

5

Atmospheric Chemistry

5.1 Introduction

In recent years there has been an increasing interest in atmospheric chemistry. Since the oceans are in intimate contact with the atmosphere and may act as a source or sink for atmospheric gases, it is appropriate to briefly examine this area of science. The early interest in the atmosphere was related to the formation of photochemical smog in various cities. Smog is formed by complicated interactions of unburned hydrocarbons from automobiles and power plants and nitrogen oxides. The sun provides the necessary energy to furnish reactive species. More recently interest in atmospheric chemistry has focused on the formation of acid rain (HNO_3 and H_2SO_4) from the oxidation of NO_x and SO_2 gases that result from the oxidation of fossil fuels. The decrease in the ozone layer resulting from the use of chlorofluorohydrocarbons (CFCs), has also prompted new interest in atmospheric chemistry. Interest has also been focused on the increasing concentration of gases that can absorb infrared (IR) energy. These gases (CO_2 , CH_4 , etc.) contribute to the warming of the atmosphere, or the so-called greenhouse effect.

Since many of the chemical reactions of interest occur near the surface of the earth, it is important to briefly examine the various layers of the atmosphere. The atmosphere can be divided into four layers (see Figure 5.1): the troposphere (0 to 10 km), the stratosphere (10 to 50 km), the mesosphere (50 to 100 km), and the thermosphere (100 to 1000 km). These layers are marked by changes in the temperature of the atmosphere. From the surface to 10 km the temperature decreases to a minimum at the tropopause. In the stratosphere the temperature increases to a maximum at the stratopause. In the mesosphere the temperature decreases to a minimum at the mesopause. In the thermosphere the temperature increases again as the atmosphere diminishes. The changes in the temperature of the atmosphere are related to the concentration of gases and the chemical reactions that occur at various levels of the ocean. The height above the surface of the earth is similar to the depth of water in the oceans. Since both fluids are compressible, changes in the height or depth can change the temperature. The effect is easier to characterize in the atmosphere since the gases behave in a near ideal manner and can be approximated using the ideal gas equation. The change in pressure with height (z) is related to the density (ρ) and acceleration of gravity (g) ($dp/dz = -\rho z$).

For an ideal gas the change in the adiabatic temperature with height can be determined ($dT/Dz = -Mg/C_p$, where M is the molecular weight and C_p is the heat capacity). This equation gives a change in the temperature of $-9.8^\circ/\text{kilometer}$. The decrease in the temperature of the atmosphere from the surface to the tropopause is due to this adiabatic cooling. The increase in the temperature between the stratosphere and the mesosphere, which goes through a maximum at the stratopause, is the result of the adsorption of energy

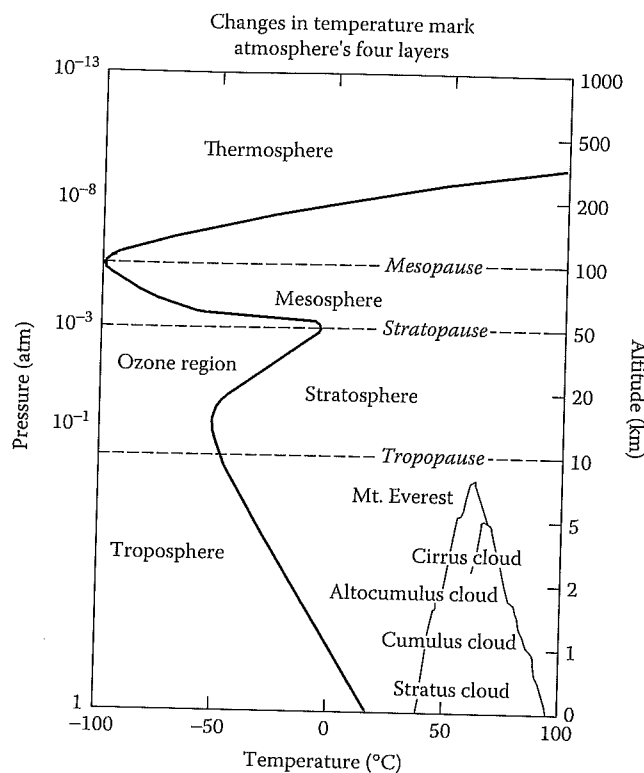


FIGURE 5.1
Changes in the temperature in the layers of the atmosphere.

by ozone molecules (O_3). As the atmosphere thins above the mesopause, the temperature increases into outer space.

Chemical reactions between the major constituents of the atmosphere occur at slow rates. The formation of active species occurs because of the influence of light and causes a number of rapid reaction chains. The chemistry of the lower atmosphere is often referred to as tropospheric photochemistry since it is driven by the absorption of photons.

The flux of solar photons as a function of wavelength is shown in Figure 5.2. Most of the radiation below 290 nm does not reach the troposphere. Photons with wavelengths shorter than 240 nm are absorbed by O_2 and N_2 molecules in the thermosphere. This results in the formation of ozone, O_3 :



where M represents another molecule of oxygen or nitrogen that is unchanged in the reaction. The concentration of O_3 formed in this manner peaks in the lower stratosphere (see Figure 5.3). The ultraviolet radiation can also stimulate dissociation of O_3 :



This reaction is responsible for the absorption of light between 240 to 300 nm. The electronically excited oxygen, $O(^1D)$, formed in the dissociation of O_3 is responsible for the

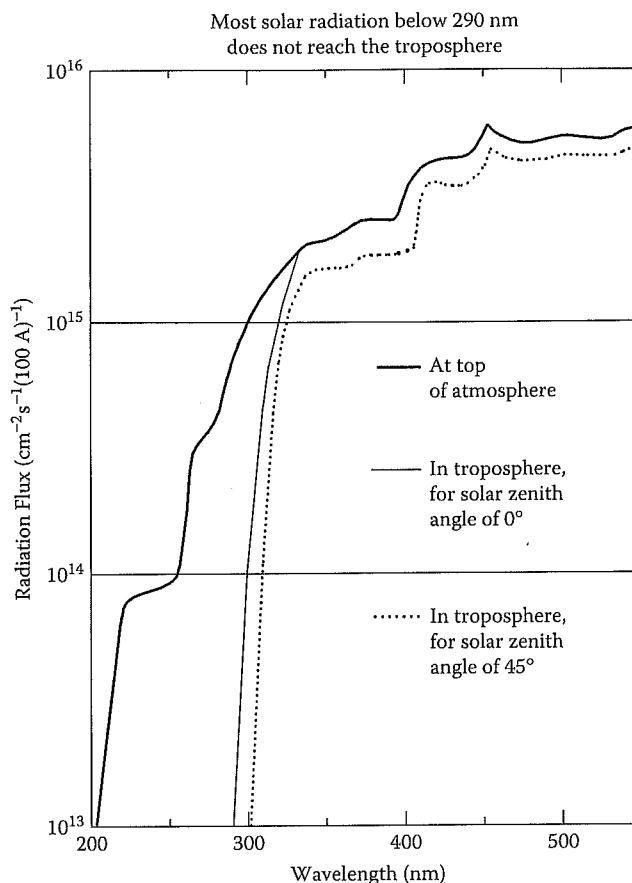


FIGURE 5.2
The solar radiation that reaches various layers in the troposphere.

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More will be said about these reactions later. The O_3 that is broken apart by photons forms oxygen atoms that quickly reform O_3 by reactions with O_2 . This leads to a steady state buildup of O_3 . The O_3 dies off when it collides with an O atom, forming two oxygen molecules



Other reactions that destroy O_3 in the stratosphere (such as reactions with atomic Cl) will be discussed later. The maximum in the concentration of ozone in the stratosphere can be attributed in the upper portion to the exponential decrease in O_2 and in the lower portion to the fall-off in the intensity of UV light as the solar light penetrates into the increasing dense atmosphere.

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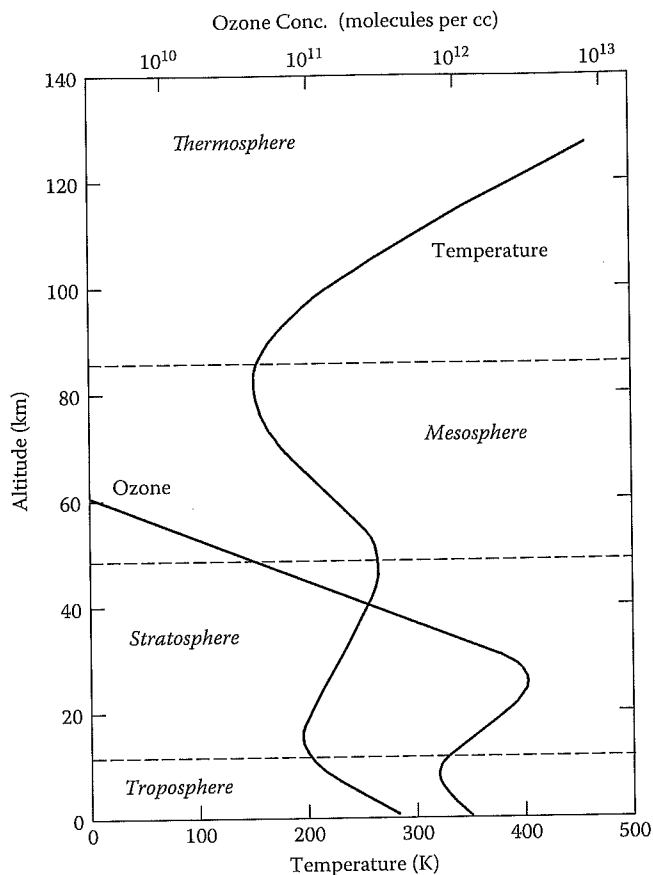
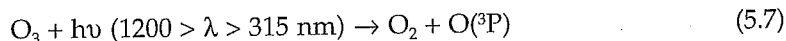


FIGURE 5.3

The concentration of ozone in various layers of the atmosphere.

Since the light reaching the troposphere has wavelengths above 300 nm, there is not enough energy available to break O–O bonds that have a bond strength of 120 kcal mol⁻¹. This means that O₂ cannot oxidize reduced gases in the troposphere. At one time it was thought that O₃ and H₂O₂ were oxidizers in the troposphere. Now the OH radical is thought to be the oxidizer.

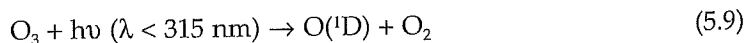
The production of OH· radicals is initiated by the photolysis of O₃. Ozone is present in the troposphere at concentrations from 10 to 100 ppb and has a bond energy of 26 kcal mol⁻¹. Solar photons with wavelengths between 315 and 1200 nm can dissociate O₃ and produce an oxygen atom in its ground electronic state:



The O(³P) atom rapidly reforms ozone by reaction with O₂ in a three-body reaction:



where M is N₂ or O₂. This sequence results in no net chemical effect. When ozone reacts with wavelengths shorter than 315 nm, an electronically excited oxygen atom is produced:



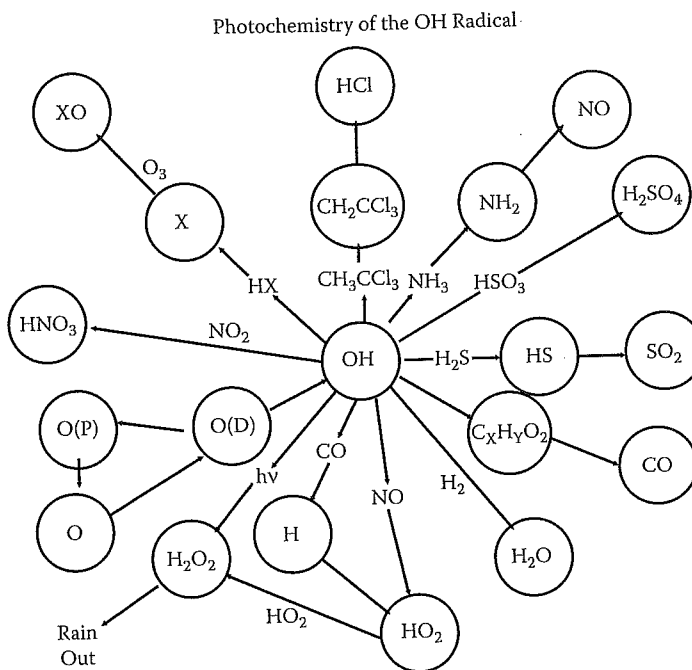


FIGURE 5.4
The photochemical control of OH· radicals on trace gases.

The $O(^1D)$ to $O(^3P)$ transition is forbidden and results in a relatively long lifetime for $O(^1D)$ of 100 seconds. The $O(^1D)$ most often collides with N_2 or O_2 (M):

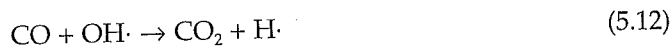


This ultimately reacts with O_2 to form O_3 , which also results in no net chemical change. Occasionally $O(^1D)$ collides with water to generate two hydroxyl radicals:

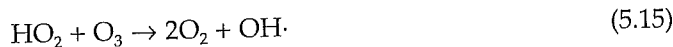


This reaction sequence is the primary source of hydroxyl radicals in the troposphere. The $OH\cdot$ radical formed in this manner is thought to control the concentration of many trace gases (see Figure 5.4).

The removal of $OH\cdot$ from the atmosphere results from the reactions



Both the $H\cdot$ and the $\cdot CH_3$ radicals combine rapidly with O_2 to form hydroperoxyl (HO_2) and methperoxyl (CH_3O_2) radicals. The hydroperoxyl radical, however, can regenerate $OH\cdot$ radicals:



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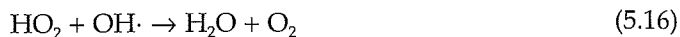
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It can also lead to the chain termination



The hydrogen peroxide (H_2O_2) is removed in rain. The chemistry of the methyloxy radical (CH_3O_2) is quite complicated and not all of its reactions are known at present. Mathematical models have been used to simulate these reactions, and the average $\text{OH}\cdot$ concentration is about 2 to 20×10^5 radicals per cm^3 , with the highest levels in the tropics. Model calculations predict that about 20% more $\text{OH}\cdot$ radicals should be found in the southern hemisphere. This is caused by the higher CO concentrations in the northern hemisphere. Direct measurements of $\text{OH}\cdot$ radicals in the atmosphere are difficult to make because of their low concentration and high reactivity. The largest loss of the OH radical in the troposphere is the oxidation of CO, which is controlled by the concentration of CO. The distributions of CO shown in Figure 5.5 have been measured as a function of time in a number of locations

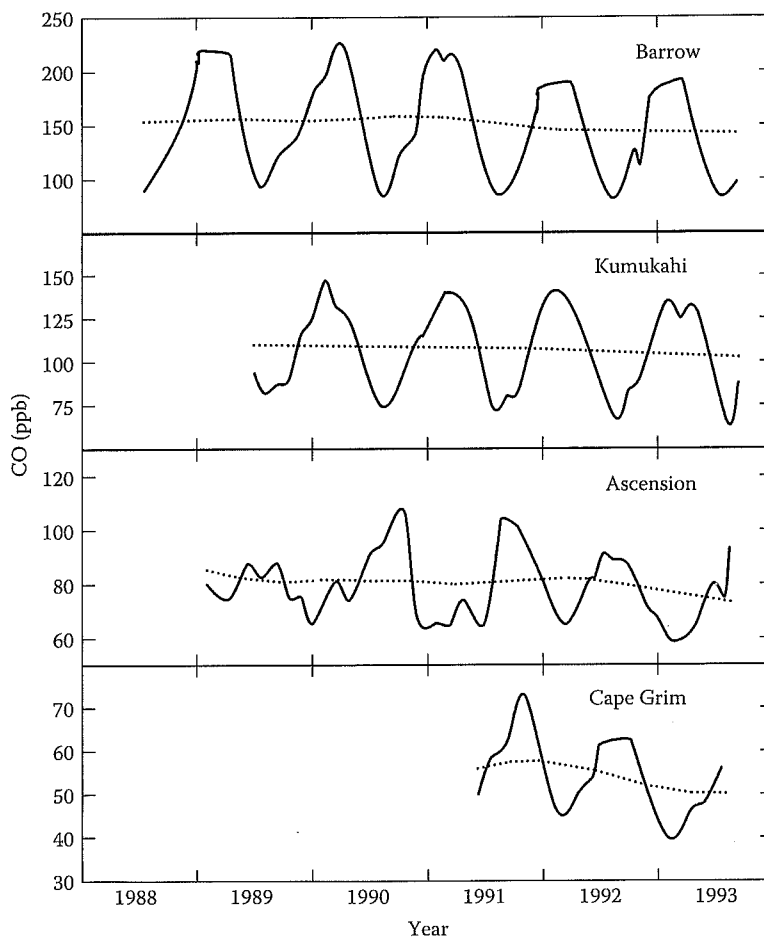


FIGURE 5.5
The changes in the concentration of CO in the atmosphere at different locations as a function of time.

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(Novelli 1994). The levels range from 45 to 250 ppb, decreasing from the north to the south. The levels are highest in the late winter and early spring and decrease in the summer.

Over the past 2 to 5 years the CO appears to have decreased in the northern latitudes by 7.3 ppb year⁻¹ and in the southern latitudes by 4.2 ppb year⁻¹. This recent decrease is opposite to the 1 to 2% increase that has occurred in the northern hemisphere over the past 30 years. The input of CO into the atmosphere is dominated by fossil fuel combustion, industrial emissions, biomass burning, and oxidation of CH₄ and non-methane hydrocarbons. The reaction with OH· accounts for 90 to 95% of the sinks. This decrease cannot be fully explained as the result of more efficient use of fossil fuels. It may be related to higher levels of OH· radicals in the atmosphere or possibly caused by the decrease of O₃ in the stratosphere from the eruption of Mount Pinatubo in June 1991. The decrease in O₃ may have resulted in an increase in the UV radiation reaching the troposphere and increased production of OH· radicals from the photolysis of O₃. A number of other factors can influence the sources and sinks of CO. Further measurements are needed to confirm the downward trend. It is interesting to note that the decreases of CO₂, methane, and nitrous oxide also showed a slowdown in their increase beginning in 1991, while the input of oxygen showed an increase. Although these results may be caused by independent effects, they point out how small changes in the conditions in the atmosphere can lead to dramatic changes in the concentrations of gases.

5.1.1 Composition of the Atmosphere

The atmosphere is composed of major gases (N₂, O₂, Ar, H₂O, and CO₂ [mole fraction]), minor gases (Ne, He, CH₄, and CO [measured as parts per million]), and a number of trace gases (O₃, NO, N₂O, and SO₂ [measured as parts per billion]; CCl₂F₂, CF₄, and NH₃ [measure as parts per trillion]; radicals such as OH· [measured as atoms or molecules per cubic centimeter]). In addition to gases, the atmosphere also has condensed phases (clouds, aerosols) that contain numerous compounds (H₂SO₄, HNO₃, etc.). The mole fractions of the major conservative gases of the atmosphere are given in Table 5.1. The errors (±) of the mole fractions reflect the constancy and precision of the composition. The composition of some minor gases in the atmosphere are given in Table 5.2. These gases originate from biological, industrial, and photochemical processes. The concentration of the minor gases varies according to variations in their industrial and biological sources.

TABLE 5.1

Abundance of the Major Conservative Atmospheric Gases

Gas	Mole Fraction in Dry Air (X _i)
N ₂	0.78084 ± 0.00004
O ₂	0.20946 ± 0.00002
Ar	(9.34 ± 0.01) × 10 ⁻³
CO ₂	(3.5 ± 0.1) × 10 ⁻⁴
Ne	(1.818 ± 0.004) × 10 ⁻⁵
He	(5.24 ± 0.004) × 10 ⁻⁶
Kr	(1.14 ± 0.01) × 10 ⁻⁶
Xe	(8.7 ± 0.1) × 10 ⁻⁸

Source: Data from Kester, 1975.

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TABLE 5.2

The Composition of Minor Gases in the Atmosphere

Species	X _i Actual	Reliability	Source	Sink
CH ₄	1.7 × 10 ⁻⁶	High	Biog.	Photochem.
CO	0.5 – 2 × 10 ⁻⁷	Fair	Photo., Anthr.	Photochem.
O ₃	5 × 10 ⁻⁸ (clean) 4 × 10 ⁻⁷ (polluted) 10 ⁻⁷ to 6 × 10 ⁻⁶ (stratosphere)	Fair	Photo.	Photochem.
NO + NO ₂	10 ⁻⁸ – 10 ⁻¹²	Low	Lightning, Anthr. Photo.	Photochem.
HNO ₃	10 ⁻⁹ – 10 ⁻¹¹	Low	Photo.	Rainout
NH ₃	10 ⁻⁹ – 10 ⁻¹⁰	Low	Biog.	Photo., Rainout
N ₂ O	3 × 10 ⁻⁷	High	Biog.	Photo.
H ₂	5 × 10 ⁻⁷	High	Biog., Photo.	Photo.
OH	10 ⁻¹⁵ – 10 ⁻¹²	Very low	Photo.	Photo.
HO ₂	10 ⁻¹¹ – 10 ⁻¹³	Very low	Photo.	Photo.
H ₂ O ₂	10 ⁻¹⁰ – 10 ⁻¹⁸	Very low	Photo.	Rainout
H ₂ CO	10 ⁻¹⁰ – 10 ⁻⁹	Low	Photo.	Photo.
SO ₂	10 ⁻¹¹ – 10 ⁻¹⁰	Fair	Anthr., Photo.	Photo., Volcanic
CS ₂	10 ⁻¹¹ – 10 ⁻¹⁰	Low	Anthr., Biol.	Photo.
OCS	5 × 10 ⁻¹⁰	Fair	Anthr., Biol., Photo.	Photo.
CH ₃ CCl ₃	0.7–2 × 10 ⁻¹⁰	Fair	Anthr.	Photo.

The distribution of gases in the atmosphere are a function of their molecular weight and reactivity (Figure 5.6). High molecular weight gases (Xe, Kr) are concentrated near the earth, while lighter gases (H₂, He) extend to the outer atmosphere. The distribution of gases in the atmosphere is related to their lifetimes. The atmospheric lifetimes vary from seconds to hundreds of years (see Figure 5.7). These lifetimes can be compared to interhemispheric mixing times of years to intrahemispheric mixing times of months. Water has the shortest lifetime in the atmosphere (6 to 15 days, from the equator to the polar regions). Gases such as methane and carbon monoxide that have continental sources have different distributions between the hemispheres because of their different lifetimes (see Figure 5.8). The long lifetime of methane (7 years) results in a nearly uniform distribution between hemispheres, while the more reactive carbon monoxide (65 days) is concentrated near its sources in the north. The slow movement of gases between hemispheres is caused by the intertropical convergence zone (ITCZ). The ITCZ is caused by air rising near the equator. This prevents mixing across the two hemispheres and results in interhemispheric mixing times of 1 to 2 years. The fast intrahemispheric mixing can be demonstrated by following the movement of dust and particles from the El Chichon volcanic eruption in 1982 (see Figure 5.9). The eruption occurred April 4 and moved completely around the northern hemisphere by April 25.

The concentrations of trace gases in the atmosphere are controlled by a complex combination of processes. Factors that affect the temporal and spatial variability of gases are the source (strength and variability) and sinks (mechanisms and variability) and lifetime. The variability close to the sources (polluted air) is dominated by the variations in the source (automobile traffic), while the variability in remote areas (over the oceans) is controlled by the sinks or lifetimes. The variability of the concentrations of trace gases is inversely related to the residence time. The concentrations of trace gases in the atmosphere are higher than would be expected based on thermodynamic calculations. The principal sources of these gases are:

1. Biogenic (CH₄, NH₃, N₂O, H₂, CS₂, OCS)
2. Photochemical (CO, O₃, NO₂, HNO₃, H₂, OH, HO₂, H₂O₂, H₂CO)

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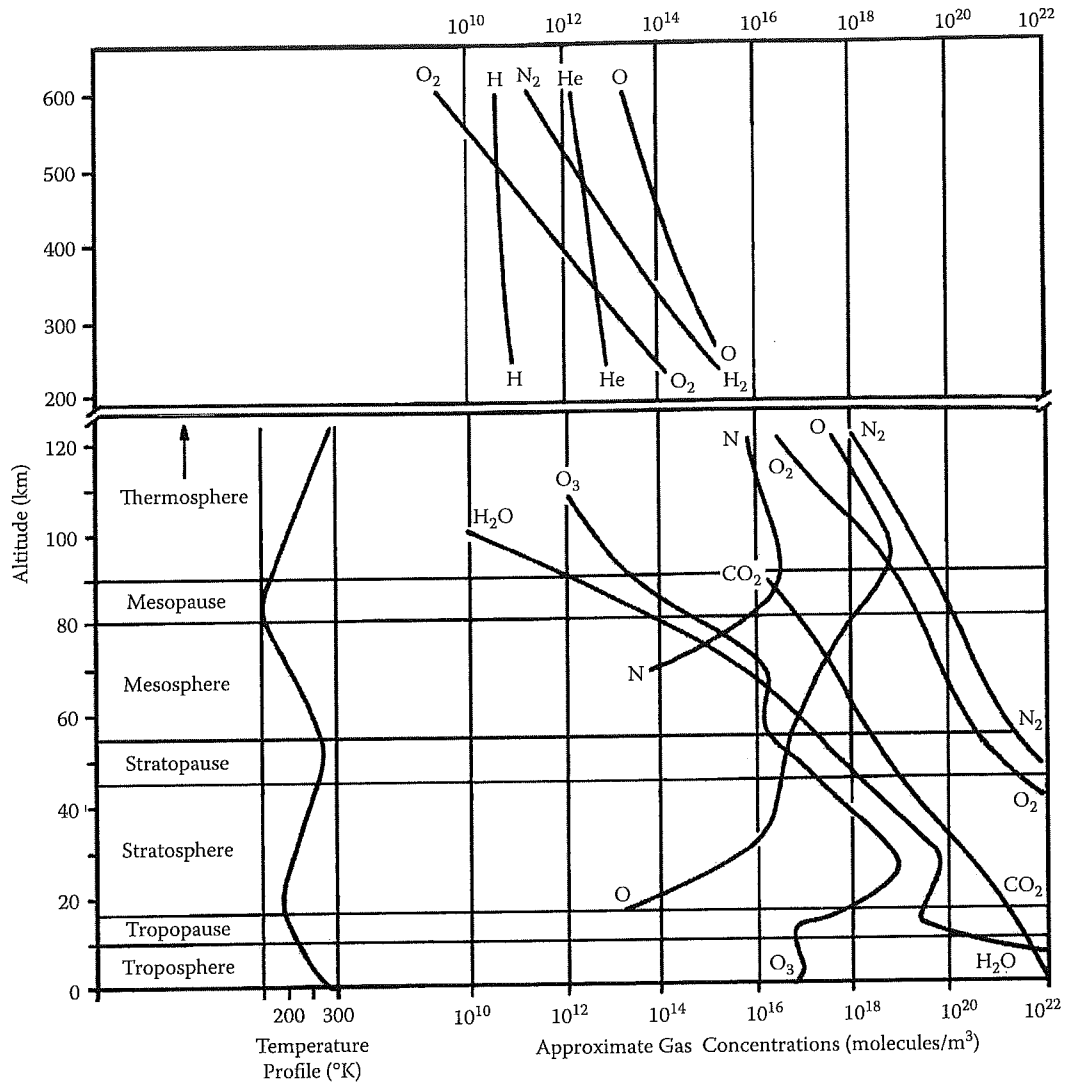


FIGURE 5.6
The approximate concentration of gases in the atmosphere as a function of altitude.

3. Lightning (NO , NO_2)
4. Volcanic (SO_2)

The sinks of these gases are largely photochemical, with the exception of H_2O_2 , HNO_3 , and H_2SO_4 , which are lost because of rainout.

All three phases of water exist in the atmosphere. The partial pressure of water under ordinary conditions is quite small (30 to 40 mbar, which corresponds to 25 gm^3). In typical clouds little of this is in the condensed phase (stratus clouds have 0.3 to 1 gm^3).

These clouds are important since they deliver water from the atmosphere to the earth's surface and they scavenge a number of materials from the air and deliver them to the surface. The formation of clouds is due to particles that act as cloud condensation nuclei

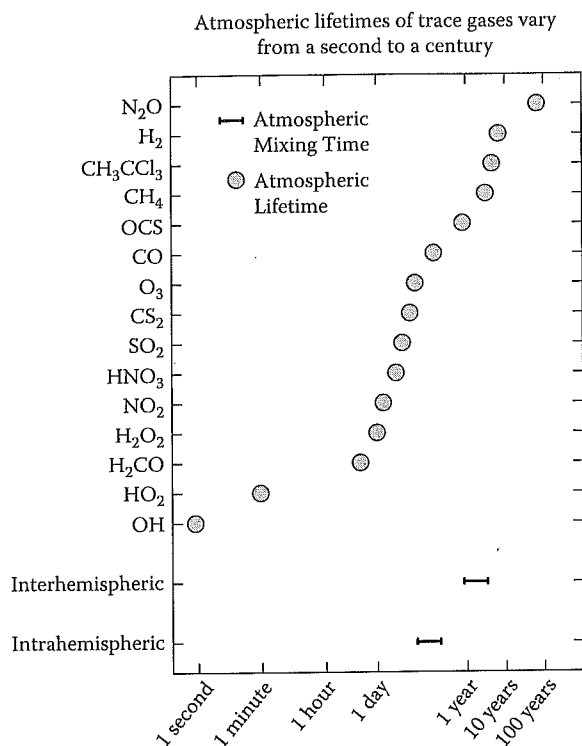


FIGURE 5.7
The atmospheric lifetimes of trace gases in the troposphere.

(CCN). These particles must be small enough to have small settling velocities. They are soluble in water. In the past it was thought that NaCl from sea spray was the main CCN. More recent studies indicate that sulfate particles (H_2SO_4 and $[\text{NH}_4]_2\text{SO}_4$) dominate. Following the growth of droplets by condensation, further growth occurs by collisions. Large water particles and heavy precipitation occur when ice is present (typically at temperatures of -5 to -20°C). Ice particles that grow during collisions while falling can result in the formation of hail (if frozen) or rain (if it melts). The compounds dissolved in CCN can be made up of dissolved gases (SO_2 , NH_3 , HCHO , H_2O_2 , HNO_3) and salts ($[\text{NH}_4]_2\text{SO}_4$, NaCl , etc.). More will be said about sulfur compounds later.

5.2 Nitrogen Gases

The reactive nitrogen species in the lower atmosphere (Table 5.3) are NO , NO_2 , and HNO_3 . These species are coupled by a series of reactions that cycle the various species. The reactions of these species are shown in Figure 5.10. The reaction of nitric oxide with hydroperoxyl radicals is of special interest:



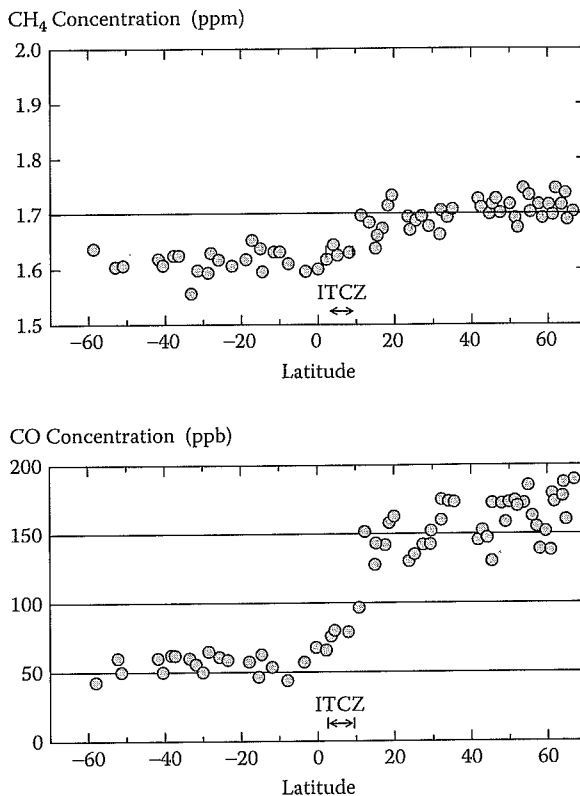


FIGURE 5.8 The distribution of methane (top) and carbon monoxide (bottom) between the hemispheres.

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This reaction regenerates OH· from HO₂. It also leads to the generation of ozone by the following:



where M = N₂ or O₂. As with CO, large amounts of NO are produced from the burning of fossil fuels (e.g., in automobiles). Although CO causes the OH· levels to decrease, NO can enhance the OH· levels, especially in remote areas. The nitrogen oxides are rapidly removed from the atmosphere as HNO₃, which is soluble in rainwater. It also can be attached to aerosols and particles and removed as dry deposition. The HNO₃ in rainwater is one of the components of acid rain. Although the importance of HNO₃ as a component of acid rain has been known to affect the pH of rain, recent work (see Figure 5.11) indicates that atmospheric sources of nitrate may also contribute to the eutrophication of the Chesapeake Bay.

The N₂O in the atmosphere can also reduce the stratospheric ozone (see Figure 5.12). Bacterially produced N₂O can break down at high altitudes by the absorption of light:

(5.18)



NO, NO₂, and HNO₃.
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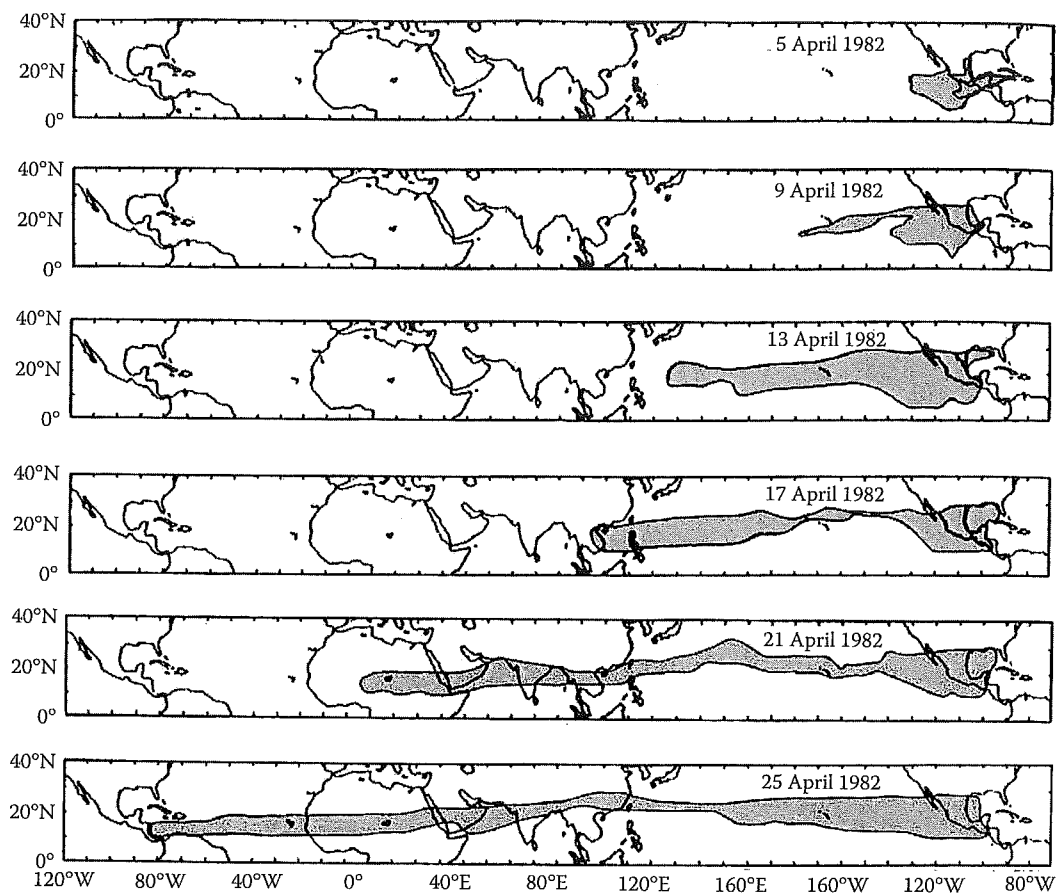


FIGURE 5.9

The movement of dust and particles in the northern hemisphere after the El Chichon Volcano eruption.

The NO formed can react with O₃ in a chain reaction:



TABLE 5.3

Concentration of Atmospheric Nitrogen Compounds

Species	Concentration	Source	Sink
N ₂	78.9084%	Primitive Volatile	Biological, Lightning
NH ₃	0–10 ppbv	Biological	Precipitation
RNH ₂	—	Biological	Precipitation
N ₂ O	0.1–0.4 ppmv	Biological	Photolysis in stratosphere
NO	0–0.5 ppmv	Oxidation	HNO ₃
NO ₂	—	NO oxidation	HNO ₃
HNO ₂	—	OH + NO	Precipitation
HNO ₃	—	OH + NO	Precipitation

Source: Data from Carlson, R.J., 1992.

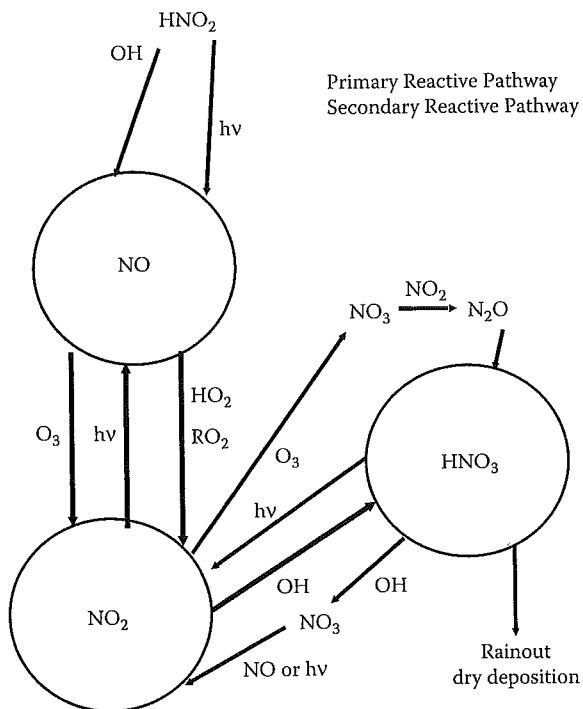
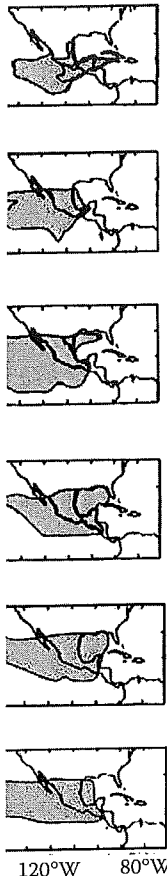


FIGURE 5.10
The major reactive nitrogen species in the troposphere.

The net reaction is



The concern that sulfur species cause acid rain has led to an interest in the sulfur cycle. Biogenic processes emit a number of sulfur species (H_2S , CH_3SCH_3 , OCS). These reduced

Atmospheric sources of nitrate to Chesapeake Bay
likely to increase by year 2030

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(5.23)

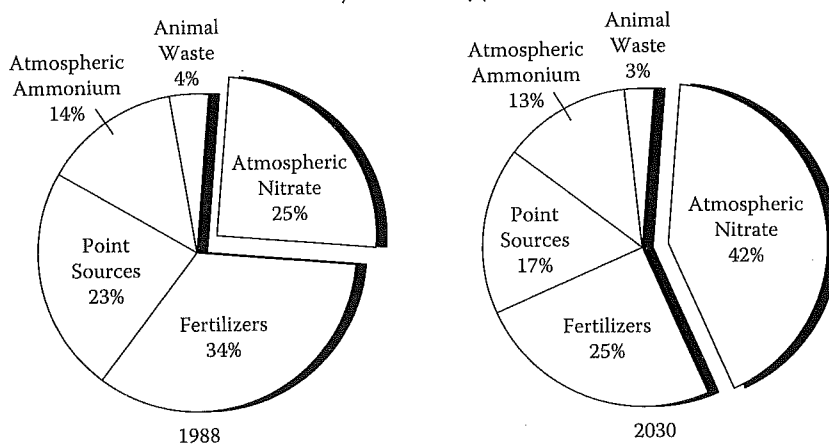


FIGURE 5.11
The atmospheric sources of nitrate to Chesapeake Bay.

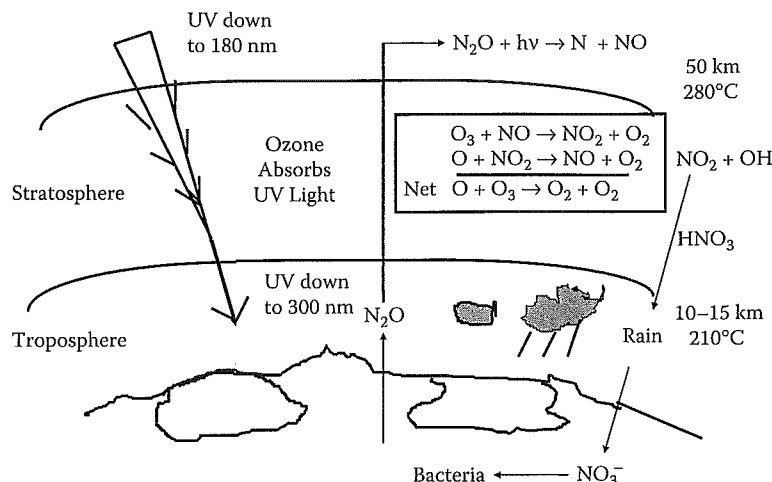


FIGURE 5.12
The effect of nitrogen oxides on the concentration of stratospheric ozone.

species are oxidized to SO_2 by $OH\cdot$ radicals. SO_2 can also be directly injected into the atmosphere as a by-product of the oxidation of fossil fuels. The lifetime of SO_2 is between a few days to a month. Removal occurs in rainout and wet and dry deposition (see Figure 5.13) after the oxidation of SO_2 to H_2SO_4 . The H_2SO_4 is incorporated into cloud droplets and aerosols. The oxidation can occur in the gas phase, the solution phase, or on particles (see Figure 5.14).

The term *acid rain* was first used by Angus Smith to describe the effect industrial emissions had on the precipitation in Great Britain. The pH of water in equilibrium with atmospheric CO_2 has a value of 5.6. In uncontaminated areas the pH is closer to 5.0 because of natural levels of acids. In most urban areas the pH is normally lower than 5.0. In Europe

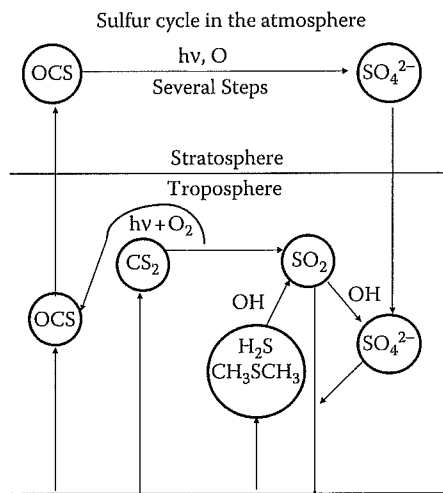


FIGURE 5.13
The sulfur cycle in the atmosphere.

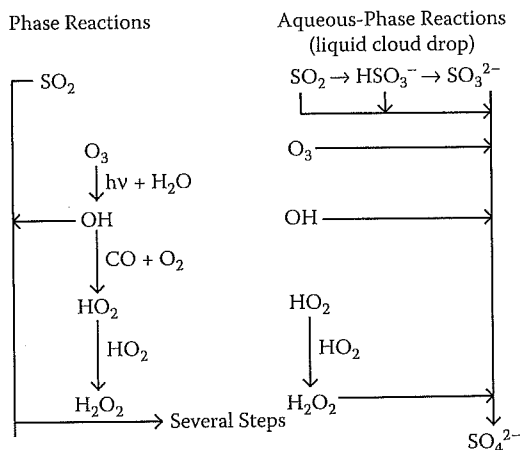


FIGURE 5.14
The gas and liquid phase reactions of sulfur in the atmosphere.

and North America, 90% of the sulfur comes from the burning of fossil fuels (Table 5.4). The lower pH of the rain (pH = 4.6 to 4.7) is normally attributed to the concentrations of HNO₃ and H₂SO₄ formed by the oxidation of NO_x and SO₂. Organic acids may also be important components of acidic rain, especially in remote areas. Many areas are sensitive to acid rain. These include many northern lakes that have low alkalinity (<50 μM) and vast forest areas.

The effects of acid rain have led to lower alkalinity to Mg²⁺ and Ca²⁺ ratios. Fish can tolerate values of pH as low as 5.5. Juvenile fish and many organisms can be affected at pHs above 5.5. This can cause starvation of predatory fish. Acidic streams have frequently had fish kills caused by pulses of acid waters during the spring snow melt. The lower pH of lakes and streams can also cause aluminum to be released from the sediments. Ionic aluminum, Al³⁺, appears to be toxic, while the hydrolyzed forms are nontoxic (Al[OH]₂⁺, Al[OH]₂⁺, etc.). Recent studies have shown that exchange reactions of H⁺ with sediments

TABLE 5.4

Composition of Marine Rainwater from the Mediterranean and North Atlantic

Ion	North Atlantic	Mediterranean
pH	4.3–5.8	4.03–6.88
H ⁺	1.7–50.1 μM	0.1–93.3 μM
NH ₄ ⁺	—	4–40
Na ⁺	1.7–64.6	17–1620
Mg ²⁺	1–653	3–211
K ⁺	1–130	1–42
Ca ²⁺	2–119	2–112
NO ₃ ⁻	1–38	4–97
Cl ⁻	8–6900	20–2260
SO ₄ ²⁻	2–341	9–115
HCO ₃ ⁻	4.1	9–152

Source: Data from Losno, R., et al., *Atm. Environ.*, 25A, 763, 1991.

may lessen the effect of acid rain on a lake. The recovery of a lake may be fast if the basic components of the soil are not lost. It is unlikely, however, that the original pH will be reached for years, and widespread stocking will be necessary to bring back game fish and the resultant food chains.

5.3 Greenhouse Gases

The likelihood that CO_2 increases will cause global climate changes is now well accepted. Less is known, however, of the effects of other trace gases on the climate. Gases such as CH_4 , O_3 , N_2O , and CFCs such as CCl_3F (CFC-11) and CCl_2F_2 (CFC-12) can contribute to the increasing temperature of the troposphere. Solar radiation is absorbed by the atmosphere, providing energy for many processes. The UV energy coming to the top of the atmosphere is shown in Figure 5.15. The IR energy back-irradiated to the atmosphere is a function of the temperature of the earth (285 K or 12°C). The amount of solar energy that affects the earth is shown in Figure 5.16. For the global climate to be balanced, the absorbed radiation must be equal to the outgoing radiation. The trapping of some of the thermal radiation by particles and molecules increases the surface temperature by 10 to 15°C compared to what it would be without these molecules. This process of absorption of (IR) energy radiated from the earth is called the greenhouse effect.

The effect of the various gases in the atmosphere in adsorbing the IR energy is shown in Figure 5.17. Clouds and water vapor are dominant contributors to this process. Other atmospheric gases, although present in small amounts, can also contribute to this trapping of thermal radiation. Gases that absorb strongly in the IR region where water vapor and CO_2 do not strongly absorb can have the biggest effects. The so-called window that exists between 7,500 nm and 12,000 nm is of particular importance because water vapor and

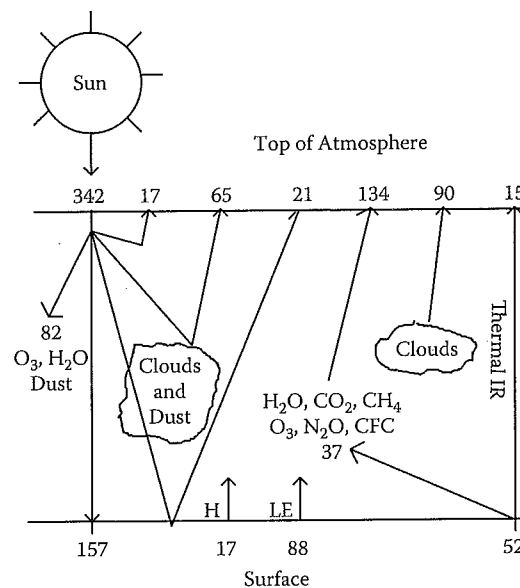


FIGURE 5.15
The amount of energy that affects the earth.

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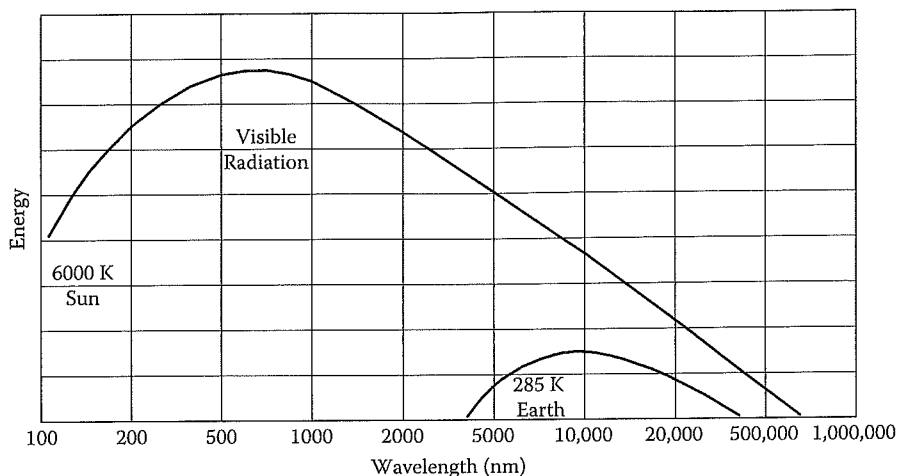


FIGURE 5.16
The visible radiation reaching the earth and the infrared radiation emitted by the earth.

CO₂ do not absorb in this region, and the earth's emission is at a maximum at 10,000 nm. Without these active constituents, the earth would lose thermal radiation as a black body (~387 W m⁻²). The actual radiative flux at the top of the atmosphere is 239 W m⁻², so ~148 W m⁻² (38%) is trapped. Changes in the trapping of 1 W m⁻² (0.3%) can change the balance sufficiently to change the climate. The current trapping by trace constituents of the atmosphere is given in Table 5.5. The pre-industrial estimates of the trace gas concentrations and the change in thermal trapping are given in Table 5.6. Since the concentrations of all the greenhouse gases are increasing, these changes will become larger in future years.

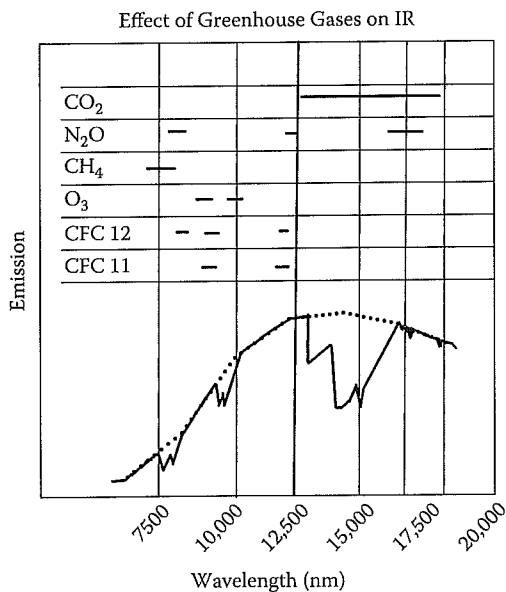


FIGURE 5.17
The adsorption of infrared radiation by gases in the atmosphere.

TABLE 5.5
Trapping of IR Radiation by Trace Gases (ΔQ , $W m^{-2}$)

Gas	Present Level	Present ΔQ	Lifetime
CO ₂	345 ppm	2.0	10–15 years
CH ₄	1.7 ppm	1.7	7–10
O ₃	10–100 ppb	1.3	0.5
N ₂ O	340 ppb	1.3	100
CFC-11 ^a	0.22 ppb	0.06	75
CFC-12 ^b	0.38 ppb	0.12	100
		6.5	

^a CCl₃F

^b CCl₂F₂

One would expect from comparing the two tables that there has been approximately a 200% increase in the ΔQ caused by industrial processes. It is difficult, however, to translate the increases in ΔQ to an increase in the global temperature. Although some measurements (see Figure 5.18) indicate that the temperature has increased, it is hard to attach a reliable estimate of changes in ΔQ with changes in ΔT . The increase of CO₂ over the past 260 years has been well documented (Figure 5.19). This increase in the CO₂ is caused by the increased use of fossil fuels (coal, petroleum, and natural gas [Figure 5.20]). The contributions of the emissions of fossil fuel CO₂ by the United States is compared to other countries in Figure 5.21. The present contributions of Asia are equivalent to the US and will be greater than the US in the future. Although the United States has 5% of the world population, we produce 20% of the fossil fuel CO₂. This is shown more clearly in Figure 5.22, where the per capita fossil fuel emissions are shown for various countries. The United States produces 30% more per capita than the nearest country (Australia).

The measurements of the pCO₂ in the atmosphere by Keeling and Whorf (2004) starting in 1958 at the Mauna Loa Observatory in Hawaii demonstrates that CO₂ is increasing (Figure 5.23). The annual cycling of pCO₂ in the atmosphere shown after the removal of the increases (Figure 5.24) is caused by variations in the photosynthesis and respiration of land plants. The maximum occurs in April and May, and the minimum occurs in September and October. In recent years the values of pCO₂ have been measured at other locations (Figure 5.25). The increases are the same (1.5 ppm/year) as at Mauna Loa, but the yearly variations are larger in Alaska and smaller in the South Pole. The concentration of CO₂ in the atmosphere in the past has been determined by measuring the concentration of CO₂ in the air trapped in ice cores (Figure 5.19, squares). The extension of the pCO₂ record back

TABLE 5.6
Pre-Industrial Trapping of IR Radiation
of Trace Gases

Gas	Past Level	Past ΔQ
CO ₂	275 ppm	1.3
CH ₄	0.7 ppm	0.6
O ₃	0–25% less	0 to 0.2
N ₂ O	285 ppb	0.05
CFC-11	0	0
CFC-12	0	0
		2.2

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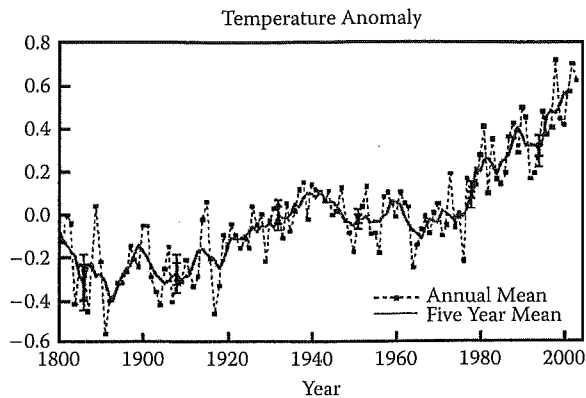


FIGURE 5.18
 The average global air temperature over the past century.

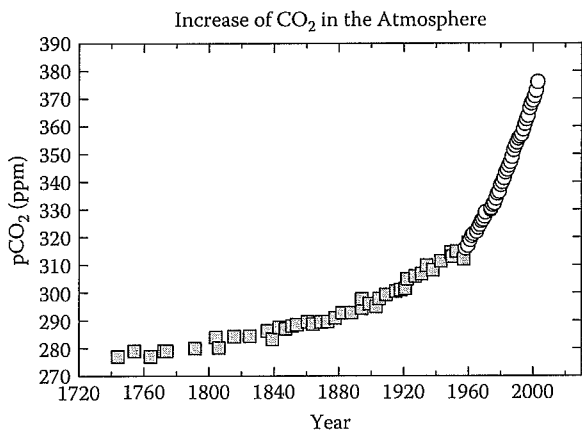


FIGURE 5.19
 The increase of the partial pressure of carbon dioxide in the atmosphere over the past three centuries.

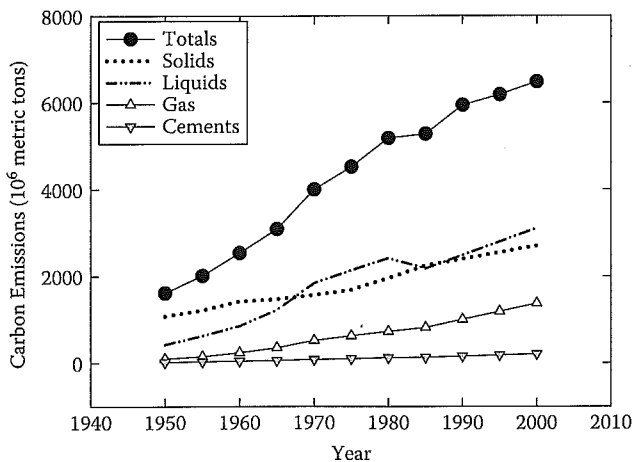


FIGURE 5.20
 The CO₂ emissions into the atmosphere from fossil fuel consumption (liquids and gases) and cement.

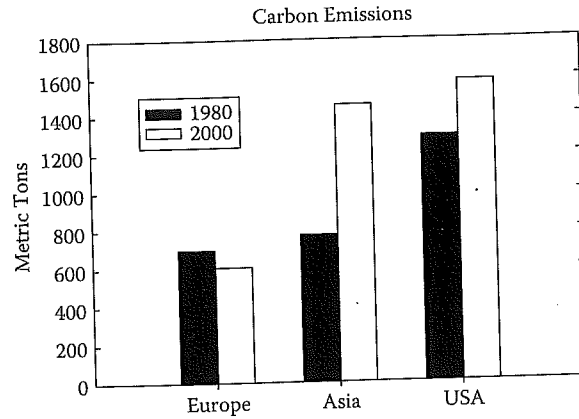


FIGURE 5.21
The emissions of fossil fuel CO₂ by various regions.

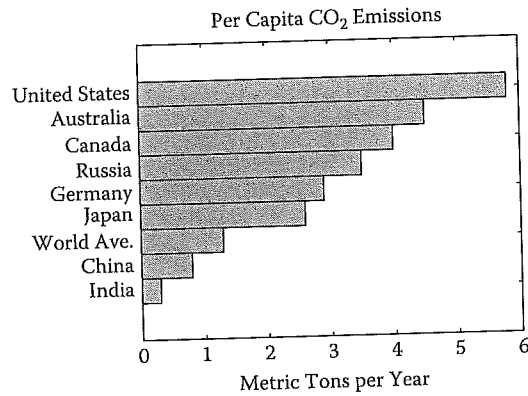


FIGURE 5.22
The per capita emissions of fossil fuel CO₂ by various countries.

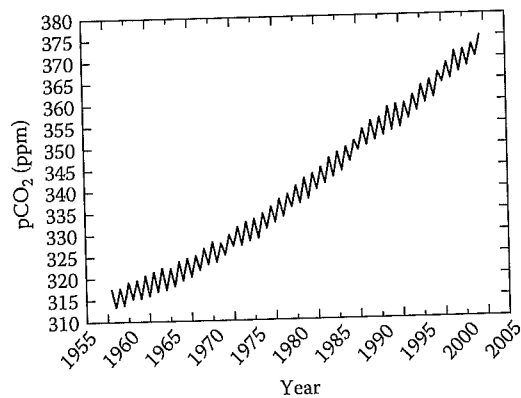


FIGURE 5.23
The increase of carbon dioxide in Hawaii showing the annual cycling over the last 24 years. (Data from Keeling and Whorf, 2004.)

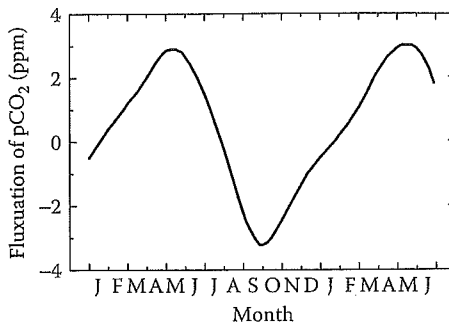


FIGURE 5.24
The mean annual cycling of carbon dioxide in the atmosphere.

10,000 years shows that the level of CO₂ in the atmosphere has increased and decreased through time. The levels are lower during glacial times and higher during nonglacial times. These increases and decreases in CO₂ have followed the global temperatures (Figure 5.26). We do not know if the fluctuations in CO₂ caused the changes in the temperature or visa versa.

Recent work has also demonstrated that CH₄ has increased dramatically as well (see Figure 5.27). The sources of methane to the atmosphere (550 Tg year⁻¹) are shown in Figure 5.28. The largest sources are from wetlands (21%) and rice paddies (20%). Other sources include cattle (15%), biomass burning (10%), natural gas (8%), termites (7.4%), landfills (7.4%), coal (6.5%), and the oceans (2%). The increase in methane is not well understood. The inputs into the atmosphere in the southern hemisphere (from the oceans) appear to have an annual cycle, while the inputs into the northern hemisphere (from industry) have a more complicated signal.

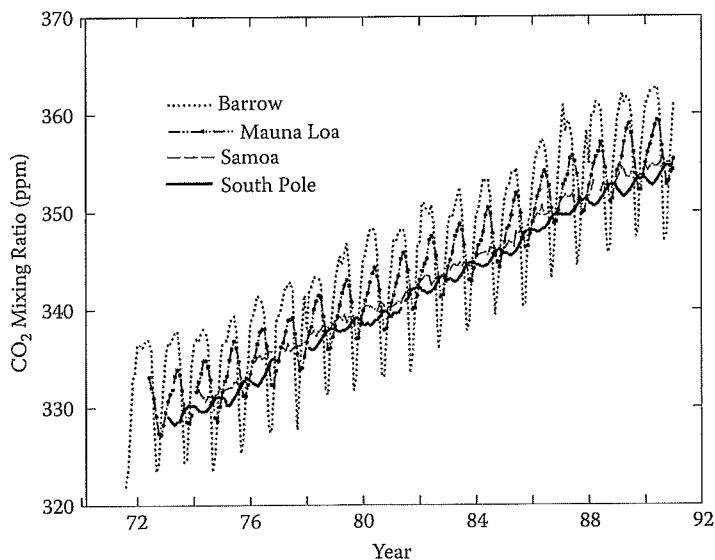


FIGURE 5.25
The difference in the annual cycling of carbon dioxide in the atmosphere at various locations.

rs. (Data from Keeling

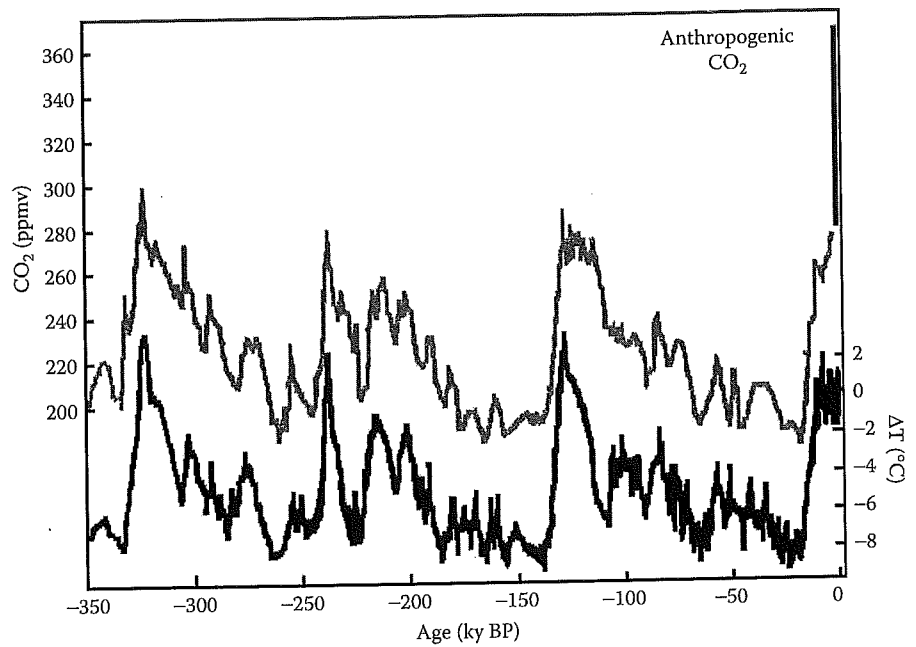


FIGURE 5.26

The variations of carbon dioxide, methane, and changes in temperature as recorded in the Vostok ice core during the last climate cycle.

Various workers have attempted to estimate the long-term effects of the addition of greenhouse gases to the atmosphere. The projected increases of the gases in 2050 are given in Table 5.7. A number of workers have attempted to estimate the effect the projected increase of trace gases will have on the temperature in the next century. The models used to make these estimates are quite complicated and may not be reliable; however, at present this is the best one can do. The increases in temperature estimated by assuming various increases in trace gases are given in Table 5.8. Although CO_2 makes up to 75% of the increase, other gases are important and will become more important in the future

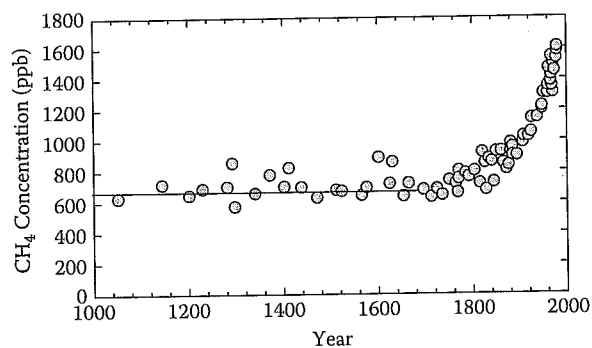


FIGURE 5.27

The increase in atmospheric methane concentrations.

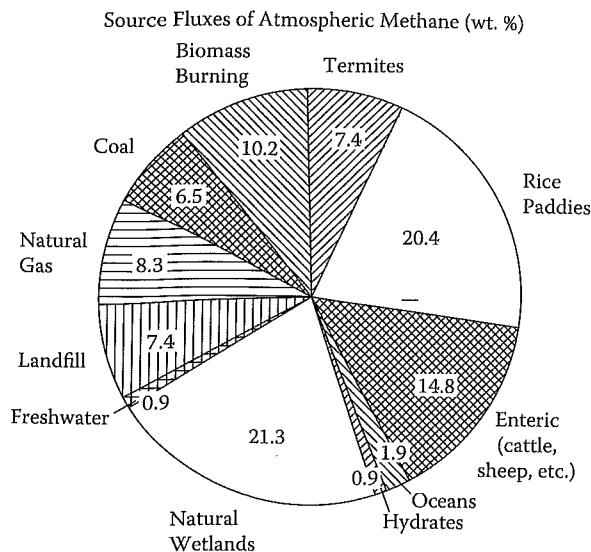
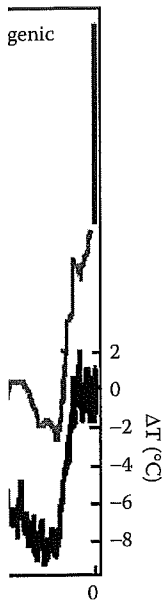


FIGURE 5.28 The relative inputs of methane into the atmosphere.

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TABLE 5.7

Trapping of IR Radiation by Trace Gases in 2050

Gas	2050 Levels	ΔQ
CO ₂	440-600 ppm	0.9-3.2
CH ₄	2.1-4.0 ppm	0.2-0.9
O ₃	15-50% more	0.2-0.6
N ₂ O	350-450 ppb	0.1-0.3
CFC-11	0.7-3.0 ppb	0.23-0.7
CFC-12	2.0-4.8 ppb	0.6-1.4
		2.2-7.2

TABLE 5.8

Estimated Increase in Temperature Caused by Increases in the Concentration of Trace Gases

Gas	Assumed Increase	Temp. Change (°C)
CO ₂	2	2.6
H ₂ O	2	0.65
O ₃	0.75	-0.4
N ₂ O	2	0.65
NH ₃	2	0.12
HNO ₃	2	0.08
CH ₄	2	0.26
SO ₂	2	0.02
CFCs	20	0.65
		4.63

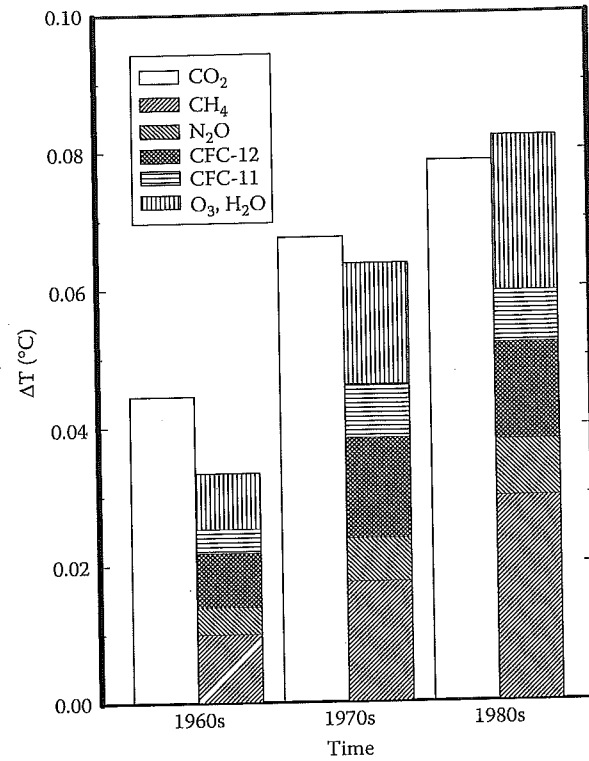


FIGURE 5.29

The relative effects of various trace gases on greenhouse warming.

(see Figure 5.29). Recently it has become apparent that volcanic eruptions can produce gases and particles that can influence global temperature (see Figure 5.30). The decrease in global temperature may be the result of the formation of more clouds (from the SO₂) or reflection (from the particles).

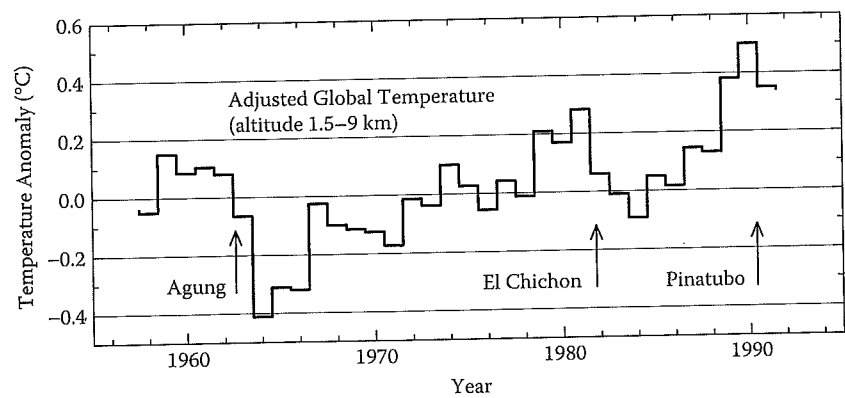


FIGURE 5.30

The effect of volcanic eruptions on the average global temperature.

5.4 Effects of Global Change

At the present time most scientists agree that:

Certain gases are transparent to incoming solar UV but adsorb IR.
Atmospheric concentrations of greenhouse gases are increasing.
As the gases increase, so will the average global temperature.

Some questions that are not known at the present time with certainty are:

What is the timing and severity of the warming?
What are the regional distributions of the impacts?
What are the magnitudes of the feedback processes?

It is useful to briefly review the state of our understanding of these issues. As discussed earlier, the increase of CO₂ in the atmosphere is largely related to the burning of fossil fuels. The increase of greenhouse gases in the atmosphere and the resultant increase in the temperature of the earth can cause some global changes. Some of those include:

Sea level rise: The increase in the temperature can cause an increase in the volume of seawater and a subsequent increase of sea level. The increased temperature can also melt ice on land, which would increase the sea level. For example, if the ice on Antarctica melts, the sea level may rise by 170 m.

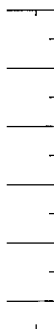
Extreme weather events: These can result from the higher temperature of the surface waters in the oceans. Hurricanes, for example, can become more frequent and stronger in warmer waters. Some have speculated that if the temperatures of North Atlantic surface waters become too warm, they will not be able to sink to form North Atlantic deep water. This could have large-scale climate effects on the earth.

Spread of tropical diseases: The warmer waters in tropical regions may result in an increase in tropical diseases such as malaria and typhoid fever.

Species extinctions: The increase in the temperature of ocean waters may cause coral bleaching of reefs.

There is some evidence that the ice cover in the Arctic Ocean is thinning because of global warming. These results come from submarine measurements from 1957 to 1997. The ice has decreased by as much as 3 m over the past 40 years. Some predict that the ice will completely disappear in the Arctic in the summer in 50 years. There is also some evidence that surface ocean waters have increased over the past 20 years. For example, the heat content of the waters have increased over the past 50 years. This means that part of the increase in the temperature of the atmosphere has been used to heat up the surface waters of the oceans. Although current measurements indicate that the sea level is rising, we cannot accurately predict what it will be in the future. We can, however, estimate the level based on the possible increases in the temperature. If the temperature increases by 3°C over the next 50 years, the sea level could rise by 80 cm, or 32 inches. Recently, some have predicted that if the ice on Antarctica melts, the ocean will rise by as much as 70 m (~200 ft). This increase in sea level can cause an inundation of water in some coastal areas and result in more serious coastal

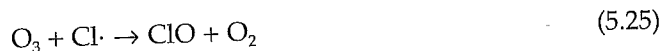
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flooding from hurricanes and typhoons. Some websites for more information on global warming are www.ipcc.ch, www.ucsusa.org, and www.iclei.org.

5.5 Loss of Ozone

It has been known for some time that gases produced by man can contribute to the loss of ozone in the stratosphere. The effect of naturally produced N_2O was discussed earlier (see Figure 5.12). Chlorine can also reduce O_3 by the following reactions (see Figure 5.31)



The net reaction is



Free atomic chlorine is produced by the photodissociation of CFCs (CFC-11 and CFC-12):



These CFCs reach the high altitudes where light of sufficient energy can cause dissociation because of their long lifetimes (CFC-11, $\tau = 75$ years; CFC-12, $\tau = 110$ years). As mentioned earlier, $NO\cdot$ and $OH\cdot$ radicals can also reduce ozone:

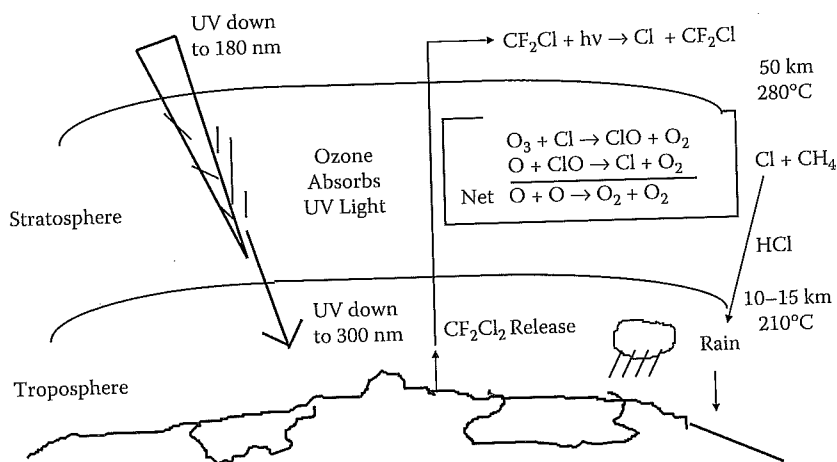


FIGURE 5.31
The effect of chlorine on the concentration of ozone in the stratosphere.

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The net effect of both reaction paths is the destruction of two ozone molecules (the primary reaction with O_3 and the destruction of $\text{O}\cdot$ that would have formed O_3).

The reactive species are removed by reactions that produce stable species or water-soluble species that are rained out

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Figure 5.31)



Photodissociation or other free radical reactions can reverse these reactions:



With increasing CFC production (see Figure 5.32) one would expect that the formation of $\text{Cl}\cdot$ by photodissociation would be more important in removing O_3 in future years. Even though the aerosol usage of CFCs has decreased, nonaerosol usage has increased. The increase of

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and CFC-12):

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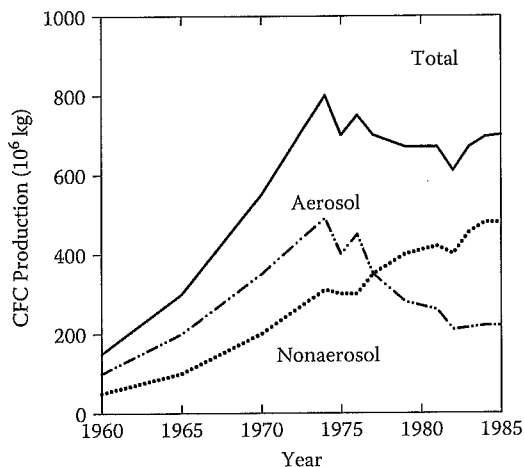


FIGURE 5.32
The production of CFCs from 1960 to 1985.

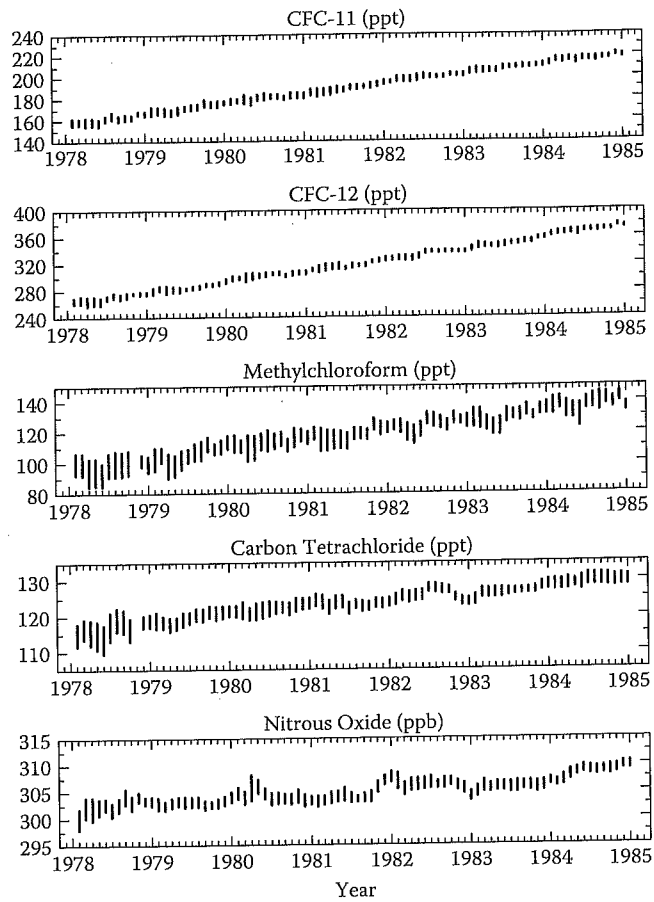


FIGURE 5.33
The increase in the concentration of chlorinated compounds and nitrogen oxide in the atmosphere.

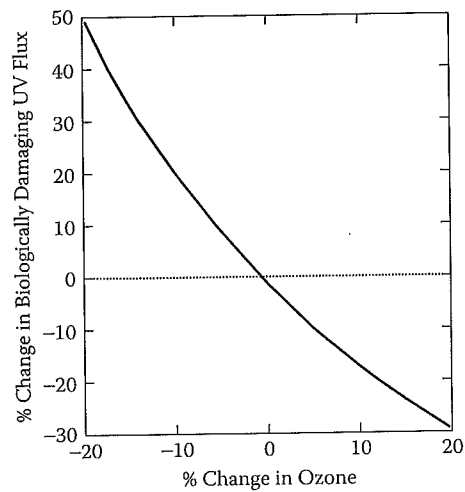


FIGURE 5.34
The changes in the biologically damaging ultraviolet (UV) flux as a function of changes in ozone levels.

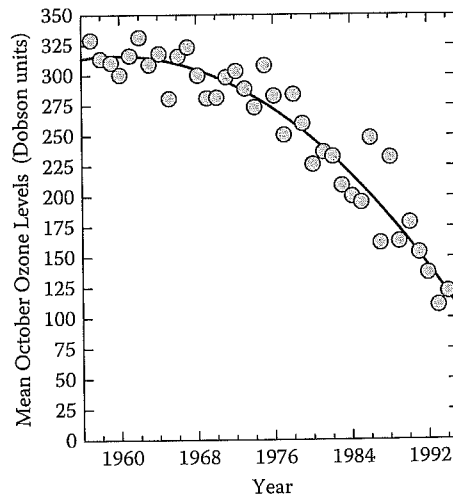


FIGURE 5.35
The decline of springtime ozone over the Antarctic over the past 33 years.

CFCs, methychloroform, carbon tetrachloride, and nitrous oxides since 1978 has been documented by direct measurements (see Figure 5.33). The decrease in O₃ levels will increase the amount of UV radiation that reaches the earth. This is shown in Figure 5.34. This plot includes all the wavelengths weighted according to how damaging they are to biological systems (300 to 345 nm). A 100% decrease of O₃ will increase the damaging UV flux by about 18%.

Recent attention to the destruction of O₃ has concentrated in the Antarctic region over the past 30 years (see Figure 5.35) in the springtime. This has caused the so-called ozone hole over the South Pole (Figure 5.36). This springtime loss of ozone extends well north of



FIGURE 5.36
The ozone hole in the Antarctic region.

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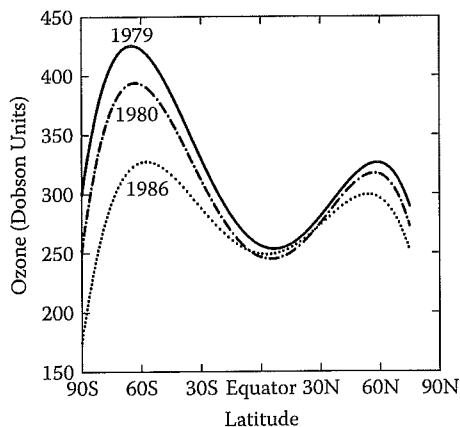


FIGURE 5.37
The levels of ozone as a function of latitude.

Antarctica (see Figure 5.37). It should be pointed out that one Dobson unit equals a concentration of O_3 of one molecule in every 10^9 total molecules. Recent work has shown that the size of the ozone hole has increased considerably over the past 20 years (see Figure 5.38). Since the global concentrations of O_3 show large variations (see Figure 5.39), it is difficult to distinguish trends over time.

The loss of ozone in Antarctica in the springtime has been attributed to the formation of ClO (see Figure 5.40). The large effects in the springtime have been attributed to a dynamic uplifting of the lower stratosphere as well as catalytic cycles involving Cl. One

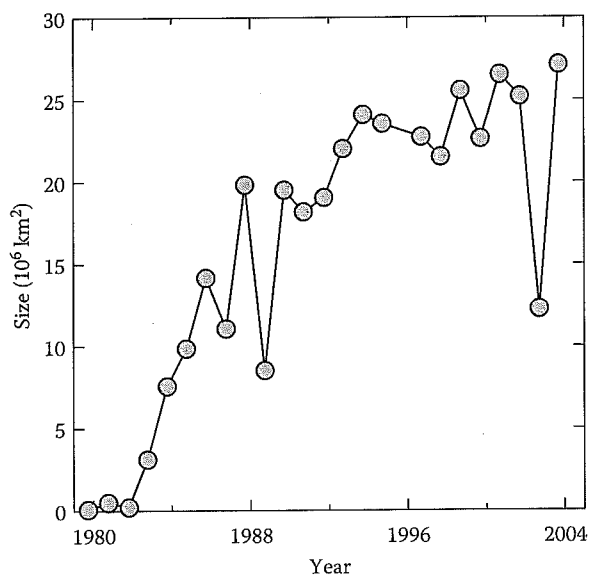


FIGURE 5.38
The increase in the size of the ozone hole in the Antarctic.

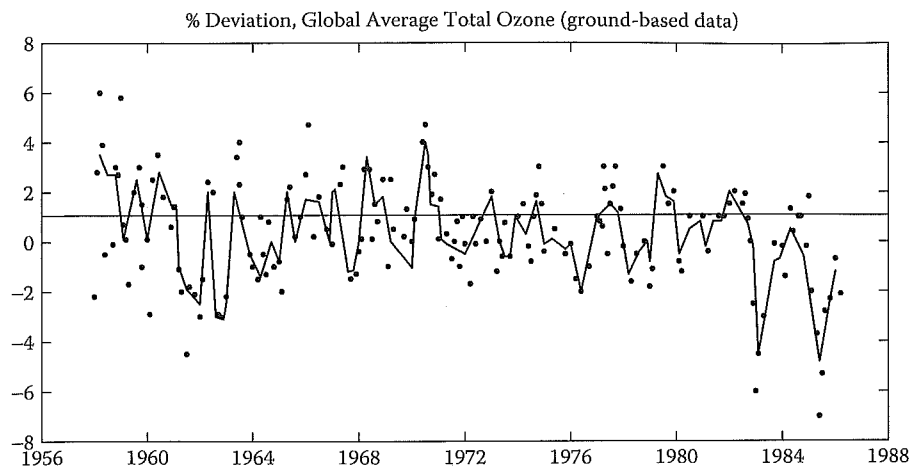
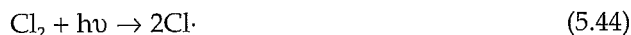


FIGURE 5.39
The fluctuations of the global average total ozone as a function of time.

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The reaction of Cl or ClO with CH₄ and NO₂ can produce inert compounds:

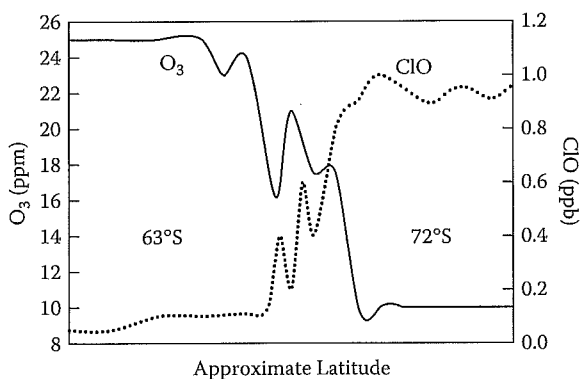
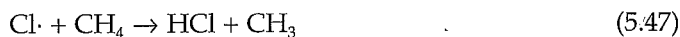
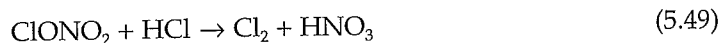
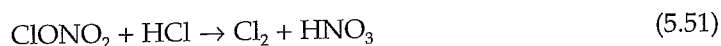


FIGURE 5.40
The relationship between O₃ and ClO in the Antarctic.

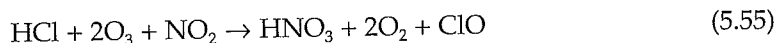
Low levels of NO_2 are needed to prevent the formation of ClONO_2 . Reactions on ice have been proposed to explain how the inert compound becomes active:



The unique meteorology of Antarctica results in a circulation of air in the stratosphere that is different from the northern hemisphere. A stream of air called the polar vortex tends to circle the South Pole in the winter. Air trapped in the vortex gets very cold (-90°C) and forms clouds even in very dry conditions. These clouds provide ice crystals that have been shown by laboratory studies to cause molecules of HCl and ClONO_2 to react. The Cl_2 gas formed is released to the gas phase, whereas HNO_3 remains in the ice. The Cl_2 reacts with light to produce $2\text{Cl}\cdot$ that further reacts with O_3 to produce more ClO . The total reaction sequence is



The net reaction is



The HCl gets rid of NO_2 and forms ClO that further removes O_3 . Although these reactions explain the formation of the ozone hole formed in Antarctica, further work is needed to predict the loss of O_3 in the global atmosphere. As man continues to add gases that upset the natural balance to the atmosphere, there will continue to be changes in the climate that affect life on the earth.

Recent work has also indicated that iodine may be important along with chlorine and bromine in the destruction of ozone. The loss of ozone in temperate regions above 20 km have puzzled scientist for years. Chlorine and bromine are important at higher altitudes, but they cannot account for the loss in the lower stratosphere. The reaction sequence for iodine are postulated to be (Solomon and Ravishankara, 1994)



The possible affect of iodine on the depletion of ozone is complicated by the fact that trifluoromethyl iodide (CF_3I) has been proposed as a possible replacement for ozone-depleting halons used to fight fires. It was thought that this compound would not pose

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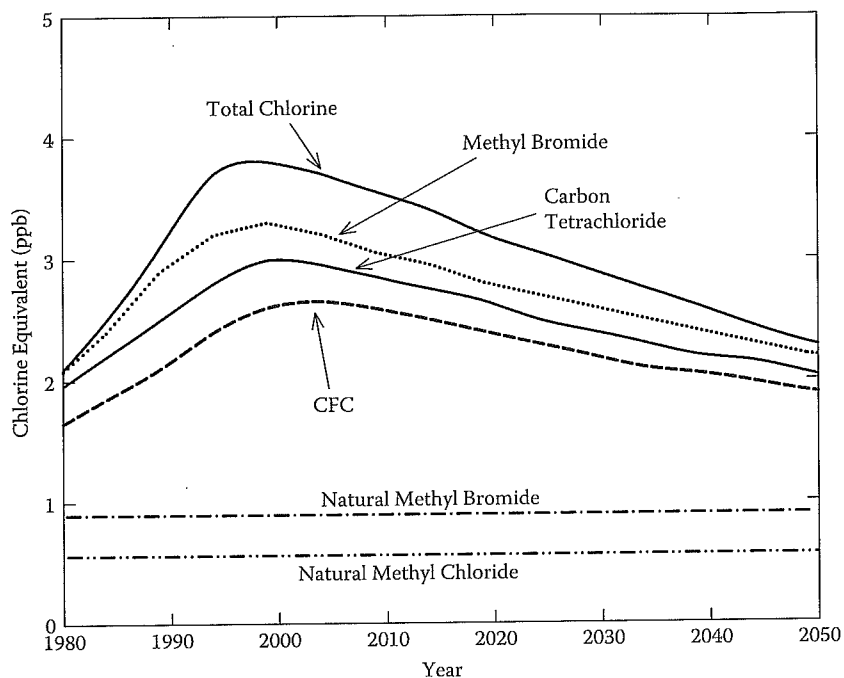


FIGURE 5.41 The levels of chlorine in the stratosphere as a result of the Montreal Protocol.

a problem for the depletion of the ozone layer because the carbon iodine bonds are readily photolysed by sunlight and never reach the stratosphere. Naturally formed methyl iodine produced by marine life is thought to be much higher than the present industrial emissions. As scientists rush to make further measurements of iodine, the jury will remain out.

Finally, although the Montreal accord stopped the use of CFCs, the levels of chlorine in the stratosphere will decrease at a slow rate (see Figure 5.41). Thus, the decrease in the ozone levels will continue for some time.

5.6 The Global Sulfur Cycle

In recent years there has been interest in the global sulfur cycle (Saltzman and Cooper, 1989). This interest is related to the production of reduced sulfur compounds from the burning of sulfur fuels (SO₂) and the production of reduced sulfur compounds from plants (dimethylsulfide [DMS]). These compounds can be oxidized to H₂SO₄ that can serve as CCN and affect the climate. The estimates of the natural sulfur emissions (Tmol S year⁻¹) are given in Table 5.9. The total levels of 1.2 to 2.8 Tmol year⁻¹ can be compared to the 2.5 ± 0.3 Tmol year⁻¹ for man-made sulfur emissions (T = tera = 10¹²). From this comparison it is apparent that the natural levels, although not well known, are the same order of magnitude as the man-made levels. This has led to an increased interest in the natural

TABLE 5.9
Concentration of Atmospheric Sulfur Compounds

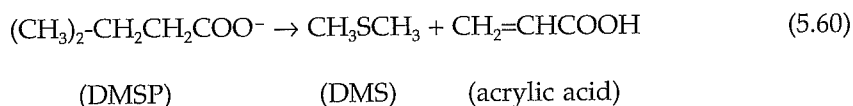
Species	Concentration	Sources	Sinks
SO ₂	0-0.5 ppmv (urban) 20-200 pptv (remote)	Fossil fuels (oxid) Biological (DMS)	Oxidation to SO ₄ Oxidation to SO ₂
H ₂ S	0-40 pptv	Biological	Oxidation to SO ₂
CH ₃ SH	>ppbv	Paper pulping	Oxidation to SO ₂
CH ₃ CH ₂ SH	>ppbv	Paper pulping	Oxidation to SO ₂
OCS	500 pptv		Destruction in stratosphere
CH ₃ SCH ₃	20-200 pptv	Oceanic plankton	Oxidation to SO ₂
CH ₃ SSCH ₃	Small		Oxidation to SO ₂
CS ₂	10-20 pptv		Destruction in stratosphere

biogeochemistry of sulfur and the cycling of sulfur across the air-sea interface. The uncertainties in the natural sulfur cycle are due to:

1. Difficulty in measuring H₂S at low levels in unpolluted areas
2. Problems in measuring fluxes from forest and brush ecosystems
3. Poor geographical coverage of existing data

The most important sources are from the burning of fossil fuels and the oceans.

The reduction of sulfate to volatile sulfur compounds is due to biological processes. The major volatile coming from the oceans is DMS. The DMS is produced from dimethylsulfonium propionate (DMSP) produced in marine algae from the protein methionine.



DMSP is thought to be osmotic or osmoregulatory in marine algae. It is present at high levels in dinoflagellates, coccolitophores, and cyanobacteria. Since the surface waters are supersaturated with DMS, it is released to the atmosphere, especially during phytoplankton blooms. The contribution of DMS from land and ocean plants is nearly equal to the industrial input of reduced sulfur (SO₂). DMS has a lifetime of 8 to 49 h. It can be oxidized by OH radicals in the day and nitrate radicals at night. The major products from the oxidation of DMS are SO₂ and methanesulfonic acid (CH₃SO₃H [MSA]). The SO₂ can be quickly oxidized to SO₄²⁻, while MSA is fairly stable and slowly oxidized to SO₂. Other products of the oxidation include dimethyl sulphoxide (DMSO) and dimethyl sulphone (DMSO₂). MSA is a strong acid and its atmospheric chemistry is dominated by aqueous processes. It is thus very rapidly incorporated into aerosols by nucleation and coagulation. The sulfur compounds present in aerosol in the atmosphere are listed in Table 5.10. The Mg, Ca, and Na sulfates come largely from marine sources.

Due to its stability, MSA has been used as a tracer for biogenic sulfur (DMS) emissions in ice cores (Saltzman et al., 1997). The amount of non-sea-salt sulfate (NSS) in marine aerosols can be calculated by assuming that the salt-derived sulfate is related to sodium by its seawater value

$$\text{NSS-SO}_4 = [\text{SO}_4^{2-}]_T - X[\text{Na}^+] \quad (5.61)$$

TABLE 5.10

Compounds in Aerosol Particles in the Atmosphere

Species	Formula
Sulfuric acid	H ₂ SO ₄
Sulfurous acid	H ₂ SO ₃
Sulfonic acid	R-SO ₃ H
Nitric acid	HNO ₃
Ammonium sulfate	(NH ₄) ₂ SO ₄
Ammonium bisulfate	NH ₄ HSO ₄
Ammonium nitrate	NH ₄ NO ₃
Magnesium sulfate	MgSO ₄
Calcium	CaSO ₄
Sodium sulfate	Na ₂ SO ₄

Source: Data from Carlson, R.J., 1992.

where $X = 0.2517$ and $[Na^+]$ is the concentration of sodium in the aerosol. The NSS can be produced by the burning of fossil fuels, volcanoes, biomass burning, and the oxidation of DMS. The ratio of MSA/NSS-SO₄ can be used to discriminate between the biogenic and non-biogenic contributions to the marine sulfur budget.

The distribution of DMS exhibits a pattern that is similar to primary production. The higher the biological activity, the higher the production of DMS. It is high near the marine boundary layer and decreases with height in the atmosphere. The distribution of MSA in aerosols from the photochemical oxidation of DMS is similar. The NSS-SO₄ is low at the marine boundary layer and increases with height showing a correlation with SO₂ (see Figure 5.42). The long-range transport of SO₂ can result in elevated levels of SO₂ and NSS-SO₄ in the high troposphere.

The aerosols of MSA and SO₄ can act as CCN and influence the albedo (reflectance) of the upper atmosphere and the earth's climate (Figure 5.43). Some have speculated that

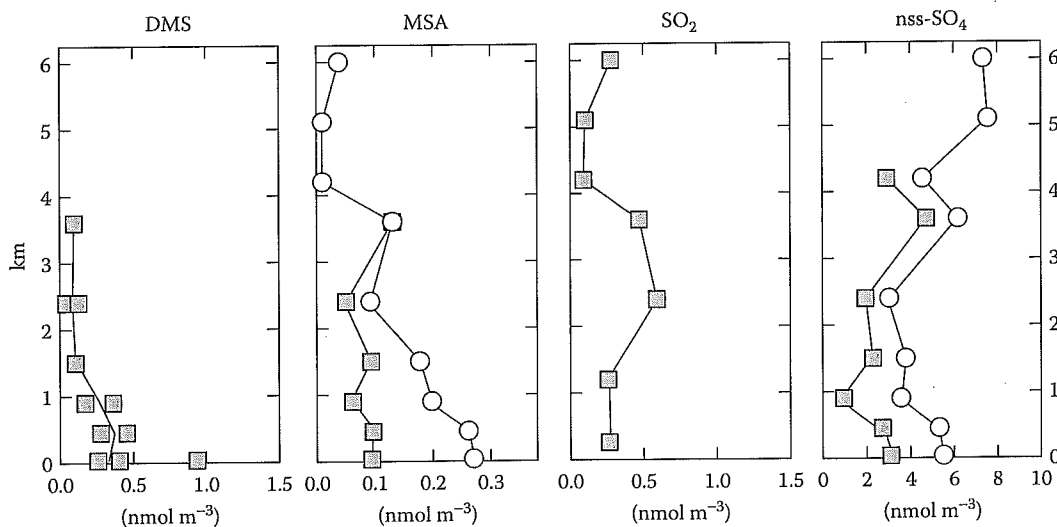


FIGURE 5.42 The vertical distribution of dimethylsulfide (DMS), methanesulfonate aerosol (MSA), sulfur dioxide (SO₂), and non-sea-salt sulfate (nss-SO₄) in the atmosphere over the northeastern Pacific.

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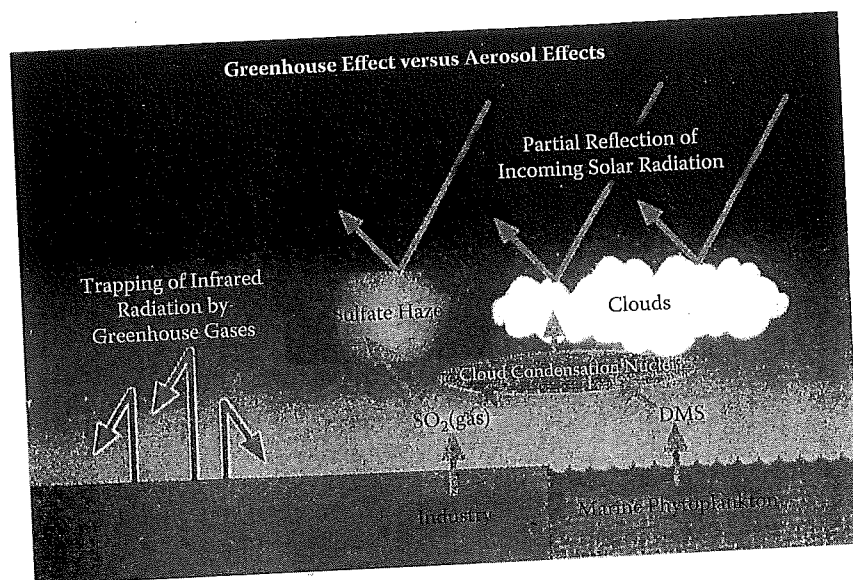


FIGURE 5.43 The effect of aerosols and greenhouse gases on the balance of incoming and outgoing radiation.

this can lead to a so-called feedback effect. The growth of plants in the surface of the oceans can result in the formation of clouds and a resulting cooling of the earth that counteracts the effects of the greenhouse gases.

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