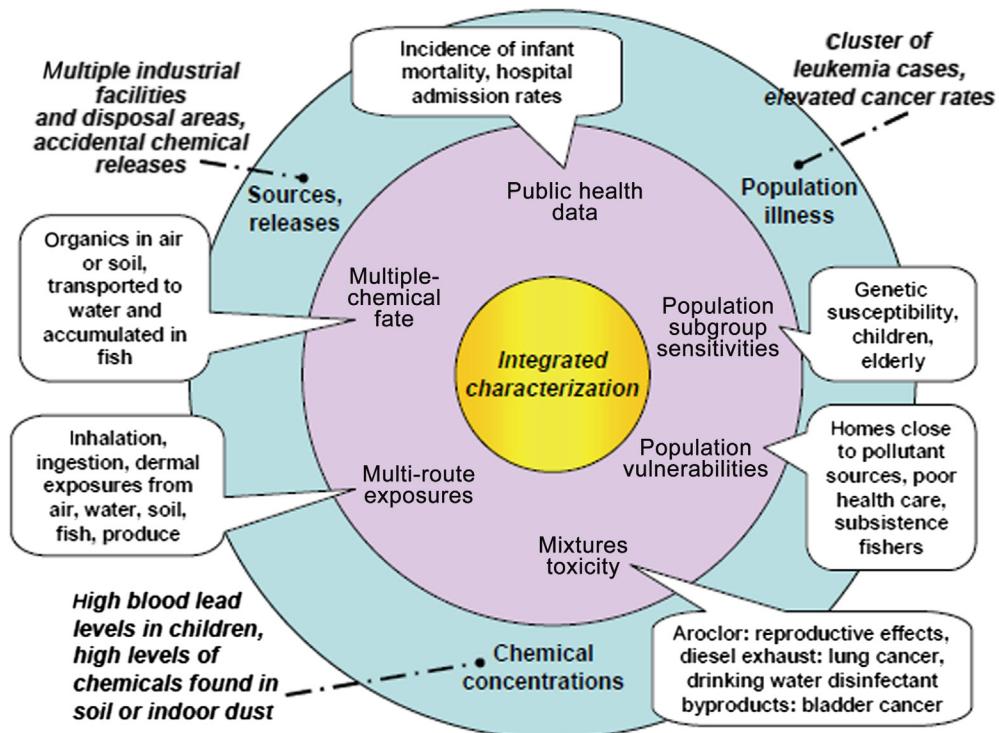


**FIGURE 27.49 Key steps in a cumulative risk assessment.** The interdependence of exposure and toxicity assessments is indicated by blue arrows. (For interpretation of the references to color in this figure legend, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Concepts, methods and data sources for cumulative health risk assessment of multiple chemicals, exposures and effects: a resource document. EPA/600/R-06/013F. Washington (DC): <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=190187>; 2007 [accessed 01.10.13].

and health status. As such, exposure and dose models are discussed in greater detail in Chapter 8.

Fluid mechanics and dynamics as model inputs covered in this chapter are also addressed in Chapter 9,

but at a smaller scale (i.e. within the lung). Diffusion, deposition, and other mechanical processes in the respiratory system are included in the discussion of respiratory health effects. Rather than the focus on scales from



**FIGURE 27.50 Initiating factors and data needs to begin building an exposure model for cumulative risk assessment.** U.S. Environmental Protection Agency. Concepts, methods and data sources for cumulative health risk assessment of multiple chemicals, exposures and effects: a resource document. (For color version of this figure, the reader is referred to the online version of this book.) EPA/600/R-06/013F. Washington (DC): <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=190187>; 2007 [accessed 01.10.13].

regional to community for ambient dispersion and receptor models, and rather than the microenvironmental and personal scales of the exposure models, respiratory scale models focus on air movement and contaminant transfer to and from the lungs and alveoli. Again, many are the same processes as those in the larger atmosphere, but the differences can be quite substantial.

## QUESTIONS

- Flow characteristics inside urban street canyons were studied in a laboratory water channel. The approaching flow direction was horizontal and perpendicular to the street axis. The street width was adjusted to form street canyons of aspect ratios 0.5, 1.0, and 2.0. The velocity field and turbulent intensity were measured with a laser Doppler anemometer at various locations within the street canyons, which were used to elucidate the flow pattern inside the street canyons. What kind of model is this?
- A model assumes that an individual particle moves independently of the motions of all other particles and that the movements of one and the same particle in different time intervals are independent processes, so long as these time intervals are not chosen too small. The model includes a time interval, which is very small compared to the observable time intervals, but nevertheless so large that in two successive time intervals, the particle movement is assumed to be events that are independent of each other. What kind of model is this?
- The mass balance can be determined for any control volume. Thus, consider a house to be such a control volume:

We can construct a simple *box model* for this control volume using the mass balance equation:

$$V \frac{dC}{dt} = QC_A + E - QC - kCV$$

Some  $k$  values in inverse seconds for some important indoor pollutants (from Lawrence Berkeley National Laboratory) are

- Formaldehyde (HCHO) =  $1.11 \times 10^{-4}$
- Nitric acid (NO) = 0.0
- Aerosols (fine particles  $<0.5 \mu\text{m}$  aerodynamic diameter) =  $1.33 \times 10^{-4}$
- Rn =  $2.11 \times 10^{-6}$
- Sulfur dioxide (SO<sub>2</sub>) =  $6.39 \times 10^{-5}$
- Carbon monoxide = 0.0

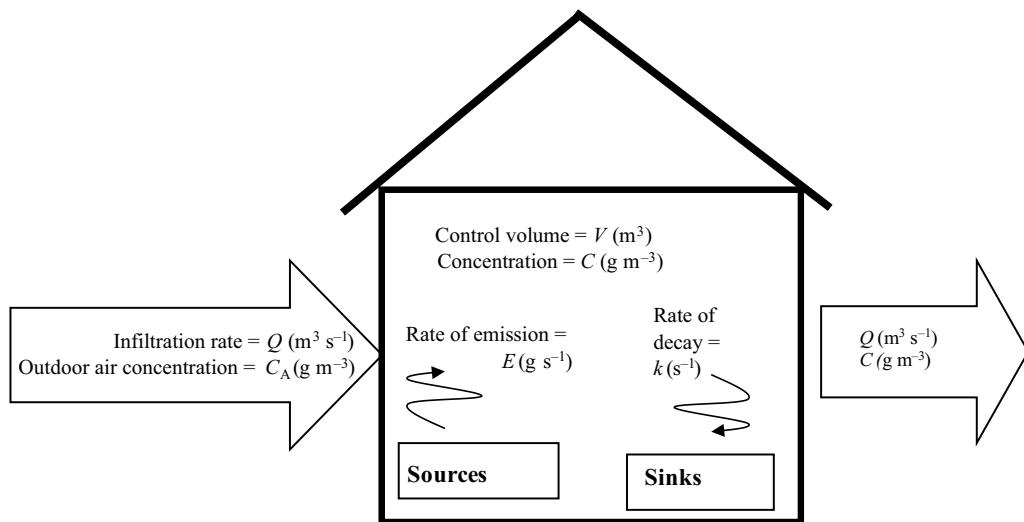
To find the time-dependent concentration (i.e. the general solution), use

$$C_t = \frac{\frac{E}{V} + C_A \frac{Q}{V}}{\frac{Q}{V} + k} \left[ 1 - \exp \left( - \left( \frac{Q}{V} + k \right) t \right) \right] + C_0 \exp \left[ - \left( \frac{Q}{V} + k \right) t \right]$$

And, for steady state conditions (i.e.  $\frac{dC}{dt} = 0$ ), the indoor concentrations are simplified to

$$C = \frac{QC_A + E}{Q + kV}$$

Further, if the pollutant does not appreciably decay (i.e.  $k \approx 0$ ); it is considered to be a *conservative pollutant*. Many indoor studies use conservative tracers (e.g. perfluorides). So, when



outdoor concentrations of a conservative compound are negligible, and the initial indoor concentration is zero, we can further simplify the mass balance to

$$C_t = \frac{E}{Q} \left[ 1 - \exp \left( - \left( \frac{Q}{V} \right) t \right) \right]$$

You are heating your apartment with an unvented kerosene heater for 1 h. The air volume of your apartment is  $200 \text{ m}^3$ . If the heater emits  $\text{SO}_2$  at a rate of  $50 \mu\text{g s}^{-1}$ , and the ambient (outdoor air) and initial concentrations in your apartment are both  $100 \mu\text{g m}^{-3}$ , the ventilation (air exchange rate) is  $50 \text{ l s}^{-1}$ , and your ceiling fan is sufficiently mixing the air (i.e. the control volume is assumed to be well mixed), what is the indoor concentration of  $\text{SO}_2$  in your apartment after 1 h?

4. How long will it take after shutting off the heater (i.e.  $E = 0$ ), to reach the same concentrations of  $\text{SO}_2$  as that found outside the house?
5. How can GIS and kriging be used to enhance the interpretation of air pollution measurements?
6. Assuming that you have been working on your car's engine in a garage with the same dimensions and air exchanges as the apartment above, and that the concentrations of carbon monoxide were also  $625.39 \mu\text{g m}^{-3}$ . How long will it take to reach  $0 \mu\text{g m}^{-3}$  CO, assuming the outdoor concentration is  $0 \mu\text{g m}^{-3}$  CO? In other words, how long will it take to flush the CO? What could you do to increase the flushing rate? Find the time needed to reach a relatively safe indoor CO concentration of 300 ppb, with  $k = 2 \times 10^{-10} \text{ s}$ . After all, even conservative gases like CO breakdown (e.g. by reactions with hydroxyl radicals).

Compare the results and try to explain any differences in theory vs practical applications. What is going on here? Be creative and bold in thinking about the differences. This is one of the interesting differences between engineering and basic science.

7. Consider the mathematics of the time-dependent equation when applied to a conservative pollutant ( $k = 0$ ) at an ambient concentration = 0. Although mathematically possible, is it practically possible?
8. Characterize the conditions typical of low-pressure systems, particularly as they relate to ventilation. Characterize the conditions typical of high-pressure systems, particularly as they relate to ventilation.
9. What atmospheric characteristics are usually associated with stagnating high-pressure systems?
10. What factors contribute to a high mixing height?
11. Discuss the similarities of the three major episodes of pollution (Meuse Valley, Donora, and London).

12. A railroad tank car has derailed and overturned, and some material is leaking out and apparently evaporating. The car is labeled "Toxic". In order to take appropriate emergency action, which meteorological factors would you consider and how would you assess them?
13. A 100-m tall stack emits  $2 \text{ g Hg}^0$  per second. Assume an effective height of emission at 120 m, constant wind speed of  $0.1 \text{ m s}^{-1}$  and a mixing height of 150 m. If the Hg does not react chemically after emission, what is the surface concentration of  $\text{Hg}^0$  in a plume 1000 m downwind, with 20 m crosswind distance is 50 m,  $\sigma_y = 50 \text{ m}$  and  $\sigma_z = 80 \text{ m}$ ?
14. In the above scenario, if the mixing height changes to 40 m, what would the  $\text{Hg}^0$  concentration be at this point?
15. The same stack is also releasing a compound with a first-order reaction rate of  $10^{-1} \text{ s}$ . At an emission rate of  $20 \text{ kg s}^{-1}$ , what would its concentration be for the scenarios described in the previous three questions?
16. In addition to air pollutants, what meteorological factor has a profound effect on decreasing visibility, and what is the approximate threshold of its influence?
17. What pollution factors may affect atmospheric precipitation?
18. What is the approximate lowering of the centroid of a dispersing cloud of particles at 2 km from the source whose mass medium diameter is  $30 \mu\text{m}$  and whose particle density is  $1 \text{ g cm}^{-3}$  in a  $5 \text{ m s}^{-1}$  wind?
19. Prior to the onset of rain at the rate of  $2.5 \text{ mm h}^{-1}$ , the average concentration of 10- $\mu\text{m}$  particles in a pollutant plume is  $80 \mu\text{g m}^{-3}$ . What is the average concentration after 30 min of rain at this rate?
20. In a situation under stable conditions with a wind speed of  $4 \text{ m s}^{-1}$  and  $\sigma_a = 0.12$  radians, the wind is blowing directly toward a receptor of 1 km from the source. How much must the wind shift, in degrees, to reduce the concentration to 10% of its previous value? (At  $2.15\sigma$  from the peak, the Gaussian distribution is 0.1 of the value at the peak.)
21. If the variation in wind speed with height is well approximated with a power law wind profile having an exponent equal to 0.15, how much stronger is the wind at 100 m above ground than at 10 m?
22. At a particular downwind distance, a dispersing plume is approximately 40 m wide. Which of the following three turbulent eddy diameters—5 m, 30 m, or 100 m—do you believe would be more effective in further dispersing this plume?
23. A pollutant is released from an effective height of 50 m and has a ground-level concentration of  $300 \mu\text{g m}^{-3}$  at a position directly downwind where

- the  $\sigma_z$  is 65 m. How does the concentration at 50 m above this point, that is, the plume centerline, compare with this ground-level concentration?
24. At a downwind distance of 800 m from a 75-m source having plume rise of 180 m,  $\sigma_y$  is estimated as 84 m and  $\sigma_z$  is estimated as 50 m. If one considers buoyancy-induced dispersion as suggested by Pasquill, by how much is the plume centerline concentration reduced at this distance?
25. Consider the parameters that need to be measured and the instrumentation needed to make the measurements for monitoring dispersion of effluent from a 30-m stack.
26. A tracer experiment includes sampling on an arc at 1000 m from the source. If the horizontal spread is expected to result in a  $\sigma_y$  between 120 and 150 m at this distance, and if the wind direction is within  $\pm 15^\circ$  azimuth of that forecast, how many samplers should be deployed and what should be that spacing? It is desirable to have more than seven measurements within  $\pm 2\sigma_y$  of the plume centerline and at least one sample on each side of the plume.
27. For a tracer release that can be considered to be at ground level, approximate the vertical dispersion  $\sigma_z$  at the downwind distance where measurements indicate that the concentration peak is  $7 \times 10^{-8} \text{ g m}^{-3}$ , the horizontal  $\sigma_y$  is 190 m, and the CWI concentration is  $3.16 \times 10^{-5} \text{ g m}^{-3}$ . The tracer release rate is  $0.01 \text{ g s}^{-1}$  and the wind speed is  $3.7 \text{ m s}^{-1}$ .
28. At 8:00 p.m. hydrogen sulfide exits an effective stack height of 50 m at  $60 \text{ mg s}^{-1}$ . The wind speed is  $2.5 \text{ m s}^{-1}$  under cloudy conditions. What is the maximum surface concentration on the plume centerline downwind from the stack? Assume the H<sub>2</sub>S odor threshold = 470 ppt and sketch the area of odor detection.
29. The maximum 1-h concentration at an urban monitoring station is  $800 \mu\text{g m}^{-3}$ . If the concentration varies with averaging time with a power law relation when the power is  $-0.3$ , what is the expected maximum concentration for a 1-week averaging time?
30. How can a toxicokinetic model make use of predictions of indoor air concentrations of a pollutant by a stochastic model?
31. Assume that a landfill surface is  $5700 \text{ m}^2$  of untreated soil. The soil air 3 m beneath the lining has a concentration of  $285 \text{ g cm}^{-3}$  THC. If the diffusion coefficient is  $0.03 \text{ cm}^2 \text{ s}^{-1}$  for the landfill porous media and assuming that the air is well mixed, what are the flux density of the vapor and the rate of vapor release by molecular diffusion for this landfill?
32. A model that deduces contaminant losses from chemical reactions and includes mass transfer coefficients and deposition rates is operating at what level?
33. What are the two major classes of model uncertainty?
34. The movement of an aerosol in a wind tunnel will differ from the movement of the same aerosol in the real world. Some of the scaling factors are known, but many are not. If a scaled model of a town and surrounding terrain are built in a wind tunnel study, which indicates that the an incinerator continuously emitting 1 mg of dioxin per second results in a concentration of 1 ppb dioxin at a local school. What types of uncertainty must be acknowledged in this study?
35. Consider ways that air pollution models can inform and be informed by food chain and food web models to predict ecological impacts from air pollutants. Give an example of each.
36. Assuming that the buoyancy flux parameter  $F$  is greater than 55 in both situations, what is the proportional final plume rise for stack A compared to stack B if A has an inside diameter three times that of B?
37. How much greater is the penetration of a plume through an inversion of  $1^\circ\text{C}$  per 100 m than through an inversion of  $3^\circ\text{C}$  per 100 m? Assume that the wind speed is  $3 \text{ m s}^{-1}$ , ambient air temperature is 29 K, and the stack characteristics are  $T_s = 415 \text{ K}$ ,  $d = 3 \text{ m}$ , and  $v_s = 20 \text{ m s}^{-1}$ .
38. What is the steady state concentration derived from the box model for a 10-km city with average emissions of  $2 \times 10^{-5} \text{ g m}^{-2} \text{ s}^{-1}$  when the mixing height is 500 m and the wind speed is  $4 \text{ m s}^{-1}$ ?
39. In formulating and applying a gradient transfer model, what are two of the major difficulties?
40. What is the advantage in using trajectory models for estimating air pollutant concentrations at specific air monitoring stations?
41. What is the major difficulty in estimating the maximum short-term (hours) impact of two point sources 1 km apart?
42. Using simplified techniques for estimating the concentrations from area sources, what is the annual average PM concentration for a city with an average wind speed of  $3.6 \text{ m s}^{-1}$  and area emission rate of  $8 \times 10^{-7} \text{ g s}^{-1} \text{ m}^{-2}$ ?
43. What are the major limitations in modeling pollutant transformations in urban areas?
44. From the results of the application of the EURMAP model to Europe, what pollutant and mechanism seem to cause the least pollution by a nation to itself?
45. Which measure of scatter is likely to be larger, the mean absolute error or the root-mean-square error?

46. Contrast the fractional error for a measurement of 20 and an estimate of 4 to the fractional error for a measurement of 4 and an estimate of 20.

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# Air Quality Status and Trends

## 28.1 INTRODUCTION

For most of Canada, the United States, and Western Europe, the pollutants known to affect public health have decreased in concentrations in the ambient air. As indicated in Table 3.3 in Chapter 3, for example, in the United States, the National Ambient Air Quality Standards (NAAQS) for protection of human health and welfare have shown a continuing decrease for these “criteria air pollutants”, i.e. carbon monoxide (CO), nitrogen dioxide ( $\text{NO}_2$ ), sulfur dioxide ( $\text{SO}_2$ ), ground-level ozone ( $\text{O}_3$ ), lead (Pb), and particulate matter (PM). However, this does not mean that the air is necessarily “clean” throughout the world or even the entirety of North America and Europe, as many areas still do not meet health standards for these criteria pollutants (see Figure 26.1 in Chapter 26).

Unfortunately, many or even most of the world’s population have not experienced such improvements. Serious risks to health continue in many of the world’s urban areas from exposure to PM and  $\text{O}_3$  in both developed and developing countries. Air pollution levels have been linked to increased human mortality or morbidity, even at relatively low concentrations. In particular, elevated concentrations of many pollutants in the indoor air may pose a risk to the health of over half of the world’s population. In homes where biomass fuels and coal are used for cooking and heating, PM concentrations can be 10–50 times higher than the guideline values set by the World Health Organization (WHO). The source of much of these pollutants is the combustion of fossil fuels.<sup>1</sup>

The representativeness of measurement data from large-scale ambient monitoring has continuously improved as new technologies have become more reliable. This is in large part due to two factors. First, the areas that did not meet the ambient air quality standards in the twentieth century were more extensive than today. This is especially true for CO,  $\text{SO}_2$ , and  $\text{NO}_2$ . Second, the standards increasingly have been ratcheted down as new evidence of health effects were documented by improved biomedical research and engineering

technologies to detect these pollutants at increasingly lower concentrations.

In addition, three other factors must be considered with respect to overall air quality trends. First, the criteria pollutants are in many ways merely indicators of overall ambient air quality. For example, many toxic air pollutants in addition to the criteria pollutants are in the ambient air, but are not being measured at the air monitoring sites. Some of these have either not been decreasing at the rates of criteria pollutants or in some areas are increasing in concentration. Second, the monitoring sites for criteria pollutants are meant to have relatively large spatial coverage, so they would miss many pollutants at a finer scale, e.g. hot spots in neighborhoods. Third, ambient concentrations are weak indicators at best for actual exposures to many pollutants, including those with indoor sources. This is true for both criteria pollutants, e.g. PM, and air toxics, e.g. formaldehyde.

The standards for PM have incrementally changed to address finer particle sizes, especially  $\text{PM}_{2.5}$  (aerodynamic diameter smaller than  $2.5\ \mu\text{m}$ ). Indeed, there is increasing emphasis on even finer particles, i.e. ultrafines  $<100\ \text{ng}$ . Ground-level  $\text{O}_3$  status is more complicated. Like the other pollutants, more continues to be known, but much is still not understood about  $\text{O}_3$  formation in the troposphere. In addition, the sources, especially mobile sources, are increasing in many parts of the world, with the increase in the number of motor vehicles. However, this is offset to some extent by more stringent emission standards for new vehicles and increased surveillance and inspection activities in certain areas for older vehicles. The more stringent standards address volatile organic compounds (VOCs) and oxides of nitrogen ( $\text{NO}_x$ ), which are the key precursors for the formation of ozone in the troposphere. In addition,  $\text{O}_3$  formation depends on sunlight penetration, so climate change could also affect the amount of incoming solar radiation, which would change the photochemistry. Again, this is complicated, since any pollutants added to the ambient air that decrease radiation (e.g. PM) would decrease  $\text{O}_3$  formation if they absorb or

reflect solar radiation. Conversely, any climate change that increases incoming solar radiation, e.g. increased precipitation of aerosols or long-range transport of O<sub>3</sub> precursors could increase O<sub>3</sub> formation.

In addition, it is important to keep in mind that these six pollutants do not include many other compounds that are known or suspected to be toxic, especially the hazardous air pollutants listed in Table 7.2 in Chapter 7. Many of these compounds are difficult to measure and model. As the state-of-the-sciences improve, they will be found in many more locations throughout the world.

### 28.1.1 Averaging Time

The variability inherent in air pollutant transport and dispersion, the temporal variability of source strengths and the scavenging and conversion mechanisms in the atmosphere affect the residence time of chemicals in the atmosphere. These and other factors result in variability in the concentration of a pollutant arriving at a receptor. Thus, a continuous record of the concentration of a pollutant at a receptor, as measured by an instrument with rapid response, may resemble the graph shown in Figure 28.1(A). If, however, instead of measuring with a rapid-response instrument, the measurement at the receptor site was made with sampling and analytical procedures that integrated the concentration arriving at the receptor over various time periods, e.g. 15 min, 1 h, or 6 h, the resulting information would look variously like Figures 28.1(B)–(D), respectively. It should be noted that from the information in Figure 28.1(A), it is possible to derive mathematically the information in Figure 28.1(B)–(D), and it is possible to derive the information in Figures 28.1(C) and (D)

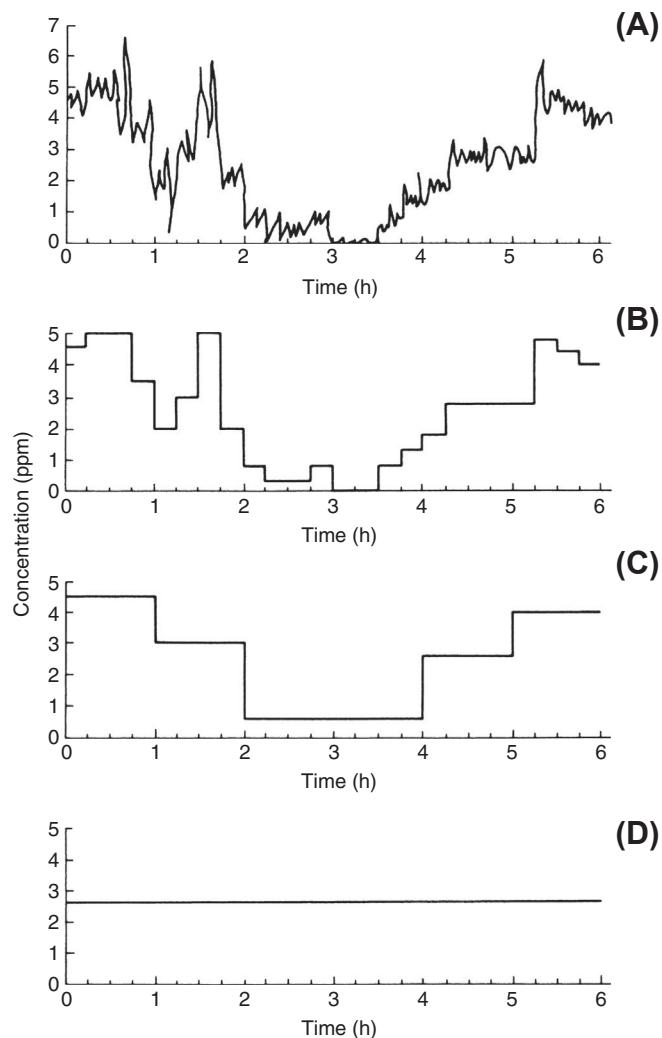
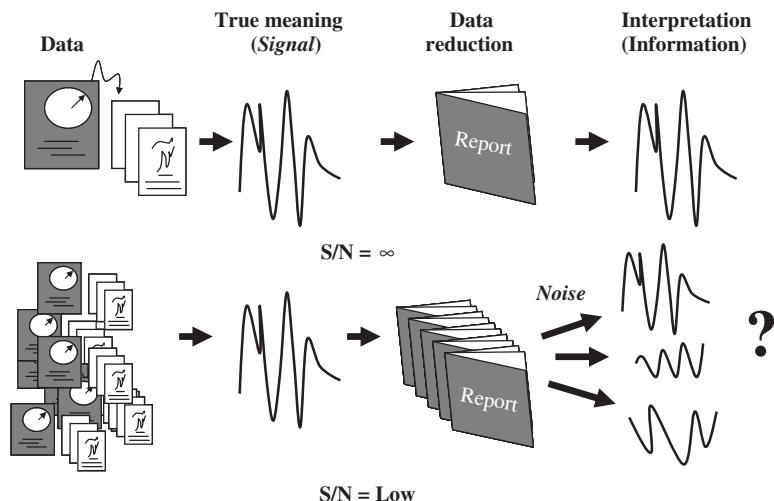


FIGURE 28.1 The same atmosphere measured by (A) a rapid-response instrument and by sampling and analytical procedures that integrate the concentration arriving at the receptor over a time period of (B) 15 min, (C) 1 h, and (D) 6 h.

FIGURE 28.2 Scientific communication of air quality measurements depends on high-quality data that is properly reduced and interpreted in order to become useful information for users. However, even data that are properly collected may become noisy if their volume is so large that they are not able to be interpreted in a timely manner. This leads to a low signal to noise (S/N) ratio.



from that in [Figure 28.1\(B\)](#). The converse is not true. With only the information from [Figure 28.1\(D\)](#) available, [Figures 28.1\(A\)–\(C\)](#) could never be constructed, nor could [Figures 28.1\(A\) and \(B\)](#) be constructed from [Figure 8.3\(C\)](#), nor [Figure 28.1\(A\)](#) from [Figure 28.1\(B\)](#). In these examples, the time intervals involved in [Figures 28.1\(B\)–\(D\)](#)—15 min, 1 h, and 6 h, respectively—are the averaging times of the measurement of pollutant exposure at the receptor.

The averaging time of the rapid-response record ([Figure 28.1\(A\)](#)) is an inherent characteristic of the instrument and the data acquisition system. It can become almost an instantaneous record of concentration at the receptor. However, in most cases this is not desirable, because such an instantaneous record cannot be put to any practical air pollution control use. What such a record reveals is something of the turbulent structure of the atmosphere, and thus it has some utility in meteorological research. In communications science parlance, an instantaneous recording has too much noise (see [Figure 28.2](#) on the previous page), preventing a proper interpretation of the measurements. It is therefore necessary to filter or damp out the noise in order to extract the useful information about pollution concentration at the receptor that the signal is trying to reveal. This damping is achieved by building time lags into the response of the sampling, analysis, and recording systems (or into all three); by interrogating the

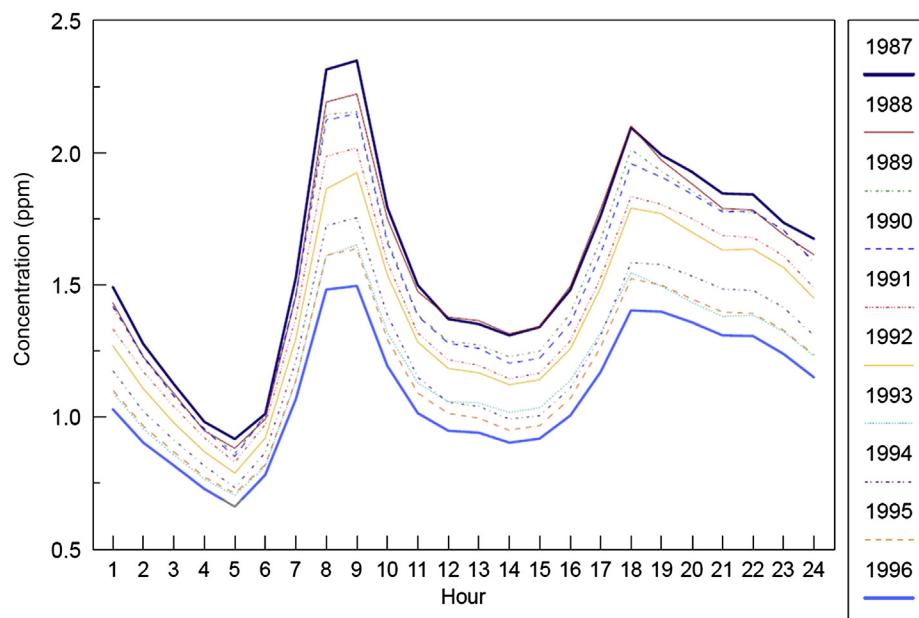
instantaneous output of the analyzer at discrete time intervals, e.g. once every minute or once every 5 min, and recording only this extracted information; or by a combination of damping and periodic interrogation.

### 28.1.2 Temporal Cycles

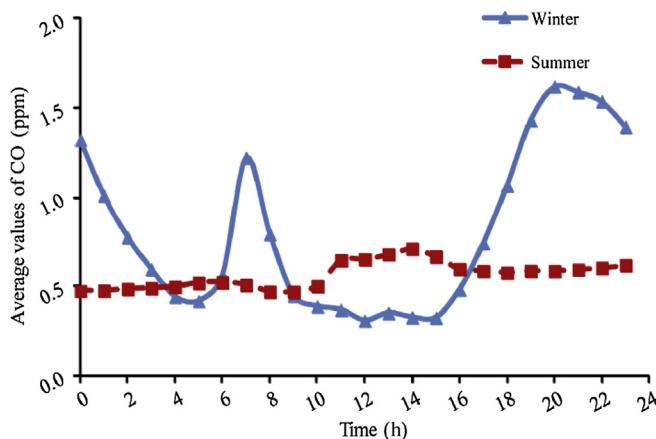
The most significant of the principal cyclic influences on variability of pollution concentration at a receptor is the diurnal cycle (see [Figures 28.3 and 28.4](#)). First, there is a diurnal pattern to source strength. In general, emissions from almost all categories of sources are less at night than during the day. Factories and businesses shut down or reduce activity at night. There is less automotive, aircraft, and railroad traffic, use of electricity, cooking, home heating, and refuse burning at night. Second, there is a diurnal pattern to transport and diffusion.

The next significant cycle is the weekend–weekday cycle. This is entirely a source strength cycle associated with the change in the pattern of living on weekends as compared with weekdays.

The curves in [Figure 28.3](#) are bimodal, and resemble the winter curve in [Figure 28.4](#). However, the summer curve is relatively flat with mild spike midday. Note that the CO data in [Figure 28.3](#) are a composite of several US urban areas, whereas the CO data in [Figure 28.4](#) are only from one city in Kuwait. Thus, it would be premature to attribute the cycle profiles to particular sources,



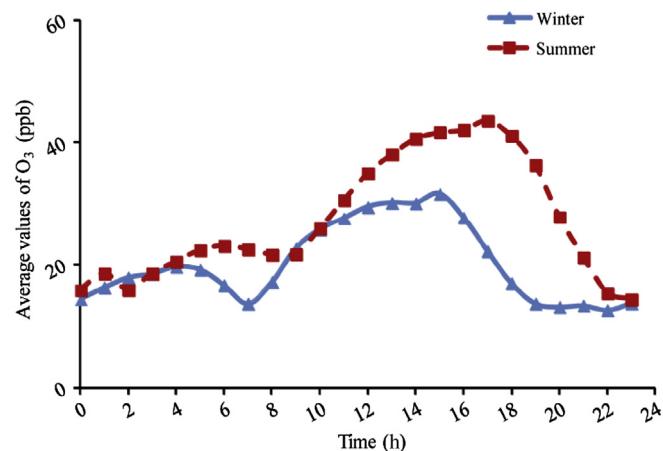
**FIGURE 28.3** Diurnal patterns in hourly carbon monoxide (CO) concentrations averaged across 2778 monitoring stations located throughout the United States for the 10-year period, 1987–1996. The trends are derived from the composite average of these direct measurements. (For color version of this figure, the reader is referred to the online version of this book.) US Environmental Protection Agency. National air quality and emissions trends report. <http://www.epa.gov/oar/aqtrnd97/chapter2.pdf>; 1997 [accessed 25.11.13].



**FIGURE 28.4** Diurnal patterns in hourly average nitrogen dioxide for winter and summer seasons for Al Jahra City, Kuwait, in 2010. (For color version of this figure, the reader is referred to the online version of this book.) Alenezi R, Al-Anzi B, Abusam A, Ashfatiue A. Seasonal influence on the ambient air quality in Al Jahra City for year 2010. J Environ Prot 2012;3:1711–8. <http://dx.doi.org/10.4236/jep.2012.312186>.

given the many variables, e.g. seasonal climate, population, traffic, and types of sources.

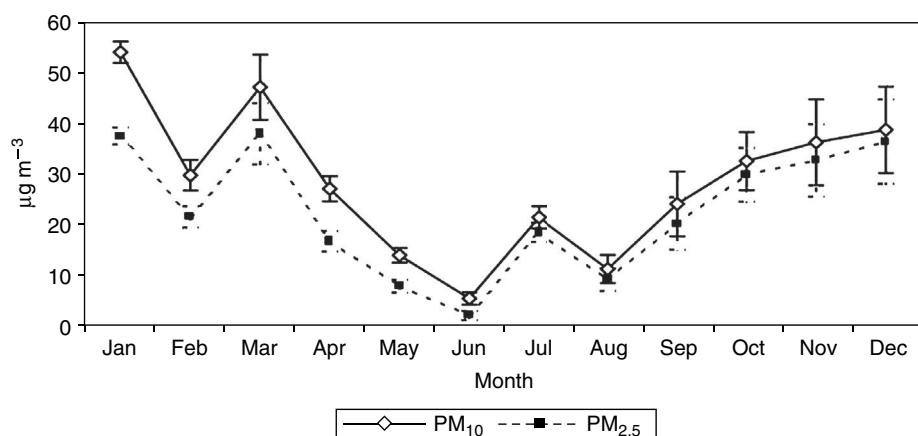
On an annual basis, some year-to-year changes in source strength may be expected as a community, a region, a nation, or the world increases in population or changes its patterns of living. Source strength will be reduced if control efforts or changes in technology succeed in preventing more pollution emission than would have resulted from increases in population (see Figure 28.5). These changes over time are called trends. Although an annual trend in source strength is expected, no such trend is expected in climate or weather, even though each year will have its own individuality with



**FIGURE 28.6** Hourly average ozone for winter and summer seasons for Al Jahra, Kuwait, in 2010. (For color version of this figure, the reader is referred to the online version of this book.) Alenezi R, Al-Anzi B, Abusam A, Ashfatiue A. Seasonal influence on the ambient air quality in Al Jahra City for year 2010. J Environ Prot 2012;3:1711–8. <http://dx.doi.org/10.4236/jep.2012.312186>.

respect to its weather. However, there is at present an ongoing debate as to whether global mean temperatures will continue to increase due to increasing concentration of global greenhouse gases (GHGs), especially carbon dioxide and methane. If so, this would be a climatic trend.

In addition to atmospheric concentration trends, emission trends are commonly displayed for air pollutant measurements. For example, emissions of industrial smoke in Great Britain, which decreased from 1.4 million tons per year in 1953 to 0.1 million tons per year in 1972; domestic smoke emission was reduced from 1.35 million tons per year in 1953 to 0.58 million tons per year in 1972; and

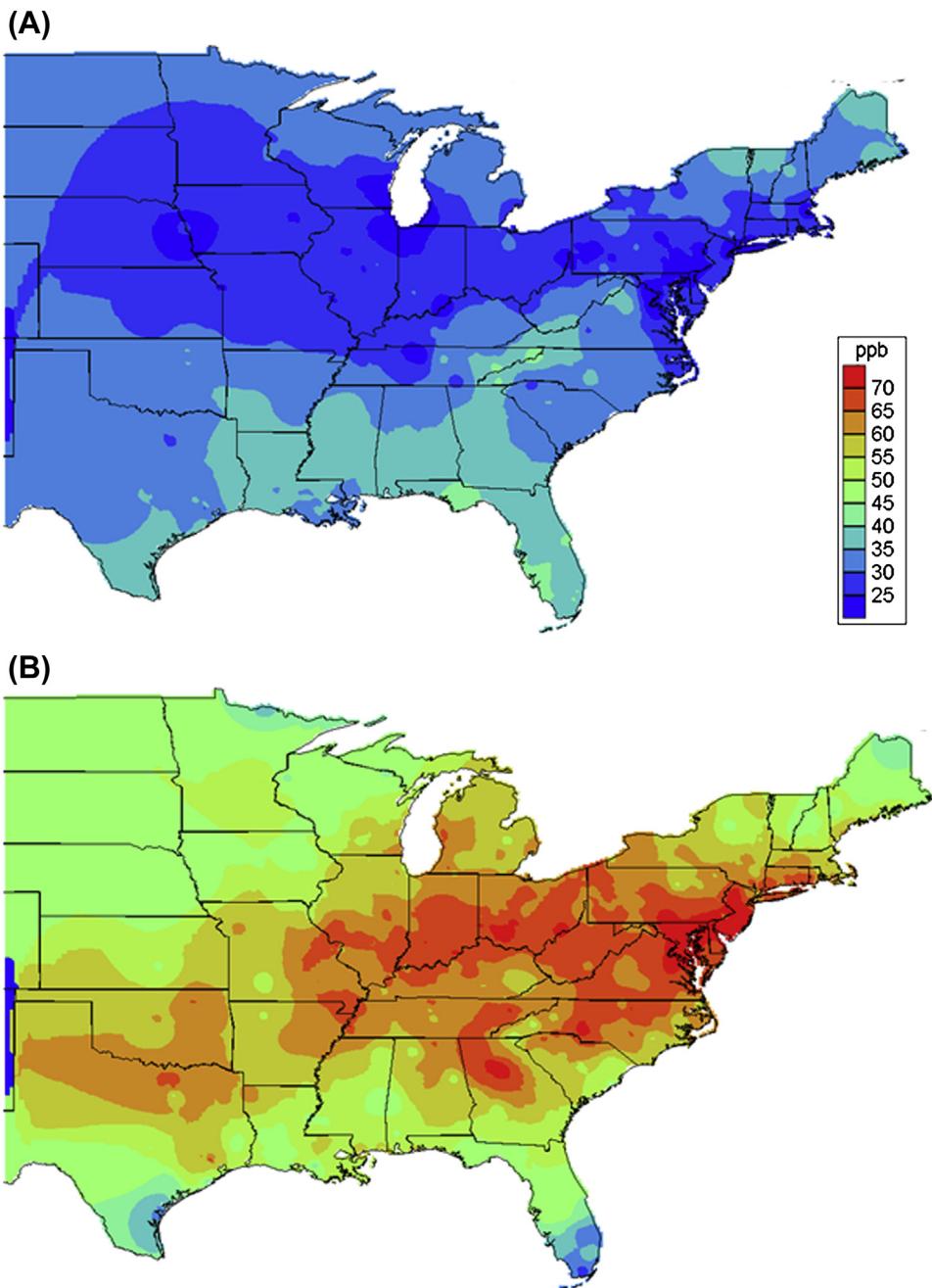


**FIGURE 28.5** Seasonal variations of airborne particulate concentrations in Hyderabad, India (178.10°–178.50° N latitude and 78.10°–78.50° E longitude). The climate of the study area is of semiarid type with total rainfall of 700 mm occurring mostly during monsoon season corresponding to July–October. Measurements were gathered approximately at hourly intervals for 4–5 days, with the sampling duration of 6 min during January–December, 2003. Latha KM, Badarinath KVS. Seasonal variations of PM<sub>10</sub> and PM<sub>2.5</sub> particles loading over tropical urban environment. Int J Environ Health Res 2005;15(1):63–68.

the number of London fogs ("smogs") capable of reducing visibility at 9 a.m. to less than 1 km was reduced from 59 per year in 1946 to 5 per year in 1976.

Each pollutant has a unique profile. For example, annual trends in urban ozone can be more subtle, with less apparent response to changes in emissions, than many other compounds because of the complex

interaction among precursors (hydrocarbons and oxides of nitrogen) and meteorology, including solar radiation. Ground-level O<sub>3</sub> is particularly sensitive to seasonal effects, but not so much in the lower latitudes, since the difference in incoming solar radiation is much less seasonably variable in the tropics (see Figure 28.6) than in the middle latitudes (see Figure 28.7).



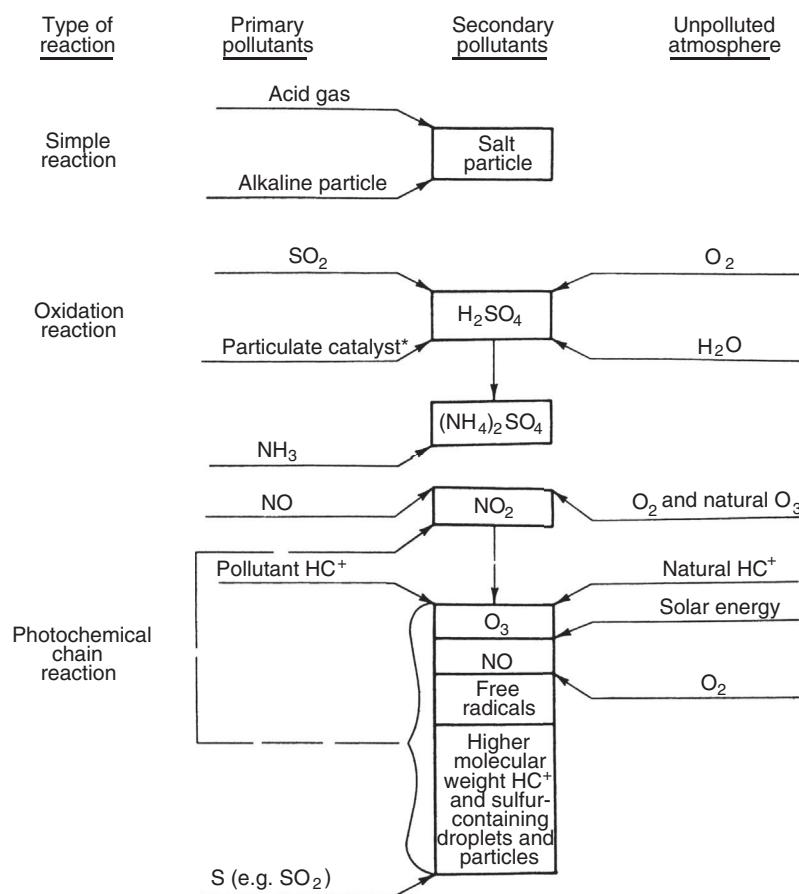
**FIGURE 28.7** Average daily maximum ozone concentrations for 1991–1995 for winter (A) and summer (B) seasons for eastern United States. (For color version of this figure, the reader is referred to the online version of this book.) Husar RB. Seasonal pattern of ozone over the OTAG region. Center for Air Pollution Impact and Trend Analysis. Washington University-St. Louis. <http://capita.wustl.edu/NESCAUM/Reports/otagseas/otagseas.html>; 1997 [accessed 25.11.13].

### 28.1.3 Primary and Secondary Pollutants

A substantial portion of the gas and vapors<sup>a</sup> emitted to the atmosphere in appreciable quantity from anthropogenic sources tends to be relatively simple in chemical structure: carbon dioxide, carbon monoxide, sulfur dioxide, and nitric oxide from combustion processes; hydrogen sulfide, ammonia, hydrogen chloride, and hydrogen fluoride from industrial processes. The solvents and gasoline fractions that evaporate are alkanes, alkenes, and aromatics with relatively simple structures.

In addition, more complex molecules such as polycyclic aromatic hydrocarbons (PAHs) and dioxins

are released from industrial processes and combustion sources and are referred to as toxic pollutants. Substances such as these, emitted directly from sources, are called primary pollutants. They are certainly not innocuous, as will be seen when their adverse effects are discussed in later chapters. However, the primary pollutants do not, of themselves, produce all of the adverse effects of air pollution. Chemical reactions may occur among the primary pollutants and the constituents of the unpolluted atmosphere (Figure 28.8). The atmosphere may be viewed as a reaction vessel into which reactants are added, and in which a tremendous array of new chemical compounds



**FIGURE 28.8 Primary and secondary pollutants.** Note: \*A catalyst is not always necessary to form sulfuric acid ( $H_2SO_4$ ) in the particulate phase; in the aqueous (aq) phase, formaldehyde can help oxidize  $SO_2$  to  $H_2SO_4$  in the particle phase. In the gas phase, the reaction is  $SO_2 + O_2 \rightarrow SO_3$ , which is followed by a heterogeneous reaction of  $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$ . However, about 70% of atmospheric sulfate is formed in cloud droplets and only a small fraction comes from condensation of  $H_2SO_4$  on particles or is formed in the aqueous phase of aerosols.<sup>2a,2b</sup>

<sup>a</sup> The terms gas and vapor are often used synonymously; however, a vapor is a gaseous substance that is a solid or liquid at standard temperature and pressure (STP), i.e. at 0 °C and 101.325 kPa. Thus, CO<sub>2</sub> is a gas, but ethanol is predominantly a liquid under these conditions. Note that not all of ethanol is liquid, since it is vaporizing. However, with increasing temperature and constant pressure, a greater amount of ethanol will move to the gas phase in accordance with Henry's law (see Chapter 18). That is, at lower temperatures only a small number of ethanol molecules are sufficiently excited to move to the gas phase, but with increasing temperature, the number of molecules escaping increases. Thus, when these ethanol molecules are measured in the gas phase, this is considered to be a vapor measurement.

are produced. These new compounds are generated by gases and vapors reacting with each other and with the particles in the air. The pollutants manufactured in the air are called secondary pollutants; they are responsible for most of the smog, haze, and eye irritation and for many of the forms of plant and material damage attributed to air pollution. In air pollution parlance, the primary pollutants that react are termed the precursors of the secondary pollutants. With the knowledge that each secondary pollutant arises from specific chemical reactions involving specific primary reactants, we must control secondary pollutants by controlling how much of each primary pollutant is allowed to be emitted. Note that the use of primary and secondary pollutants used here is different from the regulatory definitions of primary and secondary pollutants, i.e. many countries set primary standards to protect public health and secondary standards to protect welfare.

## 28.2 TROPOSPHERIC OZONE AND SMOG

The WHO's recently lowered the ground-level O<sub>3</sub> guidelines level to 120 µg m<sup>-3</sup>, based on recently documented associations between daily mortality and ozone levels occurring below this level. Indeed, several European studies have shown that with each increment of 10 µg m<sup>-3</sup> increase in O<sub>3</sub> concentrations, daily mortality increases by 0.3% and cardiovascular diseases by 0.4%.<sup>1</sup>

One of the major changes required when the US Clean Air Act was amended in 1990 (Section 182) was the call for greater attention to photochemical oxidant smog in the lower atmosphere, which is arguably the most widespread and persistent urban air pollution problem around the world. The causes of this and the lesser problem of CO and PM<sub>2.5</sub> pollution in urban areas are largely due to the diversity and number of urban air pollution sources. One component of urban smog, hydrocarbons, comes from motor vehicle emissions, petroleum refineries, chemical plants, dry cleaners, gasoline stations, house painting, and printing shops. Another key component, nitrogen oxides, comes from the combustion of fuel for transportation, utilities and industries.

Although there are other reasons for continued high levels of ozone pollution, such as growth in the number of stationary sources of hydrocarbons and continued growth in automobile travel, the remaining sources of hydrocarbons are the most difficult to control. These are the small sources, those that emit less than 100 tons of hydrocarbons per year. These sources, such as auto shops and dry cleaners, may individually emit less

than 10 tons per year but collectively emit many hundreds of tons of pollution.

Title I of the 1990 Clean Air Act Amendments (CAA90) allows the US Environmental Protection Agency (USEPA) to define the boundaries of "nonattainment" areas for ozone, CO, and PM<sub>10</sub>. Emission standards for these areas are based on a new set of "nonattainment categories". The USEPA has established a classification system for ozone design values (goals) and attainment deadlines. Table 28.1 lists these parameters.

In the United States, if a nonattainment area is classified as serious, based on ambient ozone measurements, then the state must implement actions to come into compliance within 9 years. The CAA90 also specifies the size and, therefore, the number of sources subject to regulatory control as a function of nonattainment classification. Table 28.2 illustrates these requirements for ozone nonattainment classifications of extreme and severe; the state must include sources with combined NO<sub>x</sub> and VOC emissions of 10 tons per year in their control plans.

As mentioned, nonattainment areas must implement different control measures, depending on their classification. Marginal areas, for example, are the closest to meeting the standard. They are required to conduct an inventory of their ozone-causing emissions and institute a permit program. Nonattainment areas with more serious air quality problems must implement various control measures. The worse the air quality, the more the control areas will have to implement.

TABLE 28.1 Classification of Ozone Nonattainment Areas (in Increasing Order of Severity)

Classification	Ozone Design Values (ppm)
Marginal	0.121 up to 0.138
Moderate	0.138 up to 0.160
Serious	0.160 up to 0.180
Severe	0.180 up to 0.280
Extreme	0.280 and above

TABLE 28.2 Clean Air Act Amendments, Title I, Emission Sources Requiring Control

United States Ozone Nonattainment Classification	Allowable Emissions of Combined Oxides of Nitrogen + Volatile Organic Compounds (tons per year)
Extreme and severe	10
Serious	50
Moderate and marginal	100

**TABLE 28.3** Types of Data Collected at a Photochemical Assessment Monitoring Stations (PAMS) Site

<b>OZONE, NITROGEN OXIDES, VOLATILE ORGANIC SUMS</b>	
Ozone	
Nitric acid	
Nitrogen dioxide	
Oxides of nitrogen	
Total nonmethane organic compounds	
Sum of targeted hydrocarbons	
<b>SURFACE METEOROLOGICAL</b>	
Temperature	
Wind speed	
Wind direction	
Relative humidity	
Solar radiation	
Ultraviolet radiation	
Barometric pressure	
Precipitation	
<b>HYDROCARBONS*</b>	
Ethylene	2,3-Dimethylpentane
Acetylene	3-Methylhexane
Ethane	2,2,4-Trimethylpentane
Propylene	<i>n</i> -Heptane
Propane	Methylcyclohexane
Isobutane	2,3,4-Trimethylpentane
1-Butene	Toluene
<i>n</i> -Butane	2-Methylheptane
<i>t</i> -2-Butene	3-Methylheptane
<i>c</i> -2-Butene	<i>n</i> -Octane
Isopentane	Ethylbenzene
1-Pentene	<i>m&amp;p</i> -Xylenes
<i>n</i> -Pentane	Styrene
Isoprene	<i>o</i> -Xylene
<i>t</i> -2-Pentene	<i>n</i> -Nonane
<i>c</i> -2-Pentene	Isopropylbenzene
2,2-Dimethylbutane	<i>n</i> -Propylbenzene
Cyclopentane	<i>m</i> -Ethyltoluene
2,3-Dimethylbutane	<i>p</i> -Ethyltoluene
2-Methylpentane	1,3,5-Trimethylbenzene

*Continued***TABLE 28.3** Types of Data Collected at a Photochemical Assessment Monitoring Stations (PAMS) Site—cont'd

3-Methylpentane	<i>o</i> -Ethyltoluene
2-Methyl-1-pentene	1,2,4-Trimethylbenzene
<i>n</i> -Hexane	<i>n</i> -Decane
Methylcyclopentane	1,2,3-Trimethylbenzene
2,4-Dimethylpentane	<i>m</i> -Diethylbenzene
Benzene	<i>p</i> -Diethylbenzene
Cyclohexane	<i>n</i> -Undecane
2-Methylhexane	
<b>CARBONYLS</b>	
Formaldehyde	
Acetone	
Acetaldehyde	

\* Table note: The hydrocarbons are listed according to elution sequence, i.e. the order in which the compound leaves the column and is detected. Generally, the lower the boiling point, the sooner the compound will leave the gas chromatography (GC) column. VOCs are generally separated using GC. However, this is not the case for liquid chromatography. For example, for high-performance liquid chromatography, reverse phase chromatography is widely used. The stationary phase is made of nonpolar organic chains fused to silica and the mobile phase is usually a mixture of aqueous and organic solvents. Here, compounds that are more polar exit the column and move to the mobile phase first. For volatile organic compounds, the elution sequence is for GC separation, unless otherwise stated, e.g. ethylene will separate before isoprene, which will separate before 1,2,3-trimethylbenzene.

Source: Ref. 3.

The new law also establishes similar programs for areas that do not meet the federal health standards for the pollutants carbon monoxide and PM. Areas exceeding the standards for these pollutants are divided into "moderate" and "serious" classifications. Depending on the degree to which they exceed the carbon monoxide standard, areas are required to implement programs introducing oxygenated fuels and/or enhanced emission inspection programs, among other measures. Depending on their classification, areas exceeding the PM standard will have to implement either Reasonably Available Control Technology or Best Available Control Technology, among other requirements.

Numerous sampling sites that have been added to the US network are known as Photochemical Assessment Monitoring Stations (PAMS). Since smog results from atmospheric photochemical reaction involving VOCs and oxides of nitrogen ( $\text{NO}_x$ ), the stationary networks in the United States had to improve ozone ( $\text{O}_3$ ) and include reliable chemical speciation of the  $\text{O}_3$  precursors.

In addition, meteorological information had to be improved in order to match the photochemical data gathered at each site. Table 28.3 provides the target parameters for PAMS sites.

The improved network is aimed at providing sound information that can be used by air pollution control agencies as they evaluate, track progress, and refine control strategies for attaining the ozone air quality standards.<sup>3</sup> The current standard<sup>4</sup> is 75 ppb for the fourth highest daily maximum 8-h concentration annually, averaged over 3 years.<sup>b</sup> The PAMS network design consists of five types of sites (see Figure 28.9).<sup>5</sup> The siting requirements are described in the Discussion Box: Photochemical Assessment Monitoring Station Siting Criteria.

In the United States, the ground-level ozone has been a more persistent problem than the other gas-phase criteria pollutants. It has decreased in average concentrations in recent decades, but has actually shown a slight increase since 2009. Indeed, the standard of 75 ppb, which is based on the annual fourth maximum of daily maximum 8-h averages, is actually being exceeded by the nationwide average concentration (see Figure 28.10).

Meteorology can have a major impact on O<sub>3</sub> and other air pollutant concentrations. For example, O<sub>3</sub> forms optimally on hot, sunny days in a stable (stagnant) air mass. Figure 28.11 compares national O<sub>3</sub> concentrations as observed to those corrected for weather conditions.

## PHOTOCHEMICAL ASSESSMENT MONITORING STATION SITING CRITERIA

The PAMS network consists of four types of monitoring sites:

### **Site #1**

Upwind and background characterization site. These stations are located so as to characterize background O<sub>3</sub> concentrations and incoming O<sub>3</sub> that has been transported into the area. This site also includes background and incoming concentrations for the precursor compounds. The locations are based on the predominant morning upwind direction from the local area of highest precursor emissions and at a distance needed for urban scale measurements, i.e. near the upwind edge of the photochemical grid model domain.

### **Site #2**

Maximum ozone precursor emissions impact site. These sites are established to monitor the magnitude and type of precursor emissions in the area where maximum precursor emissions representative of a Metropolitan Statistical Area (MSA) or a Consolidated Metropolitan Statistical Area (CMSA) are expected to impact and are suited for the monitoring of urban air toxic pollutants. The #2 sites are located immediately downwind (using the same morning wind direction as for locating

site #1) of the area of maximum precursor emissions and are typically placed near the downwind boundary of the primary area of precursor emissions mix to obtain neighborhood scale measurements (often the central business district). The size of the area may dictate placing a second site at the second most predominant morning wind direction.

### **Site #3**

This site is intended to monitor maximum O<sub>3</sub> concentrations downwind (typically 10 to 30 mi) from the area of maximum precursor emissions. These data will provide an estimate of the scale of the pollution.

### **Site #4**

These sites are intended to characterize the extreme downwind transported concentrations of O<sub>3</sub> and precursor compounds moving out of the area. Combined with background information (site #1), the data from these sites help to show the contribution of transport to downwind areas. These sites are typically located near the downwind edge of the photochemical grid model domain, i.e. in the predominant afternoon downwind direction from the local area of maximum precursor emissions at a distance sufficient to obtain urban scale measurements.

<sup>b</sup> The ozone rule was finalized on March 12, 2008. The 1997 ozone standard (0.08 ppm, annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years) and related implementation rules continue to be in force. In 1997, the 1-hour ozone standard (0.12 ppm, not to be exceeded more than once per year) was revoked in all areas, although some areas have continued obligations under that standard (so-called antibacksliding). The 1-hour ozone standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is less than or equal to 1.<sup>5</sup>

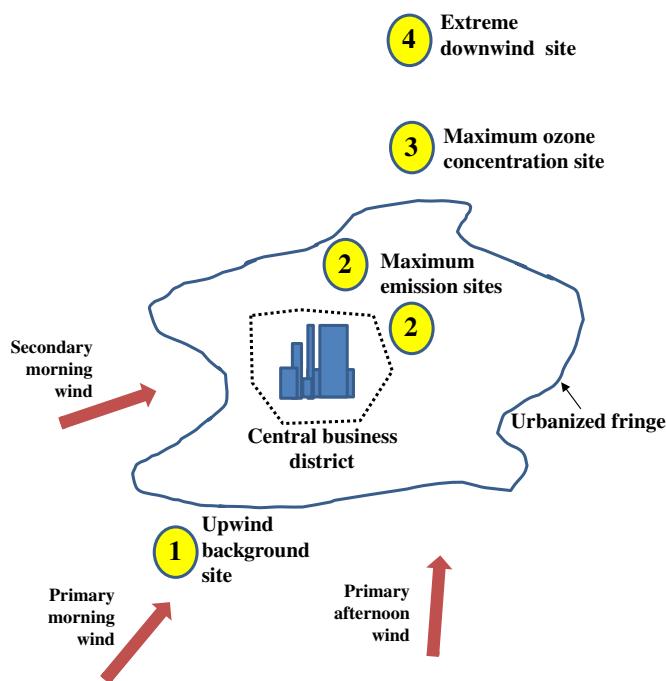


FIGURE 28.9 Photochemical assessment monitoring stations (PAMS) network design. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 3.

### 28.3 CARBON MONOXIDE

Carbon monoxide (CO) concentrations vary considerably across the globe, with much seasonal variability (see Figure 28.12). For example, the seasonal shifts in carbon monoxide in central Africa are tied to the widespread agricultural burning that shifts north and south of the equator with the seasons. Combustion, e.g. biomass burning and internal combustion engines, is an important source of carbon monoxide pollution in other regions of the Southern Hemisphere, such as the Amazon and Southeast Asia.<sup>6</sup>

In the United States, concentrations of 8-h CO decreased 52% between 2001 and 2010, as shown in Figure 28.13. From 2000 to 2012, the national CO average decreased by 57%. For several years, measured CO concentrations have been below the 8-h standard (9 ppm) and 1-h standard (35 ppm). The decrease was fairly evenly distributed throughout the United States.

### 28.4 NITROGEN DIOXIDE

The WHO guideline values for NO<sub>2</sub> are  $40 \mu\text{g m}^{-3}$  annual mean and  $200 \mu\text{g m}^{-3}$  1-h mean. At short-term concentrations exceeding  $200 \mu\text{g m}^{-3}$ , NO<sub>2</sub> causes significant inflammation of the airways. In addition, NO<sub>2</sub> is a precursor for both tropospheric ozone and particulates. If forms nitrate aerosols, which are a major constituent of PM<sub>2.5</sub>; and in the presence of ultraviolet light, NO<sub>2</sub> forms O<sub>3</sub>. The major sources of anthropogenic emissions of NO<sub>2</sub> are combustion processes. Exposure

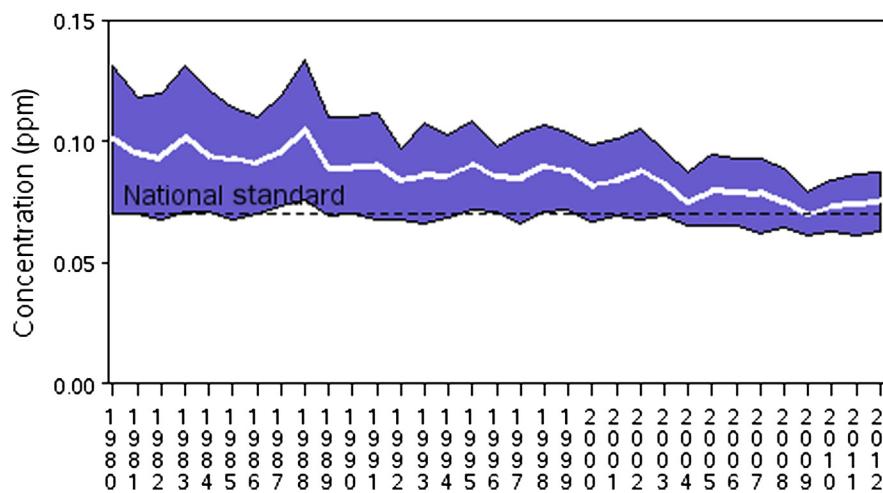


FIGURE 28.10 Trends for the 8-h ozone concentrations in the United States, based on annual fourth maximum 8-h average at 230 nationwide sites. Nationally, average O<sub>3</sub> concentrations decreased 25% between 1980 and 2012, but have appeared to be increasing in recent years. The sharpest decline occurred in the 1980s, leveling off in the 1990s, with another substantial decline after 2002. About 90% of sites have concentrations below the top line and 10% of the sites have concentrations below the bottom line. The center white line is the mean concentration for all sites. The dashed line is the national standard. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Air trends: ozone. <http://www.epa.gov/airtrends/ozone.html>; 2013 [accessed 27.08.13].

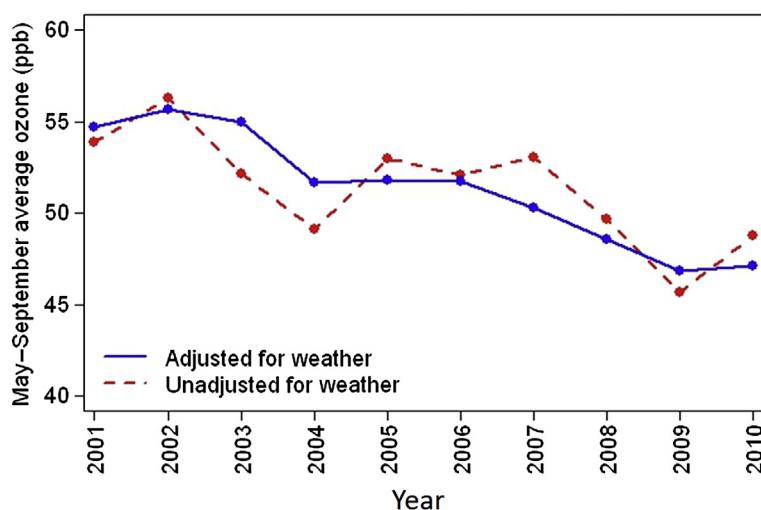


FIGURE 28.11 Trends for the 8-h ozone ( $O_3$ ) concentrations in the United States, based on annual fourth maximum 8-h average at 180 nationwide sites. The dotted line shows the trend in observed ozone concentrations at selected monitoring sites, whereas the solid line shows the underlying ozone trend at those sites with weather effects removed using a statistical model. Above-average temperatures and below-average humidity across most of the United States in 2007 contributed to increased  $O_3$  formation while below-average temperatures and above-average humidity across much of the United States in the summer of 2009 contributed to decreased ozone formation. The statistical model accounts for these effects by adjusting the seasonal average ozone trend downward in 2007 and upward in 2009. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Air trends: ozone. <http://www.epa.gov/airtrends/ozone.html>; 2013 [accessed 27.08.13].

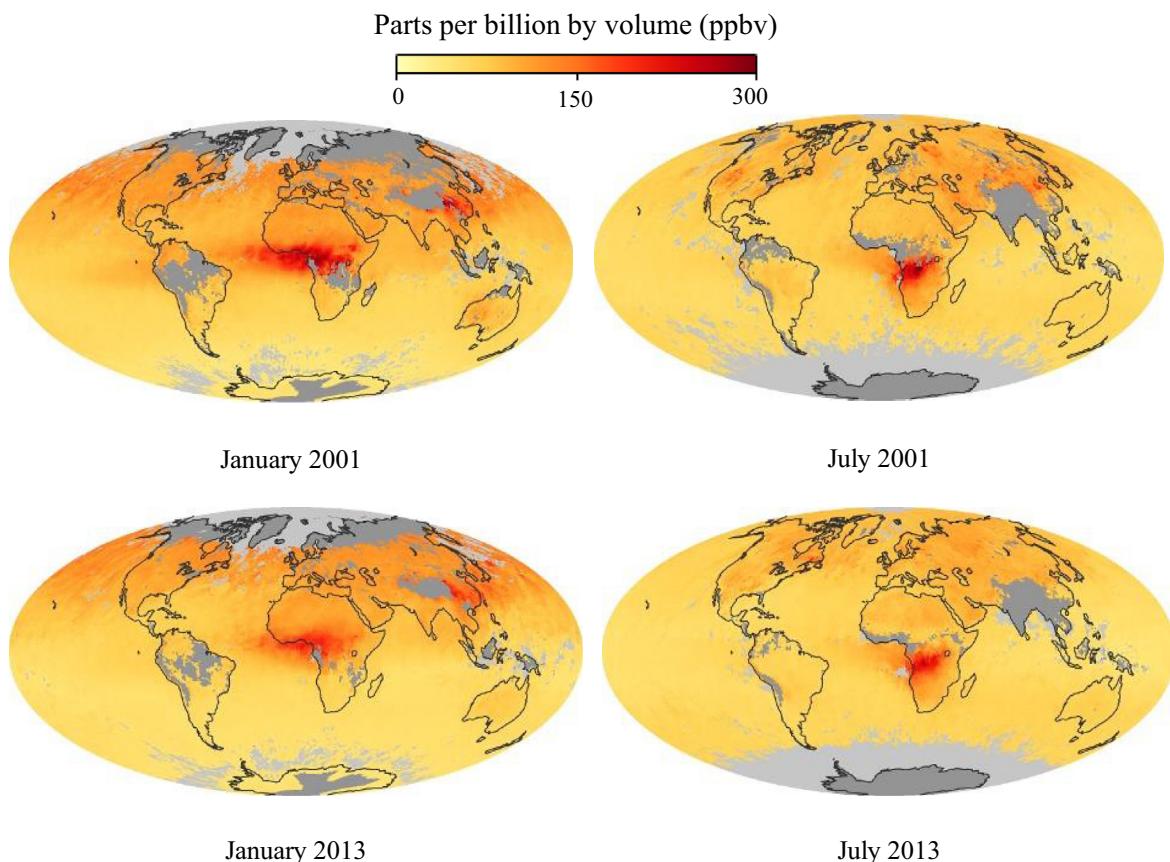
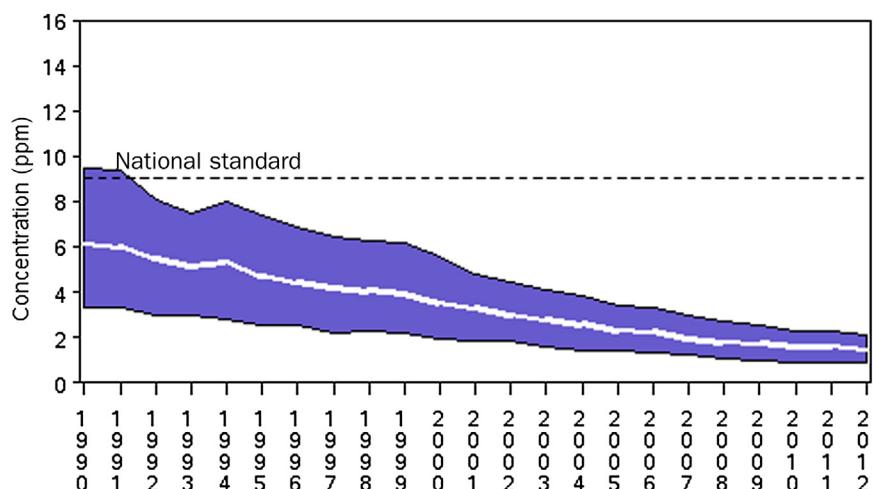


FIGURE 28.12 Global distribution of carbon monoxide. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 6.

**FIGURE 28.13** Trends for the second carbon monoxide concentrations in the United States, based on annual second maximum 8-h average at 148 nationwide sites. Note: About 90% of sites have concentrations below the top line and 10% of the sites have concentrations below the bottom line. The center white line is the mean concentration for all sites. The dashed line is the national standard. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Air trends: carbon dioxide. <http://www.epa.gov/airtrends/carbon.html>; 2013 [accessed 25.11.13].



to NO<sub>2</sub> has been linked to bronchitis in asthmatic children. Reduced lung function has been documented at NO<sub>2</sub> concentrations currently experienced in urban areas in Europe and North America.<sup>1</sup>

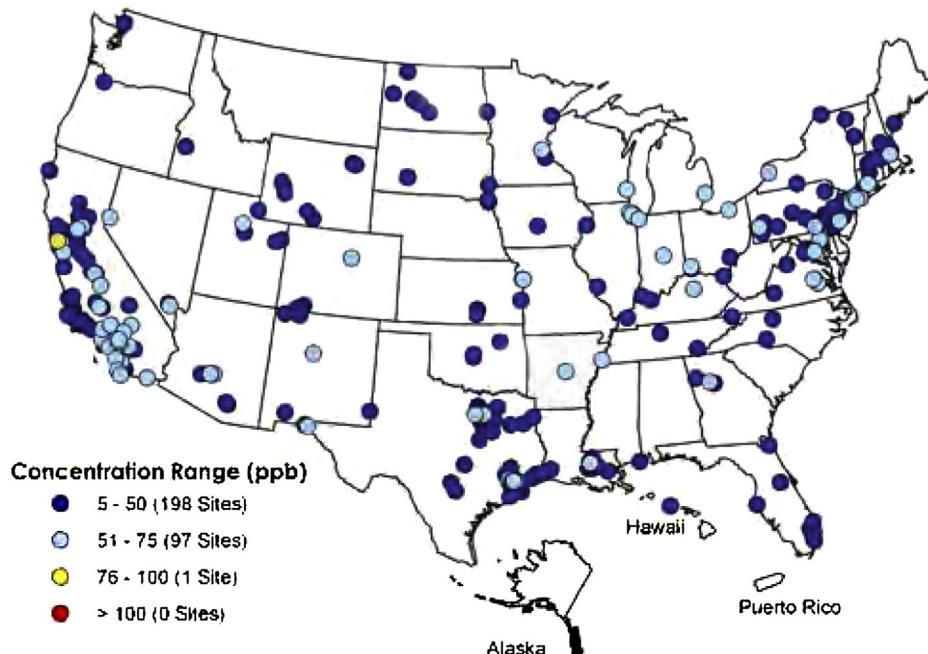
In 2010, the United States strengthened its health-based NO<sub>2</sub> ambient air quality standard, lowering it to 100 ppb for the 1-h, 3-year average of the 98th percentile of the annual distribution of daily maximum 1-h average concentrations. The current annual average NO<sub>2</sub> standard remains 53 ppb. Although this new standard is a 3-year average, Figure 28.14 shows a snapshot of the 98th percentile of the 1-h daily maximum NO<sub>2</sub> concentration for 2010.<sup>7</sup> Nationally, annual mean concentrations of NO<sub>2</sub> have shown a continual decline in

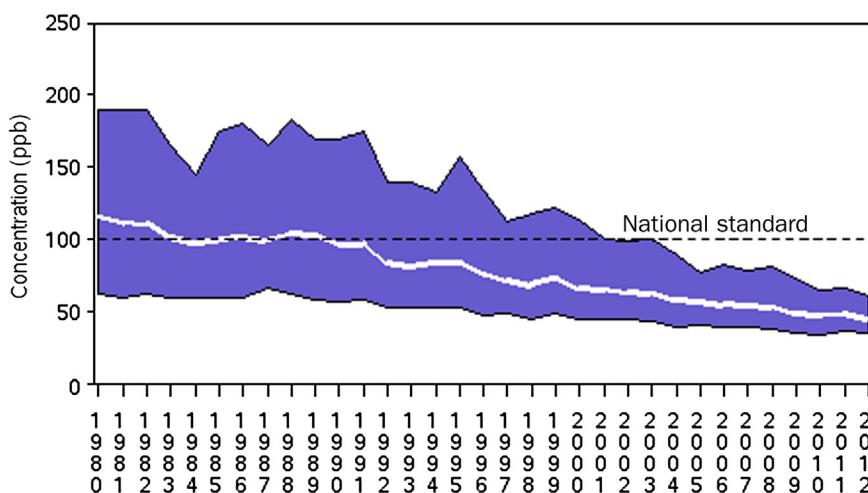
recent decades. The NO<sub>2</sub> concentrations decreased 60% between 1980 and 2012 (see Figure 28.15).

## 28.5 SULFUR DIOXIDE

The WHO guideline levels for SO<sub>2</sub> are 20  $\mu\text{g m}^{-3}$  24-h mean and 500  $\mu\text{g m}^{-3}$  10-min mean. The WHO recommends that the SO<sub>2</sub> concentration of  $\mu\text{g m}^{-3}$  should not be exceeded over average periods of 10 min duration, based on studies showing that people with asthma experience changes in pulmonary function and respiratory symptoms after periods of exposure to

**FIGURE 28.14** Nitrogen dioxide concentrations (parts per billion) in 2010 at ambient air monitoring sites. Concentrations are for 98th percentile of daily 1-h maximum. Note: The 1-h standard is actually the 3-h average of the 98th percentile of the daily maximum 1-h average, but the information presented includes those for the year 2010. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Our nation's air – status and trends through 2010. <http://www.epa.gov/airtrends/2011/report/lead.pdf>; 2011 [accessed 14.08.13].





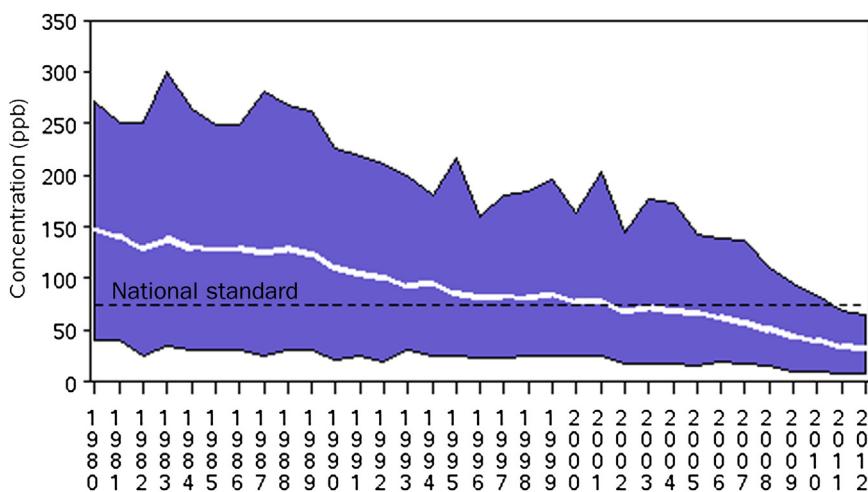
**FIGURE 28.15** Seasonally weighted annual concentrations for nitrogen dioxide in the ambient air in the United States. The chart shows the annual 99th percentile of the daily maximum 1-h average for 30 monitoring sites. (For color version of this figure, the reader is referred to the online version of this book.)

SO<sub>2</sub> as short as 10 min. The recent lowering of the 24-h guideline from 125 to 20 µg m<sup>-3</sup> was based on recent findings that the health effects are now known to be associated with much lower levels of SO<sub>2</sub> than previously believed. Thus, a greater degree of protection is needed. In addition, the lower recommendation has the added benefit of decreasing other air pollutants, e.g. secondary aerosols (see Figure 28.8).<sup>1</sup> In addition to health benefits, the lower standard should also ameliorate acid deposition impacts on ecosystems and materials.

Sulfur dioxide is produced from the burning of fossil fuels (coal and oil) and the smelting of mineral ores that contain sulfur. The main anthropogenic source of SO<sub>2</sub> is the burning of sulfur-containing fossil fuels for domestic heating, power generation, and motor vehicles. SO<sub>2</sub> can affect the respiratory system and the functions of the lungs, and causes irritation of the eyes. Inflammation

of the respiratory tract causes coughing, mucus secretion, aggravation of asthma and chronic bronchitis, and makes people more prone to infections of the respiratory tract. Hospital admissions for cardiac disease and mortality increase on days with higher SO<sub>2</sub> levels. When SO<sub>2</sub> combines with water, it forms sulfuric acid; this is the main component of acid rain, which is a cause of deforestation.<sup>3</sup>

In the United States, ambient SO<sub>2</sub> concentrations have shown an improving trend over recent decades (see Figure 28.16). Nationally, annual mean concentrations of SO<sub>2</sub> decreased about 50% between 2001 and 2010. In 2010, annual SO<sub>2</sub> concentrations were the lowest measured of the 10-year period. A site in Hawaii measured concentrations above the level of the annual standard (30 ppb) and four Hawaiian sites had concentrations greater than the 24-h standard (140 ppb), likely due to volcanic emissions.



**FIGURE 28.16** Seasonally weighted annual concentrations for sulfur dioxide in the ambient air in the United States. The chart shows the annual 99th percentile of the maximum 1-h average for 163 monitoring sites. (For color version of this figure, the reader is referred to the online version of this book.)

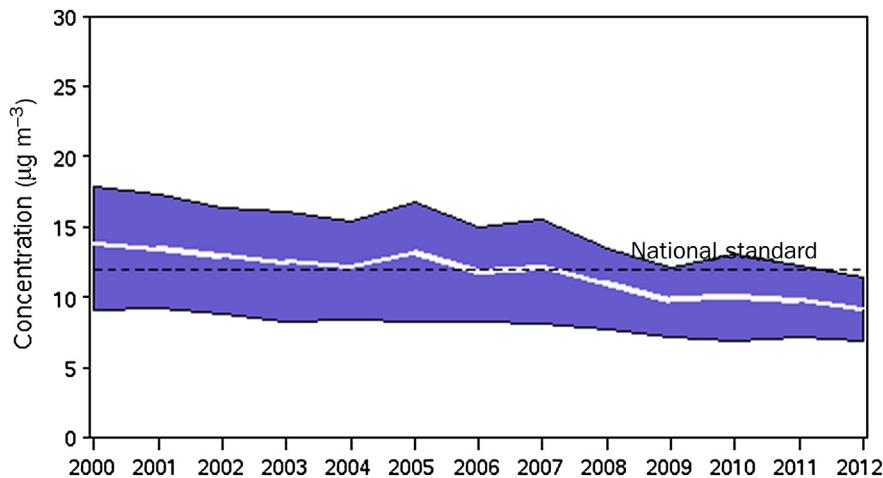
## 28.6 PARTICULATE MATTER

Around the world, more people are exposed to unhealthy concentrations of PM of various sizes than to any other pollutant. PM is composed of various compounds, including but not limited to sulfates, nitrates, ammonia, sodium chloride, carbon, mineral dust, and water. It is a complex mixture of solid and liquid particles of both inorganic and organic constituents that are suspended in the air. The PM is identified according to aerodynamic diameter, usually distinguished between coarse or PM<sub>10</sub> (particles with an aerodynamic diameter smaller than 10 µm) or fine PM<sub>2.5</sub> (aerodynamic diameter smaller than 2.5 µm). Smaller particles generally are more dangerous since, when inhaled, they may reach the peripheral regions of the bronchioles, and interfere with gas exchange inside the lungs.<sup>1</sup>

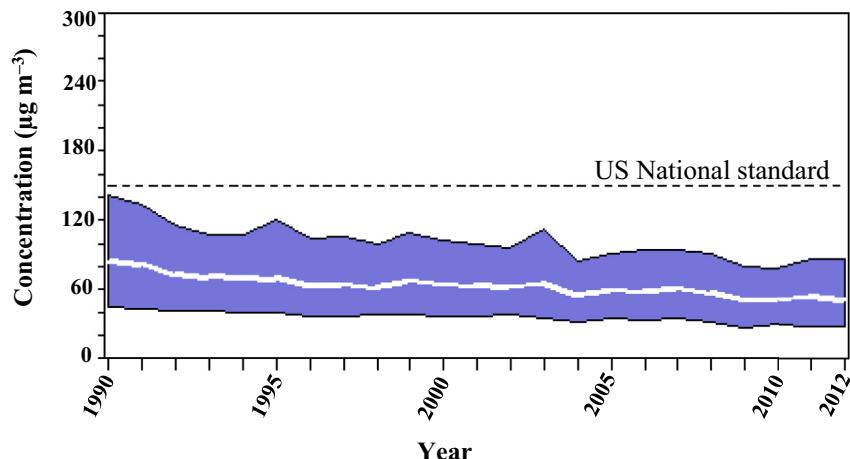
The WHO guideline values for PM<sub>2.5</sub> are 10 µg m<sup>-3</sup> annual mean and 25 µg m<sup>-3</sup> 24-h mean. The WHO guideline values for PM<sub>10</sub> are 20 µg m<sup>-3</sup> annual mean and 50 µg m<sup>-3</sup> 24-h mean. Diseases associated with PM exposure occur in most countries, in both urban and rural populations. In developing countries, exposure to pollutants from indoor combustion of solid fuels on open fires or traditional stoves increases health risks among young children. Indoor air pollution from solid fuel use also presents a major risk to humans of all ages. The mortality in urban areas with high PM pollution exceeds that observed in relatively cleaner cities by 15–20%. In Europe, the average life expectancy is 8.6 months lower due to exposure to PM<sub>2.5</sub> produced by human activities.<sup>1</sup>

In the United States, both PM<sub>2.5</sub> and PM<sub>10</sub> concentrations have fallen continuously (see Figures 28.17 and 28.18). Between 2000 and 2012, PM<sub>2.5</sub> concentrations

**FIGURE 28.17 Trends for seasonally weighted annual average of fine particulate (i.e. PM<sub>2.5</sub>) concentrations in the United States, based on 570 nationwide sites.** Note: About 90% of sites have concentrations below the top line and 10% of the sites have concentrations below the bottom line. The center white line is the mean concentration for all sites. The dashed line is the national standard. (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Air trends: carbon dioxide. <http://www.epa.gov/airtrends/carbon.html>; 2013 [accessed 25.11.13].



**FIGURE 28.18 Trends for seasonally-weighted annual average of coarse particulates (i.e. PM<sub>10</sub>) concentrations in the United States, based on the annual second maximum 24-hour average for 239 nationwide sites.** Note: About 90% of sites have concentrations below the top line and 10% of the sites have concentrations below the bottom line. The center white line is the mean concentration for all sites. The dashed line is the national standard. U.S. Environmental Protection Agency. Air trends: particulate matter. <http://www.epa.gov/airtrends/pm.html#pmnat>; 2014 [accessed 19.5.14].



fell 33%, from 1990 to 2012,  $\text{PM}_{10}$  concentrations dropped by 33%.

## 28.7 AIRBORNE LEAD

Long-term trends can be determined from samples measured by stationary air quality monitoring networks. For example, Figure 28.19 shows the long-term decrease in ambient concentrations of lead (Pb) in the atmosphere in the United States, resulting from reducing Pb in gasoline and improved control technologies. The ambient Pb concentrations have continued to decrease, i.e. approximately 71% between 2001 and 2010 (see Figure 28.20). These monitoring sites are chosen to determine the concentrations of an air pollutant within the expected zone of influence for a source or set of sources. In this case, 39 sampling stations have been sited near large stationary sources. For comparisons, 63 sites were chosen away from stationary industrial sources. For Pb, average concentrations near a stationary source expected to emit Pb (e.g. metal processing, battery manufacturing, and mining) are about eightfold higher than at a site that is not near a stationary industrial source. There are significant year-to-year changes in lead concentrations at sites near stationary sources; these reflect changes in emissions due to changes in operating schedules and plant closings.<sup>8</sup>

From the 196 sites shown in Figure 28.21, the Pb standard set in 2008 ( $0.15 \mu\text{g m}^{-3}$ ) was exceeded at 34 sites,

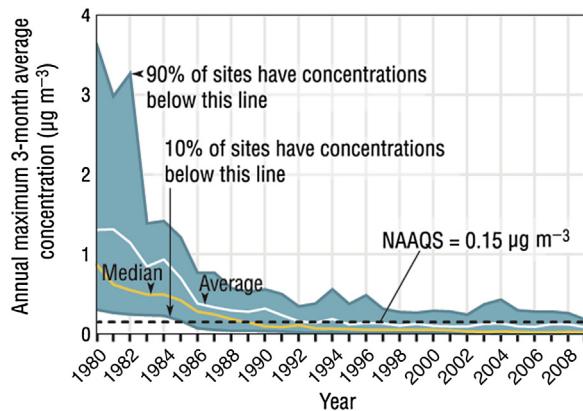


FIGURE 28.19 Ambient lead (Pb) concentrations between 1980 and 2009, decreased on average 93% nationally in the United States. The largest and most rapid decrease occurred during the 1980s and early 1990s, much of which can be attributed to decreasing lead content in gasoline. The trend is based on data from 20 monitoring sites in 14 US counties out of 122 total sites that were operational in 2009. The number reporting 3-month average lead concentrations above the level of the 2008 NAAQS ( $0.15 \mu\text{g m}^{-3}$ ) fell from 19 to 2 over the same time period. Also shown are the 90th and 10th percentiles based on the distribution of annual statistics. (For color version of this figure, the reader is referred to the online version of this book.)

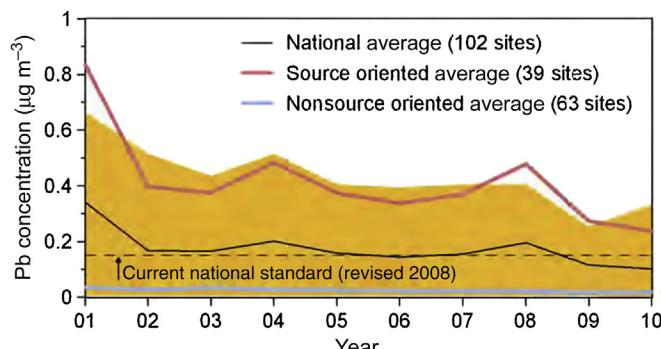


FIGURE 28.20 National lead (Pb) air quality trend, 2001–2010 (maximum 3-month average in  $\mu\text{g m}^{-3}$ ). About 90% of sites are shown in the orange area. (For interpretation of the references to color in this figure legend, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Our nation's air – status and trends through 2010. <http://www.epa.gov/airtrends/2011/report/lead.pdf>; 2011 [accessed 14.08.13].

all of which are located near stationary lead sources. Beginning in 2010 in the United States, additional monitoring is required near stationary lead sources estimated to emit 0.50 or more tons per year (tpy) of Pb. This means that as many as 270 new locations have been added.

## 28.8 AIR TOXICS

As mentioned, in addition to the criteria pollutants there are numerous compounds that cause health problems, especially chronic illnesses. There are limited data for such compounds at the international or national scale, given the variability of sources. However, there are numerous data on specific areas from measurements using equipment such as those discussed in Chapter 25. In Europe, for example, the mean ambient air concentration of benzene<sup>9</sup> in urban areas is as high as  $20 \mu\text{g m}^{-3}$  and in rural areas less than  $1 \mu\text{g m}^{-3}$ . In occupational, indoor, and other settings, benzene concentrations can be much higher. The European concentrations of formaldehyde<sup>11</sup> are shown in Table 28.4.

Benzene and formaldehyde are but two organic compounds in a long list of air toxics. In addition, there are entire classes of compounds, especially the dioxins, furans, and PAHs, that are grouped together, as well as combinations of organic and inorganic compounds, e.g. coke oven emissions, which are reported. These are often reported along with levels of concern.

In Europe, PAHs may be represented by concentrations of a single compound, e.g. benzo(a)pyrene, or dioxins may be represented by the most toxic congener, 2,4,7,8-tetrachlorodibenzo-*para*-dioxin. A unit risk for benzo(a)pyrene is estimated to be  $8.7 \times 10^{-5}$  per  $\text{ng m}^{-3}$ , which translates to excess cancer lifetime risks of  $10^{-4}$  at  $1.2 \text{ ng m}^{-3}$ ,  $10^{-5}$  at  $0.12 \text{ ng m}^{-3}$ , and  $10^{-6}$  at

FIGURE 28.21 Maximum 3-month average lead (Pb) concentrations ( $\mu\text{g m}^{-3}$ ) at 196 Pb monitoring sites in 2010 (maximum 3-month averages). (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Our nation's air: status and trends through 2010. EPA-454/R-12-001. Research Triangle Park (NC); 2011.

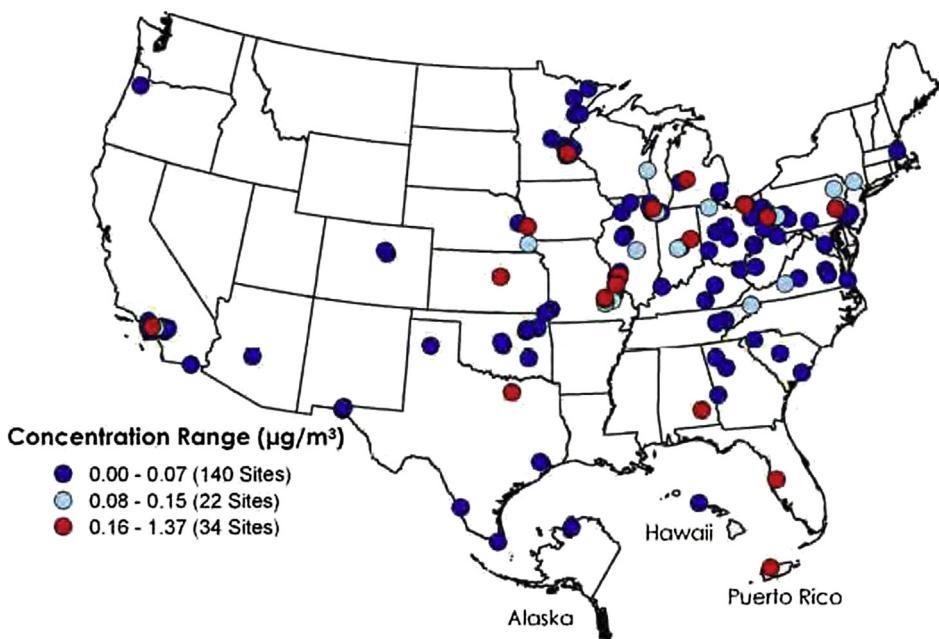


TABLE 28.4 Mean Exposure Concentrations to Formaldehyde in Various Settings in Europe

Setting	Concentrations ( $\text{mg m}^{-3}$ )	Exposure ( $\text{mg day}^{-1}$ )
Ambient air (10% of time; $2 \text{ m}^3 \text{ day}^{-1}$ )	0.001–0.02	0.002–0.04
Indoor air home (65% of time; $10 \text{ m}^3 \text{ day}^{-1}$ )		
Conventional	0.03–0.06	0.3–0.6
Mobile home	0.1	1.0
Environmental tobacco smoke	0.05–0.35	0.5–3.5
Workplace (25% of time; $8 \text{ m}^3 \text{ day}^{-1}$ )		
Without occupational exposure*	0.03–0.06	0.2–0.5
With occupational exposure	1.0	8.0
Environmental tobacco smoke	0.05–0.35	0.4–2.8
Smoking (20 cigarettes day $^{-1}$ )	60–130	0.9–2.0 <sup>§</sup>

\* These ranges assume normal concentration in conventional buildings.

§ Total amount in smoke.

Source: Ref. 9.

0.012  $\text{ng m}^{-3}$ .<sup>10</sup> For example, if a jurisdiction requires that the air toxics not increase lifetime cancer risks more than one in a million, if benzo(a)pyrene concentrations are measured to be  $0.020 \text{ ng m}^{-3}$ , then actions would be necessary to decrease them by at least  $0.008 \text{ ng m}^{-3}$  so that the ambient air concentrations would be at most  $0.012 \text{ ng m}^{-3}$ .

## 28.9 ACID DEPOSITION

Sulfur dioxide and nitrogen oxide emissions are transformed in the atmosphere and return to the earth in rain, fog, or snow. Approximately, 20 million tons of  $\text{SO}_2$  are emitted annually in the United States, mostly from the burning of fossil fuels by electric utilities. Acid rain damages lakes, harms forests and buildings, contributes to reduced visibility, and is suspected of damaging health.

The CAAA90 required a permanent 10 million ton reduction in sulfur dioxide ( $\text{SO}_2$ ) emissions from 1980 levels. To achieve this, the USEPA allocated allowances of 1 ton of sulfur dioxide in two phases. The first phase, effective January 1, 1995, required 110 power electric plants to reduce their emissions to a level equivalent to the product of an emissions rate equal to 2.5 lbs of  $\text{SO}_2$  per million Btu (mm Btu) times the average mm Btu of their 1985–1987 fuel use. Plants that use certain control technologies to meet their phase I reduction requirements were able to receive a 2-year extension of compliance until 1997. The law also had a special allocation of 200,000 annual allowances per year each of the 5 years of phase I to power plants in Illinois, Indiana, and Ohio.

The second phase, effective January 1, 2000, required approximately 2000 utilities to reduce their emissions to a level equivalent to the product of an emissions rate of  $(1.2 \text{ lbs of } \text{SO}_2 \text{ mm Btu}^{-1}) \times (\text{the average mm Btu of their 1985–1987 fuel use})$ . In both phases, affected sources were required to install systems that continuously monitor emissions in order to track progress and assure compliance.

The law provided for utilities to trade allowances within their systems and/or buy or sell allowances to and from other affected sources. Each source must have sufficient allowances to cover its annual emissions. If not, the source is subject to a \$2000 per ton excess emissions fee and a requirement to offset the excess emissions in the following year.

Nationwide, plants that emit SO<sub>2</sub> at a rate below 1.2 lbs mm Btu<sup>-1</sup> were able to increase emissions by 20% between a baseline year and 2000. Bonus allowances will be distributed to accommodate growth by units in states with a statewide average below 0.8 lbs mm Btu<sup>-1</sup>. Plants experiencing increases in their utilization in the last 5 years also receive bonus allowances; 50,000 bonus allowances per year are allocated to plants in 10 Midwestern states that make reductions in phase I. Plants that repower with a qualifying clean coal technology were able to receive a 4-year extension of the compliance date for phase II emission limitations.

The law also includes specific requirements for reducing emissions of nitrogen oxides, based on USEPA regulations to be issued not later than mid-1992 for certain boilers and 1997 for all remaining boilers.

Title IV was designed to reduce total SO<sub>2</sub> emissions by approximately 50% over a 10-year period. Provisions of the title are designed to introduce economic flexibility for the electric power industry, to recognize controls already implemented by progressive utilities and to reduce the economic impact on high-sulfur coal regions of the United States.

## 28.10 STRATOSPHERIC OZONE

The CAAA90 was built on the market-based structure and requirements on existing USEPA regulations to phase out the production of substances that deplete the ozone layer. The law requires a complete phase-out of alkyl halides like chlorofluorocarbons (CFCs) and halons with interim reductions and some related changes to the existing Montreal Protocol, revised in June 1990.<sup>11</sup> The most common CFC is dichlorodifluoromethane (known as R-12 or Freon-12). Many CFCs have been widely used as refrigerants and propellants (in aerosol applications), as well as solvents. The manufacture of such compounds has been phased out, and substituted with physical processes (e.g. manual pumps) or with products such as R-410A, which is a mixture of difluoromethane (CH<sub>2</sub>F<sub>2</sub>) and pentafluoroethane (CHF<sub>2</sub>CF<sub>3</sub>). The alkyl halides contain bromine (Br) or chlorine (Cl), but the only halogen in R-410A is fluorine (F), which does not contribute to ozone depletion.

Under CAAA90 provisions, the USEPA must list all regulated substances along with their ozone-depletion potential, atmospheric lifetimes, and global warming

potentials within 60 days of enactment. In addition, the USEPA was required to ensure that class I chemicals be phased out on a schedule similar to that specified in the Montreal Protocol—CFCs, halons, and carbon tetrachloride by 2000; methyl chloroform by 2002—but with more stringent interim reductions. Class II chemicals, hydrochlorofluorocarbons (HCFCs) will be phased out by 2030. The CAAA90 also requires USEPA to publish a list of safe and unsafe substitutes for class I and II chemicals and to ban the use of unsafe substitutes. The law required nonessential products releasing class I chemicals to be banned within 2 years of enactment. In 1994, a ban went into effect for aerosols and noninsulating foam using class II chemicals, with exemptions for flammability and safety. Regulations for this purpose are in place.

The Montreal Protocol required the United States to reduce its consumption of HCFCs by 35% below the US baseline cap. As of January 1, 2003, the USEPA banned production and import of HCFC-141b, the most ozone-destructive HCFC. This action allowed the United States to meet its obligations under the Montreal Protocol. All baseline allowances for production and import of HCFC-22 and HCFC-142b have been issued. The Montreal Protocol requires the United States to reduce its consumption of HCFCs by 75% below the US baseline. In the European Union and the United States, virgin HCFCs cannot be used in new air conditioning or similar units as of 2010. In other parts of the world, the phase-out date varies by nation. As a result, heating, ventilation, and air conditioning system manufacturers may not produce new air conditioners and heat pumps containing R-22. By January 1, 2015, the United States must reduce its consumption of HCFCs by 90% below the US baseline. Finally, by 2020, the Montreal Protocol requires the United States to reduce its consumption of HCFCs by 99.5% below the US baseline. Refrigerant that has been recovered and recycled/reclaimed will be allowed beyond 2020 to service existing systems, but chemical manufacturers will no longer be able to produce R-22 to service existing air conditioners and heat pumps.<sup>12</sup>

## 28.11 GLOBAL GHGs

Since the 1980s, many scientists have accepted that human activities play a significant role in warming of the planet. Global surface temperatures increased 0.74 °C between 1906 and 2005. Eleven of the 12 years between 1993 and 2006 had the highest recorded surface temperatures since 1850.<sup>13</sup> The years 2005 and 2010 were the hottest on record. Sea levels have risen about 1.8 mm per year since 1961, and 3.1 mm per year since 1993, due to melting ice from polar ice sheets and glaciers.

The production of global GHGs, chiefly carbon dioxide ( $\text{CO}_2$ ) and methane ( $\text{CH}_4$ ), is largely responsible for the increase in global temperatures. GHGs warm the earth by preventing solar radiation from being reflected into outer space. Increased concentrations of GHGs in the atmosphere are associated with global warming. Anthropogenic GHGs, which have risen steadily since 1750,<sup>c</sup> increased 70% from 1970 to 2004. Numerous human activities, including transportation, manufacturing, urban development, indoor heating, electric power generation, cement manufacture, and agriculture, produce GHGs.

If no actions are taken to stabilize or reduce emissions of anthropogenic GHGs, global temperatures and sea levels may continue to rise. According to various estimates, average global temperatures can be expected to rise between 1.1 and 6.4 °C in the next century, and sea levels will rise between 0.18 and 0.59 m, unless steps are taken to stabilize GHG emissions. Global temperatures and sea levels will continue to rise even if GHG emissions remain at current levels, due to time lags between GHG levels and geological and biological responses, such as removal of  $\text{CO}_2$  from the air by plants.

Much of the debate within the scientific community has involved two aspects of climate change. First, how much of any observed and projected mean global temperature increase is the result of human activities (anthropogenic sources of GHGs)? Second, how certain are the estimates of future global climate change? It is important to acknowledge this debate and recent controversies regarding the data and models being used. In fact, global climate change is similar to other modeling efforts in that accuracy of prediction depends on the quality and representativeness of the data and the algorithms. Errors in assumptions and improper weighting of variables will lead to incorrect predictions. Indeed, climate is a function of many variables and the contribution of each variable is not known with very much precision. Only more data over time will help in defining the role of each variable. Global GHGs, whether from natural or anthropogenic sources, play an important role in the atmosphere's warming, so information about their emissions and atmospheric concentrations is a worthwhile aspect of air pollution science.

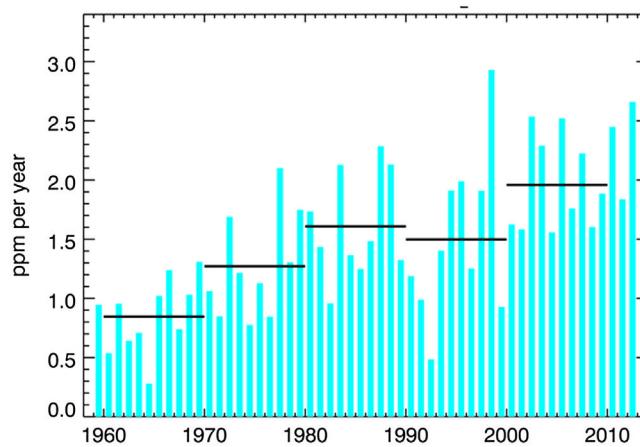
Some pollutants are the same as those released from natural sources, but due to human activities, these are found in higher quantities or different places than would be released by natural systems. For example, forests release formaldehyde, but at much lower concentrations than certain manufacturing facilities or even from furniture and other household items. Other pollutants would not be produced by natural systems, such as many of the toxic organic compounds, like the CFCs discussed in the previous section.

The GHGs fall into both categories, notably  $\text{CO}_2$  and  $\text{CH}_4$ . Indeed,  $\text{CO}_2$  is not only the product of photosynthesis and respiration (natural), but also the product of combustion (natural and anthropogenic). Likewise,  $\text{CH}_4$  is a product of microbial degradation, which is part of the decomposition components of food webs and volcanic emissions (natural) as well as released from livestock and other feeding operations and manufacturing facilities (anthropogenic).

Based on atmospheric measurements, there indeed has been a continuous increase in the concentration of atmospheric  $\text{CO}_2$  in recent centuries. At the beginning of rapid industrialization at the end of the eighteenth century, the mean global  $\text{CO}_2$  concentration is estimated to have been 280 ppmv (parts per million measured as volumes). In 2011, the mean concentration had increased to 392 ppmv. This increase correlates with a mean global temperature of the earth rising to about 0.8 °C over this time period.<sup>14</sup> (see Figure 1.4 in Chapter 1). The trend continues, as shown in Figure 28.22.

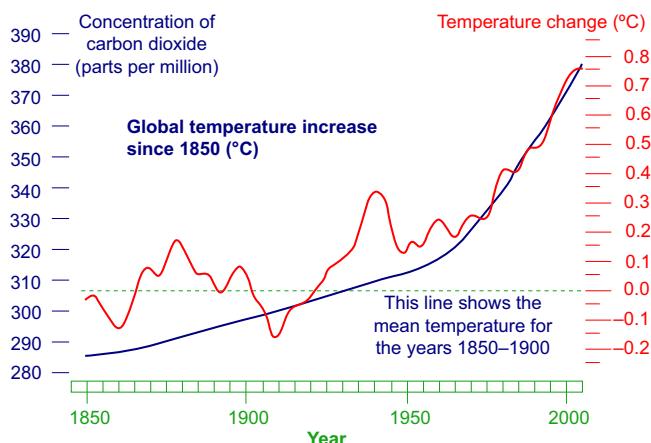
Mean GHG concentrations, particularly  $\text{CO}_2$ , are highly correlated with mean global temperature. Correlation is not necessarily causation, but it does add weight of evidence that GHGs are contributing to climate change (our second question). It is impossible to stop the production of  $\text{CO}_2$  for 10 years and see if it makes a difference. However, the correlation between the temperature rise and the increase in  $\text{CO}_2$  concentration is remarkable (especially over the past 100 years) and is supported by the International Panel on Climate Change 2007 and 2011 reports (see Figure 28.23).

Radiative forcing is an important feature of GHGs, i.e. the influence that this gas has on the balance of incoming



**FIGURE 28.22 Annual mean carbon dioxide growth rates measured at Mauna Loa.** Decadal averages of the growth rate are plotted as horizontal black lines. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 14.

<sup>c</sup>This year is used to distinguish pre-Industrial Revolution for post-Industrial Revolution eras.



**FIGURE 28.23** The correlation of the earth's average temperature and the concentration of carbon dioxide in the atmosphere. (For color version of this figure, the reader is referred to the online version of this book.) *Practical Action. Causes of climate change.* <http://www.climatechoices.org.uk/pages/cchange3.htm>; 2013 [accessed 26.11.13].

and outgoing energy in the earth-atmosphere system and is an index of the importance of the factor as a potential climate change mechanism.<sup>15</sup> Thus, forcing is the effectiveness of a particular gas to promote global warming (or cooling, as is the case with aerosols). The gases of most importance in forcing are listed in Table 28.5. Climate change results from natural internal processes and from external forcings. Both are affected by persistent changes in the composition of the atmosphere brought about by changes in land use, release of contaminants, and other human activities.

Radiative forcing can be expressed as the change in the net vertical irradiance within the atmosphere. Radiative forcing is often calculated after allowing for stratospheric temperatures to readjust to radiative equilibrium, while holding all tropospheric properties fixed at their unperturbed values. Commonly, radiative forcing is considered to be the extent to which injecting a unit of a GHG into the atmosphere changes global average temperature, but other factors can affect forcing, as shown in Figures 28.24 and 28.25. Note that these radiant gases include halocarbons, with the CFCs, which

**TABLE 28.5** Relative Forcing of Increased Global Temperature

Gas	Percentage of Relative Radiative Forcing
Carbon dioxide, CO <sub>2</sub>	64
Methane, CH <sub>4</sub>	19
Halocarbons (predominantly chlorofluorocarbons, CFCs)	11
Nitrous oxide, N <sub>2</sub> O	6

are notorious for their role in another atmospheric problem, i.e. destruction of the stratospheric ozone layer.

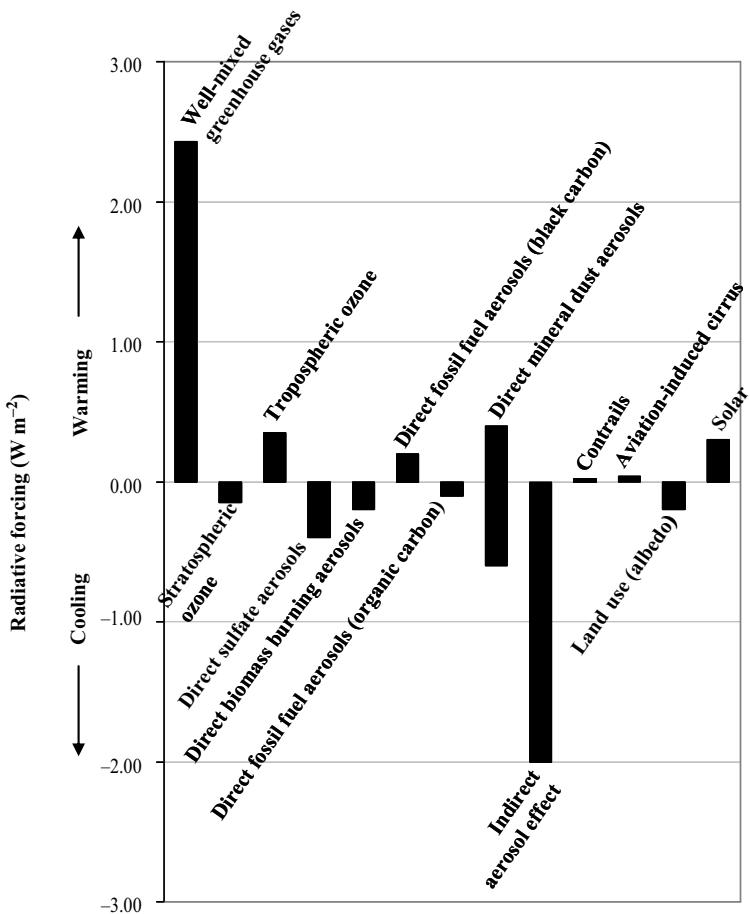
There is much uncertainty about the effects of the presence of these radiant gases (see Table 28.6), but the overall effect of the composite of gases is well understood. The effectiveness of CO<sub>2</sub> as a global warming gas has been known for over 100 years. However, the first useful measurements of atmospheric CO<sub>2</sub> were not taken until 1957. The data from Mauna Loa show that even in the 1950s the CO<sub>2</sub> concentration had increased from the baseline 280 to 315 ppm; and this has continued to climb over the last 50 years at a nearly constant rate of about 1.6 ppm per year. The most serious problem with CO<sub>2</sub> is that the effects on global temperature due to its greenhouse effect are delayed. Even in the completely impossible scenario of not emitting any new CO<sub>2</sub> into the atmosphere, CO<sub>2</sub> concentrations will continue to increase from our present 370 ppm to possibly higher than 600 ppm. The effect of this is discussed below.

Overall, total radiative forcings for CO<sub>2</sub>, O<sub>3</sub>, CH<sub>4</sub>, and N<sub>2</sub>O are 1.66, 0.30, 0.48, and 0.16 W m<sup>-2</sup>, respectively. The relative global warming potential for CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O are 1, 25, and 298 respectively, and the concentrations of CO<sub>2</sub>, O<sub>3</sub>, CH<sub>4</sub>, and N<sub>2</sub>O in the atmosphere are 392, 0.034, 1.77, and 0.32 ppmv, respectively. The mean CH<sub>4</sub> concentration has more than doubled from 0.72 ppmv in the year 1750, to its present value, but appears to have stabilized over the past decade.

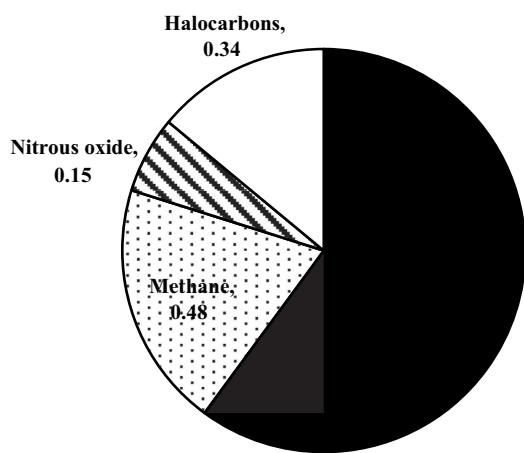
In addition to GHG concentrations, other factors must be considered in climate change, including solar radiation changes, volcanic activity, and the earth's orbital characteristics.<sup>16</sup> However, numerous scientists consider the increase in GHG concentrations to be the largest factor.<sup>17</sup>

## 28.12 INDOOR AIR QUALITY

Indoor air may be contaminated by such sources as fuel-fired cooking or space heating ranges, ovens, or stoves that discharge their gaseous and aerosol combustion products to the room; by solvents evaporated from coatings, paints, adhesives, cleaners, or other products; by formaldehyde, radon, and other products emanating from building materials; and by other pollutant sources indoors.<sup>18</sup> If some of these sources exist inside a building, the pollution level of the indoor air might be higher than that of the outside air. However, if none of these sources are inside the building, the pollution level inside would be expected to be lower than the ambient concentration outside because of the ability of the surfaces inside the building—walls, floors, ceilings, furniture, and fixtures—to adsorb or react with gaseous pollutants and to attract and retain particulate



**FIGURE 28.24** The global mean radiative forcing (watts per square meter) of the climate system for the year 2000, relative to the year 1750. The International Panel on Climate Change (IPCC) has applied a “level of scientific understanding” (LOSU) index to each forcing (see Table 28.6). This represents the Panel’s subjective judgment about the reliability of the forcing estimate, involving factors such as the assumptions necessary to evaluate the forcing, the degree of knowledge of the physical/chemical mechanisms determining the forcing, and the uncertainties surrounding the quantitative estimate of the forcing. *IPCC. Climate change 2001: the scientific basis, Chapter 6 – Radiative forcing of climate change; 2001.*



**FIGURE 28.25** Relative contribution of well-mixed greenhouse gases to the  $+2.43 \text{ W m}^{-2}$  radiative forcing shown in Figure 8.6. *Intergovernmental Panel on Climate Change. Climate change 2001: the scientific basis. Chapter 6 – Radiative forcing of climate change; 2001.*

pollutants, thereby partially removing them from the air breathed by occupants of the building. This adsorption and retention would occur even if doors and windows were open, but the difference between outdoor and indoor concentrations would be even greater if they were closed, in which case air could enter the building only by infiltration through cracks and walls.

For example, VOCs, such as the carbonyls (aldehydes and ketones), are frequently found in residences. Various sources of carbonyls are often present inside homes, but little is known about their indoor source strengths, that is, the amount generated indoors *versus* outdoors. A recent study<sup>19</sup> using a database established in the relationships of indoor, outdoor, and personal air (RIOPA) estimated indoor source strengths of 10 carbonyls and outdoor contributions to measured indoor concentrations of these carbonyls. A mass balance

TABLE 28.6 Level of Scientific Understanding (LOSU) of Radiative Forcings

Forcing Phenomenon	LOSU
Well-mixed greenhouse gases	High
Stratospheric O <sub>3</sub>	Medium
Tropospheric O <sub>3</sub>	Medium
Direct sulfate aerosols	Low
Direct biomass burning aerosols	Very low
Direct fossil fuel aerosols (black carbon)	Very low
Direct fossil fuel aerosols (organic carbon)	Very low
Direct mineral dust aerosols	Very low
Indirect aerosol effect	Very low
Contrails	Very low
Aviation-induced cirrus	Very low
Land use (albedo)	Very low
Solar	Very low

Source: Intergovernmental Panel on Climate Change. Climate change 2001: the scientific basis, Chapter 6 – Radiative forcing of climate change; 2001.

model was applied to analyze paired indoor and outdoor carbonyl concentrations simultaneously measured in 234 RIOPA homes. Table 28.7 shows indoor and outdoor concentrations of carbonyls. Scatter plots of paired

indoor and outdoor carbonyl concentrations are shown in Figure 28.26.

Table 28.8 indicates that the study found variations in the estimated decay rate (rate of chemical breakdown) constants across the RIOPA homes. Across-home estimates of indoor source strengths are presented in Figure 28.26.

Myriad factors influence indoor air pollutant concentrations, but air volume and indoor source strength have been shown to be the most influential parameters in determining indoor concentrations for compounds with strong indoor sources, whereas the outdoor concentration had the most significant impact for compounds mainly generated from outdoor sources. Interestingly the air exchange rates and the decay rate constant were the least sensitive parameters in the model used to determine the indoor concentrations for the RIOPA homes.

In addition to indoor combustion sources, chemicals are brought indoors. The indoor environment can be quite different than the environmental conditions for which partitioning coefficients and persistence estimates are based. For example, indoor environments can have much higher levels of exposure since many relatively reactive compounds become persistent indoors, given the lower rates of photodegradation and biodegradation, as well as the presence of many sorbing substrates (e.g. carpet twill) into which chemicals can be sequestered. In addition, the manner and the frequency of product use can greatly increase exposure levels. The indoor residential environment is where people spend a

TABLE 28.7 Residential Indoor and Outdoor Carbonyl Concentrations ( $\mu\text{g m}^{-3}$ ) Measured in 234 Homes

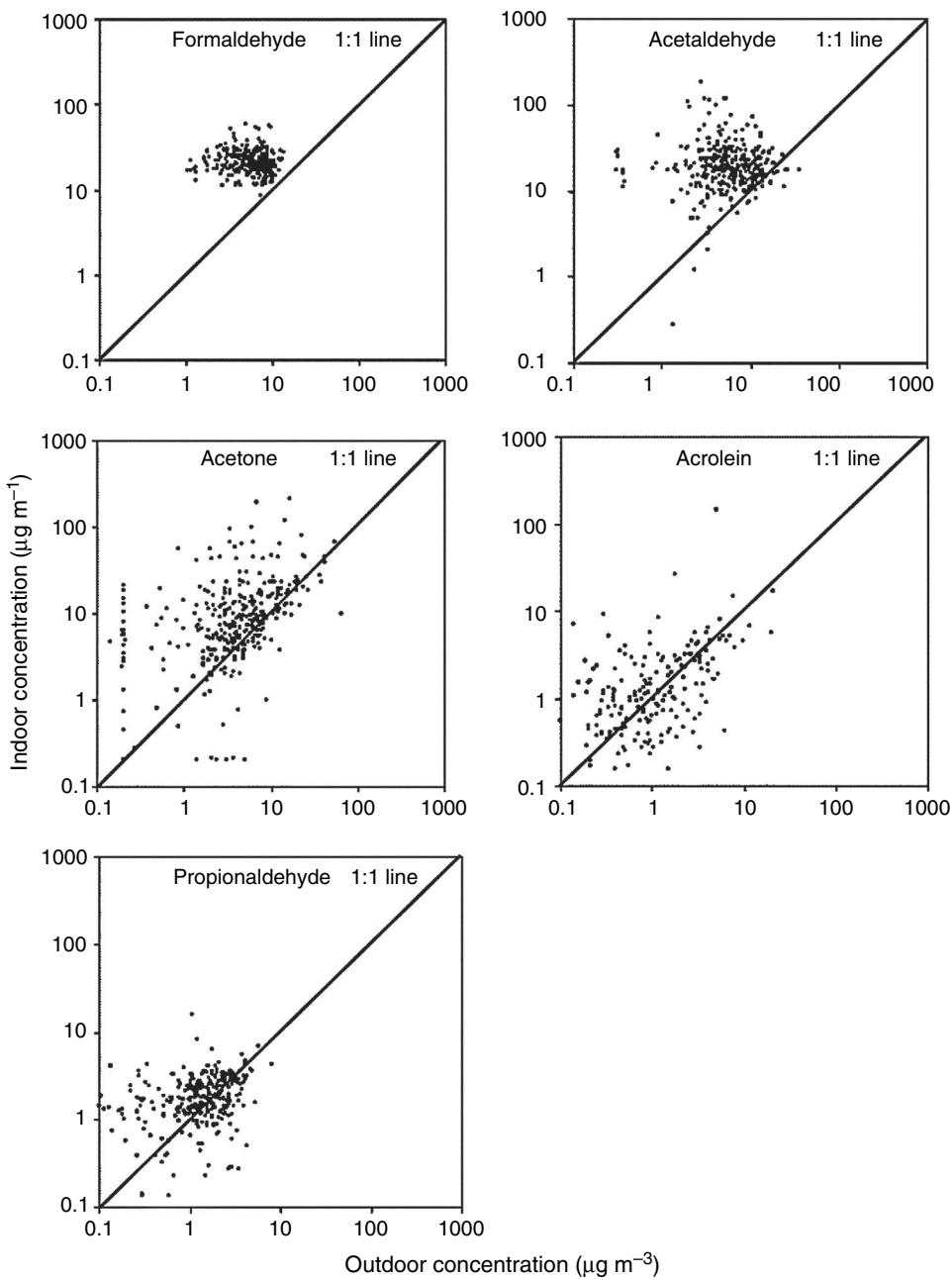
Compounds	Indoor Samples (N = 353)				Outdoor Samples (N = 353)				P-value*
	5 Percentile	Median	95 Percentile	% above MDL	5 Percentile	Median	95 Percentile	% above MDL	
Formaldehyde	12.5	20.1	32.5	100	2.21	6.42	9.95	100	<0.001
Acetaldehyde	7.53	18.6	50.2	100	1.47	5.44	14.9	98	<0.001
Acetone	0.98	8.08	45.8	97	MDL	4.19	19.5	91	<0.001
Acrolein	MDL	0.59	5.54	71	MDL	0.46	4.58	68	<0.125
Propionaldehyde	0.23	1.74	3.65	97	0.05	1.37	3.68	95	<0.001
Crotonaldehyde	MDL	0.44	2.51	72	MDL	0.26	2.03	63	<0.002
Benzaldehyde	0.98	2.92	5.25	98	MDL	1.88	4.21	94	<0.001
Glyoxal	1.12	2.53	4.37	100	0.44	1.81	3.48	99	<0.001
Methylglyoxal	1.13	2.75	4.77	99	0.26	2.05	3.99	96	<0.001
Hexaldehyde	1.63	3.81	9.94	100	0.23	2.01	4.69	99	<0.001

\* P values based on Wilcoxon signed-ranked test for residential indoor and outdoor carbonyl concentration differences in medians.

P < 0.05 indicates the difference is significant at  $\alpha = 0.05$ .

MDL, measurement detection limit.

Source: Liu W, Zhang J, Zhang L, Turpin BJ, Weisel CP, Morandi MT, et al. Estimating contributions of indoor and outdoor sources to indoor carbonyl concentrations in three urban areas of the United States. *Atmos Environ* 2006;40(12):2202–14.



**FIGURE 28.26** Scatter plots of carbonyl concentrations measured in residential indoor and outdoor air of homes (indoor concentration vs outdoor concentration,  $N = 353$ ). Liu W, Zhang J, Zhang L, Turpin BJ, Weisel CP, Morandi MT, et al. Estimating contributions of indoor and outdoor sources to indoor carbonyl concentrations in three urban areas of the United States. *Atmos Environ* 2006;40(12):2202–14.

large majority of time, is where susceptible individuals, especially the very young and elderly and those who are sick or disabled, tend to spend even more of their time,<sup>20a,20b</sup> and is where most consumer products tend to be stored and used. It is recognized that depending on their purpose, exposure to chemicals in consumer products can result through either direct or indirect routes of contact.<sup>21a–21c</sup> Historical examples

demonstrating both the exposure and health risk potential of chemicals in consumer products that have led to their subsequent mitigation include lead in paint and chlorpyrifos in household pesticides.

Many materials used and dusts generated in buildings and other enclosed spaces are allergenic to their occupants. Occupants who do not smoke are exposed to tobacco and its associated gaseous and particulate

TABLE 28.8 Estimated Carbonyl Decay Rate Constants Using Data Collected from 234 Homes

Compounds ( $k, 1 \text{ h}^{-1}$ )	N	5th Percentile	25th Percentile	Median	75th Percentile	95th Percentile	Ratio 95%/5%
Acetaldehyde	19	0.023	0.057	0.23	0.66	1.4	61.3
Acetone	75	0.011	0.078	0.34	0.97	4.0	360
Acrolein	153	0	0.072	0.54	3.2	14	NA
Propionaldehyde	121	0.011	0.085	0.39	1.4	2.0	183
Crotonaldehyde	152	0	0.098	0.62	3.9	12	NA
Benzaldehyde	79	0.019	0.082	0.24	0.61	1.5	78.9
Glyoxal	71	0.032	0.053	0.15	0.48	8.1	253
Methylglyoxal	76	0.020	0.062	0.17	0.45	1.2	60
Hexaldehyde	29	0.032	0.073	0.32	1.2	3.6	113

Source: Liu W, Zhang J, Zhang L, Turpin BJ, Weisel CP, Morandi MT, et al. Estimating contributions of indoor and outdoor sources to indoor carbonyl concentrations in three urban areas of the United States. *Atmos Environ* 2006;40(12):2202–14.

emissions from those who do. This occurs to a much greater extent indoors than in the outdoor air. Many ordinances have been established to limit or prohibit smoking in public and work places.

Indoor air quality continues to be of interest to both the scientific community and homeowners. In fact, indoor environmental quality is one of the keystone areas for green architecture and engineering, as well as sustainable buildings and construction.

that is more generally understandable. It also is a systems tool that can combine data and information from different sources to provide multi-pollutant summaries. Such indices must provide benchmarks, such as how a particular region's atmospheric concentrations of a specific air pollutant or suite of pollutants compares to the rest of the country or the rest of the world. This is often presented as percentiles, e.g. an urban area's mean concentration of  $O_3$  is at the 90th percentile, which means that this region is worse than 90% of the rest of the nation for ground-level  $O_3$ .

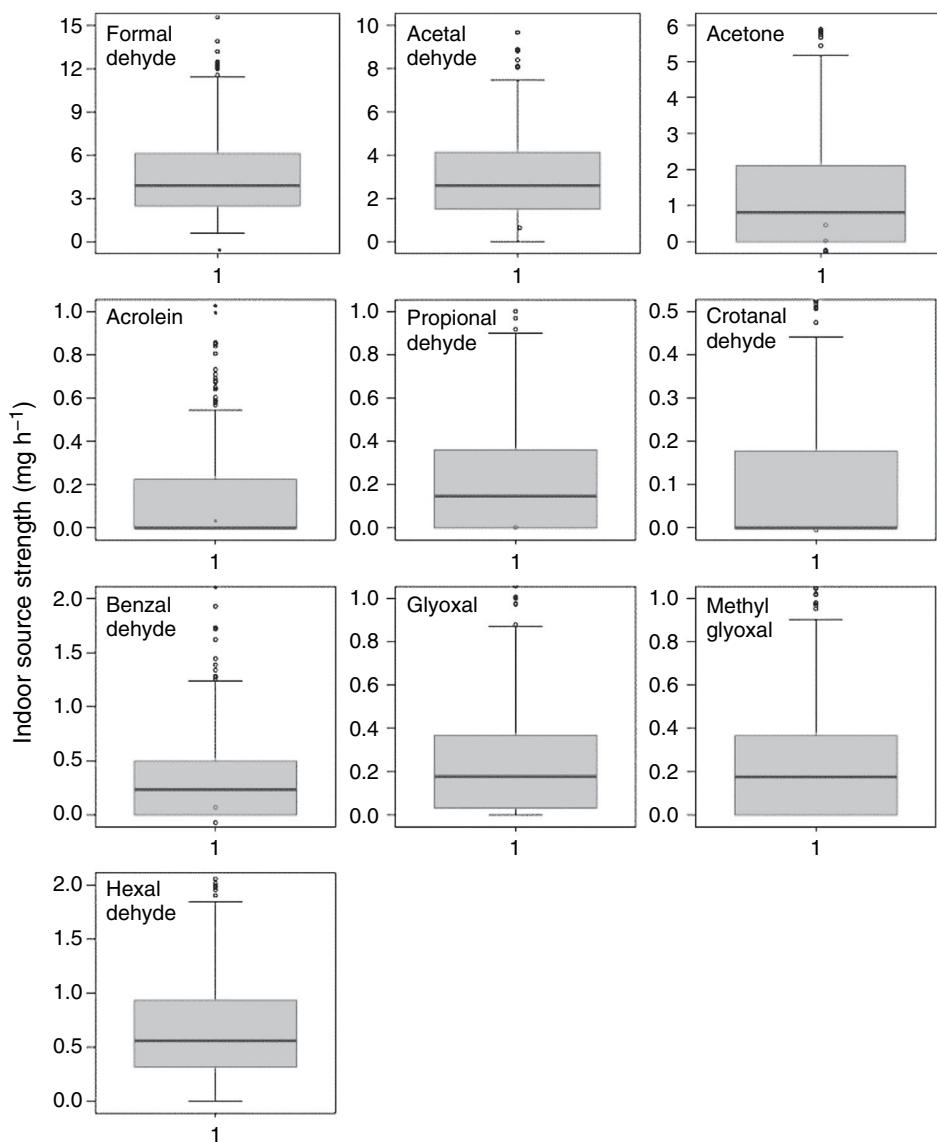
Air quality indices must also allow comparisons to level at which adverse responses could occur. The index comparison must address each pollutant's characteristic response times: short term (i.e. seconds or minutes), intermediate term (i.e. hours or days), and long term (i.e. months or years) (see Table 28.9). Thus, indices usually have fine or other indication where no adverse responses are expected or where a particular segment of the population is vulnerable (e.g. red may mean that this level is bad for everyone, but orange may mean it is particularly bad for children with asthma). Such information is derived from data

## 28.13 AIR QUALITY INDICES

After air quality is measured and interpreted, it must be shared widely with scientists, engineers, physicians, and the general public. This means that it must be summarized in a way that is understandable to a large audience. One of the ways this is done for air quality in different geographic areas is to reduce the data using an index, such as the air quality index (AQI). An index is a very useful device for digesting complex and complicated information in a manner

TABLE 28.9 Examples of Characteristic Response Times for Different Receptor Categories

Receptor Category	Characteristic Response Times		
	Short-term (seconds–minutes)	Intermediate-term (hours–days)	Long-term (months–years)
Human	Odor, visibility, nasopharyngeal, and eye irritation	Acute respiratory disease	Chronic respiratory disease and lung cancer
Animal, vegetation	Field crop loss and ornamental plant damage	Field crop loss and ornamental plant damage	Fluorosis of livestock, decreased fruit, and forest yield
Material	Acid droplet pitting and nylon hose destruction	Rubber cracking, silver tarnishing, and paint blackening	Corrosion, soiling, and materials deterioration



**FIGURE 28.27 Estimated indoor carbonyl source strengths in the RIOPA homes.** The box plots summarize the median, lower quartile, upper quartile, lower range, and upper range of the distribution of indoor source strengths. “ $\circ$ ” represents outliers with more than 1.5 box lengths from the upper or lower edge of the box. Some outliers were not presented in the plots because of the scale limit, S. Liu W, Zhang J, Zhang L, Turpin BJ, Weisel CP, Morandi MT, et al. *Estimating contributions of indoor and outdoor sources to indoor carbonyl concentrations in three urban areas of the United States*. *Atmos Environ* 2006;40(12):2202–14.

such as that presented in Figure 28.27. This figure displays response curves, which remain on the concentration duration axes because they are characteristic of the receptors, not of the actual air quality to which the receptors are exposed. The odor response curve, e.g. to hydrogen sulfide, shows that a single inhalation requiring approximately 1 s can establish the presence of the odor but that, due to odor fatigue, the ability to continue to recognize that odor can be lost in a matter of minutes. Nasopharyngeal and eye irritation, e.g. by ozone, is similarly subject to acclimatization due to tear and mucus production. The three

visibility lines correlate with the concentration of suspended PM in the air. Corrosion of metal, painted surfaces, or nylon hose is shown by a line starting at 1 s and terminating in a matter of minutes, i.e. when the acidity of the droplet is neutralized by the material attacked.

Indices can present data in numerous ways. For example, vegetation damage can be measured biologically or socioeconomically. Using the latter measure, there is a 0% loss when there is no loss of the sale value of the crops or ornamental plants but a 100% loss if the crop is damaged to the extent that it cannot be sold.

These responses are related to dose, i.e. concentration times duration of exposure, as shown by the percent loss curves on the chart. A number of manifestations of material damage, e.g. rubber cracking by ozone, require an exposure duration long enough for the adverse effects to be significant economically. That is, attack for just a few seconds or minutes will not affect the utility of the material for its intended use, but attack for a number of days will.

The biological response line for acute respiratory disease is a dose-response curve, which for a constant concentration becomes a duration-response curve. The shape of such a curve reflects the ability of the human body to cope with short-term, ambient concentration respiratory exposures, and the overwhelming of the body's defenses by continued exposure.

The choice of data to represent response by animals is highly variable and depends on the type of index, e.g. ecological or agricultural. For example, fluorosis of livestock is not induced until there has been a long enough period of deposition of a high enough ambient concentration of fluoride to increase the level of fluoride in the forage. Since the forage is either eaten by livestock or cut for hay at least once during the growing season, the duration of deposition ends after the growing season. The greater the duration of the season, the greater the time for deposition, hence the shape of the line labeled "fluorosis". Long-term vegetation responses—decreased yield of fruit and forest—and long-term material responses—corrosion, soiling, and material deterioration—are shown on the chart as having essentially the same response characteristics as human chronic respiratory disease and lung cancer.

The relationship of these response curves to ambient air quality is shown by lines A, B, and C, which represent the maximum or any other chosen percentile line from a display such as Figure 28.28, which shows actual air quality. Where the air quality is poor (line A), essentially all the adverse effects displayed will occur. Where the air quality is good (line C), most of the intermediate and long-term adverse effects displayed will not occur. Where the air quality is between good and poor, some of the intermediate and long-term adverse effects will occur, but in an attenuated form compared with those of poor air quality.

Indices have been devised for categorizing the air quality measurements of several individual pollutants by one composite number. The index used by the USEPA, for example, is authorized by Section 319 of the Clean Air Act and is called the AQI (Table 28.10). Comparable values for international standards are shown in Table 28.11.

The AQI includes the category "unhealthy for sensitive groups"; breakpoints for the ozone ( $O_3$ ) subindex in terms of 8-h average  $O_3$  concentrations, along a subindex for fine PM ( $PM_{2.5}$ ) as well as subindices for coarse PM ( $PM_{10}$ ), carbon monoxide (CO), and sulfur dioxide ( $SO_2$ ). The AQI is designed to convey information to the public regarding daily air quality and its associated health risks. The scientific understanding of pollutants, especially PM and  $O_3$ , continues to improve. As such, air quality indices will need to incorporate this knowledge, so changes in categories and benchmarks should be expected. These criteria pollutants have no threshold below which health effects are not likely to

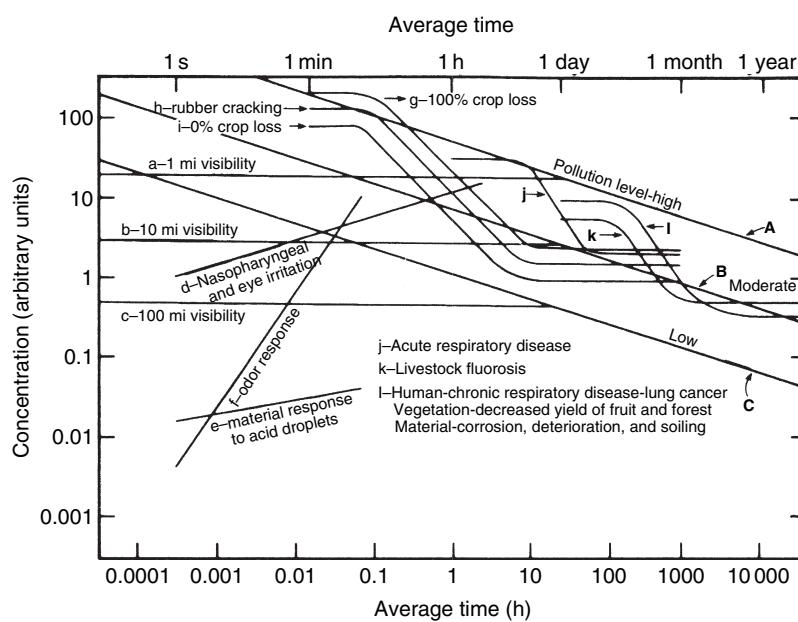


FIGURE 28.28 Adverse response times and relative concentrations of air pollutants.

TABLE 28.10 Air Quality Index (AQI) for Criteria Air Pollutants in the United States

Category	AQI						
	Good	Moderate	Unhealthy for Sensitive Groups*	Unhealthy	Very Unhealthy	Hazardous	
Index value	0–50	51–100	101–150	151–200	201–300	301–400	401–500
<b>Pollutant</b>							
Carbon monoxide (ppm)	0–4.4	4.5–9.4	9.5–12.4	12.5–15.4	15.5–30.4	30.5–40.4	40.5–50.4
Nitrogen dioxide (ppm)	—	—	—	—	0.65–1.24	1.25–1.64	1.65–2.04
Ozone (average concentration for 1 h in ppm)	—	—	0.125–0.164	0.165–0.204	0.205–0.404	0.405–0.504	0.505–0.604
Ozone (average concentration for 8 h in ppm)	0–0.064	0.065–0.084	0.085–0.104	0.105–0.124	0.125–0.374	—	—
PM <sub>2.5</sub> ( $\mu\text{g m}^{-3}$ )	0–15.4	15.5–40.4	40.5–65.4	65.5–150.4	150.5–250.4	250.5–350.4	350.5–500.4
PM <sub>10</sub> ( $\mu\text{g m}^{-3}$ )	0–54	55–154	155–254	255–354	355–424	425–504	505–604
Sulfur dioxide (ppm)	0–0.034	0.035–0.144	0.145–0.224	0.225–0.304	0.305–0.604	0.605–0.804	0.805–1.004

\* Each category corresponds to a different level of health concern. The six levels of health concern and what they mean are

- “Good”: The AQI value for your community is between 0 and 50. Air quality is considered satisfactory, and air pollution poses little or no risk.
- “Moderate”: The AQI for your community is between 51 and 100. Air quality is acceptable; however, for some pollutants there may be a moderate health concern for a very small number of people. For example, people who are unusually sensitive to ozone may experience respiratory symptoms.
- “Unhealthy for Sensitive Groups”: When AQI values are between 101 and 150, members of sensitive groups may experience health effects. This means they are likely to be affected at lower levels than the general public. For example, people with lung disease are at greater risk from exposure to ozone, while people with either lung disease or heart disease are at greater risk from exposure to particle pollution. The general public is not likely to be affected when the AQI is in this range.
- “Unhealthy”: Everyone may begin to experience health effects when AQI values are between 151 and 200. Members of sensitive groups may experience more serious health effects.
- “Very unhealthy”: AQI values between 201 and 300 trigger a health alert, meaning everyone may experience more serious health effects.
- “Hazardous”: AQI values over 300 trigger health warnings of emergency conditions. The entire population is more likely to be affected.

Source: US Environmental Protection Agency.

TABLE 28.11 World Health Organization Guidelines for Criteria Air Pollutants Used for Comparison and Benchmarks of Air Pollution in Air Quality Indices

	PM <sub>10</sub> ( $\mu\text{g m}^{-3}$ )	PM <sub>2.5</sub> ( $\mu\text{g m}^{-3}$ )	Basis for the Selected Level
Interim target-1 (IT-1)	70	35	These levels are associated with about a 15% higher long-term mortality risk relative to the AQG level
Interim target-2 (IT-2)	50	25	In addition to other health benefits, these levels lower the risk of premature mortality by approximately 6% (2–11%) relative to the IT-1 level
Interim target-3 (IT-3)	30	15	In addition to other health benefits, these levels reduce the mortality risk by approximately 6% (2–11%) relative to the IT-2 level
Air Quality Guideline (AQG)	20	10	These are the lowest levels at which total, cardiopulmonary and lung cancer mortality have been shown to increase with more than 95% confidence in response to long-term exposure to PM <sub>2.5</sub>
<b>WHO AQGS AND INTERIM TARGETS FOR PARTICULATE MATTER*: 24-H CONCENTRATIONS<sup>§</sup></b>			
Interim target-1 (IT-1)	150	75	Based on published risk coefficients from multicenter studies and meta-analyses (about 5% increase of short-term mortality over the AQG value)
Interim target-2 (IT-2)	100	50	Based on published risk coefficients from multicenter studies and meta-analyses (about 2.5% increase of short-term mortality over the AQG value)
Interim target-3 (IT-3) <sup>¶</sup>	75	37.5	Based on published risk coefficients from multicenter studies and meta-analyses (about 1.2% increase in short-term mortality over the AQG value)
AQG	50	25	Based on relationship between 24-h and annual PM levels

**TABLE 28.11** World Health Organization Guidelines for Criteria Air Pollutants Used for Comparison and Benchmarks of Air Pollution in Air Quality Indices—cont'd

	Daily Maximum 8-h Mean ( $\mu\text{g m}^{-3}$ )	Basis for the Selected Level	
<b>WHO AQG AND INTERIM TARGET FOR OZONE: 8-H CONCENTRATIONS</b>			
High levels	240	Significant health effects; substantial proportion of vulnerable populations affected	
Interim target-1 (IT-1)	160	Important health effects; does not provide adequate protection of public health. Exposure to this level of ozone is associated with <ul style="list-style-type: none"> <li>• Physiological and inflammatory lung effects in healthy exercising young adults exposed for periods of 6.6 h</li> <li>• Health effects in children (based on various summer camp studies in which children were exposed to ambient ozone levels)</li> <li>• An estimated 3–5% increase in daily mortality<sup>  </sup> (based on findings of daily time-series studies)</li> </ul>	
AQG	100	Provide adequate protection of public health, although some health effects may occur below this level. Exposure to this level of ozone is associated with <ul style="list-style-type: none"> <li>• An estimated 1–2% increase in daily mortality<sup>  </sup> (based on findings of daily time-series studies)</li> <li>• Extrapolation from chamber and field studies based on the likelihood that real-life exposure tends to be repetitive and chamber studies exclude highly sensitive or clinically compromised subjects, or children</li> <li>• Likelihood that ambient ozone is a marker for related oxidants</li> </ul>	
	Annual mean ( $\mu\text{g m}^{-3}$ )		
<b>WHO AQGS FOR NITROGEN DIOXIDE: ANNUAL MEAN</b>			
AQG	40	Recent indoor studies have provided evidence of effects on respiratory symptoms among infants at NO <sub>2</sub> concentrations below 40 $\mu\text{g m}^{-3}$ . These associations cannot be completely explained by coexposure to PM, but it has been suggested that other components in the mixture (such as organic carbon and nitrous acid vapor) might explain part of the observed association	
	1-h mean ( $\mu\text{g m}^{-3}$ )		
<b>WHO AQGS FOR NITROGEN DIOXIDE: 1-H MEAN</b>			
AQG	200	Epidemiological studies have shown that bronchitic symptoms of asthmatic children increase in association with annual NO <sub>2</sub> concentration, and that reduced lung function growth in children is linked to elevated NO <sub>2</sub> concentrations within communities already at current North American and European urban ambient air levels. A number of recently published studies have demonstrated that NO <sub>2</sub> can have a higher spatial variation than other traffic-related air pollutants, for example, particle mass. These studies also found adverse effects on the health of children living in metropolitan areas characterized by higher levels of NO <sub>2</sub> even in cases where the overall city-wide NO <sub>2</sub> level was fairly low. Since the existing WHO AQG short-term NO <sub>2</sub> guideline value of 200 $\text{m}^{-3}$ (1-h) has not been challenged by more recent studies, it is retained	
	24-h Average ( $\mu\text{g m}^{-3}$ )	10-min Average ( $\mu\text{g m}^{-3}$ )	Basis for the Selected Level
<b>WHO AQGS AND INTERIM TARGETS FOR SO<sub>2</sub>: 24-H AND 10-MIN CONCENTRATIONS</b>			
Interim target-1 (IT-1) <sup>#</sup>	125	—	
Interim target-2 (IT-2)	50	—	Intermediate goal based on controlling either motor vehicle emissions, industrial emissions and/or emissions from power production. This would be a reasonable and feasible goal for some developing countries (it could be achieved within a few years), which would lead to significant health improvements that, in turn, would justify further improvements (such as aiming for the AQG value)
AQG	20	500	

\* The use of PM<sub>2.5</sub> guideline value is preferred.

<sup>#</sup>99th percentile (3 days per year).

<sup>\*</sup>For management purposes. Based on annual average guideline values precise number to be determined on basis of local frequency distribution of daily means. The frequency distribution of daily PM<sub>2.5</sub> or PM<sub>10</sub> values usually approximates to a log-normal distribution.

<sup>||</sup>Deaths attributable to ozone. Time-series studies indicate an increase in daily mortality in the range of 0.3–0.5% for every 10  $\mu\text{g m}^{-3}$  increment in 8-h ozone concentrations above an estimated baseline level of 70  $\mu\text{g m}^{-3}$ .

<sup>#</sup>Formerly the WHO Air Quality Guideline (WHO, 2000).

Source: World Health Organization; 2006 Report No. WHO/SDE/PHE/OEH/06.02.

TABLE 28.12 Levels of Health Concern and Cautions in Using the US Air Quality Index

Index Values	Levels of Health Concern	Cautionary Statements*			
		Ozone	Particulate Matter	Carbon Monoxide	Sulfur Dioxide
0–50	Good	None	None	None	None
51–100*	Moderate	Unusually sensitive people should consider reducing prolonged or heavy exertion outdoors	Unusually sensitive people should consider reducing prolonged or heavy exertion	None	People with asthma should consider reducing exertion outdoors
101–150	Unhealthy for sensitive groups	Active children and adults, and people with lung disease, such as asthma, should reduce prolonged or heavy exertion outdoors	People with heart or lung disease, older adults, and children should reduce prolonged or heavy exertion	People with heart disease, such as angina, should reduce heavy exertion and avoid sources of CO, such as heavy traffic	Children, asthmatics, and people with heart or lung disease should reduce exertion outdoors
151–200	Unhealthy	Active children and adults, and people with lung disease, such as asthma, should avoid prolonged or heavy exertion outdoors. Everyone else, especially children, should reduce prolonged or heavy exertion outdoors	People with heart or lung disease, older adults, and children should avoid prolonged or heavy exertion. Everyone else should reduce prolonged or heavy exertion	People with heart disease, such as angina, should reduce moderate exertion and avoid sources of CO, such as heavy traffic	Children, asthmatics, and people with heart or lung disease should avoid outdoor exertion. Everyone else should reduce exertion outdoors
201–300	Very unhealthy	Active children and adults, and people with lung disease, such as asthma, should avoid all outdoor exertion. Everyone else, especially children, should avoid prolonged or heavy exertion outdoors	People with heart or lung disease, older adults, and children should avoid all physical activity outdoors. Everyone else should avoid prolonged or heavy exertion	People with heart disease, such as angina, should avoid exertion and sources of CO, such as heavy traffic	Children, asthmatics, and people with heart or lung disease should remain indoors. Everyone else should avoid exertion outdoors
301–500	Hazardous	Everyone should avoid all physical activity outdoors	People with heart or lung disease, older adults, and children should remain indoors and keep activity levels low. Everyone else should avoid all physical activity outdoors	People with heart disease, such as angina, should avoid exertion and sources of CO, such as heavy traffic. Everyone else should reduce heavy exertion	

\* Nitrogen dioxide can cause respiratory problems in children and adults who have respiratory diseases, such as asthma. The AQI for nitrogen dioxide is not included here because ambient nitrogen dioxide concentrations in the United States have been below the national air quality standard for the past several years. These concentrations are sufficiently low so as to pose little direct threat to human health. Nitrogen dioxide, however, is a concern because it plays a significant role in the formation of tropospheric ozone, particulate matter, haze, and acid rain. As concentrations increase, the proportion of people prone to experience health effects and the seriousness of these effects are expected to increase. Thus, the 1997 standards were intended to include an ample margin of safety (as required by Section 109(b) of the Clean Air Act Amendments). The margin includes special concern about protecting the health of sensitive individuals. However, they were not considered risk free and exposures to ambient concentrations just below the numerical level of the standards may be problematic for the most sensitive individuals. On the other hand, exposures to levels just above the NAAQS are not expected to be associated with health concerns for most healthy individuals. Such is the complicated nature of individual response to air pollutants, and one of the objectives of the revised index is to provide sufficient information to allow sensitive people to avoid unhealthy exposures.

occur. For example, sensitivity varies by pollutant, but research may well add new sensitive groups to those currently target. At present, when the AQI exceeds 100, the sensitive groups of concern to be at greatest risk include

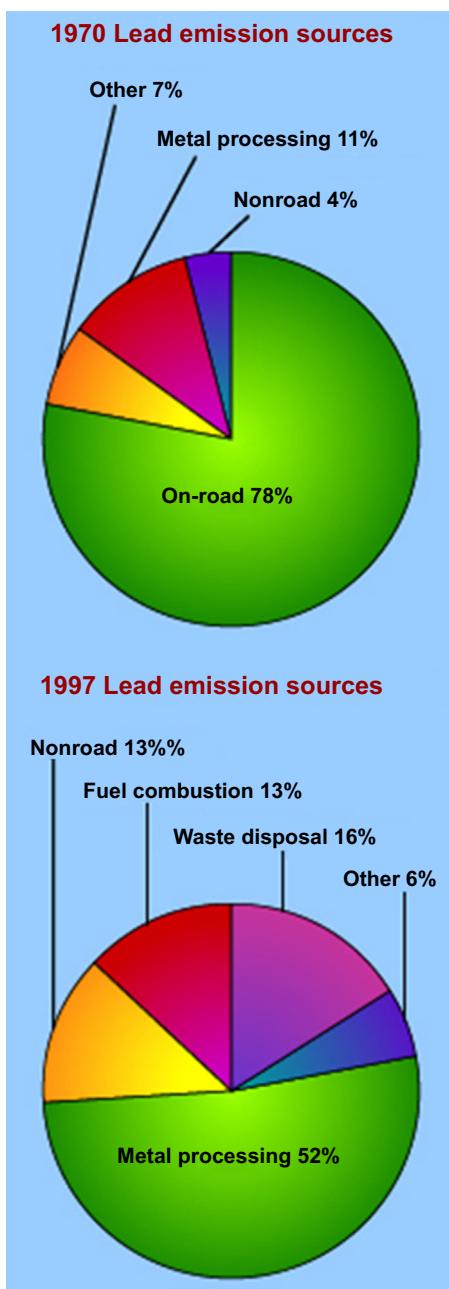
- Ozone: Children and people with asthma.
- PM<sub>2.5</sub>: People with respiratory or heart disease, the elderly and children.
- PM<sub>10</sub>: People with respiratory disease.
- Carbon monoxide: People with heart disease.

- *Sulfur dioxide*: People with asthma.
- *Nitrogen dioxide*: Children and people with respiratory disease.

The thresholds and precautionary statements for the US criteria air pollutants included in the AQI are shown in [Table 28.12](#).

## QUESTIONS

1. Give an example of a pollutant that can be well characterized by a few sites strategically located in a county.
2. What function does the inlet manifold serve in air pollution monitoring equipment?
3. A liquid sorbent sampling system is set up for SO<sub>2</sub>. At installation the sorbent liquid's pH is 7 and decreases an average 0.02 pH min<sup>-1</sup> under normal atmospheric conditions. The sorbent reliability is pH between 6 and 9. Can this system be used to collect daily SO<sub>2</sub> samples?
4. Explain the difference between a standard that is part of the NAAQS and significant harm level under the US Clean Air Act.
5. How does the range of concentrations of air pollutants of concern to the industrial hygienist differ from that of concern to the air pollution specialist? To what extent are air sampling and analytical methods in factories and in the ambient air the same or different?
6. Using the data in [Figure 28.1](#), draw the variation in concentration over the 6-h period as it would appear using sampling and analytical procedures that integrate the concentrations arriving at the receptor over 30 min and 2 h, respectively.
7. What is the drawback of using an instantaneous reading from an air pollution monitoring device compared to integrating over an averaging period? What is the disadvantage of a very long averaging period?
8. Would you expect CO concentrations near a large stadium in south Chicago to resemble the general temporal pattern near a large roadway connecting the Loop (downtown) to a large Chicago area suburb? Why or why not? How about SO<sub>2</sub>? Ozone? Benzene? PAHs?
9. Give two reasons for the seasonal variations in CO in Al Jahra City, Kuwait.
10. Explain the seasonal variability in the eastern United States for ground-level ozone. Show at least one chemical reaction that has nearly the same available reactants but that does not lead to the product, i.e. O<sub>3</sub>.
11. Describe an air quality measurement system used to assess the levels and types of aeroallergens.
12. Prepare a table describing air quality levels in your community or, if too small, in the nearest community to you that has such data available.
13. Discuss the extent and usefulness of dissemination by the media of the AQI values in the communities in which you have lived.
14. What do these findings tell you about the source strength of carbonyls shown in [Tables 28.7 and 28.8](#) and [Figures 28.26 and 28.27](#)? How and why do you think these source strengths differ for various carbonyls? What actions and controls would you recommend to reduce exposures to each of these carbonyls?
15. Using the strict definition of primary and secondary pollutants, which is ground-level ozone? Which is most CO in the atmosphere? Which is sulfuric acid?
16. Give an example of PM as a primary pollutant. Give an example of PM as a secondary pollutant.
17. What is the purpose of an upwind or background air pollutant monitoring site?
18. The trend in ambient tropospheric ozone concentrations in the United States has shown a steady drop in recent years, but not nearly as steep as that for several other pollutants. Explain the difficulties in addressing this pollutant.
19. Why is there a need for meteorological adjustments for air pollutant readings, especially for tropospheric ozone?
20. Propose factors contributing to the global CO "hot spot" in central Africa.
21. What are the two main reasons to decrease NO<sub>x</sub> concentrations in the ambient air?
22. In looking at ambient Pb concentration trends in recent decades, why is the annual mean not necessarily a good indication of success or failure? Which statistic(s) are preferable? Why?
23. What is the difference between an emission factor and an emission limit or emission standard?
24. Reflect on the possible reasons for the differences in source contributions to lead (Pb) emissions shown in [Figures 28.19, 28.20, and 28.21](#) since the 1990s. Review the literature for US and European sources of lead during this time, e.g. the USEPA's Air Pollution Control Orientation Course. Why did the relative contribution of mobile sources fall sharply over the past three decades?



25. Consider the various beneficial and adverse outcomes of a pollutant at the global scale. For example, CO<sub>2</sub> is an essential part of photosynthesis and has very low human toxicity; however, above background levels it contributes slightly to acid rain, is a major global GHG; but has no direct effect on stratospheric ozone. Write a similar profile for methane, NO<sub>x</sub>, nitrous oxide, sulfur dioxide, sulfate aerosols, CFCs, and ozone.

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# Air Pollutant Emissions

## 29.1 INTRODUCTION

Chapter 24 discussed the various types of air pollution sources, both natural and anthropogenic, as well as the means of measuring pollutants after they have been emitted. This chapter's focus is on ways to remove, treat and, hopefully, eliminate pollutants before they are emitted. The technologies for controlling vary by type of pollutant and the processes that have led to producing the pollutant. The first major distinction is the physical phase, i.e. the amount of pollutant that is in the vapor-phase and the amount in the aerosol-phase.

For most natural sources, the means of control are limited, since the releases occur often over large areas and times of release are difficult to predict. These controls are often aimed at personal exposures. For example, first responders must wear respirators and other control technologies when they are near wildfires; whereas, residents are evacuated to limit exposure to the pollutants (if they have not already been evacuated for safety reasons). The same is true for exposure to naturally occurring asbestos, i.e. the best means of protection against inhalation is to keep people away from known areas. Certainly, some controls are put in place for natural sources of air pollution, such as dust control (e.g. periodic wetting) and paving where vehicles may need to access areas.

Most of this chapter addresses anthropogenic sources. These range in scale from personal to economic sectors.

### 29.1.1 Emissions from Industrial Sources

A great deal of industrial pollution comes from manufacturing products from raw materials—(1) iron and steel from ore, (2) lumber from trees, (3) gasoline and other fuels from crude oil, and (4) stone from quarries. Each of these manufacturing processes produces a product, along with several waste products, which include air pollutants. Often, part or all of the

polluting material can be recovered and converted into a usable product. Indeed, matter and energy that exit the facility via stacks, vents, pipes, and by other means represents a major financial loss. Thus, industry is increasingly embracing green and sustainable processes, not just for environmental reasons, but for economic ones as well (see Chapter 30).

Industrial pollution is also emitted by industries that convert products to other products—(1) automobile bodies from steel, (2) furniture from lumber, (3) paint from solids and solvents, and (4) asphaltic paving from rock and oil.

Industrial sources are stationary, and each facility emits relatively consistent qualities and quantities of pollutants. A paper mill, for example, will be in the same place tomorrow that it is today, emitting the same quantity of the same kinds of pollutants unless a major process change is made. Control of industrial sources can usually be accomplished by applying known technology. The most effective regulatory control is that which is applied uniformly within all segments of industries in a given region, e.g. “Emission from all asphalt plant dryers in this region shall not exceed 230 mg of particulate matter per standard dry cubic meter of air”.

### 29.1.2 Emissions from Utilities

The electric power generating utilities (see Figure 29.1) are an integral part of modern life in developed and increasingly in developing nations.

Utilities are in the business of converting energy from one form to another and transporting that energy. If a large steam generating plant, producing 2000 MW, burns a million kilograms per hour of 4% ash coal, it must somehow dispose of 40,000 kg of ash per hour. Some will be removed from the furnaces by the ash-handling systems, but some will go up the stack with the flue gases. If 50% of the ash enters the stack and the fly ash collection system is 99% efficient, 200 kg of ash per hour will be emitted to the atmosphere. For a



**FIGURE 29.1 Coal-fired electric generating station.** (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Huntley R. Emission inventories – the basics. [http://www.epa.gov/ttn/chief/eidocs/basicempreparationtraining\\_april2003.pdf](http://www.epa.gov/ttn/chief/eidocs/basicempreparationtraining_april2003.pdf); 2003 [accessed 27.11.13].

typical generating plant, the gaseous emissions would include 341,000 kg of oxides of sulfur per day and 185,000 kg of oxides of nitrogen per day. If this is judged as excessive pollution, the management decision can be to (1) purchase lower-ash or lower-sulfur coal, (2) change the furnace so that more ash goes to the ash pit and less goes up the stack, or (3) install more efficient air pollution control equipment. In any case, the cost of operation will be increased and this increase will be passed on to the consumer.

Another type of utility that is a serious air pollution source is the one that handles the wastes of modern society. The principal concern with solid waste and sewage is land, surface water, and ground water pollution, but an overloaded, poorly designed, or poorly operated sewage treatment plant can cause an air pollution problem which will arouse citizens to demand immediate action. In many countries around the world, open dumps still exist. These may catch fire and release harmful plumes of smoke and fumes. Even in more economically developed nations, landfills remain sources of dust and smoke, as are fires in abandoned mine shafts and in industrial waste disposal and reclamation sites. These are certainly sources of public complaint, even though it may be explained to the same public that it is the “cheapest” way to dispose of their solid waste. The public has shown its

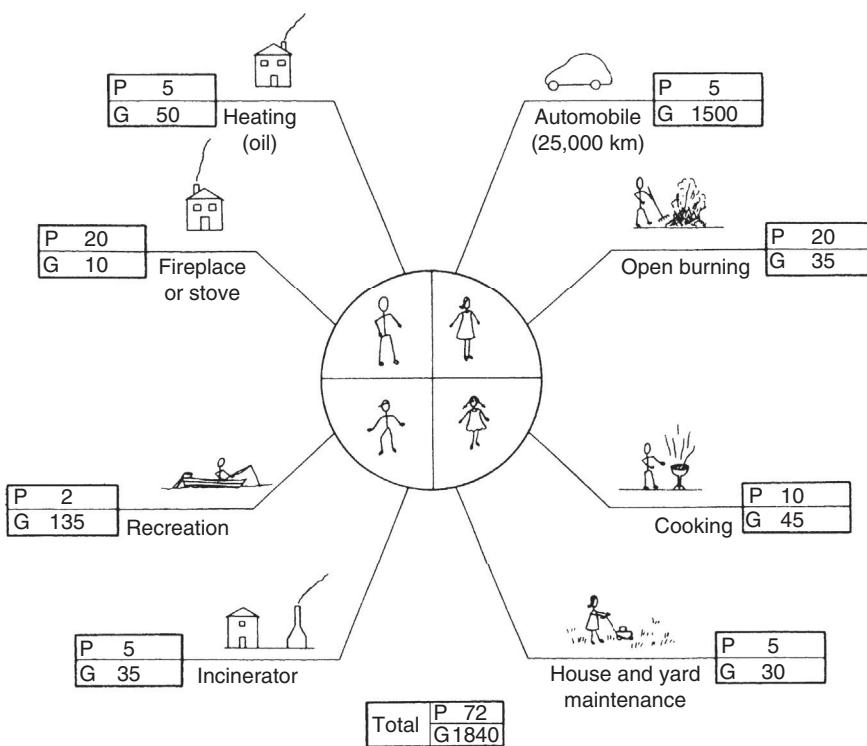
willingness to ban burning dumps and pay the additional cost of adequate waste disposal facilities to have a pollution-free environment.

### 29.1.3 Emissions from Residential and Personal Sources

Even in Western society, which has moved toward centralized industries and utilities, there remain many personal sources of air pollution, including: (1) automobiles, (2) home furnaces, (3) home fireplaces and stoves, (4) backyard barbecue grills, and (5) open burning of refuse and leaves. **Figure 29.2** illustrates the personal emissions of a typical US family. The collective contribution of individual actions, such as backyard burning can be substantial. For example, significantly higher levels of dioxins are produced by burning trash in burn barrels than in municipal incinerators. Household burn vessels receive limited oxygen, so the combustion occurs at relatively low temperatures. This produces products of incomplete combustion (PIC), including halogenated dioxins and furans, in addition to smoke and other pollutants. Conversely, large incinerators in many countries are required by regulations to have pollution control systems that reduce dioxin emissions primarily by preventing their formation, e.g. specification of incineration time, temperature, and mixing. Backyard burning is also particularly dangerous because it releases pollutants at ground level where they are more readily inhaled or incorporated into the food chain.<sup>1</sup>

The energy release and air pollution emissions from personal sources in the United States are greater than those from industry and utilities combined. In any major city in the United States, the mass of pollutants emitted by the vast numbers of private automobiles exceeds that from any other source.

Control of these personal sources of pollution takes the form of (1) regulation (fireplaces and stoves may be used only when atmospheric mixing is favorable), (2) change of lifestyle (sell the automobile and ride public transportation), (3) change from a more polluting to a less polluting source (convert the furnace to natural gas), or (4) change the form of pollution (instead of burning leaves, haul them to the city landfill for composting). Whatever method is used for control of pollution from personal sources, it is usually difficult and unpopular to enforce. It is difficult to get citizens to believe that their new, highly advertised, shiny, unpaid-for automobiles are as serious a pollution problem as the smoking factory stack on the horizon. It is also a very ineffective argument to point out that the workers at that factory put more pollution into the air each day by driving their automobiles to and from work, or by mowing their



**FIGURE 29.2** Estimated emissions from a U.S. family of four. P = particulate matter in kg per year; G = gas-phase pollutants in kg per year.

lawns on Saturday, than does the factory with its visible plume of smoke.

## 29.2 COMBUSTION EMISSIONS

The emissions mentioned in the previous section in large part result from thermal processes. Combustion is the most widely used class of chemical reactions to provide energy and to manufacture products. Combustion occurs as the rapid union of a substance with oxygen accompanied by the evolution of light and heat.<sup>2</sup>

The economies of highly industrialized nations are heavily dependent on combustion. Much of the transportation by automobile, rail, and airlines is based on internal combustion engines that burn gasoline or diesel fuels. Small internal combustion engines are deceptively important sources of air pollutants. In fact, with the advent of low emitting vehicles (LEVs), lawn mower usage for 1 h emits about as much as driving a car 100 miles (650 miles for a vehicle made before 1990). A push mower emits as much hourly pollution as 11 cars and a riding mower emits as much as 34 cars. Since small engine use exceeds three billion hours per year in the United States, the US EPA proposed a rule in 2007 to reduce small engine exhaust of hydrocarbons by 35% and oxides of nitrogen emissions by 60%. In addition, fuel evaporative emissions of hydrocarbons

are expected to fall by 45% if the rule is implemented. To meet exhaust emission standards, manufacturers are expected to use catalytic converters for the first time in numerous small watercraft, lawn, and garden equipment. The rule also lays out fuel evaporative standards, national standards for vessels powered by stern-drive or inboard engines, and CO standards for gasoline-powered engines used in recreational watercraft.<sup>3</sup> Combustion is the relatively simple phenomenon of oxidizing a substance in the presence of heat. Chemically, efficient combustion is:

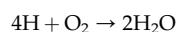
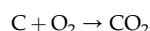


The coefficients and subscript depend on the specific fuel composition. Most thermal processes, however, do not reach complete combustion. More complex combustion reactions are shown in Table 29.1. They are usually oxygen limited, leading to the generation of a wide variety of compounds, many that are toxic. Other reactions besides combustion also produce air pollutants. Decomposition of a substance in the absence of oxygen is known as pyrolysis. In fact, a single fire can have pockets of both combustion and pyrolytic processes. This lack of homogeneity results in temperatures varying in both space and time. Plastic fires, for example, can release over 450 different organic compounds.<sup>3</sup> The relative amount of combustion and pyrolysis in a

TABLE 29.1 Balanced Combustion Reactions for Selected Organic Compounds

Chlorobenzene	$C_6H_5Cl + 7O_2 \rightarrow 6CO_2 + HCl + 2H_2O$
Tetrachloroethene (TCE)	$C_2Cl_4 + O_2 + 2H_2O \rightarrow 2CO_2 + HCl$
Hexachloroethane (HCE)	$C_2Cl_6 + \frac{1}{2}O_2 + 3H_2O \rightarrow 2CO_2 + 6HCl$
Post-chlorinated polyvinyl chloride (CPVC)	$C_4H_5Cl_3 + 4\frac{1}{2}O_2 \rightarrow 4CO_2 + 3HCl + H_2O$
Natural gas fuel (methane)	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
PTEE Teflon	$C_2F_4 + O_2 + 2H_2O \rightarrow 2CO_2 + 4HF$
Butyl rubber	$C_9H_{16} + 13O_2 \rightarrow 9CO_2 + 8H_2O$
Polyethylene	$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

Wood is considered to have the composition of  $C_{6.9}H_{10.6}O_{3.5}$ . Therefore, the combustion reactions are simple carbon and hydrogen combustion



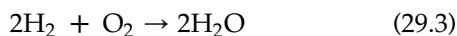
Source: U.S. Environmental Protection Agency.

fire affects the actual amounts and types of compounds released.

Temperature is also important, but there is no direct relationship between temperature and pollutants released. For example, Figure 29.3 shows that in a plastics fire (i.e. low-density polyethylene pyrolysis) compounds are generated at lower temperatures, but for others the optimal range is at higher temperatures. The aliphatic compounds in this fire (i.e. 1-dodecene, 9-nonadecane, and 1-hexacosene) are generated in higher concentrations at lower temperatures (about 800 °C), and the aromatics need higher temperatures (see Figures 29.3 and 29.4).

Combustion is used primarily for heat by changing the potential chemical energy of the fuel to thermal energy. This occurs in a fossil fuel-fired power plant, a home furnace, or an automobile engine. Combustion is also used as a means of destruction for our unwanted materials. This decreases the volume of a solid waste by burning the combustibles in an incinerator. We subject combustible gases, with undesirable properties such as odors, to a high temperature in an afterburner system to convert them to less objectionable gases.

The efficient reaction can be seen as two simple reactions that produce carbon dioxide and water:



The problems with the combustion reaction occur because the process also produces many other products. These can be gases, e.g. carbon monoxide (CO),  $CO_2$ , oxides of sulfur ( $SO_x$ ), oxides of nitrogen ( $NO_x$ ), smoke, fly ash, metals, metal oxides, metal salts, aldehydes, ketones, acids, polycyclic aromatic hydrocarbons (PAHs), halogenated organic compounds that include

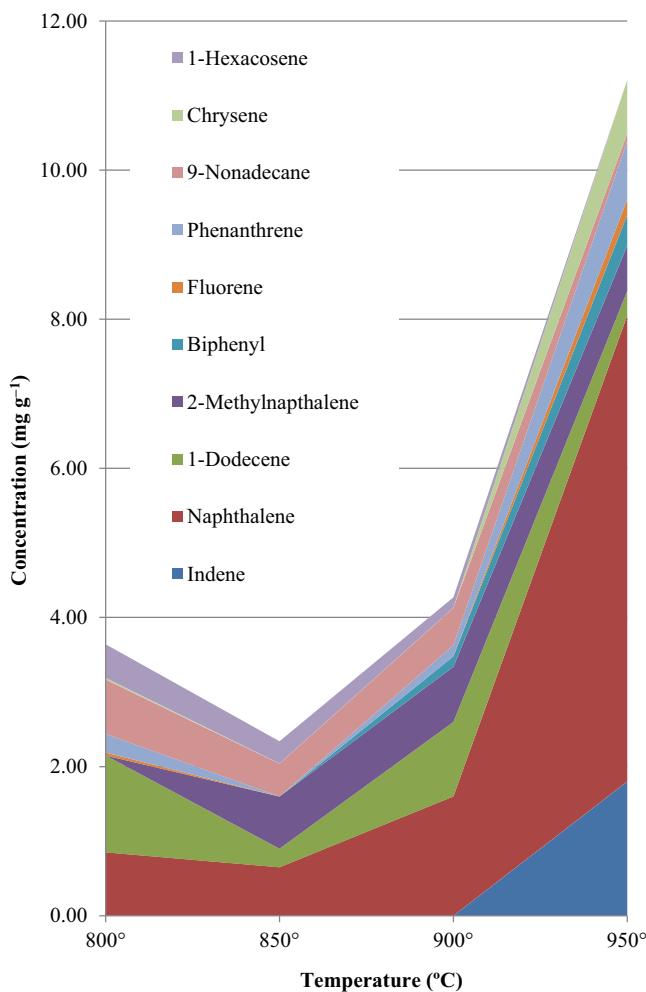
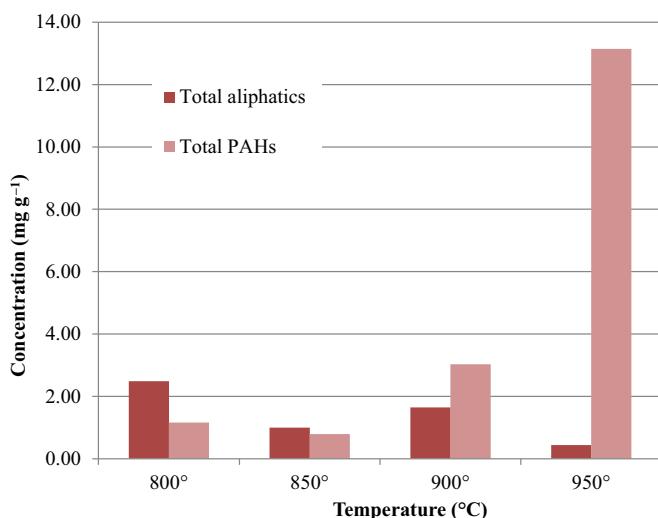


FIGURE 29.3 Selected hydrocarbon compounds generated in a low-density polyethylene fire (pyrolysis; low oxygen conditions) in four temperature regions. (For color version of this figure, the reader is referred to the online version of this book.) Data from: Hawley-Fedder RA, Parsons ML, Karasek FW. Products obtained during combustion of polymers under simulated incinerator conditions. J Chromatogr 1984;314: 263–272.



**FIGURE 29.4** Total aliphatic (chain) hydrocarbons *versus* polycyclic aromatic hydrocarbons (PAHs) generated in a low-density polyethylene fire (pyrolysis) in four temperature regions. (For color version of this figure, the reader is referred to the online version of this book.) Data from: Hawley-Fedder RA, Parsons ML, Karasek FW. Products obtained during combustion of polymers under simulated incinerator conditions. J Chromatogr 1984;314:263–272.

hexachlorobenzene and the dioxins and furans, volatile organic compounds (VOCs) and many others. For a number of decades now combustion engineers have devoted considerable attention to the relatively small quantities of materials emitted from the combustion process that are considered to be air pollutants. Prior to them an automotive engineer, for example, was not overly concerned about the 1% of carbon monoxide in the exhaust of the gasoline engine. By getting this 1% to burn to carbon dioxide inside the combustion chamber, the engineer could expect an increase in gasoline mileage of something less than one-half of 1%. This 1% of carbon monoxide, however, is 10,000 ppm by volume, and a number of such magnitudes cannot be ignored by an engineer dealing with air pollution problems. This is now a key aspect of any engine design.

Combustion is extremely complicated but is generally considered to be a free radical chain reaction. Several reasons exist to support the free radical mechanism:

- (1) Simple calculations of the heats of disassociation and formation for the molecules involved do not agree with the experimental values obtained for heats of combustion.
- (2) A great variety of end products may be found in the exhaust from a combustion reaction. Many complicated organic molecules have been identified in the effluent from a system burning pure methane with pure oxygen.
- (3) Inhibitors, such as tetraethyl lead and methylcyclopentadienyl manganese tricarbonyl (MMT), can greatly change the rate of reaction.<sup>d</sup>

When visualizing a combustion process, it is useful to think of it in terms of the three *Ts*: time, temperature, and turbulence. Time for combustion to occur is necessary. A combustion process that is just initiated, and suddenly has its reactants discharged to a chilled environment, will not go to completion and will emit excessive pollutants. A high enough temperature must exist for the combustion reaction to be initiated. Combustion is an exothermic reaction (it gives off

<sup>d</sup> MMT ( $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$ ) is an octane enhancer, which was approved as a fuel additive in the US. Some decades ago, the US EPA determined that MMT, added at 1/32 g per gallon of manganese (Mn), will not cause or contribute to regulated emissions failures of vehicles. Some have expressed concerns that the use of MMT may harm on-board diagnostic equipment (OBD) which monitors the performance of emissions control devices in the vehicle. Currently, the US EPA considers the data collected to be inconclusive with regard to OBD. After completing a 1994 risk evaluation on the use of MMT in gasoline, the US EPA was unable to determine if there is a risk to the public health from exposure to emissions of MMT gasoline. Like lead, manganese is also neurotoxic, so the US EPA has required the manufacturer perform testing to support a more definitive risk evaluation, including health pharmacokinetic (PK) studies and one emission characterization. Completed final reports for all of these studies have been submitted to EPA. These final reports can be found in the Federal Docket Management System (FDMS) at [www.regulations.gov](http://www.regulations.gov) identified by docket number EPA-HQ-OAR-2004-0074. In addition to the already completed tests, the manufacturer is now in the process of developing physiologically based pharmacokinetic (PBPK) models for manganese which are being derived from data generated from the completed testing. The manufacturer anticipates that these PBPK models will be completed in 2008. The US EPA is presently reviewing exposure and risk information and may refine its risk evaluation or may ask for further testing based on the results of the submitted testing and resulting model now being developed, as well as any other available data. See [http://www.epa.gov/otaq/regulations/fuels/additive/mmt\\_cmts.htm](http://www.epa.gov/otaq/regulations/fuels/additive/mmt_cmts.htm).

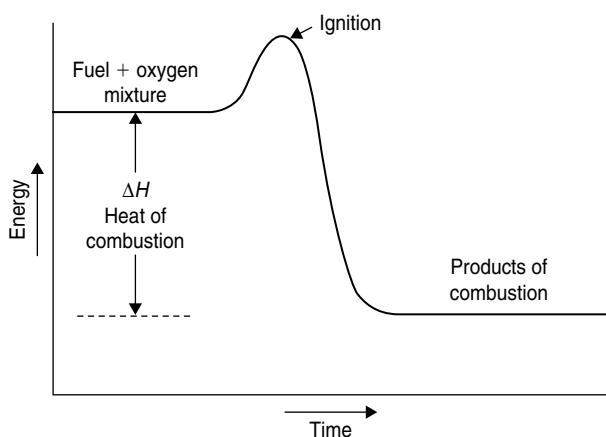


FIGURE 29.5 Energies involved in combustion.

heat), but it also requires energy to be initiated (see Figure 29.5). Turbulence is necessary to ensure that the reacting fuel and oxygen molecules in the combustion process are in intimate contact at the proper instant, when the temperature is high enough to cause the reaction to begin.

The physical state of the fuel for a combustion process dictates the type of system to be used for burning. A fuel may be composed of volatile material, fixed carbon, or both. The volatile material burns as a gas and exhibits a visible flame, whereas the fixed carbon burns without a visible flame in a solid form. If a fuel is in the gaseous state, such as natural gas, it is very reactive and can be fired with a simple burner.

If a fuel is in the liquid state, such as fuel oil, most of it must be vaporized to the gaseous state before combustion occurs. This vaporization can be accomplished by supplying heat from an outside source, but usually the liquid fuel is first atomized and then the finely divided fuel particles are sprayed into a hot combustion chamber to accomplish the gasification. With a solid fuel, such as coal or wood, a series

of steps are involved in combustion. These steps occur in a definite order, and the combustion device must be designed with these steps in mind. Figure 29.6 indicates what happens to a typical solid fuel during the combustion process.

The cycle of operation of the combustion source affects air pollutant formation. A steady process, such as a large steam boiler, operates with a fairly uniform load and a continuous fuel flow. The effluent gases, along with any air pollutants, are discharged steadily and continually from the stack. An automobile engine, on the other hand, is a series of intermittent sources. The emissions from the automotive engine will be vastly different from those from the boiler in terms of both quantity and quality. A four-cylinder automotive engine operating at 2500 rpm has 5000 separate combustion processes started and completed each minute of its operation. Each of these lasts about 0.01 s from beginning to end.

A comparison of typical emissions from various common combustion sources may be seen in Table 29.2. The emissions from combustion processes may be predicted to some extent if the variables of the processes are completely defined. Figure 29.7 indicates how the emissions from a combustion source would be expected to vary with the temperature of the reaction. No absolute values are shown, as these will vary greatly with fuel type, independent variables of the combustion process, etc.

### 29.3 STATIONARY EMISSION SOURCES

Emissions from industrial processes are varied and often complex.<sup>4</sup> These emissions can be controlled by applying the best available technology. The emissions may vary slightly from one facility to another, using apparently similar equipment and processes, but inspite

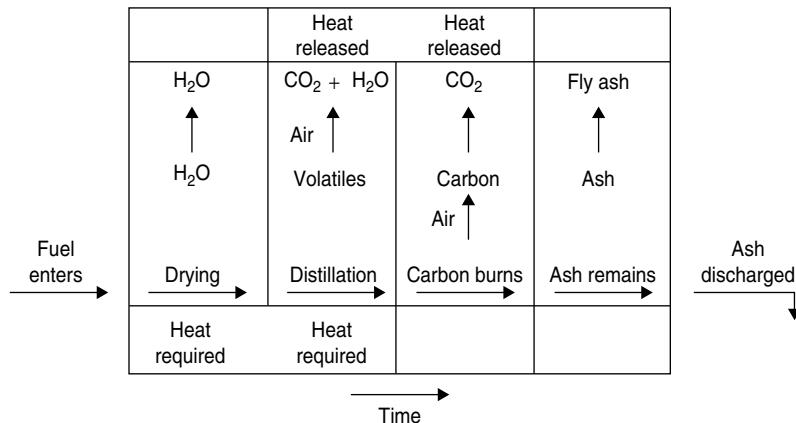


FIGURE 29.6 Physical and chemical processes during solid fuel combustion.

TABLE 29.2 Comparison of Pollutant Emissions Produced from Various Combustion Processes

Contaminant	Power Plant Emission (g kg <sup>-1</sup> fuel)			Refuse Burning Emission (g kg <sup>-1</sup> refuse)		Uncontrolled Automotive Emission (g kg <sup>-1</sup> fuel)	
	Coal	Oil	Gas	Open	Multiple	Gasoline	Diesel
Carbon monoxide	Nil	Nil	Nil	50.0	Nil	165.0	Nil
Oxides of sulfur (SO <sub>2</sub> )	(20)x	(20)x	(16)x	1.5	1.0	0.8	7.5
Oxides of nitrogen (NO <sub>2</sub> )	0.43	0.68	0.16	2.0	1.0	16.5	16.5
Aldehydes and ketones	Nil	0.003	0.001	3.0	0.5	0.8	1.6
Total hydrocarbons	0.43	0.05	0.005	7.5	0.5	33.0	30.0
Total particulate	(75)y	(2.8)y	Nil	11	11	0.05	18.0

x = percentage of sulfur in fuel; y = percentage of ash in fuel.

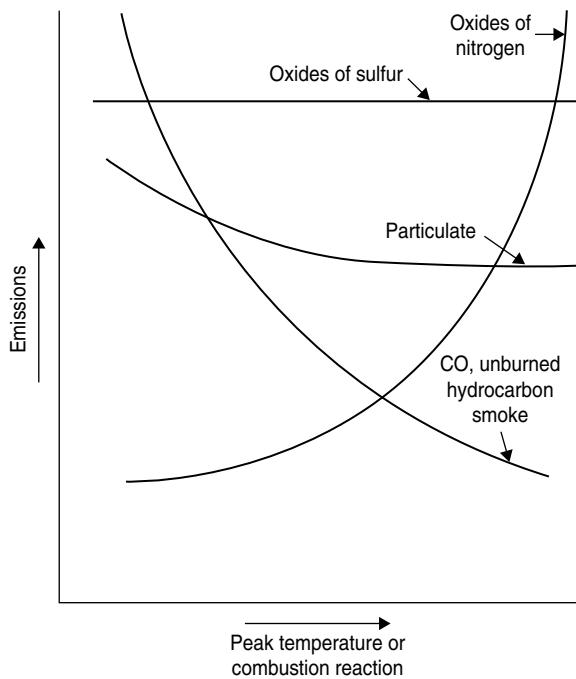


FIGURE 29.7 Emissions from combustion as a function of peak combustion temperatures.

of this slight variation, similar control technology is usually applied.<sup>5</sup> For example, a method used to control the emissions from steel mill X may be applied to control similar emissions at plant Y. It should not be necessary for plant Y to spend excessive amounts for research and development if plant X has a system that is operating satisfactorily. The solution to the problem is often to look for a similar industrial process, with similar emissions, and find the type of control system used. That said, good engineering must always consider the details in any design. Thus, even seemingly small differences between two similar processes (e.g. quantity, flow rates, holding times, materials, and reactor size and

shape) can lead to dramatically different waste products, not to mention unforeseen safety and liability issues. Consequently, the following discussions are merely guidelines that must be adapted for each facility.

### 29.3.1 Chemical and Allied Products

The emissions from a chemical process can be related to the specific process. A plant manufacturing a resin might be expected to emit not only the resin being manufactured but also some of the raw material and some other products which may or may not resemble the resin. A plant manufacturing sulfuric acid can be expected to emit sulfuric acid fumes and SO<sub>2</sub>. A plant manufacturing soap products could be expected to emit a variety of odors.

Depending on the process, the emissions could be any one or a combination of dust, aerosols, fumes, or gases. The emissions may or may not be odorous or toxic. Some of the primary emissions might be innocuous but later react in the atmosphere to form an undesirable secondary pollutant. A flowchart and material balance sheet for the particular process are very helpful in understanding and analyzing any process and its emissions.<sup>6</sup>

In any discussion of the importance of emissions from a particular process for an area, several factors must be considered—(1) the percentage of the total emissions of the area that the particular process emits, (2) the degree of toxicity of the emissions, and (3) the obvious characteristics of the source (which can be related to either sight or smell).

### 29.3.2 Resins and Plastics

Resins are solid or semisolid, water-insoluble,<sup>3</sup> organic substances with little or no tendency to crystallize. They are the basic components of plastics and are

also used for coatings on paper, particleboard, and other surfaces that require a decorative, protective, or special-purpose finish. The common characteristic of resins is that heat is used in their manufacture and application, and gases are exhausted from these processes. Some of the gases that are economically recoverable may be condensed, but a large portion is lost to the atmosphere. One operation, coating a porous paper with a resin to form battery separators, was emitting to the atmosphere about 85% of the resin purchased. This resin left the stacks of the plant as a blue haze, and the odor was routinely detected more than 2 km away. Since most resins and their by-products have low-odor thresholds, disagreeable odor is the most common complaint against any operation using them.

### 29.3.3 Varnish and Paints

In the manufacture of varnish, heat is necessary for formulation and purification. The same may be true of operations preparing paints, shellac, inks, and other protective or decorative coatings. The compounds emitted to the atmosphere are gases, some with extremely low-odor thresholds. Acrolein, with an odor threshold of about  $4000 \mu\text{g m}^{-3}$ , and reduced sulfur compounds, with odor thresholds of  $2 \mu\text{g m}^{-3}$ , are both possible emissions from varnish cooking operations. The atmospheric emissions from varnish cooking appear to have little or no recovery value, whereas some of the solvents used in paint preparation are routinely condensed for recovery and returned to the process. If a paint finish is baked to harden the surface by removal of organic solvents, the solvents must either be recovered, destroyed, or emitted to the atmosphere. The last course, emission to the atmosphere, is undesirable and may be prohibited by the air pollution control agency.

However, the reactants and other materials used to produce or modify resins and plastics (e.g. polymers) may include chemicals with high aqueous solubility, such as the neurotoxic compound, acrylamide ( $650,000 \text{ mg l}^{-1}$ ). This means that such ancillary chemicals can find their way to the air via water vapor or water films on particles. They may also move to other environmental compartments (e.g. contaminating surface and ground water).

### 29.3.4 Acid Manufacture

Acids are used as basic raw materials for many chemical processes and manufacturing operations. Figure 29.8 illustrates an acid plant with its flow diagram. Sulfuric acid is one of the major inorganic chemicals in modern industry. The atmospheric discharges from a sulfuric acid plant can be expected to contain gases including

$\text{SO}_2$  and aerosol mists, containing  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$ , in the submicron to  $10\text{-}\mu\text{m}$  size range. The aerosol mists are particularly damaging to paint, vegetation, metal, and synthetic fibers.

Other processes producing acids, such as nitric, acetic, and phosphoric acids, can be expected to produce acid mists from the processes themselves as well as various toxic and nontoxic gases. The particular process must be thoroughly studied to obtain a complete listing of all the specific emissions.

### 29.3.5 Soaps and Detergents

Soaps are made by reacting fats or oils with a base. Soaps are produced in a number of grades and types. They may be liquid, solid, granules, or powder. The air pollution problems of soap manufacture are primarily odors from the chemicals, greases, fats, and oils, although particulate emissions may occur during drying and handling operations. Detergents are manufactured from base stocks similar to those used in petroleum refineries, so the air pollution problems are similar to those of refineries.

### 29.3.6 Phosphate Fertilizers

Phosphate fertilizers are prepared by beneficiation of phosphate rock to remove its impurities, followed by drying and grinding. The  $\text{PO}_4$  in the rock may then be reacted with sulfuric acid to produce normal superphosphate fertilizer. Over 100 plants operating in the United States produce approximately a billion kilograms of phosphate fertilizer per year. Figure 29.9 is a flow diagram for a normal superphosphate plant which notes the pollutants emitted. The particulate and gaseous fluoride emissions cause greatest concern near phosphate fertilizer plants.

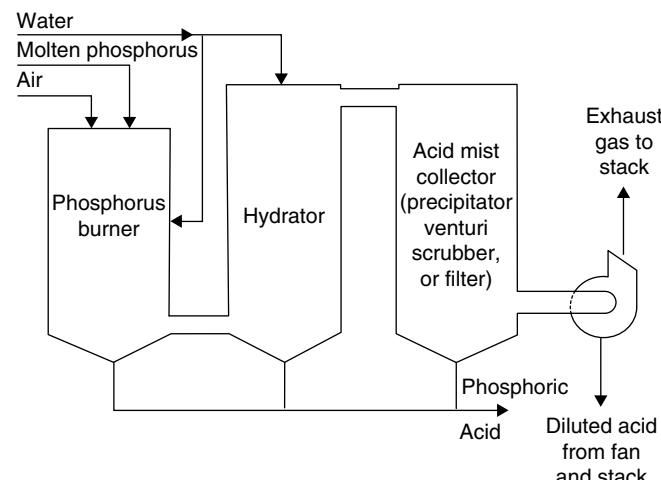


FIGURE 29.8 Flow diagram for a phosphoric acid plant.

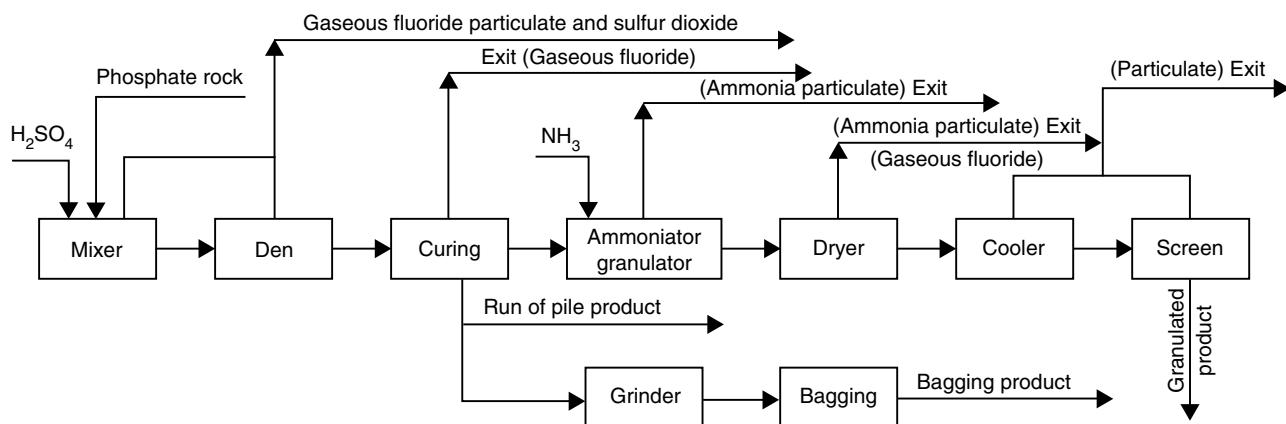


FIGURE 29.9 Flow diagram for a normal superphosphate plant.

### 29.3.7 Other Inorganic Chemicals

Production of the large quantities of inorganic chemicals necessary for modern industrial processes can result in air pollutant emissions as undesirable by-products. Table 29.3 lists some of the more common inorganic chemicals produced, along with the associated air pollutants potentially emitted from the specific process.<sup>7</sup>

### 29.3.8 Petroleum and Coal

Petroleum and coal are the principal fuels that supply the majority of the energy in all industrial countries. This fact gives an indication of the vast quantities of materials handled and also hints at the magnitude of the air pollution problems associated with obtaining the resource, transporting it, refining it, and transporting it again (see Chapter 5). The emission problems from burning fossil fuel have been previously discussed.

TABLE 29.3 Miscellaneous Inorganic Chemicals and Associated Air Pollution Emissions

Inorganic Chemical Produced	Associated Air Pollution Emissions
Calcium oxide (lime)	Lime dust
Sodium carbonate (soda ash)	Ammonia—soda ash dust
Sodium hydroxide (caustic soda)	Ammonia—caustic dust and mist
Ammonium nitrate	Ammonia—nitric oxides
Chlorine	Chlorine gas, hydrochloric acid (HCl)
Bromine	Bromine gas and compounds, chlorine gas, radionuclides

#### 29.3.8.1 Petroleum

Petroleum products are obtained from crude oil. In the process of getting the crude oil from the ground to the refinery, many possibilities for emission of hydrocarbon and reduced sulfur gaseous emissions occur. In many cases, these operations take place in relatively remote regions and affect only those employed by the industry, so that little or no control is attempted.

In the United States in 2011, petroleum refineries released 26 million kg of toxic pollutants, with 58% directly emitted from refinery stacks or indirectly as fugitive emissions.<sup>8</sup> As shown in Figure 29.10, an improperly controlled petroleum refinery is a potential source of large tonnages of atmospheric emissions. All refineries are odorous, the degree being a matter of the housekeeping practices around the refinery. Since refineries are essentially closed processes, emissions are not normally considered a part of the operation. Refineries do need pressure relief systems and vents, and emissions from them are possible. Most refineries use very strict control measures for economic as well as regulatory reasons. The recovery of 1 or 2% of a refinery throughput which was previously lost to the atmosphere can easily pay for the cost of the control equipment. The expense of the catalyst charge in some crackers and regenerators requires that the best possible control equipment be used to prevent catalyst emissions to the atmosphere.

Potential air pollutants from a petroleum refinery could include: (1) hydrocarbons from all systems, leaks, loading, and sampling; (2) sulfur oxides from boilers, treaters, and regenerators; (3) carbon monoxide from regenerators and incinerators; (4) nitrogen oxides from combustion sources and regenerators; (5) odors from air and steam blowing, condensers, drains, and vessels; and (6) particulate matter from boilers, crackers, regenerators, coking, and incinerators.

Loading facilities must be designed to recover all vapors generated during filling of tank trucks or tanker

FIGURE 29.10 A petroleum refinery with numerous sites of potential emissions. Ref. 8.



ships. Otherwise these vapors will be lost to the atmosphere. Since they may be both odorous and photochemically reactive, serious air pollution problems could result. The collected vapors must be returned to the process or disposed of by some means.

An increasingly important concern is the likelihood of an uncontrolled fire caused by an accident or by a terrorist act at the refinery. This can be the source of large and highly toxic plumes. Thus, refineries need special measures for protection and security, coupled with vigorously diligent monitoring, operation, and maintenance. Every refinery also needs an up-to-date contingency plan.

### 29.3.8.2 Coal

The air pollution problems associated with combustion of coal are of major concern. These problems generally occur away from the coal mine. The problems of atmospheric emissions due to mining, cleaning, handling, and transportation of coal from the mine to the user are of lesser significance as far as the overall air pollution problems are concerned. Whenever coal is handled, particulate emission becomes a problem. The emissions can be either coal dust or inorganic inclusions. Control of these emissions can be relatively expensive if the coal storage and transfer facilities are located near residential areas. This is particularly problematic in developing nations. For example, China's economic and industrial expansion over the past decade has been largely supported by coal combustion (about two-thirds of energy use). This leads to three types of problems:

1. Coal is among the worst fuels in terms of production of greenhouse gases, mainly CO<sub>2</sub>.
2. Coal often has high sulfur and ash content, so it is a major source of oxides of sulfur and particulate matter, respectively.
3. Coal contains heavy metals, particularly mercury, so it is also a major contributor to air toxics.

### 29.3.9 Primary Metals Industry

Metallurgical equipment has long been an obvious source of air pollution. The effluents from metallurgical furnaces are submicron-size dusts and fumes and hence are highly visible. The emissions from associated coke ovens are not only visible but odorous as well.

#### 29.3.9.1 Ferrous Metals

Iron and steel industries have been concerned with emissions from their furnaces and cupolas since the industry started. In recent decades, most of the companies controlling these operations have opened new, controlled plants to replace older, higher-emitting plants. Table 29.4 illustrates the changes in the steelmaking processes that have occurred in the United States.

Air-polluting emissions from steelmaking furnaces include metal oxides, smoke, fumes, and dusts to make up the visible aerosol plume. They may also include gases, both organic and inorganic. If steel scrap is melted, the charge may contain appreciable amounts of oil, grease, and other combustibles that further add to the organic gas and smoke loadings. If the ore used has appreciable

TABLE 29.4 Changes in Steel-making Processes in the United States

Year	Production by Specific Process (%)				
	Bessemer	Open Hearth	Electric	Basic Oxygen Furnace	Total
1920	21	78	1	0	100
1940	6	92	2	0	100
1960	2	89	7	2	100
1970	1	36	14	48	100
1980	1	22	31	46	100
1990	0	4	37	59	100

fluoride concentrations, the emission of both gaseous and particulate fluorides can be a serious problem.

Emissions from foundry cupolas are relatively small but still significant, in some areas. An uncontrolled 2-m cupola can be expected to emit up to 50 kg of dust, fumes, smoke, and oil vapor per hour. Carbon monoxide, oxides of nitrogen, and organic gases may also be expected. Control is possible, but the cost of the control may be prohibitive for the small foundry which only has one or two heats per week.

Steel-making is commonly associated with coke ovens. Coke is coal that has undergone pyrolysis, i.e. heated up to 1000–1400 °C in the absence of oxygen, so it is not burned. This process intentionally releases gaseous components of the coal to produce nearly pure carbon.<sup>9</sup>

Coke oven emissions are complex mixtures of gas, liquid, and solid phases, usually including a range of about 40 PAHs, as well as other PICs; notably formaldehyde, acrolein, aliphatic aldehydes, ammonia, carbon monoxide, nitrogen oxides, phenol, cadmium, arsenic, and mercury. More than 60 organic compounds have been collected near coke plants. A metric ton of coal yields up to 635 kg of coke, up to 90 kg of coke breeze (large coke particulates), 7–9 kg of ammonium sulfate, 27.5–34 l of coke oven gas tar, 55–135 l of ammonia liquor, and 8–12.5 l of light oil. Up to 35% of the initial coal charge is emitted as gases and vapors. Most of these gases and vapors are collected during by-product coke production. Coke oven gas is comprised of hydrogen, methane, ethane, carbon monoxide, carbon dioxide, ethylene, propylene, butylene, acetylene, hydrogen sulfide, ammonia, oxygen, and nitrogen. Coke oven gas tar includes pyridine, tar acids, naphthalene, creosote oil, and coal-tar pitch. Benzene, xylene, toluene, and solvent naphthas may be extracted from the light oil fraction. Coke production in the US increased steadily between 1880 and the early 1950s, peaking at 65 million metric tons in 1951. In 1976, the United States was second in the world with 48 million metric tons of coke, i.e. 14.4% of the world production. By 1990, the US produced 24 million metric tons, falling to fourth in the world. A gradual decline in production has continued; production has decreased from 20 million metric tons in 1997 to 15.2 million metric tons in 2002. Demand for blast furnace coke also has declined in recent years because technological improvements have reduced the amount of coke consumed per amount of steel produced by as much as 25%.

Obviously, the volatilized gases are air pollutants. In fact, coke ovens are the source of thousands of compounds, many that are toxic. Coke facilities have recognized that many of these gases are also economically valuable, so technologies exist and are being applied to recover, separate, and sell them for profit. Some of the processes shown in Table 29.4 no longer need coke

to produce steel. This is an example of green engineering.

### 29.3.9.2 Nonferrous Metals

Around the turn of the century, one of the most obvious effects of industry on the environment was the complete destruction of vegetation downwind from copper, lead, and zinc smelters. This problem was caused by the smelting of the metallic sulfide ores. As the metal was released in the smelting process, huge quantities of sulfur were oxidized to SO<sub>2</sub>, which was toxic to much of the vegetation fumigated by the plume. Present smelting systems go to great expense to prevent the uncontrolled release of SO<sub>2</sub>, but in many areas the recovery of the ecosystem will take years and possibly centuries.

Early aluminum reduction plants were responsible for air pollution because of the fluoride emissions from their operations. Fluoride emissions can cause severe damage to vegetation and to animals feeding on such vegetation. The end result was an area surrounding the plant devoid of vegetation. Such scenes are reminiscent of those downwind from some of the uncontrolled copper smelters. New aluminum reduction plants are going to considerable expense to control fluoride emissions. Some of the older plants are finding that the cost of control will exceed the original capital investment in the entire facility. Where the problem is serious, control agencies have developed extensive sampling networks to monitor emissions from the plant of concern.

Emissions from other nonferrous metal facilities are primarily metal fumes or metal oxides of extremely small diameter. Zinc oxide fumes vary from 0.03 to 0.3 μm and are toxic. Lead and lead oxide fumes are extremely toxic and have been extensively studied. Arsenic, cadmium, bismuth, and other trace metals can be emitted from many metallurgical processes.

### 29.3.10 Stone and Clay Products

The industries which produce and handle various stone products emit considerable amounts of particulate matter at every stage of the operation. These particulates may include fine mineral dusts of a size to cause damage to the lungs. Depending on the type of rock, mineral fibers can also be released, notably asbestos. The threshold values for such dusts have been set quite low to prevent disabling diseases for the worker, including lung cancer, mesothelioma, pleural diseases, asbestosis, and silicosis.

In the production of clay, talc, cement, chalk, etc., an emission of particulate matter will usually accompany each process. These processes may involve grinding, drying, and sieving, which can be enclosed and controlled to prevent the emission of particles. In

many cases, the recovered particles can be returned to the process for a net economic gain.

During the manufacture of glass, considerable dust, with particles averaging about 300 µm in size, will be emitted. Some dusts may also be emitted from the handling of the raw materials involved. Control of this dust to prevent a nuisance problem outside the plant is a necessity. When glass is blown or formed into the finished product, smoke and gases can be released from the contact of the molten glass with lubricated molds. These emissions are quite dense but of a relatively short duration.

### 29.3.11 Forest Products Industry

#### 29.3.11.1 Wood Processing

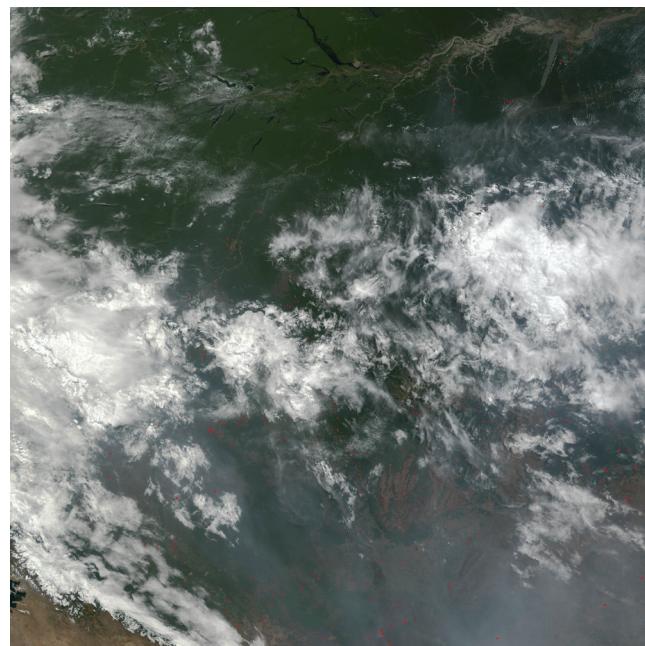
Trees are classified as a renewable resource which is being utilized in most portions of the world on a sustained yield basis. A properly managed forest will produce wood for lumber, fiber, and chemicals indefinitely. Harvesting this resource can generate considerable dust and other particulates. Transportation over unpaved roads causes excessive dust generation. The cultural practice of burning the residue left after a timber harvest, called *slash burning*, is still practiced in some areas and is a major source of smoke, gaseous, and particulate air pollution in the localities downwind from the fire (see [Figure 29.11](#)). Visibility reduction from such burning can be a serious problem.

Processing the harvested timber into the finished product may involve sawing, peeling, planing, sanding, and drying operations, which can release considerable amounts of wood fiber and lesser amounts of gaseous material to the atmosphere. Control of wood fiber emissions from the pneumatic transport and storage systems can be a major problem of considerable expense for a plywood mill or a particleboard plant.

#### 29.3.11.2 Pulp and Paper

Pulp and paper manufacture is increasing in the world at an exponential rate. The demand for paper will continue as new uses are found for this product. Since most paper is manufactured from wood or wood residue, it provides an excellent use for this renewable resource.

The most widely used pulping process is the kraft process, as shown in [Figure 29.12](#), which results in recovery and regeneration of the chemicals. This occurs in the recovery furnace, which operates with both oxidizing and reducing zones. Emissions from such recovery furnaces include particulate matter, very odorous reduced sulfur compounds, and oxides of sulfur. Bleaching has been a substantial source of dioxins, but many processors have now modified their operations to use substantially less chlorine, greatly reducing the dioxin

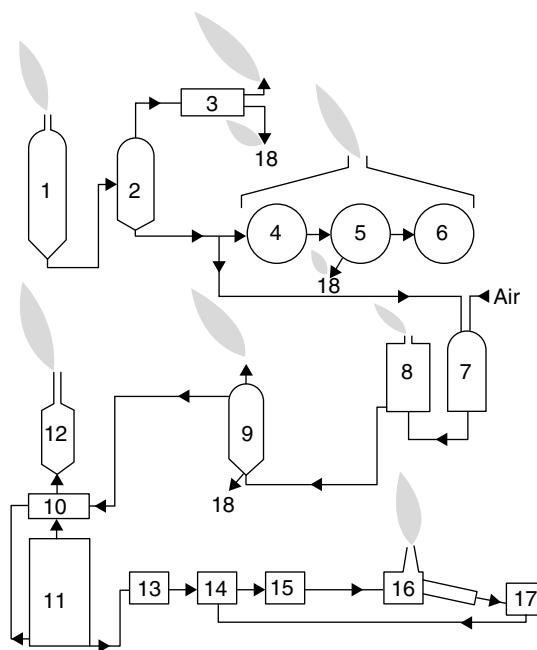


**FIGURE 29.11 Plume from slash burning in the Amazon region of South America.** From the rainforests around the Amazon River (top) in Brazil, through the central highlands and into Bolivia to the southwest, numerous fires (highlighted in red) were burning throughout the region on September 8, 2002. The fires were detected by the Moderate Resolution Imaging Spectroradiometer (MODIS) on NASA's Terra satellite, and their locations are marked with red dots in this true-color image. Thick smoke and clouds are shrouding the highlands in the southern portion of the image. (For the interpretation of the references to color in this figure legend, the reader is referred to the online version of this book.) Photo by Allen J., based on data from the National Aeronautics and Space Administration, 2005, Goddard Space Flight, Space Visualization Studio, Maryland.

formation. If extensive and expensive control is not exercised over the kraft pulp process, the odors and aerosol emissions will affect a wide area. Odor complaints have been reported over 100 km away from these plants. A properly controlled and operated kraft plant will handle huge amounts of material and produce millions of kilograms of finished products per day, with little or no complaint regarding odor or particulate emissions.

### 29.3.12 Noxious Trades

As the name implies, these operations, if uncontrolled, can cause a serious air pollution problem. The main problem is the odors associated with the process. Examples of such industries are tanning works, confined animal feeding operations (CAFOs), rendering plants, and many of the food processing plants such as fish meal plants. In most cases, the emissions of particulates and gases from such plants are not of concern, only the odors. However, other air pollutants are also common (e.g. chromium in tanning and nitric oxide (NO) near



**FIGURE 29.12 Schematic diagram of the kraft pulping process.** 1, digester; 2, blow tank; 3, blow heat recovery; 4, washers; 5, screens; 6, dryers; 7, oxidation tower; 8, foam tank; 9, multiple effect evaporator; 10, direct evaporator; 11, recovery furnace; 12, electrostatic precipitator; 13, dissolver; 14, causticizer; 15, mud filter; 16, lime kiln; 17, slaker; 18, sewer. Ref. 6.

CAFOs). Requiring these industries to locate away from the business or residential areas is no longer acceptable as a means of control.

## 29.4 AIR EMISSIONS FROM HAZARDOUS WASTES

In Chapter 32, we generally address air pollution as a byproduct of another process, such as manufacturing. Air pollution controls are also a necessary component of directly treating other forms of wastes. The goal is to treat the waste to reduce the toxicity, to decrease exposures and, ultimately, to eliminate or at least properly the risks from hazardous substances in the waste. The type of technology applied depends on the intrinsic characteristics of the contaminants and on the substrate in which they reside. The choice must factor in all of the physical, chemical, and biological characteristics of the contaminant with respect to the matrices and substrates (if soil and sediment) or fluids (air, water, or other solvents) where the contaminants are found. Chapter 32 provides the basics of most air pollution control technologies, but when addressing particularly hazardous air pollutants, a number of additional factors must be considered. The selected approach must meet criteria

for treatability (i.e. the efficiency and effectiveness of a technique in reducing the mobility and toxicity of a waste). The comprehensive remedy must consider the effects of each action taken will have on past and proceeding steps.

Eliminating or reducing pollutant concentrations in a waste stream begins with assessing the physical and chemical characteristics of each contaminant, and matching these characteristics with the appropriate treatment technology. All of the kinetics and equilibria, such as solubility, fugacity, sorption, and bioaccumulation factors, will determine the effectiveness of destruction, transformation, removal, immobilization of these contaminants. For example, Table 29.5 ranks the effectiveness of selected treatment technologies on organic and inorganic contaminants typically found in contaminated slurries, soils, sludges, and sediments. As shown, there can be synergies (e.g. innovative incineration approaches are available that not only effectively destroy organic contaminants, but in the process also destroys the inorganic cyanide compounds). Unfortunately, there are also antagonisms among certain approaches, such as the very effective incineration processes for organic contaminants that transform heavy metal species into more toxic and more mobile forms. The increased pressures and temperatures are good for breaking apart organic molecules and removing functional groups that lend them toxicity, but these same processes oxidize or in other ways transform the metals into more toxic or more bioavailable forms. So, when mixtures of organic and inorganic contaminants are targeted, more than one technology may be required to accomplish project objectives, and care must be taken not to make trade one problem (e.g. polychlorinated biphenyls, PCBs) for another (e.g. more mobile species of cadmium).

The characteristics of the substrate (e.g. solid waste, soil, sediment, or water) will affect the performance of any contaminant treatment or control. For example, sediment, sludge, slurries, and soil characteristics that will influence the efficacy of treatment technologies include particle size, solids content, and high contaminant concentration (see Table 29.6).

Particle size may be the most important limiting characteristic for application of treatment technologies to sediments. Most treatment technologies work well on sandy soils and sediments. The presence of fine-grained material adversely affects treatment system emission controls because it increases particulate generation during thermal drying, it is more difficult to dewater, and it has greater attraction to the contaminants (particularly clays). Clayey sediments that are cohesive also present materials handling problems in most processing systems. Solids content generally ranges from high (i.e. usually the *in situ* solids content (30–60% solids by weight)) to low (e.g. hydraulically

TABLE 29.5 Effect of the Characteristics of the Contaminant on Decontamination Efficiencies

Treatment Technology	Organic Contaminants					Inorganic Contaminants		
	PCBs	PAHs	Pesticides	Petroleum Hydrocarbons	Phenolic Compounds	Cyanide	Mercury	Other Heavy Materials
Conventional incineration	D	D	D	D	D	D	xR	pR
Innovative incineration*	D	D	D	D	D	D	xR	I
Pyrolysis*	D	D	D	D	D	D	xR	I
Vitrification*	D	D	D	D	D	D	xR	I
Supercritical water oxidation	D	D	D	D	D	D	U	U
Wet air oxidation	pD	D	U	D	D	D	U	U
Thermal desorption	R	R	R	R	U	U	xR	N
Immobilization	pI	PI	pI	pI	pI	pI	U	I
Solvent extraction	R	R	R	R	R	pR	N	N
Soil washing <sup>§</sup>	pR	pR	pR	pR	pR	pR	pR	pR
Dechlorination	D	N	pD	N	N	N	N	N
Oxidation <sup>¶</sup>	N/d	N/d	N/d	N/d	N/d	N/d	U	xN
Bioremediation <sup>  </sup>	N/pd	N/d	N/d	D	D	N/d	N	N

\* This process is assumed to produce a vitrified slag.

<sup>§</sup>This effectiveness of soil washing is highly dependent on the particle size of the sediment matrix, contaminant characteristics, and the type of extractive agents used.

<sup>¶</sup>The effectiveness of oxidation depends strongly on the types of oxidant(s) involved and the target contaminants.

<sup>||</sup>The effectiveness of bioremediation is controlled by a large number of variables as discussed in the text.

PCBs, polychlorinated biphenyls; PAHS, polycyclic aromatic hydrocarbons.

#### Primary designation

D = effectively destroys contaminant.

R = effectively removes contaminant.

I = effectively immobilizes contaminant.

N = no significant effect.

N/D = effectiveness varies from no effect to highly efficient depending on the type of contaminant within each class.

#### Prefixes

p = partial.

x = may cause release of non-target contaminant.

U = effect not known.

Source: Ref. 10.

TABLE 29.6 Effect of Particle Size, Solids Content, and Extent of Contamination on Decontamination Efficiencies

Treatment Technology	Predominant Particle Size			Solids Content		High Contaminant Concentration	
	Sand	Silt	Clay	High (slurry)	Low ( <i>in situ</i> )	Organic Compounds	Metals
Conventional incineration	N	X	X	F	X	F	X
Innovative incineration	N	X	X	F	X	F	F
Pyrolysis	F	X	X	F	X	F	F
Vitrification	X	F	F	X	F	F	X
Supercritical water oxidation	X	F	F	X	F	F	X
Wet air oxidation	F	X	X	F	X	F	N
Thermal desorption	F	X	X	F	X	F	N
Immobilization	F	X	X	F	X	X	N
Solvent extraction	F	F	X	F	X	X	N
Soil washing	F	F	X	N	F	N	N
Dechlorination	U	U	U	F	X	X	N
Oxidation	F	X	X	N	F	X	X
Bioslurry process	N	F	N	N	F	X	X
Composting	F	N	X	F	X	F	X
Contained treatment facility	F	N	X	F	X	X	X

F, sediment characteristic favorable to the effectiveness of the process; N, sediment characteristic has no significant effect on process performance; U, effect of sediment characteristic on process is unknown; and X, sediment characteristic may impede process performance or increase cost.

Source: Ref. 10.

dredged sediments (10–30% solids by weight)). Treatment of slurries is better at lower solids contents; but this can be achieved even for high solids contents by water addition at the time of processing. It is more difficult to change from a lower to a higher solids content, but evaporative and dewater approaches, such as those used for municipal sludges, may be employed. Also, thermal and dehalogenation processes are decreasingly efficient as solids content is reduced. More water means increased chemical costs and increased need for wastewater treatment.

Elevated levels of organic compounds or heavy metals in high concentrations must also be considered. Higher total organic carbon (TOC) content favors incineration and oxidation processes. The TOC can be the contaminant of concern or any organic, since they are combustibles with caloric value. Conversely, higher metal concentrations may make a technology less favorable by increasing contaminant mobility of certain metal species following application of the technology.

A number of other factors may affect selection of a treatment technology other than its effectiveness for treatment (some are listed in Table 29.7). For example, vitrification and supercritical water oxidation have only been used for relatively small projects and would require more of a proven track record before implementing them for full-scale sediment projects. Regulatory

compliance and community perception are always a part of decisions regarding an incineration system. Land use considerations, including the amount of acreage needs, are commonly confronted in solidification and solid-phase bioremediation projects (as they are in sludge farming and land application). Disposing of ash and other residues following treatment must be part of any process. Treating water effluent and air emissions must be part of the decontamination decision-making process.<sup>10</sup>

## 29.4.2 Pre-control Considerations

### 29.4.2.1 Estimating Contaminant Migration

Estimating potential contaminant releases (i.e. “losses” as defined by environmental regulators) from various combinations of treatment technologies is difficult due to the variability of chemical and physical characteristics of contaminated media (especially soils and sediments), the strong affinity of most contaminants for fine-grained sediment particles, and the limited track record or “scale-up” studies for many treatment technologies. Off-the-shelf models can be used for simple process operations, such as extraction or thermal vaporization applied to single contaminants in relatively pure systems. However, such models have not been

TABLE 29.7 Important Factors When Selecting Decontamination and Treatment Approaches

Treatment Technology	Implementability at Full Scale	Regulatory Compliance	Community Acceptance	Land Requirements	Residuals Disposal	Wastewater Treatment	Air Emissions Control
Conventional incineration	✓	✓	✓				✓
Innovative incineration	✓	✓	✓	✓			✓
Pyrolysis		✓					✓
Vitrification	✓	✓					✓
Supercritical water oxidation	✓						✓
Wet air oxidation							
Thermal desorption					✓	✓	✓
Immobilization				✓			✓
Solvent extraction					✓	✓	✓
Soil washing					✓	✓	✓
Dechlorination							✓
Oxidation	✓						
Bioslurry process	✓						✓
Composting				✓			✓
Contained treatment facility				✓		✓	✓

✓, the factor is critical in the evaluation of the technology.

Source: Ref. 10.

TABLE 29.8 Selected Waste Streams Commonly Requiring Treatability Studies

Contaminant Loss Stream	Treatment Technology Type						
	Biological	Chemical	Extraction	Thermal Desorption	Thermal Destruction	Immobilization	Particle Separation
Residual solids	X	X	X	X	X	X	X
Wastewater	X	X	X	X			X
Oil/organic compounds			X	X			X
Leachate							X*
Stack gas				X	X		
Adsorption media			X	X			
Scrubber water						X	
Particulates (filter/cyclone)				X	X		

\* Long-term contaminant losses must be estimated using leaching tests and contaminant transport modeling similar to that used for sediment placed in a confined disposal facility. Leaching could be important for residual solids for other processes as well.

Source: Ref. 10.

appropriately evaluated for a number of other technologies because of the limited database on treatment technologies, such as for contaminated sediments or soils.<sup>10</sup>

#### 29.4.2.2 Treatability Tests

Standard engineering practice for evaluating the effectiveness of treatment technologies for any type of contaminated media (solids, liquids, or gases) requires first performing a treatability study for a sample that is representative of the contaminated material.<sup>10</sup> The performance data from treatability studies can aid in reliably estimating contaminant concentrations for the residues following treatment, as well as possible waste streams generated by a technology. Treatability studies may be performed at the bench-scale (in the laboratory) or at pilot-scale level (e.g. a real-world study, but limited in number of contaminants, in spatial extent, or to a specific, highly controlled form of a contaminant, e.g. one pure congener of PCBs, rather than the common mixtures). Most treatment technologies include post-treatment or controls for waste streams produced by the processing. The contaminant losses can be defined as the residual contaminant concentrations in the liquid or gaseous streams released to the environment. For technologies that extract or separate the contaminants from the bulk of the sediment, a concentrated waste stream may be produced that requires treatment offsite at a hazardous waste treatment facility, where permit requirements may require destruction and removal efficiencies greater than 99.9999% (i.e. the so-called rule of “six nines”). The other source of loss for treatment

technologies is the residual contamination in the sediment after treatment. After disposal, treated wastes are subject to leaching, volatilization, and losses by other pathways. The significance of these pathways depends on the type and level of contamination that is not removed or treated by the treatment process. Various waste streams for each type of technology that should be considered in treatability evaluations are listed in Table 29.8.

#### 29.4.3 Contaminant Treatment and Control Approaches<sup>a</sup>

The life cycle viewpoint is instructive in controlling hazardous air pollutants. Five steps in sequence define an event that results in environmental contamination of the air, water, or soil pollution. These steps individually and collectively offer opportunities to intervene and to control the risks associated with hazards and thus protect public health and the environment. The steps address the presence of waste at five points in the life cycle:<sup>10</sup>

Source →

Release →

Transport →

Exposure →

Response

As a first step, the contaminant source must be identifiable. A hazardous substance must be released from

<sup>a</sup> The principal sources for this section are collaborations with two prominent environmental engineers, Ross E. McKinney and J. Jeffrey Peirce.

the source, be transported through the air, water, or soil environment, reach a human, animal, or plant receptor in a measurable dose, and the receptor must have a quantifiable detrimental response in the form of death or illness. Intervention can occur at any one of these steps to control the risks to public health and to the environment. Of course, any intervention scheme and subsequent control by the engineer must be justified by the environmental engineer as well as the public or private client in terms of scientific evidence, sound engineering design, technological practicality, economic realities, ethical considerations, and the laws of local, state, and national governments.

#### **29.4.3.1 Intervention at the Source of Contamination**

A contaminant must be identifiable, either in the form of an industrial facility that generates waste byproducts, a hazardous waste processing facility, a surface or subsurface land storage/disposal facility, or an accidental spill into a water, air, or soil receiving location. The intervention must minimize or eliminate the risks to public health and the environment by utilizing technologies at this source that are economically acceptable and based on applicable scientific principles and sound engineering designs.

In the case of an industrial facility producing hazardous waste as a necessary byproduct of a profitable item, as considered here for example, the engineer can take advantage of the growing body of knowledge that has become known as life cycle analysis.<sup>10</sup> In the case of a hazardous waste storage facility or a spill, the engineer must take the source as a given and search for possibilities for intervention at a later step in the sequence of steps as discussed below.

Under the life cycle analysis method of intervention, the environmental manager considers the environmental impacts that could incur during the entire life cycle of (1) all of the resources that go into the product; (2) all the materials that are in the product during its use; and (3) all the materials that are available to exit from the product once it or its storage containers are no longer economically useful to society. Few simple examples exist that describe how *life cycle analysis* is conducted but consider for now any one of a number of household cleaning products. Consider that a particular cleaning product, a solvent of some sort, must be fabricated from one of several basic natural resources. Assume for now that this cleaning product currently is petroleum based. The engineer could intervene at this initial step in the life cycle of this product, as the natural resource is being selected, and consequently the engineer could preclude the formation of a source of hazardous waste by suggesting instead the production of a water-based solvent.

Similarly, intervention at the production phase of this product's life cycle and suggested fabrication techniques can preclude the formation of a source of certain contaminants from the outset. In this case the recycling of spent petroleum materials could provide for more household cleaning products with less or zero hazardous waste generation, thus controlling the risks to public health and the environment. Another example is that of "co-generation", which may allow for two manufacturing facilities to co-locate so that the "waste" of one is a "resource" for the other. An example is the location of a chemical plant near a power generation facility, so that the excess steam generated by the power plant can be piped to the nearby chemical plant, obviating the need to burn its own fuel to generate the steam needed for chemical synthesis. Another example is the use of an alcohol waste from one plant as a source for chemical processes to another.

As discussed in Chapter 30, the product under consideration must be considered long before any switches are flipped and valves turned. For example, a particular household cleaning product may result in unintended human exposure to buckets of solvent mixtures that fumigate the air in a home's kitchen or pollute the town's sewers as the bucket's liquid is flushed down a drain. In this way, life cycle analysis is type of systems engineering where a critical path is drawn, and each decision point considered.

Under the plan, the disposal of this solvent's containers must be considered from a long-term risk perspective. The challenge is that every potential and actual environmental impact of a product's fabrication, use, and ultimate disposal must be considered. This is seldom, if ever, a "straight line projection".

#### **29.4.3.2 Intervention at the Point of Release**

Once a contaminant source has been identified, the next step is to intervene at the point at which the waste is released into the environment. This point of release could be at the top of a stack or vent from the source of pollution to a receiving air shed, or it could be a more indirect release, such as from the bottom-most layer of a clay liner in a hazardous waste landfill connected to surrounding soil material. Similarly this point of release could be a series of points as a contaminant is released along a shoreline from a plot of land into the air, from an evaporation pond, from a landfill, near a river or through a plane of soil underlying a storage facility (i.e. a so-called "non-point source").

#### **29.4.3.3 Intervention as the Contaminant Is Transported in the Environment**

Wise site selection of facilities that generate, process, and store contaminants is the first step in preventing or reducing the likelihood that they will move. For

example, the distance from a source to a receptor is a crucial factor in controlling the quantity and characteristics of waste as it is transported.

Meteorology is a primary determinant of the opportunities to control the atmospheric transport of contaminants. For example, manufacturing, transportation, and hazardous waste generating, processing, and storage facilities must be sited to avoid areas where specific local weather patterns are frequent and persistent. These avoidance areas include ground-based inversions, elevated inversions, valley winds, shore breezes, and city heat islands. In each of these venues, the pollutants become locked into air masses with little of no chance of moving out of the respective areas. Thus the concentrations of the pollutants can quickly and greatly pose risks to public health and the environment. In the soil environment the engineer has the opportunity to site facilities in areas of great depth-to-groundwater, as well as in soils (e.g. clays) with very slow rates of transport. In this way, engineers and scientists must work closely with city and regional planners in early in the site selection phases.<sup>b</sup>

#### **29.4.3.4 Intervention to Control the Exposure**

As mentioned in Chapter 1, the receptor of contamination can be a human, other fauna in the general scheme of living organisms, flora, or materials or constructed facilities. In the case of humans, as we discussed previously, the contaminant can be ingested, inhaled, or dermally contacted. Such exposure can be direct with human contact to, for example, particles of lead that are present in inhaled indoor air. An exposure also can be indirect as in the case of human ingestion of the cadmium and other heavy metals found in the livers

exposure to air pollutants, from the “greening” of statutes through the de-zinc process associated with low pH rain events to the crumbling of stone bridges found in nature. Isolating potential receptors from exposure to hazardous air pollutants, the engineer has an opportunity to control the risks to those receptors.

The opportunities to control exposures to contaminants are directly associated with the ability to control the amount of hazardous pollutants delivered to the receptor through source control and siting of control systems and hazardous waste management facilities. One solution to environmental contamination could be to increase their dilution in the air, water, or soil environments. We will discuss specific examples of this type of intervention later in this chapter.

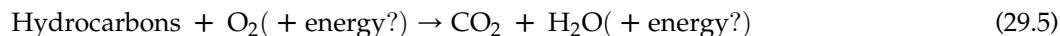
#### **29.4.3.5 Intervention at the Point of Response**

Opportunities for intervention are grounded in basic scientific principles, engineering designs and processes, and applications of proven and developing technologies to control the risks associated with contaminants. Let us consider thermal processing as a class of hazardous control technology that is widely used in treating wastes, but which has a crucial air pollution component.

### **29.4.4 Thermal Treatment Processes**

#### **29.4.4.1 Thermodynamics and Stoichiometry**

Contaminants, if completely organic in structure, are, in theory, completely destructible using principles based in thermodynamics with the engineering inputs and outputs summarized as:



of beef cattle that were raised on grasses receiving nutrition from cadmium-laced municipal wastewater treatment biosolids (commonly known as “sludge”).

Heavy metals or chlorinated hydrocarbons similarly can be delivered to domestic animals and animals in the wild. Construction materials are also sensitive to

Contaminants are mixed with oxygen, sometimes in the presence of an external energy source, and in fractions of seconds or several seconds the byproducts of gaseous carbon dioxide and water are produced to exit the top of the reaction vessel while a solid ash is produced to exit the bottom of the reaction vessel.<sup>c</sup>

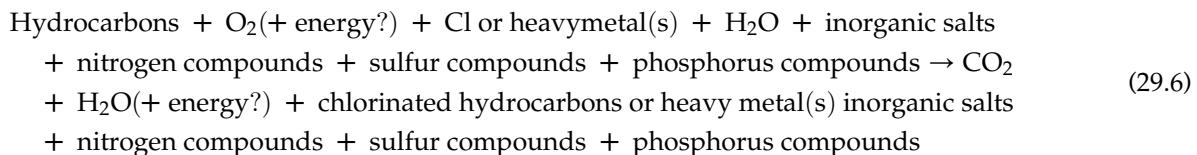
<sup>b</sup> This goes beyond zoning. Obviously, the engineer should be certain that the planned facility adheres to the zoning ordinances, land use plans, and maps of the state and local agencies. However, it behooves all of the professionals to collaborate, hopefully before any land is purchased and contractors are retained. Councils of Government (COG) and other “A-95” organizations can be rich resources when considering options on siting. They can help avoid the need for problems long before implementation, to say nothing of contentious zoning appeal and planning commission meetings and perception problems at public hearings.

<sup>c</sup> Numerous textbooks address the topic of incineration in general and hazardous waste incineration in particular. For example, see Refs 29–32.

3K Energy may also be produced during the reaction and the heat may be recovered. A derivative problem in this simple reaction could be global warming associated with the carbon dioxide.

Conversely, if the contaminant of concern to the engineer contains other chemical constituents, in particular chlorine and/or heavy metals, the original simple input and output relationship is modified to a very complex situation:

and microbiological characteristics of the waste also over the planning period of the project. The space required for the incinerator itself ranges from several square yards to possibly on the back of a flat bed truck to several acres to sustain a regional incinerator system. Laboratory testing and pilot studies matching a given waste to a given incinerator must be conducted prior to the design, citing, and construction of each incinerator. Generally, the same reaction applies to



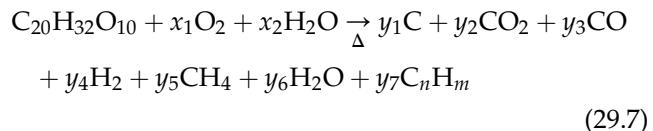
With these contaminants the potential exists for destruction of the initial contaminant, but actually exacerbating the problem by generating more hazardous off-gases containing chlorinated hydrocarbons and/or ashes containing heavy metals are produced (e.g. the improper incineration of certain chlorinated hydrocarbons can lead to the formation of the highly toxic chlorinated dioxins, furans, and hexachlorobenzene). All of the thermal systems discussed below have common attributes. All require the balancing of the three "T's" of the science, engineering, and technology of incineration of any substance:

1. Time of incineration
2. Temperature of incineration
3. Turbulence in the combustion chamber

The advantages of thermal systems include: (1) the potential for energy recovery; (2) volume reduction of the contaminant; (3) detoxification as selected molecules are reformulated; (4) the basic scientific principles, engineering designs, and technologies are well understood from a wide range of other applications including electric generation and municipal solid waste incineration; (5) application to most organic contaminants which compose a large percentage of the total contaminants generated worldwide; (6) the possibility to scale the technologies to handle a single gallon per pound (liter per kilogram) of waste or millions of gallon per pound (liter per kilogram) of waste; and (7) land areas that are small compared to many other facilities (e.g. landfills).

Each system design must be customized to address the specific contaminants under consideration, including the quantity of waste to be processed over the planning period as well as the physical, chemical,

most thermal processes, i.e. gasification, pyrolysis, hydrolysis, and combustion<sup>11,12</sup>:



The coefficients  $x$  and  $y$  balance the compounds on either side of the equation. The delta under the arrow indicates heating. In many thermal reactions,  $\text{C}_n\text{H}_m$  includes the alkanes,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ ,  $\text{C}_5\text{H}_{12}$ , and benzene,  $\text{C}_6\text{H}_6$ . The actual reactions from test burns for commonly incinerated compounds are provided in Table 10.1.

Of all of the thermal processes, incineration is the most common process for destroying organic contaminants in industrial wastes. Incineration simply is heating wastes in the presence of oxygen to oxidize organic compounds (both toxic and non-toxic). The principal incineration steps are shown in Figure 29.13.

#### 29.4.4.2 Applying Thermal Processes for Treatment

A word of warning when choosing incineration as the recommended technology: The mere mention of "incineration" evokes controversy in communities. There have been real and perceived failures. It is also important to note that incineration alone does not "destroy" heavy metals; it simply changes the valence of the metal. In fact, incineration can increase the leachability of metals via oxidation, although processes like slagging (operating at sufficiently high temperatures to melt and remove combustible materials) or vitrification (producing

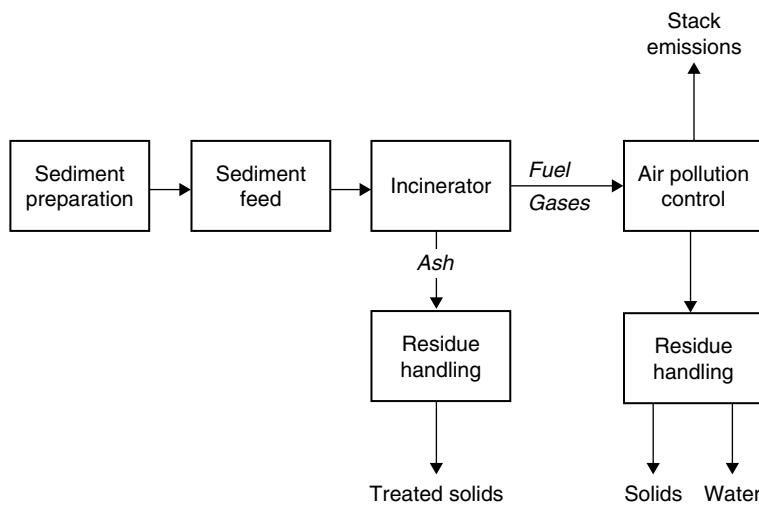


FIGURE 29.13 Steps in the incineration of contaminants. *Ref. 10.*

non-leachable, basalt-like residue) actually reduce the mobility of many metals.

Leachability is a measure of the ease with which compounds in the waste can move into the accessible environment. The increased leachability of metals would be problematic if the ash and other residues are to be buried in landfills or stored in piles. The leachability of metals is generally measured using the toxicity characteristic leaching procedure (TCLP) test, discussed earlier. Incinerator ash that fails the TCLP must be disposed of in a waste facility approved for hazardous wastes. Enhanced leachability would be advantageous only if the residues are engineered to undergo an additional treatment step of metals. Again, the engineer must see incineration of but one component within a systematic approach for any contaminant treatment process.

There are a number of places in the incineration flow of the contaminant through the incineration process where new compounds may need to be addressed. As mentioned, ash and other residues may contain high levels of metals, at least higher than the original feed. The flue gases are likely to include both organic and inorganic compounds that have been released as a result of temperature induced volatilization and/or newly transformed PICs with higher vapor pressures than the original contaminants.

The disadvantages of hazardous waste incinerators include: (1) the equipment is capital intensive, particularly the refractory material lining the inside walls of each combustion chamber that must be replaced as cracks form whenever a combustion system is cooled and/or heated; (2) the operation of the equipment requires very skilled operators and is more costly when fuel must be added to the system; (3) ultimate disposal

of the ash is necessary and particularly troublesome and costly if heavy metals and/or chlorinated compounds are found during the expensive monitoring activities; and (4) air emissions may be hazardous and thus must be monitored for chemical constituents and controlled.

Given these underlying principles of incineration, seven general guidelines emerge:

1. Only liquid purely organic contaminants are true candidates for combustion.
2. Chlorine-containing organic materials deserve special consideration if in fact they are to be incinerated at all; special materials used in the construction of the incinerator, long (many seconds) of combustion time, high temperatures ( $>1600^{\circ}\text{C}$ ), with continuous mixing if the contaminant is in the solid or sludge form.
3. Feedstock containing heavy metals generally should not be incinerated.
4. Sulfur-containing organic material will emit sulfur oxides which must be controlled.
5. The formation of nitrogen oxides can be minimized if the combustion chamber is maintained above  $1100^{\circ}\text{C}$ .
6. Destruction depends on the interaction of a combustion chamber's temperature, dwell time, and turbulence.
7. Off-gases and ash must be monitored for chemical constituents, each residual must be treated as appropriate so the entire combustion system operates within the requirements of the local, state, and federal environmental regulators, and hazardous components of the off-gases, off-gas treatment processes, and the ash must reach ultimate disposal in a permitted facility.

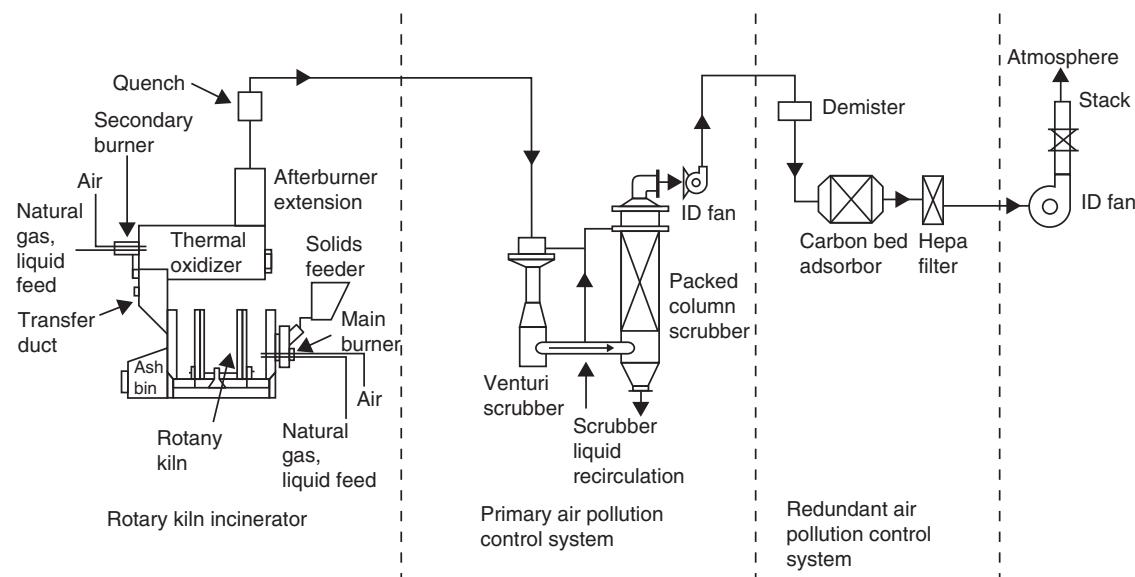


FIGURE 29.14 Rotary kiln system. Ref. 26.

### 29.4.5 Thermal Destruction Systems

The types of thermal systems vary considerably. Five general categories are available to destroy contaminants: (1) rotary kiln; (2) multiple hearth; (3) liquid injection; (4) fluidized bed; and (5) multiple chamber.

#### 29.4.5.1 Rotary Kiln

The combustion chamber in a rotary kiln incinerator as illustrated in Figure 29.14 is a heated rotating cylinder that is mounted at an angle with possible baffles added to the inner face to provide the turbulence necessary for the target three "T's" for the contaminant destruction process to take place. Engineering design decisions, based on the results of laboratory testing of a specific contaminant, include: (1) angle of the drum; (2) diameter and length of the drum; (3) presence and location of the baffles; (4) rotational speed of the drum; and (5) use of added fuel to increase the temperature of the combustion chamber as the specific contaminant requires. The liquid, sludge, or solid hazardous waste is input into the upper end of the rotating cylinder, rotates with the cylinder-baffle system, and falls with gravity to the lower end of the cylinder. The heated upward moving off-gases are collected, monitored for chemical constituents, and subsequently treated as appropriate prior to release, while the ash falls with gravity to be collected, monitored for chemical constituents, and also treated as needed before ultimate disposal. The newer rotary kiln systems<sup>4</sup> consist of a primary combustion chamber, a transition volume, and a fired afterburner chamber. After exiting the afterburner, the flue gas is passed through a quench section followed by a primary air

pollution control system (APCS). The primary APCS can be a venture scrubber followed by a packed-column scrubber. Downstream of the primary APCS, a backup secondary APCS, with a demister, an activated carbon adsorber, and a high-efficiency particulate air (HEPA) filter can collect contaminants not destroyed by the incineration.

The rotary kiln is applicable to the incineration of most organic contaminants, it is well suited for solids and sludges, and in special cases liquids and gases can be injected through auxiliary nozzles in the side of the combustion chamber. Operating temperatures generally vary from 800 to 1650 °C. Engineers use laboratory experiments to design residence times of seconds for gases and minutes or possibly hours for the incineration of solid material.

#### 29.4.5.2 Multiple Hearth

In the multiple hearth illustrated in Figure 29.15 generally contaminants in solid or sludge form are fed slowly through the top vertically stacked hearth; in special configurations hazardous gases and liquids can be injected through side nozzles. Multiple hearth incinerators, historically developed to burn municipal wastewater treatment biosolids, rely on gravity and scrapers working in the upper edges of each hearth to transport the waste through holes from upper hotter hearths to lower cooler hearths. Heated upward moving off-gases are collected, monitored for chemical constituents, and treated as appropriate prior to release; the falling ash is collected, monitored for chemical constituents, and subsequently treated prior to ultimate disposal.

Most organic wastes generally can be incinerated using a multiple hearth configuration. Operating

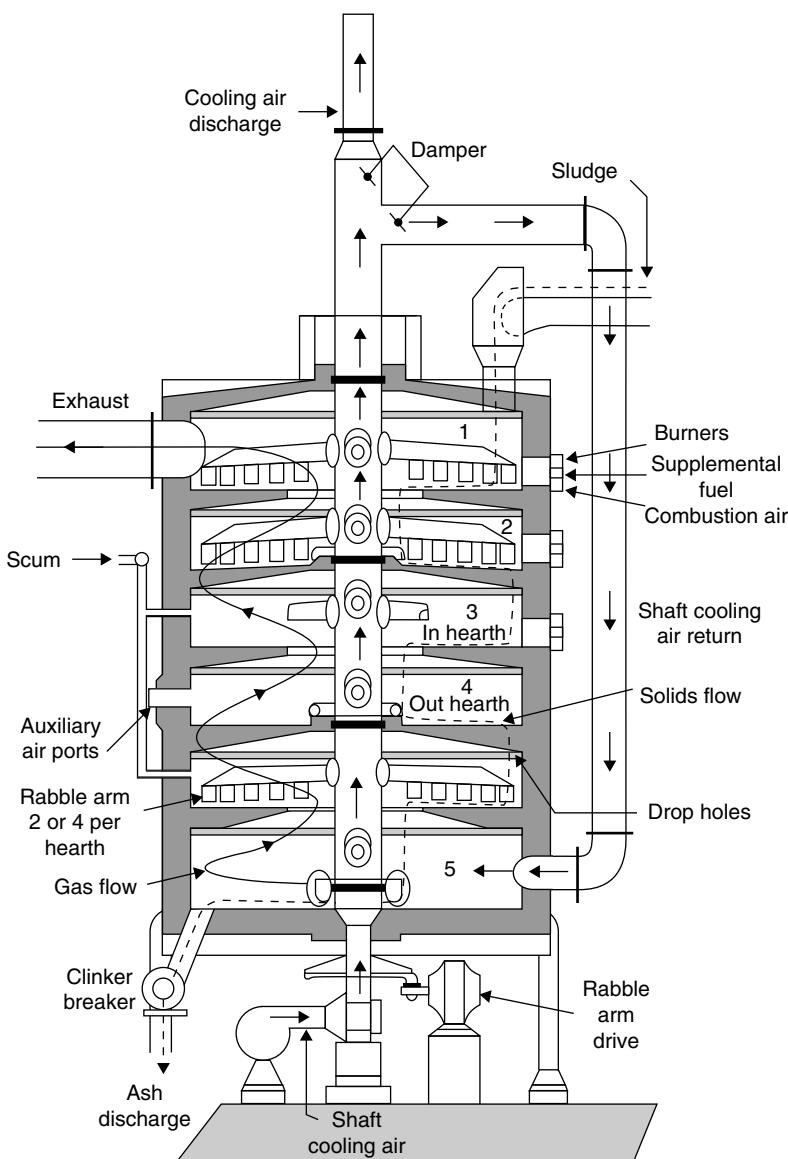


FIGURE 29.15 Multiple hearth incineration system. Ref. 27.

temperatures generally vary from 300 to 980 °C. These systems are designed with residence times of seconds if gases are fed into the chambers to several hours if solid materials are placed on the top hearth and allowed to eventually drop to the bottom hearth exiting as ash.

#### 29.4.5.3 Liquid Injection

Vertical or horizontal nozzles spray liquid hazardous wastes into liquid injection incinerators specially designed for the task or as a retrofit to one of the other incinerators discussed here. The wastes are atomized through the nozzles that match the waste being handled with the combustion chamber as determined in laboratory testing. The application obviously is limited to liquids that do not clog these nozzles, though some

success has been experienced with hazardous waste slurries. Operating temperatures generally vary from 650 to 1650 °C (1200–3000 °F). Liquid injection systems (Figure 29.16) are designed with residence times of fractions of seconds as off-gases, the upward moving off-gases are collected, monitored for chemical constituents, and treated as appropriate prior to release to the lower troposphere.

#### 29.4.5.4 Fluidized Bed

Contaminated feedstock is injected under pressure into a heated bed of agitated inert granular particles, usually sand, as the heat is transferred from the particles to the waste, and the combustion process proceeds as summarized in Figure 29.17. External heat is applied

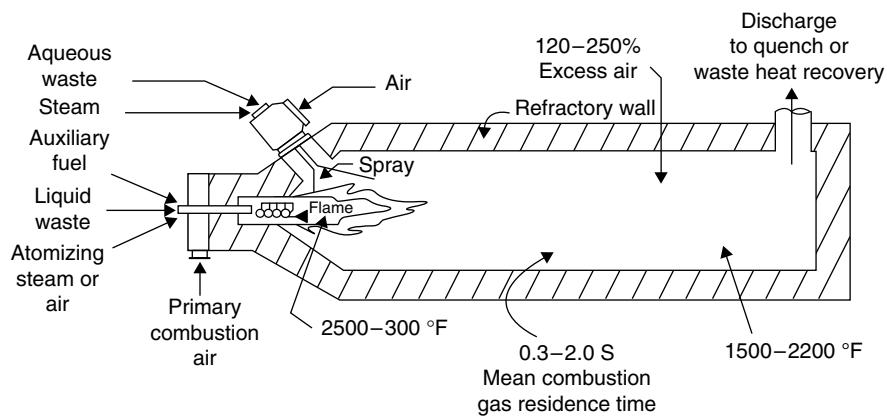


FIGURE 29.16 Prototype of liquid injection system. Ref. 27.

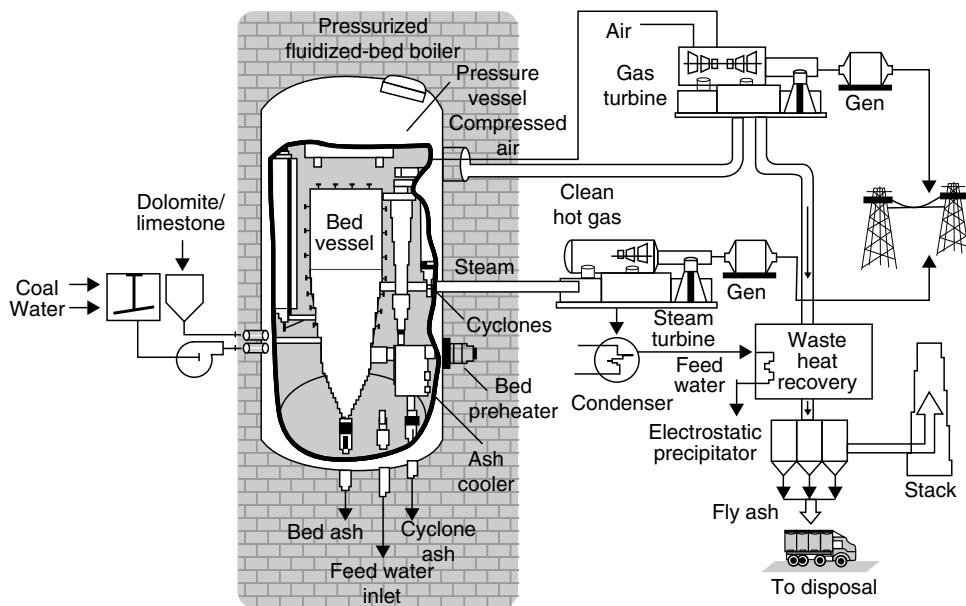


FIGURE 29.17 Pressurized fluidized bed system. US Department of Energy. TIDD PFBC demonstration project. 1999.

to the particle bed prior to the injection of the waste and continually is applied throughout the combustion operation as the situation dictates. Heated air is forced into the bottom of the particle bed and the particles become suspended among themselves during this continuous fluidizing process. The openings created within the bed permit the introduction and transport of the waste into and through the bed. The process enables the contaminant to come into contact with particles that maintain their heat better than, for example, the gases inside a rotary kiln. The heat maintained in the particles increases the time the contaminant is in contact with a heated element and thus the combustion process could become more complete with fewer harmful byproducts. Off-gases are collected, monitored for chemical constituents, and treated as appropriate prior to release, and the falling ash is collected, monitored for chemical

constituents, and subsequently treated prior to ultimate disposal.

Most organic wastes can be incinerated in a fluidized bed, while the system is best suited for liquids. Operating temperatures generally vary from 750 to 900 °C. Liquid injection systems are designed with residence times of fractions of seconds as off-gases, the upward moving off-gases are collected, monitored for chemical constituents, and treated as appropriate prior to release to the lower troposphere.

#### 29.4.5.5 Multiple Chamber

Contaminants are turned to a gaseous form on a grate in the ignition chamber of a multiple chamber system. The gases created in this ignition chamber travel through baffles to a secondary chamber where the actual combustion process takes place. Often the secondary

chamber is located above the ignition chamber to promote natural advection of the hot gases through the system. Heat may be added to the system in either the ignition chamber or the secondary chamber as required for specific burns.

The application of multiple chamber incinerators generally is limited to solid wastes with the waste entering the ignition chamber through an opened charging door in batch, not continuous, loading. Combustion temperatures typically hover near 540 °C for most applications. These systems are designed with residence times of minutes to hours for solid hazardous wastes as off-gases are collected, monitored for chemical constituents, and treated as appropriate prior to release to the lower troposphere. At the end of each burn period the system must be cooled so that the ash can be removed prior to monitoring for chemical constituents and subsequent treatment prior to ultimate disposal.

## 29.4.6 Destruction Removal

### 29.4.6.1 Calculating Destruction Removal

Federal hazardous waste incineration standards require that hazardous organic compounds meet certain destruction efficiencies. These standards require that any hazardous waste undergo 99.99% destruction of all hazardous wastes and 99.9999% destruction of extremely hazardous wastes like dioxins. Recall that destruction removal efficiency (DRE) is calculated as:

$$\text{DRE} = \frac{W_{\text{in}} - W_{\text{out}}}{W_{\text{in}}} \times 100 \quad (29.8)$$

where,  $W_{\text{in}}$  is the rate of mass of waste flowing into the incinerator and  $W_{\text{out}}$  is the rate of mass of waste flowing out of the incinerator.

For example, let us calculate the DRE if during a stack test, the mass of pentachlorodioxin is loaded into incinerator at the rate of 10 mg min<sup>-1</sup> and the mass flow rate of the compound measured downstream in the stack is 200 pg min<sup>-1</sup>. Is the incinerator up to code for the thermal destruction of this dioxin?

$$\begin{aligned} \text{DRE} &= \frac{W_{\text{in}} - W_{\text{out}}}{W_{\text{in}}} \times 100 \\ &= \frac{10 \text{ mg min}^{-1} - 200 \text{ pg min}^{-1}}{10 \text{ mg min}^{-1}} \times 100 \end{aligned}$$

Since 1 pg = 10<sup>-12</sup> g and 1 mg = 10<sup>-3</sup>, then 1 pg = 10<sup>-9</sup> mg. So

$$\begin{aligned} &\frac{10 \text{ mg min}^{-1} - 200 \times 10^{-9} \text{ mg min}^{-1}}{10 \text{ mg min}^{-1}} \times 100 \\ &= 999,999.98\% \text{ removal} \end{aligned}$$

Even if pentachlorodioxin is considered to be "extremely hazardous", this is better than the "rule of six nines" so the incinerator is operating up to code.

If we were to calculate the DRE during the same stack test for the mass of tetrachloromethane (CCl<sub>4</sub>) loaded into incinerator at the rate of 100 l min<sup>-1</sup> and the mass flow rate of the compound measured downstream is 1 ml min<sup>-1</sup>. Is the incinerator up to code for CCl<sub>4</sub>? This is a lower removal rate since 100 l are in and 0.001 are leaving, so the DRE = 99.999. This is acceptable, i.e. better removal efficiency than 99.99% by an order of magnitude, so long as CCl<sub>4</sub> is not considered an extremely hazardous compound. If it were, then it would have to meet the rule of six nines (it only has five).

By the way, both of these compounds are chlorinated. As mentioned, special precautions must be taken when dealing with such halogenated compounds, since even more toxic compounds than those being treated can end up being generated. Incomplete reactions are very important sources of environmental contaminants. For example, these reactions generate PICs, such as dioxins, furans, carbon monoxide (CO), polycyclic aromatic hydrocarbons (PAHs), and hexachlorobenzene. Thus, the formation of unintended byproducts is always a possibility with thermal systems. An extensive discussion can be found in Chapter 7, for example, on the various processes that can lead to the formation of dioxins and furans. In particular, see the thermal relationships in Table 7.5 and Figure 7.6.

## 29.4.7 Other Thermal Processes

### 29.4.7.1 Processes Other than Incineration

Incineration is frequently used to decontaminate soils with elevated concentrations of organic hazardous constituents. High-temperature incineration, however, may not be needed to treat soils contaminated with most volatile organic compounds (VOCs). Also, in waste feeds with heavy metals, high temperature incineration will likely increase the volatilization of some of these metals into the combustion flue gas (see Tables 29.9 and 29.10). High concentrations of volatile trace metal compounds in the flue gas pose increased challenges to air pollution control. Thus, other thermal processes, i.e. thermal desorption and pyrolysis, can provide an effective alternative to incineration.

When successful in decontaminating soils to the necessary treatment levels, thermally desorbing contaminants from soils have the additional benefits of lower fuel consumption, no formation of slag, less volatilization of metal compounds, and less complicated air pollution control demands. So, beyond monetary costs and ease of operation, a less energy (heat) intensive system can be more advantageous in terms of actual pollutant removal efficiency.

**TABLE 29.9** Conservative Estimates of Heavy Metals and Metalloids Partitioning to Flue Gas as a Function of Solids Temperature and Chlorine Content\*

Metal or Metalloid	871 °C		1093 °C	
	Cl = 0%	Cl = 1%	Cl = 0%	Cl = 1%
Antimony	100%	100%	100%	100%
Arsenic	100%	100%	100%	100%
Barium	50%	30%	100%	100%
Beryllium	5%	5%	5%	5%
Cadmium	100%	100%	100%	100%
Chromium	5%	5%	5%	5%
Lead	100%	100%	100%	100%
Mercury	100%	100%	100%	100%
Silver	8%	100%	100%	100%
Thallium	100%	100%	100%	100%

\* The remaining percentage of metal is contained in the bottom ash. Partitioning for liquids is estimated at 100% for all metals. The combustion gas temperature is expected to be 100–1000 °F higher than the solids temperature.

Source: Ref. 32.

#### 29.4.7.2 Pyrolysis

Pyrolysis is the process of chemical decomposition induced in organic materials by heat in the absence of oxygen. It is practicably impossible to achieve a completely oxygen-free atmosphere, so pyrolytic systems run with less stoichiometric quantities of oxygen. Because some oxygen will be present in any pyrolytic

system, there will always be a small amount of oxidation. Also, desorption will occur when volatile or semi-volatile compounds are present in the feed.

During pyrolysis<sup>5</sup> organic compounds are converted to gaseous components, along with some liquids, as coke, i.e. the solid residue of fixed carbon and ash. CO, H<sub>2</sub>, CH<sub>4</sub>, and other hydrocarbons are produced. If these gases cool and condense, liquids will form and leave oily tar residues and water with high concentrations of TOC. Pyrolysis generally takes place well above atmospheric pressure at temperatures exceeding 430 °C. The secondary gases need their own treatment, such as by a secondary combustion chamber, by flaring, and partial condensation. Particulates must be removed by additional air pollution controls, e.g. fabric filters or wet scrubbers.

Conventional thermal treatment methods, such as rotary kiln, rotary hearth furnace, or fluidized bed furnace, are used for waste pyrolysis. Kilns or furnaces used for pyrolysis may be of the same design as those used for combustion (i.e. incineration) discussed earlier, but operate at lower temperatures and with less air than in combustion.

The target contaminant groups for pyrolysis include semivolatile organic compounds (SVOCs), including pesticides, PCBs, dioxins, and PAHs. It allows for separating organic contaminants from various wastes, including those from refineries, coal tar, wood preservatives, creosote-contaminated and hydrocarbon-contaminated soils, mixed radioactive and hazardous wastes, synthetic rubber processing, and paint and coating processes. Pyrolysis systems may be used to treat a variety of

**TABLE 29.10** Metal and Metalloid Volatilization Temperatures

Metal or Metalloid	Without Chlorine		With 10% Chlorine	
	Volatility Temperature (°C)	Principal Species	Volatility Temperature (°C)	Principal Species
Chromium	1613	CrO <sub>2</sub> /CrO <sub>3</sub>	1611	CrO <sub>2</sub> /CrO <sub>3</sub>
Nickel	1210	Ni(OH) <sub>2</sub>	693	NiCl <sub>2</sub>
Beryllium	1054	Be(OH) <sub>2</sub>	1054	Be(OH) <sub>2</sub>
Silver	904	Ag	627	AgCl
Barium	841	Ba(OH) <sub>2</sub>	904	BaCl <sub>2</sub>
Thallium	721	Tl <sub>2</sub> O <sub>3</sub>	138	TiOH
Antimony	660	Sb <sub>2</sub> O <sub>3</sub>	660	Sb <sub>2</sub> O <sub>3</sub>
Lead	627	Pb	-15	PbCl <sub>4</sub>
Selenium	318	SeO <sub>2</sub>	318	SeO <sub>2</sub>
Cadmium	214	Cd	214	Cd
Arsenic	32	As <sub>2</sub> O <sub>3</sub>	32	As <sub>2</sub> O <sub>3</sub>
Mercury	14	Hg	14	Hg

Source: Ref. 33.

organic contaminants that chemically decompose when heated (i.e. “cracking”). Pyrolysis is not effective in either destroying or physically separating inorganic compounds that coexist with the organics in the contaminated medium. Volatile metals may be removed and transformed but their mass balance, of course, will not be changed.

#### 29.4.7.3 Emerging Thermal Technologies

Other promising thermal processes include high-pressure oxidation and vitrification.<sup>6</sup> High-pressure oxidation combines two related technologies, i.e. wet air oxidation and supercritical water oxidation, which combine high temperature and pressure to destroy organics. Wet air oxidation can operate at pressures of about 10% of those used during supercritical water oxidation, an emerging technology that has shown some promise in the treatment of PCBs and other stable compounds that resist chemical reaction. Wet air oxidation has generally been limited to conditioning of municipal wastewater sludges, but can degrade hydrocarbons (including PAHs), certain pesticides, phenolic compounds, cyanides, and other organic compounds. Oxidation may benefit from catalysts.

Vitrification uses electricity to heat and destroy organic compounds and immobilize inert contaminants. A vitrification unit has a reaction chamber divided into two sections: the upper section to introduce the feed material containing gases and pyrolysis products, and the lower section consisting of a two-layer molten zone for the metal and siliceous components of the waste. Electrodes are inserted into the waste solids, and graphite is applied to the surface to enhance its electrical conductivity. A large current is applied, resulting in rapid heating of the solids and causing the siliceous components of the material to melt as temperatures reach about 1600 °C. The end product is a solid, glass-like material that is very resistant to leaching.

#### 29.4.8 Indirect Air Impacts

In addition to direct treatment, air pollution is also a concern for other means of treating hazardous wastes, especially when these wastes are stored or treated more passively, such as in a landfill or aeration pond. Leachate collection systems (see Figure 29.18) provide a way to collect wastes that can then be treated. However, such “pump and treat” systems can produce air pollutants. Actually, this is often intentional. For example, groundwater is treated by drilling recovery wells to pump contaminated groundwater to the surface. Commonly used groundwater treatment approaches include air stripping, filtering with granulated activated carbon (GAC), and air sparging. Air stripping transfers volatile compounds from water to air (see Figure 29.19). Groundwater is allowed to drip downward in a tower filled with a permeable material through which a stream of air flows upward. Another method bubbles pressurized air through contaminated water in a tank. The air leaving the tank (i.e. the off-gas) is treated with methods described in Chapter 32 for removing gaseous pollutants. Filtering groundwater with GAC entails pumping the water through the GAC to trap the contaminants. In air sparging, air is pumped into the groundwater to aerate the water. Most often, a soil venting system is combined with an air sparging system for vapor extraction, with the gaseous pollutants treated, as in air stripping.

Regulatory agencies often require two or three pairs of these systems as design redundancies to protect the integrity of a hazardous waste storage or treatment facility. A primary leachate collection and treatment system must be designed like the bottom of the landfill bathtub. This leachate collection system must be graded to promote the flow of liquid within the landfill from all points in the landfill to a central collection point(s) where the liquid can be pumped to the surface for subsequent monitoring and treatment. Crushed stone and perforated pipes are used to channel the liquid along the

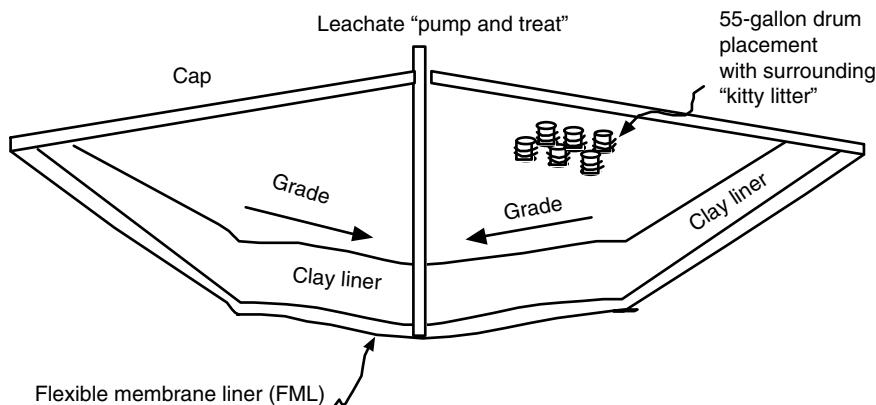


FIGURE 29.18 Leachate collection system for a hazardous waste landfill. Ref. 28.

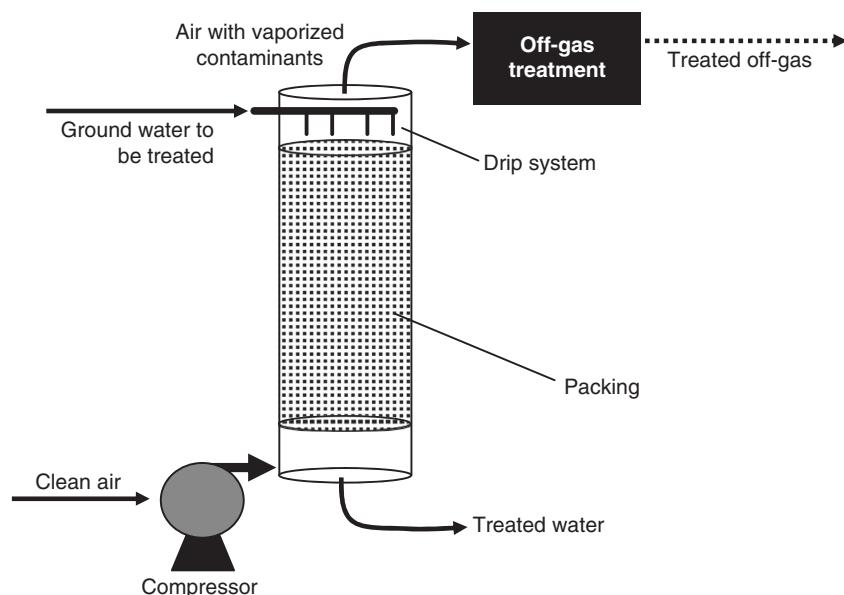


FIGURE 29.19 Schematic diagram of air stripping system to treat volatile compounds in water.

top layer of this compacted clay liner to the pumping locations.

Thus, directly treating hazardous wastes physically and chemically, as with thermal systems and indirectly controlling air pollutants as when gases are released from pump and treat systems require a comprehensive approach. Otherwise, we are merely moving the pollutants to different locations or even making matters worse by either rendering some contaminants more toxic or exposing receptors to dangerous substances.

## 29.5 MOBILE EMISSION SOURCES

A mobile source of air pollution can be defined as one capable of moving from one place to another under its own power. According to this definition, an automobile is a mobile source and a portable asphalt batching plant is not. The regulatory definition seems to center around the internal combustion engine. Generally, mobile sources imply transportation, but sources such

as construction equipment, gasoline-powered lawn mowers, and gasoline-powered tools are included in this category.<sup>13</sup>

Mobile sources therefore consist of many different types of vehicles, powered by engines using different cycles, fueled by a variety of products, and emitting varying amounts of both simple and complex pollutants. Table 29.11 includes the more common mobile sources.

The predominant mobile air pollution source in all industrialized countries of the world is the motor vehicle, powered by a four-stroke cycle (Otto cycle) engine fuel with gasoline. In the United States, over 253 million automobiles were registered for use.<sup>13</sup> When one considers the present reliability, cost, and life expectancy of the internal combustion engine, it is not difficult to see why it has remained so popular. A modern automotive engine traveling 100,000 km will have about  $2.5 \times 10^8$  power cycles.

The emissions from a gasoline-powered vehicle come from many sources.

TABLE 29.11 Main Pollutants Emitted by Different Internal Combustion Engines

Power Plant Type	Fuel	Major Emissions	Vehicle Type
Otto cycle	Gasoline	HC, CO, CO <sub>2</sub> , NO <sub>x</sub>	Auto, truck, bus, aircraft, marine, motorcycle, tractor
Two-stroke cycle	Gasoline	HC, CO, CO <sub>2</sub> , NO <sub>x</sub>	Motorcycle, outboard motor particulate
Diesel	Diesel oil	NO <sub>x</sub> , particulate, SO <sub>x</sub> , CO <sub>2</sub>	Auto, truck, bus, railroad, marine, tractor
Gas turbine (jet)	Turbine	NO <sub>x</sub> , particulate, CO <sub>2</sub>	Aircraft, marine, railroad
Steam	Oil, coal	NO <sub>x</sub> , SO <sub>x</sub> , particulate, CO <sub>2</sub>	Marine

With time, motor vehicle emission standards have become increasingly stringent for the typical air pollutants, especially hydrocarbons, NO<sub>x</sub>, CO, and PM. With most of today's automobiles using unleaded gasoline, lead emissions are no longer a major concern in the West, but are still a problem in numerous other parts of the world. Currently, certain countries limit emissions of these pollutants from crankcases, fuel tanks and, especially, exhaust from engines. In the U.S., these emission standards for mobile sources have become increasingly lowered. The so-called Tier 2 standards are presently in effect (see [Table 29.12](#)), but newer standards, i.e. the Tier 3 program will soon replace them.

Beginning in 2017, Tier 3 would set new vehicle emissions standards and lower the sulfur (S) content of gasoline. These emission standards will treat the vehicle and its fuel as an integrated system. That is, the proposed vehicle standards would reduce both tailpipe and evaporative emissions from passenger cars, light-duty trucks, medium-duty passenger vehicles, and some heavy-duty vehicles.

The proposed gasoline S standard is expected to improve the on-board emission control systems for both existing and new vehicles, thus increasing the likelihood of meeting more stringent vehicle emissions standards. Removing S allows the vehicle's catalyst to work more efficiently. Lower sulfur gasoline also facilitates the development of some lower-cost technologies to improve fuel economy and decrease GHG emissions. The proposed tailpipe standards include different phase-in schedules that vary by vehicle class but generally phase in between model years 2017 and 2025. In addition to the gradual phase-in schedules, other proposed flexibilities include credits for early compliance and the ability to offset some higher-emitting vehicles with extra-clean models.<sup>15</sup>

The proposed fuel S standards that are part of Tier 3 not only address mobile sources, but address emissions at stationary sources, e.g. they include an averaging, banking, and trading (ABT) program that would allow refiners and importers to spread out their investments through an early credit program and rely on ongoing nationwide averaging to meet the S standard. The ABT and other means of meeting implementing standards for air toxics are discussed in the next section.

## **29.6 MEANS OF IMPLEMENTING EMISSION STANDARDS**

The most common rationale for developing emission limits for stationary sources is the application of the best practicable means for control. Under this rationale, the degree of emission limitation achievable at the best designed and operated installation in a category sets

the emission limits for all other installations of that category. As new technology is developed, what was the best practicable means in 1993 is likely not still the best attainable in 2013. This moving target means must be provided administratively to allow the facility which complied with a best practicable means limit to be considered in compliance for a reasonable number of years thereafter. It is important to note that best practicable means limits are set without regard to present or background air quality or the air quality standards for the specific pollutants emitted, the number and location of sources affected by the limit, and the meteorology or topography of the area in which they are located. However, an additional limit on minimum stack height, or buffer zone, based on these noted factors may be coupled with a best practicable means limit on mass or emission.

The other major rationales for developing emission limits have been based on some or all of the noted factors—air quality, air quality standards, number and location of sources, meteorology, and topography. These include the rollback approach, which involves all these factors except source location, meteorology, and topography; and the single-source mathematical modeling approach, which considers only the air quality standard and meteorology, ignoring the other factors listed.

Some variants of best practicable means were spelled out in the US Clean Air Act of 1977. One is the requirement that Best Available Control Technology (BACT) for a specific pollutant be employed on new "major sources" that are to be located in an area that has attained the National Ambient Air Quality Standard (NAAQS) for that pollutant. The BACT was also required for pollutants for which there is no NAAQS (e.g. total reduced sulfur (TRS), for which emission limits are specified by a federal New Source Performance Standard (NSPS)). BACT must be at least as stringent as NSPS but is determined on a case-by-case basis.

Another variant is the lowest achievable emission rate (LAER) for a specific pollutant required for a new source of that pollutant to be located in a nonattainment area (i.e. one which has not attained the NAAQS for that pollutant). LAER is the lowest emission rate allowed or achieved anywhere without regard to cost or energy usage. LAER is intended to be more stringent than BACT or NSPS and is also determined on a case-by-case basis.

This changed with the passage of the Clean Air Act Amendments of 1990 (CAA90) and the subsequent regulations. The Maximum Achievable Control Technology (MACT) standards continued for some years, but incrementally have been phased-out in favor of standards to address the margin of risk that remained from the technology-based standards. This is known as residual risk. Section 112(f) of the CAA90 directs the U.S. Environmental Protection Agency (U.S. EPA) to

TABLE 29.12 Emission Limits for Light-duty Vehicles

Engine Type and Pollutant	Prior to Control <sup>II</sup> 1968–1969	1968–1969 1970–1971	1970–1971 1972	1973–1974	1975–1976	1977–1979	1980	1981	1982–1986	1987–1993	Tier 1 <sup>III</sup> 1994–2003 <sup>§</sup>	Interim Tier 2 <sup>III</sup> 2004–2006	Tier 2 <sup>III</sup> 2007+
Gasoline HC (total)	11	§§	2.2	3.4	3.4	1.5	1.5	0.41	0.41	0.41	0.41	0.41	0.41
NMHC	#	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	0.25	(0.31)	¶¶
NMOG	#	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	(0.156)
CO	80	§§	23	39	39	15	15	7.0	3.4	3.4	3.4	(4.2)	3.4
Cold-temp. CO <sup>¶</sup>	#	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	10	¶¶	¶¶
NO <sub>x</sub>	4	¶¶	¶¶	¶¶	¶¶	3.0	3.1	2.0	2.0	1.0	1.0	0.4	(0.6)
Particulates	#	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	0.08	(0.10)	0.08
Formaldehyde	#	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	0.015	(0.018)
Diesel HC (total)	11	¶¶	¶¶	¶¶	¶¶	1.5	1.5	0.41	0.41	0.41	0.41	(¶¶)	¶¶
NMHC	#	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	0.25	(0.31)	¶¶
NMOG	#	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	(0.156)
CO	80	¶¶	¶¶	¶¶	¶¶	15	15	7.0	3.4	3.4	3.4	(4.2)	3.4
NO <sub>x</sub>	4	¶¶	¶¶	¶¶	¶¶	3.1	2.0	2.0	1.0	1.0	1.0	(1.25)	0.6
Particulates	#	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	¶¶	0.08	(0.10)	0.02

Formaldehyde #	1968 7-mode	1968 CVS-72	1968 CVS-72	1968 CVS-75	1968 (0.018)	0.015	(0.018)								
Test procedure*	7-mode	CVS-72	CVS-72	CVS-75											
Useful life**, intermediate <sup>§,  </sup> (full)	1968 5 years/ 50,000 miles														
Useful life, intermediate <sup>§,  </sup> (full)	5 years/ 50,000 miles	5 years/ 100,000 miles	10 years/ 100,000 miles	10 years/ 100,000 miles	10 years/ 100,000 miles	10 years/ 100,000 miles	10 years/ 100,000 miles								

\* The test procedure for measuring exhaust emissions has changed several times over the course of vehicle emissions regulations. The 7-mode procedure was used through model year 1971 and was replaced by the CVS-72 procedure beginning in model year 1972. The CVS-75 procedure became the test procedure as of model year 1975. While it may appear that the total HC and CO standards were relaxed in 1972–74, these standards were actually more stringent due to the more stringent nature of the CVS-72 test procedure. Additional standards for CO and composite standards for NMHC and NO<sub>x</sub> tested under the new Supplemental Federal Test Procedure will be phased-in beginning with model year 2000; these standards are not shown in this table.

\*\* All emissions standards must be met for a useful life of 5 years/50,000 miles. Beginning with model year 1994, a second set of emissions standards must also be met for a full useful life of 10 years/100,000 miles; these standards are shown in parentheses. Tier one exhaust standards were phased-in during 1994–96 at a rate of 40%, 80%, and 100%, respectively.

† The cold CO emissions standard is measured at 20 F (rather than 75 F) and is applicable for a 5 year/50,000 mile useful life.

‡ The “Prior to control” column reports emissions estimates of a typical newly manufactured car in the years before exhaust emissions certification standards were implemented.

# No estimate available.

\*\* Manufacturers can opt to certify vehicles for a full useful life of 15 years/150,000 miles and have either (1) intermediate useful life standards waived or (2) receive additional NO<sub>x</sub> credits.

§ In 1968–1969, exhaust emissions standards were issued in parts per million rather than grams per mile and are, therefore, incompatible with this table.

|| No standard has been set.

||| The term “tier” refers to a level of standards and is associated with specific years. Interim Tier two refers to an intermediate level of standards that move manufacturers toward compliance with Tier 2 standards. Interim Tier two and Tier 2 standards are established as “bins”. Each bin is a set of standards for NO<sub>x</sub>, CO, NMHC, formaldehyde, and particulate matter; HC and NMHC standards are dropped for Tier two and Interim Tier 2. Manufacturers may certify any given vehicle family to any of the bins available for that vehicle class as long as the resulting sales-weighted corporate average NO<sub>x</sub> standard is met for the full useful life of the vehicle. The Tier two corporate average NO<sub>x</sub> standard is 0.07 g mile<sup>-1</sup>. Interim corporate-based average NO<sub>x</sub> standards are based on vehicle type. The interim sales-weighted average for light-duty vehicles (LDVs) is 9.3 g mile<sup>-1</sup>. For LDVs, Tier 2 standards will be phased-in at a rate of 25% in 2004, 50% in 2005, 75% in 2006, and 100% in 2007. During this period, all LDVs not meeting the Tier 2 standards must meet Interim Tier 2 standards.

Source: 40 CFR 86, Subpart A (July 1, 2000); Federal Register. 65(28):6851–6858.

prepare a report to Congress on the methods to be used to address this residual risk from sources that emit hazardous air pollutants (HAPs) have been promulgated and applied. The U.S. EPA presents a discussion of how it intends to provide the CAAA90's mandate to "provide an ample margin of safety to protect public health" or to set more stringent standards, if necessary, "to prevent, taking into consideration costs, energy, safety, and other relevant factors, an adverse environmental effect". This includes both human and ecological risk. The U.S. EPA published the Residual Risk Report to Congress in March 1999.

All of the MACT regulations for 174 industry source categories have been reviewed to decrease emissions of toxic air pollutants listed in the Clean Air Act (see Table 5.2 in Chapter 5 for the nearly 200 listed compounds). The 1989 National Emission Standard for Hazardous Air Pollutants (NESHAPs) for benzene<sup>1</sup> presented the following risk management framework for cancer risk, which reflects the two-step approach suggested by the court. The benzene rule preamble states that in determining acceptable risk:

The Administrator believes that an MIR [maximum individual risk] of approximately 1 in 10 thousand should ordinarily be the upper-end of the range of acceptability. As risks increase above this benchmark, they become presumptively less acceptable under Section 112, and would be weighed with the other health risk measures and information in making an overall judgment on acceptability. Or, the Agency may find, in a particular case, that a risk that includes MIR less than the presumptively acceptable level is unacceptable in light of the other health risk factors.

The Risk and Technology Review (RTR) is a combined effort to evaluate both risk and technology as required by CAAA90 after the application of MACT standards. Section 112(f)(2) directs the U.S. EPA to conduct risk assessments on each source category subject to MACT standards and to determine if additional standards are needed to reduce residual risks. Section 112(d)(6) of the CAA requires the U.S. EPA to review and revise the MACT standards, as necessary, taking into account developments in practices, processes and control technologies.<sup>16</sup>

The maximum individual risk (MIR), the distribution of risks in the exposed population, incidence, the science policy assumptions and uncertainties associated with risk measures, and the weight of evidence that a pollutant is harmful to health are all key determinants used to the estimate safety and risk posed by a HAP. To ensure protection of public health and the environment, the Section 112(f) requires a human health risk and adverse environmental effects based "needs test" in the second regulatory phase of the air toxics program. As mentioned, this residual risk standard setting considers the need for additional national standards

on stationary emission sources following regulation under Section 112(d) to provide an ample margin of public safety, and also mandates that the U.S. EPA determine whether residual risk standards are necessary to prevent adverse environmental effects, taking into consideration "costs, energy, safety, and other relevant factors" in deciding what level is protective. Adverse environmental effect is defined in Section 112(a)(7) as "any significant and widespread adverse effect, which may reasonably be anticipated, to wildlife, aquatic life, or other natural resources, including adverse impacts on populations of endangered or threatened species or significant degradation of environmental quality over broad areas".

In 2005 the U.S. EPA issued final amendments to reduce emissions of toxic air pollutants, or air toxics, from coke oven batteries; these were the first of a series of emissions reductions under the new residual risk standards. Across the industry, this rule will require reductions of allowable emissions from 11.3 tons per year under the 1993 MACT to 9.8 tons per year under the amendments. This rule was also designed to ensure that the affected batteries do not increase their emissions back to the levels allowed in 1993. The final amendments include more stringent requirements for certain processes at several coke oven batteries to address health risks remaining after implementing EPA's October 1993 air toxics emission MACT standards.

The final amendments also include requirements for new or reconstructed coke oven batteries that reflect improvements in emission control practices that have occurred in the years since the 1993 MACT standards. This applies to coke oven emissions from nine batteries at five coke plants for which the 1993 MACT standard applied. There are approximately 14 other coke oven plants in the country that are not affected by this rule because they chose to install more stringent controls than the MACT the LAER, beginning in 1993. Because these LAER batteries opted to reduce their emissions by more than the 1993 MACT required, they do not have to comply with residual risk rule until the year 2020. The final amendments apply to charging, leaks, and bypass stacks at coke oven batteries. Emissions from these processes occur at the start of the process of turning coal into coke, primarily as the coke ovens are heating up. Thus, residual risk measures focus in a number of areas, beyond technology.

When owners wish to build a new source which will add a certain amount of a specific pollutant to an area that is in nonattainment with respect to that pollutant, they must, under US federal regulations, document a reduction of at least that amount of the pollutant from another source in the area. They can effect this reduction, or "offset", as it is called, in another plant they

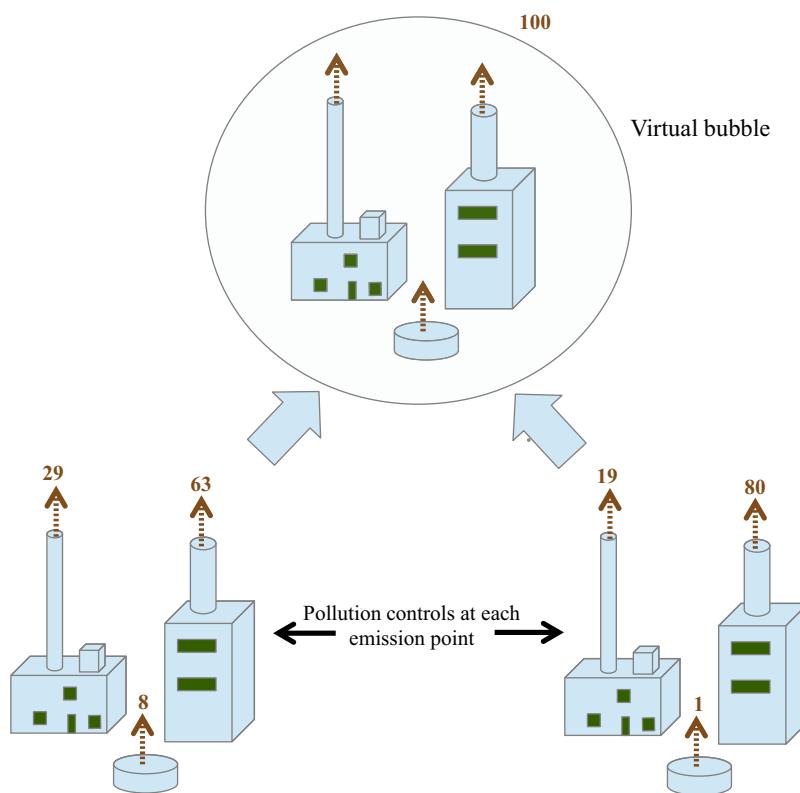
own in the area or can shut down that plant. However, if they do not own another such plant or do not wish to shut down or effect such reduction in a plant they own, they can seek the required reduction or offset from another owner. Thus, such offsets are marketable credits that can be bought, sold, traded, or stockpiled ("banked") as long as the state or local regulatory agency legitimizes, records, and certifies these transactions. The new source will still have to meet NSPS, BACT or MACT, and/or LAER standards, whichever are applicable.

### 29.6.1 Averaging, Banking, and Trading Emissions

Emissions trading programs generally can be accomplished by netting, offsets, bubbles, and banking. Netting allows large new sources and major modifications of existing sources to be exempted from certain review procedures if existing emissions elsewhere in the same facility are reduced by a sufficient amount. An offsets allows a major new source to locate in an area that does not attain a given air quality standard, i.e. a non-attainment area, if emissions from an existing source are decreased by at least as much as the new source would contribute, after installation of stringent controls. A bubble allows a regulated entity to combine the limits for several different sources into one

combined limit and to determine compliance based on that aggregate limit instead of from each source individually. The name alludes to an imaginary "bubble" placed over the several sources. Banking allows a regulated entity to accumulate emission credits for future use or sale if it takes actions to lower emissions below the relevant standard. These approaches all have a common objective of flexibility to comply with traditional source-specific command and-control standards, but achieving or providing even less emissions to improve local air quality.<sup>16</sup>

When a new stationary source has been added to a group of existing stationary sources under the same ownership in the same industrial complex, the usual practice has been to require the new source independently to meet the offset, NSPS, BACT, and/or LAER, disregarding the other sources in the complex. Under the more recent "bubble concept" (Figure 29.20) adopted by some states with the approval of the U.S. EPA, the addition of the new source is allowed, whether or not it meets NSPS, BACT, or LAER, provided the total emission of the relevant regulated pollutants from the total complex is decreased. This can be accomplished by obtaining the required offset from one or more of the other sources within the complex, by shutdown, or by improvement in control efficiency. The bubble concept has been subject to litigation and may require a ruling or challenge to make it acceptable.



**FIGURE 29.20 Bubble concept.** This pollution control concept places an imaginary bubble over an entire industrial plant, evaluating emissions from the facility as a whole instead of requiring control point-by-point on emission sources. Numbers represent emissions from individual sources, some of which can be fugitive sources, and from the entire industrial plant. This hypothetical complex would produce 100 units of pollution in any of the three scenarios depicted. (For color version of this figure, the reader is referred to the online version of this book.)

## 29.6.2 Fugitive and Secondary Emission Sources

To estimate the potential for emission of a new source or source complex, it is necessary to consider two other source categories, "fugitive" and "secondary" sources. Fugitive emissions are those from other than point sources, such as unpaved plant roads, outdoor storage piles swept by the wind, and surface mining. Secondary sources are those small sources with emissions of a different character from those of a major source, necessary for the operation of the major source, or source complex.

## 29.6.3 Indirect Sources

A facility, building, structure, installation, or combination of these that generates or attracts mobile source activity is known as an indirect source of air pollution. The very existence of such a source results in emissions of any pollutant (or the precursor of an air pollutant, e.g. hydrocarbons and NO<sub>x</sub> for ground-level O<sub>3</sub>) for which there is a state ambient air quality standard. Examples include parking areas of shopping malls, sports arenas, and other facilities that attract large numbers of motor vehicles, frequently arriving and leaving over relatively short periods of time. Of somewhat similar character are traffic interchanges, as at an intersection of major highways, each highway being a line source in its own right.

## 29.6.4 Proportional Emission Predictions

The proportional modeling or rollback approach assumes that emissions and atmospheric concentrations are proportional and linearly-related, i.e. that a given percentage reduction in emission will result in a similar percentage reduction in atmospheric concentrations. This is most likely a valid assumption for a nonreactive gas such as carbon monoxide, whose principal source is the automobile, however, it is not recommended for many pollutants and/or those with more complicated and complex physics and chemistry, e.g. ground-level O<sub>3</sub>.<sup>e</sup> The simple rollback model is

$$R = \frac{g(P) - D}{g(P) - B} \times 100 \quad (29.9)$$

Where,  $R$  is the required percentage reduction in emission,  $P$  is the present air quality,  $D$  is the air quality standard,  $B$  is the background concentration, and  $g$  is the growth factor in emissions (e.g.  $g$  is projected to a year

in the future when emissions are expected to apply to all vehicles on the road).

The basic steps<sup>18</sup> for the rollback model are:

1. Determine representative monitoring station(s) and the design value;
2. Determine background as the lowest pollutant concentration value recorded at an upwind monitoring location on the same day or during the same time period;
3. Prepare a micro-scale inventory of the sources that emit the pollutant for the time period the monitor measured;
4. Calculate the percentage for each source based upon the entire inventory;
5. Calculate the relative contribution from each source to the concentration measured for the time period;
6. Estimate the anticipated increase or decrease in emissions from each source;
7. Apply the same percentage of increase or decrease in emissions from each source to the relative contribution calculated for the same source; and
8. Calculate the anticipated ambient concentration after source emissions change.

As mentioned, rollback is a substantial oversimplification of the processes involved in air pollution, so basing emission reduction on rollback is fraught with error. Indeed, proportional modeling is mentioned in the U.S. air quality modeling only for PM and lead (Pb). Proportional models are not recommended for PM screening analysis, unless such techniques are used in conjunction with receptor modeling. Refined models are recommended for PM<sub>10</sub>. However, where possible, particle size, gas-to-particle formation, and their effect on ambient concentrations may be considered. For point sources of small particles and for source-specific analyses of complicated sources, the appropriate recommended steady-state plume dispersion model should be used. Receptor models have proven useful for helping validate emission inventories and for corroborating source-specific impacts estimated by dispersion models. The Chemical Mass Balance (CMB) model is useful for apportioning impacts from local sources. Other receptor models, e.g. the Positive Matrix Factorization (PMF) model and Unmix, which do not have some of CMB's constraints, have also been applied. In regulatory applications, dispersion models have been used in conjunction with receptor models to attribute source (or source category) contributions.<sup>7</sup>

For lead (Pb) an entire major urban area or to model areas without significant sources of Pb emissions, as a

<sup>e</sup> Preferred methods include dispersion modeling, source/receptor models such as the Chemical Mass Balance (CMB) models, and advanced regional models (e.g. the Urban Airshed Model; link: <http://www.epa.gov/scram001/photochemicalindex.htm>).

minimum a proportional model may be used for air quality analysis. However, urban or other dispersion models are encouraged in these circumstances where the use of such models is feasible. In modeling the effect of traditional line sources (such as a specific roadway or highway) on lead air quality, dispersion models applied for other pollutants can be used.<sup>19</sup>

### 29.6.5 Fuel Standards

To reduce emissions from fuel-burning sources, one can limit the sulfur, ash, or volatile content of fuels.<sup>4</sup> The U.S. EPA required major gasoline retailers to begin to sell one grade of unleaded gasoline by July 1, 1974. This mandate was primarily focused on protecting emissions control systems (e.g. catalytic converters). It was at this time that the working definition of "unleaded" gasoline was to mean "gasoline containing not more than 0.05 g of lead per gallon and not more than 0.005 g of phosphorus per gallon" (38FR1255, January 10, 1973). The major Pb species was tetraethyl lead (TEL). The agency also called for the gradual phase-out of leaded gasoline. The schedule for reduction of lead content in automobile gasoline was 1.7 g per gallon ( $\text{g gal}^{-1}$ ) in 1975, to 1.4  $\text{g gal}^{-1}$  in 1976, 1.0  $\text{g gal}^{-1}$  in 1977, 0.8  $\text{g gal}^{-1}$  in 1978, and 0.5  $\text{g gal}^{-1}$  in 1979 (38FR33741, December 6, 1973). Subsequent regulations reduced the allowable lead content to 0.1  $\text{g gal}^{-1}$  in 1986 (50FR9397, March 7, 1985), and prohibited leaded gas use after 1995 (61FR3837, February 2, 1996). The EPA established a limit of 1.1  $\text{g gal}^{-1}$  for the content of leaded gasoline beginning on July 1, 1985, 0.5  $\text{g gal}^{-1}$  after July 1, 1985 and  $\text{g gal}^{-1}$  after January 1, 1986. An EPA program to allow trading in lead credits among refiners facilitated this schedule of lead reduction. On July 1, 1983 EPA allowed refiners and importers of gasoline to trade lead reduction credits to meet the limit for the average lead content of gasoline. Refiners and importers that reduced the average lead content of their gasoline below the EPA limit generated credits that could be sold to refiners or importers that exceeded the limit. Once the limit for the average content of leaded gasoline reached 0.1  $\text{g gal}^{-1}$ , trading was no longer allowed because of concern that gasoline with less than 0.1  $\text{g gal}^{-1}$  could cause excessive valve seat wear in older vehicles. In 1985 EPA allowed refiners to bank lead credits for subsequent use before the end of 1987.<sup>20</sup>

Many other countries have imposed similar bans and phase-outs of TEL. In most industrialized countries, a phase-out of TEL from motor fuels was completed by the early 2000s. Technological advances have helped, e.g. in automotive engineering and petroleum chemistry. Safer methods for making higher octane blending stocks ameliorated the need for TEL, as did other antiknock additives of varying toxicity including metallic

compounds, e.g., methylcyclopentadienyl manganese tricarbonyl (MMT, discussed earlier in the chapter and in Chapter 13); and oxygenating compounds, e.g. methyl tertiary-butyl ether (MTBE, discussed in Chapter 3).<sup>21</sup> As of June 2011, unleaded automotive gasoline is available almost universally throughout the world and the only countries in which leaded gasoline is the only type available are Burma and Afghanistan; Leaded gasoline also remains available in Algeria, Georgia, Iraq, North Korea, and Yemen.<sup>22</sup>

## 29.7 AIR TOXICS EMISSIONS

Hazardous air pollutants are known in most air pollution control communities as toxic air pollutants or air toxics. These are the pollutants that cause or are strongly suspected to cause cancer or other serious health effects, including reproductive and developmental effects or birth defects. They are also often associated with adverse environmental and ecological effects. The Clean Air Act Amendments of 1990 require the US Environmental Protection Agency (EPA) to control 188 air toxics (see Table 5.2 in Chapter 5). Examples of toxic air pollutants include benzene, which is found in gasoline; perchloroethylene, which is emitted from some dry cleaning facilities; and methylene chloride, which is used as a solvent and paint stripper by a number of industries.

The Clean Air Act allows for petitions to modify the list (e.g. in 2006, caprolactam, hydrogen sulfide, and methyl ethyl ketone were undergoing modification).

Most air toxics originate from human-made sources, including mobile and stationary sources, similar to the criteria pollutants discussed in this chapter. However, many are predominantly or nearly exclusively indoor air pollutants.

Two types of stationary sources routinely emit air toxics:

- Major sources* emit 10 tons per year of any of the listed toxic air pollutants, or 25 tons per year of a mixture of air toxics. Major sources may release air toxics from equipment leaks, when materials are transferred from one location to another, or during discharge through emission stacks or vents.
- Area sources* are smaller-size facilities that release lesser quantities of air toxics. These sources emit less than 10 tons per year of a single air toxic, or less than 25 tons per year of a combination of air toxics. Though emissions from individual area sources are often relatively small, collectively their emissions can be of concern—especially in heavily populated communities with many sources.

The 1990 Clean Air Act Amendments direct the EPA to set standards for all major sources of air toxics (and

some area sources that are of particular concern). The EPA published the initial list of source categories in 1992 in the *Federal Register* (57FR31576, July 16, 1992), which has since been revised and updated frequently. The list designates whether the sources are considered to be major or area sources.

## 29.8 EMISSION INVENTORY

An emission inventory is a list of the amount of pollutants from all sources entering the air in a given time period. The boundaries of the area are fixed.<sup>22</sup>

The tables of emission inventory are very useful to control agencies as well as planning and zoning agencies. They can point out the major sources whose control can lead to a considerable reduction of pollution in the area. They can be used with appropriate mathematical models to determine the degree of overall control necessary to meet ambient air quality standards. They can be used to indicate the type of sampling network and the locations of individual sampling stations if the areas chosen are small enough. For example, if an area uses very small amounts of sulfur-bearing fuels, establishing an extensive SO<sub>2</sub> monitoring network in the area would not be an optimum use of public funds. Emission inventories can be used for publicity and political purposes: "If natural gas cannot meet the demands of our area, we will have to burn more high-sulfur fuel, and the SO<sub>2</sub> emissions will increase by 8 tons per year".

The method used to develop the emission inventory does have some elements of error, but the other two alternatives are expensive and subject to their own errors. The first alternative would be to monitor continually every major source in the area. The second method would be to monitor continually the pollutants in the ambient air at many points and apply appropriate diffusion equations to calculate the emissions. In practice, the most informative system would be a combination of all three, knowledgeably applied.

The US Clean Air Act Amendments of 1990 strengthened the emission inventory requirements for plans and permits in nonattainment areas.<sup>24</sup> The amendments state:

**Inventory**—Such plan provisions shall include a comprehensive, accurate, current inventory of actual emissions from all sources of the relevant pollutant or pollutants in such area, including such periodic revisions as the Administrator may determine necessary to assure that the requirements of this part are met.

**Identification and quantification**—Such plan provisions shall expressly identify and quantify the emissions, if any, of any such pollutant or pollutants which will be allowed, from

the construction and operation of major new or modified stationary sources in each such area. The plan shall demonstrate to the satisfaction of the Administrator that the emissions quantified for this purpose will be consistent with the achievement of reasonable further progress and will not interfere with the attainment of the applicable national ambient air quality standard by the applicable attainment date.

### 29.8.1 Inventory Calculation and Construction

The general equation for emissions estimation is:

$$E = A \times E_F \times \left( \frac{1 - E_R}{100} \right) \quad (29.10)$$

Where,  $E$  = emissions;  $A$  = activity rate;  $E_F$  = emission factor; and  $E_R$  = overall emission reduction efficiency (%).

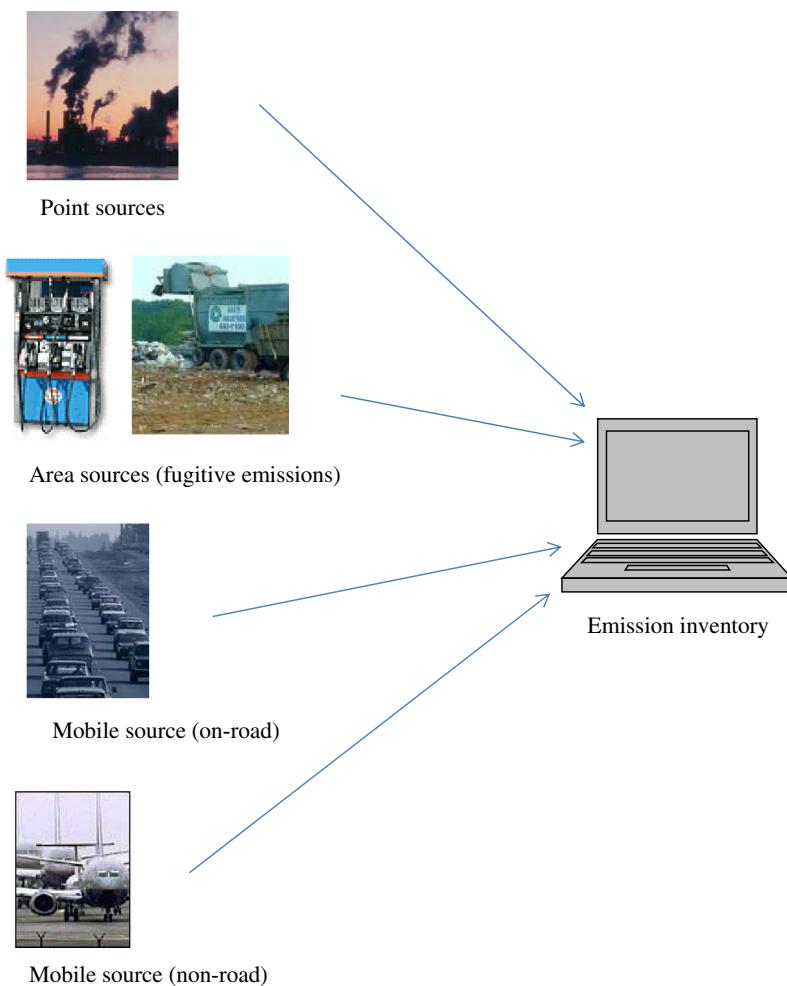
To develop an emission inventory for an area, one must (1) list the types of sources for the area, such as cupolas, automobiles, and home fireplaces (see Figure 29.21); (2) determine the type of air pollutant emission from each of the listed sources, such as particulates and SO<sub>2</sub>; (3) examine the literature to find valid emission factors for each of the pollutants of concern (e.g. "particulate emissions for open burning of tree limbs and brush are 10 kg per ton of residue consumed"); (4) through an actual count, or by means of some estimating technique, determine the number and size of specific sources in the area (the number of steelmaking furnaces can be counted, but the number of home fireplaces will probably have to be estimated); and (5) multiply the appropriate numbers from (3) and (4) to obtain the total emissions and then sum the similar emissions to obtain the total for the area.<sup>25</sup>

A typical example will illustrate the procedure. Suppose the amount of CO from oil furnaces emitted per day, during the heating season, in a small city of 50,000 population needs to be determined:

1. The source is oil furnaces within the boundary area of the city.
2. The pollutant of concern is carbon monoxide.
3. Emission factors for carbon monoxide are listed in various ways (240 g per 1000 l of fuel oil, 50 g per day per burner, 1.5% by volume of exhaust gas, etc.). For this example, use 240 g per 1000 l of fuel oil.
4. Fuel oil sales figures, obtained from the local dealers association, average 40,000 l per day.
5.  $\frac{240 \text{ g CO}}{1000 \text{ l}} \times \frac{40,000 \text{ l}}{\text{day}} = 9.6 \text{ kg CO day}^{-1}$

### 29.8.2 Emission Factors

Valid emission factors for each source of pollution are the key to the emission inventory. It is not uncommon to find emission factors differing by 50%, depending on the



**FIGURE 29.21 Types of sources included in emission inventory.** (For color version of this figure, the reader is referred to the online version of this book.) U.S. Environmental Protection Agency. Huntley R. Emission inventories – the basics. [http://www.epa.gov/ttn/chief/eidocs/basicemipreparationtraining\\_april2003.pdf](http://www.epa.gov/ttn/chief/eidocs/basicemipreparationtraining_april2003.pdf); 2003 [accessed 27.11.13].

researcher, variables at the time of emission measurement, etc. Since it is possible to reduce the estimating errors in the inventory to  $\pm 10\%$  by proper statistical sampling techniques, an emission factor error of 50% can be overwhelming. It must also be realized that an uncontrolled source will emit at least 10 times the amount of pollutants released from one operating properly with air pollution control equipment installed.<sup>24</sup>

Actual emission data are available from many handbooks, government publications, and literature searches of appropriate research papers and journals. In addition, online support is available, especially the Technology Transfer Network/Clearinghouse for Inventories and Emissions Factors, accessible at <http://www.epa.gov/ttn/chief/index.html>. This site provides information on emission factors, inventory, modeling, along with a knowledge base for emissions monitoring.

It is always wise to verify the data, if possible, as to the validity of the source and the reasonableness of the final number. Some emission factors, which have been in use for years, were only rough estimates proposed by someone years ago to establish the order of magnitude of the particular source.

Emission factors must be also critically examined to determine the tests from which they were obtained. For example, carbon monoxide from an automobile will vary with the load, engine speed, displacement, ambient temperature, coolant temperature, ignition timing, carburetor adjustment, engine condition, etc. However, in order to evaluate the overall emission of carbon monoxide to an area, we must settle on an average value that we can multiply by the number of cars, or kilometers driven per year, to determine the total carbon monoxide released to the area.

### 29.8.3 Data Gathering

To compile the emission inventory requires a determination of the number and types of units of interest in the study area. It would be of interest, for example, to know the number of automobiles in the area and the number of kilometers each was driven per year. This figure would require considerable time and expense to obtain. Instead, it can be closely approximated by determining the liters of gasoline sold in the area during the year. Since a tax is collected on all gasoline sold for highway use, these figures can be obtained from the tax collection office.

Data regarding emissions are available from many sources. Sometimes the same item may be checked by asking two or more agencies for the same information. An example of this would be to check the liters of gasoline sold in a county by asking both the tax office and the gasoline dealers association. Sources of information for an emission inventory include: (1) city, county, and state planning commissions; (2) city, county, and state chambers of commerce; (3) city, county, and state industrial development commissions; (4) census bureaus; (5) national associations such as coal associations; (6) local associations such as the County Coal Dealers Association; (7) individual dealers or distributors of oil, gasoline, coal, etc.; (8) local utility companies; (9) local fire and building departments; (10) data gathered by air pollution control agencies through surveys, sampling, etc.; (11) traffic maps; and (12) insurance maps.

### 29.6.5 Data Reduction and Compilation

The final emission inventory can be prepared on a computer, with a program written so that changes can easily be made. There will be times when major changes occur and the inventory must be completely changed. Imagine the change that would take place when natural gas first becomes available in a commercial–residential area which previously used oil and coal for heating.

To determine emission data, as well as the effect that fuel changes would produce, it is necessary to use the appropriate thermal conversion factor from one fuel to another. [Table 29.13](#) lists these factors for fuels in common use.

A major change in the emissions for an area will occur if control equipment is installed. This can be shown in the emission inventory to illustrate the effect on the community.

By keeping the emission inventory current and updating it at least yearly as fuel uses change, industrial and population changes occur, and control equipment is added, a realistic record for the area is obtained.

**TABLE 29.13** Thermal Conversion Factors for Fuels

Fuel	Joule $\times 10^6$
Bituminous coal	30.48 per kg
Anthracite coal	29.55 per kg
Wood	20.62 per kg
Distillate fuel oil	38.46 per kg
Residual fuel oil	41.78 per l
Natural gas	39.08 per m <sup>3</sup>
Manufactured gas	20.47 per m <sup>3</sup>

### QUESTIONS

- What percentage range of sulfur in most fossil fuels is converted to SO<sub>2</sub> in a utility boiler?
- Of temperature, pH, O<sub>2</sub> concentration, N-content of fuel, water salinity and Cu-content in chamber wall, which factor(s) is/are rate-limiting in the formation of NO<sub>x</sub> in a boiler?
- Calculate the heat generated by dissociation and formation as one molecular weight of methane, CH<sub>4</sub>, burns to carbon dioxide and water. How does this heating value compare to the tabular heating value for methane?
- Many control districts have banned the use of private backyard incinerators. Would you expect a noticeable increase in air quality as a result of this action?
- Show a free radical reaction which results in ethane in the effluent of a combustion process burning pure methane with pure oxygen.
- Using a rollback model, what required percentage reduction in emission of SO<sub>2</sub> would be needed to meet an ambient standard of 75 ppb SO<sub>2</sub>, if the present SO<sub>2</sub> concentration is 3.5 µg m<sup>-3</sup>, the background concentration is 1.2 µg m<sup>-3</sup> and the growth factor in emissions is 12%.
- How can the background concentration, such as in the question above, be established? What are some of the uncertainties associated with this estimate?
- A power plant burns oil that is 4% ash and 3% sulfur. At 50% excess air, what particulate (mg m<sup>-3</sup>) emissions would you expect?
- Suppose a 40,000-l gasoline tank is filled with liquid gasoline with an average vapor pressure of 20 mm Hg. At 50% saturation, what weight of gasoline would escape to the atmosphere during filling?
- If a major freeway with four lanes of traffic in one direction passes four cars per second at 100 km per hour during the rush period, and each car carries

- two people, how often would a commuter train of five cars carrying 100 passengers per car have to be operated to handle the same load? Assume the train would also operate at  $100 \text{ km h}^{-1}$ .
11. An automobile traveling  $50 \text{ km h}^{-1}$  emits 0.1% CO from the exhaust. If the exhaust rate is  $80 \text{ m}^3 \text{ min}^{-1}$ , what is the CO emission in grams per kilometer?
12. A sand and gravel facility using the processes 600,000 tons of product per year. What would the predicted emissions of  $\text{PM}_{10}$  be if the emission factor is 0.05 lb per ton of product, without PM controls? If the facility adds wet suppression and fugitive dust controls (about 80%  $\text{PM}_{10}$  removal), how would the emission change?
13. Assume above emission factor is being applied to all sand and gravel facilities by a metropolitan area that is not attaining the ambient  $\text{PM}_{10}$  standard. Air quality models estimate that 500 tons of  $\text{PM}_{10}$  will have to be removed from total emissions to meet the standard. If all 10 sand and gravel operations in the nonattainment area are presently uncontrolled with  $5 \times 10^8 \text{ kg}$  product, what percentage of the needed reduction would be provided if the air pollution agency requires wet suppression and fugitive dust controls at all such facilities? What if the largest operation ( $1 \times 10^8 \text{ kg}$  product) already has these controls in place, and the agency decides that the rest of the facilities need to use the same controls, how much  $\text{PM}_{10}$  will be reduced from this action? Calculate the  $\text{PM}_{10}$  emission reduction needed if, rather than 80% removal, the relationship between controls and actual reduction in emissions has uncertainty, so that wet suppression and fugitive dust controls have been found to range between 57% and 92%.
14. In the question above, what level of control (percent removal) would be needed to ensure sand and gravel operations contribute 21% of the total  $\text{PM}_{10}$  reduction to meet the ambient standard?
15. Following a report of a possible leak from a nuclear power plant, the spokesperson applies the term "half-life" to iodine-131 and methane. Identify any differences in the use of this term for these two substances.
16. List the following in increasing amounts from the exhaust of an idling automobile:  $\text{O}_2$ ,  $\text{NO}_x$ ,  $\text{SO}_x$ ,  $\text{N}_2$ , unburned hydrocarbons,  $\text{CO}_2$ , and CO.
17. In the U.S., what is the major objective of Tier 3 mobile source standards?
18. A processing facility emits 30 tons of iron oxide, 1 ton of  $\text{SO}_2$  and 50 tons of PM each year. If these are its only emission, is it considered a major source under NESHAPS? Another source emits 1 ton acrolein, 1 ton of CO, 4 tons of  $\text{SO}_2$ , 5 tons formaldehyde, 7 tons of hexane, and 8 tons of diethyl sulfate each year. Is it a major source under NESHAPS.
19. What technologies can be adapted to moderate the increased air pollution associated with industrial development in developing nations? What are some of the important things to keep in mind when transferring such technologies to other cultures?
20. Your company's waste stream contains a large percentage of clay-sized particles with a high content of organic compounds and chromium. Which treatment technologies are good candidates for this waste? What other assumptions do you need to make and how may these assumptions be eliminated from your decision; i.e. how can you close the "data gap"?
21. What if 20% of the organic fraction in the above waste stream is chlorinated? How would that affect your selection of treatment approaches?
22. Your city has decided to use supercritical oxidation to treat a low solid content PCB-contaminated waste. What problems, if any, do you see with this approach?
23. What characteristics of a waste increase the likelihood that it should be treated thermally? When is incineration preferable to pyrolysis and vice versa?
24. What precautions should be taken in selecting a treatment process for a halogenated waste? For a heavy metal-laden waste?
25. What are the "three T's" of thermal destruction? Give an example of problems that may ensue if each is neglected?
26. Show by means of a flow diagram or sketch how you would treat and dispose of the fly ash collected from a municipal incinerator. The fly ash contains toxic and nontoxic metals, nonmetallic inorganics, and organic halogen compounds.
27. What is the best thermal destruction system for a liquid pharmaceutical waste contaminated with 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)? How about for soil contaminated with 2,3,7,8-TCDD? What is the major difference in these two wastes?
28. A waste containing 10 ppb of 2,3,7,8-TCDD is incinerated in the U.S. How much of the TCDD would be allowed to exit the incinerator's stack?
29. What is the best thermal destruction system for liquid solvents? Support your answer.
30. Is the multiple hearth system good for treating a liquid waste that breaks down at temperatures  $>1000^\circ\text{C}$ ? If the waste also contains Hg and Ni, what is the preferable treatment approach?
31. What are the major concerns about thermal destruction of PCBs and hexachlorobenzene?

32. What is the difference between air stripping and sparging? Give a situation where stripping would be preferred and one where sparging is better. Explain.
33. Identify two air pollutants wherein odor may be a promising indicator of air quality. What are the limitations of using odor beyond a screening level?
34. Identify an air pollutant where a standard or recommended air concentration to protect health is higher than the typical odor recognition threshold and one where the health level is lower than the typical odor recognition threshold.
35. If humans lose their olfactory acuity with age, how might this factor affect risk management and engineering decisions associated with H<sub>2</sub>S?
36. One definition of acceptable indoor air quality is when "there are no known contaminants at harmful concentrations as determined by cognizant authorities and with which a substantial majority (80% or more) of the people exposed do not express dissatisfaction". From a scientific perspective, identify and explain any problems with this definition.
37. In 1986, a plume of radioactive material was released from the Chernobyl, Ukraine. A large amount of material was released during the first few minutes of the meltdown, but the emission attenuated over the next several months, with the total radiation from the emissions estimated at  $5 \times 10^7$  Ci. The long-range transport was intercontinental, with elevated isotope readings in Scandinavia and beyond. Assuming an instantaneous release of  $10^7$  Ci of radioactive gases and fine PM that remain suspended in the atmosphere during the entire time of atmospheric transport in a plume moving  $3 \text{ m s}^{-1}$ , what is the maximum surface concentration of radioactive gases and PM (curies  $\text{m}^{-3}$ ) at the surface 1000 km away in Scandinavia? Also assume that atmosphere has the stability class C and that mixing in the *x* direction is the same as mixing in the *y* direction.
38. Consider the following information from an accident report filed with the US EPA and write a brief contingency plan that would prevent such an incident occurring at any refinery:

At about 10:15 a.m., on October 16, 1995, an explosion and fire occurred at Plant No. 1 of the Pennzoil Products Company refinery in Rouseville, Pennsylvania. After the initial explosion, flames quickly engulfed a large area of the refinery, including areas under construction, storage trailers, a trailer where contractors took work breaks, and many storage tanks. The flames ignited several tanks containing naphtha and fuel oil. During the fire, several loud explosions could be heard as compressed gas cylinders and other sealed containers exploded.

The explosions hurled some plant debris beyond the fence line. Thick black smoke spread throughout the area. The fire forced Pennzoil employees and contractors at the plant, residents of the town of Rouseville and an elementary school, and the Pennzoil office across Route eight from the facility, to evacuate. Firefighters extinguished the fire at about 12:30 p.m. that same day. Three workers were killed in the fire and three others were injured. Two of the injured died later as a result of their injuries. The fire resulted in extensive damage to the facility. Minor "sheening" was reported on the stream that runs past the refinery, but there were no reports of any materials spilled into the stream or environmental damage.

A welding operation was in progress on a service stairway located between two waste liquid storage tanks (tanks 487 and 488) at the time of the incident. These tanks contained mixtures of waste hydrocarbons and water. A hot work (welding, cutting) permit had been prepared, as required by Occupational Safety and Health Administration (OSHA) standard, which included combustible gas detection prior to welding to ensure the safety of the work.

The EPA Chemical Accident Investigation Team (CAIT) identified the immediate cause of the fire and the conditions which triggered the serious consequences. The immediate cause of the fire was the ignition of flammable vapors in storage tank 487. Although the CAIT could not determine the exact mechanism, there are at least two likely scenarios: undetected flammable vapors emitted from tank 487 were ignited by an ignition source which then flashed back into the tank; or an electrical discharge in the tank 487, generated by the arc welding, ignited flammable vapors in the tank.

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# Air Pollution Control Technologies

## 30.1 ENGINEERING CONTROL CONCEPTS

### 30.1.1 Introduction

The application of control technology to air pollution problems assumes that a source can be reduced to a predetermined level to meet a regulation or some other target value. Control technology cannot be applied to an uncontrollable source, such as a volcano, nor can it be expected to control a source completely to reduce emissions to zero. The cost of controlling any given air pollution source is usually an exponential function of the percentage of control and therefore becomes an important consideration in the level of control required.<sup>1</sup> Figure 30.1 shows a typical cost curve for control equipment.

If the material recovered has some economic value, the picture is different. Figure 30.2 shows the previous cost of control with the value recovered curve superimposed on it. The plant manager looking at such a curve would want to be operating in the area to the left of the intersection of the two curves, whereas the local air pollution forces would insist on operation as far to the right of the graph as the best available control technology would allow.

Control of any air pollution source requires a complete knowledge of the contaminant and the source.

The engineers controlling the source must be thoroughly familiar with all available physical and chemical data on the effluent from the source. They must know the rules and regulations of the control agencies involved, including not only the air pollution control agency but also any agencies, which may have jurisdiction over the construction, operation, and final disposal of the waste from the source.<sup>2</sup>

In many cases, heating or cooling of the gaseous effluent will be required before it enters the control device. The engineer must be thoroughly aware of the gas laws, thermodynamic properties, and reactions involved to secure a satisfactory design. For example, if a gas is cooled below its dewpoint, the gas will condense onto surfaces. If water is sprayed into the hot gas for cooling, it adds greatly to the specific volume of the mixture. As the gases pass through hoods, ducts, fans, and control equipment, temperatures and pressures change which in turn will change specific volumes and velocities.<sup>3</sup> In addition, compounds may react with the water, e.g. they may undergo hydrolysis and form acids, which may add to the corrosiveness and shorten equipment life.

The control of atmospheric emissions from a process will generally take one of the three forms depending on the process, fuel, types, availability of control

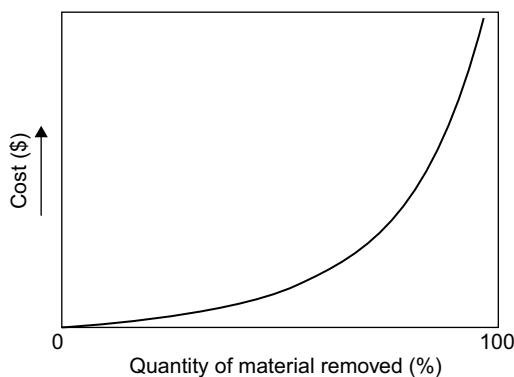


FIGURE 30.1 Air pollution control equipment cost.

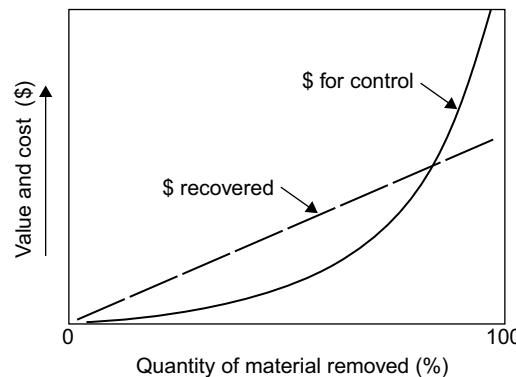


FIGURE 30.2 Control equipment cost with value recovered.

equipment, etc. The three general methods are (1) process change to a less polluting process or to lowered emission from the existing process through a modification or change in operation, (2) change to a fuel that will give the desired level of emissions, and (3) installation of control equipment between the point of pollutant generation and its release to the atmosphere. Control may consist of either removal of the pollutant or conversion to a less polluting form.<sup>3</sup>

### 30.1.2 Process Change

A process change can be either a change in operating procedures for an existing process or the substitution of a completely different process. In recent years, this has been labeled "pollution prevention". Consider a plant manager who for years has been using solvent A for a degreasing operation. By past experimentation, it has been found that with the conveyor speed at 100 units per hour, with a solvent temperature of 80 °C, one gets maximum cleaning with solvent, a loss that results in the lowest overall operating cost for the process.

A new regulation is passed requiring greatly reduced atmospheric emissions of organic solvents, including solvent A. The manager has several alternatives:

1. Change to another more expensive solvent, which by virtue of its lower vapor pressure would emit less organic matter.
2. Reduce the temperature of the solvent and slow down the conveyor to get the same amount of cleaning. This may require the addition of another line or another 8 h shift.
3. Put in the necessary hooding, ducting, and equipment for a solvent recovery system which will decrease the atmospheric pollution and also result in some economic solvent recovery.
4. Put in the necessary hooding, ducting, and equipment for an thermal oxidizing (afterburner) system which will burn the organic solvent vapors to a less polluting emission, but with no solvent recovery.

In some cases, the least expensive control is achieved by abandoning the old process and replacing it with a new, less polluting one. Any increased production and/or recovery of material may help offset a portion of the cost. It has proved to be cheaper to abandon old steel mills and to replace them with completely new furnaces of a different type than to modify the old systems to meet pollution regulations. Kraft pulp mills found that the least costly method of meeting stringent regulations was to replace the old, high-emission recovery furnaces with a new furnace of completely different design. The kraft mills have generally asked for, and received,

additional plant capacity to offset partially the cost of the new furnace type.

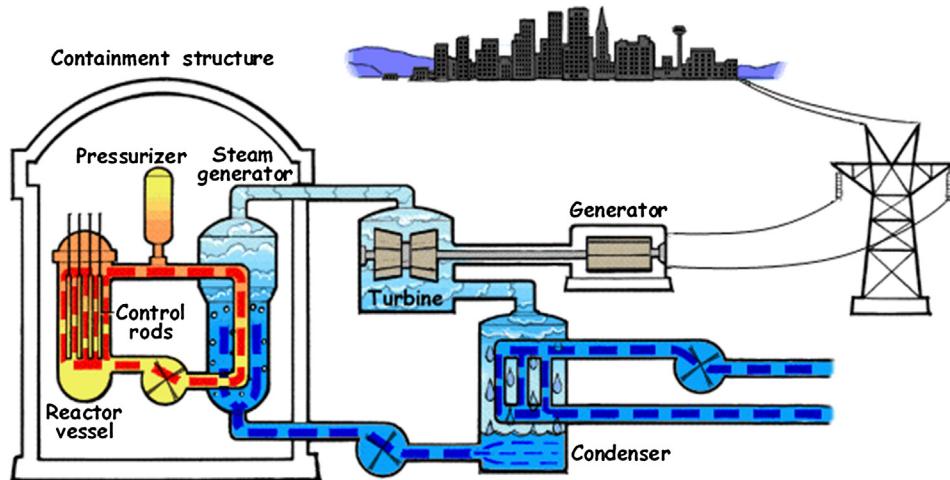
### 30.1.3 Fuel Change

For certain air pollution control situations, a change to a less polluting fuel may be the ideal solution to the problem, at least in the near-term. If a power plant is emitting large quantities of SO<sub>2</sub> and fly ash, conversion to natural gas could very well be cheaper than installing the necessary control equipment to decrease the pollutant emissions to meet the permitted values. If the drier at an asphalt plant is emitting 350 mg of particulate matter per standard cubic meter of effluent when fired with heavy oil of 4% ash, a switch to either oil of a lower ash content or natural gas may allow the operation to meet an emission standard of 250 mg per standard cubic meter.

In the twentieth century, fuel switching based on meteorological or air pollution forecasts was a common practice to reduce the air pollution burden at critical times. Some control agencies allowed power plants to operate on residual oil during certain periods of the year when pollution potential was low. Some large utilities for years have followed a policy of switching from their regular coal to a more expensive but lower-sulfur coal when stagnation conditions were forecast.

Caution should be exercised when considering any change in fuels to reduce emissions. This is particularly true when fuel is expensive. Specific considerations might be the following:

1. What are the current and potential fuel supplies? In many areas, natural gas is already in short supply. It may not be possible to convert a large plant with current allocations or pipeline capacity.
2. Most large boilers use a separate fuel for auxiliary or standby purposes. One actual example was a boiler fired with wood residue as the primary fuel and residual oil as the standby. A change was made to natural gas as the primary fuel, with residual oil kept for standby. This change was made to lower particulate emissions and to achieve a predicted slightly lower cost. Because of gas shortages, the plant now operates on residual oil during most of the cold season, and the resulting particulate emission greatly exceeds that of the previously burned wood fuel. In addition, an SO<sub>2</sub> emission problem exists with the oil fuel that never occurred with the wood residue. Overall costs have not been lowered because natural gas rates have increased since the conversion.
3. Charts or tables listing supplies or reserves of low-sulfur fuel may not tell the entire story. For example, a large percentage of low-sulfur coal is owned by steel companies and is therefore not



**FIGURE 30.3** Schematic of a pressurized power reactor components. (For color version of this figure, the reader is referred to the online version of this book.) Source: US Nuclear Regulatory Commission. *The Pressurized Water Reactor (PWR)*. <http://www.nrc.gov/reading-rm/basic-ref/students/animated-pwr.html> [accessed 19.5.2014].

generally available for use in power generating stations even though it is listed in tables published by various agencies.

- Strong competition exists for low-pollution fuels. While one area may be drawing up regulations to require use of natural gas or low-sulfur fuels, it is probable that other neighboring areas are doing the same. Although there may have been sufficient premium fuel for one or two areas, if the entire region changes, not enough exists. Such a situation has resulted in extreme fuel shortages during cold spells in some large cities. The supply of low-sulfur fuels has been exhausted during period of extensive use.

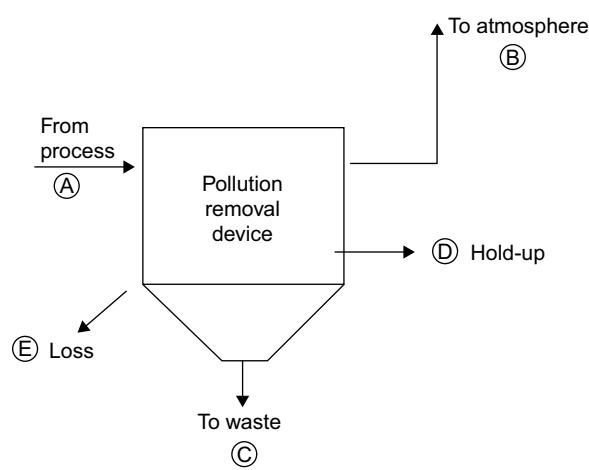
Nuclear reactors (Figure 30.3) used for power generation has been questioned from several environmental points of view. These appear to be relatively pollution free compared to the more familiar fossil fuel-fired plant, which emits carbon monoxide and carbon dioxide, oxides of nitrogen and sulfur, hydrocarbons, and fly ash. However, waste and spent-fuel disposal problems may offset the apparent advantages. These problems (along with steam generator leaks) have been the cause for premature closures of nuclear power plants.

#### 30.1.4 Pollution Removal

In many situations, sufficient control over emissions cannot be entirely obtained by fuel or process change. In cases such as these, the levels of the pollutants of concern in the exhaust gases or process stream must be decreased to allowable values before they are released to the atmosphere.

The equipment for the pollutant removal system includes: hoods, ducting, controls, fans, and disposal or recovery systems that might be necessary. The entire system should be engineered as a unit for maximum efficiency and economy. Many systems operate at less than maximum efficiency because a portion of the system has been designed or adapted without sufficient consideration of the other portions.<sup>4</sup>

Efficiency of the control equipment is normally specified before the equipment is purchased. If a plant is emitting a pollutant at  $500 \text{ kg h}^{-1}$  and the regulations allow an emission of only  $25 \text{ kg h}^{-1}$ , it is obvious that at least 95% efficiency is required of the pollution control system. This situation requires the regulation to state "at least 95% removal on a weight basis". The regulation should further specify how the test would be made to determine the efficiency. Figure 30.4 shows the situation as it exists.



**FIGURE 30.4** Typical pollution control device as shown for efficiency calculations.

The efficiency for the device shown in Figure 30.4 may be calculated in several ways:

$$\text{Efficiency, \%} = 100 \left( \frac{C}{A} \right), \text{ but since } A = B + C \quad (30.1)$$

$$\begin{aligned} \text{Efficiency, \%} \\ = 100 \left( \frac{C}{B+C} \right) \text{ or } 100 \left( \frac{A-B}{A} \right) \text{ or } 100 \left( \frac{A-B}{B+C} \right) \end{aligned} \quad (30.2)$$

The final acceptance test would probably be made by measuring two of the three quantities and using the appropriate equation. For a completely valid efficiency test, the effect of hold-up ( $D$ ) and loss ( $E$ ) must also be taken into account.

To remove a pollutant from the carrying stream, some property of the pollutant that is different from the carrier must be exploited. The pollutant may have different size, inertia, electrical, or absorption properties. Removal requires that the equipment be designed to apply the scientific principles necessary to perform the separation.

### 30.1.5 Disposal of Pollutants

If a pollutant is removed from the carrying gas stream, disposal of the collected material becomes of vital concern. If the collected material is truly inert, it may be disposed of in a sanitary landfill. If it is at the other end of the scale, it is probably considered as a toxic waste and strict laws governing its disposal apply. Disposal of hazardous wastes is regulated by governmental agencies.<sup>5-11</sup>

In the United States, the Resource Conservation and Recovery Act (RCRA) of 1976 is the major legislation covering the disposal of solid and hazardous wastes.<sup>2</sup> This act provides a multifaceted approach to solving the problems associated with the generation of approximately 5 US billion metric tons of solid waste each year in the United States. It places particular emphasis on the regulation of hazardous wastes. This law established the Office of Solid Waste within the US Environmental Protection Agency and directed the agency to publish hazardous waste characteristics and criteria.

If a waste is designated as hazardous under the RCRA, regulations are applied to generators, transporters, and those who treat, store, or dispose of that waste. Regulations regarding hazardous wastes are enforced by the federal government, while the individual states are responsible for enforcing the provisions of the RCRA which apply to nonhazardous wastes. The act also provides for research, development, and demonstration grants for waste disposal.

The US Environmental Protection Agency, Office of Solid Waste Management Programs, defines hazardous waste as "wastes or combinations of wastes which pose a substantial present or potential hazard to human health or living organisms because they cause, or tend to cause, detrimental cumulative effects".

Hazardous wastes can be categorized in a way that shows their potential or immediate effect. A common system for categorizing substances is (1) toxic substances (acute or chronic damage to living systems), (2) flammable, (3) explosive or highly reactive, (4) irritating and/or sensitizing, (5) corrosive (strong oxidizing agents), (6) radioactive, (7) bioaccumulative and/or biomagnified substances (with toxic effects), and (8) genetically interactive substances (mutagenic, teratogenic, and carcinogenic). It is possible for a substance to be placed in any number of these categories, but placement in only one category is sufficient for it to be considered hazardous.<sup>5-11</sup>

Table 30.1 indicates the four main types of hazardous material, with examples of substances of each type. Not presented in Table 30.1 are radioactive materials, which are considered as a separate type of hazardous waste.<sup>12</sup>

Table 30.2 lists some of the currently used pretreatments and ultimate disposal methods for hazardous wastes.<sup>13</sup> Pretreatment refers almost entirely to thickening or dewatering processes for liquids or sludges. This process not only reduces the volume of the waste but also allows easier handling and transport.

The general purpose of ultimate disposal of hazardous wastes is to prevent the contamination of susceptible environments. Surface water runoff, ground water leaching, atmospheric volatilization, and biological accumulation are processes that should be avoided during the active life of the hazardous waste. As a rule, the more persistent a hazardous waste is (i.e. the greater its resistance to breakdown), the greater the need to isolate it from the environment. If the substance cannot be neutralized by chemical treatment or incineration and still maintains its hazardous qualities, the only alternative is usually to immobilize and bury it in a secure chemical burial site.

## 30.2 AIR POLLUTION CONTROL DEVICES

The best means of addressing air pollutants is to prevent their existence through waste minimization and prevention. These techniques have improved but, unfortunately, the most common way to control air pollution remains pollution removal and treatment. For pollution removal to be accomplished, the polluted carrier gas must pass through a control device or system, which

TABLE 30.1 Hazardous Material Types

Miscellaneous Inorganics	Halogens and Interhalogens	Miscellaneous Organics	Organic Halogen Compounds
Metals	Bromine pentafluoride	Acrolein	Aldrin
Antimony	Chlorine	Dinitrophenol	Chlordane
Bismuth	Chlorine pentafluoride	Tetrazene	1,1-Dichloro-2,2-bis ( <i>p</i> -chlorophenyl) ethane (DDD) Dichloro-diphenyl-trichloroethane (DDT)
Cadmium	Chlorine trifluoride	Nitroglycerine	Dieldrin
Chromium	Fluorine	Nitroaniline	Endrin
Cobalt	Perchloryl fluoride	Chloroacetophenone (CN tear gas)	Potassium cyanide
Copper			Heptachlor
Lead			Lindane
Mercury			Parathion
Nickel			Methyl bromide
Selenium			Polychlorinated biphenyls (PCBs)
Silver			
Tellurium			
Thallium			
Tin			
Zinc			
Nonmetallics			
Cyanide (ion)			
Hydrazine			
Fluorides			
Phosgene			

collects or destroys the pollutant and releases the cleaned carrier gas to the atmosphere. The control device or system selected must be specific for the pollutant of concern. If the pollutant is an aerosol, the device used will, in most cases, be different from the one used for a gaseous pollutant. If the aerosol is a dry solid, a different device must be used than for liquid droplets.

Not only the pollutant itself but also the carrier gas, the emitting process, and the operational variables of the process affect the selection of the control system. Table 30.3 illustrates the large number of variables which must be considered in controlling pollution from a source.<sup>14a,14b,14c,14d</sup>

After the control system is installed, its operation and maintenance become a major concern. Important reasons for an operation and maintenance (O&M) program are (1) the necessity of continuously meeting emission regulations, (2) prolonging control equipment life, (3) maintaining productivity of the process served by the control device, (4) reducing operation costs,

(5) promoting better public relations and avoiding community alienation, and (6) promoting better relations with regulatory officials.<sup>15</sup>

The O&M program has the following minimum requirements: (1) an equipment and record system with equipment information, warranties, instruction manuals, etc.; (2) lubrication and cleaning schedules; (3) planning and scheduling of preventive maintenance; (4) a storeroom and inventory system for spare parts and supplies; (5) listing of maintenance personnel; (6) costs and budgets for O&M; and (7) storage of special tools and equipment.

### 30.3 PARTICULATE MATTER CONTROL DEVICE PHYSICS

Controlling particulate matter (PM) emissions takes advantage of physical principles. Unlike gases, which flow with the air, particles deposit differentially within

TABLE 30.2 Ultimate Waste Disposal Methods

Process	Purpose	Wastes	Problems (Remarks)
Cementation and vitrification	Fixation	Sludges	Expensive
	Immobilization	Liquids	
	Solidification		
Centrifugation	Dewatering	Sludges	
	Consolidation	Liquids	
Filtration	Dewatering	Sludges	Expensive
	Volume reduction	Liquids	
Thickening (various methods)	Dewatering	Sludges	
	Volume reduction	Liquids	
Chemical addition (polyelectrolytes)	Precipitation	Sludges	Can be used in conjunction with other processes
	Fixation	Liquids	
	Coagulation		
Submerged combustion	Dewatering	Liquids	Acceptable for aqueous organics
<b>MAJOR ULTIMATE DISPOSAL METHODS</b>			
Deep well injection	Partial removal from biosphere	Oil field brines; low toxicity, low-persistence wastes; refinery wastes	Monitoring difficulty Need for special geological formations
	Storage		Ground water contamination
Incineration	Volume reduction	Most organics	If poor process control, unwanted emissions produced
	Toxicity destruction		Can produce NO <sub>x</sub> , SO <sub>x</sub> , halo acids
Recovery	Reuse	Metals	Sometimes energy prohibitive
		Solvents	
Landfill	Storage	Inert to radioactive	Volatilization
<b>MAJOR WASTE DISPOSAL METHODS</b>			
Land application	Isolation		Leaching to ground water
Land burial	Dispersal		Access to biota
Ocean disposal	Dispersal	Acids, bases	Contact with ocean ecosystem
	Dilution	Explosives	Containers unstable
	Neutralization	Chemical war agents	
	Isolation (?)	Radioactive wastes	
<b>MINOR DISPOSAL METHODS</b>			
Biological degradation	Reduction of concentration	Biodegradable organics	Most hazardous wastes do not now qualify
	Oxidation		
Chemical degradation (chlorination)	Conversion	Some persistent pesticides	
	Oxidation		
Electrolytic processes	Oxidation	Organics	
Long-term sealed storage	Isolation	Radioactive	How good are containers?
	Storage		
Salt deposit disposal	Isolation	Radioactive	Are salt deposits stable in terms of waste lifetimes?

**TABLE 30.3** Key Characteristics of Air Pollution Control Devices and Systems

Factor Considered	Characteristic of Concern
General	Collection efficiency Legal limitations such as best available technology Initial cost Lifetime and salvage value Operation and maintenance costs Power requirement Space requirements and weight Materials of construction Reliability Reputation of manufacturer and guarantees Ultimate disposal/use of pollutants
Carrier gas	Temperature Pressure Humidity Density Viscosity Dewpoint of all condensables Corrosiveness Inflammability Toxicity
Process	Gas flow rate and velocity Pollutant concentration Variability of gas and pollutant flow rates, temperature, etc.
Pollutant (if gaseous)	Allowable pressure drop Corrosiveness Inflammability Toxicity Reactivity
Pollutant (if particulate)	Size range and distribution Particle shape Agglomeration tendencies Corrosiveness Abrasiveness Hygroscopic tendencies Stickiness

**TABLE 30.3** Key Characteristics of Air Pollution Control Devices and Systems—cont'd

Factor Considered	Characteristic of Concern
	Inflammability
	Toxicity
	Electrical resistivity
	Reactivity

the airway by mechanical processes (see Figure 9.7 in Chapter 9). Pollution control equipment to remove PM makes use of several physical mechanisms:

- Gravitational settling
- Inertial impaction
- Centrifugal inertial force
- Brownian motion
- Electrostatic attraction
- Thermophoresis
- Diffusiophoresis

The importance of each varies according to the class of equipment. Each mechanism applies a combination of forces to a particle that makes it to move. The design of the control equipment takes advantage of this motion, i.e. moving the particle toward a collecting surface. Obviously, engineering must apply physical principles within a domain of uncertainty, so the more that is known about the mass and energy relationships of the particle, the air stream and the surfaces of the control equipment, the more that can be included in a design. These basic relationships are summarized as:

$$\sum F = m_p \cdot a_p = m_p \frac{dv_p}{dt} \quad (30.3)$$

where,  $\Sigma F$  is the sum of all forces acting on a particle ( $\text{g cm s}^{-2}$ );  $m_p$ , particle mass (g);  $a_p$ , particle acceleration ( $\text{cm s}^{-2}$ );  $v_p$ , particle velocity; and  $t$ , time (s). In English units, these relationships are expressed as:

$$\sum F = \frac{m_p \cdot a_p}{g_c} \quad (30.4)$$

where,  $\Sigma F$ , sum of all forces acting on a particle (foot pounds,  $\text{lbf}_f$ );  $m_p$ , particle mass (international avoirdupois pound,  $\text{lb}_m$ ), and  $a_p$ , particle acceleration ( $\text{ft s}^{-2}$ ). The foot pound is the product of  $\text{lb}_m$  and  $g_0$  (i.e. the standard gravitational field). That is, 1  $\text{lb}_f$  is equal to the force exerted by 1  $\text{lb}_m$  in a gravitational field. The gravitational constant ( $g_c$ ) is expressed as:

$$g_c = 32.2 \frac{\text{lb}_m \cdot \text{ft}}{\text{lb}_f \cdot \text{s}^2} \quad (30.5)$$

All of these mechanisms are involved in particle movement. In practice, much of the motion that accounts for efficient particle removal involves three basic processes:

1. Initial capture of particles on surfaces
2. Gravity settling of solids into the hopper
3. Removal of solids from the hopper

For example, high-efficiency particulate control systems, e.g. fabric filters and electrostatic precipitators apply these processes; although the initial step of capturing varies considerably (e.g. one uses filtration whereas the other uses electrostatics). Also, the means of using gravity will vary among devices. Thus, this discussion differentiates the particle collection mechanisms that control the effectiveness of initial capture of the incoming particles and gravity settling of the collected solids.

The distribution of PM sizes is the first information that is needed when designing, selecting, and installing equipment. The type of source, operation conditions, and other factors lead to significant differences in the particle size ranges, even from within the same industry or other source category. In addition, the type of control equipment may use the same physical mechanisms as other equipment, but in varying proportions.

Indeed, technologies even within the same class, e.g. filtration, are not limited to filter mechanisms. For example, a pulse jet fabric filter uses inertial impaction, Brownian motion, and electrostatic attraction to capture particles in the size range of 100  $\mu\text{m}$  to less than 0.01  $\mu\text{m}$  onto the accumulated layers of dust on the exterior surfaces of the bags. Thus, the bags must be cleaned regularly. Large aggregates of dust cake become dislodged from the filter surface and drop into the hopper. These visible agglomerations of solids are several orders of magnitude larger than the individual particle, i.e. between 10,000 and 50,000  $\mu\text{m}$  (1.0–5.0 cm). Thus, the aggregate mass causes them to readily fall into the hopper. Unfortunately, poor O&M, e.g. improper filter cleaning, will allow for dislodging much smaller agglomerations; thus greatly decreasing the settling rate. This means that even with a very efficient capture of PM, the control equipment can become much less efficient if not followed by well-maintained gravity settling systems.

The principle of pressure differential is crucial to particulate removal. The laws of potentiality state that flow moves from high to low pressure. So, if pressure can decrease significantly below that of the atmosphere, air will move to that pressure trough. If there is a big pressure difference between air outside and inside, the flow will be quite rapid. So, the “vacuum” (it is really a pressure differential) is created inside the vacuum cleaner

using an electric pump. When the air rushes to the low pressure region it carries particles with it. Increasing velocity is proportional to increasing mass and numbers of particles that can be carried. This is the same principle as the “competence” of a stream, which is high (i.e. can carry heavier loads) in a flowing river, but the competence declines rapidly at the delta where stream velocity approaches zero. This causes the river to drop its particles in descending mass, i.e. sedimentation of heavier particles first, but colloidal matter remaining suspended for much longer times.

Two of the most common types of particle collection systems in industry are cyclones and fabric filter systems. Both the cyclone and the fabric filter are all designed to remove particles. In the United States, air quality standards were first directed at total suspended particulates (TSP) as measured by a high-volume sampler, i.e. a device that collected a large range of sizes of particles (aerodynamic diameters up to 50  $\mu\text{m}$ ), with added emphasis on smaller particles with time. Presently, ultrafine particles (aerodynamic diameter  $\leq 100 \text{ nm}$ ) are a major new emphasis. Some of the older PM removal systems will fall short in removing them, but will likely still need to employ the same principles mentioned above, but in different ways. For example, coarse PM will still need to be removed, but after this process, other mechanisms will be needed for the ultrafines.

Particle size is also important because of the relationship between the diameter of a sphere and the sphere's surface area. In the discussion of multistage impactors in Chapter 25 (Figure 25.25), each stage removes particles of progressively smaller diameter. The PM collected on each stage is an indication that inertial forces can be used to collect PM. As shown in Table 30.4, with each order of magnitude decrease in diameter, the surface area increases by two orders of magnitude. Thus, a 1  $\mu\text{m}$  particle has six orders of magnitude greater surface area than a 1 mm particle. This difference in size-to-surface areas ratio affects sorption, which means that smaller particles will be more likely to sorb materials, including toxic compounds.

TABLE 30.4 Relationship between Spherical Particle Diameter, Volume, and Surface Area

Diameter ( $\mu\text{m}$ )	Volume ( $\text{cm}^3$ )	Area ( $\text{cm}^2$ )
0.1	$5.23 \times 10^{-16}$	$3.14 \times 10^{-10}$
1.0	$5.23 \times 10^{-13}$	$3.14 \times 10^{-8}$
10.0	$5.23 \times 10^{-10}$	$3.14 \times 10^{-6}$
100.0	$5.23 \times 10^{-7}$	$3.14 \times 10^{-4}$
1000.0	$5.23 \times 10^{-4}$	$3.14 \times 10^{-2}$

### 30.3.1 Gravity

After initial capture, gravity is the next important mechanism. Thus, the forces exerted on the particle must be calculated to estimate the extent to which a particle or clumps formed from particle aggregates can be collected by gravitational settling. These forces are the gravitational force ( $F_G$ ), buoyant force ( $F_B$ ), and the drag force ( $F_D$ ). The gravitational force causes the PM mass to fall. This is expressed as:

$$F_G = m_p \cdot g = \rho_p \cdot V_p \cdot g \quad (30.6)$$

where,  $F_G$  is the gravitational force ( $\text{g cm s}^{-2}$ );  $m_p$ , particle mass (g);  $g$ , particle acceleration due to gravity ( $980 \text{ cm s}^{-2}$ );  $\rho_p$ , particle density ( $\text{g cm}^{-3}$ ); and  $V_p$ , particle volume ( $\text{cm}^3$ ).

If the particle is assumed to be spherical, the volume term in Eqn (30.13) can be simplified as:

$$V_p = \frac{\pi d_p^3}{6} \quad (30.7)$$

where  $d_p$  is the physical diameter of the particle (cm). Thus, substituting this term in Eqn (30.13) gives:

$$F_G = \frac{\pi d_p^3 \rho_p g}{6} \quad (30.8)$$

### 30.3.2 Buoyancy

It is important to note that the forces included in the sum of all forces in Equations 30.3 and 30.4 can be in the same or in opposite directions. A force in the opposite direction of gravity is buoyancy. Buoyancy force ( $F_B$ ) resists gravity, so the greater the buoyancy, the more likely a particle will remain suspended in the air. This can be expressed as:

$$F_B = m_g \cdot g = \rho_g \cdot V_p \cdot g \quad (30.9)$$

where,  $F_B$  is the buoyancy force ( $\text{g cm s}^{-2}$ );  $m_g$ , mass of displaced gas (g);  $g$ , particle acceleration due to gravity ( $980 \text{ cm s}^{-2}$ );  $\rho_g$ , carrier gas density ( $\text{g cm}^{-3}$ ); and  $V_p$ , particle volume ( $\text{cm}^3$ ). Again, assuming a spherical particle, this equation can also be simplified:

$$F_B = \frac{\pi d_p^3 \rho_g g}{6} \quad (30.10)$$

Note that  $F_B$  depends on the density of the gas, which is usually air. Even in very polluted carrying gases, the gas is predominantly air. Thus,  $\rho_g$  is on the order of  $10^{-2} \text{ lb}_m \text{ ft}^{-3}$ ; whereas the  $F_G$  depends on  $\rho_p$ , which is on the order of  $10^2 \text{ lb}_m \text{ ft}^{-3}$ . This density difference

means that in most practical situations, the buoyant force is orders of magnitude smaller than the gravitational force and is usually neglected.

### 30.3.3 Drag

As the particle begins to move downward due to  $F_G$ , it encounters a resistive force that increases with increasing downward velocity. This is the third important force acting on a particle, i.e. drag force:

$$F_D = \frac{A_p \cdot \rho_g \cdot V_p^2 \cdot C_D}{2} = \frac{\pi d_p^2 \rho_g v_p^2 \cdot C_D}{8} \quad (30.11)$$

where,  $F_D$  is the drag force ( $\text{g cm s}^{-2}$ );  $A_p$ , cross-sectional area of the particle (cm), which equals  $\frac{\pi d_p^2}{4}$ ;  $\rho_g$ , gas density ( $\text{g cm}^{-3}$ ); and  $C_D$ , drag coefficient (dimensionless).

The drag force results from the gas in front of the particle that is being displaced as the particle moves. This imparts momentum on the gas. Thus,  $F_D$  equals the momentum per unit time imparted by the gas on the particle. Some of the particle velocity ( $v_p$ ) is imparted to the gas as gas velocity ( $v_g$ ). The amount of energy that  $v_p$  gives to  $v_g$  is related to a factor of friction, which is the drag coefficient ( $C_D$ ) (see Figure 30.5).

The drag coefficient is related to particle velocity and the flow pattern of the gas around the particle. This flow is determined by the Reynolds number ( $N_R$  or  $Re$ ).<sup>a</sup> As discussed in Chapter 16, as velocity increases, a fluid's flow ceases to be laminar and becomes turbulent. The  $N_R$  is expressed as the ratio of inertial to viscous forces in a fluid:

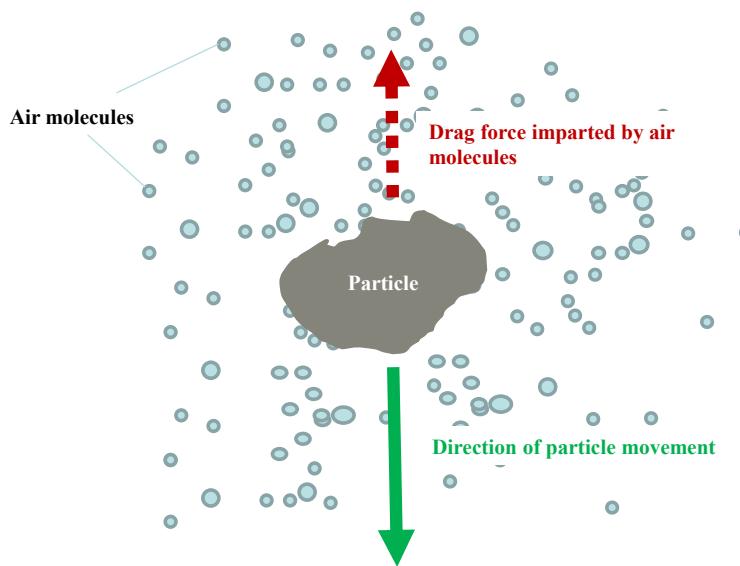
$$N_R = \frac{\text{Inertial Forces}}{\text{Viscous Forces}} \quad (30.12)$$

The inertial forces are proportional to the velocity and density of the fluid, as well as to the diameter of the conduit in which the fluid is moving. An increase in any of these factors will lead to a proportional increase in the momentum of the flowing fluid. The coefficient of viscosity or absolute viscosity ( $\mu$ ) represents the total viscous force of the fluid, so,  $N_R$  can be calculated as:

$$N_R = \frac{D_e v \rho}{\mu} \quad (30.13)$$

where,  $D_e$  is the conduit's equivalent diameter, which evaluates the fluid flow as a physical length. Recall that  $\mu \rho^{-1}$  is the kinematic viscosity  $v$ , so the Reynolds

<sup>a</sup> Note that the symbol in Chapter 16 for the general fluid dynamics aspects of the Reynolds number is  $N_R$ . The symbol  $Re$  is commonly used in air pollution science and engineering, so it is used here. The underlying theory and practice is the same; only the symbols differ.



**FIGURE 30.5** Drag force of air imparted onto a particle moving as a result of gravitational force. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Ref. 16.

number can be stated as the relationship between the size of the conduit, the average fluid velocity  $v$ , and  $v$ :

$$N_R = \frac{d_e v}{v} \quad (30.14)$$

At very low velocities, the mass moves in discrete layers parallel to one another. The only movement across the fluid layers is molecular motion, which creates viscosity. Such a flow is laminar (see Figure 16.14 in Chapter 16). The dimensionless particle Reynolds ( $Re_p$  or  $N_{R_p}$ ) number can also be expressed in terms similar to those of the forces, but adding gas viscosity:

$$Re_p = \frac{d_p v_p \rho_g}{\mu_g} \quad (30.15)$$

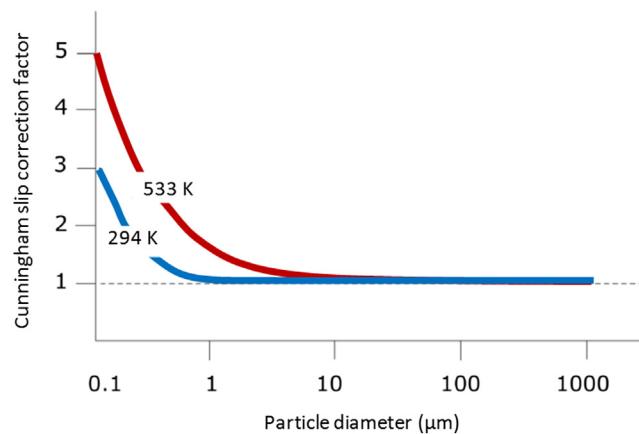
where,  $\mu_g$  is the gas viscosity ( $\text{g cm}^{-1} \text{s}^{-1}$ ).

As mentioned, three particle flow regions exist: laminar, transition, and turbulent (see Figure 30.6). For low values of the particle Reynolds number ( $Re_p \ll 1$ ), the flow is considered laminar.<sup>b</sup> Laminar flow is defined as the flow in which the fluid moves in layers smoothly over an adjacent particle surface. For much greater values of the particle Reynolds number (e.g.  $Re_p > 1000$ ), the flow is turbulent.<sup>c</sup> Turbulent flow is characterized by erratic motion of fluid, with a violent interchange of momentum throughout the fluid near the particle surface. For particle Reynolds numbers between 1 and 1000, the flow is in the transition region, i.e. the flow can be either laminar or turbulent, depending on the local conditions. In most air pollution control

applications, particles less than  $100 \mu\text{m}$  are in the laminar flow region. Transition and turbulent flow conditions are relevant primarily to the gravity settling of large agglomerates in fabric filters and electrostatic precipitators.

The experimental data that are the basis for Figure 30.7 can be used to relate the values of  $C_D$  and  $Re_p$  as expressed in equations for each particle Reynolds region.<sup>17</sup> The drag coefficient in the laminar flow region ( $Re_p < 1$ ) is:

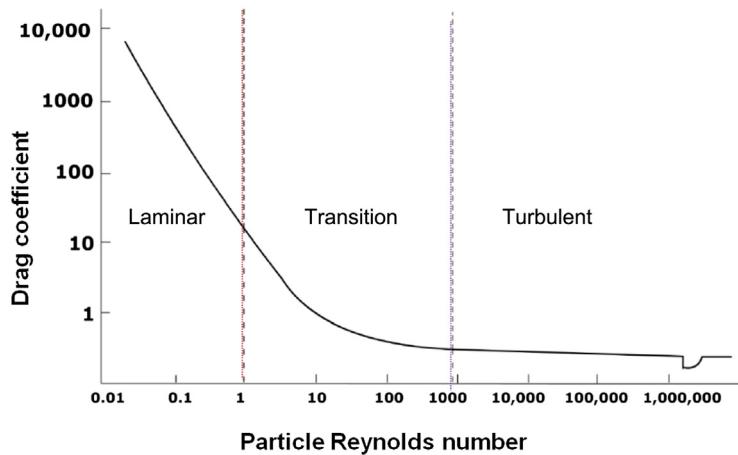
$$C_D = \frac{24}{Re_p} \quad (30.16)$$



**FIGURE 30.6** Cunningham slip correction factor as a function of temperature and particle diameter. Ref. 17.

<sup>b</sup> The laminar region is also known as the Stokes region.

<sup>c</sup> The turbulent region is also known as the Newton region.



The drag coefficient in the transition flow region ( $1 < \text{Re}_p < 1000$ ) is:

$$C_D = \frac{18.5}{\text{Re}_p^{0.6}} \quad (30.17)$$

The drag coefficient in the turbulent flow region ( $\text{Re}_p > 1000$ ) is:

$$C_D = 0.44 \quad (30.18)$$

These equations apply to particles with diameters  $>3 \mu\text{m}$ , i.e. those where the gas is continuous around the particle. For smaller particles, the gas appears as distinct molecules. Such small-diameter particles can slip between the gas molecules, which means they fall faster than relationships developed for continuous media predict. English mathematician Ebenezer Cunningham deduced in 1910 that the drag coefficient should be reduced for small particles.<sup>18</sup> This means that the drag coefficient equation for the laminar region must be modified to include a term called the Cunningham slip correction factor ( $C_C$ ):

$$C_D = \frac{24}{\text{Re}_p \cdot C_C} \quad (30.19)$$

An approximation of the slip correction (see Figure 30.6) can be based on the temperature and the particle diameter:

$$C_C = 1 + \frac{6.21 \times 10^{-4} T}{d_p} \quad (30.20)$$

where  $T$  is the absolute temperature (K) and  $d_p$ , the particle diameter ( $\mu\text{m}$ ).

Applying the slip corrections and substituting terms allow drag forces to be calculated for each flow region. The drag force for the laminar region is:

$$F_D = \frac{3\pi\mu_g v_p d_p}{C_C} \quad (30.21)$$

FIGURE 30.7 Relationship between drag coefficient and particle Reynolds number. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 17.

The drag force for the transition flow region is:

$$F_D = 2.30(d_p \cdot v_p)^{1.4} \cdot \mu_g^{0.6} \cdot \rho_g^{0.4} \quad (30.22)$$

The drag force for the turbulent flow region is:

$$F_D = 0.05\pi(d_p \cdot v_p)^2 \cdot \rho_g \quad (30.23)$$

where,  $\mu_g$  is the gas viscosity ( $\text{g cm}^{-1} \text{s}^{-1}$ );  $d_p$ , particle diameter (cm);  $\rho_g$ , gas density ( $\text{g cm}^{-3}$ );  $v_p$ , particle velocity relative to the gas ( $\text{cm s}^{-1}$ ); and  $C_C$ , Cunningham slip factor (dimensionless).

With buoyancy not a factor, the two forces dominating particle deposition are gravity and drag. As the particle accelerates, its velocity increases. As shown in Figure 30.6, gravity and drag work against one another, either keeping the particle suspended and moving it toward settling. Thus, another way of considering Eqn (30.3) is to show when this balance is achieved when the two forces are equal:

$$\sum F = F_G - F_D = m_p \cdot a_p = m_p \frac{dv_p}{dt} = 0 \quad (30.24)$$

The drag force on the particle also increases with increasing velocity. At some point, velocity will become high enough that the drag force will be as large as the gravitational force. At this point, the gravitational and drag force balance, i.e. the net force is zero, and the particle will no longer accelerate, reaching a constant velocity. This constant velocity is known as the terminal settling velocity ( $v_t$ ).

Terminal velocities differ for the three regions and can be derived by substituting the terms:

$$\text{Laminar flow: } v_t = \frac{g \cdot C_C \cdot \rho_p \cdot d_p^2}{18\mu_g} \quad (30.25)$$

$$\text{Transition flow: } v_t = \frac{0.153g^{0.71} \cdot \rho_p^{0.71} \cdot d_p^{1.14}}{\mu_g^{0.43} \cdot \rho_g^{0.29}} \quad (30.26)$$

$$\text{Turbulent flow: } v_f = 1.74 \left( \frac{g \cdot \rho_p \cdot d_p}{\mu_g} \right)^{0.5} \quad (30.27)$$

For example, at 20 °C, the  $K$  value of a 10 µm particle in air (density =  $1.2 \times 10^{-3}$  g cm $^{-3}$ ; viscosity =  $1.8 \times 10^{-4}$  g cm $^{-1}$  s $^{-1}$ ) with a particle density of 1.0 g cm $^{-3}$  would be:

$$K = 1.0 \times 10^{-3} \text{ cm} \left( \frac{(980 \text{ cm s}^{-2}) \times (1.0 \text{ g cm}^{-3}) \times (1.2 \text{ g} \times 10^{-3} \text{ cm}^{-3})}{(1.80 \times 10^{-4} \text{ g cm}^{-1} \text{ s}^{-1})^2} \right)^{0.33} \approx 0.3$$

where  $v_t$  is the terminal particle settling velocity (cm s $^{-1}$ );  $g$ , particle acceleration due to gravity (980 cm s $^{-2}$ );  $C_C$ , Cunningham slip correction factor (dimensionless);  $\mu_g$ , gas viscosity (g cm $^{-1}$  s $^{-1}$ );  $d_p$ , particle diameter (cm);  $\rho_p$ , particle density (g cm $^{-3}$ );  $\rho_g$ , gas density (g cm $^{-3}$ ); and  $v_p$ , particle velocity relative to the gas (cm s $^{-1}$ ).

The slip correction and Reynolds numbers can now be used to determine the flow region in which the parti-

Thus, this is in the laminar flow region. Note that for more viscous gases, the  $K$  value would be much smaller, since the term for gas viscosity in the denominator is squared (squaring numbers <1 decreases the product). Thus, more viscous gases have larger laminar flow regions (i.e. flow is less likely to be turbulent) than less viscous gases.

Assuming  $C_C = 1.0$ , the terminal velocity for this particle is:

$$v_t = \frac{g \cdot C_C \cdot \rho_p \cdot d_p^2}{18 \mu_g} = \left( \frac{(980 \text{ cm s}^{-2}) \times (1.0 \text{ g cm}^{-3}) \times (10 \times 10^{-4} \text{ cm})^2}{18 \times (1.80 \times 10^{-4} \text{ g cm}^{-1} \text{ s}^{-1})} \right)^{0.33} \approx 0.3 \text{ cm s}^{-1}.$$

cles are settling in the pollution control equipment. This is found by using a characteristic value, i.e. the  $K$  value, for each type of flow:

$$K = d_p \left( \frac{g \cdot \rho_p \cdot \rho_g}{\mu_g^2} \right)^{0.33}$$

This particle, i.e. diameter = 10 µm, is actually considered a coarse particle in the ambient air, but is relatively small with regard to gravity-based settling equipment. For example, a larger particle, e.g. diameter = 100 µm, and a denser particle, e.g.  $\rho_p = 2$  of 1.0 g cm $^{-3}$ , would be well within the transitional flow regime:

$$K = 1.0 \times 10^{-2} \text{ cm} \left( \frac{(980 \text{ cm s}^{-2}) \times (2.0 \text{ g cm}^{-3}) \times (1.2 \text{ g} \times 10^{-3} \text{ cm}^{-3})}{(1.80 \times 10^{-4} \text{ g cm}^{-1} \text{ s}^{-1})^2} \right)^{0.33} \approx 38$$

Therefore, for this particle, the terminal velocity would be calculated using Eqn (30.16):

$$v_t = \frac{0.153 g^{0.71} \cdot \rho_p^{0.71} \cdot d_p^{1.14}}{\mu_g^{0.43} \cdot \rho_g^{0.29}} = \frac{[0.153 \times (980 \text{ cm s}^{-2})]^{0.71} \times (2.0 \text{ g cm}^{-3})^{0.71} \times (1.0 \times 10^{-2} \text{ cm})^{1.14}}{(1.80 \times 10^{-4} \text{ g cm}^{-1} \text{ s}^{-1})^{0.43} \times (1.2 \times 10^{-3} \text{ g cm}^{-3})^{0.29}} \approx 86 \text{ cm s}^{-1}.$$

The units for the variables are the same as the previous equations, with the gravitational acceleration ( $g$ ) = 980 cm s $^{-2}$ .

Each flow region type has a  $K$  value range:

Laminar region:  $K < 2.62$

Transitional region:  $2.62 < K < 69.12$

Turbulent region:  $K > 69.12$

Obviously, with this greater terminal velocity, the denser and larger particle would be much more amenable to gravitational collection equipment. These equations have been used to calculate the terminal settling velocities of a wide range of particles with physical diameters  $\geq 10^{-2}$  µm. Table 30.5 indicates that terminal settling velocities are negligible for the very fine PM, i.e. diameters  $< 2.5$  µm and even for much of the coarse PM fraction,

**TABLE 30.5** Terminal Settling Velocities for Spherical, Unit-Density Particles in Air at 25 °C

Particle Size ( $\mu\text{m}$ )	Terminal Settling Velocity at 25 °C ( $\text{cm s}^{-1}$ )	Flow Condition
0.1	0.000087	Laminar
1.0	0.0035	Laminar
2.5	0.2	Laminar
10.0	0.304	Laminar
50.0	7.5	Laminar
80.0	19.3	Laminar
100.0	31.2	Transitional
200.0	68.8	Transitional
1000.0	430.7	Transitional
10,000.0	1583	Turbulent
100,000.0	5004	Turbulent

Source: Ref. 17.

i.e.  $< 10 \mu\text{m}$ . This indicates that PM control devices that employ only gravitational settling are primarily used for very coarse PM and are useful for initial separation and as precleaners designed to decrease the large-particle fraction before entering a next stage of treatment, or in front of air movers and other ancillary equipments. They are particularly useful for gravity settling to remove large agglomerated masses or clumps of dust that have been collected on fabric filter, precipitator plates, or other collection surfaces. These large clumps of material have high terminal settling velocities (e.g. the bottom rows in Table 30.5).

Another important force that acts in similar way as gravitation is centrifugal force. This is discussed in detail later in this chapter.

### 30.3.4 Particle Morphology

The assumption in these force equations that a particle is spherical, however, is not actually the case in most air pollutant scenarios. Indeed, another particle characteristic that influences removal is the relationship between aerodynamic diameter and shape or morphology. For example, the settling velocities in Table 30.5 are assumed to be for spheres, but these values would differ for other shapes. The unit-density sphere mentioned in the table's caption is a correction for both density, i.e.  $\rho_p = 1 \text{ g cm}^{-3}$  = the density of water at STP and the condition of the air (i.e. calm), but should also be corrected for the different morphology of a particle compared to that of a sphere.

Few particles are spheres; however, so particles that appear to be different in physical size and shape can have the same aerodynamic diameter, as shown in

**Table 30.6.** Conversely, some particles that appear similar can have somewhat different aerodynamic diameters. Particles can be spheres, hollow spheres, irregular shapes, flakes, fibers, aggregates, and condensation flocs.<sup>19</sup>

### 30.3.5 Mechanisms of Particulate Removal

The principal PM removal technologies are inertial and gravitational separation, fabric filtration, and electromagnetics. Filtration is an important technology in every aspect of environmental engineering (i.e. air pollution, wastewater treatment, drinking water, and even hazardous waste and sediment cleanup). Basically, filtration consists of four mechanical processes: (1) diffusion, (2) interception, (3) inertial impaction, and (4) electrostatics (see Figure 6.33 in Chapter 6). Diffusion is important only for very small particles ( $< 0.1 \mu\text{m}$  diameter) because the Brownian motion allows them to move in a "random walk" away from the air stream. Interception works mainly for particles with diameters between 0.1 and 1  $\mu\text{m}$ . The particle does not leave the air stream but comes into contact with the filter medium (e.g. a strand of fiberglass or fabric fiber). Inertial impaction, as explained in the cyclone discussion, collects particles sufficiently large to leave the air stream by inertia (diameters  $> 1 \mu\text{m}$ ).

Electrostatics consist of electrical interactions between the atoms in the filter and those in the particle at the point of contact (Van der Waal's force), as well as electrostatic attraction (charge differences between particle and filter medium). These are the processes at work in large-scale electrostatic precipitators (ESPs) that are employed in coal-fired power plant stacks around the world for particle removal. Other important factors affecting filtration efficiencies include the thickness and pore diameter of the filter, the uniformity of particle diameters and pore sizes, the solid volume fraction, the rate of particle loading onto the filter (e.g. affecting particle "bounce"), the particle phase (liquid or solid), capillarity and surface tension (if either the particle or the filter media are coated with a liquid), and characteristics of air or other carrier gases, such as velocity, temperature, pressure, and viscosity.

Environmental engineers have been using filtration to treat air and water for several decades. Air pollution controls employing fabric filters (i.e. baghouses), remove particles from the air stream by passing the air through a porous fabric. The fabric filter is efficient at removing fine particles and can exceed efficiencies of 99%. Based solely on an extrapolation of air pollution control equipment, a filter should be better than a cyclone. However, this does not take into operational efficiencies and effectiveness, which are very important to the consumer and the engineer. Changing the bag and insuring that it does not exceed its capacity must be monitored closely by the

TABLE 30.6 Morphology's Effect on Particle Diameter ( $d$ ) and Density ( $\rho_p$ ) for Three Particles with the Same Aerodynamic Diameter ( $d_p$ )

	Shape	Density ( $\rho_p$ ) and diameter ( $d$ )	Aerodynamic diameter ( $d_p$ )
	Solid sphere	$\rho_p = 2.0 \text{ g cm}^{-3}$ $d = 1.4 \mu\text{m}$	
	Hollow sphere	$\rho_p = 0.5 \text{ g cm}^{-3}$ $d = 2.8 \mu\text{m}$	$d_p = 2.0 \mu\text{m}$
	Irregular	$\rho_p = 2.3 \text{ g cm}^{-3}$ $d = 1.3 \mu\text{m}$	

Adapted from: Ref. 19.

user. Also, the efficiency of the equipment is only as good as the materials being used. For example, a filter's efficiency depends on interception, inertial impaction, and electromagnetics; and to a lesser extent diffusion. However, the cyclone only requires optimization for inertia.

Selecting the correct control device is a matter of optimizing efficiencies. In some environments, e.g. research "clean rooms" in laboratories and assembly operations (e.g. semiconductors, high-efficiency particle air (HEPA)), filters are fitted to equipment to enhance removal efficiency. Efficiency is often expressed as a percentage. So a 99.99% HEPA filter is efficient enough to remove 99.99% particles from the air stream. This means that if 10,000 particles enter the filter, on average only one particle would pass all the way through the filter. This is exactly the same concept that we use for incinerator efficiency, but it is known as destruction removal efficiency (DRE), since it depends on at least two forms of energy: (1) thermal destruction of pollutants into simpler, less toxic compounds; and (2). motion for the physical removal of the breakdown products. For example, in the United States, federal standards require

that hazardous compounds can only be incinerated if the process is 99.99% efficient, and for the more toxic compounds (i.e. "extremely hazardous wastes") the so-called "rule of six nines" applies (i.e. DRE >99.9999%). The HEPA and DRE calculations are simply restatements of Eqn (30.1):

$$\text{DRE or HEPA efficiency} = \frac{M_{\text{in}} - M_{\text{out}}}{M_{\text{in}}} \times 100 \quad (30.28)$$

Thus, if  $10 \text{ mg min}^{-1}$  of a hazardous compound is fed into the incinerator, only  $0.001 \text{ mg min}^{-1} = 1 \mu\text{g min}^{-1}$  is allowed to exit the stack for a hazardous waste. If the waste is an extremely hazardous waste, only  $0.00001 \text{ mg min}^{-1} = 0.01 \mu\text{g min}^{-1} = 10 \text{ ng min}^{-1}$  is allowed to exit the stack. This is the same concept that is used throughout environmental engineering to calculate treatment and removal efficiencies. For example, assume that raw wastewater enters a treatment facility with  $300 \text{ mg l}^{-1}$  biochemical oxygen demand ( $\text{BOD}_5$ ),  $200 \text{ mg l}^{-1}$  suspended solids (SS), and  $10 \text{ mg l}^{-1}$  phosphorous (P). If the plant must meet effluent standards of  $<10 \text{ mg l}^{-1}$   $\text{BOD}_5$ ,  $<10 \text{ mg l}^{-1}$  SS, and  $<1 \text{ mg l}^{-1}$  P, the removal rates of these contaminants must be 97%

for  $\text{BOD}_5$ , 95% for SS, and 90% for P, respectively. The pure efficiency values may be misleading because the ease of removal can vary significantly with each contaminant. In this case, gravitational settling in the primary stages of the treatment plant can remove most of the SS, and the secondary treatment stage removes most of the BOD, but more complicated, tertiary treatment is needed for removing most of the nutrient P.

Although the fine and ultrafine PM have received the largest focus recently, there remain important reasons to remove the mass in the coarse fraction of particles, i.e. ranging between 2.5 and 10  $\mu\text{m}$  aerodynamic diameter. These may consist of potentially toxic components, for example, resuspended road dust, brake lining residues, industrial byproducts, tire residues, heavy metals, and aerosols generated by organisms spores (known as "bioaerosols"), such as tree pollen and mold spores. A large fraction of these coarse particles may deposit to the upper airways, causing health scientists to link them to asthma. And, since asthma appears to be increasing in children, their role in triggering asthma and other respiratory diseases needs to address a compliment of ultrafine, fine, and coarse particles.

Thus, equipment selection has been complicated by some fairly simple technical specifications. Efficiency is an important part of effectiveness, although the two terms are not synonymous. As we discussed, efficiency is simply a metric of what you get out of a system compared to what you put in. However, you can have a bunch of very efficient systems that may in to be ineffective. They are all working well as designed, but they may not be working on the right things, or their overall configuration is not optimal to solve the problem at hand. So, the correct control device is the one that gives not only optimal efficiency, but also that effectively addresses the specific pollution problem at hand.

## 30.4 REMOVAL OF DRY PM

The moisture content and stickiness of the air stream and particles are very important factors on equipment selection. Generally, dry aerosols differ so much from the carrier gas stream that their removal should present no major difficulties. The aerosol is different physically, chemically, and electrically from the gas in which it is suspended. It has vastly different inertial properties than the carrying gas stream and can be subjected to an electric charge. It may be soluble in a specific liquid. With such a variety of removal mechanisms that can be applied, it is not surprising that PM, such as mineral dust, can be removed by a filter, wet scrubber, or ESP with equally satisfactory results.

### 30.4.1 Inertial Collectors

Inertial collectors, which include cyclones, baffles, louvers, and rotating impellers, operate on the principle that the aerosol material in the carrying gas stream has a greater inertia than the gas. Since the drag forces on the particle are a function of the diameter squared and the inertial forces are a function of the diameter cubed, it follows that as the particle diameter increases, the inertial (removal) force becomes relatively greater. Inertial collectors, therefore, are most efficient for larger particles. The inertia is also a function of the mass of the particle, so that heavier particles are more efficiently removed by inertial collectors. These facts explain why an inertial collector will be highly efficient for removal of 10- $\mu\text{m}$  rock dust and very inefficient for 5- $\mu\text{m}$  wood particles. It would be very efficient, though, for 75- $\mu\text{m}$  wood particles.

The most common inertial collector is the cyclone, which is used in two basic forms: the tangential inlet and the axial inlet (see Figure 30.8). In actual industrial practice, the tangential inlet type is usually a large (1–5 m in diameter) single cyclone, while the axial inlet cyclone is relatively small (about 20 cm in diameter and arranged in parallel units for the desired capacity).

For any cyclone, regardless of type, the radius of motion (i.e. curvature), the particle mass, and the particle velocity determine the centrifugal force exerted on the particle. This centrifugal force may be expressed as

$$F = MA \quad (30.29)$$

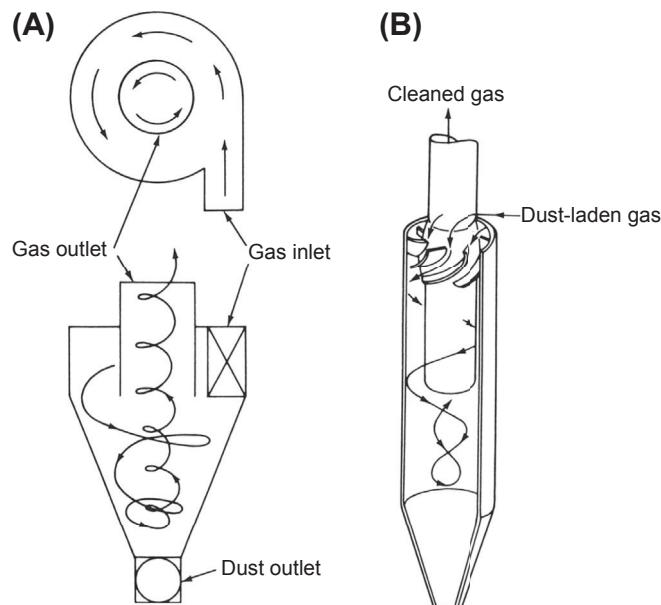


FIGURE 30.8 Two common cyclone configurations : (A) tangential inlet and (B) axial inlet. (For color version of this figure, the reader is referred to the online version of this book.)

where,  $F$  is the force (centrifugal);  $M$ , mass of the particle; and  $A$ , acceleration (centrifugal), and

$$A = \frac{V^2}{R} \quad (30.30)$$

where  $V$ , the velocity of particle; and  $R$ , the radius of curvature. Therefore:

$$F = \frac{MV^2}{R} \quad (30.31)$$

Other types of inertial collectors which might be used for particulate separation from a carrying gas stream depend on the same theoretical principles developed for cyclones. Table 30.7 summarizes the effect of the common variables on inertial collector performance.

Although decreasing the radius of curvature and increasing the gas velocity both result in increased efficiency, the same changes cause increased pressure drop through the collector. Design of inertial collectors for maximum efficiency at minimum cost and minimum pressure drop is a problem which lends itself to computer optimization. Unfortunately, many inertial collectors, including the majority of the large single cyclones, have been designed to fit a standard-sized sheet of metal rather than a specific application and gas velocity. As tighter emission standards are adopted, the major use of inertial collectors will be to preclean in front of more sophisticated fine PM and gas control devices.

In a cyclone (Figure 30.9), air is rapidly circulated causing suspended particles to change directions. Due to their inertia, the particles continue in their original direction and leave the air stream (see Figure 30.10). This works well for larger particles because of their relatively large masses (and greater inertia), but very fine particles are more likely to remain in the air stream and stay suspended. The dusty air is introduced in the cyclone from the top through the inlet pipe tangential to the cylindrical portion of the cyclone. The air whirls

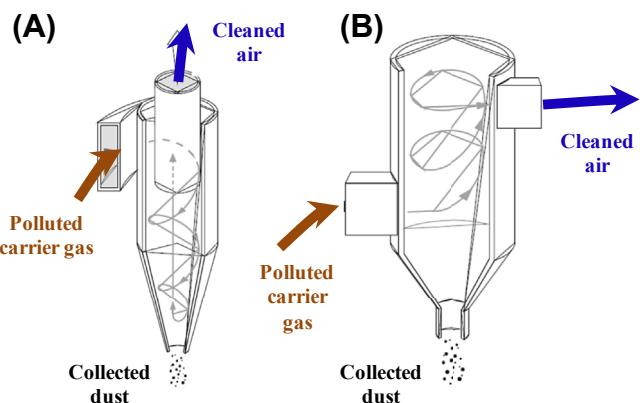


FIGURE 30.9 Schematic of simple cyclone separators: (A) Top inlet type; (B) Bottom inlet type. Adapted from: U.S. Environmental Protection Agency (2004). (For color version of this figure, the reader is referred to the online version of this book.) Air Pollution Control Orientation Course, <http://www.epa.gov/air/oqps/eog/course422/ce6.html>; accessed November 30, 2013.

downward to form a peripheral vortex, which creates centrifugal forces. As a result, individual particles are hurled toward the cyclone wall and, after impact, fall downward where they are collected in a hopper. When the air reaches the end of the conical segment, it will change direction and move upward toward the outlet. This forms an inner vortex. The upward airflow against gravitation allows for additional separation of particles. The cyclone vacuum cleaner applies the same inertial principles, with the collected dust hitting the sides of the removable cyclone separator and falling to its bottom.

### 30.4.1.1 Centrifugal Force in a Cyclone

The geometry of pollution control equipment is important. For example, circular designs are usually preferable to avoid pockets of zero to very low airflows, which can attract PM and increase the frequency of cleaning. In addition, inertial forces are often very effective when PM-laden air flows in a circular route within a cylinder (see Figure 30.11).

The approach used to estimate terminal settling velocity due to gravity can be used for the motion of a particle due to centrifugal force ( $F_C$ ). The drag and centrifugal forces balance at some point:

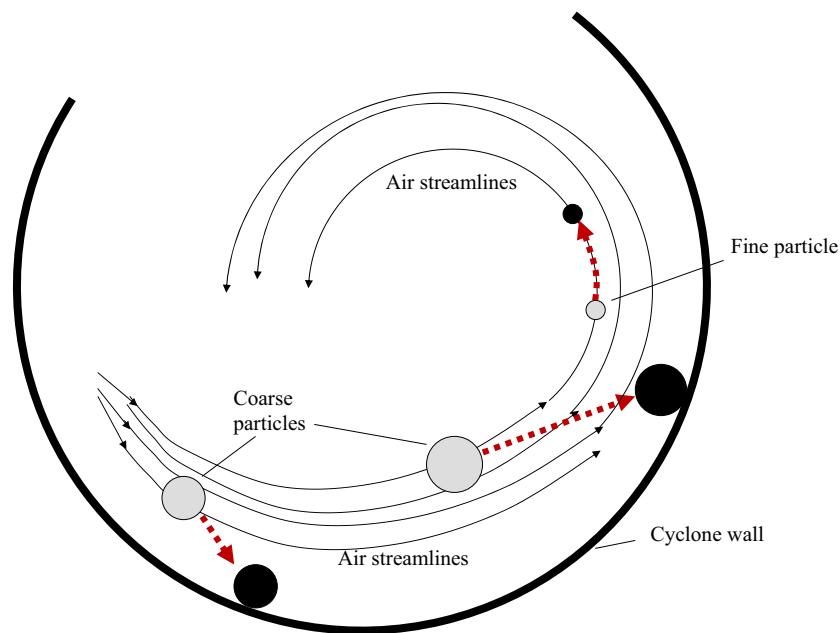
$$\sum F = F_C - F_D = 0 \quad (30.32)$$

$$F_C = \frac{m_p v_\tau^2}{R} \quad (30.33)$$

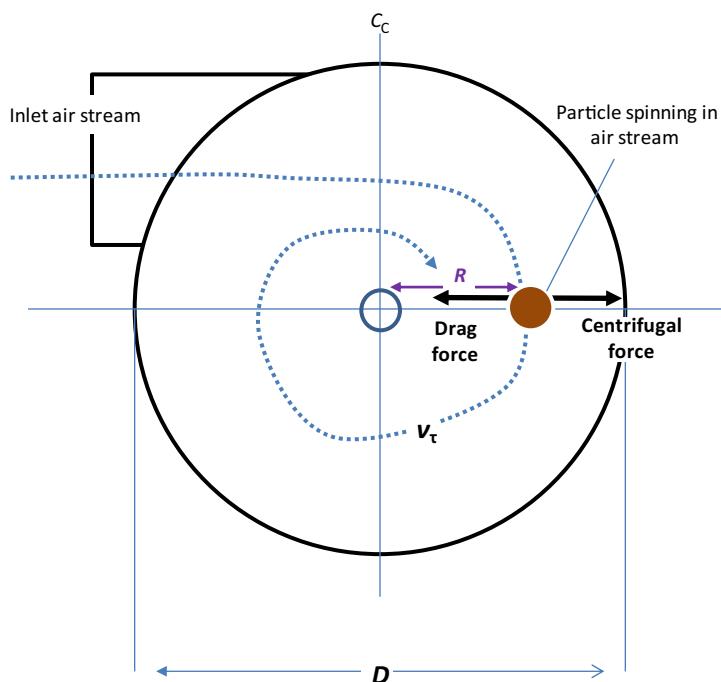
where  $F_C$  is the centrifugal force ( $\text{g cm s}^{-2}$ );  $m_p$ , particle mass (g);  $v_\tau$ , tangential velocity of the gas ( $\text{cm s}^{-1}$ ); and  $R$ , radial position of the particle (cm). The combined

TABLE 30.7 Effect of Independent Variables on Inertial Collection Efficiency

Independent Variable of Concern	Increase or Decrease to Improve Efficiency
Radius of curvature	Decrease
Mass of particle	Increase
Particle diameter	Increase
Particle surface/volume ratio	Decrease
Gas velocity	Increase
Gas viscosity	Decrease



**FIGURE 30.10 Inertial forces in a cyclone separator.** The inertia of heavier particles (mainly coarse fraction, with some very dense fine particles) is high enough that they leave the air stream of the vortex created by the cyclone inside configuration. The particle next collides with the cyclone wall. The fine and ultrafine particles, having smaller mass, continue moving with the air stream, thus remaining suspended and not collected until the stream velocity decreases to a point where it can no longer carry the particle. If this velocity is never reached, the particle will exit the cyclone. (For color version of this figure, the reader is referred to the online version of this book.)



**FIGURE 30.11 Centrifugal force demonstrated by the top view cutaway schematic of a cyclone.**  $v_t$ , tangential velocity of the air;  $D$ , cyclone inside diameter;  $R$ , radial position of the particle;  $C_C$ , Cunningham. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Ref. 17.

term  $\frac{\nu_t^2}{R}$  is similar to the  $g$  (gravitational constant) term used to calculate gravitational settling.

The particle mass can also be expressed in terms of particle density and volume:

$$F_C = \frac{\pi d_p^3 \rho_p v_t^2}{6R} \quad (30.34)$$

where,  $d_p$  is the physical particle density (cm) and  $\rho_p$ , particle density ( $\text{g cm}^{-3}$ ). And, for fine PM with laminar Reynolds numbers, the drag force is:

$$F_D = \frac{3\pi\mu_g v_p d_p}{C_C} \quad (30.35)$$

Equations (30.30) and (30.31) can be substituted into Eqn (30.28) to find particle's velocity in the cylinder:

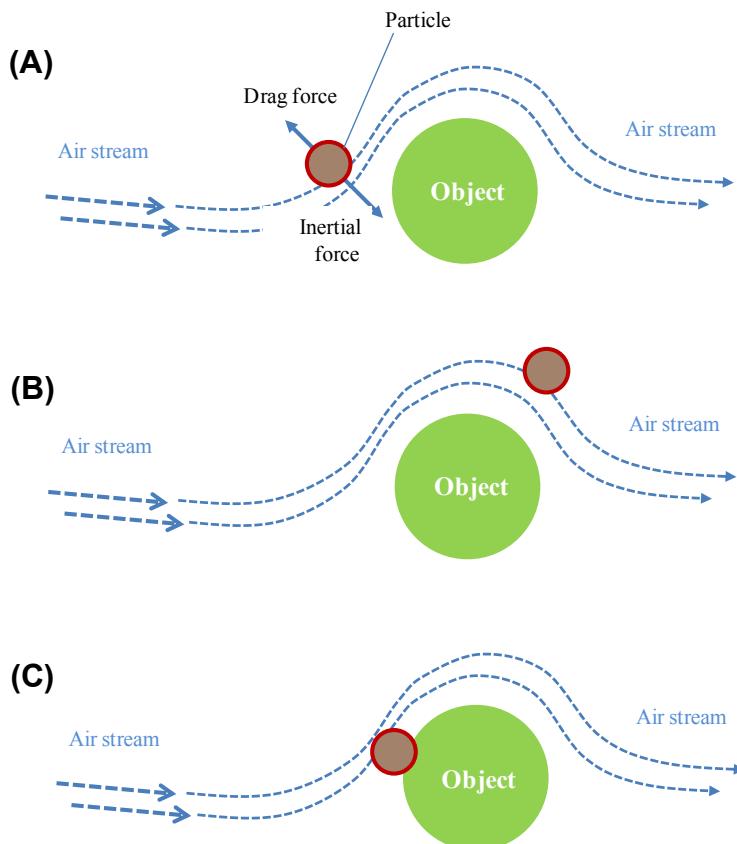
$$v_p = \frac{C_C d_p^2 \rho_p v_t}{18\mu_g R} \quad (30.36)$$

Thus, the particle velocity across the air streamlines and its velocity moving toward the walls of the cyclone are proportional to the square of the particle's diameter.

As is the case for settling velocities, the larger the particle the more effective the cyclone will be at PM removal. Also, no matter the size, the radial velocity of the particle is proportional to the square of the air-stream tangential velocity and inversely proportional to the radius of the cyclone. Thus, when selecting a cyclone system, these factors need to be known, since they determine the amount of spin within the cyclone. Higher air-stream velocities will increase radial velocities, which increase the amount of PM collected. It is important not to "oversize" a cyclone, since a small radius causes a sharper turn of the air stream, which improves cyclone PM collection efficiencies.

### 30.4.1.2 Inertial Impaction

A moving particle in the air stream can come into contact with surfaces of stationary and slower moving objects. The air-stream flows around the object, but due to the particle's inertia the particle is displaced across the air-stream lines. As such, it moves into the object and, if there is sufficient inertia, contacts the object and is captured (see Figure 30.12). The object can be a plate or other target surface.



**FIGURE 30.12 Inertial impactation.** The air-stream flows around the object (A). If the momentum of the air stream around the object and drag force is higher than the inertial force, the object will miss the object (B). However, if the inertial force sufficiently exceeds the drag force and the particle velocity is high enough, the particle will contact the object and be captured (C). (For color version of this figure, the reader is referred to the online version of this book.)

Note the similarities of the inertial force competing with the drag force to the gravitational and centrifugal forces discussed earlier. Indeed, impaction efficiencies may be evaluated with the same approaches used for gravitational and centrifugal forces. For particles with  $Re < 1$ , impaction effectiveness can relate to a dimensionless inertial impaction parameter ( $\Psi$ ), calculated as:

$$\Psi = \frac{C_C d_p^2 3 y_p \rho_p}{18 \mu_g D_C} \quad (30.37)$$

where,  $C_C$  is the Cunningham slip correction factor (dimensionless);  $d_p$ , physical particle diameter (cm);  $y_p$ , difference in velocity and collection object ( $\text{cm s}^{-1}$ );  $D_C$ , diameter of the collection object (cm);  $\rho_p$ , density of particle; and  $\mu_g$ , gas velocity ( $\text{g cm}^{-1} \text{s}^{-1}$ ). If the Stokes number (Stk) is used as the inertial impaction parameter rather than  $\Psi$ , the parameter will be twice the value calculated in Eqn (30.37) since, rather than a coefficient of 18 in the denominator, the Stk denominator has a coefficient of 9.

With increasing  $\Psi$  values, particles are more likely to move radially toward a collection surface. Conversely, smaller  $\Psi$  values mean that the particle is likely to remain in the air stream and miss the target collection surface. Therefore, larger diameter, faster moving, and denser particles are more likely to be captured by inertial impaction. Also, smaller collection targets (e.g. fine wires or filter fibers) increase the likelihood of inertial capture.

### 30.4.1.3 Brownian Motion

As mentioned, molecular diffusion is only an important collection mechanism for very small particles (e.g.  $< 0.2 \mu\text{m}$  diameters). These ultrafine PM or nanoparticles can be deflected slightly by coming into contact with gas molecules. This deflection is the result of kinetic energy from fast-moving gas molecule imposed upon the small particle. The dimensionless diffusional collection parameter ( $\Psi_D$ ) is analogous to the inertial impaction parameter discussed in the previous section:

$$\Psi_D = \frac{X_p}{D_C v_p} \quad (30.38)$$

where,  $X_p$  is the particle diffusivity ( $\text{cm}^2 \text{s}^{-1}$ );  $D_C$ , collection target's diameter (cm); and  $v_p$ , relative velocity between the particle and the target object. Particle diffusivity is expressed as:

$$X_p = \frac{C_C k T}{3 \pi \mu_g d_p} \quad (30.39)$$

where,  $k$  is the Boltzmann constant ( $\text{g cm}^2 \text{s}^{-1} \text{K}^{-1}$ );  $C_C$ , Cunningham slip correction factor (dimensionless);  $d_p$ , particle's physical diameter;  $T$ , absolute temperature (K); and  $\mu_g$ , gas viscosity ( $\text{g cm}^{-1} \text{s}^{-1}$ ).

As  $\Psi_D$  increases, so does the tendency of a particle to be collected by applying Brownian motion. Thus, very small particles in low viscosity gases are the best candidates for collection by molecular diffusive processes. However, the additional collection provided by diffusion becomes negligible above  $0.3 \mu\text{m}$  diameter.

### 30.4.1.4 Electrostatic Mechanisms

Field charging and diffusion (or ion) charging are employed in PM collection equipment. Field charging works best for particles larger than  $2 \mu\text{m}$ , with collection rapidly diminishing with decreasing diameter. The opposite is true for diffusion charging. Diffusion charging is most effective for particles with diameters  $< 0.4 \mu\text{m}$ , and improves with diminishing diameters.

Diffusion charging occurs from collisions between particles and unipolar ions in the air stream. The collisions result from random walks (Brownian) of both ions and very small particles. The diffusion charging continues until the surface gains particles that have sufficient charge to repel the ions. Diffusion charging needs no electrical field, but if one exists it will influence particles that have acquired a charge. The charged particles will move according to the electrical field lines in the direction of the lower field strength. Thus, the collection surface would ideally have a large charge differential with the particles.

Field charging results from the creation of a strong electrical field having a high unipolar ion concentration. The ions need a large enough mass to cause local disruptions of the electrical field lines. The ions travel toward the particle surface along the field lines intersecting the particle. The electrical charge transfer will continue until the particle has an electrical field strength sufficient to repel the electric field (i.e. it has reached a saturation charge).

The number of charges imparted to a particle from field charging is a function of square of the particle diameter. This charge level is reached rapidly and, once charged, the particles are strongly influenced by the electrical field that makes for a force toward the collection surface. The particle charge is often expressed as the product of the number of charges ( $n$ ) times the smallest unit of charge (i.e. the charge of an electron, which is  $4.8 \times 10^{-10}$  statcoulombs). The force on a particle with  $n$  units of charge in an electric field ( $E$ ) is expressed as:

$$F_E = n \cdot e \cdot E \quad (30.40)$$

where,  $F_E$  is the electrostatic charge (dyne);  $n$ , number of charges;  $e$ , charge of electron ( $4.8 \times 10^{-10}$  statcoulombs); and  $E$ , electrical field strength (statvolts  $\text{cm}^{-1}$ ).

Electric fields create forces orders of magnitude greater than gravity. The particle velocities within electric fields can be estimated in the same way as gravity settling and centrifugal force:

$$F_E - F_D = 0 \quad (30.41)$$

$$n \cdot e \cdot E - \frac{3\pi\mu_g d_p v_p kT}{C_C} = 0 \quad (30.42)$$

The migration or drift velocity toward the collecting service ( $\omega$ ) applies to particles in the laminar flow region. For  $Re_p > 1$ , the mathematics become much more complicated. This migration is expressed as:

$$\omega = \frac{n \cdot e \cdot E \cdot C_C}{3\pi\mu_g d_p v_p} \quad (30.43)$$

For example,<sup>d</sup> what is the migration velocity of a 2  $\mu\text{m}$  unit-density particle carrying 800 units of charge in an electric field of 2  $\text{kV cm}^{-1}$ ? The gas temperature is 20  $^{\circ}\text{C}$ .

- To solve this problem, the following relationships are used:
- 300 V = 1 statvolt
- 1 statvolt = 1 statcoulomb  $\text{cm}^{-1}$
- 1 dyne = 1 statcoulomb $^2 \text{ cm}^{-2} = 1 \text{ g cm s}^{-2}$
- $C_C = 1.09$  (as calculated in Example 4-2)

The electric field in centimeter–gram–second units is:

$$E = 2 \frac{\text{kV}}{\text{cm}} = 2000 \frac{v}{\text{cm}} \left( \frac{\text{statvolt}}{300 \text{ volts}} \right) = 6.67 \frac{\text{statvolts}}{\text{cm}}$$

$$= 6.67 \frac{\text{statcoulom bs}}{\text{cm}^2}$$

$$\omega = \frac{neEC_C}{3\pi\mu_g d_p} = \frac{(800)(4.8 \times 10^{-10} \text{ statcoulom bs})(6.67 \frac{\text{statcoulom bs}}{\text{cm}^2})(1.09)}{3\pi(1.8 \times 10^{-4} \text{ g cm s}^{-1})(2 \times 10^{10} \text{ cm})} = 8.23 \text{ cm s}^{-1}$$

The migration velocity of the 2  $\mu\text{m}$  particle is much greater than the settling velocity of the same sized particle. Again, this illustrates that electrical fields can provide much larger force than gravity.

### 30.4.1.5 Thermophoresis and Diffusiophoresis

The remaining forces on particles that can be deployed for pollutant collection are thermophoresis and diffusiophoresis; both relatively weak compared to those already discussed.<sup>17</sup>

Temperature differences on either side of a particle can lead to particle movement, i.e. thermophoresis. The particle is deflected toward the colder side, since energy is transported from higher to lower potentials.

Similarly, a particle can move due to differences in concentrations of molecules in one part of a particle than another. This difference leads to an increase in molecular collisions, with the particle moving toward the region of lower concentration. The major means of achieving diffusiophoresis is to use water vapor that is migrating with the bulk air stream toward colder liquid (e.g. scrubber liquid) onto which the water condenses. An air stream with 15%  $\text{H}_2\text{O}$  vapor by volume and liquid with relatively constant low temperature can enhance collection efficiency substantially. For example, a study found that after a 30 inches of water column (in WC), pressure drop venturi downstream from an industrial incinerator had removed 90% of the PM and cooled the gases to 77  $^{\circ}\text{C}$  water and saturated the air stream with  $\text{H}_2\text{O}$  vapor, further cooling the air stream to 27  $^{\circ}\text{C}$  in a 3-m counter current packed-bed cooling tower cooled removed another 60% of fine PM.<sup>20</sup>

Thus, if condensation or evaporation of water is taking place, phoresis can make for particle movement. High moisture conditions lead to temperature and concentration gradients. However, typical temperature and concentration conditions in a gas stream lead to very little phoresis, so extra measures, such as the packed-bed cooling tower mentioned above, need to be provided.

### 30.4.1.6 Net Effects of Forces

For most dry pollutant collection scenarios, particle size is the key factor. Particle with diameters  $>100 \mu\text{m}$

are generally effectively collected with inertial impaction, electrostatics and, to a lesser extent from gravitational settling. Particles with diameters ranging from 10  $\mu\text{m}$  to 100  $\mu\text{m}$ , respond well to inertial and electrical

<sup>d</sup>This example is taken from: U.S. Environmental Protection Agency. APTI 413: control of particulate matter emissions. Chapter 4: particle collection mechanisms; 2012.

forces, i.e. proportional to the square of the particle diameter. However, the efficiencies diminish dramatically with smaller diameters, to a point where molecular diffusion becomes a force of choice for very small particles (<0.3 µm diameters).<sup>17</sup> Of course, a quick perusal of the equations in this chapter would indicate that no single parameter dictates the choice of the equipment. For example, gas velocity and electrical field strengths can be modulated to improve PM collection substantially.

### 30.4.2 Filtration

A filter removes PM from the carrying gas stream because the particulate impinges on and then adheres to the filter material. As time passes, the deposit of PM becomes greater and the deposit itself then acts as a filtering medium. When the deposit becomes so heavy that the pressure necessary to force the gas through the filter becomes excessive, or the flow reduction severely impairs the process, the filter must either be replaced or cleaned.

The filter medium can be fibrous, such as cloth; granular, such as sand; a rigid solid, such as a screen; or a mat, such as a felt pad. It can be in the shape of a tube, sheet, bed, fluidized bed, or any other desired form. The material can be natural or man-made fibers, granules, cloth, felt, paper, metal, ceramic, glass, or plastic. It is not surprising that filters are manufactured in an infinite variety of types, sizes, shapes, and materials.

The theory of filtration of aerosols from a gas stream is much more involved than the sieving action which removes particles in a liquid medium. The mechanisms mentioned in Chapter 6 and shown in Figure 6.33 account for the filtration of most particles, although diffusion is important only for very small particles. Note that the particles are often depicted as spheres (e.g. in Figures 6.33 and 30.10). In practice, the particles and filter elements are seldom spheres or cylinders. Thus, decisions on the optimal equipment should not simply be based on size and mass, but also morphology of the particles.

Direct interception occurs when the fluid streamline carrying the particle passes within one-half of a particle diameter of the filter element. Regardless of the particle's size, mass or inertia, it will be collected if the streamline passes sufficiently close. Inertial impaction occurs when the particle would miss the filter element if it followed the streamline, but its inertia resists the change in direction taken by the gas molecules and it continues in a sufficiently direct course to be collected by the filter element. Electrostatic attraction occurs because the particle, the filter, or both possess sufficient electrical charge to overcome the inertial forces; the particle is then collected instead of passing the filter element. Note that size separation ("sieving") plays little or no role in filtration.

#### 30.4.2.1 Filter Efficiency

Particles can be measured as either mass or count. Particle count is the number of particles in a given band of mass, such as particles with aerodynamic diameters greater than 10 µm (coarse fraction), those with diameters less than 10 µm, but greater than 2.5 µm (PM<sub>10</sub> fraction), and those with diameters less than 2.5 µm (PM<sub>2.5</sub> fraction, also known as the fine fraction). However, the bands can be further subdivided. For example, there has been concern recently about the so-called "nanoparticles". These have diameters less than 100 nm. Filtration is the most common method used to measure particles in the air. So, a sample, taken from a filter could show bands within the fine fraction, may resemble that shown in Table 30.8.

Since filtration is important in both measuring and controlling particle matter, expressions of filter efficiency are crucial to air pollution technologies. Equation (30.3) provides the overall efficiency of any air pollution removal equipment. The efficiency ( $E$ ) equation can be restated specifically for particles:

$$E = \frac{N_{\text{in}} + N_{\text{out}}}{N_{\text{in}}} \quad (30.44)$$

TABLE 30.8 Mass of Particles Collected on a Filter (Fictitious Data)

Size Range (µm)	Count (Number of Particles)	Mass (µg)	Flow Rate (l min <sup>-3</sup> )	Integration Time (min)	Mass Concentration (µg m <sup>-3</sup> )	Description
>10	2	100	16	60	96	Re-entrained dust
>2.5 < 10	20	10	16	60	9.6	Tailpipe emission
>0.01 < 2.5	200	1	16	60	0.96	Suspended colloids
>0.01	20,000	0.1	16	60	0.096	Nanoparticles; mainly carbon (fullerenes = C-60)

$$E = \frac{C_{\text{in}} + C_{\text{out}}}{C_{\text{in}}} \quad (30.45)$$

where,  $N$  is the number of particles (count) and  $C$  is the mass concentration (subscripts: in, entering; out, exiting).

Pollution control equipment often characterizes efficiency in terms of the fraction entering *versus* that exiting the filter known as particle penetration ( $P$ ):

$$P = \frac{N_{\text{out}}}{N_{\text{in}}} = 1 - E \quad (30.46)$$

$$P = \frac{C_{\text{out}}}{C_{\text{in}}} = 1 - E \quad (30.47)$$

Since  $P$  is the inverse of  $E$ , an inefficient filter is one that allows a large number or mass of particles to penetrate the filter. Thus, the air pollution engineer needs to specify the tolerances for filtration in any design of measurement or control technologies. Inherent to penetration calculations is the velocity of air entering the system. The front (entry side) of the filter is known as the face, so face velocity ( $U_0$ ) is the air's velocity just before the air enters the filter:

$$U_0 = \frac{Q}{A} \quad (30.48)$$

where,  $Q$  is the volumetric flow and  $A$  is the area of the cross section through which the air is passing. However, since the flow is restricted to the void spaces of the filter, the actual velocity in the filter itself is higher than the face velocity (same air mass through less volume). This is true for flow through any porous medium, such as polyurethane traps (see Figure 11.2 in Chapter 11) and columns of sorbant granules, like XAD resins (see Figure 11.3 in Chapter 11). Thus the velocity within the filter ( $U_{\text{filter}}$ ) is:

$$U_{\text{filter}} = \frac{Q}{A(1 - \alpha)} \quad (30.49)$$

where  $\alpha$  is the packing density (solidity),<sup>e</sup> which is inverse to the filter (or trap) porosity:

$$\alpha = \frac{V_{\text{ff}}}{V_{\text{total}}} = 1 - \phi \quad (30.50)$$

where,  $V_{\text{ff}}$  is the filter fiber volume;  $V_{\text{total}}$ , total filter volume; and  $\phi$ , porosity.

The filter configuration is similar to that of a sieve; however, filters are quite different from sieves, given that size separation is not even listed as one of the

mechanisms for PM removal. In fact, fibrous filters are more akin to numerous microscopic layers of filters, each with a specific probability of catching a particle, depending on the particle's shape and size. Therefore, the efficiency is enhanced with filter thickness. Thus, size capture is not one of the most important mechanisms for collection, compared to inertial impaction, interception, and electrostatics.

Other less important mechanisms that result in aerosol removal by filters are (1) gravitational settling due to the difference in mass of the aerosol and the carrying gas, (2) thermal precipitation due to the temperature gradient between a hot gas stream and the cooler filter medium which causes the particles to be bombarded more vigorously by the gas molecules on the side away from the filter element, and (3) Brownian deposition as the particles are bombarded with gas molecules that may cause enough movement to permit the aerosol to come into contact with the filter element. Brownian motion may also cause some of the particles to miss the filter element because they are moved away from it as they pass by.

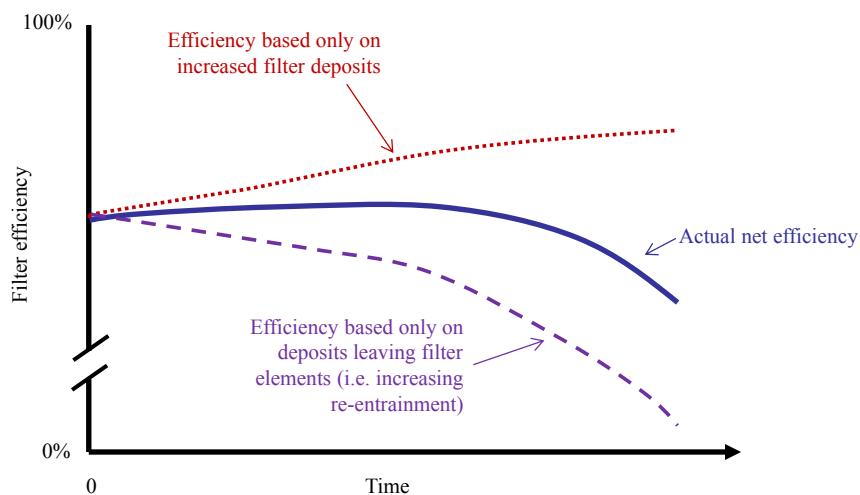
Regardless of the mechanism which causes the aerosol to come in contact with the filter element, it will be removed from the air stream only if it adheres to the surface. Aerosols arriving later at the filter element may then, in turn, adhere to the collected aerosol instead of the filter element. The result is that actual aerosol removal seldom agrees with theoretical calculations. One should also consider that certain particles do not adhere to the filter element even though they touch it. As time passes, the heavier deposits on the filter surface will be dislodged more easily than the light deposits, resulting in increased re-entrainment. Because of plugging of the filter with time, the apparent size of the filter element increases, causing more interception and impaction.

The contravening effects of all of these variables on the particle buildup and re-entrainment are shown in [Figure 30.13](#). In this hypothetical example, the net aerosol collection efficiency actually increases slightly compared to that of the clean filter (time = 0); due to the combination of attractions to filter element and newly deposit mass onto the filter elements. After time, however, the re-entrainment of deposits decreases the filter efficiency, leading to the time when filters become much less efficient and need cleaning and replacement.

### 30.4.2.2 Fabric Filter System Configurations

The types of industrial filtration systems vary considerably. Fabric filters, commonly known as baghouses,

<sup>e</sup> Packing density is analogous to bulk density in soil science, i.e. inversely proportional to porosity. Bulk density is calculated as the dry weight of soil divided by its volume. The volume includes that of the soil particles and the pores among particles, often expressed in g cm<sup>-3</sup>.



**FIGURE 30.13** Change of filtration efficiency with time. (For color version of this figure, the reader is referred to the online version of this book.)

can be highly efficient in removing PM. Filtration technologies have continuously improved from the early versions in the mid-twentieth century, with some systems efficiently removing ultrafine ( $\sim 100$  nm diameter) particles. The mechanisms include those discussed under inertia separations systems, e.g. impaction, electrostatics, and molecular (Brownian) diffusion.

Like other air pollution control equipment, filtration is only as efficient as the O&M allows, with filters susceptible to chemical degradation, physical damage (e.g. punctures, flexing, and abrasion) and thermal breakdown. Chemical, physical, and thermal susceptibility vary by filter materials (see [Table 30.9](#)). In addition, dust cake fissures can allow excessive penetration. Also,

problems can result during cleaning and bag replacement, such as excessive pressure drop.

A common configuration of a fabric filter system, i.e. the shaker filter, is shown in [Figure 30.14](#). The filter bags are fabricated from woven material, with the material and weave selected to fit the specific application. Cotton and synthetic fabrics are used for relatively low temperatures, and glass cloth fabrics can be used for elevated temperatures, up to  $290^{\circ}\text{C}$ .

The basic operating principle of all fabric filters is that they capture particles directly in the filter material or in the dust layers that form on these materials. Thus, the first mechanism at work is inertial impaction, which is quite effective for capturing PM with diameters

**TABLE 30.9** Thermal and Acid Resistance of Common Fabric Filter Materials

Filter Material	Common or Trade Name	Maximum Temperature ( $^{\circ}\text{F}$ )		Acid Resistance	Resistance to Abrasion and Flex
		Continuous	Surges		
Natural fiber, cellulose	Cotton	180	225	Poor	Good
Polyolefin	Polyolefin	190	200	Good to excellent	Excellent
Polypropylene	Polypropylene	200	225	Excellent	Excellent
Polyamide	Nylon <sup>®</sup>	200	225	Excellent	Excellent
Acrylic	Orlon <sup>®</sup>	240	260	Good	Good
Polyester	Dacron <sup>®</sup>	275	325	Good	Excellent
Aromatic polyamide	Nomex <sup>®</sup>	400	425	Fair	Excellent
Polyphenylene sulfide	Ryton <sup>®</sup>	400	425	Good	Excellent
Polyimide	P-84 <sup>®</sup>	400	425	Good	Excellent
Fiberglass	Fiberglass	500	550	Fair	Fair
Fluorocarbon	Teflon <sup>®</sup>	400	500	Excellent	Fair
Stainless steel	Stainless steel	750	900	Good	Excellent
Ceramic	Nextel <sup>®</sup>	1300	1400	Good	Fair

Source: Ref. 21.

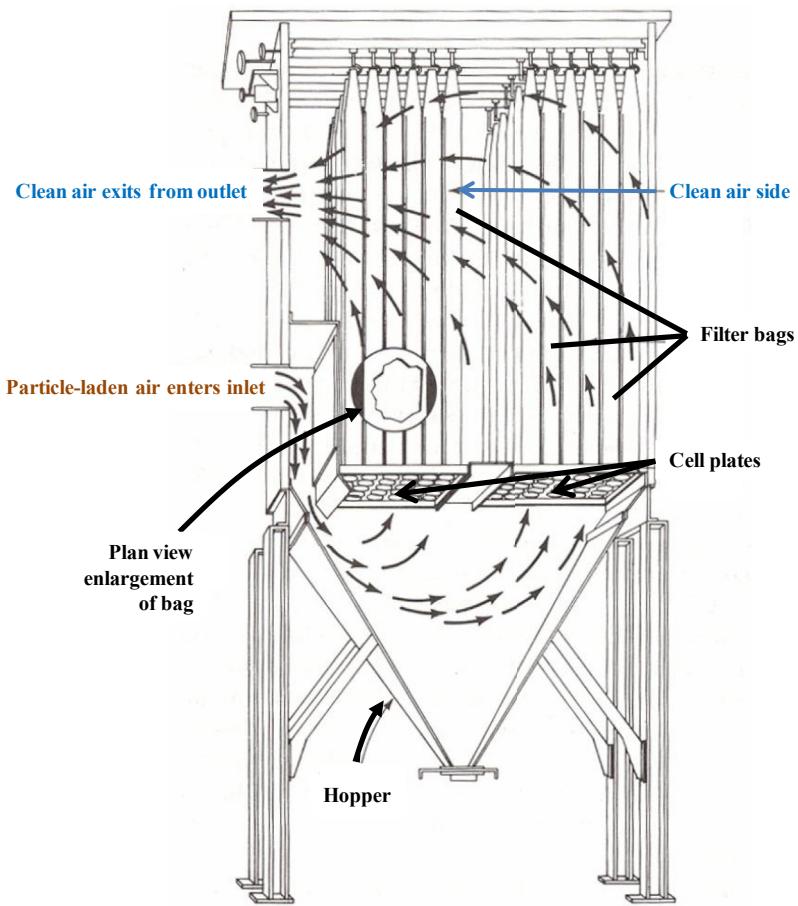


FIGURE 30.14 Common baghouse configuration (shaker filter). (For color version of this figure, the reader is referred to the online version of this book.) Ref. 21.

$\geq 1 \mu\text{m}$ , given the tortuosity of the pathways taken by particles and the many opportunities to contact objects, i.e. myriad situations like those depicted in Figure 30.12(C).

Static charge also builds in the fabric and dust cake, so electrostatic attraction also adds PM capture efficiency. However, since the charges can be either negative or positive, particles will oscillate between attraction and repulsion depending on the net charge differential between the filter and particles. Opposite or neutral polarity leads to particle attraction. Size separation or sieving can also add to PM capture after a dust layer forms.<sup>21</sup>

Brownian diffusion can add to the attraction of very small particles, especially given the protracted time and length required to traverse the filter and dust cake. In addition, the pore spaces are quite small, so the distance to surfaces is small enough that the diffusion path is very short.

The filtration collection curve is somewhat U-shaped, i.e. filters collect large and very small particles. Filtration is very efficient for  $\text{PM}_{10}$  and larger particles and reasonably efficient for ultrafines ( $<100 \text{ nm}$ ), but not nearly as

efficient for those particles in between. And, these efficiencies only occur after a sufficient dust layer forms on the filter material. Thus, efficiency is decreased substantially after cleaning or installation of new fabric. Thus, the cleaning schedule must be optimized between preventing excessive blockage and destroying efficient dust cake layers.

Other types of industrial filtration systems include (1) fixed beds or layers of granular material such as coke or sand; some of the original designs for cleaning large quantities of gases from smelters and acid plants involved passing the gases through such beds; (2) plain, treated, or charged mats or pads (common throwaway air filters used for hot air furnaces and for air conditioners are of this type); (3) paper filters of multiple plies and folds to increase filter efficiency and area (the throwaway dry air filters used on automotive engines are of this type); (4) rigid porous beds which can be made of metal, plastic, or porous ceramic (these materials are most efficient for removal of large particles such as the  $30 \mu\text{m}$  particles from a wood sanding operation); and (5) fluidized beds in which the granular material of the

bed is made to act as a fluid by the gas passing through it. Most fluidized beds are used for heat or mass transfer. Their use for filtration has not been extensive.

### 30.4.2.3 Fabric Filter Operation, Maintenance, and Performance Evaluation

The filter ratio for baghouses, also called the gas-to-cloth ratio or air-to-cloth ( $A/C$ ) ratio,<sup>21</sup> varies from 0.6 to  $1.5 \text{ m}^3$  of gas per minute per square meter of fabric. The air-to-cloth ( $A/C$ ) ratio,<sup>21</sup> which is an expression of the air-stream flow rate through the fabric cloth:

$$A/C = \frac{Q_g}{A_{\text{fabric}}} \quad (30.51)$$

where,  $A/C$  is expressed as length time<sup>-1</sup>( $\text{L T}^{-1}$ );  $Q_g$  is the actual gas flow rate ( $\text{L}^2 \text{T}^{-1}$ ), and  $A_{\text{fabric}}$  is the fabric surface area ( $\text{L}^2$ ).

With increasing  $A/C$  ratios, the velocities of the gas moving through filter media and dust layers also increase. At high  $A/C$ , ultrafine particles may pass unscathed and not be captured or re-entrained if loosely retained after capture. When either occurs it is known as filter bleed-through. In addition to particle size, bleed-through is also increased with the amount of flex and movement of the bags and decreased with the thickness of dust layers on the fabric. Other inherent material properties may also affect bleed-through, e.g. pore collapse.

One means of knowing whether the dust layer is optimal is by measuring pressure drop. The pressure drop across the fabric is a function of the filter ratio; it ranges from about 80 mm of water for the lower filter ratios up to about 200 mm of water for the higher ratios. Before selecting any bag filter system, a thorough engineering study should be made, followed by a consultation with different bag and baghouse manufacturers. Lower than optimal static pressure drop may mean that there is insufficient thickness of the dust cake; whereas higher than optimal pressure drop may indicate that the gas flow is overly constricted. This flow constriction can be caused by mechanical and electrical failures in air moving equipment. Thus, monitoring equipment can be located to indicate flange-to-flange static pressure drop (at the outlet and inlet ducts) and/or at the unfiltered side of the system to indicate media static pressure drop.

The pressure drop through the filter is a function of two separate effects. The clean filter has some initial pressure drop. This is a function of filter material, depth of the filter, the superficial gas velocity, which is the gas velocity perpendicular to the filter face, and the viscosity of the gas. Pressure drop increases from the initial clean filter's resistance as particles begin to adhere to form a cake on the filter surface. This cake increases in thickness

as approximately a linear function of time, and the pressure difference necessary to cause the same gas flow also becomes a linear function with time. Usually, the pressure available at the filter is limited so that as the cake builds up the flow decreases. Timing of filter cleaning can be based, therefore, on (1) increased pressure drop across the filter, (2) decreased volume of gas flow, or (3) time elapsed since the last cleaning.

Put simply, media static pressure drop can be expressed as the sum of the pressure drop across the filter media plus the pressure drop across the dust cake:

$$\Delta P_{\text{total}} = \Delta P_{\text{media}} + \Delta P_{\text{dust-cake}} \quad (30.52)$$

Pressure drop is often expressed as inches of water column (in. WC).<sup>f</sup> The drop in static pressure across the filter media ( $\Delta P_{\text{media}}$ ) is approximated as:

$$\Delta P_{\text{media}} = k_1 \cdot v_f \quad (30.53)$$

where  $k_1$  is the filter media resistance constant ( $\frac{\text{in. WC}}{(\text{ft min}^{-1})(\text{lb}_m \text{ ft}^{-2})}$ ) and  $v_f$ , velocity through the filter ( $\text{ft min}^{-1}$ ). The drop in static pressure through the dust cake ( $\Delta P_{\text{dust-cake}}$ ) is approximated as:

$$\Delta P_{\text{dust-cake}} = k_2 \cdot c_i \cdot v_f^2 \cdot t \quad (30.54)$$

where,  $k_2$  is the filter media resistance constant ( $\frac{\text{in. WC}}{(\text{ft min}^{-1})(\text{lb}_m \text{ ft}^{-2})}$ );  $c_i$ , the PM concentration ( $\text{lb}_m \text{ ft}^{-3}$ ); and  $t$ , filtration time (min).

With substitutions, the total pressure drop is:

$$\Delta P_{\text{total}} = (k_1 \cdot v_f) + (k_2 \cdot c_i \cdot v_f^2 \cdot t) \quad (30.55)$$

The filter drag ( $S_f$ ) can be found by dividing both the sides of Eqn (30.55) by the velocity ( $v_f$ ):

$$S_f = \frac{\Delta P_{\text{total}}}{v_f} = k_1 + (k_2 \cdot c_i \cdot v_f \cdot t) \quad (30.56)$$

where  $S_f$  is the filter drag force (in. WC  $\text{ft}^{-1} \text{ min}^{-1}$ ).

These and other general predictions of pressure drop are gross approximations given the variability in dust cake thickness and other real-world conditions.

The bags must be periodically cleaned to remove the accumulated PM (note in Figure 30.13 the general downward trend in efficiency with time). Bag cleaning methods vary widely with the manufacturer and with baghouse style and use. Methods for cleaning include (1) mechanical shaking by agitation of the top hanger, (2) reverse flow of gas through a few of the bags at a time, (3) continuous cleaning with a reverse jet of air passing through a series of orifices on a ring as it moves up and down the clean side of the bag, and (4) collapse and pulsation cleaning methods.

<sup>f</sup> 1 WC = 0.25 kPa.

Common fabric filter cleaning mechanisms include shaking, reverse air, and pulse jets. Shaker systems are cleaned after stopping the gas flow, allowing the bags to relax (usually less than 1 min) and shaking the bags for 10–100 cycles with a rocker-arm assembly in 1–5 cycles per second. The cleaning cycles are usually controlled by a timing device which deactivates the section being cleaned. The dusts removed during cleaning are collected in a hopper at the bottom of the baghouse and then removed, through an air lock or star valve, to a bin for ultimate disposal.

The reverse air filtration system construction and operation resembles that of shaker collectors, including a tube sheet that separates the bags in the upper portion of the collector from the hoppers. The open bottoms of

the bags are attached to the tube sheet and the closed tops are attached to an upper support. Gases enter through the hopper and pass up through the filter bag, depositing the dust cake inside the bag. Cleaner air exits through an outlet duct. Reverse air collectors usually employ woven fabrics; as well as membrane bags and felted bags. Their typical A/C ratio is 0.8–1.8 cm s<sup>-1</sup>.<sup>21</sup>

There are two basic types of pulse jet collectors: top-access and side-access; with the top-access pulse jet more common (see Figure 30.15). In pulse jet collectors, the tube sheet is located near the top of the unit and the bags are suspended from it. This free-hanging design is needed to facilitate bag replacement, to direct gas stream movement upward and to avoid abrasive surfaces near the bottom of the bags. The pulse jet cleaning occurs

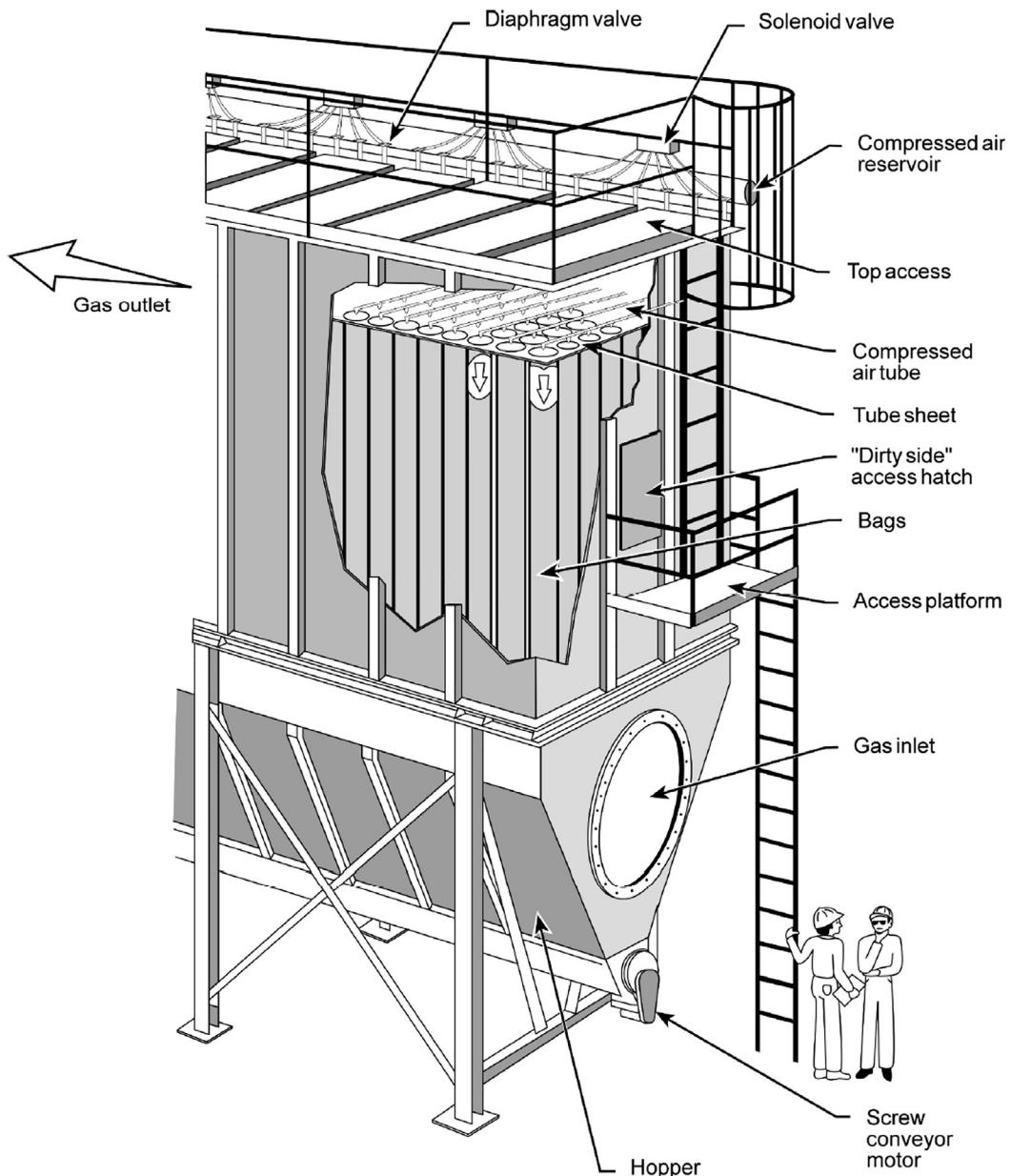


FIGURE 30.15 Pulse jet fabric filter with top-access. Ref. 21.

from compressed air that passes through a drier, if gas has too much moisture, which can condense upon cooling and increase blinding. The compressed air is filtered to remove oil droplets that condense from lubricating oils in the compressor, heated and delivered by compressed tubes to the bags.<sup>21</sup>

Cartridge filter systems are similar to pulse jet fabric filter systems, with filter elements supported on a tube sheet that is usually mounted near the top of the filter housing. Filtering is performed by the filter media and the dust cake supported on the exterior of the filter media. The filter media is usually cellulose, polypropylene, or other flex-resistant material covered with felt. Cartridges are usually shorter than pulse jet bags. They can be cylindrical but may also have other shapes to increase the surface area. Their short filter element makes it less susceptible to being scratched by suspended matter in the air stream and allows cleaning with compressed air in a process similar to pulse jet cleaning.

The actual performance of filtration systems is a function of numerous factors, so the evaluation of performance is multifactorial as well. These factors include the type of fabric, the  $A/C$  ratio, approach velocity, filter bag spacing and size, bag access, design of cleaning system and hopper, bypass dampening, and the type and locations of monitoring instrumentation.

The  $A/C$  ratio is the most useful means of sizing fabric filters. Gross  $A/C$  is the actual gas flow rate at maximum operating conditions divided by the total area of fabric in the system:

$$(A/C)_{\text{gross}} = \frac{Q_{\max}}{A_{\text{total}}} \quad (30.57)$$

where,  $(A/C)_{\text{gross}}$  is the gross air-to-cloth ratio [ $(\text{ft}^3 \text{ min}^{-1}) \text{ ft}^{-2}$ ];  $Q_{\max}$ , maximum actual flow rate ( $\text{ft}^3 \text{ min}^{-1}$ ); and  $A_{\text{total}}$ , total fabric area ( $\text{ft}^2$ ).

The net  $A/C$  ratio is commonly used for systems that have multiple compartments, with one or more of them separated from the gas flow during cleaning, maintenance, or as a regularly scheduled part of a modular system:

$$(A/C)_{\text{nets}} = \frac{Q_{\max}}{A_{\text{net}}} \quad (30.58)$$

where,  $(A/C)_{\text{nets}}$  is the net air-to-cloth ratio [ $(\text{ft}^3 \text{ min}^{-1}) \text{ ft}^{-2}$ ];  $Q_{\max}$ , maximum actual flow rate ( $\text{ft}^3 \text{ min}^{-1}$ ); and  $A_{\text{net}}$ , isolated compartment's fabric area ( $\text{ft}^2$ ).

Bag area of a cylindrically shaped bag or shaker is:

$$A = \pi DL \quad (30.59)$$

where,  $A/C$  is the bag surface area ( $\text{ft}^2$ );  $D$ , bag diameter (ft); and  $L$ , bag length (ft). This assumes that filtration

only occurs on the side of the bag, not on the top or bottom. If the bag is a pleated cylindrical cartridge, the area is:

$$A = 2ndh \quad (30.60)$$

where,  $A$  is the cartridge surface area ( $\text{ft}^2$ );  $n$ , number of pleats;  $d$ , depth of pleat (ft); and  $h$ , pleat height (ft).

To illustrate how  $A/C$  is useful in performance evaluation, consider two examples.<sup>g</sup>

The air-to-cloth ratio used for a system depends on the particle size distribution, fabric characteristics, particulate matter loadings, and gas stream conditions. Low values for a design air-to-cloth ratio are generally used when the particle size distribution includes a significant fraction of very fine PM or if particulate loading is high. The air-to-cloth ratios for cartridge filters are usually maintained at values less than approximately  $4 (\text{ft}^3 \text{ min}^{-1}) \text{ ft}^2$ . General  $A/C$  ratio values for shaker, reverse air, and pulse jet fabric filters in various settings are provided in Table 30.10. However, this is merely a general guideline, since sites and situations vary. In addition, air-to-cloth ratio requirements have been decreasing in recent decades, commensurate with more stringent PM emission limits.

Other aspects of filter system performance should be part of the evaluation. This includes inspection of the extent of gravity settling of dust cake agglomerates, sheet, and particles that can be released during cleaning. Collection efficiency and static pressure drops can result when fine PM matter, with its inherently low settling velocities, returns to the filter surface. Thus, a sufficient amount of time is needed to allow for particles that have been resuspended to re-settle. Also, gas entering the hopper instead of the collector side during on-line cleaning (e.g. pulse jets) can block particle and aggregates from settling.

The gas approach velocity of a pulse jet system is directly proportional to the  $A/C$  ratio. Thus, large dust agglomerates or sheets rather than small aggregates or individual particles should be released during cleaning. For example, consider two identical pulse jet systems with the following design characteristics:

Design Characteristic	First Unit	Second Unit
Compartment area, $\text{ft}^2$	130	130
Number of bags	300	300
Bag diameter, in.	6	6
Bag height, ft	10	10
Air-to-cloth ratio, $(\text{ft}^3 \text{ min}^{-1}) \text{ ft}^{-2}$	5	8

<sup>g</sup> These examples are taken from: U.S. Environmental Protection Agency. APTI 413: control of particulate matter emissions. Chapter 8: fabric filters; 2012.

Example 1: A reverse air baghouse has 20 compartments with 360 bags in each compartment. Each bag has a diameter of 11 in. and is 30 ft long. At an actual gas flow rate of 1.2 million cubic feet per minute and assuming that two compartments are presently out of service, calculate the gross and net air-to-cloth ratios.

### Solution

$$\text{Bag area} = \pi DL$$

$$\text{Area/bag} = \pi(11 \text{ in.})(\text{ft}/12 \text{ in.})30 \text{ ft} = 86.35 \text{ ft}^2/\text{bag}$$

The gross air-to-cloth ratio is calculated assuming that all the bags are in service.

$$\text{Total number of bags} = (360 \text{ bags/compartment})(20 \text{ compartments}) = 7200 \text{ bags}$$

$$\text{Total fabric area} = (7200 \text{ bags})(86.35 \text{ ft}^2/\text{bag}) = 621,720 \text{ ft}^2$$

$$(A/C)_{\text{gross}} = \frac{1.2 \times 10^6 \text{ ft}^3 \text{ min}^{-1}}{621,720 \text{ ft}^2} = \frac{1.93 \text{ ft}^3 \text{ min}^{-1}}{\text{ft}^2}$$

The net air-to-cloth ratio is calculated by subtracting the compartments that are not in filtering service.

$$\text{Total number of bags} = (360 \text{ bags/compartments})(18 \text{ compartments}) = 6480 \text{ bags}$$

$$\text{Total fabric area} = (6480 \text{ bags})(86.35 \text{ ft}^2/\text{bag}) = 559,548 \text{ ft}^2$$

$$(A/C)_{\text{gross}} = \frac{1.2 \times 10^6 \text{ ft}^3 \text{ min}^{-1}}{559,548 \text{ ft}^2} = \frac{2.14 \text{ ft}^3 \text{ min}^{-1}}{\text{ft}^2}$$

Example 2: A cartridge baghouse has four compartments with 16 cartridges per compartment, a cartridge length of 2 ft, and a cartridge diameter of 8 in. Use a pleat depth of 1.5 in. and a total of 36 pleats in the cartridge. Use an actual gas flow rate of  $4000 \text{ ft min}^{-1}$ . Assume one compartment is out of service. Calculate the gross and net air-to-cloth ratios.

### Solution

$$\text{Cartridge area} = 2ndh$$

$$\text{Area/cartridge} = 2(36 \text{ pleats})(15 \text{ in.}/(12 \text{ in. per ft}))(2 \text{ ft}) = 18 \text{ ft}^2$$

The gross air-to-cloth ratio is calculated assuming that all the bags are in service.

$$\text{Total number of cartridges} = (16 \text{ cartridges/compartment})(4 \text{ compartments}) = 64 \text{ cartridges}$$

$$\text{Total fabric area} = (64 \text{ cartridges})(18 \text{ ft}^2 \text{ per cartridge}) = 1152 \text{ ft}^2$$

$$(A/C)_{\text{gross}} = \frac{4000 \text{ ft}^3 \text{ min}^{-1}}{1152 \text{ ft}^2} = \frac{3.47 \text{ ft}^3 \text{ min}^{-1}}{\text{ft}^2}$$

The net air-to-cloth is calculated by subtracting the compartment that are not in the filtering service

$$\text{Total number of cartridges} = (16 \text{ cartridges/compartment})(3 \text{ compartments}) = 48 \text{ cartridges}$$

$$\text{Total fabric area} = (48 \text{ cartridges})(18 \text{ ft}^2 \text{ per cartridge}) = 864 \text{ ft}^2$$

$$(A/C)_{\text{gross}} = \frac{4000 \text{ ft}^3 \text{ min}^{-1}}{864 \text{ ft}^2} = \frac{4.62 \text{ ft}^3 \text{ min}^{-1}}{\text{ft}^2}$$

TABLE 30.10 Air-to-Cloth Ratios for Selected Industrial Processes

Process	Shaker	Reverse Air	Pulse Jet
Basic oxygen furnaces	2.5–3.0	1.5–2.0	6–8
Brick manufacturers	2.5–3.2	1.5–2.0	9–10
Coal-fired boilers	1.5–2.5	1.0–2.0	3–5
Electric arc furnaces	2.5–3.0	1.5–2.0	6–8
Ferroalloy plants	2.0	2.0	9
Gray iron foundries	2.5–3.0	1.5–2.0	7–8
Lime kilns	2.5–3.0	1.5–2.0	8–9
Municipal incinerators	1.5–2.5	1.0–2.0	2.5–4.0
Phosphate fertilizer	3.0–3.5	1.8–2.0	8–9
Portland cement kilns	2.0–3.0	1.2–1.5	7–10

Source: Ref. 21.

The bag area is calculated using the product of the bag circumference times bag length:

$$\begin{aligned}\text{Bag area} &= \pi DL = \pi(6 \text{ in.})(1 \text{ ft}/12 \text{ in.})(10 \text{ ft}) \\ &= 15.7 \text{ ft}^2 \text{ per bag.}\end{aligned}$$

$$\text{Total bag area} = (300 \text{ bags})(15.7 \text{ ft}^2 \text{ per bag}) = 4710 \text{ ft}^2.$$

Total gas flow rate of first unit

$$= \frac{5 (\text{ft}^3 \text{ min}^{-1})}{\text{ft}^2} (4.710 \text{ ft}^2) = 23,550 \text{ ft}^3 \text{ min}^{-1}$$

Total gas flow rate of second unit

$$= \frac{8 (\text{ft}^3 \text{ min}^{-1})}{\text{ft}^2} (4.710 \text{ ft}^2) = 37,680 \text{ ft}^3 \text{ min}^{-1}$$

The area for gas flow at the bottom of the pulse jet bags is identical in both the units.

$$\begin{aligned}\text{Area for flow} &= \text{total area} - \text{bag projected area} \\ &= \text{total area} - (\text{number of bags}) \\ &\quad \times (\text{circular area of bag at bottom}) \\ &= 130 \text{ ft}^2 - (300)(\pi D^2/4) \\ &= 130 \text{ ft}^2 - 58.9 \text{ ft}^2 = 71.1 \text{ ft}^2\end{aligned}$$

$$\begin{aligned}\text{Gas approach velocity for first unit} &= \frac{23,550 \text{ ft}^3 \text{ min}^{-1}}{71.1 \text{ ft}^2} \\ &= 331 \text{ ft min}^{-1}\end{aligned}$$

Gas approach velocity for second unit

$$= \frac{37,680 \text{ ft}^3 \text{ min}^{-1}}{71.1 \text{ ft}^2} = 530 \text{ ft min}^{-1}$$

The approach velocity in pulse jet systems is directly proportional to the bag length. An increase in the second unit's length from 10 to 16 ft, for example, would

increase the approach velocity substantially to about  $850 \text{ ft min}^{-1}$ , so long as the A/C ratio is constant. This, combined with the longer path that fine PM would have to travel in the more elongated bag would increase problems caused by additional gravity settling.

The type of instrumentation should be properly matched to the equipment. As a minimum, for fabric filters this likely includes instrumentation for static pressure drop measurement, inlet and outlet gas temperature measurements, and opacity monitors.

It should be noted that often times a number of different air pollution control devices are used in sequences and series. For example, when addressing a very toxic compound, particulates and gases must be removed and/or treated. In these configurations, both inertial and filtration equipment may be deployed, along with scrubbers and sorbing media for gases (see Figure 30.16).

## 30.5 ELECTROSTATIC PRECIPITATORS

High-voltage ESPs have been widely used throughout the world for particulate removal since Frederick Cottrell invented the first one early in the twentieth century. Most of the original units were used for recovery of process materials, but today gas cleaning for air pollution control is often the main reason for their installation. The ESP has distinct advantages over other aerosol collection devices:

1. It can easily handle high-temperature gases, which makes it a likely choice for boilers, steel furnaces, etc.;
2. It has an extremely small pressure drop, so that fan costs are minimized;
3. It has an extremely high-collection efficiency if operated properly on selected aerosols (many cases are on record, however, in which relatively low efficiencies were obtained because of unique or unknown dust properties);
4. It can handle a wide range of particulate sizes and dust concentrations (most precipitators work best on particles smaller than  $10 \mu\text{m}$ , so that an inertial pre-cleaner is often used to remove the large particles); and,
5. If it is properly designed and constructed, its operating and maintenance costs are lower than those of any other type of particulate collection system.

Three of the disadvantages of ESPs are:

1. The initial cost is the highest of any particulate collection system;
2. A large amount of space is required for the installation, and,
3. ESPs are not suitable for combustible particles such as grain or wood dust.

The particles move advectively with the gas stream that is moving through the ESP unit (see Figure 30.17).

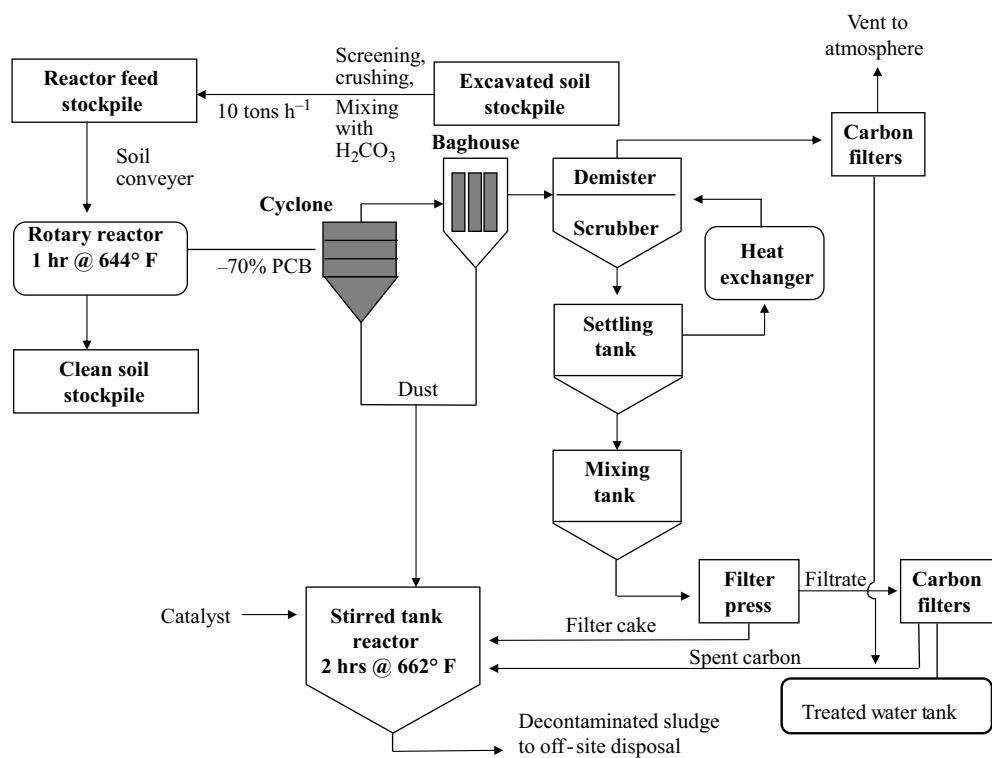


FIGURE 30.16 Schematic of a treatment system for treating soil that had to be contaminated with polychlorinated biphenyls (PCBs). PCBs are semivolatile compounds that can exist both as aerosols and vapors. After incineration with a rotary kiln, the dust removal relies on both a cyclone and a baghouse to capture various sizes of PM. The vapors are captured after dust removal, with a final stage employing sorption onto granulated activated carbon. *Federal Remediation Technologies Roundtable. Screening matrix and reference guide. 4th ed. Washington (DC).*

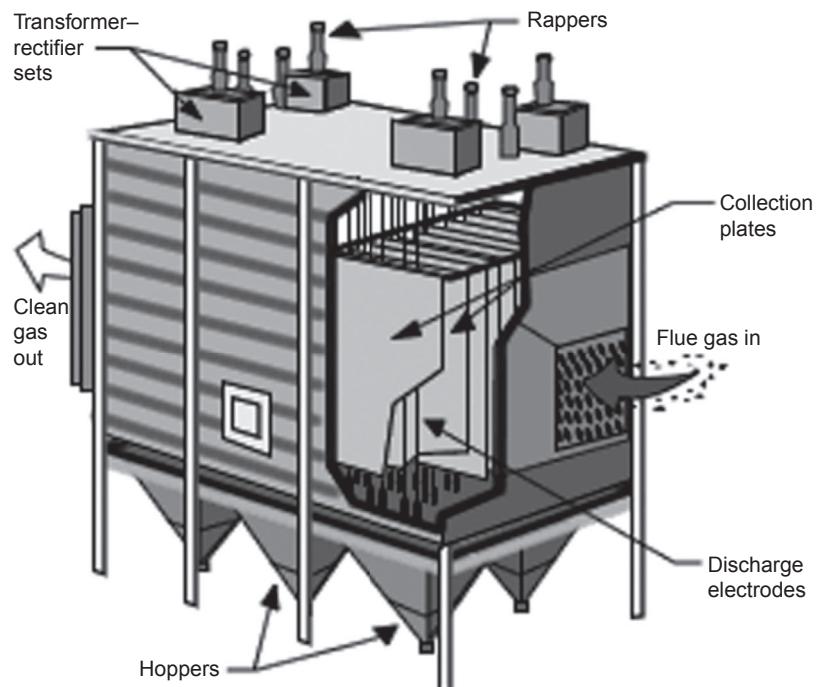


FIGURE 30.17 Commercial plate-type ESP. U.S. Environmental Protection Agency. Basic concepts in environmental sciences—module 6: air pollutants and control techniques. <http://www.epa.gov/eogapti1/module6/matter/control/control.htm>; [accessed 30.06.07].

The particles become charged and then are attracted by the charge differential to either side. The particles migrate toward the collection surface, where they are captured. The accumulated solids or liquids are deposited into the hoppers (or sumps for liquids) which are below the electrical zone.

The ESP works by charging dust with ions and then collecting the ionized particles on a surface. The collection surfaces may consist of either tubular or flat plates. For cleaning and disposal, the particles are then removed from the collection surface, usually by rapping the surface.

The alternating power supplied to the primary control cabinet is at a constant 480 V and 60 cycles per second. A transformer-rectifier (T-R) set provides this power. The primary alternating power is converted to a secondary pulse-type direct power in the T-R set. The relatively low primary voltage is stepped up to a secondary voltage of more than 50,000 V. The voltage applied to the discharge electrodes is called the secondary voltage because the electrical line is on the transformer's secondary side, i.e. the high-voltage generating side.<sup>22</sup> With increasing supply of primary voltage, the secondary voltage applied to the discharge electrodes increases. A high-voltage (30 kV or more) DC field is established between the central wire electrode and the grounded collecting surface.

The voltage is high enough that a visible corona can be seen at the surface of the wire. The result is a cascade of negative ions in the gap between the central wire and the grounded outer surface. Any aerosol entering this gap is both bombarded and charged by these ions. The aerosols then migrate to the collecting surface because of the combined effect of this bombardment and the charge attraction. When the particle reaches the collecting surface, it loses its charge and adheres because of the attractive forces existing. It should remain there until the power is shut off and it is physically dislodged by rapping, washing, or sonic means.

The electrical discharges from the precipitator discharge electrodes are termed corona discharges and are needed to charge the particles. Within the negative corona discharge, electrons are accelerated by a very strong electrical field and strike and ionize gas molecules. Each collision of a fast-moving electron with a gas molecule produces an additional electron and a positively charged gas ion. The corona discharges can be described as an "electron avalanche" since large numbers of electrons are generated during multiple electron-gas molecule collisions.<sup>22</sup>

The positive gas ions generated in the ionization process turn back toward the discharge electrode. Some positive gas ions deposit on particles within the corona, adding a positive charge. The positively charged particles collect on negative discharge electrodes, and must

be cleaned sufficiently often to continue inducing charge.

Electrons released in the corona discharges are captured by gas molecules, further from the discharge electrode, where the electrical field strength is lower. The negatively charged gas ions move toward the grounded collection plates. Some are captured by particles, inducing a negative charge. The particles quickly reach a maximum charge, i.e. saturation charge, at which the electrostatic field created by the captured ions is sufficiently strong to deflect additional gas ions approaching the particle.<sup>22</sup> The magnitude of the saturation charge is dependent on the particle size:

$$q = (3\pi\epsilon_0 E)d_p^2 \quad (30.61)$$

where,  $q$  is the charge on particle;  $\epsilon_0$ , permittivity of free space ( $8.85 \times 10^{-12} \text{ F m}^{-1}$ );  $E$ , strength of electrical field ( $\text{V m}^{-1}$ ); and  $d_p$ , physical diameter of particle.

Since gas ions have small surfaces on which to deposit, small particles have low saturation charges. Thus, saturation charge increases with surface area and with the square of the particle diameter. Large particles accumulate higher electrical charges on their surface and, therefore, are more strongly affected by the applied electrical field.

Upon attaching ions, particles are influenced by the strong, nonuniform electrical field between the discharge electrode and the grounded collection plate. As a result, the charged particles migrate toward the grounded plates at a velocity given by:

$$\omega = \frac{qE_p C_C}{3\pi d_p \mu_g} \quad (30.62)$$

where,  $\omega$  is the migration velocity;  $q$ , charge on particle;  $E_p$ , electrical field near collector plate;  $C_C$ , Cunningham slip correction factor;  $\mu_g$ , gas viscosity; and  $d_p$ , physical diameter of particle.

Simultaneously to the migration from the charge differential, drag forces, which depend on the particle mass or the cube of the particle diameter, are inducing particle to move unabated through the precipitator. Thus, very small particles deposit near the inlet, while increasingly larger particles deposit deeper into the precipitator. Often, particles larger than about  $30 \mu\text{m}$  diameter can be removed with precleaning. Otherwise, the ESP would have to be much longer. Small-sized particles charge more slowly but, once they acquire a charge, they move rapidly to the collection plate.

Particles with  $>1.0 \mu\text{m}$  diameters accumulate charged gas ions by locally disrupting the electrical field. As a result, the gas ions are momentarily directed to the particle surface rather than the collection plate, known as contact charging. Particles with  $<0.1 \mu\text{m}$  diameters have insufficient mass to disrupt the electrical field.

Rather, very small particles accumulate charges as in their random walks through the gas ions, known appropriately as diffusion or ion charging. The combined effect of contact and diffusion charging creates a particle size collection efficiency relationship that is efficient for very small particles, dropping to a low of <70% for  $\sim 0.5 \mu\text{m}$  diameter particles, and increasing in efficiency, nearing 100% for PM<sub>10</sub>. The high-collection efficiencies for PM  $> 1.0 \mu\text{m}$  diameter is due to the result of improved effectiveness of contact charging for large particles. Increased diffusion charging is the reason for good collection efficiencies for particles smaller than  $0.1 \mu\text{m}$  diameter. The sub-optimal range between  $0.1$  and  $1.0 \mu\text{m}$  diameter results from size-dependence limitations of both of these charging mechanisms. Electrostatic systems are notoriously weak in collecting particles in this size range.

In a tube-type ESP, the tubes are 8–25 cm in diameter and 1–4 m long. They are arranged vertically in banks with the central wires, about 2 mm in diameter, suspended in the center with tension weights at the bottom. Many innovations, including square, triangular, and barbed wires, are used by different manufacturers.

A plate-type ESP is similar in principle to the tubular type except that the airflows across the wires horizontally, at right angles to them. The particles are collected on vertical plates, which usually have fins or baffles to strengthen them and prevent dust re-entrainment. [Figure 30.17](#) illustrates a large plate-type precipitator. These precipitators are usually used to control and collect dry dusts.

Problems with ESPs develop because the final unit does not operate at ideal conditions. Indeed, ESP operation is vulnerable to particle characteristics. Gas channeling through the unit can result in high dust loadings in one area and light loads in another. The end result is less than optimum efficiency because of much re-entrainment. The chemical composition of the dust cake affects conductance and resistance. Actually, electrons can flow through the dust cake in two ways. Electrons can pass directly through each dust particle until reaching the metal surface (bulk conductance); or they can be conducted surface-to-surface (surface conductance), e.g. vapor-phase conductive compounds sorb to the particles. Obviously, bulk conductance requires that the particle material have sufficient conductivity. The resistivity of the dust greatly affects its re-entrainment in the unit. If a high-resistance dust collects on the plate surface, the effective voltage across the gap is decreased.

It should also be noted that resistance is temperature dependent. For example, resistivity of inorganic oxides is orders of magnitudes lower at gas temperatures  $< 150^\circ\text{C}$  than at  $180^\circ\text{C}$ . Resistivity is also orders of magnitudes lower at gas temperatures  $> 200^\circ\text{C}$  than at  $180^\circ\text{C}$ . Thus, the range between  $150$  and  $200^\circ\text{C}$  is to be avoided,

with temperatures between  $250$  and  $350^\circ\text{C}$  nearly optimal, depending on the specific dust material.<sup>22</sup>

Some power plants burning high-ash, low-sulfur coal have reported very low efficiency from the precipitator because the ash needed more SO<sub>2</sub> to decrease its resistivity. The suggestion that precipitator efficiency could be greatly improved by adding SO<sub>2</sub> or SO<sub>3</sub> to the stack gases has met, not surprisingly, with skepticism given these compounds' reputations as potent air pollutants. However, combustion of coal and other fossil fuels often generate sufficient H<sub>2</sub>SO<sub>4</sub> and other particle surface conditioning agents that lower dust layer resistivities to allow for conductance through dust layers.

Electrostatic precipitators work well in many settings; however some need to be avoided or at least customized to address certain unwanted properties of substances in gas streams. These include fly ash with extremely low resistivities, sticky PM, and flammable and explosive substances. In addition, ESPs produce ozone (O<sub>3</sub>), so operators must ensure that waste streams do not produce unacceptable amounts of this pollutant, i.e. tradeoff between PM and O<sub>3</sub>.

## 30.6 SCRUBBERS

Scrubbers, or wet collectors, have been used as gas cleaning devices for many years. They predominantly collect PM by applying two basic physical mechanisms already discussed, i.e. inertial impaction and Brownian motion. The wet-scrubbing process uses two processes to remove an aerosol from the gas stream. The first is to wet the particle by the scrubbing liquid. As shown in [Figure 30.18](#), this process is essentially the same whether the system uses a spray to atomize the scrubbing liquid or a diffuser to break the gas into small bubbles. In either case, it is assumed that the particle is trapped when it travels from the supporting gaseous medium across the interface to the liquid scrubbing medium. Some relative motion is necessary for the particle and liquid–gas interface to come into contact. In the spray chamber, this motion is provided by spraying the droplets through the gas so that they impinge on and make contact with the particles. In the bubbler, inertial forces and severe turbulence achieve this contact. In either cases, the smaller the droplet or bubble, the greater is the collection efficiency. In the scrubber, the smaller the droplet, the larger will be the surface area for a given weight of liquid, with a greater likelihood of wetting the particles. In a bubbler, smaller bubbles mean not only that more interface area is available but also that the particles have a shorter distance to travel before reaching an interface where they can be wetted.

The second process employed by wet collectors is to remove the wetted particles on a collecting surface,

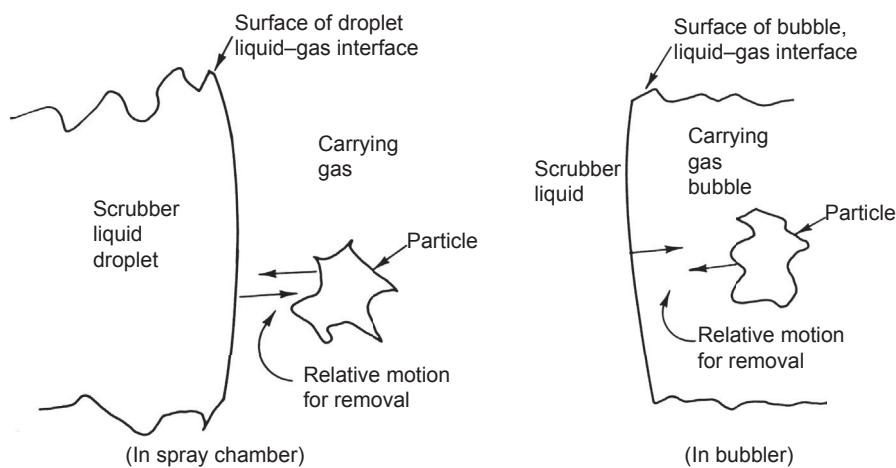


FIGURE 30.18 Wetting of aerosols in a spray chamber or bubbler.

followed by their eventual removal from the device. The collecting surface can be in the form of a bed or simply a wetted surface. One common combination follows the wetting section with an inertial collector which then separates the wetted particles from the carrying gas stream. Thus, collection has two phases; first the particle is captured within a droplet; then the droplets aggregate into a slurry which must be removed and treated.

Increasing either the gas velocity or the liquid droplet velocity in a scrubber will increase the efficiency because of the greater number of collisions per unit time. The ultimate scrubber in this respect is the venturi scrubber, which operates at extremely high gas and liquid velocities with a very high pressure drop across the venturi throat. Figure 30.19 illustrates a configuration of a venturi scrubber unit.

Large amounts of water are involved in scrubbing, so the scrubbing liquid is recirculated to minimize the amount of liquid needing to be treated and discharged. The scrubbing liquid is collected in the sump of the scrubber and mist eliminator delivered by gravity to a recirculation tank having a liquid residence time of several minutes. This provides sufficient time to introduce alkali additives and to adjust the pH back to the proper range, if necessary. A centrifugal pump recirculates the liquid back to the scrubber vessel from the recirculation tank. Some scrubber systems use spray nozzles to atomize the scrubbing liquid. To project droplets across an entire circular area, a full-cone nozzle is used most frequently. This improves the effective gas–liquid contact. Full-cone nozzles usually provide mean diameters of 100–1000 µm that are log-normally distributed.<sup>23</sup>

The liquid-to-gas ratio (L:G) is the rate of liquid flow to a scrubber, expressed as volume per volume (e.g. gallons of liquid per 1000 actual cubic feet of gas flow). To collect PM, wet scrubber systems generally operate with L:G ratios between 4 and 20 gal:1000 actual cubic feet

(acf). Higher ratios do not appear to improve performance. Plus, higher L:G changes the droplet distribution within the scrubber, which adversely affects collection efficiencies. Low L:G can dramatically decrease efficiency by decreasing the number of available target objects for particle impaction. At low L:G ratio conditions, a portion of the particle-laden gas stream may pass through the collection zone without encountering a liquid target. The L:G ratio can be defined based either on the inlet or outlet gas flow rates, or based on either actual or standard gas flow rates. A practical definition of L:G is:

$$L : G = \frac{Q_{i-l}}{Q_{o-g}} \quad (30.63)$$

where,  $Q_{i-l}$  is the the inlet liquid flow (gallons per minute, gpm) and  $Q_{o-g}$ , the outlet gas flow (actual  $\text{ft}^3 \text{ min}^{-1}$ , acfm).

$Q_{o-g}$  is used because it is already measured as part of an emission test program and is considerably easier to obtain an accurate flow measurement at the scrubber outlet, because this is where PM being loaded into the gas stream is decreased and where sampling ports are available. Indeed, most scrubber inlet ducts are not well suited for testing gas flow rates.

L:G ratios needs to be above the minimum level necessary to ensure proper gas–liquid distribution. In most gas-atomized scrubbers, this minimum value is approximately 4 gallons:1000 acf. In other type of scrubbers, the value can be as low as 2 gal:1000 acf.

These calculations can be illustrated with an example. What is the design liquid-to-gas ratio for a scrubber system that has an outlet gas flow rate of 10,000 acfm, a pump discharge rate of 110 gpm, and a liquid purge rate of 20 gpm? The purge stream is withdrawn from the pump discharge side.

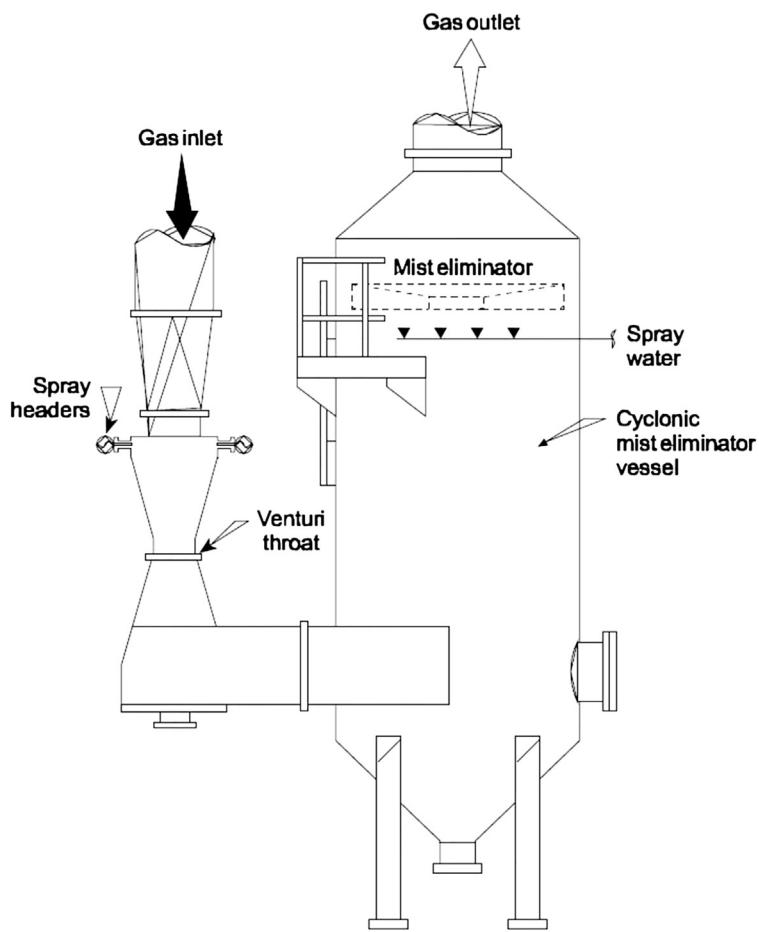


FIGURE 30.19 Venturi scrubber and mist eliminator vessel. Ref. 16.

$$\text{Solution: } L : G = \frac{Q_{i-1}}{Q_{o-g}}$$

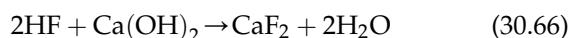
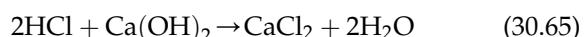
$$Q_{i-1} = 110 - 10 \text{ gpm} = 90 \text{ gpm}$$

$$\text{Therefore, } L : G = \frac{90 \text{ gpm}}{10^4 \text{ acfm}} = 9 \times 10^{-3} \frac{\text{gal.}}{\text{acf}} = \frac{9 \text{ gal.}}{1000 \text{ acf}}$$

The chemical composition of the particles and gases in the air stream often require pretreatment. For example, if acid gases, e.g.  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , and  $\text{HF}$ , are present, an alkali addition system is used on wet scrubber systems that collect acidic PM or to treat gas streams that have acidic gases or vapors that could absorb in the liquid stream. In addition,  $\text{CO}_2$  formed in most combustion processes can also be absorbed, with the  $\text{H}_2\text{CO}_3^*$  lowering the pH. The most common alkalis used in

scrubbers are liming agents (e.g.  $\text{CaCO}_3$  or  $\text{Ca(OH)}_2$ ), soda ash ( $\text{Na}_2\text{CO}_3$ ), and sodium hydroxide ( $\text{NaOH}$ ).

The amount of alkali needed depends on the quantities of acidic gases captured and the molar ratios necessary for the following reactions:



For example,<sup>h</sup> assuming an  $\text{HCl}$  removal efficiency of 95%, what is the amount of calcium hydroxide (lime) needed to neutralize the  $\text{HCl}$  absorbed from a gas stream with 50 ppmv  $\text{HCl}$  and a flow rate of 10,000 scfm? This can be calculated using Reaction (30.65).

<sup>h</sup>This example is taken from: U.S. Environmental Protection Agency. APTI 413: control of particulate matter emissions. Chapter 9: wet scrubbers; 2012.

Solution:

$$50 \text{ ppmv} = \frac{50 \text{ ft}^3 \text{ HCl}}{10^6 \text{ ft}^3 \text{ total}} = 0.00005 \frac{\text{ft}^3 \text{ HCl}}{\text{ft total}} = 0.00005 \frac{\text{lb - mole HCl}}{\text{lb - mole total}}$$

$$\text{HCl absorbed} = 10,000 \text{ scfm} \left( \frac{\text{lb - mole}}{385.4 \text{ scf}} \right) \left( 0.00005 \frac{\text{lb - mole HCl}}{\text{lb - mole total}} \right) (0.95) = 0.00123 \frac{\text{lb - mol}}{\text{min}}$$

$$\begin{aligned} \text{Ca(OH)}_2 \text{ required} &= \left( \frac{1 \text{ lb - mole Ca(OH)}_2}{2 \text{ lb - mole HCl}} \right) \left( 0.00123 \frac{\text{lb - mole HCl}}{\text{min}} \right) \\ &= 0.00062 \frac{\text{lb - mole}}{\text{min}} \left( 74 \frac{\text{lb Ca(OH)}_2}{\text{lb - mole}} \right) \left( 60 \frac{\text{min}}{\text{h}} \right) \\ &= 2.75 \text{ lb h}^{-1} \end{aligned}$$

### 30.6.1 Mist Elimination

Scrubber vessels generate relatively large water droplets that become entrained in the gas stream. Most contain captured particles that must be removed by mist eliminators from the gas stream before being emitted to the atmosphere. In addition to minimizing the carry-over of PM-containing droplets to the atmosphere, mist eliminators also protect downstream equipment, e.g. fans and other air movers, from PM-laden droplets, and minimize water losses. Solids accumulate as a result of the impaction of solids-laden water droplets, and due to the chemical precipitation of dissolved solids from the scrubbing liquid. Mist eliminators usually have at least one spray nozzle to remove these accumulated solids. The four most common types of mist eliminators are chevrons, mesh or woven pads, tube banks, and cyclones.<sup>1</sup> Static pressure drops across their surfaces range from 0.5 in. WC to more than 4 in. WC.<sup>23</sup>

### 30.6.2 Scrubber Performance

Scrubber manufacturers have extensive databases regarding the performance of their commercial brands of scrubbers for removing pollutants from different types of industrial sources. While useful, these data must be augmented by additional site-specific and specific PM characterization information before installing a system, beginning with the site-specific inlet particle

size distribution and uncertainties around this distribution (e.g. does the distribution vary according to certain operations and maintenance schedules?). Scrubber performance depends on many factors, including:

1. Particle size distribution
2. Mean and maximum gas flow rates
3. Mean and maximum inlet gas temperatures
4. Chemical composition of PM and gas stream, including concentrations of corrosive materials present in the inlet gas stream
5. Concentrations of potentially explosive materials present in the inlet gas stream
6. Makeup water availability
7. Purge liquid treatment and disposal requirements
8. Process type, raw materials, and fuels
9. Source operating schedule
10. Area available for scrubber and wastewater treatment
11. Alkali supply requirements
12. Emission test data

This site-specific information together with the historical performance data informs the decision of whether a scrubber is applicable to the pollutant stream and, if so, which type. The data also provide a basis for the design of the scrubber system components, including estimates of static pressure drops across the system.

Scrubbers have distinct advantages and disadvantages. For example, venturi scrubbers have high-collection efficiencies, can handle mists and are capable

<sup>1</sup>For a detailed discussion of these four systems, see: U.S. Environmental Protection Agency. APTI 413: control of particulate matter emissions. Chapter 8: wet scrubbers. <http://www.4cleanair.org/APTI/413Combined.pdf>; 2012 [accessed 05.12.13].

of handling flammable and explosive dusts (a distinct advantage over ESPs). Their design is simple, relatively easy to install and maintain. They provide cooling of hot gases and can neutralize corrosive PM and gases.<sup>24</sup> However, venturi scrubbers, like all wet scrubbers, produce large amounts of wastewater and sludge that must be treated. The final exhaust must be reheated. In addition, these systems have high-pressure drops and require protection from weather (e.g. freezing).<sup>25</sup>

### 30.6.3 Dry Scrubbers

Gravel bed filters that recirculate the gravel filter medium using an external cleaning or washing system are known as dry scrubbers. Some units also use an electrostatic field across the gravel bed to enhance removal of the particulate material. The dry scrubber may have to be followed by a baghouse for the effluent to achieve acceptable emission standards. The advantage of dry scrubbers is their ability to remove large quantities of particulate pollutants, such as fly ash, from hot gas streams.

### 30.6.4 Bioscrubbers

Bioscrubbers are an example of an integrated environmental control system. They have a suspended microbial population in a flowing water phase. Absorption takes place in typical wet-scrubbing equipment, e.g. spray towers, plate towers, or packed beds. The effluent from the wet scrubber is then transferred to a separate aerated vessel, where degradation of the contaminants is performed by suspended microbes. Nutrients, acids, or bases are added to the recirculated water to maintain conditions conducive to microbial populations that lead to optimal pollutant removal. This can be an enhancement to a scrubber and particularly useful in the enhancement of not only removing, but also biodegrading hazardous air pollutants, in both gas and particulate phases.

## 30.7 REMOVAL OF LIQUID DROPLETS AND MISTS

The term mist generally refers to liquid droplets from submicron size to about 10 µm. If the diameter exceeds 10 µm, the aerosol is usually referred to as a *spray* or simply as *droplets*. Mists tend to be spherical because of their surface tension and are usually formed by nucleation and the condensation of vapors.<sup>26</sup> Larger droplets are formed by bursting bubbles, by entrainment from surfaces, by spray nozzles, or by splash-type liquid distributors. The large droplets tend to be elongated relative to their direction of motion because of the action of drag forces on the droplets.<sup>25</sup>

Mist eliminators are widely used in air pollution control systems to prevent free moisture from entering the atmosphere. Usually, such mist eliminators are found downstream from wet scrubbers. The recovered mist is returned to the liquid system, resulting in lowered liquid makeup requirements.

As is the case for dry particles, mist aerosols and droplets differ substantially physically for the carrying gas stream, including diameter, density, and phase (e.g. gas *versus* liquid). Indeed, some particles in mist collection systems are the size of ordinary raindrops. Thus, most of the removal mechanisms are similar to those employed for the removal of dry particulates.

Mist collection is further simplified because the particles are spherical and tend to resist re-entrainment. In addition, mists tend to agglomerate after coming in contact with the surface of the collecting device. Control devices developed particularly for condensing mist are discussed separately.

### 30.7.1 Filtering Liquids

Filters for mists and droplets have larger pores and open areas than those used for dry particles. If a filter is made of many fine, closely spaced fibers, it will become wet due to the collected liquid. Such wetting leads to matting of the fibers, retention of greater amounts of liquid, which leads eventually to a blocked filter. Water droplets in the dust cake can severely increase the resistance to gas flow. At the very least, the water fills voids in the dust cake which would normally be the route of the carrying gas. At some point, the water-filled pore space in the dust cake becomes sufficient to pack the PM or to form a layer of mud, rendering the filter impervious to airflow. The problem is known as fabric blinding. Moisture can come from numerous sources, including entrained condensed droplets; droplets carried in with the compressed air, e.g. in pulse jet fabric filters; or from excessive gas cooling in baghouses, e.g. those serving combustion sources that produce high vapor concentrations of water; and other compounds can cause water condensation in the dust cakes.

Water is the most common but not the exclusive liquid that can cause blinding. Indeed, almost any liquid can cause or exacerbate fabric blinding. In addition to liquids formed from previously volatilized vapors mentioned above, liquids can be actually used in the pollution control equipment itself. For example, oil droplets can deposit in the upper, clean side surfaces of the fabric filters and prevent airflow. This means that proper O&M requires filtering of the entire inlet gas stream in the unaffected lower portions of the part of the filter (e.g. jet bag). Indeed, blinding agents do not even have to be "wet". High-velocity carrying gas

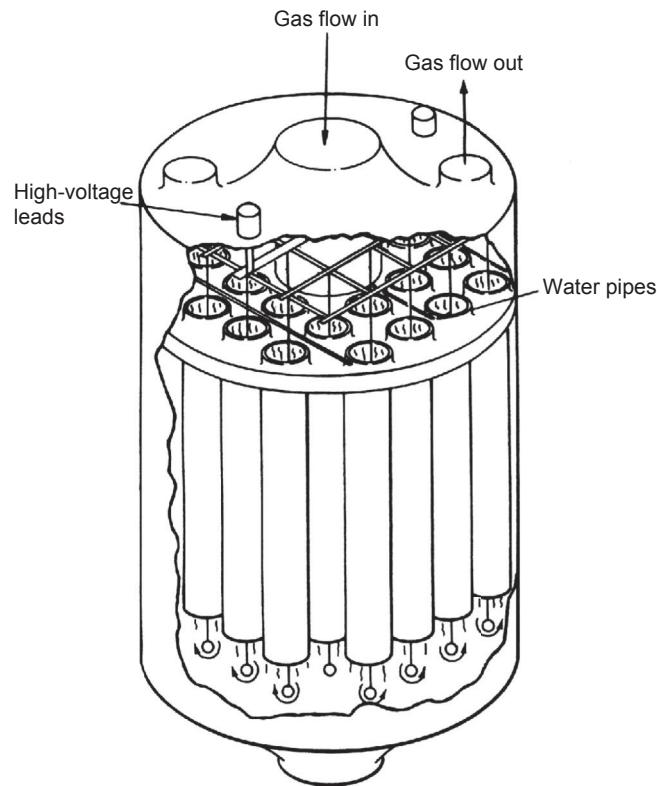
laden with ultrafine particles can be driving these very small particles into the filter fabric before a protective residual dust layer has formed. Newly installed in baghouse compartment with several seasoned bags are particularly vulnerable to such blinding. This is because the seasoned bags already have a residual dust cake layer; thus the gas velocities through the new bag are excessively high. The carrying gas will follow the path of least resistance, i.e. through the clean pores of the newly installed bags. Ultrafine particle blinding is possible after installing new bags at sources that generate high concentrations of  $PM \leq \mu\text{m}$  aerodynamic diameter. To ameliorate this problem, the new bags can be conditioned prior to service by passing through air containing resuspended coarse particulate.<sup>16</sup>

This is a major difference between dry and wet filtration. Thus, rather than closely spaced fiber weaves, wet filtration system is usually composed of either knitted wire or wire mesh packed into a pad. This looser filtration medium yields a lower pressure drop than the media of the filters used for dry PM. The reported pressure drop across wire mesh mist eliminators is 1–2 cm of water at face velocities of  $5 \text{ m s}^{-1}$ . The essential collection mechanisms employed for filtration of droplets and mists are inertial impaction and, to a lesser extent, direct interception.

### 30.7.2 Electrostatic Precipitators for Mists and Droplets

ESPs for liquid droplets and mists are essentially of the wetted wall type. Figure 30.20 shows a wet-wall precipitator with tubular collection electrodes.<sup>1</sup> In wet ESPs, the upper ends of the tubes form weirs, and water flows over the tube ends to irrigate the collection surface. The collecting electrode becomes coated with a water film. The PM collected in the wet type electrostatic precipitator is discharged along with the collecting electrode washing liquid. Thus, wastewater treatment is necessary.

Figure 30.21 shows an alternative type of wet precipitator with plate-type collection electrodes. In this design, sprays located in the ducts formed by adjacent collecting electrodes serve to irrigate the plates.<sup>1</sup> These are often supplemented by overhead sprays to ensure that the entire plate surface is irrigated. The design of such precipitators is similar to that of conventional systems except for the means of keeping insulators dry, measures to minimize corrosion, and provisions for removing the slurry.<sup>j</sup>



**FIGURE 30.20 Wet-wall ESP with tubular collection electrodes.**  
Oglesby Jr S, Nichols GB. Electrostatic precipitators. In: Stern AC, editor. Air pollution. 3rd ed., vol. 4. New York (NY): Academic Press; 1977; Theodore L, Buonicore AJ. Air pollution control equipment: selection, design, operation and maintenance. Englewood Cliffs (New Jersey): Prentice-Hall.

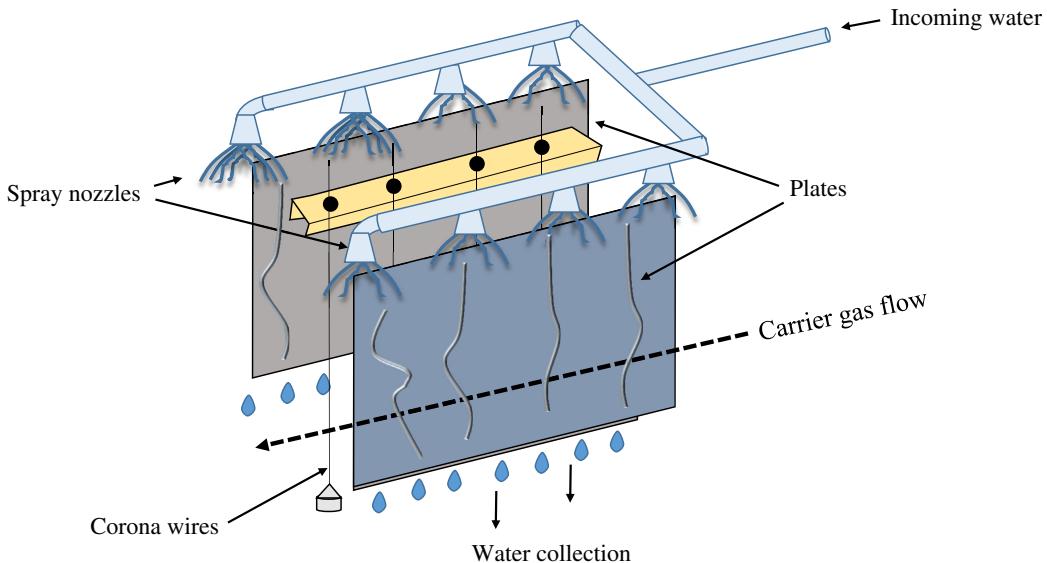
### 30.7.3 Inertial Collection of Mists and Droplets

Inertial collectors for mists and droplets are widely used. They include cyclone collectors, baffle systems, and skimmers in ductwork. Inertial devices can be used as primary collection systems, precleaners for other devices, or mist eliminators. The systems are relatively inexpensive and reliable, and have low-pressure drops.

Cyclone mist eliminators and collectors have virtually the same efficiency for both liquid aerosols and solid particles. To avoid re-entrainment of the collected liquid from the walls of the cyclone, an upper limit is set to the tangential velocity that can be used. The maximum tangential velocity should be limited to the inlet velocity. Even at this speed, the liquid film may creep to the edge of the exit pipe, from which the liquid is then re-entrained.

Baffle separators of the venetian blind, V, W, and wave types are widely used for spray removal. They

<sup>i</sup>Oglesby Jr S, Nichols GB. Electrostatic precipitators. In: Stern AC, editor. Air pollution. 3rd ed., vol. 4. New York (NY): Academic Press; 1977; Theodore L, Buonicore AJ. Air pollution control equipment: selection, design, operation and maintenance. Englewood Cliffs (New Jersey): Prentice-Hall.



**FIGURE 30.21** Wet ESP with plate collection electrodes. (For color version of this figure, the reader is referred to the online version of this book.)

have small space requirements and low-pressure drops. They operate by diverting the gas stream and ejecting the droplets onto the collector baffles. Efficiencies of single stages may be only 40–60%, but by adding multiple stages, efficiencies approaching 100% may be obtained.

#### 30.7.4 Scrubbers for Mists and Droplets

A widely used type of scrubber for mists and droplets is the venturi scrubber. It has been used for the collection of sulfuric acid and phosphoric acid mists with very high efficiency. The scrubbing contact is made at the venturi throat, where very small droplets of the scrubbing liquid (usually water) are injected. At the throat, gas velocities as high as  $130 \text{ m s}^{-1}$  are used to increase collision efficiencies. Water, injected for acid mist control, ranges from 0.8 to  $2.0 \text{ l m}^{-3}$  of gas. Collection efficiencies approaching 100% are possible, but high efficiencies require a gas pressure drop of 60–90 cm of water across the scrubber. Normal operation, with a submicron mist, is reported to be in the 90–95% efficiency range.<sup>27</sup>

One problem in using scrubbers to control mists and droplets is that the scrubber also acts as a condenser for volatile gases. For example, a hot plume containing volatile hydrocarbon gases, such as the exhaust from a gas turbine, may be cooled several hundred degrees by passing through a scrubber. This cooling can cause extensive condensation of the hydrocarbons, resulting in a plume with a high opacity. For example, when jet engine exhaust is cooled in a test cell using water sprays, droplet loadings can be 10–100% greater than those measured from the plane's exhaust due to the condensation of hydrocarbons which were normally exhausted as gases.<sup>27</sup>

#### 30.7.5 Other Systems

Many unique systems have been proposed, and some used, to control the release of mists and droplets. Ceramic candles are thimble-shaped, porous, acid-resistant ceramic tubes. Although efficiencies exceeding 98% have been reported, the candles have high maintenance requirements because they are very fragile.

Electric cyclones utilize an electrode in the center of the cyclone to establish an electric field within the cyclone body. This device is more efficient than the standard cyclone. It is probably more applicable to mists and droplets than to dry particulates, due to possible fire or explosion hazards with combustible dusts.

Sonic agglomerators have been used experimentally for sulfuric acid mists and as mist eliminators. Commercial development is not projected at this time because the energy requirements are considerably greater than those for venturi scrubbers of similar capacity.

### 30.8 COMPARISON OF PARTICULATE REMOVAL SYSTEMS

When selecting a system to remove particulate from a gas stream, many choices concerning equipment can be made. The selection could be made on the basis of cost, gas pressure drop, efficiency, temperature, resistance, etc. Table 30.11 summarizes these factors for comparative purposes. The tabular values must not be considered absolute because great variations occur between types and manufacturers. No table is a substitute for a qualified consulting engineer or a reputable manufacturer's catalog.

TABLE 30.11 Comparison of Particulate Removal Systems

Type of Collector	Particle Size Range ( $\mu\text{m}$ )	Removal Efficiency	Space Required	Maximum Temperature ( $^{\circ}\text{C}$ )	Pressure Drop (cm H <sub>2</sub> O)	Annual Cost (US\$ per year m <sup>-3</sup> )*
Baghouse (cotton bags)	0.1–0.1	Fair	Large	80	10	28.00
	1.0–10.0	Good	Large	80	10	28.00
	10.0–50.0	Excellent	Large	80	10	28.00
Baghouse (dacron, nylon, orlon)	0.1–1.0	Fair	Large	120	12	34.00
	1.0–10.0	Good	Large	120	12	34.00
	10.0–50.0	Excellent	Large	120	12	34.00
Baghouse (glass fiber)	0.1–1.0	Fair	Large	290	10	42.00
	1.0–10.0	Good	Large	290	10	42.00
	10.0–50.0	Good	Large	290	10	42.00
Baghouse (Teflon)	0.1–1.0	Fair	Large	260	20	46.00
	1.0–10.0	Good	Large	260	20	46.00
	10.0–50.0	Excellent	Large	260	20	46.00
Electrostatic precipitator	0.1–1.0	Excellent	Large	400	1	42.00
	1.0–10.0	Excellent	Large	400	1	42.00
	10.0–50.0	Good	Large	400	1	42.00
Standard cyclone	0.1–1.0	Poor	Large	400	5	14.00
	1.0–10.0	Poor	Large	400	5	14.00
	10.0–50.0	Good	Large	400	5	14.00
High-efficiency cyclone	0.1–1.0	Poor	Moderate	400	12	22.00
	1.0–10.0	Fair	Moderate	400	12	22.00
	10.0–50.0	Good	Moderate	400	12	22.00
Spray tower	0.1–1.0	Fair	Large	540	5	50.00
	1.0–10.0	Good	Large	540	5	50.00
	10.0–50.0	Good	Large	540	5	50.00
Impingement scrubber	0.1–1.0	Fair	Moderate	540	10	46.00
	1.0–10.0	Good	Moderate	540	10	46.00
	10.0–50.0	Good	Moderate	540	10	46.00
Venturi scrubber	0.1–1.0	Good	Small	540	88	112.00
	1.0–10.0	Excellent	Small	540	88	112.00
	10.0–50.0	Excellent	Small	540	88	112.00
Dry scrubber	0.1–1.0	Fair	Large	500	10	42.00
	1.0–10.0	Good	Large	500	10	42.00
	10.0–50.0	Good	Large	500	10	42.00

\* Includes costs for water and power, operation and maintenance, capital equipment and insurance (in 1994 US\$).

## 30.9 REMOVAL OF GASEOUS POLLUTANTS

Gaseous pollutants may be easier or more difficult to remove from the carrying gas stream than aerosols, depending on the individual situation. Certainly, the fact that the air stream and the pollutants are of the same physical phase removes some of the complexities of PM removal. Of course, any separation system relying on differences in inertial properties will not work for gases.

Gases may be reactive to other chemicals, which is an important chemical property that can be used to collect vapor-phase pollutants. Four general methods of separating gaseous pollutants are currently in use. These are: (1) absorption in a liquid, (2) adsorption on a solid surface, (3) condensation to a liquid, and (4) conversion into a less polluting or nonpolluting gas.

### 30.9.1 Absorption Devices

Absorption of pollutant gases is accomplished by using a selective liquid in a wet scrubber, packed tower, or bubble tower. Pollutant gases commonly controlled by absorption include sulfur dioxide, hydrogen sulfide, hydrogen chloride, chlorine, ammonia, oxides of nitrogen, and low-boiling hydrocarbons.

The scrubbing liquid must be chosen with specific reference to the gas being removed. The gas solubility in the liquid solvent should be high so that reasonable quantities of solvent are required. The solvent should have a low vapor pressure to reduce losses, be noncorrosive, inexpensive, nontoxic, nonflammable, chemically stable, and have a low freezing point. It is no wonder that water is the most popular solvent used in absorption devices. The water may be treated with an acid or a base to enhance removal of a specific gas. If carbon dioxide is present in the gaseous effluent and water is used as the scrubbing liquid, a solution of carbonic acid will gradually replace the water in the system.

In many cases, pure water is a poor scrubbing solvent, especially if the targeted vapor has low aqueous solubility. Sulfur dioxide, for example, is only slightly soluble in water, so a scrubber of very large liquid capacity would be required. SO<sub>2</sub> is readily soluble in an alkaline solution, so scrubbing solutions containing ammonia or amines are used in commercial applications.

Chlorine, hydrogen chloride, and hydrogen fluoride are examples of gases that are readily soluble in water, so water scrubbing is very effective for their control. For years, hydrogen sulfide has been removed from refinery gases by scrubbing with diethanolamine. More recently, the light hydrocarbon vapors at petroleum refineries and loading facilities have been absorbed, under pressure,

in liquid gasoline and returned to storage. All of the gases mentioned have economic importance when recovered and can be valuable raw materials or products when removed from the scrubbing solvent. This is another reminder of the need for a systems approach and to consider the entire life cycle of a process (see Chapter 5).

### 30.9.2 Adsorption Devices

Adsorption of pollutant gases occurs when certain gases are selectively retained on the surface or in the pores or interstices of prepared solids. The process may be strictly a surface phenomenon with only molecular forces involved, or it may be combined with a chemical reaction occurring at the surface once the gas and adsorber are in intimate contact. The latter type of adsorption is known as chemisorption.

The solid materials used as adsorbents are usually very porous, with extremely large surface-to-volume ratios. Activated carbon, alumina, and silica gel are widely used as adsorbents depending on the gases to be removed. Activated carbon, for example, is excellent for removing light hydrocarbon molecules, which may be odorous. Silica gel, being a polar material, does an excellent job of adsorbing polar gases. Its characteristics for removal of water vapor are well known.

Solid adsorbents must also be structurally capable of being packed into a tower, resistant to fracturing, and capable of being regenerated and reused after saturation with gas molecules. Although some small units use throwaway canisters or charges, the majority of industrial adsorbents regenerate the adsorbent to recover not only the adsorbent but also the adsorbate, which usually has some economic value.

The efficiency of most adsorbents is very near 100% at the beginning of operation and remains extremely high until a breakpoint occurs when the adsorbent becomes saturated with adsorbate. At this breakpoint, the slope of the percentage of mass of gaseous fluid that is not sorbed increases dramatically with time. It is at the breakpoint that the adsorber should be renewed or regenerated. This is shown graphically in [Figure 30.22](#).

Industrial adsorption systems are engineered so that they operate in the region before the breakpoint and are continually regenerated by units. [Figure 30.23](#) shows a schematic diagram of such a system, with steam being used to regenerate the saturated adsorbent. [Figure 30.24](#) illustrates the actual system shown schematically in [Figure 30.23](#).

### 30.9.3 Condensers

In many situations, the most desirable control of vapor-type discharges can be accomplished by condensation. Condensers may also be used ahead of other air

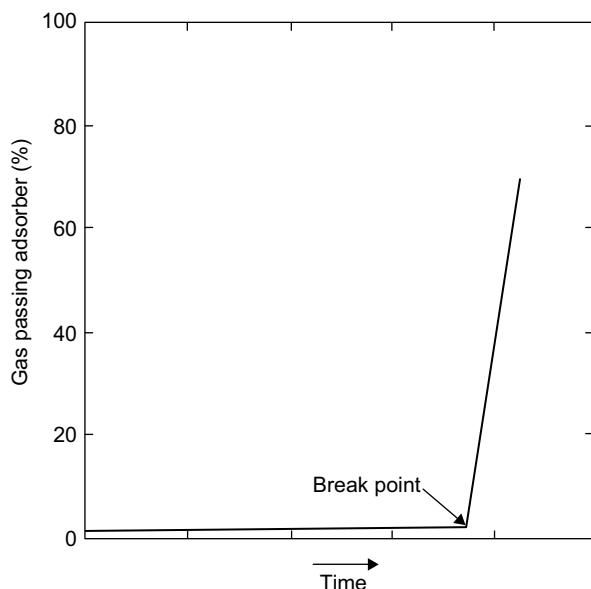


FIGURE 30.22 Adsorbent breakpoint at saturation with adsorbate.

pollution control equipment to remove condensable components. The reasons for using condensers include (1) recovery of economically valuable products, (2) removal of components that might be corrosive or damaging to other portions of the system, and (3) reduction of the volume of the effluent gases.

Although condensation can be accomplished either by reducing the temperature or by increasing the pressure, in gas-removal practice it is usually done by temperature reduction only.

Condensers may be of one or two general types depending on the specific application. Contact condensers operate with the coolant, vapors, and condensate intimately mixed. In surface condensers, the coolant does not come in contact with either the vapors or the condensate. The usual shell-and-tube condenser is of the surface type. [Figure 30.25](#) illustrates a contact

condenser which might be used to clean or preclean a hot corrosive gas.

[Table 30.12](#) lists several applications of condensers currently in use. For most operations listed, air and noncondensable gases should be kept to a minimum, as they tend to reduce condenser capacity.

### 30.9.4 Conversion to Less Polluting Substances

A widely used system for the control of organic gaseous emissions is oxidation of the combustible components to water and carbon dioxide. The thermal processes discussed in Chapter 29 apply to all phases of hazardous substances, including the gas phase. In fact, thermal processes like incineration often work much better for homogenous gas-phase reactions as opposed to heterogenous reactions involving solids, liquids, and gases.

Other systems such as the oxidation of  $\text{H}_2\text{S}$  to  $\text{SO}_2$  and  $\text{H}_2\text{O}$  are also used even though the  $\text{SO}_2$  produced is still considered a pollutant. The tradeoff occurs because the  $\text{SO}_2$  is much less toxic and undesirable than the  $\text{H}_2\text{S}$ . The odor threshold for  $\text{H}_2\text{S}$  is about three orders of magnitude less than that for  $\text{SO}_2$ . For oxidation of  $\text{H}_2\text{S}$  to  $\text{SO}_2$ , the usual device is simply an open flare with a fuel gas pilot or auxiliary burner if the  $\text{H}_2\text{S}$  is below the stoichiometric concentration. If the  $\text{SO}_2$  is above emission or other operation limits, it will also have to be treated (e.g. by scrubbing).

Thermal oxidizers (also known as afterburners) are widely used as control devices for oxidation of undesirable combustible gases. The two general types are (1) direct-flame thermal oxidizers, in which the gases are oxidized in a combustion chamber at or above the temperature of autogenous ignition and (2) catalytic combustion systems, in which the gases are oxidized at temperatures considerably below the autogenous ignition point.

Direct-flame thermal oxidizers are the most commonly used air pollution control device in which

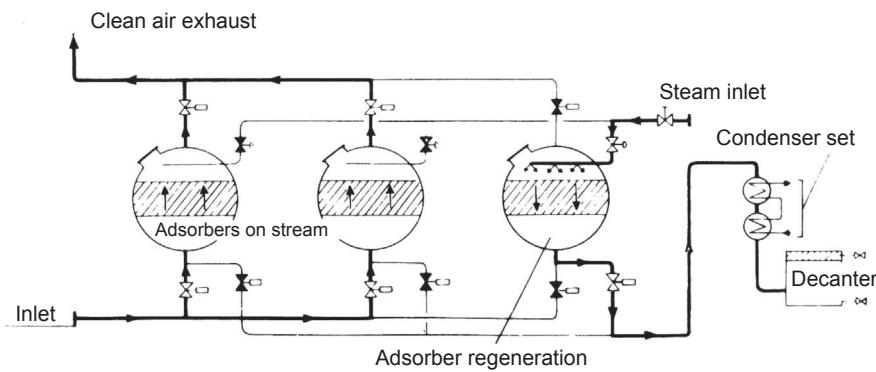
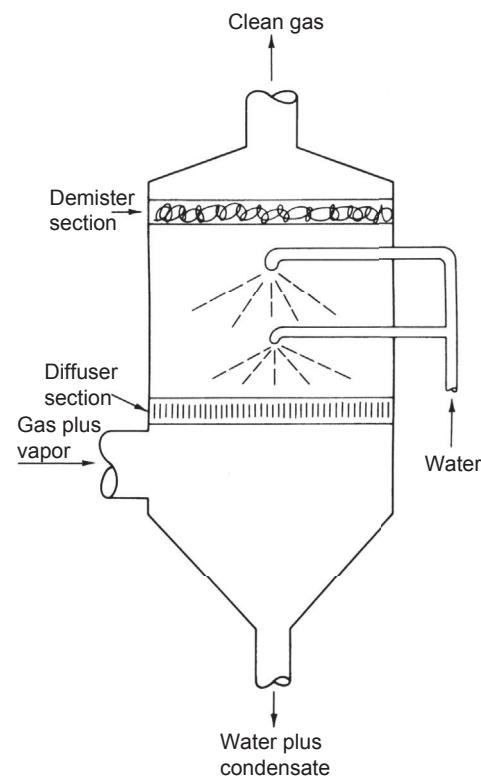


FIGURE 30.23 Flow diagram of adsorber. *The British Ceca Company, Ltd.*



**FIGURE 30.24** Pollution control facility in Milford foundry, New Hampshire includes an adsorption tower. Gaseous emissions are introduced at the base of the treatment column, where a gas diffuser ensures that they are evenly distributed through the system. The gas then contacts purification liquid in the packing of sorbents (e.g. zeolite) in the absorption zone. A second diffuser ensures that the purification liquid is evenly spread. *Environ-Access, Inc.* Environmental fact sheet. Treatment of air and gas: treatment of gaseous emissions through a wet scrubber—MESAR Environair Inc. (F2-03-96), Sherbrooke (Quebec, Canada).

combustible aerosols, vapors, gases, and odors are to be controlled. The components of the thermal oxidizer are shown in Figure 30.26. They include the combustion chamber, gas burners, burner controls, and exit temperature indicator. Usual exit temperatures for the



**FIGURE 30.25** Contact condenser.

destruction of most organic materials are in the range of 650–825 °C, with retention times of 0.3–0.5 s at the elevated temperatures.

Direct-flame thermal oxidizers are efficient and economical when properly operated. Costs to operate and maintain these systems are similar to those of the auxiliary gas fuel systems. Operating and maintenance costs are essentially those of the auxiliary gas fuel. For larger industrial applications, the overall cost of the oxidizer operation may be considerably reduced by using heat recovery equipment as shown in Figure 30.27. In fact, this is an example of the sustainable engineering

**TABLE 30.12** Selected Condenser Applications for Gas-phase Air Pollutant Removal

	Petrochemical	Basic Chemical	Miscellaneous
Petroleum Refining	Manufacturing	Manufacture	Industries
Gasoline accumulator	Polyethylene gas vents	Ammonia	Dry cleaning
Solvents	Styrene	Chlorine solutions	Degreasers
Storage vessels	Copper napthenates		Tar dipping
Lube oil refining	Insecticides		Kraft paper
	Phthalic anhydride		
	Resin reactors		
	Solvent recover		

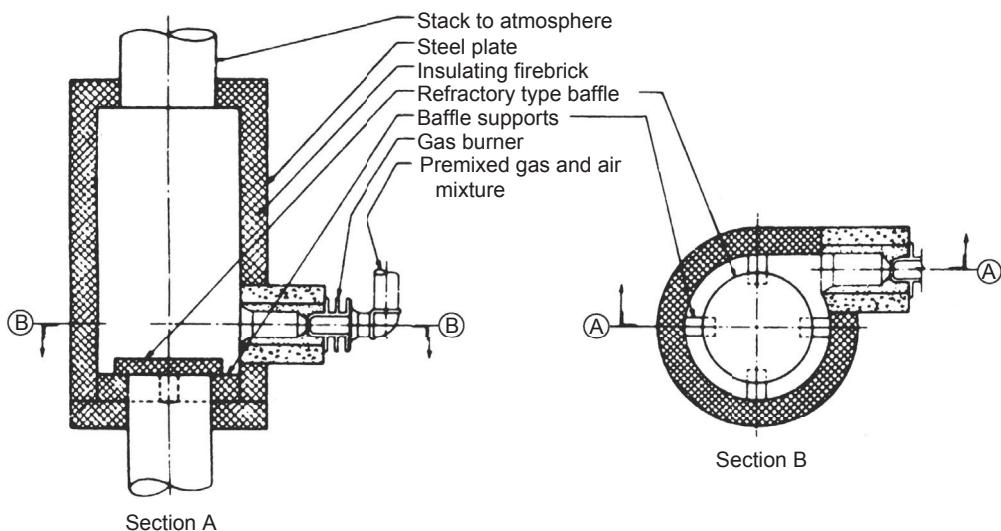


FIGURE 30.26 Direct-fired afterburner. Los Angeles Air Pollution Control District.

approach known as cogeneration. In some innovative schemes, heat recovery can provide heat for reactors in neighboring industries. Boilers and kilns also provide efficient pollutant destruction of volatile organic compounds and other vapor-phase pollutants in numerous industrial settings. Thermal processes are treated in greater detail in Chapter 29 [in particular, note the thermal oxidizing (afterburner) system following the rotary kiln in Figure 29.14].

Catalytic afterburners are currently used primarily in industry for the control of solvents and organic vapor emissions from industrial ovens. They are used as emission control devices for gasoline-powered automobiles.

The main advantage of the catalytic afterburner is that the destruction of the pollutant gases can be accomplished at a temperature range of about 315–485 °C, which results in considerable savings in fuel costs. However, the installed costs of the catalytic systems are higher than those of the direct-flame afterburners because of the expense of the catalyst and

associated systems, so the overall annual costs tend to balance out.

In most catalytic systems there is a gradual loss of activity due to contamination or attrition of the catalyst, so the catalyst must be replaced at regular intervals. Other variables that affect the proper design and operation of catalytic systems include gas velocities through the system, amount of active catalyst surface, residence time, and preheat temperature necessary for complete oxidation of the emitted gases.

### 30.9.5 Biological Control Systems

Waste streams with low to moderate concentrations of volatile organic compounds (VOCs) may be treated with biological systems. These are similar to biological systems used to treat wastewater, classified as three basic types: (1) biofilters; (2) biotrickling filters; and (3) bioscrubbers.

Biofilms of microorganisms (bacteria and fungi) are grown on porous media in biofilters and biotrickling

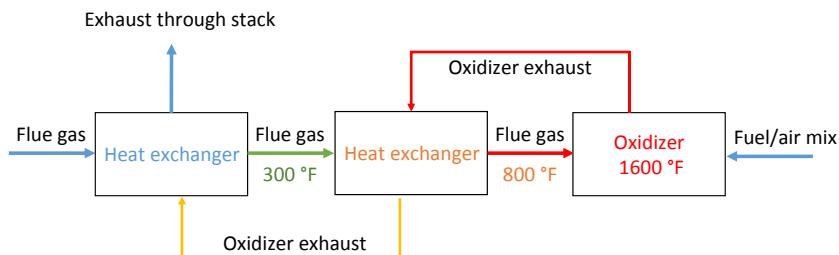


FIGURE 30.27 Thermal oxidizer schematic. This system employs a thermal oxidizer (burner) at one of the chambers. Other designs use tangentially fired burners and tangential fume inlets to lengthen residence time and enhance mixing. (For color version of this figure, the reader is referred to the online version of this book.) Source: Ohio Environmental Protection Agency. Thermal fume and catalytic incinerators. <http://www.epa.state.oh.us/portals/27/engineer/eguides/thermal.pdf> [accessed 19.05.14].

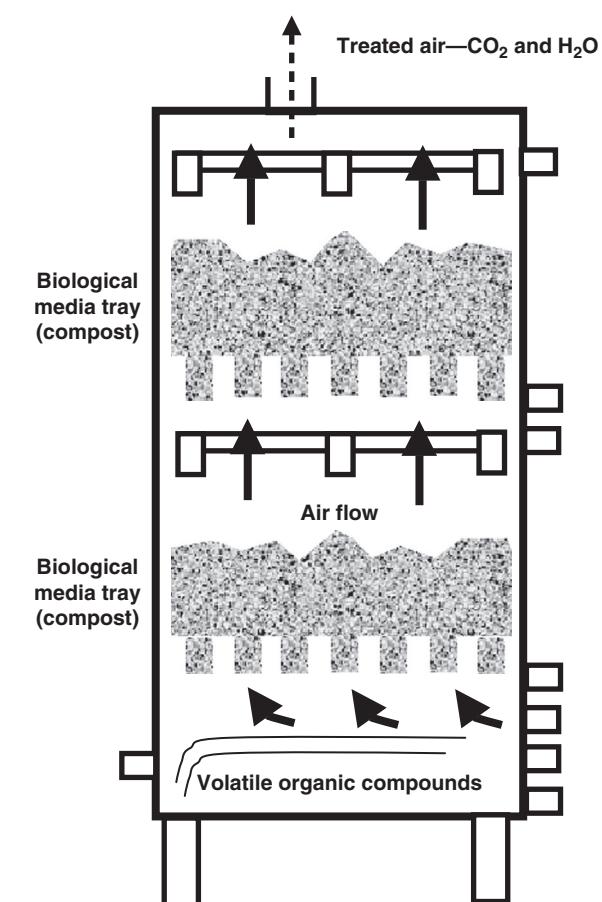
systems. The air or other gas containing the VOCs is passed through the biologically active media, where the microbes breakdown the compounds to simpler compounds, eventually to carbon dioxide (if aerobic), methane (if anaerobic), and water. The major difference between biofiltration and trickling systems is how the liquid interfaces with the microbes. The liquid phase is stationary in a biofilter (see [Figure 30.7](#)), but liquids move through the porous media of a biotrickling system (i.e. the liquid “trickles”).

A particularly valuable form of biofiltration uses compost as the porous media. Compost contains numerous species of beneficial microbes that are already acclimated to organic wastes. Industrial compost biofilters have achieved removal rates at the 99% level. Bio-filters are also the most common method for removing VOCs and odorous compounds from air streams. In addition to a wide array of volatile chain and aromatic organic compounds, biological systems have successfully removed vapor-phase inorganics, such as ammonia, hydrogen sulfide, and other sulfides including carbon disulfide, as well as mercaptans.

The operational key is the biofilm. The gas must interface with the film. In fact, this interface may also occur without a liquid phase (see [Figure 30.28](#)). According to Henry's law, the compounds partition from the gas phase (in the carrier gas or air stream) to the liquid phase (biofilm). Compost has been a particularly useful medium in providing this partitioning.

The bioscrubber is a two-unit setup. The first unit is an adsorption unit (see previous discussion in this chapter). This unit may be a spray tower, bubbling scrubber, or packed column. After this unit, the air stream enters a bioreactor with a design quite similar to an activated sludge system in a wastewater treatment facility. Bioscrubbers are much less common in the United States than biofiltration systems.

All three types of biological systems have relatively low operating costs since they are operated near ambient temperature and pressure conditions. Power needs are generally low ( $<10 \text{ cm H}_2\text{O m}^{-1}$  or  $<1.2 \text{ in. WC ft}^{-1}$  of packed bed). Other costs include amendments (e.g. nutrients) and humidification. Another advantage is the usual small amount of toxic byproducts, as well as low rates of emissions of greenhouse gases (oxides of nitrogen and carbon dioxide), compared to thermal systems. Success is highly dependent on the degradability of the compounds present in the air stream, their fugacity, and solubility needed to enter the biofilm (see [Figure 30.29](#)), and pollutant loading rates. Care must be taken in monitoring the porous media for incomplete biodegradation, the presence of substances that may be toxic to the microbes, excessive concentrations of organic acids and alcohols, and pH. The system should



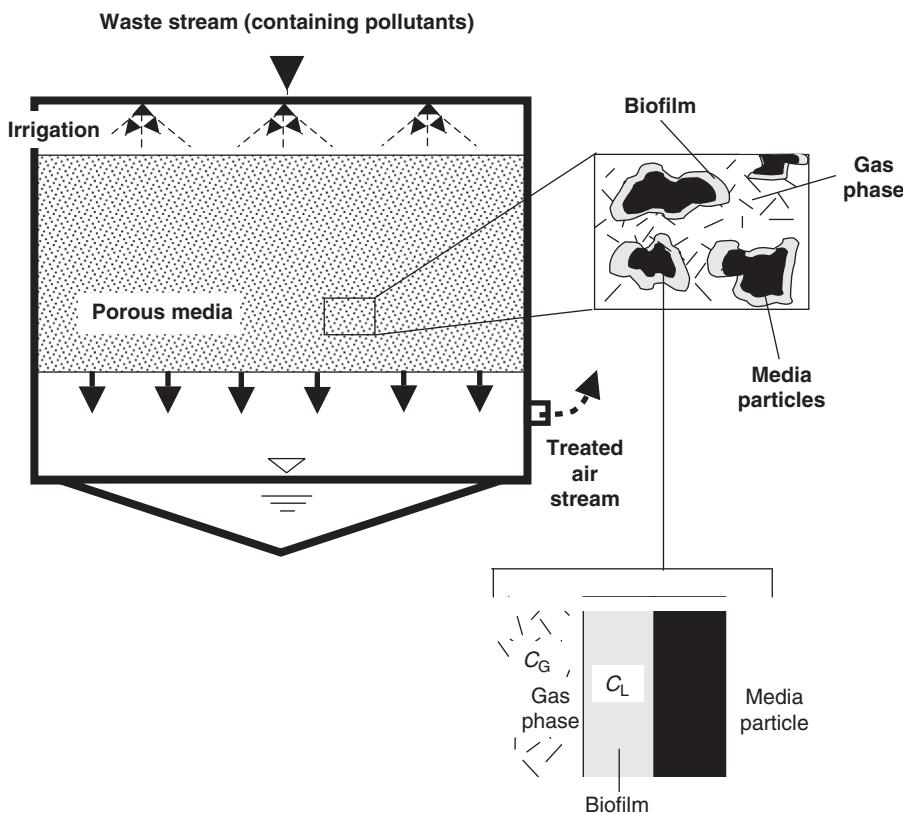
**FIGURE 30.28** Schematic of packed-bed biological control system to treat volatile compounds. Air containing gas-phase pollutants ( $C_G$ ) traverse porous media. The soluble fraction of the volatilized compounds in the air-stream partition into the biofilm ( $C_L$ ) according to Henry's Law:  $C_L = \frac{C_G}{H}$  where  $H$  is the Henry's law constant. Adapted from: Ref. 29.

also be checked for shock and the presence of dust, grease, or other substances that may clog the pore spaces of the media.<sup>28</sup>

### 30.9.6 Comparison of Gaseous Pollutant Removal Systems

As with particulate removal systems, it is apparent that many choices are available for removal of gases from effluent streams. [Table 30.13](#) presents some of the factors that should be considered in selecting equipment.

For the control of  $\text{SO}_2$ , several systems are currently in development and use. [Table 30.14](#) briefly explains these systems. Likewise, numerous systems are available for removing oxides of nitrogen ( $\text{NO}_x$ ). In this case, the removal includes gas phase N species other than NO and  $\text{NO}_2$ , including the greenhouse gas,  $\text{N}_2\text{O}$ . Generally oxides of N can be reduced by lowering peak operating



**FIGURE 30.29 Biofiltration without a liquid phase used to treat vapor-phase pollutants.** Air carrying the volatilized contaminants upward through porous media (e.g. compost) containing microbes acclimated to breakdown the particular contaminants. The wastes at the bottom of the system can be heated to increase the partitioning to the gas phase. Microbes in the biofilm surrounding each individual compost particle metabolize the contaminants into simpler compounds, eventually converting them into carbon dioxide and water vapor.

TABLE 30.13 Comparison of Gaseous Pollutant Removal Systems

Type of Equipment	Pressure Drop (cm H <sub>2</sub> O)	Installed Cost (1990 US\$ per m <sup>3</sup> )	Annual Operating Cost (1990 US\$ per m <sup>3</sup> )
Scrubber	10	9.80	14.00
Absorber	10	10.40	28.00
Condenser	2.5	28.00	7.00
Direct-flame afterburner	1.2	8.20	8.40 + Gas
Catalytic afterburner	2.5	11.60	28.00 + Gas
Biological control systems	Low (e.g. <1 in compost)	Variable (low to moderate)	Variable (low to moderate)

TABLE 30.14 Potential Sulfur Dioxide Control Approaches

Method	Remarks
Limestone or lime injection (dry)	Calcined limestone or lime reacts with sulfur oxides. They are then removed with a dry particulate control system.
Limestone or lime injection (wet)	Calcined limestone or lime reacts with sulfur oxides, which are then removed by wet scrubbers.
Sodium carbonate	Sodium carbonate reacts with sulfur oxides in a dry scrubber to form sodium sulfite and CO <sub>2</sub> . Sodium sulfite is then removed with a baghouse.
Citrate process	Citrate is added to scrubbing water to enhance SO <sub>2</sub> solution into water. Sulfur is then removed from the citrate solution.
Copper oxide adsorption	Oxides of sulfur react with copper oxide to form copper sulfate. Removal with a dry particulate control system follows.
Caustic scrubbing	Caustic neutralizes sulfur oxides. This method is used on small processes.

temperatures and decreasing the time at which operations are at peak temperatures. Also, these oxides can be reduced by burning and re-burning, as well as by chemical reduction reactions, both catalyzed and noncatalyzed. Other methods include substituting O<sub>2</sub> for air in combustion processes, absorption, oxidation followed by sorption and various combinations of these approaches. Carbon dioxide removal, i.e. sequestration, processes are discussed in Chapter 21.

### **30.10 MERCURY REMOVAL**

Gas-phase mercury is a particularly important and difficult substance to remove from gas streams, including emissions from coal-fired power plants. When Hg-laden coal is burned, the Hg is vaporized in the furnace and exits as Hg<sup>0</sup>. Up to 98% of the Hg is then oxidized to Hg<sup>2+</sup>, which has high aqueous solubility.

Factors that enhance mercury control are low temperature in the system (<150 °C), the use of an effective mercury sorbent and a method to collect the sorbent. Generally, high concentrations of carbon in the fly ash enhance mercury sorption onto PM, with the ash then removed by the PM control device, e.g. an electrostatic precipitator, wet flue gas desulfurization system (wFGD), and combinations of these and other technologies. Additionally, the presence of hydrogen chloride (HCl) in the flue gas stream can result in the formation of mercuric chloride (HgCl<sub>2</sub>), which is readily adsorbed onto carbon-containing PM. Conversely, sulfur dioxide (SO<sub>2</sub>) in flue gas can act as a reducing agent to convert oxidized mercury to elemental mercury, which is more difficult to collect.<sup>29</sup>

The most common techniques for removing Hg are carbon filter beds, wet scrubbing, selenium filters, and activated carbon injection. Gas-phase oxidized Hg can be collected by absorption to aqueous solution in the wFGD and removed with wFGD waste. Once captured from the gas phase, Hg<sup>2+</sup> can persist in wFGD liquids in a water-soluble form, partition to the solid phase or be reduced to Hg<sup>0</sup>.

#### **30.10.1 Carbon Filter Beds**

Three carbon filter designs have been used to remove Hg: cross flow, counter current, and counter-cross flow. The cross-flow design has been applied to utility boilers and waste combustors, the counter current design to waste combustors and the counter-cross flow design to utility boilers. In the cross-flow filters, the flue gas flows horizontally through the filter bed, while the adsorbent migrates through the filter from top to bottom. The bed is about 1 m thick and is divided into three layers. The

first layer removes PM, heavy metals (including mercury), organic compounds, and SO<sub>2</sub>. Removal of HCl occurs primarily in the second layer. The third layer acts as a safety layer. The three layers are separated by perforated metal sheets. On the outlet side, there is a slotted sheet designed to prevent particles from being carried out of the filter with the flue gas. Additionally, an impact separator is located downstream of the slotted sheet, functioning as a safety barrier against particle emissions.

Pressure drop is the primary rate-limiting factor for carbon removal from the bed. The designed pressure drop across the bed is 1.5–1.9 cm (6–7.5 in.) of water. The pressure drop across the whole system including fans and ducting is about 30 cm (12 in.) of water. Because of PM collection in and compaction of each layer, approximately 10–13 cm (4–5 in.) of material is periodically sloughed from each layer. Because of greater vibration of particles and, thus, greater settling of the particles within the first layer, carbon is sloughed from this layer on the shortest time interval, typically once every 6–8 h. The second layer is sloughed once every day, and the third layer is sloughed once every 2 weeks. Based on these removal rates and bed thicknesses, the mass of carbon in the filter is fully replaced at an average rate of once every year.<sup>29</sup>

Spent carbon can be disposed of by combustion if the unit is equipped with a wet-scrubbing system. The combustion process degrades organic compounds captured in the carbon and the wet scrubber collects the heavy metals and acid gases.

#### **30.10.2 Wet Scrubbing**

Wet-scrubbing controls acid gases, metals, PM, and semivolatile organic compounds (SVOCs), e.g. chlorinated dioxins and furans. Single-stage scrubbers can be used to remove acid gases. Two-stage scrubbers can be used for acid gases and metals. Three-stage systems having a two-stage scrubber followed by a high-efficiency wet particulate control system are designed for improved control of fine particulates, metals, and SVOCs. Single-stage scrubbers can also be installed following other pollution controls for increased pollutant control (i.e. polishing scrubbers).

Hydrophilic Hg compounds, e.g. HgCl and HgO, can be effectively captured (>90%) in the wet scrubber. If there is significant Hg<sup>0</sup> in the flue gas, however, collection efficiencies will be limited. The captured mercury is precipitated out during wastewater treatment with additives (i.e. sodium sulfide and dithiocarbamate). Three-stage systems have shown Hg removal efficiencies of over 90%. The amount of hydrophilic Hg species in the gas stream is a major factor determining effectiveness of this control approach.<sup>29</sup>

### 30.10.3 Selenium Filters

Selenium (Se) filters operate based on the affinity between Hg and Se. The Hg-laden flue gas passes through the filter, which consists of ceramic grains impregnated with metallic selenium. The gas pathway through the filter is tortuous, which increases the contact between the mercury and the selenium, forming mercury selenite (HgSe). Selenium filters are effective on flue gas streams with inlet mercury concentrations of up to  $9 \text{ mg scm}^{-3}$  (3900 g per million scf). At very low Hg concentrations, removal efficiency decreases due to the dramatic decrease in Hg–Se molecular collisions. At higher Hg concentrations, the lifetime of the filter is short. Because the removal of mercury in the filter is based on the formation of HgSe, the selenium in the filter is eventually exhausted. The selenium filter is designed to convert approximately 50 kg of mercury to HgSe per cubic meter of filter material ( $3 \text{ lbs ft}^{-3}$ ). The combination of pressure drop, Hg content in the flue gas, and the mechanical construction of the filter drive filter life. On average, the filter lifetime is 5 years, after which the filter element is replaced. Once the lifetime of the filter mass has expired, the HgSe must be properly disposed as a hazardous waste. Se filter Hg removal effectiveness has been shown for metal smelters and crematories, but not yet for a utility boiler.

### 30.10.4 Activated Carbon Injection

Powdered activated carbon can be injected into the gas upstream of air pollution control devices. Since activated carbon has many internal pores and large surface area, it can adsorb a broad range of trace contaminants, including Hg. After injection into the flue gas and adsorption of Hg and other contaminants, the activated carbon is captured in the PM control device. The factors affecting the performance of activated carbon injection are the temperature of the flue gas, the amount of activated carbon injected, the concentration of each Hg species in the flue gas, the extent of contact between the carbon and Hg, and the type of carbon used. Flue gas temperature is crucial because Hg volatilizes at temperatures above 150–200 °C. The flue gas temperature needs to be within, or preferably below, this range for the mercury to adsorb onto the carbon. The combustion device and the corresponding composition of the flue gas will affect this temperature range. In an MWC, where there is a substantial amount of HCl resulting in the formation of  $\text{HgCl}_2$ , temperatures within and below the noted range have proven to be effective when injecting carbon. Test data from an MWC retrofitted with activated carbon injection indicate mercury removals

greater than 95%. Pilot testing on a coal-fired utility boiler indicated that a temperature under 90–120 °C was necessary for effective mercury removal. With activated carbon injection, efficient distribution of the carbon in the flue gas is also important. The amount of carbon needed to achieve a specific level of mercury removal will vary depending on the fuel being burned, the amount of carbon inherent to the system, and the type of PM control device. At a given carbon feed rate, a fabric filter provides more Hg control than an ESP because of the additional Hg adsorption that occurs on the bags of the fabric filter (due to the increased gas contact time). Mercury is predominately removed upstream of an ESP-equipped facility; however, the nominal residence time of 1 s or less limits the capture. In addition, Hg is not effectively collected across the ESP, further requiring substantially higher carbon feed rates than the fabric filter-equipped facilities.<sup>29</sup>

## 30.11 REMOVAL OF ODORS

An odor can be described as a physiological response to activation of the sense of smell.<sup>1</sup> It can be caused by a chemical compound (e.g.  $\text{H}_2\text{S}$ ) or a mixture of compounds (e.g. coffee roasting). Generally, if an odor is objectionable, any perceived quantity greater than the odor threshold will be a cause for complaint. The control of odors, therefore, becomes a matter of reducing them to less than their odor thresholds, preventing them from entering the atmosphere, or converting them to a substance that is not odorous or has a much higher odor threshold. Odor masking is not recommended for a practical, long-term odor control system.

### 30.11.1 Odor Reduction by Dilution

If the odor is not a toxic substance and has no harmful effects at concentrations below its threshold, dilution may be the least expensive control technique. Dilution can be accomplished either by using tall stacks or by adding dilution air to the effluent. Tall stacks may be more costly if only capital costs are considered, but they do not require the expenditure for energy that is necessary for dilution systems. In addition, if the emission contains other pollutants, taller stacks will increase the distance traveled by the pollutant and, thus, will contribute to the long-range transport and the potential cumulative effects of these pollutants.

The odor threshold for most atmospheric pollutants may be found in the literature.<sup>1</sup> By properly applying the diffusion equations, one can calculate the height of a stack necessary to reduce the odor to less than its

threshold at the ground or at a nearby structure. A safety factor of two orders of magnitude is suggested if the odorant is particularly objectionable.

Odor control by the addition of dilution air involves a problem associated with the breakdown of the dilution system. If a dilution fan, motor, or control system fails, the odorous material will be released to the atmosphere. If the odor is objectionable, complaints will be noted immediately. Good operation and maintenance of the dilution system become an absolute requirement, and redundant systems should be considered.

### 30.11.2 Odor Removal

It is sometimes possible to close an odorous system to prevent the release of the odor to the atmosphere. For example, a multiple-effect evaporator can be substituted for an open contact condenser on a process emitting odorous, noncondensable gases.

Another possible solution to an odor problem is to substitute a less noxious or more acceptable odor within a process. An example of this type of control is the substitution of a different resin in place of a formaldehyde-based resin in a molding or forming process.

Many gas streams can be deodorized by using solid adsorption systems to remove the odor before the stream is released to the atmosphere. Such procedures are often both effective and economical.

### 30.11.3 Odor Conversion

Many odorous compounds may be converted to compounds with higher odor thresholds or to nonodorous substances. An example of conversion to another compound is the oxidation of  $\text{H}_2\text{S}$ , odor threshold 0.5 ppb, to  $\text{SO}_2$ , odor threshold 0.5 ppm. The conversion results in another compound with an odor threshold three orders of magnitude greater than that of the original compound.

An example of conversion to a nonodorous substance would be the passage of a gas stream containing butyraldehyde,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ , with an odor threshold of 40 ppb, through a direct-fired afterburner which converts it to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , both nonodorous compounds. It should be noted that using a direct-fired afterburner, particularly one without heat recovery, to destroy 40 ppb is not an economical use of energy, and some other odor control system may be more desirable.

The next chapter describes how the technologies addressed in this chapter are applied in various industrial and transportation sectors.

## QUESTIONS

1. Why is the viscosity of the carrier gas a key characteristic of a pollution control device? Hint: Consider the force equations.
2. How does gas viscosity change with increasing temperature?
3. Give an example of specifications you would make in selecting a particle collection device for a factory that uses highly corrosive ( $\text{pH} > 12$ ) aerosols.
4. What is the problem when aggregates smaller than those called for in the design specifications are released from dust cake in PM control equipment?
5. What is the main role of gravity settling in high-efficiency particulate control systems?
6. How is the collection efficiency of a cyclonic collector related to the particle size?
7. Two aerosols each have  $3.14 \times 10^{-10} \text{ cm}^2$  surface area and  $8.00 \times 10^{-3} \mu\text{g}$  mass, but one has half the physical diameter? How will this difference affect settling?
8. An aerosol has  $10 \mu\text{m}$  aerodynamic diameter and weighs  $1.6 \times 10^{-3} \mu\text{g}$ . Another has  $2.5 \mu\text{m}$  aerodynamic diameter and weighs  $3.2 \times 10^{-3} \mu\text{g}$ . How will these differences affect gravity settling? How will they affect inertial impaction?
9. As the diameter of an aerosol decreases, what happens to the Cunningham slip factor?
10. Assuming the temperature is  $20^\circ\text{C}$ , if the particle Reynolds number is 0.5, what is the drag coefficient for  $2.5 \mu\text{m}$  diameter particle?
11. Assuming the temperature is  $20^\circ\text{C}$ , if the Reynolds number for the same particle were 1200, what is the particle's drag coefficient?
12. Based on the relationship between flow condition and terminal settling velocity, what can be done to the design of a gravity system to improve its collection efficiency?
13. Identify physical features of an aerosol that make it more difficult to collect by gravity.
14. What are the major forces at work in a cyclone?
15. What are the major forces at work in an inertial impactor?
16. How is the collection efficiency of an air pollution control device using inertial impaction (e.g. particulate wet scrubber) related to the particle size?
17. Why is  $\text{PM}_{10}$  not effectively collected by molecular diffusion?
18. How does the effectiveness of Brownian motion relate to the particle size?
19. Why is a very dirty filter not very efficient in collecting PM? Why is a very clean filter also not very efficient at collecting PM?

20. Add a maintenance event to [Figure 30.13](#) and extend the time. What shape are the curves?
21. Which types of fabric filter systems collect the dust cake on the exterior surface of the filter media?
22. What is the purpose of using off-line cleaning in a multi-compartment pulse jet collector?
23. What fabrics have a long-term temperature limitation above 400 °F?
24. What types of contaminants can be present in untreated compressed air used to clean pulse jet fabric filters and cartridge fabric filters?
25. What problem/problems is/are created if a pulse jet bag does not seal properly to the tube sheet?
26. A reverse bag constructed of fiberglass has very low tension and is sagging severely at the connection to the tube sheet thimble. What problem or problems could be created by this condition?
27. What forces are used to remove particles in woven and felted bags?
28. What forces are used to remove particles in a membrane bag?
29. Polypropylene and polyamide have excellent acid resistance and excellent resistance against abrasion and flex. Why would other less resistant materials be used in fabric filter systems?
30. Why is pressure drop across fabric filter media important?
31. A reverse air baghouse is with 36 compartments, 200 bags in each compartment. Each bag has a diameter of 270 cm and is 9 m in length. At an actual gas flow rate of  $5 \times 10^4 \text{ m}^{-3} \text{ s}^{-1}$  and assuming that eight compartments are presently out of service, calculate the gross and net air-to-cloth ratios.
32. Would the specifications described above work well for a reverse air system to control emissions from a municipal incinerator? How about for a pulse jet system for a refractory plant?
33. What problem occurs at excessive air-to-cloth ratios?
34. Calculate the gas approach velocity for a pulse jet baghouse having a single compartment, 60 rows of bags with 10 bags each, and a bag diameter of 6 in. Assume that the internal dimensions of the compartment are  $6.5 \times 40$  ft. Use a gas flow rate of 66,000 acfm.
35. Would a 150 µm size particle or particle agglomerate successfully settle by gravity in the pulse jet baghouse described in the previous question? Assume a temperature of 20 °C, a particle density of  $1.0 \text{ g cm}^{-3}$ , and that the transitional region terminal settling velocity equation is appropriate for this particle size.
36. Calculate the static pressure difference between the clean gas plenum of a top-access type pulse jet baghouse and the ambient air. Assume that the

- inlet static pressure to the baghouse is 4 in. WC and the static pressure drop across the baghouse is 5 in. WC.
37. Before installing a pulse jet fabric filter with an air-to-cloth ratio of  $2.5 \text{ ft min}^{-1}$  to clean a 10,000 scfm air stream at 250 °F, determine the filtering area required for this operation and, using the information below, choose an appropriate filter bag and determine how many will be needed.

Filter Bag	A	B	C	D
Tensile strength	Excellent	Very good	Fair	Excellent
Maximum temperature (°F)	260	275	260	220
Relative cost per bag	2.6	3.8	1.0	2.0
Size	$4\frac{3}{4}'' \times 10'$	$6'' \times 10'$	$6'' \times 14'$	$6'' \times 14'$

38. If the carrier gas and the aerosols being collected are very similar physically and chemically, is an ESP likely to be a good device?
39. Demonstrate mathematically that fly ash with extremely low resistivity is not a good candidate for collection by electrostatic precipitation.
40. An ESP is designed and operated to collect PM at 95% efficiency at 150 °C, using fuel with an S-content of 2.5%. If a 0.5% S-content fuel is substituted, what is the new collection efficiency?
41. What problems can occur if moisture and/or conductive solids accumulate on the surfaces of the high-voltage frame support insulators?
42. What factors influence the dust layer resistivity for a precipitator operating at less than 350 °F?
43. How is saturation charge related to particle diameter?
44. What is a generally good temperature range to decrease electrical resistivity of dust cake?
45. What is the difficult-to-control particle size range for ESPs?
46. Calculate the liquid-to-gas ratio for a scrubber system with a gas flow rate of  $4000 \text{ ft}^3 \text{ s}^{-1}$  and a recirculation liquor flow rate of  $2000 \text{ gal min}^{-1}$ . Is this value in the normal range for a particulate matter wet scrubber?
47. When might the oxidation of H<sub>2</sub>S not be preferable as an air pollution control approach? What can be done to address this problem?
48. Why is substituting oxygen for air a means of decreasing NO<sub>x</sub> emissions?
49. Which is better for removing PM with physical diameters <1 µm, a venturi scrubber, or a baghouse with nylon bags? Explain. Which is better for removing PM with physical diameters >10 µm, an

- ESP, or spray tower? Explain. How might the chemical composition of the PM affect collection efficiencies and change your answers?
50. What two processes from dry systems are combined in a wet scrubber?
51. One of the criticisms of wet scrubbers is that they transform an air pollution problem into a water pollution problem. Is this true? Support your answer chemically.
52. Why is a dry scrubber often much more efficient than a wet scrubber at removing fly ash from hot gas streams?
53. Give two similarities between a bioscrubber for air pollutants and trickling filter for water pollutants. Give two differences.
54. What can be done to enhance SO<sub>2</sub> removal efficiency by a wet scrubber?
55. What is the difference between absorption and adsorption as methods to remove gaseous air pollutants?
56. Suggest a reason that increasing L:G ratios above 20 gal:1000 acf do not appreciably improve wet scrubber performance.
57. What happens to an adsorption system when the adsorbent becomes saturated with adsorbate?
58. An activated carbon is used to remove a volatile organic solvent from the gas stream. The temperature of the air entering the bed decreases from 35 to 32 °C and the humidity of the air increases by 15%. How has this changed the saturation capacity?
59. Why are absorbers often installed in series?
60. Where do you take the toluene measurement to determine if a VOC absorption system has toluene breakthrough?
61. When does Henry's law not apply to absorption processes?
62. How do temperature ranges differ for a catalytic oxidizer *versus* a thermal oxidizer? Why is the difference?
63. How can increases above the recommended temperature range adversely impact the catalytic oxidizer?
64. What are the two units needed when using a bioscrubber to remove gaseous air pollutants?
65. Name two forms of mercury that can be captured with 90% or higher efficiency using a wet scrubber? What inherent property of these compounds is responsible for this efficiency?
66. What causes a selenium filter to lose its ability to capture mercury?
67. What is an effective control technology for mercury removal from a gas stream with a large amount of low aqueous solubility Hg species?

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# Controlling Air Pollution from Sources

## 31.1 INTRODUCTION

Control of sources of air pollution requires the application of the control concepts and approaches discussed in Chapter 30, but the control devices usually need to be adapted and tailored to the specific operations of various industrial and other economic sectors. In some cases, more than one system or device must be used to achieve satisfactory control. The general methods of control are:

1. modifications to a less polluting process;
2. changes in types of supplies (e.g. more efficient filters, sorbants, catalysts, reagents, cartridges, and air movers);
3. improved operation and maintenance (O&M) that produce less emissions from the existing process by improved operation;
4. fuel change to a fuel which will give the desired level of emissions; and
5. installation of control equipment.

Arguably the best approach is to integrate all of these methods into the life cycle perspective and design facilities in ways that achieve the same objectives, but in a manner that does not generate the pollution or at least in a way that decreases the amount of the pollutant or produces pollutants that are not as harmful as those that would be produced with the *status quo*. For example, each of these five steps could incorporate the principles of green chemistry, e.g. safer reagents, green engineering, and design for the environment (DfE). This applies to every stationary source discussed in this chapter (see Table 31.1). For example, health risks, social expectations, and environmental impacts and other societal risks and benefits associated with a device, structure, product, or activity can be visualized at various stages of the manufacturing, marketing, and application stages. These ideas were introduced in Chapter 5 and will be revisited in the next chapter.

Many industrial, transportation, construction, and other sectors have embraced these ideas, so the

approaches discussed in this chapter must be seen within a larger context of overall design, installation, O&M of specific equipment. With more sustainable practice, the need for some will be eliminated entirely, whereas others may be used for a smaller fraction of pollutants in the waste and gas streams. However, it has always been more efficient for the engineer to design air pollution control into the source when it is first considered, rather than to leave it until the process is operational and found to be in violation of emission standards.

TABLE 31.1 Functions That Must Be Integrated into Stationary Source Design

Baseline studies of natural and built environments
Analyses of project alternatives
Feasibility studies
Environmental impact studies
Assistance in project planning, approval, and financing
Design and development of systems, processes and products
Design and development of construction plans
Project management
Construction supervision and testing
Process design
Startup operations and training
Assistance in operations
Management consulting
Environmental monitoring
Decommissioning of facilities
Restoration of sites for other uses
Resource management
Measuring progress for sustainable development

Source: American Society of Mechanical Engineers. <http://www.professionalpractice.asme.org/communications/sustainability/2.htm>; 2006 [accessed 23.05.06].

As discussed in Chapter 29, emission standards are generally divided between stationary and mobile sources. Thus, this chapter addresses these separately. However, many of the same principles being applied at the larger, more centralized systems of stationary sources can be applied to smaller, more distributive mobile sources. There are, of course, scaling differences that need to be incorporated, but processes such as catalysis, filtration, fuel mix, inertial impaction, and electrostatics can be applied in any air pollution setting, whether stationary or mobile.

## 31.2 STATIONARY SOURCE CONTROL TECHNOLOGIES

Most new large stationary sources of air pollution in the United States are regulated under the Clean Air Act Amendments of 1990 and are legally required to comply with the Amendments. This is also true for most of the developed, industrialized world. Similar emission standards are being developed in rapidly developing areas of the world as well.

Indeed, some of the world is experiencing air pollution levels similar to those experienced by Western urban areas during the worst episodes of the twentieth century. The rapid development of heavy chemical industries, energy consumption, and motor vehicle ownership in South Asia has resulted in substantial emissions of sulfur dioxide ( $\text{SO}_2$ ), oxides of nitrogen ( $\text{NO}_x$ ), and volatile organic compounds (VOCs), as well as the generation of secondary pollutants like by  $\text{PM}_{2.5}$ , ground-level  $\text{O}_3$ , and acidic deposition. In China in 2010, the annual average value from  $\text{PM}_{2.5}$  pilot monitoring stations in seven cities was  $40\text{--}90 \mu\text{g m}^{-3}$ , which is 14–157% higher than the U.S. National Ambient Air Quality Standards (NAAQS). Ozone monitoring pilots show that  $\text{O}_3$  concentrations exceeded Grade II NAAQS for 20% of the days in the year in some cities, and the maximum  $\text{O}_3$  concentration per hour in some regions exceeded the European alert level (240 ppb). The pollution is visible to the naked eye, with complex air pollution diminishing visibility and creating haze for about 100 days per year in the Beijing–Tianjin–Hebei, Yangtze Delta, and Pearl River Delta regions. In some cities haze occurs for more than 200 days a year.<sup>1</sup> Addressing these issues calls for steps to prevent the protracted path that the United States and Europe followed that eventually led to the Clean Air Act of 1970 and similar laws in Europe. The current and projected ambient air quality in these rapidly developing areas are leading to conditions similar to those that led to the high mortality episodes of in the Meuse Valley, Belgium,<sup>2</sup> Donora, Pennsylvania<sup>3</sup> Poza Rica, Mexico, and other urban areas of North America and Europe in the twentieth century.

There is a growing appreciation of this problem. In 2012, China announced plans to require key regions (including the metropolitan areas) to decrease ambient concentration of  $\text{SO}_2$  and  $\text{PM}_{10}$  by 10%,  $\text{NO}_2$  by 7%, and  $\text{PM}_{2.5}$  by 5%. In addition, three key regions, i.e. Beijing–Tianjin–Hebei, Yangtze River Delta, Pearl River Delta will have to reduce  $\text{PM}_{2.5}$  concentration by 6% by 2015. This means that if these plans are to be realized, substantial emission controls will need to be put into place for both particulate and gas phase pollutants released from both stationary and mobile sources. For example, the plan calls for lowering  $\text{SO}_2$ ,  $\text{NO}_x$ , and stationary source emissions of particulates by 12%, 13%, and 10%, respectively. The  $\text{SO}_2$  target is 4% more stringent than the national target, i.e. 8%. The  $\text{NO}_x$  emissions decrease would be 3% higher than the national target, i.e. 10%.<sup>5</sup>

Existing stationary sources may require modification of existing systems or installation of newer, more efficient control devices to meet more restrictive emission standards. Such changes are often required by control agencies when it can be shown that a new control technology is superior to older systems or devices being used. This is usually referred to as application of the best available control technology (BACT). The BACT standards have been incrementally replaced with risk-based standards, meaning that sources may need to apply more stringent technologies as well as important measures to reduce emissions further (e.g. pollution prevention).

Installation of control systems may have a positive economic benefit, which will offset a portion of their cost. Such benefits include tax deduction provisions, recovery of materials previously emitted, depreciation schedules favoring the owner of the source and banking or sale of the emission offset credits if the source is in a nonattainment area, i.e. flexibly complying with traditional source-specific command and control standards, but with even less emissions to improve local air quality.<sup>5</sup>

### 31.2.1 Thermal Systems

Thermal energy, power generation, and incineration have several factors in common. All rely on combustion, which causes the release of air pollutants; all exhaust their emissions at elevated temperatures; and all produce large quantities of ash when they consume solid or residual fuels. The ratio of the energy used to control pollution to the gross energy produced can be a deciding factor in the selection of the control system. These processes have important differences, which influence the selection of specific systems and devices for individual facilities.

Eliminating or reducing pollutant concentrations that would otherwise need to be destroyed thermally should be the first step in deciding which incinerator and other thermal process, if any is appropriate for the waste and gas streams. This begins by assessing the physical and chemical characteristics of each contaminant, and matching these characteristics with the appropriate control technology. The scientific concepts of Chapters 16 through 19 must be part of this decision. These especially include the kinetics and equilibria, e.g. solubility, fugacity, sorption, and bioaccumulation factors, which will determine the effectiveness of destruction, transformation, removal, and immobilization of these contaminants. In Chapter 32, these properties will be discussed within the context of sustainable approaches to address organic and inorganic contaminants typically found in air pollution scenarios, e.g. contaminated slurries and sludges.

There can be synergies, e.g. innovative thermal approaches are available that not only effectively destroy organic contaminants, but in the process also destroys the inorganic cyanic compounds. Unfortunately, there are also antagonisms among approaches, such as the very effective incineration processes for organic contaminants that transform heavy metal species into more toxic and more mobile forms. The increased pressures and temperatures are good for breaking apart organic molecules and removing functional groups that lend them toxicity, but these same factors oxidize or in other ways transform the metals into worse forms. So, when mixtures of organic and inorganic contaminants are targeted, more than one technology may be required to accomplish project objectives, and care must be taken not to trade one problem (e.g. polychlorinated biphenyls, PCBs) for another (e.g. a more mobile species of cadmium).<sup>6</sup>

### **31.2.1.1 Energy-Producing Industries**

Stationary energy-producing systems are of two general types, residential and commercial space heating and industrial steam generation. The smaller systems (residential and commercial heating) are usually regulated only with respect to their smoke emission, even though they may produce appreciable amounts of other air pollutants.<sup>7</sup> The large industrial systems which generate steam for process use and space heating (where superheated or high-temperature saturated steam is used for a process, e.g. cogeneration, exhausted from the process at a lower energy level, and then introduced into a space heating system, where it gives up a large amount of latent energy, condensing to hot water) are required to comply with rigid standards in most countries.

Petroleum and coal supply the majority of the energy in all industrial countries. This fact gives an indication of the vast quantities of materials handled and also hints at the magnitude of the air pollution problems associated

with obtaining the resource, transporting it, refining it, and transporting it again. The emission problems from burning fossil fuel have been previously discussed.

Petroleum products are obtained from crude oil. In the process of getting the crude oil from the ground to the refinery, many possibilities for emission of hydrocarbon and reduced sulfur gaseous emissions occur. In many cases, these operations take place in relatively remote regions and affect only those employed by the industry, so that little or no control is attempted.

Control of atmospheric emissions from petroleum refining can be accomplished by process change, installation of control equipment, and improved housekeeping and maintenance. In many cases, recovery of the pollutants will result in economic benefits. [Table 31.2](#) lists some of the control measures that can be used at petroleum refineries.

The amount of emissions from a petroleum refinery varies according to type of operations, the amount and rate of crude oil being processed and the operations and management practices in and around the refinery. A modern petroleum refinery is a complex system of chemical and physical operations. The crude oil is first separated by distillation into fractions such as gasoline, kerosene, and fuel oil. Some of the distillate fractions are converted into more valuable products by cracking, polymerization, or reforming. The products are treated to remove undesirable components, such as sulfur, and then blended to meet the final product specifications. Some of the emission sources for these processes are listed in [Table 31.3](#).

Since refineries are essentially closed processes, emissions are not normally considered a part of the operation. Refineries do need pressure relief systems and vents, and emissions from them are possible. Most refineries use very strict control measures for economic as well as regulatory reasons. The recovery of 1% or 2% of a refinery throughput which was previously lost to the atmosphere can easily pay for the cost of the control equipment. The expense of the catalyst charge in some crackers and regenerators requires that the best possible control equipment be used to prevent catalyst emissions to the atmosphere.

Potential air pollutants from a petroleum refinery could include: hydrocarbons from all systems, leaks, loading, and sampling; sulfur oxides ( $\text{SO}_x$ ) from boilers, treaters, and regenerators; carbon monoxide (CO) from regenerators and incinerators;  $\text{NO}_x$  from combustion sources and regenerators; odors from air and steam blowing, condensers, drains, and vessels; and particulate matter (PM) from boilers, crackers, regenerators, coking, and incinerators.

Loading facilities must be designed to recover all vapors generated during filling of tank trucks or tanker ships. Otherwise these vapors will be lost to the

**TABLE 31.2** Control Measures for Air Pollutants from Petroleum Refining

Source	Control Method
Storage vessels	Vapor recovery systems; floating roof tanks; pressure tanks; vapor balance; painting tanks white
Catalyst regenerators	Cyclones—precipitator—CO boiler; cyclones—water scrubber; multiple cyclones
Accumulator vents	Vapor recovery; vapor incineration
Blowdown systems	Smokeless flares-gas recovery
Pumps and compressors	Mechanical seals; vapor recovery; sealing glands by oil pressure; maintenance
Vacuum jets	Vapor incineration
Equipment valves	Inspection and maintenance
Pressure relief valves	Vapor recovery; vapor incineration; rupture disks; inspection and maintenance
Effluent waste disposal	Enclosing separators; covering sewer boxes and using liquid seals; liquid seals on drains
Bulk loading facilities	Vapor collection with recovery or incineration; submerged or bottom loading
Acid treating	Continuous-type agitators with mechanical mixing; replace with catalytic hydrogenation units; incinerate all vented cases; stop sludge burning
Acid sludge storage and shipping	Caustic scrubbing; incineration, vapor return system
Spent caustic handling	Incineration; scrubbing
Doctor treating	Steam strip spent doctor solution to hydrocarbon recovery before air regeneration; replace treating unit with other, less objectionable units (Merox)
Sour water treating	Use sour water oxidizers and gas incineration; conversion to ammonium sulfate
Mercaptan disposal	Conversion to disulfides; adding to catalytic cracking charge stock; incineration; using material in organic synthesis
Asphalt blowing	Incineration; water scrubbing (nonrecirculating type)
Shutdowns, turnarounds	Depressurize and purge to vapor recovery

Source: Ref. 8.

**TABLE 31.3** Sources of Emissions from Oil Refining

Type of Emission	Source
Hydrocarbons	Air blowing, barometric condensers, blind changing, blowdown systems, boilers, catalyst regenerators, compressors, cooling towers, decoking operations, flares, heaters, incinerators, loading facilities, processing vessels, pumps, sampling operations, tanks, turnaround operations, vacuum jets, waste effluent handling equipment
Sulfur oxides	Boilers, catalyst regenerators, decoking operations, flares, heaters, incinerators, treaters, acid sludge disposal
Carbon monoxide	Catalyst regenerators, compressor engines, coking operations, incinerators
Nitrogen oxides	Boilers, catalyst regenerators, compressor engines, flares
Particulate matter	Boilers, catalyst regenerators, coking operations, heaters, incinerators
Odors	Air blowing, barometric condensers, drains, process vessels, steam blowing, tanks, treaters, waste effluent handling systems
Aldehydes	Catalyst regenerators, compressor engines
Ammonia	Catalyst regenerators

Source: Elkins HF. *Petroleum refining*. In: Stern AC, editor. *Air pollution*. 3rd ed., vol. 4. New York, NY: Academic Press; 1977.

atmosphere. Since they may be both odorous and photochemically reactive, serious air pollution problems could result. The collected vapors must be returned to the process or disposed of by some means.

An increasingly important concern is the likelihood of an uncontrolled fire caused by an accident or by a terrorist act at the refinery. This can be the source of large and highly toxic plumes. Thus, refineries need special measures for protection and security, coupled with vigorously diligent monitoring, operation, and maintenance. Every refinery also needs an up-to-date contingency plan.

The air pollution problems associated with combustion of coal are of major concern. Combustion may occur near the mine, i.e. a mine mouth operation, or many miles away from the mine (e.g. with coal shipped to distant power plants via rail and barge). The problems of atmospheric emissions due to mining, cleaning,

handling, and transportation of coal from the mine to the user are of lesser significance as far as the overall air pollution problems are concerned. Whenever coal is handled, particulate emission becomes a problem. The emissions can be either coal dust or inorganic inclusions. Control of these emissions can be relatively expensive if the coal storage and transfer facilities are located near residential areas. This is particularly problematic in developing nations. For example, China's economic and industrial expansion over the past decade has been largely supported by coal combustion (about two-thirds of energy use). This leads to three types of problems:

1. Coal is among the worst fuels in terms of production of greenhouse gases, mainly carbon dioxide ( $\text{CO}_2$ ).
2. Coal often has high sulfur and ash content, so it is a major source of oxides of sulfur and particulate matter, respectively.
3. Coal contains heavy metals, particularly mercury, so it is also a major contributor to air toxics.

Control of air pollution from energy-producing industries is a function of the fuel used and the other variables of the combustion process. The system must be thoroughly analyzed before a control system is chosen. The important variables are listed in Table 30.3 in Chapter 30. For particulate matter control, the variables of process control such as improved combustion, fuel cleaning, fuel switching, and load reduction through conservation should be considered before choosing an add-on control system. If the particulate matter emission is still found to be in excess of standards, then control devices must be used. These include inertial devices (such as multiple cyclones), baghouses, wet and dry scrubbers, electrostatic precipitators (ESPs), and some of the previously discussed novel devices. Series combinations of control devices may be necessary to achieve the required level of particulate matter emission. A commonly used system is a multiple cyclone followed by a fine-particle control system, such as a baghouse, scrubber, or ESP.

Opacity reduction is the control of fine-particulate matter ( $<1\ \mu\text{m}$  diameter). It can be accomplished through the application of the systems and devices discussed for control of particulate matter and by use of combustion control systems to reduce smoke and aerosol emission. In addition, operational practices such as continuous soot blowing and computerized fuel and air systems should be considered.

Sulfur dioxide reduction to achieve required emission levels may be accomplished by switching to lower-sulfur fuels. Use of low-sulfur coal or oil, or even biomass such as wood residue as a fuel, may be less expensive than installing an  $\text{SO}_2$  control system after the process. This is particularly true in the wood

products industry, where wood residue is often available at a relatively low cost.

If an  $\text{SO}_2$  control device is necessary, the first decision is whether to use a wet or dry system. Many times this decision is based on the local situation regarding the disposal of the collected residue (sludge or dry material). Wet scrubbing systems, using chemical additions to the scrubbing liquid, are widely used. Various commercial systems have used lime or limestone, magnesium oxide, or sodium hydroxide slurries to remove the  $\text{SO}_2$ . Dry removal of  $\text{SO}_2$  can be accomplished by adding the same chemicals used in wet scrubbers, but adding them in a spray drier and then removing the spent sulfates with a bag house or ESP. This results in the collection of a dry material which may be either disposed of by land filling or used as a raw material for other processes. The electric power generating industry has had many years of experience with  $\text{SO}_2$  control systems. These methods are discussed in more detail in the next section.

Control of oxides of nitrogen can be accomplished by catalysts or absorbents, but most control systems have concentrated on changing the combustion process to reduce the formation of  $\text{NO}_x$ . Improved burners, change in burner location, staged combustion, and low-temperature combustion utilizing fluidized-bed systems are all currently in use. These combustion improvement systems do not generate waste products, so no disposal problems exist.

### 31.2.1.2 Power Generation

In general, plants-producing electric power are much larger than those producing steam for space heating or process use. Therefore, the mass of emissions is much greater and the physical size of the control equipment larger.

The extensive control of particulate matter, opacity,  $\text{SO}_2$ , and  $\text{NO}_x$  required on new power plants is very expensive. The high-projected cost of environmental control for a new coal-fired electric generating plant has made utility companies reluctant to risk the US billions of dollars necessary to use coal as a major fuel, particularly when they have perceived that emission standards are being redefined and changed.<sup>9</sup> Figure 31.1 illustrates the complexity of the current technology for the various alternative systems.

Figure 31.1(A) presents the integrated environmental control potential for maximum control of particulate matter and  $\text{SO}_2$ . Cooling tower water blowdown and treatment by-products may be used to satisfy scrubber makeup requirements. Fly ash and scrubber sludge will be produced separately. If the catalytic  $\text{NO}_x$  process is required, the integration issues will be increased significantly.

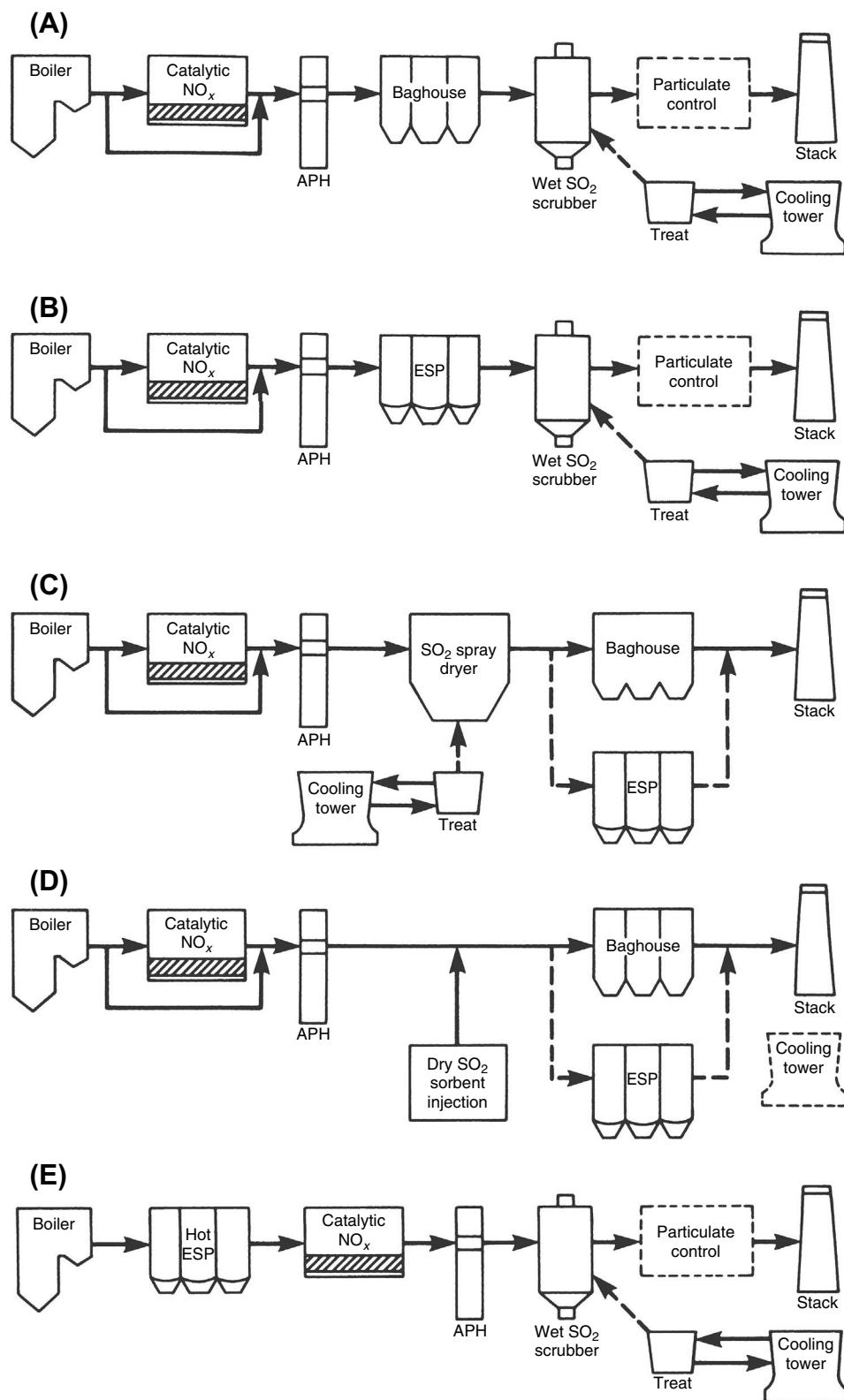


FIGURE 31.1 Integrated environmental control system for fossil fuel burning electric generating plants. Ref. 9.

**Figure 31.1(B)** is similar to **Figure 31.1(A)** except that an ESP is used for particulate control. This represents the most common approach for compliance when configured without a catalytic NO<sub>x</sub> unit.

**Figure 31.1(C)** is distinctly different from the first two in the type of SO<sub>2</sub> control processes used and the sequence of the particulate matter and SO<sub>2</sub> controls. It is a promising approach for up to 90% SO<sub>2</sub> control of western United States coal, and there is a single waste product. Other features include the collection of particulate matter at temperatures below 90 °C and the possibility for spray dryer cooling tower water integration. This system may or may not include a catalytic NO<sub>x</sub> unit.

**Figure 31.1(D)** represents the simplest, least expensive, and lowest water consumer of all the alternatives. There is a single solid waste product. The key element

is the integrated SO<sub>2</sub>/particulate control process. Using sodium-based sorbents, compliance may be achievable for western United States coals.

**Figure 31.1(E)** includes a hot ESP for fly ash collection prior to a catalytic NO<sub>x</sub> unit. Having a hot ESP dictates the use of a conventional wet scrubber and perhaps the need for a second particulate matter control device at the end of the system. Fly ash and scrubber sludge would be separate by-products, but sludge could be contaminated with NH<sub>4</sub> from the catalytic NO process.

**Figure 31.2** illustrates a wet SO<sub>2</sub> desulfurization system using a spray tower absorber. **Figure 31.3** illustrates a rotary atomizer injecting an alkaline slurry into a spray dryer for SO<sub>2</sub> control.

Selection and installation of an integrated air pollution control system do not end the concern of the utility

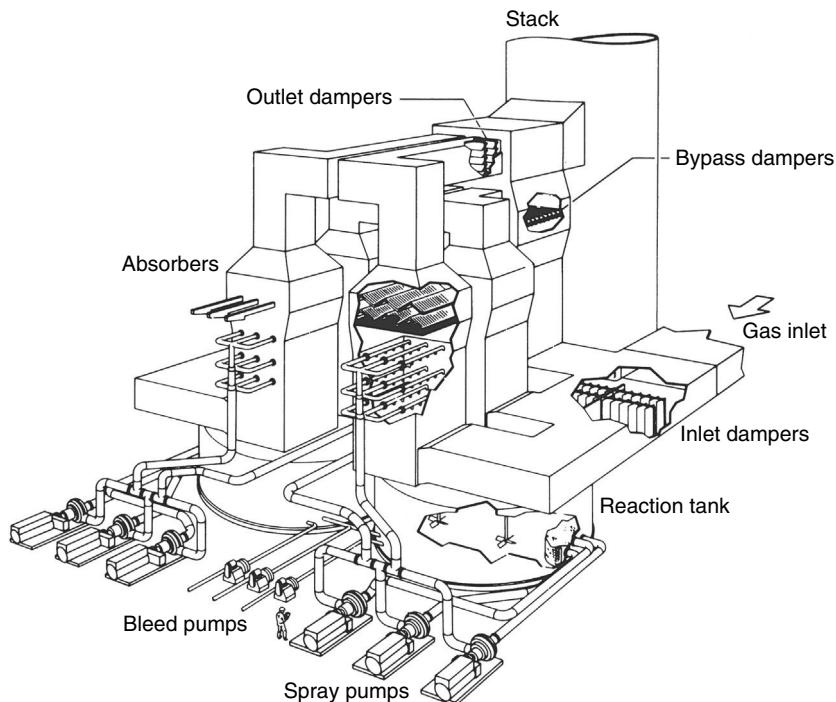


FIGURE 31.2 Cutaway drawing of a flue gas desulfurization (FGD) spray tower absorber. CE Power Systems, Combustion Engineering, Inc.

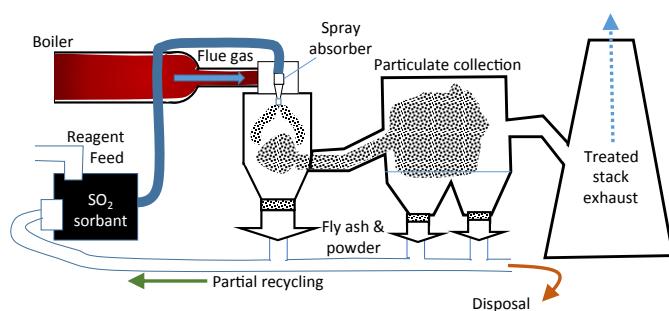


FIGURE 31.3 Alkaline slurry SO<sub>2</sub> spray dryer.

industry. Maintenance and operational problems of the system are considered by many engineers to be the weak link in the chain of power generation equipment.<sup>10</sup> This is particularly important for SO<sub>2</sub> removal.

Generally to treat SO<sub>2</sub>, the exhaust gas passes through a scrubber where a spray mixture of limestone and water reacts with the SO<sub>2</sub>. Newer scrubbers are typically being designed to remove 95% or more of the SO<sub>2</sub> from the gas stream of fossil-fuel power plants. When SO<sub>2</sub> combines with limestone, a primary by-product is calcium sulfate (CaSO<sub>4</sub>). This substance can be used as wallboard and cement, and as a soil amendment.<sup>11</sup>

Wet flue gas desulfurization (FGD) scrubbers can be classified as either nonregenerable or regenerable. Non-regenerable FGD processes produce a sludge that must be disposed of properly. This does not mean that the scrubbing liquid cannot be recycled or regenerated, but that no directly useful product is obtained from the eventual sludge. Conversely, regenerable processes generate a product from the sludge that may be sold to partially offset the cost of operating the FGD system. Regenerated products include elemental S, H<sub>2</sub>SO<sub>4</sub>, and gypsum. Over 90% of FGD processes are nonregenerable, likely due to the greater simplicity and less costs, at least at present. About 80% of FGD systems in the United States are wet systems using lime or limestone as a reagent.<sup>12</sup>

The reliability of the FGD system is defined as the time the system operates properly divided by the time it should have operated. Wet limestone systems have been designed for high efficiency SO<sub>2</sub> removal, up to 98%, but most wet limestone systems appear to be designed for 90% SO<sub>2</sub> removal. All limestone forced oxidation (LSFO) systems installed after 1990 are designed to remove SO<sub>2</sub> at a rate greater than 90%. The low efficiency designs are used generally for low-S fuel fossil fuel burning facilities.<sup>13</sup> High velocity LSFO processes appear to be able to remove over 99% of SO<sub>2</sub> under test conditions.<sup>14</sup> The SO<sub>2</sub> reduction efficiency at lime spray drying installations are about 90% for flue gas from burning 2% S coal.

The primary factors cited for low FGD reliability are (1) plugging, scaling, and corrosion of scrubber internals, mist eliminators, and reheaters; (2) need for open-loop operation and blowdown of scrubber liquor to reduce the corrosive substance concentration and dissolved solids content; (3) corrosion and failure of stack liners; and (4) plugging and failure of piping, pumps, and valves. Probably more critical are failures of dampers, ducts, and baffles, because this may require plant shutdown to perform maintenance.

Other methods, which should be mentioned because they show potential benefits for pollution reduction from utility stacks include (1) coal cleaning and treatment, (2) atmospheric pressure and pressurized fluidized-bed combustors, (3) conversion of solid fuels

to liquid or gaseous fuels, and (4) combustion modification through staged combustors or other systems.

Tall stacks are no longer considered to be an acceptable alternative for controlling emissions from electric power generating plants. Although they may allow much of the pollution plume to miss nearby areas, they contribute to the long-range transport of these pollutants. This leads to acidic deposition and other regional, continental, and global pollution problems.

### 31.2.1.3 Incineration

Thermal removal processes are discussed in detail in Chapter 29, but these techniques are applied in many industries other than hazardous waste destruction. Indeed, the principles employed for hazardous wastes were initially borrowed from industry, e.g. kilns for cement making.

Incineration continues to be an important means of dealing with municipal waste. For example, it represents a substantial component of solid waste management in many countries (Table 31.4). Municipal waste incinerators are particularly problematic, since their waste streams include a wide range of materials. Some are already hazardous and others can become hazardous after the combustion processes involved in incinerators.

Incineration is similar to combustion-generated energy and power processes in that fuel combines with oxygen. The incineration process, however, is designed as a waste disposal process, and if any energy is recovered, it is considered as a secondary system. Ideally, incineration will reduce the need for combustors,<sup>7</sup> conversion of solid fuels to liquid or gaseous fuels, and combustion modification through staged combustors or other systems.

It is important to note that the term "incineration" is specifically reserved for oxidative thermal processes with excess air. However, in general use, the term often includes thermal processes in the absence of O<sub>2</sub> (i.e. pyrolysis) and low O<sub>2</sub> (e.g. gasification). Indeed, this is not just a matter of thermodynamic theory, but is a factor in air pollution control. For example, pyrolytic processes produce H<sub>2</sub>, CO, hydrocarbons, ash, and pyrolysis oil; all of which need to be addressed in the gas stream. Below the stoichiometric air required for combustion, gasification produces H<sub>2</sub>, CH<sub>4</sub>, methane (CO<sub>2</sub>), CO, slag, and ash.

An incinerator will usually have a fuel of varying chemical composition and physical properties, as well as varying moisture content and heating value. In addition, the fuel fired in one locality may be vastly different from that fired by an incinerator of similar size and design in another locality. Refuse production in the United States has been estimated to average 2.5 g per person per day in 1970, increasing to 10 kg per person per day by the year 2000.

The air pollutants from incinerators consist of particulate matter (e.g. fly ash, carbon, metals and metal oxides

TABLE 31.4 Number and Total Capacity of the Existing Incinerators in 17 European Countries

Country	Number	Capacity (Mt year <sup>-1</sup> )	Country	Number	Capacity (Mt year <sup>-1</sup> )
Austria	5	0.5	Luxembourg	1	0.15
Belgium	17	2.4	Portugal	3	1.2
Denmark	32	2.7	Spain	9	1.1
Finland	1	0.07	Sweden	30	2.5
France	210	11.7	Netherlands	11	5.3
Germany	59	13.4	UK	17	3.0
Greece	0	0	Norway	11	0.65
Ireland	0	0	Switzerland	29	3.3
Italy	32	1.7			

Mt = million metric tons.

Source: Quina MJ, Bordado JCM, Quinta-Ferreira RM. Air pollution control in municipal solid waste incinerators. In: Mohamed Khallaf, editor. The impact of air pollution on health, economy, environment and agricultural sources; 2011. doi: 10.5772/17650. ISBN: 978-953-307-528-0, InTech.

and visible smoke), combustible gases such as CO and organic products of incomplete combustions (PICs), including polynuclear organic material (POM), and noncombustible gases such as NO<sub>x</sub>, SO<sub>x</sub>, and hydrogen chloride (HCl).

The oxides of nitrogen are formed by two mechanisms: thermal NO<sub>x</sub>, in which atmospheric nitrogen and oxygen combine at high furnace temperatures, and fuel NO<sub>x</sub>, when nitrogen-bearing compounds are incinerated. Addressing emissions of NO<sub>x</sub> and SO<sub>x</sub> is an example of advancing the state-of-the-science of both stationary and mobile source controls. These emission standards of compounds, especially NO<sub>x</sub>, have continuously become more stringent for mobile sources, e.g. to address ground-level ozone and acid rain. This has led to improved mobile source control technologies that can be adapted to stationary source. These modify the combustion process to quench combustion gases and to shorten residence times at high temperatures and O<sub>2</sub> availability. Other approaches include low excess air firing, staged combustion, and flue gas recirculation. These controls have been shown to decrease NO<sub>x</sub> emissions from electric utility boilers, oil field steam generators, and glass melting furnaces. Redesigned burners for boilers and heaters, water injection or dry low NO<sub>x</sub> combustors have been used on gas turbines. Prestratified charge and precombustion chamber systems have been applied to reciprocating internal combustion engines. These combustion modifications can be used alone or in combination with other control technologies.<sup>15</sup>

Postcombustion NO<sub>x</sub> control methods include selective catalytic reduction (SCR), selective noncatalytic reduction (SNCR), and nonselective catalytic reduction (NSCR). Selective NO<sub>x</sub> reduction methods inject ammonia (NH<sub>3</sub>) urea or other reductants into the post-combustion region. In the SCR approach, a catalyst is

added to the injection, whereas in the SNCR approach the reductant is injected in the absence of a catalyst. For rich burning internal combustion engines, CO and hydrocarbons reduce NO<sub>x</sub> nonselectively atop a catalyst bed, i.e. NSCR. The NO<sub>x</sub> emission removal efficiency of these technologies can be as high as 95%.<sup>15</sup>

It is important to note that HCl's inherent toxicity is quite high even at low concentrations, and that, its emissions are compounded with increasing amounts of halogenated polymers, notably polyvinyl chloride (PVC), in the refuse; i.e. 1 kg of pure PVC yields about 0.6 kg of HCl.

The POM emissions appear to be a function of the degree of combustion control, decreasing with increasing incinerator size (larger incinerators are more thoroughly instrumented and controlled). The measured emission rates for POM and CO vary considerably by type of incinerator and the amount and type of materials being incinerated. For example, a municipal incinerator burning 227 metric tons per day, before a settling chamber, is reported to emit 0.032 grams per metric ton (g Mg<sup>-1</sup>) POM and 0.35 grams per kilogram (g kg<sup>-1</sup>) CO, whereas a 45 metric ton per day incinerator is reported to emit 0.258 g Mg<sup>-1</sup> POM and 2.00 g kg<sup>-1</sup> CO. However, with a scrubber, the 45 metric ton per day incinerator's emissions decrease to 0.014 g Mg<sup>-1</sup> POM and 1.00 g kg<sup>-1</sup> CO. A commercial multiple chamber's emissions can be quite high, e.g. a 3 metric ton per day chamber without a control system has been reported to be 1.726 g Mg<sup>-1</sup> POM and 12.50 g kg<sup>-1</sup> CO.<sup>16</sup>

Air pollution control systems using wet scrubbers will remove some water-soluble gases, but the removal of particulate matter is the primary concern for a control system. The air pollution control system, therefore, is usually a single device such as a wet scrubber, small-diameter multiple cyclones, fabric filters, or ESPs. The



FIGURE 31.4 Chemical industry complex in West Virginia. (For color version of this figure, the reader is referred to the online version of this book.)

multicyclones are the least expensive system and the ESPs the most expensive.

Some technological enhancements of incineration offer the possibility of reduced emissions. These include “slagging” (operating at such a high temperature that incombustible materials are melted and removed as a fluid slag); fluidized beds (which are useful only on homogeneous or well-classified refuse); suspension burning in cylindrical combustion chambers, which may or may not result in slagging; and pyrolysis, which is destructive distillation in the absence of oxygen.

The emission control requirements set for municipal incinerators are extensive and complex. They vary by type of waste being incinerated and by the rules of a particular jurisdiction. A thorough study of the regulations in a particular jurisdiction is necessary for incinerator technology and control.

### 31.2.2 Chemical and Metallurgical Industries

The chemical and metallurgical industries of the world are so varied and extensive that it is impossible to cover all of the processes, emissions, and controls in a single chapter.

#### 31.2.2.1 Chemical and Allied Industries

The term chemical industry applies to a group of industries which range from small, single owner–employee operations to huge complexes employing thousands of people. Indeed, a single facility can have myriad reactors, storage vessels and other structures, each with its own vents, stack and fugitive releases (Figure 31.4). The number of environmental regulations that the chemical industry must comply with is so extensive that specialized consulting firms have been formed to aid the industry in handling them.

The emissions from a chemical process can be related to the specific process. A plant manufacturing a resin

might be expected to emit not only the resin being manufactured but also some of the raw material and some other products which may or may not resemble the resin. A plant manufacturing sulfuric acid can be expected to emit sulfuric acid fumes and SO<sub>2</sub>. A plant manufacturing soap products could be expected to emit a variety of odors. Depending on the process, the emissions could be any one or a combination of dust, aerosols, fumes, or gases. The emissions may or may not be odorous or toxic. Some of the primary emissions might be innocuous but later react in the atmosphere to form an undesirable secondary pollutant. A flowchart and material balance sheet for the particular process are very helpful in understanding and analyzing any process and its emissions.<sup>11</sup>

In any discussion of the importance of emissions from a particular process for an area, several factors must be considered—(1) the percentage of the total emissions of the area that the particular process emits, (2) the degree of toxicity of the emissions, and (3) the obvious characteristics of the source (which can be related to either sight or smell).

Each chemical in use today has a particular life cycle, beginning during extraction from the earth with releases to the environment along the way (Figure 31.5). Air pollutant emissions from these various processes must be controlled.

#### 31.2.2.1.1 INORGANIC CHEMICAL PROCESSES

Production of major inorganic chemicals in the United States exceeds 200 million metric tons per year produced in over 1300 plants.<sup>17</sup>

**31.2.2.1.1.1 ACID AND BASE MANUFACTURE** Acids are used as basic raw materials for many chemical processes and manufacturing operations. Figure 31.6 illustrates an acid plant with its flow diagram. Sulfuric acid is one of the major inorganic chemicals in modern industry. The atmospheric discharges from a sulfuric

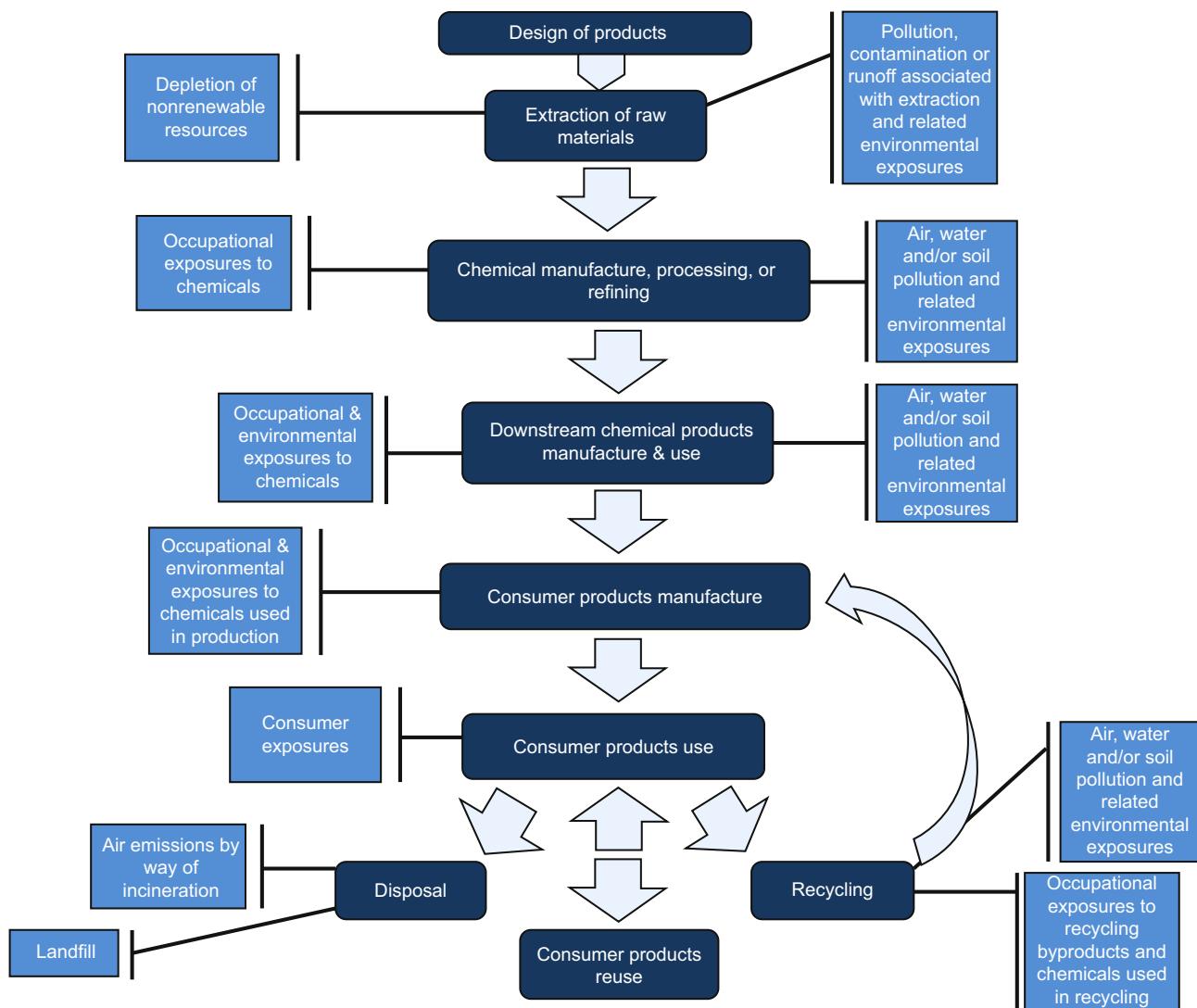


FIGURE 31.5 Life cycle of a chemical. *Anonymous (requested not to cite)*. (For color version of this figure, the reader is referred to the online version of this book.)

acid plant can be expected to contain gases including  $\text{SO}_2$  and aerosol mists, containing  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$ , in the submicron to 10- $\mu\text{m}$  size range. The aerosol mists are particularly damaging to paint, vegetation, metal, and synthetic fibers.

Other processes producing acids, such as nitric, acetic, and phosphoric acids, can be expected to produce acid mists from the processes themselves as well as various toxic and nontoxic gases. The particular process must be thoroughly studied to obtain a complete listing of all the specific emissions. The major acids produced are hydrochloric, hydrofluoric, nitric, phosphoric, and sulfuric. The emissions and usual control methods for the various acid and manufacturing processes are shown in Table 31.5.

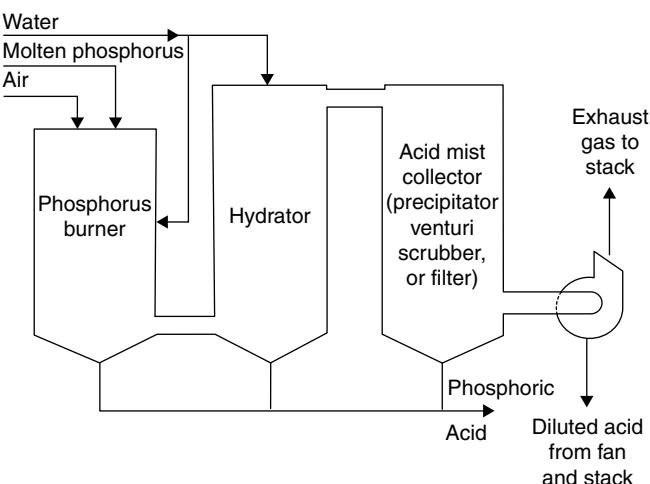


FIGURE 31.6 Flow diagram of a phosphoric acid plant.

TABLE 31.5 Air Pollution Emissions and Controls: Inorganic Acid Manufacture

Acid	Manufacturing Process	Air Pollutant Emissions	Control Methods in Use
Hydrochloric	By-product of organic chlorination, salt process, and synthetic HCl	HCl	Absorption
Hydrofluoric	Fluorspar—sulfuric acid	SiF <sub>4</sub> , HF	Scrubber (some with caustic)
Nitric	Pressure process and direct strong acid	NO, NO <sub>2</sub> , N <sub>2</sub> O <sub>4</sub>	Catalytic reduction, adsorption, absorption
Phosphoric	Elemental phosphorus	Particulate matter, fluorides	Baghouse
	Thermal process	H <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> S	Mist eliminators, alkaline scrubbers
	Wet process	SiF <sub>4</sub> , HF	Scrubber
	Superphosphoric	Fluorides	Scrubber
Sulfuric	Contact	SO <sub>2</sub> , acid mist	Scrubbers with mist eliminators, electrostatic precipitators (ESPs)

TABLE 31.6 Air Pollution Emissions and Controls: Inorganic Base Manufacture

Base	Manufacturing Process	Air Pollutant Emissions	Control Methods in Use
Calcium oxide (lime)	Rotary kilns, vertical and shaft kilns, fluidized-bed furnaces	Particulate matter	Cyclones plus secondary collectors (baghouse, electrostatic precipitator (ESP), wet scrubbers, granular bed filters, wet cyclones)
Sodium carbonate (soda ash)	Solvay (ammonia soda)	Particulate matter	Wet scrubbers
Sodium hydroxide, caustic soda	Electrolytic	Chlorine	Alkaline scrubbers
		Mercury	Chemical scrubbing and adsorbers

Major bases and caustics produced by the chemical industry are calcium oxide (lime), sodium carbonate (soda ash), and sodium hydroxide (caustic soda). The emissions and usual control methods for the various bases and their manufacturing processes are shown in Table 31.6.

**31.2.2.1.1.2 FERTILIZER PRODUCTION** Phosphate fertilizers are prepared by beneficiation of phosphate rock to remove its impurities, followed by drying and grinding. The PO<sub>4</sub> in the rock may then be reacted with sulfuric acid to produce normal superphosphate fertilizer. Over 100 plants operating in the United States produce approximately a billion kilograms of phosphate fertilizer per year. Figure 31.7 is a flow diagram for a normal superphosphate plant which notes the pollutants emitted. The particulate and gaseous fluoride emissions cause greatest concern near phosphate fertilizer plants.

Fertilizer production is dependent on the production of phosphates and nitrates. Phosphate rock preparation

generates some dry particulate matter during drying, grinding, and transferring of the rock. These emissions are controlled by wet scrubbers and baghouses. The atmospheric emissions and control methods for the production processes are shown in Table 31.7.

Ammonium nitrate fertilizer is produced by the neutralization of nitric acid with ammonia. The primary emission is the dust or fume of ammonium nitrate from the prill tower. The material is of submicron size and, therefore, highly visible. Control is usually performed by a wet scrubber followed by a mist eliminator.

Air pollutants can be emitted from several sites in Figure 31.7, including the reactor, the ammoniator-granulator, the dryer and cooler, product sizing and material transfer. There is also water pollution and the opportunity for water-to-air emissions of compounds, such as slurries and gypsum ponds that contain scrubber waste. The reactor and ammoniator-granulator produce emissions of gaseous ammonia, gaseous fluorides such as hydrogen fluoride (HF) and silicon

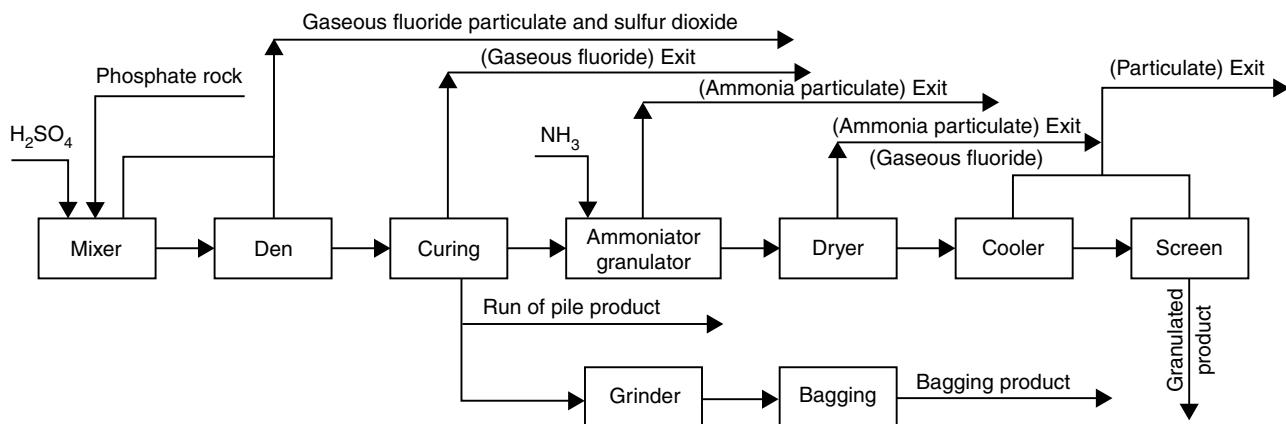


FIGURE 31.7 Flow diagram of a superphosphate plant.

TABLE 31.7 Air Pollution Emissions and Controls: Phosphate Fertilizer Plants

Process	Air Pollutant Emissions	Control Methods in Use
Normal superphosphate	SiF <sub>4</sub> , HF	Venturi or cyclonic scrubber
	Particulate matter	Wet scrubber or baghouse
Diammonium phosphate	Gaseous F, NH <sub>3</sub>	Venturi or cyclonic scrubber with 30% phosphoric acid
	Particulate matter	Cyclone followed by scrubber
Triple superphosphate, run of pile	SiF <sub>4</sub> , HF	Venturi or cyclonic scrubber
Triple superphosphate, granular	SiF <sub>4</sub> , HF, particulate matter	Venturi or packed scrubber

tetrafluoride (SiF<sub>4</sub>), as well as particulate ammonium phosphates. These are commonly combined and passed through primary and secondary scrubbers. HF is listed as a hazardous air pollutant under the 1990 Clean Air Act Amendments. Exhaust gases from the dryer and cooler also contain ammonia, fluorides and PM, which are usually combined and passed through cyclones and primary and secondary scrubbers. The PM emissions and low ammonia and fluoride concentrations from product sizing and material transfer operations are controlled in this manner. Exhaust streams from the reactor and ammoniator-granulator pass through a primary scrubber, in which phosphoric acid is used to recover ammonia and particulate. Exhaust from the dryer, cooler and screen first are sent to cyclones for PM recovery, and next to primary scrubbers. Materials collected in the cyclone and primary scrubbers are recovered and returned to the process. The exhaust is sent to secondary scrubbers, where recycled gypsum pond water serves as a scrubbing liquid to control the emissions of F-compounds. The scrubber effluent recirculates to the gypsum pond.

Primary scrubbing equipment at fertilizer plants commonly includes venturi and cyclonic spray towers,

with impingement scrubbers and spray-crossflow packed bed scrubbers serving as secondary controls. Mainly to recover ammonia, primary scrubbers often use phosphoric acid of 20 to 30 percent as scrubbing liquor. Secondary scrubbers generally use gypsum and pond water for F control. Although this is the general configuration, any combinations and variations of the set-up exist, e.g. using reactor-feed concentration phosphoric acid (40 percent P<sub>2</sub>O<sub>5</sub>) in both primary and secondary scrubbers, and some use phosphoric acid near the dilute end of the 20 to 30 percent P<sub>2</sub>O<sub>5</sub> range in only a single scrubber. Existing plants are equipped with ammonia recovery scrubbers on the reactor, ammoniator-granulator and dryer, and particulate controls on the dryer and cooler. Emission control efficiencies for ammonium phosphate plant control equipment generally range from 94 to 99 percent for ammonium, 75 to 99.8 percent for particulates, and 74 to 94 percent for fluorides.<sup>18</sup>

**31.2.2.1.1.3 HALOGEN PRODUCTION** Most of the chlorine manufactured is produced by two electrolytic methods, the diaphragm cell and the mercury cell processes. Both processes emit chlorine to the atmosphere from various streams and from handling and loading

**TABLE 31.8** Types of Inorganic Chemicals Produced by Selected Air Pollution Emissions

Inorganic Chemical Produced	Associated Air Pollution Emissions
Calcium oxide (lime)	Lime dust
Sodium carbonate (soda ash)	Ammonia—soda ash dust
Sodium hydroxide (caustic soda)	Ammonia—caustic dust and mist
Ammonium nitrate	Ammonia—nitric oxides
Chlorine	Chlorine gas, hydrochloric acid (HCl)
Bromine	Bromine gas and compounds, chlorine gas, radionuclides

facilities. If the gas streams contain over 10% chlorine, the chlorine is recovered by absorption. If the chlorine concentration is less, the usual practice is to scrub the vent gases with an alkaline solution. Mercury is emitted from the mercury cell process from ventilation systems and by-product streams. Control techniques include (1) condensation, (2) mist elimination, (3) chemical scrubbing, (4) activated carbon adsorption, and (5) molecular sieve absorption. Several mercury cell (chlor-alkali) plants in Japan have been converted to diaphragm cells to eliminate the poisonous levels of methyl mercury found in fish.

All of the bromine produced in the United States is extracted from naturally occurring brines using steam

extraction. The major air pollution concern is H<sub>2</sub>S from the stripper if H<sub>2</sub>S is present in the brine. The H<sub>2</sub>S can either be oxidized to SO<sub>2</sub> in a flare or sent to a sulfur recovery plant.

**31.2.2.1.4 OTHER INORGANIC CHEMICALS** Production of the large quantities of inorganic chemicals necessary for modern industrial processes can result in air pollutant emissions as undesirable by-products. Table 31.8 lists some of the more common inorganic chemicals produced, along with the associated air pollutants potentially emitted from the specific process.<sup>8</sup>

### 31.2.2.1.2 ORGANIC CHEMICAL PROCESSES

Most petrochemical processes are essentially enclosed and normally vent only a small amount of fugitive emissions. However, the petrochemical processes that use air-oxidation-type reactions normally vent large, continuous amounts of gaseous emissions to the atmosphere.<sup>19</sup> Six major petrochemical processes employ reactions using air oxidation. Table 31.9 lists the atmospheric emissions from these processes along with applicable control measures.

**31.2.2.1.2.1 RESINS AND PLASTICS** Resins are solid or semisolid, water-insoluble, organic substances with little or no tendency to crystallize. They are the basic components of plastics and are also used for coatings on paper, particleboard, and other surfaces that require a decorative, protective, or special-purpose finish. The common

**TABLE 31.9** Air Pollution Emissions and Controls: Petrochemical Processes

Petrochemical Process	Air Pollutant Emissions	Control Methods in Use
Ethylene oxide (most emissions from purge vents)	Ethane, ethylene, ethylene oxide	Catalytic afterburner
Formaldehyde (most emissions from exit gas stream of scrubber)	Formaldehyde, methanol, carbon monoxide, dimethyl ether	Wet scrubber for formaldehyde and methanol only; after-burner for organic vent gases
Phthalic anhydride (most emissions from off-gas from switch condensers)	Organic acids and anhydrides, sulfur dioxide, carbon monoxide, particulate matter	Venturi scrubber followed by cyclone separator and packed countercurrent scrubber
Acrylonitrile (most emissions from exit gas stream from product absorber)	Carbon monoxide, propylene, propane, hydrogen cyanide, acrylonitrile, acetonitrile NO <sub>x</sub> from by-product incinerator	Thermal incinerators (gas-fired afterburners or catalytic afterburners) None
Carbon black (most emissions from exit gas stream from baghouse, some fugitive particulate)	Hydrogen, carbon monoxide, hydrogen sulfide, sulfur dioxide, methane, acetylene Particulate matter (carbon black)	Waste heat boiler or flare (no control for SO <sub>2</sub> ) Baghouse
Ethylene dichloride (most emissions from exit gas-stream of solvent scrubber)	Carbon monoxide, methane, ethylene, ethane, ethylene dichloride, aromatic solvent	None at present, but could use a waste heat boiler or after burner, followed by a caustic scrubber for hydrochloric acid generated by combustion

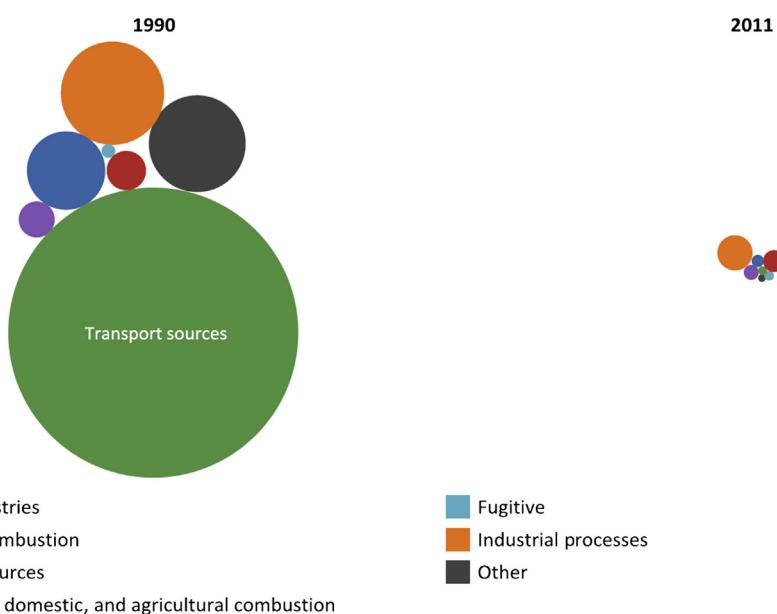
characteristic of resins is that heat is used in their manufacture and application, and gases are exhausted from these processes. Some of the gases that are economically recoverable may be condensed, but a large portion is lost to the atmosphere. One operation, coating a porous paper with a resin to form battery separators, was emitting to the atmosphere about 85% of the resin purchased. This resin left the stacks of the plant as a blue haze, and the odor was routinely detected more than 2 km away. Since most resins and their by-products have low-odor thresholds, disagreeable odor is the most common complaint against any operation using them.

**31.2.2.1.2.2 VARNISH, PAINTS, AND COATINGS** In the manufacture of varnish, heat is necessary for formulation and purification. The same may be true of operations preparing paints, shellac, inks, and other protective or decorative coatings. The compounds emitted to the atmosphere are gases, some with extremely low-odor thresholds. Acrolein, with an odor threshold of about  $4000 \mu\text{g m}^{-3}$ , and reduced sulfur compounds, with odor thresholds of  $2 \mu\text{g m}^{-3}$ , are both possible emissions from varnish cooking operations. The atmospheric emissions from varnish cooking appear to have little or no recovery value, whereas some of the solvents used in paint preparation are routinely condensed for recovery and returned to the process. If a paint finish is baked to harden the surface by removal of organic solvents, the solvents must either be recovered, destroyed, or emitted to the atmosphere. The last course, emission to the atmosphere, is undesirable and may be prohibited by the air pollution control agency.

### 31.2.2.2 Metallurgical Industries

The metallurgical industry offers some of the most challenging air pollution control problems encountered. The gas volumes are huge, and the gas may be at a high temperature. These large, hot gas volumes may convey large quantities of dust or metal oxide fumes, some of which may be highly toxic. Also, gaseous pollutants such as  $\text{SO}_2$  or  $\text{CO}$  may be very highly concentrated in the carrying stream. The process emissions to the atmosphere may have harmful effects on visibility, vegetation, animals, and inert materials, as well as being detrimental to human health. It is no wonder that the metallurgical industries have spent huge sums to control emissions.

The emission profile for heavy metals has changed dramatically in recent decades, especially for the industrialized economies. For example, in 1990 the majority of lead emissions in many countries, both developed and developing, was from the transportation sector (Figure 31.8). This was mainly due to the use of lead additives to fuel. In the United Kingdom in 2011, transport-related emissions accounted for only 3% of the total lead emissions, compared to 74% of emissions in 1990. In recent years, the main sources of lead emissions in the United Kingdom are from combustion processes during iron and steel production, metal production and combustion of lubricants in industry.<sup>17</sup> There has been a comparatively smaller decrease in emissions from iron and steel production processes due to improved abatement measures and the decreasing use of coal.<sup>20</sup>



**FIGURE 31.8** Comparison of contribution to lead emissions by sector in the United Kingdom in 1990 and in 2011. (For color version of this figure, the reader is referred to the online version of this book.) Ref. 20.

Emissions of lead from industry rose in a few UK industries, dominated by metal production. Other UK lead sources include the chemical industry and solid fuel transformation. Between 1990 and 2011 emissions from metal production and the chemical industry have fallen by 95% and 96%, respectively.<sup>20</sup>

### 31.2.2.2.1 NONFERROUS METALLURGICAL OPERATIONS

At the end of the nineteenth century, one of the most obvious environmental effects of industry was the complete destruction of vegetation downwind from copper, lead, and zinc smelters. This problem was caused by the smelting of the metallic sulfide ores. As the metal was released in the smelting process, huge quantities of sulfur were oxidized to SO<sub>2</sub>, which was toxic to much of the vegetation fumigated by the plume. Similarly, aluminum facilities emitted large amount of fluoride compounds which denuded vegetation and adversely affected farm animals.

Present smelting systems go to great expense to prevent the uncontrolled release of SO<sub>2</sub>, but in many areas the recovery of the ecosystem will take years and possibly centuries. Emissions from other nonferrous metal facilities are primarily metal fumes or metal oxides of extremely small diameter. Zinc oxide fumes vary from 0.03 to 0.3 μm and are toxic. Lead and lead oxide fumes are extremely toxic and have been extensively studied. Arsenic, cadmium, bismuth, and other trace metals can be emitted from many metallurgical processes.

Nonferrous metallurgy is as varied as the ores and finished products. Almost every thermal, chemical and physical process known to engineers is in use. Extraction of ores generates metal-laden dust. In addition, transport of the ore also involves the release of particulates. Refining the ore generates both aerosols and vapors. Flue gases from furnaces (Figure 31.9) and air moving through ventilation systems are vented to cyclones, scrubbers, baghouses, and other air pollution controls to remove PM (Figure 31.10). Smelters are examples of multicompartimental polluters. For example, to prevent air pollution, the PM that is removed from the separator is subsequently transported to on-site storage area, recycle streams or to off-site disposal sites. Thus, PM collection systems can be a significant source of heavy metal and other mineral exposures if not handled, operated, cleaned, and maintained adequately.

Every nonferrous refining process emits pollutants and requires appropriate control systems, especially primary and secondary smelting of aluminum, beryllium, copper, lead, mercury, zinc, as well as the processing of alloys.

Early aluminum reduction plants were responsible for air pollution because of the fluoride emissions from their operations. Fluoride emissions can cause severe damage to vegetation and to animals feeding on such vegetation. The end result was an area surrounding the plant devoid of vegetation. Such scenes are reminiscent of those downwind from some of the uncontrolled copper smelters. New aluminum reduction plants have invested considerable expense to control fluoride emissions. Some of the older plants have found that the cost of control exceeded the original capital investment in the entire facility. Where the problem is serious, control agencies have developed extensive sampling networks to monitor emissions from the plant of concern.

The emissions from primary aluminum reduction plants may come from the primary control system, which vents the electrolytic cells through control devices, or from the secondary system, which controls the emissions from the buildings housing the cells.

Hydrogen fluoride accounts for about 90% of the gaseous fluoride emitted from the electrolytic cell. Other gaseous emissions are SO<sub>2</sub>, CO<sub>2</sub>, CO, NO<sub>2</sub>, H<sub>2</sub>S, COS, CS<sub>2</sub>, SF<sub>6</sub>, and various gaseous fluorocarbons. Particulate fluoride is emitted directly from the process and is also formed from condensation and solidification of the gaseous fluorides.

The fluoride removal efficiency of the control equipment at primary aluminum reduction plants is shown in Table 31.10. The removal efficiency for total fluorides is a matter of great concern.

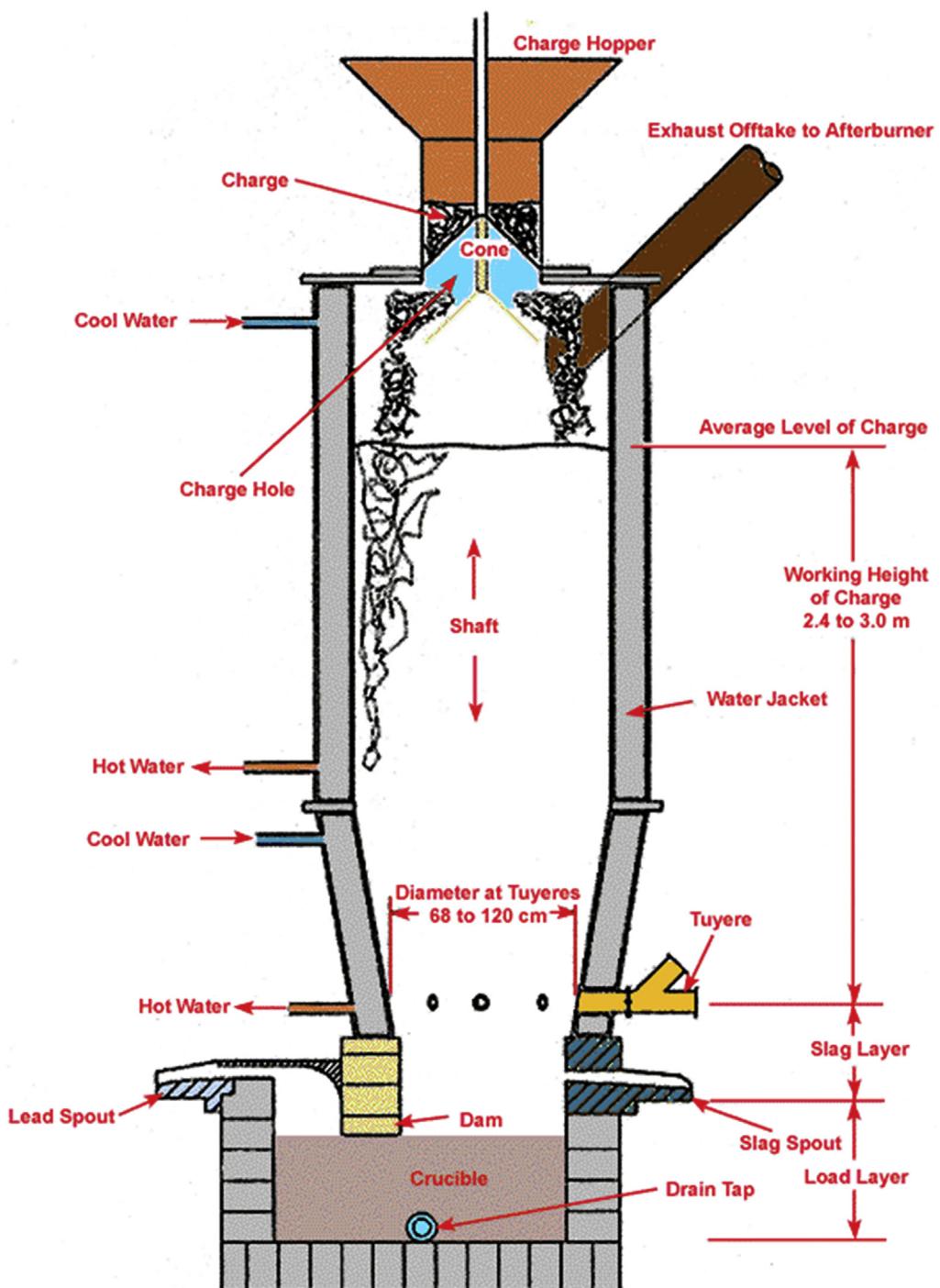
Emission rates using the BACT on the three electrolytic cell types are shown in Table 31.11.

Beryllium is extracted from the ore in the form of beryllium hydroxide, which is then converted to the desired product, metal, oxide, or alloy.<sup>21</sup> Some of these products are extremely toxic. Table 31.12 lists the emissions from the various beryllium production steps, along with the control measures commonly used.

Most copper is removed from low-grade sulfide ores using pyrometallurgical processes. The copper is first concentrated, then dewatered, and filtered. The copper smelting process consists of roasters, reverberatory furnaces, and converters. Some copper is further refined electrolytically to eliminate impurities.

Some fugitive particulate emissions occur around copper mines, concentrating, and smelting facilities, but the greatest concern is with emissions from the ore preparation, smelting, and refining processes. Table 31.13 lists the range of emissions of SO<sub>2</sub> from primary copper smelters.

Copper (Cu) ore can contain very high concentrations of sulfur compounds. In fact, Cu concentrations in ores averages only about 0.6%, with commercial



**FIGURE 31.9** Cross-sectional view of a furnace used for metal refining. The pelletized, pulverized, or otherwise mechanically altered ore enters the furnace via the charge hopper. Air is blown into the furnace through the tuyere. The exhaust contains particulate and gas-phase metal compounds. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Occupational Safety and Health Administration. Environmental controls: dust collection systems. <https://www.osha.gov/SLTC/etools/leadsmelter/environmentalcontrols/dustcollectionsystems.html>; 2013 [accessed 09.12.13].

ores being sulfides, especially chalcopyrite ( $\text{CuFeS}_2$ )<sup>22</sup> and chalcocite ( $\text{Cu}_2\text{S}$ ).<sup>23</sup> These minerals are concentrated from crushed ores to increase the Cu concentration to 10–15% copper by froth flotation or bioleaching.<sup>23</sup>

The conversion of iron sulfides into iron oxides is followed by the reaction with silica to form the silicate slag, which floats on top of the heated mass. This allows for removing the slag as iron. A copper matte remains,

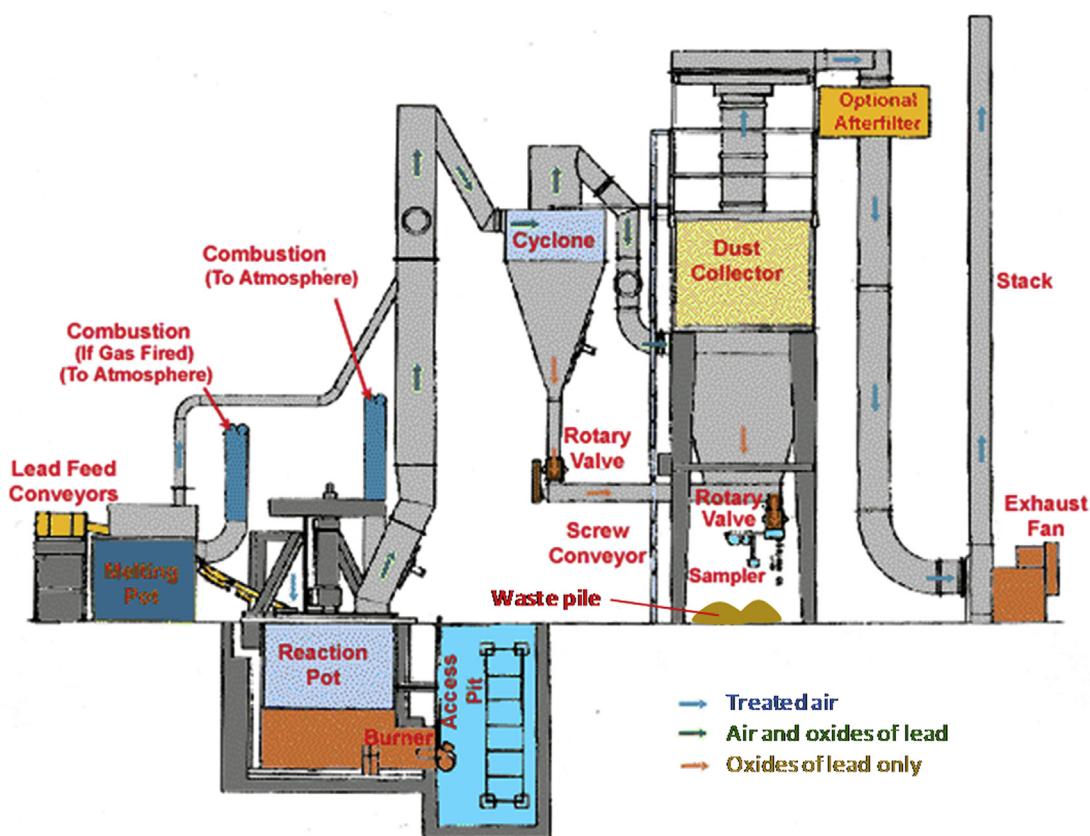


FIGURE 31.10 Collection system for a lead smelter, showing the flow of untreated air following smelting, air and oxides of lead compounds and oxides of lead only. (For color version of this figure, the reader is referred to the online version of this book.) Adapted from: Occupational Safety and Health Administration. Environmental controls: dust collection systems. <https://www.osha.gov/SLTC/etools/leadsmelter/environmentalcontrols/dustcollectionsystems.html>; 2013 [accessed 09.12.13].

consisting of  $\text{Cu}_2\text{S}$ , which is then roasted to convert sulfides into oxides:<sup>22</sup>



TABLE 31.10 Fluoride Removal Efficiencies: Selected Aluminum Industry Primary and Secondary Control Systems

Control System	Total Fluoride Removal Efficiency (%)
Coated filter baghouse	94
Fluid bed dry scrubber	99
Injected alumina baghouse	98
Wet scrubber + wet electrostatic precipitator (ESP)	99+
Dry ESP + wet scrubber	95
Floating bed	95
Spray screen (secondary)	62–77
Venturi scrubber	98
Bubbler scrubber + wet ESP	99

Thus, refining S-containing ores is another source of  $\text{SO}_2$ , in addition to burning S-containing fossil fuels. Like power plants, taller stacks designed to entrain the  $\text{SO}_2$  into the upper atmosphere to avoid local problems is no longer considered a credible means of addressing  $\text{SO}_2$  emissions from smelters and other metal refining facilities. Tall stacks for  $\text{SO}_2$  dispersion have been used in the past but are no longer acceptable as the sole means of  $\text{SO}_2$  control. Acid plants have been installed at many smelters to convert the  $\text{SO}_2$  to sulfuric acid, even though it may not be desirable from an economic standpoint.

TABLE 31.11 Emissions for Three Electrolytic Aluminum Reduction Cell Types Using Best Available Control Technology (BACT)

Cell Type	Emissions with Primary and Secondary Control	
	Fluorides ( $\text{g kg}^{-1}$ Al)	Particulate ( $\text{g kg}^{-1}$ Al)
Prebaked	0.8	3.0
Vertical stud soderberg	1.4	4.6
Horizontal stud soderberg	1.8	6.2

**TABLE 31.12** Air Pollution Emissions and Controls: Beryllium Processing

Process	Air Pollutant Emissions	Control Methods in Use
Extraction	Beryllium salts	Baghouses
	Acids	Wet collectors
	Beryllium oxides	Baghouses or high-efficiency particulate air (HEPA) filters
Machining	Beryllium dust, fume, mist	Cyclones and baghouses
	Beryllium dust	Baghouses and HEPA filters
	Beryllium oxide dust	Baghouses and HEPA filters

**TABLE 31.13** Sulfur Dioxide Emission Rates from Primary Copper Smelters

Process	Emission (g of SO <sub>2</sub> per kg of copper)
Roasting	325–675
Reverberatory furnaces	150–475
Converters	975–1075
Reverberatory furnaces*	275–800
Converters*	850–1800

\* Without roasting.

The emission of volatile trace elements from roasting, smelting, and converting processes is undesirable from both air pollution and economic standpoint. Gravity collectors, cyclones, and ESPs are used to attain collection efficiencies of up to 99.7% for dust and fumes.

Treatment of slimes for economic recovery of silver, gold, selenium, tellurium, and other trace elements requires fusion and oxidation in a furnace. The furnace gases are exhausted through a wet scrubber followed by an ESP to recover the metals.

Lead ores are crushed, ground, and concentrated in a manner similar to the processing of copper ores. Fugitive emissions from these processes include dusts,

**TABLE 31.14** Sulfur Dioxide Emission Rates from Primary Lead Smelters

Process	Emission (g of SO <sub>2</sub> per kg of lead)
Sintering	575–1075
Blast furnace	2.5–5
Dross reverberatory furnace	2.5–5

Source: Nelson KW, Varner MO, Smith TJ. Nonferrous metallurgical operations. In: Stern AC, editor. Air pollution. 3rd ed., vol. 4. New York, NY: Academic Press; 1977.

fumes, and trace metals. Smelting is usually accomplished in a blast furnace after the concentrated ore is sintered. Sintering removes up to 85% of the sulfur.

Gases from the sintering process contain SO<sub>2</sub>, dust, and metal oxide fumes. The blast furnace gases contain similar particulates plus SO<sub>2</sub> and CO. Table 31.14 indicates the expected SO<sub>2</sub> emissions.

Mercury is produced commercially by processing mercury sulfide (cinnabar). The mercury sulfide is thermally decomposed in a retort or roaster to produce elemental mercury and sulfur dioxide. The off-gases are cleaned by being passed through cyclonic separators, and the mercury is then condensed. The SO<sub>2</sub> is removed by scrubbers before the exhaust gases are released to the atmosphere. Any mercury vapors that escape are collected in refrigerated units and, usually, recovered with a baghouse or ESP. Other systems use absorption with sodium hypochlorite and sodium chloride or adsorption on activated carbon or proprietary adsorbents. The U.S. Environmental Protection Agency (EPA) has placed a limit of 2300 g of mercury emission per 24 h on any mercury smelter or process.

Zinc is processed very similarly to copper and lead. The zinc is bound in the ore as ZnS, sphalerite. Zinc is also obtained as an impurity from lead smelting, in which it is recovered from the blast furnace slag. Dusts, fumes and SO<sub>2</sub> are generated during sintering, retorting and roasting, as shown in Table 31.15.

Particulate emissions from zinc processing are collected in baghouses or ESPs. SO<sub>2</sub> in high concentrations is passed directly to an acid plant for production of sulfuric acid by the contact process.

**TABLE 31.15** Air Pollution Emissions from Primary Zinc Processing

Process	Emissions to the Atmosphere			
	Dust (g dscm <sup>-1</sup> )	Percent of Particles Less than 10 µm	SO <sub>2</sub> (%)	SO <sub>2</sub> (g kg <sup>-1</sup> Zinc)
Sintering	10	100	4.5–7.0	—
Horizontal retort	0.1–0.3	100	—	—
Roasting	—	—	—	825–1200

Nelson KW, Varner MO, Smith TJ. Nonferrous metallurgical operations. In: Stern AC, editor. Air pollution. 3rd ed., vol. 4. New York, NY: Academic Press; 1977.

TABLE 31.16 Air Pollution Emissions from Selected Nonferrous Metallurgical Processes

Metal	Type of Process	Air Pollutant Emissions	Control Methods in Use
Arsenic	By-product of copper and lead smelters	Arsenic trioxide	Baghouses or electrostatic precipitators (ESPs)
Cadmium	By-product of zinc and lead smelters	Cadmium, cadmium oxide	Baghouses
Refractory metals	Kroll process, chlorination, and magnesium reduction	Chlorine, chlorides, $\text{SiCl}_4$	Wet scrubbers
Zirconium			
Hafnium			
Titanium			
Columbium	Separation process	Ammonia	Conversion to ammonium sulfate fertilizer
Tantalum			
Vanadium			
Tungsten			
Molybdenum			

Low-concentration  $\text{SO}_2$  streams are scrubbed with an aqueous ammonia solution. The resulting ammonium sulfate is processed to the crystalline form and marketed as fertilizer.

*Other nonferrous metals and alloys:* Nonferrous metals of lesser significance include arsenic, cadmium, and refractory metals such as zirconium and titanium. Air pollution emissions from the manufacture of these metals do not constitute a major problem, although severe local problems may exist near the facility. Control of emissions is usually accomplished by a single device at the exit of the process. In many cases, the material removed by the control device has some value, either as the primary product or as a by-product. Table 31.16 shows some of the atmospheric emissions and control systems used on these metallurgical processes.

Alloys of nonferrous metals, primarily the brasses (copper and zinc), and the bronzes (copper and tin), can cause an air pollution problem during melting and casting. The type and degree of emissions depend on the furnace and the alloy. Control systems consist of hoods over the furnaces and pouring stations to collect the hot gases, ducts and fans, and baghouses or ESPs.

*Secondary metals:* These metals are those recovered from scrap. Copper (including brass and bronze), lead, zinc, and aluminum are the principal nonferrous secondary metals. Emissions from the recovery processes are similar to those from the primary metallurgical operations except that little or no  $\text{SO}_2$  or fluorides are evolved. Baghouses and ESPs are the commonly used control devices.

### 31.2.2.2 FERROUS METALLURGICAL OPERATIONS

More than half of the total pollution control costs associated with iron and steel manufacturing relate to

air emissions, and have been estimated to range from 1% to 3% of total production costs. Installation of pollution controls is about 10–20% of total plant investments. These costs are an obstacle to the global application of state-of-the-art controls in developing countries, as well as for older, financially strapped but less efficient operations.<sup>24</sup> For example, the iron and steel sector is responsible for 37% of the lead emissions in the United Kingdom in 2011, of which sinter production accounts for 74%. Emissions from sinter production have reduced by around 48% since 1990, but the proportion of annual UK lead emissions it accounts for has increased due to the decline in emissions from sectors such as transport.<sup>20</sup>

Iron and steel industries have been concerned with emissions from their furnaces and cupolas since the industry started. Pressures for control have forced the companies to such a low level of permissible emissions that some of the older operations have been closed rather than spend the money to comply. Most of the companies controlling these operations have not gone out of business but rather have opened a new, controlled plant to replace each old plant. Table 31.17 illustrates the changes in the steelmaking processes that have occurred in the United States. Indeed, virtually all steel is produced using two processes, i.e. basic oxygen furnaces (BOF) or electric arc furnaces (EAF). Both processes can integrate varying amounts of scrap, but steel of very high quality must use virgin materials. This fact and the uneven availability of acceptable scrap iron means that BOF and electric processes are not completely interchangeable. Both processes use large amounts of energy, i.e. BOF integrated processes average about 16.5 million BTU per ton (MBtu ton<sup>-1</sup>) and EAF about 5.7 MBtu ton<sup>-1</sup>.<sup>25</sup>

TABLE 31.17 Steel-Making Processes by Decade and Type in the United States

Production by Specific Process (%)					
Year	Bessemer	Open Hearth	Electric Arc	Basic Oxygen Furnace	Total
1920	21	78	1	0	100
1940	6	92	2	0	100
1960	2	89	7	2	100
1970	1	36	14	48	100
1980	1	22	31	46	100
1990	0	4	37	59	100
2000 <sup>25</sup>	0	0	47	53	100
2010 <sup>25</sup>	0	0	55	45	100

Air-polluting emissions from steelmaking furnaces include metal oxides, smoke, fumes, and dusts to make up the visible aerosol plume. They may also include gases, both organic and inorganic. If steel scrap is melted, the charge may contain appreciable amounts of oil, grease, and other combustibles that further add to the organic gas and smoke loadings. If the ore used has appreciable fluoride concentrations, the emission of both gaseous and particulate fluorides can be a serious problem (see Section 31.2.5.4 Glass Manufacturing Plants for a discussion of fluorides).

Emissions from foundry cupolas are relatively small but still significant, in some areas. An uncontrolled 2-m cupola can be expected to emit up to 50 kg of dust, fumes, smoke, and oil vapor per hour. Carbon monoxide, NO<sub>x</sub>, and organic gases may also be expected. Control is possible, but the cost of the control may be prohibitive for the small foundry which only has one or two heats per week.

Obviously, the volatilized gases are air pollutants. In fact, coke ovens are the source of thousands of compounds, many that are toxic. Coke facilities have recognized that many of these gases are also economically valuable, so technologies exist and are being applied to recover, separate, and sell them for profit. Some of the processes shown in Table 31.17 no longer need coke to produce steel. This is an example of green engineering.

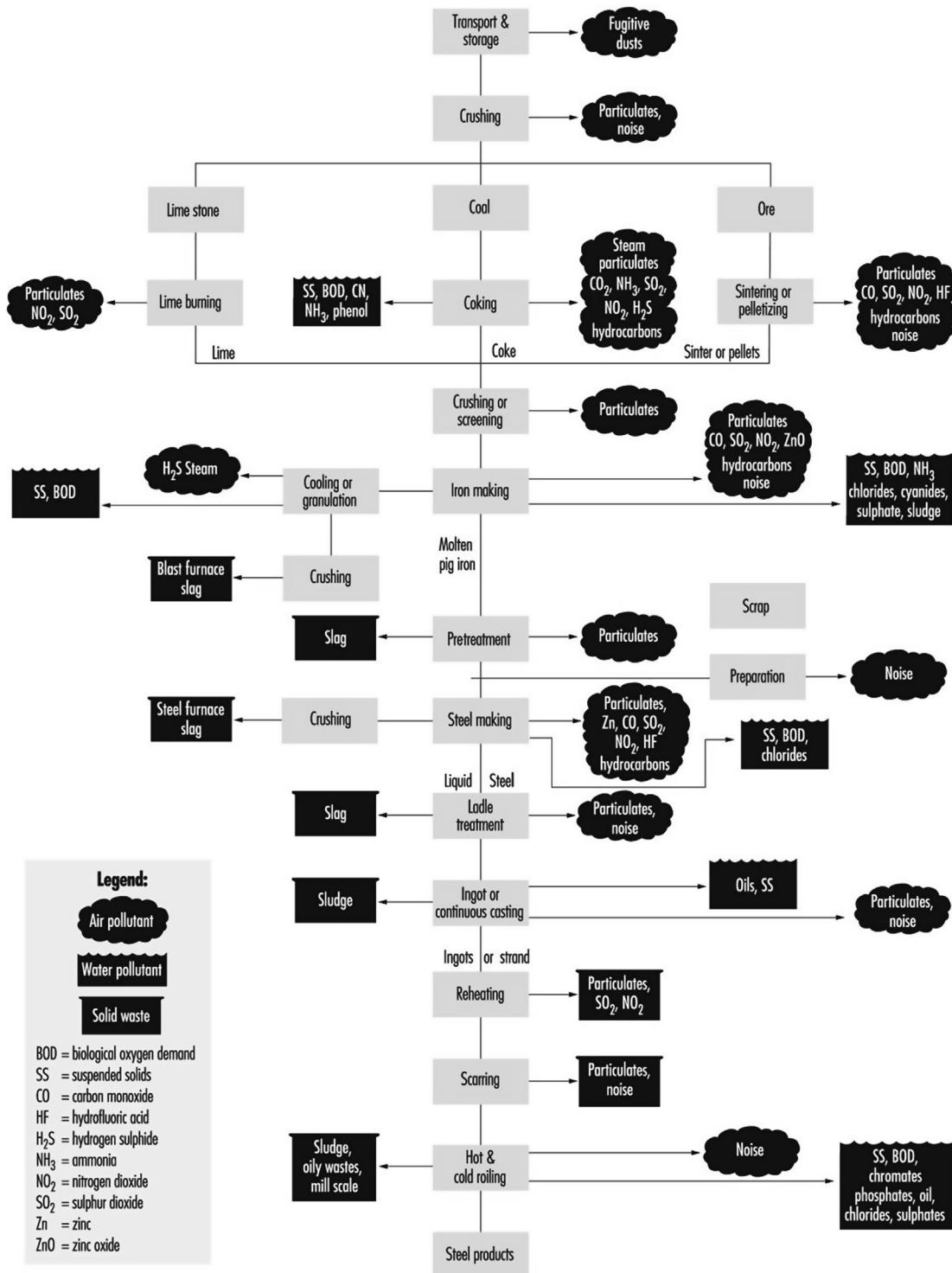
Air pollution occurs at numerous points in the manufacturing process (Figure 31.11), and the specific pollutants emitted vary according to a number of factors, including the particular refinement process, the engineering and construction of the plant, the raw materials employed, the sources and amounts of the energy required, the extent to which waste products are

recycled into the process, and the efficiency of the pollution controls. For example, the introduction of basic-oxygen steel making has permitted the collection and recycling of waste gases in a controlled manner, reducing the amounts to be exhausted, while the use of the continuous-casting process has reduced the consumption of energy, resulting in a reduction of emissions. This has increased product yield and improved quality.

In 2012, total world crude steel production was 1547.8 million metric tons (mmt). By far China was the largest steel producer with about 717 mmt, accounting 46.3% of world steel production in 2012. The European Union, Japan and the U.S. produced about 160, 107, and 89 mmt, respectively, in 2012.<sup>26</sup> Iron and steel industries are generally grouped as steel mills, which produce steel sheets or shapes, and foundries, which produce iron or steel castings. Some steel mills use electric arc furnaces with scrap steel as the raw material, but most are large, integrated mills with the following facilities:

1. *Coke making:*<sup>27</sup> Coke is produced from blended coals by either the nonrecovery beehive process or the by-product process. The by-product process produces the majority of the coke. Air pollutants from the coke-making process vary according to the point of release from the process and the time the process has been in operation. Table 31.18 shows the emissions, and their control, from the different stages of the by-product process.

Coke is produced by blending and heating bituminous coals in coke ovens to 1000–1400 °C in the absence of oxygen. Light weight oils and tars are distilled from the coal, generating various gases during the heating process. Every half an hour or so, the flows of gas, air, and waste gas are reversed to maintain uniform temperature distribution across the wall. In most modern coking systems, nearly half of the total coke oven gas produced from coking is returned to the heating flues for burning after having passed through various cleaning and co-product recovery processes. Coke oven emissions are the benzene-soluble fraction of the particulate matter generated during coke production. They are known to contain human carcinogens. These emissions comprise a highly toxic mixture of gases and aerosols. Coke oven emissions are actually complex mixtures of gas, liquid, and solid phases, usually including a range of about 40 polycyclic aromatic hydrocarbons (PAHs), as well as other PIC; notably formaldehyde, acrolein, aliphatic aldehydes, ammonia, CO NO<sub>x</sub> phenol, cadmium, arsenic, and mercury. More than 60 organic compounds have been collected near coke plants. A metric ton of coal yields up to 635 kg of coke, up to 90 kg of coke breeze (large coke



Source: UNEP 1986.

FIGURE 31.11 Pollutants generated at various points of the iron and steel manufacturing process. Ref. 26; and United Nations Environmental Program. Environmental aspects of iron and steel production: a technical review (UNEP—industry & environment technical review series) 1986; ISBN: 9280710796.

TABLE 31.18 Air Pollution Emissions and Controls Associated with Coke Making By-products

Process	Air Pollutant Emissions	Control Methods in Use
Coal and coke handling	Fugitive particulate matter	Enclose transfer points and duct to baghouses; pave and water roadways
Coke oven charging	Hydrocarbons, carbon, coal dust	Aspiration systems to draw pollutants into oven, venturi scrubbers
Coke oven discharging (pushing)	Hydrocarbons, coke dust	Hoods to fans and venturi scrubbers, low-energy scrubbers followed by ESPs (may use water spray at oven outlet)
Coke quenching	Particulate matter	Baffles and water sprays
Leaking oven doors	Hydrocarbons, carbon	Door seals with proper operation and maintenance
By-product processing	Hydrogen sulfide	Conversion to elemental sulfur or sulfuric acid by liquid absorption, wet oxidation to elemental sulfur, combustion to SO <sub>2</sub>

particulates), 7–9 kg of ammonium sulfate, 27.5–34 L of coke oven gas tar, 55–135 l of ammonia liquor, and 8–12.5 l of light oil. Up to 35% of the initial coal charge is emitted as gases and vapors. Most of these gases and vapors are collected during by-product coke production.

Coke oven gas is comprised of hydrogen, CH<sub>4</sub>, ethane, CO, CO<sub>2</sub>, ethylene, propylene, butylene, acetylene, hydrogen sulfide (H<sub>2</sub>S), ammonia, oxygen, and nitrogen. Coke oven gas tar includes pyridine, tar acids, naphthalene, creosote oil, and coal-tar pitch. Benzene, xylene, toluene, and solvent naphthas may be extracted from the light oil fraction. Coke production in the United States increased steadily between 1880 and the early 1950s, peaking at 65 mmt in 1951. In 1976, the United States was second in the world with 48 mmt of coke, i.e. 14.4% of the world production. By 1990, the United States produced 24 mmt, falling to fourth in the world. A gradual decline in production has continued; production has decreased from 20 mmt in 1997 to 15.2 mmt in 2002. Demand for blast furnace coke also has declined in recent years because technological improvements have reduced the amount of coke consumed per amount of steel produced by as much as 25%.

Steel-making is commonly associated with coke ovens. Coke is coal that has undergone pyrolysis, i.e. heated up to 1000–1400 °C in the absence of oxygen, so it is not burned. This process intentionally releases gaseous components of the coal to produce nearly pure carbon.<sup>28</sup>

2. *Sintering*: It consists of mixing moist iron ore fines with a solid fuel, usually coke, and then firing the mixture to eliminate undesirable elements and produce a product of relatively uniform size, physically and chemically stable, for charging the blast furnace. Air pollutants are emitted at different points in the process, as indicated in Table 31.19.
3. *Iron making*: It is the term used to describe how iron is produced in large, refractory-lined structures called *blast furnaces*. The iron ore, limestone, and coke are charged, heated, and then reacted to form a reducing gas, which reduces the iron oxide to metallic iron. The iron is tapped from the furnace along with the slag, which contains the impurities. A modern alternative to the blast furnace is continuous casting of iron instead of intermittent tapping. The blast furnace gas is exhausted from the top of the furnace, cooled, and cleaned of dust before it is used to fire the regenerative stoves for heating the blast furnace. The

TABLE 31.19 Air Pollution Emissions and Controls Associated with Sintering

Air Pollution Emissions and Controls: Sintering		
Process	Air Pollutant Emissions	Control Methods in Use
Waste gases (main stack gases)	Particulates, CO, SO <sub>2</sub> , chlorides, fluorides, ammonia, hydrocarbons, arsenic	Gravity separators to cyclones; then electrostatic precipitators (ESPs) or wet scrubbers with pH adjustment
Sinter machine discharge	Particulate matter	Multiple cyclones, baghouse, or low-energy wet scrubber
Materials handling	Fugitive particulate matter	Hoods over release points to baghouse or multiple cyclones
Sinter cooler	Particulate matter (trace)	Baghouse (if required)

TABLE 31.20 Air Pollution Emissions and Controls Associated with Iron Making

Process	Air Pollutant Emissions	Control Methods in Use
Blast furnace exhaust	Particulate matter	Multiple cyclone plus wet scrubber or gases wet electrostatic precipitator (ESP), two-stage wet scrubber
Slag handling	H <sub>2</sub> S, SO <sub>2</sub> (trace)	None
Casting	Particulate matter	Baghouse

atmospheric emissions from the iron making process are listed in [Table 31.20](#).

4. *Steelmaking:* The open-hearth steelmaking process produced 80–90% of the steel in the United States until the 1960s, when the basic oxygen process came into wide use. By 1990 less than 5% of U.S. steel was produced by the open-hearth process. Particulate emissions are highest during oxygen lancing with a hot metal charge in the furnace. Particulate matter loadings are reported to be in the range of 6–11 kg per metric ton of steel. Most of the particulate matter is iron or iron oxide. Control of the open-hearth particulate matter emissions is accomplished by ESPs or high-energy scrubbers. Only small quantities of SO<sub>2</sub> are emitted, but if venturi scrubbers are used for particulate matter control, they will also reduce the SO<sub>2</sub> emissions. However, severe corrosion problems have been reported for wet scrubbers on open-hearth furnaces.<sup>29</sup>

Basic oxygen furnaces (BOFs) have largely replaced open-hearth furnaces for steelmaking. A water-cooled oxygen lance is used to blow high-purity oxygen into the molten metal bath. This causes violent agitation and rapid oxidation of the carbon, impurities, and some of the iron. The reaction is exothermic, and an entire heat cycle requires only 30–50 min. The atmospheric emissions from the BOF process are listed in [Table 31.21](#).

The electric arc furnace process accounted for about 25% of the 1982 U.S. steelmaking capacity.<sup>29</sup> Most of the raw material used for the process is steel scrap. Pollutants generated by the electric furnace process are primarily particulate matter and CO. The furnaces are hooded, and the gas stream containing the particulate matter is collected, cooled, and passed to a

bag-house for cleaning. Venturi scrubbers and ESPs are used as control devices at some mills. Charging and tapping emissions are also collected by hoods and ducted to the particulate matter control device.

After the steel is tapped from the furnace, it is poured into ingots or continuously cast into slabs or billets. Many metallurgical processes are required between the furnace and the finished product. Reheat furnaces cause no air pollution problems. Scarfing processes create a fine iron oxide fume on the steel surface and also release the same fume, which must be controlled by wet scrubbers or ESPs before it reaches the atmosphere. Pickling may result in the release of acid mists. Scrubbing with special solutions may be required for control. Galvanizing is the process of applying a zinc coating and can result in release of zinc oxide emissions to the atmosphere. Control is accomplished through local collection hoods followed by ESPs, wet scrubbers, or baghouses.

5. *Ferrous foundry operations:* It produces castings of iron or steel. Many foundry air pollution problems are similar to those of steel mills but on a smaller scale. Potential emissions from foundry operations, along with the usual control methods, are shown in [Table 31.22](#).

6. *Ferroalloy production:* Ferroalloys are used to add various elements to iron or steel for specific purposes. Examples are chromium (in the form of ferrochrome) and manganese (in the form of ferromanganese) added to steel to improve its strength or hardness, or nickel and chromium added to steel to increase its corrosion resistance. In the electrolytic production of nickel, iron is not removed from nickel because nickel will be used for the production of stainless steel. The

TABLE 31.21 Air Pollution Emissions and Controls Associated with a Basic Oxygen Furnace

Process	Air Pollutant Emissions	Control Methods in Use
Hot metal transfer	Graphite and iron oxide	Multiple cyclones plus baghouses particulate matter
Charging and tapping	Particulate matter	Baghouse or venturi scrubber
Furnace waste gases	Particulate matter (7–30 kg metric ton <sup>-1</sup> of steel) Carbon monoxide	Electrostatic precipitator (ESP) or venturi scrubber Flare

TABLE 31.22 Air Pollution Emissions and Controls Associated with Iron and Steel Foundries

Process	Air Pollutant Emissions	Control Methods in Use
Cupolas	Particulate matter ( $5\text{--}22 \text{ kg ton}^{-1}$ )	Baghouses, wet scrubbers, and electrostatic precipitators (ESPs)
	Carbon monoxide $\text{SO}_2$ (25–250 ppm)	Afterburner if necessary, wet scrubber
Sand conditioning, shakeout, molding	Particulate matter	Medium-energy wet scrubbers, baghouses
Core making	Hydrocarbons	Afterburners (thermal or catalytic)

product is marketed as “ferronickel” rather than nickel. Ferrochrome, ferromanganese, and ferrosilicon are produced in high-temperature furnaces which emit copious quantities of metallic fume and particulate matter. Roasting and concentrating the ore prior to ferroalloy production produce particulate matter and oxide emissions;  $\text{SO}_2$  and CO are released during reduction; and casting produces metal oxides and fumes.

### 31.2.3 Agriculture and Forest Products Industries

The agricultural and forest products industries are dependent on renewable resources for their existence. They are also acutely aware that air pollution can damage vegetation and, therefore threaten their existence. Both industries have been exempt from many air pollution regulations in the past, but now they are finding these exemptions questioned and in some cases withdraw.<sup>30</sup>

The term agriculture refers to the operations involved in growing crops or raising animals. Dusts, smoke, gases, and odors are all emissions from various agricultural operations.

#### 31.2.3.1 Agronomy

The preparation of soils for crops, planting, and tilling raises dust as a fugitive emission. Such operations are still exempt from air pollution regulations in most parts of the world. The application of fertilizers, pesticides, and herbicides is also exempt from air pollution regulations, but other regulations may cover the drift of these materials or runoff into surface waters. This is particularly true of the materials are hazardous or toxic.

#### 31.2.3.2 Open Burning

A major source of PM, CO, and hydrocarbons is open burning of agricultural residue, as well as the cumulative emissions of smaller brush fires (Figure 31.12). National and local laws have curbed these emissions from intentional burning in several nations, but unintended wildfires, as well as controlled burning to maintain forests, woodlands, and other ecosystems. Indeed,



FIGURE 31.12 Brush fire near East St. Louis, Illinois in November 2013. (For color version of this figure, the reader is referred to the online version of this book.)

fires are a natural part of many ecological cycles, with certain tree species depending on fire for germination, for example. In the conterminous United States, there is presently only about 10% of the land burned by wild-fires as there was in the preindustrial era, with 8 times less biomass consumed, and 7 times lower emissions.<sup>31</sup>

Both legal and illegal biomass burning still occurs on large scales throughout the globe, releasing millions of metric tons of particulate matter per year are added to the atmosphere over the United States from cropland, rangeland, pastures, etc. An agricultural field releases about 8.5 kg of PM, 50 kg CO, 10 kg hydrocarbons (as  $\text{CH}_4$ ) and 1 kg  $\text{NO}_x$  per metric ton of biomass burned.<sup>32</sup> The most evident effect of such open burning is arguably the nuisance caused by the smoke, but health effects are noticed by sensitive individuals downwind from the burn.

So-called biomass burning is currently a major area of interest for many countries, both in terms of local exposures and long-range, transcontinental, and transoceanic transport (Figure 31.13). As evidence, the international community has been concerned about the release of toxic compounds. For example, wood smoke is known to contain PAHs and other toxic organics, such as dioxins. Wildfires are also major source of mercury emissions. When plants grow, they move mercury and



**FIGURE 31.13 Plume slash-and-burn forest clearing along the Rio Xingu in the state of Mato Grosso, Brazil on October 10, 2011.** The photo was taken from the International Space Station. The perspective above shows both the horizontal position and the extent of the fire lines next to the river, while also providing a sense of the vertical structure of the smoke plumes. Light colored areas within the river channel are sand bars, which show that the river is in its annual low-flow/low-water stage. The river channel is approximately 63 km long in this view. The rivers are the major route of transportation in Amazonia, so access may be the reason the fires are so near the river. (For color version of this figure, the reader is referred to the online version of this book.) National Aeronautics and Space Administration, Goddard Space Flight. <http://earthobservatory.nasa.gov/IOTD/view.php?id=71256>; 2013 [accessed 10.12.13].

other metals from the soil and soil water to their roots and sequester these metals in plant tissue. When burned, the Hg and other metals are released to the troposphere. The mean global Hg emission rate from biomass burning is estimated at<sup>a</sup>  $675 \pm 240$  mmt per year.<sup>32</sup>

If the open burning of agricultural residue is permitted, it should be scheduled to minimize the effect on populated areas. This requires burning when the wind is blowing away from the population centers, not burning during inversion periods, burning dry residue to establish a strong convection column rather than a smoldering fire, and burning only a certain number of acres at a time, so that the atmosphere does not become overloaded.

### 31.2.3.3 Orchard Heating

The practice of smudging is still carried out in many areas to protect orchards from frost. Petroleum products are burned in pots, producing both heat and smoke. Since the heat is the desirable product, smokeless heaters with return ducts to reburn the smoke are required by most air pollution control agencies. Some control agencies have passed regulations limiting the smoke to 0.5 or 1.0 g per minute per burner.

Replacement of orchard heaters by wind machines is the most desirable control measure. These large propellers force the warmer air aloft to the ground, where it mixes with the cold air, minimizing frost formation.

### 31.2.3.4 Alfalfa Dehydration and Pelletizing

Alfalfa dehydration is carried out in a direct-fired rotary dryer. The dried product is transported pneumatically to an air cooler and then to a collecting cyclone. The collected particles are ground or pelletized and then packaged for shipment. The major atmospheric emission from the process is particulate matter, which is controlled by baghouses. Odors may also be a problem, but they disperse rapidly and are no longer a problem at distances of over 1 km.

### 31.2.3.5 Animal Production

Feeding of domestic animals on a commercial basis results in large quantities of excreta, both liquid and solid. This produces obnoxious odors, which, in turn, produce complaints from citizens of the area. If the animals are concentrated in a feedlot, the odors may become so extreme that odor counteractants are necessary. However, if the feedlots are paved and regularly

<sup>a</sup> The large range of estimates is due to the variability and uncertainty associated with fire occurrence, Hg content in biomass and Hg release rates.

TABLE 31.23 Air Pollutant Emissions in England (kilotons, kt) in 2011.

Source Sector	CO	NH <sub>3</sub>	NO <sub>x</sub>	Pb	PM <sub>10</sub>	SO <sub>2</sub>	NMVOC
Energy industries	3.9%	0.0%	25.8%	6.2%	6.9%	60.4%	0.0%
Industrial combustion	25.2%	0.0%	17.3%	23.2%	10.2%	19.0%	3.4%
Transport sources	42.0%	3.8%	45.5%	3.9%	26.4%	3.0%	8.9%
Commercial combustion	6.5%	0.0%	3.4%	0.8%	9.0%	0.5%	2.1%
Public sector combustion	0.1%	0.0%	1.0%	1.5%	0.5%	1.0%	0.0%
Residential combustion	11.9%	0.6%	3.3%	6.0%	12.9%	6.0%	2.5%
Fugitive emissions (energy)	0.2%	0.0%	0.0%	4.2%	0.4%	2.4%	13.9%
Industrial processes	8.3%	2.3%	0.6%	51.5%	14.7%	5.7%	7.8%
Solvent processes	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	55.5%
Agriculture	0.0%	84.4%	0.0%	0.0%	9.1%	0.0%	0.0%
Waste	0.0%	7.5%	0.0%	0.0%	0.0%	0.0%	0.0%
Other	1.8%	1.4%	3.0%	2.8%	9.8%	2.0%	5.9%

NMVOC = nonmethane volatile organic compounds.

Derived From the National Atmospheric Emissions Inventory Database.

Source: Ref. 20.

washed down, the odors may be kept to a satisfactory minimum with much less expense.

Manure is often recycled as a solid organic fertilizer or mixed with water and sprayed as a liquid fertilizer. If the manure is repeatedly used upwind of populated areas, complaints are sure to be filed with the air pollution control agency.

Ammonia (NH<sub>3</sub>) is commonly released from animal operations. For example, in highly developed and industrialized England, emissions from livestock and their wastes comprised over 84% of the total ammonia emissions (Table 31.23). Indeed, ammonia emissions in England of ammonia were about 197 kt in 2011, a decline of 19% since 1990 and accounting for 68% of the United Kingdom total in 2011. Agricultural sources dominate the inventory with manure management representing 61% of total ammonia emissions in 2011 and 33% coming from cattle manure management alone. Ammonia emissions in England have increased in recent years, with a 3% increase between 2008 and 2011 driven by higher emissions from fertilizer application and increasing emissions from composting and biogas production via anaerobic digestion.<sup>20</sup> Note the only other criteria pollutant emitted from agricultural activities is PM<sub>10</sub>.

If uncontrolled, confined animal feeding operations (CAFOs), can cause a serious air pollution problem. The main problem is the odors associated with the process. Examples of such industries are tanning works, CAFOs, rendering plants, and many of the food processing plants such as fish meal plants. In most cases, the emissions of particulates and gases from such plants

are not of concern, only the odors. However, other air pollutants are also common (e.g. chromium [Cr<sup>6+</sup>] in tanning and nitric oxide [NO] near CAFOs). Requiring these industries to locate away from the business or residential areas is no longer acceptable as a means of control, given the possibility of transport and that vulnerable populations would fall within the plume from these sites, notwithstanding their locations.

### 31.2.3.6 Feed and Grain Milling and Handling

All grain milling involves grinding and handling of dried grain. Air streams are used for transport of the raw material and the finished products. The result is atmospheric emissions of grain dust. Originally, the control method used was cyclones; today most systems use baghouses following the cyclones. Caution must be exercised in all phases of baghouse construction, operation, cleaning, etc., as the grain dust is explosive and can cause fires accompanied by loss of property and even of lives. Particulate emissions from uncontrolled grain-processing plants range from 0.1 to 2.0 kg of particulate matter per metric ton of grain.<sup>33</sup>

### 31.2.3.7 Cotton Processing

The processing of cotton, from the field to the cloth, releases both inorganic and organic particulate matter to the atmosphere. Also, adhering pesticide residues may be emitted at the cotton gin exhaust. Table 31.24 lists the emission factors for particulate matter from cotton ginning operations.

**TABLE 31.24** Air Pollution Emissions and Controls Associated with Cotton Ginning

Process	Emissions (kg bale)*
Unloading fan	2.20
Cleaner	0.45
Stick and burr machine	1.35
Miscellaneous	1.35
Total	5.35

\* One bale weighs 277 kg.

### 31.2.3.8 Meat and Meat Products

Odors can arise during rendering, cooking, smoking, and processing. Since most of the emissions from the meat products industry are odorous organics, afterburners are used successfully as control devices. Some processors have tried to use wet scrubbers or ESPs, but the emissions are often sticky and can cause severe cleaning problems. Fish processing has similar problems and solutions.

### 31.2.3.9 Fruit and Vegetable Processing

The most severe environmental problem of fruit and vegetable processors is the potential for water pollution if the liquid wastes are not handled properly. Cooking can cause odors, which are usually controlled by using furnaces as afterburners.

One processing problem is presented by the roasting of coffee. This releases smoke, odor, and particulate matter. The particulate matter, primarily dusty and chaff, can be removed with a cyclone. The smoke and odors are usually consumed by passing the roaster exhaust gases through an afterburner. Heat recovery may be desirable if the afterburner is large enough to make it economical.

### 31.2.3.10 Miscellaneous Agricultural Industries

Other industries of interest are (1) the manufacturing of spices and flavorings, which may use activated carbon filters to remove odors from their exhaust stream; (2) the tanning industry, which uses afterburners or activated carbon for odor removal and wet scrubbers for dust removal; and (3) glue and rendering plants, which utilize sodium hypochlorite scrubbers or afterburners to control odorous emissions.

## 31.2.4 Forest Products

Trees are classified as a renewable resource which is being utilized in most portions of the world on a sustained yield basis. A properly managed forest will produce wood for lumber, fiber, and chemicals

indefinitely. Harvesting this resource can generate considerable dust and other particulates. Transportation over unpaved roads causes excessive dust generation. The cultural practice of burning the residue left after a timber harvest, called slash burning, is still practiced in some areas and is a major source of smoke, gaseous, and particulate air pollution in the localities downwind from the fire (Figure 31.13). Visibility reduction from such burning can be a serious problem.

Processing the harvested timber into the finished product may involve sawing, peeling, planning, sanding, and drying operations, which can release considerable amounts of wood fiber and lesser amounts of gaseous material to the atmosphere. Control of wood fiber emissions from the pneumatic transport and storage systems can be a major problem of considerable expense for a plywood mill or a particleboard plant.

The forest products industry encompasses a broad spectrum of operations which range from the raising of trees, through cutting and removing the timber, to complete utilization of the wood residue.<sup>34</sup>

### 31.2.4.1 Open Burning

The forest products industry (as well as governmental agencies such as the U.S. Forest Service) practices open, prescribed, burning of logging residue (slash) as a forest management tool and as an economical means of residue disposal.<sup>35</sup> This burning is usually done when meteorological conditions and fuel variables, such as moisture content, can give as clean a burn as possible with a minimum effect on populated areas. On a worldwide basis, it has been estimated that approximately 90 million metric tons of particulate matter from wild and controlled forest and range fires enter the atmosphere each year. Table 31.25 lists the pollutant emissions from forest burning.<sup>33</sup>

### 31.2.4.2 Wood-Fired Power Boilers

Wood-fired power boilers are generally found at the mills where wood products are manufactured. They are fired with waste materials from the process, such as "hogged wood", sander dust, sawdust, bark, or process trim. The major emission of concern from wood

**TABLE 31.25** Air Pollution Emission Factors from Forest Burning

Pollutant	Emission (kg metric ton <sup>-1</sup> )
Particulate matter	8.5
Carbon monoxide	22
Hydrocarbons (as CH <sub>4</sub> )	2
Nitrogen oxides (as NO <sub>2</sub> )	1

Source: Ref. 33.

boilers is particulate matter (PM). The emission rates depend primarily on the composition of the residue fuel burned, and the particle control device. Oxides of nitrogen ( $\text{NO}_x$ ) may also be emitted in significant quantities when certain types of wood residue are combusted or when operating conditions are poor.<sup>36</sup> The lignin component of wood is expected in the reaction: wood constituents can be quite variable, such as the cellulose, lignin, and other carbohydrate compounds. As a general rule of combustion, wood can be assumed to have the composition of  $\text{C}_{6.9}\text{H}_{10.6}\text{O}_{3.5}$ . However, it also contains many other elements, such as sulfur, phosphorous, and nitrogen, which are oxidized during the firing processes.

The most common control devices used to reduce PM emissions from wood-fired boilers are mechanical collectors, wet scrubbers, ESPs and fabric filters. Often, two multicyclones are used in series, allowing the first collector to remove the bulk of the dust and the second to remove diameter PM. The efficiency of this configuration varies from 25% to 65%.<sup>36</sup>

The most widely used wet scrubbers for wood-fired boilers are venturi scrubbers. With gas-side pressure drops exceeding 15 inches of water, particulate collection efficiencies  $\geq 85\%$  have been reported for venturi scrubbers operating on wood-fired boilers.<sup>36</sup>

ESPs are used when collection efficiencies above 90% are required. The ESPs are often used downstream of mechanical collector precleaners which remove larger-sized PM. Collection efficiencies of 90–99% for PM have been observed for ESPs operating on wood-fired boilers. A variation of the ESP is the electrostatic gravel bed filter. Here, PM in flue gases is removed by impaction with gravel media inside a packed bed; collection is augmented by an electrically charged grid within the bed. This gives collection efficiencies  $> 80\%$ .<sup>36</sup>

Fabric filters have had limited applications to wood-fired boilers, due to perceptions of fire danger arising from the collection of combustible carbonaceous fly ash. Steps can be taken to reduce this hazard, including the installation of a mechanical collector upstream of the fabric filter to remove large burning particles of fly ash (i.e. "sparklers"). Despite these complications, fabric filters are typically preferred for boilers firing salt-laden wood. This fuel produces fine particulates with a high salt content having a quenching effect, which decreases fire hazards. Particle collection efficiencies are typically  $\geq 80\%$ .<sup>36</sup>

Overfire air ports may be used with stoker and FBC boilers to stage the combustion process and lower  $\text{NO}_x$  emissions. In those areas of the United States where  $\text{NO}_x$  emissions must be reduced to very low concentrations, the application of SNCR to residue wood-fired boilers has been employed; the application of SCR is under consideration at this writing. Both systems are post-combustion  $\text{NO}_x$  controls in which ammonia or urea is

injected into the flue gas to selectively reduce  $\text{NO}_x$  to nitrogen and water. A SNCR in an industrial wood-fired boiler has demonstrated  $\text{NO}_x$  reduction efficiencies between 35% and 75% as the ammonia-to- $\text{NO}_x$  ratio increased from 0.4 to 3.2. Collection devices for particulate matter from wood-fired boilers are shown in Table 31.26.

The table refers to filterable PM and condensable PM fractions. The filterable fraction is comprised of the primary particles directly emitted by a source as a solid or liquid at the stack and captured on the filter of a test train. The condensable fraction consists of gaseous emissions that form particles upon condensing under ambient conditions soon after release from the stack. The filterable fraction is measured using EPA Method 5 (References: U.S. Environmental Protection Agency, 2010. Field validation of an Improved Method for Sampling and Analysis of Filterable and Condensable Particulate Matter. Research Triangle Park, NC 27711; and U.S. Environmental Protection Agency, Federal Reference Methods 1 through 5 and Method 17, 40 CFR 60, Appendix A-1 through A-3 and A-6) and the condensable fraction using Method 202.<sup>37,38</sup>

### 31.2.4.3 Driers

Driers are used in the forest products industry to lower the moisture content of the wood product being processed. Drying of dimension lumber gives it dimensional stability. This type of drying is done in steam kilns and is a batch process. No appreciable pollutants are released.

Veneer for the manufacture of plywood is dried on a continuous line in a veneer drier to assure that only dry veneer goes to the layup and gluing process. Glue will not bond if the veneer contains too much moisture. Emissions from the veneer driers are fine particulate and condensed organic material. The condensed organic material is of submicron size and appears as a blue haze coming from the stack. Control is accomplished by means of (1) a wet scrubber or (2) ducting the emissions to a wood-fired boiler, where they are burned. All of these systems must be carefully sized and operated in order to meet a 20% opacity regulation.

Wood particle and fiber driers are used to dry the raw material for particle board and similar products.<sup>39</sup> Just as with the veneer for plywood, the particles must be dried before being mixed with the resins and formed into board. Drying is accomplished in a gas-fired drier, a direct wood-fired drier, or steam coil driers. Many different types of driers are used in the industry. Emissions are fine particles and condensable hydrocarbons, which produce a highly visible plume. Control is accomplished with multiple cyclones or wet scrubbers. Fires in the control equipment and ductwork are quite common and must be expected periodically.

TABLE 31.26 Particulate Collection Efficiencies from Wood-Fired Boilers

Fuel	PM Control Device	Filterable PM		Filterable PM-10 <sup>b</sup>		Filterable PM-2.5 <sup>b</sup>	
		Emission Factor (lb MMBtu <sup>-1</sup> ) <sup>a</sup>	Emission Factor Rating	Emission Factor (lb MMBtu <sup>-1</sup> ) <sup>a</sup>	Emission Factor Rating	Emission Factor (lb MMBtu <sup>-1</sup> ) <sup>a</sup>	Emission Factor Rating
Bark/bark and wet wood	No control <sup>c</sup>	0.56	C	0.50**	D	0.43**	D
Dry wood	No control <sup>c</sup>	0.40	A	0.36**	D	0.31**	D
Wet wood	No control <sup>c</sup>	0.33	A	0.29**	D	0.25**	D
Bark	Mechanical collector <sup>d</sup>	0.54	D	0.49**	D	0.29**	D
Bark and wet wood	Mechanical collector <sup>d</sup>	0.35	C	0.32**	D	0.19**	D
Dry wood	Mechanical collector <sup>d</sup>	0.30	A	0.27**	D	0.16**	D
Wet wood	Mechanical collector <sup>d</sup>	0.22	A	0.20**	D	0.12**	D
All fuels	Electrolyzed gravel bed	0.1	D	0.074**	D	0.065**	D
All fuels	Wet scrubber	0.066	A	0.065**	D	0.065**	D
All fuels	Fabric filter	0.1	C	0.074**	D	0.065**	
All fuels	Electrostatic precipitator	0.054	B	0.04**	D	0.035**	
<u>Condensible PM</u>							
All fuels	All controls/no controls	0.017	A				

\* Units of lb of pollutant per million Btu (MMBtu) of heat input. To convert from lb MMBtu<sup>-1</sup> to lb ton<sup>-1</sup>, multiply by (HHV × 2000), where HHV is the higher heating value of the fuel, MMBtu lb<sup>-1</sup>. CPM = condensible particulate matter.

<sup>b</sup>PM<sub>10</sub> = particulate matter less than or equal to 10 μm aerodynamic diameter; PM<sub>2.5</sub> = particulate matter less than or equal to 2.5 μm aerodynamic diameter. Filterable PM = PM captured and measured on the filter in an U.S. EPA Method 5 (or equivalent) sampling train. Condensible PM = PM captured and measured in U.S. EPA Method 202 (or equivalent) sampling train.

<sup>c</sup>Factor represents boilers with no controls, Breslove separators, Breslove separators with reinjection, and mechanical collectors with reinjection.

<sup>d</sup>Mechanical collectors include cyclones and multicyclones. Emission factor rating ranges A through E, with A being the best. A factor's rating is a general indication of the reliability or robustness, of that factor. This rating is assigned using expert judgment, is based on the estimated reliability of the methods used to develop the factor, and on both the amount and the representative characteristics of the data.

\*\* = Cumulative mass percentage for bark and wet wood-fired boilers multiplied by the Filterable PM factor.

Source: Ref. 37.

#### **31.2.4.4 Pulp and Paper Processing**

Pulp and paper manufacture is increasing in the world at an exponential rate. The demand for paper will continue as new uses are found for this product. Since most paper is manufactured from wood or wood residue, it provides an excellent use for this renewable resource.

The most widely used pulping process is the kraft process (see Figure 29.12 in Chapter 29) which results in recovery and regeneration of the chemicals. This occurs in the recovery furnace, which operates with both oxidizing and reducing zones. Emissions from such recovery furnaces include particulate matter, very odorous reduced sulfur compounds, and oxides of sulfur. Bleaching has been a substantial source of dioxins, but many processors have now modified their operations to use substantially less chlorine, greatly reducing the dioxin formation. If extensive and expensive control is not exercised over the kraft pulp process, the odors and aerosol emissions will affect a wide area. Odor complaints have been reported over 100 km away from these plants. A properly controlled and operated kraft plant will handle huge amounts of material and produce millions of kilograms of finished products per day, with little or no complaint regarding odor or particulate emissions.

The kraft process has become the dominant process for pulp production throughout the world, primarily because of the recovery of the pulping chemicals. Control of air pollutant emissions in modern kraft mills is accomplished by (1) proper operation of the entire mill, (2) high-efficiency ESPs on the recovery furnace (up to 99.7% efficiency for particulate matter, which is recovered and returned to the process), (3) collection of noncondensable gases from several vent points (digesters, blow tanks, washers) and ducting them to the lime kiln, where they are completely burned, and (4) high-energy wet scrubbers on the lime kiln exhaust to remove the particulate matter and sulfurous gases.

#### **31.2.5 Other Industrial Processes**

Many industries operated throughout the world do not fall into the previous categories. Some of these are universal, such as asphalt batching plants, whereas others are regional, such as bagasse-fired boilers. Each has its own emission and control problems and requires knowledgeable analysis and engineering. Some of the more widely used processes are examined in this section.

##### **31.2.5.1 Mineral Products**

Conversion of minerals to useful products is a major worldwide industry. Mining or quarrying of minerals

can produce fugitive emissions, which may be controlled by paving work and traffic areas, wetting the materials being removed or handled, or using collection and exhaust systems at the site where the particulate matter is being generated. The usual air pollution control device is a multiple cyclone or a baghouse at the system exit. The same control techniques can be applied at other points in the process where the minerals are transported, stored, crushed and ground, concentrated, dried, and mixed.<sup>40</sup>

#### **31.2.5.2 Asphaltic Concrete Plants**

Hot mix asphalt (HMA) paving uses a mixture of size-graded, aggregate that can include reclaimed asphalt pavement (RAP), and liquid asphalt cement. To produce HMA, the aggregate is heated and mixed. If RAP is used, it and the aggregate constitute >92% total weight of the mixture. Fine aggregate (i.e. <74 µm in physical diameter) is required for the production of acceptable quality HMA. HMA paving materials can be manufactured by batch mix plants, by continuous mix (mix outside dryer drum) plant, by parallel-flow drum-mix plants or by counter-flow drum-mix plants. This order of listing reflects the chronological order of use within the HMA industry.<sup>41</sup>

More than 500 million tons of HMA is produced each year in the United States by about 3600 asphalt plants. Of these, about 2300 are batch plants, 1000 are parallel-flow drum-mix plants and 300 are counterflow drum-mix plants. About 85% being manufactured today have the counter-flow drum-mix design. Batch plants make up about 10% and parallel flow drum-mix plants account 5%. Continuous mix plants represent less than 0.5%.<sup>41</sup>

An HMA plant can be constructed as a permanent plant or with a modular, skid-mounted design or a smaller, portable plant. All plants can and do have RAP processing capabilities.<sup>41</sup>

Figures 31.14–31.16 respectively shows the configurations for a batch mix plant, a parallel-flow drum mix and a counter-flow drum-mix plant. Fugitive emissions occur at the handling areas and at the bin loading facility. The emissions of greatest concern, however, occur at the rotary drier, hot aggregate elevator, and hot aggregate handling systems. Each has the potential for releasing large quantities of uncontrolled particulate matter. Table 31.27 illustrates the large range of emissions from uncontrolled and controlled asphaltic concrete plants.

Emissions from batch mix HMA plants can be from ducted sources, i.e. those vented to the atmosphere through a stack, vent or other conveyance, or from fugitive sources. Ducted emissions are usually collected and transported by an industrial ventilation system with one or more air movers, eventually to be emitted to the

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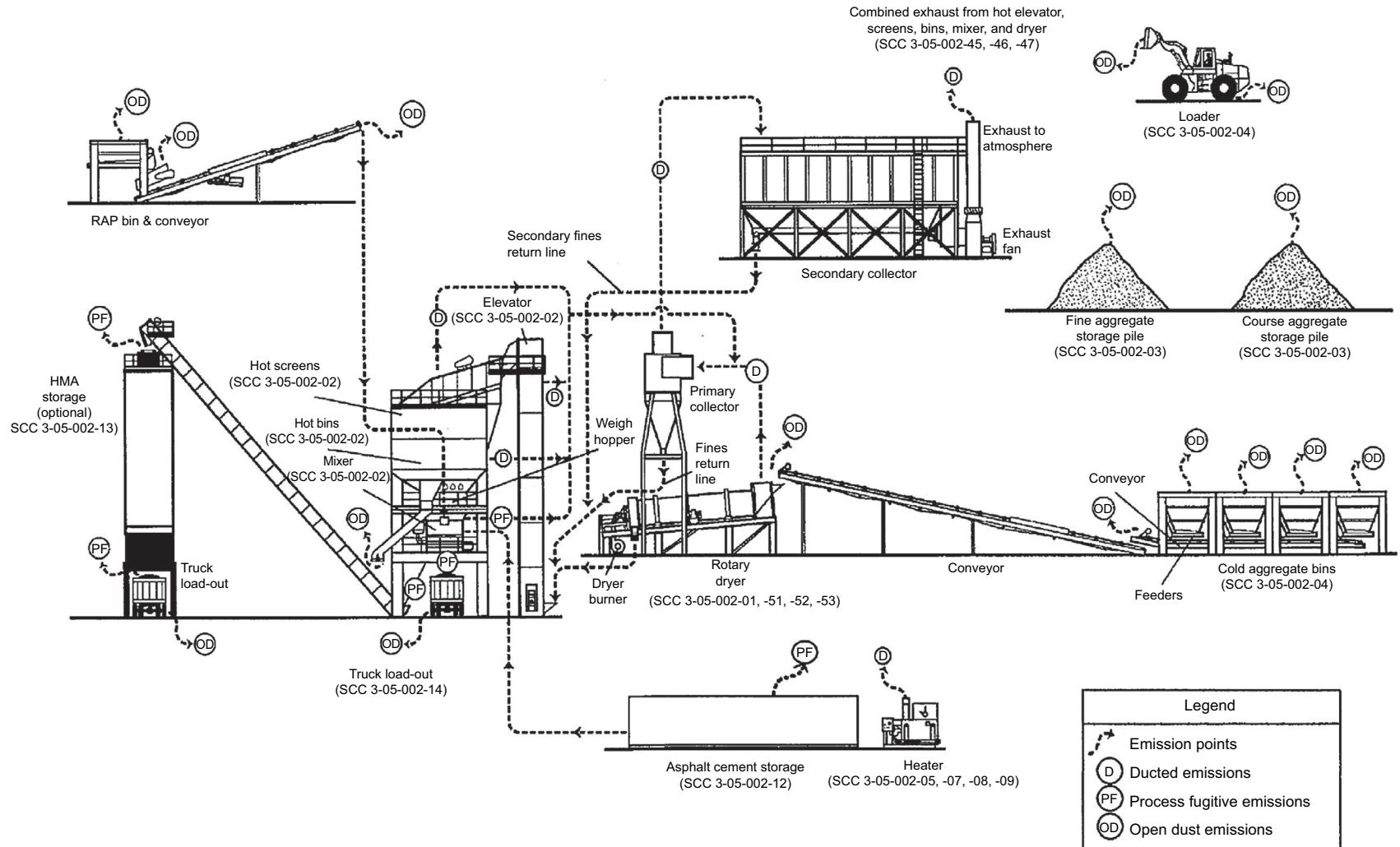


FIGURE 31.14 General process flow diagram for batch mix asphalt plants (source classification codes in parentheses). U.S. Environmental Protection Agency. Emission factor documentation for AP-42. Section 11.1 hot mix asphalt plants. Final report. Research Triangle Park, North Carolina: RTI International; 2004.

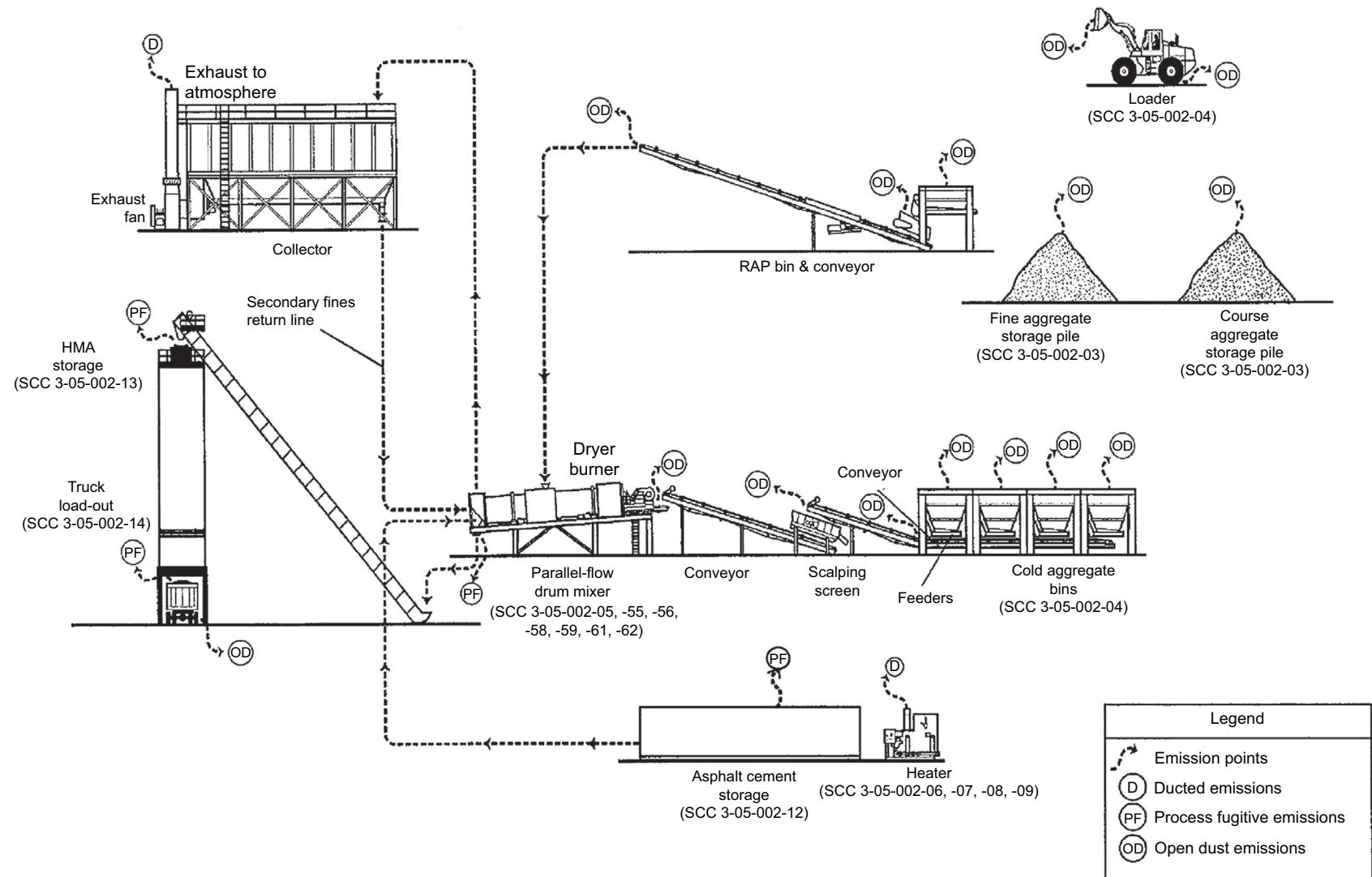


FIGURE 31.15 General process flow diagram for parallel-flow drum-mix asphalt plants (source classification codes in parentheses). Ref. 40.

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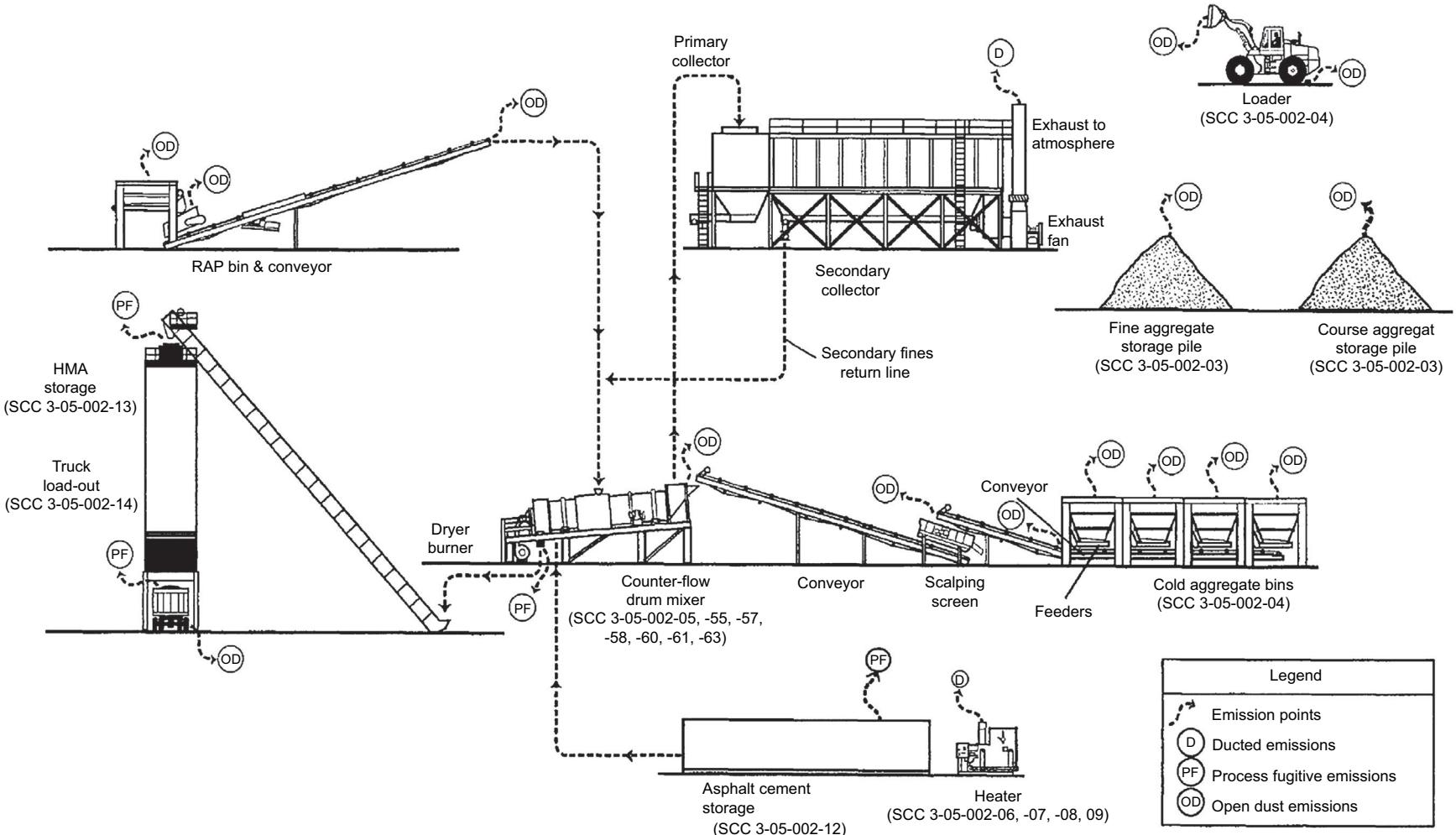


FIGURE 31.16 General process flow diagram for counter-flow drum-mix asphalt plants (source classification codes in parentheses). U.S. Environmental Protection Agency. Emission factor documentation for AP-42. Section 11.1 hot mix asphalt plants. Final report. Research Triangle Park, North Carolina: RTI International; 2004.

**TABLE 31.27** Air Pollution Emission Factors for Asphalt Concrete Plants

Type of Control	Emissions (kg metric ton <sup>-1</sup> )
Uncontrolled*	22.5
Cyclone precleaner	7.5
High-efficiency cyclone	0.85
Spray tower scrubber	0.20
Multiple centrifugal scrubber	0.15
Baffle spray tower scrubber	0.15
Orifice-type scrubber	0.02
Baghouse <sup>§</sup>	0.05

\* Almost all plants have at least a precleaner following the rotary drier. The fines collected are returned and are an important part of the mix.

<sup>§</sup>Emissions from a properly designed, installed, operated, and maintained baghouse collector can be as low as 0.0025–0.010 kg per metric ton.

Source: Ref. 41.

atmosphere through a stack. Fugitive emissions result from process and open sources and consist of a combination of gas-phase pollutants and PM. The rotary drum dryer is generally the largest source of emissions that include PM; CO, CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>x</sub>, (CO), CH<sub>4</sub>, VOCs, and various hazardous air pollutants. The pollutants are also generated at other sites in the process, including hot-side conveyors, classifiers and mixing equipment. The concentrations of organic aerosols emitted depend on the mixing temperature, with low-molecular compounds released first.<sup>41</sup>

In the parallel-flow and counterflow designs, the largest source is the rotary drum dryer, with similar pollutants as those produced by the batch mix system. The type of material used influences emission rates. For example, in test plants, total organic carbon, benzene, 2-methyl phenol SO<sub>2</sub>, NO<sub>x</sub>, CO, PM, and Pb emissions were found to increase substantially when rubber is present in the asphalt, but PAHs and CO<sub>2</sub> emissions decreased.<sup>41</sup>

Nearly all plants employ a primary dust collection system, e.g. large cyclones, for large PM, usually as a classifier to return and use product that would otherwise escape. The controls of choice are appropriately selected dry mechanical collectors, scrubbers and fabric filters. ESPs do not appear to work well for HMA. The capture of VOCs and other gas-phase pollutants can be limited by proper O&M of the burner.<sup>41</sup>

### 31.2.5.3 Cement Manufacturing

Air pollution from cement manufacturing begins with extraction of limestone and other calcareous substances. These are typically extracted from open-face quarries. The less pure the calcareous, the more likely

addition pollutants will be released. For example, if pyrite is included, SO<sub>2</sub> emissions will increase during processing. If metals are present, e.g. Al and Fe, they will be found in the emissions. In addition, gypsum and anhydrite are extracted for the Portland cement finishing process. The cement process has a high mass loss rate. For example, about 33% of the calcareous mass is lost as CO<sub>2</sub>.

Portland cement manufacture accounts for about 98% of the cement production in the United States. The raw materials are crushed, processed, proportioned, ground, and blended before going to the final process, which may be either wet or dry. In the dry process, the moisture content of the raw material is reduced to less than 1% before the blending process occurs. The dry material is pulverized and fed to the rotary kiln. Further drying, decarbonating, and calcining take place as the material passes through the rotary kiln. The material leaves the kiln as clinker, which is cooled, ground, packaged, and shipped.

For the wet process, a slurry is made by adding water during the initial grinding. The homogeneous wet mixture is fed to the kiln as a wet slurry (30–40% water) or as a wet filtrate (20% water). The burning, cooling, grinding, packaging, and shipping are the same as for the dry process.

Gas-phase and particulate matter emissions can occur at numerous points in the cement manufacturing process (Figure 31.17 and Table 31.28).

The key component of cement manufacturing is the rotary kiln, which is a long, cylindrical, slightly inclined furnace that is lined with refractory to protect the steel shell and to retain heat. The raw material mix enters the kiln at the elevated end, and the combustion fuels generally are introduced into the lower end of the kiln in a counter-current manner. The materials move continuously to the lower end by rotation of the kiln. The raw materials become more fluid and cementitious form the kiln heating. The heat source is generally the combustion of coal, natural gas, and sometimes oil.<sup>42</sup> Other supplemental fuels including waste solvents, inks, scrap rubber, and petroleum coke can be added. Indeed, the cement rotary kiln design has been emulated in hazardous waste incineration systems. Control of particulate matter emissions from the kilns, dryers, grinders, etc., is by means of standard devices and systems: (1) multiple cyclones (80% efficiency), (2) ESPs (95% efficiency), (3) multiple cyclones followed by ESPs (97.5% efficiency), and (4) baghouses (99.8% efficiency).

### 31.2.5.4 Glass Manufacturing Plants

Fiberglass is manufactured primarily from borosilicate glass by drawing the molten glass into fibers. Two fiberglass products are produced, textile, and glass wool. Soda-lime glass accounts for about 90% of the U.S.

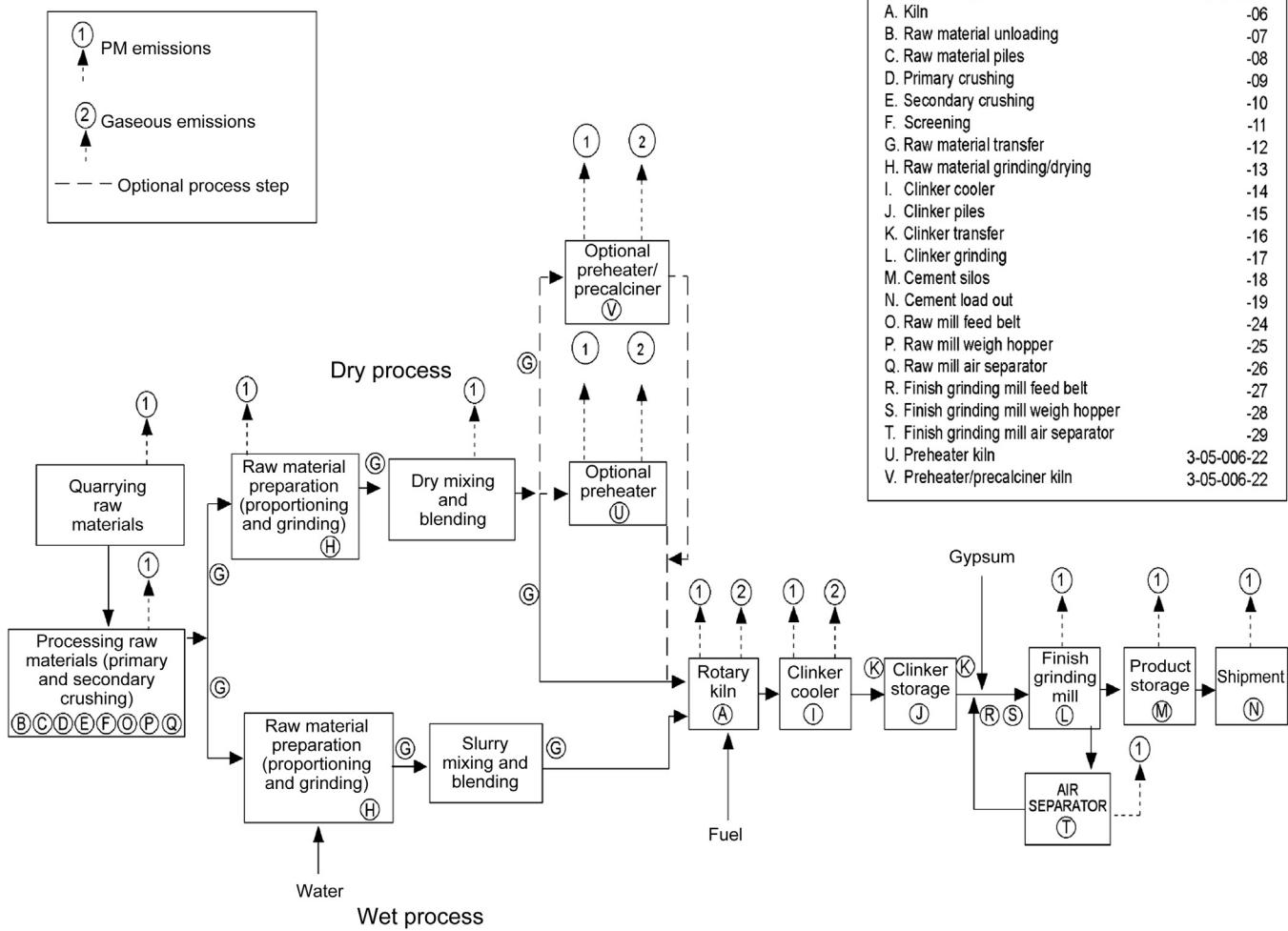


FIGURE 31.17 Process flow diagram for Portland cement manufacturing. SCC = Source classification code. Ref. 42.

TABLE 31.28 Air Pollution Emission Factors for Portland Cement Manufacturing if No Controls Are Present

Pollutant	Emissions (kg metric ton <sup>-1</sup> )			
	Dry Process		Wet Process	
	Kilns	Dryers, Grinders, etc.	Kilns	Dryers, Grinders, etc.
Particulate matter	122.0	48.0	114.0	16.0
Sulfur dioxide*	5.1			
Mineral source	Neg	—	5.1	—
Gas combustion	$2.1 \times S^{\frac{1}{2}}$	—	Neg	—
Oil combustion	$3.4 \times S$	—	$2.1 \times S^{\frac{1}{2}}$	—
Coal combustion		—	$3.4 \times S$	—
Nitrogen oxides	1.3	—	1.3	—

\* If a baghouse is used as control device, reduce SO<sub>2</sub> by 50% because of reactions with an alkaline filter cake.

<sup>§</sup>S is the percent of sulfur in the fuel.

Source: Ref. 33.

production. It is produced in large, direct-fired, continuous-melting furnaces in which the blended raw materials are melted at 1480 °C to form glass.

The expected emissions from glass furnace fired with gaseous fuel are 100 mg of PM per container produced and for pressed and brown glass when produced using soda-lime and lead recipes. This method would emit 500 mg g<sup>-1</sup> of glass produced for borosilicate recipes, and 250 mg g<sup>-1</sup> of glass produced by other methods, such as opal and fluoride recipes. Wool fiberglass recipes also have expected emission rates of 250 mg g<sup>-1</sup>. Flat glass emissions would be 225 mg g<sup>-1</sup>. A furnace fired with liquid fuel would have 30% higher PM emission rates, e.g. 130 mg g<sup>-1</sup> for container glass and 650 mg g<sup>-1</sup> for the borosilicate method.<sup>43</sup> For effective control of the PM emissions, baghouses are used.

During the manufacture of glass, considerable dust, with particles averaging about 300 mm in size, will be emitted. Some dusts may also be emitted from the handling of the raw materials involved. Control of this dust to prevent transport away from the plant is a necessity. When glass is blown or formed into the finished product, smoke and gases can be released from the contact of the molten glass with lubricated molds. These emissions are quite dense but of a relatively short duration.

Glass making also emits oxides of SO<sub>x</sub>, NO<sub>x</sub>, and CO. For example, a textile glass furnace using the

regenerative method and gas would be expected to emit 15 kg SO<sub>x</sub>, 10 kg NO<sub>x</sub>, and 15 kg CO per metric ton (Mg) of material processed, whereas an gas-recuperative furnace producing the same product would be expected to emit 1.5 kg SO<sub>x</sub>, 10 kg NO<sub>x</sub>, and 0.25 kg CO per Mg of material processed. When an electric furnace is available, emission rates of PM and gaseous pollutants decrease substantially. Fluorides are also commonly emitted during glass manufacturing, e.g. 0.06 kg 0.25 kg fluorides per Mg of material processed by either a regenerative or recuperative gas furnace. Other emissions include volatile organic compounds, phenolics, phenol, and formaldehyde.<sup>44</sup> These and other emission factors for various glass manufacturing are published by the US EPA.<sup>45</sup>

The emissions from the two processes are shown in Table 31.29.<sup>33</sup> Control is usually better achieved through proper design and operation of the manufacturing operations rather than by add-on devices.

### 31.2.5.5 Stone and Clay Product Manufacturing

The industries which produce and handle various stone products emit considerable amounts of particulate matter at every stage of the operation. These particulates may include fine mineral dusts of a size to cause damage to the lungs. Depending on the type of rock, mineral fibers can also be released, notably asbestos. The threshold values for such dusts have been set quite low to prevent

TABLE 31.29 Air Pollution Emission Factors for Fiberglass Manufacturing without Controls

Type of Process	Emissions (kg metric ton <sup>-1</sup> )				
	Particulate Matter	Sulfur Oxides as SO <sub>2</sub>	Carbon Monoxide	Nitrogen Oxides as NO <sub>2</sub>	Fluorides
<b>Textile products</b>					
Glass furnace					
Regenerative	8.2	14.8	0.6	4.6	1.9
Recuperative	13.9	1.4	0.5	14.6	6.3
Forming	0.8	—	—	—	—
Curing ovens	0.6	—	0.8	1.3	—
<b>Wool products</b>					
Glass furnace					
Regenerative	10.8	5.0	0.13	2.5	0.06
Recuperative	14.2	4.8	0.13	0.9	0.06
Electric	0.3	0.02	0.03	0.14	0.01
Forming	28.8	—	—	—	—
Curing ovens*	1.8	—	0.9	0.6	—
Cooling*	0.7	—	0.1	0.1	—

\* In addition, 0.05 kg metric ton<sup>-1</sup> for phenol and 1.7 kg metric ton<sup>-1</sup> for aldehyde during curing and cooling.

Source: Ref. 33.

disabling diseases for the worker, including lung cancer, mesothelioma, pleural diseases, asbestos, and silicosis.

In the production of clay, talc, cement, chalk, etc., an emission of particulate matter will usually accompany each process. These processes may involve grinding, drying, and sieving, which can be enclosed and controlled to prevent the emission of particles. In many cases, the recovered particles can be returned to the process for a net economic gain.

### 31.2.5.6 Sewage Treatment Plants

The concern with atmospheric emissions from sewage treatment plants involves gases and odors from the plant itself, particulate matter and gaseous emissions from the sludge incinerator if one is used, and gases, odors, and particulate matter if sludge disposal is conducted at the site. The gases and odors are combustible, so afterburners or flares are used. Some plants use the sewage gas to fire small stationary boilers or fuel gas–diesel engines for plant energy. Particulate matter from sludge incinerators is usually scrubbed with treated water from the plant, and the effluent is returned to the incoming plant stream. If the odors are too persistent, masking agents are sometimes specified to lessen the objections of the public.

### 31.2.5.7 Coal Preparation Plants

Coal preparation plants are used to reduce noncombustibles and other undesirable materials in coal before it is burned.

### 31.2.5.8 Gas Turbines

Gas turbines are used as prime movers for pumps, electric generators, and large rotating machinery. Their main economic advantage is driving high-horsepower, consistent loads. Many stationary gas turbines use the same core engine as their jet engine counterpart.

## 31.3 MOBILE SOURCE CONTROL TECHNOLOGIES

Because mobile sources of air pollution are capable of moving from one local jurisdiction to another, they are usually regulated by the national government. In the United States, state or local agencies can have more restrictive standards, if they choose. To date, only the state of California has established extensive standards more restrictive than the U.S. federal standards, and these only for gasoline-powered automobiles.

### 31.3.1 Gasoline-Powered Vehicles

Gasoline-powered motor vehicles outnumber all other mobile sources combined in the number of vehicles, the amount of energy consumed, and the mass of air pollutants emitted. It is not surprising that they have received the greatest share of attention regarding emission standards and air pollution control systems. Currently, certain countries limit emissions gasoline-powered vehicles from crankcases, fuel tanks and, especially, exhaust from engines. In the United States, these emission standards for mobile sources have become increasingly lowered. As discussed in Chapter 29, the Tier 2 standards are presently in effect (Table 29.12), but newer standards, i.e. the Tier 3 program will soon replace them.

Crankcase emissions in the United States have been effectively controlled since 1963 by positive crankcase ventilation (PCV) systems which take the gases from the crankcase, through a flow control valve, and into the intake manifold. The gases then enter the combustion chamber with the fuel–air mixture, where they are burned. Figure 31.18 shows a cross-section of a gasoline engine with the PCV system.

In the United States, evaporative emissions from the fuel tank and carburetor have been controlled by either a vapor recovery system which uses the crankcase of the engine for the storage of the hydrocarbon vapors or an adsorption and regeneration system using a canister of activated carbon to trap the vapors and hold them until such time as a fresh air purge through the canister carries the vapors to the induction system for burning in the combustion chamber.

The exhaust emissions from gasoline-powered vehicles are the most difficult to control. These emissions are influenced by such factors as gasoline formulation, air–fuel ratio, ignition timing, compression ratio, engine speed and load, engine deposits, engine condition, coolant temperature, and combustion chamber configuration. Consideration of control methods must be based

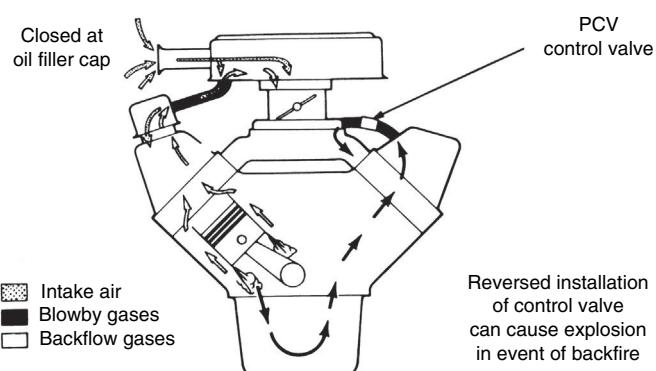


FIGURE 31.18 Positive crankcase ventilation (PCV) system.

on elimination or destruction of unburned hydrocarbons, CO, and NO<sub>x</sub>. Methods used to control one pollutant may actually increase the emission of another requiring even more extensive controls.

Control of exhaust emissions for unburned hydrocarbons and carbon monoxide has followed three routes:

1. Fuel modification in terms of volatility, hydrocarbon types, or additive content. Some of the fuels currently being used are liquefied petroleum gas (LPG), liquefied natural gas (LNG), compressed natural gas (CNG), fuels with alcohol additives, and unleaded gasoline. The supply of some of these fuels is very limited. Other fuel problems involving storage, distribution, and power requirements have to be considered.
2. Minimization of pollutants from the combustion chamber. This approach consists of designing the engine with improved fuel-air distribution systems, ignition timing, fuel-air ratios, coolant and mixture temperatures, and engine speeds for minimum emissions. The majority of automobiles sold in the United States now use an electronic sensor/control system to adjust these variables for maximum engine performance with minimum pollutant emissions.
3. Further oxidation of the pollutants outside the combustion chamber. This oxidation may be either by normal combustion or by catalytic oxidation. These systems require the addition of air into the exhaust manifold at a point downstream from the exhaust valve. An air pump is employed to provide this air. [Figure 31.19](#) illustrates an engine with an air pump and distribution manifold for the oxidation of CO and hydrocarbons (HC) outside the engine.

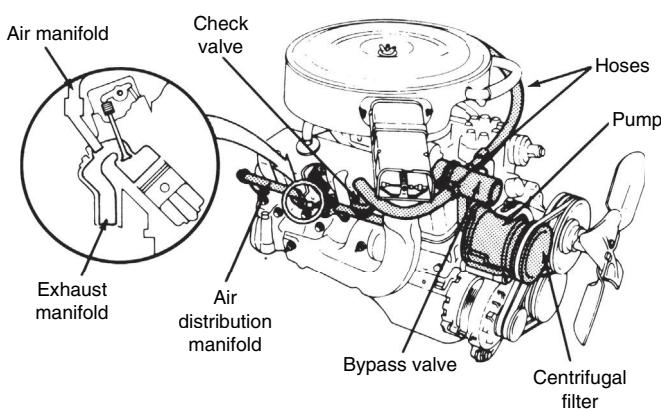
Beginning with the 1975 U.S. gasoline-powered automobiles, catalytic converters were added to nearly all models to meet the more restrictive emission standards. Since the lead used in gasoline is a poison to the catalyst

used in the converter, a scheduled introduction of unleaded gasoline was also required. The U.S. petroleum industry simultaneously introduced unleaded gasoline into the marketplace.

In order to lower emissions of oxides of nitrogen from gasoline engines, two general systems were developed. The first is exhaust gas recirculation (EGR), which mixes a portion of the exhaust gas with the incoming fuel-air charge, thus reducing temperatures within the combustion chamber. This recirculation is controlled by valving and associated plumbing and electronics, so that it occurs during periods of highest NO<sub>x</sub> production, when some power reduction can be tolerated: a cruising condition at highway speed. Other alternatives are to use another catalytic converter, in series with the HC/CO converter, which decomposes the oxides of nitrogen to oxygen and nitrogen before the gases are exhausted from the tailpipe.

A modified internal combustion engine which shows promise is the stratified-charge engine. This is a spark ignition engine using fuel injection in such a manner as to achieve selective stratification of the air/fuel ratio in the combustion chamber. The air/fuel ratio is correct for ignition at the spark plug, and the mixture is fuel lean in other portions of the combustion chamber. Only air enters the engine on the intake stroke, and the power output is controlled by the amount of fuel injected into the cylinder. Stratified-charge engines have been operated experimentally and used in some production vehicles. They show promise as relatively low-emission engines. The hydrocarbon emission levels from this engine are quite variable, the CO levels low, and the NO<sub>x</sub> levels variable but generally high.

An external combustion engine that has been widely supported as a low-emission power source is the Rankine cycle steam engine. Many different types of expanders can be used to convert the energy in the working fluid into rotary motion at a drive shaft. Expanders that have been tried or proposed are reciprocating piston engines, turbines, helical expanders, and all possible combinations of these. The advantage of the steam engine is that the combustion is continuous and takes place in a combustor with no moving parts. The result is a much lower release of air pollutants, but emissions are still not completely zero. Present technology is capable of producing a satisfactory steam-driven car, truck, or bus, but costs, operating problems, warm-up time, and weight and size must be considered in the total evaluation of the system. A simple Rankine cycle steam system is shown diagrammatically in [Figure 31.20](#).



**FIGURE 31.19** Manifold air oxidation system.

### 31.3.2 Diesel-Powered Vehicles

The diesel, i.e. compression ignition, cycle is regulated by fuel flow only, with air flow remaining constant

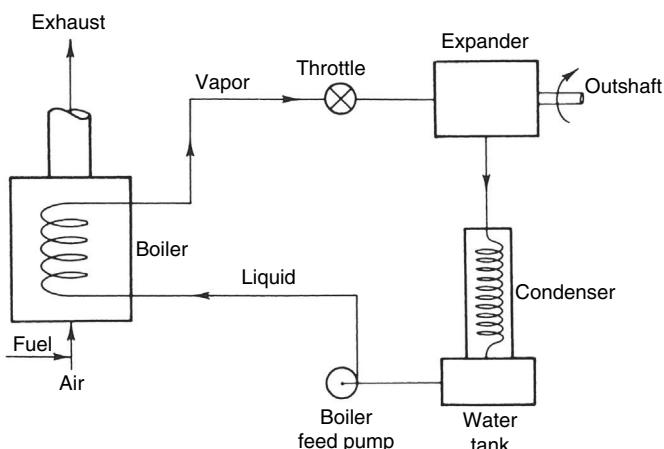


FIGURE 31.20 Rankine cycle system.

with engine speed. Because the diesel engine is normally operated well on the lean side of the stoichiometric mixture (40:1 or more), emission of unburned hydrocarbons and CO is minimized. The actual emissions from a diesel engine are (1) oxides of nitrogen, as for spark ignition engines; (2) particulate matter, mainly unburned carbon, which at times can be excessive; (3) partially combusted organic compounds, many of which cause irritation to the eyes and upper respiratory system; and (4) oxides of sulfur from the use of sulfur-containing fuels. A smoking diesel engine indicates that more fuel is being injected into the cylinder than is being burned and that some of the fuel is being only partially burned, resulting in the emission of unburned carbon.

Control of emissions from diesel-powered vehicles has received much attention in recent years. This is partially accomplished by fuel modification to obtain reduced sulfur content and cleaner burning and by proper tuning of the engine using restricted fuel settings to prevent overfueling.

Diesel fuel has begun to evolve in another, more sustainable, way. An increasing number of vehicles are running on so-called “biodiesel” fuel. This is refined from plant-based hydrocarbons, especially from waste residues (e.g. from used cooking oils). With operational adjustments, biodiesel is currently in use in buses as part of urban transit and college transportation systems.

Effective with the 1982 model year, particulate matter from diesel vehicles was regulated by the U.S. EPA for the first time, at a level of  $0.37 \text{ g km}^{-1}$  traveled.<sup>17</sup> Diesel vehicles were allowed to meet an  $\text{NO}_x$  level of  $0.93 \text{ g km}^{-1}$ <sup>17</sup> under an EPA waiver. These standards were met by a combination of control systems, primarily EGR and improvements in the combustion process. For the 1985 model year, the standards decreased to  $0.12 \text{ g}$  of particulate matter per kilometer and  $0.62 \text{ g}$  of  $\text{NO}_x$  per kilometer.

After 2005, the attention to both gaseous pollutants and PM from diesel engines has accelerated. Diesel PM is part of a complex mixture that makes up diesel exhaust. The gas phase of diesel exhaust is composed of many hazardous air pollutants, e.g. acetaldehyde, acrolein, benzene, 1,3-butadiene, formaldehyde, and PAHs. The particle phase also has many different types of particles that can be classified by size or composition. The composition of fine and ultrafine diesel particles contain elemental carbon (EC) into and onto which numerous compounds are sorbed, e.g. organic compounds, sulfate, nitrate, and heavy metals.<sup>46</sup>

Controlling the combustion process is key to controlling emissions. Diesel control technologies include oxidation catalysts, particulate filters and closed crankcase ventilation for PM and EGR, selective catalytic reduction (SCR), lean catalysts and lean traps for  $\text{NO}_x$ . Slowing ignition timing that allows certain hydrocarbons to pass through the exhaust and trigger the catalyst sooner can be effective in generating exothermic heat over the catalyst and regenerate soot. Variable valve timing similarly introduces some of the exhaust into the combustion process to lower hydrocarbon and  $\text{NO}_x$  emissions. EGR can also dilute intake air to decrease combustion temperatures and to decrease  $\text{NO}_x$  emissions. Direct *versus* port injection of fuel to the cylinders can also improve combustion efficiency.<sup>47</sup>

Catalytic mechanisms can greatly decrease numerous emissions. For example, prior to seeing the catalyst, the gas stream contains CO, hydrocarbons, PAHs,  $\text{SO}_2$ ,  $\text{NO}_x$ , and PM (including the soluble organic fraction, SOF). The flow-through diesel oxidation catalyst's (DOCs) honeycomb stainless steel substrate is coated with the metal catalyst, e.g. platinum or palladium. The catalyzed oxidative process converts the incoming pollutants to more oxidized and less toxic compounds, especially  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ . The PM entering the DOC consists of EC and gaseous and semivolatile organic compounds (SVOCs). Exiting the catalyst, most of the volatile SOF in the PM has been oxidized, along with some of the EC. The decrease in PM concentration is affected by the SOF in the particulate. For example, an oxidation catalyst can lower the SOF of the particulate by 90% under certain operating conditions, which would decrease PM emissions by up to 40–50%. PM reductions of 20–35% is common for newer model year engines. Destruction of the SOF is important given that this component of PM often contains a number of compounds of concern, including PAHs and dioxins.

The catalyst technology has advanced to include filter regeneration catalysts. In 2007, every heavy-duty diesel-powered vehicle had to include a diesel particulate filter (DPF) to decrease PM to  $<0.01 \text{ g}$  per braking horsepower-h ( $\text{g php}^{-1} \text{ h}^{-1}$ ). The DPF efficiency

depends on a prescribed regeneration to burn soot that has accumulated on the filter. The regeneration process first oxidizes unburned hydrocarbons and CO, using the heat that is generated to raise the temperature of the exhaust gas, which combusts carbonaceous soot. The second regeneration oxidizes NO<sub>x</sub> to NO<sub>2</sub>, which in turn, oxidizes C.

Oxidation catalyst efficiency can be diminished by the presence of S. In fact, SOF catalysts may also oxidize SO<sub>2</sub> to form H<sub>2</sub>SO<sub>4</sub> and water, thereby increasing acidic PM (sulfate) concentrations. This is a main reason for the lower S content required for diesel fuel.

Close crankcase ventilation consists of a multistage filter that collects, coalesces and returns emitted lubrication oil to the engine sump. The filtered gases are returned to the intake system, so that differential pressures are balanced. This can be combined with DOC and DPF systems for increased efficiencies.

These technologies are summarized in [Table 31.30](#).

### 31.3.3 Gas Turbines and Jet Engines

The modified Brayton cycle is used for both gas turbines and jet engines. The turbine is designed to produce a usable torque at the output shaft, while the jet engine allows most of the hot gases to expand into the atmosphere, producing usable thrust. Emissions from both turbines and jets are similar, as are their control methods. The emissions are primarily unburned hydrocarbons, unburned carbon which results in the visible exhaust, and oxides of nitrogen. Control of the unburned hydrocarbons and the unburned carbon may be accomplished by redesigning the fuel spray nozzles and reducing cooling air to the combustion

chambers to permit more complete combustion. U.S. airlines have converted their jet fleets to lower-emission engines using these control methods. NO<sub>x</sub> emissions may be minimized by reduction of the maximum temperature in the primary zone of the combustors.

U.S. EPA regulations for commercial, jet and turbine-powered aircraft<sup>7</sup> are based on engine size (thrust) and pressure ratio (compressor outlet/compressor inlet) for the time in each mode of a standardized takeoff and landing cycle. Once the aircraft exceeds an altitude of 914 m, no regulations apply. This does not mean that emissions are not important and do not contribute to atmospheric pollution above this level. Indeed, about 60–80% of the air space contribution of NO<sub>x</sub> results from emissions above this altitude. Similarly, 80–90% of SO<sub>2</sub> and 20–40% of VOCs in the air space comes at higher altitude.<sup>48</sup>

The gas turbine engine for automotive or truck use could be either a simple turbine, a regenerative turbine, a free turbine, or any combination. [Figure 31.21](#) shows the basic types which have been successfully tried in automotive and truck use.

### 31.3.4 Alternatives to Existing Mobile Sources

The atmosphere of the world cannot continue to accept greater and greater amounts of emissions from mobile sources as our transportation systems expand. Although the emissions have fallen in recent decades, present emissions from all transportation sources in the United States still exceed 80 million tons of CO per year, 8 million tons of VOCs, 12 million tons of NO<sub>x</sub>, 0.4 million tons of PM<sub>10</sub> and 0.5 million tons of PM<sub>2.5</sub>.<sup>49</sup>

**TABLE 31.30** Typical Improvements and Costs for Retrofitted Diesel Pollution Control Equipment

Diesel Retrofit Technology	Percentage Decrease in Pollutant Emission				Cost (In 2013 U.S. Dollars)
	PM	NO <sub>x</sub>	HC	CO	
Diesel oxidation catalyst (DOC)	20–40		40–70	40–60	Material: \$600–\$4000 Installation: 1–3 h
Diesel particulate filter (DPF): active or passive	85–95		85–95	50–90	Material: \$8000–\$50,000 Installation: 6–8 h
Partial diesel particulate filter: partial or flow-through	Up to 60		40–75	10–60	Material: \$4000–\$6000 Installation: 6–8 h
Selective catalytic reduction*		≤75			\$10,000–\$20,000 Urea \$0.80 gal <sup>-1</sup>
Closed crankcase ventilation*	Varies				
Exhaust gas recirculation*		25–40			
Lean NO <sub>x</sub> catalyst*		5–40			\$6500–\$10,000

\* Table note: May be combined with diesel oxidation catalyst (DOC) or diesel particulate filter (DPF) systems to reduce PM, HC, and CO emissions.

Source: U.S. Environmental Protection Agency. Technologies: diesel retrofit devices. <http://www.epa.gov/cleandiesel/technologies/retrofits.htm>; 2013 [accessed 10.12.13].

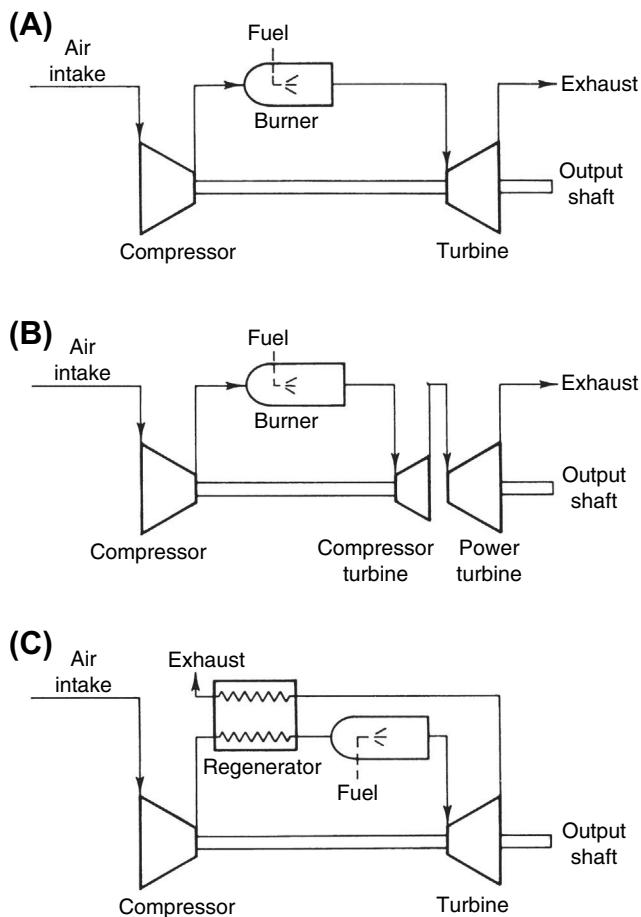


FIGURE 31.21 Schematic and flow of gas turbines (A) simple gas turbine; (B) free-turbine engine; and (C) regenerative gas turbine.

All alternatives should be considered simultaneously to achieve the desired result, an acceptable transportation system with a minimum of air pollution.

Electric drive systems have been tried as a means of achieving propulsion without harmful emissions. Currently, most battery-operated vehicles use lead–acid batteries, which give low power, limited range, and require frequent recharging. In power shortage areas this could be a severe additional load on the electrical system. Sulfuric acid, hydrogen, and oxygen emissions from millions of electric vehicles using lead–acid storage batteries for an energy source would be appreciable. Other types of batteries offer some promise, but their manufacture and costs present obstacles to their widespread automotive use. In fact, the nickel (Ni) based battery systems installed in many hybrid vehicles detract from the vehicles' overall environmental attractiveness. Viewed from a life cycle perspective, the mining of the Ni ore (e.g. from the extensive area near Sudbury, Ontario), the processing of the ore and manufacture of Ni foam, and the shipping of the foam and other components many thousands of kilometers to vehicle assembly

plants present large costs and make for a rather unsustainable network to support the batteries.

Hybrid systems consisting of two or more energy-conversion processes are now being increasingly used in very low-emission vehicles. A constant speed and load internal combustion engine driving a generator with a small battery for load surges could be made to emit less hydrocarbons, CO, and NO<sub>x</sub> than a standard automobile engine, but the cost would be much higher. Other hybrid systems which have been proposed are steam–electric and turbine–electric. The problem associated with hybrid systems is the cost of the two engines plus the cost of the added controls and system integration.<sup>9</sup> However, the prices are beginning to equilibrate, and they have become more attractive to a broader consumer base since they provide a “green” alternative to ordinary internal combustion vehicles.

Fuel cells, which rely on electrochemical generation of electric power, could be used for nonpolluting sources of power for motor vehicles. Since fuel cells are not heat engines, they offer the potential for extremely low emissions with a higher thermal efficiency than internal combustion engines. Basically, a fuel cell converts chemical energy directly into electricity by combining oxygen from the air with hydrogen gas. The cell can keep producing electricity so long as hydrogen is available. The space program has used fuel cells for many decades. However, there are still obstacles to overcome before fuel cells attain widespread use. The federal government and others, especially California, have recently stated strong interests in making fuel cells more mainstream, in the interests of energy savings (and national security), as well as for improvements in air quality.

Probably the ultimate answer to the problem of emissions from millions of private automobiles is an intelligent mix of transportation systems. It must be remembered, however, that even rail systems and bus systems do emit some air pollution. Rail systems are expensive to construct and lack flexibility. A quick calculation of the number of passengers carried per minute past a single point on a freeway in private automobiles will illustrate the difficulties of a rail system in replacing the automobile. Buses offer much greater flexibility at lower cost than rail systems, but in order to operate efficiently and effectively, they would require separate roadway systems and loading stations apart from automobile traffic.

Of course, walking and biking should be encouraged, where appropriate. This requires thoughtful city and regional land use and transportation planning, as well as innovative engineering and architectural designs (e.g. improve bike lanes) that optimize for safety, environmental quality, economic feasibility and energy efficiency.

## QUESTIONS

1. Give three examples of conversion of a pollutant to a less polluting form or substance.
2. List the advantages and disadvantages of handling household waste in a municipal sanitary landfill and using a municipal incinerator.
3. List the advantages and disadvantages of recovering energy, in the form of steam, from a municipal incinerator.
4. Diagram how best to treat and to dispose of the fly ash collected from a municipal incinerator. Assume that the fly ash contains toxic and nontoxic metals, nonmetallic inorganics, and organic halogen compounds.
5. For a given process at a plant, the cost of control can be related to the equation: dollars for control =  $10,000 + 10e^x$ , where  $x$  = percent of control/10. The material collected can be recovered and sold and the income determined from the equation: dollars recovered  $5 \cdot (1000) \cdot (\text{percent of control})$ :
  - a. At what level of control will the control equipment just pay for itself?
  - b. At what level of control will the dollars recovered per dollars of control equipment be the maximum?
  - c. What would be the net cost to the process for increased control from 97.0% to 99.5%?
6. Give an example of changing to a different fuel to decrease an emission of an air pollutant.
7. Give two examples of how improved O&M will result in less PM emissions. Give two examples of how improved O&M will result in less gaseous emissions.
8. Show the chemical reactions involved in simultaneous destruction of an organic compound and an inorganic cyanic compound.
9. You find that there are sulfur compounds, especially mercaptans, in the gas stream of a pesticide plant. What are some candidate control measures that have been applied successfully in another industry that may be applied here?
10. From an air pollution, perspective, what are three disadvantages of burning coal as an energy source?
11. A fluidized gas desulfurization system is designed to operate for 60 days at 92% SO<sub>2</sub> removal, but one average over the past five years falls below this efficiency every 47 days. Calculate its reliability. What factors could be contributing to these reliability problems?
12. Do most FGD coal-fired combustion systems combine SO<sub>2</sub> and PM removal in the same system?
13. What properties of coal have the greatest impact on FGD performance?
14. How do pressure drop, gas velocity and L:G ratios affect FGD performance in removing SO<sub>2</sub> compared to other absorption methods?
15. What happens to entrainment and cost efficiency when gas velocity is decreased in an FGD?
16. How can fly ash be removed before the gas stream enters an FGD?
17. What is the purpose of reheating stack gases in systems using FGD?
18. What are the two physicochemical mechanisms at work in a double-alkali process?
19. In a sodium FGD, when the pH becomes elevated, how does the carbonate scale form?
20. Why is the term "thermal system" preferable to "incineration" in many pollutant destruction processes that use heat?
21. What types of postcombustion controls are available to remove NO<sub>x</sub>?
22. What is a likely candidate to remove acrylonitrile from a gas stream?
23. Why is fluoride produced in the aluminum industry?
24. Would you expect fluoride to be more efficiently removed by a spray screen method or by fluid bed dry scrubber?
25. What do all of the beryllium processing control technologies discussed in this text have common?
26. How have Pb emissions changed in the United States and Europe in the past three decades?
27. What are the two major sources of S that contribute to SO<sub>2</sub> emissions from copper and other metal refining operations?
28. Why are coke oven emissions difficult to address?
29. What is the major pollutant directly produced by agricultural operations? What is the importance of qualifying this question with the term "directly"?
30. What is the major source of odors from pulp and paper operations?
31. How have forest product manufacturers been able to substantially decrease the dioxin in the waste streams?
32. What types of air pollutants are generated by HMA concrete plants? Which process in asphalt production usually accounts for most of the air pollutant emissions?
33. What factors determine the choice of PM controls in a concrete plant?
34. Do emissions from fiberglass manufacturing and from aluminum processing have any factors in common?
35. Why does fiberglass forming have such a high emission factor for PM? Why does a fiberglass regenerative process have such a high emission factor for SO<sub>2</sub>?

36. How can diesel emissions be controlled? How does a flow-through DOC work? How does S-content in the diesel fuel decrease its efficiency?
37. A hood in a factory has a collection/capture efficiency of 92% and a wet scrubber receiving this air stream has a collection efficiency of 95%. If the work in this hood is producing 100 pounds of a pollutant per hour, why do you expect to be stack emissions and the fugitive emissions from this work?
38. What types of pollutants are generally treated with condensation systems?
39. What is the vapor pressure of an organic vapor exiting in the gas stream from a condensation system?
40. Calculate the acetate removal efficiency in a direct contact condensation system at 4.4 °C in a gas stream with 800 ppm acetate.
41. Additives have been used to enhance performance of internal combustion engines. What were/are the drawbacks of Pb-based, Mn-based, and methyl tertiary-butyl ether (MTBE) additives from a systematic view of the environment?
42. Take a walk in an area that has pollution control equipment on roofs. Choose one and take pictures of the equipment from several angles. Determine the direction of flow into and out of the device. Describe the equipment in terms of type(s) of pollutants being collected. Do an investigation to find similar equipment. What are the design specifications and operational requirements? Based on your investigation, report whether this is appropriate for the types and amounts of emissions from this facility. If not, suggest alternate approaches that would be better. Support your answers with sound physics, chemistry, and if applicable, biology. Hint: Approach this systematically, considering improvements to design, O&M and possible prevention and waste reduction options.
43. What is the relationship between adsorption control technology and VOC concentration in the gas stream?
44. Which inherent properties of an organic compound determine its removal efficiency by adsorption?
45. Would you recommend adsorption with activated carbon to remove PCBs from a gas stream? How about trichloroethylene?
46. Explain the relationship between surface attraction and energy, both potential and kinetic, during adsorption and desorption of VOCs. How does this explain why adsorbed VOCs are often thermally desorbed?
47. What factors determine a compound's adsorption isotherm?

48. What is the LEL and why must it be known when using sorption control technologies for organic vapors?

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## P A R T V I

# THE FUTURE FOR AIR POLLUTION SCIENCE AND ENGINEERING

Environmental science and engineering are evolving endeavors. When public and scientific interests began to accelerate in the second half of the twentieth century, pollutants of any type and in any environmental compartment were addressed on a contaminant-by-contaminant control basis. Each law and regulation addressed a single compartment. As evidence, the U.S. Congress passed the Clean Air Act for air, the Clean Water Act for water, and so on. During the 1980s, this command and control paradigm continued, but added at least an acknowledgment for the need to prevent pollution and to minimize the volume and toxicity of wastes. All of these, along with subsequent life cycle approaches, have been aimed at reducing risks to acceptable levels.

Toxic substances, including the hazardous air pollutants, also had to be addressed. Since the first editions of this book, pollution prevention and green engineering have become mainstays in every environmental field, including air pollution science and engineering. Greener, more sustainable, and systems approaches that incorporate natural processes and that mimic and borrow from those processes have received attention from researchers and practitioners alike.

An important challenge is to improve the metrics used to evaluate air quality outcomes in light of the scientific advances. As evidence, the notion of life cycle introduced in Chapter 5 and discussed throughout this book is often, arguably too often, based on a cost–benefit economic model of demonstrating the return on investment that can be expected over the life of a system. While this approach is crucial to applying a financial model to demonstrate the return on investment of air quality options, the concept must also be applied beyond the comparison of initial investment as a fraction of the total cost of operating and maintaining a system. It must also evolve to include an expanded definition beyond pure economics.

Decisions about air quality must account for the less tangible impacts on the individual, society, and ecology that may not fit neatly in a data spreadsheet. On this point, the environment is usually deferential to economics. This is odd, given a choice of a healthier environment or more money, many of us would and do choose the latter. Part of this has to do with the metrics mentioned above. How we measure and describe air quality does indeed influence the value it receives.

The critical path of engineering and other design professions that view a project from conception to completion has changed very little over the thousands of years since man began to shape the environment to create shelter from the elements. The first builders harvested locally available materials and assemblies grew from trial and error and observation of the structures found in nature. Trial and error created the feedback loop that guided the technical development of these structures. Codifying existing practice on topics ranging from building materials to proportional relationships based on the human body, the text served as an influential reference for centuries. Vitruvius wrote of architecture as an imitation of nature and a central tenant of his writing was the suggestion that structure must contain three essential qualities, “firmitas, utilitas and venustas”. *Firmitas* translated from Latin is firmness or strength, *utilitas* suggests commodity or usefulness, and *venustus* is a quality of delight or beauty.<sup>1</sup>

The ideal air quality perspective is one that envisions an optimal level of air quality, and then lays out all the necessary steps to achieve that desired state, including the physical and social sciences. The result must not only be acceptable within the rigid confines of science, but must also include the values held dear by society. The scientific revolution during the Renaissance did not distinguish boundaries between the roles of artist, architect, and engineer. The Renaissance master builder

was the evidence of an evolution of the rationalizing of the process with the introduction of science and engineering principles. The emergence of architectural treatises, increased physical challenges of larger spans, and a desire for increasingly rich aesthetic expression all contributed to the growing complexity in navigating this pathway from conception to completion. The master builder of the Renaissance played the roles of architect, engineer, material scientist, and builder, simultaneously serving as the source of inspiration, technical resolution, and achievement and maintenance of the desired state. This is understandably a daunting and tall order for those who are steeped in technical knowledge, who shy from the perceived “softness” or subjectivity of the social sciences and humanities. However, this is the milieu in which air quality decisions are made.

This book ends on an optimistic note, i.e. one that envisions a more systematic and sustainable approach to air quality. The grand challenges for engineers, scientists, and others engaged in air quality careers call for a systems approach. This approach must, however, be based on a solid foundation. The foundation is a sound understanding of the physical, chemical, biological, and engineering fundamentals of air pollution.

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# Sustainable Approaches

## 32.1 INTRODUCTION

The immediacy and urgency of the pollution problems in the 1950s and 1960s led to an air quality strategy that focused mainly on cleaning up existing problems. There were numerous episodes in which people were suffering from the acute problems associated with high concentrations of what are now known as conventional or criteria pollutants, especially particulate matter (PM), carbon monoxide (CO), nitrogen dioxide ( $\text{NO}_2$ ) and sulfur dioxide ( $\text{SO}_2$ ), as well as what was collectively known as "smog".

The remediation that was needed allowed little time and effort devoted to preventing the pollution in the first place. As engineers so often do, they dedicated their skills and creativity to finding ways to remove and treat the pollutants. Their success in this effort over that past half-century is nothing short of phenomenal. The technologies described in Chapters 29, 30, and 31 for the most part did not exist in 1960 and, if they did, they were rudimentary means of testing for and cleaning up air pollution. Indeed, when this effort started, only the most noticeable and easily measured pollutants were even addressed. And, when this was done, it was at detection levels at several orders of magnitude higher than health and environmental thresholds.

As measurement, control technologies, and predictive and descriptive models have improved, there has been a growing, commensurate capacity to begin to think about ways to address problems before they begin. This can be traced to an evolution of engineering air pollution controls. This evolution was not just in better methods, but also in a new engineering and science ethos. The end-of-stack technologies continue to be as important as ever and continue to improve in efficiency and effectiveness. However, the ethos today also includes a more systematic view of the pollutant, the environment and the receptors of the pollutant (see Figure 32.1).

There are numerous industrial, commercial, and governmental green initiatives, including design for

the environment (DfE), design for disassembly (DfD) and design for recycling (DfR).<sup>2a,2b</sup> As shown in Figure 32.1, adhering to a systems view begins with concern about future generations, i.e. it is not only important to achieve an acceptable condition but that the level of acceptability be sustained. Solving an immediate problem may well be unacceptable if it leads to consequences in time. It is preferable to avoid air pollution than to treat it. DfD is a mindset that is akin to the engineering concept of reliability. Sustainable engineering must consider the time horizon before and after the useful life of a device or system.

Engineering reliability is based on a "failure density", or  $f(t)$ , which is a function of the likelihood that an adverse outcome will occur, but note that it is not a function of the severity of the outcome. The  $f(t)$  is not affected by whether the outcome is very severe (complete shutdown of all pollution control equipment) or relatively benign (unforeseen need for cartridge replacement). The likelihood that something will fail at a given time interval can be found by integrating the hazard rate over a defined time interval:

$$P\left\{t_1 \leq T_f \leq t_2\right\} = \int_{t_1}^{t_2} f(t)dt \quad (32.1)$$

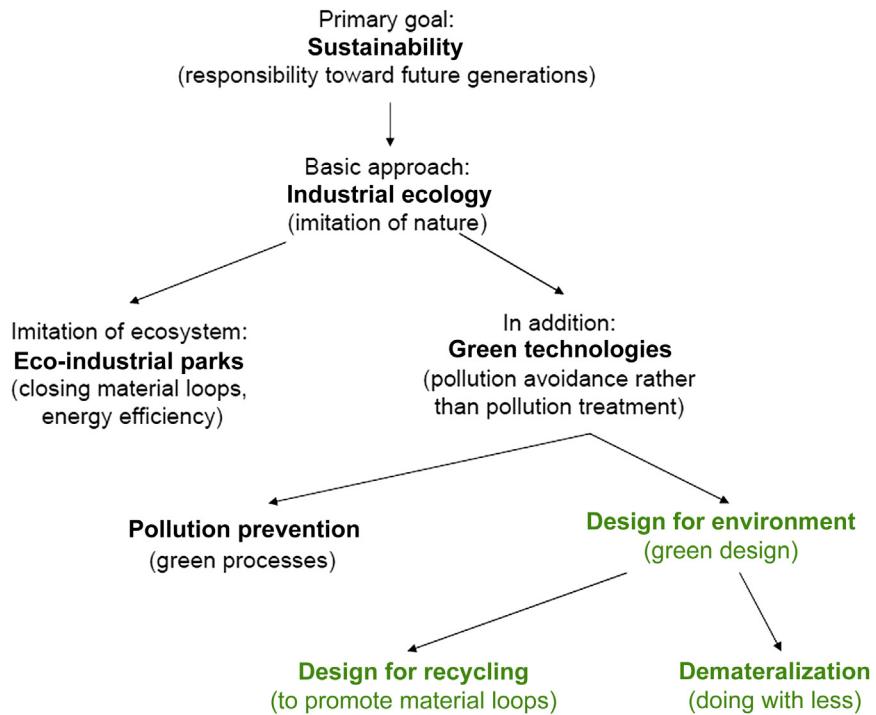
where  $T_f$  = time of failure.

Thus, the reliability function  $R(t)$  of a system at time  $t$  is the cumulative probability that the system has not failed in the time interval from  $t_0$  to  $t$ :

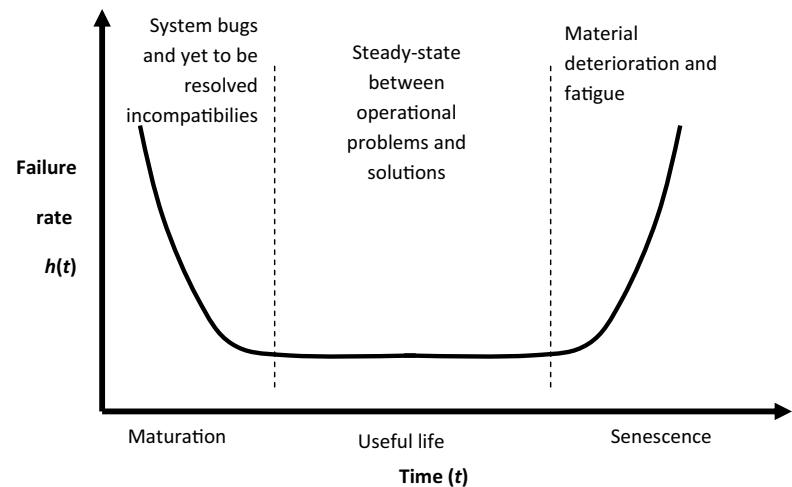
$$R(t) = P\left\{T_f \geq t\right\} = 1 - \int_0^t f(x)dx \quad (32.2)$$

Reliability can be improved by extending the time (increasing  $t_f$ ), thereby making the system more resistant to failure. For example, proper engineering design of a cyclone by limiting the number of moving parts may extend the expected life for decades. However, the design cannot completely eliminate failure, i.e.  $R(t) = 0$ ;

**FIGURE 32.1** Systems approaches to air pollution, beginning with a sustainable view. The green lettering indicates decisions that have to be made very early in the corporate decision-making process. Ref. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the online version of this book.)



**FIGURE 32.2** Prototypical reliability curve, i.e. the **bathtub distribution**. The highest rates of failure,  $h(t)$ , occur during the early stages of system implementation and when the systems, processes, or equipment become obsolete or being to deteriorate. For well-designed systems, the steady state period can be protracted, e.g. decades. *Vallero DA. Paradigms lost: learning from environmental mistakes, mishaps, and misdeeds. Burlington, Massachusetts: Butterworth-Heinemann; 2005.*



it simply protracts the time before the failure occurs (increases  $T_f$ ). Even with the simple cyclone, it can be damaged by natural catastrophes or, more likely, by corrosion from chemicals in the gas stream.

Equation (32.2) illustrates built-in vulnerabilities, such as unscientifically sound facility siting practices or the inclusion of inappropriate design criteria, e.g. cheapest land. Such mistakes or malpractice shortens the time before a failure. Thus, reliability is also a term of efficiency. Lack of insight to recognize these

inefficiencies upfront leads to premature failures (e.g. power failures to the electrostatic precipitator, unexpected chemical compounds in the gas stream that foul a catalytic converter, or operator errors).

The common graphical representation of engineering reliability is the so-called bathtub curve (Figure 32.2). The U-shape indicates that failure will more likely occur at the beginning and near the end of the life of a system, process, or equipment. The flaw of the reliability curve is that it implies that the process only begins after we are

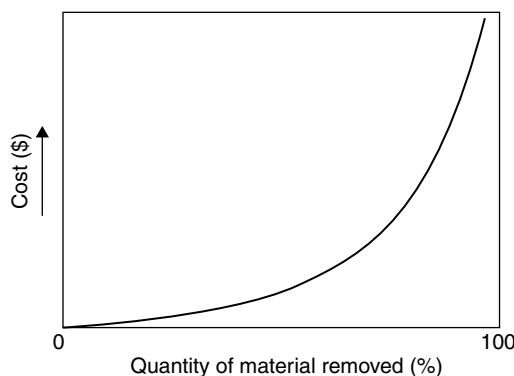


FIGURE 32.3 Hypothetical cost curve for pollution control equipment.

called on to design a solution. Indeed, failure can occur even before the proposals for control equipment are written. Perhaps, given corporate inertia, the optimal approach had been eliminated for reasons of immediacy and initial costs. In this case, the engineer may not have even considered what would have been the best option.

When selecting pollution control equipment, for example, one of the selection criteria should be to have a strategy to address what remains after the equipment's function has ceased, e.g. will long-term disposal or special handling be needed (such as radioactive isotopes in monitoring equipment and potentially toxic materials in control equipment filters and cartridges). Obviously, the best strategy is to have nothing to address, i.e. zero waste at end-of-life. The DfD and DfR approaches require that the entire life cycle be considered before installation, especially the times near the end of useful life of the system. For example, is the control device merely shifting the environmental burden to another part of the environment, e.g. making an air pollutant into a solid waste or water pollutant?

These rubrics sometimes replace, but often are integrated with the traditional pollution control paradigms. Thus, the present era of air pollution control is transitional between the traditional, retroactive "collection and treatment" approach and a fully regenerative and sustainable approach. The application of the control technologies discussed in Chapters 30 and 31 involves numerous variables. Some are objective and science based. Others concern costs and feasibility. Still others are policy and rules based. The cost of controlling any given air pollution source is usually an exponential function of the percentage of control and therefore becomes an important consideration in the level of control required. Figure 32.3 shows a typical cost curve for control equipment.

If the material recovered has some economic value, the picture is different. Figure 32.4 shows the previous cost of control with the value recovered curve

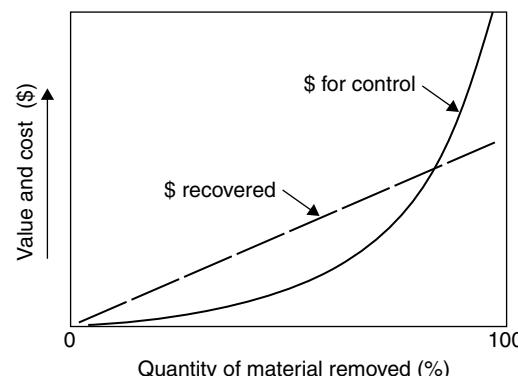


FIGURE 32.4 Hypothetical cost curve for pollution control equipment, with value recovered.

superimposed on it. The plant manager looking at such a curve will strive to operate in the region to the left of the intersection of the two curves, whereas the local air pollution forces would insist on operation as far to the right of the graph as the best available control technology would allow.

Control of any air pollution source requires a complete knowledge of the contaminant and the source. Preventing the formation of a pollutant also requires an understanding of the physical and chemical properties of the precursors of that pollutant and the conditions that promote or inhibit its formation. Thus, the engineers controlling the source must be thoroughly familiar with all available physical and chemical data on the effluent from the source. They must know the rules and regulations of the control agencies involved, including not only the Air Pollution Control Agency but also any agencies that may have jurisdiction over the construction, operation, and final disposal of the waste from the source.<sup>3</sup>

In many cases, heating or cooling of the gaseous effluent will be required before it enters the control device. To develop a satisfactory design, the engineer must be thoroughly aware of the gas laws, thermodynamic properties, and reactions involved. For example, if a gas is cooled there will be condensation when the temperature drops below the dew point. If water is sprayed into the hot gas for cooling, it adds greatly to the specific volume of the mixture. As the gases pass through hoods, ducts, fans, and control equipment, temperatures and pressures change and hence, also, specific volumes and velocities.<sup>4</sup>

## 32.2 UTILITY AND THE BENEFIT–COST ANALYSIS

On the surface, the choice of whether to pursue an air pollution control option is a simple matter of benefits vs

costs. Is it more or less costly to control the emissions of air pollutant "A" using approach "1", "2", or "n"? Engineers make much use of the benefit-cost ratio (BCR), owing to a strong affinity for objective measures of successes. Thus, utility is an engineering measure of success of any successful engineering enterprise. After all, engineers are expected to provide reasonable and useful products. Two useful engineering definitions of utilitarianism (Latin *utilis*, useful) are imbedded in BCR and life cycle analysis (LCA):

1. The belief that the value of a thing or an action is determined by its utility.
2. The concept that effort should be directed toward achieving the most benefit for the greatest number.

The BCR is a useful metric due to its simplicity and seeming transparency. To determine whether a project is worthwhile, one simply sums all of the benefits and puts them in the numerator and sums all of the costs and puts them in the denominator. If the ratio is greater than 1, the option's benefits exceed its costs.

One obvious problem with the BCR is that some costs and benefits are much easier to quantify than others. Some, like those associated with quality of life, are nearly impossible to quantify and monetize accurately. Further, the comparison of action vs no-action alternatives cannot always be captured within a BCR. Opportunity costs and risks are associated with taking no action and staying with the status quo (e.g. not applying a new technology may miss an opportunity for improved efficiency).

Simply comparing the status quo to costs and risks associated with a new technology may be biased toward no action or proven technologies. Costs in time and money are not the only reasons for avoiding action. The new technology may have problems over time that are not yet apparent from experience with limited applications.

Often, selecting a critical path, including various waste streams, is a matter of optimization, which is proven analytical tool in engineering. However, the greater the number of contravening risks that are possible, the more complicated such optimization routines become. As seen in Chapter 5, the product flows, critical paths, and life cycle inventories of various options can become quite complicated for complex problems, such as decisions about the optimal sources of energy.

Alternative fuels provide an illustrative example of these complexities. The greater availability of ethanol may introduce unforeseen risks that, if not managed properly, could interfere with quality of life of distant and future populations and could add costs to the public (e.g. air pollutants and topsoil loss) with little or no net benefit. So it is not simply a matter of benefits *versus* cost; it is often a matter of trading one risk for another.

Generally, addressing a contravening risk is a matter of optimization, which is a proven analytical tool in engineering. However, the greater the number of contravening risks that are possible, the more complicated such optimization routines become.

The product flows, critical paths, material manifests, and inventories can become quite large and uncertain for complex issues like selecting fuels that meet environmental, societal, and economic demands. Indeed, one of the present challenges of LCA approaches discussed in Chapter 5 is having a reliable life cycle inventory (LCI). To date, LCIs have often been proprietary, limited in available material and energy data for numerous processes, and devoid of general standards for quality. In particular, LCIs contain very little information about product usage and potential exposure to the ingredients in products. There is progress in this area; such as the establishment of the US LCI Database by the National Renewable Energy Laboratory. This effort is finding ways to develop publicly available LCI data modules for commonly used materials, products, and processes. These data will support efforts to develop product LCA-based decision support systems and tools. It will also provide benchmark data for generating or assessing company, plant, or new technology data, as well as to provide for a broad data resource base for conducting LCAs generally.<sup>5</sup> Risk trade-off is likely to occur in ethanol and biofuel decisions. For example, when regulatory agencies mandate more ethanol usage, they must also enforce new air pollution laws associated with the fuel. These added regulations can be associated with indirect, countervailing risks. As a result, new facilities will likely need to be constructed (see Figure 32.5), each with its costs and pollution emissions. These costs and emission may not be well understood since the technologies are either new or scaled up substantially. In addition, the price of feedstock (especially corn in the case of corn-based ethanol) may increase safety risks via "income" and "stock" effects.

The income effect results from decreasing funds for other fuel ventures to pay the capital costs associated with ethanol, which makes it more difficult for a company or backers to invest in other services that would have provided improved fuel efficiency. The stock effect results when the capital costs increase to a point where companies have to wait to purchase new facilities, so they are left with substandard manufacturing. Thus, the engineer is frequently asked to optimize for two or more conflicting variables in many situations. The success of ethanol in displacing fossil fuels depends on the efficiency with which it can be produced and used. Complicating matters, the use of fossil fuels in their production and/or operation is part of ethanol production, as it is for all biofuels. Societal benefits and costs are tied to ethanol's energy balances.



**FIGURE 32.5 Ethanol processing facility in Illinois.** Note the large silos to store the grain. (For color version of this figure, the reader is referred to the online version of this book.)

Another accountability challenge is whether losses are included in calculations. From a thermodynamics standpoint, the nation's increased ethanol use could actually increase demands for fossil fuels, such as the need for crude oil-based infrastructures, including farm chemicals derived from oil, farm vehicle, and equipment energy use (planting, cultivation, harvesting, and transport to markets) dependent on gasoline and diesel fuels, and even embedded energy needs in the ethanol processing facility (crude oil-derived chemicals needed for catalysis, purification, fuel mixing, and refining). A comprehensive LCA is a vital tool for ascertaining the actual efficiencies.<sup>a</sup>

The questions surrounding alternative fuels and ethanol, specifically, can be addressed using a three-step methodology. First, the efficiency calculations must conform to the physical laws, especially those of thermodynamics and motion. Second, the “greenness”, as a metric of sustainability and effectiveness can be characterized by LCAs. Third, the policy and geopolitical options and outcomes can be evaluated by decision force field analyses. In fact, these three approaches are sequential. The first must be satisfied before moving to the second. Likewise, the third depends on the first two methods. No matter how politically attractive or favorable by society, an alternative fuel must comport with the conservation of mass and energy. Further, each step in the life cycle (e.g. extraction of raw materials, value-added manufacturing, use, and disposal) must be considered in any benefit–cost or risk–benefit analysis. Finally, the societal benefits and risks must be

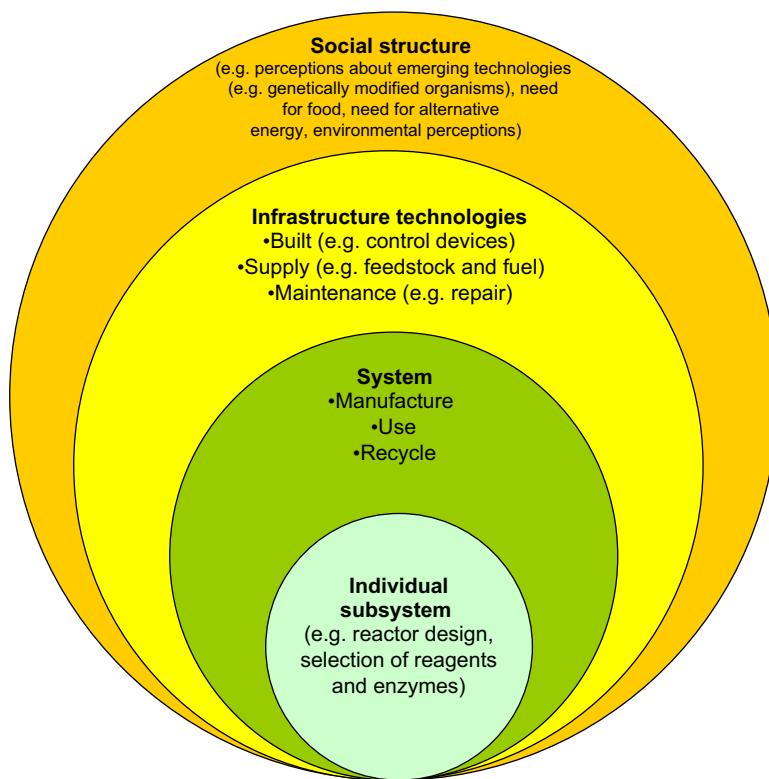
viable for an alternative fuel to be accepted. Thus, even a very efficient and effective fuel may be rejected for societal reasons (e.g. religious, cultural, historical, or ethical).

The challenge of the scientist, engineer, and policy maker is to sift through the myriad data and information to ascertain whether ethanol truly presents a viable alternative fuel. Of the misrepresentations being made, some clearly violate the physical laws. Many ignore or do not provide correct weights to certain factors in the life cycle. There is always the risk of mischaracterizing the social good or costs, a common problem with the use of benefit–cost relationships.

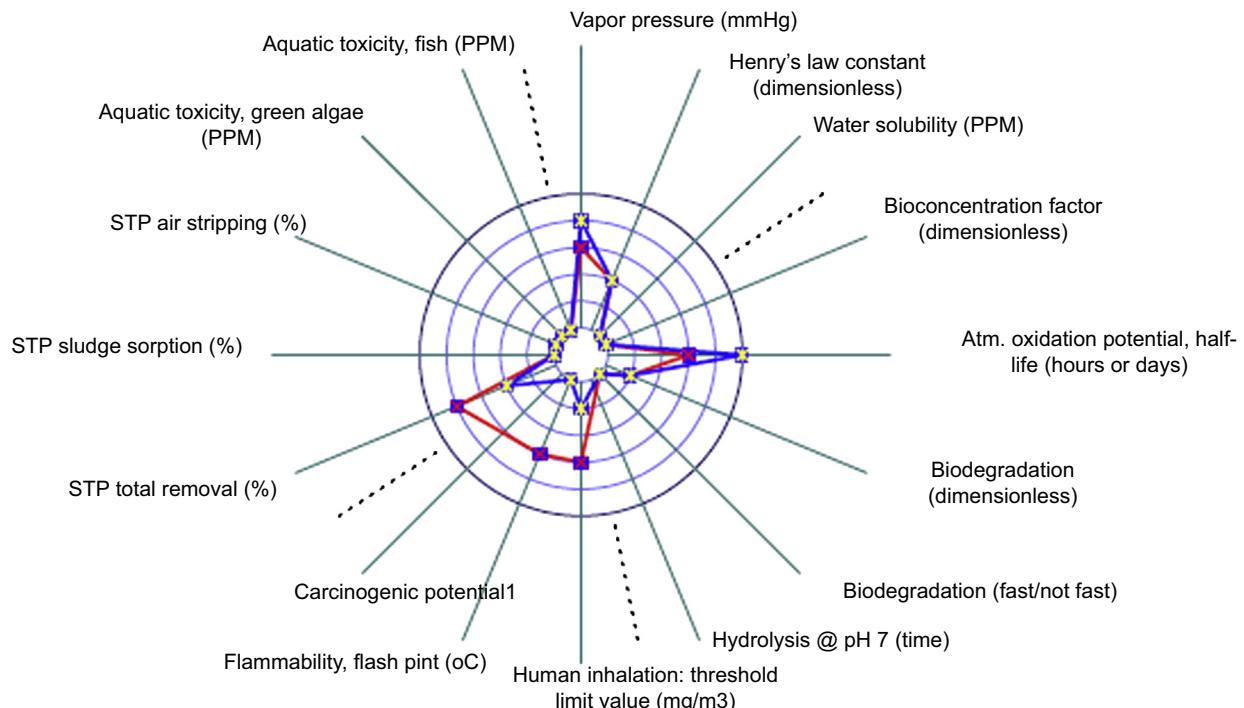
Industrial ecology employs the life cycle, including the technical intricacies involved in manufacturing, using and decommissioning of a product or system, the infrastructure technologies need to support the product, and the social structure in which the product is made and used (see Figure 32.6). The factory or other facility must be viewed within the context of spheres of influence; the processes influence and are influenced by each adjacent sphere.

Decision force fields can be adapted specifically to sustainable designs. For example, if the primary concern is managing the emissions of hazardous air pollutants (HAPs), decision force fields can be based on the various physical and chemical properties of a substance using a multiple objective plot (see Figure 32.7). Here, two different products can be visually compared in terms of the sustainability, based on toxicity (carcinogenicity), mobility, and partitioning

<sup>a</sup> Another indirect impact of ethanol fuel switching involves operation and maintenance (O&M) costs. Very commonly, O&M is not effectively valued in cost and risk comparisons. For example, ethanol may be much more damaging to fuel systems, such as clogging jets in carburetors and fuel lines, especially in small engines. These additional costs must be part of any LCA, benefit/cost ratios, or other decision tool.



**FIGURE 32.6 Spheres or layers of influence in a system.** The system consists of interdependencies among each layer. (For color version of this figure, the reader is referred to the online version of this book.) *Adapted from: Allenby BR, Graedel TE. Industrial ecology. New York (NY): Prentice Hall; 1995.*



**FIGURE 32.7 Hypothetical multiple objective plot of two candidate reagents that can be used to manufacture the same product.** Both reagents appear to have an affinity for the air. Product #1 (open squares) has a larger half-life (i.e. is more persistent), whereas product #2 (closed squares) is more carcinogenic, flammable, and likely to be taken up by the lungs. Based on these factors, it appears, at least at the screening level, that product #1 is comparatively better from a sustainability standpoint. (For color version of this figure, the reader is referred to the online version of this book.) *Crittenden J. (used with permission).*

(e.g. sorption, vapor pressure, and Henry's law constants), persistence, and treatability by different methods (e.g. wastewater treatment facilities, pump and treat, etc.). The shape of the curve and the size of the peaks are relative indicators of toxicity and persistence of a potential problem (the inverse of sustainability of healthy conditions).

The plot criteria are selected to provide an estimate of the comparative sustainability of candidate products. It is important to tailor the criteria to the design needs. In the instance of Figure 32.7, this is mainly addressing the toxic hazard and risk of the substances<sup>6</sup>:

*Vapor pressure*—This sector is a chemical property that tells us the potential of the chemical to become airborne. The low end of the scale is  $10^{-8}$  mmHg; high end is  $10^2$  mmHg and above.

*Henry's law*—This property tells us how the chemical partitions in air and water. Nonvolatile substances have a value of  $4 \times 10^{-7}$  (unitless), moderate volatility is between  $4 \times 10^{-4}$  and  $4 \times 10^{-2}$ , and volatile chemicals are at or above 4. The values are limitless because they are a ratio of concentration in air and water.

*Solubility*—This property alludes to the potential of the chemical to enter water. Very soluble chemicals are on the order of 10,000 ppm and nonsoluble entities have aqueous solubility less than 0.1 ppm.

*Bioconcentration*—This sector specifies the tendency/potential of the chemical to be taken up by biological entities (algae, fish, animals, humans, etc.). A low potential is defined as 250 (unitless) or less, while a high potential is found at 1000 or above.

*Atmospheric oxidation, half-life (days)*—This property helps to define the fate of the chemical once it enters the atmosphere. A short half-life is desirable as the chemical will have little time to cause adverse effects. A rapid half-life would be on the order of 2 h or less. A slow half-life is between 1 and 10 days; longer than 10 days is a persistent chemical.

*Biodegradation*—This sector defines the ability of the environment to break down the chemical. A short biodegradation time is ideal so that the chemical does not persist. There are two sectors of biodegradation; one is dimensionless and one has units of time. A biodegradation factor on the order of hours is very quick, whereas a factor on the order of years is long.

*Hydrolysis*—This describes the potential of the chemical to be broken down into a by-product and water. It has units of time for a pH of 7. A long hydrolysis time is on the order of many years.

*Flammability*—This describes the chemical's flash point (degrees Centigrade).

*Human inhalation*—This defines the threshold limit for inhalation of the chemical below which there will be no observed effect in humans; 500 mg m<sup>-3</sup> and above is a high concentration for which there is little effect. The

chemical becomes more of a problem when the limit is 50 mg m<sup>-3</sup> or less.

*Carcinogenicity*—This is the potential for the chemical to cause cancer. This data is usually somewhat uncertain due to inaccurate dose-response curves.

*Sewage treatment plant (STP) total removal*—This is the percentage of the chemical that is removed in a wastewater treatment process; 90–100% removal is desirable, whereas 0–10% removal describes a chemical that is tough to treat.

*STP sludge sorption*—This is a percentage of how much of the chemical will adsorb to the sludge in a wastewater treatment plant. This can be important when the sludge is disposed in a landfill or agriculturally land applied. About 0–10% sorption is ideal so that the chemical does not get recycled back to the environment; 90–100% sorption to sludge solids makes disposal difficult.

*STP air removal*—A percentage of the chemical that is removed to the air from waste water treatment. About 0–10% is ideal so that little extra air treatment is needed; 90–100% air removal requires significant air treatment.

*Aquatic toxicity (green algae) (parts per million)*—This sector defines the chemical's toxicity to green algae. A toxic effect on algae can disrupt the entire food chain of an ecosystem. Toxicity is measured on a concentration scale. A low toxicity would be at high concentrations ( $>100$  ppm). A high toxicity would be at concentrations on the parts per billion or parts per trillion scale.

*Aquatic toxicity (fish) (parts per million)*—This defines the toxicity of the chemical to a specific fish species. For example, in the Pacific Northwest, a chemical that is toxic to salmon can cause millions of dollars in economic damage. A low toxicity would be at high concentrations ( $>100$  ppm). A high toxicity would be at concentrations on the parts per billion or parts per trillion scale.

Certainly, green design considers more than toxicity. The ecosystem view calls for a search for materials and processes that improve recycling and reuse, avoid consumer misuse and consider disassembly. These can also be evaluated using multiple objective plots. The best of these can be considered the benchmark, which is a type of index that conveniently displays numerous factors with appropriate weightings. A weakness of this approach is the reliance on inherent human and aquatic toxicity, rather than cumulative risk. Although inhalation is one of the criteria, other exposure routes and pathways, e.g. ingestion and dermal, must be included in a comprehensive LCA.

A way to visualize the interrelationships within and between factors represented by such complex data is the decision matrix. The matrix helps to ensure that all of the right factors are considered in the planning and design phase and that these factors are properly

implemented and monitored throughout the project. Integrated engineering approaches require that the engineer's responsibilities extend well beyond the construction, operation, and maintenance stages. This approach has been articulated by the American Society of Mechanical Engineers. The integrated matrix helps DfE to be visualized, which allows for the engineer to see the technical and other factors associated with each component of the design, as well as the relationships among these components. For example, health risks, social expectations and environmental impacts, and other societal risks and benefits associated with a device, structure, product, or activity can be visualized at various stages of the manufacturing, marketing, and application stages. This yields a number of two-dimensional matrices (see Figure 32.8) for each relevant design component.

And, each respective cell indicates both the importance of that component but the confidence (expressed as scientific certainty) that the engineer can have about the underlying information used to assess the importance (see legend to Figure 32.8).

The matrix approach is qualitative or at best semi-quantitative, but like the multiple objective plots, provides a benchmark for comparing alternatives that would otherwise be incomparable. To some extent, even numerical values can be assigned to each cell to compare them quantitatively, but the results are at the discretion of the analyst, who determines how different areas are weighted. The matrix approach can also focus on design for a more specific measure, such as energy efficiency or product safety, and can be extended to corporate activities as a system.

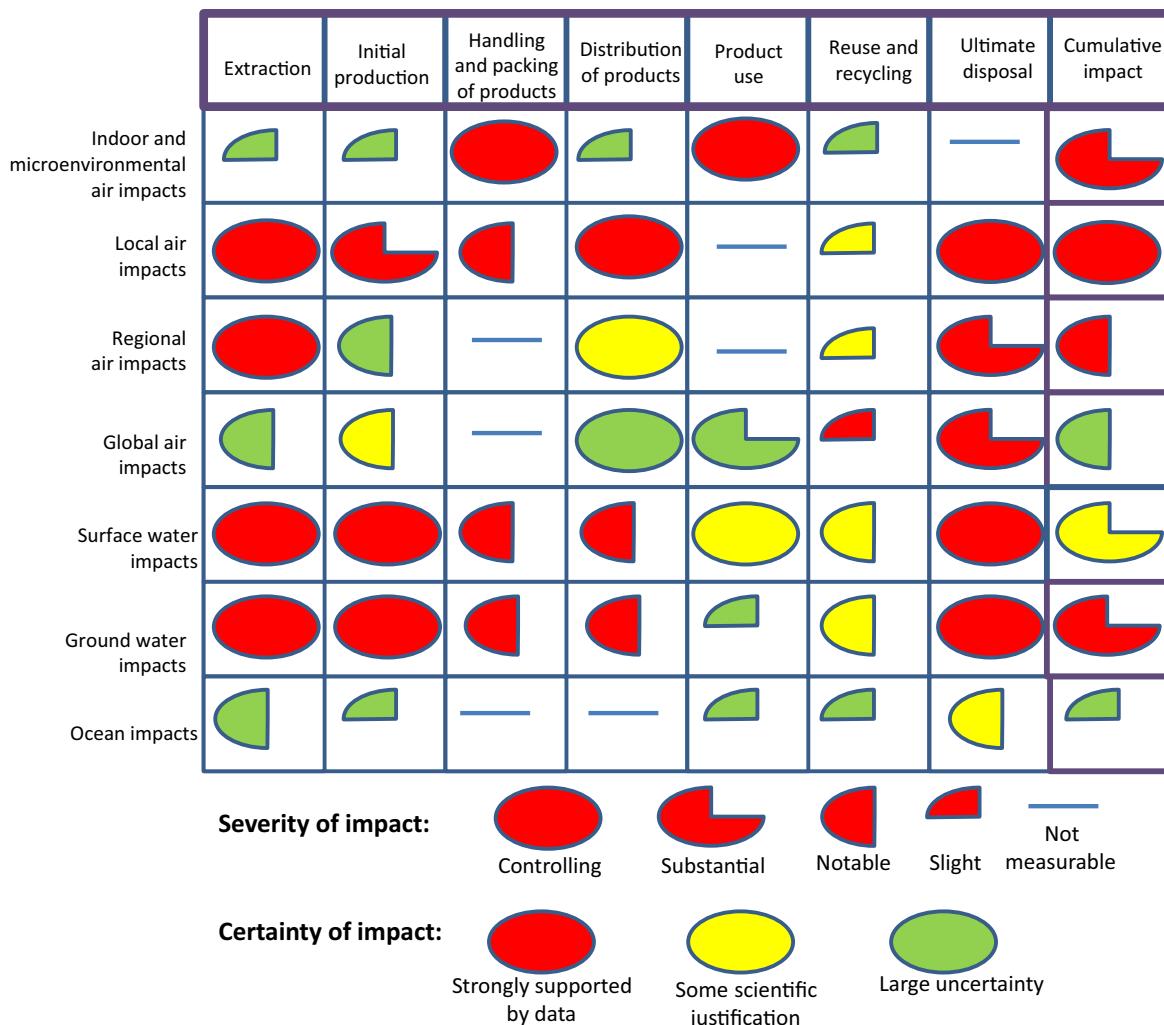


FIGURE 32.8 An engineering matrix used to characterize the sustainability of a hypothetical product. In this case, the product is associated with personal and regional air pollution, as well as with other environmental impacts. Note: This figure differs substantially, but was inspired by one previously used by the American Society of Mechanical Engineers in a professional development course on sustainable design. (For color version of this figure, the reader is referred to the online version of this book.) American Society of Mechanical Engineers; <http://www.professionalpractice.asme.org/communications/sustainability/2.htm>; [accessed 25.05.06].

The key point about benchmarking is the importance of a systematic and prospective viewpoint in design. Whatever tools we can use to help us to model and to predict consequences of available alternatives is an important aspect of green design.

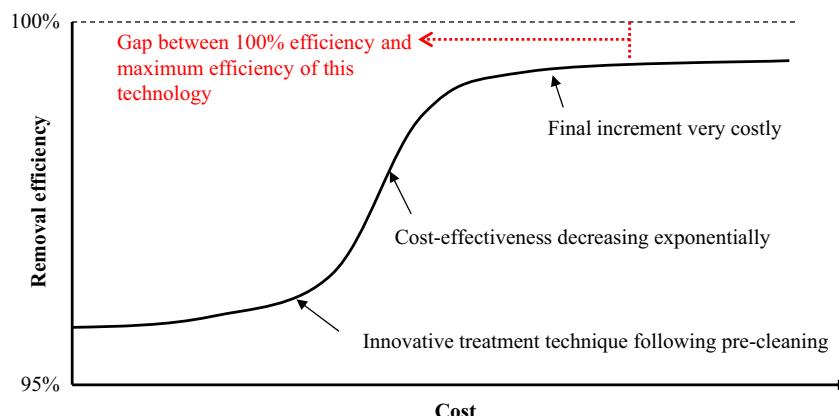
The emissions trading programs, e.g. netting, offsets, bubbles, and banking, mentioned in Chapter 29 have been tested and work well for some pollutants. In many cases, less pollution is produced using these innovative methods than with the traditional “stack-by-stack” and “pipe-by-pipe” approach, i.e. pollution command and control. Such policy and regulatory innovations call for some improved technology-based approaches as well as better quality-based approaches, such as leveling out the pollutant loadings and using less expensive technologies to remove the first large bulk of pollutants, followed by higher operations and maintenance (O&M) technologies for the more difficult to treat stacks and pipes. But, the net effect can be a greater reduction of pollutant emissions and effluents than treating each stack or pipe as an independent entity. This is a foundation for most sustainable design approaches, i.e. conducting a LCA, prioritizing the most important problems, and matching the technologies and operations to address them. The problems will vary by size (e.g. pollutant loading), difficulty in treating, and feasibility. The easiest ones are the big ones that are easy to treat (so-called low hanging fruit). By doing the first successfully, good will and confidence grows, which may help overcome the corporate inertia need to address the more difficult problems. However, the most intractable problems are often those that are small but very expensive and difficult to treat, i.e. less feasible. This is a common problem in pollution control. The first increments of removal or treatment are relatively inexpensive and achievable with off-the-shelf technologies, but the cost-efficiency ratio increases substantially and becomes quasi-asymptotic with each increment of removal (see [Figure 32.9](#), which modifies

the typical cost curve discussed in Chapter 4 to show the combination of technical and cost constraints when selecting pollution control equipment). Thus, the environmental science requires that expectations be managed from both a technical and an operational perspective.

The selection of any pollution control technology is based on the intrinsic characteristics of the contaminants and on the substrate in which they reside. The choice must factor in all of the physical, chemical, and biological characteristics of the contaminant with respect to the matrices and substrates (e.g. if sorbed to PM, the particle shape and diameter) and the characteristics of the gas stream (air and other gases and suspended PM).

Eliminating or reducing pollutant concentrations begins with assessing the physical and chemical characteristics of each contaminant, and matching these characteristics with the appropriate treatment technology. All of the kinetics and equilibria discussed in Part II, such as solubility, fugacity, sorption, and bioaccumulation factors, will determine the effectiveness of destruction, transformation, removal, and immobilization of these contaminants. There can be synergies (e.g. innovative incineration approaches are available that not only effectively destroy organic contaminants, but in the process also destroys the inorganic cyanic compounds). Unfortunately, there are also antagonisms among certain approaches, such as the very effective incineration processes for organic contaminants that transform heavy metal species into more toxic and more mobile forms. Increasing pressures and temperatures not only degrade organic molecules and remove functional groups that make for more toxic and bioaccumulating compounds, but may also oxidize or in other ways transform the metals into more toxic forms.

Thus, elevated concentrations of organic compounds or heavy metals are an example of a constraint in selecting controls or changing processes. Certainly, proper air



**FIGURE 32.9** Hypothetical cost-efficiency curve of an advanced air pollution removal device following pre-cleaning (e.g. by a cyclone). The initially 96% removal efficiency is achieved at much less cost than the remaining 4%. In this case, removal >99% is not only expensive but also unattainable technically, i.e. removal efficiency has reached an asymptote. (For color version of this figure, the reader is referred to the online version of this book.)

pollution prevention and control must account for the entire life cycle of a potential hazard.<sup>7</sup> Off-the-shelf models can be used for simple process operations, such as extraction or thermal vaporization applied to single contaminants in relatively pure systems. However, such models have not been appropriately evaluated for a number of other technologies because of the limited database on treatment technologies for many pollutants. This requires a comprehensive review of the state-of-the-science to ensure the data and models indeed apply to the setting and treatment scenarios at hand. If very similar scenarios and data are not available, testing under the actual manufacturing conditions is likely need.

The emerging discipline of industrial ecology acknowledges this need for a more encompassing, systems view. The entire manufacturing process can be viewed as an ecosystem. This manufacturing ecosystem perspective has a very different set of environmental performance metrics than the tradition compartmental approach. This is based on finding opportunities for improvement across the breadth of the entire enterprise, including devices, installation, operations, cleaning, upkeep, change-outs, and other operations and processes across all facilities and buildings. Traditionally, such elements have been typically considered separately and often independently, including span of control of the people. This view calls for the integration of the flows of resources spanning the disciplines of manufacturing engineers, energy and facility engineers, building architects, O&M personnel and managers. This systems perspective of a factory can be measured and predicted using models of the material, energy, and waste (MEW) flows. The MEW flows integrate manufacturing operations, supporting facilities, and operations.<sup>8</sup>

The MEW perspective is also useful for occupational safety and health. Segregation of processes from humans may be accomplished by designing sections of the facility to be operated without the need for humans to habitate them. Obviously, this is done in the heavy industrial sections where temperature, pressure, and chemical concentrations are very high. However, it could also include other functions that are aligned. These areas would not only be able to have higher concentrations of PM and gas-phase compounds, but could even be free of oxygen, e.g. pure N<sub>2</sub> assembly areas that would eliminate oxidation and improve fire safety while also lowering the likelihood of product contamination.<sup>1</sup>

The control of atmospheric emissions from a process will generally take one of three forms depending on the process, fuel, types, availability of control equipment, etc. The three general methods are (1) process change to a less polluting process or to lowered emission from the existing process through a modification or

change in operation, (2) change to a fuel that will give the desired level of emissions, and (3) installation of control equipment between the point of pollutant generation and its release to the atmosphere. Control may consist of either removal of the pollutant or conversion to a less polluting form.<sup>9</sup>

### **32.3 PROCESS CHANGE**

One of the steps toward a sustainable approach toward air quality was attention to the industrial processes that lead to the generation of the pollutant. Plant managers, engineers, and even financial officers, not to mention regulators, began to ask, "Are there ways that we can get the same product or service with less pollution?" Actually, the engineer and environmental officers may have asked that question, but the others might have asked it somewhat differently, "Are there things we can do to prevent so much of our valuable matter and energy exiting the facility in places other than in our product?" Thus, pollution was seen as an indicator of inefficiency in the process, which can be described using both environmental and economic metrics.

A process change can be either a change in operating procedures for an existing process or the substitution of a completely different process. In recent years, this has been labeled "pollution prevention". Consider a plant manager who for years has been using solvent A for a degreasing operation. By past experimentation, it has been found that with the conveyor speed at 100 units per hour, with a solvent temperature of 80 °C, one gets maximum cleaning with solvent a loss that results in the lowest overall operating cost for the process.

A new regulation is passed requiring greatly reduced atmospheric emissions of organic solvents, including solvent A. The manager has several alternatives:

1. Change to another more expensive solvent, which by virtue of its lower vapor pressure would emit less organic matter.
2. Reduce the temperature of the solvent and slow down the conveyor to get the same amount of cleaning. This may require the addition of another line or another 8 h shift.
3. Put in the necessary hooding, ducting, and equipment for a solvent recovery system, which will decrease the atmospheric pollution and also result in some economic solvent recovery.
4. Put in the necessary hooding, ducting, and equipment for an after-burner system, which will burn the organic solvent vapors to a less polluting emission, but with no solvent recovery.

In some cases, the least expensive control is achieved by abandoning the old process and replacing it with a new, less polluting one. Any increased production and/or recovery of material may help offset a portion of the cost. It has proved to be cheaper to abandon old steel mills and to replace them with completely new furnaces of a different type than to modify the old systems to meet pollution regulations. Kraft pulp mills found that the least costly method of meeting stringent regulations was to replace the old, high-emission recovery furnaces with a new furnace of completely different design.

Process change is often incentivized if it is deemed to have a societal value even greater than the specific value to a company. For example, some of the Kraft mills at first received some relief and support to provide additional plant capacity to offset partially the cost of the new furnace type. The initial costs of a complete process change can be quite high, but is often paid back with time.

Another way to compare options, e.g. energy production, is the payback ratio, which is the ratio of total costs, mass, or energy produced during a system's normal lifespan, divided by the costs, mass, or energy needed to build, install, maintain, and operate that system. A high ratio indicates good environmental performance or effectiveness. If a system has an energy-payback ratio between 1 and 1.5, its costs are about the same as the savings or it consumes nearly as much energy as it generates. This would mean the net gain in energy production is zero, so this not a viable energy source.

Another useful and similar metric is known as the energy return on the energy investment (EROEI). Energy production and use can never been 100% efficient, given the second law of thermodynamics and losses with each conversion. For instance, the chemical energy of crude oil well is diminished during extraction, processing, and transport on its way to the end use, and is further diminished by losses at the end use, e.g. inefficiencies within the internal combustion engine. The EROEI is the ratio of the energy obtained from the resource to the energy expended in production, but is actually an enhancement of the expression of net energy, i.e. the energy produced minus the energy expended. Thus, an  $\text{EROEI} \leq 1$  means that the net energy  $\leq 0$ . Thus, the problems with ethanol mentioned above can be expressed as an EROEI. Arguably, for corn-based ethanol production, if the fossil fuel life cycles are included in the calculation, EROEI is lower than if this is calculated later in the life cycle, since farming and handling of corn is so fossil fuel dependent. Thus, ethanol's EROEI can be substantially improved with a

whole plant-type method *versus* the fruit-only fermentation process. The EROEI is also a useful tool for comparing stationary and mobile sources. For example, one could describe electric cars as being either nuclear or coal-fired vehicles, since most electricity is generated from these two stationary source types. Thus, the life cycles of an electric *versus* gasoline fueled vehicle could be compared using the EROEI.

Indeed, the process change is seldom a choice between two process types, but often includes numerous options, each with its own crossover and combinations of process change options with their own collective crossover. Sometimes, combining options is synergistic. That is, one option may be to use less toxic raw materials and another option may be to change the operating temperature in reactor to decrease the generation of a caustic and toxic substance. However, the combination of these two options may not only lead to the elimination of the substance in the gas stream, but also may greatly increase the efficiency of fabric filters downstream, as well as extend the time needed for cleaning and replacement. This is not only beneficial financially, but also could greatly lower the amount of PM released. Recall from Chapter 30, that each filter cleaning and/or replacement is followed by an increase in PM until the dust cake is formed. Thus, the combined process option changes could obviate the need to add pollution control equipment for the caustic pollutant, improve filtration efficiency, and reduce PM emissions.

Conversely, some option combinations can be antagonistic. Solving a problem in one part of the system, e.g. installing complicated, high O&M control technologies, could introduce problems downstream if the line is shut down too often. Another example would be to add a sorbant to improve an upstream technology that generates particles with low electrical conductance, thus interfering with and lowering efficiencies of electrostatic precipitators downstream. Thus, when evaluating and considering process change options, it is important to consider the systematic effects of each option and the combinations of various options.

As engineers often find, the technical aspects of redesigning a process may well be the easiest part. For many industries, this may be the only way to improve efficiency (e.g. steel making will always require the iron, carbon, and energy, but the process leading to a particular grade of steel can vary). Inventories and data bases already exist, since the raw materials and energy use are part of the financial bottom line. Such information is available for the engineer's mass and energy balance calculations (input and output). The chemistry and physics are also well understood. Good industrial practice minimizes the "black boxes" of a process; otherwise,

adjustments in production and output of products would be very risky (i.e. a catalyst concentration may have a very tight tolerance range, outside of which the process does not work well or at all). Finally, the loss term in the thermodynamic balances are well understood. If (raw material A) + (raw material B) – (losses of A and B) = (Product C – losses), the plant manager needs precise and accurate data on these loss terms. These data document what leaves the process through vents, stacks, pipes, and other conveyances, as well as via fugitive emissions. Many of these losses are indeed air pollutants. Thus, the engineer can recommend process changes that can eliminate and decrease pollution, with attendant cost predictions.

The hardest part of process change may be the ability to predict success. Many excellent emerging technologies work well at the bench or microcosm scale, but when scaled up under real-world conditions are much less efficient. Or, if they do work, can be infeasible in terms of production rate or product quality. Often, companies do not have the luxury of time and resources to conduct the needed developmental work to apply the new technology to their process. They may also be leery of possible risks and liabilities of new processes, especially if the status quo is working, albeit not perfectly. Each company has a unique threshold for risk and uncertainty. The engineer needs to recommend process changes with these thresholds in mind. There is also the phenomenon of "corporate inertia". Every organization fears change to varying extents. The maxim is often, "If it ain't broke, don't fix it".

### **32.4 FUEL CHANGE**

In the past, for many air pollution control situations, a change to a less polluting fuel offered the ideal solution to the problem. If a power plant was emitting large quantities of SO<sub>2</sub> and fly ash, conversion to natural gas was cheaper than installing the necessary control equipment to reduce the pollutant emissions to the permitted values. If the drier at an asphalt plant was emitting 350 mg of PM per standard cubic meter of effluent when fired with heavy oil of 4% ash, it was probable that a switch to either oil of a lower ash content or natural gas would allow the operation to meet an emission standard of 250 mg m<sup>-3</sup>.

Fuel switching based on meteorological or air pollution forecasts was, in the past, a common practice to reduce the air pollution burden at critical times. Some control agencies allowed power plants to operate on residual oil during certain periods of the year when pollution potential was low. Some large utilities for years have followed a policy of switching from their

regular coal to a more expensive but lower sulfur coal when stagnation conditions were forecast.

Caution should be exercised when considering any change in fuels to reduce emissions. This is particularly true considering today's fuel costs. Specific considerations might be the following:

1. What are current and potential fuel supplies? In many areas natural gas is already in short supply. It may not be possible to convert a large plant with current allocations or pipeline capacity.
2. Most large boilers use a separate fuel for auxiliary or standby purposes. One actual example was a boiler fired with wood residue as the primary fuel and residual oil as the standby. A change was made to natural gas as the primary fuel, with residual oil kept for standby. This change was made to lower particulate emissions and to achieve a predicted slightly lower cost. Because of gas shortages, the plant now operates on residual oil during most of the cold season, and the resulting particulate emission greatly exceeds that of the previously burned wood fuel. In addition, an SO<sub>2</sub> emission problem exists with the oil fuel that never occurred with the wood residue. Overall costs have not been lowered because natural gas rates have increased since the conversion.
3. Charts or tables listing supplies or reserves of low-sulfur fuel may not tell the entire story. For example, a large percentage of low-sulfur coal is owned by steel companies and is therefore not generally available for use in power-generating stations even though it is listed in tables published by various agencies.
4. Strong competition exists for low-pollution fuels. While one area may be drawing up regulations to require use of natural gas or low-sulfur fuels, it is probable that other neighboring areas are doing the same. Although there may have been sufficient premium fuel for one or two areas, if the entire region changes, not enough exists. Such a situation has resulted in extreme fuel shortages during cold spells in some large cities. The supply of low-sulfur fuels has been exhausted during period of extensive use.

The use of nuclear reactors to generate electricity has been questioned from several environmental points of view. This approach appears to be relatively pollution free compared to the more familiar fossil fuel-fired plant, which emits carbon monoxide and carbon dioxide, oxides of nitrogen and sulfur, hydrocarbons, and fly ash. However, waste and spent-fuel disposal problems may offset the apparent advantages. These problems, as well as steam generator leaks and natural disasters (such as the recent tsunami aftermath in

Japan), have led to concerns about nuclear power plants throughout the world.

### **32.5 REMOVAL OF POLLUTANTS**

In many situations, sufficient control over emissions cannot be obtained exclusively by fuel or process change. In cases such as these, the concentrations of the pollutants of concern in the exhaust gases or process stream must be decreased to allowable values before they are released to the atmosphere. This is the prototypical approach to air pollution and is the focus of Chapters 30 and 31. In the foreseeable future, depending on the pollutant, facility, and environmental setting, variations of combinations of these approaches will have to be used to address air pollutants, but with a movement toward prevention, waste minimization, and interventions earlier in the life cycle.

The equipment for the pollutant removal system includes all hoods, ducting, controls, fans, and disposal or recovery systems that might be necessary. Even a seemingly insignificant component can be very important if its function is rate limiting. For example, a valve that is mismatched to the gas stream and fouls at a much faster rate than another valve, can lead to substantial and avoidable emissions and costs.

Indeed, a systems approach would include a review of each component to decide if a better one exists or, preferably, to "design out" any problematic component. A useful engineering pedagogy is to ask students how they can improve a series of switches in a system. Students often jump into an assignment with vigor and start looking for better materials in terms of conductance and durability. They may even do some research to see if a particular part of the switch is composed of toxic materials or find substitutes that could be more recyclable. However, they are less likely to remove some or all of the switches, even if they have no purpose. For example, there may never be access to a room, or the equipment is designed to stay on in every scenario. Indeed, the switch could even be a safety hazard if it were shut off, e.g. a backup pump to move hazardous materials to reserve tank in the event of an overflow. In such cases, the component can and should be designed out of the process. Obviously, before removing a component, the engineer must be quite certain about the intended function.

The entire system should be engineered as a unit for maximum efficiency and economy. Many systems operate at less than maximum efficiency because a portion of the system was designed or adapted without consideration of the other portions.<sup>9</sup> In a manner of speaking, this requires a sensitivity analysis of every component of the entire process, not just the air pollution control equipment. That is, if a small change somewhere in

the process can lead to substantially decreased concentrations of a pollutant or its precursor, this is an opportunity for improved efficiency. This means that the persons addressing air pollution controls at a facility must have a working knowledge not only of all of the environmental compartments (air, water, solid waste, radiation, etc.), but also of the manufacturing process. Again, this is the only way to calculate a meaningful mass and energy balance.

Efficiency of the control equipment is normally specified before the equipment is purchased. If a plant is emitting a pollutant at  $500 \text{ kg h}^{-1}$  and the regulations allow an emission of only  $25 \text{ kg h}^{-1}$ , it is obvious that at least 95% efficiency is required of the pollution control system. This situation requires the regulation to state "at least 95% removal on a weight basis". The regulation should further specify how the test would be made to determine the efficiency.

The thermodynamic efficiency for the device shown in Figure 32.4 may be calculated in several ways:

$$\text{Efficiency, \%} = 100 \times \frac{C}{A} \quad (32.3)$$

However, since  $A = B + C$ :

$$\begin{aligned} \text{Efficiency, \%} &= 100 \times \left( \frac{C}{B+C} \right) \quad \text{or} \\ &100 \times \left( \frac{A-B}{A} \right) \quad \text{or} \quad 100 \times \left( \frac{A-B}{B+C} \right) \end{aligned} \quad (32.4)$$

The final acceptance test would probably be made by measuring two of the three quantities and using the appropriate equation. For a completely valid efficiency test the effect of holdup ( $D$ ) and loss ( $E$ ) must also be taken into account.

To remove a pollutant from the carrying stream, some property of the pollutant that is different from the carrier must be exploited. The pollutant may have different size, inertia, electrical, or absorption properties. Removal requires that the equipment be designed to apply the scientific principles necessary to perform the separation.

### **32.6 DISPOSAL AND WASTE MINIMIZATION OF POLLUTANTS**

If a pollutant is removed from the carrying gas stream, disposal of the collected material becomes of vital concern. If the collected material is truly inert, it may be disposed of in a sanitary landfill. If it is at the other end of the scale, it is probably considered as a toxic waste and strict laws governing its disposal apply. Disposal of hazardous wastes is regulated by governmental agencies. Thus, in addition to efficiency

calculations, the flow in [Figure 32.4](#) is also useful for green engineering and waste minimization. For example, a pollutant can be degraded in the device, e.g. thermally, to decrease the amount of a toxic substance that reaches the waste ( $C$ ), the need for disposal is eased.

In the United States, the Resource Conservation and Recovery Act (RCRA) of 1976 is the major legislation covering the disposal of solid and hazardous wastes.<sup>10</sup> This act provides a multifaceted approach to solving the problems associated with the generation of approximately  $5 \times 10^9$  metric tons ( $5 \times 10^{12}$  kg) of solid waste each year in the United States. It places particular emphasis on the regulation of hazardous wastes. This law established the Office of Solid Waste within the US Environmental Protection Agency (EPA) and directed the agency to publish hazardous waste characteristics and criteria.

If a waste is designated as hazardous under the RCRA, regulations are applied to generators, transporters, and those who treat, store, or dispose of that waste. Regulations regarding hazardous wastes are enforced by the federal government, while the individual states are responsible for enforcing the provisions of the RCRA that apply to nonhazardous wastes. The act also provides for research, development, and demonstration grants for waste disposal.

The general purpose of ultimate disposal of hazardous wastes is to prevent the contamination of susceptible environments. Surface water runoff, groundwater leaching, atmospheric volatilization, and biological accumulation are processes that should be avoided during the active life of the hazardous waste. As a rule, the more persistent a hazardous waste is (i.e. the greater its resistance to breakdown), the greater the need to isolate it from the environment. If the substance cannot be neutralized by chemical treatment or incineration and still maintains its hazardous qualities, the only alternative is usually to immobilize and bury it in a secure chemical burial site.

### 32.7 GREEN PRINCIPLES AND AIR QUALITY

From a thermodynamics standpoint, a sustainable system is one that is in equilibrium or changing at a tolerably slow rate. In the food chain, for example, plants are fed by sunlight, moisture, and nutrients, and then become food themselves for insects and herbivores, which in turn act as food for larger animals. The waste from these animals replenishes the soil, which nourishes plants, and the cycle begins again.<sup>11</sup>

At the largest scale, manufacturing, transportation, commerce, and other human activities that promote

high consumption and wastefulness of finite resources cannot be sustained. At the individual designer scale, the products and processes must be considered for their entire lifetimes and beyond. The operationalizing of the quest for sustainability is defined as green engineering, a term that recognizes that engineers are central to the practical application of the principles sustainability to everyday life.<sup>12</sup>

Green engineering treats environmental quality as an end in itself. The US EPA has defined green engineering as

... the design, commercialization, and use of processes and products, which are feasible and economical while minimizing (1) generation of pollution at the source and (2) risk to human health and the environment. The discipline embraces the concept that decisions to protect human health and the environment can have the greatest impact and cost effectiveness when applied early to the design and development phase of a process or product.<sup>13</sup>

Green engineering approaches are benefiting from the phenomenal improvements in computational abilities (see [Table 32.1](#)) and other tools that were not available at the outset of the environmental movement, or even at the turn of the 21st century. Increasingly, companies and governmental agencies have come to recognize that improved efficiencies save time, money, and other resources in the long run. Hence, decision makers are thinking systematically about the entire product stream in numerous ways:

- applying sustainable development concepts, including the framework and foundations of "green" design and engineering models;
- applying the design process within the context of a sustainable framework: including considerations of commercial and institutional influences;
- considering practical problems and solutions from a comprehensive standpoint to achieve sustainable products and processes;
- characterizing waste streams resulting from designs;
- understanding how first principles of science, including thermodynamics, must be integral to sustainable designs in terms of mass and energy relationships, including reactors, heat exchangers, and separation processes;
- applying creativity and originality in group product and building design projects.

Traditionally, air pollution considerations have been approached by engineers as constraints on their designs. For example, hazardous substances generated by a manufacturing process were dealt with as a waste stream (including releases and emissions from vents and stacks) that must be contained and treated to fall below a designated concentration in the emission or other release fluid (i.e. air or water). The pollutant

TABLE 32.1 Green Principles

Principle	Description	Example	Role of Computational Toxicology
Waste prevention	Design chemical syntheses and select processes to prevent waste, leaving no waste to treat or clean up.	Use a water-based process instead of an organic solvent-based process.	Informatics and data mining can provide candidate syntheses and processes.
Safe design	Design products to be fully effective, yet have little or no toxicity.	Using microstructures, instead of toxic pigments, to give color to products. Microstructures bend, reflect, and absorb light in ways that allow for a full range of colors.	Systems biology and “omics” (genomics, proteomics, and meta-bonomics) technologies can support predictions of cumulative risk from products used in various scenarios.
Low-hazard chemical synthesis	Design syntheses to use and generate substances with little or no toxicity to humans and the environment.	Select chemical synthesis with toxicity of the reagents in mind upfront. If a reagent ordinarily required in the synthesis is acutely or chronically toxic, find another reagent or new reaction with less toxic reagents.	Computational chemistry can help predict unintended product formation and reaction rates of optional reactions.
Renewable material use	Use raw materials and feedstocks that are renewable rather than those that deplete nonrenewable natural resources. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or that must be extracted by mining.	Construction materials can be from renewable and depleting sources. Linoleum flooring, for example, is highly durable, can be maintained with nontoxic cleaning products, and is manufactured from renewable resources amenable to being recycled. Upon demolition or reflooring, the linoleum can be composted.	Systems biology, informatics, and “omics” technologies can provide insights into the possible chemical reactions and toxicity of the compounds produced when switching from depleting to renewable materials.
Catalysis	Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.	The Brookhaven National Laboratory recently reported that it has found a “green catalyst” that works by removing one stage of the reaction, eliminating the need to use solvents in the process by which many organic compounds are synthesized. The catalyst dissolves into the reactants. Also, the catalyst has the unique ability of being easily removed and recycled because, at the end of the reaction, the catalyst precipitates out of products as a solid material, allowing it to be separated from the products without using additional chemical solvents.*	Computation chemistry can help to compare rates of chemical reactions using various catalysts.

(Continued)

TABLE 32.1 Green Principles—cont'd

Principle	Description	Example	Role of Computational Toxicology
Avoiding chemical derivatives	Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.	Derivatization is a common analytical method in environmental chemistry, i.e. forming new compounds that can be detected by chromatography. However, chemists must be aware of possible toxic compounds formed, including leftover reagents that are inherently dangerous.	Computational methods and natural products chemistry can help scientists start with a better synthetic framework.
Atom economy	Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.	Single atomic and molecular-scale logic used to develop electronic devices that incorporate DfD, DfR, and design for safe and environmentally optimized use.	The same amount of value, e.g. information storage and application, is available on a much smaller scale. Thus, devices are smarter and smaller, and more economical in the long-term. Computational toxicology enhances the ability to make product decisions with better predictions of possible adverse effects, based on the logic.
Nanomaterials	Tailor-made materials and processes for specific designs and intent at the nanometer scale ( $\leq 100$ nm).	Emissions, effluent, and other environmental controls; design for extremely long life cycles. Limits and provides better control of production and avoids overproduction (i.e. "throwaway economy").	Improved, systematic catalysis in emission reductions, e.g. large sources like power plants and small sources like automobile exhaust systems. Zeolite and other sorbing materials used in air pollution treatment and emergency response situations can be better designed by taking advantage of surface effects; this decreases the volume of material used.
Selection of safer solvents and reaction conditions	Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.	Supercritical chemistry and physics, especially that of carbon dioxide and other safer alternatives to halogenated solvents are finding their way into the more mainstream processes, most notably dry cleaning.	To date, most of the progress has been the result of wet chemistry and bench research. Computational methods will streamline the process, including quicker "scale-up".
Improved energy efficiencies	Run chemical reactions and other processes at ambient temperature and pressure whenever possible.	To date, chemical engineering and other reactor-based systems have relied on "cheap" fuels and, thus, have optimized on the basis of thermodynamics. Other factors, e.g. pressure, catalysis, photovoltaics, and	Heat will always be important in reactions, but computational methods can help with relative economies of scale. Computational models can test feasibility of new energy-efficient systems, including intrinsic and

## Design for degradation

Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.

fusion, should also be emphasized in reactor optimization protocols.

extrinsic hazards, e.g. to test certain scale-ups of hydrogen and other economies. Energy behaviors are scale dependent. For example, recent measurements of  $H_2SO_4$  bubbles when reacting with water have temperatures in the range of those found on the surface of the sun.<sup>§</sup>

## Real-time analysis to prevent pollution and concurrent engineering

Include in-process, real-time monitoring, and ensure adequate control during syntheses to minimize or eliminate the formation of by-products.

Biopolymers, e.g. starch-based polymers can replace styrene and other halogen-based polymers in many uses. Geopolymers, e.g. silane-based polymers, can provide inorganic alternatives to organic polymers in pigments, paints, etc. These substances, when returned to the environment, become their original parent form.

Computation approaches can simulate the degradation of substances as they enter various components of the environment. Computational science can be used to calculate the interplanar spaces within the polymer framework. This will help to predict persistence and to build environmentally friendly products, e.g. those where space is adequate for microbes to fit and biodegrade the substances.

## Accident prevention

Design processes using chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

Scenarios that increase probability of accidents can be tested.

Real-time environmental mass spectrometry can be used to analyze whole products, obviating the need for any further sample preparation and analytical steps. Transgenic species, while controversial and ethically challenging, can also serve as biological sentries, e.g. organisms that change colors in the presence of toxic substances.

\* US Department of Energy, Research News. <http://www.eurekalert.org/features/doe/2004-05/dnl-brc050604.php>; 2005 [accessed 22.03.05].

<sup>§</sup>Flannigan DJ, Suslick KS. Plasma formation and temperature measurement during single-bubble cavitation. *Nature* 2005;434:52–55.

Adapted from: US Environmental Protection Agency. Green Chemistry. <http://www.epa.gov/greenchemistry/principles.html>; [accessed 12.04.05]. Other information from discussions with Michael Hays, US EPA, National Risk Management Research Laboratory, April 28, 2005.

generation had to be constrained by selecting certain manufacturing types, increasing waste handling facilities, and if these were not completely effective, limiting rates of production. Green engineering emphasizes that these processes are often inefficient financially and environmentally, calling for a comprehensive, systematic life cycle approach.<sup>b</sup> Green engineering attempts to achieve four goals:

1. Waste minimization or dematerialization
2. Materials management
3. Pollution prevention
4. Product enhancement

Waste reduction involves finding efficient material uses. It is compatible with other engineering efficiency improvement programs, such as total quality management and real-time or just-in-time manufacturing. The overall rationale for waste reduction is that if materials and processes are chosen intelligently at the beginning, less waste will result. In fact, a relatively new approach to engineering is to design and manufacture a product simultaneously rather than sequentially, known as concurrent engineering. Combined with DfE and industrial ecology, concurrent engineering approaches may allow air quality improvements under real-life, manufacturing conditions. However, changes made in any step must consider possible effects on the rest of the design and implementation.

As mentioned, there is a formal process for answering questions of material and product use and waste production. This is known as the LCA, short for life cycle assessment or life cycle analysis. Such an assessment is a comprehensive approach to pollution prevention by analyzing the entire life of a product, process, or activity, encompassing raw materials, manufacturing, transportation, distribution, use, maintenance, recycling, and final disposal. In other words, assessing its life cycle should yield a complete picture of the environmental impact of a product.

The first step in the LCA is to gather data on the flow of a material. Once the quantities of various components of such a flow are known, the environmental effect of each step in the production, manufacture, use, and recovery/disposal is estimated.

LCAs are performed for several reasons, including the comparison of products for purchasing and a comparison of products by industry. In the former case, the total environmental effect of glass returnable bottles, for example, could be compared to the environmental effect of nonrecyclable plastic bottles. If all of the factors going into the manufacture, distribution, and disposal of

both types of bottles are considered, one container might be shown to be clearly superior.

LCAs often suffer from a dearth of data. Some of the information critical to the calculations is virtually impossible to obtain. For example, something as simple as the tonnage of solid waste collected in the United States is not readily calculable or measurable. And even if the data were there, the procedure suffers from the unavailability of a single accounting system. Is there an optimal level of pollution, or must all pollutants be removed 100% (a virtual impossibility)? If there is air pollution and water pollution, how must these be compared?

Once the life cycle of a material or product has been analyzed, the next engineering step is to manage the life cycle. If the objective is to use the least energy and to cause the least detrimental effect on the environment, then it is clear that much of the onus is on the manufacturers of these products. The users of the products can have the best intentions for reducing adverse environmental effects, but if the products are manufactured in such a way as to make this impractical or difficult, then the fault is with the manufacturers. On the other hand, if the manufactured materials are designed to be used with little environmental insult and easy to separate and recycle, then most likely energy is saved, wastes are reduced, and the environment is protected. Many examples can be found of industrial firms decreasing emissions or the production of other wastes, or of facilitating the recovery of waste products, which in the process saved money. Some automobile manufacturers, for example, are modularizing the engines so that junked parts can be easily reconditioned and reused.

There are various, but similar definitions of “pollution prevention” including:

The use of materials, processes, or practices that reduce or eliminate the creation of pollutants or wastes at the source. It includes practices that reduce the use of hazardous materials, energy, water, or other resources and practices that protect natural resources through conservation or more efficient use.<sup>14</sup>

In the broadest sense, pollution prevention is the idea of eliminating waste, regardless of how this might be done. Originally, pollution prevention was applied to industrial operations to reduce either the amount of the wastes being produced or to change the wastes’ characteristics in order to make them more readily disposable. Many industries changed to water-soluble paints, for example, thereby eliminating organic solvents, cleanup time, etc., and often in the process saving considerable

<sup>b</sup> This is another reminder that amount of pollution is most often an indicator of inefficiency. This inefficiency is in the context of both thermodynamics (i.e. mass and energy balances) and economics (e.g. supply and demand and willingness to pay).

money. In fact, the concept was first introduced as “pollution prevention pays”, emphasizing that many of the changes would actually save the companies money. In addition, the elimination or reduction of hazardous and otherwise difficult wastes also has a long-term effect—it reduces the liability the company carries as a consequence of its disposal operations.

Much of Europe had already directly or indirectly codified life cycle approaches, when with the passage of the Pollution Prevention Act in 1990, the United States officially joined the cadre of nations that encourage pollution prevention by setting appropriate standards for pollution prevention activities, to assist federal agencies in reducing wastes generated, to work with industry and to promote the elimination of wastes by creating waste exchanges and other programs, seek out and eliminate barriers to the efficient transfer of potential wastes, and to do this with the cooperation of the individual states.

In general, the procedure for the implementation of pollution prevention activities is to

1. recognize a need,
2. assess the problem,
3. evaluate the alternative, and
4. implement the solutions.

Many industries and industry groups have welcomed this governmental action, recognizing that pollution prevention can and often does result in the reduction of costs to the industry. Thus, recognition of the need quite often is internal and the prerogative of the company to initiate pollution prevention actions.

A first step is to assess the processes within an industrial operation. During the assessment phase, a common procedure is to perform a “waste audit”, which is the black box mass balance, using the company as the black box. An example of such an audit is provided in the Example Box: Water Audit.

### EXAMPLE BOX: WASTE AUDIT <sup>1,5</sup>

A manufacturing company is concerned about the air emissions of volatile organic carbons. These chemicals can volatilize during the manufacturing process, but the company is not able to estimate accurately the rate of volatilization, or even which chemicals are going to the vapor phase. The company conducts an audit of three of their most widely used volatile organic chemicals with the following record of findings:

Material	Purchase quantity (barrels)
<b>PURCHASING DEPARTMENT RECORDS:</b>	
Carbon tetrachloride* (CCl <sub>4</sub> )	48
Methyl chloride <sup>§</sup> (CH <sub>2</sub> Cl <sub>3</sub> )	228
Trichloroethylene (C <sub>2</sub> HCl <sub>3</sub> )	505
Material	Average concentration (mg l <sup>-1</sup> )
<b>WASTEWATER TREATMENT PLANT INFLUENT:</b>	
Carbon tetrachloride	0.343
Methylene chloride	4.04
Trichloroethylene	3.23

\* The correct name is tetrachloromethane, but the compound was in such common use throughout the twentieth century and was referred to as carbon tetrachloride that the name is still frequently used in the engineering and environmental professions.

<sup>§</sup>Also known as chloromethane.

The average influent flow rate to the treatment plant is 0.076 m<sup>3</sup> s<sup>-1</sup>.

Hazardous waste manifests (what leaves the company by truck, headed to a hazardous waste treatment facility):

Material	Barrels	Concentration (%)
Carbon tetrachloride	48	80
Methyl chloride	228	25
Trichloroethylene	505	80

Unused barrels at the end of the year:

Material	Barrels
Carbon tetrachloride	1
Methyl chloride	8
Trichloroethylene	13

How much volatile organic compound (VOC) is escaping?

Conduct a black box mass balance, as

$$[A_{\text{acc}}] = [A_{\text{in}}] - [A_{\text{out}}] + [A_{\text{prod}}] - [A_{\text{cons}}} \quad (32.5)$$

where

$A_{\text{acc}}$  = mass of A per unit time accumulated

$A_{\text{in}}$  = mass of A per unit time in

(Continued)

### EXAMPLE BOX: WASTE AUDIT <sup>15</sup> (cont'd)

$A_{out}$  = mass of A per unit time out

$A_{prod}$  = mass of A per unit time produced

$A_{cons}$  = mass of A per unit time consumed

The materials with reported mass (i.e. "A") are the three VOCs. Note that  $A_{prod}$  and  $A_{cons}$  together comprise the typical net loss or gain term in a thermodynamic mass balance equation, e.g. designated as  $r$  in Eqn (18.34) in Chapter 18.

Barrels must be converted to cubic meters and the density of each chemical must be known. Each barrel is  $0.12 \text{ m}^3$ , and the density of the three chemicals is 1548, 1326, and  $1476 \text{ kg m}^{-3}$ . The mass per year of carbon tetrachloride accumulated is

$$\begin{aligned}[A_{acc}] &= 1 \text{ barrel/year} \times 0.12 \text{ m}^3/\text{barrel} \times 1548 \text{ kg m}^{-3} \\ &= 186 \text{ kg year}^{-1}\end{aligned}$$

Similarly,

$$[A_{in}] = 48 \times 0.12 \times 1548 = 8916 \text{ kg year}^{-1}$$

The mass out is in three parts; mass discharge to the wastewater treatment plant, mass leaving on the trucks to the hazardous waste disposal facility, and the mass volatilizing. So the  $[A_{out}] = [0.343 \text{ g m}^{-3} \times 0.076 \text{ m}^3 \text{ s}^{-1} \times 86,400 \text{ s day}^{-1} \times 365 \text{ day year}^{-1} \times 10^{-3} \text{ kg g}^{-1}] + [48 \times 0.12 \times 1548 \times 0.80] + A_{air}$

$$= 822.1 + 7133 + A_{air}$$

where  $A_{air}$  is the mass per unit time emitted to the air.

Since there is no carbon tetrachloride consumed or produced,

$$186 = 8916 - [822.1 + 7133 + A_{air}] + 0 - 0.$$

$$\text{and } A_{air} = 775 \text{ kg year}^{-1}.$$

If a similar balance is done on the other chemicals, it appears that the loss to air of methyl chloride is about  $16,000 \text{ kg year}^{-1}$  and the trichloroethylene is about  $7800 \text{ kg year}^{-1}$ .

If the intent is to cut total VOC emissions, it is clear that the first target should be the methyl chloride, at least in terms of the mass released. But, another important consideration in preventing pollution is relative risk.

Although methyl chloride is two orders of magnitude more volatile than the other pollutants, all three compounds are likely to be found in the atmosphere. Thus, inhalation is a likely exposure pathway.

Since risk is the product of exposure times hazard ( $R = E \times H$ ), we can compare the risks by applying a hazard value (e.g. cancer potency). We can use the air emissions calculated above as a reasonable approximation of exposure via the inhalation pathway<sup>a</sup> and the inhalation cancer slope factors to represent the hazard. These slope factors are published by the US EPA and are found to be

$$\text{Carbon tetrachloride} = 0.053 \text{ kg day mg}^{-1}$$

$$\text{Methyl chloride} = 0.0035 \text{ kg day mg}^{-1}$$

$$\text{Trichloroethylene} = 0.0063 \text{ kg day mg}^{-1}$$

The relative risk for the three compounds can be estimated by removing the units (i.e. we are not actually calculating the risk, only comparing the three compounds against each other, so we do not need units). If we were calculating risks, the units for exposure would be mass of contaminant per body mass per time, e.g. milligrams per kilogram per day, whereas the slope factor unit is the inverse of this kilogram day per milligram so risk itself is a unitless probability.

$$\text{Carbon tetrachloride} = 0.053 \times 775 = 41$$

$$\text{Methyl chloride} = 0.0035 \times 16,000 = 56$$

$$\text{Trichloroethylene} = 0.0063 \times 7800 = 49$$

Thus, in terms of relative risk, methyl chloride is again the most important target chemical, but the other two are much closer. In fact, given the uncertainties and assumptions, from a relative risk perspective, the importance of removing the three compounds is nearly identical, owing to the much higher cancer potency of  $\text{CCl}_4$ .

<sup>a</sup> Even without calculating the releases, it is probably reasonable to assume that the exposures will be similar since the three compounds have high vapor pressures (more likely to be inhaled): carbon tetrachloride = 115 mmHg, methyl chloride = 4300 mmHg, trichloroethylene = 69 mmHg.

Materials changes often involve the substitution of one chemical for another, which is less toxic or requires less hazardous materials for cleanup. The use of trivalent chromium ( $\text{Cr}^{3+}$ ) for chrome plating instead of the much more toxic hexavalent chrome has found favor, as has the use of water-soluble dyes and paints.

Process modifications usually involve the greatest investments, and can result in the most rewards. For example, a countercurrent wash water use instead of a once-through batch operation can significantly reduce the amount of wash water needing treatment, but such a change requires pipes, valves, and a new process protocol. In industries where materials are dipped into

solutions, such as in metal plating, the use of drag out recovery tanks, an intermediate step, has resulted in the savings of the plating solution and reduction in waste generated.

## 32.8 SOCIOECONOMIC COSTS AND BENEFITS

Pollution prevention has the distinct advantage over stack controls in that most of the time the company or other prospective air pollution source (e.g. university facilities and maintenance departments, city public works departments, and state highway departments) not only eliminates or greatly reduces the release of hazardous materials but also saves money. The most obvious costs are those normally documented in company and departmental records, such as direct labor, raw materials, energy use, capital equipment, site preparation, tie-ins, employee training, and regulatory recordkeeping (e.g. permits).<sup>16</sup> However, there are numerous other savings, including those resulting from not having to spend time on submitting compliance permits and suffering potential fines for noncompliance. Future liabilities weigh heavily where hazardous wastes have to be buried or injected, as well as air pollution control equipment that cannot meet prospective emission standards. Additionally, there are the intangible benefits of employee relations and safety (see Table 32.2).

In many ways, the transition from command and control approaches to prevention has been incremental; an evolution rather than a revolution. Regulatory requirements and good engineering practice will continue to call for better approaches in both areas. Control technologies and pollution prevention are not separate endeavors. In fact, the life cycle view prohibits such dichotomies. They are both crucial tools in green design. The advances will continue toward sustainability and beyond, e.g. regenerative materials and technologies. By focusing on the function and eliminating inefficiencies, we can expect even better results will be attained. Engineers and other designers are dedicated to continuous improvement and total quality. As such, regenerative strategies for design, manufacturing, use, and reuse will increasingly be embraced. Process modifications usually involve the largest investments of human and financial resources, and can result in the most rewards. For example, using wash water countercurrently instead of a once-through batch operation can significantly reduce the amount of wash water needing treatment. However, such a change requires new and redirect conduits, pipes, and valves; all necessitating a new process protocol. In industries where materials are dipped into solutions, such as in metal plating, the use of drag-out recovery tanks as an intermediate step has

TABLE 32.2 Pollution Cost Categories

Cost Category	Typical Cost Components
Usual/normal	Direct labor Raw materials Energy and fuel Capital equipment and supplies Site preparation Tie-ins Training Permits: administrative and scientific
Hidden or direct	Monitoring Permitting fees Environmental transformation Environmental impact analyses and assessments Health and safety assessments Service agreements and contracts Legal Control instrumentation Reporting and recordkeeping Quality assurance planning and oversight
Future liabilities	Environmental cleanup, removal, and remedial actions Personal injury Health risks and public insults More stringent compliance requirements Inflation
Less tangible	Consumer reaction and loss of investor confidence Employee relations Lines of credit (establishing and extending) Property values Insurance premiums and insurability Greater regulatory oversight (frequency, intensiveness, onus) Penalties Rapport and leverage with regulators

*Adapted from: Ref. 16.*

resulted in the savings of the plating solution and reduction in the volume of waste generated.

Pollution prevention has the distinct advantage over stack controls in that most of the time the company not

only eliminates or greatly reduces the release of hazardous materials, and may also reduce energy requirements. The potential for future costs and liabilities weigh heavily on decisions about air pollution prevention and control. Indeed, solving an air pollution problem is a systems problem. Removing a contaminant from the gas stream, only to have it concentrated in solid or liquid phase, must include a plan for addressing this new problem, i.e. where and how to handle this new hazardous wastes. Additionally, there are intangible benefits, such as employee relations, occupational safety, and trust from the public. A company or departmental ethos must be one of stewardship and concern for the next generations. Green engineering and sustainable approaches to prevent air pollution must be part of that ethos.

## QUESTIONS

- What is the difference, from the standpoint of air quality, between pollution prevention and DfE?
- To produce fuels from plastic waste, shredded plastics undergo pyrolysis at about 400 °C. As the plastics boil, gas is separated as a fuel that is then distilled and filtered. What is the advantage of pyrolysis over incineration in this process? How does the type of plastic affect the type and amount of air pollution from this process, e.g. polyethylene and polypropylene vs polyvinyl chloride? What is the problem with using shredded polyethylene terephthalate in this process?
- Find a flowchart of the steps involved before a pound of sausage makes it to the meat section of a grocery store. Identify at least two places in the flow that could be changed to decrease the emission of an air pollutant, but still allow the pound of sausage to be produced.
- Find a flow chart of the steps involved before a pound of smart phone makes it to the retail store. Identify at least two places in the flow that could be changed to decrease the emission of an air pollutant, but still allow the phone to be produced with the same features.
- How would the changes you recommended in the two previous questions affect costs?
- For a given process at a plant, the cost of control can be related to the equation: dollars for control =  $10,000 + 10e^x$ , where  $x$  = percent of control/10. The material collected can be recovered and sold and the income determined from the equation: dollars recovered =  $(1000)(\text{percent of control})$ . At what level of control will the control equipment just pay for itself? At what level of control will the dollars recovered per dollars of control equipment be the maximum?
- In the previous question, what would be the net cost to the process for increased control from 97.0 to 99.5%?
- Give three examples of conversion of a pollutant to a less polluting form or substance.
- List the advantages and disadvantages of a municipal sanitary landfill and a municipal incinerator.
- List the advantages and disadvantages of recovering energy, in the form of steam, from a municipal incinerator.
- Consider the black box balance example. Calculate the amount of vapors escaping from 500 barrels of carbon tetrachloride (85%), with 10 barrels remaining; 1000 barrels of methyl chloride (30%) with 100 barrels remaining; and, 2000 barrels of trichloroethylene (TCE) (85%) with 200 barrels remaining. Which of the three VOCs presents the greatest risks? What are the relative risks of from the three compounds? Explain your answers from various viewpoints, including toxicology, exposure potential, engineering, and sustainability.
- Consider a facility in your hometown. What three steps could be taken in the life cycle to improve air pollution emissions?
- Give an example of a company in your home state that has turned an environmental problem into a profit. What were the major drivers? What were the obstacles that had to be overcome?
- The adage, “one man’s trash is another man’s treasure” applies to air pollution. Draw curves like those in [Figure 32.4](#) of a HAP produced during manufacturing that has been recovered in the real world.
- How can landfill gas (LFG) collection efficiencies be improved to decrease emissions of greenhouse gasses and make the operations more cost-effective? How does this differ between passive and active LFG system?
- How can planting flora on a large scale help to prevent air pollution? What factors must be considered?
- Conduct a benefit-cost study of the sludge (biosolids) handling system in your area. Was the approach based on appropriate valuations, e.g. financial, water quality, air quality, etc.? Is the sludge being incinerated? If so, do you agree with the justification? If it is not being incinerated, are there other sources of air pollution? How could the process be improved?

18. How can engineering reliability prediction be used to estimate and decrease air pollution? Suggest ways that the optimal life of a process or product can be increased and failures decreased that will result in less air pollution.
19. Solid waste is a seemingly intractable problem for many municipalities around the globe. Incineration is not only a means by which the volume of the waste can be decreased substantially, but also a major source of air pollution. Apply the principles discussed in this book and with the perspective of industrial ecology, and suggest a means by which mercury and dioxins can be decreased in the solid waste combustion gas stream.
20. Draw a diagram like Figure 32.7 for a product in your medicine cabinet. Explain the distortions, e.g. points away from the center. How can this diagram become more sustainable? Consider the function of this product. Is there an alternate means of achieving this function that has a better diagram?
21. Figure 32.8 dates to the late 1990s. How has this function, i.e. computing, changed since then with regard to the ellipses? How have air pollutant emissions been affected by these changes?
22. Why can energy production and use never be zero? Consider the steps prior to starting a vehicle in the morning back to extraction of resources needed to make the vehicle's materials and those needed to make the vehicle move. Describe the air pollution at each of these steps.
23. The mayor of a city in northern Ontario, Canada, is recommending the city change its fuel from conventional diesel for its 10 buses to B100 biodiesel. Each bus travels 500 km per day, 7 days per week at about  $2 \text{ km l}^{-1}$ . The mayor's rationale is that he expects improved efficiency and decreasing air pollutant emissions, especially  $\text{NO}_x$ . Is he correct?
24. On average, a city's buses currently emit  $2.2 \text{ g km}^{-1} \text{ CO}$ ,  $0.5 \text{ g km}^{-1}$  of hydrocarbons, and  $0.2 \text{ g km}^{-1} \text{ PM}$ . What would be the expected new air pollutant emissions for a city with 20 buses, each traveling 500 km per day, 7 days per week at about  $2 \text{ km l}^{-1}$  if the city switched from conventional diesel to B20 diesel? To B100 diesel?
25. Over a testing period, 800 g of an air pollutant has been found in the waste from a pollution control device that has received 1000 g of that air pollutant from the process, and 175 g is measured exiting the device. What is the efficiency of the device? If the pollution device is found to have a loss of 55 g and a holdup of 45 g, what does this tell you about the test's validity?
26. Why are process changes often an expensive way to address air pollution? What can be done to lower the costs and decrease emissions?

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# Grand Challenges

## 33.1 INTRODUCTION

The number of “experts” in air pollution in the middle of the twentieth century was quite small. Indeed, they likely would not have even referred to themselves as air pollution experts; preferring to be called meteorologist, engineer, physicist, chemist, or earth scientist. The disciplines of atmospheric science and more specifically, those of the atmospheric physicist or chemist or environmental engineer, have grown in expertise and confidence exponentially since the first edition of this book. In the years since, the information on air quality and knowledge of how and why the atmosphere becomes polluted have allowed for continuously improving decisions that have led to a much cleaner atmosphere.

Air pollution was a seemingly intractable problem for most of the developed world in the twentieth century. The improvement has been remarkable, especially for the health-related criteria air pollutants. More recently, substantial and sustained progress has also been made in decreasing atmospheric concentrations of hazardous air pollutants, i.e. the air toxics.

Unfortunately, much of this progress has been in the developed and richest parts of the world. Millions of people live in the developing and poorer parts of the world that have seen little improvement. Indeed, in those countries with the fastest growing economies and increasing industrialization, the problems have worsened dramatically. In fact, these growing economies in many instances are retracing the steps taken by the United States, Japan, and Europe during the petrochemical revolution after the Second World War, which led to so many pollution problems, episodes, and disasters.

In 2008, the US National Academy of Engineering announced the “Grand Challenges” facing the engineering profession in the twenty-first century. The 14 challenges fall into four themes that are essential for humankind: sustainability, health, reducing vulnerability, and enhancing the joy of living. The Academy’s list of challenges included a wide range of goals that engineers can help to meet.<sup>1</sup> Improving and sustaining

environmental quality is a key part of almost every challenge. Addressing air pollution is a direct need for several of the challenges, e.g. designing means of managing the hydrologic, nitrogen, and carbon biogeochemical cycles (see Chapters 20, 21, and 22).

Air pollution science and engineering have their own grand challenges for this century. Some are scientific and technical. Some are policy-driven and political. Some are educational and informational. There are challenges at every scale, with threats ranging from those causing harm to an individual cell to those endangering living things on the entire planet. Cancer is an example of the former. Climate change is an example of the latter. All of the challenges are, in a way, responses to a moral imperative to protect the health and wellbeing of humans, to sustain a livable environment, and to protect the quality of ecosystems.

In mere decades, the cadres of air pollution experts have been blessed in being able to witness the remarkable paradigm shift in attitudes from almost complete exploitation to empathy. Unfortunately, many of these same experts are frustrated in what seems *déjà vu* in other parts of the world, with tradeoffs between clean air and growing economies. This is particularly frustrating in that this is actually often a false choice. The transition of air quality strategies from “command and control” to pollution prevention to sustainable and regenerative approaches belies the belief that economic improvement must be accompanied by a modicum of environmental damage. Indeed, one of the great thermodynamic lessons of sustainable design and life cycle perspectives is that pollution is almost always an indication of wastefulness and inefficiency. If something is leaking out of a vessel or exiting a stack, it has gone from being a resource to becoming a pollutant.

One means of avoiding the mistakes of the past in these growing economies is to apply the lessons learned that have led to substantial improvement of air quality in the West. The growth in reliable data and information has fueled the expansion of scientific and engineering knowledge and, yes, even wisdom. This all needs to be shared with those nations that are in the process of

repeating the missteps. This is the first grand challenge for the air pollution scientific community.

### **33.2 GRAND CHALLENGE #1: SHARED KNOWLEDGE OF LESSONS LEARNED**

The information age is either rife with Pandora's Boxes or treasure troves, depending on one's perception and the topic at hand. For the air pollution expert, it is endowed with treasure troves. What would have taken months to transfer technologies across the oceans via meetings, symposia, conferences, and on-site visits, can now be shared in nanoseconds via the Internet.

Another asset is the international air quality science community that has grown substantially from the middle of the previous century to present day. As air pollution knowledge has grown, so has the willingness of the science pioneers to share their expertise and technologies. Throughout the last quarter of the twentieth century, emerging technologies were shared among Western nations, with Eastern Europe and the previous Soviet Union states, and with south Asia and with many other parts of the world, notwithstanding the geopolitical obstacles and cultural differences.<sup>a</sup> These transfers included exponential advances in the state-of-the science in both conventional pollutants and air toxics.

The advances must continue and increase to address the air pollution problems throughout the world, but with sensitivity to the socioeconomics and uniqueness of other cultures. For example, many of the new applications and sensors work well only within a strong telecommunications network, which is not universally available. This leads to the next grand challenge.

### **33.3 GRAND CHALLENGE #2: EXTENDING AIR POLLUTION INFORMATION**

Computational tools have grown rapidly. Data on air pollutant concentrations, air pollution exposures, and health status of populations and individuals can be mined to provide insights that were simply not possible before. Informatic tools are available to interpret data and to observe patterns of air pollutants to make heretofore impossible associations with effects on humans and ecosystems.

Computational methods are being applied to fluid dynamics, toxicology, and other sciences to build models that explain the movement and change of pollutants, to assess potential exposures, and to explain the kinetics and dynamics of these pollutants and their metabolites in humans and other organisms. Computational and informatics tools can also be applied in new ways to inform and to select options for controlling the emissions, including the expected change to ambient air quality with each option. Better statistical tools are also needed to compare options, e.g. Bayesian approaches that update outcomes (i.e. posterior distributions) with various control strategies.

Spatiotemporal tools are also becoming increasingly reliable. Air pollution curricula are increasing the use of geographic information systems, geostatistical methods (e.g. kriging), and land use regression techniques. Such tools can be very useful in preliminary screening of air pollution exposures and in linking potential sources to measured concentrations.

All of these tools already exist, but they need to continue to be fitted to air pollution needs. This may be particularly challenging for complicated mixtures, e.g. urban air toxics and coke oven emissions, as well as real-world indoor pollutant mixtures. These tools are only now being applied to human activities and the use of products. Such psychosocial predictions are difficult given the many variables of humans in various microenvironments, but this is a much better depiction of how a person comes into contact with an air pollutant compared to the commonly used measures of a population's central tendencies (e.g. means and medians).

This brings up the next grand challenge, i.e. addressing indoor and microenvironmental exposures to air pollutants.

### **33.4 GRAND CHALLENGE #3: NEED TO CHARACTERIZE REAL-WORLD EXPOSURES**

It is tempting to conclude that the measurements of a few air pollutants at a few hundred monitoring sites accurately explain air pollution. Indeed, these are a great improvement over having no such sites, or a few that have been sited near a likely source of a known pollutant or in a highly polluted urban area. However, these measurements are dedicated mainly to criteria pollutants and to a handful of the many possible hazardous air pollutants. Even if the data were accurate and representative of ambient air, this would not represent a person's actual

<sup>a</sup> Robert Stevens, a prolific air pollution expert formerly with the U.S. EPA, recounted how two scientists from a Baltic nation were clandestinely able to develop a method for measuring airborne mercury, basically in their "garage".

exposure. For this, measurements are needed in each place and for each activity for that person every day.

Thus, there is a need for measurements of pollutants indoors, in vehicles and in other microenvironments that can be aggregated to show the entire pollutant exposure profile for the individual. This calls for improved sensors, e.g. passive monitors, and applications (e.g. tablet and smart phone programs). From these databases, more reliable models can be built.

These models must account for at least three modes of personal exposure: (1) outdoor, which is quite likely different from the measurements at a central site, given micrometeorology and nearby sources; (2) indoor, which is a function of indoor sources and penetration of outdoor concentrations; and (3) other microenvironments, each with its own air pollution loading and mixing terms.

Indoor exposures to air pollutants in poorer regions can be at much higher concentrations than in those in higher socioeconomic status (SES) areas. For example, more wood and biomass fueled cooking and heating occur indoors in lower SES areas in many parts of the world. These can be large sources of particulate matter, carbon monoxide and air toxics, such as the polycyclic aromatic hydrocarbons. Thus, a highly exposed population is less likely to have the means to provide accurate measurements with today's technologies.

Interestingly, the challenge will probably need advances in both very low-tech and very high-tech portable, remote measurement systems. The existing system of collecting a sample and conducting laboratory analysis may not work well for remote areas. This calls for low-maintenance adaptive technologies (e.g. passive monitors with no need for a pump) and low-maintenance high-technology systems (e.g. solar powered, long-life battery powered systems, with satellite links). Sophisticated analyses, e.g. organic chemical analysis, will have to be conducted in many of these areas using portable and open-path technologies. These are currently in use, but are limited in the number of chemicals detected and have transport and other logistical challenges, which will need to be improved for wider use.

The next challenge is how to use these more reliable data to improve air quality.

### **33.5 GRAND CHALLENGE #4: IMPROVEMENTS AND ADAPTATIONS TO CONTROL TECHNOLOGIES**

Measuring and modeling of what is in the air is very important, but only the beginning. When something harmful is found in the air, the logical question is what can be done to decrease these concentrations to a "safe" level. Thus, helping emerging nations document

air quality using the proven measurement and modeling must be followed by improved means of treatment and removal of myriad compounds in air emissions. Actually, this can be said for every nation, especially for air toxics. As detection limits decrease, it becomes more likely that additional troublesome air pollutants will be found in what was before considered to be relatively unpolluted air.

The sources of both criteria and hazardous air pollutants are expected to continue and likely to increase in many parts of the world. For example, it is presently unlikely that the emerging nations will diminish the use of coal in the coming decades. Indeed, the use is likely to increase. Thus, the typical pollutants released during the combustion of coal, including mercury and sulfur dioxide, will increase in concentrations in many of the world's most populated urban areas. Of course, the technologies for removing particulate and gaseous pollutants discussed in Chapters 31 and 32 can and should be applied in China, India, and other regions with increasing coal combustion.

Even if the stationary sources burning coal and other fossil fuels in these areas comply with regulated and recommended control technologies, this is likely to be insufficient to ensure healthful air quality given the large and rapidly growing number of mobile sources (i.e. vehicles) and the highly distributive system of heating and other combustion sources in these countries.

In most of Europe, Japan, and North America, heating is often by electricity from centralized, stationary sources that burn coal. Thus, control technologies against coal's pollutants can be applied at the power plant. In many other countries, coal and other combustibles are burned at myriad buildings throughout the region. Control technologies in these cases would have to be at the point-of-use, which would be much more difficult to install, to maintain, and to ensure compliance. This calls for adapting and miniaturizing successful large-scale stationary sources. In addition, these must be low-maintenance, long-lasting, and cost-effective.

Another important aspect of this challenge is building a knowledge base on when and how to intervene when pollution occurs. This is akin to an anthropological approach, where the air pollution scientist or engineer places himself or herself into the setting. For example, if in the process of studying a neighborhood for possible sources of air pollution, an air pollution expert who observes exposures or potential exposures could recommend control and prevention methods on the spot, e.g. installation of air cleaning equipment or training on furnace and stove maintenance or reductions in sources of pollutants like lead from paint. It is proper for scientists, especially research scientists, to keep an arms-length relationship to maintain

objectivity and validity of findings. However, addressing an immediate indoor or other microenvironmental exposure and recommending avoidance behaviors to reduce exposure takes primacy over data quality.

### **33.6 GRAND CHALLENGE #5: SYSTEMS AND SUSTAINABLE THINKING**

Human populations and ecosystems are highly complex. They are threatened by complicated and multifaceted hazards. Thus, they must be viewed systematically. Every hazard exists within a milieu of life cycles. Every substance released into the environment has a life cycle. It is during this life cycle that the substance has become a pollutant. The process can be likened to a sensitivity analysis, i.e. identifying and giving weights to the factors that lead to an outcome, i.e. greater weighted factors will change the outcome more dramatically than will lesser weighted factors. For example, if one particular species of plant is eliminated from a habitat, the weight of the loss of that species would be very high if it were the exclusive prey of a predator. Its weight would be lower if all the consumers in the niche were not selective in their prey. Such sensitivities can be documented for any habitat and be part of any vulnerability assessment prior to stresses and certainly before these stresses reach disaster thresholds.

Unfortunately, there will undoubtedly be future air pollution problems that are not presently foreseen. Preventing or ameliorating them when they happen is an exercise in prediction. Models are used to predict an event or series of events. The processes that led to an actual environmental problem are difficult enough to identify completely; but predicting how events in the causal chain will interrelate is impossible to predict with much accuracy.

Identifying the factors that have contributed to the occurrence of air pollution problem is complicated. Indeed, the interaction of variables that lead to an environmental problem is almost always chaotic. Few credible information sources are available about what was occurring during/at any given period of time. Almost always, measured data are not sufficient to characterize the movement and change of materials in the environment in a way that fully explains air pollution; so scientists and engineers must rely on models to extrapolate and interpolate to find meaning.

Global greenhouse gas emissions continue to rise. Numerous toxic compounds continue to be released. Risks to human health persist. Sensitive ecosystems are threatened. As mentioned, such problems are not readily nor completely resolved by the "command and

control" approaches. Innovations and market forces (e.g. incentives and emissions banking and trading) must also be part of the solution.

Hopefully, this book is among the resources for preserving and extending what we have learned in the past few decades. Ideally, it is also a baseline for the next generation of air pollution prevention and control systems.

The problems will best be addressed by new thinking that is underpinned by sound science. The fundamentals of air pollution are based in the physical sciences, but their application to address present and future air pollution problems must also rely on the innovations from every aspect of contemporary society.

Philosopher Immanuel Kant is famous for the categorical imperative, which says that the right thing to do requires that a person must "...act only on that maxim whereby thou canst at the same time will that it should become a universal law".<sup>2</sup> In other words, in deciding whether an act is right or wrong, it is our duty to think about what would happen if everyone acted in the same way. This should sound familiar to those of us concerned about the environment and public health. In fact, it is the essence of sustainability. The only way to ensure that something is protected for the future is to think through all of the possible outcomes and select only those that will sustain a better world.

Kant's imperative is the rationale that underpins environmental mottos and quotations:

- Think globally, act locally.
- We are not going to be able to operate our spaceship earth successfully nor for much longer unless we see it as a whole spaceship and our fate as common. It has to be everybody or nobody. (R. Buckminster Fuller)
- Now, as never before, the old phrase has a literal meaning: We are all in the same boat. (Jacques Cousteau)
- When one tugs at a single thing in nature, he finds it attached to the rest of the world. (John Muir)
- A thing is right when it tends to preserve the integrity, stability, and beauty of the biotic community. It is wrong when it tends otherwise. (Aldo Leopold)
- Nothing ever goes away. (Barry Commoner)
- Only within the moment of time represented by the present century has one species—man—acquired significant power to alter the nature of his world. (Rachel Carson)

The philosopher gives us reasons to act, but the scientist and engineer must give us credible ways to act. The air pollution expert now requires a deep understanding of systems that operate once the design is implemented and, ideally, forms a foundation for the exploration and discovery of innovative ways to minimize risks to health

and safety, increase design reliability, and improve the environment. With a better understanding of sustainable processes, new stewardship strategies will emerge to supplant old ways of thinking, especially replacing those antiquated templates that depend on the subjugation of nature to achieve human ends. Actually, it may not be correct to classify these approaches as “new”, since it was only within the past couple of centuries that we abandoned many sustainable views of how humans are to care for the environment. A quick perusal of the words of Saint Francis of Assisi or Chief Seattle remind us of this responsibility.

Understanding air quality depends on a foundation in the laws of thermodynamics and motion. All engineering and science curricula are built on this foundation. It is encouraging that over the past few decades, air pollution strategies have become more integrated. Simply shifting an air pollutant from the atmosphere to the hydrosphere is neither a systematic nor a sustainable solution. This is done, for example, when arsenic, mercury or another toxic substance is removed from the gas stream, caught in a slurry, which is then regularly delivered to a pit or pile. This may indeed be the best approach in terms of air pollution, but the sustainable approach would also address the new, more concentrated As- or Hg-laden slurry. The good news is that multicompartamental solutions are happening and must continue.<sup>b</sup> Fewer experts draw a “bright line” that considers the job completed once the pollutant leaves the atmosphere.

### 33.7 GRAND CHALLENGE #6: TRANSDISCIPLINARY SCIENCE

The motivation behind the systematic view and the sustainability framework is actually quite familiar to engineers, even if the terms themselves are not. Both are manifestations of the “critical path” and “reverse engineering”. The critical path is used by designers to ensure that all the necessary steps are included in the flow toward the completed design. Even a problem with a seemingly small step in this path can mean failure. Delays in any of the critical components can propagate to a level in which the design is threatened in quality or the design objectives are compromised or missed. The “perfect” design is worthless if it is too late to matter.

Reverse engineering is simply the critical path in reverse. It is a structured way to keep the end in mind

and to ascertain all the steps that have led to a success or failure. In addition, reverse engineering shows which steps are essential, which steps are desirable but not necessarily essential (e.g. improving timeliness or quality, but their absence does not truncate the critical path), which steps are unnecessary and which steps are counterproductive.

Interestingly, many things scientists and engineers do fall outside of the first two types. Often, however, the steps that are unnecessary from a scientific standpoint may well be essential and desirable from a policy or feasibility standpoint. For example, if control technology X has a 95% removal efficiency and control technology Z’s removal efficiency is 90% for the same air pollutant, there is no technical need to justify choosing control technology X. However, if the cost is prohibitively higher, X may not be chosen, unless it is the only way to meet emission limits.

The systems view even affects the critical path. In the example above, if the more efficient technology is less costly, that would be ideal from an air pollution control perspective. However, if this technology leads to the generation of a hazardous waste that is very difficult and costly to handle, store, and reuse, this would detract from this option. Indeed, the generation of the waste is an example of a step that is counterproductive to achieve a sustainable solution to the air pollution problem.

Systems scientists are now comfortable with reaching out to other scientific disciplines in their research. Indeed, that is the essence of systems science. Similarly, practitioners are becoming more comfortable with such multidisciplinary efforts, e.g. systems engineering and systems medicine that include all of the physical, chemical, and biological sciences. As evidence, recent Nobel prizes and other science awards have been shared among physicists, chemists, engineers, and physicians. Including nontechnical stakeholders in the critical path is more challenging. Often, however, a step that appears to be technically “unnecessary” and “counterproductive” may actually be essential from a feasibility and implementation perspective. Such steps obviously will not change the scientific principles, but will be needed to educate and involve those affected by the design. The step also helps to ensure that technically feasible options are also culturally appropriate. For example, the best place to site a noisy piece of air pollution equipment from an emissions standpoint may not be the best place from a neighborhood quality standpoint, or a chain link

<sup>b</sup> As this book went to print, North Carolina was addressing a massive spill in to the Dan River. Its source was one of several large coal ash piles near power plants. Arsenic and heavy metals were found in the water; not surprising, since ash remains after the volatile components are emitted during combustion. Thus, ash is actually a means of “refining” the coal’s metals and metalloids, which will be mobilized either slowly (e.g. leaching into ground water) or rapidly (e.g. a spill into the adjacent river).

fence may be a perfectly acceptable barrier between industrial operations and residences from an access perspective, but not aesthetically.

The truly unnecessary steps that occur during air pollution prevention and control efforts can be limited or eliminated by monitoring the critical paths. The key question is always, "Is this the best and only step to meet this sub-objective on the path to the final objective, e.g. an emission limit?" A corollary question would be, "If a previous step were changed, would this step even be needed to meet the objective?"

Thus, future solutions to air pollution will increasingly rely on multidisciplinary teams. These teams will have to go beyond each member simply providing information to a team lead. They must be "transdisciplinary". That is, each member retains the knowledge of his or her field, but actually works across and beyond this discipline. Transdisciplinary teams include every necessary scientific discipline, plus other nontechnical stakeholders, so that the solutions automatically are systematic.<sup>3</sup> This prevents the need to have to translate and adapt the scientifically sound approach, i.e. "retrofit" the solution to accommodate cultural, social, economic, and other perspectives. The transdisciplinary team will have already designed the solution accordingly. This is particularly crucial when trying to adapt a design or technology that works well in one culture to another cultural setting. Indeed, this was a major flaw that led to the Bhopal toxic plume disaster (see discussion in Chapter 4). For the disaster to occur, there had to be several essential steps leading to the explosion and emission of the toxin, e.g. critical mass of chemical product, an overfilled reserve tank and possibly even sabotage. The damage incurred by the disaster was exacerbated by other cultural factors, especially a lack of appreciation of squatting and allowing so many people to build makeshift housing so near the factory, which increased the magnitude and duration of their exposure to the toxin.

Any failsafe mechanism and control technology can only work well with hands-on management, which always exists within a specific social milieu and context. In the Bhopal case, the context included cultural differences that obviated a sufficient understanding of the written and unwritten codes of Western civilization (e.g. safety manuals written only in English; different perspectives of land ownership and squatting). The lesson here is that when control technologies and other air pollution strategies are adopted and adapted in different cultural settings, air pollution experts will need to appreciate that what is the standard of practice in one country or state is likely to be at least somewhat different in another. Of course, this does not allow the practitioner to violate any of his or her codes of ethics or other professional canons and standards, but it does

mean that a "one size fits all" solution will not work without at least some customization in other settings.

### **33.8 GRAND CHALLENGE #7: TRANSLATIONAL SCIENCE**

In addition to the synergies of a transdisciplinary team approach, the scientific fundamentals of air pollution have to be translated to be understood by various audiences. Translational science is a metaphorical two-way street. Science from one discipline is translated to others for some common purpose. In return, the common purpose advances the specific discipline. For example, biochemistry contributes to medicine and ecology, which help to explain concepts and to enhance hypotheses and models that would be restricted by pure reductionism. Explaining lung cancer, for example, needs not only reductionist biochemistry (e.g. DNA-pollutant interactions), but also the contribution of reductionist physics (e.g. diffusion into the cell), reductionist mechanics (e.g. respiratory responses), and other assimilations of "pure" science. In return, each of these fields advances with enhancements to the understanding of genetic molecular structures and substitutions, biochemical gradients, respiration mechanics, etc. that could not be understood outside of this translational system.

Social and cultural factors are usually more complex than physical and biological scientific factors. For example, the uncertain, yet looming threat of global climate change can be attributed in part to technological and industrial progress. But using straight-line trends or even sophisticated climatological models will be insufficient to predict the extent and degree of damage. The number of variables necessary to define climate is so large and the interrelationships among them so complex, even the highly advanced computational methods and climatological models have large uncertainties when used to predict climate change. Even more complicated are the predictions of human behavior and decision making. For example, to what extent will future people engage in avoidance behaviors, such as spending more time indoors, exposing them to different array of pollutants? How will human populations respond to any shifts of insect vector-borne diseases? How will companies respond to emission reductions in their siting decisions?

The good news is that emergent technologies are beginning to assuage some of the contributing factors, e.g. improvements to alternative sources of energy, such as wind and solar, which in turn could lead to less global demand for fossil fuels. Conversely, these same factors could lead to complacencies or even lead to other, previously unknown and unexpected

environmental problems, e.g. changes in migratory patterns if wind turbines interfere with bird habitats.<sup>4</sup>

For centuries, societal momentum has been toward urbanization and increasing the size of economies, which is indicated by higher rates of industrial output. Society also demands the control of the consequences caused by these same endeavors, including air pollution emission limits after the fact. These seemingly conflicting demands are often quite rational at a personal level. For example, radiation is both a cause and a cure for cancer. Advances in radioisotope technology are part of the arsenal to treat cancer, but exposure to these same radioactive wastes leaving hospitals can increase the risk of contracting cancer. Likewise, cleanup of polluted waters and sediments can be accomplished using combustion and incineration to break down some very persistent contaminants, but combustion in general is problematic in its release of products of complete combustion (carbon dioxide) or incomplete combustion (e.g. dioxins, furans, polycyclic aromatic hydrocarbons, and carbon monoxide). In almost every discussion in this book, air pollution has emerged as a byproduct of an enterprise that is deemed useful and is in demand, at least for some period of time, by large sectors of the population.

This apparent dichotomy between societal aspirations and problems calls for advances in science and technology. Unfortunately, these very same technologies may lead to a whole new set of problems.<sup>5</sup> Sting, the singer-philosopher, sums up this dichotomy as his having never seen a "miracle of science that did not go from a blessing to a curse".<sup>6</sup> While the lyrics are apparently intended to be overly pessimistic, e.g. it is likely that Sting uses electricity, wireless communications, nanotechnologies, and other miracles of science that not so long ago seemed impossible, his sentiments are instructive. Every technological advancement has some degree of uncertainty and the potential for downstream problems.

Cross-cultural transport of environmental problems is continuing and growing in certain parts of the globe. For example, computer materials and other wastes are shipped from the Western Hemisphere to Bangladesh for recycling that exposes unprotected workers to contaminants at extraordinarily high concentrations of pollutants; well above levels acceptable in the West. Beyond moral problems associated with such practices, this is also a reminder of the interconnectedness of all people. This is evident in the banning of substances. A number of pesticides, including DDT, have been banned in Europe, Canada, and the United States. People in the West, however, continue to be exposed to several of these substances by importing food that has been grown where these pesticides are not banned. In fact, Western nations may still allow the pesticides to be formulated at home, but do not allow their application and use. So, the pesticide comes back in the imported products;

known as the "circle of poisons". In addition to products, these very persistent and toxic substances also find their way back to the banning nations from long-range atmospheric transport and residual concentrations in the food chain.

Products that contain dangerous materials like asbestos, lead, mercury, polybrominated compounds, and polychlorinated biphenyls were once considered acceptable and were even required by law or policy to protect the public safety and health, such as asbestos-containing and polybrominated materials to prevent fires; DDT, and other persistent pesticides for vector control in an effort to prevent disease; and methyl *tert*-butyl ether as a fuel additive to prevent air pollution. Subsequently, these products were all found to cause environmental and health problems.

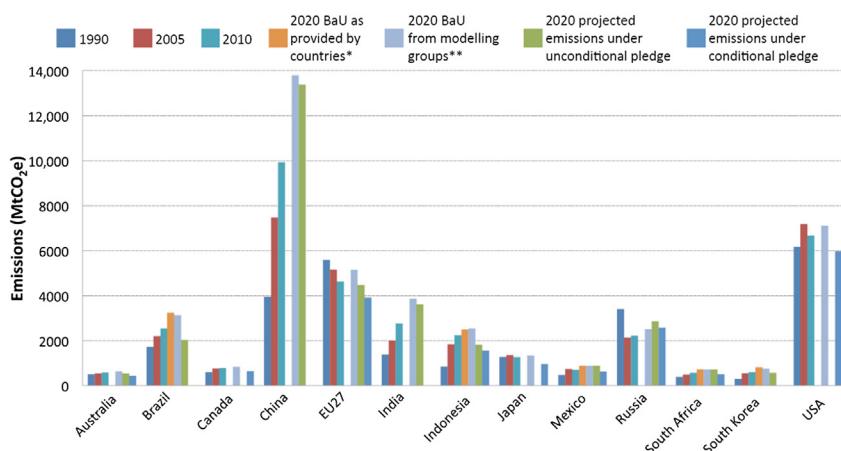
Global problems include climate change, acid rain, and the depletion of ozone in the stratosphere. They affect everyone on the planet to some degree. The good news is that nations have been reasonably successful in improvements in several cross-boundary problems. Notably, the United States has decreased emissions of acid-forming pollutants that have harmed ecosystems in Canada and Scandinavia. Most of the world has banned and required substitutes for ozone-depleting substances, like the most chemically active chlorofluorocarbons. There have been dramatic decreases in lead emissions from vehicles, first in developed economies and increasingly in developing nations.

Western nations have taken actions that have lowered the emissions or at least the rate of increase of global greenhouse gas (GHG) emissions. Europe has made substantial reductions in GHG emissions and the US has slowed the rate of growth of these emissions. Unfortunately, even if all countries meet their most ambitious formal commitments, there will still be a shortfall in emission reductions that would be needed to reduce climate change threats sufficiently. Meanwhile, the mix of nations contributing has changed. Indeed, the West may soon no longer be the largest contributor to GHG emissions (see Figure 33.1).<sup>7</sup>

Developing countries generally emit CO<sub>2</sub> at higher rates per unit of GDP than developed countries, especially if the share of forestry emissions is high (e.g. Brazil and Indonesia). The GHG emission rates, i.e. all GHGs combined and expressed as a CO<sub>2</sub> equivalent, are growing at a rapid rate in China, India, Brazil, and Indonesia.

Regarding CO<sub>2</sub> specifically, its emissions grew by 1.0 Gt from 2010 to 2011, or 3.2%. Coal accounted for 45% of total energy-related CO<sub>2</sub> emissions in 2011, followed by oil (35%) and natural gas (20%). This yearly increase was 6.1% in countries outside the most developed economies, but was slightly offset by a 0.6% reduction in emissions by the developed nations. China was the

**FIGURE 33.1 Regional year 1990, 2005, 2010, and 2020 greenhouse gas emissions for G20 countries (and European Union countries as a group) that have made pledges to reduce emission.** Emissions are reported in units of annual gigatons of carbon dioxide equivalent (GtCO<sub>2</sub> per year). Carbon dioxide equivalents of non-CO<sub>2</sub> gases are computed from the 100-year global warming potentials. Note: \* = where available; \*\* = based on median of modeling results. Ref. 7. (For color version of this figure, the reader is referred to the online version of this book.)



biggest source of the global increase in emissions, i.e. 720 million tonnes (Mt) or an increase of 9.3%, primarily due to higher coal consumption. India's emissions grew by 140 Mt, or 8.7%, displacing Russia as the fourth largest emitter behind China, the United States, and the European Union. Despite these increases, per-capita CO<sub>2</sub> emissions in China and India still remain just 63% and 15% of the CO<sub>2</sub> released, respectively, of that released per-capita in the developed nations.<sup>8</sup>

Total CO<sub>2</sub> emissions in the United States in 2011 fell by 92 Mt, or 1.7%, mainly due to fuel switching from coal to natural gas in power generation and a mild winter, which decreased demand for electrical auxiliary heating. US emissions fell by 430 Mt (7.7%) between 2006 and 2011, the largest reduction of all countries or regions, which can be linked to efficiency improvements, higher oil prices, and the economic downturn leading to fewer vehicle miles traveled, along with a substantial shift from coal to gas in the power sector. CO<sub>2</sub> emissions in the EU in 2011 were lower by 69 Mt, or 1.9%, due largely to the economic recession and attendant drop in industrial production and a relatively warm winter that reduced heating needs. By contrast, Japan's emissions increased by 28 Mt or 2.4%, as a result of a substantial increase in a switch from nuclear to fossil fuels for power generation due to taking the Fukushima plant off-line.<sup>9</sup>

The transfer of GHG and other pollutant control and prevention strategies among nations is complicated and dynamic, as indicated above. The grand challenge for the air pollution experts will be how to do this in a scientifically sound and culturally effective way.

### 33.9 GRAND CHALLENGE #8: FUTURE GENERATIONS

The previous discussion addressed distant peoples. Another challenge is to address the temporal aspect of sustainable air quality, i.e. future human populations

and future ecosystems. There are two basic ways of achieving acceptable air quality, i.e. risk-based decision making and precaution-based decision making. Much of this book has been devoted to the former, i.e. use of scientifically sound information to assess the risk and to use this assessment to select appropriate means of reducing that risk. Indeed, this is the major paradigm for conventional and hazardous air pollution control strategies. However, when the risks are highly uncertain and outcomes are substantial, severe, and potentially irreversible, then a modicum of precaution is needed beyond the confines of the risk assessment process.

Many scientists and policy makers have recommended taking the precautionary approach to climate change. That is, even if the data are uncertain, corrective actions that do not have sufficient risks themselves should be taken. The caveat is needed since corrective actions often have their own risks, e.g. fuel additives to improve air emissions but that have been subsequently found to damage other parts of the environment.

Another aspect of future people is education. This book, for example, is a part of air pollution education within an engineering or science framework. However, air pollution education begins long before and continues well after formal education at the university level. This book also serves as a manual for careers after the formal education. However, there is a dearth of useful educational tools for the next generation, i.e. those before advanced placement high school courses.

This need is not for lack of demand. The author has met with very young students (e.g. 3-year-old preschoolers), who have an amazing grasp of some very technical air pollution topics. For example, more than half of the control technologies discussed in this book addresses particulates. Young children understand texture (Figure 33.2). From this understanding, with some prodding and guidance, they can extrapolate this



**FIGURE 33.2** Illustration of four textures, i.e. four particle sizes, as conceived and drawn by a 4-year-old prekindergartener, Chloe Jayne Randall, St. Thomas More School, Chapel Hill, North Carolina. *Photo by D.A. Vallero (2013).* (For color version of this figure, the reader is referred to the online version of this book.)

knowledge to an understanding of the particles shown in Figure 3.2 in Chapter 3.

The lesson here is that the fundamentals of air pollution can begin to be grasped and taught at increasingly complex levels from a very early age. New pedagogies are needed to reach presently ignored groups, especially those who are being exposed and will be exposed and who will be affected by the air quality decisions that are being made now. Thus, it is the hope of the author that the investment made by the reader will not only lead to cleaner air but also that the propagation of this expertise will expand to recruit the next generation of experts. Each generation is morally obligated to invest in the next. Certainly, their challenges will be great, but the author is convinced that today's 4-year olds will be the new experts to build on today's knowledge to realize opportunities for a cleaner environment that today's air pollution experts cannot even conceive.

## QUESTIONS

1. List three ways that science lessons learned in addressing air pollution can be transferred to developing countries. How about engineering lessons? Policy and regulatory lessons?
2. Consider how computational fluid dynamics has changed meteorology in recent years? How can

similar computational methods in other sciences be used to estimate, predict, and address air pollution?

3. Since the highest levels of exposure to some of the most dangerous air pollutants occur indoors, how do means of decreasing exposures differ from those employed for the criteria air pollutants in ambient air?
4. Choose an environmental motto mentioned in this chapter. How does systems thinking relate to it?
5. What is the difference between multidisciplinary science and transdisciplinary science as they related to air pollution prevention and control?
6. Compare a risk-based approach to a precautionary approach to address global environmental and air pollution problems. Describe a problem best addressed with each.
7. Identify a pollution problem that the previous generation had thought would be difficult or impossible to address, but which is now being addressed. Explain how the paradigm shifted.
8. Identify a pollution problem that is presently thought by many to be difficult or impossible to address. How can the paradigm be shifted?

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# Abbreviations and Symbols

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Air pollution science and engineering employs basic and derived information from the physical, chemical, biological, and social sciences. As such, the abbreviations and symbols used in equations, reactions, and descriptions of properties and mechanisms vary according to the specific aspect of air pollution being discussed. The following abbreviations and symbols are used in this text and/or other air pollution writings. The same symbol or abbreviation may be applied differently in different chapters. Thus, the specific context must be understood.

$\underline{D}$	dispersion tensor (length time <sup>-1</sup> )	$\mu$	chemical potential (mass length <sup>2</sup> time <sup>-2</sup> )
$\bar{v}$	average linear velocity (length time <sup>-1</sup> )	$\mu_E$	microenvironment
$\bar{V}$	average speed (length time <sup>-1</sup> )	$\mu_g$	gas viscosity (mass length <sup>-1</sup> time <sup>-1</sup> )
$\eta_e$	effective porosity (dimensionless)	$\mu_m$	arithmetic mean
$\Delta G_f^{*0}$	free energy formation at steady state	$\mu_M$	micromole
$K_{1a_{G/A}}$	global volumetric mass transfer coefficient (time <sup>-1</sup> )	$0$	initial (subscript)
-	single bond	$A$	area, surface area (length <sup>2</sup> )
$\sigma$ or $\sigma^\circ$	surface tension (forces length <sup>-1</sup> )	$a$	acceleration (length time <sup>2</sup> )
$\sigma$ or SD	standard deviation	$A$	activity rate (in emission calculation)
$\sigma^2$	variance	$A$	air (subscript)
$\phi_g$	microgram	$A$	aqueous phase
$\phi_m$	micron or micrometer	$A$	atomic weight
$\sigma_n$	normal shear stress (mass length <sup>-1</sup> time <sup>-2</sup> )	$A/C$	air-to-cloth ratio (filtration; length time <sup>-1</sup> )
$\frac{\Delta}{\Delta x}$	energy (heat) required for reaction	$AA$	atomic absorption detection
$\frac{dy}{dx}$	ordinary derivative of $x$ with respect to $y$	$A_{aw}$	airway surface area (length <sup>2</sup> )
$S_A^*$	substrate concentration at the gas–aqueous interface	$ABL$	atmospheric boundary layer
$\bar{y}$	sample mean	$abs$	absorbed
$\frac{\bar{y}}{\bar{Y}}$	source mean	$ABT$	averaging, banking, and trading
$\frac{\partial y}{\partial x}$	partial derivative of $x$ with respect to $y$	$AC$	activated carbon
[C]	molar concentration	$AC$	alternating current (electricity)
=	mean or average (capped symbol or letter)	$ACGIH$	American Conference of Governmental and Industrial Hygienists
$\nabla$	double bond	$AChE$	acetylcholine esterase
$\nabla$	(nabla) gradient of a scalar field, especially in Navier–Stokes equations	$ACM$	asbestos-containing material
$\nabla$	(nabla) water table	$ACS$	American Cancer Society
$\cong$	approximately equal to	$ACToR$	Aggregated Computational Toxicology Resource
$\approx$	almost equal to	$ADAF$	age-dependent adjustment factor (cancer risk)
$\equiv$	triple bond	$ADD$	average daily dose
$\rightarrow$	kinetic reaction	$ADME$	absorption, distribution, metabolism, and excretion (or elimination)
$\leftrightarrow$	equilibrium reaction	$ADP$	adenosine diphosphate
$^{\circ}\text{C}$	degrees Celsius or Centigrade (temperature)	$AF$	absorption factor
$^{\circ}\text{F}$	degrees Fahrenheit (temperature)	$AF$	atrial fibrillation
$^{\circ}\text{K}$	degrees Kelvin (temperature)	$A_{fabric}$	fabric surface area (length <sup>2</sup> )
$^{\circ}\text{lat}$	latitude (degrees)	$AFO$	animal feeding operation
$^{\circ}\text{long}$	longitude (degrees)	$AIHA$	American Industrial Hygiene Association
$^{\circ}\text{R}$	degrees Rankine (temperature)	$AIRS$	Aerometric Information Retrieval System (U.S.)
$\mu$ or $\mu_v$	dynamic viscosity (mass length <sup>-1</sup> time <sup>-1</sup> )	$ALAD$	aminolevulinic acid dehydratase
		$amu$	atomic mass unit
		$A_p$	cross-sectional area of the particle (length <sup>2</sup> ) = $\frac{\pi d_p^2}{4}$
		$a_p$	particle acceleration
		$AP-1$	activator protein-1
		$APCD$	air pollution control device
		$APCD$	air pollution control district
		$APCS$	air pollution control system
		$APE$	alkylphenolethoxylates
		$APG$	assigned protection factor
		$aq$	aqueous phase
		$AQCD$	Air Quality Criteria Document (U.S.)
		$AQI$	air quality index
		$AQMA$	air quality maintenance area
		$AQS$	Air Quality System (part of AIRS; U.S.)
		$ASCE$	American Society of Civil Engineers
		$ASME$	American Society of Mechanical Engineers

<b>ASPECT</b>	airborne spectral photometric environmental collection technology	<b>CMB</b>	chemical mass balance (model)
<b>AT or <math>t_{\text{averaging}}</math></b>	averaging time for exposure (time)	<b>CNG</b>	compressed natural gas
<b>atm</b>	atmosphere (unit of pressure)	<b>CNS</b>	central nervous system
<b>ATP</b>	adenosine triphosphate	<b>COE</b>	U.S. Army Corps of Engineers (also USACE)
<b>ATSDR</b>	Agency for Toxic Substances and Disease Registry (U.S.)	<b>COHb</b>	carboxyhemoglobinemia
<b>ATUS</b>	American Time Use Survey	<b>COPD</b>	chronic obstructive pulmonary disease
<b>aw</b>	airway (script)	$C_{\text{org}}$	substrate organic matter (mass of organic carbon per mass of substrate)
<b>AWMA</b>	Air and Waste Management Association	<b>cos</b>	cosine
<b>B</b>	background pollutant concentration (rollback model)	<b>COX2</b>	cyclooxygenase-2
<b>B(a)P</b>	benzo(a)pyrene	$c_p$	specific heat at constant pressure
<b>B/C</b>	benefit-to-cost ratio	$c_p$	cycles per second (1 cps = 1 Hz)
<b>BACT</b>	best available control technology	<b>CTEPP</b>	equilibrium concentration of the solute in the solid phase
<b>BAF</b>	bioaccumulation factor	$c_v$	cancer slope factor ( $[\text{mass mass}^{-1} \text{ time}^{-1}]^{-1}$ )
$b_{\text{ag}}$	absorption of light by $\text{NO}_2$ gas	<b>CVD</b>	Children's Total Exposure to Persistent Pesticides and Other Persistent Organic Pollutants Study
$b_{\text{ap}}$	absorption of light by particles	<b>CWA</b>	specific heat at constant volume
<b>BCF</b>	bioconcentration factor	<b>CWS</b>	cardiovascular disease
<b>BCR</b>	benefit/cost ratio	$C_xH_yO_z$	Clean Water Act (U.S.)
$b_{\text{ext}}$	light extinction coefficient	<b>CYP450</b>	Canada-wide standards
<b>BF</b>	bioavailability (percent of substance absorbed per day)	$d$	organic compound (hypothetical or representative)
<b>BOEM</b>	Bureau of Energy Management (U.S.)	$D$	cytochrome P450 enzyme
<b>BOF</b>	basic oxygen furnace	$D$	membrane thickness (length)
<b>BP</b>	blood pressure	$D$	air quality standard (rollback model)
<b>BPA</b>	Bonneville Power Administration	$d$	day
$b_{\text{rg}}$	scattering of light by gaseous molecules (Rayleigh scattering)	$D$	destroyed
$b_{\text{scat}}$	scattering of light by particles	$D$	diameter (length)
<b>Btu or BTU</b>	British Thermal Unit (power) = 1060 J	$D$	dose
<b>BW</b>	body weight (mass)	$D$	index of community diversity
<b>C</b>	chemical concentration ( $[\text{mass mass}^{-1}]$ , $[\text{volume volume}^{-1}]$ , or $[\text{mass volume}^{-1}]$ )	$D$	inside diameter of cyclone
$c$	speed of light ( $3 \times 10^8 \text{ m s}^{-1}$ )	$D$	intermedia or intercompartmental transport term (fugacity models)
$C_a$	airborne chemical concentration ( $\text{mass volume}^{-1}$ of air in breathing zone)	$D$	mass of pollutant per body mass
<b>CA</b>	carbonic anhydrase	$d_0$	transfer coefficient or compartmental rate constant (for fugacity)
<b>CAA</b>	Clean Air Act (U.S.)	$D_A$	proportionality constant (diffusion)
<b>CAAA90</b>	Clean Air Act Amendments of 1990 (U.S.)	<b>DANT</b>	nondiffusive transfer coefficient for fugacity
<b>CAFO</b>	confined animal feeding operation	<b>DAS</b>	diaminonitrotoluene
<b>cal</b>	calorie	$D_C$	data acquisition system
<b>CAM</b>	compliance assurance monitoring	$D_C$	diameter of the collection object (length)
<b>CARB</b>	California Air Resources Board	<b>DCE</b>	direct current (electricity)
$C_c$	Cunningham slip correction factor	$D_D$	dichloroethene
<b>CCA</b>	chromated copper arsenate	<b>DDD</b>	diffusive transfer coefficient for fugacity
$C_D$	drag coefficient (dimensionless)	<b>DDE</b>	dichlorodiphenyl dichloroethane
<b>CDC</b>	Centers for Disease Control and Prevention (U.S.)	<b>DDT</b>	dichlorodiphenyl dichloroethylene
<b>CDD</b>	chlorinated dibenzodioxin	<b>DES</b>	dichlorodiphenyl trichloroethane
<b>CDF</b>	chlorinated dibenzofuran	<b>DfD</b>	diethylstilbestrol
<b>CEM</b>	continuous emissions monitoring	<b>DfE</b>	design for disassembly
<b>CEQ</b>	Council on Environmental Quality (U.S.)	<b>DfR</b>	design for the environment
<b>CERCLA</b>	Comprehensive Environmental Response, Compensation and Liability Act (Also known as Superfund; U.S.)	<b>DHHS</b>	design for recycling
<b>CFC</b>	chlorofluorocarbon	<b>DHS</b>	Department of Health and Human Services (U.S.)
<b>CFR</b>	Code of Federal Regulations (U.S.)	$d_i$	Department of Homeland Security (U.S.)
<b>CHAD</b>	Consolidated Human Activity Database	<b>DI</b>	percentage difference (precision)
<b>CHIEF</b>	Clearinghouse for Inventories and Emission Factors (U.S.)	<b>DIAL</b>	daily intake
<b>CI</b>	confidence interval	$d_L$	differential absorption lidar
<b>Ci</b>	curie (radioactivity unit)	<b>DNA</b>	deciliter (volume)
$C_{ij}$	concentration of exposure by person $i$ in microenvironment $j$	<b>DNAPL</b>	deoxyribonucleic acid
<b>CMAQ</b>	Community Multi-scale Air Quality Model (U.S.)	<b>DNT</b>	dense (high density) nonaqueous phase liquid
		<b>DO</b>	dinitrotoluene
		<b>DOAS</b>	dissolved oxygen
		<b>DOC</b>	differential optical absorption spectroscopy
		<b>DOE</b>	diesel oxidation catalyst
			Department of Energy (U.S.)

DOI	Department of the Interior (U.S.)	<i>f</i>	Coriolis parameter
DOI	digital object identifier	<i>F</i>	energy flux
DOS	Department of State (U.S.)	<b>F</b>	favorable
DOT	Department of Transportation (U.S.)	<i>F</i>	force (mass length time <sup>-2</sup> )
DP	degradation product	<i>F</i>	frequency (probability and statistics)
<i>d<sub>p</sub></i>	physical particle diameter (length)	<i>f</i>	fugacity
D <sub>pa</sub> or <i>d<sub>pa</sub></i>	aerodynamic diameter of a particle (length)	<i>f</i>	fugacity (subscript)
DPF	diesel particulate filter	<b>F<sub>B</sub></b>	buoyancy force (mass length time <sup>-2</sup> )
D <sub>ps</sub> or <i>d<sub>ps</sub></i>	Stokes particle diameter (length)	<b>F<sub>C</sub></b>	centrifugal force (mass length time <sup>-2</sup> )
DQO	data quality objective	<b>F<sub>D</sub></b>	drag force (mass length time <sup>-2</sup> )
DRE	destruction removal efficiency	<b>F<sub>E</sub></b>	electrostatic charge (force)
DWH	Deepwater Horizon	<b>FFDCA</b>	Federal Food, Drug and Cosmetic Act (U.S.)
<i>e</i>	charge of electron ( $4.8 \times 10^{-10}$ statcoulombs)	<b>FGD</b>	flue gas desulfurization
<i>E</i>	electrical field strength (potential; voltage length <sup>-1</sup> )	<b>FHWA</b>	Federal Highway Administration (U.S.)
<i>E</i>	bulk modulus (fluid stress divided by strain)	<b>FID</b>	flame ionization detection
<i>E</i>	element (chemical)	<b>FIFRA</b>	Federal Insecticide, Fungicide and Rodenticide Act (U.S.)
<i>E</i>	emission	<b>FOARAM</b>	Federal Ocean Acidification Research and Monitoring Act (U.S.)
<i>E</i>	energy required in a reaction	<i>foc</i>	weight fraction of organic carbon in compartmental matrix (dimensionless)
<i>e</i>	Euler's number = 2.71,828,183...	<b>FONSI</b>	finding of no significant impact
<i>E</i>	event (probability and statistics)	<b>FQPA</b>	Food Quality Protection Act (U.S.)
<i>E</i>	exposure	<b>FR</b>	Federal Register (U.S.)
<i>E</i>	extractive	<b>FRM</b>	federal reference method (U.S.)
<i>E</i>	particle collection efficiency; inverse of penetration (filtration)	<b>ft</b>	foot (length)
<i>E<sub>0</sub></i>	strength of electrical field (volts length <sup>-1</sup> )	<b>FTIR</b>	Fourier-transform infrared
<b>E10</b>	Fuel mix of 90% gasoline and 10% ethanol	<b>g</b>	gas or vapor phase (subscript or parenthetic)
<b>E85</b>	Fuel mix of 15% gasoline and 85% ethanol	<b>G</b>	gas-phase emissions (mass time <sup>-1</sup> )
<i>EC</i>	average exposure concentration	<b>G</b>	Gibbs free energy
<i>EC</i>	elemental carbon	<b>g</b>	gram
<b>ECA</b>	European Chemicals Agency	<b>g</b>	gravitational force
<b>ECD</b>	electron capture detection	<b>g</b>	gravitational gas hold-up
<b>ED</b>	exposure duration (time)	<b>g</b>	growth factor (rollback model)
<b>EDC</b>	endocrine disrupting compound	<b>g</b>	nondiffusive flow rate (for fugacity)
<b>EDD</b>	electronic data delivery	<b>G</b>	standard gravitational field
<b>EDS</b>	energy dispersive spectroscopy	<i>g<sub>0</sub></i>	granulated activated carbon
<b>EDSP</b>	endocrine disruptor screening program	<b>GAC</b>	gallon (volume)
<i>E<sub>F</sub></i>	emission factor (in emission calculation)	<b>gal</b>	gas chromatography
<i>EF</i>	exposure frequency (time)	<b>GC</b>	gravitational constant = $32.2 \frac{\text{lb}_m \cdot \text{ft}}{\text{lb}_t \cdot \text{s}^2} = 980 \text{ cm s}^{-2}$
<b>EGR</b>	exhaust gas recirculation	<i>g<sub>c</sub></i>	gross domestic product
<b>EH</b>	epoxide hydrolase	<b>GDP</b>	global greenhouse gas
<b>EIA</b>	Energy Information Administration (U.S.)	<b>GHG</b>	gigahertz ( $10^9$ Hz)
<i>E<sub>ing</sub></i>	ingestion exposure (mass per time)	<b>GHz</b>	advection rate (fugacity models)
<i>E<sub>inh</sub></i>	inhalation exposure (mass per time)	<i>G<sub>i</sub></i>	gastrointestinal
<b>EIS</b>	Emission Inventory System (U.S.)	<b>GIS</b>	geographic information system
<b>EIS</b>	environmental impact statement	<b>GLP</b>	good laboratory practice
<b>EJ</b>	environmental justice	<b>GPS</b>	global positioning system
<b>EL</b>	exposure length (time per time)	<b>grad</b>	gradient; grad $f = \nabla f(x, y)$ in a plane and $\nabla f(x, y, z)$ in space
<b>ELF</b>	extremely low frequency	<b>GSP</b>	global warming potential
<b>EMEP</b>	Cooperative Program for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe	<b>GST</b>	glutathione S-transferase
<b>EMR</b>	electromagnetic radiation	<b>GT</b>	glucosyltransferases
<b>EPA or U.S. EPA</b>	Environmental Protection Agency (U.S.)	<b>h or hr</b>	hour
<i>E<sub>R</sub></i>	percent overall emission reduction efficiency (in emission calculation)	<i>h</i>	elevation
<b>ERDEM</b>	Exposure Related Dose Estimating Model	<b>H</b>	enthalpy
<i>erg</i>	energy and work unit ( $10^{-7}$ J)	<b>H</b>	hazard
<b>EROEI</b>	energy return on energy investment	<b>H</b>	headspace height
<b>ERPG</b>	Emergency Response Planning Guidelines (U.S.)	<b>H</b>	heat (subscript [mass length <sup>-1</sup> time <sup>-2</sup> ])
<b>ESP</b>	electrostatic precipitator	<b>H</b>	Henry's Law (subscript)
<b>ETS</b>	environmental tobacco smoke	<i>h</i>	horizontal (subscript)
<b>EVT</b>	extreme value theory	<b>HAP</b>	Planck's constant ( $6.62 \times 10^{-27}$ erg s)
<b>exp(x)</b>	exponential ( $e^x$ )	<b>HC</b>	hazardous air pollutant
<i>E<sub>v</sub></i>	energy at frequency <i>v</i>	<b>HCB</b>	hydrocarbon
			hexachlorobenzene

HCFC	hydrochlorofluorocarbon	$K_{\text{G/A}}$	partition coefficient between the gaseous and aqueous phases
HCH	hexachlorocyclohexane	$K_{\text{H}}$	Henry's Law partitioning coefficient
HEDS	Human Exposure Database System (U.S.)	$k_{\text{inh}}$	inhalation rate (volume of air per unit time)
HEPA	high efficiency particulate air (filter)	$\text{km}$	kilometer (length)
HHM	hierarchical holographic modeling	$K_{\text{oa}}$	Octanol-air partitioning coefficient
HI	hazard index	$K_{\text{oc}}$	Organic-carbon partitioning coefficient
HMIWI	hospital/medical/infectious waste incinerators	$K_{\text{ow}}$	Octanol-water partitioning coefficient
HON	hazardous organic NESHPAs	$k_{\text{p}}$	rate of chemical energy storage by primary producers
hPa	hectopascal (unit of pressure)	$\text{kPa}$	kilopascal (unit of pressure)
HPG	hypothalamic-pituitary-gonadal (axis)	$K_{\text{sp}}$	solubility product constant
HPLC	high performance liquid chromatography	$K_{\text{w}}$	water dissociation equilibrium constant
HPV	high production volume (chemical class)	$\text{kWh}$	kilowatt-hour
HQ	hazard quotient	$L \text{ or } l$	liter
HR	hazard ratio	$l$	liquid phase (subscript or parenthetic)
HRS	Hazard Ranking System (U.S.)	LADD	lifetime average daily dose
HRV	heart rate variability	LAER	lowest achievable emission rate
HSWA	Hazardous and Solid Waste Amendments (U.S.)	$\text{lb}$	pound (weight)
HVAC	heating, ventilation, and air conditioning	$\text{lb}_f$	foot-pound (force)
HYSPLIT	Hybrid Single Particle Lagrangian Integrated Trajectory (model)	$\text{lb}_m$	international avoirdupois pound (weight)
Hz	hertz (cycles $s^{-1}$ )	LC	liquid chromatography
$h\nu$	photon	$LC_{50}$	lethal concentration-50 (lethal to 50% of tested organisms)
$i$	group, species, subgroup of total (subscript)	LCA	life cycle analysis or life cycle assessment
I	immobilized	LCI	life cycle inventory
I	in situ	$LD_{50}$	lethal dose-50 (lethal to 50% of tested organisms)
I	intake dose	LEL	lower explosive limit
I	intensity	LEV	low emissions vehicle
I/M	inspection and maintenance program	lidar	remote sensing of distance using a laser (combination of light and radar)
IAEA	International Atomic Energy Agency	$\ln(x)$	natural log of x
ICRP	International Commission on Radiological Protection	LNAPL	light (low density) nonaqueous phase liquid
ID	interior diameter	LOAEC	lowest observed adverse effect concentration
IDL	instrument detection limit	LOAEL	lowest observed adverse effect level
IDLH	immediately dangerous to life or health	LoD	limit of detection (also known as DL, detection limit)
IF	intermediate frequencies	log	logarithm
IMPROVE	interagency monitoring of protected visual environments (U.S.)	LoQ	limit of quantitation
in Hg	inches of mercury (unit of pressure)	LOSU	level of scientific understanding
IN	mass or energy inflow to control volume; influent (subscript)	LPG	liquefied propane gas
IOGAPS	integrated organic gas and particulate sampler	LRTAP	long-range transboundary air pollutants
IOM	Institute of Medicine (U.S.)	LTP	local temperature and pressure
IPCC	Intergovernmental Panel on Climate Change	$L_v$	distance at which a black object is just barely visible
IQ	intelligence quotient	$m$	mass
IR	intake rate ([mass time $^{-1}$ ] or [volume per time])	$\text{m}$	meter
IR	infrared	M	mole (gram molecular weight)
IR-DIAL	infrared-differential absorption lidar	M	relatively nonreactive molecule in a reaction
IRIS	Integrated Risk Information System	MACT	maximum achievable control technology
ISCLT	Industrial Source Complex Long Term (model)	max	maximum (subscript)
IUR	inhalation unit risk	MCE	mixed cellulose ester
J	Joule (energy unit)	MCL	maximum contaminant level (drinking water)
J	soil-to-air flux	Me	metal
$k$	Boltzmann's constant ( $1.37 \times 10^{-16} \text{ erg K}^{-1}$ )	MEI	maximum exposed individual
K	partitioning coefficient	MFAA	Millipore cellulose ester membrane
$k$	reaction rate constant	$m_g$	mass of displaced gas
$k_1$	filter media resistance constant	MHz	megahertz ( $10^6 \text{ Hz}$ )
$k_2$	filter dust cake resistance constant	MIC	methylisocyanate
$K_a$	acid equilibrium constant	min	minimum (subscript)
$K_{\text{AW}}$	Air-water partitioning coefficient	min	minute (time)
$K_b$	base equilibrium constant	MIR	maximum individual risk
$K_D$	Soil sorption partitioning coefficient	$\text{mm Hg}$	millimeters of mercury (unit of pressure)
$k_e$	rate at which the producers use energy (via respiration)	mm	millimeter
$K_F$	Freundlich isotherm constant	$\text{mM}$	millimole
$\text{kg}$	kilogram (mass)		

mmBTU	$10^6$ BTU	NMDA	N-methyl-D-aspartate
MMT	methylcyclopentadienyl manganese tricarbonyl	NMHC	nonmethane hydrocarbon
mmt	million metric tons	NMMAPS	National Mortality and Morbidity Air Pollution Study (U.S.)
MOA	mode of action	NMOG	nonmethane organic gases
mol	mole (gram molecular weight)	NMVOC	nonmethane volatile organic compound
$m_p$	particle mass	NOAA	National Oceanic and Atmospheric Administration (U.S.)
MQO	model quality objective	NOAEC	no observed adverse effect concentration
MRL	minimum risk level	NOAEL	no observed adverse effect level
MS	mass spectroscopy	NOES	National Occupational Exposure Survey (U.S.)
MSAT	mobile source air toxic	$N_{out}$	number of particles (count) exiting a system (e.g. filter)
MSDS	material safety data sheet	NO <sub>x</sub>	oxides of nitrogen; specifically NO and NO <sub>2</sub>
Mt	malonyltransferases	NO <sub>y</sub>	oxides of nitrogen; specifically NO <sub>x</sub> and NO <sub>2</sub>
MT	metallothionein	NO <sub>z</sub>	HNO <sub>3</sub> + HONO + N <sub>2</sub> O <sub>5</sub> + HO <sub>2</sub> NO <sub>3</sub> + PAN + organic nitrates
MTBE	methyl tertiary-butyl ether	NPL	National Physics Laboratory (UK)
MUC	maximum use concentration	NPL	National Priorities List (U.S.)
mV	millivolts (potential)	NPP	net primary product (or productivity)
MW	megawatt	NPRI	National Pollutant Release Inventory (Canada)
MW	molecular weight	$N_R$	Reynolds number
$n$	number of charges (electrostatics)	NRC	National Research Council (U.S.)
N	concentration (number)	$N_{Rp}$	dimensionless particle Reynolds number
N	Newton (unit of force)	NSF	National Science Foundation (U.S.)
N	not significant	NSR	new source review
$n$	number (e.g. number of moles)	NTP	National Toxicology Program (U.S.)
N	transport process rate (fugacity $\times$ compartmental rate constant)	NTSIP	National Toxic Substance Incidents Program (U.S.)
N-100	respirator protection efficiency against particulate aerosols (99.97%), but not resistant to oil	NVOC	nonvolatile organic compound
NA	nonaqueous phase	O	octanol (subscript)
NA	nonattainment	O&M	operation and maintenance
NAA	neutron activation analysis	O(1D)	O atom in an excited singlet state
NAAQS	National Ambient Air Quality Standard (U.S.)	OA	organic acid
NAD	nicotinamide adenine dinucleotide	OC	organic carbon (subscript)
NADP	National Atmospheric Deposition Program (U.S.)	OC/EC	organic carbon-to-elemental carbon ratio
NADP*	nicotinamide adenine dinucleotide phosphate reduced form of NADP <sup>+</sup>	OECD	Organisation for Economic Co-operation and Development
NADPH	National Academy of Engineering (U.S.)	OMI	ozone monitoring instrument
NAE	national air monitoring station (U.S.)	OP	organophosphorous (pesticide class)
NAMS	nonaqueous phase liquid	OP-FTIR	open path Fourier transform infrared
NAPL	National Academy of Sciences (U.S.)	OSHA	Occupational Safety and Health Administration (U.S.)
NAS	National Aeronautics and Space Administration (U.S.)	OUT	mass or energy outflow from control volume; effluent (subscript)
NASA	NAT	P or p	pressure
	N-acetyltransferase	p	momentum
	NATA	p	partial
ND, n.d.	National Air Toxics Assessment (U.S.)	p	particle (subscript)
NDIR	not detected	P	particle penetration; inverse of efficiency (filtration)
NEA	nondispersive infrared	P	particulate matter emissions (mass time <sup>-1</sup> )
NEI	Nuclear Energy Agency	P	present air quality (rollback model)
NEPA	National Emissions Inventory (U.S.)	P <sup>0</sup>	probability
NESHAP	National Environmental Policy Act (U.S.)	P <sub>1</sub>	vapor pressure
	National Standard for Hazardous Air Pollutants (U.S.)	P-100	net primary productivity (or production)
ng	nanogram	p <sub>a</sub>	oil-proof respirator protection efficiency against particulate aerosols (99.97%)
NHANES	National Health and Nutrition Examination Survey (U.S.)	p <sub>a</sub>	partial pressure of chemical substance gas in inhaled air
NHATS	National Human Adipose Tissue Survey (U.S.)	p <sub>a</sub>	partial pressure of gas a
NHEXAS	National Human Exposure Assessment Survey (U.S.)	p <sub>a</sub>	pascal (unit of pressure)
NHIS	National Health Interview Survey (U.S.)	PA	preliminary assessment
$N_{in}$	number of particles (count) entering a system (e.g. filter)	PAD	population adjusted dose
NIOSH	National Institute for Occupational Safety and Health	PAH	polycyclic aromatic hydrocarbon (sometimes polyaromatic hydrocarbon)
NIST	National Institute of Standards and Technology (U.S.)		
NLEV	National Low Emissions Vehicle Program (U.S.)		
nM	nanomole		

PAL	point, area and line (model)	R	gas constant
PAL-DS	point, area, and line model with deposition and settling	R	percentage emission reduction (rollback model)
PAMS	photochemical assessment monitoring station	R	radial position of particle (centrifugal force calculation)
PAN	peroxyacetyl nitrate	r	radius
$p_b$	partial pressure of chemical substance gas in blood	R	remote
PBDE	pentabromodiphenyl ether	R	removed
PBPD	physiologically-based pharmacodynamic	R	risk
PBPK	physiologically-based pharmacokinetic	r	thermodynamic loss term
PBT	persistent, bioaccumulating, and toxic	$R(t)$	reliability function
PC	particle concentration	$R'$	universal gas constant ( $8.315 \text{ J K}^{-1} \text{ mol}^{-1}$ )
PC	polycarbonate	R-100	oil-resistant respirator protection efficiency against particulate aerosols (99.97%)
PC	polycarbonate	$\mathbf{R}^2$ or r	coefficient of determination
PCB	polychlorinated biphenyl	RACT	reasonably available control technology
PCDD/F	pentachlorodibenzodioxins and furans	RAT	rapid assessment tool
PCE	tetrachloroethene	RCRA	Resource Conservation and Recovery Act (U.S.)
pCi	picocurie (radioactivity unit)	Re	Reynolds number
PCM	phase contrast microscopy	REACH	Registration, Evaluation, Authorisation, and Restriction of Chemicals (Europe)
PDF	probability density function	REL	recommended exposure limit
PFOA	perfluorooctanoic acid	REL-TWA	recommended exposure limit (time-weighted average)
PFOS	perfluorooctane sulfonate	$\mathbf{Re}_p$	dimensionless particle Reynolds number
pH	negative log of $\text{H}^+$ or $\text{H}_3\text{O}^+$ concentration	RF	radio frequency
PHED	Pesticide Handlers Exposure Database (U.S.)	RfC	reference concentration
PIC	product of incomplete combustion	RfD	reference dose
PID	photoionization detector	RIOPA	Relationship Between Indoor, Outdoor and Personal Air Study (U.S.)
$pK_a$	negative log of the acid dissociation constant	RNA	ribonucleic acid
$p_L$	supercooled liquid vapor pressure	RO <sub>2</sub>	radical made of a chain of organic compounds with $\text{O}_2$ substituted for H
PLM	polarized light microscopy	ROD	record of decision
PM	particulate matter	ROS	reactive oxygen species
PM <sub>10</sub>	Particulate matter, <10 micron diameter	RR	relative risk
PM <sub>2.5</sub>	Particulate matter, <2.5 micron diameter	RT	residence time
pMC	percent modern carbon	RT	retention time
PMF	positive matrix factorization	RX	organic compound
PMN	premanufacture notification	s or sec	second (time)
PNS	peripheral nervous system	S	entropy
pOH	negative log of $\text{OH}^-$ concentration	S	severity of risk
POM	polynuclear organic material	S	solid or sorbed phase (subscript or parenthetic)
POP	persistent organic pollutant	S	solid phase concentration
ppb	parts per billion	S	solubility
ppbv	parts per billion by volume	S	Sorption
PPE	personal protection equipment	S	source or sink
ppm	parts per million	S/N	signal-to-noise ratio
ppmv	parts per million by volume	$\mathbf{S}^2$	variance
ppt	parts per trillion	$s^2$	variance of the source
PQAO	primary quality assurance organization	$S_A$	substrate concentrations in the aqueous phase
PQL	practical quantitation limit	SAR	structure-activity relationships
PRTR	Pollutant Release and Transfer Register (Mexico)	SARA	Superfund Amendments and Reauthorization Act (U.S.)
PSD	prevention of significant deterioration (U.S.)	SATB	surface area of the tracheobronchial region
PSI	pollution standard index (replaced by AQI)	SCR	selective catalytic reduction
psi	pounds per square inch (pressure)	SD or $\sigma$	standard deviation
PTFE	polytetrafluoroethylene	SDWA	Safe Drinking Water Act (U.S.)
PUF	polyurethane foam	SE	standard error
$P_v$	velocity pressure	SEM	scanning electron microscopy
PVC	polyvinyl chloride	SES	socioeconomic status
Q	airflow	$S_f$	filter drag force
$q$	electric charge on particle	SF	slope factor
Q	ionic product	$S_G$	substrate concentrations in the bulk gas phase
QA	quality assurance	$S_h$	horizontal surface
QAPP	quality assurance project plan		
QC	quality control		
$Q_g$	gas flow rate ( $\text{length}^2 \text{ time}^{-1}$ )		
QM-A	Whatman QM-A, quartz micro-fiber filter		
QSAR	quantitative structure-activity relationships		
R or r	correlation coefficient		
r	chemical production or degradation rate		

<b>SHEDS</b>	Stochastic Human Exposure and Dose Simulation (model)	<b>UFP</b>	ultrafine particles
<b>SHS</b>	second-hand smoke	<b>UGT</b>	UDP-glucuronyltransferase
<b>sin</b>	sine	<b>UNEP</b>	United Nations Environmental Program
<b>SIP</b>	State Implementation Plan (U.S.)	<b>UNFCCC</b>	United Nations Framework Convention on Climate Change
<b>SLAMS</b>	state and local air monitoring station (U.S.)	<b>UNICEF</b>	United Nations Children's Fund
<b>SMR</b>	standard morbidity ratio	<b>USCG</b>	United States Coast Guard
<b>SMR</b>	standard mortality ratio	<b>USDA</b>	U.S. Department of Agriculture
<b>SNCR</b>	selective noncatalytic reduction	<b>USF&amp;W</b>	U.S. Fish and Wildlife Services
<b>SOF</b>	soluble organic fraction	<b>USGS</b>	U.S. Geological Survey
<b>SOM</b>	soil organic matter	<b>UST</b>	underground storage tank
<b>SOP</b>	standard operating procedure	<b>UV</b>	ultraviolet
<b>SO<sub>x</sub></b>	oxides of sulfur	<b>UVCB</b>	chemical substances of unknown or variable composition, complex reaction products, and biological materials (U.S.)
<b>SPMS</b>	special purpose monitoring station	<b>UV-DOAS</b>	differential optical absorption spectroscopy in UV range
<b>SS</b>	steady state (subscript)	<b>UVF</b>	ultraviolet fluorescence
<b>ST</b>	sulfotransferase	<b>V</b>	fluid velocity
<b>Stk</b>	Stokes number	<b>V</b>	speed
<b>STP</b>	standard temperature and pressure	<b>v</b>	stochastic or aleatory uncertainty
<b>SVOC</b>	semivolatile organic compound	<b>V</b>	vapor phase (subscript or parenthetic)
<b>T</b>	temperature	<b>V</b>	volume
<b>t</b>	tonne	<b>V<sub>aw</sub></b>	airway volume (length <sup>3</sup> )
<b>T</b>	total (subscript)	<b>VC</b>	vinyl chloride
<b>t<sub>0</sub></b>	initial time	<b>V<sub>D</sub></b>	volume of distribution
<b>t<sub>1/2</sub></b>	half-life	<b>V<sub>e</sub></b>	minute volume (volume time <sup>-1</sup> )
<b>TAGA</b>	trace atmospheric gas analyzer	<b>v<sub>f</sub></b>	velocity through the filter (length time <sup>-1</sup> )
<b>tan</b>	tangent	<b>V<sub>ff</sub></b>	filter fiber volume
<b>TC</b>	total carbon	<b>v<sub>g</sub></b>	gas velocity
<b>TCDD</b>	tertachlorodibenzo- <i>para</i> -dioxin	<b>v<sub>g</sub></b>	geostrophic velocity
<b>TCDF</b>	tertachlorodibenzofuran	<b>vis</b>	visible light range
<b>TCE</b>	trichloroethene	<b>v<sub>max</sub></b>	frequency of maximum radiation intensity (Wien's displacement law)
<b>TCLP</b>	toxicity testing leaching procedure	<b>VMT</b>	vehicle miles traveled
<b>TCM</b>	tetrachloromercurate	<b>VOC</b>	volatile organic compound
<b>TDL</b>	tunable diode laser	<b>v<sub>p</sub></b>	particle velocity
<b>TDS</b>	total dissolved solids	<b>V<sub>p</sub></b>	particle volume
<b>TEAM</b>	Total Exposure Assessment Methodology Study	<b>V<sub>total</sub></b>	total filter volume
<b>TEL</b>	tetraethyl lead	<b>W</b>	body weight
<b>TEM</b>	transmission electron microscopy	<b>W</b>	water (subscript)
<b>T<sub>f</sub></b>	time of failure	<b>WHO</b>	watt (unit of power; J s <sup>-1</sup> )
<b>T<sub>ij</sub></b>	time spent in microenvironment <i>j</i> by person <i>i</i>	<b>WOE</b>	World Health Organization
<b>TL</b>	typical lifetime	<b>WWT</b>	weight of evidence
<b>TLV</b>	threshold limit value	<b>WWTP</b>	wastewater treatment
<b>TLV-C</b>	threshold limit value (ceiling)	<b>x</b>	wastewater treatment plant
<b>TLV-STEL</b>	TLV threshold limit value-short-term exposure limit	<b>x</b>	at distance <i>x</i> from <i>x</i> = 0 (subscript)
<b>TNT</b>	trinitrotoluene	<b>x</b>	distance (horizontal)
<b>TOMS</b>	total ozone mapping spectrometer	<b>XAD</b>	sorbing material; ion exchange resin
<b>TPTH</b>	triphenyltin hydroxide	<b>XRD</b>	X-ray diffraction spectrometry
<b>tpy</b>	tons per year	<b>XRF</b>	X-ray fluorescence
<b>T-R</b>	transformer-rectifier	<b>y</b>	at distance <i>y</i> from <i>y</i> = 0 (subscript)
<b>TRI</b>	Toxic Release Inventory (U.S.)	<b>y</b>	distance (width)
<b>TRS</b>	total reduced sulfur	<b>Y</b>	modeling result/outcome
<b>TS</b>	total sulfur	<b>y<sub>p</sub></b>	year (time)
<b>TSCA</b>	Toxic Substances Control Act (U.S.)	<b>y</b>	difference in velocity between the particle and collection object (length time <sup>-1</sup> )
<b>TSP</b>	total suspended particulate	<b>Z</b>	at distance <i>z</i> from <i>z</i> = 0 (subscript)
<b>TVA</b>	Tennessee Valley Authority	<b>Z</b>	atomic number
<b>TWA</b>	T wave alternans	<b>Z</b>	distance (vertical)
<b>TWA</b>	time-weighted average	<b>Z</b>	fugacity capacity
<b>U</b>	epistemic uncertainty	<b>α</b>	zenith angle (degrees)
<b>U</b>	internal energy	<b>γ</b>	packing density (solidity)
<b>U</b>	unknown	<b>Δ</b>	specific weight (mass length <sup>-3</sup> )
<b>UAM</b>	urban airshed model		change
<b>UEL</b>	upper explosive limit		
<b>UF<sub>inter</sub></b>	interspecies uncertainty		
<b>UF<sub>intra</sub></b>	intrasppecies uncertainty		
<b>UF<sub>other</sub></b>	RfC or RfC uncertainty other than UF or UF <sub>intra</sub>		

$\delta$	solar declination (degrees)	$\sigma$	Stefan–Boltzmann constant
$\Delta G^*$	standard change in Gibbs free energy	$\tau$	tortuosity
$\Delta P_{\text{dust-cake}}$	pressure drop across dust cake on filter	$\tau_s$	shear stress (mass length <sup>-1</sup> time <sup>-2</sup> )
$\Delta P_{\text{media}}$	pressure drop across filter media	$v$ or $v_v$	kinematic viscosity (length <sup>2</sup> time <sup>-1</sup> ) = dynamic viscosity divided by density ( $\mu \rho^{-1}$ )
$\Delta P_{\text{total}}$	total pressure drop	$v$	specific volume (reciprocal of density; length <sup>3</sup> mass <sup>-1</sup> )
$\epsilon_0$	permittivity of free space ( $8.85 \times 10^{-12} \text{ F m}^{-1}$ )	$\varphi$	angle (degrees or radians)
$\eta$	hour angle (degrees)	$\varphi$	filter porosity
$\theta$	potential temperature	$\varphi$	fugacity coefficient
$\lambda$	average or expected counts or events per unit time (Poisson equation)	$\varphi^\circ$	latitude (degrees)
$\lambda$	degradation term in chemical decay	X	fraction, ratio or coefficient
$\lambda$	wavelength (length, often nm)	$X_p$	leaving group from organic compound
$v_p$	relative velocity between the particle and the target object	$\psi$	particle diffusivity (length <sup>2</sup> time <sup>-1</sup> ); surface deposition
$v_\tau$	tangential velocity of gas	$\Psi_D$	diffusional collection parameter (dimensionless)
$\pi$	3.14159...	$\Omega$	migration velocity (electrostatics)
$\rho$	density (volume length <sup>-3</sup> )	$\Omega$	angular speed of the Earth's rotation
$\rho_0$	standard density (1 g m <sup>-3</sup> )	$\omega$	solar azimuth (degrees)
$\rho_g$	gas density (mass length <sup>-3</sup> )	$\omega$	spherical particle mass
$\rho_p$	particle density (volume length <sup>-3</sup> )		

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Note: Page numbers followed by "f" indicate figures; "t", tables; "b", boxes.

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