

Air Pollution



Shown here is an aerial view of Dallas, Texas and the greater Kansas City metropolitan area are both participating in the new initiative called Sustainable Skylines, through the U.S. Environmental Protection Agency.

LEARNING OBJECTIVES

The atmosphere has always been a sink—a place of deposition and storage—for gaseous and particulate wastes. When the amount of waste entering an area of the atmosphere exceeds the atmosphere’s ability to disperse or break down the pollutants, problems result. After reading this chapter, you should understand . . .

- The two major ways that pollution affects living things: by direct contact down here and by altering the atmosphere above us;
- Why air pollution from human activities, combined with meteorological conditions, may exceed the atmosphere’s natural ability to remove wastes;
- What the major categories and sources of air pollutants are;
- How “acid rain” is produced and how its environmental impacts might be minimized;
- Why air quality standards are important;
- Why the economics of air pollution is controversial and difficult;
- What the major indoor air pollutants are, where they come from, and why they cause some of our most serious environmental health problems;
- “Green buildings” and other major strategies for controlling and minimizing indoor air pollution;
- The “ozone hole” and the science of ozone depletion.



CASE STUDY

Sustainable Skylines: Dallas and Kansas City

Sustainable Skylines is an initiative that has been launched by the Environmental Protection Agency (EPA). Its objective is to achieve sustainable air quality by reducing the six major air pollutants, as well as other toxic air pollutants and greenhouse gases. Cities that participate in the program are encouraged to integrate energy, land use, transportation, and air quality planning in order to achieve measurable improvements within a three-year period. As of 2009, two cities participated—Dallas, Texas, and Kansas City, Kansas and Missouri (the greater Kansas City metropolitan area). The EPA hopes to have ten cities invested in the program by 2010. Among the projects included in a particular sustainable Skyline venture are the following:

- Reducing emissions from landscape equipment by improved irrigation of lawns and turf management, as well as retrofitting small off-road equipment to achieve reduced emissions of air pollutants.
- Reducing vehicle emissions by increasing public transportation and reducing the distances traveled in vehicles.
- Replacing existing taxis with “green taxis” that emit far less pollution.
- Encouraging “**green buildings**” with healthier interior environments and landscaping that benefit the local external environment.

- Reducing emissions from idling vehicles and retrofitting diesel engines to reduce emissions.
- Programs to encourage planting trees in the city to develop a tree canopy in as many areas as possible.

Each city that participates in the Sustainable Skylines Program will have its own local programs and policies, developed in collaboration with the city’s inhabitants and city leaders, along with public and private partners. For example, in Dallas, Texas, the description of activities has the goal of helping to reduce the urban “heat island” effect. Urban areas are often warmer than surrounding areas due to the abundance of equipment and lights, as well as surfaces that absorb heat. Cities with little vegetation also have less evaporative cooling. This is a particular problem in Dallas, which has a naturally warm climate much of the year. As a result, the goal of the Sustainable Skylines Program for Dallas is to increase the number of shaded surfaces and green vegetated surfaces of roofs and surrounding buildings in order to reduce the heat island effect and cool the city.

In the greater Kansas City area, the objectives are to encourage a variety of sustainable environmental projects with social benefits. They plan to address such issues as transportation, energy, land use, resource efficiency, green buildings, and air quality, with a focus on projects that will result in cleaner, healthier air for this large urban area.

21.1 Air Pollution in the Lower Atmosphere

A Brief Overview

As the fastest-moving fluid medium in the environment, the atmosphere has always been one of the most convenient places to dispose of unwanted materials. The atmosphere has been a sink for waste disposal ever since we first used fire, and people have long recognized the existence of atmospheric pollutants, both natural and human-induced. Leonardo da Vinci wrote in 1550 that a blue haze formed from materials

emitted into the atmosphere by trees. What he had observed is a natural photochemical smog from hydrocarbons given off by living trees. This haze, whose cause is still not fully understood, gave rise to the name Smoky Mountains for the range in the southeastern United States.

The phenomenon of acid rain was first described in the 17th century, and by the 18th century it was known that plants in London were damaged by air pollution. Beginning with the Industrial Revolution in the 18th century, air pollution became more noticeable. The word *smog* was introduced by a physician at a public-health conference in 1905 to denote poor air quality resulting from a mixture of smoke and fog.

Stationary and Mobile Sources of Air Pollution

The two major categories of air pollution sources are stationary sources and mobile sources. **Stationary sources** have a relatively fixed location and include point sources, fugitive sources, and area sources.

- *Point sources*, discussed in Chapter 10, emit pollutants from one or more controllable sites, such as power-plant smokestacks (Figure 21.1).
- *Fugitive sources* generate air pollutants from open areas exposed to wind. Examples include burning for agricultural purposes (Figure 21.2), as well as dirt roads, construction sites, farmlands, storage piles, surface mines, and other exposed areas.
- *Area sources*, also discussed in Chapter 10, are well-defined areas within which are several sources of air pollutants—for example, small urban communities, areas of intense industrialization within urban complexes, and agricultural areas sprayed with herbicides and pesticides.

Mobile sources of air pollutants include automobiles, trucks, buses, aircraft, ships, trains, and anything else that pollutes as it moves from place to place.²

General Effects of Air Pollution

Air pollution affects many aspects of our environment, including its visual qualities, vegetation, animals, soils, water quality, natural and artificial structures, and human health. Air pollutants affect visual resources by discoloring the atmosphere and by reducing visual range and atmospheric clarity. We cannot see as far in polluted air, and



FIGURE 21.1 This steel mill in Beijing, China, is a major source of air pollution.



FIGURE 21.2 Burning sugarcane fields, Maui, Hawaii—an example of a fugitive source of air pollution.

what we do see has less color contrast. These effects were once limited to cities but now extend to some wide-open spaces of the United States. For example, near the Four Corners, where New Mexico, Arizona, Colorado, and Utah meet, emissions from two large fossil-fuel-burning power plants have altered visibility in a region where visibility used to be 80 km (50 mi) from a mountaintop on a clear day.¹ The power plants are two of the largest pollution sources in the U.S.

Air pollution's numerous effects on vegetation include damage to leaves, needles, and fruit; reduced or suppressed growth; increased susceptibility to diseases, pests, and adverse weather; and disruption of reproductive processes.^{1, 2}

Air pollution is a significant factor in the human death rate in many large cities. For example, it has been estimated that in Athens, Greece, the number of deaths is several times higher on days when the air is heavily polluted; and in Hungary, where air pollution has been a serious problem in recent years, it may contribute to as many as 1 in 17 deaths. The United States is certainly not immune to health problems related to air pollution. The most polluted air in the nation is in the Los Angeles urban area, where millions of people are exposed to it. An estimated 175 million people live in areas of the United States where exposure to air pollution contributes to lung

disease, which causes more than 300,000 deaths per year. Air pollution in the United States is directly responsible for annual health costs of over \$50 billion. In China, whose large cities have serious air pollution problems, mostly from burning coal, the health cost is now about \$50 billion per year and may rise to about \$100 billion per year by 2020.

Air pollutants can affect our health in several ways, depending on the dose or concentration and other factors, including individual susceptibility (see the discussion of dose–response in Chapter 10). 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. People suffering from respiratory diseases are the most likely to be affected. Healthy people tend to acclimate to pollutants, but this is a physiological tolerance; as explained in Chapter 10, it doesn't mean that the pollutants are doing no harm (Figure 21.3).

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. For example, sulfate and nitrate may attach to small particles in the air, facilitating their inhalation deep into lung tissue. There, they may do greater damage than a combination of the two pollutants would be expected to, based on their separate effects. This phenomenon has obvious health consequences; consider joggers breathing deeply and inhaling

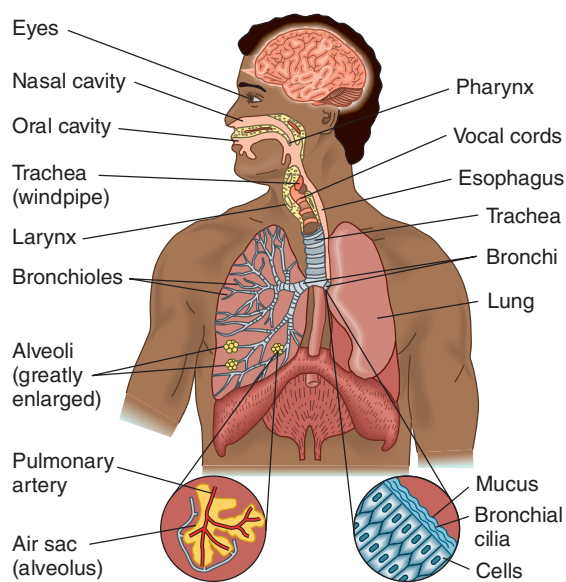


FIGURE 21.3 Idealized diagram showing some of the parts of the human body (brain, cardiovascular system, and pulmonary system) that can be damaged by common air pollutants. The most severe health risks from normal exposures are related to particulates. Other substances of concern include carbon monoxide, photochemical oxidants, sulfur dioxide, and nitrogen oxides. Toxic chemicals and tobacco smoke also can cause chronic or acute health problems.

particulates as they run along the streets of a city. The effects of air pollutants on vertebrate animals in general include impairment of the respiratory system; damage to eyes, teeth, and bones; increased susceptibility to disease, parasites, and other stress-related environmental hazards; decreased availability of food sources (such as vegetation affected by air pollutants); and reduced ability for successful reproduction.²

Air-pollution deposits can also make soil and water toxic. In addition, soils may be leached of nutrients by pollutants that form acids. Air pollution's effects on man-made structures include discoloration, erosion, and decomposition of building materials (see the discussion of acid rain later in this chapter).

The Major Air Pollutants

Nearly 200 air pollutants are recognized and assessed by the EPA and listed in the Clean Air Act. They can be classified as primary or secondary. **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.

The major air pollutants occur either as particulate matter (PM) or in gaseous forms. Particulates are very small particles of solid or liquid substances and may be organic or inorganic. Gaseous pollutants include sulfur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO), ozone (O_3) and volatile organic compounds (VOCs), such as hydrocarbons (compounds containing only carbon and hydrogen that include petroleum products), hydrogen sulfide (H_2S), and hydrogen fluoride (HF).

The primary pollutants that account for nearly all air-pollution problems are carbon monoxide (58%), volatile organic compounds (11%), nitrogen oxides (15%), sulfur oxides (13%), and particulates (3%). In the United States today, about 140 million metric tons of these substances enter the atmosphere from human-related processes. If these pollutants were uniformly distributed in the atmosphere, the concentration would be only a few parts per million by weight. Unfortunately, pollutants are not uniformly distributed but tend to be produced, released, and concentrated locally or regionally—for example, in large cities.

In addition to pollutants from human sources, our atmosphere contains many pollutants of natural origin, such as sulfur dioxide from volcanic eruptions; hydrogen sulfide from geysers and hot springs, as well as from biological decay in bogs and marshes; ozone in the lower atmosphere as a result of unstable meteorological

conditions, such as violent thunderstorms; a variety of particles from wildfires and windstorms;¹ and natural hydrocarbon seeps, such as La Brea Tar Pits in Los Angeles.

The data in Table 21.1 suggest that, except for sulfur and nitrogen oxides, natural emissions of air pollutants exceed human-produced emissions. Nevertheless, it is the human component that is most abundant in urban areas and leads to the most severe problems for human health.

Criteria Pollutants

The six most common pollutants are called **criteria pollutants** because the EPA has set specific limits on the levels of these six and they are responsible for most of our air-pollution problems. The six are sulfur dioxide, nitrogen oxides, carbon monoxide, ozone, particulates, and lead.

Sulfur Dioxide

Sulfur dioxide (SO₂) is a colorless and odorless gas normally present at Earth's surface in low concentrations. A significant feature of SO₂ is that once emitted into the atmosphere, it can be converted into fine particulate sulfate (SO₄) and removed from the atmosphere by wet or dry deposition. The major anthropogenic (human) source of sulfur dioxide is the burning of fossil fuels, mostly coal in power plants (see Table 21.1). Another major source comprises a variety of industrial processes, ranging from petroleum refining to the production of paper, cement, and aluminum.¹⁻⁴

Adverse effects of sulfur dioxide depend on the dose or the concentrations (see Chapter 10) and include injury or death to animals and plants, as well as corrosion of paint and metals. Crops, such as alfalfa, cotton, and barley, are especially susceptible. Sulfur dioxide can severely damage the lungs of people and other animals, especially in the sulfate form. It is also an important precursor to acid rain (see A Closer Look 21.1).¹⁻⁴

U.S. emission rates of SO₂ from 1970 to 2007 are shown in Table 21.2. Emissions peaked at about 32 million tons in the early 1970s and since then have fallen 60%, to about 13 million tons, as a result of effective emission controls.

Nitrogen Oxides

Although nitrogen oxides (NO_x) occur in many forms in the atmosphere, they are emitted largely as nitric oxide (NO) and nitrogen dioxide (NO₂), and only these two forms are subject to emission regulations. The more important of the two is NO₂, a yellow-brown to reddish-brown gas. A major concern with NO₂ is that it may be converted by complex reactions in the atmosphere to an ion, NO₃²⁻, within small water particulates, impairing visibility. As mentioned earlier, both NO and NO₂ are major contributors to smog, and NO₂ is also a major contributor to acid rain (see A Closer Look 21.1). Nitrogen oxides contribute to nutrient enrichment and eutrophication of water in ponds, lakes, rivers, and the ocean (see Chapter 19). Nearly all NO₂ is emitted

Table 21.1 MAJOR NATURAL AND HUMAN-PRODUCED COMPONENTS OF SELECTED AIR POLLUTANTS

AIR POLLUTANTS	EMISSIONS (% OF TOTAL)		MAJOR SOURCES OF HUMAN-PRODUCED COMPONENTS	PERCENT
	NATURAL	HUMAN-PRODUCED		
Particulates	85	15	Fugitive (mostly dust)	85
			Industrial processes	7
			Combustion of fuels (stationary sources)	8
Sulfur oxides (SO _x)	50	50	Combustion of fuels (stationary sources, mostly coal)	84
			Industrial processes	9
Carbon monoxide (CO)	91	9	Transportation (automobiles)	54
Nitrogen dioxide (NO ₂)		Nearly all	Transportation (mostly automobiles)	37
			Combustion of fuels (stationary sources, mostly natural gas and coal)	38
Ozone (O ₃)	A secondary pollutant derived from reaction with sunlight NO ₂ , and oxygen (O ₂)		Concentration present depends on reaction in lower atmosphere involving hydrocarbons and thus automobile exhaust	
Hydrocarbons (HC)	84	16	Transportation (automobiles)	27
			Industrial processes	7

Table 21.2 U.S. EMISSIONS OF CRITERIA POLLUTANTS FROM 1970–2007

	MILLIONS OF TONS PER YEAR							
	1970	1980	1985	1990	1995	2000	2005	2007
Carbon Monoxide (CO)	200	178	170	144	120	102	89	81
Lead	ND	0.074	0.023	0.005	0.004	0.002	0.003	0.002
Nitrogen Oxides (NO _x)	~27	27	26	25	25	22	19	17
Volatile Organic Compounds (VOC)	~30	30	27	23	22	17	15	15
Particulate Matter (PM)								
PM ₁₀	ND	6	4	3	3	2	2	2
PM _{2.5}		ND	ND	2	2	2	1	1
Sulfur Dioxide (SO ₂)	32	26	23	23	19	16	15	13
Totals	ND	267	250	220	191	161	141	129

Notes:

- In 1985 and 1996 EPA refined its methods for estimating emissions. Between 1970 and 1975, EPA revised its methods for estimating PM emissions.
- The estimates for 2002 are from 2002 NEI v2; the estimates for 2003 and beyond are preliminary and based on 2002 NEI v2.
- No data (ND)

Source: Environmental Protection Agency, 2008.
Air Trends accessed June 10, 2008 @ www.epa.gov.

from anthropogenic sources. The two main sources are automobiles and power plants that burn fossil fuels.^{1, 2}

Nitrogen oxides have various effects on people, including irritation of eyes, nose, throat, and lungs and increased susceptibility to viral infections, including influenza (which can cause bronchitis and pneumonia).^{1, 2} Dissolved in water, nitrogen oxides form acids that can harm vegetation. But when the oxides are converted to nitrates, they can promote plant growth.

U.S. emission rates of NO_x from 1970 to 2007 are shown in Table 21.2. Emissions are primarily from combustion of fuels in power plants and vehicles. They have been reduced by about 30% since 1980.

Carbon Monoxide

Carbon monoxide (CO) is a colorless, odorless gas that, even at very low concentrations, is extremely toxic to humans and other animals. The high toxicity results from a physiological effect: Carbon monoxide and hemoglobin have a strong natural attraction for one another; if there is any carbon monoxide in the vicinity, the hemoglobin in our blood will take it up nearly 250 times faster than it will oxygen and carry mostly carbon monoxide, rather than oxygen, from the atmosphere to the internal organs. Effects range from dizziness and headaches to death. Many people have been accidentally asphyxiated by carbon monoxide from incomplete combustion of fuels in campers, tents,

and houses. Carbon monoxide is particularly hazardous to people with heart disease, anemia, or respiratory disease. It may also cause birth defects, including mental retardation and impaired fetal growth. Its effects tend to be worse at higher altitudes, where oxygen levels are lower. Detectors (similar to smoke detectors) are now commonly used to warn people if CO in a building reaches a dangerous level.

Approximately 90% of the carbon monoxide in the atmosphere comes from natural sources. The other 10% comes mainly from fires, automobiles, and other sources of incomplete burning of organic compounds, but these are easily concentrated locally, especially by enclosures, so this 10% causes most of the health problems. Emissions of CO peaked in the early 1970s at about 200 million metric tons and declined 60% to about 81 million metric tons by 2007 (Table 21.2). This significant reduction stemmed largely from cleaner-burning engines despite an increased number of vehicles.

Ozone and Other Photochemical Oxidants

Photochemical oxidants are secondary pollutants arising from atmospheric interactions of nitrogen dioxide and sunlight. Ozone, of primary concern here, is a form of oxygen in which three atoms of oxygen occur together rather than the normal two. A number of other photochemical oxidants, known as PANs (peroxyacyl nitrates), occur with photochemical smog.

Ozone is relatively unstable and releases its third oxygen atom readily, so it oxidizes or burns things more readily and at lower concentrations than does normal oxygen. Released into the air or produced in the air, ozone may injure living things. However, since these include bacteria and other organisms, it is sometimes used for sterilizing purposes—for example, bubbling ozone gas through water is one way to purify water.

Ozone in the lower atmosphere is a secondary pollutant produced on bright, sunny days in areas where there is significant primary pollution. The major sources of ozone, as well as other oxidants, are automobiles and industrial processes that release nitrogen dioxide by burning fossil fuels. Because of the nature of its formation, ozone is difficult to regulate and thus is the pollutant whose health standard is most frequently exceeded in U.S. urban areas.^{5,6}

The adverse environmental effects of ozone and other oxidants, like those of other pollutants, depend in part on the dose or concentration of exposure and include damage to plants and animals, as well as to materials, such as rubber, paint, and textiles. Ozone's effects on plants can be subtle. At very low concentrations, it can slow growth without visible injury. At higher concentrations, it kills leaf tissue and, if pollutant levels remain high, whole plants. The death of white pine trees along highways in New England is believed to be due in part to ozone pollution. In animals, including people, ozone causes various kinds of damage, especially to the eyes and respiratory system. Many millions of Americans are often exposed to ozone levels that damage cell walls in lungs and airways. Tissue reddens and swells, and cellular fluids seep into the lungs. Eventually, the lungs lose elasticity and are more susceptible to bacterial infection, and scars and lesions may form in the airways. Even young, healthy people may be unable to breathe normally, and on especially polluted days breathing may be shallow and painful. Ground-level ozone decreased by 9% from 1990 to 2007.^{1,2,6}

While too much ozone causes problems down here, too little of it has become a problem in the stratosphere. Because of the effect of sunlight on normal oxygen, ozone forms a natural layer high in the stratosphere that protects us from harmful ultraviolet radiation from the sun. However, the emission of certain chemicals in the lower atmosphere has led to serious ozone depletion in the stratosphere. We will discuss the ozone-depletion story later in the chapter. Suffice it to say here that it is becoming an environmental success story at the global level.

Particulate Matter: PM_{10} , $PM_{2.5}$, and Ultrafine Particles

Particulate matter (PM) is made up of tiny particles. The term *particulate matter* is used for varying mixtures of particles suspended in the air we breathe, but in regulations these are divided into three categories: PM_{10} ,

particles up to 10 micrometers (μm) in diameter; $PM_{2.5}$, particles between 2.5 and 0.18 microns; and UP, **ultrafine particles** smaller than 0.18 micrometers in diameter, released into the air by vehicles on streets and freeways. For comparison, the diameter of a human hair is about 60 to 150 μm (Figure 21.4).

Nearly all industrial processes, as well as the burning of fossil fuels, release particulates into the atmosphere. Farming, too, adds considerable particulate matter to the atmosphere, as do windstorms in areas with little vegetation and volcanic eruptions. Particles are everywhere, and high concentrations and/or specific types of particles pose a serious danger to human health, including aggravation of cardiovascular and respiratory diseases. Major particulates include asbestos (especially dangerous, discussed in detail in Chapter 10)² and small particles of heavy metals, such as arsenic, copper, lead, and zinc, which are usually emitted from smelters and other industrial facilities. Particulates can reduce visibility and affect climate (see Chapter 20).² Much particulate matter is easily visible as smoke, soot, or dust; other particulate matter is not easily visible.

Fine particles— $PM_{2.5}$ and smaller—are easily inhaled into the lungs, where they can be absorbed into the bloodstream or remain embedded for a long time. Among the most significant of these particles are sulfates and nitrates. As already explained, these are mostly secondary pollutants produced in the atmosphere by chemical reactions between normal atmospheric constituents and sulfur dioxide and nitrogen oxides. These reactions are important in the formation of sulfuric and nitric acids in the atmosphere and are further discussed when we consider acid rain.^{1,2}

Ultrafine particles (UP), released into the air by motor vehicles, are so small that they cannot be easily filtered and can enter the bloodstream. Rich in organic compounds and other reactive chemicals, they may be the most hazardous components of air pollution, especially with respect to heart disease. They evidently can contribute to inflammation (cell and tissue damage by oxidation), reducing the protective quality of “good” cholesterol and leading to plaque buildup in the arteries that can result in heart attack and stroke. Those most at risk are the young, the elderly, and individuals living near a freeway, or exercising near heavy traffic, or spending a lot of time in traffic (sitting in slow-moving traffic can roughly triple your short-term risk of a heart attack). The risk to an individual is very small, but when millions of people are exposed to a small risk, large numbers are affected. The prudent approach is to limit your exposure. For example, avoid jogging or bike riding near heavy traffic for extended periods.³

Particulate matter is measured as *total suspended particulates* (TSPs). Values for TSPs tend to be much higher in large cities in developing countries, such as Mexico,

China, and India, than in developed countries, such as Japan and the United States.

Particulates affect human health, ecosystems, and the biosphere. In the United States, particulate air pollution is estimated to contribute to the death of 60,000 people annually.⁷ Studies estimate that 2 to 9% of human mortality in cities is associated with particulate pollution, and that the mortality risk is about 15 to 25% higher in cities with the highest levels of fine particulate pollution.⁸ Particulates are linked to both lung cancer and bronchitis (see Figure 21.4) and are especially hazardous to the elderly and to people who have respiratory problems, such as asthma. There is a direct relationship between particulate pollution and increased hospital admissions for respiratory distress.

Dust raised by road building and plowing not only makes breathing more difficult for animals (including humans) but also can be deposited on green plants, interfering with absorption of carbon dioxide and oxygen and release of water (transpiration). On a larger scale, particulates associated with large construction projects—such as housing developments, shopping centers, and industrial parks—may injure or kill plants and animals and damage surrounding areas, changing species composition, altering food chains, and thereby affecting ecosystems. The terrorist attacks that destroyed the Twin Towers in New York City on September 11, 2001, sent huge amounts of particles of all sizes into the air, causing serious health problems that continue even today in people who were exposed to it.

Modern industrial processes have greatly increased the total amount of suspended particulates in Earth's atmosphere. These particulates block sunlight and can cause **global dimming**, a gradual reduction in the solar

energy that reaches Earth's surface. Global dimming cools the atmosphere and has lessened the global warming that has been predicted. Its effects are most apparent in the midlatitudes of the Northern Hemisphere, especially over urban regions or where jet air traffic is more common. Jet plane exhaust emits particulates high in the atmosphere. That this could affect the climate was suggested in 2001, when civil air traffic was shut down for two days after the September 11 attacks in New York. During those two days, the daily temperature range over the United States was about 1°C higher than usual.⁹ Of course, this may have been just a coincidence.

Table 21.2 shows that anthropogenic emissions of PM₁₀ in the United States from 1970 to 2007 declined by about two-thirds (66%).

Lead

Lead (a heavy metal) is an important constituent of automobile batteries and many other industrial products. Leaded gasoline (still used in some countries) helps protect engines and promotes more effective fuel consumption. However, the lead is emitted into the air with the exhaust and has thereby been spread widely around the world, reaching high levels in soils and waters along roadways. Once released, lead can be transported through the air as particulates to be taken up by plants through the soil or deposited directly on their leaves. Thus, it enters terrestrial food chains. When lead is carried by streams and rivers, deposited in quiet waters, or transported to oceans or lakes, it is taken up by aquatic organisms and enters aquatic food chains. Lead is toxic to wildlife and people. It can damage the nervous system, impair learning, and reduce IQ and memory. In children it can also contribute to behavioral problems. (Recall that this is the subject of the Critical Thinking section in Chapter 10.) In adults it can contribute to cardiovascular and kidney disease, as well as anemia.^{1, 2}

Lead reaches Greenland as airborne particulates and in seawater and is stored in glacial ice. The concentration of lead in Greenland glaciers was essentially zero in A.D. 800 and reached measurable levels with the beginning of the Industrial Revolution in the mid-18th century. The lead content of the glacial ice increased steadily from 1750 until about 1950, when there was a sudden upsurge in the rate of lead accumulation, reflecting rapid growth in the use of leaded gasoline. The accumulation of lead in Greenland's ice illustrates that our use of heavy metals in the 20th century reached the point of affecting the entire biosphere.

Lead has now been removed from nearly all gasoline in the United States, Canada, and much of Europe. In the United States, lead emissions have declined about 98% since the early 1980s (Table 21.2). The reduction and eventual elimination of lead in gasoline are a good start in reducing levels of anthropogenic lead in the biosphere.

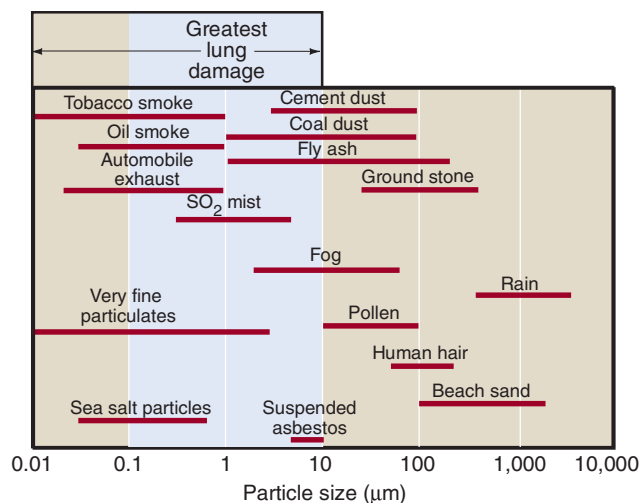


FIGURE 21.4 Sizes of selected particulates. The shaded area shows the size range that produces the greatest lung damage. (Source: Modified from Fig. 7–8, p. 244 in *Chemistry, Man and Environmental Change: An Integrated Approach*, by J. Calvin Giddings. Copyright © 1973 by J. Calvin Giddings. Reprinted by permission of Harper Collins Publishers, Inc.).

A CLOSER LOOK 21.1

Acid Rain

Acid rain is precipitation in which the pH is below 5.6. The pH, a measure of acidity and alkalinity, is the negative logarithm of the concentration of the hydrogen ion (H^+). Because the pH scale is logarithmic, a pH value of 3 is 10 times more acidic than a pH value of 4 and 100 times more acidic than a pH value of 5. Automobile battery acid has a pH value of 1. Many people are surprised to learn that all rainfall is slightly acidic; water reacts with atmospheric carbon dioxide to produce weak carbonic acid. Thus, pure rainfall has a pH of about 5.6, where 1 is highly acidic and 7 is neutral (see Figure 21.5). (Natural rainfall in tropical rain forests has been observed in some instances to have a pH of less than 5.6; this is probably related to acid precursors emitted by the trees.)

Acid rain includes both wet (rain, snow, fog) and dry (particulate) acidic depositions. The depositions occur near and downwind of areas where the burning of fossil fuels produces major emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x). Although these oxides are the primary contributors to acid rain, other acids are also involved. An

example is hydrochloric acid emitted from coal-fired power plants.

Acid rain has likely been a problem at least since the beginning of the Industrial Revolution. In recent decades, however, it has gained more and more attention, and today it is a major, global environmental problem affecting all industrial countries. In the United States, nearly all of the eastern states are affected, as well as West Coast urban centers, such as Seattle, San Francisco, and Los Angeles. The problem is also of great concern in Canada, Germany, Scandinavia, and Great Britain. Developing countries that rely heavily on coal, such as China, are facing serious acid rain problems as well.

Causes of Acid Rain

As we have said, sulfur dioxide and nitrogen oxides are the major contributors to acid rain. Amounts of these substances emitted into the environment in the United States are shown in Table 21.1. As shown earlier in Table 21.2, emissions of SO_2 peaked in the 1970s and declined to about 13 million metric tons per year by 2007; and nitrogen oxides leveled off at about 25 million metric tons per year in the mid-1980s and had dropped to 17 million metric tons by 2007.

In the atmosphere, reactions with oxygen and water vapor transform SO_2 NO_x into sulfuric and nitric acids, which may travel long distances with prevailing winds and be deposited as acid precipitation—rainfall, snow, or fog (Figure 21.6). Sulfate and nitrate particles may also be deposited directly on the surface of the land as dry deposition and later be activated by moisture to become sulfuric and nitric acids.

Again, sulfur dioxide is emitted primarily by stationary sources, such as power plants that burn fossil fuels, whereas nitrogen oxides are emitted by both stationary and mobile sources, such as automobiles. Approximately 80% of sulfur dioxide and 65% of nitrogen oxides in the United States come from states east of the Mississippi River.

Sensitivity to Acid Rain

Geology, climate, vegetation, and soil help determine the effects of acid rain, because these differ widely in their “buffers”—chemicals that can neutralize acids. Sensitive areas are those in which the type of bedrock (such as granite) or soils (such as those consisting largely of sand) cannot buffer acid input. Limestone bedrock provides the best buffering because it is made up mainly of calcium carbonate ($CaCO_3$), the mineral known as calcite. Calcium carbonate reacts with the hydrogen in the water and neutralizes the acid.

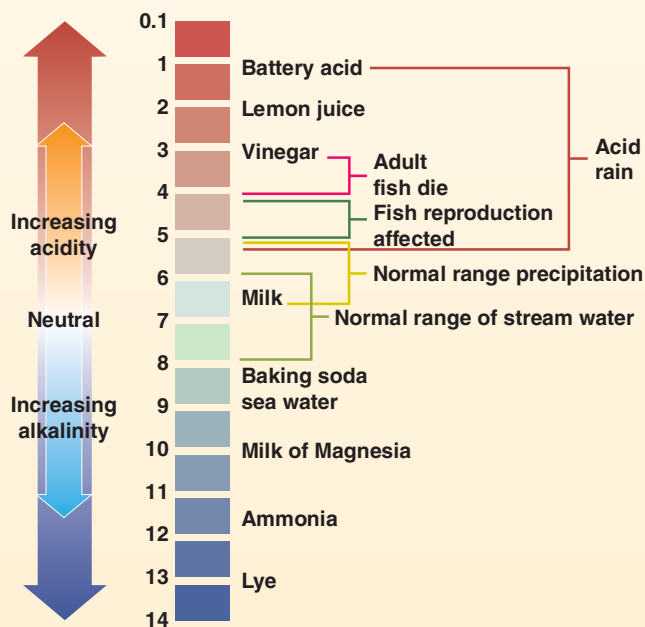


FIGURE 21.5 The pH scale shows the levels of acidity in various fluids. The scale ranges from less than 1 to 14, with 7 being neutral: pHs lower than 7 are acidic; pHs greater than 7 are alkaline (basic). Acid rain can be very acidic and harmful to the environment. (Source: <http://ga.water.usgs.gov/edu/phdiagram.html>. Accessed August 12, 2005.)

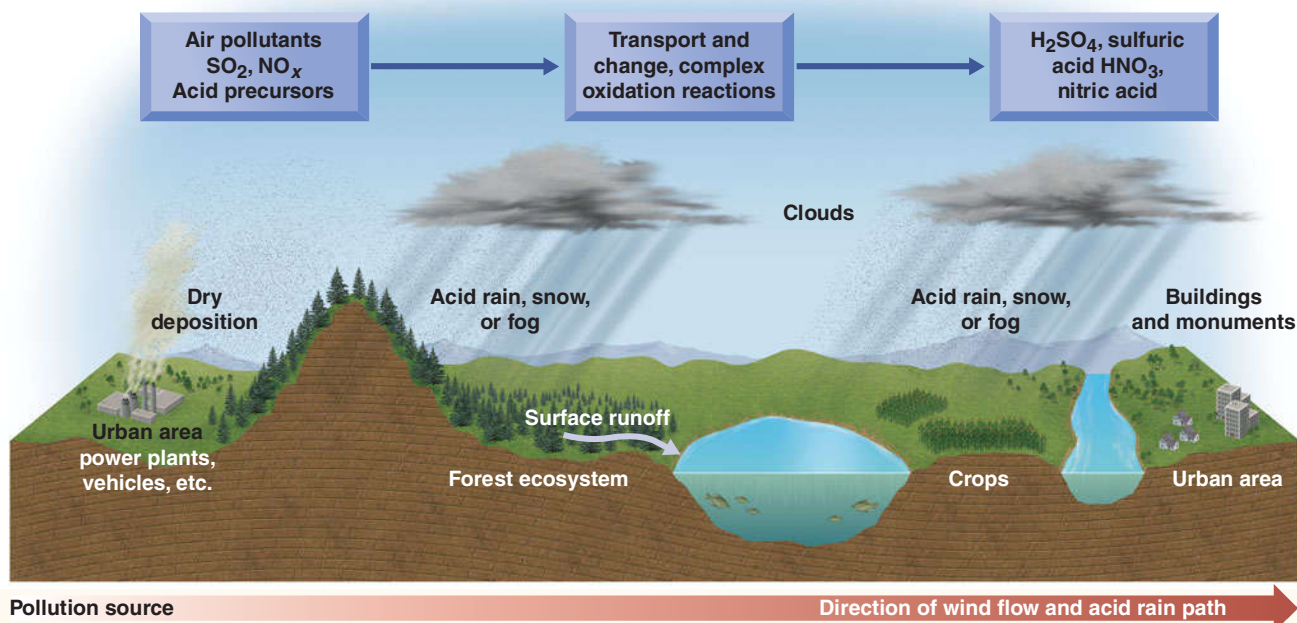


FIGURE 21.6 Idealized diagram showing selected aspects of acid rain formation and paths.

Soils may lose their fertility when exposed to acid rain, either because nutrients are leached out by acid water or because the acid in the soil releases elements that are toxic to plants.

Acid Rain's Effects on Forest Ecosystems

It has long been suspected that acid precipitation damages trees. Studies in Germany led scientists to cite acid rain and other air pollution as the cause of death for thousands of acres of evergreen trees in Bavaria. Similar studies in the Appalachian Mountains of Vermont (where many soils are naturally acidic) suggest that in some locations half the red spruce trees have died in recent years. Some high-elevation forests of the Appalachian Mountains, including the Great Smoky Mountains and Shenandoah National Park, have been impacted by acid rain, acid fog, and dry deposition of acid. Symptoms include slowed tree growth, leaves and needles that turn brown and fall off, and in extreme cases the death of trees. The acid rain does not directly kill trees; rather, it weakens them as essential nutrients are leached from soils or stripped from leaves by acid fog. Acidic rainfall also may release toxic chemicals, such as aluminum, that damage trees.¹⁰

Acid Rain's Effects on Lake Ecosystems

Records from Scandinavian lakes show an increase in acidity accompanied by a decrease in fish. The increased acidity has been traced to acid rain caused by industrial processes in other countries, particularly Germany and Great Britain. Thousands of lakes, ponds, and streams in the eastern United States are sensitive to acidification, including the Adirondacks and Catskill Mountains of New York State and others in the

Midwest and in the mountains of the Western U.S. Little Echo Pond in Franklin, New York, is one of the most acidic lakes, with a measured pH of 4.2.¹⁰

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. For example, crayfish produce fewer eggs in acidic water, and the eggs produced often grow into malformed larvae.

Second, acid rain dissolves chemical elements necessary for life in the lake. Once in solution, the necessary elements leave the lake with water outflow. Thus, elements that once cycled in the lake are lost. Without these nutrients, algae do not grow, animals that feed on the algae have little to eat, and animals that feed on these animals also have less food.^{10, 11}

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. Elevated concentrations of aluminum are particularly damaging to fish because the metal can clog the gills and cause suffocation. The heavy metals may pose health hazards to people, too, because the metals may become concentrated in fish and then be passed on to people, mammals, and birds that eat the fish. Drinking water from acidic lakes may also have high concentrations of toxic metals.

Not all lakes are vulnerable to acidification. Acid is neutralized in waters with a high carbonate content (in the form of the ion HCO_3^-). Therefore, lakes on limestone or other rocks rich in calcium or magnesium carbonates can readily buffer river and lake water against acids. Lakes with high

concentrations of such elements are called hard water lakes. Lakes on sand or igneous rocks, such as granite, tend to lack sufficient buffering to neutralize acids and are more susceptible to acidification.¹²

Acid Rain's Effects on Human Society

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. Classical buildings on the Acropolis in Athens and in other cities show considerable decay (chemical weathering) that accelerated in the 20th century as a result of air pollution. The problem has grown to such an extent that buildings require restoration, and the protective coatings on statues and other monuments must be replaced quite frequently, at a cost of billions of dollars a year. Particularly important statues in Greece and other areas have been removed and placed in protective glass containers, leaving replicas standing in their former outdoor locations for tourists to view.¹¹

Stone decays about twice as rapidly in cities as it does in less urban areas. The damage comes mainly from acid rain and humidity in the atmosphere, as well as from corrosive

groundwater.¹⁵ This implies that measuring rates of stone decay will tell us something about changes in the acidity of rain and groundwater in different regions and ages. It is now possible, where the ages of stone buildings and other structures are known, to determine whether the acid rain problem has changed over time.

Control of Acid Rain

We know what causes acid precipitation—the solution is what we are struggling with. One solution to lake acidification is rehabilitation by the periodic addition of lime, as has been done in New York State, Sweden, and Ontario. This solution is not satisfactory over a long period, however, because the continuing effort is expensive. A better approach is to target the components of acid rain, the emissions of sulfur dioxide and nitrogen oxides. As noted, sulfur dioxide emissions in the United States are down about 60% since 1970—a big improvement that is significantly reducing acid rain. Emissions were lowered by a market-based SO₂ cap-and-trade program of the U.S. Environmental Protection Agency's Acid Rain Program, by which utilities receive pollution allowances that they can trade or sell if they lower emissions from their power plants (see Chapter 7 for a discussion of cap and trade).¹⁴

Air Toxics

Toxic air pollutants, or **air toxics**, are among those pollutants known or suspected to cause cancer and other serious health problems after either long-term or short-term exposure. The most serious exposure to air toxics occurs in California and New York, with Oregon, Washington, DC, and New Jersey making up the rest of the top five. States with the cleanest air include Montana, Wyoming, and South Dakota.

Air toxics include gases, metals, and organic chemicals that are emitted in relatively small volumes. They cause respiratory, neurological, reproductive, or immune diseases, and some may be carcinogenic. A 2006 EPA report estimated that the average risk of cancer from exposure to air toxics is about 1 in 21,000. The assessment concluded that benzene poses the most significant risk for cancer, accounting for 25% of the average individual cancer risk from all air toxics. Again, the effect on an individual's health depends on a number of factors, including duration and frequency of exposure, toxicity of the chemical, concentration of the pollutant the individual is exposed to, and method of exposure, as well as an individual's general health.¹⁵

Among the more than 150 known toxic air pollutants are hydrogen sulfide, hydrogen fluoride, various chlorine gases, benzene, methanol, and ammonia. In 2006 the EPA released an assessment of the national health risk from air toxics. It focused on exposure from breathing

the pollutants; it did not address other ways people are exposed to them.

Standards and regulations established for more than 150 air toxics are expected to reduce annual emissions from 1990 levels. Even though vehicle miles will likely increase significantly by 2020, emissions of gaseous air toxics (such as benzene) from vehicles on highways are projected to decline about 80% from 1990 levels. Following are several examples of air toxics.

Hydrogen Sulfide

Hydrogen sulfide (H₂S) is a highly toxic corrosive gas, easily identified by its rotten-egg odor. Hydrogen sulfide is produced from natural sources, such as geysers, swamps, and bogs, and from human sources, such as petroleum refineries and metal smelters. The potential effects of hydrogen sulfide include functional damage to plants and health problems ranging from toxicity to death for humans and other animals.⁴

Hydrogen Fluoride

Hydrogen fluoride (HF) is a gas released by some industrial activities, such as aluminum production, coal gasification, and burning of coal in power plants. Hydrogen fluoride is extremely toxic; even a small concentration (as low as 1 ppb) may cause problems for plants and animals. It is potentially dangerous to grazing animals because some forage plants can become toxic when exposed to this gas.¹

Mercury

Mercury is a heavy metal released into the atmosphere by coal-burning power plants, other industrial processes, and mining. Natural processes—such as volcanic eruptions and evaporation from soil, wetlands, and oceans—also release mercury into the air. Its toxicity to people is well documented and includes neurological and development damage, as well as damage to the brain, liver, and kidneys. Mercury from the atmosphere may be deposited in rivers, ponds, lakes, and the ocean, where it accumulates through biomagnification and both wildlife and people are exposed to it.²

Volatile Organic Compounds

Volatile organic compounds (VOCs) include a variety of organic compounds. Some of these compounds are used as solvents in industrial processes, such as dry cleaning, degreasing, and graphic arts. Hydrocarbons (compounds of hydrogen and carbon) comprise one group of VOCs. Thousands of hydrocarbons exist, including natural gas, or methane (CH_4); butane (C_4H_{10}); and propane (C_3H_8). Analysis of urban air has identified many hydrocarbons, and their potential adverse effects are numerous. Some are toxic to plants and animals, and others may be converted to harmful compounds through complex chemical changes that occur in the atmosphere. Some react with sunlight to produce photochemical smog.

Globally, our activities produce only about 15% of hydrocarbon emissions. In the United States, however, nearly half the hydrocarbons entering the atmosphere are emitted from anthropogenic sources. The largest of these sources in the United States is automobiles. Anthropogenic sources are particularly abundant in urban regions. However, in some southeastern U.S. cities, such as Atlanta, Georgia, natural emissions (in Atlanta's case, apparently from trees) probably exceed those from automobiles and other human sources.³

Like emissions of sulfur dioxide and nitrogen oxide, VOCs peaked in the 1970s and have been reduced by 50% (Table 21.2) thanks to effective government-mandated emission controls for automobiles.

Methyl Isocyanate

Some chemicals are so toxic that extreme care must be taken to ensure they do not enter the environment. This was demonstrated on December 3, 1984, when a toxic liquid from a pesticide plant leaked, vaporized, and formed a deadly cloud of gas that settled over a 64 km² area of Bhopal, India. The gas leak lasted less than an hour; yet more than 2,000 people were killed and more than 15,000 injured. The colorless gas that resulted from the leak was methyl isocyanate ($\text{C}_2\text{H}_3\text{NO}$), which causes severe irritation (burns on contact) to eyes, nose, throat, and lungs. Breathing the gas in concentrations of only a few parts per million (ppm) causes violent coughing, swelling of the lungs, bleeding, and death. Less exposure can cause a variety of problems, including blindness.

Methyl isocyanate is an ingredient of a common pesticide known in the United States as Sevin, as well as two other insecticides used in India. An industrial plant in West Virginia also makes the chemical. Small leaks not leading to major accidents occurred there both before and after the catastrophe in Bhopal.

Clearly, chemicals that can cause widespread injury and death should not be stored near large population centers. In addition, chemical plants should have reliable accident-prevention equipment, as well as personnel trained to control and prevent problems.

Benzene

Benzene (C_6H_6) is a gasoline additive and an important industrial solvent. Generally, it is produced when carbon-rich materials, such as oil and gasoline, undergo incomplete combustion. It is also a component of cigarette smoke. Automobiles, trucks, airplanes, trains, and farm machinery are major sources of environmental benzene.¹⁵

Acrolein

Acrolein (CH_2CHCHO) is a volatile hydrocarbon that is extremely irritating to the eyes, nose, and respiratory system in general. It is produced by manufacturing processes that involve combustion of petroleum fuels and is a component of cigarette smoke.¹⁵

Variability of Air Pollution

Pollution problems vary greatly among the different regions of the world and even within just the United States. For example, as noted earlier, in the Los Angeles basin and many U.S. cities, nitrogen oxides and hydrocarbons are particularly troublesome because they combine in the presence of sunlight to form photochemical smog. Most of the nitrogen oxides and hydrocarbons are emitted from automobiles and other mobile sources. In other U.S. regions, such as Ohio and the Great Lakes region, air quality also suffers from emissions of sulfur dioxide and particulates from industry and from coal-burning power plants, which are point sources.

Air pollution also varies with the time of year. For example, smog is usually a problem in the summer, when there is a lot of sunlight. Particulates are a problem in dry months, when wildfires are likely, and during months when the wind blows across the desert. For example, drought and heat in August of 2010 resulted in wildfires in Russia that produced a thick hazardous smoke and resulting very poor air quality in Moscow. The combination of heat and air pollution at the height of the pollution event killed about 700 people per day in Moscow.

Pollution from particulates is a problem in arid regions, where there is little vegetation and the wind easily picks up and transports fine dust. Las Vegas, Nevada, the fastest-growing urban area in the United States in the 1990s,

now has some of the most polluted air in the southwestern United States. The brown haze over Las Vegas is due mostly to the nearly 80,000 metric tons of PM_{10} that enter the air in that region from the desert environment. About 60% of the dust comes from new construction sites, dirt roads, and vacant land. The rest is natural windblown dust. Las Vegas also has a carbon monoxide problem from vehicles, but it is the particulates that are causing concern, possibly leading to future EPA sanctions and growth restrictions.

Haze from Afar

Air pollution has become global and is not limited to urban areas. One example of this is Alaska's North Slope, a vast strip of land approximately 200 km (125 mi) wide that many consider to be one of the few unspoiled wilderness areas left on Earth. It seems logical to assume that air quality in the Arctic environments of Alaska would be pristine, except perhaps near areas where petroleum is being vigorously developed. However, ongoing studies suggest that the North Slope has an air-pollution problem that originates in Eastern Europe and Eurasia.

It is suspected that pollutants from burning fossil fuels in Eurasia are transported via the jet stream, at speeds that may exceed 400 km/hr (250 mi/hr), northeast over the North Pole to the North Slope of Alaska. There, they slow, stagnate, and produce a reddish-brown air mass known as "Arctic haze." The concentrations of air pollutants, including oxides of sulfur and nitrogen, are comparable to those of some eastern U.S. cities, such as Boston. Air quality problems in remote areas, such as Alaska, have significance as we try to understand air pollution at the global level.¹⁶

A curious global event occurred in the spring of 2001 when a white haze consisting of dust from Mongolia and industrial particulate pollutants arrived in North America. The haze affected one-fourth of the United States and could be seen from Canada to Mexico. In the United States, pollution levels from the haze alone were as high as two-thirds of federal health limits and caused respiratory problems. The haze demonstrates that pollution from Asia is carried by winds across the Pacific Ocean. Today we know from satellite observation that air pollutants transported by winds from East Asia to North America account for about 15% of the total pollutants originating from the United States and Canada.¹⁷

Urban Air Pollution: Chemical and Atmospheric Processes

Now that we have introduced and discussed the various types of air pollutants. This preparation allows for a more detailed discussion of the processes and chemistry of urban **smog**.

There are two major types of urban smog: photochemical smog, sometimes called L.A.-type smog or brown air; and sulfurous smog, sometimes referred to as London-type smog, gray air, or industrial smog. **Sulfurous smog** is produced primarily by the burning of coal or oil at large power plants. Sulfur oxides and particulates combine under certain conditions to produce a concentrated sulfurous smog. **Photochemical smog** is directly related to automobile use.

Figure 21.7 shows a characteristic pattern in the way nitrogen oxides, hydrocarbons, and oxidants (mostly ozone) vary during a typically smoggy day in Southern California. Early in the morning, when commuter traffic begins to build up, concentrations of nitrogen oxide (NO) and hydrocarbons begin to increase. At the same time, nitrogen dioxide (NO_2) may decrease because sunlight breaks it down to produce NO plus atomic oxygen ($\text{NO} + \text{O}$). The atomic oxygen (O) is then free to combine with molecular oxygen (O_2) to form ozone (O_3). As a result, the concentration of ozone also increases after sunrise. Shortly thereafter, oxidized hydrocarbons react with NO to increase the concentration of NO_2 by mid-morning. This causes the NO concentration to decrease and allows ozone to build up, producing a midday peak in ozone and a minimum in NO. As the smog develops, visibility may be greatly reduced as light is scattered by the pollutants. Figure 21.8 shows Los Angeles on a clear day, in sharp contrast to the way the city looks on a smoggy day.

What are the chances that a deadly smog will occur somewhere in the world? Unfortunately, the answer is all too good, given the amount of air pollution in some large cities. Beijing, for example, might be a candidate; the city uses an immense amount of coal, and coughing is so pervasive that residents often refer to it as the "Beijing cough." Another likely candidate is Mexico City, which has one of the worst air-pollution problems anywhere in the world today.

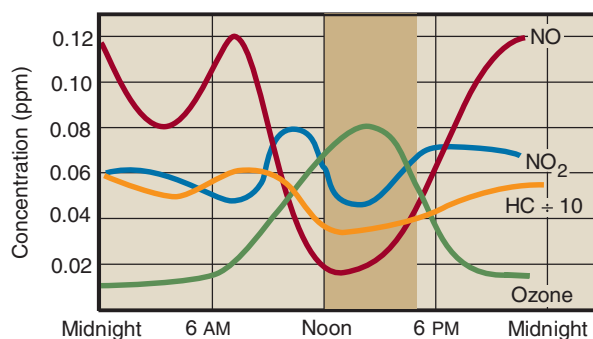


FIGURE 21.7 Development of photochemical smog over the Los Angeles area on a typical warm day.