

The Atmosphere

OUTLINE

Introduction	49	Atmospheric Deposition	74
Structure and Circulation	50	<i>Processes</i>	74
		<i>Regional Patterns and Trends</i>	76
Atmospheric Composition	55	Biogeochemical Reactions in the	
Gases	55	Stratosphere	79
Aerosols	59	Ozone	79
		Stratospheric Sulfur Compounds	86
Biogeochemical Reactions in the			
Troposphere	63	Models of the Atmosphere and Global	
Major Constituents—Nitrogen		Climate	87
and Oxygen	63		
Carbon Dioxide	65	Summary	89
Trace Biogenic Gases	65		

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 conditions in which we live—our supplies of food and water, our health, and our economy. 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 the oceans and land, resulting in a global circulation of elements.

We begin our discussion with a brief consideration of the structure, circulation, and composition of the atmosphere. Then we 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 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. Finally, we discuss human impacts on the global atmosphere, as seen in ozone depletion and climate change.

STRUCTURE AND CIRCULATION

The atmosphere is held on 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:

$$F = M(g), \quad (3.1)$$

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). Decline in atmospheric pressure (P in bars) with altitude (A in km) is approximated by the logarithmic relation:

$$\log P = -0.06(A), \quad (3.2)$$

over the whole atmosphere (Figure 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 2000), and jet aircraft flying at high altitudes require cabin pressurization for their passengers.

Certain atmospheric constituents, such as ozone, aerosols, and clouds absorb and reflect 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 (Figure 3.2). The overall reflectivity or *albedo* of the Earth, as measured by changes in "earthshine" received by the Moon, is about 30% (Goode et al. 2001). The Earth's albedo has apparently increased slightly in recent years, presumably due to particulate air pollutants (Pallé et al. 2009, Wang et al. 2009). Greater albedo reduces the radiation reaching Earth's surface (i.e., global dimming).

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 (Figure 3.1). Because warm air is less dense and rises, the troposphere is well mixed. The top of the troposphere extends to 8 to 17 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.

Above the troposphere, the stratosphere is defined by the zone in which temperatures increase with altitude, extending to about 50 km (Figure 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*.

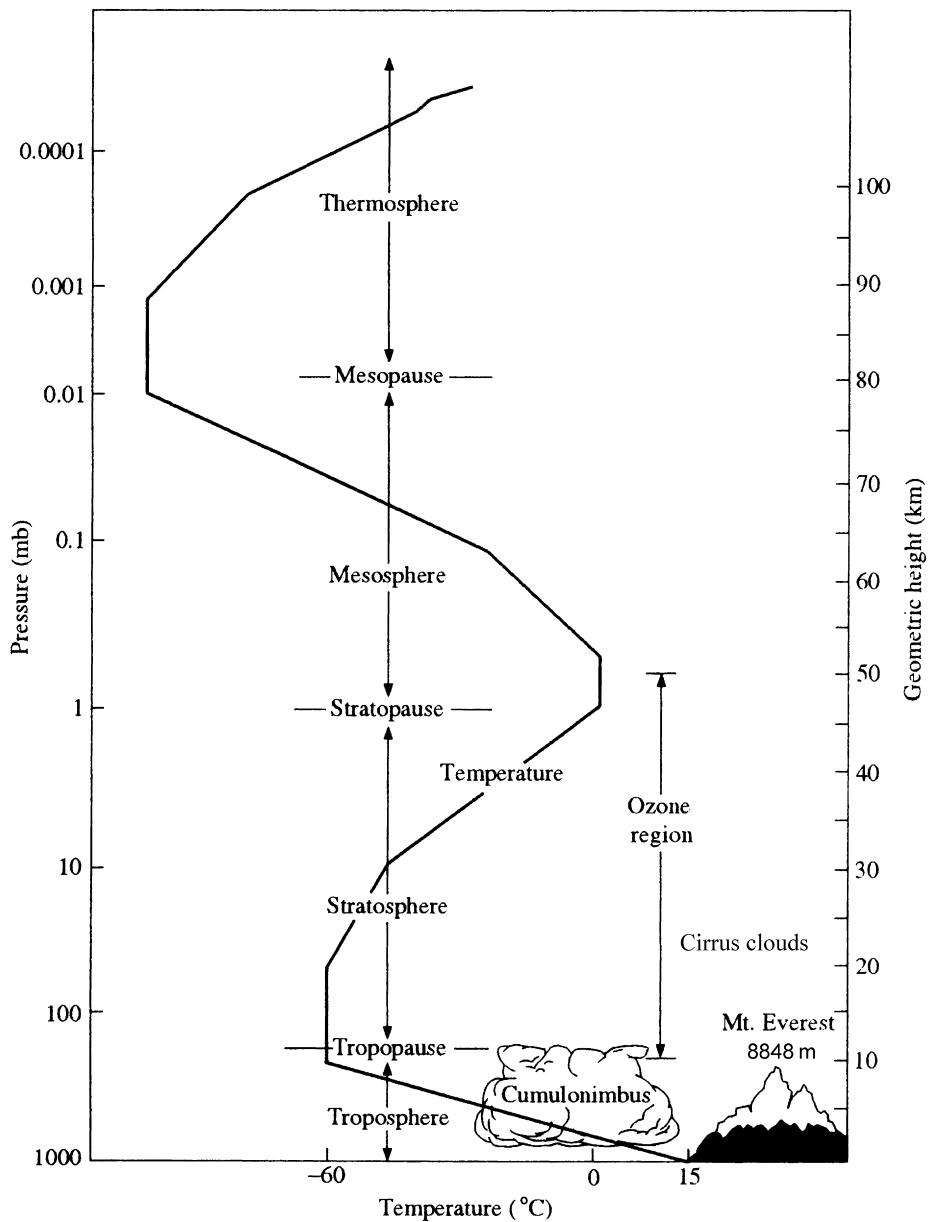


FIGURE 3.1 Vertical structure and zonation of the atmosphere, showing the temperature profile to 100-km altitude. Note the logarithmic decline in pressure (*left axis*) as a function of altitude.

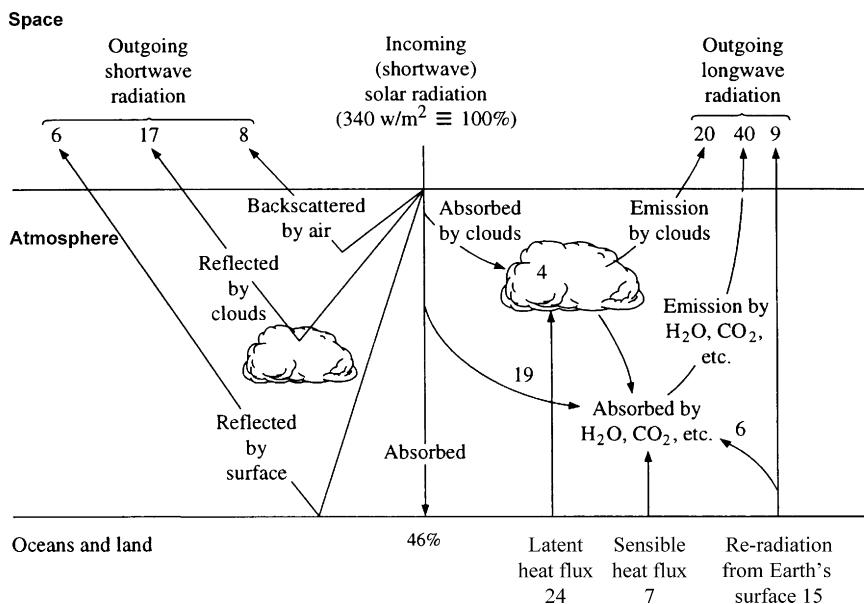


FIGURE 3.2 The radiation budget for Earth, showing the proportional fate of the energy that Earth receives from the Sun, about 340 W/m^2 largely in short wavelengths. About one-third of this radiation is reflected back to space and the remaining is absorbed by the atmosphere (23%) or the surface (46%). Long-wave radiation (infrared) 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. Source: Modified from MacCracken (1985).

Thus, materials that enter the stratosphere remain there for long periods, allowing for high-altitude 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 (Figure 3.3). 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*, the tropical and polar circulation patterns drive an indirect circulation in each hemisphere between 40° and 60° latitude, producing regional storm systems and the prevailing west winds that we experience in the temperate zone (Figure 3.3).

The tropospheric air in each hemisphere mixes on a time scale of a few months (Warneck 2000), allowing for regional transport of air pollutants that persist for more than a few days. For instance, in 1995 carbon monoxide (CO) from Canadian forest fires contributed to air

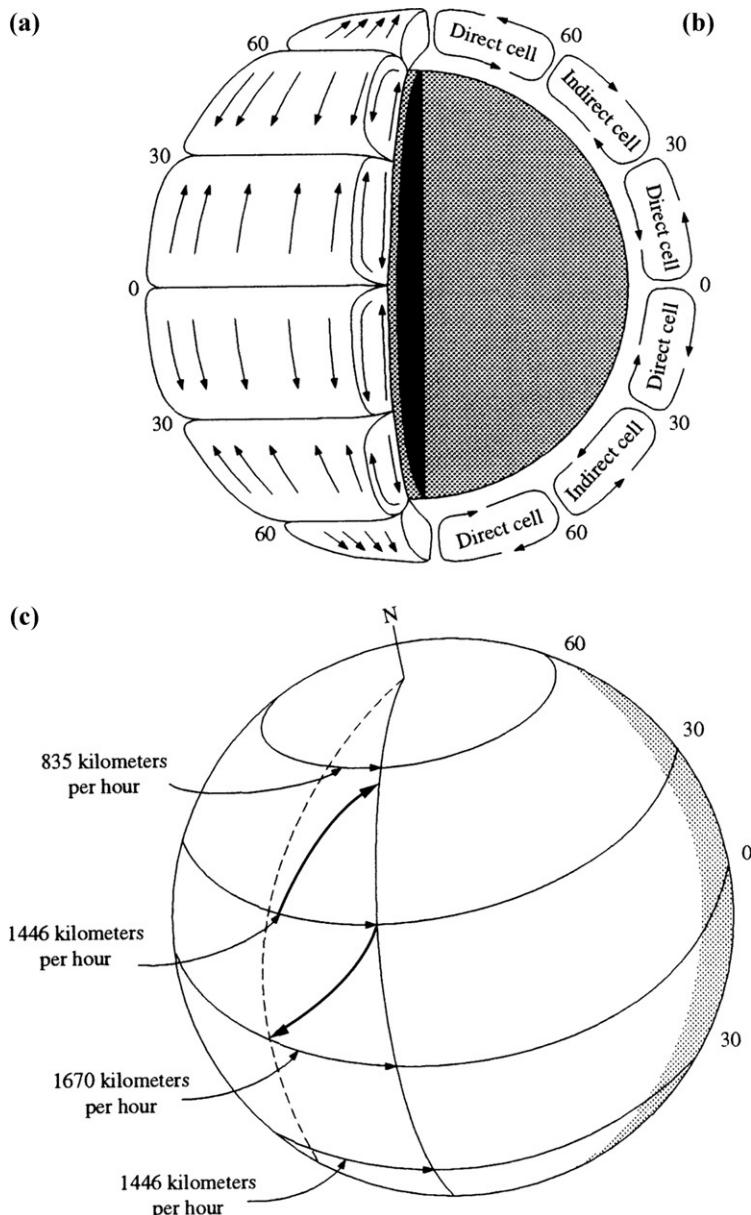


FIGURE 3.3 Generalized pattern of global circulation showing (a) surface patterns, (b) vertical patterns, and (c) the origin of the Coriolis force. As air masses move across different latitudes, they are deflected by the Coriolis force, which arises because of the different speeds of the Earth's rotation at different latitudes. For instance, if you were riding on an air mass moving at a constant speed south from 30° N latitude, 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. *Source: Modified from Oort (1970) and Gross (1977).*

pollutant loads in the eastern United States (Wotawa and Trainer 2000). The eruption of the Eyjafjallajökull volcano in Iceland on April 13 and 14, 2010 produced a cloud of volcanic ash over Poland several days later (Pietruczuk et al. 2010, Langmann et al. 2012) and disrupted airplane travel over much of Europe for several weeks. Vertical mixing in the troposphere is driven by convection, especially in thunderstorms, so that much of the air in the upper troposphere is less than a week old (Brunner et al. 1998, Bertram et al. 2007). 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 ([Figure 3.4](#)).

Exchange between the troposphere and the stratosphere is driven by several processes (Warneck 2000). In the tropical Hadley cells, rising air masses carry some tropospheric air to the stratosphere (Holton et al. 1995, Fueglistaler et al. 2004). 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, Hocking et al. 2007), thunderstorms (Dickenson et al. 1987, Randel et al. 2010), and eddy diffusion (Warneck 2000).

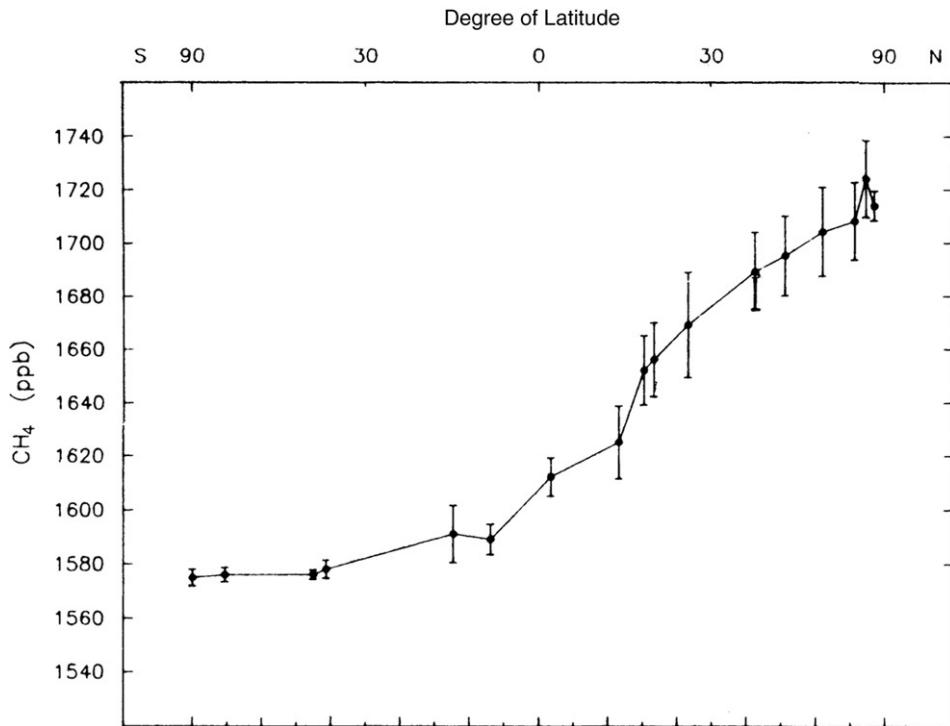


FIGURE 3.4 The latitudinal variation in the mean concentration of methane (CH₄) in Earth's atmosphere. *Source:* From Steele et al. (1987). Used with permission of Reidel Publishing.

Atmospheric scientists have examined the exchange of air mass between the troposphere and the stratosphere by following the fate of industrial pollutants released to the troposphere and radioactive contaminants released to the stratosphere in tests of atomic weapons during the 1950s and early 1960s (Warneck 2000). In these considerations, the concept of mean residence time is useful. For any reservoir that is in steady state, *mean residence time* (MRT) is defined as

$$\text{MRT} = \text{Mass}/\text{flux}, \quad (3.3)$$

where flux may be either the input or the loss from the reservoir.¹ Since the stratosphere is not well mixed vertically, the mean residence time of stratospheric air increases with altitude (Waugh and Hall 2002). However, the return of stratospheric air to the troposphere, about 4×10^{17} kg/yr (Seo and Bowman 2002), amounts to about 40% of the stratospheric mass each year, leading to an overall mean residence time of 2.6 years for stratospheric air. Thus, when a large volcano injects sulfur dioxide into the stratosphere, about half of it will remain after 2 years and about 5% will remain after 7.5 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). The mean residence times of these gases are much longer than the rate of atmospheric mixing. Thus, the concentrations of N₂, O₂, and all noble gases (He, Ne, Ar, Kr, and Xe) are globally uniform and time-invariant.

Several hundred trace gases, including a wide variety of volatile organic compounds (VOCs), are also found in the atmosphere. The most abundant volatile organic compound from vegetation is isoprene, which is commonly emitted from many coniferous forest species (Guenther et al. 2000, Fuentes et al. 2000). For comparison, [Table 3.2](#) shows the volatile emission from several species of desert shrubs in the southwestern United States, where monoterpene compounds dominate the flux (Geron et al. 2006). The various volatile organic compounds derived from vegetation are known as nonmethane hydrocarbons (NMHC). Humans also add a wide variety of trace gases to the atmosphere, including oxygenated organic gases, such as acetone and alcohols (Piccot et al. 1992, Chameides et al. 1992, Singh et al. 2001).

Most trace gases are highly reactive and thus have short mean residence times, so it is not surprising that they are minor constituents in the atmosphere (Atkinson and Arey 2003). 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 (e.g., Idso et al. 2001) 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

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., $1/\text{MRT}$). 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.

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} or $\mu\text{l/l}$)			
Carbon dioxide	CO ₂	400	3.11×10^{18}
Neon	Ne	18.2	6.49×10^{16}
Helium	He	5.24	3.70×10^{15}
Methane	CH ₄	1.83	5.19×10^{15}
Krypton	Kr	1.14	1.69×10^{16}
Parts-per-billion constituents (ppb = 10^{-9} or nl/l)			
Hydrogen	H ₂	510	1.82×10^{14}
Nitrous oxide	N ₂ O	320	2.49×10^{13}
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 ₃ F	280	6.79×10^{12}
CFC 12	CCl ₂ F ₂	550	3.12×10^{13}
Methylchloride	CH ₃ Cl	620	5.53×10^{12}
Methylbromide	CH ₃ Br	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 514×10^{19} g.

Source: Updated from Trenberth and Guillemot (1994).

1985). Winds mix the concentrations of these gases to their average tropospheric background concentration within a short distance downwind of local sources. While spatial heterogeneity in atmospheric concentrations can help us identify important source areas, we can best perceive global changes in atmospheric composition, such as the current increase in CH₄, 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 (Figure 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 spatial variation. For example, the average volume of water in the atmosphere is equivalent to about 13,000 km³ at any time, or 24.6 mm above any point on the Earth's surface (Trenberth 1998). The average daily precipitation would be about 2.73 mm if it were deposited evenly around the globe. Thus, the mean residence time for water vapor in the atmosphere is

$$24.6 \text{ mm} / 2.73 \text{ mm day}^{-1} = 9.1 \text{ days.} \quad (3.4)$$

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 (Figure 3.5). This relationship between variation in concentration and residence time in the atmosphere

TABLE 3.2 Emission of Volatile Organic Compounds ($\mu\text{gC g}^{-1} \text{ h}^{-1}$) from Desert Shrubs of the U.S. Southwest

Species	Isoprene	α-Pinene	β-Pinene	Camphene	Myrcene	d-Limonene	Γ-Monoterpenes
<i>Ambrosia deltoidea</i>	<0.1	0.06 (0.02)	0.31 (0.18)	0.51 (0.18)	2.3 (1.1)	1.0 (0.32)	4.1 (1.6)
<i>Ambrosia dumosa</i>	<0.1	1.6 (0.93)	3.0 (1.5)	0.06 (0.03)	1.1 (0.82)	2.0 (0.87)	7.9 (3.4)
<i>Atriplex canescens</i>	<0.1	0	0	0.17 (0.17)	0.13 (0.12)	0	0.31 (0.29)
<i>Chrysothamnus nauseosus</i>	<0.1	0.28 (0.28)	0	0	0.16 (0.16)	0.21 (0.02)	0.65 (0.46)
<i>Ephedra nevadensis</i>	10 (4.0)	0.05 (0.01)	0.03 (0.017)	0.01 (0.006)	0.09 (0.06)	0.11 (0.06)	0.30 (0.04)
<i>Hymenoclea salsola</i>	<0.1	1.4 (0.31)	0.06 (0.06)	0.02 (0.02)	0.35 (0.26)	0.30 (0.30)	2.6 (0.57)
<i>Krameria erecta</i>	<0.1	0.02 (0.02)	0.06 (0.001)	0.03 (0.003)	0.14 (0.05)	0.05 (0.003)	0.30 (0.03)
<i>Larrea tridentata</i>	<0.1	0.37 (0.18)	0.12 (0.04)	0.44 (0.18)	0.30 (0.13)	0.74 (0.31)	2.0 (0.48)
<i>Lycium andersonii</i>	<0.1	0.10 (0.03)	0.27 (0.10)	0.11 (0.01)	0.39 (0.02)	0.27 (0.06)	1.1 (0.18)
<i>Psorothamnus fremontii</i>	35 (10)	0.50 (0.19)	0	0	1.0 (0.24)	0.50 (0.18)	2.0 (0.2)

Source: From Geron et al. (2006).

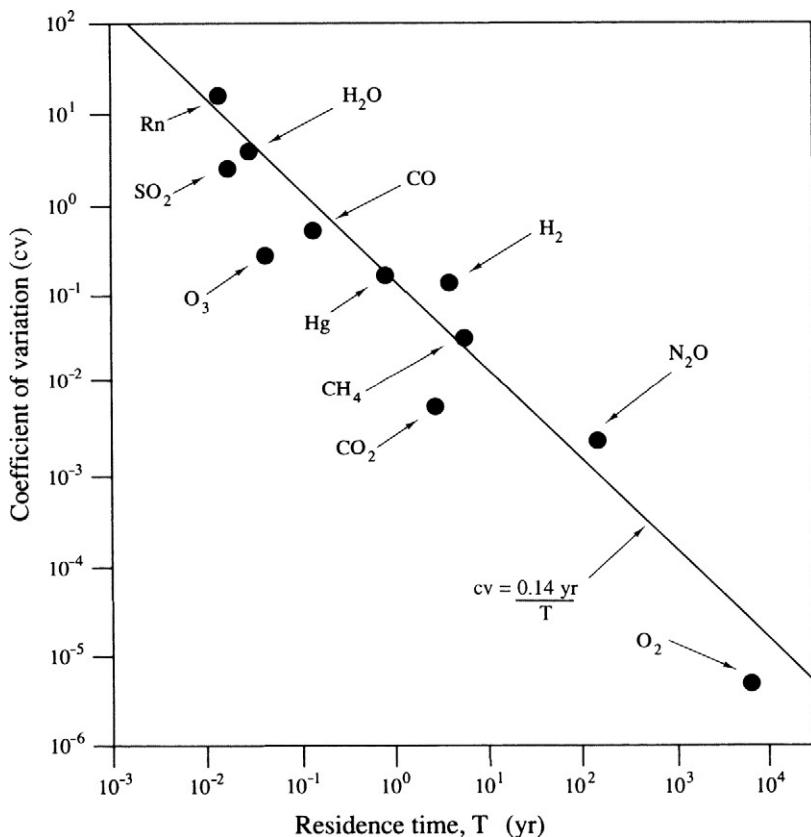


FIGURE 3.5 Variability in the concentration of atmospheric gases, expressed as the coefficient of variation among measurements, as a function of their estimated mean residence times in the atmosphere. *Source: Modified from Junge (1974), as updated by Slinn (1988).*

extends to trace organic species (e.g., propane), which have residence times of a few days (Jobson et al. 1999).

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 CO₂ by plants, CO₂ shows a minor seasonal and latitudinal variation (\pm about 1%) in its global concentration of ~400 ppm (Figures 1.1 and 3.6). In contrast, painstaking analyses are required to show *any* variation in the concentration of O₂ 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 of <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 and thus long-lived in the troposphere (Rowland 1989). This allows chlorofluorocarbons to mix into the stratosphere, where they lead to the destruction of ozone by ultraviolet light (see pp. 82–83).

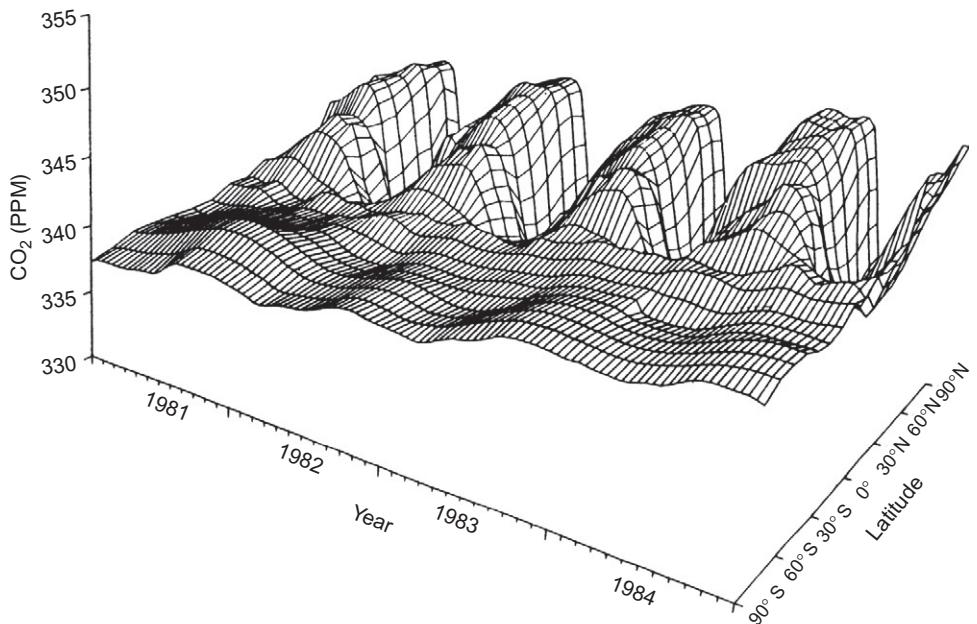


FIGURE 3.6 Seasonal fluctuations in the concentration of atmospheric CO₂ (1981–1984), shown as a function of 10° latitudinal belts (Conway et al. 1988). Note the smaller amplitude of the fluctuations in the Southern Hemisphere, reaching peak concentrations during the Northern Hemisphere's winter.

Aerosols

In addition to gaseous components, the atmosphere contains particles, known as aerosols, that arise from a variety of sources (Table 3.3). Soil particles are dispersed by wind erosion (also known as deflation weathering or eolian transport) from arid and semiarid regions (Pye 1987, Engelstaedter et al. 2003, Ravi et al. 2011). Particles with diameter <1.0 μm are held aloft by turbulent motion and are subject to long-range transport. Current estimates suggest that up to 2×10^{15} g/yr of soil particles enter the atmosphere from arid and barren agricultural soils (Zender et al. 2004), and about 20% of these particles are involved in long-range transport. The flux of soil dust has increased due to human cultivation, especially in semiarid lands (Tegen et al. 2004, Mulitza et al. 2010) and increases during droughts. 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 (Mahowald et al. 2005b, Chapter 9). Similarly, dust from the Sahara supplies nutrients to phytoplankton in the Atlantic Ocean (Talbot et al. 1986, Wu et al. 2000, Jickells et al. 2005) and phosphorus to Amazon rainforests (Swap et al. 1992, 1996; Perry et al. 1997; Okin et al. 2004). Dust from desert soils is monitored by several satellites, including NASA's MODIS satellite (Tanre et al. 2001, Kaufman et al. 2002; see Figure 3.7). 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, Yang et al. 2009).

TABLE 3.3 Global Production and Atmospheric Burden of Aerosols from Natural and Human-Derived Sources

	Mass emission 10^{12}g/yr	Mass Burden Tg	Number Produced per year	Number Burden
Carbonaceous aerosols				
Primary organic (0–2 μm)	95	1.2	–	$310 \cdot 10^{24}$
Biomass burning	54	–	$7 \cdot 10^{27}$	–
Fossil fuel	4	–	–	–
Biogenic	35	0.2	–	–
Black carbon (0–2 μm)	10	0.1	–	$270 \cdot 10^{24}$
Open burning and biofuel	6	–	–	–
Fossil fuel	4.5	–	–	–
Secondary organic	28	0.8	–	–
Biogenic	25	0.7	–	–
Anthropogenic	3.5	0.08	–	–
Sulfates				
Biogenic	57	1.2	–	–
Volcanic	21	0.2	–	–
Anthropogenic	122	1.4	–	–
Nitrates				
	18	0.49	–	–
Industrial dust, etc.				
	100	1.1	–	–
Sea salt				
$d < 1 \mu\text{m}$	180	3.5	$7.4 \cdot 10^{26}$	–
$d = 1\text{--}16 \mu\text{m}$	9940	12	$4.6 \cdot 10^{26}$	–
Total	10,130	15	$1.2 \cdot 10^{27}$	$27 \cdot 10^{24}$
Mineral (soil) dust				
<1 μm	165	4.7	$4.1 \cdot 10^{25}$	–
1–2.5 μm	496	12.5	$9.6 \cdot 10^{25}$	–
2.5–10 μm	992	6	–	–
Total	1600	18 ± 5	$1.4 \cdot 10^{26}$	$11 \cdot 10^{24}$

Source: From Andreae and Rosenfeld (2008).

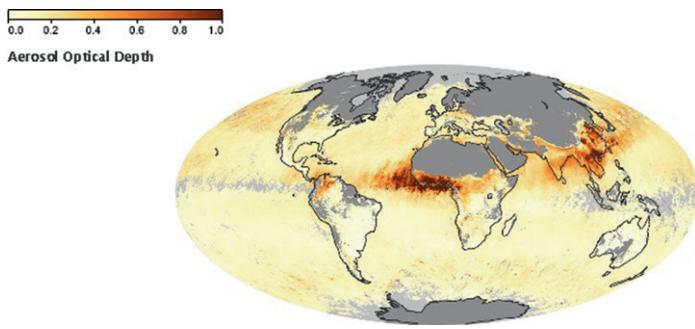


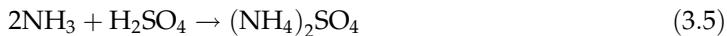
FIGURE 3.7 Aerosols in Earth's atmosphere, measured as AOD by the NASA MODIS satellite during March 2010. Optical depth is the fraction of light absorbed by aerosols in a column of air. Note high amounts of aerosols exiting the southern Sahel region of Africa, blowing westward to the Amazon, and high concentrations of aerosols emitted from the deserts of China, blowing eastward across the Pacific Ocean. Source: From http://earthobservatory.nasa.gov/GlobalMaps/view.php?d1=MODAL2_M_AER_OD.

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 remains 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 (see [Figure 3.16](#) later). Other global estimates of seasalt production are similar (Erickson and Duce 1988, Gong et al. 1997, Sofiev et al. 2011).

Organic particles are produced from a wide variety of sources, including pollen, plant fragments, and bacteria (Després et al. 2012). 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 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 inject finely divided rock material—volcanic ash—into the atmosphere where it is deposited over large areas ([Table 3.4](#)), contributing to soil development in regions that are downwind from major eruptions (Watkins et al. 1978, Dahlgren et al. 1999, Zobel and Antos 1991). Volcanic gases and ash that are transported to the stratosphere by violent eruptions undergo global transport, affecting climate for several years (Langway et al. 1995, McCormick et al. 1995, Briffa et al. 1998).

Small particles, known as secondary aerosols, 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 $(\text{NH}_4)_2\text{SO}_4$ may be produced by a subsequent reaction with atmospheric ammonia (NH_3 ; Behera and Sharma 2011):



(Ammonia is derived from a variety of sources, primarily associated with agricultural activities; [Chapter 12](#).) Sulfate aerosols are also produced during the oxidation of dimethylsulfide released from the ocean ([Chapter 9](#)). Sulfate aerosols increase the albedo of the Earth's atmosphere, so estimates of the abundance of sulfate aerosols are an important component of global climate models (Kiehl and Briegleb 1993, Mitchell et al. 1995). Secondary aerosols are also produced from volatile organic compounds, such as isoprene, that are released from plants (Kavouras et al. 1998, O'Dowd et al. 2002, Henze and Seinfeld 2006, Jimenez et al. 2009, Pöschl et al. 2010).

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

TABLE 3.4 Composition of Airborne Particulate Volcanic Ash Sample Collected during Mt. St. Helens Eruption in Washington State on May 19, 1980

Constituent	Particulate sample	Average ash
Major elements (%)		
SiO ₂	≡65.0	65.0
Fe ₂ O ₃	6.7	4.81
CaO	3.0	4.94
K ₂ O	2.0	1.47
TiO ₂	0.42	0.69
MnO	0.054	0.077
P ₂ O ₅	–	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

Source: From Fruchter et al. (1980); and Hooper et al. (1980), used with permission of American Association for the Advancement of Science.

at the Earth's surface (Bertine and Goldberg 1971). Fine particulate air pollution has significant human health effects (Samet et al. 2000, Pope et al. 2009, Anenberg et al. 2010). Fortunately, the mass of industrial aerosols has declined in many developed countries where pollution controls have been instituted (Renberg and Wik 1984). One of the most widespread anthropogenic aerosols, particles of lead from automobile exhaust, has declined in global abundance over the past 30 years due to a reduction in the use of leaded gasoline (Boutron et al. 1991). In other regions, where air pollution is unregulated, concentrations of aerosols have increased in recent years (Streets et al. 2008, Dey and Girolamo 2011), contributing to observations of global dimming. Overall, human activities probably account for about 10% of the burden of aerosols in today's atmosphere (Table 3.3).

Small particles ($<1.0 \mu\text{m}$)² 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 2000, Raes et al. 2000). Nanoparticles ($<0.3 \mu\text{m}$), derived from a variety of natural and

² The U.S. EPA designates small aerosols, those $<2.5 \mu\text{m}$, as PM_{2.5}.

manufactured sources (Kumar et al. 2010, Hendren et al. 2011), are of particular concern to human health. The mass of aerosols declines with increasing altitude from values ranging between 1 and 50 $\mu\text{g}/\text{m}^3$ 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 2000). 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 they carry the largest mass of material through the atmosphere.

The composition of tropospheric aerosols varies greatly depending on the proximity of continental, maritime, or anthropogenic sources (Heintzenberg 1989, Murphy et al. 1998). 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 $>0.1 \mu\text{m}$ 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 Kahl 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* or *multiphase reactions* (Ravishankara 1997). Such reactions are responsible for the ultimate removal of many reactive gases from the atmosphere.

BIOGEOCHEMICAL REACTIONS IN THE TROPOSPHERE

Major Constituents—Nitrogen and Oxygen

It is perhaps not surprising that the major constituents of the atmosphere, N_2 , O_2 , and Ar, have nearly uniform concentrations and long mean residence times in the atmosphere. Argon is inert and has accumulated in the Earth's atmosphere since the earliest degassing of its crust ([Chapter 2](#)). From a biogeochemical perspective, N_2 is practically inert; reactive N is found only in molecules such as NH_3 and NO . Collectively the reactive nitrogen gases are sometimes called “odd” nitrogen, because the molecules have an odd number of N atoms (versus N_2 or N_2O).³ Despite its abundance in the atmosphere, N_2 is so inert that the rate of formation of odd, or reactive, nitrogen is the primary factor that limits the growth of plants on land and in the oceans (Delwiche 1970, LeBauer and Treseder 2008). Among atmospheric gases, only argon and the other noble gases are less reactive.

³ The term “odd nitrogen” is not ideal. In practice it refers only to the various oxidized forms of nitrogen in the atmosphere, including N_2O_5 , but not to NH_3 , which also has an odd number of N atoms.

Conversion of N₂ to reactive compounds, *N fixation*, occurs in lightning bolts, but the estimated global production of NO by lightning ($<5 \times 10^{12}$ g N/yr; Chapter 12) is too low to account for a significant turnover of N₂ in the atmosphere. By far the most important source of fixed nitrogen for the biosphere derives from the bacteria that convert N₂ to NH₃ in the process of biological nitrogen fixation (Eq. 2.10). 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 (Chapters 6 and 9). Including human activities, global nitrogen fixation is not likely to exceed 450×10^{12} g N/yr, with the production of synthetic nitrogen fertilizer now accounting for about one-third of the total (Chapter 12).

The natural rate of nitrogen fixation would remove the pool of N₂ from the atmosphere in about 40 million years.⁴ Fortunately, denitrification (Eq. 2.20) returns N₂ to the atmosphere. 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 N₂ in the atmosphere. While the biosphere is responsible for the maintenance of N₂ in Earth's atmosphere over geologic time, it plays a minor role in stabilizing the concentration of atmospheric N₂ over shorter periods, since the pool of N₂ in the atmosphere is so large (Walker 1984).

In Chapter 2 we discussed the accumulation of O₂ in the atmosphere during the evolution of life on Earth. The atmosphere now contains only a small portion of the total O₂ released by photosynthesis through geologic time (Figure 2.8). However, the atmosphere contains much more O₂ 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 pool of atmospheric oxygen content by only 0.45% (Chapter 5). The accumulation of O₂ in the atmosphere 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 2.3). The rate of burial is determined by the area and depth of the ocean floor that is subject to anoxic conditions (Walker 1977, Hartnett et al. 1998). Because the area and depth vary inversely with the concentration of atmospheric O₂, the balance between the burial of organic matter and its oxidation maintains O₂ at a steady-state concentration of about 21% (see also Chapters 9 and 11).

A large amount of O₂ has been consumed in weathering of reduced crustal minerals, especially Fe and S, through geologic time (Figure 2.8); the current rate of exposure of these minerals would consume all atmospheric oxygen in about 70 million years (Lenton 2001; see Figure 11.8). However, the rate of exposure is not likely to vary greatly in response to changes in atmospheric O₂, so weathering is not the major factor controlling O₂ in the atmosphere. In sum, despite the potential reactivity of O₂, its rate of reaction with reduced compounds is rather slow, and O₂ is a stable component of the atmosphere. The mean residence time of O₂ in the atmosphere is on the order of 4000 years, largely determined by exchange with the biosphere (compare Figures 3.5 and 11.8). As such O₂ is well mixed and uniform in the atmosphere. Annual photosynthesis and respiration cause seasonal variations in O₂ concentration of about $\pm 0.002\%$ (Figure 1.1).

⁴ Mass of N in the atmosphere (Table 3.1) divided by the global rate of biological nitrogen fixation (270×10^{12} gN/yr) gives a mean residence time of 14,300,000 years for N₂ in the atmosphere. Thus, $k = 7.0 \times 10^{-8}$ and $3/k = 43$ million years.

Carbon Dioxide

Carbon dioxide is not reactive with other gases in the atmosphere. The concentration of CO₂ is affected by interactions with the Earth's surface, including the reactions of the carbonate–silicate cycle (Figure 1.3), gas exchange with seawater following Henry's Law (Eq. 2.4), and annual cycles of photosynthesis and respiration by land plants (Figures 1.1 and 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 CO₂ in the atmosphere is captured by photosynthesis. The annual exchange of CO₂ with seawater, particularly in areas of cold, downwelling water and high productivity (Chapter 9), is about 1.5× as large as the annual uptake of CO₂ by land plants. Both plant and ocean uptake are likely to increase with increasing concentrations of atmospheric CO₂, potentially buffering fluctuations in its concentration (Chapters 5, 9, and 11). Following Eq. 3.3, the mean residence time for CO₂, determined by the total flux from the atmosphere (the sum of land and ocean uptake), is about 5 years, so CO₂ shows some seasonal and latitudinal variation in the atmosphere (Figures 1.1 and 3.6).

The carbonate–silicate cycle (Figure 1.3) also buffers the concentration of CO₂ in the atmosphere, but does not affect the concentration of atmospheric CO₂ significantly in periods of less than ~10,000 years (Hilley and Porder 2008). 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 CO₂ is a non-steady-state condition, caused by the combustion of fossil fuels and destruction of land vegetation. CO₂ 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 CO₂ would return to a steady state, and after several hundred years nearly all of the CO₂ released by humans would reside in the oceans. In the meantime, higher concentrations of CO₂ are likely to cause significant atmospheric warming through the "greenhouse effect" (refer to Figure 3.2).

Trace Biogenic Gases

Volcanoes are the original source of volatiles in the Earth's atmosphere (Chapter 2) and a small continuing source of some of the reduced gases (H₂S, H₂, NH₃, CH₄) that are found in the atmosphere today (Table 2.2). However, in most cases, the concentrations of these gases in today's atmosphere are dominated by supply from the biosphere, particularly by microbial activity (Monson and Holland 2001). Methane is largely produced by anaerobic decomposition in wetlands (Chapters 7 and 11), nitrogen oxides by soil microbial transformations (Chapters 6 and 12), 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 (Crutzen 1983). These and other trace gases are found at concentrations well in excess of what is predicted from equilibrium geochemistry in an atmosphere with 21% O₂ (Table 3.5).

Unlike major atmospheric constituents, many of the trace biogenic gases in the atmosphere are highly reactive, showing short mean residence times and variable concentrations in space and time (refer to Figure 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

TABLE 3.5 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	1830	9 years	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 ₂ O	10 ⁻²²	320	120 years	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) ₂ S		0.004–0.06	1 day	50
Hydrogen sulfide	H ₂ S		<0.04	4 days	100
Carbonyl sulfide	COS	0	0.50	5 years	20
Sulfur dioxide	SO ₂	0	0.02–0.10	3 days	50

^a Approximate values in equilibrium with an atmosphere containing 21% O₂ (Chameides and Davis 1982).

^b For short-lived gases, the value is the range expected in remote, unpolluted atmospheres.

these gases from the atmosphere. Sinks 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 (Prinn 2003).

Despite its abundance, O₂ does not directly oxidize reduced gases in the atmosphere. Instead, a small proportion of the oxygen is converted to the powerful atmospheric oxidants ozone (O₃) and hydroxyl radical (OH) through a series of reactions driven by sunlight (Logan 1985, Thompson 1992). Ozone and OH are the primary gases that oxidize many of the trace gases to CO₂, HNO₃, and H₂SO₄.

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 O₂ 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 (e.g., Hocking et al. 2007), where it contributes to the budget of ozone in the troposphere (Table 3.6). However, observations of high ozone

TABLE 3.6 Tropospheric Ozone Budget

Source or sink	Pre-industrial	Present	Human impact
Stratospheric injection	+696	+696	0
Tropospheric production (i.e., dirty atmosphere reactions)	+199	+686	+487
Tropospheric sink (i.e., clean atmosphere reactions)	-435	-558	-123
Dry deposition	-459	-825	-366

Note: All values in Tg (10^{12} g) of O_3 /year.

Source: From Levy *et al.* (1997).

concentrations in the smog of polluted cities (e.g., Los Angeles) alerted atmospheric chemists to reactions by which ozone is produced in the troposphere (Warneck 2000).

When NO_2 is present in the atmosphere, it is dissociated by sunlight ($h\nu$),



followed by a reaction producing ozone:



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



which is an equilibrium reaction, so high concentrations of NO tend to drive the reaction backward. Sunlight is essential to form ozone by these pathways, so they are known as photochemical reactions. At night, ozone is consumed by reactions with NO_2 to form nitric acid (Brown *et al.* 2006b).

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.⁵ 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, Lelieveld *et al.* 2004, Cooper *et al.* 2010).

Ozone is subject to further photochemical reaction in the troposphere,



where $h\nu$ is ultraviolet light with wavelengths $<318\text{ nm}$ and $O(^1D)$ is an excited atom of oxygen. Reaction of $O(^1D)$ with water yields hydroxyl radicals:



⁵ NO_x (pronounced “knocks”) 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—for example, HNO_3 and $CH_3C(O)O_2NO_2$ (peroxyacetyl nitrate or PAN).

The formation of hydroxyl radicals is strongly correlated with the amount of ultraviolet radiation (Rohrer and Berresheim 2006). Hydroxyl radicals may further react to produce HO₂ and H₂O₂,



which are other short-lived oxidizing compounds in the atmosphere (Thompson 1992, Crutzen et al. 1999).

Hydroxyl radicals exist with a mean concentration of about 1×10^6 molecules/cm³ (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 for only 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 et al. 1997).

Because of its short mean residence time, the global mean concentration of OH radicals must be estimated indirectly. For this purpose, atmospheric chemists have relied on methyl-chloroform (trichloroethane), a gas that is known to result only from human activity. Methyl-chloroform has a mean residence time of about 4.8 years (Prinn et al. 1995), so it is reasonably well mixed in the atmosphere. In the laboratory, it reacts with OH,



and the rate constant, K , for the reaction is 0.85×10^{-14} cm³ molecule⁻¹ sec⁻¹ at 25°C (Talukdar et al. 1992). Then, knowing the industrial production of CH₃CCl₃, its accumulation in the atmosphere and K , one can calculate the concentration of OH that must be present, namely,

$$\text{OH} = (\text{Production} - \text{Accumulation})/K. \quad (3.14)$$

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,

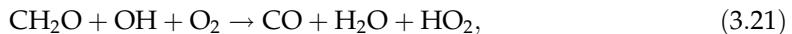


for which the net reaction is



Note that the hydroxyl radical has acted as a catalyst to initiate the oxidation of CH₄ and its byproducts by O₂. Other volatile organic compounds are also oxidized through this pathway, which yields formaldehyde (CH₂O; Atkinson 2000, Atkinson and Arey 2003).

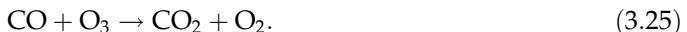
The formaldehyde that is produced in these reactions is further oxidized to carbon monoxide,



and CO is oxidized by OH to produce CO_2 ,

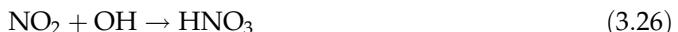


for which the net reaction is



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 can also react with NO_2 and SO_2 in homogeneous gas reactions:



and the latter reaction is followed by a heterogeneous reaction with raindrops:



which removes sulfur dioxide from the atmosphere, causing acid rain. Sulfur dioxide is also oxidized by hydrogen peroxide, according to Chandler et al. (1988):



The reaction of OH with NO_2 is very fast, and it produces nitric acid that is removed from the atmosphere by a heterogeneous interaction with raindrops (Munger et al. 1998). The reactions with SO_2 are much slower, accounting for the long-distance transport of SO_2 as a pollutant in the atmosphere (Rodhe 1981). Hydrogen sulfide (H_2S) and dimethylsulfide ($(\text{CH}_3)_2\text{S}$), released from anaerobic soils (Chapter 7) and the ocean surface (Chapter 9), are also removed by reactions with OH and other oxidizing compounds, 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 radicals 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 3.5). The mean residence time for methane is much longer, accounting for its more uniform distribution (Figure 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 declined only slightly (or perhaps not at all) in recent years (Prinn et al. 1995, 2005; Montzka et al. 2011b). Increasing deposition of formaldehyde in the Greenland snowpack indicates increasing oxidation of methane in the atmosphere (Eq. 3.20; Staffelbach et al. 1991).

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 O₃, and thus OH, during the oxidation of reduced gases (Jenkin and Clemitshaw 2000, Sillman 1999). When the concentration of NO is >10 ppt, which we will define as a “dirty” atmosphere (Jacob and Wofsy 1990), the oxidation of carbon monoxide begins by reaction with hydroxyl radical and proceeds as follows (Crutzen and Zimmermann 1991):



The net reaction is



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



In both cases, NO acts as a catalyst leading to the oxidation of reduced gases by oxygen.

Figure 3.8 shows the contrasting pathways of carbon monoxide oxidation in clean and dirty atmospheres. Crutzen (1988) points out that the oxidation of one molecule of CH₄ could consume up to 3.5 molecules of OH and 1.7 molecules of O₃ when the NO concentration is low, whereas it would yield a net gain of 0.5 OH and 3.7 O₃ in polluted environments (see also Wuebbles and Tamarasis 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 >10 ppt are present over most of the Earth’s land surface (Chameides et al. 1992, Levy et al. 1999). 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 O₃ over rural areas of the southeastern United States (Figure 3.9) (Jacob et al. 1993, Kleinman et al. 1994, Kang et al. 2003) and in remote tropical regions (Crutzen et al. 1985, Zimmerman et al. 1988, Jacob and Wofsy 1990, Andreae et al. 1994a). In urban areas, where the concentration of NO_x is especially high due to industrial pollution, effective control of atmospheric O₃ levels may also depend on the regulation of volatile hydrocarbons (Chameides et al. 1988, Seinfeld 1989). In rural areas, ozone formation is usually limited

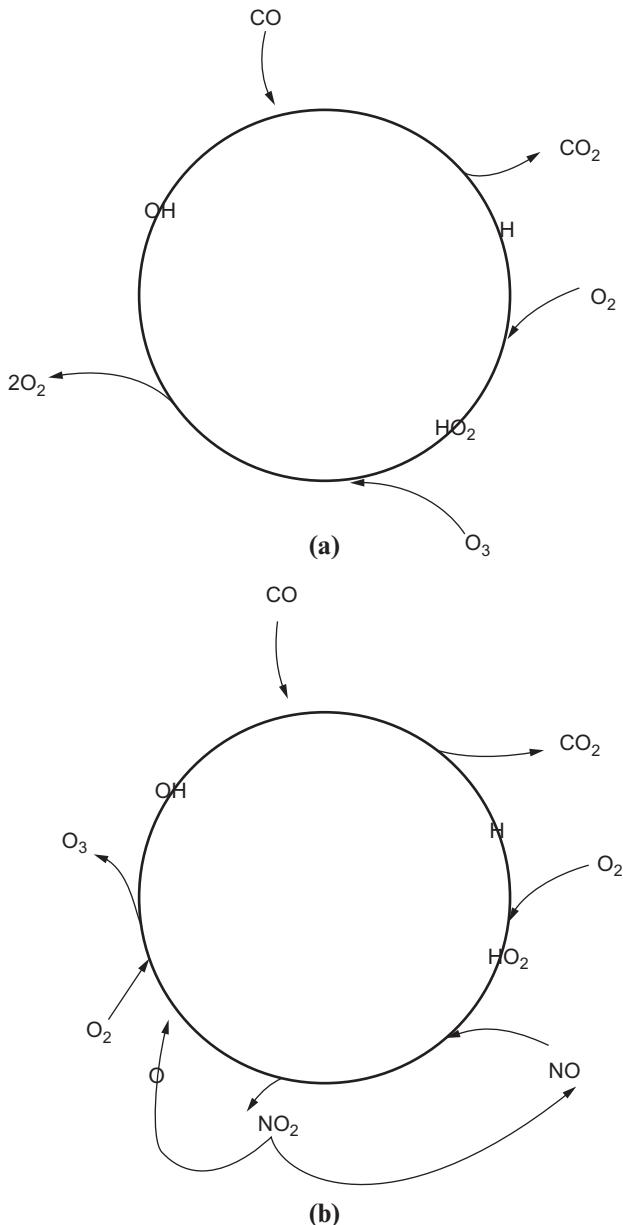


FIGURE 3.8 Reaction chain for the oxidation of CO in (a) clean and (b) dirty atmospheric conditions.

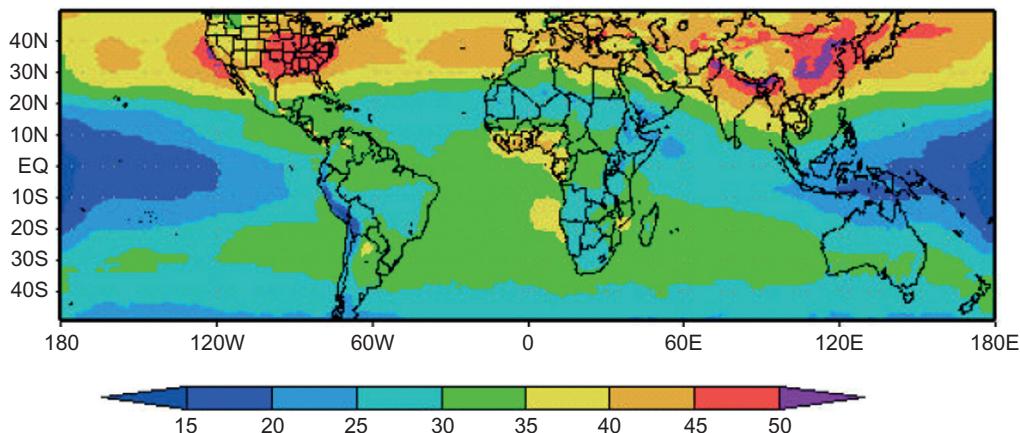


FIGURE 3.9 Distribution of ozone in Earth’s atmosphere, for summer months, averaged over 1979–1991. Note high ozone concentrations over the eastern United States and China. Data are in Dobson units (see page 83). Source: From Fishman et al. (2003). Used with permission of European Geosciences Union.

by the concentration of NO_x , especially during the growing season, when vegetation actively emits volatile organic compounds (Figure 3.10; Aneja et al. 1996).

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 can contribute to greenhouse warming. Some models predict an increase in O_3 (Isaksen and Hov 1987, Hough and Derwent 1990, Thompson 1992, Prinn 2003) in the atmosphere as a result of increasing human emissions of NO, creating dirty atmosphere conditions over much of the planet. Indeed, measurements in Europe in the late 1800s indicate lower concentrations of tropospheric ozone than today (Volz and Kley 1988, Marenco et al. 1994). 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, 2005; Montzka et al. 2011b). Concentrations of H_2O_2 , derived from OH (Eqs. 3.11 and 3.12), 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 (Figure 3.11). Several recent papers suggest additional pathways leading to the formation of OH (Li et al. 2008, Hofzumahaus et al. 2009), so that its production may not be restricted to the photochemical reactions outlined in Eqs. 3.8 through 3.10. Soil microbes that produce nitrite (NO_2^-) are a potential source of nitrous acid (HONO) in the atmosphere and OH radicals (Su et al. 2011).

Some of the O_3 produced over the continents undergoes long-distance transport (Jacob et al. 1993, Parrish et al. 1993, Cooper et al. 2010, Brown-Steiner and Hess 2011), resulting in the appearance of O_3 and its byproducts at considerable distances from their source (Figure 3.9). In some rural areas, concentrations of O_3 from local production and transport from nearby cities inhibit the growth of agricultural crops and trees (Chameides et al. 1994). 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, Kang et al. 2003).

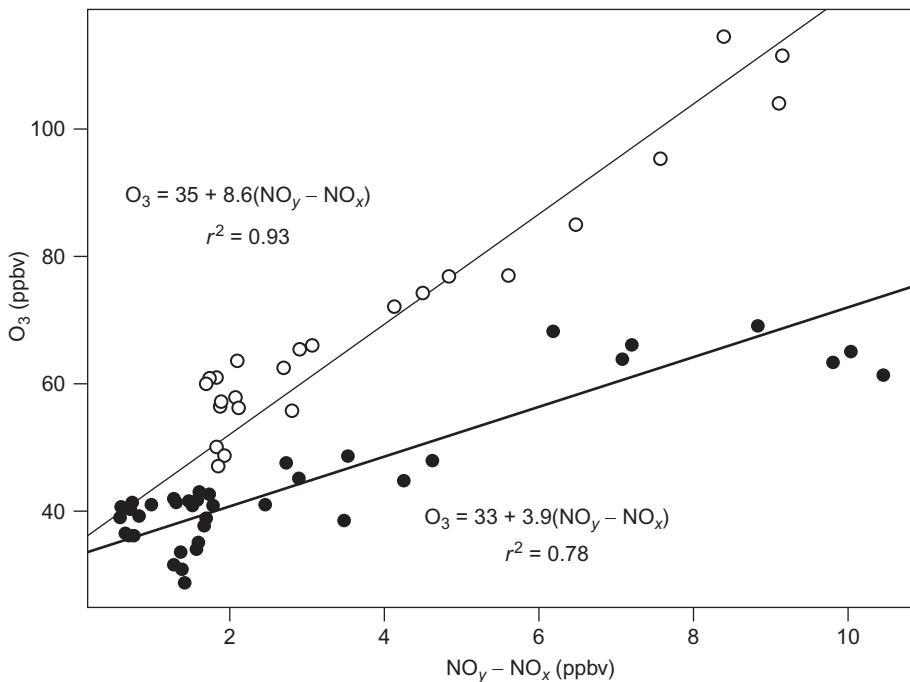


FIGURE 3.10 Ambient O_3 versus $NO_y - NO_x$ concentrations in the atmosphere at Harvard forest in northern Massachusetts in the United States, May 6–12, 1990 (●) and August 24–30, 1992 (○). Source: From Hirsch *et al.* (1996). Used with permission of American Geophysical Union.

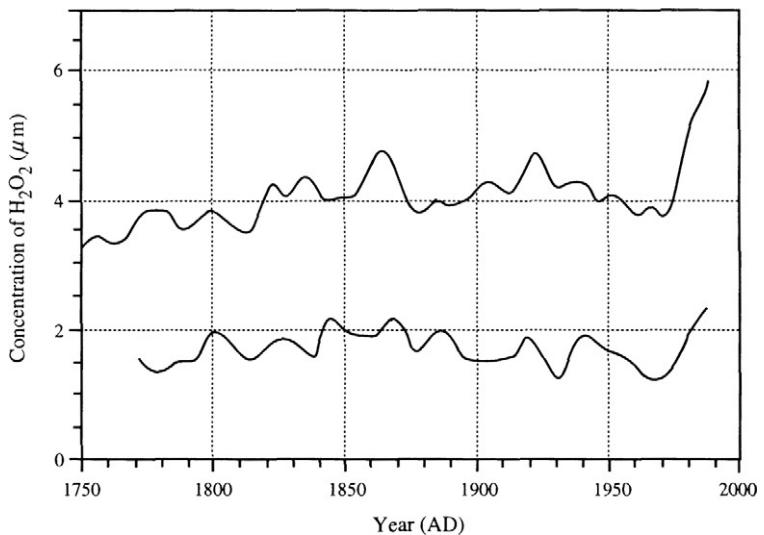


FIGURE 3.11 Variation in the mean annual H_2O_2 concentration over the past 200 years as seen in two cores from the Greenland ice pack. Source: Modified with permission of Macmillan from Sigg and Neftel (1991).

ATMOSPHERIC DEPOSITION

Elements of biogeochemical interest are deposited on the Earth's surface as a result of rainfall, dry deposition, and the direct absorption of gases from the atmosphere. The importance of each of these processes differs for different regions and for different elements (Gorham 1961).

Processes

In many forests, a large fraction of the annual uptake and circulation of nutrient elements in vegetation may be derived from the atmosphere (Miller et al. 1993b, Kennedy et al. 2002a, Avila et al. 1998). The atmosphere accounts for nearly all of the nitrogen and sulfur that circulates in terrestrial ecosystems, with rock weathering providing only smaller amounts (see Table 4.5 and 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 dissolved content in both fractions represents the results of heterogeneous reactions between gases and raindrops in the atmosphere.

The relative contribution of rainout and washout varies depending on 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 that has fallen (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 Wötzl 1970, Bator and Collett 1997). This inverse relation explains why extremely high concentrations of dissolved constituents are found in fog waters (Weathers et al. 1986, Waldman et al. 1982, Clark et al. 1998, Elbert et al. 2000). Capture of fog and cloud water by vegetation is an important component of the deposition of nutrient elements from the atmosphere in some high-elevation and coastal ecosystems (Lovett et al. 1982, Waldman et al. 1985, Ewing et al. 2009, Weathers et al. 2000).

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

$$\text{Washout} = \frac{\text{Ionic concentration in rain(mg/liter)}}{\text{Ionic concentration in air(mg/m}^3\text{)}}. \quad (3.37)$$

With units of m^3/liter , this ratio gives an indication of the volume of atmosphere cleansed by each liter of rainfall as it falls. 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, Wesely and

Hicks 1999). Dryfall of dusts downwind of arid lands is often spectacular; Liu et al. (1981) reported $100 \text{ g m}^{-2} \text{ hr}^{-1}$ of dustfall in Beijing, China, as a result of a single dust storm on April 18, 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, Muhs et al. 2001). 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 to 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. 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, Chadwick et al. 1999, Okin et al. 2004). Dry deposition contributes about 30 to 60% of the deposition of sulfur in New Hampshire (Likens et al. 1990; compare Tanaka and Turekian 1995). Similarly, 34% of the atmospheric inputs of nitrogen to Harvard Forest (Massachusetts) are derived from dry deposition (Munger et al. 1998). Organic nitrogen compounds deposited from the atmosphere are decomposed by soil microbes, providing additional plant nutrients (Neff et al. 2002a, Mace et al. 2003, Zhang et al. 2012b).

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 (Hosker and Lindberg 1982, Lindberg et al. 1986, Sparks et al. 2003, Turnipseed et al. 2006). Uptake of pollutant O_3 , 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, where dry deposition was nearly half of the total annual deposition of nitrogen from the atmosphere. Vegetation can also be a source or a sink for atmospheric NH_3 , depending on the ambient concentration in the atmosphere (Langford and Fehsenfeld 1992, Sutton et al. 1993, Pryor et al. 2001). Plants can also remove volatile organic compounds from the air (Simonich and Hites 1994).

The 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):

$$\text{Deposition velocity} = \frac{\text{Rate of dryfall}(\text{mg/cm}^2/\text{sec})}{\text{Concentration in air}(\text{mg/cm}^3)}. \quad (3.38)$$

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 $5.8 \text{ m}^2/\text{m}^2$ and an ambient concentration of $0.82 \mu\text{g N m}^{-3}$ 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, Petroff et al. 2008).

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 CO_2 (Sabine et al. 2004) and SO_2 (Beilke and Lamb 1974) and as a source of NH_3 (Quinn et al. 1987, 1988).

Regional Patterns and Trends

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). Coastal areas are dominated by atmospheric inputs from the sea, with large inputs 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, in rainfall (Figure 3.12; Young et al. 1988, Sequeira 1993,

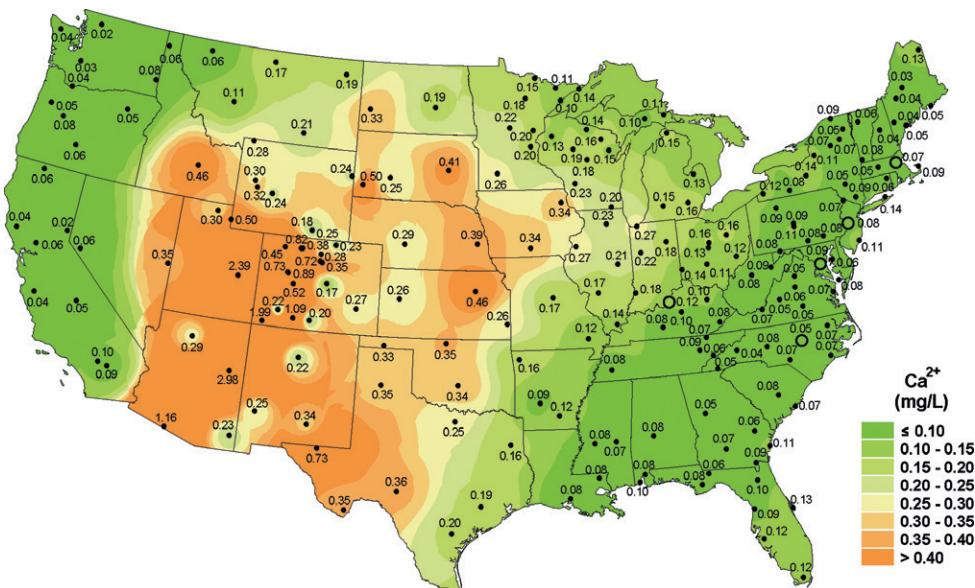


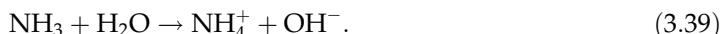
FIGURE 3.12 Mean calcium concentration (mg/l) in wetfall precipitation in the United States for 2009. Source: From the National Atmospheric Deposition Program/National Trends Network (2009); <http://nadp.sws.uiuc.edu>.

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 (refer to Table 9.1)—we may presume 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. (1982b) used this approach to deduce nonmarine sources of Ca and SO_4 in the rainfall in coastal California (Figure 3.13).

Iron (Fe) and aluminum (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 2000). High concentrations of Al in dryfall on Hawaii were traced to springtime dust storms on the central plains of China (Parrington et al. 1983). Soil mineralogy in dusts from the 1930s' Great Plains dust bowl can be identified in layers of the Greenland ice pack (Donarummo et al. 2003). 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 (Eqs. 3.27 and 3.28; Cogbill and Likens 1974, 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). In contrast, ammonia (NH_3) is a net source of alkalinity in rainwater, since its dissolution produces OH^- :



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), namely (from Gorham et al. 1984),

$$\text{H}^+ = [\text{NO}_3^- + 2\text{SO}_4^{2-}] - [\text{NH}_4^+ + 2\text{Ca}^{2+}] \quad (3.40)$$

In Kanpur, India, ammonia dominated the neutralization of acidity in rainfall during the wet season, while Ca played a similar role in the dry season, when more soil dust was present in the atmosphere (Shukla and Sharma 2010).

Globally, about 40% 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-} , which is related to pollutant emissions of SO_2 in areas upwind (Likens et al. 2005). Similar relationships are seen between emissions of NO_x and the NO_3^- content of rain (Butler et al. 2003, 2005). In the western United States, the relationship between acidity and the acid-forming anions is less clear because they have often reacted with soil aerosols containing CaCO_3 (Epstein and Oppenheimer 1986, Oppenheimer et al. 1985, Young et al. 1988, Reheis and Kihl 1995).

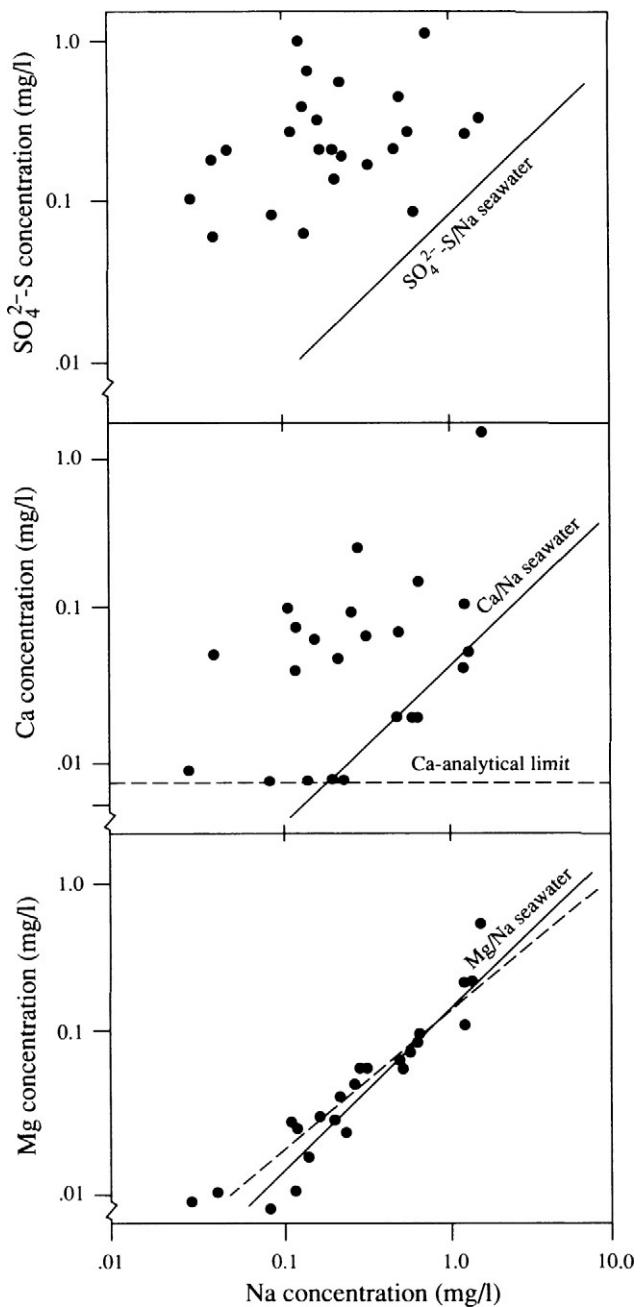


FIGURE 3.13 Concentrations of SO_4^{2-} , Ca, and Mg in wetfall precipitation near Santa Barbara, California, plotted as a logarithmic function of Na concentration in the same samples (Schlesinger et al. 1982b). The *solid line* represents the ratio of these ions to Na in seawater. Ca and SO_4^{2-} are enriched in wetfall relative to seawater, whereas Mg shows a correlation (*dashed line*) that is not significantly different from the ratio expected in seawater.

In the past 100 years, increases in the concentration of NO_3^- and SO_4^{2-} in the Greenland and Tibetan snowpacks have reflected the changes in the abundance of anthropogenic pollutants due to industrialization in the Northern Hemisphere (Mayewski et al. 1986, 1990; Thompson et al. 2000). 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 and eastern Tennessee suggest a recent decline in the concentrations of SO_4^{2-} that may reflect improved control of emissions (Likens et al. 1984, 2002; compare Kelly et al. 2002, Zbieranowski and Aherne 2011, Lutz et al. 2012b). Improvements in air quality as a result of the implementation of the Clean Air Act in 1990 have resulted in significant decreases in the acidity of rainfall over the eastern United States and Canada (Figure 3.14; Hedin et al. 1987). Similarly, the uppermost layers of ice in glaciers of the French Alps and Greenland show lower concentrations of SO_4^{2-} and NO_3^- , presumably due to control of pollutant emissions in upwind sources in recent years (Preunkert et al. 2001, 2004, Fischer et al. 1998).

Even with pollutant abatement, long-term records suggest that many natural ecosystems 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). Excess deposition of nitrogen 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 (Chapters 4 and 6). Atmospheric deposition of nitrogen makes a significant contribution to the nutrient load and eutrophication of lakes (Bergström and Jansson 2006), estuaries (Nixon et al. 1996, Latimer and Charpentier 2010), and coastal waters (Paerl et al. 1999). 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, Liang et al. 1998). Although pollutant emissions have declined in North America and Europe, increasing emissions are seen from India and China (Lelieveld et al. 2001, Richter et al. 2005, Stern 2006). The airborne concentrations of many air pollutants can now be measured using satellite technology (Richter et al. 2005, Clarisse et al. 2009, Martin 2008).

BIOGEOCHEMICAL REACTIONS IN THE STRATOSPHERE

Ozone

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



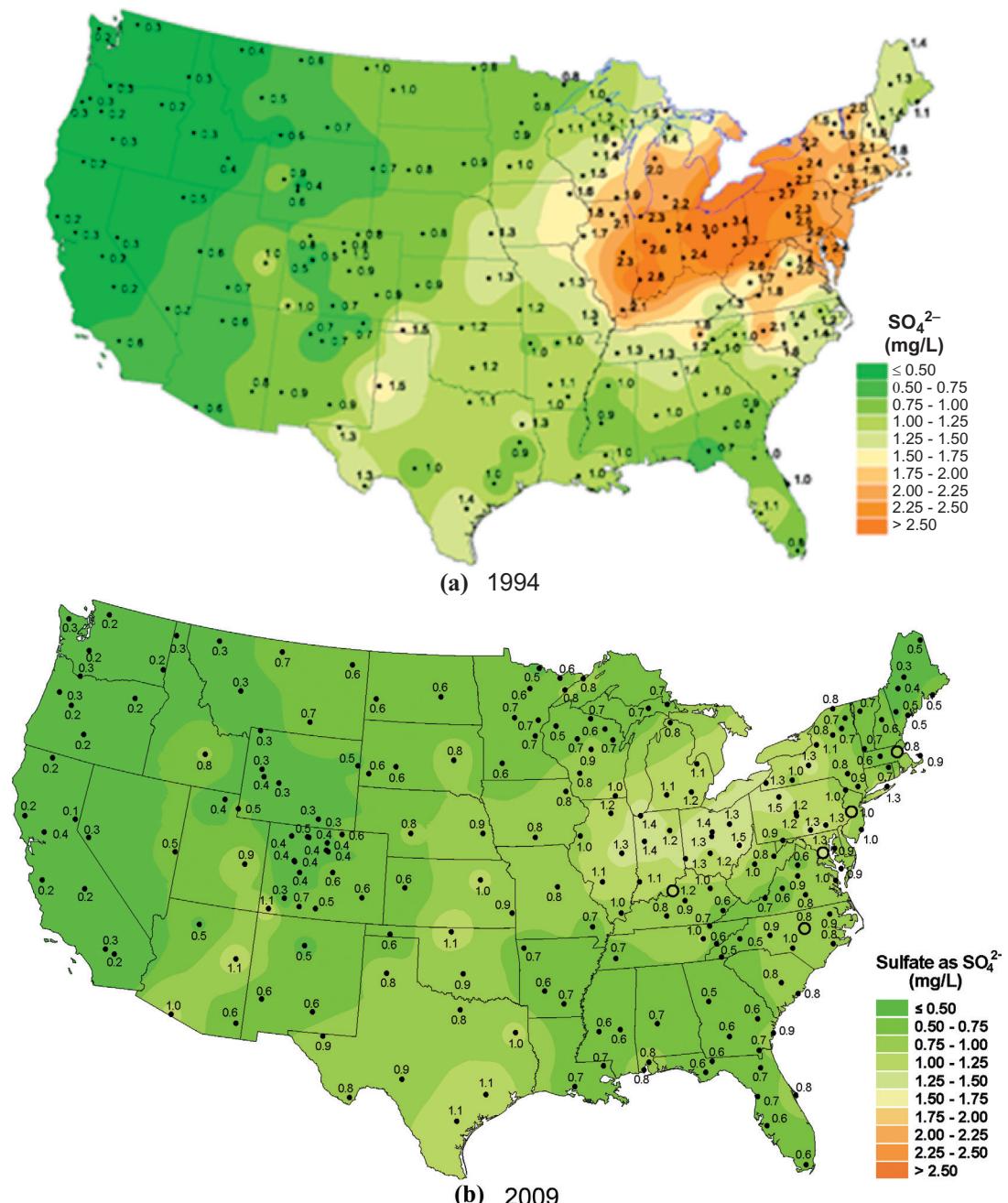


FIGURE 3.14 Sulfate (SO_4^{2-}) concentration (mg/l) measured in samples of wetfall precipitation across the United States, showing the effect of the Clean Air Act in reducing SO_2 emissions and thus SO_4^{2-} deposition between (a) 1994 and (b) 2009. Source: From the National Atmospheric Deposition Program/National Trends Network (2009); <http://nadp.sws.uiuc.edu>.

Some ozone from the stratosphere mixes down into the troposphere, where the production of O₃ by these reactions is limited because there is less ultraviolet light (refer to [Table 3.6](#)). Most of the remaining ozone is destroyed by a variety of reactions in the stratosphere.

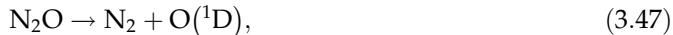
Absorption of ultraviolet light at wavelengths between 200 and 320 nm destroys ozone:



This absorption warms the stratosphere (refer to [Figure 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 (Wennberg et al. 1994),



and by reactions stemming from the presence of nitrous oxide (N₂O), which mixes up from the troposphere. Tropospheric N₂O is produced in a variety of ways ([Chapters 6 and 12](#)), but it is inert in the lower atmosphere. The only significant sink for N₂O is photolysis in the stratosphere. About 80% of the N₂O reaching the stratosphere is destroyed in a reaction producing N₂ (Warneck 2000),



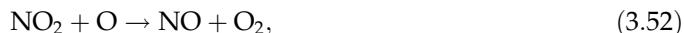
and about 20% in reactions with the O(¹D) produced in [Eq. 3.47](#), mainly



but with a small amount forming NO:



The nitric oxide (NO) produced in reaction 3.49 destroys ozone in a series of reactions,



for which the net reaction is



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 N₂O; only a small

amount is contributed by high-altitude aircraft. Eventually NO_2 is removed from the stratosphere by reacting with OH to produce nitric acid (Eq. 3.26), which mixes down to the troposphere and is removed by the heterogeneous reaction with raindrops.⁶

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



for a net reaction of

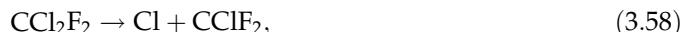


Although each Cl produced may cycle through these reactions and destroy many molecules of O_3 , Cl is eventually converted to HCl and removed from the stratosphere by downward mixing and heterogeneous interaction with cloud drops in the troposphere (Rowland 1989, Solomon 1990).

The balance between ozone production (refer to Eqs. 3.41 and 3.42) and the various reactions that destroy ozone maintains a steady-state concentration of stratospheric O_3 with a peak of approximately 7×10^{18} molecules/m³ at 30 km altitude (Warneck 2000). Although the photochemical production of O_3 is greatest at the equator, the density of the ozone layer is normally thickest at the poles.

Since the mid-1980s, field measurements have indicated that the total density of ozone molecules in the atmospheric column has declined significantly over Antarctica (Farman et al. 1985; Figure 3.15) and globally (Herman 2010). The decline, as much as 0.3%/yr, was 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, McKenzie et al. 1999) and increased incidence of skin cancer and cataracts in humans (Norval et al. 2007). Greater uvB radiation at the Earth's surface is likely to reduce marine production in the upper water column of the Southern Ocean around Antarctica (Smith et al. 1992b, Arrigo et al. 2003). Ultraviolet radiation also causes deleterious effects on land plants (Caldwell and Flint 1994, Day and Neale 2002). Because previous, steady-state ozone concentrations were maintained in the face of natural photochemical reactions that produce and consume ozone, attention focused on how this balance might have been disrupted by human activities (Cicerone 1987, McElroy and Salawitch 1989, Rowland 1989).

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):



⁶ Atmospheric chemists refer to this reaction as denitrification. It is not to be confused with the denitrification performed by certain bacteria, which remove NO_3^- and produce N_2 in anaerobic soils and sediments (Chapter 7).

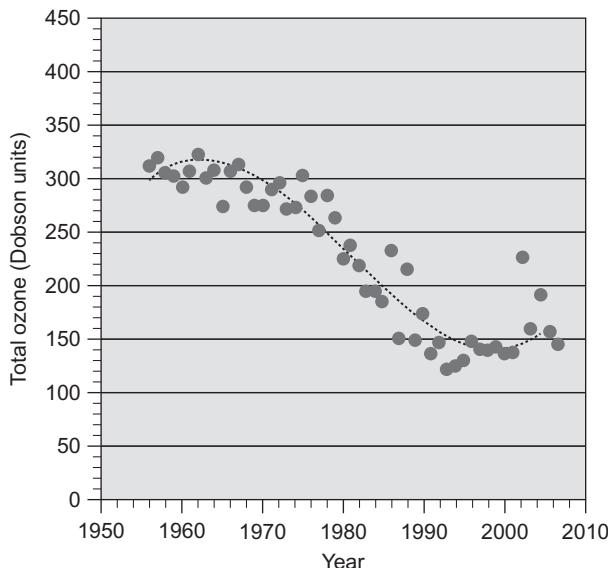
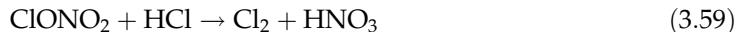


FIGURE 3.15 The decline in ozone (O_3) over Antarctica since the 1950s, and its recovery in recent years as a result of the Montreal Protocol, instituted in 1989. The customary unit for the total number of ozone molecules in an atmospheric column, the Dobson unit, is equivalent to 2.69×10^{16} molecules/cm² of the Earth's surface. Source: From Kump et al. (2010). Used with permission of Pearson/Prentice Hall.

which can destroy ozone by the reactions of Eqs. 3.54 through 3.56. 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:



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 (Solomon 1990).

The relative importance of chlorofluorocarbons versus natural sources of chlorine in the stratosphere is apparent in a global budget for atmospheric chlorine (Figure 3.16). 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 seasalt aerosols 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, Textor et al. 2003). After the Mount 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 the ocean surface, by plants in coastal salt marshes and upland forests, by

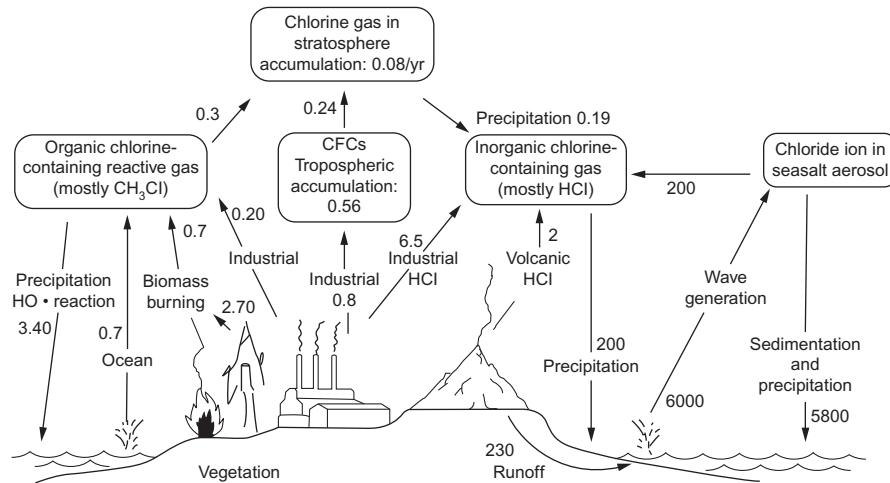


FIGURE 3.16 A global budget for Cl in the troposphere and the stratosphere. All data are given in 10^{12} g Cl/yr. Sources: Modified and updated from Möller (1990), Graedel and Crutzen (1993), and Graedel and Keene (1995), with new data from McCulloch et al. (1999) and other sources listed in Table 3.7.

litter decomposition (Keppler et al. 2000, Hamilton et al. 2003), and by forest fires (Table 3.7). There is no strong industrial source that might be indicated by an increase in the concentration of CH_3Cl in the Antarctic ice pack during the past 100 years (Butler et al. 1999, Saltzman et al. 2009), or by a significant difference in the concentration of methylchloride between the Northern and Southern Hemispheres (Beyersdorf et al. 2010). The current budget for CH_3Cl is imbalanced, with sources slightly exceeding sinks, but methylchloride has a mean residence time of about 1.3 years in the atmosphere, so a small portion mixes into the stratosphere.

In the global Cl budget, the relatively small industrial production of chlorofluorocarbons, which are inert in the troposphere, is the dominant source of Cl delivered to the stratosphere (Figure 3.16; Russell et al. 1996). Increasing concentrations of these compounds have been strongly implicated in ozone destruction (Rowland 1989, Butler et al. 1999). Happily, with the advent of the Montreal Protocol in 1989, 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, Montzka et al. 1996, Solomon et al. 2006) and that the ozone hole may be starting a slow recovery (Figure 3.15; Yang et al. 2008, Newman et al. 2006). Indeed, the main cause of continued human impacts on stratospheric ozone may stem from our continuing contributions to the rise in N_2O in Earth's atmosphere (Ravishankara et al. 2009; Chapter 12).

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 source of methylbromide (CH_3Br), which is used as an agricultural fumigant (Yagi et al. 1995). Methylbromide is also released from the ocean's surface, coastal vegetation, and biomass burning (Table 3.7). Sinks of CH_3Br include uptake by the oceans and soils and oxidation by OH radical. After rising throughout the Industrial Revolution (Saltzman et al. 2008, Khalil et al. 1993a), the atmospheric concentration of methylbromide appears to have

TABLE 3.7 Budgets of CH₃Cl and CH₃Br in the Atmosphere (Tg/yr)

Sources	CH ₃ Cl	CH ₃ Br	References
Ocean surface	0.65–0.76	0.10	Thompson et al. 2002, Yoshida et al. 2006, Anbar et al. 1996
Coastal vegetation	0.05–0.17	0.0014–0.014	Rhew et al. 2000, Hu et al. 2010, Manley et al. 2006
Tropical forests	0.91–1.5		Yokouchi et al. 2002a, Saito et al. 2008, Blei et al. 2010
Other vegetation (by difference)	1.4		Yoshida et al. 2006
Biomass burning	0.55–0.90	0.029	Andreae and Merlet 2001, Yoshida et al. 2006, Thompson et al. 2002
Industrial uses	0.11–0.16	0.05	McCulloch et al. 1999, Thompson et al. 2002
Total of sources (best estimates)	4.28	0.19	
Sinks			
Ocean uptake		0.12	Anbar et al. 1996
Soil uptake	0.25	0.022–0.042	Shorter et al. 1995, Serca et al. 1998
Reaction with OH	3.37	0.09	Thompson et al. 2002
Loss to stratosphere	0.28	0.006	Thompson et al. 2002
Total of sinks (best estimates)	3.90	0.24	

declined in recent years (Yokouchi et al. 2002b, Yvon-Lewis et al. 2009). The global budget of CH₃Br and its mean residence time (about 0.8 years; Colman et al. 1998) in the atmosphere are poorly constrained—sinks exceed sources (Table 3.7). However, some CH₃Br persists long enough to reach the stratosphere, where it can lead to ozone destruction.

Among other halogen-containing gases, the lifetimes of bromoform (CHBr₃; Quack and Wallace 2003) and methyl iodide (CH₃I; Campos et al. 1996, Bell et al. 2002, Butler et al. 2007, Yokouchi et al. 2008), both produced by marine phytoplankton, and various inorganic fluoride compounds (e.g., CH₃F) are too short for appreciable mixing into the stratosphere. The observed increase of fluoride in the stratosphere appears solely due to the upward transport of chlorofluorocarbons, and it is an independent verification of their destruction in the stratosphere by ultraviolet light (Russell et al. 1996). However, F is ineffective as a catalyst for ozone destruction.

Satellite observations have greatly aided our understanding of changes in stratospheric ozone. The loss of ozone from the atmosphere has been monitored since 1979 when the first Total Ozone Mapping Spectrometer (TOMS) began records of the abundance of O₃ in a column extending from the bottom to the top of the atmosphere (Figure 3.17). Both the

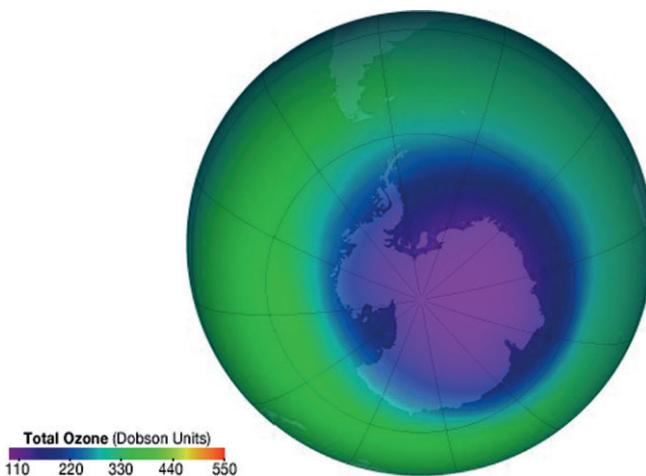


FIGURE 3.17 The average abundance of ozone in the atmosphere of the Southern Hemisphere during October 2006. The ozone “hole,” seen in blue and purple, is actually an area where the abundance of ozone in the stratosphere is reduced—perhaps better described as a thinning rather than a hole. Source: From http://ozonewatch.gsfc.nasa.gov/monthly/monthly_2006-10.html.

area and the minimum column abundance of ozone appear to have stabilized in recent years, after strong declines at the beginning of the record (refer to Figure 3.15).⁷ Similar, though less extensive, ozone losses are reported for the Arctic (Solomon et al. 2007, Manney et al. 2011).

Stratospheric Sulfur Compounds

Sulfate aerosols in the stratosphere are important to the albedo of the Earth (Warneck 2000). A layer of sulfate aerosols, known as the Junge layer, is found in the stratosphere at about 20 to 25 km altitude. Its origin is twofold. Large volcanic eruptions can inject SO₂ into the stratosphere, where it is oxidized to sulfate (Eqs. 3.27 and 3.28). Large eruptions have the potential to increase the abundance of stratospheric sulfate 100-fold (Arnold and Bührke 1983, Hofmann and Rosen 1983), and the sulfate aerosols persist in the stratosphere for several years, cooling the planet (McCormick et al. 1995, Briffa et al. 1998). During periods without volcanic activity, the dominant source of stratospheric sulfate derives from carbonyl sulfide (COS)⁸ 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 (refer to Table 3.5), so about one-third of the annual production mixes to the stratosphere. Additional COS may be lofted to the stratosphere in the smoke plumes of large wildfires (Notholt et al. 2003).

Carbonyl sulfide that reaches the stratosphere is oxidized by photolysis, forming sulfate aerosols which contribute to the Junge layer (Chin and Davis 1993). Eventually, these aerosols are removed from the stratosphere by downward mixing of stratospheric air.

⁷ See <http://ozoneaq.gsfc.nasa.gov/> and <http://ozenewatch.gsfc.nasa.gov/>.

⁸ Also abbreviated OCS.

The concentration of COS in the atmosphere today is higher than in preindustrial times (Montzka et al. 2004), although it seems to have declined slightly in recent years (Rinsland et al. 2002, Sturges et al. 2001).

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 (2D) models 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 1981, Asman and van Jaarsveld 1992, Berge and Jakobsen 2002). Three-dimensional (3D) models attempt to follow the fate of particular parcels of air as they move both horizontally and vertically in the atmosphere. These dynamic 3D models are known as *general circulation models* (GCMs) for the globe ([Figure 3.18](#)).

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 climate models predict that a substantial warming of the atmosphere (2–4.5°C) will accompany increasing concentrations of CO₂, N₂O, CH₄, and chlorofluorocarbons in the atmosphere (IPCC 2007).⁹ Largely stemming from fossil fuel combustion, the concentration of CO₂ is now higher than at any time in the past 20 million years (Pearson and Palmer 2000). During the past 150 years, the concentrations of CO₂, CH₄, and N₂O have risen above levels seen at any time during the past 10,000 years—spanning the entire history of human civilization (Flückiger et al. 1999). Atmospheric warming, resulting from the absorption of infrared (heat) radiation by these gases emitted from the Earth's surface, is known as the greenhouse effect or radiative forcing ([Figure 3.2](#)). The predicted warming of future climate is greatest near the poles, where there is normally the greatest net loss of infrared radiation relative to incident sunlight (Manabe and Wetherald 1980). Dramatic, recent declines in the extent of Arctic sea ice suggest that these predictions are already proving correct (Serreze et al. 2007; [Chapter 10](#)). For the same reason, future nighttime and wintertime temperatures worldwide are likely to show large changes relative to today's conditions. Presumably the oceans will warm more

⁹ Through its industrial use as a solvent, nitrogen trifluoride (NF₃) is potentially an important contributor to Earth's greenhouse effect, but it is not included in most assessments of climate change (Prather and Hau 2008, Weiss et al. 2008).

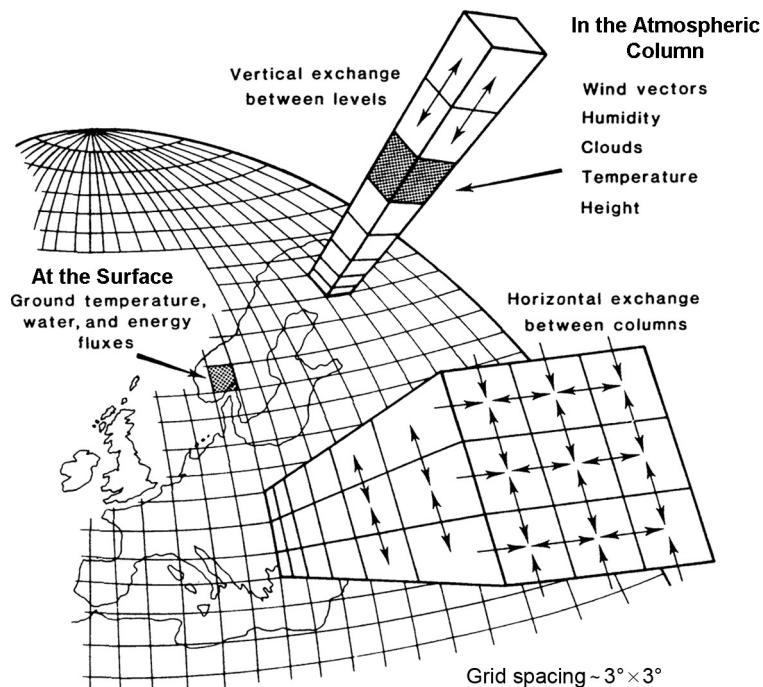


FIGURE 3.18 Conceptual structure of a dynamic three-dimensional general circulation model for the Earth's atmosphere, indicating the variables that must be included for a global model to function properly. Source: From Henderson-Sellers and McGuffie (1987). Copyright © 1987. Reprinted by permission of John Wiley & Sons, Ltd.

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 (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, Soden et al. 2005, Willett et al. 2007). Thus, most models predict that higher concentrations of CO₂ and other trace gases in the atmosphere will make the Earth a warmer and more humid planet.

Incoming solar radiation delivers about 340 W/m² to the Earth (Figure 3.2).¹⁰ The natural greenhouse effect warms the planet about 33°C by trapping 153 W/m² of outgoing radiation (Ramanathan 1988).¹¹ For the past 30 years or so, there has been a small increase in the Sun's luminosity (+0.12 to +0.16 W/m²) (IPCC 2007, Foukal et al. 2006, Pinker et al. 2005), but the human impact on radiative forcing due to increasing concentrations of atmospheric trace gases currently adds about 2.3 W/m² to the natural greenhouse effect (IPCC 2007), causing measurable

¹⁰ The Sun's radiation, measured outside Earth's atmosphere, delivers 1379 W/m², known as the solar constant (McElroy 2002). A one-dimensional model for the Earth's radiation budget shows an annual input of ~340 W/m⁻², because only ¼ of the Earth's surface is exposed to sunlight at any moment.

¹¹ The Earth's greenhouse effect is dominated by H₂O and CO₂. O₂ and N₂ provide only a trivial contribution to Earth's radiation balance, together adding 0.28 W/m² to the greenhouse effect (Hopfner et al. 2012).

changes in the spectral distribution of radiation leaving the Earth (Harries et al. 2001). Aerosols tend to cool the atmosphere, and increases in aerosols due to human activities are thought to reduce the global radiative forcing by about 1.2 W/m^2 (i.e., global dimming; IPCC 2007, Bellouin et al. 2005, Mahowald 2011). It is interesting to note that aerosol concentrations were higher (Patterson et al. 1999, Lambert et al. 2008) and CO_2 concentrations and temperatures were lower (Figure 1.2) during the last glacial period.

Long-term records from tree rings and ice cores suggest that substantial warming of the global climate is now occurring, coincident with rising CO_2 (Mann et al. 1999; Thompson et al. 2000). Recent temperatures in Europe are greater than at any point in the past 500 years (Luterbacher et al. 2004). These changes in climate cannot be explained by natural phenomena alone (Crowley 2000, Stott et al. 2000). 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. Already, several long-term records suggest increases in the ocean's temperature worldwide (Barnett et al. 2005, Levitus et al. 2001).

Differential warming of the atmosphere and oceans will also change global patterns of precipitation and evapotranspiration (Manabe and Wetherald 1986, Rind et al. 1990, Zhang et al. 2007), causing substantial changes in soil moisture of most areas outside the tropics. Arid regions, such as the southwestern United States, are especially likely to experience increased drought (Cook et al. 2004, Seager et al. 2007), consistent with recent trends in rainfall in this region (Milly et al. 2005).

Climate change affects biogeochemistry (and vice versa) in a variety of ways. Land plants and ocean waters take up substantial quantities of CO_2 from the atmosphere, potentially slowing the rate of climate change (Chapters 5, 9, and 11). Clearing vegetation alters the albedo of the Earth's land surface, potentially altering radiative forcing. Warmer temperatures may increase the rate of decomposition of soil carbon now frozen in Arctic permafrost (Dorrepaal et al. 2009, Schuur et al. 2009), and trigger the release of methane now frozen in ocean sediments, resulting in positive feedbacks that further exacerbate global warming (Chapter 11). Changes in climate are likely to affect the distribution of many plants and animals, potentially causing many extinctions (Thomas et al. 2004a); they also impact a wide range of conditions affecting human health and economic activity.

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 inputs 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. Changes in stratospheric ozone and global climate are early warnings of the human impact on the atmosphere of our planet.

Recommended Readings

- Brasseur, G.P., J.J. Orlando, and G.S. Tyndall. 1999. *Atmospheric Chemistry and Global Change*. Oxford University Press.
- Graedel, T.E. and P.J. Crutzen. 1993. *Atmospheric Change*. Freeman.
- Henderson-Sellers, A. and K. McGuffie. 1987. *A Climate Modelling Primer*. Wiley.
- Jacob, D.J. 1999. *Introduction to Atmospheric Chemistry*. Princeton University Press.
- McElroy, M.B. 2002. *The Atmospheric Environment*. Princeton University Press.
- Seinfeld, J.H. and S.N. Pandis. 2006. *Atmospheric Chemistry and Physics*. Wiley.
- Walker, J.C.G. 1977. *Evolution of the Atmosphere*. Macmillan.
- Warneck, P. 2000. *Chemistry of the Natural Atmosphere* (second ed). Academic Press/Elsevier.
- Wayne, R.P. 1991. *Chemistry of Atmospheres*. Clarendon Press.

PROBLEMS

- 3.1 If you are vacationing in Aspen, Colorado (8000 ft elevation), what is the mass of the atmosphere above you, relative to that at sea level?
- 3.2 For any planet, the equilibrium surface temperature is determined by the balance between the radiation received and the radiation lost to space. The input is determined by

$$\text{Input} = [F(1 - A)\pi(R^2)]/4,$$

where

F is the solar constant; for Earth $F = 1379 \text{ W/m}^2$

A is the albedo of the surface

R = radius of the planet

The loss of radiation is determined by the emission of infraradiation:

$$\text{Loss} = (\sigma)T^4\pi R^2,$$

where

σ is the Stefan-Boltzmann constant ($5.673 \times 10^{-8} \text{ W/m}^2/\text{K}^{-4}$)

T is the temperature in degrees Kelvin

R = radius of the planet

Thus, if the input of radiation increases, the temperature will rise. But with a rise in temperature there is a dramatic increase in loss (i.e., temperature to the 4th power), so eventually the input and loss will again be equal. At that time, the planet will be in thermal equilibrium but at a higher surface temperature. This is essentially the origin of the “greenhouse effect” on Earth, which is driven not by changes in the Sun’s luminosity but by the tendency for radiatively active gases (such as CO₂ and H₂O) to reduce the loss of infrared radiation from Earth’s surface.

- (a) If the albedo of Earth was 0 (i.e., if the Earth were a perfect black-body absorber), what would be its equilibrium temperature?
- (b) Actually, the albedo of Earth is about 0.30. What should be its equilibrium temperature? Compared to the mean temperature on Earth, what is the “greenhouse effect”?

- 3.3 The mass of tropospheric air that is injected into the stratosphere results in a mean residence time for stratospheric air of 2.6 years. Presumably, each year, the same volume of air mixes down from the stratosphere into the troposphere. What is the mean residence time of tropospheric air with respect to the stratosphere? Given their 100-year mean residence time in Earth’s atmosphere, what does this say about the circulation of CFCs in our atmosphere?
- 3.4 What percent of the emissions of a gas with constant emissions and a mean residence time of 120 days in the troposphere will mix into the stratosphere?
- 3.5 The deposition velocity of NH₃ in forests and other natural ecosystems is often about 10 to 50 mm/sec (Sutton et al. 1993). Given the range of concentrations of NH₃ in the atmosphere (Table 3.5), what is the expected range of dry deposition of NH₃ in terrestrial ecosystems?
-