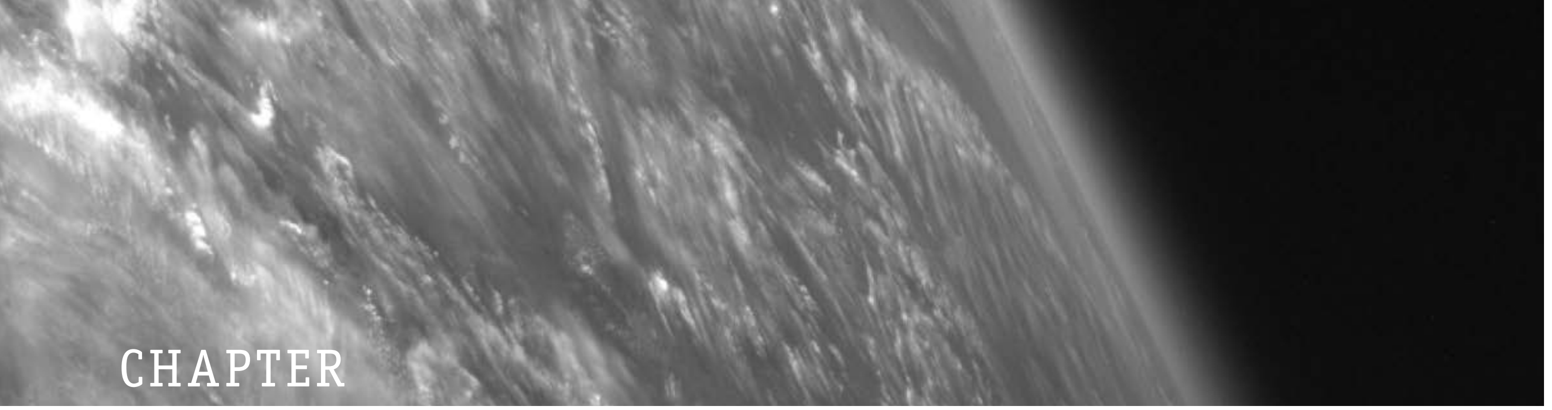


CHAPTER 3

CHAPTER OUTLINE

Image courtesy of NASA/JPL/UCSD/JSC.

The Earth's Atmosphere

THE **ATMOSPHERE** IS A THIN BLANKET OF GAS THAT ENVELOPS THE EARTH. It provides the carbon dioxide that plants need for photosynthesis and the oxygen that animals need for respiration. It is also the ultimate source of nitrogen for plant growth. Freshwater reaches the Earth from the atmosphere in the form of dew, rain, and snow. The atmosphere shields us from the sun's cancer-causing ultraviolet (UV) radiation and also moderates the Earth's climate. Without it, the Earth would experience the extremes of hot and cold that are found on planets that have little or no atmosphere.

The atmosphere is obviously vital for human existence, but we have nevertheless been polluting it for years. By the end of the nineteenth century, huge quantities of coal were being burned to fuel the Industrial Revolution, and smokestacks belching great brown clouds into the atmosphere became a sign of prosperity. By the middle of the twentieth century, the automobile had become another significant source of air pollution. Today, in the United States, pollution from these sources has been greatly reduced as a result of legislation, but we face other problems. Our continued dependence on fossil fuels for energy is introducing increasingly large quantities of carbon dioxide into the atmosphere. In this chapter and the next one, we examine how this practice may be causing the atmosphere to become warmer—a trend that could have disastrous consequences for the world's climate.

Here we first examine the major layers of the atmosphere and their composition, followed by the important balance of energy reaching the Earth from the sun. The absorption of infrared (IR) radiation by atmospheric gases, the increased concentration of these gases in the atmosphere, and their effects on **global warming** are then discussed.

The Major Layers in the Atmosphere

The gases that make up the atmosphere are held close to the Earth by the pull of gravity. With increasing distance from the Earth's surface, the temperature, density, and composition of the atmosphere gradually change. On the basis of air temperature, the atmosphere can be divided vertically into four major layers: the **troposphere**, the **stratosphere**, the **mesosphere**, and the **thermosphere** (**Figure 3.1**).

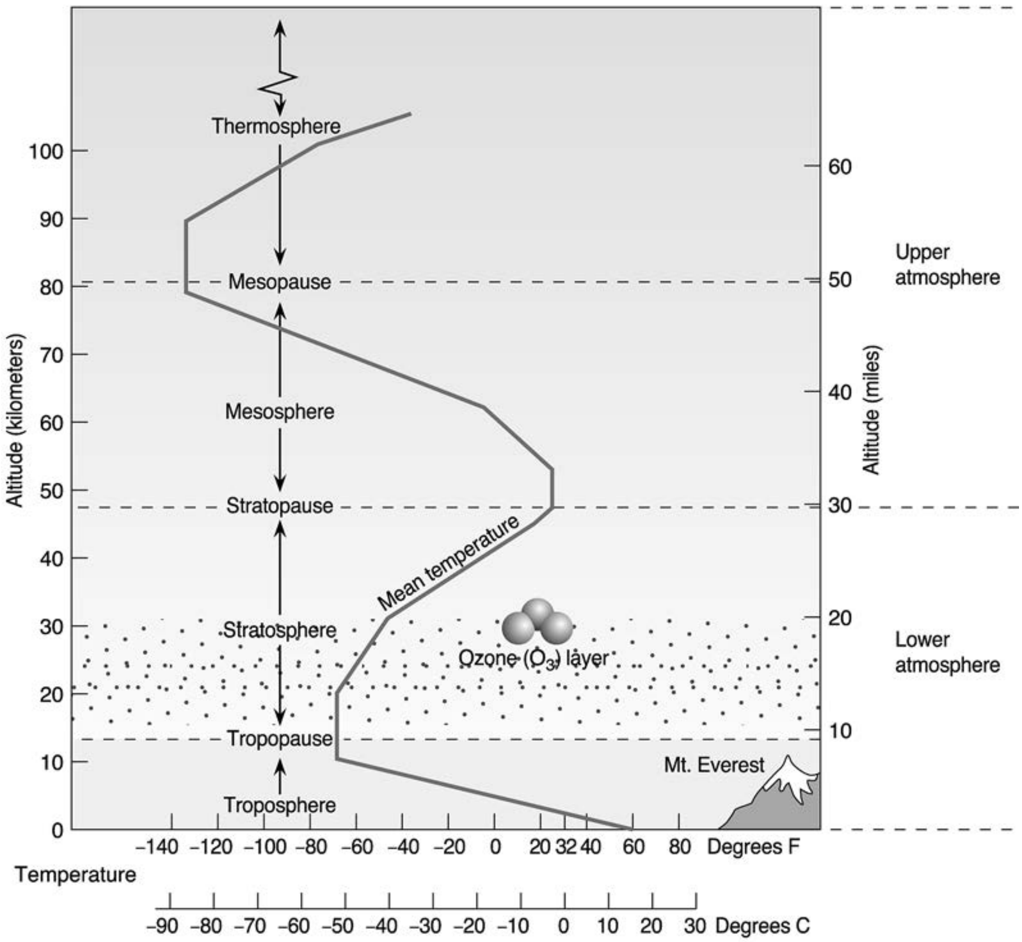


Figure 3.1 The Earth's atmosphere is subdivided vertically into four major regions based on the air-temperature profile. The ozone layer that protects us from the sun's UV radiation is in the stratosphere.

Temperature Changes in the Atmosphere

As shown in Figure 3.1, the Earth's atmosphere is stratified as a result of temperature and density relationships that result from the interaction of physical and photochemical (induced by sunlight) processes. The troposphere extends above the Earth to a distance of 10 to 16 kilometers (6 to 10 miles). The temperature of this layer of the atmosphere decreases steadily as the distance from the Earth's warm surface increases until it reaches approximately –57°C (–70°F).

The lower part of the troposphere (0 to 3,000 meters), which interacts directly with the surface of the Earth, is known as the **boundary layer.** Pollutants emitted near the ground accumulate in the boundary layer. The temperature of the air in this region responds to changes in ground temperature in less than 1 hour. Most weather occurs in the boundary layer of the troposphere.

The temperature of the **free troposphere** (the upper part of the troposphere), by comparison, responds to changes in ground temperatures over a longer period. The temperature of the free troposphere decreases with rising altitude (approximately 6.5°C/km). The temperature of this region decreases with increasing altitude for a number of reasons. First, the top of the free troposphere continuously radiates energy upward, cooling the upper troposphere. Second, the troposphere itself does not efficiently absorb solar radiation. Third, this region receives warmed air that rises from the surface. Because atmospheric pressure also decreases with increased altitude, the warm air enters a region of lower pressure. The warm air expands and as a result cools, resulting in a decrease of temperature with increasing height.

The region called the **tropopause** is at the top of the troposphere. The low temperature (–57°C) of this region serves as barrier that freezes water vapor as ice crystals that fall back to the surface of the Earth. If water vapor was able to rise above this layer, it could reach higher altitudes where it could be photodissociated by intense UV radiation. If this happened, the H_2 and O_2 generated through this process would be lost into space, and as a result, the amount of water on Earth would be constantly decreasing.

Above the troposphere is the stratosphere, which extends to approximately 50 km (30 miles) and includes the ozone layer. The temperature remains constant in the lower part of the stratosphere but begins to rise with increasing altitude, reaching a maximum of approximately –1°C (30°F) at the **stratopause,** which is the boundary between the stratosphere and the mesosphere. The formation of ozone in the stratosphere, which absorbs UV radiation from incoming solar radiation and converts the radiant energy into heat, causes this rise in temperature. Collectively, the troposphere and the stratosphere are known as the **lower atmosphere.**

The **upper atmosphere** extends beyond the stratosphere and is divided into the mesosphere and the thermosphere. Continuing outward through the mesosphere, the temperature again falls. At an altitude of between approximately 80 and 90 km (50 and 56 miles), the lowest temperature in the atmosphere, approximately –90°C (–130°F), is reached. Above the mesosphere, the temperature rises once more and reaches a maximum of approximately 1,200°C (2,192°F) in the thermosphere. This rise in temperature is caused by the few gaseous molecules in the thermosphere absorbing the most energetic radiation emanating from the sun.

Pressure and Density Changes in the Atmosphere

The gases in the atmosphere exert a pressure on the surface of the Earth. Although we are not aware of it and have adapted to it, humans and everything else on the Earth's surface are constantly subjected to this pressure **(Figure 3.2)**. We are adversely affected by even relatively small variations in atmospheric pressure. For example, people flying in a jet aircraft through the stratosphere, where the air is thin, could not survive if cabin pressure were not adjusted to match the air pressure normally found on the Earth's surface.

With increasing distance from the Earth, the pull of gravity becomes weaker, and air density (mass per unit volume) decreases. The troposphere and stratosphere together account for 99.9% of the mass of the atmosphere; almost half of this mass is concentrated within

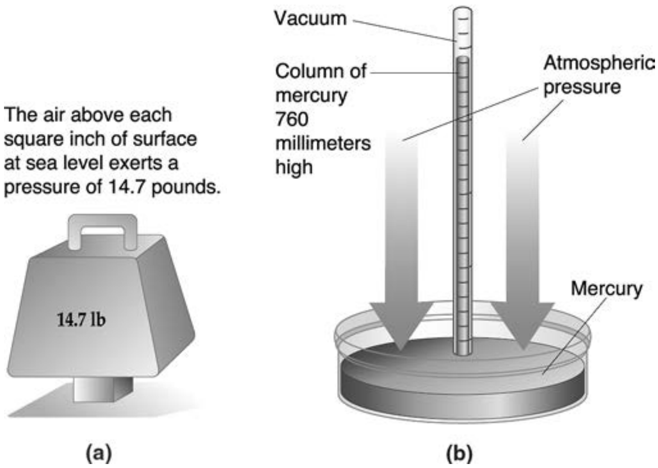


Figure 3.2 (a) At sea level, the air above each inch of the Earth's surface exerts a pressure of 14.7 pounds. (b) At sea level and 0°C, the average pressure of the atmosphere supports a column of mercury 740 to 770 mm in height.

6 km (3.6 miles) of the Earth's surface. As the air becomes thinner with increasing distance from the Earth's surface, atmospheric pressure decreases rapidly. At an altitude of 6 km (3.6 miles), atmospheric pressure is reduced to approximately 50% of the value at sea level. Although the actual atmospheric pressure at any location depends on weather conditions and altitude, the average value used is 1 atmosphere (atm), 760 torr, or 101,325 Pa. The standard unit for pressure is the **pascal** (Pa). A related unit sometimes used to report pressures is the bar (1 bar equals 10^5 Pa).

Composition of the Atmosphere

The major components in the atmosphere are nitrogen (N_2) and oxygen (O_2), which make up approximately 78% and 21% of the volume of the atmosphere, respectively **(Table 3.1)**. Minor components are the noble gas argon (0.93%) and carbon dioxide (0.038%). Smaller amounts of the other noble gases (neon, helium, and krypton) and methane are present as well. The percentage of carbon dioxide (0.038%) in the atmosphere is extremely small, but carbon dioxide is the essential raw material for photosynthesis; thus this very small amount is vital for life itself on Earth. Carbon dioxide also plays an important role in maintaining the Earth's heat balance.

Water vapor is not included in Table 3.1 because its concentration in the air is variable. Depending on temperature, precipitation, rate of evaporation, and other factors at a particular location, the percentage of water vapor in the atmosphere may be as low as 0.1% or as high as 5%. It generally lies between 1% and 3%, making water the third most abundant constituent of the air. The amount of water in the atmosphere depends on the temperature, because the vapor pressure of water increases with temperature. **Table 3.2** shows the partial pressure exerted by water as a function of temperature.

The partial pressures of water vapor, pH_2O, are equilibrium values and represent the maximum pressure that water vapor can exert at that temperature. If the pressure of all gases in the atmosphere is 1.0 atmosphere pressure, you can see that the percentage of water vapor varies from less than 1% at 0°C to more than 5% at 35°C. Notice that the vapor pressure of water at its freezing point is not zero—this explains why even snow can evaporate. Usually, the atmosphere is not saturated with water vapor. The **relative humidity** expresses just how saturated with water vapor the atmosphere is. Using the data in Table 3.2, the partial pressure of water vapor can be calculated if the relative humidity is also known.

EXAMPLE 3.1

Relative Humidity

Calculate the partial pressure of water at 25°C if the relative humidity is 80%.

Step 1: Obtain from Table 3.2 the saturated partial pressure of water vapor in air at 25°C.

Step 2: Multiply the saturated partial pressure of water vapor by the relative humidity expressed as a fraction.

$$pH_2O = (0.03126\text{ atm})(0.80) = 0.0250\text{ atm}$$

Because complete mixing of the troposphere would take several years, water is very unevenly distributed in the atmosphere. The distribution of water is consistent with variations in the weather from place to place.

Table 3.1

Composition of Pure Dry Air at Ground Level

Gas	Percent by Volume	Parts per Million
Nitrogen (N_2)	78.08	780,840
Oxygen (O_2)	20.94	209,440
Argon (Ar)	0.93	9,340
Carbon dioxide (CO_2)	0.04	370
All other gases	0.01	10

Table 3.2

Saturated Partial Pressure of Water Vapor in Air

Temperature °C	pH_2O, atm
–10	0.00257
–5	0.00396
0	0.00603
10	0.01683
20	0.02307
25	0.03126
30	0.04187
35	0.05418

If water vapor is excluded, the concentration of the major components of the air is remarkably constant. In the absence of pollution, no matter where you may be on the surface of the Earth, the air that you breathe is the same. This homogeneity results from the mixing that is brought about by the continuous circulation of the air in the troposphere.

In addition to water vapor and gases, the atmosphere contains many airborne particles, which are the centers around which ice crystals and water droplets form. Under favorable conditions, these droplets coalesce to produce clouds and ultimately rain. Airborne particles range in size from those that are visible, such as dust, to others that can be seen only with a high-powered microscope. Minute particles with diameters of less than approximately 10 µm are termed **aerosols;** larger particles are called **particulates.** Both types of particles can be either liquids or solids.

Relative to their size, small particles have very large surface areas that act as sites for chemical interactions. Depending on the nature of the particle and of the impacting molecule (or other species), chemical reactions may occur at the surface of a particle or within it. If impacting molecules become attached to the particle's surface, the process is termed **adsorption.** If, as in the case of liquid particles, molecules are drawn inside and dissolved, the process is termed **absorption.**

Particulates are studied in more detail when we consider their role as pollutants later in this chapter.

Units Used to Describe Atmospheric Chemistry

Parts per Million, Parts per Billion, and Parts per Trillion

The most commonly used units of concentration for atmospheric gases are the "parts per million" (ppm), the "parts per billion" (ppb), and "parts per trillion" (ppt) classifications. Unlike in solids and liquids, where the "parts per ________" are expressed as mass, in gases, these units are expressed as the number of molecules of a pollutant in air. The **ideal gas law** (PV = nRT) states that the volume of gas is proportional to the total numbers of molecules present. The terminology used to emphasize that the relationship is based on number of molecules, or volume, is to place the letter "v" as part of the unit. Thus an ozone concentration of 10 ppmv indicates that there are 10 ozone molecules for every 1 million air molecules; this measurement of molecules was made by volume. This means there are 2 L of pollutant in 1 million L of air, assuming that the temperature and atmospheric pressure of each are the same. Because the partial pressure of gas is proportional to its number of moles, 2 ppmv would have 2×10^{-6} atmospheres partial pressure of pollutant if the total atmospheric pressure was 1 atmosphere.

Molecules per Cubic Centimeter

The concentrations of many atmospheric pollutants are expressed in pollutant molecules per cubic centimeter (cm^3) of air. One liter equals 1,000 cm^3. To convert a concentration of 5 ppm carbon monoxide to molecules of CO per cubic centimeter at 1 atmosphere pressure and 25°C, use the ideal gas law:

$$PV = nRT$$

Because we know there are 5 CO molecules for every 1 million air molecules, we need to calculate the volume, in cm^3, that 1 million molecules of air would occupy. First calculate the number of moles:

$$n = \frac{1.0 \times 10^{6} \text{ molecules}}{6.023 \times 10^{23}} = 1.66 \times 10^{-18} \text{ mol}$$

Then rearrange the ideal gas law and substitute:

$$V = nRT/P = \frac{(1.66 \times 10^{-18})(0.082 \text{ L-atm/mol K})(298 \text{ K})}{1.0 \text{ atm}}$$

$$V = 4.06 \times 10^{-17} \text{ L}$$

Now convert liters into cubic centimeters:

$$\left(4.06 \times 10^{-17} \text{ L}\right) \frac{\left(1{,}000 \text{ cm}^3\right)}{1.0 \text{ L}} = 4.06 \times 10^{-14} \text{ cm}^3$$

Because we know that five molecules of CO occupy the volume of 1 million air molecules, we can now complete the calculation:

$$\frac{5 \text{ molecules CO}}{4.06 \times 10^{-14} \text{ cm}^3} = 1.23 \times 10^{14} \text{ molecules/cm}^3$$

Micrograms per Cubic Meter

Another unit that is often used to express the concentration of a pollutant in air is micrograms per cubic meter ($\mu g/m^3$). To convert the micrograms per cubic meter unit to ppm or ppb, all that is needed is the mass of the pollutant. As an example, assume a measurement has shown the atmosphere to contain 230 $\mu g/m^3$ of nitrogen dioxide (NO_2) on a day that was

27°C and 1 atm atmospheric pressure. Express this concentration in ppb. The units for ppb are as follows:

$$\text{ppb } NO_2 = \frac{\text{molecules of } NO_2}{\text{1 billion molecules of air}}$$

First we have to compute how many NO_2 molecules there are in 230 μg:

$$230 \times 10^{-6}\text{ g } NO_2 \times \frac{1 \text{ mol } NO_2}{46.0 \text{ g } NO_2} \times \frac{6.02 \times 10^{23} \text{ molecules of } NO_2}{1 \text{ mol } NO_2}$$

$$= 3.01 \times 10^{18} \text{ molecules of } NO_2$$

Next, using the ideal gas law, we can compute how many molecules of air are in 1 m^3 of air. Use the conversion factor 1.0 L = 10^{-3} m^3.

$$n = PV/RT = \frac{(1.0 \text{ atm})(1.0 \text{ m}^3)(1.0 \text{ L}/10^{-3}\text{m}^3)}{(0.082 \text{ L-atm/mol K})(300 \text{ K})} = 40.7 \text{ mol}$$

Now find how many air molecules are in 40.7 mol:

$$(40.7 \text{ mol})(6.023 \times 10^{23}) = 2.45 \times 10^{25} \text{ molecules of air}$$

So,

$$\frac{3.01 \times 10^{18} \text{ molecules of } NO_2}{2.45 \times 10^{25} \text{ molecules of air}} = (1.23 \times 10^{-7}) \quad \frac{(10^9)}{(10^9)} = \frac{123 \text{ molecules of } NO_2}{10^9 \text{ molecules of air}}$$

$$= 123 \text{ ppb}$$

Energy Balance

Electromagnetic Radiation

The energy source that sustains all life on Earth is the sun. It provides the light energy that plants need for photosynthesis and the heat that warms the Earth. It controls our climate, drives our weather systems, and regulates the life cycles of all plant and animal species. The radiant energy—**electromagnetic radiation (EMR)**—that the sun continually transmits through space reaches the Earth in many forms. The most familiar forms are light and radiant heat; other forms include cosmic rays, X-rays, UV radiation, microwaves, and radio waves **(Figure 3.3)**. The sun has a surface temperature of approximately 5,800°K and acts as a "black body" emitter. As can be seen in **Figure 3.4**, as the temperature of a black body emitter rises, its emission of EMR increases, and the wavelength of the EMR shifts to increasingly shorter wavelengths (λ). Planck has described the energy (*E*) of the EMR:

$$E = \frac{hc}{\lambda}$$

where

E = energy in joules (J)
λ = wavelength in meters
$h = 6.626 \times 10^{-34}$ Js, Planck's constant
$c = 2.998 \times 10^8$ m/s, the speed of light

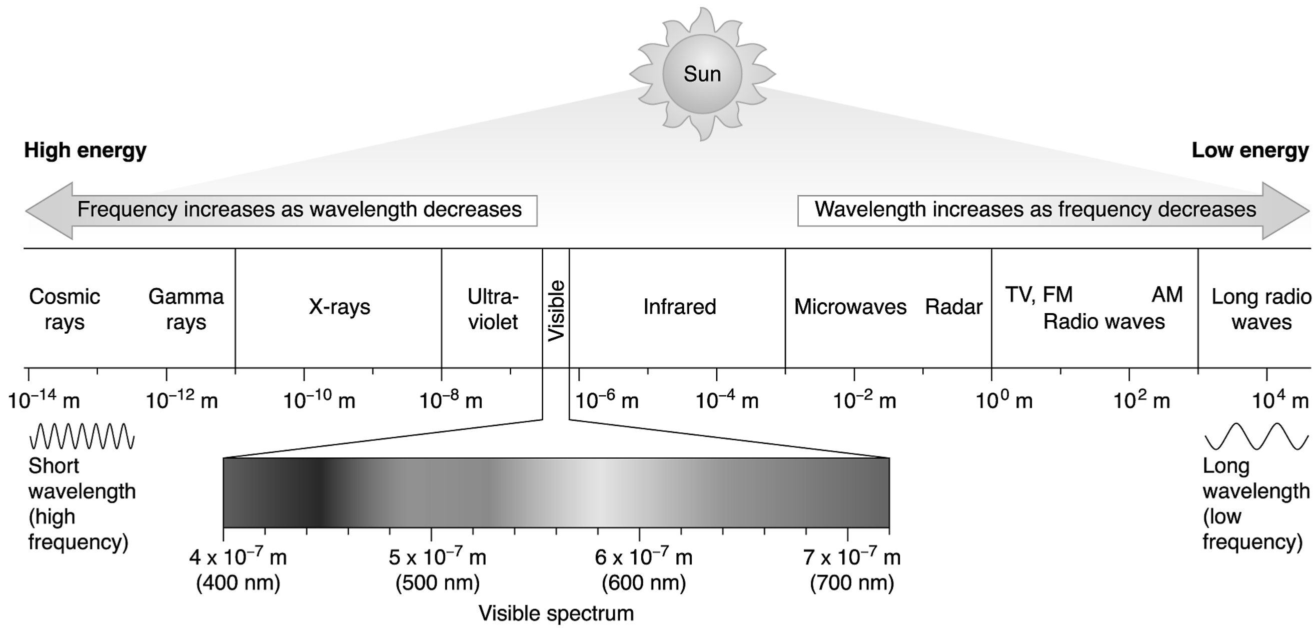


Figure 3.3 The electromagnetic spectrum. As the wavelength of EMR increases from cosmic rays to radio waves, the energy and frequency of the waves decrease. The visible wavelengths make up a very small part of the electromagnetic spectrum (1 nm is equal to 10^{-9} m).

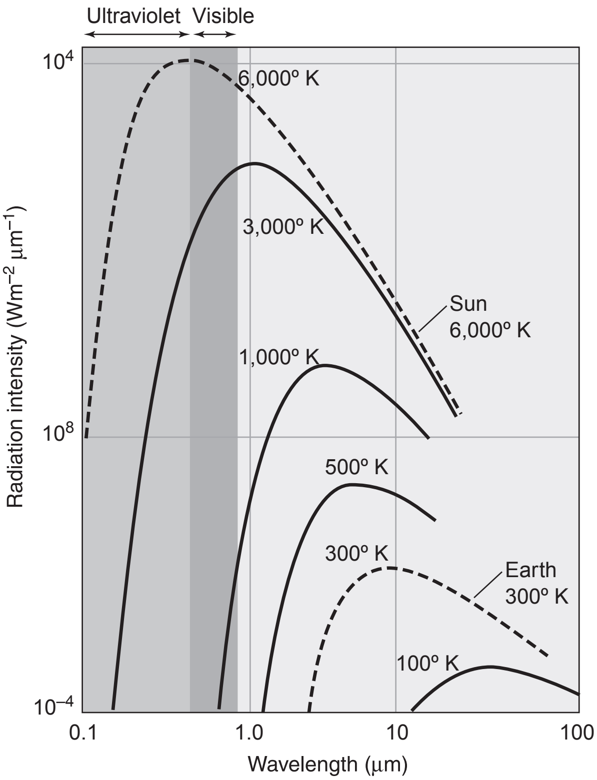


Figure 3.4 Emission spectrum of a black body. *Source:* Adapted from F. Grum and R.J. Becherer, *Optical Radiation Measurements, Volume I: Radiometry,* New York: Plenum, 1979.

As the EMR shifts to increasingly shorter wavelengths, the energy of the EMR increases. To approximate the wavelength of maximum emission, **Wein's displacement law** is used:

$$\lambda_{max} = \frac{2,897}{T}$$

where

λ_{max} = wavelength in micrometers (μm)
T = temperature in K

The emission from the 5,800°K sun has a maximum at approximately 500 nm, which is in the visible spectrum.

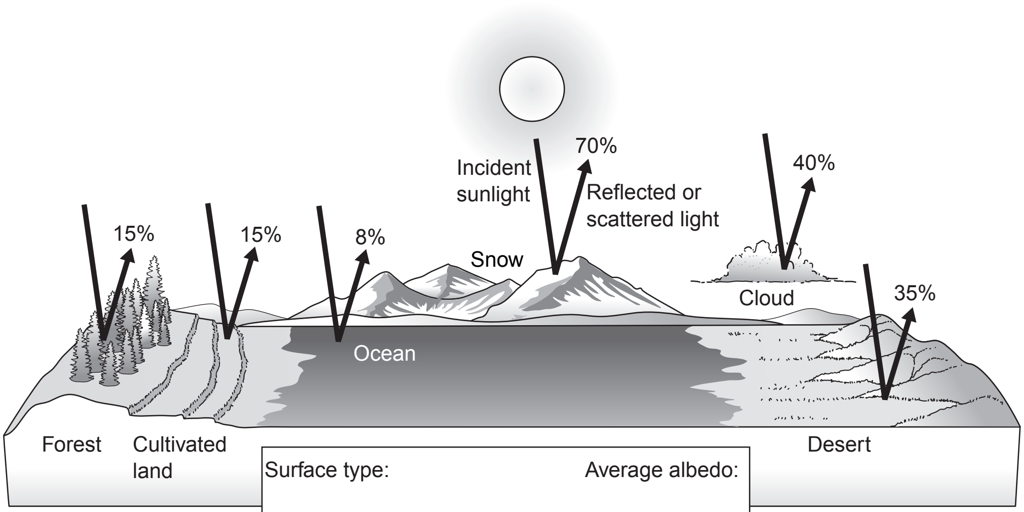
EXAMPLE 3.2

Calculate the wavelength of maximum radiative emission from the Earth.

Solution

1. The average surface temperature of the Earth is 288°K.
2. Use Wein's displacement law:

$$\lambda_{max} = \frac{2,897}{288} = 10.1\,\mu m$$



Surface type:	Average albedo:
Forest land	10–20%
Agricultural land	10–20%
Deserts	25–40%
Snow cover (above 60° latitude)	60–80%
Oceans (70° latitude and above)	15–20%
Oceans (below 70° latitude)	6–10%
Clouds (average over all types)	35–40%
Overall average	**31%**

Figure 3.5 Albedo varies depending on cloud cover and the type of surface.

Only approximately 69% of the total solar radiation or **solar flux** reaching the Earth is actually absorbed at the Earth's surface; the remaining 31% of the solar flux is reflected back into space. The solar flux that is reflected is referred to as Earth's **albedo.** Many factors, including clouds, dust, smoke, and volcanic ash, cause the albedo. The albedo of different surface types can be seen in **Figure 3.5.** The reflectivity of the Earth's surface also varies depending on location. Of the 69% of the solar flux that is absorbed, 23% is absorbed by water droplets in clouds and other gaseous molecules such as ozone in the atmosphere. The remaining 46% is absorbed at the Earth's surface and is used as an energy source for biomass growth and for thermal warming of the planet's surface. The average solar flux reaching the Earth (at the top of the stratosphere) is 1,368 W/m^2.

All of the energy that the Earth absorbs from the sun is eventually lost as EMR. The average surface temperature of the Earth is 288°K (15°C). The Earth loses EMR as a black body reradiating energy. The previously mentioned equation allows us to calculate the maximum wavelength of this reradiating EMR, which is 10 μm, which corresponds to the emission line for a 288°K black body emitter. Figure 3.4 shows that the Earth reradiates EMR as infrared.

The Earth's Heat Balance

Solar energy is transmitted through space as EMR. The amount of solar energy that reaches the outer limits of the Earth's upper atmosphere is enormous; if all of it penetrated to the Earth's surface and were retained, the very high temperature would have prevented the development of any life on Earth. Fortunately, as solar radiation travels through the atmosphere, interactions with gases and particulates prevent approximately half of it from penetrating to the Earth's surface. The 69% of solar energy that eventually reaches the Earth includes the entire visible region of the spectrum together with smaller portions of the adjacent UV and IR regions. This incoming radiation is largely absorbed at the surface and is then reradiated back to space. If this radiation away from the surface did not occur, the Earth would become increasingly warm as solar energy continued to flow in. Outgoing radiation from the Earth is in the longer wavelength IR region.

As mentioned earlier, the solar flux (F_s) is 1,368 W/m^2. To estimate the amount of energy reaching the Earth, consider an area of πr^2, where r is the Earth's radius. The total amount of solar energy absorbed by the Earth (E_{in}) is equal to the solar flux times the area of the Earth minus the portion that is reflected back into space. The reflected portion is the albedo (A). Albedo varies greatly depending on the surface. Snow and ice, for example, reflect more incoming radiation than does a parking lot paved with black asphalt. The incoming radiation that is absorbed must be balanced with the radiation that is emitted to calculate an equilibrium temperature for Earth.

$$E_{in} = F_s(1 - A)(\pi r^2)$$

where

E_{in} = total amount of solar energy absorbed by the Earth
A = albedo

The Earth gives off radiation as a sphere. The energy reradiating from the entire area of its surface (E_{out}) can be estimated by the **Stefan Boltzmann law:**

$$E_{out} = 4\pi r^2 \ S_b \ T^4$$

where

T = Kelvin temperature of the Earth
$S_b = 5.67 \times 10^{-8}$ Wm^{-2}K^{-4}, Stephan Boltzmann constant
E_{out} = energy reradiationg from the entire area of the Earth's surface

Over time, the steady-state total energy that the Earth absorbed from the sun equals the energy that it reradiates:

$$E_{in} = E_{out}$$

$$F_S(1 - A)(\pi r^2) = 4\pi r^2 \ S_b \ T^4$$

Rearranging this equation gives

$$T = \left(\frac{(1-A)\,F_S}{4\ S_b}\right)^{1/4}$$

knowing that

$F_s = 1{,}368\ \text{Wm}^{-2}$

$A = 0.31$

$$T = \left(\frac{(1 - 0.31)(1{,}368\ \text{Wm}^{-2})}{4\ (5.67 \times 10^{-8}\ \text{Wm}^{-2}\text{K}^{-4})}\right)^{1/4}$$

$$T = 254°\text{K or} -19°\text{C}$$

This calculation allows us to predict an average global surface temperature of –19°C. The experimentally measured average temperature of the Earth is 15°C (288°K), and this temperature

Table 3.3

Calculated and Actual Temperatures of the Surfaces of Planets and the Moon

Planet	Distance from Sun, 10^9 m	Calculated Temperature K	Actual Temperature K	ΔT
Venus	108	252	730	+478
Earth	150	255	288	+34
Earth's moon	150	270	274	+4
Mars	228	217	218	+1

Source: Adapted from M. Z. Jacobson. *Atmospheric Pollution* (Cambridge, UK: Cambridge University Press, 2002), p. 314.

is 34°C higher than calculated. The calculation, however, assumes that all radiation leaves the Earth and is lost into space. If some of the IR radiation is absorbed by gases in the atmosphere and is not lost, then the Earth's temperature would be expected to be higher.

If the same equation is used to calculate the temperature of other nearby planets and the results are compared with the actual temperature, an interesting correlation is revealed. **Table 3.3** shows the difference between the calculated and actual temperatures on the surfaces of several other nearby planets and Earth's moon. The calculated and actual temperatures for Mars and Earth's moon closely agree. Both of these objects have very thin atmospheres that could not absorb IR radiation emitted from the surface of the planet.

The surface temperature of Venus is more than 475°K warmer than the temperature expected from the calculation. Venus is closer to the sun than the other planets and receives more incident radiation. Early in this planet's evolution, liquid water and ice were melted and evaporated. The water vapor was exposed to intense UV radiation from the sun, which photolyzed the water to atomic hydrogen and the hydroxyl radical.

$$H_2O + h\nu \rightarrow H^{\cdot} + OH^{\cdot}$$

$$2H^{\cdot} \rightarrow H_2$$

Over time, the atomic hydrogen formed hydrogen gas (H_2), which was able to escape Venus's gravity and was lost into space. Because of the loss of hydrogen, water could not re-form. At the same time, volcanic outgassing released CO_2. Because there was no water left, there was no means to dissolve the CO_2 and convert it to carbonate rock—a process that took place on Earth during the same time period. As a result, CO_2 built up in Venus's atmosphere, producing a runaway greenhouse effect. Today, Venus has a surface atmospheric pressure that is 90 times greater than that of Earth, and this atmosphere is mostly CO_2. It is this high concentration of CO_2 that absorbs reradiated IR radiation from the surface of Venus and renders the planet more than 475°K hotter than expected.

Earth is located at a distance from the sun that makes it an ideal place to support life. The comparison of Earth to Venus and Mars produces the **Goldilocks' hypothesis.** According to this hypothesis, Venus is too hot to support life because it is too close to the sun, and its atmosphere has too high of a concentration of greenhouse gases. Mars is too cold to support life because it is too far away from the sun and has little atmosphere. Earth, however, is the ideal distance from the sun and has a low concentration of greenhouse gases that warm the planet enough to allow water to exist as a gas, liquid, and solid and to support life.

Although the amount of energy reaching the top of the Earth's atmosphere facing the sun is 1,368 watts per square meter per second, the average amount of energy reaching

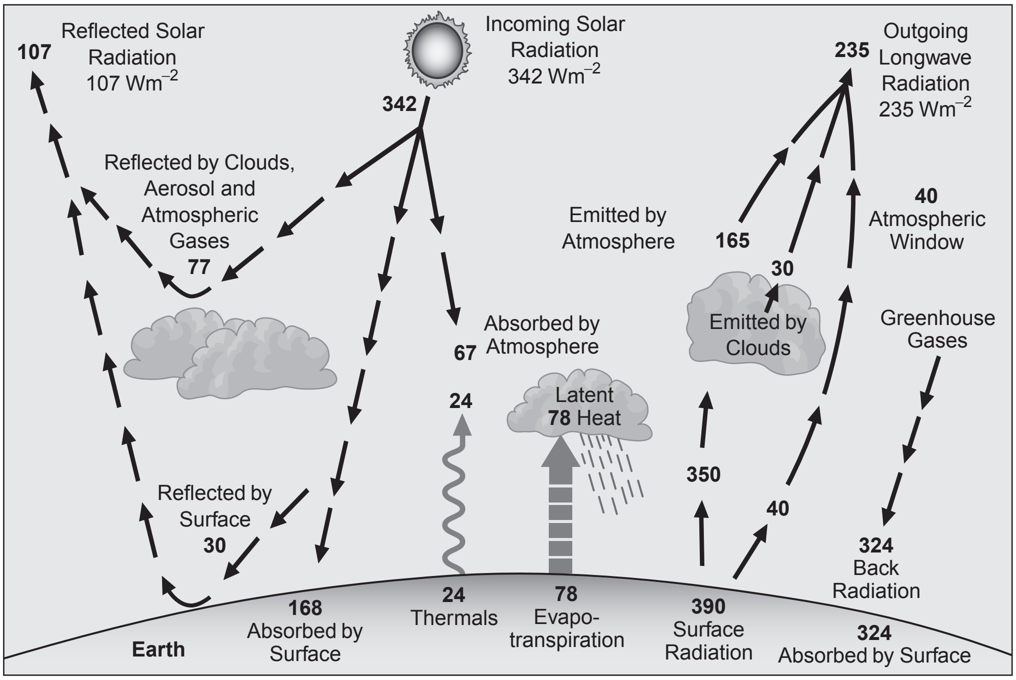


Figure 3.6 An estimate of the Earth's energy balance. *Source:* Adapted from J.T. Kiehl and K.E. Trenberth, Earth's annual global mean energy budget. *Bull. Am. Meteor. Soc.*, 1997;78:197–208.

the entire planet is approximately one fourth of this, or 342 Wm^{-2}. As can be seen in **Figure 3.6**, approximately 30% of the incoming solar radiation (107 Wm^{-2}) is reflected back to space. Light-reflecting areas of the Earth's surface, such as those covered with snow, ice, or deserts, reflect roughly one third of the energy (30 Wm^{-2}), while aerosols suspended in the atmosphere reflect the rest (77 Wm^{-2}).

The amount of light reflected by aerosols can be dramatically altered by natural and anthropogenic events that suspend light-scattering materials in the troposphere. Volcanic eruptions, for instance, eject dust very high into the atmosphere and are a natural way that the Earth's albedo can be increased. The dust ejected by the eruption of Mount Pinatubo in 1991 reflected sunlight for several years, for example, and the increased albedo caused a slight drop in global average temperature at the ground. The same mechanism also can operate on a smaller scale. Where large quantities of smoke are released, local areas can be cooler during the daytime than they would otherwise because of the enhanced scattering of sunlight back into space. These sources are termed **anthropogenic** events because they are caused by human activity.

The energy not reflected back into space is absorbed by the Earth's surface and atmosphere (235 Wm^{-2}). The Earth keeps an energy balance by reradiating the same amount of energy back into space in the form of IR radiation. The calculation shown earlier indicated that to emit 235 Wm^{-2}, a surface would have to have a mean temperature of −19°C. This is much colder than the Earth's global mean surface temperature, which is 14°C. A closer inspection of the Earth's atmosphere indicates that the atmosphere's temperature at 5 km above the surface is −19°C.

The Earth's surface is warmer than expected because of the presence of greenhouse gases in the atmosphere that absorb the IR radiation that would have otherwise been lost into space. They are called **greenhouse gases** because they warm the atmosphere in much the same way as a greenhouse warms the air inside the structure so that plants can grow.

A greenhouse, which is made from glass panels, is designed to allow incoming radiation from the sun to fall on plants inside. Because IR radiation cannot pass through glass, it becomes trapped inside the greenhouse, while outside it is reflected back to space. Thus the greenhouse remains warm even in the cold of winter.

The Earth is a sphere, and more solar energy strikes a square meter of its surface in the tropics than the equivalent area at higher latitudes because of the inclination of the planet toward the sun. Energy is distributed from the tropical regions to higher latitudes by atmospheric and oceanic circulation as well as by storms. The energy required to evaporate water from the sea or other bodies of water is called *latent heat* (Figure 3.6); this latent heat is released when water vapor condenses into clouds. In fact, circulation of the atmosphere is set into motion primarily by the release of latent heat. Atmospheric circulation then induces circulation of water in the ocean by the action of winds on the surface. Because of the Earth's rotation, the atmosphere tends to move in more of an west-east direction.

A variety of climatic feedback mechanisms can amplify (*positive feedback*) or diminish (*negative feedback*) the mechanisms that affect global energy. One such feedback loop is the *ice–albedo feedback loop*. This loop begins with increasing concentrations of greenhouse gases that cause more IR energy to be absorbed by the atmosphere, which in turn heats the atmosphere and causes more ice to melt. When the ice melts, darker surfaces below the ice are exposed, which absorb more solar radiation than does ice. This effect causes more warming and a reinforcing cycle is created. The understanding of climatic feedback loops has been a major focus of scientists for the past 20 years.

Particles in the Atmosphere

Suspended Particulate Matter

Natural sources of airborne particles, which may be either solid or liquid, include smoke and ash from forest fires and volcanic eruptions, dust, sea salt spray, pollen grains, bacteria, and fungal spores. Aerosols and particulates that are liquid are generally called *mist*, which includes fog and raindrops. A significant quantity of harmful particulate matter is also emitted as a result of human activities **(Figure 3.7)**.

Eventually, all particulate matter is deposited on the Earth's surface. Relatively large particles (diameters of greater than 10 µm) settle under the influence of gravity within 1 to 2 days. Medium-sized particles (diameters of 1 to 10 µm) remain suspended for several days. Fine particles (diameters of less than 1 µm) may remain in the troposphere for several weeks and in the stratosphere for up to 5 years. Aerosols, acting as nuclei for the formation of droplets in clouds, reach the ground when the droplets condense and fall as rain or snow. Fine particles can be transported considerable distances by winds before settling to the ground or being washed out by falling rain or snow.

Aerosol Particles

The effect of particulate matter on the heat flux of the atmosphere depends mostly on particle size and not as much on the total concentration of particles. Large, dark particles absorb light and add to the warming of the atmosphere. Small particles, regardless of their color, scatter incident sunlight and increase the albedo of the atmosphere.

Natural sources of light-scattering aerosols are estimated to produce 50% to 75% of all atmospheric aerosols. There are two major natural sources of aerosols: (1) ammonium sulfates generated during microbial degradation of decaying biomass and organic matter in soil and water and (2) reactive organic molecules that are released from natural sources. A good example of the latter is the release of a group of organic molecules called *terpenes*, which come from coniferous trees that include pine, spruce, and fir trees. One of these terpenes, α-pinene, produces the smell that we associate with pine forests.

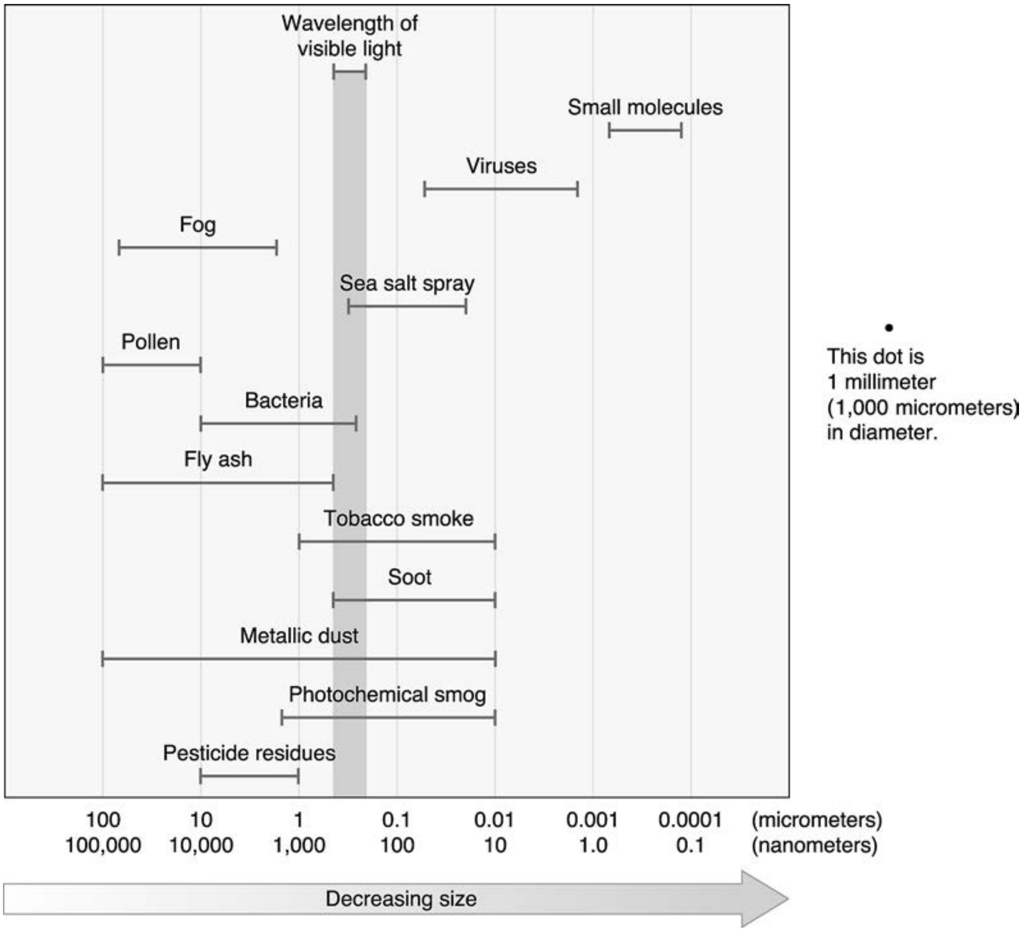


Figure 3.7 Suspended particulate matter of many types and sizes enters the atmosphere from both natural and anthropogenic sources.

Light scattering by aerosols with dimensions that are significantly smaller than the wavelength of the radiation is called **Rayleigh scattering.** Its intensity is proportional to the inverse fourth power of the wavelength ($S = 1/\lambda^4$). Blue light, which has a shorter wavelength, is scattered more than red light. This is why the sky, which we see in scattered light, appears blue, and the sunset, which we see in transmitted light, appears red. The blue haze of the Great Smoky Mountains of Tennessee is caused by light scattering from small aerosols formed by the oxidation of terpenes emitted from the conifer forests.

As can be seen in **Figure 3.8,** the size distribution of particles in the atmosphere varies widely, but there are a larger number of smaller particulates with radii in the range of 0.01 to 0.1 μm. Larger particles of sea spray, pollen, and dust settle out of the atmosphere more quickly than do the smaller particles.

One way to measure the total amount of suspended particulate matter is the **total suspended particulate (TSP)** test. With this method air is drawn through a preweighed filter at a rate of 1 m^3h^{-1}. The total time that air is pumped is recorded so that the total volume of air passing through the filter will be known. At the end of the test, the filter is weighed again so that the total weight of particulate matter is known. TSPs as high as 200 $\mu g/m^3$ have been measured in large cities; individual measurements as high as 500 $\mu g/m^3$ have been measured in very dusty locations such as the desert. Rural farming areas average TSPs in the range of 10 to 50 $\mu g/m^3$. The effects of airborne particulates on health and the environment depend

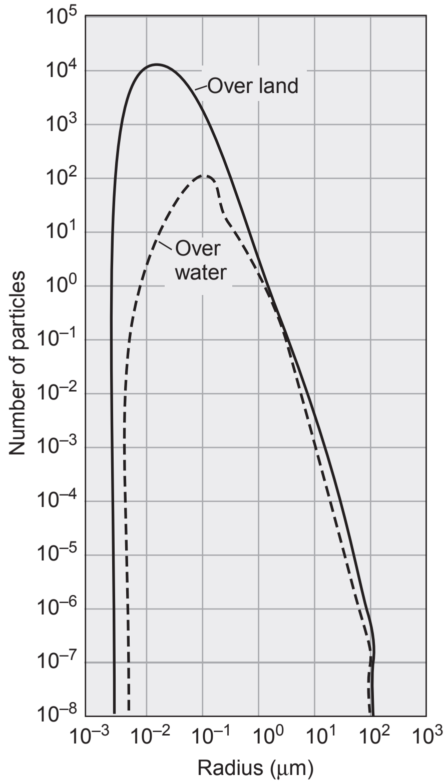


Figure 3.8 Distribution (by size) of particles in the lower atmosphere.

on both the size and the nature of the particles. Very fine particles (diameters of less than approximately 1 μm) are the most hazardous to human health. They are not filtered by hairs and mucus in the nose, which means they are drawn deep into the lungs, where they can remain indefinitely, causing tissue damage and contributing to the development of the lung disease emphysema. These particles take with them any toxic chemicals that are attached to their surfaces or are dissolved within them, such as sulfuric acid.

The **Clean Air Act** Amendments of 1970 for the first time set U.S. standards for the fraction of particles that are easily inhaled and deposited in the lung. Inhalable particulates were defined as those particles with a diameter smaller than 10 μm and are referred to as **PM_{10}.** In 1997, in a revision of the Clean Air Act, another standard was added for particles of diameter 2.5 μm or smaller, the **$PM_{2.5}$.** The current federal standard for $PM_{2.5}$ is 65 μg/m^3 for a 24-hour average concentration.

The Clean Air Act grants the Environmental Protection Agency (EPA) the authority to set and review national air quality standards for PM. Using a nationwide network of monitoring sites, this federal agency has developed ambient air quality trends for particle pollution. Air quality monitors are set up across the country to measure concentrations of PM. Average PM air quality from 1990–2009, in terms of $PM_{2.5}$ and PM_{10}, can be seen in **Figure 3.9.** Nationally, the average PM_{10} concentrations decreased 38% over this period; $PM_{2.5}$ has also decreased 27% since 1999. For information on PM standards, sources, health effects, and programs to reduce PM, see the EPA website (www.epa.gov).

Epidemiologic studies in the 1970s found a link between short-term increases in the PM_{10} of 10 μg/m^3 and an increase in hospitalization and healthcare visits for respiratory and cardiovascular disease and enhanced outbreaks of asthma and coughing. Although studies have identified an association between exposure to outdoor air pollution and health, in

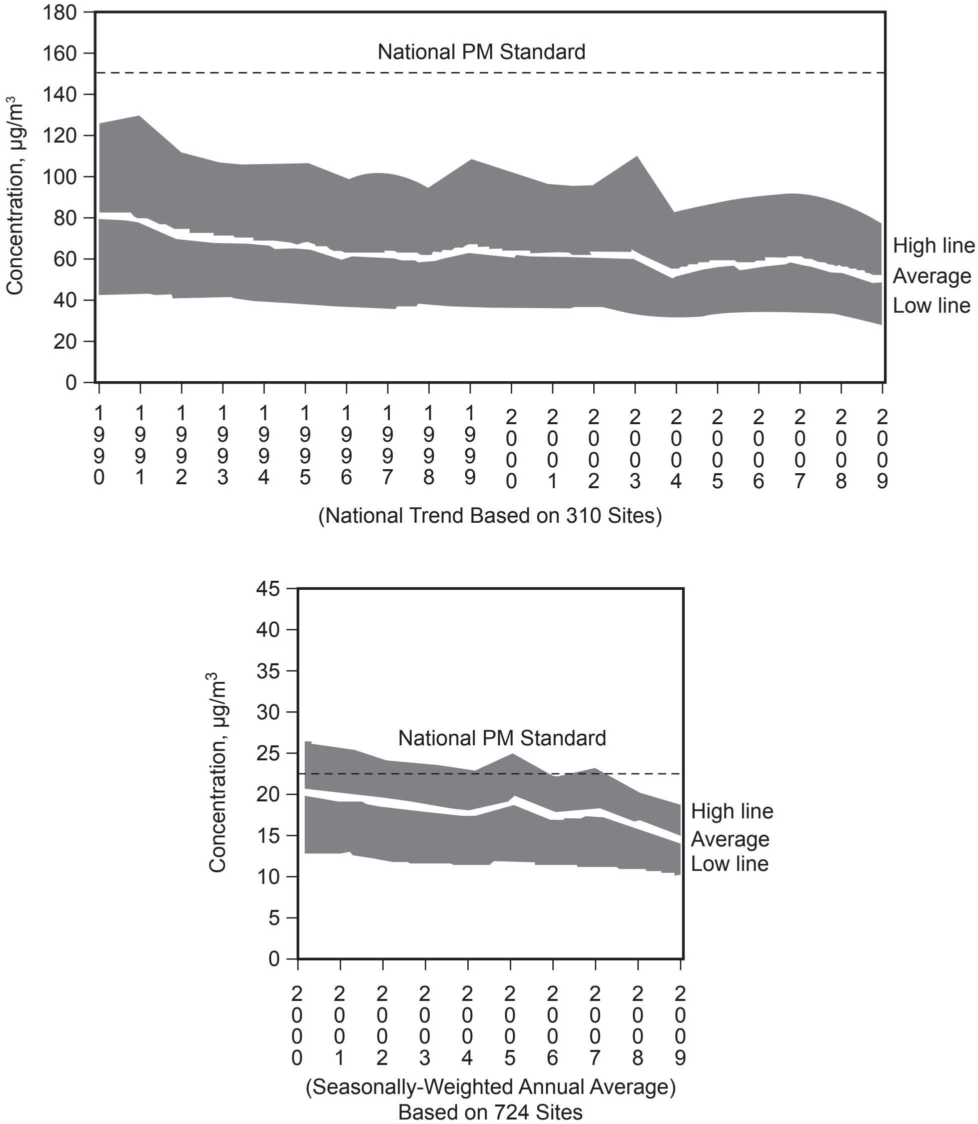


Figure 3.9 Average U.S. atmospheric PM concentration, 1990–2009, as reported by the EPA. Modified from U.S. Environmental Protection Agency, Particulate Matter.

today's world we spend most of our time indoors. The concentration of particles indoors is often greater than outdoors.

Anthropogenic Sources of Particulate Matter

Suspended particulate matter is the most visible form of air pollution. The major source of such particles is the combustion of coal by electric power-generating plants **(Figure 3.10)**. One product of the incomplete combustion of coal is **soot,** a finely divided, impure form of elemental carbon; the structure of this molecule contains a series of benzene rings that are fused. Graphite, another form of elemental carbon, has fused benzene rings, forming a flat, layered structure, whereas soot particles are close to spherical. Soot is also present in black smoke that is emitted by diesel-powered trucks. In the past, diesel engines, which operate at lower temperatures than gasoline engines, produced as much as 3 g of soot per kilogram of

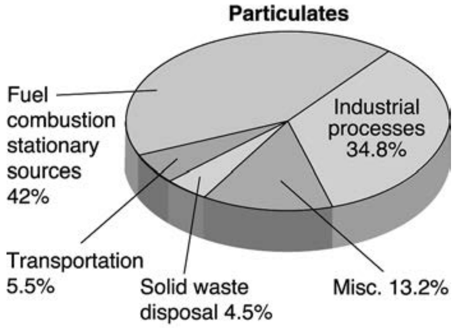


Figure 3.10 Nationwide emissions of particulates according to source.

diesel fuel, whereas gasoline engines of the same era produced only 0.1 g of soot per kilogram of gasoline. Over the years, EPA has been lowering the standards for the emission of soot from diesel trucks. In 1988, diesel trucks were allowed to emit 0.6 g/hp-hr. With the implementation of EPA's 2010 standards, however, diesel trucks are now allowed to emit only 0.01 g/hp-hr. Because soot is black, suspended soot particles absorb incoming radiation from the sun. Other suspended particulates are near-white in color and reflect incoming radiation from the sun.

Other products of coal combustion include metallic and nonmetallic oxides that are formed from minerals present in the coal. These materials, called **fly ash,** are swept up smokestacks in drafts from roaring furnaces and emitted into the atmosphere. Several methods are used to trap and measure fly ash (as described later in this chapter). Fly ash particles are small enough to be respirable. Their composition depends on the quality of the coal being burned and the temperature of the combustion. These particles are composed primarily of the following metallic and nonmetallic oxides: SiO_2, Al_2O_3, Fe_2O_3, and CaO. They also are known to sometimes contain toxic metals such as arsenic, lead, and cadmium.

Other anthropogenic sources of particulate emissions are solid-waste incineration, mining and ore processing, construction sites, and agricultural activities. Toxic metal particles, cement dust, and pesticide and fertilizer residues that are released in these activities are all potentially hazardous.

Residence Times of Particles

The most important physical process that determines the residence time of an aerosol is the **settling rate** of the particles. Settling occurs because the force of gravity pulls the particles and deposits them on the surface of the Earth. For particles in which the diameter exceeds 1 μm, the settling velocity ν is given by **Stokes' law:**

$$\nu = \frac{gd^2\left(p_1 - p_2\right)}{18\eta}$$

where

$g = 9.80\ \mathrm{m/s^2}$ the acceleration caused by gravity
d = diameter of particle in meters
p_1 = density of the particle expressed in $\mathrm{g/m^3}$
p_2 = density of air in $\mathrm{g/m^3}$

Because $p_1 >>> p_2$, $(p_1 - p_2)$ is approximately equal to p_1, and $\eta = 1.9 \times 10^{-2}$ g/ms, which is the viscosity of air at atmospheric pressure and 25°C.

The settling rate for a particle of fly ash that is 2 μm in diameter and has a density (p_1) of 1.0 g/mL is calculated as follows:

Step 1: Convert the density of the particle into g/m^3:

$$p_1 = \frac{1.0\ g}{mL} = \left(\frac{1.0\ g}{mL} \times \frac{1 \times 10^6\ mL}{1.0\ m^3}\right) = 1.0 \times 10^6\ \frac{g}{m^3}$$

Step 2: Plug the values into the equation:

$$\nu = \frac{gd^2 p_1}{18\eta} = \frac{\left(9.80\,m/s^2\right)\left(2 \times 10^{-6}\,m\right)^2\left(1.0 \times 10^6\,g/m^3\right)}{18\left(1.9 \times 10^{-2}\,g/ms\right)}$$

where

$\nu = 114.6 \times 10^{-6}$ m/s
$\nu = 0.011$ cm/s

This particle has a settling velocity of 0.011 cm/s.

Step 3: The settling rate is the distance that the particle will drop in a specific unit of time. The settling rate per day will be as follows:

$$\left(8.6 \times 10^4\ s/day\right)\left(114.6 \times 10^{-6}\ m/s\right) = 9.8\ m/day$$

If the fly ash particle described here was released into the atmosphere from a 100-meter-tall smokestack, it would take 10 days for it to settle on the ground. Stokes' law predicts that the residence time of a particle in air will increase as the radius decreases. The residence times of particles in tropospheric air are often estimated by assuming that they fall 10 m/day.

Control of Particulate Emissions

One method that industry uses to control particulate emissions is **electrostatic precipitation (Figure 3.11a)**. In this process, gases and particulate matter are passed through a high-voltage chamber before leaving the chimney stacks. A negatively charged central electrode imparts a negative charge to the particles, which are then attracted to the positively charged walls of the chamber. As their charges are neutralized, the particles clump together and fall to the bottom, where they can be collected.

A second method for controlling particulate emissions is **bag filtration,** in which lined-up fabric bags function essentially like the bag in a household vacuum cleaner **(Figure 3.11b)**. Gases can pass through the finely woven bags, but particulate matter cannot; particles with diameters of 0.01 to 10 μm are effectively filtered. Unfortunately, the bags are sensitive to temperature and humidity and can become clogged by fine particles. The bags are shaken at intervals to dislodge particles, which are collected in a hopper located underneath the bags. Although both electrostatic precipitation and bag filtration remove more than 98% of particulates, they fail to remove the finest ones, which are the most dangerous.

Another less efficient method of controlling particulate emission is **cyclone separation,** in which the particle-laden gases are subjected to a centrifugal force. The spiraling particles hit the walls, settle, and fall to the bottom, where they are collected. Stokes' law determines how many of the airborne particulates will be removed. The centrifugal force of the cyclone greatly increases the settling rate. Particles that are larger than 1 μm in diameter are more efficiently removed than are smaller particles. All three methods produce solid wastes, which must be disposed of and which mostly end in landfills.

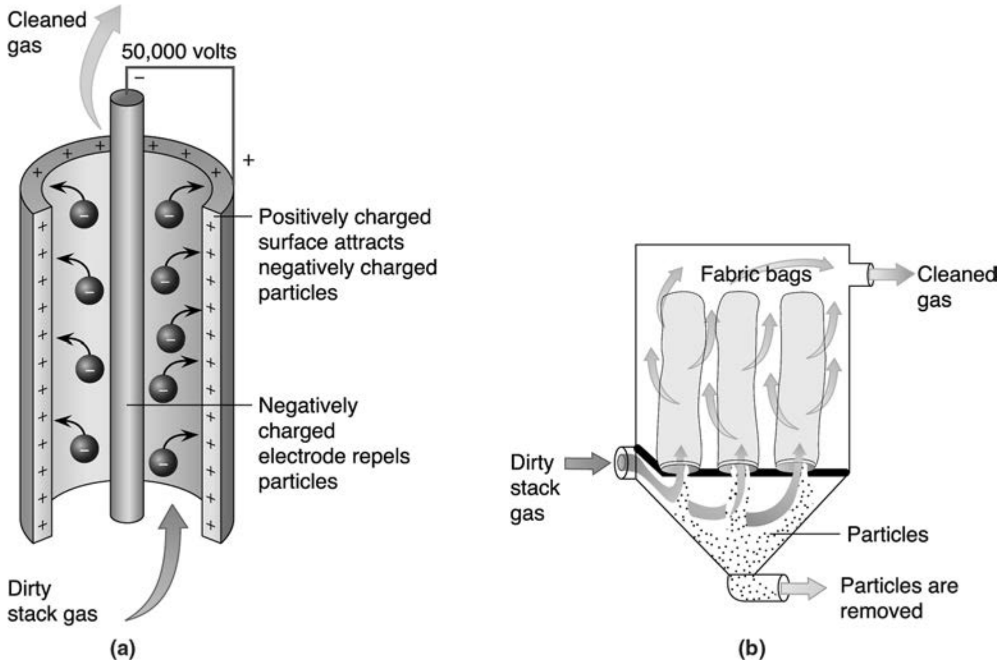


Figure 3.11 Two methods for controlling emissions. (a) In electrostatic precipitation, the dirty gas is passed though a chamber, where particles acquire a negative charge from a negatively charged central electrode. The now negatively charged particles are attracted to the positively charged wall of the chamber, where they are deposited. (b) In bag filtration, the dirty gas is forced through fabric bags, which trap particles. The bags are shaken at intervals, causing the particles to fall into a hopper.

Although the 1970 Clean Air Act mandated standards for particulate emissions, many areas failed to meet the requirements because of difficulties in enforcing the law. Under the 1990 amendments to the act, areas not in compliance must take steps to meet the standards.

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Keywords

absorption
adsorption
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albedo
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Clean Air Act
cyclone separation
electromagnetic radiation (EMR)
electrostatic precipitation
fly ash
free troposphere

global warming
Goldilocks' hypothesis
greenhouse gases
ideal gas law
lower atmosphere
mesosphere
particulates
pascal (Pa)
PM_{10}
PM_{25}
Rayleigh scattering
relative humidity
settling rate
solar flux
soot
Stefan Boltzmann law
Stokes' law
stratopause
stratosphere
thermosphere
total suspended particulate (TSP)
tropopause
troposphere
upper atmosphere
Wein's displacement law

Questions and Problems

1. What is the concentration of each of the following gases in clean, dry air? Express the concentration in percent and parts per million.
   a. O_2
   b. CO_2
   c. N_2
   d. Ar
2. Draw a diagram showing the four main layers into which the atmosphere can be divided. Label your diagram to show the following:
   a. The distance the two layers closest to the Earth extend out from the Earth's surface
   b. The changes in temperature with increasing distance from the surface of the Earth
   c. The location of the ozone layer
3. Explain why the stratosphere, which is more than 20 miles thick, has a smaller total mass than the troposphere, which is less than 10 miles thick.
4. Calculate the partial pressure of water in the Earth's atmosphere if the temperature is 20°C and the relative humidity is 50%.
5. The percentage of water vapor in the atmosphere is variable. It generally lies in the range of which of the following?
   a. 0.05% to 1%
   b. 1% to 3%
   c. 5% to 10%
   d. 10% to 20%
6. Define the term *relative humidity*.
7. Calculate the relative humidity for the following atmospheric conditions:
   a. A temperature of 25°C and a partial pressure of 0.0275 atm for water
   b. A temperature of 20°C and a partial pressure of 0.0205 atm for water
8. Draw a diagram to show how atmospheric pressure varies with altitude.
9. If the surface temperature of Venus is 730°K, what is the wavelength of the radiation it emits as a black body? Does it emit IR radiation?
10. If the temperature of the sun increased from 5,800°K to 8,500°K, how would the wavelength of its emission change? What effect would this have on plants and mammals?
11. Define the term *albedo*. Arrange the following surfaces in order of lowest albedo to highest albedo: desert, ice, grassland, forest, water, asphalt.
12. Describe the difference between an aerosol and a particulate.

13. Define the following:
    a. Mist
    b. Fog
    c. Soot
    d. Fly ash
    e. Smog
14. Give four examples of particulate matter that arise from the following:
    a. Natural sources
    b. Anthropogenic sources
15. Describe Raleigh scattering by particulates.
16. Why is the sky blue?
17. Describe the TSP test.
18. Define the following:
    a. $PM_{2.5}$
    b. PM_{10}
19. Explain how the surface areas of particulates and aerosols are a factor in causing them to be health hazards.
20. How does the size of a particle influence its effect on health?
21. Calculate the settling rate for the following:
    a. A particle of fly ash that is 2.5 μm in diameter with a density of 1.2
    b. A particle of soot that is 1.0 μm in diameter with a density of 0.7
    c. Which of the two particles would settle out of the air first?
22. Estimate the resonance time of a fly ash particle that is released from a 300-ft smoke stack.
23. Describe three different methods for removing particulate matter from industrial emissions. What is done with the solid particles after they are removed from the air?
24. How does the unit ppbv differ from the unit ppb?
25. The airborne concentration of NO_2 over Chicago on a day with a temperature of 25°C and an atmospheric pressure of 1.0 atm is measured to be 46 ppmv. How much $\mu g/m^3$ of NO_2 is present in the atmosphere?
26. A stratospheric measurement of ozone indicates that gas is present at a level of 50 ppbv. Express this concentration:
    a. In ppmv
    b. In $\mu g/m^3$
    c. In $molecules/cm^3$
27. The atmospheric concentration of methane over Iowa in the summer is measured to be 9×10^{13} molecules per cm^3. Express this concentration of methane in ppmv.
28. Calculate the temperature of the Earth if anthropogenic airborne particulates increased the average albedo of the Earth to 0.38. Assume there is no greenhouse effect. Compare this temperature to the temperature calculated in Table 3.3 and describe how the increased tropospheric particulate concentration affects global temperature.
29. Why is the variation between calculated temperature and actual temperature for Earth greater than that for Earth's moon? Both bodies are the same distance from the sun.
30. Describe the runaway greenhouse effect that took place on Venus.
31. Draw the structure of a hydroxyl radical.
32. The following species are all present in the atmosphere. Which are free radicals?

    O_3, NO, N_2O, ClO, N_2O, OH

33. Describe Goldilocks' hypothesis.
34. Describe what is meant by a "positive" atmospheric feedback mechanism. Give an example.

35. Describe what is meant by a “negative” atmospheric feedback mechanism. Is a negative feedback mechanism, by definition, detrimental to the atmosphere?
36. Assume that polar ice caps have an albedo of 80% and that the sea near the poles has an albedo of 20%. Explain how a small increase in global ambient temperature could cause a rapid melting of much of the polar ice caps.
37. Assume that the snowpack in northern Canada has an albedo of 75%. Explain how the deposition of soot from coal-burning power plants would affect global ambient temperature.
38. Outgoing radiation from the Earth has been measured by satellite to be 235 Wm^{-2}. Three major sources contribute to this total. Describe each and the amount that it contributes.
39. Explain how volcanic eruptions can cause year-long cooling in the mean global surface temperature. Why does the effect of an eruption last so long?
40. Because the Earth is a sphere, does more solar energy strike a given surface area in the tropics or in the northern latitudes? Explain.