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Air Pollution

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AIR POLLUTION

1. Introduction

Air pollution is a relative term. Air is polluted when it contains substances at concentrations that cause harm to human health, as well as when it damages ecosystems and other socially valued materials, such as materials and structures. Air near the earth's surface consists almost entirely (dry volume, 99.997%) of four gases, molecular nitrogen (N_2 , 78.00%), oxygen (O_2 , 20.94%), argon (Ar, 0.93%), and carbon dioxide (CO_2 , 0.04%). Of these, only the concentrations of CO_2 have been increasing from just under 0.03% since the industrial revolution. Because Ar is a noble gas and the other three gases are very stable and nonreactive under atmospheric conditions of temperature and pressure, the atmosphere's dry composition remains very stable. Of course, 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 (eg, organic liquids), as well as liquid- and solid-phase constituents (aerosols or particulate matter (PM) held in suspension) (1,2).

Air pollution discussions often focus on how a particular part of the troposphere or stratosphere deviates in quality from a norm. Such deviations vary by scale: air pollution influencing a single-cell organism may be a few cubic nanometers (nm^3) in volume, whereas the atmosphere influencing and being influenced by biome shift encompasses many cubic kilometers (km^3). For humans, most exposure to pollutants occurs in comparatively small parcels of the atmosphere, known as microenvironments. Indeed, the highest exposure to many harmful air pollutants occurs as a "personal cloud" (3).

Air pollutants are categorized into two phases, aerosols and gas-phase pollutants. The terms particulates and aerosols are generally synonymous, ie, liquid and solid phases, but are distinguished from gases and vapors.

Besides N_2 , O_2 , H_2O , Ar, and CO_2 , most other atmospheric constituents exist in trace amounts. With the exceptions of molecular hydrogen (H_2) and nitrous oxide (N_2O), the remaining predominant gases are relatively nonreactive and stable under atmospheric conditions (4). From a mass balance perspective, nitrogen (N) and oxygen (O) exist in numerous chemical compounds in the atmosphere. Nitrogenous compounds include a number of air pollutants, especially nitrogen dioxide (NO_2), and many essential compounds, eg, nitrates, nitrites, and ammonia. At $3.9 \times 10^{18} kg$, the amount of N_2 is six orders of magnitude larger than the atmosphere's second most abundant N-compound, N_2O .

Carbon (C) is the distinguishing element for organic compounds, ie, those with C–C and/or H–C bonds, but it is also part of many inorganic compounds, including CO_2 , a global greenhouse gas (GHC), and carbon monoxide (CO), an air pollutant that causes cardiovascular and other health effects. Indeed, C is a major constituent of many air pollutants, including PM in various forms, as well as many of the most toxic air pollutants, eg, dioxins, polychlorinated biphenyls (PCBs), and many pesticides, and GHGs, eg, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons.

Several of the abundant compounds in the atmosphere are greenhouse gases, most notably CO_2 , methane (CH_4), and N_2O . Indeed, H_2O is also a greenhouse gas since, by definition, it traps heat in the atmosphere. That is, the portion of the

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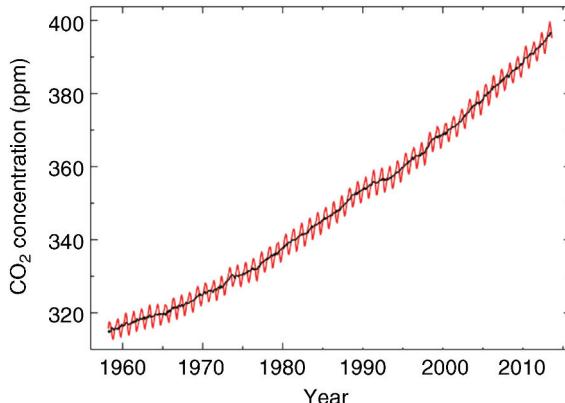


Fig. 1. Monthly mean atmospheric carbon dioxide concentrations (ppm by volume) at Mauna Loa Observatory, Hawaii. The CO₂ data (red curve) presented as the mole fraction in dry air at Mauna Loa Observatory constitute the longest record of direct measurements in the atmosphere. The black curve represents the seasonally corrected data. Data are reported as a dry mole fraction defined as the number of molecules of CO₂ divided by the number of molecules of dry air multiplied by 1 million (ppm). (Adapted from Reference 2.)

incoming solar radiation that is reradiated as infrared wavelengths is either trapped by greenhouse gases or allowed to leave the atmosphere. In particular, as the most abundant greenhouse gas, CO₂ 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 Fig. 1).

The most abundant organic molecule in the atmosphere, CH₄, is also a potent GHG. Its atmospheric concentration increased dramatically after the industrial revolution, but is no longer increasing. It is produced from anaerobic processes. These include agriculture, eg, livestock and rice paddies, but also landfills, fossil fuel extraction and gas distribution, and biomass burning (4). These anthropogenic sources produce about the same amount of CH₄ as natural sources, which include reduced, anoxic portions of wetlands and portions of ecosystems undergoing organic decomposition. Methane is a more potent GHG than CO₂, absorbing 22 times the energy per unit mass. However, at about 9 yr, its atmospheric residence time could be far less than that of CO₂, which is estimated to be between 5 and 100 yr (see Table 1). The reason for the variable atmospheric lifetime for CO₂ is the fluctuating rates of removal (eg, photosynthesis), production (eg, combustion and respiration) processes, and the atmospheric exchanges with water and land surfaces.

Each gas mixes in the air at different altitudes; ie, they have unique mixing ratios (see Fig. 2). The mixing ratio is the number density of the gas divided by number density of all gases in dry air. Only N₂ and the noble gases have nearly constant mixing ratios below 100 km, given their chemical stability. Since most CH₄ and N₂O 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

Table 1. Approximate Concentrations (ppb) and Rate of Concentration Change (ppb yr^{-1}) of Select Greenhouse Gases That Are Affected by Human Activities^a

	CO_2	CH_4	N_2O	CFC-11 (chlorofluoro- carbon-11)	HFC-23 (hydrofluoro- carbon-23)	CF_4 (perfluoro- methane)
preindustrial concentration	2.8×10^5	700	270	0	0	4.0×10^{-2}
concentration in 1998	3.7×10^5	1745	314	0.27	14	8.0×10^{-2}
rate of concentration change ^c	1.5×10^{6b}	7.0 ^b	0.8	-1.4×10^{-3}	5.5×10^{-4}	1.0×10^{-3}
atmospheric lifetime (yr)	5–200 ^d	12 ^e	114 ^e	45	260	$>5.0 \times 10^4$

^aRef. 5.

^bRate has fluctuated between 0.9 and 2.8 ppm yr^{-1} for CO_2 and between 0 and 13 ppb yr^{-1} for CH_4 over the period of 1990–1999.

^cRate is calculated over the period of 1990–1999.

^dNo single lifetime can be defined for CO_2 because of the different rates of uptake by different removal processes.

^eThis lifetime incorporates the indirect effect of the gas on its own residence time.

decreasing temperatures in the troposphere. The stratospheric O_3 layer is also apparent at 35 km in Figure 2 (2).

Essential compounds include micronutrients needed by plant life and other organisms in ecosystems. However, even essential substances can become pollutants in the wrong concentrations. Thus, expression of chemical concentration is crucial to understand 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 (ie, N_2 , O_2 , and H_2O) in percent volume of air. Thus, this is a unitless expression, ie, volume of constituent per volume of air. However, smaller air constituents, including all air pollutants, are expressed either as a number density, ie, molecules per unit volume, such as molecules cm^{-3} , or as a mass density, such

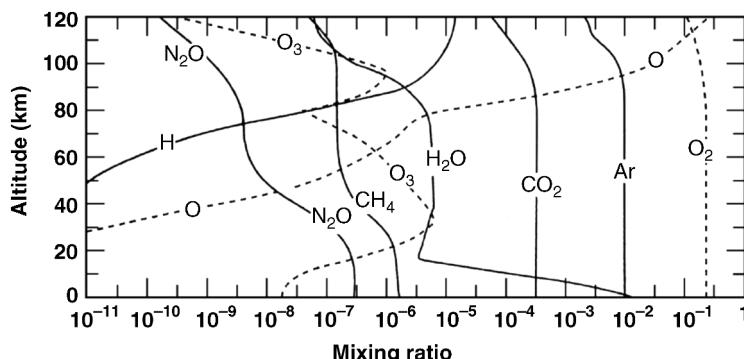


Fig. 2. Atmospheric mixing ratios for ozone and abundant atmospheric gases, other than molecular nitrogen and noble gases (given they are well mixed up to 100-km altitude). (Adapted from Reference 4.)

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as $\mu\text{g m}^{-3}$. An example of a number density expression of an air pollutant would be 1.2×10^{12} formaldehyde (CH_2O) molecules per $\text{cm}^3 = 1.2 \times 10^{18}$ molecules per m^3 (1,2).

Chemical concentration may be expressed as combinations of mass and volume. For example, air pollutant concentrations are often expressed as micrograms per cubic meter of air ($\mu\text{g m}^{-3}$). Concentrations of specific, trace gases are important in air pollution. Synoptic meteorology and climatology may refer to “organic vapor” concentrations to describe the many volatile and semivolatile organic compounds (SVOCs), whereas air pollution meteorologists would be concerned about the specific gases at concentrations $< 1 \mu\text{g m}^{-3}$, and how these substances vary in time and space (1). For example, ambient volatile organic compound (VOC) concentrations differ between rural and urban areas, and near and far from roadways. They also show seasonal differences in the same urban area (Fig. 3). For example, formaldehyde concentrations in urban areas are generally higher in summer, whereas the concentrations of benzene, another VOC, are generally higher in the winter (Fig. 4). Atmospheric concentrations can vary even more in different microenvironments than in the ambient air (see Table 2).

Even though 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. Concentrations are even more variable between ambient and indoor air, as indicated in Table 2.

The variability in chemical concentrations can be even higher among various types of microenvironments. For example, the two types of homes listed in Table 2 show very different mean and maximum concentrations, with manufactured homes having much higher values than conventional homes. This likely indicates that manufactured homes include sources of formaldehyde that are greater than those of conventional homes, eg, 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 (1).

2. Transformation, Transport, and Fate of Air Pollutants

Air pollution scales may be categorized from cellular to global, but ambient air pollution is often subdivided as local, urban, regional, continental, and global. The spheres of influence of the air pollutants themselves range from molecular (eg, gases and nanoparticles) to planetary (eg, diffusion of greenhouse gases throughout the troposphere). The local scale covers up to about 5 km of the earth’s surface. The urban scale extends to the order of 50 km. The regional scale is from 50 to 500 km. Continental scales are from 500 to several thousand kilometers. Of course, the global scale extends worldwide (1).

The movement of pollutants is known as transport. Fate is an expression of what the 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 chemical form on its way to its fate. It will be physically transported and undergo coincidental chemical processes, known as transformations, such as

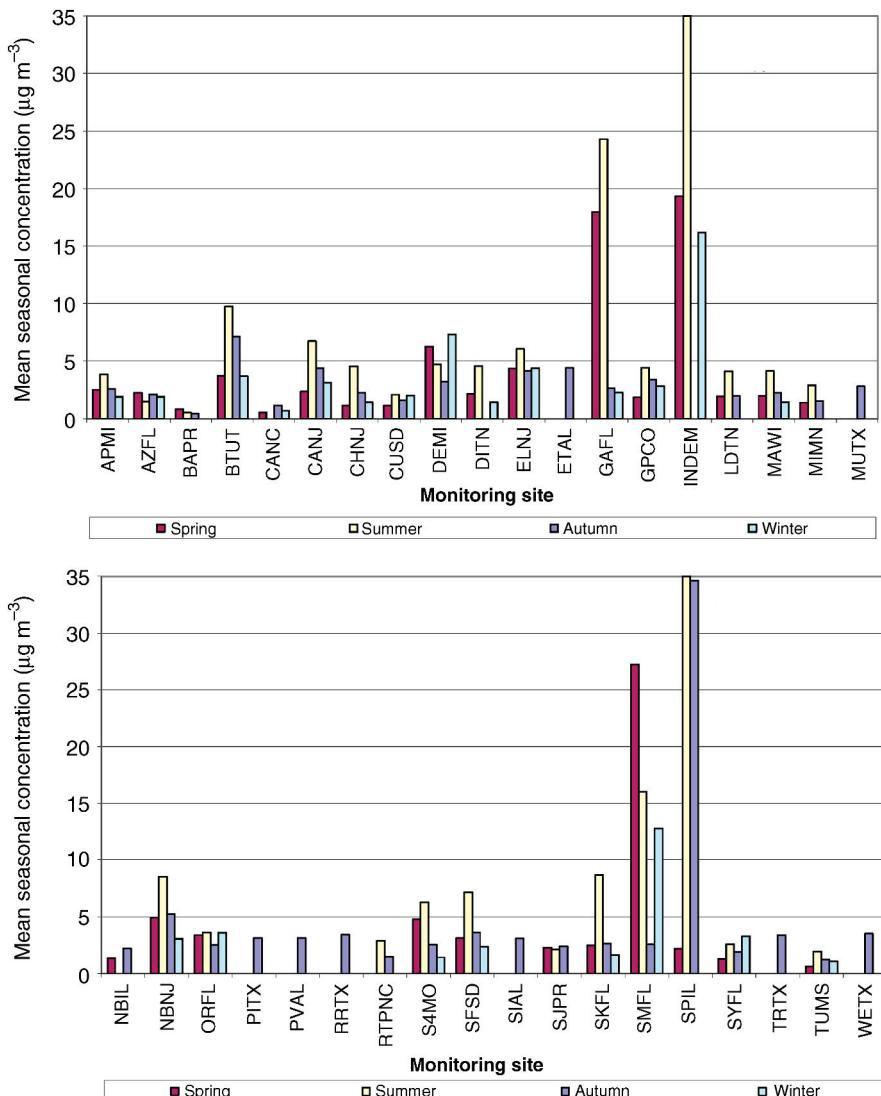


Fig. 3. Measured concentrations of formaldehyde in several urban areas. APMI = Allen Park, Detroit, Michigan; AZFL = Azalea Park, St. Petersburg, Florida; BAPR = Barcelona, Puerto Rico; BTUT = Bountiful, Utah; CANC = Candor, North Carolina; CANJ = Camden, New Jersey; CHNJ = Chester, New Jersey; CUSD = Custer, South Dakota; DITN = Dickson, Tennessee; ELNJ = Elizabeth, New Jersey; ETAL = East Thomas, Birmingham, Alabama; FLFL = Davie, Florida; GAFL = Gandy in Tampa, Florida; GRMS = Grenada, Mississippi; INDEM = Gary, Indiana; ITCMI = Sault Sainte Marie, Michigan; LDTN = Loudon, Tennessee; MAWI = Madison, Wisconsin; MIMN = Minneapolis, Minnesota; MUTX = Murchison Middle School in Austin, Texas; NBNJ = New Brunswick, New Jersey; ORFL = Winter Park, Florida; PCOK = Site 1 in Ponca City, Oklahoma; PGMS = Pascagoula, Mississippi; PITX = Pickle Research Center, Austin, Texas; POOK = Site 2 in Ponca City, Oklahoma; PVAL = Providence, Rhode Island; RRTX = Round Rock, Texas; RTPNC = Research Triangle Park, North Carolina; SFSD = Sioux Falls, South Dakota; SIAL = Sloss Industries, Birmingham, Alabama; SJPR = San Juan, Puerto Rico; SMFL = Simmons Park in Tampa, Florida; SPIL = Schiller Park in Chicago, Illinois; TRTX = Travis High School in Austin, Texas; TUMS = Tupelo, Mississippi; WETX = Webberville Road in Austin, Texas. (Adapted from Reference 6.)

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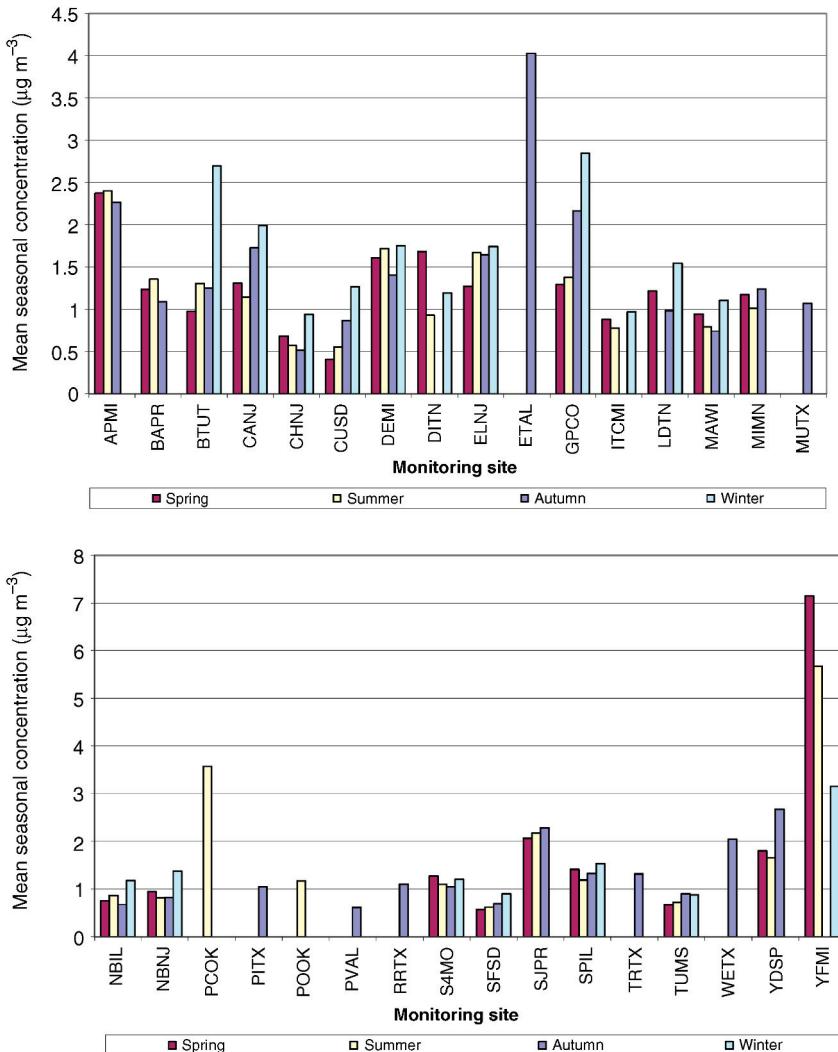


Fig. 4. Measured concentrations of benzene in several urban areas. APMI = Allen Park, Detroit, Michigan; AZFL = Azalea Park, St. Petersburg, Florida; BAPR = Barcelona, Puerto Rico; BTUT = Bountiful, Utah; CANC = Candor, North Carolina; CANJ = Camden, New Jersey; CHNJ = Chester, New Jersey; CUSD = Custer, South Dakota; DITN = Dickson, Tennessee; ELNJ = Elizabeth, New Jersey; ETAL = East Thomas, Birmingham, Alabama; FLFL = Davie, Florida; GAFL = Gandy in Tampa, Florida; GRMS = Grenada, Mississippi; INDEM = Gary, Indiana; ITCMI = Sault Sainte Marie, Michigan; LDTN = Loudon, Tennessee; MAWI = Madison, Wisconsin; MIMN = Minneapolis, Minnesota; MUTX = Murchison Middle School in Austin, Texas; NBAL = North Birmingham, Alabama; NBNJ = New Brunswick, New Jersey; ORFL = Winter Park, Florida; PCOK = Site 1 in Ponca City, Oklahoma; PGMS = Pascagoula, Mississippi; PITX = Pickle Research Center, Austin, Texas; POOK = Site 2 in Ponca City, Oklahoma; PVAL = Providence, Rhode Island; RRTX = Round Rock, Texas; RTPNC = Research Triangle Park, North Carolina; SFSD = Sioux Falls, South Dakota; SIAL = Sloss Industries, Birmingham, Alabama; SJPR = San Juan, Puerto Rico; SMFL = Simmons Park in Tampa, Florida; SPIL = Schiller Park in Chicago, Illinois; TRTX = Travis High School in Austin, Texas; TUMS = Tupelo, Mississippi; WETX = Webberville Road in Austin, Texas; YDSP = El Paso, Texas; YFMI = Yellow Freight in Detroit, Michigan. (Adapted from Reference 6.)

Table 2. Formaldehyde Concentrations Measured at Various Locations in California^a

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 and 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)

^aRef. 7.

photochemical and biochemical reactions (see Fig. 5). 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 less dense molecule. This 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 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 in the fish. If the fish is eaten by humans, the ultimate fate of the air pollutant released from the stacks and vents is human tissue. Thus, the fate is a consequence of physics, chemistry, and biology (1).

Environmental engineering has a slightly different perspective of fate. Engineers seek to control and to design systems to accomplish outcomes. For example, engineers employ remediation reactions, such as thermal and mechanical separation processes, abiotic chemical reactions, such as precipitation and hydrolysis, and biological processes, such as microbial metabolic biochemical reactions, to break down toxic substances into simpler, less toxic compounds.

Spatial and temporal scales are important factors in air pollution. For example, inhalation rates vary somewhat from one city to the next and certainly vary with latitude (eg, different outdoor activities in Northern latitudes than in the Tropics). Temporal variability occurs over large time horizons, from very long 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 quality decisions must also account for the pollutant source, the potentially exposed population (eg, infants and pregnant women), the time frame of exposure, all possible exposure routes and pathways, the type of microenvironment, and all human activities. An individual can be exposed to pollutants continuously, with exposures varying according to activities and locations. This so-called personal cloud often results in increased personal exposures to air pollutants compared with indoor concentrations, or compared with the time-weighted indoor and outdoor concentrations (see Fig. 6). 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.

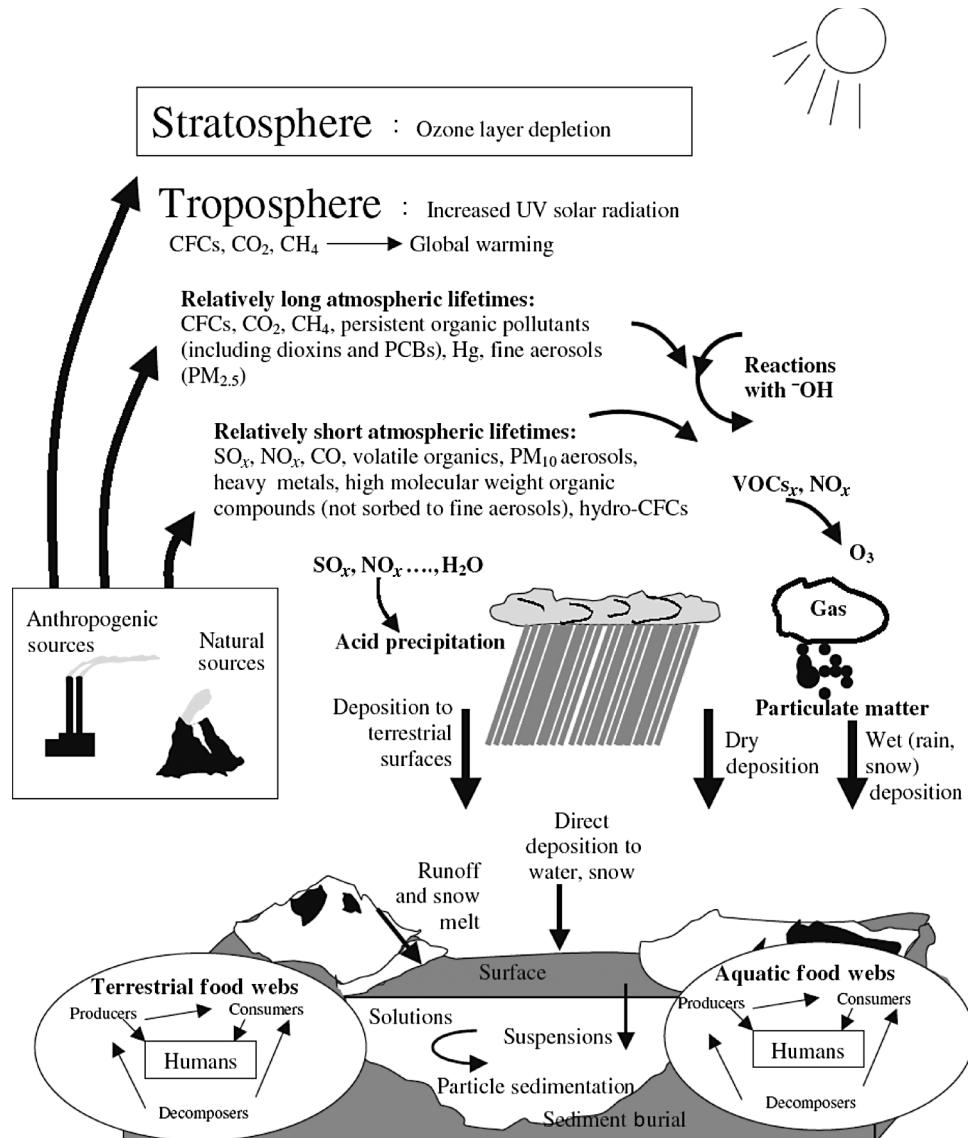


Fig. 5. The physical movement and accumulation of contaminants after release. (Reprinted with permission from Reference 9. Copyright 2004, Elsevier.)

Air pollutants are transported predominantly by advection; ie, they move with the flow of the fluid where they reside, ie, the air. An air pollutant plume is never homogeneous in that the pollutant usually has higher concentrations near the source, but it will also have pockets of higher and lower concentrations given variability of terrain, structures, albedo, clouds, temperature, and moisture. Even a small compartment, eg, a room in a house, is never completely mixed, with regions of varying pollutant concentrations. Advection is caused by differences in

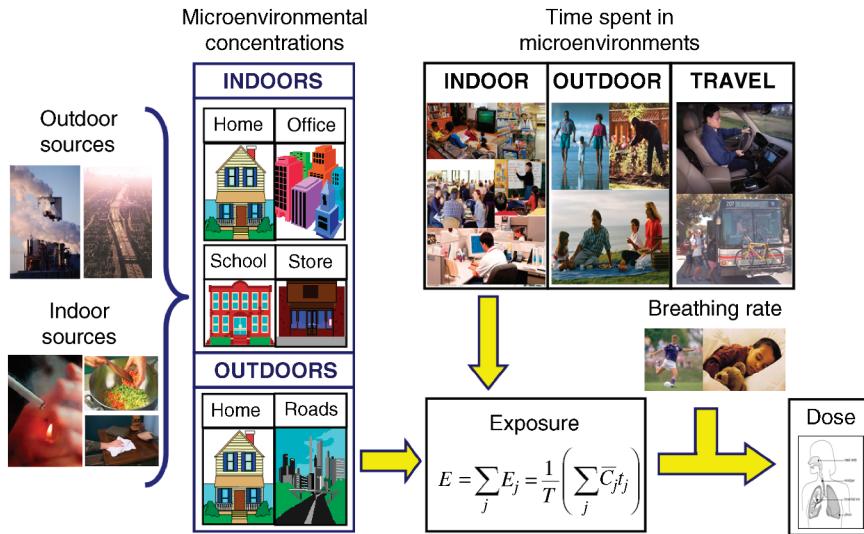


Fig. 6. Various scales of air pollution that contribute to personal exposures. People spend varying amounts of time indoors and outdoors in numerous locations. Each person has a unique exposure profile due to varying airborne concentrations of pollutants and time spent in each microenvironment. In addition, unique characteristics of the person and activity, eg, breathing rate, also change the amount of pollutant absorbed, which leads to a unique dose of the pollutant. In this case, the exposure (E) equation includes the sum of all exposure events (j), which are each the mean concentration (\bar{C}) integrated with respect to time of the event j per exposure duration (T). (Adapted from Reference 3.)

pressure (p), ie, force per unit area:

$$p = \frac{F}{A}$$

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.

3. Criteria Air Pollutants

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 problems, 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 the six so-called criteria air pollutants:

1. Particulate matter (PM)
2. Ozone (O_3)

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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. Environmental Protection Agency (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. Primary standards are aimed at protecting public health. Secondary standards protect social welfare, especially 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 problematic not only 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 (eg, 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 (10).

Pollutant sources can be stationary, such as a power plant stack, or mobile, such as an automobile’s exhaust. In the United States, each state establishes a plan, known as a state implementation plan (SIP), which includes control strategies to address air pollution in nonattainment areas. The SIP addresses stationary sources by requiring control strategies to decrease the amount of a criteria pollutant emitted by industrial facilities and other stationary sources. The SIP also addresses various sources using baselines and projection inventories of pollutants from stationary and mobile sources. The inventories target control strategies for on-road and off-road mobile sources. The SIP inventories are based on emission data from major regulated facilities, as well as calculated emissions from minor stationary sources (ie, area source calculations) (11).

3.1. Regulations Designed to Prevent Criteria Air Pollution. The New Source Review (NSR) addresses potential air pollution from a proposed construction. The nonattainment NSR rules are designed to help attain and maintain compliance with the NAAQS, applying to pollutants for a nonattainment area. The nonattainment NSR rules assume 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 (12).

Similarly, Prevention of Deterioration (PSD) rules are designed to curtail the transport of criteria air pollutions to areas that are presently meeting standards, ie, those meeting NAAQS. The Clean Air Act defines the amount of

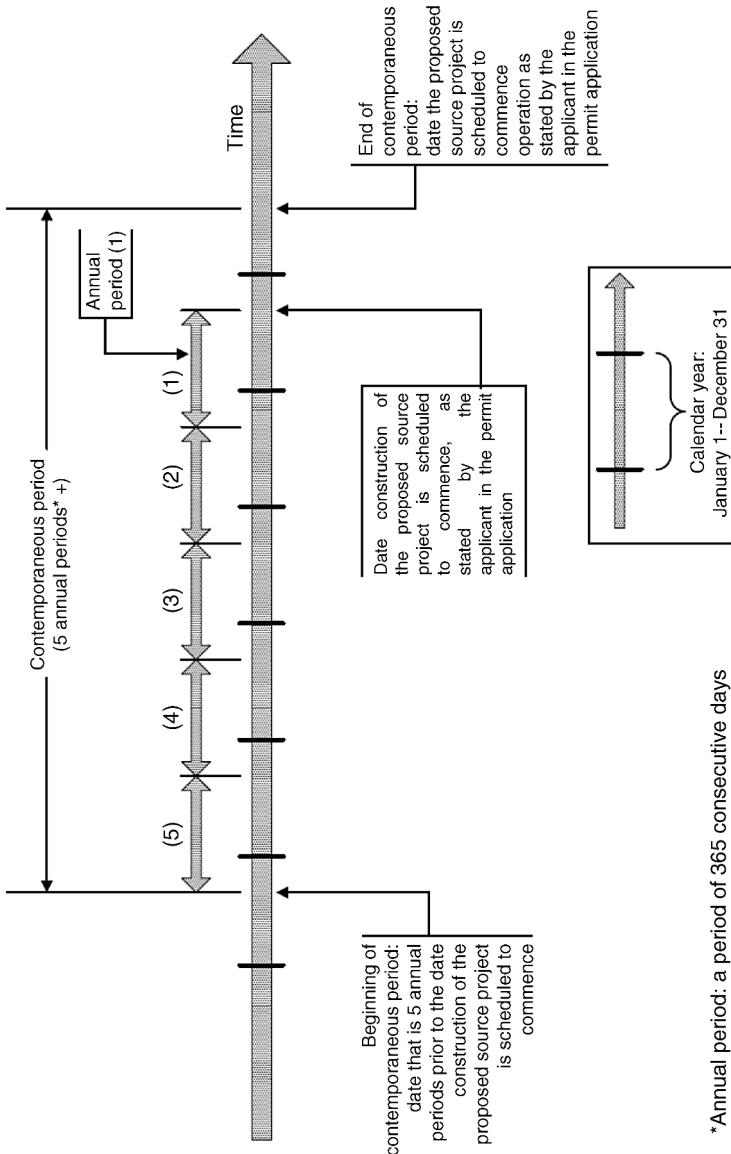
deterioration that can be considered “insignificant.” The PSD is designed to protect both public health and welfare, and to preserve, protect, and enhance the air quality in national parks, national wilderness areas, national monuments, national seashores, and other areas of particular, cultural value. The PSD also requires that economic growth occur in a manner consistent with the preservation of existing clean air resources. The PSD provisions also consider possible cumulative effects. 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 by aggregating emission changes that have occurred at a source over a contemporaneous time period (see Fig. 7).

4. Hazardous Air Pollutants

As of 2013, 187 air pollutants are listed as “hazardous” under section 112 of the Clean Air Act. Most of these are carcinogenic, mutagenic, and/or toxic to neurological, endocrine, reproductive, and developmental systems. They are commonly known as “air toxics.” The list includes many more than 189 chemical compounds, since some of those listed include multiple chemical compounds. The coke oven emission category, for example, actually includes thousands of chemical species, and the metals are listed as metals and their compounds. The U.S. EPA publishes a list of source categories and issues Maximum Achievable Control Technology (MACT) standards that must be met for each category after a specified time limit. Beyond the MACT standards, chronic health risks are likely to remain, even when the MACT is achieved, ie, “residual risk.”

The residual risk provision sets additional standards to protect public health with an “ample margin of safety,” as well as additional standards needed to prevent adverse environmental effects. A source that can demonstrate that it will not contribute a risk to greater than one in a million additional cancers (10^{-6}) may achieve the ample margin of safety. The ample margin needed to protect populations from noncancer toxins will likely involve the application of some type of hazard quotient (HQ), ie, ratio of the potential exposure to the substance to the level at which no adverse effects are expected. An $HQ < 1$ means that the exposure levels to a chemical should not lead to adverse health effects. Conversely, an $HQ > 1$ means that adverse health effects are possible. Due to large scientific uncertainties, the ample margin of safety threshold currently ranges from $HQ = 0.2$ to $HQ = 1.0$. Thus, a source that can demonstrate that it will not contribute to greater than the threshold for noncancer risk (whether it is 0.2, 1.0, or a yet-to-be-established HQ) would achieve the ample margin of safety requirements for air toxics (1,13).

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 <10 tons per year of a single air toxic, or <25 tons per year of a combination of air toxics (13).



*Annual period: a period of 365 consecutive days

Fig. 7. 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 nonattainment areas. (Adapted from Reference 11.)

The MACTs are specific to each source category. For instance, semiconductor manufacturing, semiconductor packaging, printed wiring board manufacturing, and display manufacturing may be similar, but each handles and releases a unique set of air toxics, which includes organic, organometallic, and metal compounds (1).

4.1. National-Scale Air Toxics Assessment. The National-Scale Air Toxics Assessment (NATA) is a screening tool to reflect risks of cancer and other serious health effects from inhaling air toxics.

The NATA assessments are based on information about sources, erring on overestimating rather than underestimating risks. The estimates are based on chronic exposure from outdoor sources, providing a snapshot of the outdoor air quality and the risks if air toxic emissions remain unchanged.

The NATA follows a four-step process (14).

1. Compiling a national air toxics emissions inventory of outdoor stationary and mobile sources, ie, the National Emissions Inventory (NEI).
2. Estimating ambient concentrations based on 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 conducted in 1996 and the most recent assessment was done in 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 8.

The route of exposure is assumed to be inhalation, so the NATA does not include other routes (eg, ingestion and dermal exposure to the same air toxic). Cumulative cancer risks from all compounds listed as carcinogenic or likely to be carcinogenic to humans are estimated by combining the risks at the census tract level (15). In 2005, the combined upper bound lifetime cancer risk from these compounds exceeded 10 in 1 million risk. Over 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 U.S. national average risk is 36 in a million.

Ideally, HQs would pool pollutants that cause the same adverse effects by the same toxic mechanism to reflect cumulative risk. However, because detailed information on mechanisms is sparse or absent for most air toxics, a more conservative method was used for NATA. Many pollutants in NATA are irritants and neurotoxins. Additive effects are represented by a “hazard index,” ie, the sum of the HQs of the air toxic compounds that affect the respiratory or nervous system. In 2005, the respiratory hazard index was dominated by the compound acrolein. The respiratory hazard index was >1.0 for most of the U.S. population, and exceeded 10 for over 22 million people. The neurological hazard index was 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.

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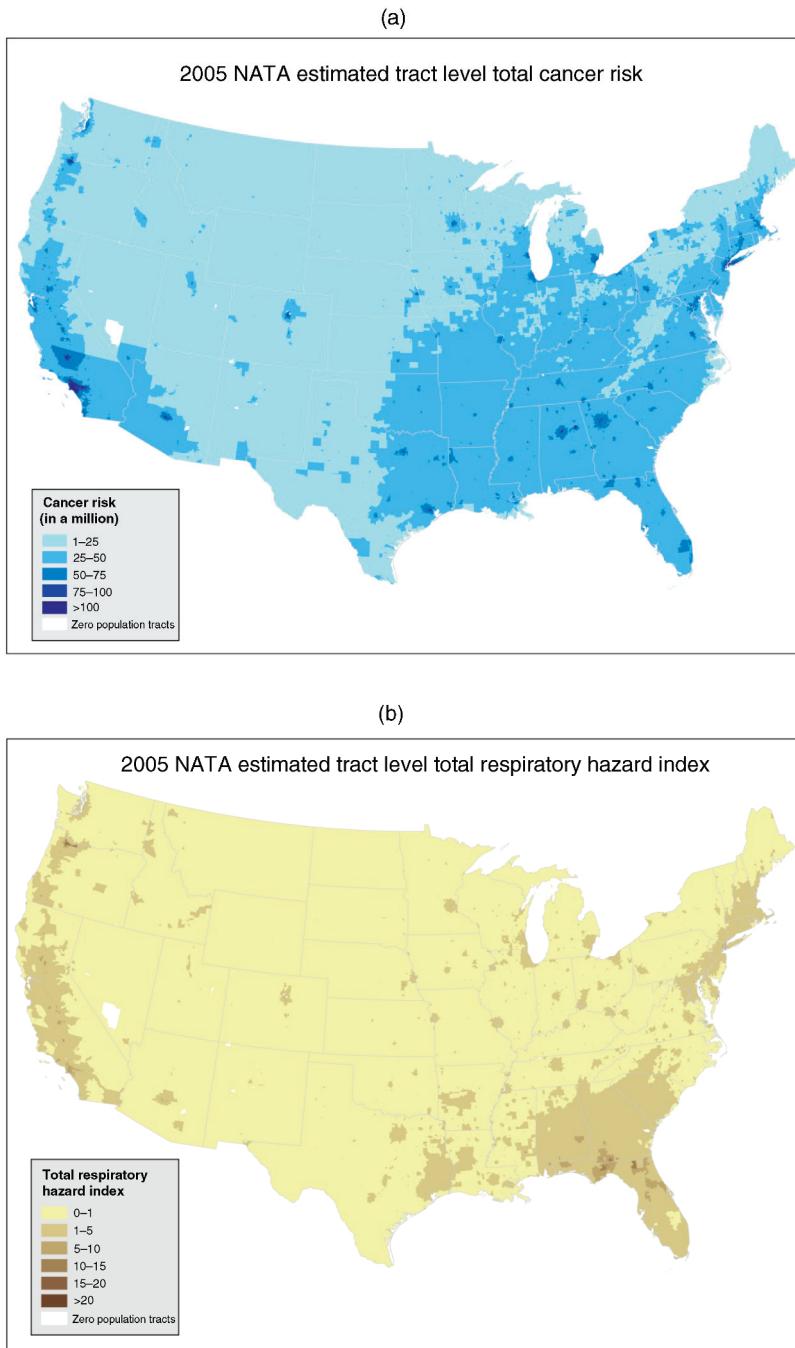


Fig. 8. National Air Toxics Assessment. (a) 2005 census tract level total cancer risk. (b) 2005 National Air Toxics Assessment census tract level total respiratory (noncancer) hazard index. (Adapted from Reference 15.)

4.2. Airborne Carcinogens. The pathway to carcinogenesis varies both inside and outside of the body. The compound released into the atmosphere may be a carcinogen or it may be a carcinogen precursor (top of Fig. 9) that is transformed in the atmosphere into a carcinogen. The compound may also be transformed into

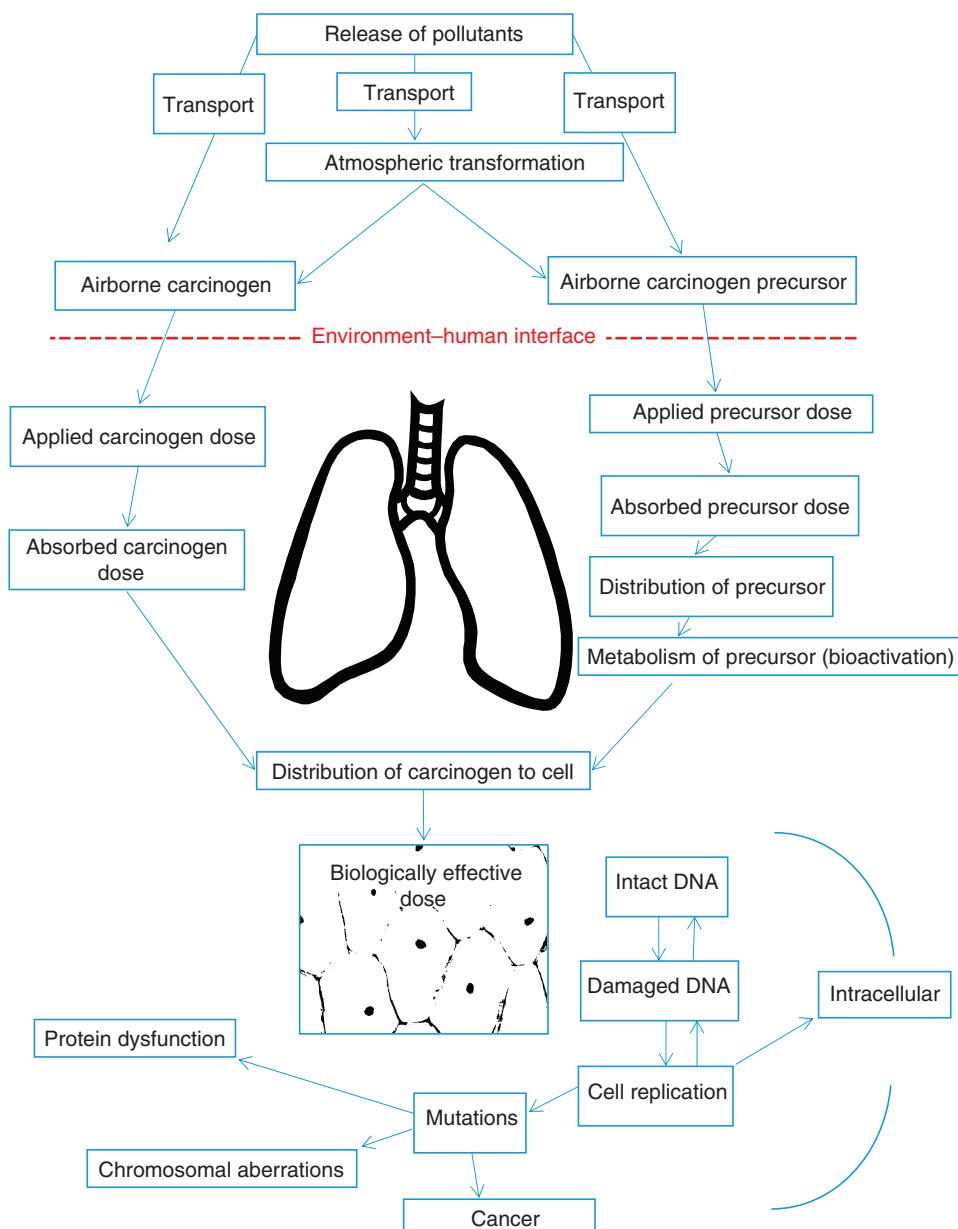


Fig. 9. Steps leading to carcinogenesis from an air pollutant, including metabolic processes and endogenous chemicals, with a number of steps within the cell involving damage and repair of DNA. (Reprinted with permission from Reference 1. Copyright 2014, Elsevier.)

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a precursor that is not yet carcinogenic, but will become a carcinogen after exposure due to endogenous processes (see Fig. 9).

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 based upon the dose-response curves from animal research and human epidemiology. The quasi-linear segments of these curves provide cancer slope factors (CSFs), which are published by environmental regulatory agencies (eg, the U.S. EPA's Integrated Risk Information System, IRIS, www.epa.gov/iris). Long-term exposure may be expressed as the lifetime average daily dose (LADD):

$$\text{cancer risk} = \text{CSF} \times \text{LADD}$$

where

$$\text{LADD} = \frac{C \cdot \text{IR} \cdot \text{EL} \cdot \text{AF} \cdot \text{ED}}{\text{BW} \cdot \text{TL}}$$

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), expressed in mass per body weight per day (eg, mg kg⁻¹ day⁻¹), must be estimated or modeled:

$$\text{DI} = \frac{\text{concentration (mg volume}^{-1}) \times \text{intake (volume day}^{-1})}{\text{body mass (kg)}}$$

Chronic daily intake (CDI) can be estimated by averaging DI over long-term exposure (eg, 70 yr for LADD) (1).

The average lifetime may be assumed to be 70 yr. However, exposure duration (ED) is often less than the total lifetime. For example, ED would be 25 yr for air pollution concentrations from a source that was in operation for 25 yr. Body weight may be assumed to be 70 kg; frequency of exposure may be <365 days yr⁻¹. For example, the frequency of exposure would be 250 days yr⁻¹ if that is the number of days that a person spends in a particular microenvironment, eg, workplace, during the 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, eg, 2.5 m³ h⁻¹ × 8 h day⁻¹. However, as indicated in Table 3, inhalation rates can be highly variable.

An air pollution exposure equation 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 mg kg⁻¹ day⁻¹. Since the intake of air pollutants is almost entirely via inhalation, the contaminant concentration in the air can be used exclusively:

$$I = C_A \times \frac{\text{IR}}{\text{BW}} \times \frac{\text{ET} \times \text{EF} \times \text{ED}}{\text{AT}}$$

Table 3. Tracheobronchial Region Default Values for Humans of Different Ages and Activity Patterns^a

	Minute volume ^b (V_e), L min ⁻¹	Surface area ^b (SA), cm ²	V_e/SATB , L min ⁻¹ cm ⁻²	Tracheobronchial regional gas dose ratio	NOAEL (human equivalent concentration)
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-yr M	14.0	2520	0.0056	1.1	0.18
15-yr F	10.9	2250	0.0048	1.3	0.21
10 yr	10.6	1830	0.0058	1.1	0.18
5 yr	6.1	1340	0.0046	1.4	0.22
1 yr	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

^aRef. 17.^bThese values are from Ref. 18.

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where C_A is the contaminant concentration in air (mg m^{-3}), IR is the inhalation rate ($\text{m}^3 \text{ h}^{-1}$), BW is the body weight (kg), ET is the exposure time (h day^{-1}), EF is the exposure frequency (days yr^{-1}), ED is the exposure duration (yr), and AT is the averaging time (days over which exposure is averaged).

Similarly, an exposure concentration (EC) is a time-weighted average (TWA) 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 be almost the same. However, estimating cancer risks from chronic exposure involves both the C_A measured at a point of exposure point and scenario-specific parameters, such as the ED and frequency:

$$\text{EC} = \frac{C_A \times \text{ET} \times \text{EF} \times \text{ED}}{\text{AT}}$$

The value of AT for chronic exposures is $\text{ED} \times \text{years} \times 365 \text{ days yr}^{-1} \times 24 \text{ h day}^{-1}$. 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 (19). It is common to see EC combined with an inhalation unit risk (IUR), which is similar to the CSF; ie, 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 $\text{IUR} = 2 \times 10^{-6} \mu\text{g}^{-1} \text{ m}^{-3}$, 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 m^3 of air.

The C_A must include all physical phases, ie, both the pollutant in vapor phase and that in aerosol phase. The aerosol phase consists of the amount of the compound in liquid and solid phases, as well as any amount is sorbed in or on particulates. 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 of these phases. These values must be normalized, eg, all expressed in units of mass per volume (eg, mg m^{-3}) or mass per mass (eg, mg kg^{-1}).

Many air toxics are organic compounds that are highly diverse in their physical characteristics and chemical composition. Volatile organic compounds, for example, exist in the ambient air almost entirely in the gas phase since their vapor pressures in the environment are usually $>10^{-2} \text{ kPa}$. For VOCs, then, C_A may be almost equal to vapor-phase concentrations. Conversely, relatively nonvolatile organic compounds (NVOCs) with vapor pressures $<10^{-5} \text{ kPa}$ 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 be equal to the total amount of the air pollutant in PM collected. However, SVOCs, with vapor pressures between 10^{-2} and 10^{-5} kPa , can exist in substantial concentrations

in both the gas and particle phases in the ambient air. The SVOCs include some of the most important pollutants, including dioxins, PCBs, polycyclic aromatic hydrocarbons (PAHs), organochloride and organophosphate pesticides, and numerous other persistent organic pollutants (POPs).

5. Acid Rain

Acid rain is specifically the so-called wet deposition of low pH precipitation, but acidified substances also reach the earth's surface by dry deposition of "acid aerosols" and by acid fog (eg, airborne droplets of water that contains sulfuric acid or nitric acid). Generally, acid deposition contains not simply materials of $\text{pH} < 7$, but usually of $\text{pH} < 5.7$, since in most of the world, rainfall pH is about 5.7, due to the ionization of absorbed CO_2 . Aquatic biota can be significantly harmed by slight changes in pH. Acidified soils and surface waters result from both the increase in acidity of the precipitation and the ability of the receiving waters and soil to resist the change in soil pH, ie, soil buffering capacity. Human-generated (anthropogenic) acidic materials, especially the oxides of sulfur and the oxides of nitrogen, contribute substantially to acid deposition.

In the United States, measures to address acid deposition follow a two-phase, market-based system to decrease sulfur dioxide emissions from power plants by more than 50%, with total annual emissions capped at 8.9 million tons. This translates into 10 million tons from the 1980 baseline levels. 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 decreasing phase I plant emissions. All sources were required to install continuous emission monitors to assure compliance. This approach has been applied to emissions of the oxides of nitrogen (NO_x). However, decreases in the oxides of sulfur (SO_x) have been based on performance standards, rather than the two-phase system (1).

6. Stratospheric Ozone Depletion

In the late 1970s, the scientific community presented strong evidence of stratospheric ozone reacting with halogenated compounds found in refrigerants, propellants, and other chemicals (see Fig. 10). 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 CFCs.

Depletion of O_3 begins with the release of chemicals into the atmosphere, ie, depletion occurs as an indirect result of air pollutants. Direct exposure takes place when a toxic chemical is absorbed, distributed, and metabolized to induce harmful effects. Conversely, air pollutant carcinogenesis can be indirect, ie, disease or damage results from earlier reactions that allow for exposures to other agents. In the case of O_3 depletion, the agent is ultraviolet electromagnetic radiation. Like

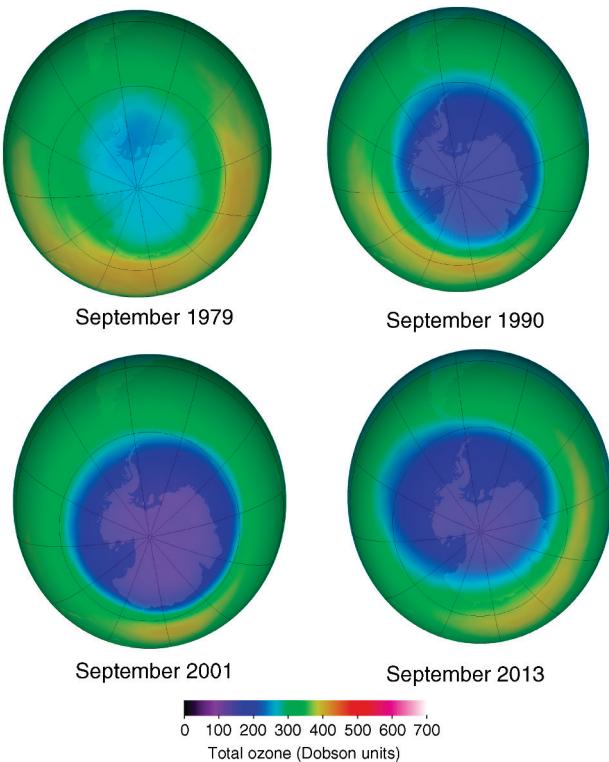


Fig. 10. Change in September monthly mean concentration of ozone (O_3) in the stratosphere indicated by false-color view of total ozone over the Antarctic pole. The purple and blue colors indicate the lowest concentrations of ozone, and the yellow and red colors show higher indications. Dobson unit = 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. (Reprinted with permission from Reference 1. Copyright 2014, Elsevier.)

the direct exposure, the cellular genetic 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 ultraviolet (uv) radiation reaching the earth's surface that would have otherwise been trapped (see Fig. 11).

In addition to O, other free radicals catalyze ozone destruction, including Cl^\bullet , OH^\bullet , HOO^\bullet , and NO^\bullet . Many reactions occur between O_3 and various chemicals, but the net O_3 depletion reaction is



Similar 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 Cl^\bullet , F^\bullet , FO^\bullet , and ClO^\bullet . Catalysis is an important part of the process. That is, a molecule acts as the catalyst by reacting with an O_3 molecule to remove one of

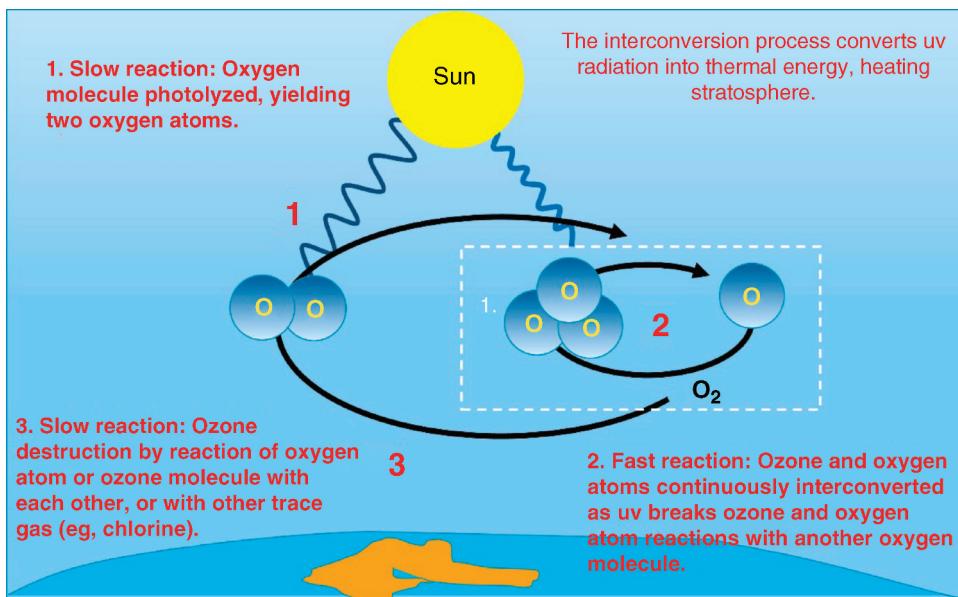
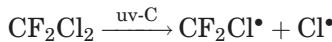


Fig. 11. Production and destruction of ozone in the stratosphere. (Adapted from Reference 21.)

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 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 (CF_2Cl_2) is an important ozone-depleting compound that releases Cl^\bullet , in a reaction catalyzed photochemically. The CFC rises in the atmosphere until it reacts with uv light:



The chlorine atom is highly reactive and can undergo many types of reactions that destroy O_3 . In addition, the other product, CF_2Cl^\bullet , can then react with OH^\bullet :



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. This change has been associated with an increase in the incidence of skin cancer, especially the most virulent form, melanoma. The

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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 United States, 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 O₃ 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 (22).

7. Air Pollution Risk and Damage

The World Health Organization (WHO) estimates that air pollution causes about 1.5 million premature deaths (23). This is likely an underestimate, since air pollution also contributes indirectly to many public health problems.

For example, food supply is threatened when tropospheric ozone damages crop yields by hastening senescence and abscission of leaves, reducing stomatal aperture and thereby carbon uptake, and decreasing photosynthetic carbon fixation (24). Indeed, high concentration of O₃ is presently depressing yields of crops important to global food supply (eg, average global yield reductions as high as 5.5% for corn, 14% for wheat, and 15% for soybeans). And, since climate change may lead to emission increases of hydrocarbon and oxides of nitrogen in many areas, tropospheric O₃ 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 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 (1).

The first step in assessing air pollution risk is to identify the hazard. The hazards associated with air pollution are generally differentiated among harm to human health, impairment to ecosystems, and damage to socially important resources, such as monuments, buildings, and infrastructure.

Air pollutant hazard primarily focuses on the toxicity of a chemical compound. 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 longer time frames than used for laboratory rats. 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; eg, copper compounds can be highly toxic to fish (1).

A compound may cause toxicity 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. In addition to toxicity, chemical hazards include other potential harm, including fire hazard, explosiveness, corrosivity, and chemical reactivity. Hazards may also be biological (biohazards) and physical (eg, radioactive). Hazard assessment is particularly important to first response and emergency situations. Indeed, spills and accidents may at first be physical hazards, eg, a highly reactive compound leaking from a ruptured tank, but the reactions may subsequently 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 pollutants transported in the air.

The threshold level is the lowest amount needed to induce harmful effects in an organism. In addition to this inherent toxicity of the compound (eg, 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; eg, a chlorinated compound is inherently more difficult to break down than is its nonhalogenated counterpart), and its likelihood to accumulate in living tissue (eg, mercury and lead can build up in tissue over years and decades with long-term exposures).

7.1. Exposure. An exposure is any contact between a receptor and the air pollutant (see Fig. 6). The receptor can be human, other species, ecosystems, or even inanimate objects, eg, buildings and monuments. For chemical and biological pollutants, this contact can come about from a number of exposure pathways (eg, air, water, and soil) and routes (eg, inhalation, ingestion, dermal, and nasal). Physical agents, such as ionizing, uv, and electromagnetic radiation, may also act along these pathways, but often have 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, chemical undergoes two steps. First, the receptor is exposed, ie, comes into contact with the agent. Next, the 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. 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 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 primary

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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 exposure is inhalation for air pollutants, 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 (eg, 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 (eg, headache, lung damage, liver damage, or cancer) (25).

Exposure can be calculated by multiplying the concentration of the agent (eg, air pollutant) with the duration of the contact. Exposure occurs immediately when the agent contacts the receptor at a single point in time and space (26). These instantaneous exposures are summed for the total ED to arrive at a time-integrated exposure (E) expressed in mass per volume (eg, $\mu\text{g m}^{-3}$):

$$E = \int_{t_1}^{t_2} C(t)dt$$

where $t_2 - t_1 = \text{ED}$ (expressed in units of time) and $C = \text{EC}$ as a function of time (mass/volume). This equation is a gross oversimplification of air pollution exposure, since the actual exposure would require this calculation for every exposure event in every location for each person's activity over the entire averaging time, eg, 24 h or a year.

Dividing the time-integrated exposure by the ED 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 twice 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 (eg, the amount of the contaminant that is applied or absorbed by a person). The target may also be an organ or other tissue in the receptor (eg, 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. Indeed, the

biomarker may not be parent compound, but a metabolite of the compound, eg, a person exposed to nicotine would have a certain amount of its metabolite, cotinine, and a person exposed to PAHs may have 1-hydroxypyrene in urine.

Exposure can be expressed for an individual, for certain groups (eg, 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 various microenvironments and age groups. This can be calculated as an inhalation exposure (E_j)

$$E_j = \sum_{i=1}^n C_i \times IR_{ij} \times t_{ij}$$

where E_j is the daily exposure for the j th group (mg day^{-1}), n denotes settings (eg, different microenvironmental and outdoor locations), $i = 1, 2, 3, \dots, n$ is type of each different setting (eg, $i = 1$ is indoors, $i = 2$ is driving in traffic, and $i = 3$ is outdoors), $j = 1, 2, 3$ refers to different age groups (eg, $j = 1$ is adults, $j = 2$ is children, and $j = 3$ is infants), C_i is the air pollutant concentration in the i th setting (mg m^{-3}), IR_{ij} is the inhalation rate in the i th setting of the j th group ($\text{m}^3 \text{ h}^{-1}$), and t_{ij} is the daily exposure time span in the i th environment of the j th group (h day^{-1}).

7.2. Respiratory System. The primary function of the human respiratory system is to deliver O_2 to the bloodstream and to remove CO_2 from the body. These two processes occur concurrently as the breathing cycle is repeated. Air containing O_2 flows into the nose and/or mouth and down through the upper airway to the alveolar region, where O_2 diffuses across the lung wall to the bloodstream. The counterflow involves transfer of CO_2 from the blood to the alveolar region and then up the airways and out the nose. 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 12. This system may be divided into three regions, namely, 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 12 illustrates the continued bifurcation of the trachea to form many branching pathways of increasingly smaller diameter by 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 (1).

The behavior of particles and gases in the respiratory system is greatly influenced by the region of the lung in which they are located (27). 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.

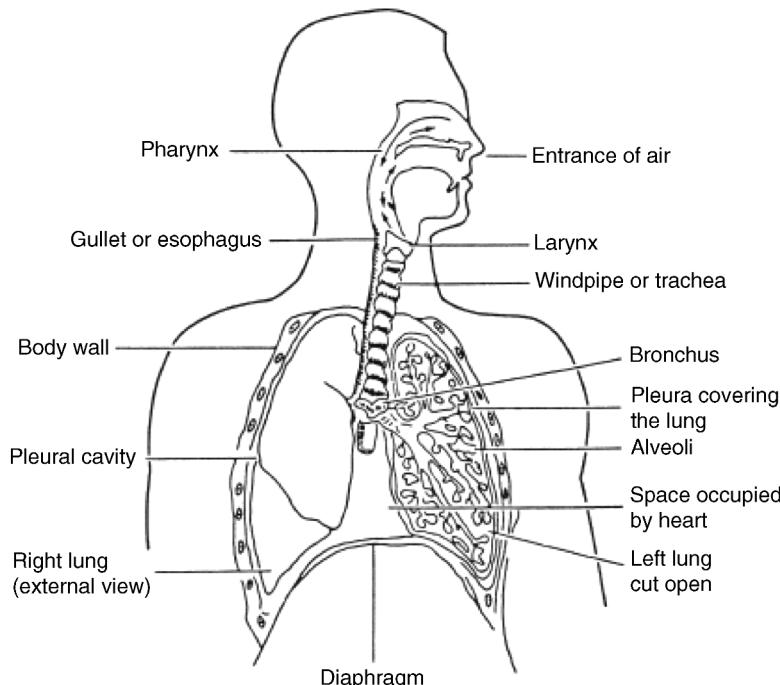


Fig. 12. Anatomy of the human respiratory system. (Reprinted with permission from Reference 1. Copyright 2014, Elsevier.)

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 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 <0.01 to $>50 \mu\text{m}$ in diameter. The relationship between the aerodynamic size of particles and the regions where they are deposited is shown in Figure 13. 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 (1).

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 remove particles from the upper airways. The tracheobronchial walls have fiber cilia that sweep the mucous fluid upward, transporting particles to the top of the trachea,

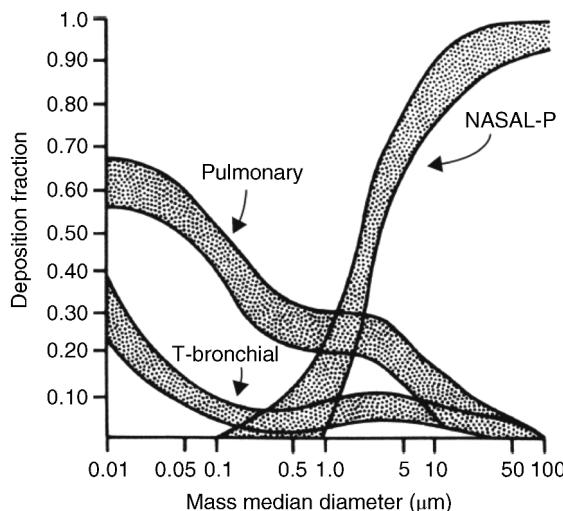


Fig. 13. Particle deposition as a function of particle diameter in various regions of the lung. The nasopharyngeal region consists of the nose and throat; the tracheobronchial (T-bronchial) region consists of the windpipe and large airways; and the pulmonary region consists of the small bronchi and the alveolar sacs. (Reprinted with permission from Reference 28. Copyright 1966, Health Physics.)

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, 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_2 are absorbed in the upper airways, whereas less soluble gases such as NO_2 and O_3 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 (1).

Since the location of particle deposition in the lungs is a function of aerodynamic diameter and density, changing the characteristics of aerosols can greatly affect their likelihood to elicit an effect. Larger particles ($>5 \mu\text{m}$) 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 $<1 \mu\text{m}$ 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 (1).

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, eg, small aerodynamic diameter, are undesirable for an air pollutant. 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 (29). Air pollutant particles with these properties would have to be removed since they are readily bioavailable (1).

Absorption is essential to drug delivery, but needs to be avoided in air pollution (eg, respirators can be used to prevent intake and absorption). The same is true for distribution. It is usually desirable to have more drug, but less pollutant distribution. 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, eg, 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, ie, producing a metabolite that is more toxic than the parent or a previous metabolite (1).

8. Effects on Plant Life

The effects of air pollution on plants range from minor damage to small habitats to biome scale. Historically, these effects have been classified as visible symptoms and nonvisual or subtle effects (30). 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 is 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 reduction 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 (1).

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. 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 (31).

The major air pollutants that are phytotoxic to plants are ozone, sulfur dioxide, nitrogen dioxide, fluorides, and peroxyacetyl nitrate (PAN). Physiological or biochemical changes have been observed in plants exposed to air pollutants, including alterations in net 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.

Air pollutant-associated damage affects plant life in ecosystems and agriculture. For example, certain native and crop species exposed to O₃ 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 (eg, harsh weather), diminished insect pest infestation, and reduced ability to compete with weed species (1).

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, eg, 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. Direct and indirect ecosystem risks often combine to exacerbate risks, such as when organisms that are already stressed from direct pollutant exposure (eg, SO₂) are further stressed by changes in humidity and temperature (1).

9. Material Damage

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 (SO₂), which reacts in the atmosphere to become sulfuric acid (H₂SO₄). 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 United States, which translates into \$61 million per year (32).

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 with surfaces and crevices as acid aerosols and the dissolution of many types of materials by acid-forming gases. 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 rust, verdigris, and other oxides form on metals. The

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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, eg, SO₂ that is converted to sulfates during deposition reacts with calcite (made up of calcium carbonate, CaCO₃) in limestone and marble, and gypsum (calcium sulfate dihydrate) (32).

Conversely, the natural process of metal corrosion from exposure to natural environmental elements is enhanced by exposure to anthropogenic pollutants, in particular SO₂ or other acidic substances, which render the protective film less effective. The rate of deterioration is determined by the pollutant concentration, the deposition rate, and the stone'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 stones 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.

10. Occupational Air Pollutants

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 in air pollution, control devices are not deployed. Thus, the allowable concentration of an air pollutant will vary according to the protection needed in ambient air and various personal and workplace microenvironments (see Fig. 6). The information in Figure 14 is used frequently to compare 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, eg, 8 h day⁻¹, 5 days week⁻¹ for 30 yr, compared with general exposures, eg, 24 h day⁻¹, 7 days week⁻¹ 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 14. 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 (34).

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

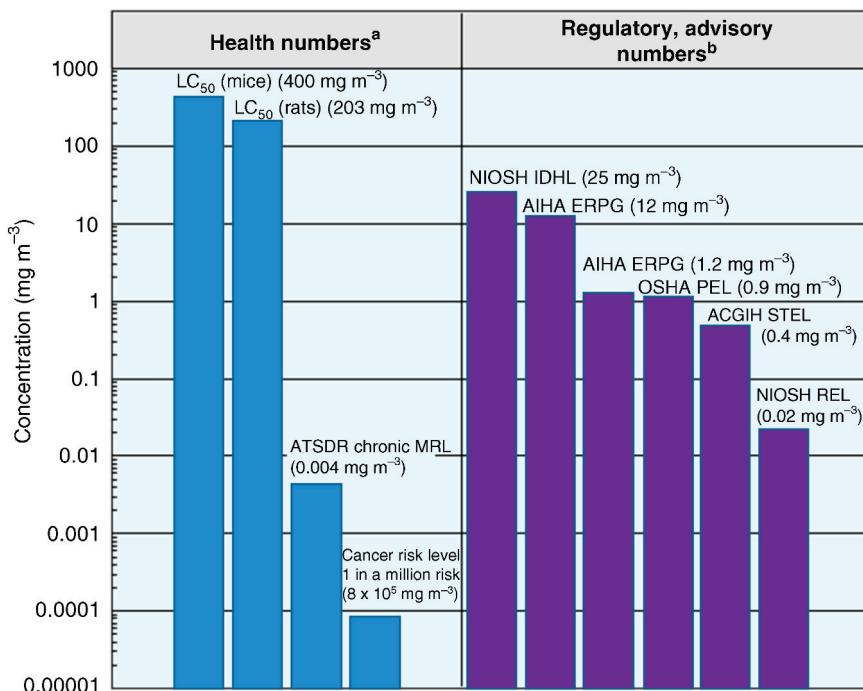


Fig. 14. Health data for inhalation exposure to formaldehyde as of 1999. Conversion of concentrations in air (at 25°C) from ppm to mg m⁻³: mg m⁻³ = (ppm) × (molecular weight of the compound)/24.45. For formaldehyde: 1 ppm = 1.23 mg m⁻³. AIHA ERPG: American Industrial Hygiene Association's emergency response 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 TWA exposure, the concentration of a substance that should not be exceeded at any time during a workday; LC₅₀ (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 TWA exposure and/or ceiling; OSHA PEL: Occupational Safety and Health Administration's permissible exposure limit expressed as a TWA, 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. (Adapted from Reference 33.)

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exposure limit (PEL) for each air pollutant. The PEL is set to protect workers day in and day out for their entire career, ie, a long-term exposure.

There are three types of PELs:

1. The TWA is the average employee exposure over a time period that a person is expected work. This is usually 8 h, so the 8-h TWA is very commonly used. It is based on measurements taken near or on the work, ie, personal exposure. The measured level 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 exceedance 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 a 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 ceilings or STELs. Others have ceilings and STELs instead of TWA values.

The recommended levels of workplace exposure are based on research; eg, 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, ie, the threshold limit values (TLVs). Both, the TLV and REL are advisory, but the PEL is a legal requirement that carries penalties when exceeded.

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

1. The REL-TWA: 8-h TWA concentration.
2. The REL-TWA: 15-min TWA concentration.
3. REL-C: ceiling concentration—not to be exceeded.
4. IDHL: 30-min concentration that is immediately dangerous to life and health.

Some industrial operations may require work in higher workplace exposures. This is permitted only if the workers wear appropriate PPE, especially respirators. Assigned protection factors (APFs) define the level of respiratory protection expected to be provided by a respirator or class of respirators (35). The APFs range from 5 to 10,000. 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 type of respirator needed:

$$\text{MUC} = \text{PEL} \times \text{APF}$$

11. Measuring and Predicting Air Pollution

Air pollution varies in type and scale. Its extent and characteristics must be documented to begin with. The progress made by control and prevention actions must be evaluated by comparing air quality over time and space. Ultimately, these air quality changes must be compared with improvements in human health, ecosystem condition, and public welfare, eg, less material destruction from air pollutants.

A reliable measurement of air pollution is the first step in providing data to support decisions needed to reduce 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 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 be very complex. Measurements are also needed to evaluate models and ground truth models, ie, evaluating the model's predictions against a well-designed and controlled set of predictions. Such measurement results are often called "knowns" with which modeled ("predicted") results are compared.

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. Such information is useful in siting monitors. For example, this wind rose (see Fig. 15) would be useful if an air pollutant is only released in the spring (eg, 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 vary intra-annually and sources are seldom limited to a single month. For most air pollution monitoring, the annual wind rose is preferred to monthly. The disadvantage of an annual wind rose is that it may wash out an important extreme condition, eg, 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.

Models can represent complicated air pollution scenarios in an understandable way. Conceptual models 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. 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

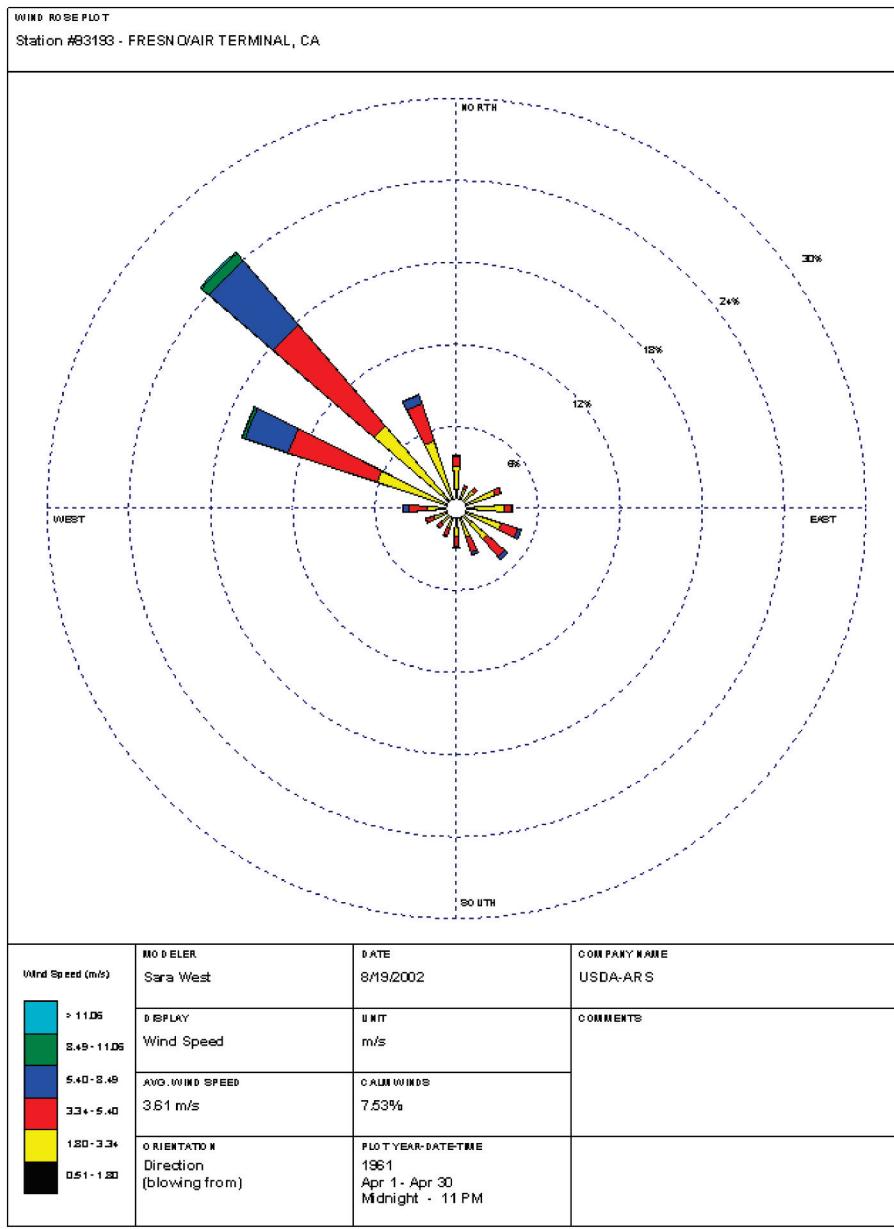


Fig. 15. April wind rose for Fresno, California. (Adapted from Reference 36.)

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, chambers or full-size test houses can 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 (37).

Air pollutant 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; ie, 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. The term "stochastic" has also been applied to aspects of a model related to an individual, eg a "virtual person".

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 incorporate both statistical and deterministic approaches, for example, when one part of a system tends to be more random, while another has a very strong basis in physical principles. Numerous models are available to address the movement of chemicals through a single environmental medium, 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 (eg, carpet), in the air as dust and vapors, and in exchanges with surfaces. Numerical models, such as computational fluid dynamics, apply mathematical expressions to approximate a system (36).

12. Controlling Particulate Matter Emissions

Removal of air pollutants to control emissions differs by type of pollutant. The major difference is between particulates and gas-phase pollutants.

12.1. Filtration. A filter removes particles from the carrying gas stream because the particulate impinges on and then adheres to the filter material. With time, PM deposits increase, and the deposit material then acts as a filtering medium. When the deposit becomes sufficiently thick 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 (1).

Filtration of aerosols from a gas stream is much more involved than size separation or sieving. 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 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.

Particles can be measured either as mass or count. Particle count is the number of particles in a given band of mass, such as particles with aerodynamic diameters $>10\text{ }\mu\text{m}$ (coarse fraction), those with diameters $<10\text{ }\mu\text{m}$, but $>2.5\text{ }\mu\text{m}$ (PM_{10} fraction), and those with diameters $<2.5\text{ }\mu\text{m}$ ($\text{PM}_{2.5}$ fraction, also known as the fine fraction). However, these size ranges can be further subdivided. For example, there has been concern recently about the so-called "ultrafines" or nanoparticles. These have at least one dimension with diameters $<100\text{ nm}$. Filtration is the most common method used to measure particles in the air (1).

12.2. Electrostatic Precipitation. High voltage electrostatic precipitators (ESPs) have been widely used throughout the world for particulate removal since they were perfected by Fredrick Cottrell 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 operate with 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 $10\text{ }\mu\text{m}$, so that an inertial precleaner 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. In an ESP, the particles move advectively with the gas stream, which is travelling horizontally through the ESP unit. The particles become charged and then are attracted by the charge differential to either side, where they are captured.

Three disadvantages of ESPs are as follows: (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 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.

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. It should remain there until the power is shut off, and it is physically dislodged by rapping, washing, or sonic means.

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 air flows 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.

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 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. Some power plants burning high ash, low sulfur coal have reported very low efficiency from the precipitator because the ash needed more SO₂ to decrease its resistivity. The suggestion that precipitator efficiency could be greatly improved by adding SO₂ or SO₃ to the stack gases has, not surprisingly, met with much skepticism.

12.3. Inertial Collectors. Inertial collectors, whether cyclones, baffles, louvers, or 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-μm rock dust and very inefficient for 5-μm wood particles. It would be very efficient, though, for 75-μm wood particles.

The most common inertial collector is the cyclone, which is used in two basic forms—the tangential inlet and the axial inlet.

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 (curvature), the particle mass, and the particle velocity are the three factors that determine the centrifugal force exerted on the particle. Other types of inertial collectors that might be used for particulate separation from a carrying gas stream depend on the same theoretical principles developed for cyclones.

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 that 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.

12.4. Scrubbers. Scrubbers, or wet collectors, have been used as gas cleaning devices for many years. However, the process has two distinct mechanisms that result in the removal of the aerosol from the gas stream. The first mechanism involves wetting the particle by the scrubbing liquid. 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 in 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 case, the smaller the droplet or bubble, the greater the collection efficiency. In the scrubber, the smaller the droplet, the greater the surface area for a given weight of liquid and the greater the chance for 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 mechanism important in wet collectors is removal of the wetted particles on a collecting surface, 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 that then separates the wetted particles from the carrying gas stream.

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 prototypical 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.

Dry scrubbers are gravel bed filters that recirculate the gravel filter medium using some type of external cleaning or washing system. 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 to clean the effluent to acceptable standards. The advantage of dry scrubbers is their ability to remove large quantities of particulate pollutants, such as fly ash, from hot gas streams.

13. Controlling Gas-Phase Emissions

Current methods of separating gaseous pollutants from an air stream include (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. Following are discussions of devices that employ these methods.

13.1. 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, water is a poor scrubbing solvent. Sulfur dioxide, for example, is only slightly soluble in water, so a scrubber of very large liquid capacity would be required. Sulfur dioxide 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.

13.2. 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 disposable canisters or charges, the majority of industrial adsorbers regenerate the adsorbent to recover not only the adsorbent but also the adsorbate, which usually has some economic value.

The efficiency of most adsorbers 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.

Industrial adsorption systems are engineered so that they operate in the region before the breakpoint and are continually regenerated by units.

13.3. 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 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.

13.4. Conversion to Nonpollutant Material. A widely used system for the control of organic gaseous emissions is oxidation of the combustible components to water and carbon dioxide. Other systems such as the oxidation of H₂S to SO₂ and H₂O are also used even though the SO₂ produced is still considered as pollutant. The trade-off occurs because the SO₂ is much less toxic and undesirable than the H₂S. The odor threshold for H₂S is about three orders of magnitude less than that for SO₂. For oxidation of H₂S to SO₂, the usual device is simply an open flare with a fuel gas pilot or auxiliary burner if the H₂S is below the stoichiometric concentration. If the SO₂ is above the emission or other operation limits, it will also have to be treated (eg, by scrubbing).

Afterburners are widely used as control devices for oxidation of undesirable combustible gases. The two general types are (1) direct-flame afterburners, 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 afterburners are the most commonly used air pollution control devices in which combustible aerosols, vapors, gases, and odors are to be controlled. The components of the afterburner include the combustion chamber, gas burners, burner controls, and exit temperature indicator. Usual exit temperatures for the destruction of most organic materials are in the range of 650–825°C, with retention times at the elevated temperature of 0.3–0.5 s.

Direct-flame afterburners 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 afterburner operation may be considerably reduced by using heat recovery equipment. In fact, this is an example of the green engineering 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. 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 (1).

13.5. Biological Control Systems. Waste streams with low to moderate concentrations of VOCs may be treated with biological systems. These are similar to biological systems used to treat wastewater, classified into three basic types: (1) biolfilters, (2) biotrickling filters, and (3) bioscrubbers.

Biofilms of microorganisms (bacteria and fungi) are grown on porous media in biofilters and biotrickling systems. The air or other gas containing the VOCs is passed through the biologically active media, where the microbes break down 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, but liquids move through the porous media of a biotrickling system (ie, the liquid “trickles”) (1).

One type of biofiltration uses compost as the porous media. Compost contains numerous species of beneficial microbes that are already acclimated to breaking down organic wastes. Thus, this medium has a head start in degrading organic compounds. Industrial compost biofilters have achieved removal rates at the 99% level. Biofilters 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. 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.

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The bioscrubber is a two-unit setup. The first unit is an adsorption unit described above. 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 (1).

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 for air movement and pressure drops are low. Other costs include amendments (eg, nutrients) and humidification. Another advantage is the usual small amount of toxic by-products, as well as low rates of emissions of greenhouse gases (oxides of nitrogen and carbon dioxide), compared with 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, 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 also be checked for shock and the presence of dust, grease, or other substances that may clog the pore spaces of the media (1).

14. Preventing Air Pollution

Control technologies have improved substantially in recent years, but the best approach is preventing the occurrence of air pollution. This can be achieved by viewing the entire life cycle of a process and considering it as a system. To begin, air quality is part of the larger environmental systems, which include the atmosphere, the hydrosphere, and the biosphere. Air pollution results from myriad sources and processes. As such, the fundamentals of air pollution include transfers and transformations among air, water, soil, sediment, and biota.

The acceptability of a process can be aided by conducting a life cycle (LCA; see Fig. 16). One of the key requirements is that a process be sustainable. A sustainable solution is one that assures that not only a level of air quality be met continuously for the foreseeable future, but all environmental values are sustained (38). Proper design must consider the raw materials, energy, labor, and other aspects of a project before extraction from the earth, manufacture, operating life, and end of life (including disposal and recycling). The LCA must consider values beyond its utility at hand. For example, how does an air quality decision affect the fabric of the community, including the vitality, history, and connections within the neighborhood and the other neighborhoods to which it is connected?

Consider the choice of whether to burn 100 L fuel A to manufacture 1000 kg of product Y using a process that releases 100 kg of SO₂ per year versus burning 150 L of fuel B to manufacture the same amount of product Z, but releasing 300 kg of SO₂ 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, earlier in the life cycle fuel A requires that 1 ton of earth be removed to produce the 100 L of fuel A, but fuel B requires no extraction (it is generated from recycled food oils, eg, biodiesel). This likely means that, early in the life cycle, fuel A results in more environmental harm than does fuel B. It could

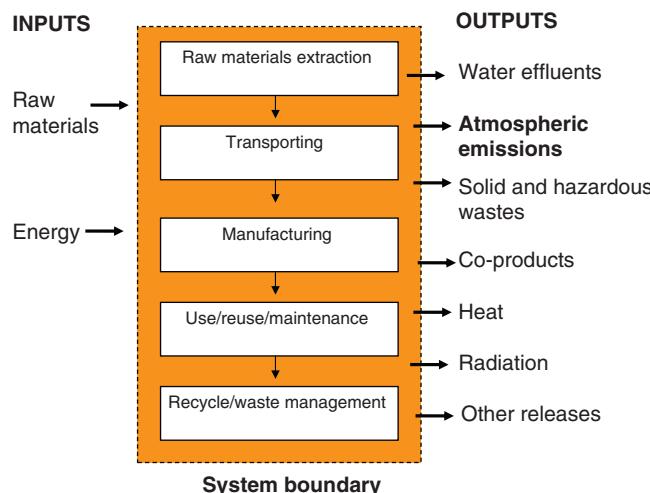


Fig. 16. Life cycle stages of a process following the conservation law, with material and energy balances. (Adapted from Reference 39.)

be that the extraction processes do not emit a large amount of air pollutants, although they usually do in the form of fugitive dust (PM). However, they are likely to damage ecosystems, soils, and water systems. Furthermore, the two fuels will have different costs and benefits at the other levels.

The above example shows that upstream effects, eg, extraction of ore, can override downstream effects, eg, air emissions. The key is to find a process that serves function, with the least amount of damage and the greatest reward. Such optimization is informed by an LCA. Unfortunately, air quality decisions have focused mainly on emissions of pollutants during separate processes, not from a comprehensive life cycle perspective. Upstream, mining emissions were not necessarily connected to refining emissions. Indeed, the different mining and the refining operations have received separate permits. The same is true for distributors of ores, crude oil, and fuel. Pipelines are regulated differently from rail, which has different requirement from trucks. Finally, operators and users of the fuel are regulated separately and differently from those who provide the fuel. Not only is the system segmented among air, water, and other environmental media, but it is segmented within the air medium. Most environmental laws and regulations address a single compartment, ie, the Clean Air Act for air, the Clean Water Act for water, etc.

Increasingly, however, pollution prevention and green engineering have become mainstays in every environmental field. Greener approaches that incorporate natural processes and that mimic and borrow from those processes have received attention from researchers and practitioners alike. This is leading to broader applications of the LCA and a step toward a more comprehensive and systematic approach to environmental quality and air quality specifically.

14.1. Process Change. Pollution is as an indicator of inefficiency in a process. A process change can be either a change in operating procedures for an

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existing process or the substitution of a completely different process. In recent years, this has been labeled "pollution prevention."

For example, consider a hypothetical decision to be made by a plant manager who for years used solvent A for a degreasing operation. He has found that operating at a conveyor speed of 100 units per hour, using a solvent temperature of 80°C, maximum cleaning with low solvent loss would result 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 that will decrease the atmospheric pollution and also result in some economic solvent recovery.
4. Put in the necessary hooding, ducting, and equipment for an afterburner system that 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 may be less expensive to abandon old steel mills, for example, 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 cost of a complete process change can be quite high, but is often paid back with time.

Another way to compare options, eg, 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, eg, 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, ie, the energy produced minus the energy expended. Thus, an $\text{EROEI} \leq 1$ means that the net energy ≤ 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 that calculated later in the life cycle, since farming and handling of corn are 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 to 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 greatly increase the efficiency of fabric filters downstream, as well as extend the time needed for cleaning and replacement. This not only is beneficial financially, but also could greatly lower the amount of PM released. 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, eg, 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 sorbent to improve an upstream technology that generates particles with low electrical conductance, thus interfering with and lowering efficiencies of ESP 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 (eg, steelmaking will always require the iron, carbon, and energy, but the process leading to a particular grade of steel can vary). Inventories and databases 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 (ie, a catalyst concentration may have a very tight tolerance range, outside of which the

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process does not work well or at all). Finally, the air pollutant component of the loss term in the thermodynamic balances is difficult to quantify. 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.

Other improvements include change to a less polluting fuel. For example, if a power plant emits large quantities of SO₂ and fly ash, conversion to natural gas may be much less expensive than installing the necessary control equipment to reduce the pollutant emissions to the permitted values. If the drier at an asphalt plant were emitting 350 mg of PM per standard cubic meter of effluent when fired with heavy oil of 4% ash, it is 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⁻³.

Pollution prevention has the distinct advantage over air emission controls in that the company not only eliminates or greatly reduces the release of pollutants, but also saves money. Direct costs include labor, raw materials, energy use, capital equipment, site preparation, tie-ins, employee training, and regulatory recordkeeping (eg, permits). In addition, there are indirect cost savings, eg, time saved from submitting compliance permits and suffering potential fines for noncompliance. One important intangible benefit is that removing a hazardous substance or dangerous situation from a process for environmental reasons can also lead to a cleaner work environment and decreased occupational risks.

DISCLAIMER

The views expressed in this article are those of the author and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency.

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