Global Atmospheric Change

CHAPTER 8

"The observed increase [in temperatures] could be largely due to natural variability; alternatively, this variability and other man-made factors could have offset a still larger man-made greenhouse warming."

—*IPCC 1990*

"The balance of evidence suggests a discernible human influence on global climate."

—*IPCC 1995*

"There is new and stronger evidence that most of the warming observed over the last 50 years is attributable to human activities."

—*IPCC 2001*

"Most of the observed increase in globally averaged temperatures since the mid-twentieth century is very likely due to the observed increase in anthropogenic greenhouse gas concentrations."

—*IPCC 2007*

"Be Worried. Be Very Worried"

—*Time, April 3, 2006*

8.1 Introduction

The preceding four quotes from the Intergovernmental Panel on Climate Change (IPCC) demonstrate a cautious evolution in the degree of certainty expressed by climate scientists about the role played by human activities in causing the past half-century's rapid rise in global average temperature. The *Time* magazine cover story in April 2006, with the provocative title "Be Worried. Be *Very* Worried" well captured the growing awareness among the general public that dealing with global warming is perhaps the most important environmental challenge of the twenty-first century.

While the atmosphere is made up almost entirely of nitrogen and oxygen, other gases and particles existing in very small concentrations determine to a large extent the habitability of our planet. In this chapter, we will focus on several of these other gases, including carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), and ozone (O_3), as well as a category of man-made gases called *halocarbons* that includes chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), carbon tetrachloride (CCl_4), methylchloroform (CH_3CCl_3), and halons. The two problems of greenhouse effect enhancement, leading to global climate change, and stratospheric ozone depletion, which increases our exposure to life-threatening ultraviolet radiation, are linked to changes in these trace gases and are the subject of this chapter.

The problems of global warming and stratospheric ozone depletion are linked by their shared dependence on minute changes in our global atmosphere, and they are, by their very nature, problems whose solutions require international cooperation. The IPCC was established in 1988 by the World Meteorological Organization (WMO) and the United Nations Environment Program (UNEP) to (1) assess available scientific information on climate change, (2) assess the environmental and socioeconomic impacts of climate change, and (3) formulate appropriate response strategies (IPPC, 1995). The IPCC provided the technical documentation that led to the United Nations Framework Convention on Climate Change (UNFCCC), which was signed by 150 nations, including the United States, at the UN Conference on Environment and Development in Rio de Janeiro in 1992. The UNFCCC is a climate treaty that laid the groundwork for nations to stabilize greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous interference with the climate system. It took effect on March 21, 1994, after 50 countries ratified the treaty. The subsequent Kyoto Protocol had its origins in UNFCCC.

Another effort by WMO and UNEP to organize the scientific community around the issue of stratospheric ozone depletion led to the signing of the Montreal Protocol on Substances That Deplete the Ozone Layer in 1987. The Montreal Protocol, and subsequent Amendments framed in London (1990), Copenhagen (1992), and Vienna (1995), has been extraordinarily important both in terms of its success in reducing emissions of ozone depleting substances and its clear demonstration that nations can come together to address global environmental problems.

Much of this chapter is based on the multivolume scientific assessment reports on climate change and ozone depletion that have been written as part of the WMO and UNEP efforts.

8.2 | The Atmosphere of Earth

When the Earth was formed, some 4.6 billion years ago, it probably had an atmosphere made up of helium and compounds of hydrogen such as molecular hydrogen, methane, and ammonia. That early atmosphere is thought to have escaped into space, after which our current atmosphere slowly began to form. Through volcanic activity, gases such as carbon dioxide, water vapor, and various compounds of nitrogen and sulfur were released over time. Molecular oxygen (O_2) eventually began to form both as a result of photodissociation of water vapor and by photosynthesis by plants that were evolving underwater where life was protected from the sun's intense, biologically damaging ultraviolet radiation. As atmospheric oxygen levels gradually increased, more and more ozone (O_3) was formed in the atmosphere. It is thought that the absorption of incoming ultraviolet radiation by that ozone provided the protection necessary for life to begin to emerge onto the land.

Table 8.1 shows the composition of the Earth's atmosphere as it exists now, expressed in volumetric fractions (see Section 1.2 for a reminder of the difference between gaseous concentrations expressed by volume and by mass). The values given are for "clean," dry, air and don't include the relatively small but extremely important amounts of water vapor and particulate matter. While most of the values in the table are essentially unchanging, that is not the case for the principal greenhouse gases carbon dioxide CO_2, methane CH_4, and nitrous oxide N_2O, which are rising.

It is convenient to think of the atmosphere as being divided into various horizontal layers, each characterized by the slope of its temperature profile. Starting at the Earth's surface, these layers are called the *troposphere, stratosphere, mesosphere,* and *thermosphere*. The troposphere and mesosphere are characterized by decreasing temperatures with altitude, while the stratosphere and thermosphere show increasing temperatures. The transition altitudes separating these layers are called the

TABLE 8.1

Composition of Clean Dry Air (Fraction by Volume in Troposphere, 2006)

Constituent	Formula	Percent by Volume	Parts per Million
Nitrogen	N_2	78.08	780,800
Oxygen	O_2	20.95	209,500
Argon	Ar	0.93	9,300
Carbon dioxide	CO_2	0.038	380
Neon	Ne	0.0018	18
Helium	He	0.0005	5.2
Methane	CH_4	0.00017	1.7
Krypton	Kr	0.00011	1.1
Nitrous oxide	N_2O	0.00003	0.3
Hydrogen	H_2	0.00005	0.5
Ozone	O_3	0.000004	0.04

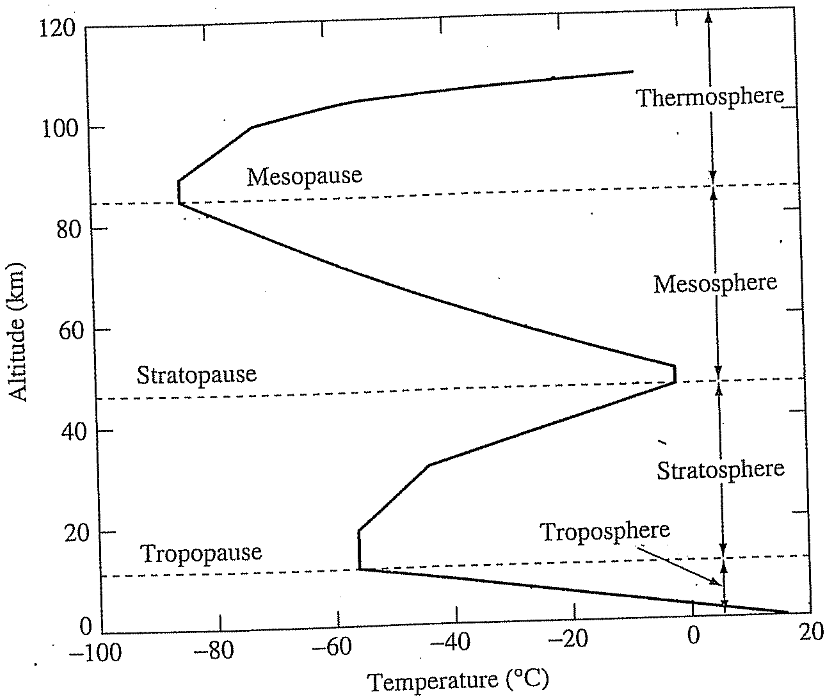


FIGURE 8.1 The U.S. Standard Atmosphere, showing the four major layers.

tropopause, stratopause, and *mesopause*. Obviously, the conditions in the actual atmosphere of Earth vary with time and location, but a useful, idealized temperature profile, known as the *U.S. Standard Atmosphere,* provides a convenient starting point for atmospheric studies (Figure 8.1).

More than 80 percent of the mass of the atmosphere and virtually all of the water vapor, clouds, and precipitation occur in the troposphere. At mid-latitudes, the troposphere extends up to 10 or 12 km (about the altitude of a typical commercial airline flight). At the poles, it may be only about 5 to 6 km, while at the equator it is about 18 km. In the troposphere, temperatures typically decrease at 5 to 7°C per km, which is essentially the wet adiabatic lapse rate corresponding to the rate of change of temperature as water-saturated air rises (see Section 7.10). The troposphere is usually a very turbulent place; that is, strong vertical air movements lead to rapid and complete mixing. This mixing is good for air quality since it rapidly disperses pollutants.

Above the troposphere is a stable layer of very dry air called the stratosphere. Pollutants that find their way into the stratosphere may remain there for many years before they eventually drift back into the troposphere, where they can be more easily diluted and ultimately removed by settling or precipitation. In the stratosphere, short-wavelength ultraviolet energy is absorbed by ozone (O_3) and oxygen (O_2), causing the air to be heated. The resulting temperature inversion is what causes the stratosphere to be so stable. The troposphere and stratosphere combined account for about 99.9 percent of the mass of the atmosphere. Together they extend only about 50 km above the surface of the Earth, a distance equal to less than 1 percent of the Earth's radius.

Beyond the stratosphere lies the mesosphere, another layer where air mixes fairly readily, and above that the thermosphere. The heating of the thermosphere is due to the absorption of solar energy by atomic oxygen. Within the thermosphere is a relatively dense band of charged particles, called the *ionosphere*. (Before satellites, the ionosphere was especially important to worldwide communications because of its ability to reflect radio waves back to Earth.)

8.3 | Global Temperature

The common definition of climate suggests it is the prevailing or average weather of a place as determined by temperature and other meteorological conditions over a period of years. Average temperature, then, is but one measure of climate; many others, including precipitation, winds, glaciation, and frequency of extreme events such as typhoons and hurricanes, are also important parameters. Long-term variations in average temperature, however, are the single most important attribute of climate change.

Climatologists have used a number of clues to piece together past global temperatures, including evidence gathered from historical documents, tree rings, changes in ice volume and sea level, fossil pollen analysis, and geologic observations related to glacial movements. One of the most fruitful approaches involves the analysis of concentrations of various stable isotopes of hydrogen and oxygen as found in ice cores and sea-floor sediments.

Isotopes and Temperature

Recall that atoms of a particular element all have the same number of protons but may have varying numbers of neutrons. The sum of the protons and neutrons, called the mass number, identifies which isotope of that element we are talking about. Some isotopes are radioactive, such as radon-222 (^{222}Rn), and their decay rate can be used to date various geological events. Other isotopes are stable, which means they can be used to track the movement of substances in the environment over geologic time.

Consider water, H_2O. Hydrogen, with one proton, has two stable isotopes, ^{1}H and ^{2}H (also called deuterium, D). Oxygen, with eight protons, has three stable isotopes, ^{16}O, ^{17}O, and ^{18}O. Thus we can imagine many different combinations of atoms making up molecules of water, including the two most important "heavier water" molecules $^1H^2H^{16}O$ and $^1H^1H^{18}O$.

When water evaporates from the oceans, it contains a mix of isotopes of hydrogen and oxygen. Heavier water containing ^{18}O or deuterium (^{2}H) evaporates less readily and condenses more quickly than light water, which means those heavy isotopes get left behind as water vapor from the ocean travels toward the poles. That means snow falling in the Arctic and Antarctic will have lower concentrations of deuterium (D or ^{2}H) and ^{18}O than seawater. This separation of light isotopes from heavier ones is temperature dependent. As it gets colder, less and less of the heavier deuterium and ^{18}O make it to the poles. The $^2H/^1H$ and $^{18}O/^{16}O$ ratios in precipitation that forms glaciers and ice sheets therefore decrease when it gets colder and increase when it gets warmer, thus providing a very important historic measure of global temperature.

The relative abundance of ^{2}H and ^{18}O in seawater is so important that standardized concentrations have been established called the *Vienna Standard Mean Ocean Water* (VSMOW) ratios. The VSMOW ratio of $^2H/^1H$ is 0.00015575 (1 deuterium per 6,422 atoms of conventional hydrogen) and the standardized $^{18}O/^{16}O$ ratio is 0.0020052 (1 part ^{18}O to 499 parts ^{16}O). The shifts in isotope ratios are compared to the standard using a parts-per-thousand $\delta X(^0/_{00})$ notation. For example, the $\delta^{18}O(^0/_{00})$ concentration is expressed as

$$\delta^{18}O(^0/_{00}) = \left[\frac{(^{18}O/^{16}O)\text{ sample}}{(^{18}O/^{16}O)\text{ standard}} - 1\right] \times 10^3 \qquad (8.1)$$

Negative values of $\delta^{18}O$ or δD represent isotope ratios below the standard, while positive numbers correspond to higher ratios. For example, $\delta^{18}O(^0/_{00}) = -10$ means the concentration of ^{18}O is lower than the standard by 10 parts per thousand ("10 per mil"), or 1 percent. Changes in δD and $\delta^{18}O$ in precipitation seem to be linearly related to temperature. For $\delta^{18}O$, the change is about 0.7 per °C, while for deuterium, it is about 6 per mil per °C (McGuffie and Henderson-Sellers, 2005).

EXAMPLE 8.1 Deuterium in an Ice Core

Suppose a deuterium measurement taken near the surface of an ice core yields an isotope ratio of $^2H/^1H = 8.753 \times 10^{-5}$.

a. Find the corresponding $\delta D(^0/_{00})$ using the VSMOW standard for deuterium.

b. Suppose an ice sample from a deeper, and older, depth in the core shows $\delta D(^0/_{00}) = -445$. Using the estimate of 5.6 $\delta D(^0/_{00})$ per °C, how much colder was it at the time that ice layer was created?

Solution

a. Using the VSMOW standard of 0.00015575 for deuterium in (8.1) gives

$$\delta D(^0/_{00}) = \left[\frac{(^2H/^1H)\text{ sample}}{(^2H/^1H)\text{ standard}} - 1\right] \times 10^3$$

$$\delta D(^0/_{00}) = \left[\frac{8.753 \times 10^{-5}}{0.00015575} - 1\right] \times 10^3 = -438$$

b. The 7 per mil drop in δD from -438 to -445 translates to about $7/5.6 \times 1°C = 1.25°C$ colder than the present.

As the world's ice volume increases, it selectively removes ^{16}O from the hydrologic cycle and concentrates the remaining ^{18}O in the decreasing volume of the oceans. Hence, marine organisms that build their shells out of calcium carbonate in seawater will have a higher ratio of ^{18}O to ^{16}O in their shells when it is cold and more of the world's water is locked up in glaciers and ice. By dating marine sediments extracted from deep sea cores, and observing the ratio of the two oxygen isotopes in their carbonates, a historic record of the volume of ice storage on Earth can be created. Figure 8.2 shows a reconstruction of climate based on $\delta^{18}O$ in benthic

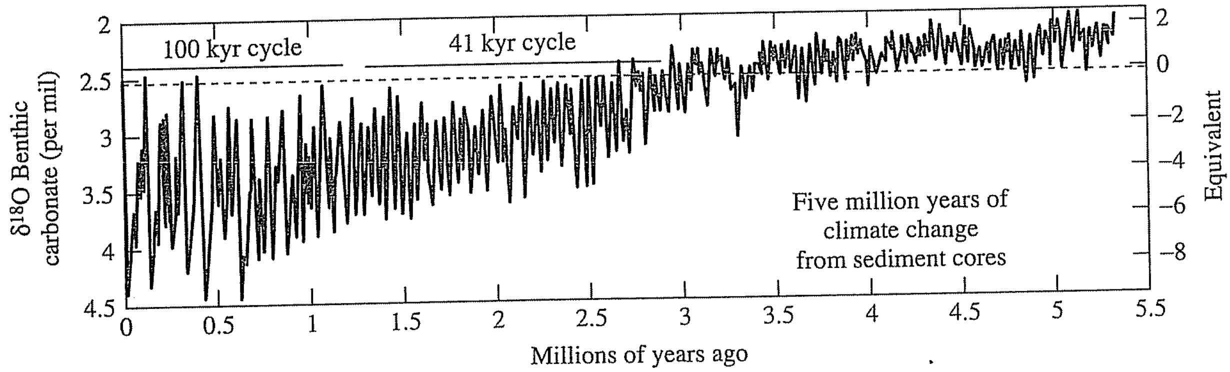


FIGURE 8.2 Five million years of climate change from deep sea sediment cores. (*Source:* Lisiecki and Raymo, 2005.)

carbonates over the past 5 million years. The temperature scale calibration is based on a comparison with ice core data. Notice the isotope record in ocean sediments moves in the opposite direction to the isotope record in glacial ice. That is, for example, while warmer temperatures cause *decreases* in ^{18}O in oceans and sediments, warmer temperatures cause *increases* in ^{18}O in that year's layer of glacial ice.

The Antarctic and Greenland Ice Cores

Analysis of ice cores taken in Greenland and Antarctica have provided a remarkable picture of the climate and composition of the Earth's atmosphere over hundreds of thousands of years of history. Isotopic analysis of glacial ice provides the temperature record, while analysis of the composition of the air bubbles captured in the ice as it was formed gives a corresponding record of the concentrations of various atmospheric gases as well as wind-blown dust and ash.

The Vostok station in Antarctica is the site from which a number of significant cores have been drilled, the deepest of which extends 3,623-meters into the ice. The Vostok core provides a climate record that extends back some 420,000 years and includes four past glacial cycles. The record-holding ice core in terms of the length of its historical record, as opposed to its depth, is the 3,270-m *European Project for Ice Coring in Antarctica* (EPICA) core drilled into an ice summit called Dome C located several hundred miles away from Vostok. The EPICA core goes back in time by more than 720,000 years and covers 8 previous glacial cycles.

Figure 8.3 shows a very strong correlation between atmospheric carbon dioxide and methane concentrations taken from air bubbles in the Antarctic cores compared

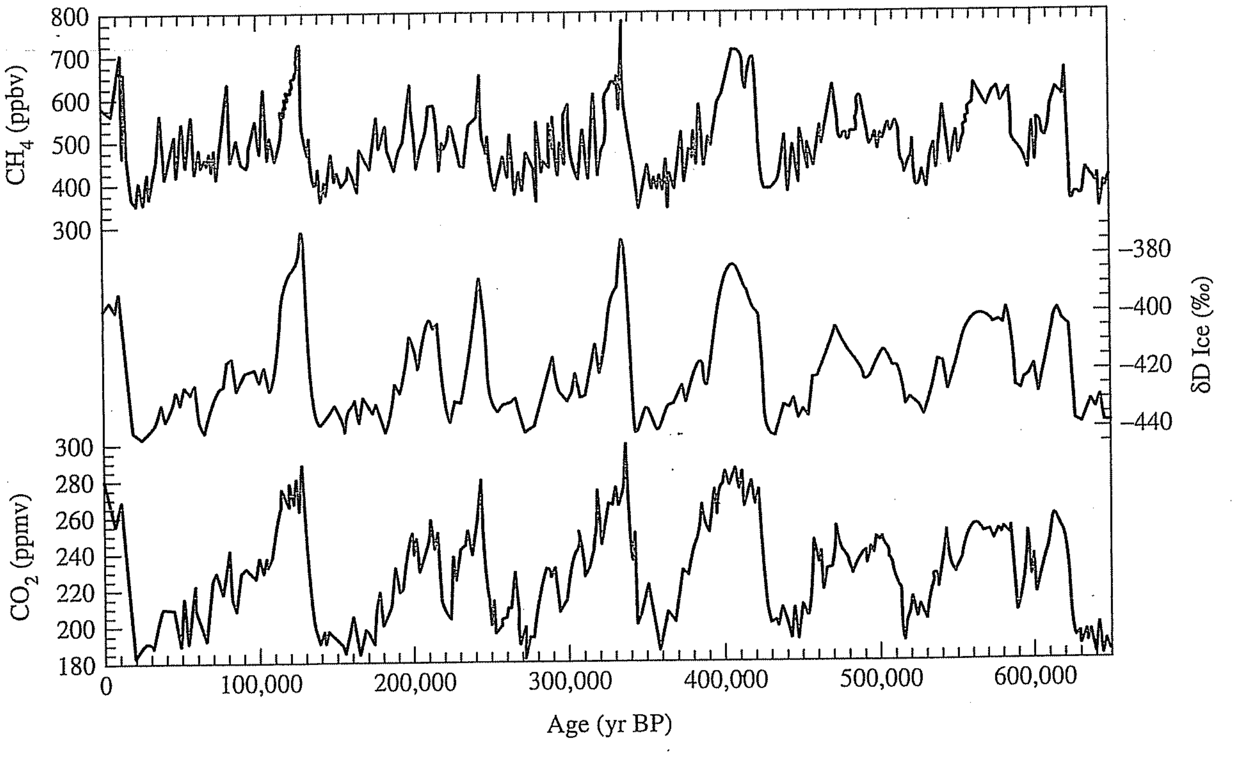


FIGURE 8.3 Antarctic carbon dioxide and methane concentrations correlate well with the climate proxy δD. The current CO_2 concentration (390 ppm in 2007) is far higher than it has been over the past 650,000 years.
(*Source:* Data from Siegenthaler et al., 2005, and Spahni et al., 2005.)

with the δD temperature surrogate. During glacial periods, the greenhouse gases CO_2 and CH_4 are low; during the warmer interglacial periods, they are high. Perhaps the most startling feature in the figure is how much higher the current CO_2 concentration is (390 ppm in 2007) than it has been in over 650,000 years. What the data do not make clear is whether it is changing concentrations of greenhouse gases that cause temperature changes or vice versa. Switches from glacial to interglacial periods may well be triggered by other phenomena, such as natural variations in the Earth's orbit, coupled with positive feedbacks between warming and increased greenhouse gas emissions.

In the opposite hemisphere, a number of cores have been drilled into the the 3-km-thick glacial cap in Greenland. The Greenland data show cycles of gradual cooling, followed by rapid warming, during the last glacial period. These cycles, which have a period of between 500 and 2,000 years, are called *Dansgaard-Oeschger* events after their discoverers. They seem to be linked to another phenomenon, called *Heinrich* events, in which it is thought that enormous flotillas of icebergs periodically drifted across the North Atlantic; their melting deposited unusual layers of sediments on the seafloor that were used to identify and date these events. One of the most startling observations from Greenland ice cores is the speed with which large, *regional* temperature jumps can occur. During the last glacial period, 10,000 to 110,000 years ago, the temperature of Greenland showed jumps of 5 to 7°C within just a decade or two. Global temperatures, on the other hand, do not seem to have changed nearly that rapidly in the past. Over the past 10,000 years (the present interglacial period), it seems unlikely that global mean temperatures have ever changed faster than 1°C per century (IPCC, 1995, 3.6.3).

More Recent Global Temperature

While ice cores and seafloor sediments provide indirect methods of estimating temperatures over many hundreds of thousands of years of Earth history, ever since the mid-nineteenth century, the temperature record has been based on actual measurements. Most of the data are from actual thermometer readings taken at weather stations across the globe, including ships at sea, augmented more recently with satellite data. Adjustments have been made to discount the impact of warming caused by the growth of cities around meteorological stations. Dark surfaces in urban areas absorbing heat from the sun, along with waste heat from energy consumption, cause elevated temperatures referred to as the urban heat island effect. To offset the bias caused by urban warming, nighttime satellite images are used to identify stations outside of brightly lit urban areas. Greater reliance is then placed on data sets taken from those unlit areas and other rural areas across the globe. After these adjustments, the remaining urban influence on the global record is estimated to be less than 0.1°C (Hansen et al., 2001).

Figure 8.4 shows the Goddard Institute for Space Sciences (GISS) estimate of the mean annual global temperature expressed as a deviation, or anomaly, from a fixed reference temperature. In this graph, the reference is the 1951–1980 average global temperature, estimated to be 14°C. Eleven of the years between 1995 and 2006 rank among the 12 warmest years in the instrumental record of global surface temperature (IPCC, 2007). The current average temperature is probably the highest it has been since the beginning of the current interglacial period, which began some

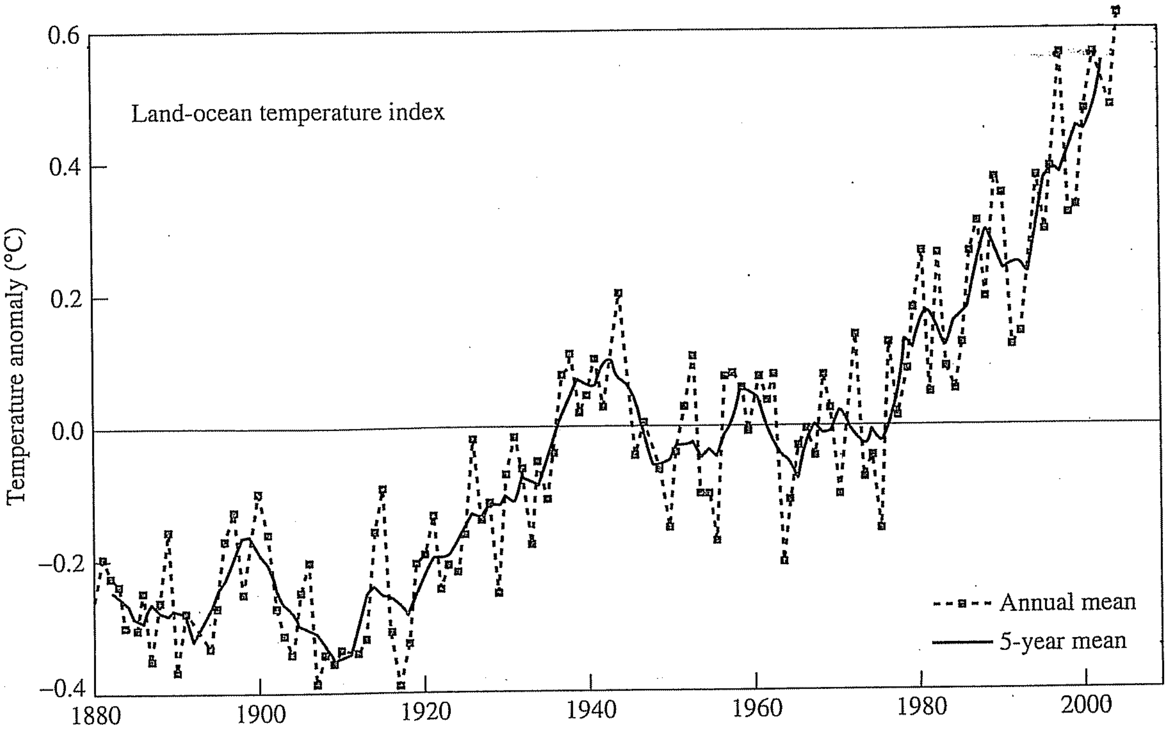


FIGURE 8.4 Global mean annual temperature anomaly referenced to the 14°C estimated average for 1951–1980. The Earth has warmed about 0.8°C since 1990.
(*Source:* NASA Goddard Institute for Space Studies Web site, 2006.)

12,000 years ago. While the overall temperature trend has been steeply upward, the period between about 1940 and 1980 shows an actual decline in temperature. That cooling is attributed to particulates, especially sulfates, caused by rapidly growing fossil fuel combustion during a period of time when emission controls were not yet in widespread use. Those aerosols reflecting sunlight back into space are thought to have masked the ongoing global warming caused by greenhouse gas emissions. When power plant emissions began to be controlled, global warming reemerged and the post-1980 temperature increases have averaged about 0.28°C per decade. The more recent 1992–1994 cool spell is attributed to the increased reflection of sunlight off the atmosphere caused by the eruption of Mount Pinatubo in the Philippines, in June 1991.

Attempts have been made to combine the measured temperature anomaly with other temperature proxies such as historical documents, tree rings, corals, ice cores, and lake sediments to reconstruct patterns of the past thousand or so years of temperature change. These attempts focus on the Northern Hemisphere mean temperature since there isn't much data available for the rest of the globe. One such study is shown in Figure 8.5. Several periods of time are sometimes noted, including a "Medieval Warm Period" from roughly 900 to 1300, during which some regions of the globe experienced unusual warmth, and the "Little Ice Age" from about 1500 to 1900, when the opposite occurred.

The overall shape of the 1,000-year profile shown in Figure 8.5 has picked up the nickname of the temperature "hockey stick." The hockey stick has been a source of some controversy, with some arguing that the current temperature and rate of change of temperature might not be without precedent in the past 1,000 years, and therefore the warming we are now observing may be a natural phenomenon. The

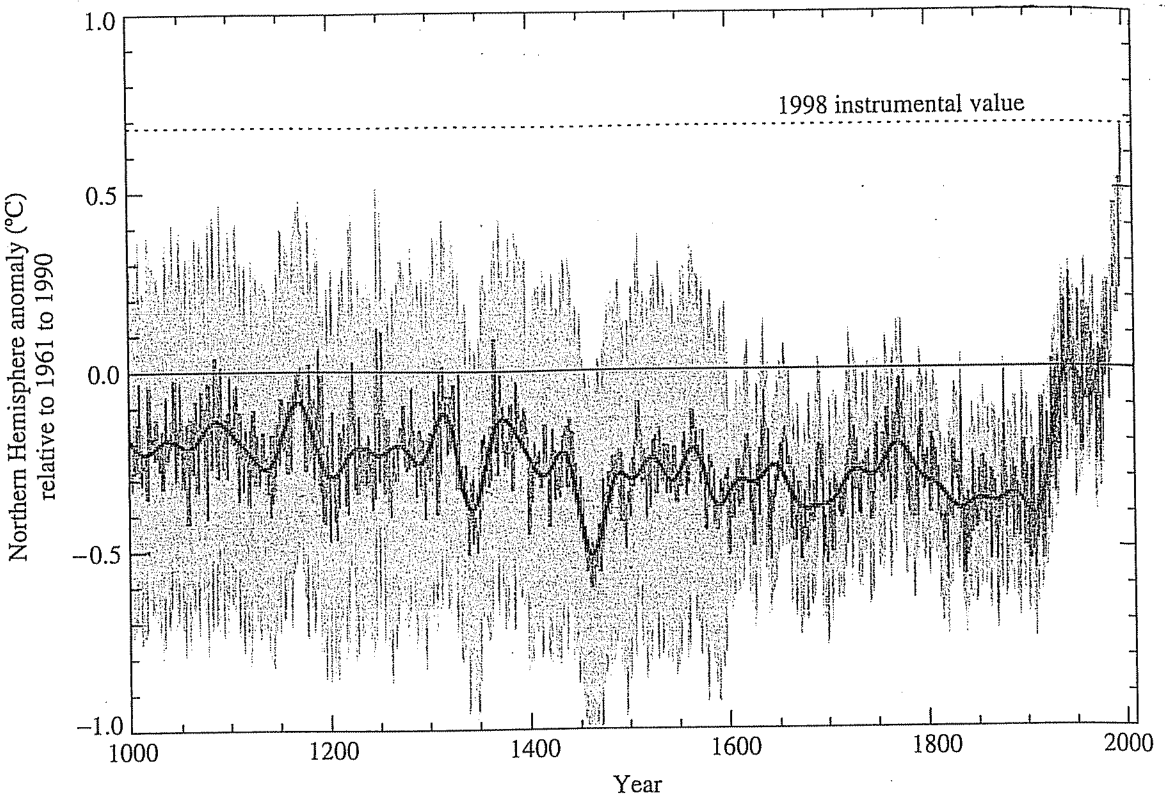


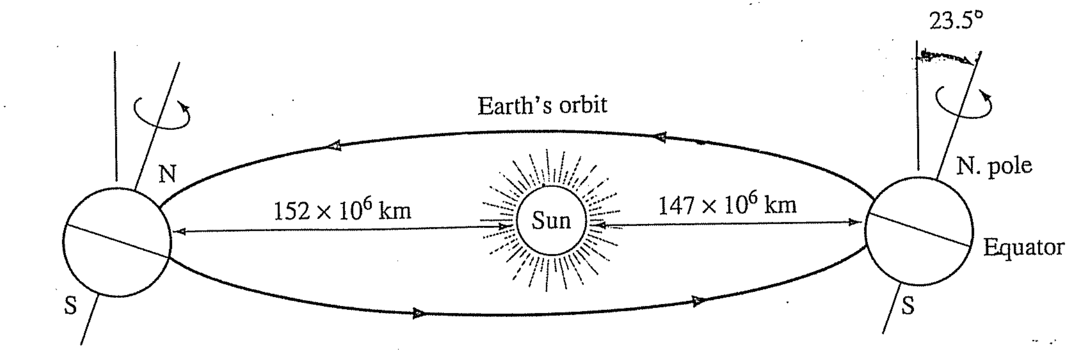
FIGURE 8.5 The Northern Hemisphere temperature anomaly, sometimes referred to as the "hockey stick."
(*Source:* IPCC, 2001.)

data set from which the graph has been drawn has enough uncertainty in it to keep this controversy alive, but the National Research Council took up the issue in 2006 and concluded that there is a high level of confidence that the global mean surface temperature during the past few decades is higher than at any time over the preceding four centuries, but beyond that there is less confidence. Whether or not the warming is unprecedented, the current rapid increase in anthropogenic greenhouse gas emissions, the well understood physics and chemistry of the atmosphere, and direct measurements of greenhouse gas impacts, all tell us the climate is changing, and we have a lot to do with causing that change.

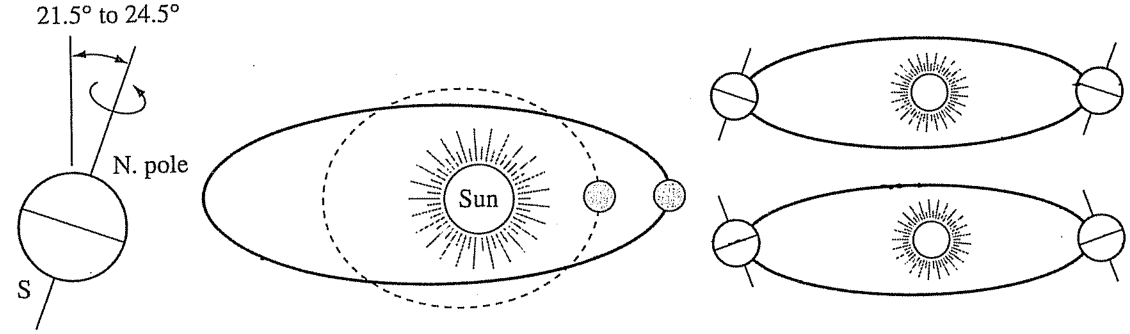
Orbital Variations and Sunspots

The history and future of the Earth's orbit around the sun can be calculated precisely. The connection between orbital variations and climate were first proposed in the 1930s by an astronomer, Milutin Milankovitch, and the orbital cycles are now referred to as *Milankovitch* oscillations. Changes in the orbit affect the amount of sunlight striking the Earth as well as the distribution of sunlight both geographically and seasonally. Those variations are thought to be quite influential in the timing of the coming and going of ice ages and interglacial periods.

There are three primary orbital cycles. The shape of the Earth's orbit oscillates from elliptical to more nearly circular with a period of 100,000 years (*eccentricity*). The Earth's tilt angle with respect to its orbit fluctuates from 21.5° to 24.5° with a period of 41,000 years (*obliquity*). Finally, there is a 23,000-year period associated



(*a*) The current orbit



(*b*) Obliquity 41,000 years (*c*) Eccentricity 100,000 years (*d*) Precession 23,000 years

FIGURE 8.6 Orbital variations affect the timing of ice ages: (*a*) the current orbit; (*b*) the tilt angle variation, with period 41,000 years; (*c*) eccentricity variation, with period 100,000 years; (*d*) precession, with period 23,000 years.

with the precession, or wobble, of the Earth's spin axis (*precession*). This precession determines where in the Earth's orbit a given hemisphere's summer occurs. Figure 8.6 illustrates these variations.

Careful analysis of the historical record of global temperatures does show a primary cycle between glacial episodes of about 100,000 years, mixed with secondary oscillations with periods of 23,000 years and 41,000 years that match the Milankovitch theory reasonably well. Although these orbital variations only change the total annual dosage of sunlight by about 0.1 percent, the impacts on seasons and the resulting patterns of oceanic and atmospheric heat distribution around the globe are thought to be significant enough to trigger major climate changes.

Another factor that affects the amount of solar radiation reaching the top of the Earth's atmosphere is variations in the intensity of radiation emitted from the sun itself. For example, the sun spins on its axis making one complete rotation every 27 days. There are darker and brighter areas on the solar surface that cause variations of up to 0.2 percent in the amount of solar radiation reaching the Earth over that 27-day period. Those variations occur so rapidly, however, that they are not thought to be particularly important in determining average global climate.

Of greater importance is an 11-year cycle of sunspots that were first described by an amateur astronomer, Heinrich Schwabe, in 1843 (Figure 8.7). During peak periods of magnetic activity on the sun, the surface has large numbers of cooler, darker regions, called *sunspots,* that in essence block solar radiation, accompanied by other regions, called *faculae,* that are brighter than the surrounding surface. The

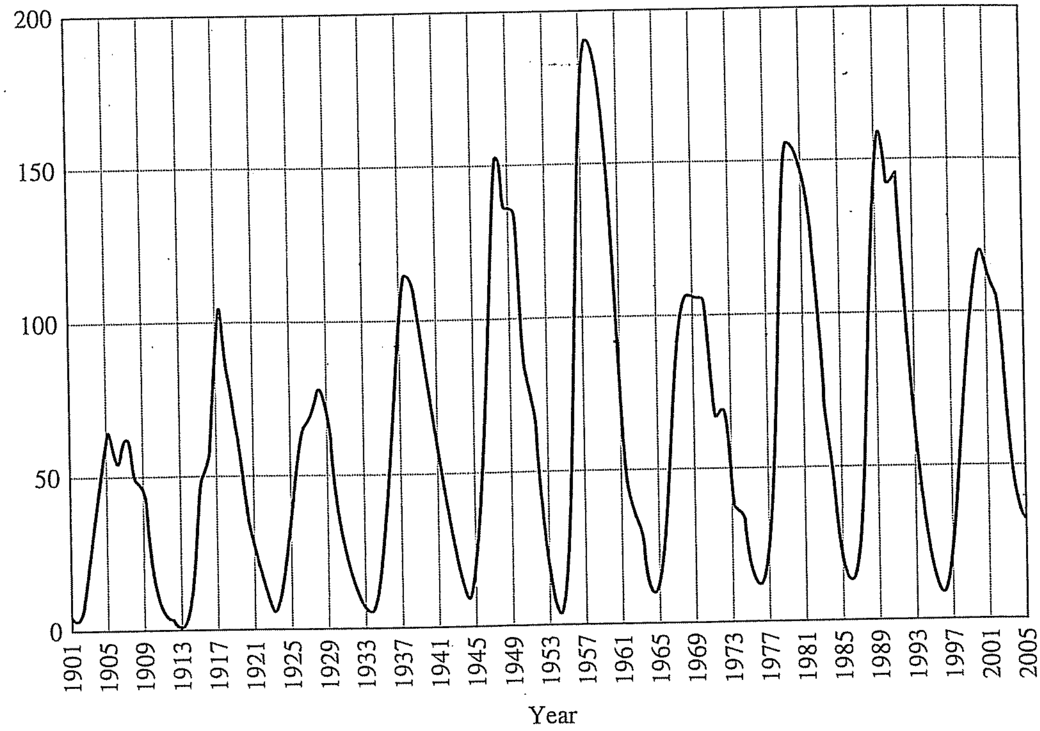


FIGURE 8.7 Mean annual sunspot number showing the 11-year Schwabe cycle.

net effect of sunspots that dim the sun, and faculae that brighten it, is an increase in solar intensity during periods of increased numbers of sunspots. The variation in solar radiation reaching the Earth as a result of these cycles is roughly 0.1 percent, which is thought to be enough to change the Earth's temperature by roughly 0.2°C. Sunspot activity helps provide an explanation for the continuous up and down jiggling of the Earth's temperature that complicates the problem of deciding whether a true global warming "signal" is emerging from the "noise."

A Simple Global Temperature Model

Measurements of historical global temperatures show that our planet has maintained its average temperature within a limited range, but within those bounds, it seems to be continuously changing. If we hope to predict future impacts of anthropogenic changes in our environment, we need to develop mathematical models that explain the past. Mathematically modeling of global climate and predicting the impacts of changes in key environmental parameters is an extremely important but difficult task. Such models range from very simple back-of-the-envelope calculations, to complex, three-dimensional *General Circulation Models* (GCMs, also known as *Global Climate Models*) that attempt to predict climate on a regional, seasonal, and annual basis. The most sophisticated of these models can take weeks to run on a supercomputer, yet they must still be considered primitive. In comparison, our treatment here is just the briefest of introductions. For a much more thorough introduction, see McGuffie and Henderson-Sellers (2005).

The simplest starting point for modeling climate begins with models that focus on factors influencing the single parameter, *temperature*. Obviously, other factors

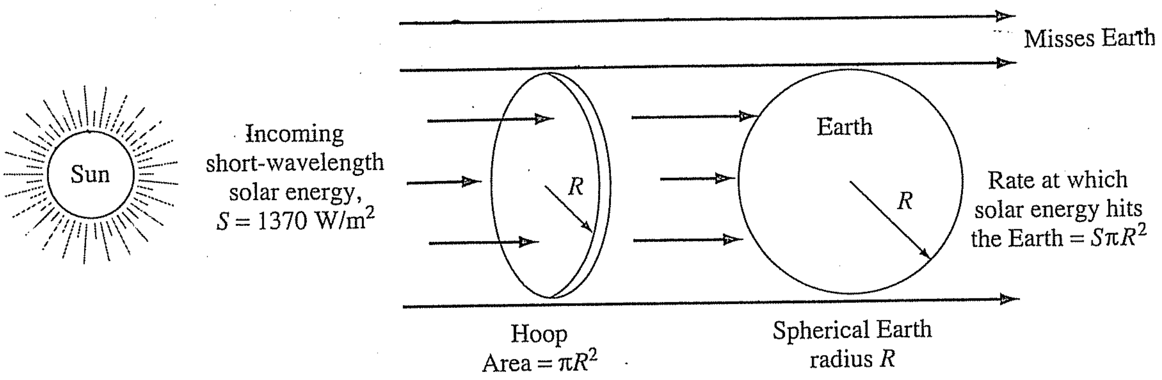


FIGURE 8.8 Solar energy passing through a "hoop" with the same radius as that of the Earth, hits the Earth. Radiation that misses the hoop also misses the Earth.

such as precipitation patterns, winds and storms, ocean currents, soil moisture, sea ice, glacial cover, and so forth are exceedingly important, but they are more difficult to approach with simple models. Even beginning with just temperature as the single quantity of interest, we could try to find out how temperature varies in all four dimensions (latitude, longitude, altitude, time), which is the domain of very complex GCMs. At the other end of the complexity scale is a simple "zero-dimensional" model in which a single average global temperature is obtained that is not a function of location or time. The following is such a model.

The basic zero-dimensional energy balance model equates solar energy absorbed by the Earth with the energy that the Earth radiates back to space. Radiation from the sun arrives just outside the Earth's atmosphere with an average annual intensity, called the *solar constant, S*, currently equal to about 1,370 watts/m^2. A simple way to calculate the total rate at which energy hits the Earth is to note that all of the flux passing through a "hoop" having radius equal to that of the Earth, and placed normal to the incoming radiation, strikes the Earth's surface. From Figure 8.8, we can write

$$\text{Rate at which solar energy strikes the Earth} = S\pi R^2 \text{ (watts)} \tag{8.2}$$

where

S = the solar constant, taken to be 1,370 W/m^2
R = the radius of the Earth (m)

Some of the incoming solar energy that hits the Earth is reflected back into space, as shown in Figure 8.9. Such reflected energy is not absorbed by the Earth or its atmosphere and does not contribute to their heating. The fraction of incoming solar radiation that is reflected is called the *albedo,* and for the Earth, the global annual mean value is now estimated to be about 31 percent. What isn't reflected is absorbed, which leads to the following expressions.

$$\text{Energy reflected by Earth} = S\pi R^2\alpha \tag{8.3}$$

$$\text{Energy absorbed by Earth} = S\pi R^2(1 - \alpha) \tag{8.4}$$

where α = the Earth's albedo, taken to be 0.31.

On the other side of the energy balance equation is the rate at which Earth sends energy back to space. Since there can be no heat transfer from the Earth to

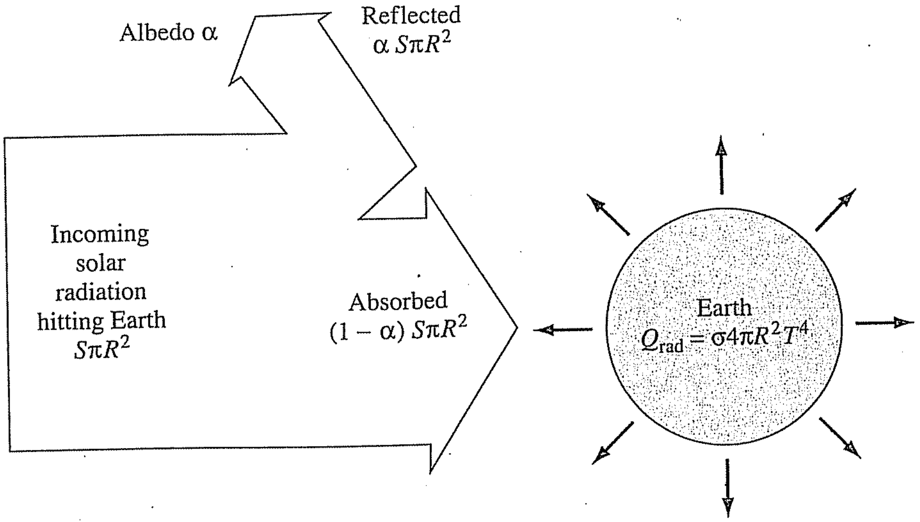


FIGURE 8.9 Simple global temperature model.

space by conduction or convection, the only way for the Earth to get rid of energy is by radiation. Recall from Section 1.4 that every object radiates energy at a rate that is proportional to its surface area times its absolute temperature raised to the fourth power (Eq. 1.35). For this model, we will assume the Earth is a blackbody; that is, it radiates as much as any object with the same temperature and area possibly can (emissivity = 1). We also assume it is isothermal; that is, the temperature is the same everywhere on the planet. Since the area of a spherical object is $4\pi R^2$, we can write

$$\text{Energy radiated back to space by earth} = \sigma 4\pi R^2 T_e^4 \tag{8.5}$$

where

σ = Stefan-Boltzmann constant = 5.67×10^{-8} W/m²-K⁴

and

T_e = earth's "effective" blackbody temperature (kelvins)

If we go on to assume steady-state conditions, that is, the Earth's temperature is not changing with time, we can equate the rate at which energy from the sun is absorbed (8.4), with the rate at which energy is radiated from Earth back to space (8.5):

$$S\pi R^2(1 - \alpha) = \sigma 4\pi R^2 T_e^4 \tag{8.6}$$

Solving for T_e,

$$T_e = \left[\frac{S(1 - \alpha)}{4\sigma}\right]^{1/4} \tag{8.7}$$

Substituting appropriate values into (8.7) yields

$$T_e = \left[\frac{1{,}370\ \text{W/m}^2(1 - 0.31)}{4 \times 5.67 \times 10^{-8}\ \text{W/m}^2\text{K}^4}\right]^{1/4} = 254\ \text{K} = -19^\circ\text{C} \tag{8.8}$$

Notice the conversion from kelvins to Celsius (°C = K − 273). The actual value of the Earth's average surface temperature is currently about 288 K (15°C). While we are off by only 12 percent, which might seem a modest error, in terms of life on Earth, the 254 K (−19°C) estimate for T_e is terribly wrong. We need to find an explanation for why the Earth is (fortunately) not that cold. The key factor that makes our model differ so much from reality is that it does not account for interactions between the atmosphere and the radiation that is emitted from the Earth's surface. That is, it does not include the greenhouse effect.

8.4 | The Greenhouse Effect

The surface of the Earth is 34°C higher than what is predicted by (8.8). To understand the reason for the higher temperature, it is helpful to begin by recalling the discussion in Chapter 1 concerning the relationship between the spectrum of wavelengths radiated by an object and its temperature. Wien's displacement rule (Eq. 1.43), repeated here, gives the wavelength at which a blackbody spectrum peaks as a function of its absolute temperature:

$$\lambda_{\max}(\mu\text{m}) = \frac{2{,}898}{T(\text{K})} \tag{8.9}$$

The sun can be represented as a blackbody with temperature 5,800 K, so its spectrum peaks at 0.5 μm. The Earth, at 288 K, has its peak at 10.1 μm. Figure 8.10 shows these two spectra. Recall from Chapter 1 that the area under these curves, between any two wavelengths, is the total radiant energy in that range of frequencies. For example, the area under the curve of incoming solar radiation just outside the atmosphere is the total solar radiant flux; that is, it is the solar constant, 1,370 W/m^2. Notice nearly all the incoming solar energy as it arrives just outside the Earth's atmosphere has wavelengths less than 3 μm, while the outgoing energy radiated by the Earth has essentially all of its energy in wavelengths greater than 3 μm. With so little overlap, it is convenient to speak of solar energy as being *short-wavelength* radiation, while energy radiated from the Earth's surface is *long-wavelength,* or *thermal,* radiation. The infrared (IR) portion of the spectrum begins at about 0.7 μm and extends out to 100 μm, so some of the incoming solar radiation and all of the outgoing thermal radiation is IR.

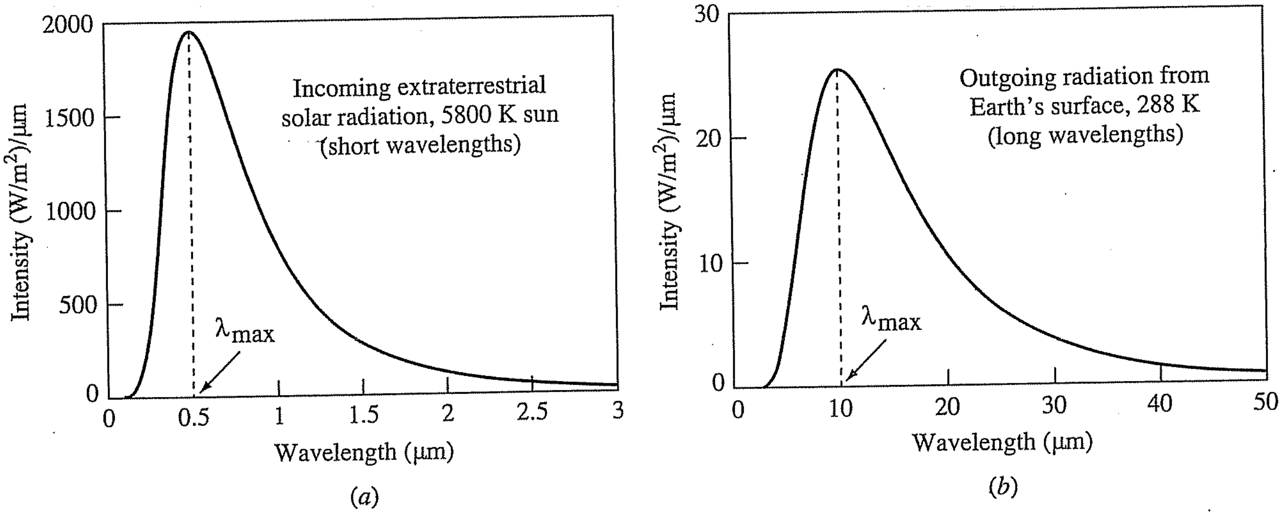
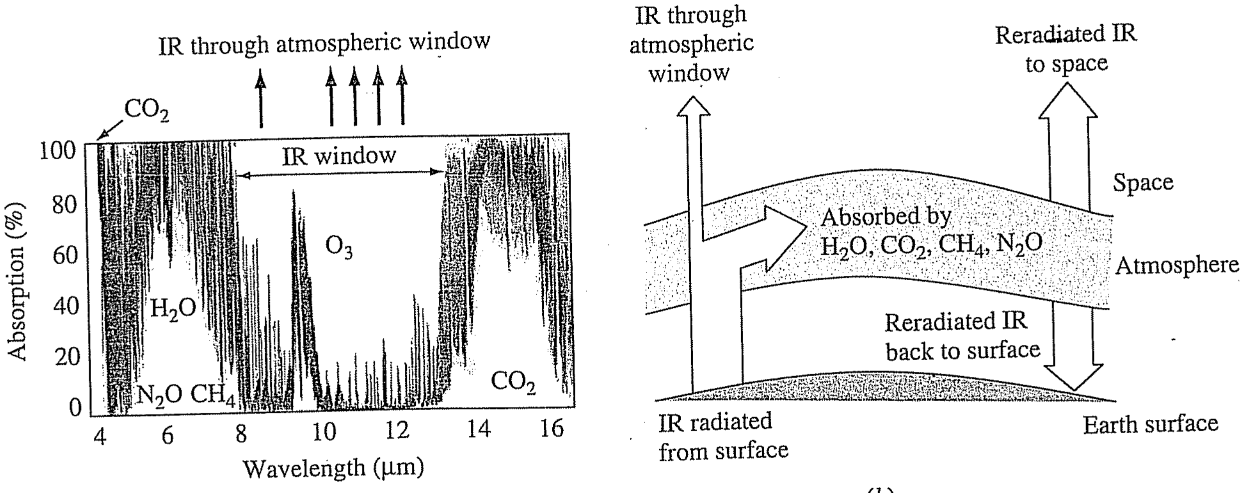


FIGURE 8.10 Blackbody radiation at 5,800 K and 288 K. (*a*) Incoming solar radiation just outside of the Earth's atmosphere. (*b*) Radiation from the Earth's surface at 288 K.



(*a*) (*b*)

FIGURE 8.11 Some IR radiated from the Earth's surface passes through a relatively clear IR window between about 7 and 13 μm (*a*). Most, however, is absorbed by greenhouse gases in the atmosphere (*b*).

As radiant energy attempts to pass through the atmosphere, it is affected by various gases and aerosols in the air. Those atmospheric constituents can let the radiant energy pass through unaffected, they can scatter the energy by reflection, or they can stop it by absorption. The key phenomenon of interest here is the ability of gases to absorb radiant energy. As the atoms in gaseous molecules vibrate toward and away from each other (vibrational energy) or rotate around each other (rotational energy), they absorb and radiate energy in specific wavelengths. When the frequency of these molecular oscillations is close to the frequency of the passing radiant energy, the molecule can absorb that energy. This absorption occurs over a rather limited range of frequencies, not just at the oscillatory frequency of the molecule, and results in an absorptivity spectrum, which is a plot of the fraction of incoming radiant energy that is absorbed as a function of wavelength.

Figure 8.11*a* shows the absorption spectra for the key greenhouse gases of concern in this chapter, along with the their effect on outgoing infrared (IR) radiation emitted by the Earth's surface. Most of the long-wavelength energy radiated by the Earth is absorbed by a combination of radiatively active gases, most important of which are water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and ozone (O_3). Water vapor, which is by far the most important greenhouse gas, strongly absorbs thermal radiation with wavelengths less than 8 μm and greater than 18 μm. Carbon dioxide shows a strong absorption band centered at 15 μm, as well as bands centered at 2.7 μm and 4.3 μm. Between 7 μm and 13 μm there is a relatively clear sky for outgoing thermal radiation, referred to as the *atmospheric radiative window*. Radiation in those wavelengths easily passes through the atmosphere, except for a small, but important, absorption band between 9.5 μm and 10.6 μm associated with O_3.

Radiatively active gases that absorb wavelengths longer than 4 μm are called greenhouse gases. This absorption heats the atmosphere, which, in turn, radiates energy back to the Earth as well as out to space, as shown in Figure 8.11*b*. These greenhouse gases act as a thermal blanket around the globe, raising the Earth's surface temperature beyond the equivalent temperature calculated earlier. The importance of

TABLE 8.2

Application of the Simple Model (8.7) to Compute Effective Temperatures, Compared with Actual Surface Temperatures

Planet	Distance to Sun (10^6 km)	Atmosph. Pressure (atm)	Solar Constant S (W/m^2)	Albedo α (%)	Effective Temp. T_e (K)	Surface Temp. T_s (K)	Greenhouse Warming (°C)
Venus	108	90	2,620	76	229	750	521
Earth	150	1	1,370	31	254	288	34
Mars	228	0.006	589	25	210	218	8

Note: Mars, with little atmosphere, shows almost no greenhouse effect while on Venus it is quite pronounced.
Source: Hoffert, 1992.

water vapor as a greenhouse gas is quite evident on clear nights, when the Earth cools much more rapidly than it does on cloudy nights. It is also interesting to note that the term *greenhouse effect* is based on the concept of a conventional greenhouse with glass acting much like the aforementioned gases. Glass, which easily transmits short-wavelength solar energy into the greenhouse, absorbs almost all of the longer wavelengths radiated by the greenhouse interior. This radiation trapping is partly responsible for the elevated temperatures inside the greenhouse, although much of the effect is simply due to the reduction in convective cooling of the interior space caused by the enclosure. The elevated interior temperature of your car after it has been parked in the sun is another common example of the greenhouse effect.

If the Earth did not already have a greenhouse effect, its temperature would be 254 K as predicted by (8.8). That is, the planet would have an average temperature of −19°C, or about −2°F. In fact, one way to quantify the magnitude of the greenhouse effect is to compare the effective temperature, T_e, given in (8.7), with the actual surface temperature, T_s

$$\text{Magnitude of greenhouse effect} = T_s - T_e \tag{8.10}$$

Thus, since the actual temperature of the Earth is 288 K, and its effective temperature is 254 K, we can say that the greenhouse effect adds 34°C of warming to the surface of the Earth.

In Table 8.2, this notion is applied to Venus and Mars. Even though the atmosphere of Mars is almost entirely carbon dioxide, there is so little atmosphere that the greenhouse effect is barely apparent. The atmospheric pressure on Venus, on the other hand, is nearly 100 times that of Earth, and its atmosphere is 97 percent CO_2. The greenhouse effect on Venus is correspondingly very pronounced. It is interesting to note that without the greenhouse effect, the greater albedo of Venus would make it cooler than the Earth in spite of its closer proximity to the Sun.

8.5 Global Energy Balance

As suggested in Figure 8.11, a simple model of the greenhouse effect treats the Earth's surface, the atmosphere, and outer space as three separate regions. Figure 8.12 expands the diagram to include incoming solar energy as well as outgoing IR and

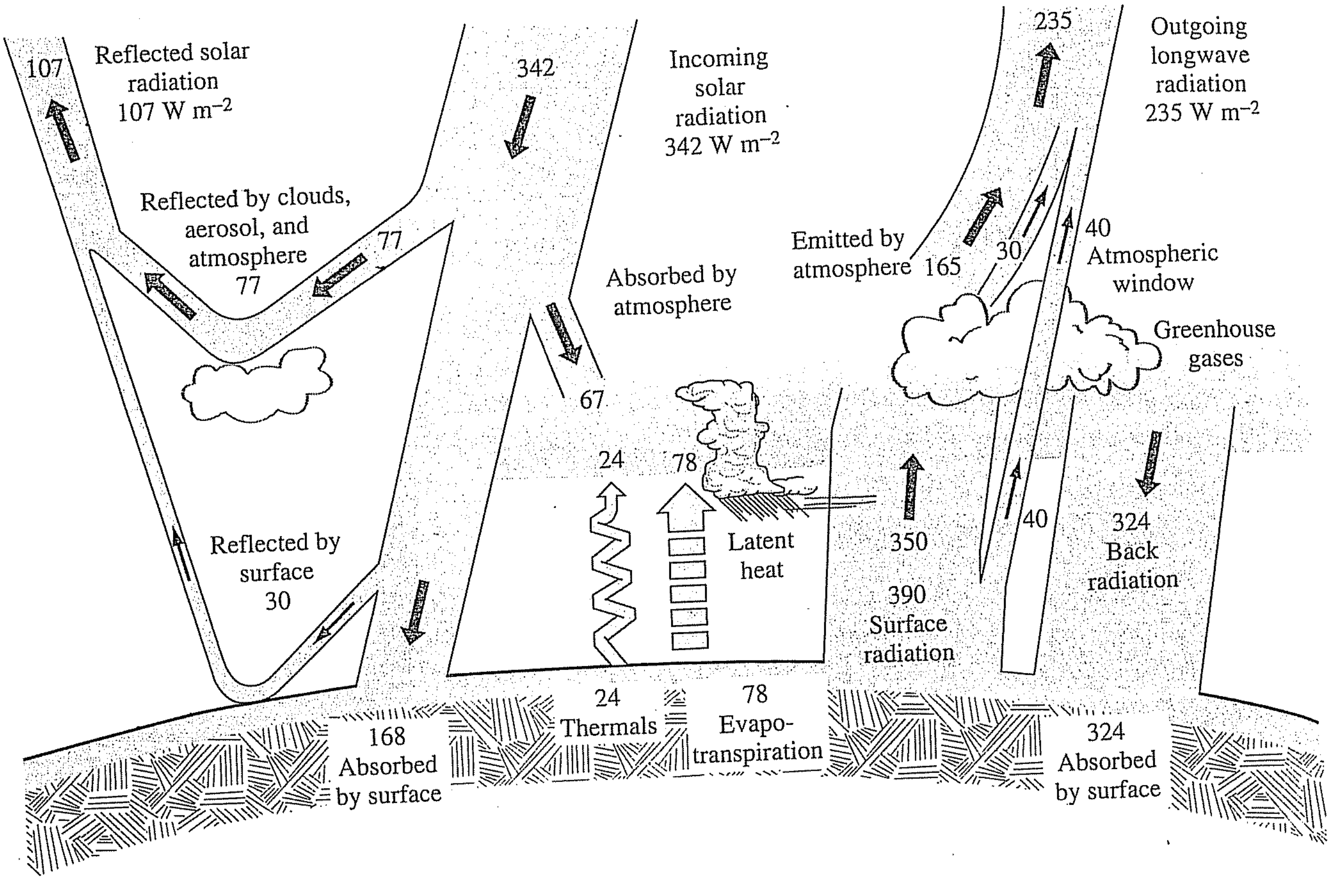


FIGURE 8.12 Average energy flows among space, the atmosphere, and the Earth's surface for a global equilibrium model. Units are watts per square meter of surface area. Values given are from Kiehl and Trenberth (1996) as they appear in IPCC (1996).

adds some quantitative detail to help us track energy flows. Some of this detail is relatively easy to derive. Begin by normalizing energy flows between these three regions by expressing them in terms of rates per unit of surface area of the Earth. For example, (8.2) indicates that the total amount of solar radiation striking the Earth is $S\pi R^2$. Distributed over the entire surface of the Earth, the average incoming solar radiation is equal to

$$\frac{\text{Incoming solar radiation}}{\text{Surface area of Earth}} = \frac{S\pi R^2}{4\pi R^2} = \frac{S}{4} = \frac{1{,}370 \text{ W/m}^2}{4} = 342 \text{ W/m}^2 \quad (8.11)$$

Since the albedo is 31 percent, the amount of incoming radiation reflected back into space per square meter of the Earth's surface is

$$\begin{aligned}\frac{\text{Solar energy reflected}}{\text{Surface area of Earth}} &= \frac{S\pi R^2\alpha}{4\pi R^2} = \frac{S}{4}\alpha \\ &= 342 \text{ W/m}^2 \times 0.31 = 107 \text{ W/m}^2\end{aligned} \quad (8.12)$$

Of this 107 W/m^2, it is estimated that 77 W/m^2 is reflected off the atmosphere itself, while the remaining 30 W/m^2 is reflected off the Earth's surface. The solar radiation that is not reflected is absorbed by the Earth and its atmosphere. Calling that absorbed energy Q_{abs} (again, with units of watts per square meter of surface) gives

$$\frac{\text{Solar radiation absorbed}}{\text{Surface area of Earth}} = Q_{abs} = \frac{S\pi R^2(1-\alpha)}{4\pi R^2} = \frac{S}{4}(1-\alpha) \tag{8.13}$$
$$= 342\ \text{W/m}^2 \times (1 - 0.31) = 235\ \text{W/m}^2$$

Of that 235 W/m^2, 67 W/m^2 is absorbed by the atmosphere, and the remaining 168 W/m^2 is absorbed by the surface of the Earth.

If we assume that global temperatures are unchanging with time, then the rate at which the Earth and its atmosphere receive energy from space must equal the rate at which energy is being returned to space. The 107 W/m^2 of reflected energy is already balanced; that is, 107 W/m^2 hits the Earth/atmosphere, and 107 W/m^2 is reflected back into space so we can ignore that component for now. The Earth and its atmosphere absorb the remaining 235 W/m^2, so the same amount must be radiated back into space. If the Earth's surface were at 254 K, it would radiate 235 W/m^2, which is just enough to balance the incoming energy. We know, however, that greenhouse gases would absorb most of that outgoing 235 W/m^2, so the required energy balance would not be realized. Therefore, to force enough energy through the atmosphere to create the necessary balance, the temperature of the Earth's surface must be higher than 254 K.

If we treat the Earth as a blackbody radiator, we can use (8.4) to estimate the rate at which energy is radiated from the Earth's surface toward the atmosphere. With the surface of the Earth at its actual temperature of 288 K, it will radiate the following amount per unit of surface area.

$$\frac{\text{Energy radiated by surface}}{\text{Surface area of Earth}} = \frac{\sigma 4\pi R^2 T_s^4}{4\pi R^2} = \sigma T_s^4 \tag{8.14}$$
$$= 5.67 \times 10^{-8}\ \text{W/m}^2\text{K}^4 \times (288\ \text{K})^4 = 390\ \text{W/m}^2$$

Of that 390 W/m^2, only 40 W/m^2 passes directly through the atmosphere, mostly through the atmospheric radiative window between 7 and 13 μm. The remaining 350 W/m^2 is absorbed by greenhouse gases in the atmosphere. The atmosphere then radiates 324 W/m^2 back to the surface.

There is also heat transfer from the surface to the atmosphere by convective heating, evaporation, and condensation of water. Convection transfers 24 W/m^2 to the atmosphere, while condensation of water vapor provides 78 W/m^2 of latent heat (see Section 1.4).

All of these energy flows are shown in Figure 8.12. If this model is an internally self-consistent equilibrium model, the rate of energy gain should equal the rate of energy loss in each of the three regions: space, the atmosphere, and the Earth's surface. Consider the following checks:

	Rate of energy gain = Rate of energy loss?	
Earth's surface:	168 + 324 + 30 = 78 + 24 + 30 + 390	(checks)
Atmosphere:	67 + 78 + 24 + 350 = 165 + 30 + 324	(checks)
Space:	107 + 165 + 30 + 40 = 342	(checks)

So, the model shows the necessary balances.

8.6 Carbon Dioxide: The Principal Greenhouse Gas

Thus far, the greenhouse effect has been described as a natural phenomenon that is responsible for Earth having an average surface temperature 34°C warmer (288 K vs 254 K) than it would have if it didn't have radiatively active gases in the atmosphere. As is now well known, anthropogenic sources of a number of gases and aerosols are enhancing the natural greenhouse effect, leading us into a future of uncertain global climate. The principal greenhouse gases are carbon dioxide, methane, nitrous oxide, and a category of carbon-based gases called *halocarbons,* which are molecules that contain atoms of carbon plus fluorine, chlorine, and/or bromine. In addition, emissions of black carbon, or soot, particles also add to atmospheric warming. We begin our exploration of these gases and particulates with the most important one, carbon dioxide. Carbon dioxide has been recognized for its importance as a greenhouse gas for over a century. The Swedish chemist Svante August Arrhenius is usually credited with the first calculations on global temperature as a function of atmospheric CO_2 content, and his results are not that far from those obtained today.

Atmospheric Concentration of CO_2

The first continuous, precise, and direct measurements of atmospheric carbon dioxide began in 1957 at the South Pole, and 1958 at Mauna Loa, Hawaii. At that time, the concentration in Mauna Loa was 315 ppm and growing at less than 1 ppm per year. In 1979, NOAA began assembling data from a network of sites to determine a global average value. The global average in 1990 was 354 ppm and growing at 1.6 ppm per year. In 2006, it reached 380 ppm, and the rate of growth had increased to about 2 ppm/yr.

Figure 8.13 shows NOAA data for monthly global CO_2 for the recent past. The oscillations are caused by seasonal variations in the rates of photosynthesis and respiration. During photosynthesis, carbon is transferred from the air into plant material (indicated by the carbohydrate, glucose, in the following reaction). During spring and summer, when plants are growing their fastest, atmospheric CO_2 levels drop, tending to reach their lowest point in the Northern Hemisphere in about October.

$$\text{Photosynthesis:} \quad 6\ CO_2 + 6\ H_2O \xrightarrow{\text{sunlight, chlorophyll}} C_6H_{12}O_6 + 6\ O_2 \qquad (8.15)$$

Reversing the preceding reaction yields the equation describing respiration, which is the process that living things use to obtain energy. During respiration, complex organic molecules are broken down, returning carbon to the atmosphere. When the rate of respiration exceeds the rate of photosynthesis, as tends to occur in the fall and winter seasons, there is a net replacement of carbon into the atmosphere, which globally results in peak concentrations around May.

$$\text{Respiration: } 6\ C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O + \text{energy} \qquad (8.16)$$

Carbon thus moves continually from the atmosphere into the food chain during photosynthesis and returns to the atmosphere during respiration.

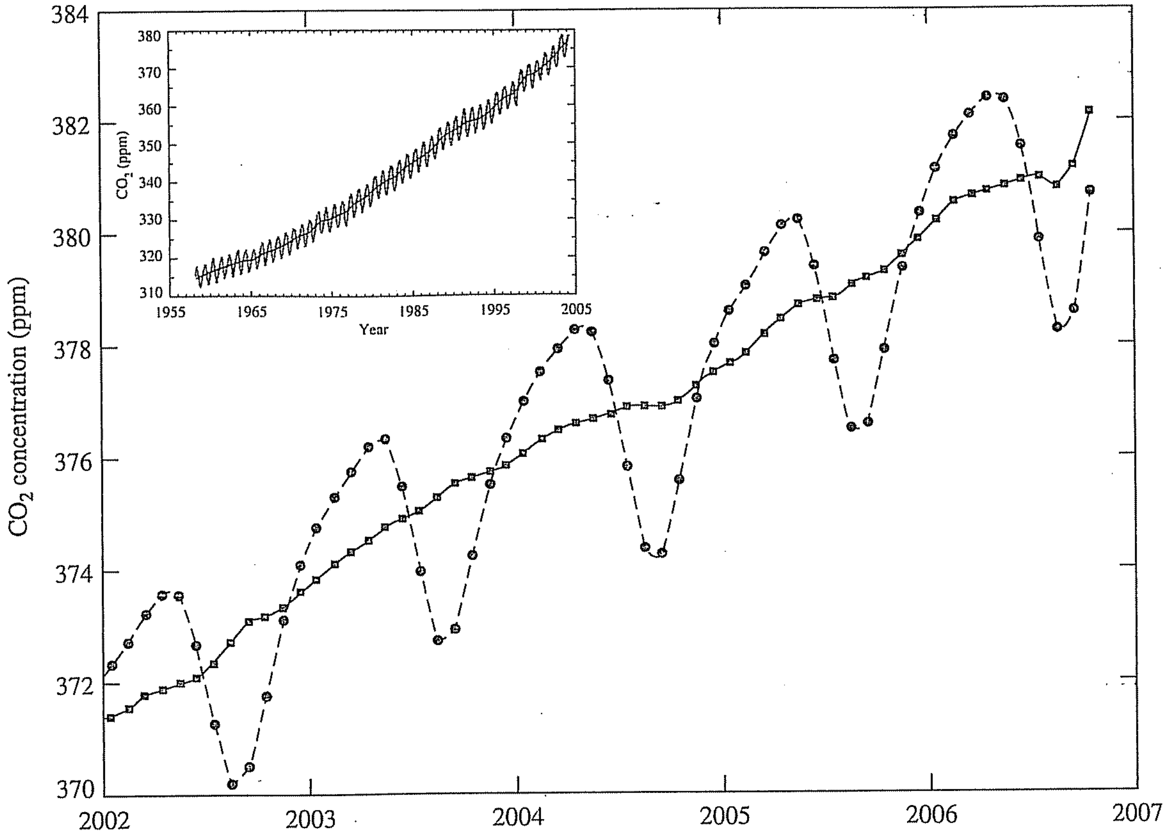


FIGURE 8.13 Recent global CO_2 concentrations. The oscillations are month-by-month mean values; the smoothed line is a moving average over 10 adjacent months. (*Source:* NOAA Web site http://www.cmdl.noaa.gov/ccgg/trends/index.php#mlo, 2006.)

Atmospheric carbon dioxide concentrations inferred from Antarctic ice cores and other evidence over the past 1,000 years, combined with more recent direct measurements, are shown in Figure 8.14. Over most of that time period, the concentration of carbon dioxide hovered at close to 280 ppm, and that is the value that is commonly used as a reference point for comparison with current readings and future projections. Carbon dioxide concentrations are now more than one-third higher than they were just before the industrial revolution.

The Carbon Cycle

The atmosphere contains about 800 GtC, where 1 GtC means 1 gigaton of carbon (10^9 metric tons or 10^{15} g). Since almost all of that carbon is stored in the form of CO_2 (less than 1 percent is in other carbon-containing compounds such as methane and carbon monoxide), in most circumstances it is reasonable to assume that atmospheric carbon is entirely CO_2. The amount of carbon locked up in terrestrial vegetation (610 GtC) is of the same order of magnitude as that in the atmosphere, but both of these amounts are dwarfed by the 39,000 GtC stored in the oceans.

Natural processes continuously transport enormous amounts of carbon back and forth among the atmosphere, biosphere, and the oceans. The carbon flux into and out of the atmosphere during photosynthesis and respiration is on the order of 60 GtC/yr. The oceans absorb around 90 Gt/C/yr and store almost all of it in the

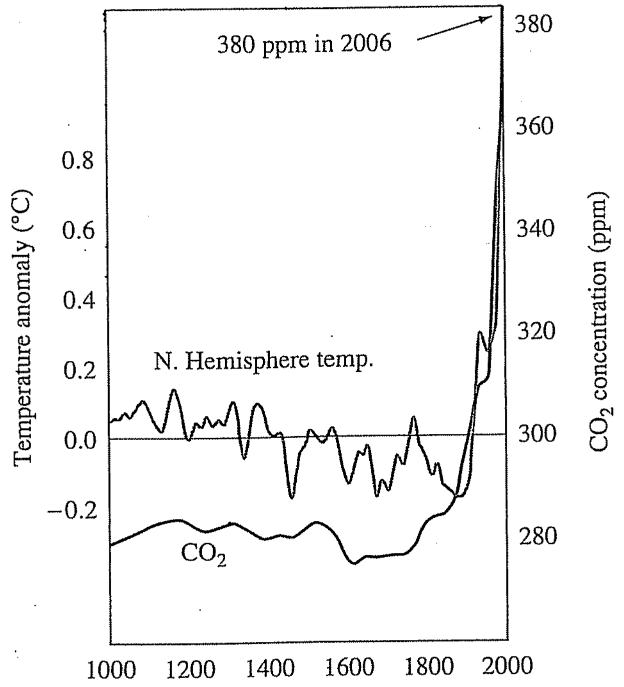


FIGURE 8.14 Carbon dioxide concentration and Northern Hemisphere temperature over the past 1,000 years.

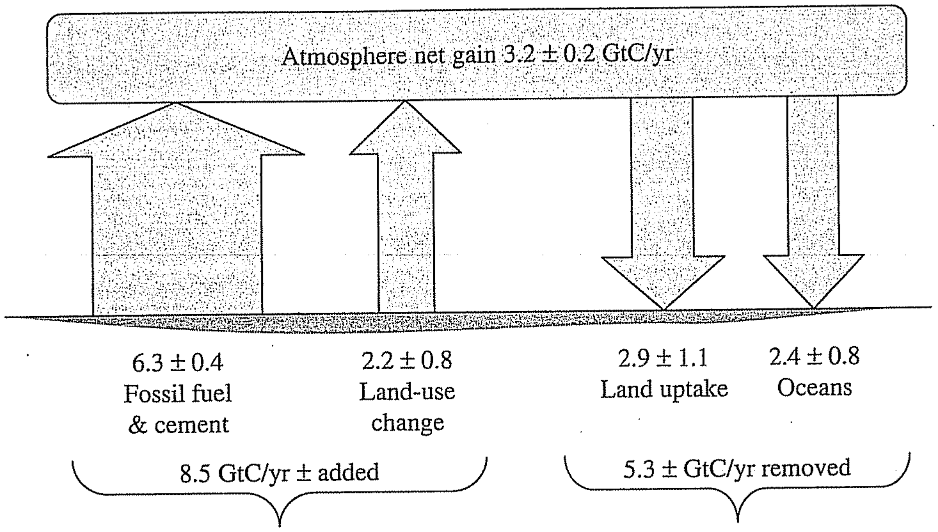


FIGURE 8.15 Human perturbations to the global carbon cycle during the 1990s. (*Source:* Based on data from Houghton, 2003.)

form of bicarbonate ions (HCO_3^-), but some becomes part of the marine food chain. A similar quantity is returned to the atmosphere. A very small portion of nonliving organic matter each year ends up in sediments. The slow, historical accumulation of that organic carbon is the source of our fossil fuels—oil, natural gas, and coal. When these are burned, ancient carbon is returned to the atmosphere.

By comparison with the natural fluxes of carbon, the additional amounts added to the atmosphere by combustion, cement production, and changes in land use are modest, but they are enough to cause a significant response by the climate system. Figure 8.15 summarizes the impact of human perturbations to the carbon fluxes into and out of the atmosphere during the 1990s. Fossil fuel combustion and cement production deliver 6.3 GtC/yr to the atmosphere, while land use changes, such as biomass burning and harvesting of forests, add another 2.2 GtC/yr. Not all of that 8.5 GtC/yr remains in the atmosphere, however. Greater carbon uptake through purposeful reforestation efforts, as well as stimulated plant growth caused by higher CO_2 levels and increased nitrogen deposition on the soils from fossil fuel combustion, removes around 2.9 GtC/yr. Finally, higher atmospheric CO_2 increases the oceans' absorption of carbon, providing an additional 2.4 GtC/yr sink.

As Figure 8.15 suggests, fossil fuel combustion and land-use changes in the 1990s added about 8.5 GtC/yr to the atmosphere. Of that amount, 5.3 GtC/yr was returned to the oceans or other terrestrial sinks, leaving about 3.2 GtC/yr remaining in the atmosphere. The ratio of the amount of anthropogenic carbon emitted to the amount that remains in the atmosphere is known as the *airborne fraction*. Using these data, the airborne fraction has been:

$$\text{Airborne fraction} = \frac{3.2\ \text{GtC/yr remaining in atmosphere}}{8.5\ \text{GtC/yr anthropogenic additions}} = 0.38 = 38\% \quad (8.17)$$

Thus, roughly speaking, somewhat less than half of the carbon we emit stays in the atmosphere. But the airborne fraction is not necessarily a fixed quantity. For example, if large areas of land are deforested, the ability of the biosphere to absorb carbon would be reduced, and the atmospheric fraction would increase. Likewise, CO_2 fertilization of terrestrial biomass can stimulate plant growth, which increases the rate of removal of atmospheric carbon, so the airborne fraction could get smaller. The airborne fraction also depends on how fast carbon is being added to the atmosphere. For scenarios with little or no growth in emissions or even declining emissions, the oceans and plants have more time to absorb carbon, so the atmospheric fraction could be lower. On the other hand, for rapidly increasing emission rates, carbon sinks cannot keep up and the fraction remaining in the atmosphere may be higher.

The following example develops another useful relationship, this time between the concentration of CO_2 and the tons of carbon in the atmosphere. This ratio, coupled with an estimate of the airborne fraction, provides the key to predicting future CO_2 concentrations for various carbon emission scenarios.

EXAMPLE 8.2 Carbon Content of the Atmosphere

Find a relationship between the concentration of carbon dioxide and the total amount of carbon in the atmosphere. The total mass of the atmosphere is estimated to be 5.12×10^{21} g.

Solution We will need to know something about the density of air. That, of course, varies with altitude, but finding it under some particular conditions will work. From Table 8.1 we know the concentration of each gas in air. Recall from Section 1.2 that 1 mole of each gas occupies $22.414 \times 10^{-3}\ \text{m}^3$ at Standard

Temperature and Pressure (0°C and 1 atmosphere), which is 44.61 mol/m^3. The following table organizes the calculation:

Gas	$\frac{\text{m}^3\text{ gas}}{\text{m}^3\text{ air}}$	×	g/mol	×	$\frac{\text{mol}}{\text{m}^3\text{ gas}}$	=	$\frac{\text{g}}{\text{m}^3\text{ air}}$
N_2	0.7808		28		44.61		975.3
O_2	0.2095		32		44.61		299.1
Ar	0.0093		40		44.61		16.6
CO_2	0.00038		44		44.61		0.75
					Total		1291.8 g/m^3

If all of the atmosphere were at standard temperature and pressure, it would have a density of 1291.8 g/m^3, and its mass would still be 5.12×10^{21} g. Putting these together gives

$$1\text{ ppm} = \frac{1\text{ m}^3\text{ CO}_2}{10^6\text{ m}^3\text{ air}} \cdot 44.61\frac{\text{mole}}{\text{m}^3\text{ CO}_2} \cdot 12\frac{\text{g C}}{\text{mole}} \cdot \frac{5.12 \times 10^{21}\text{ g air}}{1291.8\frac{\text{g air}}{\text{m}^3\text{ air}}} \cdot 10^{-15}\frac{\text{GtC}}{\text{g C}} = 2.12\text{ GtC}$$

Notice this calculation has taken advantage of the fact that volumetric concentrations (ppm) are independent of temperature or pressure.

From Example 8.2, we have the following very useful relationship:

$$1\text{ ppm CO}_2 = 2.12\text{ GtC} \tag{8.18}$$

For example, knowing the concentration of CO_2 in 2006 was 380 ppm, the total amount of carbon in the atmosphere can be estimated to be

$$380\text{ ppm} \times 2.12\text{ GtC/ppm} = 806\text{ GtC}$$

EXAMPLE 8.3 Estimating the Rate of Change of CO_2

Suppose global fossil fuel combustion emits 7.4 GtC/yr and cement production adds another 0.5 GtC. Assuming the an airborne fraction of 0.38 and assuming no change in emissions associated with land use, what rate of change in CO_2 concentration would you expect?

Solution Including the 2.2 GtC/yr land-use emissions from Figure 8.17 gives a total emission rate of 2.2 + 7.4 + 0.5 = 10.1 GtC/yr. Using the 0.38 airborne fraction along with the 2.12 GtC/ppm ratio gives

$$\Delta CO_2 = \frac{10.1\text{ GtC/yr} \times 0.38}{2.12\text{ GtC/ppm CO}_2} = 1.8\text{ ppm CO}_2\text{/yr}$$

Carbon Emissions from Fossil Fuels

Use of energy and the resulting emissions of carbon vary considerably from country to country. The United States, with less than 5 percent of the world's population, emits 22 percent of global energy-related CO_2. The second largest emitter is China,

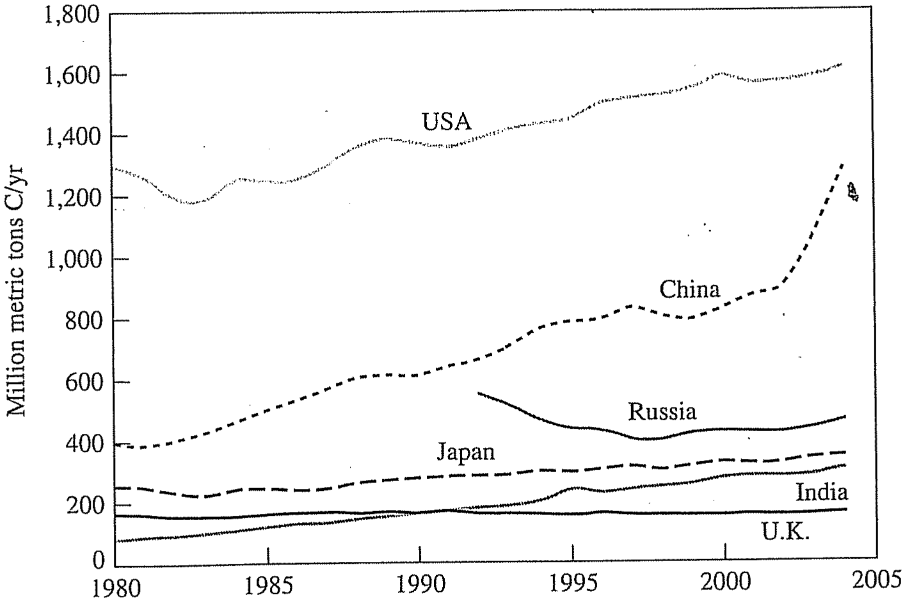


FIGURE 8.16 Fossil fuel carbon emissions.
(*Source:* EIA data, 2006.)

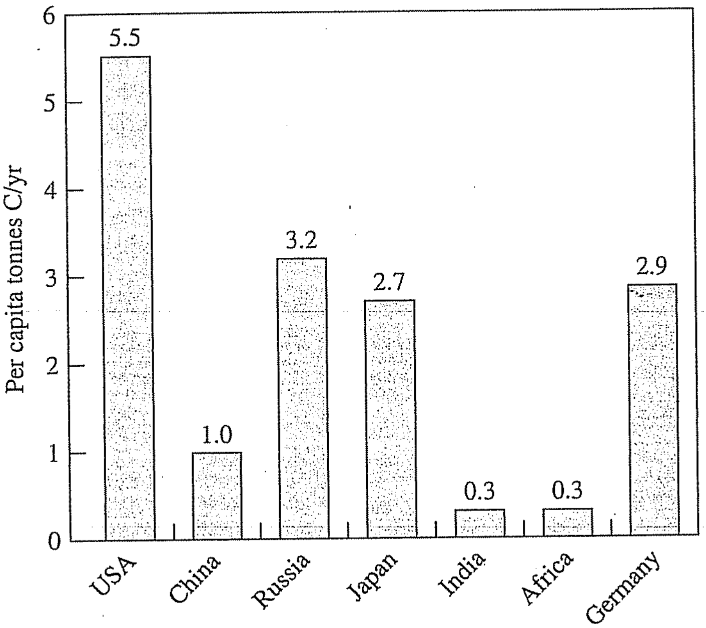


FIGURE 8.17 Per capita carbon emissions.
(*Source:* EIA data, 2006.)

and as Figure 8.16 indicates, it is very rapidly closing the gap with the United States. In fact, it is projected that China's emissions will exceed those of the United States by 2010. While China's emissions growth is certainly worrisome, two other measures provide some insight into the root cause of our global carbon problem. On a per capita basis, the United States emits far more carbon than any other country—roughly double that of most other advanced countries and more than five times as much as China (Figure 8.17). Moreover, it is the accumulated emissions from developed countries that are overwhelmingly responsible for the rising CO_2 concentrations in the atmosphere (Figure 8.18).

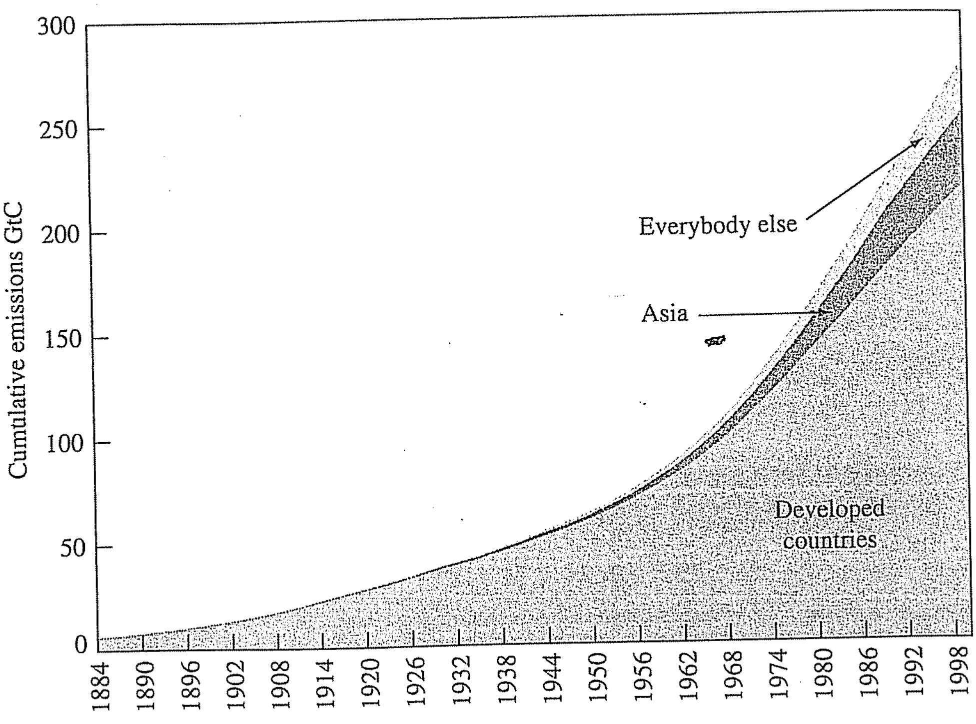


FIGURE 8.18 Cumulative carbon emissions by region.
(*Source:* E. Wanless with data from G. Marland, Oak Ridge National Labs.)

Carbon Emissions from Industrial Processes

A number of manufacturing processes result in carbon emissions on site that are not included in the usual accounting for fossil fuel combustion. The primary source of these industrial emissions is the calcination of limestone ($CaCO_3$) to create lime (CaO). These two compounds are basic materials in the production of cement, iron and steel, and glass. Other industrial emissions result from the production and use of soda ash (Na_2CO_3), the manufacture of carbon dioxide, and the production of aluminum.

The largest single industrial CO_2 source, however, results from cement production. Concrete, which is probably the most important building material in the world, is made up of a mixture of Portland cement, fine aggregate (sand), coarse aggregate (crushed stone), and water. Portland cement, which is the binding agent for concrete, derived its name in the early nineteenth century from its similarity to a particular type of stone found on the Isle of Portland in Dorset, England. It is typically on the order of 12 to 15 percent by weight of the concrete mix.

The major raw material needed for the manufacture of Portland cement is limestone ($CaCO_3$), along with a source of silicon such as clay or sand. Processing of those materials is done in high-temperature kilns, usually fired with fossil fuels whose combustion leads to CO_2 emissions. In addition, the calcination of $CaCO_3$ into lime (CaO) that occurs in those kilns emits its own CO_2 as the following reaction suggests:

$$\text{Limestone } (CaCO_3) + \text{Clay or Sand } (Si) + \text{Heat} \rightarrow \text{Cement } (CaO, SiO_2) + CO_2 \tag{8.19}$$

The average intensity of carbon emissions from cement production is about 0.222 tons of carbon per ton of cement, with about half of that being the result of calcinations and half released during combustion (Worrell et al., 2001). In addition, power plants supplying electricity for plant operations emit their own carbon, but that is usually not included in the category of industrial process emissions. All told, cement manufacturing globally contributes close to 5 percent of all anthropogenic carbon emissions. The total industrial emissions category accounts for about 0.8 GtC/yr.

As it turns out, fly ash from coal-fired power plants can be used as a replacement for some of the cement in concrete. This *fly-ash concrete* not only reduces carbon emissions by roughly one ton of CO_2 per ton of replaced cement, but it also results in a concrete that is stronger and more durable than its conventional counterpart. It also recycles a relatively useless waste product that would otherwise have to be disposed of. Concrete mixtures with more fly ash than cement are now becoming popular in the emerging green building industry.

Carbon Intensity of Fossil Fuels

The amount of carbon released per unit of energy delivered is called the *carbon intensity*. Some fuels have high carbon intensity, such as coal, and some conversion systems release no direct carbon at all, such as wind turbines or nuclear power. Interestingly, biomass fuels may also be used in ways that emit little or no carbon when new plants are grown to replace the ones that were burned. No energy system is likely to have zero carbon emissions, however, since it is hard to avoid such emissions during the mining, materials processing, and construction of any energy facility.

EXAMPLE 8.4 Carbon Intensity of Methane

Find the carbon intensity of methane based on its higher heating value (HHV) of 890 kJ/mol (which includes the energy of condensation of the water vapor formed; you might want to review Examples 2.4 and 2.5 in Chapter 2, which describe HHV and LHV). Then find the carbon intensity based on the lower heating value (LHV) of 802 kJ/mol.

Solution First, write a balanced chemical reaction for the oxidation of methane:

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$

So, burning 1 mol of CH_4 liberates 890 kJ of energy while producing 1 mol of CO_2. Since 1 mol of CO_2 has 12 g of carbon, the HHV carbon intensity of CH_4 is

$$\text{HHV carbon intensity} = \frac{12\text{ g C}}{890\text{ kJ}} = 0.0135\text{ gC/kJ} = 13.5\text{ gC/MJ}$$

Similarly, the LHV carbon intensity would be

$$\text{LHV carbon intensity} = \frac{12\text{ gC}}{802\text{ kJ}} = 0.015\text{ gC/kJ} = 15.0\text{ gC/MJ}$$

The LHV carbon intensity assumes the latent heat of the water vapor produced is not available as usable energy.

TABLE 8.3

LHV and HHV Carbon Intensities and Emissions for Typical Fossil Fuels

Fuel	LHV Carbon Intensity (gC/MJ)	HHV Carbon Intensity (gC/MJ)	2004 Global Carbon Emissions (GtC/yr)
Natural gas	15.3	13.8	1.58 (21.2%)
Petroleum	20.0	19.7	2.96 (39.8%)
Coal	25.8	24.2	2.89 (38.9%)

Sources: Carbon intensities from NAS, 1992; emissions from EIA, 2006.

We can get a quick estimate of the carbon intensity of other fuels by using the fact that the energy released during combustion of carbon-based fuels is approximately proportional to the amount of oxygen they consume (Baird, 1995). For example, if we consider coal to be purely carbon and oil to be approximately CH_2, we can write the following oxidation reactions:

Coal: $$C + O_2 \rightarrow CO_2 \tag{8.20}$$

Oil: $$CH_2 + 1.5\ O_2 \rightarrow CO_2 + H_2O \tag{8.21}$$

Natural gas: $$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O \tag{8.22}$$

The same amount of carbon is released for each of these reactions, but since energy is roughly proportional to oxygen consumption, per unit of carbon emitted we would expect about 1.5 times as much energy from oil as coal and twice as much energy from natural gas compared to coal. Turning that around, coal is more carbon-intensive than oil, and oil emits more carbon than natural gas.

The actual LHV and HHV carbon intensities for typical fossil fuels, combined with estimates of total carbon emissions, are given in Table 8.3. Note the slight difference between the carbon intensity of natural gas and the intensity of methane itself found in Example 8.4. Natural gas is mostly methane, but it also includes other hydrocarbons, which alters the calculation slightly. Since the proportions of methane and other hydrocarbons vary from one source to another, the carbon intensities given in Table 8.3 are "typical," and you are likely to find other, slightly different, values in the literature. The same goes for variations in types of coal. Another comment worth making is that energy consumption figures in the United States are often based on the higher heating value of a fuel, while most of the rest of the world, including the IPCC, uses LHV values. The LHV value makes more sense for power plants since they never recover the latent heat of their water vapor emissions, but HHV values are more appropriate for high-efficiency condensing furnaces and water heaters, which do capture that heat. To be consistent with the IPCC, in this chapter, all energy data and carbon intensities will be based on the LHV values.

The carbon intensity data given in Table 8.3 suggest that sizable reductions in carbon emissions are possible by switching from coal to natural gas. It is unfortunately the case, however, that most of the world's fossil fuel resources are in the form of coal. It is interesting to note that almost 90 percent of the world recoverable resources of coal are in just three regions: the United States, the former USSR, and China.

Table 8.4 presents data on the world's fossil fuel resources. These resources are shown as a resource base, which consists of already identified reserves plus an estimate at the 50-percent probability level of remaining undiscovered resources. The

TABLE 8.4

Energy Content of Global Fossil Fuel Resources and Occurrences, in Exajoules (EJ)

Fuel	Conventional Resources	Unconventional Resources	Total Resource Base	Additional Occurrences
Natural gas	9,200	26,900	36,100	>832,000
Petroleum	8,500	16,100	24,600	>25,000
Coal	25,200	100,300	125,500	>130,000
Totals	42,900	143,300	186,200	>987,000

Source: Nakicenovic, 1996.

resources are also described as coming from conventional sources of the type now being exploited, as well as unconventional sources that might be usable in the future. Unconventional sources of oil include oil shale, tar sands, and heavy crude; unconventional natural gas sources include gas in Devonian shales, tight sand formations, geo-pressurized aquifers, and coal seams. An additional column in Table 8.4 is labeled "additional occurrences." These are additional resources with unknown certainty of occurrence and/or with unknown or no economic significance in the foreseeable future. Enormous amounts of methane locked in methane hydrates ($CH_4 \cdot 6H_2O$) under the oceans (estimated at over 800,000 EJ) are the most important of these.

Example 8.5 suggests what might happen to the CO_2 concentration in the atmosphere if we were to burn all of the world's coal resource base.

EXAMPLE 8.5 **Burning the World's Coal**

Estimate the increase in atmospheric CO_2 if the 125,500 EJ of coal were to be burned. Assume a constant airborne fraction of 38 percent.

Solution We can first estimate the carbon content using the LHV value from Table 8.3:

$$125{,}500 \text{ EJ} \times 25.8 \text{ gC/MJ} \times 10^{12} \text{ MJ/EJ} \times 10^{-15} \text{ GtC/gC} = 3{,}238 \text{ GtC}$$

which is roughly four times as much carbon as currently exists in the atmosphere. Converting this to CO_2 and including the 0.38 airborne fraction gives

$$\Delta CO_2 = \frac{3{,}238 \text{ GtC} \times 0.38}{2.12 \text{ GtC/ppm } CO_2} = 580 \text{ ppm } CO_2$$

That would result in 2.5 times as much CO_2 in the atmosphere as we have today. In fact, it would likely be higher than that if the airborne fraction increases due to the oceans ceasing to be such a good carbon sink.

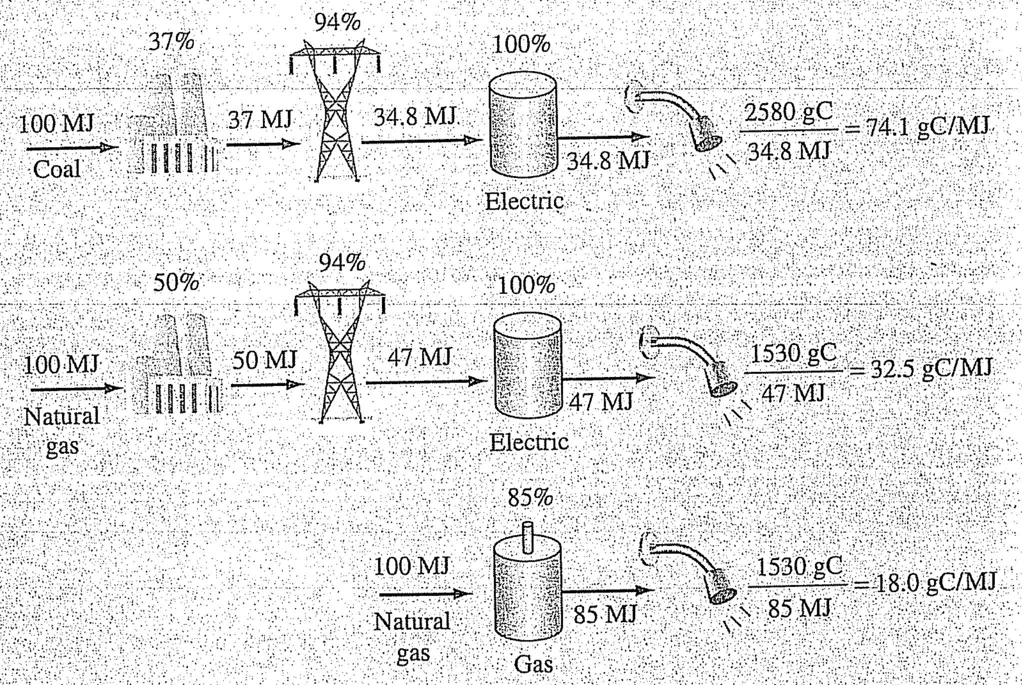
It is interesting to note that a similar calculation to that shown in Example 8.5 suggests that the oil and gas resource base has the potential to add only about one-third as much CO_2 to the atmosphere as would burning all of the world's coal resources. That calculation is less certain, however, because of the relatively unknown carbon emission factors that would be appropriate for the unconventional oil and gas resources. It is also complicated by the fact that the principal component of natural gas, methane, is a much more potent greenhouse gas than CO_2, which means methane leakage can amplify its potential global warming.

The carbon-intensity factors given in Table 8.3 suggest that switching from coal to oil or natural gas would reduce emissions significantly. For example, it would appear that switching from coal to natural gas would reduce carbon emissions by about 41 percent while delivering the same amount of energy. Example 8.6 shows how efficiency advantages as well as carbon advantages associated with using natural gas can substantially increase that advantage.

EXAMPLE 8.6 Efficiency and Carbon Intensity Combined

Compare the carbon emissions to heat household water using the following three energy systems: 1) a very good, 37 percent-efficient coal-fired power plant delivering electricity to a 100 percent-efficient electric water heater; 2) a new, 50 percent-efficient natural-gas-fired combined-cycle power plant for that same electric water heater; and 3) an 85 percent-efficient gas-fired water heater. Assume 6 percent losses in electrical transmission lines.

Solution Let us base our comparison on 100 MJ of energy provided to each system. Using the LHV values given in Table 8.3, burning 100 MJ of coal releases 2,580 g of carbon, while 100 MJ of natural gas releases 1,530 gC. As suggested here, the coal-plant system delivers 100 × 0.37 × 0.94 = 34.8 MJ to heat water; the more efficient gas-fired power plant delivers 100 × 0.50 × 0.94 = 47 MJ to heat water; and using gas in the water heater delivers 85 MJ of heat.



The carbon intensities for each system are shown in the figure. Switching from coal to gas in the power plant reduces carbon emissions for the electric water heater by 56 percent. Using gas directly in the water heater reduces carbon emissions by 75 percent (much more than the 41 percent improvement expected based just on the carbon intensity of natural gas versus coal).

Estimating Emissions: The Kaya Identity

Predicting future concentrations of carbon dioxide depends on numerous assumptions about population growth, economic factors, energy technology, and the carbon cycle itself. The usual approach involves developing a range of emission scenarios that depend on those factors and then using those scenarios to drive mathematical models of how the atmosphere and climate system will react to those inputs. At the level of treatment given in this short section, we can't begin to approach the complexity of those models; however, we can make a few simple calculations to at least give a sense of some of the important factors.

One way to build simple models of environmental problems is to start with the notion that impacts are driven by population, affluence, and technology, which is sometimes referred to as the *IPAT identity* (Ehrlich and Holdren, 1971).

$$\text{Environmental Impact} = (\text{Population}) \times (\text{Affluence}) \times (\text{Technology}) \qquad (8.23)$$

The following application of IPAT to carbon emissions from energy sources is often referred to as the *Kaya identity* (Kaya, 1990).

$$C = \text{Population} \times \frac{\text{GDP}}{\text{Person}} \times \frac{\text{Primary Energy}}{\text{GDP}} \times \frac{\text{Carbon}}{\text{Primary Energy}} \qquad (8.24)$$

where

C = carbon emission rate (GtC/yr)

$\frac{\text{GDP}}{\text{Person}} = \frac{\text{GDP}}{\text{P}}$ = per capita gross domestic product ($/person-yr)

$\frac{\text{Primary Energy}}{\text{GDP}} = \frac{\text{PE}}{\text{GDP}}$ = primary energy intensity, (EJ/$)

$\frac{\text{Carbon}}{\text{Primary Energy}} = \frac{\text{C}}{\text{PE}}$ = carbon intensity, (GtC/EJ)

Equation (8.24) incorporates the key quantities that drive our energy-related carbon emissions. It includes economic and population scenarios plus two factors that are central to energy: energy intensity and carbon intensity. Carbon intensity has already been introduced. *Energy intensity* is the amount of energy required to create a unit of economic activity as measured by gross domestic product (GDP). It is usually thought of as a surrogate for the country's energy efficiency. For example, Japan, which only needs half the energy to produce a unit of GDP, is often considered to be roughly twice as energy efficient as the United States. While there is some truth to that assertion, it sometimes masks differences in the standard of living and the climate in each country. For example, the United States has larger houses that are kept warmer in more severe winters, so if more energy is required it may have more to do with those factors than whether or not homes are better insulated in one country or the other. Japan is also a small, densely populated country with relatively short travel distances, so transportation energy would likely be less as well, even with an equivalent level of transportation efficiency.

For example, the Kaya identity for the year 2010 looks something like this:

$$\begin{aligned} C &= 6.9 \times 10^9 \text{ people} \times \$4{,}605/\text{person-yr} \times 14.9\ \text{EJ}/\$10^{12} \times 0.016\ \text{GtC/EJ} \\ &= 7.6\ \text{GtC/yr} \end{aligned}$$

TABLE 8.5

1990 to 2020 Average Annual Growth Rates (%/yr) Used in the IPCC IS92a Scenario for Energy-Related Carbon Emissions

Region	Population	$\frac{\text{GDP}}{\text{Person}}$	$\frac{\text{PE}}{\text{Person}}$	$\frac{\text{Carbon}}{\text{PE}}$
China and centrally planned Asia	1.03	3.91	−1.73	−0.32
Eastern Europe and ex-USSR	0.43	1.49	−0.66	−0.24
Africa	2.63	1.25	0.26	−0.21
United States	0.57	2.33	−1.81	−0.26
World	1.40	1.53	−0.97	−0.24

Equation (8.24) expresses the carbon emission rate as the product of four terms: population, GDP, carbon intensity, and energy intensity. Recall from Section 3.2 that if each of the factors in a product can be expressed as a quantity that is growing (or decreasing) exponentially, then the overall rate of growth is merely the sum of the growth rates of each factor. That is, assuming each of the factors in (8.23) is growing exponentially, the overall growth rate of carbon emissions r is given by

$$r = r_{\text{P}} + r_{\text{GDP/P}} + r_{\text{PE/GDP}} + r_{\text{C/PE}} \tag{8.25}$$

By adding the individual growth rates as has been done in (8.25), an overall growth rate is found, which can be used in the following emission equation:

$$C = C_0 e^{rt} \tag{8.26}$$

where

C = carbon emission rate after t yrs (GtC/yr)
C_0 = initial emission rate (GtC/yr)
r = overall exponential rate of growth (yr^{-1})

Table 8.5 shows population, economic growth, carbon intensity, and energy intensity values that have been used in one of the most-cited IPCC emission scenarios (IS92a) for energy. For the world as a whole, energy intensity and carbon intensity are both improving over time, which helps offset population and economic growth.

The cumulative emissions from a quantity growing exponentially at a rate r, over a period of time T is given by

$$C_{\text{tot}} = \int_0^T C_0 e^{rt}\,dt = \frac{C_0}{r}\left(e^{rT} - 1\right) \tag{8.27}$$

Combining (8.27) with an estimate of the atmospheric fraction, along with our 2.12 GtC/ppm CO_2 conversion factor, lets us make simple estimates of future CO_2 concentrations in the atmosphere, as Example 8.7 demonstrates.

EXAMPLE 8.7 Kaya Estimate of Future Carbon Emissions

Emissions from fossil-fuel combustion in 2010 are estimated to be 7.6 GtC/yr. In the same year, atmospheric CO_2 concentration is estimated to be 390 ppm. Assume the atmospheric fraction remains constant at 0.38.

a. Assuming the energy growth rates shown in Table 8.5 don't change, estimate the energy-related carbon-emission rate in 2050.
b. Estimate the cumulative energy-related carbon added to the atmosphere between 2010 and 2050.
c. Add into your scenario carbon emissions from industrial processes (especially cement) of 0.7 GtC/yr in 2010 and growing at 1.3%/yr. Also add a constant 0.9 GtC/yr from land-use changes. Estimate the CO_2 concentration in 2050.

Solution

a. The overall growth rate in energy-related carbon emissions is just the sum of the individual growth rates:

$$r = 1.40\% + 1.53\% - 0.97\% - 0.24\% = 1.72\% = 0.0172/\text{yr}$$

With 40 years of growth at 1.72% per year, the emission rate in 2050 would be

$$C_{2050} = C_{2010}e^{rT} = 7.6\, e^{0.0172\times 40} = 15.1 \text{ GtC/yr}$$

b. Over those 40 years, the cumulative energy emissions would be

$$C_{\text{tot}} = \frac{C_0}{r}(e^{rT} - 1) = \frac{7.6}{0.0172}(e^{0.0172\times 40} - 1) = 437 \text{ GtC}$$

c. The cumulative carbon emissions from industrial processes and land-use changes is

$$\text{Industrial } C_{\text{tot}} = \frac{C_0}{r}(e^{rT} - 1) = \frac{0.7}{0.013}(e^{0.013\times 40} - 1) = 37 \text{ GtC}$$

$$\text{Land Use } C_{\text{tot}} = 0.9 \text{ GtC/yr} \times 40 \text{ yrs} = 36 \text{ GtC}$$

Using the 2.12 GtC/ppm CO_2 ratio and a 0.38 atmospheric fraction makes our estimate of CO_2 in 2050

$$CO_2 = 390 + \frac{(437 + 37 + 36)\text{ GtC} \times 0.38}{2.12 \text{ GtC/ppm } CO_2} = 481 \text{ ppm}$$

One of the weakest aspects of the Kaya identity as expressed in (8.24) is its use of primary energy per GDP as a measure of energy efficiency. Primary energy, which is in essence energy as it is taken out of the ground, can be reduced by efficiency improvements on the supply side (e.g., more efficient electric power plants) as well as on the demand side (e.g., by making light bulbs more efficient). One way to address the two different efficiency improvements is to introduce another factor, call it *final energy FE,* which is the energy purchased by consumers (e.g., gasoline, natural gas, electricity). Another extension is based on prospects for carbon capture and

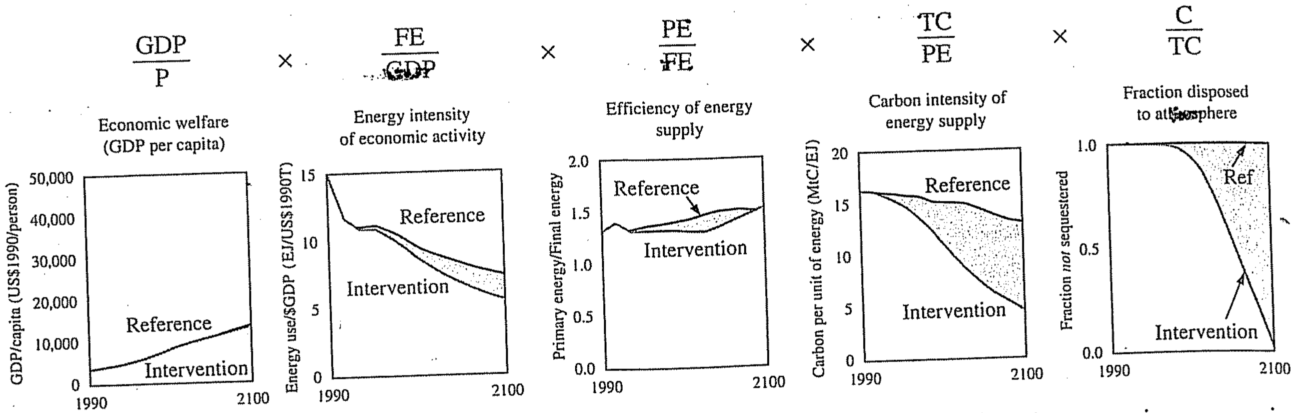


FIGURE 8.19 An expanded Kaya analysis showing a reference scenario and an intervention scenario designed to stabilize atmospheric CO_2.
(*Source:* Hummel, 2007 based on the IPCC A2-4.5 W/m^2 scenario.)

storage in the future. Letting *TC* be total carbon in the fuel and *C* be carbon actually emitted to the atmosphere, the Kaya identity can be expanded as follows:

$$\mathrm{C} = \mathrm{P} \times \frac{\mathrm{GDP}}{\mathrm{P}} \times \frac{\mathrm{FE}}{\mathrm{GDP}} \times \frac{\mathrm{PE}}{\mathrm{FE}} \times \frac{\mathrm{TC}}{\mathrm{PE}} \times \frac{\mathrm{C}}{\mathrm{TC}} \tag{8.28}$$

This much more useful disaggregation breaks the overall carbon emissions into much tighter packages for analysis. One such analysis showing a comparison between a more or less business-as-usual carbon scenario with one designed to ultimately stabilize CO_2 is shown in Figure 8.19.

A Climate Sensitivity Parameter

As we pump more and more CO_2 into the atmosphere, the marginal impact of each additional ton decreases as its absorption bands approach saturation. That suggests a nonlinear relationship between CO_2 and the resulting global warming that it causes. One commonly used representation of this phenomenon is given in (8.29).

$$\Delta T_{\mathrm{e}} = \frac{\Delta T_{2\mathrm{X}}}{\ln 2} \ln\left[\frac{(\mathrm{CO_2})}{(\mathrm{CO_2})_0}\right] \tag{8.29}$$

where

ΔT_{e} = the equilibrium, global, mean surface temperature change
$\Delta T_{2\mathrm{X}}$ = the equilibrium temperature change for a doubling of atmospheric CO_2
$(\mathrm{CO_2})_0$ = the initial concentration of CO_2
$(\mathrm{CO_2})$ = the concentration of CO_2 at another time

The increase in surface temperature that results from a doubling of CO_2 in the atmosphere is called the *climate sensitivity*, $\Delta T_{2\mathrm{X}}$. Notice what happens to (8.29) when CO_2 is double the initial amount. The change in surface temperature is what it should be, that is,

$$\Delta T_{\mathrm{e}} = \frac{\Delta T_{2\mathrm{X}}}{\ln 2} \ln\left[\frac{2(\mathrm{CO_2})_0}{(\mathrm{CO_2})_0}\right] = \frac{\Delta T_{2\mathrm{X}}}{\ln 2} \ln 2 = \Delta T_{2\mathrm{X}}$$

If the concentration of CO_2 is quadrupled,

$$\Delta T_{\mathrm{e}} = \frac{\Delta T_{2\mathrm{X}}}{\ln 2} \ln\left[\frac{4(\mathrm{CO_2})_0}{(\mathrm{CO_2})_0}\right] = \frac{\Delta T_{2\mathrm{X}}}{\ln 2} \ln\left(2^2\right) = 2\Delta T_{2\mathrm{X}}$$

In other words, the logarithmic function suggests that for every doubling of CO_2, the surface temperature goes up by the same amount. For example if ΔT_{2X} is 3°C, then the first doubling raises the surface temperature by 3°C, doubling it again to four times its initial value raises the temperature by another 3°C, and so on, as illustrated in Figure 8.20. The climate sensitivity ΔT_{2X} is a convenient benchmark that is often used to compare various general circulation computer models. It has long been estimated to be between 1.5°C and 4.5°C, with the best estimate as of 2006 being somewhere around 3.0°C.

Equilibrium Temperature and Realized Temperature

The surface temperatures dealt with thus far, T_e and ΔT_e, are known as *equilibrium* temperatures; that is, they are temperatures that would eventually be reached for a given atmospheric configuration. In reality, of course, the temperature of the Earth will not adjust instantaneously to changes in greenhouse gas concentrations. A considerable period of time is needed to warm the upper layer of the oceans and the surface of the land, which means the actual *realized* surface temperature of the Earth will lag somewhat behind the equilibrium temperature. As shown in Figure 8.21, at any

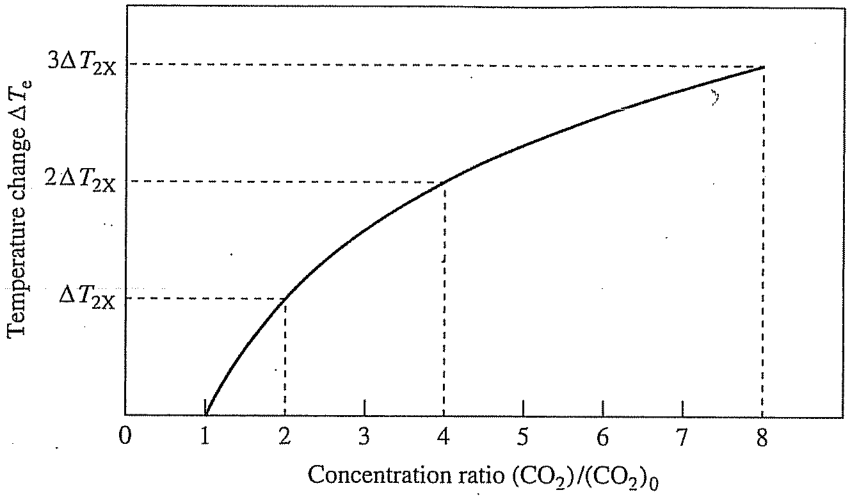


FIGURE 8.20 For every doubling of CO_2, the global equilibrium temperature increases by ΔT_{2X}.

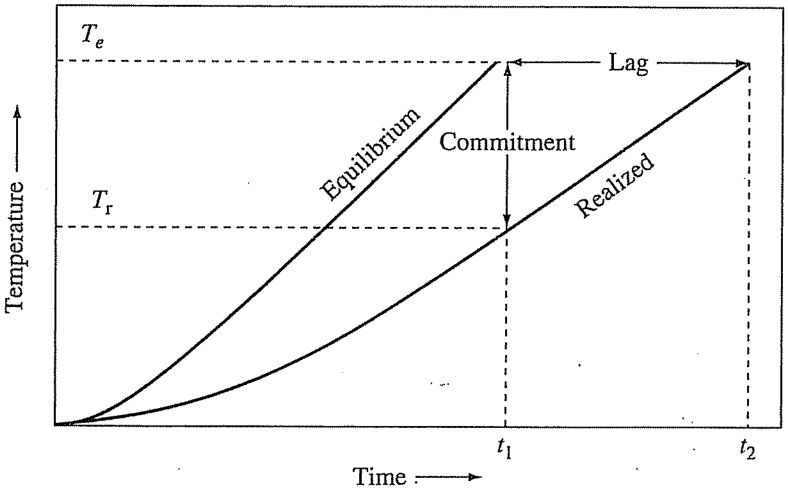


FIGURE 8.21 At time t_1, the realized surface temperature of the Earth is T_r, but even if there are no further increases in greenhouse gases, it will continue to rise to the equilibrium temperature T_e with a lag time of $t_2 - t_1$.

given time, the difference between realized and equilibrium temperature is referred to as the temperature *commitment*, while the time it takes to achieve equilibrium is the *lag time*. Coupled atmosphere-ocean general circulation models indicate that the realized temperature is roughly 60 to 85 percent of the equilibrium temperature.

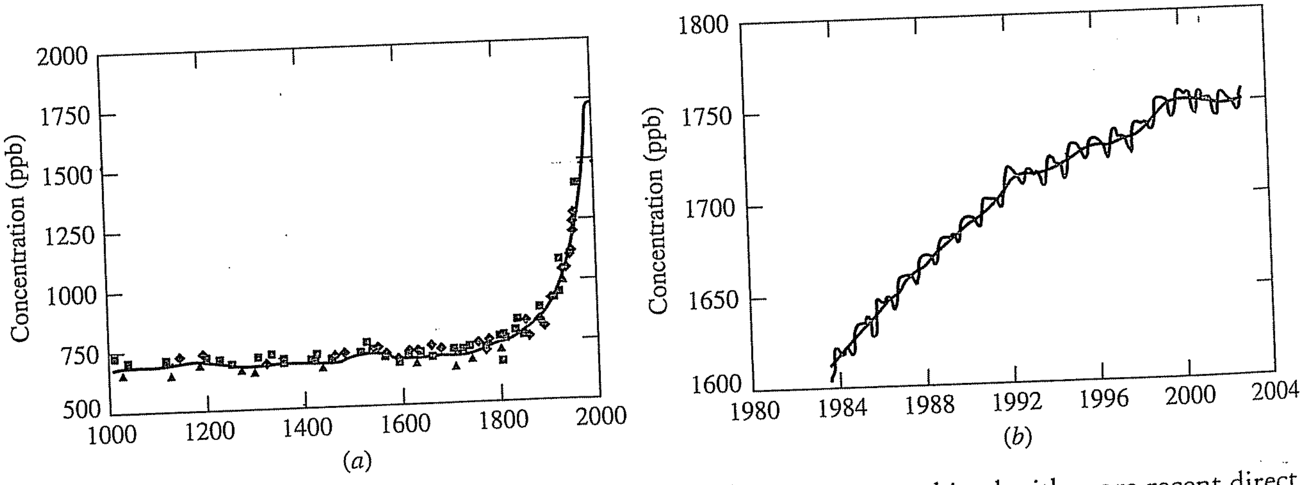
8.7 The Other Greenhouse Gases and Aerosols

While most of the attention on greenhouse gases has been directed toward CO_2 emissions, a number of other gases, as well as aerosols, contribute to our global warming problem. After introducing each one, we will see how they interact with each other and with the atmosphere to affect not only climate but also ozone depletion in the stratosphere.

Methane (CH_4)

Methane is another naturally occurring greenhouse gas that is increasing in concentration as a result of human activities. As shown in Figure 8.22, methane concentrations in the atmosphere were approximately 750 parts per billion (ppb) for many hundreds of years before they began their rapid climb in the 1800s. After a period of very rapid rise, their concentration in the atmosphere in the early years of the twenty-first century seems to be leveling off at about 1,750 ppb. Whether this is some new steady-state level or a temporary pause, remains to be seen.

Methane is produced by bacterial fermentation under anaerobic conditions, such as occurs in swamps, marshes, rice paddies, landfills, as well as in the digestive tracks of ruminants. Total emissions have been estimated to be on the order of 600 teragrams per year, of which about 60 percent are related to human activities such as agriculture, fossil fuel use, and waste disposal. Recent estimates of methane emissions from short-lived biomass and plant litter under aerobic conditions suggest methane's contribution to the observed global warming may have been significantly underestimated and a reassessment may be called for (Keppler et al., 2006).



(*a*) (*b*)

FIGURE 8.22 Methane concentrations from Antarctic ice cores (*a*) combined with more recent direct measurements (*b*).
(*Source:* IPCC, 2007.)

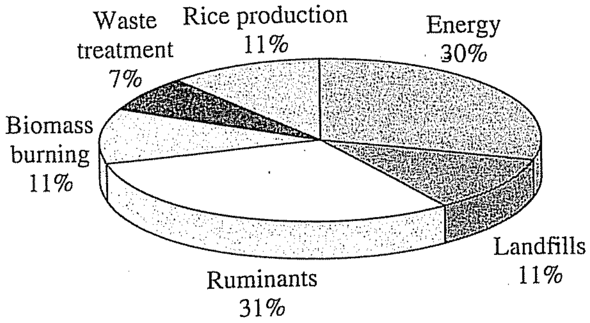


FIGURE 8.23 Anthropogenic sources of methane emissions, totaling some 370 Tg/yr. (*Source:* Based on Houweling et al., 1999.)

Almost half of anthropogenic methane emissions are the result of human food production, especially rice production and livestock, including cattle, sheep, and buffalo, which belch some 115 Tg of methane per year. Clearing and burning of biomass, in part to prepare land for grazing and crops, also contribute. Almost one-third of anthropogenic emissions are associated with fossil fuel use (Figure 8.23).

Methane has an absorption band centered at 7.7 μm, which places it right on the edge of the atmospheric window and makes it a very potent greenhouse gas. Its relatively short residence time in the atmosphere, on the order of 9 to 15 years, coupled with its high potency, suggests reducing methane emissions could be an effective means to reduce global warming on a relatively short timescale.

Methane is removed from the atmosphere primarily through reactions with the hydroxyl radical (OH), as the following reaction suggests:

$$CH_4 + OH + 9\,O_2 \rightarrow CO_2 + 0.5\,H_2 + 2\,H_2O + 5\,O_3 \qquad (8.30)$$

Methane is of course a greenhouse gas, so it has direct effects on the Earth's radiation balance. There are, however, a number of indirect effects that provide additional impacts, which reaction (8.30) helps explain. First, when methane reacts with hydroxyl (OH), the concentration of OH decreases. With less OH available, the rate of removal of CH_4 slows down, lengthening the atmospheric lifetime of the remaining methane. With a longer lifetime for CH_4 in the atmosphere, it continues to absorb infrared for a longer time, increasing its global warming potential. The second indirect effect that (8.30) implies is that as methane reacts with hydroxyl, it produces water vapor. When this reaction occurs in the troposphere, the increase in water vapor is insignificant, but in the stratosphere, it becomes quite important. Finally, (8.30) indicates the destruction of methane produces an increase in ozone, which is itself a greenhouse gas. The sum of all of these indirect effects greatly increases methane's climate impact.

There is some concern for the possibility that global warming could free large amounts of methane currently frozen in permafrost in the far northern regions of the world and could allow anaerobic decomposition of organic matter also frozen in permafrost, producing more methane. This is an important example of a positive feedback loop. Warming leading to increased releases of the greenhouse gas, methane, could reinforce the original warming.

Nitrous Oxide (N_2O)

Nitrous oxide ("laughing gas") is another naturally occurring greenhouse gas that has been increasing in concentration due to human activities (Figure 8.24). The current

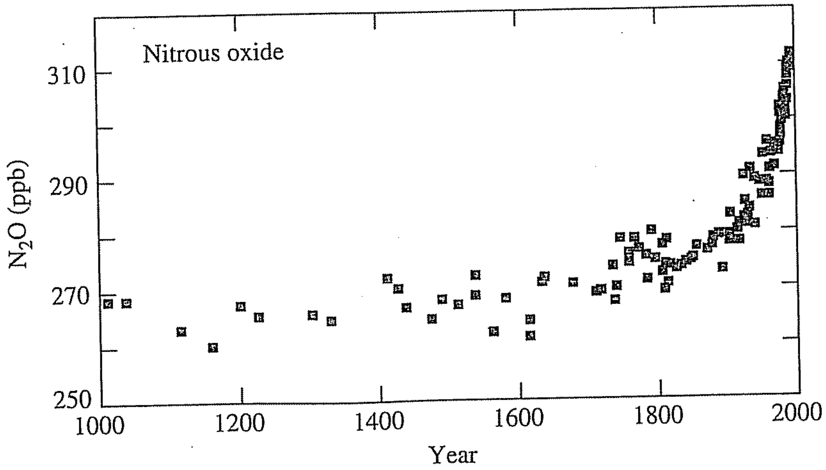


FIGURE 8.24 Increasing concentration of nitrous oxide and corresponding radiative forcing. (*Source:* IPCC, 2001.)

atmospheric concentration is about 320 ppb, which is a 16 percent increase over the preindustrial concentration of about 275 ppb.

Nitrous oxide is released into the atmosphere mostly during the nitrification portion of the nitrogen cycle:

NH_4^+	$\rightarrow$	N_2	$\rightarrow$	N_2O	$\rightarrow$	NO_2^-	$\rightarrow$	NO_3^-
Ammonium ion		Molecular nitrogen		Nitrous oxide		Nitrite ion		Nitrate ion

It is estimated that natural sources of N_2O deliver 9 Tg per year to the atmosphere, with most of that coming from oceans and wet forest soils. Anthropogenic sources, which add another 6 Tg/yr, are largely the result of forest clearing and nitrogen fertilizers. Other sources include three-way catalytic converters on cars, combustion of fuels containing nitrogen, and a variety of industrial processes such as the manufacture of nylon.

Apparently, there are no significant tropospheric sinks for N_2O, and it is only slowly degraded in the stratosphere by photolysis. As a result, it has a long atmospheric lifetime, estimated at about 120 years, which means perturbations in the natural cycle will have long-lasting repercussions. Nitrous oxide has an absorption band at 7.8 μm that is associated with a stretching of the bonds, and another at 8.6 μm associated with bending of the bond angle. The band at 7.8 μm is on the shoulder of the atmospheric window, and the band at 8.6 μm is right in the window, so N_2O is a very potent greenhouse gas.

Halocarbons

Halocarbons are carbon-based molecules that have chlorine, fluorine, or bromine in them. The carbon-to-fluorine bonds in halocarbons oscillate, and hence absorb, at wavelengths around 9 μm, and other bond stretching and bending in halocarbons also occur with frequencies in the atmospheric window, so these molecules are all potent greenhouse gases. They are environmentally important not only because they contribute to global warming, but also because chlorine and bromine atoms that find their way into the stratosphere have the ability to catalytically destroy ozone, as will be described later in this chapter.

Subcategories of halocarbons include *chlorofluorocarbons* (CFCs), which have only carbon, fluorine, and chlorine, but no hydrogen; *hydrochlorofluorocarbons* (HCFCs), which are like CFCs, but do contain hydrogen; *hydrofluorocarbons* (HFCs), which contain no chlorine; and *halons,* which are carbon-based molecules containing bromine along with fluorine and perhaps chlorine. These halocarbon gases differ from all of the other radiatively active gases in that they do not occur naturally, and their presence in the atmosphere is due entirely to human activities. Other important halocarbons include carbon tetrachloride (CCl_4), methyl chloroform (CH_3CCl_3), and methyl bromide (CH_3Br). With so many categories, it may help to show some examples, which Table 8.6 does.

Chlorofluorocarbons (CFCs) are nontoxic, nonflammable, nonreactive, and are not water soluble, which led to the belief when they were first invented that they were truly benign chemicals. But because they are inert and don't dissolve easily in water, they aren't destroyed by chemical reactions or removed from the troposphere by rain. That means they have long atmospheric lifetimes, as Table 8.6 suggests. The only known removal mechanism is photolysis by short-wavelength solar radiation, which occurs after the molecules drift into the stratosphere. It is the chlorine freed during this process that can go on to destroy stratospheric ozone. Similarly, halons, which contain bromine, have no tropospheric sinks, and their only removal mechanism is also photochemical decomposition in the stratosphere, which releases the ozone-depleting bromine.

TABLE 8.6

Examples of Halocarbons

Formula	Designation	Atmospheric Lifetime (yrs)
Chlorofluorocarbons (CFCs)		
$CFCl_3$	CFC-11	50
CF_2Cl_2	CFC-12	102
$CF_2ClCFCl_2$	CFC-113	85
Hydrochlorofluorocarbons (HCFCs)		
CHF_2Cl	HCFC-22	12.1
CH_3CFCl_2	HCFC-141b	9.4
$CF_3CF_2CHCl_2$	HCFC-225ca	2.1
Hydrofluorocarbons (HFCs)		
CF_3CH_2F	HFC-134a	14.6
CH_3CF_3	HFC-143a	48.3
Perfluorocarbons (PFCs)		
CF_4	Tetrafluoromethane	50,000
C_2F_6	Perfluoroethane	10,000
Halons		
CF_3Br	H-1301	65
CF_2ClBr	H-1211	20
Other		
CH_3CCl_3	Methyl chloroform	4.9
CH_3Br	Methyl bromide	0.7
CCl_4	Carbon tetrachloride	26

Source: IPCC, 1996.

Hydrochlorofluorocarbons (HCFCs) are being introduced as replacements for CFCs. By adding hydrogen to the molecules, they are no longer chemically inert, which means chemical reactions can destroy them in the troposphere before they have a chance to drift into the stratosphere. Notice the much shorter atmospheric lifetimes for the HCFCs in Table 8.6. HCFCs are only temporary replacements for CFCs, however, since they do still have some potential to deplete the ozone layer, and they are still potent greenhouse gases.

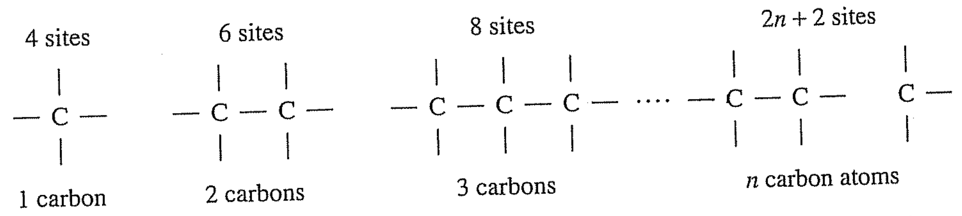
Hydrofluorocarbons (HFCs) have no chlorine at all, so they are even better than HCFCs in terms of stratospheric ozone protection. The hydrofluorocarbon CH_2FCF_3 (HFC-134a) is quickly becoming the refrigerant of choice for automobile air conditioners and refrigeration equipment. Even this chemical, however, has a sizable atmospheric lifetime (14.6 years), and, as a greenhouse gas, it is 1,400 times as potent as CO_2.

Perfluorocarbons (PFCs) are hydrocarbons containing only carbon and fluorine atoms. They are characterized by extreme stability, nonflammability, low toxicity, zero ozone depleting potential, and high global warming potential. For example, tetrafluoromethane (CF_4) has an atmospheric lifetime of 50,000 years, and its global warming potential is 6,500 times that of carbon dioxide.

Halons have the ozone-destroying element bromine in them. They are very stable molecules with no tropospheric sinks, so they only release that bromine when they eventually drift into the stratosphere and are broken apart by photolysis. The primary use of halons is in fire extinguishers. They are nontoxic and leave no residue when sprayed onto fires, so they are ideal for use in confined spaces containing critical equipment such as computers.

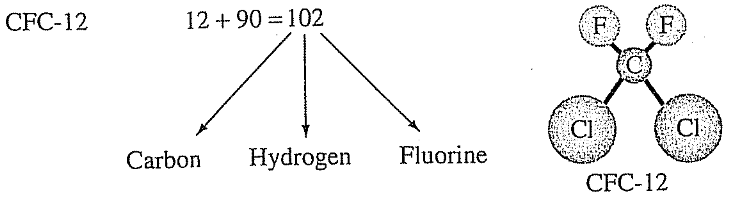
Halocarbon Numbering Systems. In Table 8.6, most of the halocarbons are identified by a simple numerical designation as well as a chemical formula. The CFCs, HCFCs, and HFCs are referred to using a number system developed years ago by DuPont. For example, trichlorofluoromethane, $CFCl_3$, is CFC-11, and the hydrochlorofluorocarbon CHF_2Cl is HCFC-22. To determine the chemical formula from a fluorocarbon number, begin by adding "90" to the number and then interpret the three-digit result as follows: The leftmost digit is the number of carbon atoms, the middle digit is the number of hydrogen atoms, and the right digit is the number or fluorines.

To determine the number of chlorine atoms, begin by visualizing molecules in which each carbon atom forms four single bonds to other atoms (if the other atoms are all hydrogens, this is the familiar alkane series: methane, ethane, propane, and so on):



A single carbon atom has four sites to fill, two carbon atoms have six sites, and so forth. All of the sites will be occupied by hydrogen, fluorine, or chlorine. So, to find the number of chlorines, just subtract the number of hydrogens and fluorines from the total available sites. Each vacant bonding site not taken up by fluorine or hydrogen is occupied by chlorine.

For example, to figure out what CFC-12 is, add 90 to 12 giving 102. So, there is 1 carbon, no hydrogens, and 2 fluorines. With 1 carbon there are 4 sites available, 2 of which are taken by fluorine, leaving 2 for chlorine.



Thus, CFC-12 is CF_2Cl_2.

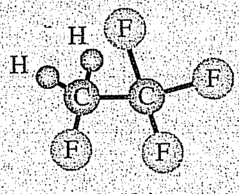
The halons also have a number system, but this one is not so complicated. Halons are given a four-digit designation, with the leftmost digit being the number of carbons, the second is fluorines, the third is chlorines, and the fourth is bromine. For example, H-1211 is CF_2ClBr.

EXAMPLE 8.8 Halocarbon Numbering

a. What is the chemical composition of CFC-115?
b. What is the CFC number for CH_2FCF_3?
c. What is H-2402?

Solution

a. CFC-115: Adding 90 to 115 gives 205. Thus, a molecule contains 2 carbons, no hydrogens, and 5 fluorines. Two carbons have 6 bonding sites, 5 of which are taken by fluorine. The remaining site is taken by chlorine. The chemical formula would therefore be C_2F_5Cl (more correctly written as $CClF_2CF_3$).
b. CH_2FCF_3 has 2 carbons, 2 hydrogens, and 4 fluorine atoms. Subtracting 90 from 224 gives 134. There is no chlorine or hydrogen, so this halocarbon is a hydrofluorocarbon, HFC-134. Notice that we can't tell whether this is CHF_2CHF_2 or CH_2FCF_3. To distinguish one isomer from another, a letter designation is added. For example, CHF_2CHF_2 is HFC-134 (1,1,2,2-tetrafluoroethane), and CH_2FCF_3 is HFC-134a (1,1,1,2-tetrafluoroethane).



HFC-134a

c. H-2402 is $C_2F_4Br_2$ ($CBrF_2CBrF_2$).

Refrigerants. Chlorofluorocarbons have many unusual properties that have led to their widespread use. For example, they are easily liquefied under pressure, and when that pressure is released, they evaporate and produce very cold temperatures.

In fact, they were originally developed to satisfy the need for a nontoxic, nonflammable, efficient refrigerant for home refrigerators. Before they were introduced in the early 1930s, the most common refrigerants were ammonia, carbon dioxide, isobutane, methyl chloride, methylene chloride, and sulfur dioxide. All had significant disadvantages. They were either toxic, noxious, highly flammable, or required high operating pressures that necessitated heavy, bulky equipment. From those perspectives, CFCs are far superior to any of the gases that they replaced. As a side note, fluorocarbons used in refrigeration equipment are often referred to with a "Refrigerant" number. For example, CFC-12 is often called "Refrigerant-12" or, more simply, R-12. The DuPont trade name Freon has also been used, so occasionally it is still called F-12. The "R" designation is also applied to other hydrocarbons such as methane (R-50) and ethane (R-170).

Until recently, most refrigerators, freezers, and automobile air conditioners used CFC-12 as the refrigerant, and large building air conditioning systems have tended to use CFC-11. CFC refrigerants do not wear out, so as long as they are sealed into equipment, the total emission rate can be small. Automobile air conditioners, however, tend to develop leaks that necessitate periodic recharging of their systems. Not long ago, when car air conditioners were serviced, the old refrigerant was usually vented to the atmosphere rather than being captured and recycled, which compounded the loss rate. As a result, automobile air conditioners used to contribute on the order of 20 percent of all emissions of CFCs in the United States. The Montreal Protocol and subsequent changes in the Clean Air Act have changed that picture significantly. Production and importation of CFCs ended in 1996, and air conditioners on new cars now tend to use HFC-134a and HFC-152a, which contain no chlorine. Only licensed facilities that use CFC recycling equipment can service older automobile air conditioners.

Aerosol Propellants. When CFCs were first hypothesized as a danger to the ozone layer by Molina and Rowland (1974), over half of worldwide emissions were from aerosol propellants for products such as deodorants, hair spray, and spray-paint cans. At that time, the United States alone was using over 200,000 tons per year of CFC-11 and CFC-12 in aerosols. The EPA responded rather quickly to the threat, and acting under the Toxic Substances Control Act, it banned the use of CFCs in nonessential aerosol propellant applications beginning in 1979. Norway, Sweden, and Canada adopted similar restrictions, but the rest of the world lagged far behind until recently. The Montreal Protocol has led to total bans in most of the developed world. Replacements for CFCs in aerosols include isobutane, propane, and carbon dioxide. In some applications, simple pumps or "roll on" systems have replaced the propellants.

Foamed Plastics. The second most common use for CFCs in general, and the most common use for CFC-11 in particular, has been in the manufacture of various rigid and flexible plastic foams found in everything from seat cushions to hamburger "clamshell" containers to building insulation. When liquid CFCs are allowed to vaporize in plastic, they create the tiny bubbles that make the plastic foamy.

Sheets of rigid "closed cell" urethane foams are used primarily as thermal insulation in buildings and refrigeration equipment. In such applications, the CFCs or HCFCs, which are poor thermal conductors, trapped in foam cells reduce the heat transfer capabilities of the product. CFCs have also been used to manufacture nonurethane, rigid foams such as extruded polystyrene (Dow's trade name is Styrofoam) used extensively for egg cartons and food service trays, and expanded polystyrene foam, which is used to make drinking cups. Since CFCs are trapped in the holes in closed-cell foams, they are only slowly released into the atmosphere as the material ages or is eventually crushed. It is estimated that the "bank" of CFCs and HCFCs trapped in rigid foam insulation is equivalent to about 19 Gt of CO_2. New production of HCFCs will be banned by 2020.

Replacements for these foams are possible. Polyisocyanurate foams made with hydrocarbon blowing agents such as pentane have no global warming potential or ozone-depletion potential, and they are excellent insulators. Fiberglass insulation, although thermally not as effective per unit of thickness, also contains no CFCs. Various cardboards and other paper products can be used to replace many of the polystyrene applications in the food industry.

Flexible foams, which are used in furniture, automobile seats, and packaging, have cells that are open to the atmosphere (open-cell). Hence, CFC release is almost immediate. These foams are made using carbon dioxide as the primary blowing agent, but the CO_2 is often augmented with methylene chloride.

Ozone (O_3)

Ozone has a strong absorption band at 9 μm, right in the middle of the atmospheric window (refer to Figure 8.11), so clearly it is a greenhouse gas of importance. It has, however, proven to be a difficult one to understand. It is not a "well-mixed" gas in the atmosphere the way all of the greenhouse gases described up to this point are. Not only does its concentration vary from place to place and time to time around the globe, but its effect on climate depends on its vertical distribution as well.

As was discussed in Chapter 7, ozone in the troposphere is formed by photochemical reactions involving relatively short-lived precursor gases, including NO_x, nonmethane-hydrocarbons, and CO. It is the principal gas in photochemical smog. And since smog is associated with the major industrialized areas of the world, it is not surprising that tropospheric ozone concentrations are higher in the Northern Hemisphere than in the Southern Hemisphere. Those concentrations also vary seasonally as sunnier summer months energize the formation of ozone. Ozone transported from the industrialized countries in the Northern Hemisphere to the Arctic has been identified as a major contributor to the current rapid warming of that region.

In the stratosphere, ozone concentrations are decreasing as a result of the attacks by chlorine and bromine released by UV-exposed CFCs and halons. These stratospheric ozone losses also vary by geographic location and by season as the annual appearance of the ozone hole over Antarctica in September and October certainly demonstrates. This ozone loss helps open the atmospheric window, which offsets some of the global warming caused by halocarbon emissions. As emissions of CFCs and halons into the atmosphere are curtailed, it is expected that ozone will recover in the early part of the twenty-first century, so this helpful impact of ozone depletion will diminish.

Aerosols

Suspensions of particles having an effective diameter of less than 10 μm are called aerosols. Some particles enter the atmosphere as solids (e.g., soil dust), and others are formed in the atmosphere when gases such as sulfur dioxide condense into liquid particles such as sulfates. Combustion of fossil fuels and biomass burning are the principal anthropogenic sources of aerosols. Natural sources of aerosols include wind-blown soil dust, evaporation of sea-spray droplets, and volcanic eruptions. While the natural emission rates from these and other sources far exceeds anthropogenic emissions, most of these particulates are so large that they quickly drop out of the troposphere. Smaller particles, especially ones that reach the stratosphere, are much more important in terms of their impact on climate as well as human health.

Aerosols have characteristics that make them considerably different from the well-mixed, long-lived greenhouse gases CO_2, CH_4, N_2O, and halocarbons. For one, they have atmospheric lifetimes that are measured in days or weeks in the troposphere, and a few years in the stratosphere, while greenhouse gases have lifetimes measured usually in decades, but for some, in thousands of years. The aerosols in the troposphere today are mostly particles that entered the atmosphere within the past few days. That means aerosol concentrations can vary considerably from week to week and from place to place. That short lifetime also implies that the radiative impacts of aerosols are likely to be regional phenomena, centered around the industrialized areas of the world, whereas greenhouse gas impacts are much more uniformly distributed around the globe. In fact, in some heavily industrialized parts of the world, the cooling caused by aerosols can be greater than the warming due to greenhouse gases. That doesn't necessarily mean, however, that such an area would experience cooling, since regional temperatures are so much affected by other factors.

Aerosols are also different from most greenhouse gases in that they cause both heating and cooling of the atmosphere. As Figure 8.25 suggests, they affect the Earth's energy balance in three ways: (1) they can reflect incoming solar radiation back into space, which increases the Earth's albedo; (2) they can provide cloud condensation nuclei, which increases cloud reflectivity and cloud lifetime, which also increases albedo; and (3) carbonaceous particles such as soot from fossil-fuel combustion can increase the atmospheric absorption of incoming solar energy. Sulfates and white smoke increase the albedo by enhancing atmospheric and cloud reflection,

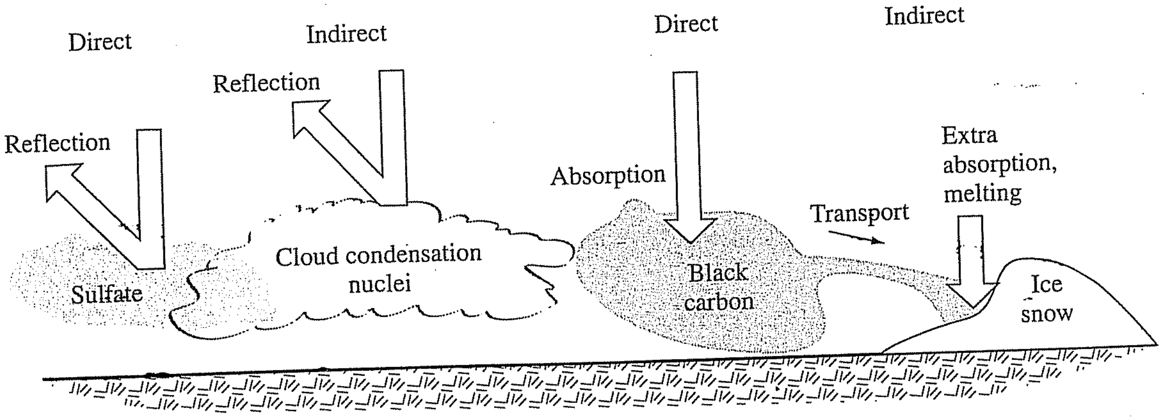


FIGURE 8.25 Aerosols provide cooling by increasing solar reflection off sulfates (direct effect) and white clouds (indirect). Black carbon warms the planet by absorbing sunlight (direct) and reducing albedo by helping to blacken and melt ice (indirect).

which helps cool the planet, and solar absorption by black smoke causes warming. The term *black carbon* (BC) is used to describe that black smoke, which consists of various carbonaceous products of incomplete combustion, including chars, charcoals, and soots.

The direct effect of black carbon absorption of incoming solar energy, warming the air itself, is amplified by its indirect effect as soot is transported and deposited onto snow-covered areas. By making the snow darker, its albedo is reduced causing further warming. And, as the soot-blackened snow melts, it exposes darker undersurfaces, further reducing albedo. These indirect albedo effects are estimated to more than double the warming impact of black carbon, making it a very important contributor to current global warming. Its importance, coupled with its extremely short atmospheric lifetime, suggest reducing black carbon may be the quickest way to slow the current rate of global warming.

8.8 Radiative Forcing of Climate Change

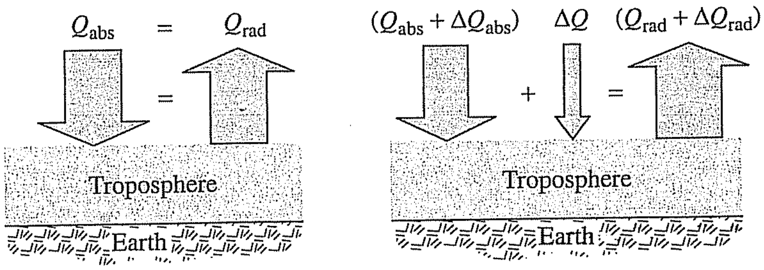
In the global equilibrium model shown earlier in Figure 8.12, the incoming 235 W/m^2 of solar energy absorbed by the Earth and its atmosphere is exactly balanced by 235 W/m^2 of outgoing long-wave radiation. If, for some reason, an additional amount of energy is added to the incoming energy, then the balance will be temporarily upset. Over time, however, the climate system will adjust to that change either by either increasing or decreasing the surface temperature of Earth until a balance is once again attained.

Mathematically, we can represent that process as follows. In Figure 8.26, the incoming energy absorbed, and outgoing energy being radiated, are shown as they exist at the top of the troposphere—that is, at the tropopause. Initially, the balanced system has energy absorbed equal to energy radiated:

$$Q_{\text{abs}} = Q_{\text{rad}} \tag{8.31}$$

When the system is perturbed by adding *radiative forcing*, ΔQ (W/m^2), to the incoming absorbed energy, a new equilibrium will eventually be established so that

$$(Q_{\text{abs}} + \Delta Q_{\text{abs}}) + \Delta Q = (Q_{\text{rad}} + \Delta Q_{\text{rad}}) \tag{8.32}$$



(a) Before (b) After

FIGURE 8.26 Radiative forcing, ΔQ, perturbs the balance between incoming solar energy absorbed, Q_{abs}, and outgoing radiant energy, Q_{rad}. (*a*) The balanced system before perturbation; (*b*) the balanced system after radiative forcing is added.

where the deltas refer to changes in the quantity in question. Subtracting (8.31) from (8.32) gives

$$\Delta Q = \Delta Q_{\text{rad}} - \Delta Q_{\text{abs}} \tag{8.33}$$

As we shall see, the value of the radiative forcing concept is that it provides a common currency for comparing the impacts of changes in individual greenhouse gases and aerosols, changes in albedo, and changes in the sun's radiation. Determining the radiative forcing associated with these has been one of the most important research areas for atmospheric scientists.

Another Climate Sensitivity Parameter

The key question, of course, is how much does the equilibrium surface temperature change ΔT_e for a given change in radiative forcing, ΔQ. The quantity that links the two is called the *mean climate sensitivity parameter* (λ) with units of °C of temperature rise per W/m^2 of radiative forcing. A linear expression for this relationship is often used:

$$\Delta T_e = \lambda \Delta Q \tag{8.34}$$

It has been established that a doubling of CO_2 is equivalent to a radiative forcing ΔQ of about 4.2 W/m^2. We already had another climate sensitivity parameter ΔT_{2X}, which is the equilibrium surface temperature change for a doubling of CO_2. The relationship between these two climate sensitivities is therefore

$$\lambda \approx \frac{\Delta T_{2X}}{4.2}\left(\frac{^\circ\text{C}}{\text{W/m}^2}\right) \tag{8.35}$$

Following a procedure outlined by the National Research Council (NRC, 2003) as a first cut at estimating λ, we might consider the Earth as a blackbody with no greenhouse effect and no complicating feedback factors, just as we did in Figure 8.9. The rate at which this Earth radiates energy (on a per-unit-of-area basis) is given by the Stefan-Boltzmann equation,

$$Q = \sigma T_e^4 \tag{8.36}$$

from which,

$$\frac{dQ}{dT} = \frac{d}{dT}(\sigma T_e^4) = 4\sigma T_e^3 \tag{8.37}$$

Using (8.8), we already have derived the equilibrium surface temperature T_e for this simplified Earth and found it to be 254 K. Substituting that value, along with the Stefan-Boltamann constant, into (8.34) gives

$$\lambda_B = \frac{1}{dQ/dT} = \frac{1}{4 \times 5.67 \times 10^{-8}\,\text{W/m}^2\text{K}^4 \times (254\text{ K})^3} = 0.27^\circ\text{C}/(\text{W/m}^2) \tag{8.38}$$

where the "B" in λ_B indicates this was derived assuming a blackbody Earth. If this sensitivity is used in (8.34) with a ΔT_{2X} forcing of 4.2 W/m^2, we would expect a doubling of CO_2 to cause an equilibrium surface temperature increase of $4.2 \times 0.27 = 1.1^\circ$C, which is far below what most general circulation models predict.

Not surprisingly, (8.38) is not a very good estimate because it does not account for any of a number of complicating feedback factors.

Ice-Albedo Feedback. Ice and snow are highly reflective. If global warming decreases their surface area, they will reflect less solar radiation (decreasing the albedo) and absorb more of it, which leads to greater warming. That is an example of a *positive feedback* effect in that a perturbation in one direction or another feeds back onto itself, increasing the original perturbation.

Water-Vapor Feedback. Water vapor is the most important greenhouse gas. Global warming increases evaporation, which enhances the absorption of long-wavelength energy radiated from the surface. That means the atmosphere warms up and radiates more energy back to the surface, which increases surface temperature. It is another positive feedback loop.

Cloud Feedbacks. Since clouds can be highly reflective, surface warming could lead to more clouds, which could increase the albedo, which could lower the surface temperature. This is an example of a *negative feedback effect,* in which feedback reduces the original perturbation. On the other hand, clouds contain water vapor, which is a greenhouse gas, so increasing clouds could lead to an enhanced greenhouse effect, which leads to more surface warming—positive feedback. Modeling both phenomena has proved to be one of the most challenging problems in climate science, but the consensus seems to be that the net effect of clouds yields a positive feedback.

Lapse-Rate Feedbacks. Water vapor and clouds in the upper troposphere are colder than the surface of the Earth, which means they radiate less energy toward space than does the surface. The difference between the two is, in essence, the greenhouse effect. If the lapse rate changes, which is the rate of decrease of temperature with altitude, then the temperature difference from surface to upper troposphere also changes, which can lead to greater or lesser greenhouse effect. When surface warming causes the lapse rate to increase, the greenhouse effect will be enhanced, which is a positive feedback.

Figure 8.27 shows one way to model feedback loops using a summing device and a feedback loop with a gain factor of g. The input is the blackbody sensitivity λ_B. The output λ is the climate sensitivity factor, including the impacts of feedback. The feedback factor g is positive for processes having positive feedback, and negative for those with negative feedback. From the diagram, we can write the following:

$$\lambda = \lambda_B + g\,\lambda \tag{8.39}$$

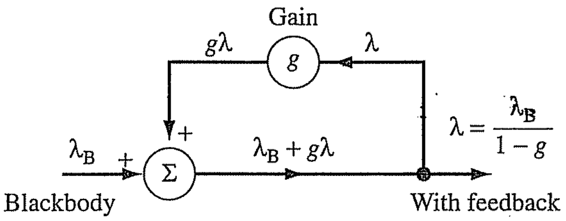


FIGURE 8.27 A simple model used to modify the blackbody climate sensitivity factor λ_B into a climate sensitivity factor λ that includes feedback phenomena.

Solving for λ gives

$$\lambda = \frac{\lambda_B}{1 - g} \tag{8.40}$$

The gain g used in the feedback model can be expressed as the sum of individual feedback factors

$$g = g_{\text{water vapor}} + g_{\text{cloud}} + g_{\text{surface ice}} + g_{\text{lapse rate}} + g_{\text{other}} \tag{8.41}$$

EXAMPLE 8.9 Climate Sensitivity with Feedback

Suppose the combined radiative forcing of greenhouse gases, aerosols, and solar intensity is 4.2 W/m^2, which is the focing that is thought to result from a doubling of CO$_2$. Using the blackbody sensitivity found in (8.38), $\lambda_B = 0.27°\text{C}/(\text{W/m}^2)$, find the global equilibrium temperature increase when the following feedback factors are included:

a. Water-vapor feedback, $g = 0.5$
b. Water-vapor feedback, $g = 0.5$, plus ice-albedo feedback, $g = 0.25$
c. Water-vapor feedback, $g = 0.5$, plus cloud feedback, $g = -0.25$
d. What feedback factor would yield an equilibrium $\Delta T_{2X} = 3.0$ K?

Solution: Including the specified feedbacks in (8.40) gives

a. The new sensitivity factor is $\lambda = \dfrac{\lambda_B}{1 - g} = \dfrac{0.27}{1 - 0.5} = 0.54°\text{C}/(\text{W/m}^2)$.

From (8.34), $\Delta T_e = \lambda \Delta Q = 0.54°\text{C}/(\text{W/m}^2) \times 4.2\ \text{W/m}^2 = 2.3°\text{C}$.

b. Including an additional $g = 0.25$ yields

$$\Delta T_e = \frac{\lambda_B}{1 - g}\Delta Q = \frac{0.27}{1 - 0.5 - 0.25} \times 4.2 = 4.5°\text{C}$$

c. With the -0.25 negative feedback provided by clouds,

$$\Delta T_e = \frac{\lambda_B}{1 - g}\Delta Q = \frac{0.27}{1 - 0.5 + 0.25} \times 4.2 = 1.5°\text{C}$$

d. From (8.35), for $\Delta T_{2X} = 3.0°\text{C}$,

$$\lambda = \frac{\Delta T_{2X}}{4.2} = \frac{3.0}{4.2} = 0.714°\text{C}/(\text{W/m}^2)$$

Rearranging (8.40) gives a feedback factor of

$$g = 1 - \frac{\lambda_B}{\lambda} = 1 - \frac{0.27}{0.714} = 0.62$$

The results shown in Example 8.9 span the typical range of climate sensitivity factors ΔT_{2X} used in global circulation models, ranging from 1.5°C to 4.5°C, and shows the feedback factor needs to be about 0.62 to produce the often-used $\Delta T_{2X} = 3°\text{C}$. Figure 8.28 points out how sensitive λ becomes as the feedback factor

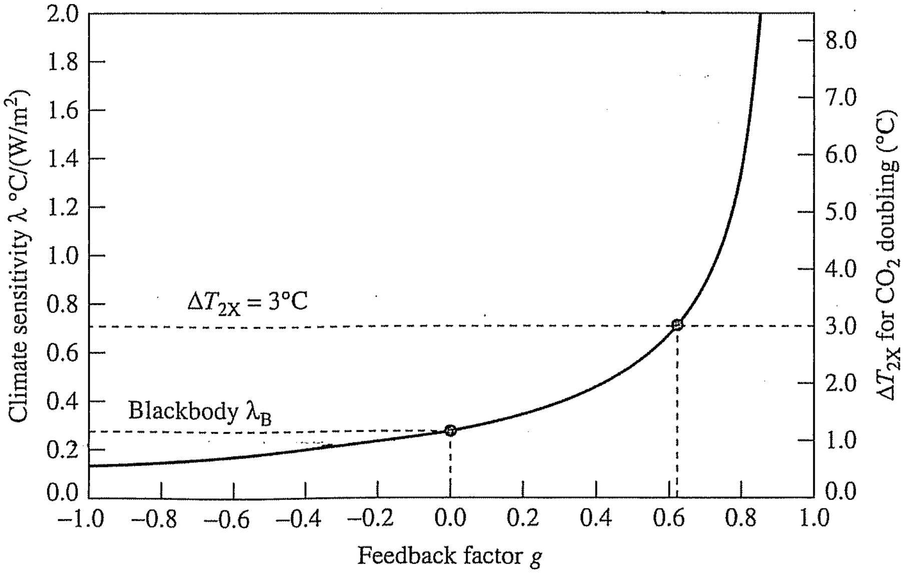


FIGURE 8.28 The climate sensitivity λ becomes very sensitive to the feedback factor as g approaches 1. An example with a 3°C equilibrium surface temperature change for a CO_2 doubling (ΔT_{2X}) is also shown.

increases. Once a strong positive feedback is present in the system, the impacts of other feedback processes are amplified.

The preceding analysis depends on a number of gross simplifications. It is a linear response model, which is really only valid for small perturbations around the equilibrium climate system. It assumes the various feedback processes (cloud, ice, lapse rate, and so on) are independent and additive, when in fact they do interact with each other. And it is an equilibrium analysis that ignores thermal capacitance and lag time responses, when the actual climate system is certainly not in equilibrium and won't be so for a good long time. Finally, the mathematics of (8.40) blows up for a feedback factor of $g = 1$, at which point the slightest radiative forcing would produce an infinite temperature change. It is introduced here as a rough guide to the relative importance of feedback processes.

Radiative Forcings Since Preindustrial Times

The concept of radiative forcing of climate change can be applied to the accumulation of greenhouse gases in the atmosphere, changes in aerosols from natural and anthropogenic sources, ozone depletion in the stratosphere, photochemically produced ozone accumulation in the troposphere, and the natural variability in solar intensity reaching Earth's outer atmosphere. Both positive and negative forcings are possible. Positive forcings contribute to global warming, while negative forcings tend to cool the Earth.

Gases and particulate matter added to the atmosphere can exert both *direct* and *indirect* radiative forcing effects. Direct forcing is caused by substances in the atmosphere that have actually been emitted from some source. Indirect forcings are those that occur when those substances go on to cause other atmospheric changes that affect radiative properties of the atmosphere. For example, aerosols have a direct effect on forcing when they absorb or reflect sunlight. Aerosols can also cause an indirect effect when they induce changes in the albedo of clouds. Halocarbons provide another example of direct and indirect effects. The direct effect of halocarbons is an increase in radiative forcing as these gases absorb long-wave radiation from the Earth. They also, however, cause an indirect effect by destroying ozone in the stratosphere. Recall from Figure 8.11 that ozone absorbs in the middle of the atmospheric window, so ozone destruction opens the window and allows the Earth to cool more readily. The direct effect of halocarbons therefore contributes to global warming, while the indirect effect of destroying ozone works in the opposite direction to help to cool the planet.

Figure 8.29 shows global average radiative forcing estimates associated with CO_2, the other greenhouse gases (CH_4, CFCs, N_2O), aerosols, land-use changes, and the estimated increase in solar intensity that has occurred in this period. Aerosol effects are broken out into the positive forcing caused by black carbon and the negative forcings caused by the indirect impact of reflective aerosols and induced cloud changes.

Several features stand out. Carbon dioxide provides the largest forcing, but the others are significant; conventional air pollution, responsible for black carbon and ozone, is also substantial; and the largest uncertainties are associated with aerosol

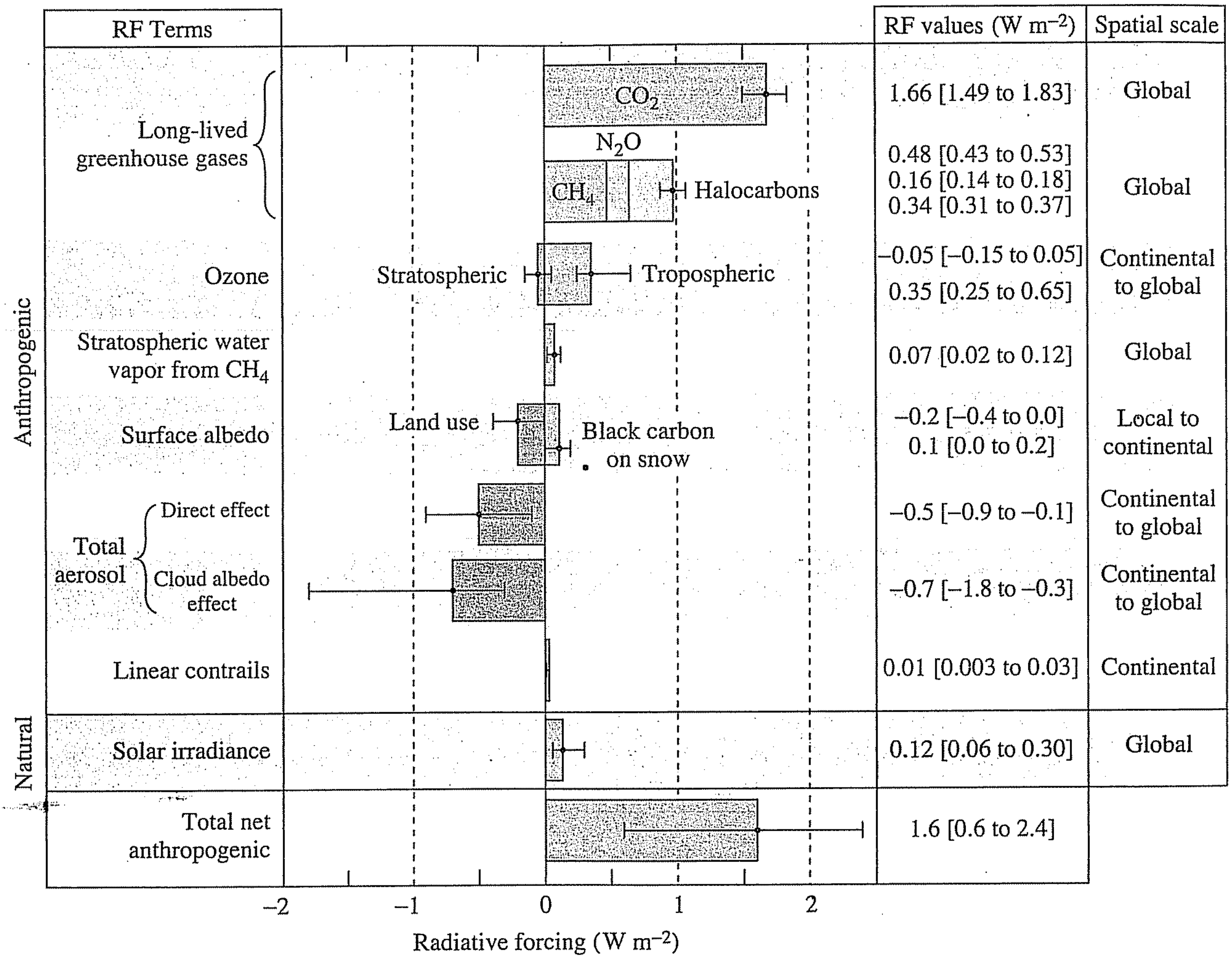


FIGURE 8.29 Global mean radiative forcing during the Industrial Era, 1750–2005, in W/m^2. Carbon dioxide is the best understood and ranks as the most important. Estimates of aerosol effects are significant and show the greatest uncertainty. Error bars are based on one standard deviation probabilities. (*Source:* IPCC, 2007.)

effects, both direct and on clouds. In spite of the significant black carbon contribution to warming, the net effect of aerosols seems to be negative, meaning global cooling, but the uncertainties shown make that not a clear assertion.

The 2007 IPCC 4th Assessment Report (AR4) asserts with very high confidence that the globally averaged net effect of human activities since 1750 has been one of warming with a radiative forcing of +1.6 W/m^2 (+0.6 to +2.4). The combined forcing due to greenhouse gases themselves is +2.3 W/m^2, and its rate of increase during the industrial era is very likely to have been unprecedented in more than 10,000 years.

EXAMPLE 8.10 Combined Forcings

Using the IPCC estimate of 1.6 W/m^2 net radiative forcing shown in Figure 8.29, along with an equilibrium temperature increase caused by those forcings of 0.8°C, find the following:

a. The climate sensitivity factor λ, °C/(W/m^2)
b. The feedback gain factor g
c. The temperature climate sensitivity ΔT_{2X} (°C)

Solution

a. From (8.34), we get the climate sensitivity:

$$\lambda = \frac{\Delta T_e}{\Delta Q} = \frac{0.8}{1.6} = 0.5°\mathrm{C}/(\mathrm{W/m^2})$$

b. From (8.40), the feedback gain factor is

$$g = 1 - \frac{\lambda_B}{\lambda} = 1 - \frac{0.27}{0.5} = 0.54$$

c. From (8.35), we estimate the temperature sensitivity for a doubling of CO$_2$:

$$\Delta T_{2X} = 4.2\lambda = 4.2 \times 0.54 = 2.27°\mathrm{C}$$

The simple summation of forcings suggested in the preceding example assumes that 1 W/m^2 of one constituent (e.g., CO$_2$) has the same impact as 1 W/m^2 of another (e.g., solar intensity). A new *radiant forcing efficacy* factor E is based on weighing each climate sensitivity in terms of its global warming impact with respect to CO$_2$.

$$E = \frac{\lambda}{\lambda_{CO_2}} \tag{8.42}$$

For example, the well-mixed greenhouse gases have an efficacy of 1.0, while the direct and indirect effect of aerosols might have an efficacy of 0.72 (National Research Council, 2005). If, for example, the forcing of greenhouse gases is 3.0 W/m^2 while aerosols have a net forcing of −1.8 W/m^2, the combined impact of the two with and without considering efficacy would be

$$(\mathrm{CO_2} + \text{aerosol})\text{-forcing without efficacy} = 3.0 + (-1.8) = 1.2\ \mathrm{W/m^2}$$

$$(\mathrm{CO_2} + \text{aerosol})\text{-forcing with efficacy} = 3.0 \times 1.0 + (-1.8) \times 0.72 = 1.7\ \mathrm{W/m^2}$$

Clearly, the efficacy factor concept could have a significant impact on models based on radiant forcing.