3

The Atmosphere

Introduction

There are several reasons to begin our treatment of biogeochemistry with a consideration of the atmosphere. The atmosphere has evolved as a result of the history of life on Earth (Chapter 2), and there is good evidence that it is now changing rapidly as a result of human activities. The atmosphere controls Earth's climate and ultimately determines the environment in which we live. Further, the atmosphere is relatively well mixed, so changes in its composition can be taken as a first index of changes in biogeochemical processes at the global level. The circulation of the atmosphere transports

biogeochemical constituents between land and sea, resulting in a global circulation of elements.

We will begin our discussion with a brief consideration of the structure, circulation, and composition of the atmosphere. Then, we will examine reactions that occur among various gases, especially in the lower atmosphere. Many of these reactions remove constituents from the atmosphere, depositing them on the surface of the land and sea. In the face of constant losses, the composition of the atmosphere is maintained by biotic processes that supply gases to the atmosphere. We will mention the sources of atmospheric gases here briefly, but they will be treated in more detail in later chapters of this book, especially as we examine the microbial reactions that occur in soils, wetlands, and ocean sediments.

Structure and Circulation

The atmosphere is held on the Earth's surface by the gravitational attraction of the Earth. At any altitude, the downward force (F) is related to the mass (M) of the atmosphere above that point,

$$F = M(g), \tag{3.1}$$

where g is the acceleration due to gravity (980 cm/sec² at sea level). Pressure (force per unit area) decreases with increasing altitude because the mass of the overlying atmosphere is smaller (Walker 1977). The decline in atmospheric pressure (P in bars) with altitude (A in km) is approximated by the logarithmic relation

$$\log P = -0.06(A), \tag{3.2}$$

over the whole atmosphere (Fig. 3.1).

Although the chemical composition of the atmosphere is relatively uniform, when we visit high mountains, we often say that the atmosphere seems "thinner" than at sea level. The abundance of molecules in each volume of the atmosphere is greater at sea level, because it is compressed by the pressure of the overlying atmosphere. Thus, the lower atmosphere, the *troposphere*, contains about 80% of the atmospheric mass (Warneck 1988), and jet aircraft flying at high altitudes require cabin pressurization for their passengers.

Certain atmospheric constituents, such as ozone, absorb portions of the radiation that the Earth receives from the Sun, so only about half of the Sun's radiation penetrates the atmosphere to be absorbed at the Earth's surface (Fig. 3.2). The land and ocean surfaces reradiate long-wave (heat) radiation to the atmosphere, so the atmosphere is heated from the bottom and is warmest at the Earth's surface (Fig. 3.1). Because warm air is less
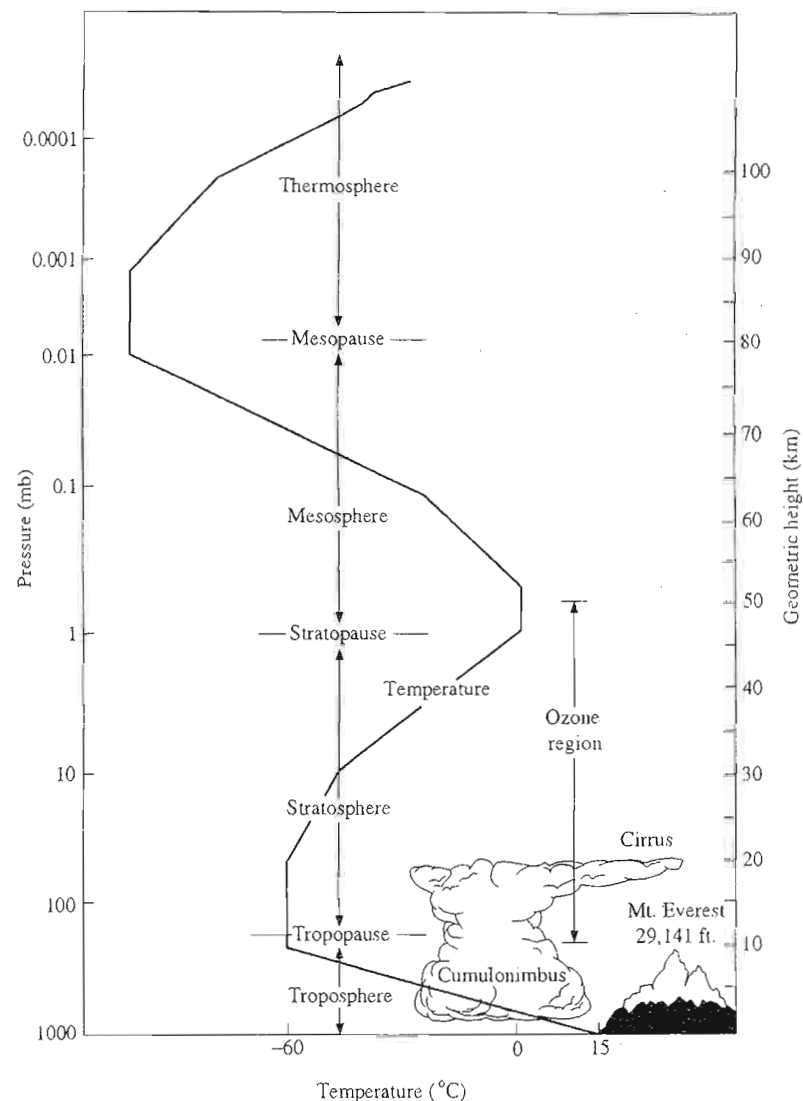
Figure 3.1 Temperature profile of the atmosphere to 100 km, showing major subdivisions of the atmosphere. Note the logarithmic decline in pressure (left-hand axis) as a function of altitude.

dense and rises, the troposphere is well mixed. The top of the troposphere extends to 10–15 km, varying seasonally and with latitude. The temperature of the upper troposphere is about −60°C, which ensures that the atmosphere above 10 km contains only small amounts of water vapor.
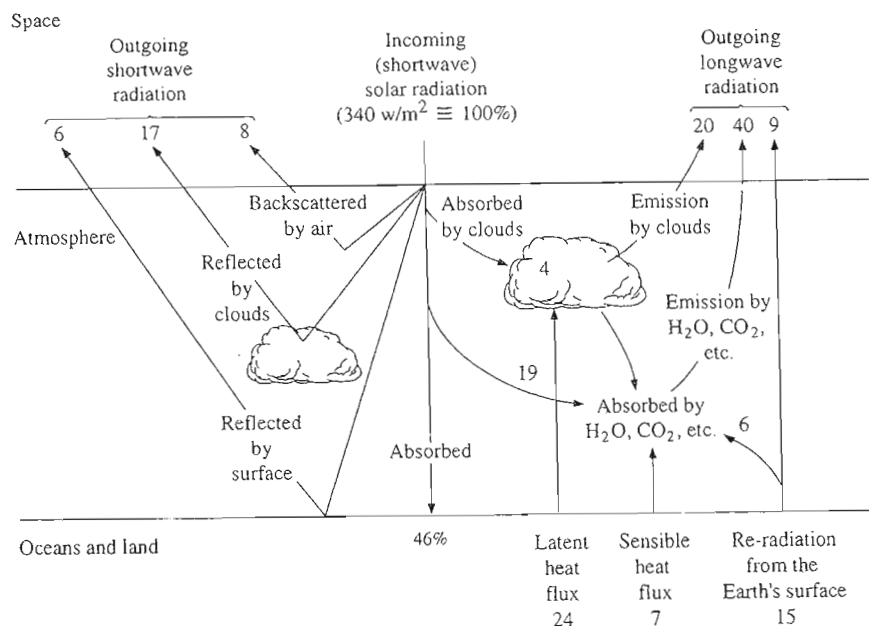
Space

Outgoing   Incoming   Outgoing
shortwave   (shortwave)   longwave
radiation   solar radiation   radiation
                (340 w/m² ≡ 100%)

6   17   8   20   40   9

Atmosphere

                Backscattered   Absorbed   Emission
                by air   by clouds   by clouds

         Reflected
         by
         clouds   Emission by
                                                   H₂O, CO₂,
                                          4   etc.

                                  19
                                          Absorbed by
         Reflected   H₂O, CO₂, etc.   6
         by
         surface   Absorbed

Oceans and land   46%   Latent   Sensible   Re-radiation
                                 heat   heat   from the
                                 flux   flux   Earth's surface
                                 24   7   15

Figure 3.2 The radiation budget for Earth, showing the proportional fate of the energy that the Earth receives from the Sun. Each year, the Earth receives about 340 W/m² of radiation, mostly in short wavelengths. About a third of this radiation is reflected back to space, and the remainder is absorbed by the atmosphere (23%) or the surface (46%). Long-wave (infrared) radiation is emitted from the Earth's surface, some of which is absorbed by atmospheric gases, warming the atmosphere (the greenhouse effect). The atmosphere emits long-wave radiation, so that the total energy received is balanced by the total energy emitted from the planet. Modified from MacCracken (1985).

Above the troposphere, the stratosphere is defined by the zone in which temperatures increase with altitude, extending to about 50 km (Fig. 3.1). The increase is largely due to the absorption of ultraviolet light by ozone. Vertical mixing in the stratosphere is limited, as is exchange across the boundary between the troposphere and the stratosphere, the *tropopause*. Thus, materials that enter the stratosphere remain there for long periods, allowing transport around the globe.

The thermal mixing of the troposphere is largely responsible for the global circulation of the atmosphere, as well as local weather patterns (Figs. 3.3a and 3.3b). The large annual receipt of solar energy at the equator causes warming of the atmosphere (sensible heat) and the evaporation of large amounts of water, carrying latent heat, from tropical oceans and rainforests. As this warm, moist air rises, it cools, producing a large amount of precipitation in equatorial regions. Having lost its moisture, the rising air mass moves both north and south, away from the equator. In a belt

centered on approximately 30° N or S latitude, these dry air masses sink to the Earth's surface, undergoing compressional heating. Most of the world's major deserts are associated with the downward movement of hot, dry air at this latitude. A similar, but much weaker, circulation pattern is found at the poles, where cold air sinks and moves north or south along the Earth's surface to lower latitudes. Known as Direct Hadley cells, these tropical and polar circulation patterns drive an indirect circulation in each hemisphere between 40° and 60° latitude, producing the regional storm systems and the prevailing west winds that we experience in the temperate zone (Fig. 3.3c).

The tropospheric air in each hemisphere mixes on a time scale of a few months (Warneck 1988). Each year, there is also complete mixing of tropospheric air between the northern and the southern hemispheres across the intertropical convergence zone (ITCZ). If a gas shows a higher concentration in one hemisphere, we can infer that a large natural or human source must exist in that hemisphere, overwhelming the tendency for atmospheric mixing to equalize the concentrations (Fig. 3.4).

Exchange between the troposphere and the stratosphere is driven by several processes (Warneck 1988). In the tropical Hadley cells, rising air masses carry some tropospheric air to the stratosphere (Holton et al. 1995). The strength of the updraft varies seasonally, as a result of variations in the radiation received from the Sun. When the height of the tropopause drops, tropospheric air is trapped in the stratosphere, or vice versa. There is also exchange across the tropopause due to large-scale wind movements (Appenzeller and Davies 1992), thunderstorms (Dickerson et al. 1987), and eddy diffusion (Warneck 1988).

Exchange between the troposphere and the stratosphere has been examined by following the fate of industrial pollutants released to the troposphere and radioactive contaminants released to the stratosphere by tests of atomic weapons during the 1950s and early 1960s (Warneck 1988). In these considerations, the concept of mean residence time is useful. For any biogeochemical reservoir, mean residence time (MRT) is defined as

$$MRT = Mass/flux, \tag{3.3}$$

where flux may be either the input or the loss from the reservoir.[1] The input of tropospheric air to the stratosphere amounts to about 75% of the stratospheric mass each year, leading to a mean residence time of 1.3 years for stratospheric air (Warneck 1988). Thus, if a large volcano injects sulfur

[1] Assuming exponential decay of a tracer from a reservoir that is in steady state, the fractional loss per year ($-k$) is equal to the reciprocal of the mean residence time in years, i.e., 1/MRT. The amount remaining in the reservoir at any time t (in years) as a fraction of the original content is equal to e^{-kt}, the half-life of the reservoir in years is $0.693/k$, and 95% will have disappeared from the reservoir after $3/k$ years.

A

B

C

835 kilometers
per hour

1446 kilometers
per hour
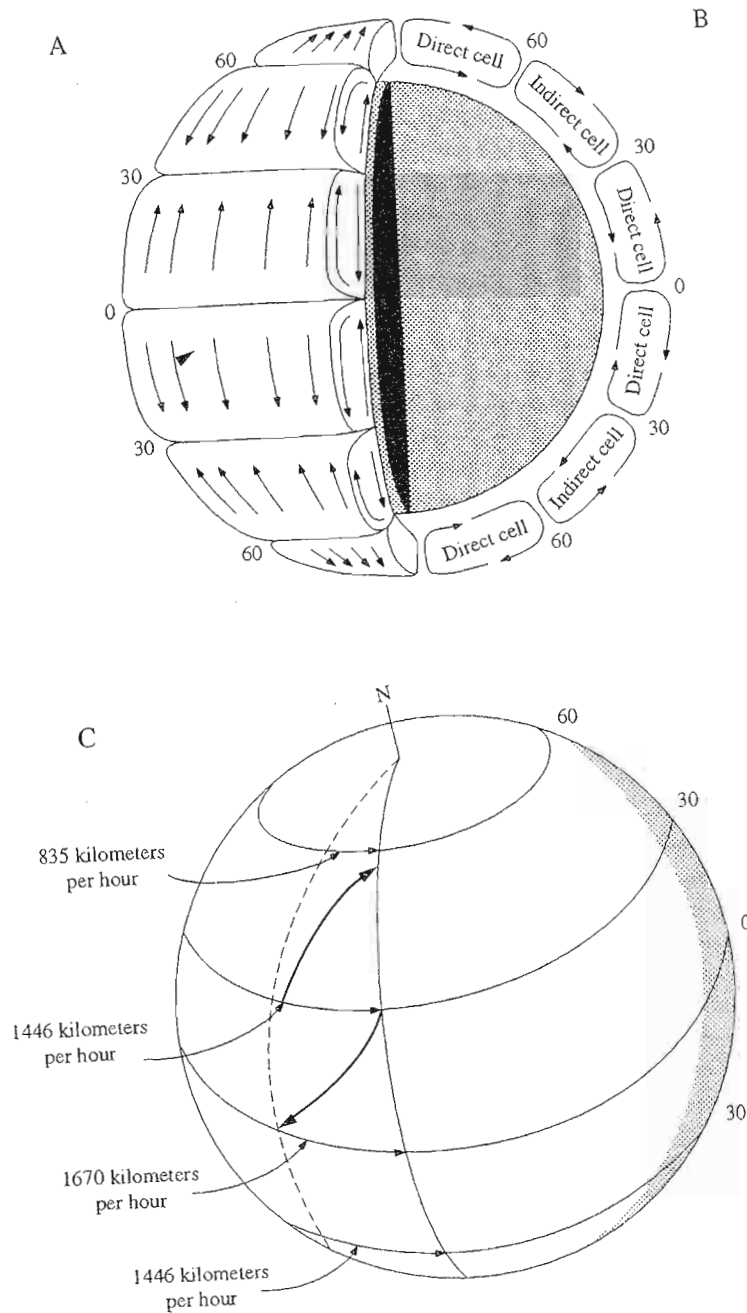
1670 kilometers
per hour

1446 kilometers
per hour

Figure 3.3 Generalized pattern of global circulation showing (a) surface patterns, (b) vertical patterns, and (c) origin of the Coriolis force. As air masses move across different latitudes, they are deflected by the Coriolis force, which arises because of the different speeds of the Earth's rotation at different latitudes. For instance, if you were riding on an air mass moving
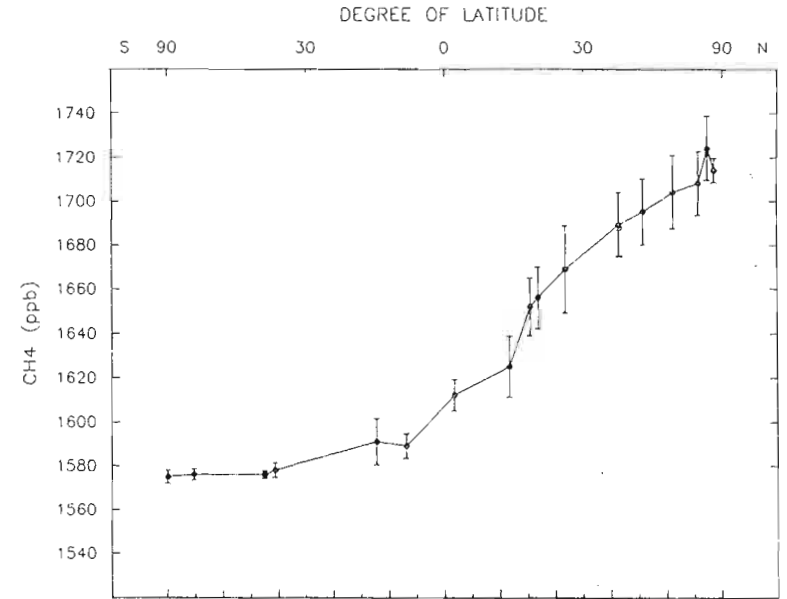
DEGREE OF LATITUDE

Figure 3.4 The latitudinal variation in the mean concentration of CH₄ (methane) in Earth's atmosphere. From Steele et al. (1987).

dioxide into the stratosphere, about half will remain after 1 year and about 5% will remain after 4 years.

Atmospheric Composition

Gases

Table 3.1 gives the globally averaged concentration of some important gases in the atmosphere. Three gases—nitrogen, oxygen, and argon—make up 99% of the atmospheric mass of 5.14×10^{21} g (Trenberth and Guillemot 1994). These gases are relatively unreactive; their mean residence times in the atmosphere are much longer than the rate of atmospheric mixing. Thus, the concentrations of N_2, O_2, and all noble gases (He, Ne, Ar, Kr, and Xe) are nearly uniform globally.

at a constant speed south from 30° N, you would begin your journey seeing 1446 km of the Earth's surface pass to the east every hour. By the time your air mass reached the equator, 1670 km would be passing to the east each hour. While moving south at a constant velocity, you would find that you had traveled 214 km west of your expected trajectory. The Coriolis force means that all movements of air in the northern hemisphere are deflected to the right; those in the southern hemisphere are deflected to the left. Modified from Oort (1970) and Gross (1977).

Table 3.1 Global Average Concentration of Well-Mixed
Atmospheric Constituents[a]

Compounds	Formula	Concentration	Total mass (g)
Major constituents (%)			
Nitrogen	N_2	78.084	3.87×10^{21}
Oxygen	O_2	20.946	1.19×10^{21}
Argon	Ar	0.934	6.59×10^{19}
Parts-per-million constituents (ppm = 10^{-6})			
Carbon dioxide	CO_2	360	2.80×10^{18}
Neon	Ne	18.2	6.49×10^{16}
Helium	He	5.24	3.70×10^{15}
Methane	CH_4	1.75	4.96×10^{15}
Krypton	Kr	1.14	1.69×10^{16}
Parts-per-billion constituents (ppb = 10^{-9})			
Hydrogen	H_2	510	1.82×10^{14}
Nitrous oxide	N_2O	311	2.42×10^{15}
Xenon	Xe	87	2.02×10^{15}
Parts-per-trillion constituents (ppt = 10^{-12})			
Carbonyl sulfide	COS	500	5.30×10^{12}
Chlorofluorocarbons			
CFC 11	CCl_3F	280	6.79×10^{12}
CFC 12	CCl_2F_2	550	3.12×10^{13}
Methylchloride	CH_3Cl	620	5.53×10^{12}
Methylbromide	CH_3Br	11	1.84×10^{11}

[a] Those with a mean residence time >1 year. Assuming a dry atmosphere with
a molecular weight of 28.97. The overall mass of the atmosphere sums to 514 $\times$
10^{19} g (Trenberth and Guillemot 1994).

Several hundred trace gases, including a wide variety of volatile hydrocarbons (Greenberg and Zimmerman 1984, Chameides et al. 1992), have also been identified in the Earth's atmosphere. Most of these gases have short mean residence times, so it is not surprising that they are minor constituents in the atmosphere. The concentration of such gases varies in space and time. For instance, we expect high concentrations of certain pollutants (ozone, carbon monoxide, etc.) over cities, and high concentrations of some reduced gases (methane and hydrogen sulfide) over swamps and other areas of anaerobic decomposition (e.g., Harriss et al. 1982, Steudler and Peterson 1985). Winds mix the concentrations of these gases to their lower, average tropospheric background concentration within a short distance downwind of local sources. Thus, we can best perceive global changes in atmospheric composition, such as the current increase in CH_4, by making long-term measurements in remote locations.

Junge (1974) related geographic variations in the atmospheric concentration of various gases to their estimated mean residence time in the atmosphere (Fig. 3.5). Gases that have short mean residence times are highly variable from place to place, whereas those that have long mean residence times, relative to atmospheric mixing, show relatively little variation. For example, the average volume of water in the atmosphere is equivalent to about 13,000 km³ at any time, or 25 mm above any point on the Earth's surface (Speidel and Agnew 1982). The average daily precipitation would be about 2.7 mm, if it were deposited evenly around the globe. Thus, the mean residence time for water vapor in the atmosphere is

$$25 \text{ mm}/2.7 \text{ mm day}^{-1} = 9.3 \text{ days}. \qquad (3.4)$$
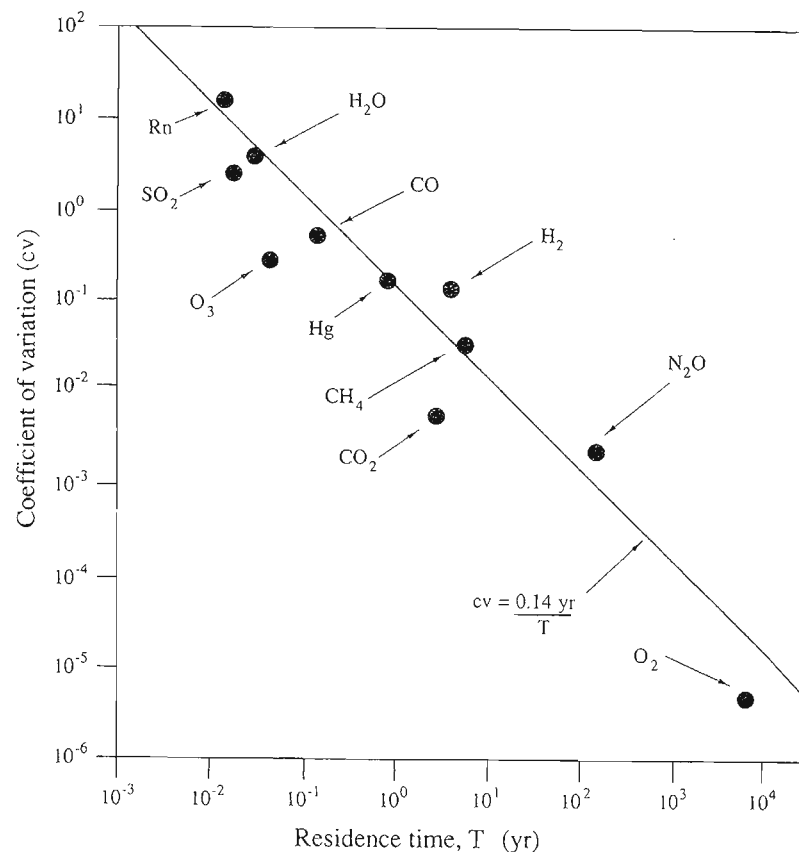

Figure 3.5 Variability in the concentration of atmospheric gases (expressed as the coefficient of variation among measurements) as a function of their estimated mean residence times in the atmosphere. Modified from Junge (1974), as updated by Slinn (1988).

This is a short time compared to the circulation of the troposphere, so we should expect water vapor to show highly variable concentrations in space and time (Fig. 3.5).

The mean residence time for carbon dioxide is about 5 years—only slightly longer than the mixing time for the atmosphere. Owing to the seasonal uptake of CO_2 by plants, CO_2 shows a minor seasonal and latitudinal variation ($\pm$ about 1%) in its global concentration of 360 ppm (Fig. 3.6). In contrast, painstaking analyses are required to show *any* variation in the concentration of O_2, because the amount in the atmosphere is so large and its mean residence time, 4000 years, is so much longer than the mixing time of the atmosphere (Keeling and Shertz 1992).

Gases with mean residence times $\ll 1$ year in the troposphere do not persist long enough for appreciable mixing into the stratosphere. Indeed, one of the most valuable, but dangerous, industrial properties of the chlorofluorocarbons is that they are chemically inert in the troposphere (Rowland 1989). This allows chlorofluorocarbons to mix into the stratosphere, where they destroy ozone in reaction with ultraviolet light.
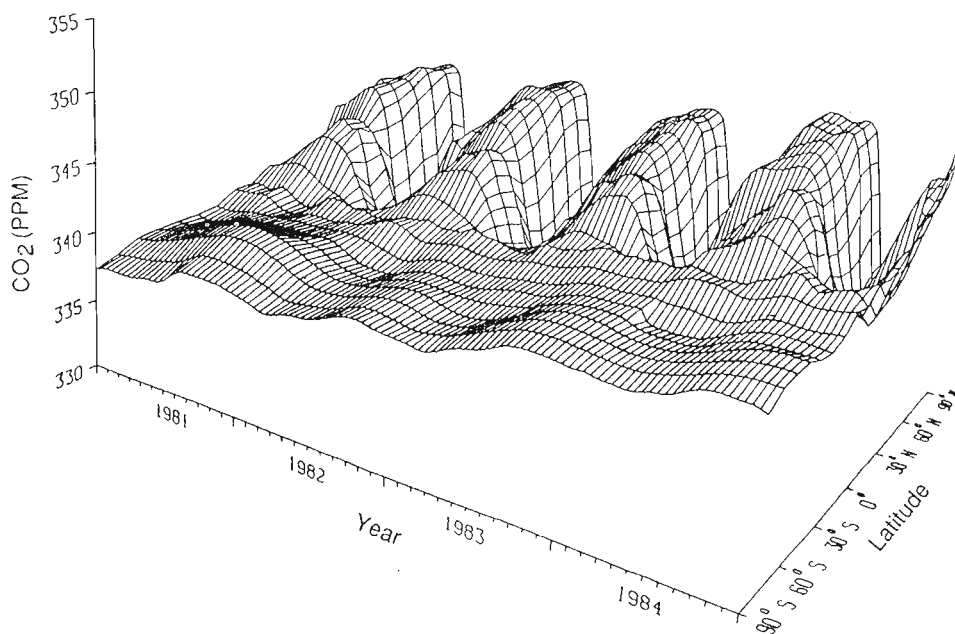
Aerosols

In addition to gaseous components, the atmosphere contains particles, known as aerosols, that arise from a variety of sources (Table 3.2). Soil minerals are dispersed by wind erosion (deflation weathering) from arid and semi-arid regions (Pye 1987, Tegen and Fung 1995). Particles with a diameter <1.0 μm are held aloft by turbulent motion and subject to long-range transport. Schütz (1980) estimates that 1×10^{15} g/yr of soil particles enter the atmosphere from arid regions, and about 20% of these particles are involved in long-range transport. Dust from the deserts of central Asia falls in the Pacific ocean (Duce et al. 1980), where it contributes much of the iron needed by oceanic phytoplankton (Chapter 9). Similarly, dust from the Sahara supplies nutrients to phytoplankton in the Atlantic ocean

Figure 3.6 Seasonal fluctuations in the concentration of atmospheric CO_2 (1981–1984), shown as a function of 10° latitudinal belts (Conway et al. 1988). Note the smaller amplitude of the fluctuations in the southern hemisphere, reaching peak concentrations during northern hemisphere minima.

Table 3.2   Global Emissions of Aerosols[a]

| Source	Global flux (10^{12}g/yr)
Natural sources	
Primary aerosols	
Soil dust	1500
Seasalt	1300
Volcanic dust	33
Organic particles	50
Secondary aerosols	
Sulfates from volatile organic sulfides (e.g., $(CH_3)_2S$)	90
Sulfates from SO_2	12
Organic condensates	55
Nitrates from NO_x	22
Sum of natural sources	3070
Anthropogenic sources	
Primary aerosols	
Industrial particles	100
Soot	20
Particles from forest fires	80
Secondary aerosols	
Sulfates from SO_2	140
Nitrates from NO_x	36
Organic condensates	10
Sum of anthropogenic sources	390
Total	3460

[a] From Jonas et al. (1995).

(Talbot et al. 1986) and phosphorus to Amazon rainforests (Swap et al. 1992). Typically, while it is in transit, soil dust warms the atmosphere over land and cools the atmosphere over the oceans, which have lower surface albedo (reflectivity) (Ackerman and Chung 1992, Kellogg 1992).

An enormous quantity of particles enter the atmosphere from the ocean as a result of tiny droplets that become airborne with the bursting of bubbles at the surface (MacIntyre 1974, Wu 1981). As the water evaporates from these bubbles, the salts crystallize to form seasalt aerosols, which carry the approximate chemical composition of seawater (Glass and Matteson 1973, Möller 1990). As in the case of soil dust, most seasalt aerosols are relatively large and settle from the atmosphere quickly, but a significant proportion remain in the atmosphere for global transport. Möller (1990) estimates a total seasalt production of 10×10^{15} g/yr, which carries about 200×10^{12} g of chloride from sea to land. Other global estimates of seasalt production are somewhat lower (Table 3.2; see also Fig. 3.12).

Forest fires produce particles of charcoal that are carried throughout the troposphere, and small organic particles (soot) are produced by the condensation of volatile hydrocarbons from the smoke of forest fires (Hahn 1980, Cachier et al. 1989). Forest fires in the Amazon are thought to release as much as 1×10^{13} g of particulate matter to the atmosphere each year (Kaufman et al. 1990). It is likely that the global production of aerosols from forest fires has increased markedly in this century as a result of higher rates of biomass burning in the tropics (Andreae 1991, Cahoon et al. 1992). Aerosols from these fires may affect regional patterns of rainfall (Cachier and Ducret 1991) and global climate (Penner et al. 1992). At the same time, in the temperate zone, control of forest fires has reduced the aerosol loading to the atmosphere over the last century (Clark and Royall 1994).

Volcanoes disperse finely divided rock materials over large areas (Table 3.3), contributing to soil development in regions that are downwind from major eruptions (Watkins et al. 1978, Dahlgren and Ugolini 1989, Zobel and Antos 1991). Volcanic gases and ash that are transported to the stratosphere by violent eruptions undergo global transport, potentially affecting climate for several years (Minnis et al. 1993, Langway et al. 1995, McCormick et al. 1995).

Small particles are also produced by reactions between gases in the atmosphere. For instance, when SO_2 is oxidized to sulfuric acid (H_2SO_4) in the atmosphere, particles rich in $(NH_4)_2SO_4$ may be produced by a subsequent reaction with atmospheric ammonia (NH_3):

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4. \qquad (3.5)$$
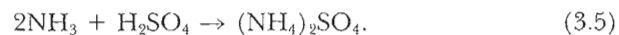
Sulfate aerosols are also produced during the oxidation of dimethylsulfide released from the ocean (Chapter 9). These aerosols increase the albedo of the Earth's atmosphere, so estimates of the abundance of sulfate aerosols

Table 3.3 Composition of an Airborne Particulate Sample Collected during the Eruption of Mt. St. Helens on May 19, 1980[a]

Constituent	Particulate sample	Average ash
Major elements (%)		
SiO_2	$\equiv 65.0$	65.0
Fe_2O_3	6.7	4.81
CaO	3.0	4.94
K_2O	2.0	1.47
TiO_2	0.42	0.69
MnO	0.054	0.077
P_2O_5[b]	—	0.17
Trace elements (ppm)		
S	3220	940
Cl	1190	660
Cu	61	36
Zn	34	53
Br	<8	~1
Rb	<17	32
Sr	285	460
Zr	142	170
Pb	36	8.7

[a] Average ash is shown for comparison. From Fruchter et al. (1980).
[b] From Hooper et al. (1980). Copyright 1980 by the AAAS.

are an important component of global climate models (Kiehl and Briegleb 1993, Mitchell et al. 1995).

Finally, a wide variety of particles are produced from human industrial processes, especially the burning of coal (Hulett et al. 1980, Shaw 1987). Globally, the release of particles during the combustion of fossil fuels rivals the mobilization of elements by rock weathering at the Earth's surface (Bertine and Goldberg 1971). Recently, the mass of industrial aerosols has declined in many developed countries where pollution controls have been instituted (Fig. 3.7). One of the most widespread anthropogenic aerosols, particles of lead from automobile exhaust, has declined in global abundance over the past 20 years due to a decline in the use of leaded gasoline (Boutron et al. 1991). Overall, human activities probably account for 10–20% of the burden of aerosols in today's atmosphere (Table 3.2).

Small particles are much more numerous in the atmosphere than large particles, but it is the large particles that contribute the most to the total airborne mass (Warneck 1988). The mass of aerosols declines with increas-
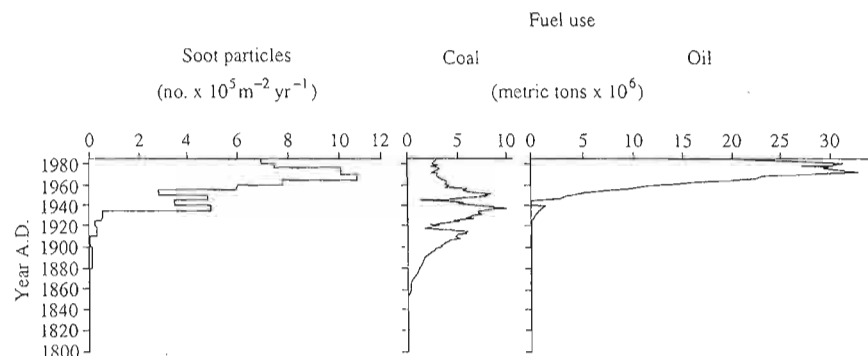
Fuel use

Soot particles   Coal   Oil

(no. x $10^5 m^{-2} yr^{-1}$)   (metric tons x 10^6)

Figure 3.7   Annual deposition of soot in Lake Koltjarn, as recorded in sediment layers, and the annual consumption of coal and oil in Sweden since 1800. The use of fossil fuel and the deposition of soot have both declined in recent years. From Renberg and Wik (1984).

ing altitude from values ranging between 1 and 50 $\mu g/m^3$ near unpolluted regions of the Earth's surface. Although there is an inverse relation between the size of particles and their persistence in the atmosphere, the overall mean residence time for tropospheric aerosols is about 5 days (Warneck 1988). Thus, aerosols are not uniform in their distribution in the atmosphere. As a result of their longer mean residence time, small particles have the greatest influence on Earth's climate and global biogeochemical transport through the atmosphere.

The composition of the tropospheric aerosol varies greatly depending upon the proximity of continental, maritime, or anthropogenic sources (Heintzenberg 1989). Over land, aerosols are often dominated by soil minerals and human pollutants (Shaw 1987, Gillette et al. 1992). Over the ocean, the composition of aerosols is a mixture of contributions from silicate minerals of continental origin and seasalt from the ocean (Andreae et al. 1986). Various workers have used ratios among the elemental constituents of aerosols to deduce the relative contribution of different sources (e.g., Moyers et al. 1977, Rahn and Lowenthal 1984).

Aerosols are important in reactions with atmospheric gases and as nuclei for the condensation of raindrops. The latter are known as cloud condensation nuclei, often abbreviated CCN. Raindrops are formed when water vapor begins to condense on aerosols >0.1 μm in diameter. As raindrops enlarge and fall to the ground, they collide with other particles and absorb atmospheric gases. Soil dusts often contain a large portion of insoluble material (Reheis and Kihl 1995), but seasalt aerosols and those derived from pollution sources are readily soluble and contribute to the dissolved chemical content of rainwater. Reactions of atmospheric gases with aerosols or raindrops are known as *heterogeneous gas reactions*. Such reactions are responsible for the ultimate removal of many reactive gases from the atmosphere.

Biogeochemical Reactions in the Troposphere

Major Constituents—N_2, O_2, and Ar

It is perhaps not surprising that the major constituents of the atmosphere, N_2, O_2, and Ar, are all relatively unreactive, showing nearly uniform concentrations and long mean residence times in the atmosphere. From a biogeochemical perspective, N_2 is practically inert; reactive N is found only in molecules such as NH_3 and NO. Collectively these compounds are known as "odd" nitrogen, because the molecules have an odd number of N atoms (versus N_2 or N_2O). In fact, despite the abundance of nitrogen in the atmosphere, N_2 is so inert that the availability of odd nitrogen is one of the primary factors that limits the growth of plants on land and in the oceans (Delwiche 1970, Vitousek and Howarth 1991). Among atmospheric gases, only argon and the other noble gases are less reactive.

Conversion of N_2 to reactive compounds, *N-fixation,* occurs in lightning bolts, but the estimated global production of NO by lightning (<3 × 10^{12} g N/yr; Chapter 12) is too low to account for a significant turnover of N_2 in today's atmosphere. By far the most important source of fixed nitrogen for the biosphere derives from the bacteria that convert N_2 to NH_3 in the process of biological nitrogen fixation (Eq. 2.12). The global rate of biological N-fixation is poorly known, because it must be extrapolated from small-scale measurements to the entire surface of the Earth. Including human activities, global nitrogen fixation is not likely to exceed $300 × 10^{12}$ g N/yr, with the production of synthetic nitrogen fertilizer now accounting for about $\frac{1}{3}$ of the total (Chapter 12).

Denitrification (Eq. 2.18) returns N_2 from the biosphere to the atmosphere. In the absence of denitrification, the global rate of nitrogen fixation would remove the pool of N_2 from the atmosphere in about 20 million years. At present, we have little evidence that the rate of either N-fixation or denitrification changes significantly in response to changes in the concentration of N_2 in the atmosphere, so it would seem that the biosphere plays a minor role in maintaining a stable concentration of atmospheric N_2 (Walker 1984).

In Chapter 2 we discussed the accumulation of O_2 in the atmosphere during the evolution of life on Earth. The atmosphere now contains only a small portion of the total O_2 released by photosynthesis through geologic time (Fig. 2.7). However, the atmosphere contains much more O_2 than can be explained by the storage of carbon in land plants today. The instantaneous combustion of all the organic matter now stored on land would reduce the atmospheric oxygen content by only 0.03% (Chapter 5).

The accumulation of O_2 is the result of the long-term burial of reduced carbon in ocean sediments (Berner 1982), which contain nearly all of the reduced, organic carbon on Earth (Table 2.2). This organic matter is largely

derived from photosynthesis in the sea, because the transport of organic carbon from land to sea in the world's rivers is very small (Schlesinger and Melack 1981). The rate of burial is determined by the area of the ocean floor that is subject to anoxic conditions (Walker 1977, 1980). Because that area varies inversely with the concentration of atmospheric O_2, the balance between the burial of organic matter and its oxidation maintains O_2 at a steady-state concentration of about 21% (see also Chapters 9 and 11).

A large amount of O_2 has been consumed in weathering of reduced crustal minerals, especially Fe and S, through geologic time (Fig. 2.7); the current rate of exposure of these minerals would consume all atmospheric oxygen in about 2 million years (see Fig. 11.7). However, the rate of exposure is not likely to vary greatly in response to changes in atmospheric O_2, so weathering is not the major factor controlling O_2 in the atmosphere. In sum, despite the potential reactivity of O_2, its rate of reaction with reduced compounds is rather slow, and O_2 is a stable component of the atmosphere. The mean residence time of O_2 in the atmosphere is on the order of 4000 years (cf. Fig. 3.5).

Carbon Dioxide

Carbon dioxide is not reactive with other gases in the atmosphere. The concentration of CO_2 is affected by interactions with the Earth's surface, including the reactions of the carbonate–silicate cycle (Fig. 1.4), gas exchange with seawater following Henry's Law (Eq. 2.5), and annual cycles of photosynthesis and respiration by land plants (Fig. 3.6). For the Earth's land surface, our best estimates of plant uptake (60×10^{15} g C/yr; Chapter 5) suggest a mean residence time of about 12.5 years before a hypothetical molecule of CO_2 in the atmosphere is captured by photosynthesis. The annual exchange of CO_2 with seawater, particularly in areas of cold, downwelling water and high productivity (Chapter 9), is about $1.5\times$ as large as the annual uptake of CO_2 by land plants. Both plant and ocean uptake are likely to increase with increasing concentrations of atmospheric CO_2, potentially buffering fluctuations in its concentration. Following Eq. 3.3, the mean residence time for CO_2, determined by the total flux from the atmosphere (the sum of land and ocean uptake), is about 5 years. The carbonate–silicate cycle (Fig. 1.4) also buffers the concentration of CO_2 in the atmosphere, but does not affect the concentration of atmospheric CO_2 significantly in periods of less than 100,000 years. We will compare the relative importance of these processes in more detail in Chapter 11, which examines the global carbon cycle.

The current increase in atmospheric CO_2 is a non-steady-state condition, caused by the combustion of fossil fuels and destruction of land vegetation (Schimel et al. 1995). CO_2 is released by these processes faster than it can be taken up by land vegetation and the sea. If these activities were to cease,

atmospheric CO_2 would return to a steady state, and after several hundred years nearly all of the CO_2 released by humans would reside in the oceans. In the meantime, higher concentrations of CO_2 are likely to cause significant atmospheric warming through the "greenhouse effect" (Fig. 3.2).

Trace Biogenic Gases

Volcanoes are the original source of volatiles in the Earth's atmosphere (Chapter 2) and are a small continuing source of some of the reduced gases (H_2S, H_2, NH_3, CH_4) that are found in the atmosphere today (Table 2.1). These and other trace gases are found at concentrations well in excess of what is predicted from equilibrium geochemistry in an atmosphere with 21% O_2 (Table 3.4). In most cases, the observed atmospheric concentrations are supplied by the biosphere, particularly by microbial activity. Methane is largely produced by anaerobic decomposition in wetlands (Chapters 7 and 11), nitrogen oxides by soil microbial transformations (Chapter 6), carbon monoxide by combustion of biomass and fossil fuels (Chapters 5 and 11), and volatile hydrocarbons, especially isoprene, by vegetation and human industrial activities (Chapter 5). The production of trace gases containing N and S contributes to the global cycling of these elements, which is controlled by the biosphere (Deevey 1970b, Crutzen 1983).

Unlike major atmospheric constituents, many of the trace biogenic gases in the atmosphere are highly reactive, showing short mean residence times

Table 3.4　Some Trace Biogenic Gases in the Atmosphere

Compound	Formula	Concentration (ppb)		Mean residence time	Percentage of sink due to OH
		Expected[a]	Actual[b]		
Carbon compounds					
Methane	CH_4	10^{-148}	1750	9 yr	90
Carbon monoxide	CO	10^{-51}	45–250	60 days	80
Isoprene	$CH_2{=}C(CH_3){-}CH{=}CH_2$		0.2–10.0	<1 day	100
Nitrogen compounds					
Nitrous oxide	N_2O	10^{-22}	311	120 yr	0
Nitric oxides	NO_x	10^{-13}	0.02–10.0	1 day	100
Ammonia	NH_3	10^{-63}	0.08–5.0	5 days	<2
Sulfur compounds					
Dimethylsulfide	$(CH_3)_2S$		0.004–0.06	1 day	50
Hydrogen sulfide	H_2S		<0.04	4 days	100
Carbonyl sulfide	COS	0	0.50	5 yr	22
Sulfur dioxide	SO_2	0	0.02–0.10	3 days	50

[a] Approximate values in equilibrium with an atmosphere containing 21% O_2 (Chameides and Davis 1982).
[b] For short-lived gases, the value is the range expected in remote, unpolluted atmospheres.

and variable concentrations in space and time (Fig. 3.5). Concentrations of these gases in the atmosphere are determined by the balance between local sources and chemical reactions—known as *sinks*—that remove these gases from the atmosphere. Losses from the troposphere are largely driven by oxidation reactions and the capture of the reaction products by rainfall. Currently the concentration of nearly all these constituents is increasing as a result of human activities, suggesting that humans are affecting biogeochemistry at the global level (Rasmussen and Khalil 1986, Mooney et al. 1987).

Despite its abundance in the atmosphere, O_2 is too unreactive to oxidize reduced gases by direct reaction in the atmosphere. However, through a variety of reactions driven by sunlight, small amounts of oxygen are converted to ozone (O_3), and further reactions yield hydroxyl radicals (OH) (Logan 1985, Thompson 1992). Ozone and OH are the primary species that oxidize many of the trace gases to CO_2, HNO_3, and H_2SO_4.

It is important to understand the natural production, occurrence, and reactions of ozone in the atmosphere. Nearly daily we read seemingly contradictory reports of the harmful effects of ozone depletion in the stratosphere and harmful effects of ozone pollution in the troposphere. In each case, human activities are upsetting the natural concentrations of ozone that are critical to atmospheric biogeochemistry.

Most ozone is produced by the reaction of sunlight with O_2 in the stratosphere, as described in the next section. Some of this ozone is transported to the Earth's surface by the mixing of stratospheric and tropospheric air. However, observations of ozone in the smog of polluted cities such as Los Angeles alerted atmospheric chemists to reactions by which ozone is produced in the troposphere (Warneck 1988). When NO_2 is present in the atmosphere it is dissociated by sunlight ($h\nu$),

$$NO_2 + h\nu \rightleftarrows NO + O, \qquad (3.6)$$
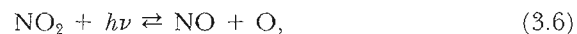
followed by a reaction producing ozone:

$$O + O_2 \rightleftarrows O_3. \qquad (3.7)$$

This reaction sequence is an example of a *homogeneous gas reaction,* i.e., a reaction between atmospheric constituents that are all in the gaseous phase. The net reaction is

$$NO_2 + O_2 \rightleftarrows NO + O_3, \qquad (3.8)$$
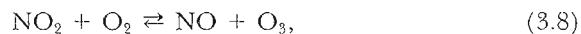
which is an equilibrium reaction, so high concentrations of NO tend to drive the reaction backward. Seinfeld (1989) indicates that the concentration of O_3 is determined by

$$O_3 \text{ (ppm)} = 0.021 \ [NO_2]/[NO]. \qquad (3.9)$$

Both NO_2 and NO, collectively known as NO_x, are found in polluted air, in which they are derived from industrial and automobile emissions.[2] Small concentrations of both of these constituents are also found in the natural atmosphere, where they are derived from forest fires, lightning discharges, and microbial processes in the soil (Chapter 6). Thus, the production of ozone from NO_2 has probably always occurred in the troposphere, and the present-day concentrations of tropospheric ozone have simply increased as industrial emissions have raised the concentration of NO_2 and other precursors to O_3 formation (Volz and Kley 1988, Hough and Derwent 1990, Thompson 1992).
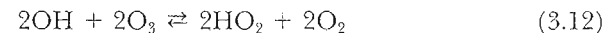
Ozone is subject to further photochemical reaction,

$$O_3 + h\nu \rightleftarrows O_2 + O(^1D), \qquad (3.10)$$
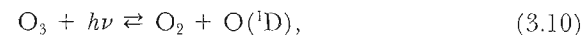
where $h\nu$ is ultraviolet light with wavelengths <310 nm and $O(^1D)$ is an excited atom of oxygen. Reaction of $O(^1D)$ with water yields hydroxyl radicals:

$$O(^1D) + H_2O \rightleftarrows 2OH. \qquad (3.11)$$

Hydroxyl radicals may further react to produce HO_2 and H_2O_2,

$$2OH + 2O_3 \rightleftarrows 2HO_2 + 2O_2 \qquad (3.12)$$

$$2HO_2 \rightleftarrows H_2O_2 + O_2, \qquad (3.13)$$

which are other short-lived oxidizing compounds in the atmosphere (Thompson 1992).

Hydroxyl radicals exist with a mean concentration of 9.7×10^5 molecules/cm^3 (Prinn et al. 1995). The highest concentrations occur in daylight (Platt et al. 1988, Mount 1992) and at tropical latitudes, where the concentration of water vapor is greatest (Hewitt and Harrison 1985). The average OH radical persists only for a few seconds in the atmosphere, so concentrations of OH are highly variable. Local concentrations can be measured using beams of laser-derived light, which is absorbed as a function of the number of OH radicals in its path (Dorn et al. 1988, Mount 1992). The global mean concentration of OH radicals must be estimated indirectly. For this purpose, atmospheric chemists rely on methylchloroform (trichloroethane), a gas that is known to result only from human activity. Methylchloroform has a mean residence time of about 4.8 years (Prinn et al.

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[2] NO_x (pronounced "knox") refers to the sum of NO + NO_2; NO_y is used to refer to the sum of NO_x plus all other oxidized forms of nitrogen [e.g., HNO_3 and peroxyacetyl nitrate (PAN)] in the atmosphere.
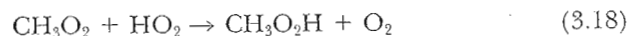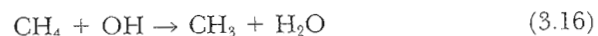
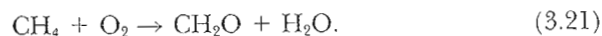1995), so it is well mixed in the atmosphere. In the laboratory, it reacts with OH,

$$OH + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3, \tag{3.14}$$
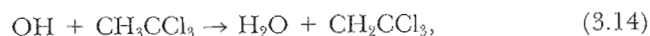
and the equilibrium constant, K, for the reaction can be carefully measured as 0.85×10^{-14} cm^3 molecule^{-1} sec^{-1} at 25°C (Talukdar et al. 1992). Then, knowing K and the concentrations of CH_3CCl_3 and CH_2CCl_3 in a gas sample taken from the troposphere, one can calculate the concentration of OH that must be present; viz.,

$$OH = \frac{[CH_2CCl_3]}{K\,[CH_3CCl_3]}. \tag{3.15}$$

Hydroxyl radicals are the major source of oxidizing power in the troposphere. For example, in an unpolluted atmosphere, hydroxyl radicals destroy methane in a series of reactions,
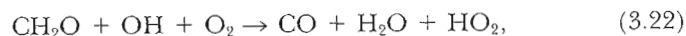
$$CH_4 + OH \rightarrow CH_3 + H_2O \tag{3.16}$$

$$CH_3 + O_2 \rightarrow CH_3O_2 \tag{3.17}$$

$$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2 \tag{3.18}$$

$$CH_3O_2H \rightarrow CH_3O + OH \tag{3.19}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2, \tag{3.20}$$

for which the net reaction is

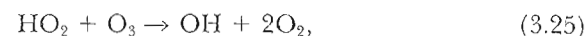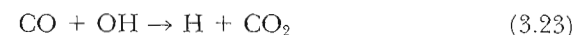$$CH_4 + O_2 \rightarrow CH_2O + H_2O. \tag{3.21}$$

Note that the hydroxyl radical has acted as a catalyst to initiate the oxidation of CH_4 and its by-products by O_2. Other volatile hydrocarbons, known as nonmethane hydrocarbons (NMHCs), released from vegetation (Lamb et al. 1987a, Guenther et al. 1994) and human activities (Piccot et al. 1992) are also oxidized through this pathway (Altshuller 1991).
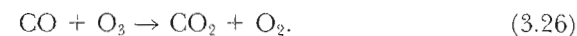
The formaldehyde that is produced in these reactions is further oxidized to carbon monoxide,

$$CH_2O + OH + O_2 \rightarrow CO + H_2O + HO_2, \tag{3.22}$$

and CO is oxidized by OH to produce CO_2,

$$CO + OH \rightarrow H + CO_2 \tag{3.23}$$

$$H + O_2 \rightarrow HO_2 \tag{3.24}$$

$$HO_2 + O_3 \rightarrow OH + 2O_2, \tag{3.25}$$

for which the net reaction is,

$$CO + O_3 \rightarrow CO_2 + O_2. \tag{3.26}$$

Thus, OH acts to scrub the atmosphere of a wide variety of reduced carbon gases, ultimately oxidizing their carbon atoms to carbon dioxide.

Hydroxyl radicals also react with NO_2 and SO_2 in homogeneous gas reactions:

$$NO_2 + OH \rightarrow HNO_3 \tag{3.27}$$
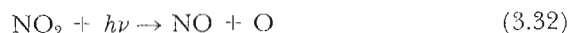
$$SO_2 + OH \rightarrow HSO_3. \tag{3.28}$$

The reaction with NO_2 is very fast, and it produces nitric acid that is removed from the atmosphere by a heterogeneous interaction with raindrops. The reaction with SO_2 is much slower, accounting for the long-distance transport of SO_2 as a pollutant in the atmosphere (Rodhe et al. 1981). HSO_3 is eventually converted to SO_4^{2-} which is removed from the atmosphere by rainfall (Warneck 1988). SO_2 is also removed from the atmosphere by reaction with H_2O_2 in raindrops (Eqs. 3.12 and 3.13), forming H_2SO_4 (Chandler et al. 1988). Similarly, hydrogen sulfide (H_2S) and dimethylsulfide ($CH_3)_2S$, released from anaerobic soils (Chapter 7) and the ocean surface (Chapter 9), are removed by reactions with OH and other oxidizing compounds, eventually leading to the deposition of H_2SO_4 (Toon et al. 1987). Thus, OH radicals cleanse the atmosphere of trace N and S gases by converting them to "acid anions" (NO_3^-, SO_4^{2-}) in the atmosphere.
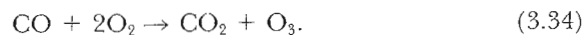
The vast majority of OH radical in the atmosphere is consumed in reactions with CO and CH_4. Although the concentration of methane is much higher than that of carbon monoxide in unpolluted atmospheres, the reaction of OH with CO is much faster. The speed of reaction of CO with OH accounts for the short mean residence time of CO in the atmosphere (Table 3.4). The mean residence time for methane is much longer, accounting for its more uniform distribution in the atmosphere (Fig. 3.5). One explanation for the current increase in methane in the atmosphere is that the anthropogenic release of CO consumes OH radicals previously available

for the oxidation of methane (Khalil and Rasmussen 1985), but other measurements suggest that OH concentrations have remained fairly constant over the last decade (Prinn et al. 1995).

In unpolluted atmospheres, all these reactions consume OH. In "dirty" atmospheres, a different set of reactions pertains, in which there can be a net *production* of O_3, and thus OH. When the concentration of NO is >3–8 ppt (= dirty), the oxidation of carbon monoxide begins by reaction with hydroxyl radical and proceeds as follows (Crutzen and Zimmermann 1991):

$$CO + OH \rightarrow CO_2 + H \tag{3.29}$$

$$H + O_2 \rightarrow HO_2 \tag{3.30}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{3.31}$$

$$NO_2 + h\nu \rightarrow NO + O \tag{3.32}$$

$$O + O_2 \rightarrow O_3. \tag{3.33}$$

The net reaction is

$$CO + 2O_2 \rightarrow CO_2 + O_3. \tag{3.34}$$

Similarly, the oxidation of methane in the presence of high concentrations of NO proceeds through a large number of steps, yielding a net reaction of

$$CH_4 + 4O_2 \rightarrow CH_2O + H_2O + 2O_3. \tag{3.35}$$

Crutzen (1988) points out that the oxidation of one molecule of CH_4 could consume up to 3.5 molecules of OH and 1.7 molecules of O_3 when the NO concentration is low, whereas it would yield a net gain of 0.5 OH and 3.7 O_3 in polluted environments (see also Wuebbles and Tamaresis 1993). Although they were first discovered in urban areas, the reactions of "dirty" atmospheres are likely to be relatively widespread in nature. NO is produced naturally by soil microbes (Chapter 6) and forest fires. Concentrations of NO >3–8 ppt are present over most of the Earth's land surface (Torres and Buchan 1988, Chameides et al. 1992). In the presence of NO, oxidation of volatile hydrocarbons emitted from vegetation, and CO emitted from both vegetation and forest fires, can account for unexpectedly high concentrations of O_3 over rural areas of the southeastern United States

(Fig. 3.8) (Jacob et al. 1993, Kleinman et al. 1994) and in remote tropical regions (Crutzen et al. 1985, Zimmerman et al. 1988, Jacob and Wofsy 1990, M.O. Andreae et al. 1994). In urban areas, where the concentration of NO_x is especially high due to industrial pollution, effective control of atmospheric O_3 levels may also depend on the regulation of volatile hydrocarbons (Chameides et al. 1988, Seinfeld 1989).

Although these reactions are both numerous and interrelated, further complexity stems from the presence of clouds, which promote heterogeneous interactions with water droplets in the atmosphere. Lelieveld and Crutzen (1991) suggest that when water droplets are present, there is no gain of OH radical in the atmosphere, even in the presence of NO_2 (Eqs. 3.8, 3.10, and 3.11), because O_3 preferentially reacts with H_2O_2 in cloud drops:

$$O_3 + H_2O_2 \rightleftarrows 2O_2 + H_2O. \tag{3.36}$$
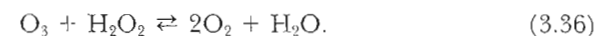
Clouds fill only about 15% of the atmosphere, but they may significantly reduce the global oxidation capacity of the troposphere (Lelieveld and Crutzen 1990).

Understanding changes in the concentration of OH and other oxidizing species in the atmosphere is critical to predicting future trends in the concentration of trace gases, such as CH_4, that potentially contribute to greenhouse warming. Some models predict an increase in OH (Prinn et al. 1992), and O_3 (Isaksen and Hov 1987, Hough and Derwent 1990, Thompson 1992) in the atmosphere as a result of increasing human emissions of NO, creating dirty atmospheric conditions over much of the planet. Indeed, measurements near Paris in the late 1800s indicate lower concentrations of tropospheric ozone than today (Volz and Kley 1988). The models are also consistent with indirect observations that the global concentration of OH has remained fairly stable in recent years, despite increasing emissions of reduced gases that should scrub OH from the atmosphere (Prinn et al. 1995).

Some of the O_3 produced over the continents undergoes long-distance transport (Jacob et al. 1993, Parrish et al. 1993, Dickerson et al. 1995),
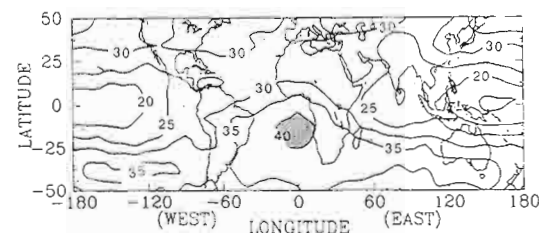

Figure 3.8 Distribution of tropospheric ozone during September through November, for the years 1979 to 1989 as determined by satellite measurements. Note the high concentration downwind (west) of central Africa, where biomass burning is widespread. From Fishman et al. (1990).

resulting in the appearance of O_3 and its by-products at considerable distances from their source. Concentrations of H_2O_2, derived from OH (Eqs. 3.12 and 3.13), have increased in layers of Greenland ice deposited during the last 200 years, suggesting a greater oxidizing capacity in the northern hemisphere as a result of human activities (Fig. 3.9; see also Jiang and Yung 1996). Other workers disagree, finding that local atmospheric conditions, rather than global changes in transport from polluted areas, determine the oxidizing capacity of the atmosphere over much of the planet (Oltmans and Levy 1992, Ayers et al. 1992).

Biogeochemical Reactions in the Stratosphere

Ozone

Ozone is produced in the stratosphere by the disassociation of oxygen atoms that are exposed to short-wave solar radiation. The reaction accounts for most of the absorption of ultraviolet sunlight ($h\nu$) at wavelengths of 180–240 nm and proceeds as follows:

$$O_2 + h\nu \rightarrow O + O \tag{3.37}$$

$$O + O_2 \rightarrow O_3. \tag{3.38}$$

Some ozone from the stratosphere mixes down into the troposphere, where the natural production of O_3 (Eqs. 3.6–3.8) is much slower because less
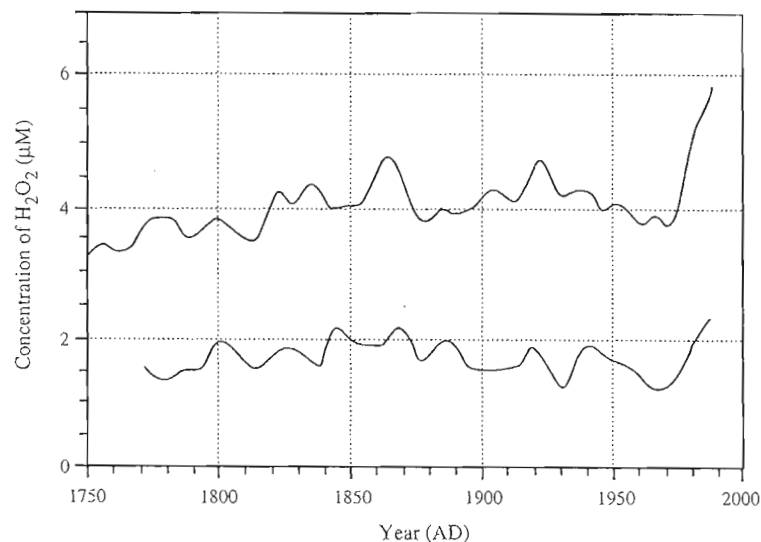
Figure 3.9 Variation in the mean annual H_2O_2 concentration in two cores from the Greenland ice pack over the past 200 years. Modified from Sigg and Neftel (1991).

ultraviolet light is available (Cicerone 1987). The remaining ozone is destroyed by a variety of reactions in the stratosphere. Absorption of ultraviolet light at wavelengths between 200 and 320 nm destroys ozone:

$$O_3 + h\nu \rightarrow O_2 + O \tag{3.39}$$

$$O + O_3 \rightarrow O_2 + O_2. \tag{3.40}$$

This absorption warms the stratosphere (Fig. 3.1) and protects the Earth's surface from the ultraviolet portion of the solar spectrum that is most damaging to living tissue (uvB).

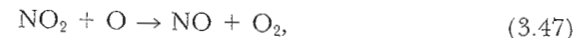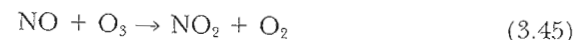Stratospheric ozone is also destroyed by reaction with OH,

$$O_3 + OH \rightarrow HO_2 + O_2 \tag{3.41}$$

$$HO_2 + O_3 \rightarrow OH + 2O_2, \tag{3.42}$$
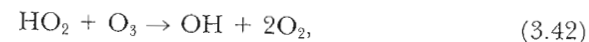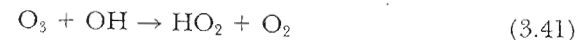
and by reactions stemming from the presence of nitrous oxide (N_2O), which mixes up from the troposphere. Tropospheric N_2O is produced in a variety of ways (Chapters 6 and 12), but it is inert in the lower atmosphere. The only known sink for N_2O is photolysis in the stratosphere. About 80% of the N_2O reaching the stratosphere is destroyed in a reaction producing N_2 (Warneck 1988),

$$N_2O \rightarrow N_2 + O(^1D), \tag{3.43}$$

and about 20% in a reaction with the $O(^1D)$ produced in Eq. 3.43:

$$N_2O + O(^1D) \rightarrow 2NO. \tag{3.44}$$
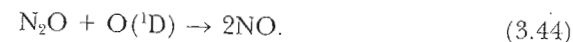
The nitric oxide (NO) produced from N_2O destroys ozone in a series of reactions,

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{3.45}$$

$$O_3 \rightarrow O + O_2 \tag{3.46}$$

$$NO_2 + O \rightarrow NO + O_2, \tag{3.47}$$

for which the net reaction is,

$$2O_3 \rightarrow 3O_2. \tag{3.48}$$

Note that the mean residence time of NO in the troposphere is too short for an appreciable amount to reach the stratosphere, where it might contribute to the destruction of ozone. Nearly all the NO in the stratosphere is produced in the stratosphere from N_2O. Eventually NO_2 is removed from the stratosphere by reacting with OH to produce nitric acid (Eq. 3.27).

Finally, stratospheric ozone is destroyed by chlorine, which acts as a catalyst in the reaction,

$$Cl + O_3 \rightarrow ClO + O_2 \tag{3.49}$$

$$O_3 + h\nu \rightarrow O + O_2 \tag{3.50}$$

$$ClO + O \rightarrow Cl + O_2, \tag{3.51}$$
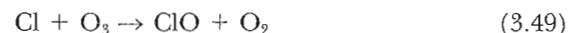
for a net reaction of,

$$2O_3 + h\nu \rightarrow 3O_2. \tag{3.52}$$

Although each Cl produced may destroy many molecules of O_3, Cl is eventually converted to HCl and removed from the stratosphere by downward mixing and heterogeneous interaction with cloud drops in the troposphere (Rowland 1989, Solomon 1990).

The balance between ozone production (Eqs. 3.37 and 3.38) and the various reactions that destroy ozone maintains a steady-state concentration of O_3 of approximately 7×10^{18} molecules/m^3, peaking at 30 km altitude (Cicerone 1987). Although the photochemical production of O_3 is greatest at the equator, the density of the ozone layer is thickest at the poles (Cicerone 1987).

Recent measurements suggest that the total density of ozone molecules in the atmospheric column has declined significantly over Antarctica (Fig. 3.10) and perhaps globally (Stolarski et al. 1992, Jones and Shanklin 1995, Bojkov and Fioletov 1995). The decline (0.3%/yr) is unprecedented and represents a perturbation of global biogeochemistry. Destruction of ozone is likely to lead to an increased flux of ultraviolet radiation to the Earth's surface (Correll et al. 1992, Kerr and McElroy 1993) and to lower stratospheric temperatures, which may alter global heat balance (Ramanathan 1988). Greater uvB radiation at the Earth's surface may already be reducing marine production in Antarctic waters (R.C. Smith et al. 1992) and perhaps the reproductive capacity of amphibians worldwide (Blaustein et al. 1994). Because previous, steady-state ozone concentrations were maintained in the face of natural photochemical reactions that produce and consume ozone, attention has focused on disruptions of this balance by human activities (McElroy and Salawitch 1989).
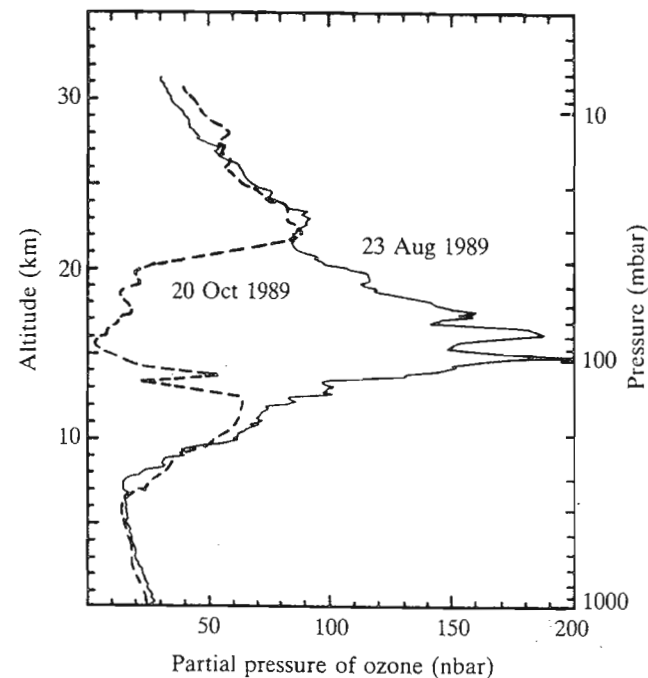
Figure 3.10   Ozone concentrations over McMurdo station, Antarctica in the spring of 1989. Note the near-complete loss of ozone at 15 km altitude (Deshler et al. 1990).

Chlorofluorocarbons (freons), which are produced as aerosol propellants, refrigerants, and solvents, have no known natural source in the atmosphere (Prather 1985). These compounds are chemically inert in the troposphere, so they eventually mix into the stratosphere where they are decomposed by photochemical reactions producing active chlorine (Molina and Rowland 1974, Rowland 1989, 1991),

$$CCl_2F_2 \rightarrow Cl + CClF_2, \tag{3.53}$$
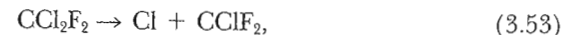
which can destroy ozone by the reactions of Eqs. 3.49 to 3.51. These reactions are greatly enhanced in the presence of ice particles, which accounts for the first observations of the O_3 "hole" in the springtime over Antarctica (Farman et al. 1985, Solomon et al. 1986). In a dry atmosphere, ClO reacts with NO_2 to form $ClONO_2$, an inactive compound that removes both gases from O_3 destruction. In the presence of ice clouds, $ClONO_2$ breaks down,

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \tag{3.54}$$

$$Cl_2 + h\nu \rightarrow 2Cl, \tag{3.55}$$
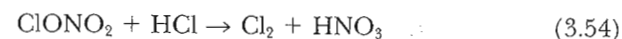
producing active chlorine for ozone destruction (Molina et al. 1987, Solomon 1990). Significantly, during the last 40 years, levels of active chlorine have increased in a mirror image to the loss of ozone from the stratosphere (Fig. 3.11).

The relative importance of chlorofluorocarbons versus natural sources of chlorine in the stratosphere is apparent in a global budget for atmospheric chlorine (Fig. 3.12). Seasalt aerosols are the largest natural source of chlorine in the troposphere, but they have such a short mean residence time that they do not contribute Cl to the stratosphere. There is also no good reason to suspect that they have increased in abundance in the last few decades. Similarly, industrial emissions of HCl are rapidly removed from the troposphere by rainfall. Especially violent volcanic eruptions can inject gases directly into the stratosphere, sometimes adding to stratospheric Cl (Johnston 1980, Mankin and Coffey 1984). However, in most cases only a small amount of Cl reaches the stratosphere, because various processes remove HCl from the rising volcanic plume (Tabazadeh and Turco 1993). After the Mt. Pinatubo eruption, which released 4.5×10^{12} g of HCl, stratospheric Cl increased by <1% (Mankin et al. 1992). The only significant natural source of Cl in the stratosphere stems from the production of methylchloride by marine algae (Wuosmaa and Hager 1990), higher plants
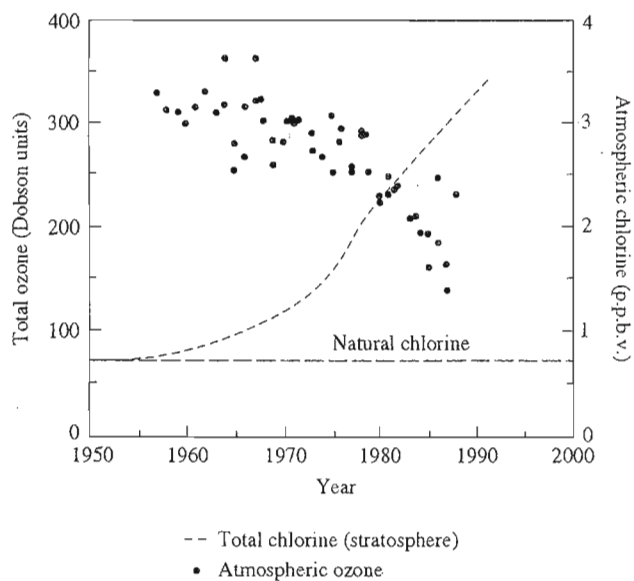
Figure 3.11 The decline in atmospheric O_3 (●) over Antarctica since 1958 corresponds to an increase in chlorine (—) in the stratosphere. The customary unit for the total number of ozone molecules in an atmospheric column, the Dobson, is equivalent to 2.69×10^{16} molecules/cm² of the Earth's surface. Modified from Solomon (1990).
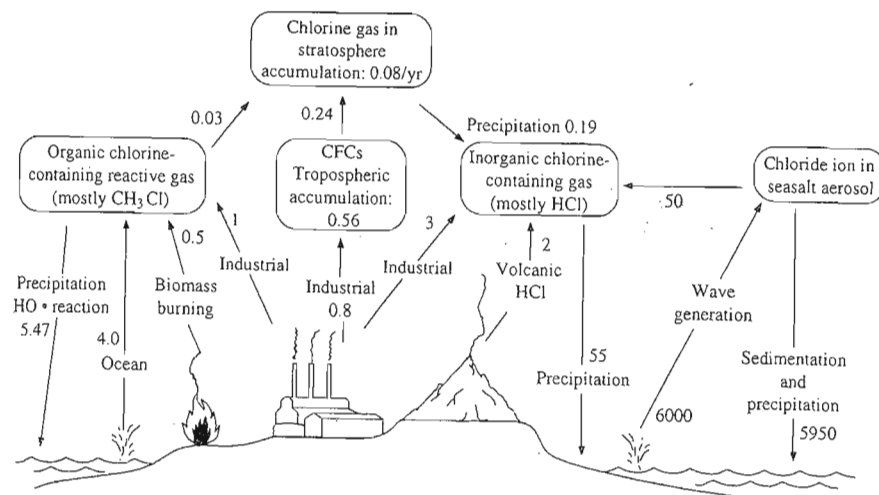
Figure 3.12 A global budget for Cl in the troposphere and the stratosphere. All data are given in 10^{12} g Cl/yr. Modified from Graedel and Crutzen (1993) and Graedel and Keene (1995).

(Saini et al. 1995), and forest fires (Crutzen et al. 1979, Laursen et al. 1992, Rudolph et al. 1995). Methylchloride has a mean residence time of about 1.8 years in the atmosphere, so a small portion of CH_3Cl mixes into the stratosphere.

In the global budget, the relatively small industrial production of chlorofluorocarbons is the dominant source of Cl delivered to the stratosphere (Fig. 3.12; Russell et al. 1996). Increasing concentrations of these compounds have been strongly implicated in ozone destruction (Rowland 1989). Happily, with the advent of the Montreal protocol, which limits the use of these compounds worldwide, there is already some evidence that the growth rate of these compounds in the atmosphere is slowing (Elkins et al. 1993).

Similar reactions are possible with compounds containing bromine; in fact, Br compounds may be even more potent in the destruction of stratospheric O_3 than Cl (Wennberg et al. 1994). Industry is a large source of methylbromide (CH_3Br), which is used as an agricultural fumigant (Yagi et al. 1995). Bromoform ($CHBr_3$) produced by marine algae (Sturges et al. 1992, Manley et al. 1992) and methylbromide by biomass burning (Manö and Andreae 1994) also contribute to the atmospheric Br budget. Sinks of CH_3Br include uptake by the oceans (Lobert et al. 1995, Anbar et al. 1996) and soils (Shorter et al. 1995). Concentrations of methylbromide in the atmosphere are increasing at about 3%/yr (Khalil et al. 1993a). The global budget of CH_3Br and its mean residence time (0.8–2 years) in the atmosphere are poorly known, but some CH_3Br may persist long enough to reach the stratosphere, where it can lead to ozone destruction. Among

other halogen-containing gases, the lifetimes of methyliodide produced by marine phytoplankton (Campos et al. 1996) and various inorganic fluoride compounds are too short for appreciable mixing into the stratosphere. Indeed, the observed increase of fluoride in the stratosphere appears solely due to the presence of chlorofluorocarbons, and it is an independent verification of their destruction in the stratosphere by ultraviolet light (Zander et al. 1994).

Satellite observations have greatly aided our understanding of changes in stratospheric ozone. The loss of ozone from the atmosphere has been monitored since 1979 by the Total Ozone Mapping Satellite (TOMS) that records the abundance of O_3 in a column extending from the bottom to the top of the atmosphere (Gleason et al. 1993). TOMS showed that the loss of ozone accelerated in the presence of stratospheric aerosols produced by the Pinatubo volcano (Herman et al. 1993, Brasseur and Granier 1992). Recently, the Upper Atmosphere Research Satellite (UARS) has observed ozone depletions over the Arctic apparently by similar processes as at the South Pole (Waters et al. 1993, Brune et al. 1991, Manney et al. 1994).

Stratospheric Sulfur Compounds

Sulfate aerosols in the stratosphere are important to the albedo of the Earth (Warneck 1988). A layer of sulfate aerosols, known as the Junge layer, is found in the stratosphere at about 20–25 km altitude. Its origin is twofold. Large volcanic eruptions can inject SO_2 into the stratosphere, where it is oxidized to sulfate (Eq. 3.28). Large eruptions have the potential to increase the abundance of stratospheric sulfate by 100-fold (Arnold and Bührke 1983, Hofmann and Rosen 1983), and the sulfate aerosols persist in the stratosphere for several years, cooling the planet (Minnis et al. 1993, McCormick et al. 1995). During periods without volcanic activity, the dominant source of stratospheric sulfate is carbonyl sulfide (COS) that mixes up from the troposphere, where it originates from a variety of sources (Chapter 13). Most sulfur gases are so reactive that they do not reach the stratosphere, but COS has a mean residence time of about 5 years in the atmosphere (Table 3.4).

Carbonyl sulfide that reaches the stratosphere is oxidized by photolysis, forming sulfate aerosols that contribute to the Junge layer (Chin and Davis 1993). Eventually, these aerosols are removed from the stratosphere by downward mixing of stratospheric air. There is some evidence that the column density of sulfate aerosols in the upper atmosphere has increased during the last few decades (Hofmann 1990). The increase in stratospheric SO_4 may result from an increasing use of high-altitude aircraft (Hofmann 1991) and other human perturbations of the global sulfur budget. Estimated sources of COS exceed known sinks (Chin and Davis 1993), but there is no observable increase in COS globally (Rinsland et al. 1992).

Models of the Atmosphere and Global Climate

A large number of models have been developed to explain the physical properties and chemical reactions in the atmosphere. When these models attempt to predict the characteristics in a single column of the atmosphere, they are known as one-dimensional (1D) and radiative-convective models. For example, Figure 3.2 is a simple 1D model for the greenhouse effect, which assumes that the behavior of the Earth's atmosphere can be approximated by average values applied to the entire surface. Two-dimensional models (2D) can be developed using the vertical dimension and a single horizontal dimension (e.g., latitude) to examine the change in atmospheric characteristics across a known distance of the Earth's surface (e.g., Brasseur and Hitchman 1988, Hough and Derwent 1990). On a regional scale these are particularly useful in following the fate of pollution emissions (e.g., Rodhe et al. 1981). Three-dimensional models (3D) attempt to follow the fate of particular parcels of air as they move both horizontally and vertically in the atmosphere. Dynamic 3D models are known as *general circulation models* (GCMs) for the globe (Fig. 3.13).

IN THE ATMOSPHERIC COLUMN

Vertical exchange between levels

Wind vectors
Humidity
Clouds
Temperature
Height

AT THE SURFACE
Ground temperature, water and energy fluxes

Horizontal exchange between columns

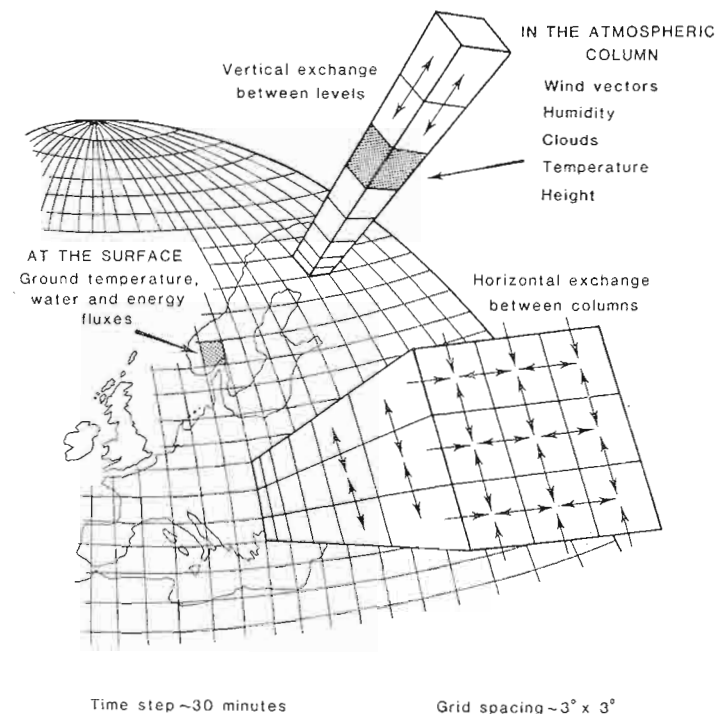Time step ~30 minutes   Grid spacing ~3° x 3°

Figure 3.13 Conceptual structure of a dynamic, three-dimensional general circulation model for the Earth's atmosphere, indicating the variables that must be included for a global model to function properly. From Henderson-Sellers and McGuffie (1987).

Many models are constructed to include both chemical reactions and physical phenomena, such as the circulation of the atmosphere due to temperature differences. Chemical transformations are parameterized using the rate and equilibrium coefficients for the reactions that we have examined in this chapter. Because there are a large number of reactions, most of these models are quite complex (e.g., Logan et al. 1981, Isaksen and Hov 1987, Lelieveld and Crutzen 1990), but they give useful predictions of future atmospheric composition when the input of several constituents is changing simultaneously.

Nearly all models suggest that substantial warming of the atmosphere (1.5 to 5.5°C) will accompany increasing concentrations of CO_2, N_2O, CH_4, and chlorofluorocarbons (Houghton et al. 1990). The warming results from the absorption of infrared (heat) radiation emitted from the surface of the Earth (Fig. 3.2). Warming will be greatest near the poles, where there is normally the greatest net loss of infrared radiation relative to incident sunlight (Manabe and Wetherald 1980). Presumably the oceans will warm more slowly than the atmosphere, but eventually warmer ocean waters will allow greater rates of evaporation, increasing the circulation of water in the global hydrologic cycle (Graham 1995; see also Chapter 10). Water vapor also absorbs infrared radiation, so it is likely to further accelerate the potential greenhouse effect (Raval and Ramanathan 1989, Rind et al. 1991). Thus, most models predict that higher concentrations of CO_2 and other trace gases in the atmosphere will make the Earth a warmer and more humid planet (Chapter 10).

Differential warming of the atmosphere will change global patterns of precipitation and evapotranspiration (Manabe and Wetherald 1986, Rind et al. 1990), causing substantial changes in the climate of most areas outside the tropics. How rapidly these changes in climate occur will be moderated by the thermal buffer capacity of the world's oceans, which can absorb enormous quantities of heat. However, the magnitude of the potential changes in climate is much larger than most changes in global climate during the last 2 million years. Although it is difficult to demonstrate any trend toward global warming from satellite observations of the planet (Spencer and Christy 1990), the global record from local weather stations suggests that warming is already in progress (Fig. 3.14). Many climatologists believe that we will see an unambiguous validation of this global experiment, in excess of normal climatic oscillations, before the end of this century (Hansen et al. 1981, Ramanathan 1988, Schneider 1994, Santer et al. 1996).

Of course, such predictions are not made without disagreement (Luther and Cess 1985). One of the largest uncertainties in climate models is the effect of tropospheric aerosols, particularly sulfate aerosols, which are reflective to incoming solar radiation. Through soil disturbance, humans have increased the abundance of soil dusts that are distributed globally by
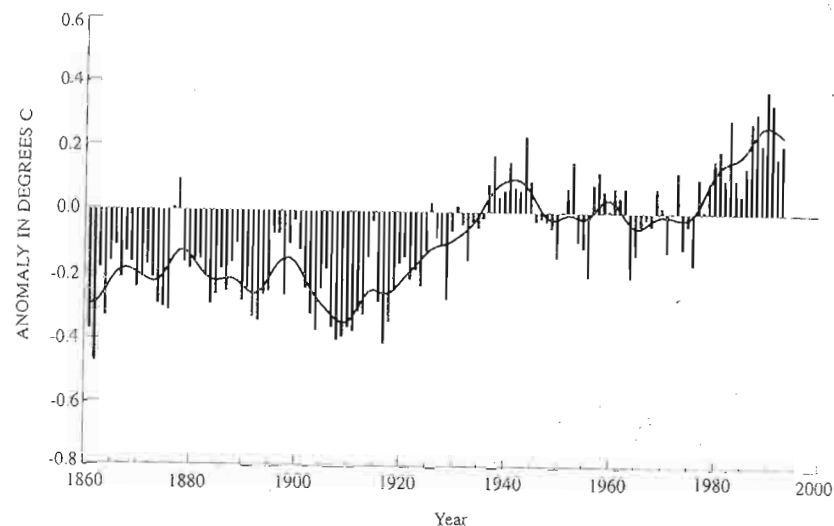
Figure 3.14 Mean global temperature, derived from measurements made on land and at sea, for the period 1861–1993, shown as deviations from the mean in the interval from 1951 to 1980. From Hadley Center for Climate Prediction and Research, United Kingdom.

wind (Tegen et al. 1996, Sokolik and Toon 1996). Despite pollution controls, sulfate aerosols have also increased in many areas of the troposphere due to human industrial activities (Langner et al. 1992). In addition to their direct effect on albedo, these aerosols increase the abundance of clouds, which amplify the reflectivity of the planet (Charlson et al. 1992). Global climate models that include the effects of aerosols produce the closest agreement with the observed trends in global temperature over the last several decades (Mitchell et al. 1995). In these models, the reflectivity of low clouds slows the rate of warming of the Earth that is expected as a result of increasing concentrations of greenhouse gases (Ramanathan et al. 1989).

Incoming solar radiation delivers about 340 W/m^2 to the Earth (Fig. 3.2). The natural greenhouse effect warms the planet about 33°C by trapping 153 W/m^2 of outgoing radiation (Ramanathan 1988). The greenhouse effect due to increasing concentrations of atmospheric trace gases currently adds about 2.1 W/m^2 to the natural greenhouse, while increasing clouds may reflect 0.3 W/m^2 to outer space (Kiehl and Briegleb 1993). It is interesting to note that aerosol concentrations were higher (De Angelis et al. 1987, Petit et al. 1990) and CO_2 concentrations were lower (Fig. 1.4) during the last glacial period, but the cause and effect relation of these observations is unclear.

Atmospheric Deposition

Processes

Elements of biogeochemical interest are deposited on the Earth's surface as a result of rainfall, dry deposition (sedimentation), and the direct absorption of gases. The importance of each of these processes differs for different regions and for different elements (Gorham 1961). Over time, cumulative deposition from the atmosphere accounts for a large fraction of the nitrogen and sulfur that is contained in terrestrial ecosystems (Chapter 6).

The chemical composition of rainfall has received great attention, as a result of widespread concern about dissolved constituents that lead to "acid rain." The dissolved constituents in rainfall are often separated into two fractions. The *rainout* component consists of constituents derived from cloud processes, such as the nucleation of raindrops. The *washout* component is derived from below cloud level, by scavenging of aerosol particles and the dissolution of gases in raindrops as they fall (Brimblecombe and Dawson 1984, Shimshock and de Pena 1989). The relative contribution of these fractions varies depending upon the length of the rainstorm. As washout cleanses the lower atmosphere, the content of dissolved materials in rainfall declines. Thus, the concentration of dissolved constituents in precipitation is inversely related to the rate of precipitation (Gatz and Dingle 1971) and to the total volume collected (Likens et al. 1984, Lesack and Melack 1991, Minoura and Iwasaka 1996). The concentration of dissolved constituents also varies inversely as a function of mean raindrop size (Georgii and Wötzel 1970). This inverse relation explains why extremely high concentrations of dissolved constituents are found in fog waters (Weathers et al. 1986, Waldman et al. 1982). Capture of fog and cloud water by vegetation dominates the deposition of nutrient elements from the atmosphere in some high-elevation and coastal ecosystems (Lovett et al. 1982, Azevedo and Morgan 1974, Waldman et al. 1985, Miller et al. 1993a).

The relative efficiency of scavenging by rainwater is often expressed as the washout ratio:

$$\text{Washout} = \frac{\text{Ionic concentration in rain (mg/liter)}}{\text{Ionic concentration in air (mg/m}^3)}. \qquad (3.56)$$

With units of m^3/liter, this ratio gives an indication of the volume of atmosphere cleansed by each liter of rainfall. Large ratios are generally found for ions that are derived from relatively large aerosols or from highly water-soluble gases in the atmosphere. Snowfall is generally less efficient at scavenging than rainfall.

The deposition of nutrients by precipitation is often called wetfall; dryfall is the result of gravitational sedimentation of particles during periods without rain (Hidy 1970). Dryfall of dusts in areas downwind of arid lands is

often spectacular; Liu et al. (1981) reported 100 g m^{-2} hr^{-1} of dustfall in Beijing, China, as a result of a single dust storm on 18 April 1980. Enormous deposits of wind-deposited soil, known as loess, were laid down during glacial periods, when large areas of semiarid land were subject to wind erosion (Pye 1987, Simonson 1995). Today, various elements necessary for plant growth are released by chemical weathering of soil minerals in these deposits (Chapter 4).

The dryfall received in many areas contains a significant fraction that is easily dissolved by soil waters and immediately available for plant uptake. Despite the high rainfall found in the southeastern United States, Swank and Henderson (1976) reported that 19–64% of the total annual atmospheric deposition of ions such as Ca, Na, K, and Mg, and up to 89% of the deposition of P, was derived from dryfall. In many forests, the majority of the annual uptake and circulation of these elements in vegetation may be derived from the atmosphere, even though rock weathering dominates overall inputs to the ecosystem and the content of runoff waters (Miller et al. 1993). Dryfall inputs of P may assume special significance to plant growth in areas where the release of P from rock weathering is very small (Newman 1995). Dry deposition contributes about 30 to 60% of the deposition of sulfur in New Hampshire (Likens et al. 1990, cf. Tanaka and Turekian 1995) and 30% of the total input of acidic substances in southern Canada (Sirois and Barrie 1988).

Dryfall is often measured in collectors that are designed to close during rainstorms. When open to the atmosphere, these instruments capture particles that are deposited vertically, known as sedimentation. In natural ecosystems, dryfall is also derived by the capture of particles on vegetation surfaces. When vegetation captures particles that are moving horizontally in the airstream, the process is known as impaction (Hidy 1970). Impaction is a particularly important process in the capture of seasalt aerosols near the ocean (Art et al. 1974, Potts 1978).

In addition to the uptake of CO_2 in photosynthesis, vegetation also absorbs N- and S-containing gases directly from the atmosphere (Whelpdale and Shaw 1974, Hosker and Lindberg 1982, Lindberg et al. 1986). Uptake of pollutant SO_2 and NO_2 by vegetation is particularly important in humid regions (McLaughlin and Taylor 1981, Rondón and Granat 1994), where plant stomata remain open for long periods. Lovett and Lindberg (1986, 1993) found that uptake of HNO_3 vapor accounted for 75% of the annual dry deposition of nitrogen (4.8 kg/ha) in a deciduous forest in Tennessee, and dry deposition was nearly half of the total annual deposition of nitrogen from the atmosphere. Vegetation also can be a source (Farquhar et al. 1979, Heckathorn and DeLucia 1995) or a sink for atmospheric NH_3 (Denmead et al. 1976), depending on the ambient concentration in the atmosphere (Langford and Fehsenfeld 1992, Sutton et al. 1993).

Total capture of dry particles and gases by land plants is difficult to measure. When rainfall is collected inside a forest, it contains materials that have been deposited on the plant surfaces, but also large quantities of elements that are derived from the plants themselves (Parker 1983, Chapter 6). Artificial collectors (surrogate surfaces) are often used to approximate the capture by vegetation (White and Turner 1970, Vandenberg and Knoerr 1985, Lindberg and Lovett 1985). The capture on known surfaces can be compared to the airborne concentrations to calculate a deposition velocity (Sehmel 1980):

$$\text{Deposition Velocity} = \frac{\text{Rate of dryfall } (\text{mg}/\text{cm}^2/\text{sec})}{\text{Concentration in air } (\text{mg}/\text{cm}^3)}. \quad (3.57)$$

In units of cm/sec, these velocities can be multiplied by the estimated surface area of vegetation (cm^2) and the concentration in the air to calculate total deposition for an ecosystem. For example, Lovett and Lindberg (1986) used a deposition velocity of 2.0 cm/sec to calculate a nitrogen deposition of 3.0 kg/ha/yr in a forest with a leaf area index of 5.8 m^2/m^2 and an ambient concentration of 0.82 μg N m^{-3} in the form of nitric acid vapor. It is often unclear if deposition velocities measured using artificial surfaces apply to natural surfaces (e.g., bark), and accurate estimates of the surface area of vegetation are difficult (Whittaker and Woodwell 1968). Clearly, further work on dry deposition is needed (Lovett 1994).

Atmospheric deposition on the surface of the sea is often estimated from collections of wetfall and dryfall on remote islands (Duce et al. 1991). The surface of the sea can also exchange gases with the atmosphere (Liss and Slater 1974), often acting as a sink for atmospheric SO_2 (Beilke and Lamb 1974) and a source of NH_3 (Quinn et al. 1987, 1988).

Regional Patterns

Regional patterns of rainfall chemistry in the United States reflect the relative importance of different constituent sources and deposition processes in different areas (Munger and Eisenreich 1983; Fig. 3.15). Coastal areas are dominated by atmospheric inputs from the sea, with large depositions of Na, Mg, Cl, and SO_4 that are the major constituents in the seasalt aerosol (Junge and Werby 1958, Hedin et al. 1995). Areas of arid and semiarid land show high concentrations of soil-derived constituents, such as Ca (Young et al. 1988, Sequeira 1993, Gillette et al. 1992). Areas downwind of regional pollution show exceedingly low pH and high concentrations of SO_4^{2-} and NO_3^- (Schwartz 1989, Ollinger et al. 1993).

The ratio among ionic constituents in rainfall can be used to trace their origin. Except in unusual circumstances nearly all the sodium (Na) in rainfall is derived from the ocean. When magnesium is found in a ratio of 0.12 with respect to Na—the ratio in seawater (Table 9.1)—one may pre-

sume that the Mg is also of marine origin. In the southeastern United States, however, Mg/Na ratios in wetfall range from 0.29 to 0.76 (Swank and Henderson 1976). Here the Mg content has increased relative to Na, presumably because the airflow that brings precipitation to this region has crossed the United States, picking up Mg from soil dust and other sources. Schlesinger et al. (1982) used this approach to deduce nonmarine sources of Ca and SO_4 in the rainfall in coastal California (Fig. 3.16).

Iron (Fe) and Al are largely derived from the soil, and ratios of various ions to these elements in soil can be used to predict their expected concentrations in rainfall when soil dust is a major source (Lawson and Winchester 1979, Warneck 1988). High concentrations of Al in dryfall on Hawaii were traced to springtime dust storms on the central plains of China (Parrington et al. 1983). Windborne particles of soil and vegetation contribute significantly to the global transport of trace metals in the atmosphere (Nriagu 1989).

In many areas downwind of pollution, a strong correlation between H^+ and SO_4^{2-} is the result of the production of H_2SO_4 during the oxidation of SO_2 and its dissolution in rainfall (Cogbill and Likens 1974, Gorham et al. 1984, Irwin and Williams 1988). Nitrate (NO_3^-) also contributes to the strong acid content in rainfall (HNO_3). These constituents depress the pH of rainfall below 5.6, which would be expected for water in equilibrium with atmospheric CO_2 (Galloway et al. 1976). Ammonia is a net source of alkalinity in rainwater, since its dissolution produces OH^-:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-. \quad (3.58)$$

Thus, the pH of rainfall is determined by the concentration of strong acid anions that are not balanced by NH_4^+ and Ca^{2+} (from $CaCO_3$), viz. (from Gorham et al. 1984),

$$H^+ = [NO_3^- + 2SO_4^{2-}] - [NH_4^+ + 2Ca^{2+}]. \quad (3.59)$$

Globally, about 22% of the atmosphere's acidity is neutralized by NH_3 (Chapter 13), with a higher proportion in the southern hemisphere where there is less industrial pollution (Savoie et al. 1993). In the eastern United States, the acidity of rainfall is often directly correlated to the concentration of SO_4^{2-}. In the western United States, when high concentrations of SO_4^{2-} are derived from industrial pollution (Epstein and Oppenheimer 1986, Oppenheimer et al. 1985), the rainfall is usually less acidic, because the acid-forming anions have reacted with soil aerosols containing $CaCO_3$ (Young et al. 1988, Reheis and Kihl 1995).

The concentrations of constituents in the Greenland snowpack reflect the changes in the abundance of anthropogenic pollutants due to industrialization in the northern hemisphere (Herron et al. 1977, Mayewski et al.
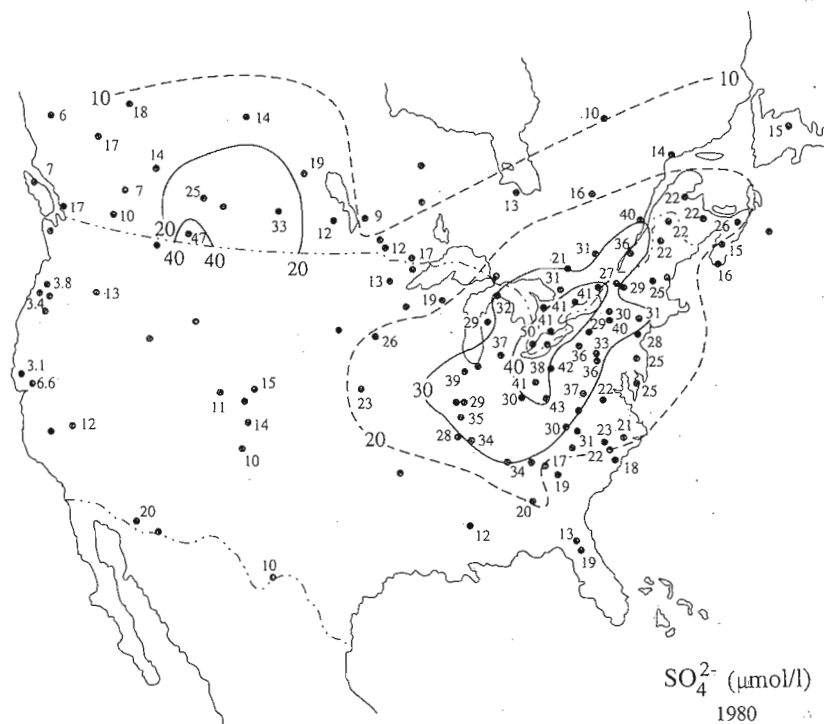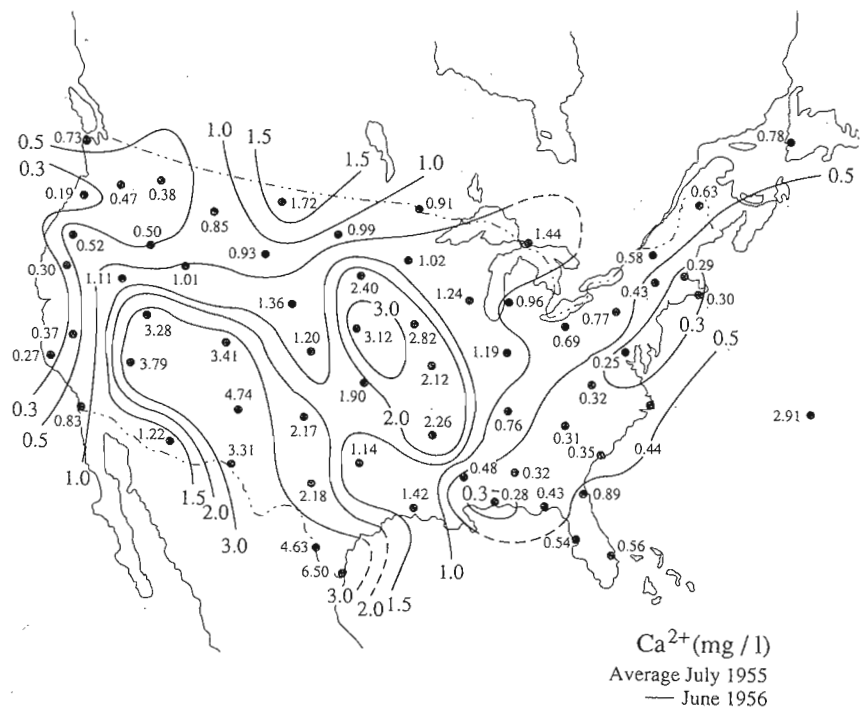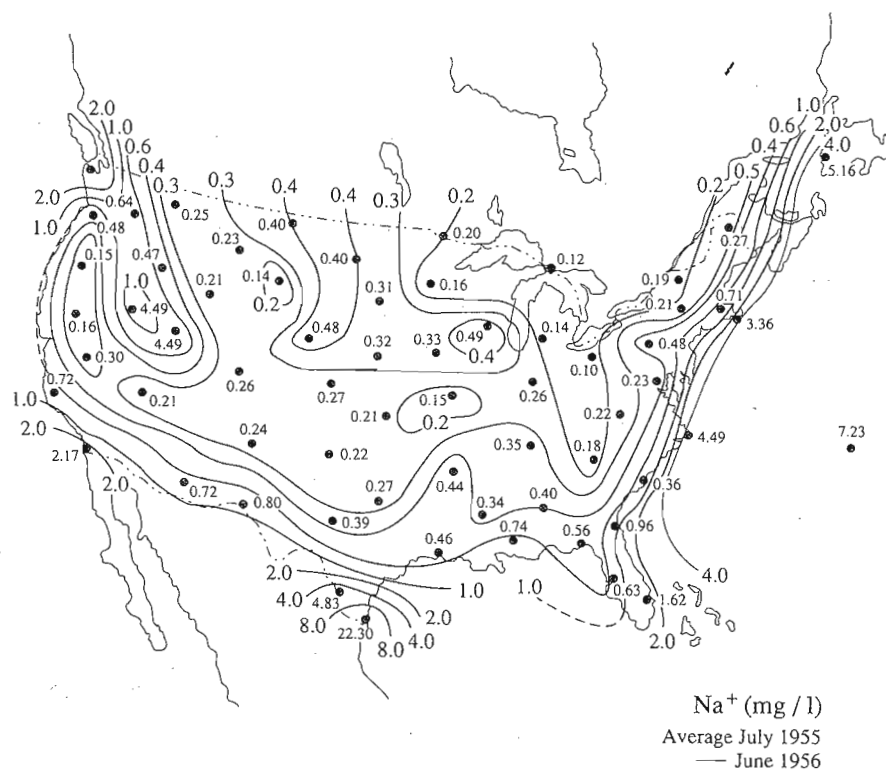
Na$^+$ (mg / l)
Average July 1955
— June 1956

Ca^{2+} (mg / l)
Average July 1955
— June 1956

SO$_4^{2-}$ (μmol/l)
1980

Figure 3.15 (*continued*)

1986, Laj et al. 1992). In recent ice on Greenland, SO$_4$ and NO$_3$ are enriched 3 to 4x over 18th century values. There are no apparent changes in the deposition of these ions in the southern hemisphere as recorded by Antarctic ice (Langway et al. 1994). Similarly, the uppermost sediments in lakes of the northern hemisphere contain higher concentrations of many trace metals, presumably from industrial sources (Galloway and Likens 1979, Swain et al. 1992). Long-term records of precipitation chemistry are rare, but the collections at the Hubbard Brook Ecosystem in central New Hampshire (USA) suggest a recent decline in the concentrations of Pb and SO$_4$ that may reflect improved control of emissions (Likens et al. 1984). Over most of the same period, however, concentrations of cations have also decreased, so the acidity of rainfall shows little change (Hedin et al. 1994).

Figure 3.15 Geographic pattern in the concentration of some major constituents in U.S. precipitation. Na and Cl are from Junge and Werby (1958) and SO$_4$ is modified from Barrie and Hales (1984).
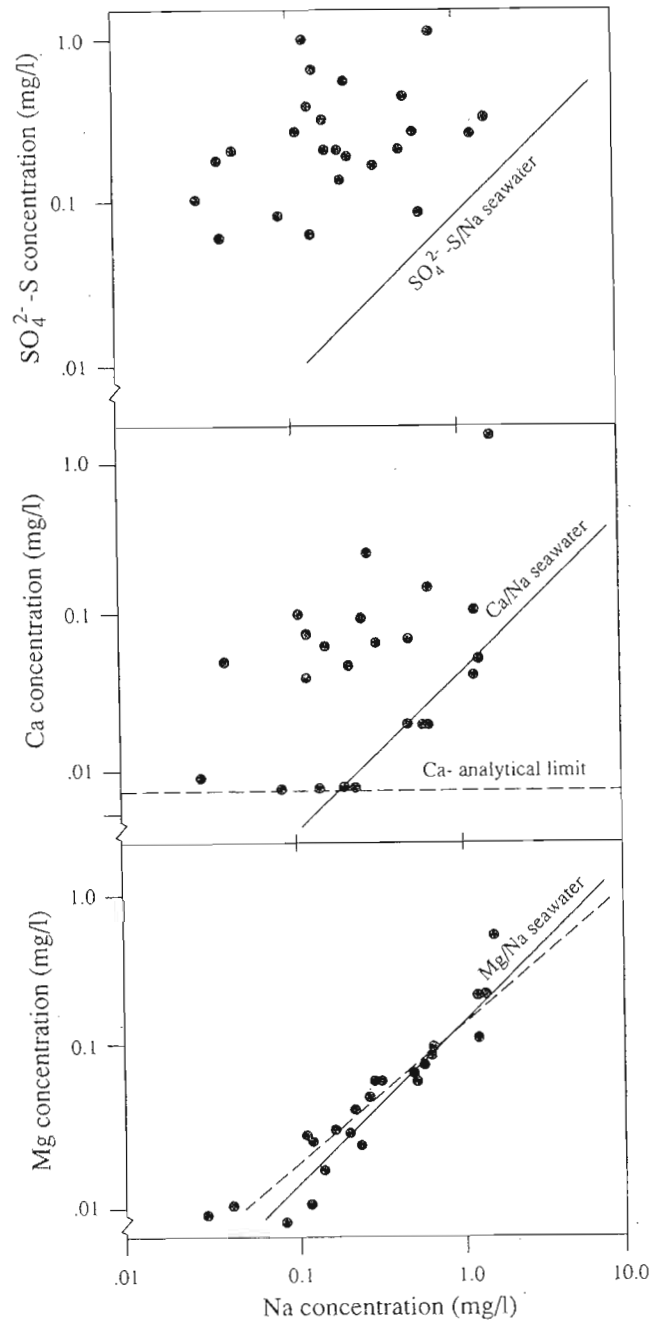
Figure 3.16 Concentrations of SO$_4$, Ca, and Mg in wetfall precipitation near Santa Barbara, California, plotted as a logarithmic function of Na concentrations in the same collections (Schlesinger et al. 1982). The solid line represents the ratio of these ions to Na in seawater. Ca and SO$_4$ are enriched in wetfall relative to seawater, whereas Mg shows a correlation (dashed) that is not significantly different from the ratio expected in seawater.

The long-term records suggest that many natural ecosystems, land and water, currently receive a greater input of N, S, and other elements of biogeochemical importance than before widespread emissions from human activities. Pollutant emissions have more than doubled the annual input of S-containing gases to the atmosphere globally (Chapter 13). The deposition of these compounds is localized (Barrie and Hales 1984). Galloway et al. (1984) calculate that the deposition of SO$_4^{2-}$ in the eastern United States is enriched by 2 to 16 times over background conditions. The western North Atlantic ocean receives about 20 to 40% of the sulfur and nitrogen oxides emitted in eastern North America (Galloway and Whelpdale 1987, Shannon and Sisterson 1992). Deposition of nitrogen in fixed compounds might be expected to enhance the growth of forests, but in combination with acidity, this fertilization effect may lead to deficiencies of P, Mg, and other plant nutrients (Waring and Schlesinger 1985). These interactions are discussed in more detail in Chapters 6 and 9.

Summary

In this chapter we have examined the physical structure, circulation and composition of the atmosphere. Major constituents, such as N$_2$, are rather unreactive and have long mean residence times in the atmosphere. CO$_2$ is largely controlled by plant photosynthetic uptake and by its dissolution in waters on the surface of the Earth. The atmosphere contains a variety of minor constituents, many of which are reduced gases. These gases are highly reactive in homogeneous reactions with hydroxyl (OH) radicals and heterogeneous reactions with aerosols and cloud droplets, which scrub them from the atmosphere. Changes in the concentration of many trace gases are indicative of global change, perhaps leading to future climatic warming and higher surface flux of ultraviolet light. The oxidized products of trace gases are deposited in land and ocean ecosystems, resulting in the input of N, S, and other elements of biogeochemical significance. Pollution of the atmosphere by the release of oxidized gases containing N and S as a result of human activities results in acid deposition in downwind ecosystems. The enhanced deposition of N and S represents altered biogeochemical cycling on a regional and global basis.

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