CHAPTER 14

AIR POLLUTANTS AND GLOBAL CLIMATE

Humans and other living things can make major local and global changes in the earth. For example, as far as we know, all the free oxygen in the atmosphere was put there by green plants using Eq. (14.1),

$$nCO_2 + nH_2O + \text{light} \rightarrow (CH_2O)_n + nO_2 \tag{14.1}$$

All of the fossil fuels (coal, oil, natural gas) in the world were produced by living things. Human beings have produced deserts by grazing livestock in numbers greater than the normal rainfall would support: the livestock simply ate away the native plants. Much of the world's farmlands were originally forests that our remote ancestors cleared. Humans have produced areas of nearly sterile soil near industrial plants in the days before air pollution control; some of those areas, devastated by exposure to high concentrations of sulfur oxides, have not yet been recolonized by plants, decades after we stopped polluting them. So it is clearly within our powers to change the surface of the earth and presumably to modify the regional and global climate.

In this chapter we consider three air pollution problems in which humans may be making large-scale changes in our planet. These pose a severe political challenge. Air pollution laws in the United States and most other countries (see Chapter 3) are based on the assumption that air pollution is a local matter. The smoky or stinky or potentially toxic factory is a nuisance or a hazard to its neighbors, who can go to the local government and ask it to clean up or close the factory. The local government has to balance the interests of the offended public with those of the factory owners and workers. These officials face all three groups at the next election. If one believes in the democratic process, then one should believe that the problem will be solved correctly. Local solutions are not available for global problems or for problems of pollutants like acid rain that cross international boundaries. No international elections can be held to settle such problems. Our political systems are responding slowly to this challenge.

In addition, we are concerned by the long lifetimes of some of the potentially climate-modifying chemicals we emit. If we decide to reduce our emissions of them, the amount already emitted and stored in the atmosphere may still cause serious problems. Some parts of the global climate *overshoot*; they continue to change in the direction they are changing even after the cause of the change has been reduced or withdrawn. Existing political and regulatory systems are not good at dealing with long-term consequences of current actions nor with systems with overshoot.

14.1 GLOBAL WARMING

Humans are putting gaseous materials into the atmosphere that may cause the earth's average temperature to rise. This is called *global warming*, or *the greenhouse effect*.

Example 14.1. Estimate the average temperature that the earth would have if it had no atmosphere.

The total radiant energy flux from the sun, just outside the earth's atmosphere, is 1.353 kW/m^2 (429 Btu/h · ft^2). The diameter of the earth is 12.75×10^6 m so that, if all the incoming solar energy were absorbed by the earth, the total heat flow in from the sun would be

$$\text{Total heat flow in from the sun} = \frac{\pi}{4}D^2 \cdot \text{flux} = \frac{\pi}{4}(12.75 \times 10^6\ \text{m})^2 \cdot 1.353\ \frac{\text{kW}}{\text{m}^2}$$
$$= 1.73 \times 10^{14}\ \text{kW} = 1.64 \times 10^{14}\ \frac{\text{Btu}}{\text{s}}$$

The total heat radiated to outer space would be this amount plus the amount produced on earth by nuclear decay and tidal friction with the moon, which together are less than 0.1 percent of the solar energy inflow and can be safely ignored. The outward radiation (assuming a zero temperature for outer space and blackbody radiation), using the surface area of the earth rather than the projected area, is

$$\text{Total heat flow out} = \pi D^2 \sigma T^4 = \pi(12.75 \times 10^6\ \text{m})^2 \cdot 5.672 \times 10^{-11}\ \frac{\text{kW}}{\text{m}^2\text{K}^4}T^4$$

where σ = the Stefan-Boltzmann constant = $5.672 \times 10^{-11}\text{kW}/(\text{m}^2 \cdot \text{K}^4)$. Setting these equal and solving for T, we find 278 K = 5°C = 41°F. ∎

This is approximately 10°C, or 18°F, below the observed average surface temperature of the earth, which is about 15°C or 59°F. Thus, the net effect of having an atmosphere is to raise the average temperature of the earth about 10°C (= 18°F) above the value it would have with no atmosphere, if the earth absorbed all incoming sunlight. This effect is even more impressive when we consider that not all the incoming solar radiation is absorbed. The earth reflects roughly 30 percent of all the incoming solar radiation back to outer space from the tops of clouds, icy surfaces, oceans, etc. (Technically, the earth's *albedo* is about 0.3.) The moon, which has no atmosphere and hence no clouds, surface water, or ice sheets, reflects about 12 percent of its incoming solar radiation. (If it absorbed it all and reflected none, we would see it as a totally black circle against the starry night sky! If it reflected the same percentage as the earth, it would be 2.5 times as bright as it is.) If the atmosphere let the same amount of sunlight in as it actually does but did not prevent the outward flow of radiant heat, then we should multiply the incoming solar radiation in Example 14.1 by 0.7, finding an average surface temperature of 254 K = −19°C = −2°F, and a frozen world.

The fact that the observed average world temperature is higher than the value in Example 14.1 demonstrates that the atmosphere must block a higher proportion of the outgoing radiation than it does of the incoming radiation.

Example 14.2. What fraction of the outgoing radiation from the earth is blocked by the atmosphere?

As just discussed, we assume that 30 percent of the incoming solar radiation is reflected away, and use an average surface temperature over the whole planet of approximately 15°C = 59°F = 288.15 K. Then setting incoming approximately equal to outgoing and solving for the fraction emitted, we have

$$\text{Fraction emitted} \approx \frac{0.7(\text{total solar input})}{\pi D^2 \sigma T^4}$$

$$= \frac{0.7(1.73 \times 10^{14})\ \text{kW}}{\pi(12.75 \times 10^6\ \text{m})^2 \cdot 5.672 \times 10^{-11}\ \dfrac{\text{kW}}{\text{m}^2\text{K}^4}(288.15\ \text{K})^4}$$

$$= 0.606$$ ■

We see that for the earth's surface temperature to average about 15°C = 59°F, the atmospheric outward transmission of radiant energy must be 60.6% of the inward transmission of solar energy. We also see that if something changes this ratio, then the earth will balance these energy flows by changing the average surface temperature. The possibility that humans may be doing one or more things to change that ratio is the cause of our concern with global warming.

Clouds block radiation, both inbound and outbound. (Cloudy days are cool and cloudy nights are warm relative to clear days and nights at the same season.) They are more or less equal in their resistance to incoming and outgoing radiation. The same is not true for clear air, which contains CO_2, H_2O, CH_4, and some other gases that can absorb radiant energy. If the wavelengths of the incoming and outgoing radiant energies were the same, then these gases would block equal amounts in both directions. But the wavelengths are quite different.

Figure 14.1 on page 514 shows the absorptive properties of the clear atmosphere (without clouds, dust, birds, insects) and some properties of the incoming solar radiation and the outgoing thermal radiation from the earth. The upper part

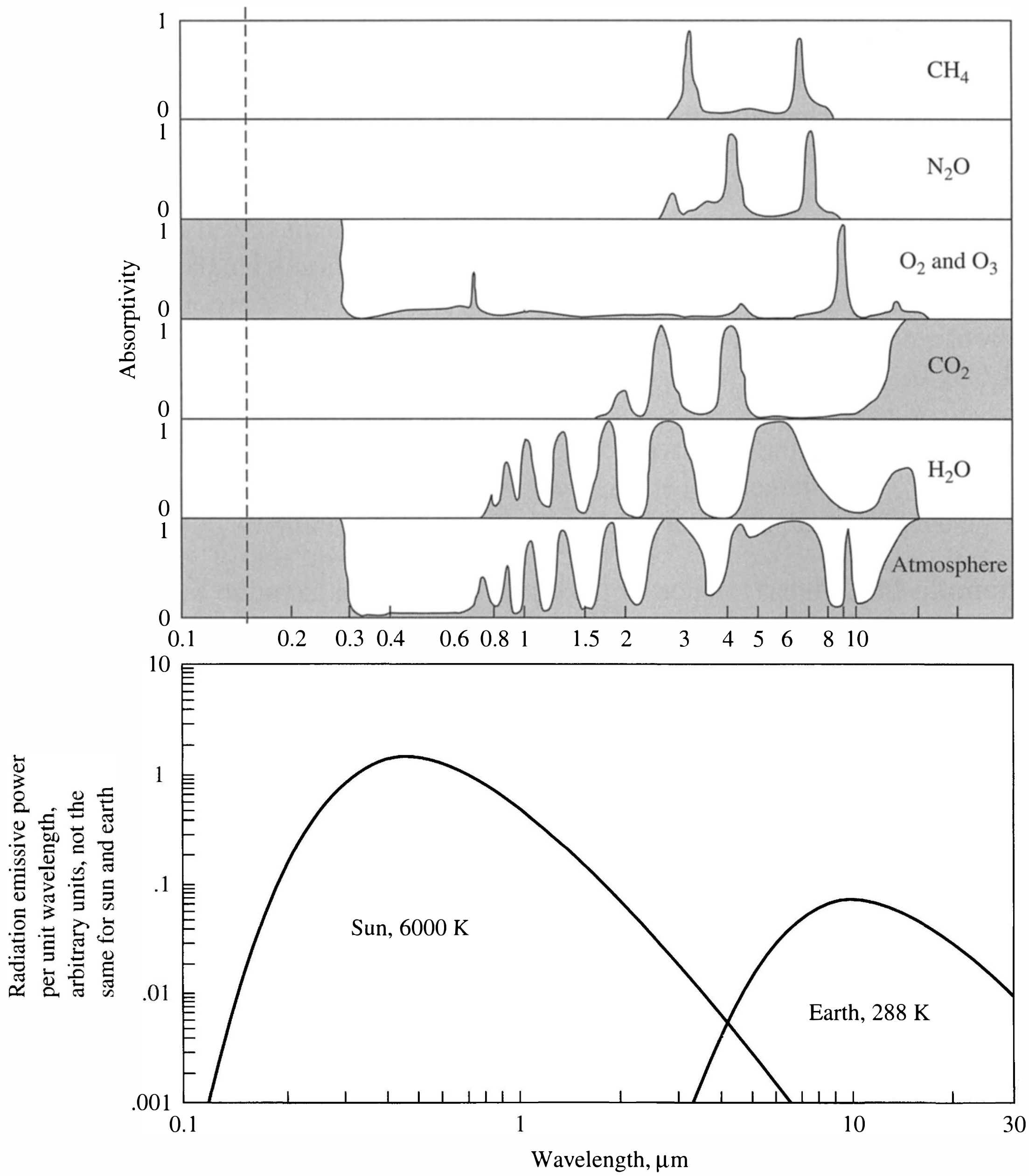

FIGURE 14.1
Absorptive properties of the atmosphere as a function of wavelength, and approximate emission spectra (see Problem 14.1) of sun and earth. The absorptive properties are after Oke [1]. At any one wavelength, the absorptive properties are the same for incoming and outgoing radiation.

of this figure shows the contribution to the absorptive properties of the atmosphere of CH_4, N_2O, O_2 and O_3, CO_2, and H_2O. The section labeled "Atmosphere" is the sum of the five sections above it. As a simple illustration of this part of the figure, if we sketched on this section the absorption curve for a sheet of blue-colored glass, which only allows blue light to pass through, the glass would show an absorptivity of 1 for all wavelengths except that of blue light (≈ 0.5 μ) and a "window" of low absorptivity for that wavelength. Applying the same logic to Fig. 14.1, we see that O_2 and O_3 block all light with wavelengths less than about 0.28 μ and that CO_2 blocks all light with wavelengths more than about 15 μ. The combined absorption spectrum for the whole atmosphere is largely transparent in the wavelength range from 0.3 μ to 0.7 μ, and has various "windows" at other wavelengths, of which the most important is the two-part window between about 8 μ and 12 μ.

The interaction of a photon with a gas molecule is quite different from that with a cloud droplet or with a fine particle (discussed later). A gas molecule will absorb a light photon if the gas molecule can make an internal rearrangement that requires the same amount of energy as that carried by the photon. One may think of this as a "tuning" or "resonance" phenomenon. (Your radio responds only to the discrete frequency to which it is tuned.) For wavelengths shorter than about 0.28 μ, the internal transitions involve shifts of electrons in their orbitals around the nuclei of one or more of the atoms that make up the molecule, but not any change in the relation of one atom to another within the molecule. For the wavelengths longer than about 1 μ the changes are not within the individual atoms but are those associated with the vibrations of the various atoms in the molecule, relative to each other. In the 0.28 to 1 μ window, the photons have too little energy to cause shifts of electron orbitals, and too much energy to be in tune with intramolecular vibrations (for the molecules in the air). The H_2O absorption peaks shown on Fig. 14.1 are caused by the various intramolecular vibration modes of the water molecule (three fundamental vibrations, plus overtones).

The lower part of the figure shows the distribution of energy in sunlight and in the infrared radiation from the earth. These are idealized values for blackbody radiators at 6000 and 288 K, which correspond roughly to the average surface temperatures of sun and earth. The real spectra are more complex, but these simplified spectra are close to correct. The quantity plotted is the fraction of the total emitted energy per micron of wavelength, which has a higher maximum (140 percent per micron) for the sun than for the earth (7 percent per micron) because the sun's spectrum is narrower. (Observe the logarithmic scale for wavelength.)

This lower section shows that radiant energy is distributed over a range of wavelengths, which is narrower for hotter bodies. Wein's law for blackbody radiation is

$$\begin{pmatrix} \text{Wavelength of} \\ \text{maximum emission} \end{pmatrix} = \lambda_{\max} = \frac{2.987 \times 10^3\ \mu\text{m} \cdot \text{K}}{T} \tag{14.2}$$

which shows that for the temperature of the sun's surface, about 6000 K, the peak intensity is at 0.50 μ, corresponding to visible light. For the earth's surface temperature of about 288 K the peak intensity is 10.3 μ, which is in the infrared region, not visible to our eyes. (We do not see the earth glowing in the dark, but if we had infrared-sensing eyes we would.) The sun's energy comes to the earth about half as visible light and about half as short-wave infrared radiation; the earth sends energy out mostly as longer-wave infrared radiation.

Comparing the lower and upper parts of the diagram, we see that sunlight comes to the surface practically unimpeded except for cloudy areas, whereas the peak radiation from the earth is close to the 8- to 12-μ window, which is not as wide nor as completely open as the window for solar energy. This is the main reason that the atmosphere is less transparent for outgoing infrared energy than it is for incoming solar energy.

Figure 14.1 is made up for the current concentrations in the atmosphere of the gases shown. It shows that CO_2, CH_4, N_2O, and H_2O all have some absorption in the 8- to 12-μ window. (The same is also true for *chlorofluorocarbons*, or CFCs, not shown on this figure but discussed later in this chapter.) If we were to increase the concentration of any or all of these gases in the atmosphere, the 8- to 12-μ window on Fig. 14.1 would become less transparent, thus making the atmosphere's ratio of outgoing to incoming transparency decline. In turn, the average temperature of the earth would rise, thus producing the so-called greenhouse effect. (This is technically a poor name; greenhouses work mostly by cutting off wind and air circulation while letting in sunlight [2]. However, this name is in common usage and will be used here. The group consisting of CO_2, CH_4, N_2O, and CFCs are collectively called *greenhouse gases*.)

Human activities are increasing the concentrations of greenhouse gases in the atmosphere. Of these gases, the strongest contributor to reducing the transparency of the 8- to 12-μ window is water vapor. However, humans do not directly influence its concentration in the atmosphere, and it is not normally a part of the discussion of the greenhouse effect. Figure 14.2 shows a very simplified view of the interactions

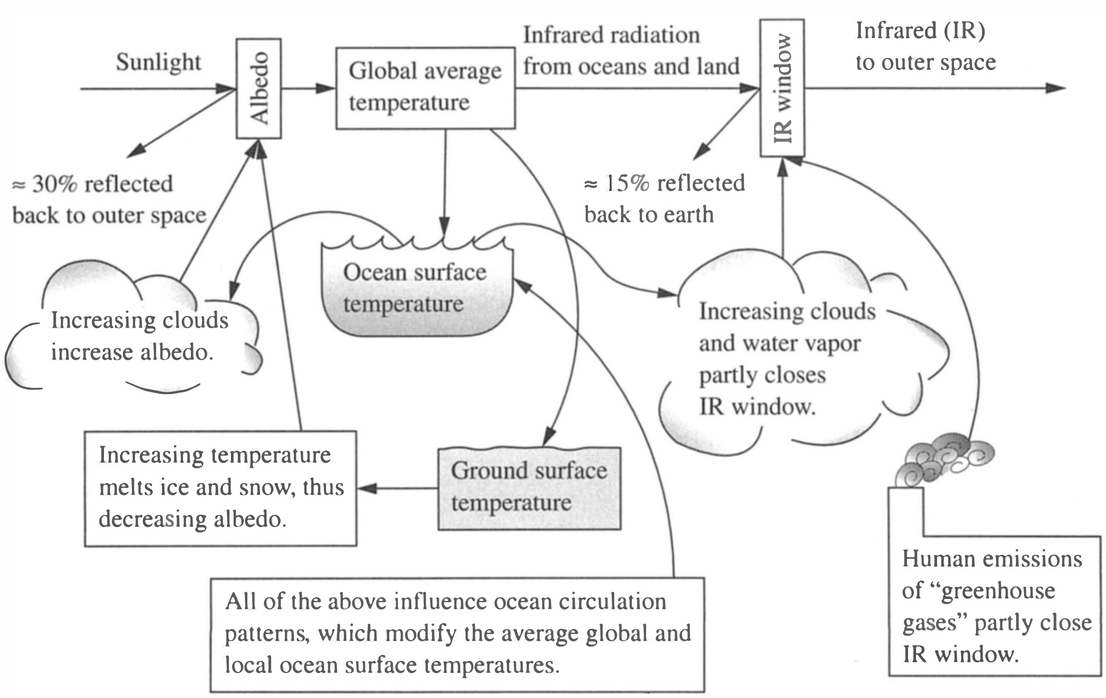

FIGURE 14.2
Simplified view of the interactions and feedback loops involved in the global warming problem. These are believed to be the major effects; there are certainly others.

and feedback loops involved in the global temperature. The previous examples have only considered the top row of the figure—sunlight in, infrared (IR) out. Increasing the global temperature by adding greenhouse gases will have positive and negative effects on the albedo by increasing cloudiness and reducing snow and ice cover, and will further close the IR window by increasing the average water vapor content of the atmosphere and the average cloudiness. Best current estimates suggest that the overall effect of all clouds is to slightly cool the earth. Perhaps the most uncertain and frightening consequences are those of changing ocean circulation patterns, like the Gulf Stream, which keeps Europe from freezing, and the El Niño currents in the central Pacific Ocean, which have very widespread weather consequences.

The previous discussion and this model are all strong simplifications of the true complexity of the earth's energy balance. They ignore the mixing and energy transport within the atmosphere and the adsorption of IR by greenhouse gases and then its partial reradiation back to the surface and its partial radiation to outer space. More detailed accounts, which do not hide this complexity, are available [3, 4].

Figure 14.3 shows the calculated relative contributions of the various greenhouse gases to the reduction of transparency of the atmosphere in the 8- to 12-μ window for the period 1980 to 1990 [5]. We see that CO_2 contributed more than half, followed by the CFCs, methane, and N_2O.

If the greenhouse effect causes the earth's mean temperature to rise even slightly, climatic changes will result. The form these changes will take is unknown. Large-scale computer modeling of the atmosphere *suggests* what will happen, but the calculations are still considered somewhat speculative. If rising temperatures were to melt the ice cap in Antarctica, the world sea level would rise several hundred feet, flooding most of the coastal cities and agricultural areas of the world. Temperature increases much smaller than those needed to melt the ice caps would cause the deserts and the temperate zones to extend farther from the equator. Agricultural

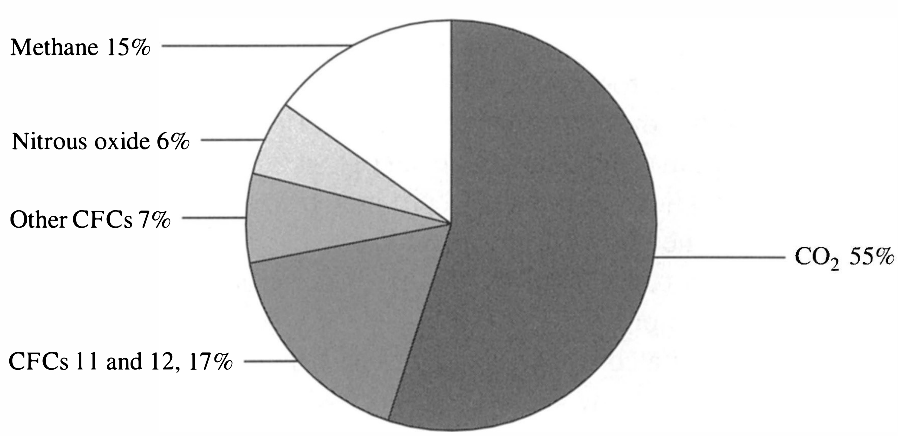

FIGURE 14.3
The contribution of human-caused greenhouse gases to the change in transparency of the 8- to 12-μ window of the atmosphere for the period 1980–1990. Tropospheric ozone may also play a role but its magnitude is uncertain [5].

areas that are currently highly productive would become dryer and hotter, while sub-Arctic regions would become warmer and wetter. Good current discussions are given in Refs. 5–7.

The best current estimates are that, for a "business as usual" projection of future emissions of all greenhouse gases, the global mean temperature will increase by 0.2° to 0.5°C (best estimate 0.3°C) per decade for the next century [5]. This change in global temperature is more rapid than any other that has occurred in the past 10 000 years (since the end of the last ice age, which was apparently quite sudden compared to the speed of other geologic events). The corresponding projection of world sea level is for a rise of 3 to 10 cm/decade (best estimate 6 cm/decade) over the same period.

The greenhouse problem has a strong overshoot. The oceans have several hundred times the heat storage capacity of the atmosphere. As greenhouse warming raises the temperature of the atmosphere, at first the cooler oceans will remove heat, slowing the rate of atmospheric temperature increase. However, as the surface layers of the ocean become warmer, that cooling effect will decline, thus producing a temperature overshoot in the atmosphere. This overshoot is likely to have a time scale of several hundred years at current emission rates [5]. Thus if we were to take steps that guaranteed that the composition of the atmosphere remained at its current state, there would still be a significant atmospheric temperature increase in the next few decades due to this overshoot.

14.1.1 Carbon Dioxide

Carbon dioxide (CO_2) is a colorless, tasteless gas that provides the "carbonation" in soft drinks and sparkling wines. It has been part of the earth's atmosphere as long as the earth has had an atmosphere. The current carbon dioxide concentration in the world atmosphere is approximately 360 ppm. At that concentration it has no known harmful effects to humans, and it is totally necessary for photosynthesis, Eq. (14.1). Our bodies produce it as we utilize foods; it leaves our bodies in exhaled breath.

Geologic records show that the CO_2 content of the world atmosphere before about A.D. 1750 was 280 ± 10 ppm and did not move out of that range for hundreds or thousands of years. About 1750 humans began to burn increasing amounts of fossil fuels, and the CO_2 content of the global atmosphere has risen. Figure 14.4 shows CO_2 concentrations from the past 30 years. During that period, the annual increase in CO_2 concentration was ≈ 1.5 ppm/yr.

Figure 14.5 shows the estimated reservoirs and flows for carbon on earth. (To convert from carbon to CO_2 multiply by 44/12). Our uncertainty in the magnitudes of the natural flows is probably greater than the magnitude of the man-made flows, but the natural flows are apparently in balance so that the increase in the atmosphere shown in Figure 14.4 is apparently due to man-made emissions.

On a geological time scale, such changes in atmospheric CO_2 content are unimportant. Over geologic time the atmosphere's CO_2 content has changed, and

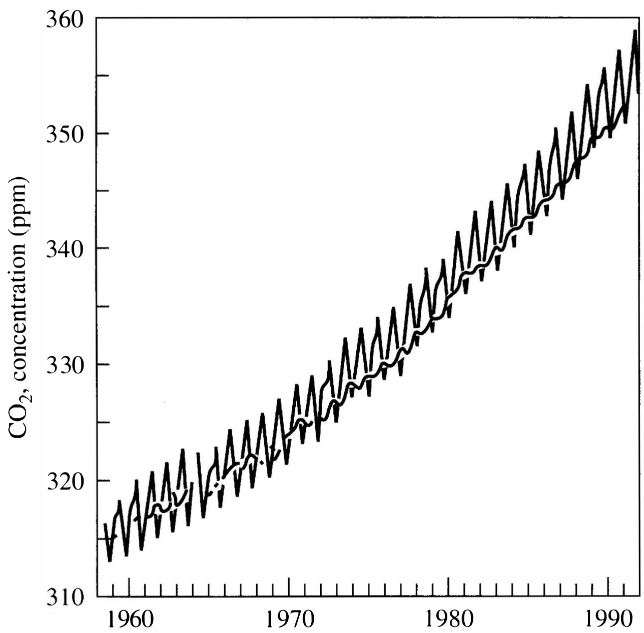

FIGURE 14.4
Recent history of the CO_2 content of the global atmosphere. The oscillating curve is from the top of Mauna Kea (13 796 ft), far from any human-caused source of CO_2 emissions. The annual oscillation of $\approx$ 6 ppm is caused by the large uptake of CO_2 by vegetation in the late spring and early summer, which produces an annual minimum. The much more regular curve is from Antarctica, which shows less seasonal variation, and generally lags on the Mauna Kea values by about 2 ppm, because most of the combustion of fossil fuels occurs in the Northern Hemisphere. (From [4], courtesy of The Cambridge University Press.)

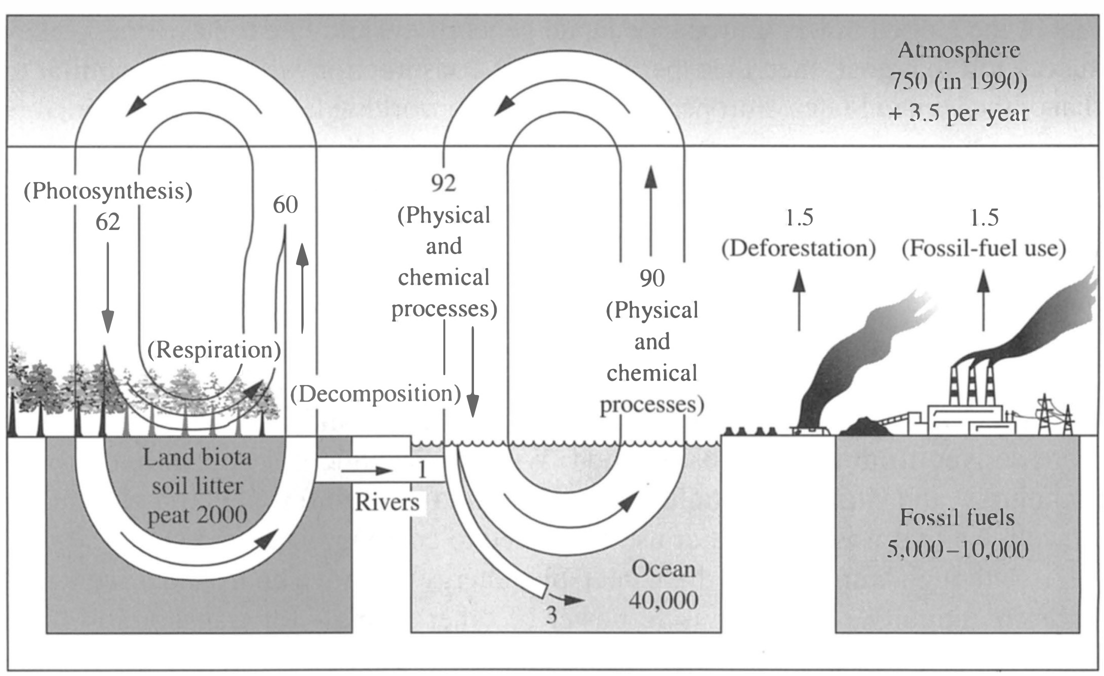

FIGURE 14.5
Estimated global flows and reservoirs of carbon (in various chemical combinations). The flow units are 10^9 metric tons (Gt)/yr; the reservoir units are Gt. We see that the oceans contain $\approx$ (40 000/750) $\approx$ 53 times as much as the atmosphere, and 4 to 8 times as much as all the fossil fuels. (From [4], courtesy of The Cambridge University Press.)

will change again. To some extent, the CO_2 content of the atmosphere serves as a global temperature regulator; when the CO_2 content rises, geologic forces are set into motion that cause it to be reduced [8]. But on a human time scale it could be a disaster. Our remote ancestors adapted to the last ice ages, but since then humans have never had to deal with climate changes as rapid as those that are predicted to occur as a result of the greenhouse effect.

If, as seems likely, increased emissions of CO_2 are the largest single cause of global warming, then our only control option is to reduce those emissions or at least reduce the rate of increase of those emissions. That may be difficult. The global annual fuel combustion CO_2 emissions are

$$\begin{pmatrix}\text{Global fuel}\\ \text{combustion}\\ CO_2\text{ emission}\end{pmatrix} = \begin{pmatrix}\text{global}\\ \text{population}\end{pmatrix}\begin{pmatrix}\text{per capita}\\ \text{fuel use}\end{pmatrix}\begin{pmatrix}CO_2\text{ emissions per}\\ \text{unit of fuel use}\end{pmatrix} \tag{14.3}$$

The first term, the global population, is growing at about 1.4 percent per year (population doubles every 50 years), and that growth rate shows little sign of slowing. The second term is highly variable from country to country. It is highest in the United States (where fuel has traditionally been cheap); next highest in Europe and Japan, where the standards of living are comparable to that in the United States, but governments have intentionally taxed fuels to keep the price relatively high to encourage fuel economy; and lowest in the Third World countries, which have much lower material standards of living than ours.

Those parts of the human population that do not have a standard of living like that in the United States, Europe, or Japan generally would like to have one. If they succeed in that goal, then their per capita fuel consumption will become similar to that of the United States, Europe, or Japan, and the worldwide average per capita fuel consumption will increase greatly. Humans use energy/fuel for food, for cooking, for light, for heat, for transportation, for industrial processes, for air conditioning, and for communication. All other uses are minor.

Over all of human history and even in many of the poorest countries today, the principal energy uses have been food, cooking fuel, light, and space heating. You may not think of food and fuel as interchangeable, but our ancestors did; they often used the same oils for cooking and for oil lamps. The only major industrial use of fuel before about 4000 B.C. was for firing pottery and bricks. The only fuels were derived from plants, mostly wood. With the invention of copper and bronze metallurgy, and later iron metallurgy, fuel began to be used for that kind of industry as well, but that was not a major use compared to cooking, heat, and light.

Although humans used the wind (solar energy) to move boats and drive windmills in antiquity, and the muscle power of other animals for transportation and industrial power (the domesticated horse, ox, camel, water buffalo, and llama are devices for converting plant materials to mechanical power), the first use of fossil fuels for driving machines was in 1776 with Watt's first general-purpose steam engine. The first use for transportation was in 1808 when Trethivic used a small, light-weight steam engine on a recreational railroad, which he called "Catch me who can." The first non-recreational steam railroad was apparently that of Stevenson in 1825. The result was the complete revolution in our ability to produce things and to move about. In the period from the domestication of the horse about 2000 B.C. to A.D. 1825, the fastest that humans could travel was the speed of a horse, about 30 miles an hour over a one-mile course, about 3–4 miles an hour going all day. From 1825 to 1900 that speed increased to 100 miles an hour all day, in fast trains. In the period from 1900 to 1990 that increased to 18 000 miles an hour for astronauts, and 600 miles an hour in commercial airlines. The change in personal mobility caused by the auto has been even more spectacular. We now think little of going 300 miles each way for a week-end outing; it takes 5 or 6 hours each way. Our great-grandparents would have needed 8 to 10 days each way for such a trip.

Humans first began to make consistent efforts to store food under refrigeration about 1860, and the effort became large-scale about 1920. As a result, we have a much more varied, tasty, healthful, and bacteriologically safe diet than our grandparents did. Air conditioning first appeared about 1900. It became available on a large scale about 1950. Since then people in the United States have spent enormous amounts of fuel cooling their homes, cars, and offices in the summer. We first had significant use of home clothes dryers about 1950. All of these appliances have made our lives more comfortable, and increased our use of fossil fuels.

To compare energy uses, we need a proper standard energy unit. The most intuitive unit is the minimal energy intake, as food, that a normal human needs, about 4 million BTU per year ($\approx$ 2750 kcal/day; the "calorie" in diet books is the kcal). That is the minimum amount of energy as fuel—food—that a "standard" human needs to live an active life for a year. Using it, we can make Table 14.1.

In the United States we use a total of about 79 times as much fuel as the minimum needed to feed ourselves. About a quarter of it goes for transportation (autos, trucks, trains, airplanes, ships), an eighth to heat houses, almost a quarter for all industry, and about a third for electricity. Of that electricity, two-thirds goes for light, heat, and air conditioning, the rest for industrial uses.

TABLE 14.1
Average U.S. per capita annual fuel usage, 1988

Food	1
Transportation	22
Residential and commercial space heat	10
Industry	18
Electricity (64% residential and commercial, 36% industrial)	28
Total	79

Note: Here, 1 = the basic food energy needed for a human = about 4 million BTU/yr
Source: Ref. 9

If we had made a similar table for the average person in the United States in 1850, or the average person in the Third World today, we would have seen that they used or use perhaps three to five times the energy they needed as food, mostly in the form of fodder for their animals and firewood for cooking and heating their homes. We use probably 15 to 30 times as much fuel per person as they do and live a much more physically comfortable life. If they are to live as we do, then world fuel consumption will grow dramatically.

The third term in Eq. (14.3) depends on the hydrogen/carbon ratio of the fuel burned. For equal amounts of energy released, the relative CO_2 release rates are approximately coal, 1.0; oil, 0.8; and natural gas, 0.6. Switching from coal to oil or from coal or oil to natural gas lowers the emission rate of CO_2. Our long-term supply of coal is much larger than that of oil or natural gas. It is possible to capture CO_2 from combustion exhaust gas and prevent its release, but only by using chemicals like CaO, whose production leads to the release of more CO_2. On a geological scale the process for removing CO_2 from the atmosphere is

$$CO_2 + Ca^{2+} + 2OH^- \rightarrow CaCO_3 + H_2O \tag{14.4}$$

which occurs in all of the the world's oceans, depositing solid $CaCO_3$ (limestone, calcite, or some other variants) on the ocean floor. It has been proposed to disperse the CO_2 from large power plants into the deep oceans in order to speed this reaction. So far that idea has not gotten beyond paper and pencil study. Its effects on the oceans are not known.

The only methods we now know to slow or stop the buildup of CO_2 in the atmosphere are to reduce the use of fossil fuels (gas, oil, coal, peat, lignite) and to stop the deforestation of the tropical rain forests. Solar, wind, hydroelectric, geothermal, and nuclear energy release no CO_2. Environmental activists suggest that we switch to solar and wind energy as one of the ways to limit CO_2 emissions. Others think we should switch to nuclear energy to solve our CO_2 emissions problem. If we decide that the global warming problem is as serious as some believe, then both of these suggestions will have to be taken very seriously. (Currently, instead of reducing the rate of fossil fuel usage, the human race is increasing it; our short-term goal is not to reduce the rate of fossil fuel usage, but to *reduce the rate of increase* in fossil fuel usage!)

The deforestation of the tropical rain forests is driven by population growth in the countries that have such forests. People without land to farm seek it by cutting down the forest. As the population grows, the demand for new agricultural and grazing land grows. The only way to stop this pressure on the remaining forests is to stop or slow the population growth in those countries.

14.1.2 Other Greenhouse Gases, Aerosols

Figure 14.3 shows that CFCs are apparently next in greenhouse effect after CO_2. They are discussed in Sec. 14.2. Next in importance is methane, the principal component of natural gas, which is formed in many anaerobic biological processes. It is the principal component of "swamp gas," is produced by bacterial decay of woody matter, and is a major component of the waste gases produced by landfills and sewage treatment plants. It is also emitted by almost all animals; our domestic dairy and meat cattle and pigs are a significant worldwide source [10].

In preindustrial times the world atmosphere contained ~ 0.7 ppm of methane. Over the past century that has increased to ~ 1.7 ppm, and it is increasing by about 0.01 ppm/yr [3]. A methane molecule is roughly 20 times as strong an infrared absorber as a CO_2 molecule (in the 8- to 12- μ window), so that even at this low concentration methane can play a significant role. The principal emissions of methane attributable to human activities are incomplete combustion (it is the most prominent hydrocarbon in automobile exhaust gases) and agricultural activities (rice paddies and animal husbandry). It is also emitted by coal mining and in the production and distribution of natural gas.

The remaining important greenhouse gas is nitrous oxide, N_2O, which formerly was often used as a dental anesthetic ("laughing gas"). It is not believed to have any harmful effects as an air pollutant except in its role as a greenhouse gas. One N_2O molecule is roughly 200 times as effective as one CO_2 molecule in reducing the transmission in the 8- to 12-μ window. The sources and sinks for N_2O are not as well known as those for the other greenhouse gases. Major human sources are not known. There is some concern that the NO_x control technologies that reduce NO with NH_3 and its near chemical relatives may produce significant amounts of N_2O.

Table 14.2, based on data from Ref. 5, summarizes current information on greenhouse gases.

The earth's average temperature can also be altered by an increase in the content of fine particles of the atmosphere. This is probably less threatening than the problem of greenhouse gases, because of the short time that fine particles spend in the atmosphere compared with the much longer time carbon dioxide and other greenhouse gases spend. However, the effects of these particles can be significant,

TABLE 14.2
Greenhouse gases

Name	Formula	Concentration in world atmosphere, 1994	Annual growth rate of concentration	Effectiveness as a greenhouse gas, per molecule, relative to CO_2
Carbon dioxide	CO_2	360 ppm	0.4%	1
Methane	CH_4	1.7 ppm	0.6%	20
CFC-11	CCl_3F	0.28 ppb	0	12 000
CFC-12	CCl_2F_2	0.48 ppb	0	16 000
Nitrous oxide	N_2O	0.31 ppb	0.25%	200

Source: Ref. 5.

as discussed in Ref. 11. For atmospheric particles to have effects lasting more than a few days, they must be injected into the stratosphere (above about 36 000 ft) because, as discussed in Chapter 5, there is little mixing between the stratosphere and the troposphere, so that particles in the stratosphere have lifetimes measured in years. In the troposphere (below that) there is fairly good atmospheric mixing, and particles are removed in days or weeks. Few human activities place many particles in the stratosphere.

Such particles can be injected into the stratosphere in large quantities by major volcanic eruptions. There they cause a lowering of the global temperature, generally for only a year or two after the eruption [12]. They lower global temperature because they are generally close in size to the wavelength of light (0.3 to 0.6 μ) and hence effective in scattering light and reducing the amount of incoming sunlight. However, these particles are much smaller than the wavelength of outgoing infrared radiation, and hence less effective in scattering it. It is widely but not universally believed that one of the causes of the extinction of the dinosaurs was the injection of a large mass of such particles into the atmosphere by a meteorite collision with the earth, which caused a severe and protracted cold spell [13, 14]. It is also widely but not universally believed that a major nuclear war would cause a "nuclear winter" by placing large amounts of particles in the high atmosphere [15].

14.2 STRATOSPHERIC OZONE DEPLETION AND CHLOROFLUOROCARBONS

The second global problem concerns the possible destruction of the stratospheric ozone layer. At ground level, ozone, O_3, is a strong eye and respiratory irritant and a major component of photochemical smog (see Fig. 1.2). It may also act as a greenhouse gas. In the stratosphere, 10 to 20 km above the earth's surface, is a layer of low-density air containing 300 to 500 ppb of ozone. Figure 14.1 shows the combined effects of O_2 and O_3; in the wavelength range below 0.28 μ, the effect is mostly due to ozone. That ozone prevents the components of sunlight with wavelengths less than about 0.28 μ from reaching the earth's surface. Ozone is the only component of the atmosphere that absorbs significantly at that wavelength (far ultraviolet). Figure 14.1 also shows that the calculated solar intensity is significant down to about 0.2 μ. (The true solar spectrum is more complex than the simple blackbody radiative flux shown here.) If that ozone layer were removed, we would expect large amounts of ultraviolet light in the wavelength range 0.2 to 0.28 μ to reach the surface of the earth.

The energy of a photon of light is proportional to (1/wavelength), so that shorter wavelength photons are more chemically active than longer wavelength photons. If high-energy photons reach the earth's surface, they will cause chemical reactions in the surfaces they contact, including human skin; they are expected to cause increased rates of skin cancer in humans. People can put on sunhats and sunscreen, but plants and animals cannot. (Sunscreens contain chemicals that are largely opaque to ultraviolet light; they convert chemically active ultraviolet light into chemically inactive