Submicron lead particles, which are formed by volatilization and subsequent condensation, attach to larger particles or they form nuclei before they are removed from the atmosphere. Once they have attained a size of several microns, they either settle out or are washed out by rain.

Nitrogen Dioxide

Bacterial action in the soil releases nitrous oxide (N_2O) to the atmosphere. In the upper troposphere and stratosphere, atomic oxygen reacts with the nitrous oxide to form nitric oxide (NO).

$$N_2O + O \rightarrow 2NO \qquad (6\text{-}10)$$

The atomic oxygen results from the dissociation of ozone. The nitric oxide further reacts with ozone to form nitrogen dioxide (NO_2).

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (6\text{-}11)$$

The global formation of NO_2 by this process is estimated to be 0.45 Pg annually.[21]

Combustion processes account for 96 percent of the anthropogenic sources of nitrogen oxides. Although nitrogen and oxygen coexist in our atmosphere without reaction, their relationship is much less indifferent at high temperatures and pressures. At temperatures in excess of 1,600 K, they react.

$$N_2 + O_2 \overset{\Delta}{\rightleftharpoons} 2NO \qquad (6\text{-}12)$$

If the combustion gas is rapidly cooled after the reaction by exhausting it to the atmosphere, the reaction is quenched and NO is the byproduct. The NO in turn reacts with ozone or oxygen to form NO_2. The anthropogenic contribution to global emissions of NO_2 by this route amounted to 0.48 Tg in 1965.[22]

Ultimately, the NO_2 is converted to either NO_2^- or NO_3^- in particulate form. The particulates are then washed out by precipitation. The dissolution of nitrate in a water droplet allows for the formation of nitric acid (HNO_3). This, in part, accounts for "acid" rain found downwind of industrialized areas.

Photochemical Oxidants

Unlike the other pollutants, the photochemical oxidants result entirely from atmospheric reactions and are not directly attributable to either people or nature. Thus, they are called *secondary pollutants.* They are formed through a series of reactions that are initiated by the absorption of a photon by an atom, molecule, free radical, or ion. Ozone is the principal photochemical oxidant. Its formation is usually attributed to the nitrogen dioxide photolytic cycle. Hydrocarbons modify this cycle by reacting with atomic oxygen to form free radicals (highly reactive organic species). The

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[21] John H. Seinfeld, *Air Pollution, Physical and Chemical Fundamentals,* p. 73.

[22] John H. Seinfeld, *Air Pollution, Physical and Chemical Fundamentals,* p. 73.

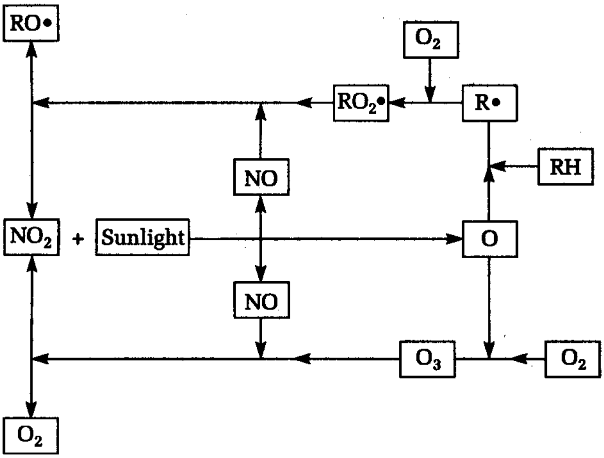

FIGURE 6-6
Interaction of hydrocarbons with atmospheric nitrogen oxide photolytic cycle. [*Source: Air Quality Criteria for Photochemical Oxidants* (U.S. Department of Health, Education and Welfare, National Air Pollution Control Administration Publication No. AP-63), Washington, DC: U.S. Government Printing Office, 1970.]

hydrocarbons, nitrogen oxides, and ozone react and interact to produce more nitrogen dioxide and ozone. This cycle is represented in summary form in Figure 6-6. The whole reaction sequence depends on an abundance of sunshine. A result of these reactions is the photochemical "smog" for which Los Angeles is famous.

Sulfur Oxides

Sulfur oxides may be both primary and secondary pollutants. Power plants, industry, volcanoes, and the oceans emit SO_2, SO_3, and SO_4^{2-} directly as primary pollutants. In addition, biological decay processes and some industrial sources emit H_2S, which is oxidized to form the secondary pollutant SO_2. In terms of sulfur, approximately 0.125 Pg are emitted annually by natural sources. Approximately 45 Tg of sulfur may be attributed to anthropogenic sources each year.[23]

The most important oxidizing reaction for H_2S appears to be one involving ozone:

$$H_2S + O_3 \rightarrow H_2O + SO_2 \qquad (6\text{-}13)$$

The combustion of fossil fuels containing sulfur yields sulfur dioxide in direct proportion to the sulfur content of the fuel:

$$S + O_2 \rightarrow SO_2 \qquad (6\text{-}14)$$

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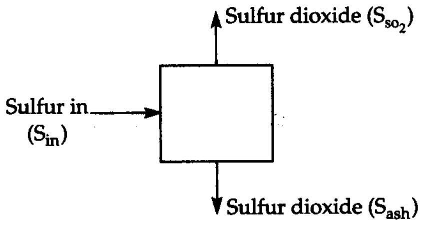
[23] John H. Seinfeld, *Air Pollution, Physical and Chemical Fundamentals,* p. 57.

This reaction implies that for every gram of sulfur in the fuel, two grams of SO_2 are emitted to the atmosphere. Because the combustion process is not 100 percent efficient, we generally assume that 5 percent of the sulfur in the fuel ends up in the ash, that is, 1.90 g SO_2 per gram of sulfur in the fuel is emitted.

Example 6-2. An Illinois coal is burned at a rate of 1.00 kg per second. If the analysis of the coal reveals a sulfur content of 3.00 percent, what is the annual rate of emission of SO_2?

Solution. Using the mass-balance approach, we begin by drawing a mass-balance diagram:



The mass balance equation may be written as

$$S_{in} = S_{ash} + S_{SO_2}$$

From the problem data, the mass of "sulfur in" is

$$S_{in} = 1.00 \text{ kg/s} \times 0.030 = 0.030 \text{ kg/s}$$

In one year,

$$S_{in} = 0.030 \text{ kg/s} \times 86{,}400 \text{ s/d} \times 365 \text{ d/y} = 9.46 \times 10^5 \text{ kg/y}$$

The sulfur in the ash is 5 percent of the input sulfur:

$$S_{ash} = (0.05)(9.46 \times 10^5 \text{ kg/y}) = 4.73 \times 10^4 \text{ kg/y}$$

The amount of sulfur available for conversion to SO_2:

$$S_{SO_2} = S_{in} - S_{ash} = 9.46 \times 10^5 - 4.73 \times 10^4 = 8.99 \times 10^5 \text{ kg/y}$$

The amount of sulfur formed is determined from the proportional weights of the oxidation reaction (Equation 6-14):

$$S + O_2 \rightarrow SO_2$$

$$\text{GMW} = 32 + 32 = 64$$

The amount of sulfur dioxide formed is then 64/32 of the sulfur available for conversion:

$$S_{SO_2} = \frac{64}{32}(8.99 \times 10^5 \text{ kg/y}) = 1.80 \times 10^6 \text{ kg/y}$$

Particle mass distributions in urban atmospheres generally exhibit two maxima. One is between 0.1 and 1 μm in diameter. The other is between 1 and 30 μm. The smaller fraction is the result of condensation. The coarse fraction consists of fly ash and dust generated by mechanical abrasion.

Small particles are removed from the atmosphere by accretion to water droplets, which grow in size until they are large enough to precipitate. Larger particles are removed by direct washout by falling raindrops.

6-6 MICRO AND MACRO AIR POLLUTION

Air pollution problems may occur on three scales: micro, meso, and macro. Micro-scale problems range from those covering less than a centimeter to those the size of a house or slightly larger. Meso-scale air pollution problems are those of a few hectares up to the size of a city or county. Macro-scale problems extend from counties to states, nations, and in the broadest sense, the globe. Much of the remaining discussion in this chapter is focused on the meso-scale problem. In this section we will address the general micro-scale and macro-scale problems recognized today.

Indoor Air Pollution

People who live in cold climates may spend from 70 to 90 percent of their time indoors. In the last two decades, researchers have become interested in identifying sources, concentrations, and impacts of air pollutants that arise in conventional domestic residences. The startling results indicate that, in certain instances, indoor air may be substantially more polluted than the outdoor air.

Carbon monoxide from improperly operating furnaces has long been a serious concern. In numerous instances, people have died from furnace malfunction. More recently, chronic low levels of CO pollution have been recognized. Gas ranges, ovens, pilot lights, gas and kerosene space heaters, and cigarette smoke all contribute (Table 6-3). Although little or no effort has been exerted to reduce or eliminate the danger from ranges, ovens, etc., the public has come to expect that the recreational habits of smokers should not interfere with the quality of the air others breathe. The results of a general ban on cigarette smoking in one office are shown in Table 6-4. Smokers were allowed to smoke only in the designated lounge area. Period 1 was prior to the implementation of the new policy. It is obvious that the new policy had a positive effect outside of the lounge.

Nitrogen oxide sources are also shown in Table 6-3. NO_2 levels have been found to range from 70 $\mu g/m^3$ in air-conditioned houses with electric ranges to 182 $\mu g/m^3$ in non-air-conditioned houses with gas stoves.[27] The latter value is quite high in comparison to the national ambient air quality limits. SO_2 levels were found to be very low in all houses investigated. On the other hand, respirable particulate

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[27] R. Hosein, *et al.*, "The Relationship Between Pollutant Levels in Homes and Potential Sources," *Transactions, Indoor Air Quality in Cold Climates, Hazards and Abatement Measures,* Pittsburgh: Air Pollution Control Association, pp. 250–260, April 1985.

TABLE 6-3
Tested combustion sources and their emission rates

Source	Range of emission rates,[a] mg/MJ				
	NO	NO_2	NO_x (as NO_2)	CO	SO_2
Range-Top Burner[b]	15–17	9–12	32–37	40–244	—[c]
Range Oven[d]	14–29	7–13	34–53	12–19	—
Pilot Light[e]	4–17	8–12	[f]	40–67	—
Gas Space Heaters[g]	0–15	1–15	1–37	14–64	—
Gas Dryer[h]	8	8	20	69	—
Kerosene Space Heaters[i]	1–13	3–10	5–31	35–64	11–12
Cigarette Smoke[j]	2.78[j]	0.73[j]	[f]	88.43[j]	—

[a] The lowest and highest mean values of emission rates for combustion sources tested in milligrams per mega-Joule (mg/MJ). Note: it takes 4.186 Joules to raise the temperature of 1.0 g of water from 14.5° C to 15.5° C at 100% efficiency.

[b] Three ranges were evaluated. Reported results are for blue flame condition.

[c] Dash (–) means combustion source is not emitting the pollutant.

[d] Three ranges were evaluated. Ovens were operated for several different settings (bake, broil, self-clean cycle, etc.).

[e] One range was evaluated with all three pilot lights, two top pilots, and a bottom pilot.

[f] Emission rates not reported.

[g] Three space heaters including one convective, radiant, and catalytic were tested.

[h] One gas dryer was evaluated.

[i] Two kerosene heaters including a convective and radiant type were tested.

[j] One type of cigarette. Reported emission rates are in mg/cigarette (800 mg tobacco/cigarette).

[*Source:* D. J. Moschandreas, *et al., Characterization of Emissions from Indoor Combustion Sources,* (Gas Research Institute Report No. 85/0075), Chicago, IL, May 1985.]

TABLE 6-4
Mean respirable particulates (RSP), CO and CO_2 levels measured on the test floor

	RSP ($\mu g/m^3$)	CO (ppm)	CO_2 (ppm)
Period 1			
Floor	26	1.67	624
Lounge	51	1.98	642
Period 2			
Floor	18	1.09	569
Lounge	189	2.40	650

Source: H. K. Lee, *et al.,* "Impact of a New Smoking Policy on Office Air Quality," *Transactions of the Air Pollution Control Association:* Pittsburgh, PA. *Indoor Air Quality in Cold Climates,* April 1985.

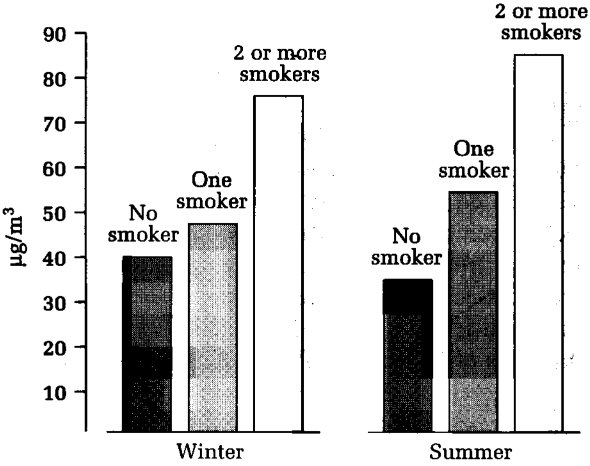

FIGURE 6-7
Respirable suspended particulate levels as a function of smoking. (*Source:* R. Hosein, *et al.*, "The Relationship Between Pollutant Levels in Homes and Potential Sources," *Transactions, Indoor Air Quality in Cold Climates, Hazards and Abatement Measures,* Pittsburgh: Air Pollution Control Association, pp. 250–260, April, 1985.)

matter (RSP) was found to increase with one smoker and to rise dramatically with two (Figure 6-7).

Radon is not regulated as an ambient air pollutant but has been found in dwellings at alarmingly high concentrations. We will address the radon issue in depth in Chapter 10. Suffice it to say at this juncture that radon is a radioactive gas that emanates from natural geologic formations and, in some cases, from construction materials. It is not generated from the activities of the householder as the pollutants discussed above.

Over 300 *volatile organic compounds* (VOCs) have been identified in indoor air. Aldehydes, alkanes, alkenes, ethers, ketones, and polynuclear aromatic hydrocarbons (PAHs) are among them. Although they are not all present all the time, frequently there are several present at the same time. Formaldehyde (CH_2O) has been singled out as one of the more prevalent, as well as one of the more toxic, compounds.[28]

Formaldehyde may not be generated directly by the activity of the homeowner. It is emitted by a variety of consumer products and construction materials including pressed wood products, insulation materials (urea-formaldehyde foam insulation in trailers has been particularly suspect), textiles, and combustion sources. In one study, CH_2O concentrations ranged from 0.0455 ppm to 0.19 ppm.[29] Some mobile homes in Wisconsin had concentrations as high as 0.65 ppm. (For comparison, the American Society of Heating, Refrigeration and Air Conditioning Engineers (ASHRAE) set a guideline concentration of 0.1 ppm.)

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[28] A. L. Hines, *et al., Indoor Air Quality & Control,* Upper Saddle River, NJ: PTR Prentice Hall, p. 21, 1993.

[29] R. S. Dumont, "The Effect of Mechanical Ventilation on Rn, NO_2, and CH_2O Concentrations in Low-Leakage Houses and a Simple Remedial Measure for Reducing Rn Concentration," *Transactions, Indoor Air Quality in Cold Climates, Hazards and Abatement Measures,* Pittsburgh, PA: Air Pollution Control Association, pp. 90–104, April 1985.

Unlike the other air pollution sources that continue to emit as long as there is anthropogenic activity (or in the case of radon, for geologic time), CH_2O is not regenerated unless new materials are brought into the residence. If the house is ventilated over a period of time, the concentration will drop.

The primary source of heavy metals indoors is from infiltration of outdoor air and soil and dust that is tracked into the building. Arsenic, cadmium, chromium, mercury, lead, and nickel have been measured in indoor air. Lead and mercury may be generated from indoor sources such as paint. Old lead paint is a source of particulate lead as it is abraded or during removal. Mercury vapor is emitted from latex-based paints that contain diphenyl mercury dodecenyl succinate to prevent fungus growth.

Indoor tobacco smoking is of particular concern because of the increasing evidence of the carcinogenic properties of the smoke. While *mainstream smoking* (taking a puff) exposes the smoker to large quantities of toxic compounds, the smoldering cigarette in the ashtray (*sidestream smoke*) also adds a considerable burden to the room environment. Table 6-5 illustrates the emission rates of mainstream and sidestream smoke from a cigarette.

TABLE 6-5
Emission of chemicals from mainstream and sidestream smoke

Chemicals	Mainstream (μg/cigarette)	Sidestream (μg/cigarette)
Gas and Vapor Phase		
Carbon monoxide	1000–20,000	25,000–50,000
Carbon dioxide	20,000–60,000	160,000–480,000
Acetaldehyde	18–1400	40–3100
Hydrogen cyanide	430	110
Methyl chloride	650	1300
Acetone	100–600	250–1500
Ammonia	10–150	980–150,000
Pyridine	9–93	90–930
Acrolein	25–140	55–130
Nitric oxide	10–570	2300
Nitrogen dioxide	0.5–30	625
Formaldehyde	20–90	1300
Dimethylnitrosamine	10–65	520–3300
Nitrosopyrolidine	10–35	270–945
Particulates		
Total suspended particles	36,200	25,800
Nicotine	100–2500	2700–6750
Total phenols	228	603
Pyrene	50–200	180–420
Benzo (a) pyrene	20–40	68–136
Naphthalene	2.8	4.0
Methyl naphthalene	2.2	60
Aniline	0.36	16.8
Nitrosonornicotine	0.1–0.55	0.5–2.5

Source: A. L. Hines, et al., *Indoor Air Quality & Control,* Upper Saddle River, NJ: Prentice Hall, 1993. Reprinted by permission.

It is doubtful that there will be any regulatory effort to reduce the emissions of these pollutants in the near future. Thus the house or apartment dweller has little recourse other than to replace gas appliances, remove or cover formaldehyde sources, and put out the smokers.

Acid Rain

Unpolluted rain is naturally acidic because CO_2 from the atmosphere dissolves to a sufficient extent to form carbonic acid (see Section 3-1). The equilibrium pH for pure rainwater is about 5.6. Measurements taken over North America and Europe have revealed lower pH values. In some cases individual readings as low as 3.0 have been recorded. The average pH in rain weighted by the amount of precipitation over the United States and lower Canada in 1985 is shown in Figure 4-15.

Chemical reactions in the atmosphere convert SO_2, NO_x, and volatile organic compounds (VOCs) to acidic compounds and associated oxidants (Figure 6-8). The primary conversion of SO_2 in the eastern United States is through the aqueous phase reaction with hydrogen peroxide (H_2O_2) in clouds. Nitric acid is formed by the reaction of NO_2 with OH radicals formed photochemically. Ozone is formed and then protected by a series of reactions involving both NO_x and VOCs.

The concern about acid rain relates to potential effects of acidity on aquatic life, damage to crops and forests, and damage to building materials. Lower pH values may affect fish directly by interfering with reproductive cycles or by releasing otherwise insoluble aluminum, which is toxic. Dramatic dieback of trees in Central Europe has stimulated concern that similar results could occur in North America. It is hypothesized that the acid rain leaches calcium and magnesium from the soil (see Figure 3-12). This lowers the molar ratio of calcium to aluminum which, in turn, favors the uptake of aluminum by the fine roots, which ultimately leads to their deterioration.

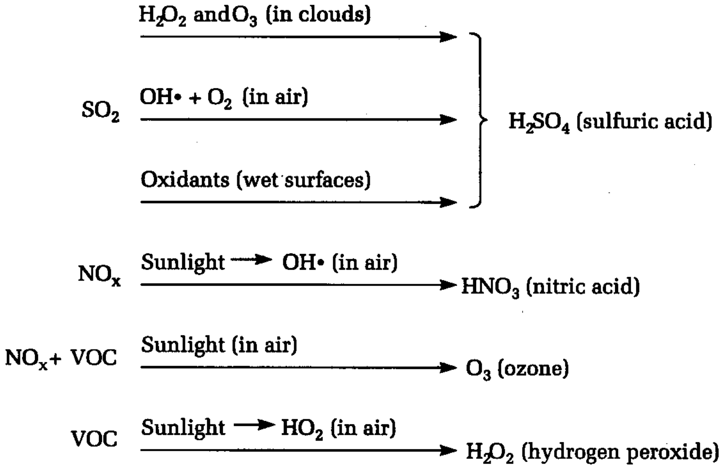

FIGURE 6-8
Acid rain precursors and products.

In 1980, Congress authorized a 10-year study to assess the causes and effects of acidic deposition. This study was titled the National Acid Precipitation Assessment Program (NAPAP). In September 1987, the NAPAP released an interim report that indicated that acidic precipitation appeared to have no measurable and consistent effect on crops, tree seedlings, or human health, and that a small percentage of lakes across the United States were experiencing pH values lower than 5.0.[30] On the other hand, oxidant damage was measurable. The NAPAP reported to Congress in 1992 that there remains no evidence of widespread decline of forest tree species caused by acidic deposition.[31] Eighty-one selected sites in the Northeast and Upper Midwest have been monitored for acidity since the early 1980s. Most of the lakes and streams experienced no measurable changes in acidity. Sulfate levels decreased while nitrate levels increased. The widespread decrease in sulfate concentration parallels the general decrease in national emissions of sulfur dioxide since 1980. However, acidic deposition has been firmly implicated as a causal factor in northeastern high-elevation red spruce decline. The effect is to reduce midwinter cold tolerance by 4° to 10°C. A major new finding was that some watersheds in regions receiving high nitrogen deposition are becoming nitrogen saturated, but there is no direct evidence of the source of the nitrate leaching from these watersheds.

While these conclusions appear to be reassuring, many uncertainties remain. These include questions about the distribution and type of natural and anthropogenic VOCs; relative importance of air pollutants versus natural stresses in causing the decline of forests above the cloud base; probability and percentage of lakes likely to become more acidic at present levels of air pollution emissions over the next few decades; importance of acidic episodes on fish populations; and possible long-term health effects of acidic aerosols.

Approximately 70 percent of the SO_2 emissions in the United States are attributable to electric utilities. In order to decrease the SO_2 emissions, the Congress developed a two-phase control program under Title IV of the 1990 Clean Air Act Amendments. Phase I sets emission allowances for 110 of the largest emitters in the Eastern half of the U.S. Phase II will include smaller utilities. The utilities may buy or sell allowances. Each allowance is equal to about 1 Mg of SO_2 emissions. If a company does not expend its maximum allowance, it may sell it to another company. This program is called a *market-based system.* As a result of this program utility emissions have decreased by 9 million Mg. In May 1993 NAPAP reported a 10 percent decrease in SO_2, a 6 percent decrease in NO_x, and a 17 percent decrease in VOC emissions.

Ozone Depletion

Without ozone, every living thing on the earth's surface would be incinerated. (On the other hand, as we have already noted, ozone can be lethal.) The presence of ozone

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[30] A. S. Lefohn and S. V. Krupa, "Conference Overview," *Acidic Precipitation, A Technical Amplification of NAPAP's Findings,* Proceedings of an APCA International Conference, Pittsburgh, PA, p. 1, January 1988.

[31] National Acid Precipitation Assessment Program, 1992 Report to Congress, pp. 5–6.

in the upper atmosphere (20 to 40 km and up) provides a barrier to ultraviolet (UV) radiation. The small amounts that do seep through provide you with your summer tan. Too much UV will cause skin cancer. Although oxygen also serves as a barrier to UV radiation, it absorbs only over a narrow band centered at a wavelength of 0.2 μm. The photochemistry of these reactions is shown in Figure 6-9. The M refers to any third body (usually N_2).

In 1974, Molina and Rowland revealed a potential air pollution threat to this protective ozone shield.[32] They hypothesized that chlorofluorocarbons (CF_2Cl_2 and $CFCl_3$—often abbreviated as CFC), which are used as aerosol propellants and refrigerants, react with ozone (Figure 6-10). The frightening aspects of this series of reactions are that the chlorine atom removes ozone from the system, and that the chlorine atom is continually recycled to convert more ozone to oxygen. It has been estimated

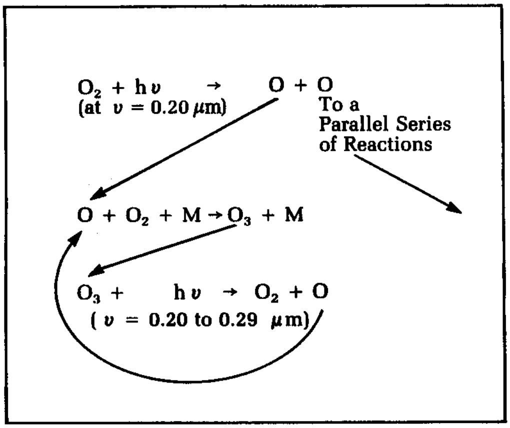

FIGURE 6-9
Photoreactions of ozone.

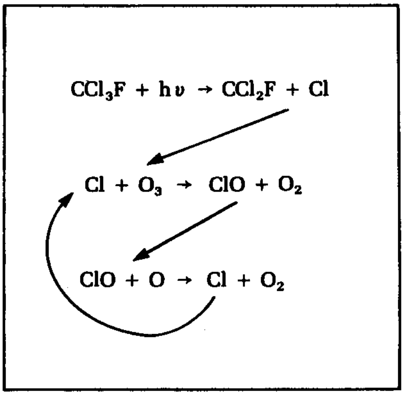

FIGURE 6-10
Ozone destruction by chlorofluoromethane.

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[32] M. J. Molina and F. S. Rowland, "Stratospheric Sink for Chlorofluoromethanes: Chlorine Atom Catalysed Destruction of Ozone," *Nature*, vol. 248, pp. 810–812, 1974.

that a 5 percent reduction in ozone could result in nearly a 10 percent increase in skin cancer.[33] Thus, CFCs that are rather inert compounds in the lower atmosphere become a serious air pollution problem at higher elevations.

By 1987, the evidence that CFCs destroy ozone in the stratosphere above Antarctica every spring had become irrefutable. In 1987, the ozone hole was larger than ever. More than half of the total ozone column was wiped out and essentially all ozone disappeared from some regions of the stratosphere.

Research confirmed that the ozone layer, on a worldwide basis, shrunk approximately 2.5 percent in the preceding decade.[34] Initially, it was believed that this phenomenon was peculiar to the geography and climatology of Antarctica and that the warmer northern hemisphere was strongly protected from the processes that lead to massive ozone losses. Studies of the North Pole stratosphere in the winter of 1989 revealed that this is not the case.[35]

In September 1987, the Montreal Protocol on Substances That Deplete the Ozone Layer was developed. The Protocol, which has been ratified by 36 countries and became effective in January 1989, proposed that CFC production first be frozen and then reduced 50 percent by 1998. Yet, under the terms of the Protocol, the chlorine content of the atmosphere would continue to grow because the fully halogenated CFCs have such long lifetimes in the atmosphere. CF_2Cl_2, for example, has a lifetime of 110 years.[36] Eighty countries met at Helsinki, Finland, in the spring of 1989 to assess new information. The delegates gave their unanimous assent to a five-point "Helsinki Declaration":

1. All join the 1985 Vienna Convention for the Protection of the Ozone Layer and the follow-up Montreal Protocol.
2. Phase out production and consumption of ozone-depleting CFCs no later than 2000.
3. Phase out production and consumption as soon as feasible of halons and such chemicals as carbon tetrachloride and methyl chloroform that also contribute to ozone depletion.
4. Commit themselves to accelerated development of environmentally acceptable alternative chemicals and technologies.
5. Make relevant scientific information, research results, and training available to developing countries.[37]

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[33] Interdepartmental Committee for Atmospheric Sciences, *The Possible Impact of Fluorocarbons and Hydrocarbons on Ozone* (Federal Council for Science and Technology, National Science Foundation Publication No. ICAS 18a-FY 75), Washington, DC: U.S. Government Printing Office, p. 3, May 1975.

[34] P. S. Zurer, "Studies on Ozone Destruction Expand Beyond Antarctic," *C&E News,* pp. 18–25, May 30, 1988.

[35] P. S. Zurer, "Scientists Find Arctic May Face Ozone Hole," *C&E News,* p. 5, February 27, 1989.

[36] M. Reisch and P. S. Zurer, "CFC Production: DuPont Seeks Total Phaseout," *C&E News,* p. 4, April 4, 1988.

[37] D. A. Sullivan, "International Gathering Plans Ways to Safeguard Atmospheric Ozone," *C&E News,* pp. 33–36, June 26, 1989.

The Montreal Protocol was strengthened in 1990 and 1992. The current terms of the treaty ban production of CFCs, carbon tetrachloride, and methyl chloroform as of January 1996. A ban on halon production took effect in January 1995.[38]

A number of alternatives to the fully chlorinated and, hence, more destructive CFCs have been developed. The two groups of compounds that emerged as significant replacements for the CFCs are hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). In contrast to the CFCs, HFCs and HCFCs contain one or more C-H bonds. This makes them susceptible to attack by OH radicals in the lower atmosphere. Because HFCs do not contain chlorine, they do not have the ozone depletion potential associated with the chlorine cycle shown in Figure 6-10. Although HCFCs contain chlorine, this chlorine is not transported to the stratosphere because OH scavenging in the troposphere is relatively efficient.

The implementation of the Montreal Protocol appears to be working. Worldwide CFC production has dropped by more than 50 percent since 1986. In 1993 alone, it dropped 15 percent.[37] Buildup of CFCs and halons has slowed, and the levels of methyl chloroform have been declining since 1991.[39,40] Because the HCFCs contribute to ozone depletion, albeit at a lower level than CFCs, it is anticipated that the peak chlorine levels will continue to rise until the year 2006 if chemical firms make use of their full allocation of HCFCs.[41]

The picture of the future development or retreat of the ozone hole is blurred by both the weather and volcanic eruptions. A very cold spring and strong winds forming a polar vortex that prevents replenishment of ozone-rich air will result in development of a large ozone hole in the Northern Hemisphere. The eruption of Mount Pinatubo in 1991 contributed sulfuric acid aerosols that cause ozone depletion that adds to the effect of anthropogenic contributions.

Greenhouse Effect

Unlike ozone, carbon dioxide is relatively transparent to shortwave ultraviolet light from the sun. It does, however, absorb and emit longwave radiation at wavelengths typical of the earth and atmosphere. Hence, CO_2 acts much like the glass on a greenhouse: It lets in shortwave radiation from the sun that heats the ground surface, but it restricts the loss of heat by radiation from the ground surface. The more CO_2 in the atmosphere, the more effective it is in restricting the outflow of radiative energy.

Since the first systematic measurements were made at Mauna Loa in Hawaii in 1958, CO_2 levels have risen from 315 ppm to 350 ppm. From analysis of air trapped in ice cores in Greenland and Antarctica, we know that preindustrial levels were about 280 ppm. The ice core records indicate that, over the last 160,000 years, no

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[38] P. Zurer, "Scientists Expect Ozone Loss to Peak about 1998," *C&E News,* p. 5, September 12, 1994.

[39] A. Newman, "CFC Phase-out Moving Quickly," *Environmental Science & Technology,* 28, p. 35A, 1994.

[40] P. Zurer, "Global Monitoring Shows Ozone Treaty Is Working," *C&E News,* pp. 7–8, July 17, 1995.

[41] J. Rose, "HCFCs May Slow Ozone Layer Recovery," *Environmental Science & Technology,* 28, p. 111A, 1994.

fluctuations of CO_2 have been larger than 70 ppm.[42] Other gases have now been recognized as contributing to the greenhouse effect. Methane (CH_4), nitrous oxide (N_2O), and CFCs are similar to CO_2 in their radiative behavior. Even though their concentrations are much lower than CO_2, these gases are now estimated to trap about 60 percent as much longwave radiation as CO_2. In recent studies, a drop-off in the rate of methane accumulation has occurred. In 1989–90, atmospheric methane was increasing at a rate of about 10 or 11 parts per billion (ppb) per year. An abrupt decrease to about 2 ppb per year occurred in 1992. This decrease has been attributed to a reduction in natural gas leaks such as those from pipelines.[43]

The bulk of the carbon dioxide that has been added to the atmosphere has been attributed to the combustion of fossil fuel. In the 1980s, massive deforestation has been identified as a possible contribution. Both the burning of timber and the release of carbon from bacterial degradation contribute. Perhaps more important, deforestation removes a mechanism for removing CO_2 from the atmosphere (commonly referred to as a *sink*). In normal respiration, green plants utilize CO_2 much as we use oxygen. This CO_2 is fixed in the biomass by photosynthetic processes. A rapidly growing rain forest can fix between 1 and 2 kg per year of carbon per square meter of ground surface. Cultivated fields, in contrast, fix only about 0.2 to 0.4 kg/m^2—and this amount is recycled by bioconsumption and conversion to CO_2.

Attempts to understand the consequences of global warming are based on mathematical models of the global circulation of the atmosphere and oceans. To date these models have a "good news–bad news" conclusion. Based on a 2° to 6°C rise in global temperature, the following good news is predicted for North America:[44]

1. A decrease in heating costs of up to 25 percent (partly offset by increased air-conditioning cost increases of 10 percent).
2. A longer growing season for crops.
3. Much easier navigation in the Arctic seas.

The bad news:

1. Drier crop conditions in the Midwest and Great Plains, requiring more irrigation.
2. Widespread melting of permanently frozen ground with adverse effects on building technology in Alaska and northern Canada.
3. A rise in sea level from 0.5 to 1.5 m that would result in an increase in the severity of flooding, damage to coastal structures, destruction of wetlands, and saltwater intrusion into drinking water supplies in coastal areas such as Florida.

There is still much speculation about the cause-effect relationship of increases in CO_2 and the possible outcomes. Although the data indicate increases in CO_2 concen-

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[42] B. Hileman, "Global Warming," *C&E News,* pp. 25–44, March 13, 1989.

[43] *C&E News,* p. 31, Feb. 28, 1994.

[44] F. K. Hare and T. C. Hutchinson, "Human Environmental Disturbances," *Environmental Science and Engineering,* J. G. Henry and G. W. Heinke, eds., Upper Saddle River, NJ: Prentice Hall, pp. 121–122, 1989.