Chapter 21

AIR POLLUTION

21.1 AIR POLLUTION IN THE LOWER ATMOSPHERE

Case Study: Beijing Air Pollution 2013
As often happens during a demographic transition, the populations of polluted areas of China have begun to demand that environmental conditions be taken into account in a growing economy. In conditions of a rising number of middle-class citizens, people become more powerful contenders in politics and the economy. Local governments have been persuaded to act to lower emissions from vehicles, which is a major source of airborne pollutants.

• A Brief Overview

There is a long history of air pollution. Written accounts can be found in the 16th century. Acid rain was described in the 17th century, and its potential to do harm was established by the 18th century. The term "smog" was coined in 1905. In the U.S., an air pollution episode in Donora, PA in 1948 caused 20 deaths and 5,000 illnesses. The Donora event was followed by a London event in 1952 that caused thousands to become ill or die prematurely.

• Stationary and Mobile Sources of Air Pollution

Air pollutants are either from stationary or mobile sources. **Stationary sources** are further described as being **point sources** (e.g. a smoke stack), **fugitive sources**, or **area sources**. Fugitive sources generate air pollutants from open areas exposed to wind (e.g. dust from a construction site). Area sources are defined areas, such as an urban community or an industrial complex. **Mobile sources** derive from transportation and other sources that move around.

• General Effects of Air Pollution

There are effects on fauna and flora as well as infrastructure. The effects on vegetation include damage to leaves, suppression of growth/photosynthesis, increased susceptibility to disease, and increased susceptibility to extreme climate. Air pollution can also make soil and water toxic, and leach minerals from soil.

Air pollution is a significant source of mortality for people in urban areas. The primary health effects include toxic poisoning, cancer, birth defects, irritation of the eyes and respiratory system. Exposure to air pollutants also increases susceptibility to hearth disease, emphysema, viral and bacterial infection. Air pollution can also damage surfaces, paint, and materials.

• The Major Air Pollutants

Air pollutants are classified as being primary or secondary. **Primary pollutants** are those emitted directly (e.g. CO), while **secondary pollutants** are produced through reactions between primary pollutants and normal atmospheric compounds. Some 140 million metric tons of primary pollutants are emitted annually in the U.S., consisting mostly of CO, NOx, SOx, and particulates. (The term "NOx" refers to multiple nitrogen oxide compounds, "SOx" for oxide compounds of sulfur.) In addition to the human sources of pollutants, there are natural pollutant sources, including forest fires (particulates and NOx), volcanic eruptions (SOx), vegetation (VOCs), ~~and~~ hot springs, geysers, ~~and~~ salt marshes (H_2S), and natural hydrocarbon seeps.

Major air pollutants either occur in **gaseous** form or as **particulate matter** (PM). Particulates are solids or liquids, and are classified according to size, e.g. PM10 is a particulate less than 10 um. The gases include SO_2 or SOx, NOx, CO, O_3, volatile organic compounds (VOCs), H_2S, and hydrogen fluoride (HF).

● Criteria Pollutants

The six most common pollutants are called **criteria pollutants**.

Sulfur dioxide gas (SO_2) is colorless, toxic and even fatal at high concentrations. It oxidizes to SO_4 in the atmosphere and combines with water to from H_2SO_4, the main component of acid rain. Combustion of coal is the major source although it is also released from several refining processes. Sulfur dioxide and its chemical products are corrosive, damaging human and animal health as well as materials and plants.

Nitrogen oxide gases (NOx) occur in several oxide forms, but largely as NO and NO_2. It contributes to acid rain as nitric acid, and is a major contributor to smog and secondary pollutants (PANs). Nearly all NOx is anthropogenic and from combustion sources. NO and NO_2 suppress plant growth, but NO_3 stimulates plant growth and contributes to aquatic eutrophication.

Carbon monoxide gas (CO) is colorless and odorless and extremely toxic to humans and animals. CO has a greater affinity for hemoglobin than O_2 (tobacco smoke contains CO, a chief reason for the tendency for smokers to form blood clots). About 90% of the CO in the atmosphere is from natural sources, the other comes from fires, autos, and other sources of incomplete burning of organic compounds. Emissions in the U.S. peaked in the early 1970s.

Ozone (O_3) and other **photochemical oxidants** result from atmospheric interactions of NO_2 and sunlight, hence they are secondary pollutants and are components of smog. O_3 is most common and is extremely reactive. It has a short half-life. It is extremely toxic to plants and animals, and in low concentrations it burns the eyes and irritates the sinuses. It attacks rubber and plastic. O_3 is sometimes manufactured for use as a sterilizing agent. It can be used instead of Cl^- to sanitize drinking water. O_3 forms naturally in the stratosphere, where it forms a protective layer that blocks UV radiation.

Particulate matter (PM 10 and PM 2.5) (less than 10 μm and 2.5 μm respectively) applies to solid particles in the air and is often visible as smoke. The composition of PM varies greatly, and includes heavy metals, arsenic and asbestos. PM 2.5 is of greatest concern because they can embed in lung tissue for long periods. 2-9% of mortality in urban areas is attributed to PMs. **Ultrafine particles**, which are small enough to enter the bloodstream, may contribute to heart disease. PM is especially high in cities. Widespread PM entering the atmosphere due to human activities has contributed to **global dimming**.

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Lead (Pb) is a constituent of auto batteries and was an additive in gasoline. Lead was phased out of gasoline when catalytic converters were added to cars, because the Pb ruined the catalytic converters. Pb poisoning causes mental retardation, neurological damage, and behavioral problems. When used in gasoline it was the major source of airborne Pb pollutions. Since the phase-out, Pb emissions have greatly declined. This is one of the success stories.

A CLOSER LOOK 21.1: Acid Rain

Acid rain is precipitation in which the pH is below 5.6. pH is a measure of the concentration of hydrogen ions. As pH decreases, the concentration of hydrogen ion rises and the concentration of hydroxyl ion (OH^-) declines. pH 7 is neutral (equal concentrations of H and OH. Acid rain is **caused** primarily by SOx emissions, with a significant contribution made by NOx. Coal-burning electric power plants are the major source of SOx for acid rain. Ironically, the problem was made worse when higher air quality standards forced electric utilities to raise the heights of their smoke stacks based on the premise that dilution is the solution to pollution. Acid rain dissolves stone monuments and bridge supports, corrodes metals, damages aquatic systems (there are lakes in the Adirondacks that are too acidic to support fish), damages the foliage on vegetation (removes protective waxes) making the leaves susceptible to fungal attack, and solubilizes aluminum in the soil (toxic to plants). The **sensitivity** of the environment to acid rain varies with the buffering capacity of the soil. Regions with thin soils over granite are most sensitive.

Case Study: High-Altitude (Stratospheric) Ozone Depletion

Ozone (O_3) is an irritating and destructive pollutant in the lower atmosphere, but in the stratosphere it acts as a screen against ultraviolet radiation that is harmful to life.

The **ozone shield** is a thick region of the atmosphere in which ozone is scattered at concentrations up to 400 parts per billion. Ozone forms after the reaction of highly energetic **ultraviolet C** (UVC) light splits O_2 molecules to form free radical oxygen that then combines with free O_2 to form O_3. Very little UVC reaches the surface. **Ultraviolet B** is also highly energetic and harmful to life. Ozone absorbs this light and prevents much of it from reaching living organisms. The amount of this radiation that reaches Earth varies with ozone concentration. Another frequency, **ultraviolet A**, is not absorbed by ozone. Some reaches the Earth and causes ~~some~~ damage to cells. The ozone hole over Antarctica grew from its first observation in the 1970s until it stabilized in the 2000s.

Much ozone depletion has been attributed to ground release of **chlorofluorocarbons** (CFCs) such as those used in propellants and air conditioning unit. Sunlight eventually destroys them, releasing free chlorine, a highly reactive free radical that catalyzes the destruction of ozone back to oxygen. CFCs are very stable in the lower atmosphere, so are not removed by conventional forces; they are susceptible to UV light in the stratosphere, allowing breakdown and the release of free Cl; the Cl can **catalyze** the breakdown of ozone, often destroying many molecules before it is removed by downward diffusion. Free chlorine can bind with nitrogen dioxide and be removed from the reaction cycle temporarily. It can be released later, so $ClONO_2$ is a reservoir for chlorine.

Ozone levels can be measured from the ground by spectrometers, from planes or satellites. Measurements over 50 years have indicated thinning of ozone in various parts of the atmosphere, usually seasonally. The thinning over the Antarctic was termed the “ozone hole”. Polar stratospheric clouds tend to sequester nitrogen oxides during the winter when temperatures drop. This sequestered nitrogen is unavailable when spring sun returns and caused the release of chlorine, resulting in the typical increased ozone thinning associated with the end of winter. Later in the year, when the polar stratospheric clouds thin, nitrogen is released ~~to~~ once again slowing the catalytic effects of free chlorine.

Ozone depletion is dangerous to people and other animals (even furred ones) due to its relation to skin cancer. Increases in ultraviolet radiation can also disrupt oceanic food chains. Hopefully ozone depletion is a success story. It was detected, measured and studied, and steps were taken for control. Ozone thinning has slowed and recovery may be noticeable by 2020, assuming our models are correct, although many released CFCs have not yet reached the upper atmosphere.

•Air Toxics

Air toxics are among those pollutants known or suspected to cause cancer or other serious health problems after exposure. They include 150 known gases, metals, and organics typically emitted in relatively small volumes.

Hydrogen sulfide (H_2S) is highly toxic, corrosive, and has a rotten egg odor. It is produced from natural sources (sulfate reduction in salt marshes, volcanoes) and industrial sources.

Hydrogen fluoride (HF) is released from industrial sources and is extremely toxic, even at 1 part per billion. It has been known to enter grazing animals after deposition on grass.

Mercury (Hg) is released from coal-burning plants, industrial sources, and mining. Hg causes neurological and developmental damage. It is deposited on soil and directly in water, where it enters the food chain and undergoes biomagnification.

Volatile organic compounds (VOCs) include a variety of chemicals, including solvents, gasoline vapors, natural gas, and may others. Many are toxic and some are carcinogenic (e.g. benzene). About 15% of VOCs emitted globally are anthropogenic, and about 50% of VOC emissions in the U.S. are anthropogenic. Catalytic converters have greatly reduced VOC emissions from autos.

Methyl isocyanate is a chemical used in pesticide production, and inhalation of it causes severe respiratory distress and death. In 1984 an accident in Bhopal, India released a cloud of methyl isocyanate that killed over 2,000 people and injured 15,000. Such chemicals need careful handling and should not be used near high-density populations.

Benzene is used in gasoline and solvents, and can be an important indoor pollutant released from glue, paint, furniture wax and detergent (CDC, http://www.bt.cdc.gov/agent/benzene/basics/facts.asp). Benzene exposure is linked to cancer and other serious human diseases.

Acrolein is released by petroleum burning and is in tobacco smoke. It has both acute and chronic effects ranging from eye and throat irritation to possible cancer. (EPA, http://www.epa.gov/iris/subst/0364.htm)

• Variability of Air Pollution

The severity of air pollution varies regionally and temporally with climate, season, source strength, and even time of day. "Haze from afar" refers to pollutants which travel long distances, even across oceans.

• Urban Air Pollution: Chemical and Atmospheric Processes

Sulfurous smog, also known as "London smog" or "gray air", is produced by burning coal or oil at large power plants. It can cause severe throat and lung irritation due to its acidic character.

Photochemical smog, also known as "L.A. smog" or "brown air" is directly linked to automobile emissions and is a particular problem in urban areas during daylight hours where concentrations of the primary pollutants are sufficiently high as they often are on the road during rush hour. Sunlight reacts with hydrocarbons and nitrogen oxides to form ozone and other irritating compounds.

Meteorological conditions can determine if air pollution is a nuisance or a major health threat. Air pollution can become severe during atmospheric inversions, which occur when a blanket of cool air is trapped at ground level and overtopped by warmer air. Since cooler air is denser than warm air, the cool air does not rise and pollutants can accumulate. The susceptibility of an area to **inversion** is a function of local topography and weather. The potential for air pollution depends on the rate of emissions, the average wind speed, the distance downwind through the city, and elevation of mixing.

21.2 CONTROLLING COMMON POLLUTANTS OF THE LOWER ATMOSPHERE

The most reasonable ways to reduce air pollution is through **reducing emissions**, **capturing them before release**, or **removal from the atmosphere**.

• Particulates

Mobile sources are difficult to control. Industrial sources can be controlled with electrostatic precipitators, scrubbers and filters, but mobile sources are more difficult.

• Automobiles

Catalytic converters are used on autos to reduce VOCs and CO. Auto emissions of NOx are reduced by recirculating exhaust gas and adjusting the air:fuel ratio, which also leads to lessening photochemical smog. Of course, reducing the number of vehicles emitting pollutants and reducing miles driven is also effective.

Interesting question for discussion: Given that transportation is one of the major sources of urban air pollution, what could be done to change the habits of people so that they would rely on alternative and cleaner forms of transportation?

• Sulfur Dioxide

SO_2 can be controlled by using **scrubbers** on smoke stacks and by using cleaner or gasified coal as a fuel source. Technology also exists to capture sulfur compounds and incorporate them into products such as sheetrock.

21.3 INDOOR AIR POLLUTION

Humans have a history of building structures and breathing the inside air, which was often contaminated by smoke from cook/heating fires. People today spend 70-90% percent of their time inside, so quality of indoor air is of major importance.

• Sources of Indoor Air Pollution

Sources include tobacco smoke, *Legionella pneumophila* (a bacterium), mold spores, radon gas from soil under the building, pesticides used in the building, asbestos from insulation and tile, formaldehyde gas from decomposing particle board, and dust mites. Unfortunately, two of the best ways to conserve energy in buildings, namely to increase insulation and eliminate air leaks, exacerbates the problem of indoor air pollution.

• Pathways, Processes, and Driving Forces

Temperature differences between the inside and outside of a building create **chimney effects**. These effects can cause outside air to be drawn in through cracks, or pollutants to be drawn from one part of a building to another.

Heating, ventilation, and air-conditioning systems move a great deal of air, and should be properly designed to provide comfort and humidity control. These systems provide an opportunity to filter air, and filters should be replaced regularly.

The combustion products from **burning tobacco** include NOx, CO, hydrogen cyanide, and about 40 carcinogenic chemicals. In the U.S. 3,000 cancer deaths and 40,000 more from heart disease are thought to be related to second hand smoke. There are still 40 million smokers in the U.S. Fortunately, many buildings have banned smoking, but people smoking in doorways still contaminate indoor air.

Radon is a naturally occurring radioactive gas that is colorless, odorless and tasteless. It is produced from the decay of ^{238}U. Radon is known to be a risk factor for lung cancer, and indoor radon gas poses risks that are 100s of times greater than those from outdoor pollutants in the air. The production of radon gas varies with the local geology and, thus, varies spatially. There are large areas of PA, NJ and NY that are notorious for high radon levels. High concentrations have been identified in other states as well. Radon enters homes by migrating up from the soil into basements and lower floors, from groundwater that sometimes is pumped into homes, and from radon-contaminated building materials such as building blocks. There are simple test kits available through commercial testing laboratories. When it is identified as a problem, it can be controlled by sealing the entry points and improving the ventilation.

The EPA estimates that 14,000 lung cancer deaths annually in the U.S. are related to radon gas exposure. This compares with a total annual mortality rate from lung cancer of about 140,000. However, there are few studies and risk estimates are controversial. The greatest risk is thought to be from the particles of a radon daughter product such as polonium-218 that adhere to dust and becomes trapped in the lung. For example, people who live in homes for about 20 years with an average concentration of radon of about 25 pCi/L are estimated to have a 1 to 2% chance of contracting lung cancer.

● Symptoms of Indoor Air Pollution

The sensitivity of people to indoor pollutants varies depending on genetic factors, lifestyle, and age. Symptoms also vary as a function of the particular pollutant. Some can be fatal under certain circumstances (e.g. CO poisoning). The problems in BRIs (building related illnesses) may be traceable to specific sources, or they may be unknown SBS (sick building syndrome). Sick building syndrome can be brought on by stress from various sources, even employment-related stress.

A case of sick building syndrome was seen in the Massachusetts Registry of Motor Vehicles. Constructed in April 1994, the first problems were reported in June of the same year. These included unpleasant odors, respiratory problems, eye irritations, rashes and other symptoms. The cooling system condensed water vapor onto ceiling tiles, which were composed of a starch that fermented when wet. Fire proofing around the ductwork was also wet and falling apart, releasing fibers into the air. The building was closed after 15 months of occupancy.

21.4 CONTROLLING INDOOR AIR POLLUTION

There are financial incentives, as much as $250 billion per year, for controlling indoor air pollution in the workplace, because of time lost from work and associated health care costs. Legislation requiring a minimum level of indoor air quality and building codes that require proper ventilation would be desirable. Such codes exist in Europe.

Education is also important. The public can protect themselves against many hazards simply by exercising good judgment and some behavior modification (e.g. not smoking indoors).

● Making Homes and Other Buildings Radon-Resistant

Radon resistance involves sealing leaks that permit radon to enter as well as making sure that buildings are adequately ventilated.

● Designing Buildings to Minimize Indoor Air Pollution
It is possible to design buildings from scratch to minimize indoor air pollutants

Study Questions

1. Since the amount of pollution emitted into the air is a very small fraction of the total material in the atmosphere, why do we have air pollution problems?

Ans: Even at these small concentration air pollutants can affect our health in several ways. Some of the primary effects are cancer, birth defects, eye and respiratory system irritation, greater susceptibility to heart disease, and aggravation of chronic diseases, such as asthma and emphysema. It is worth noting here that many air pollutants have synergistic effects—that is, the combined effects are greater than the sum of the separate effects.

2. What are the differences between primary and secondary pollutants?

Ans: Primary pollutants are emitted directly into the air. They include particulates, sulfur dioxide, carbon monoxide, nitrogen oxides, and hydrocarbons. Secondary pollutants are produced by reactions between primary pollutants and normal atmospheric compounds. For example, ozone forms over urban areas through reactions of primary pollutants, sunlight, and natural atmospheric gases. Thus, ozone is a secondary pollutant.

3. Carefully examine Figure 21.14, which shows a column of air moving through an urban area, and Figure 21.10, which shows relative concentrations of pollutants that develop on a typical warm day in Los Angeles. What linkages between the information in these two figures might be important in trying to identify and learn more about potential air pollution in an area?

Ans: The potential for air pollution in urban areas is determined by the rate of emission of pollutants per unit area, the distance that an air mass moves downwind through a city, the average speed of the wind, and the elevation to which potential pollutants can be thoroughly mixed by naturally moving air in the lower atmosphere.

4. Why is acid deposition a major environmental problem, and how can it be minimized?

Ans: Acid deposition is a problem for several reasons. Acid weakens trees as essential nutrients are leached from soils or stripped from leaves by acid fog. Acidic rainfall also may release toxic chemicals, such as aluminum. Acid rain affects lake ecosystems in three ways. First, it damages aquatic species (fish, amphibians, and crayfish) directly by disrupting their life processes in ways that limit growth or cause death. Second, acid rain dissolves chemical elements necessary for life in the lake. Third, acid rain leaches metals, such as aluminum, lead, mercury, and calcium, from the soils and rocks in a drainage basin and discharges them into rivers and lakes. Acid rain damages not only our forests and lakes but also many building materials, including steel, galvanized steel, paint, plastics, cement, masonry, and several types of rock, especially limestone, sandstone, and marble. Solution to lake acidification is rehabilitation by the periodic addition of lime, but a better approach is to target the components of acid rain, the emissions of sulfur dioxide and nitrogen oxides.

5. Why will air-pollution abatement strategies in developed countries probably be much different in terms of methods, process, and results than air-pollution abatement strategies in developing countries?

Ans: The cost of pollution-abatement technology is going to require different tradeoffs. In developed nations people may be more willing to absorb the cost of abatement. However, major shifts in behavior of people in developed countries will need to take place in order to reduce emissions from automobile and consumer goods. The science and technology necessary to reduce air pollution are well known; what we do with these tools involves a value judgment. It is clear that people value a high-quality environment, and clean air is at the top of the list. The developed countries have an obligation to take a leadership role in finding ways to use resources while minimizing air pollution. Of particular importance is finding methods and technologies that will allow for reducing air pollution while stimulating economies.

6. Discuss the processes responsible for stratospheric ozone depletion. Which are most significant? Where? Why?

Ans: include emissions of CFCs, the normal breakdown processes of CFCs, transportation of CFCs to the upper atmosphere and interaction with ozone.