The Global Carbon Cycle

INTRODUCTION

The carbon cycle is of central importance to biogeochemistry. Life is composed primarily of carbon, so estimates of the global production and destruction of organic carbon give us an overall index of the health of the biosphere—both past and present. Photosynthetic organisms capture sunlight energy in organic compounds that fuel the biosphere and account for the presence of molecular O_2 in our atmosphere. Thus, the carbon and oxygen cycles on Earth are inextricably linked, and the presence of O_2 in Earth's atmosphere sets the redox potential for organic metabolism in most habitats. Through oxidation and reduction, organisms transform the other important elements of life (e.g., N, P, and S) in reactions that capitalize on the presence of organic carbon and oxygen on Earth. When we understand the carbon cycle, we can make accurate first approximations of the movement of elements in other global cycles, recognizing the predictable stoichiometry of the chemical elements in organic matter. Finally, there is good evidence that through the burning of fossil fuels and other activities, humans have altered the global cycle of carbon, causing the atmospheric concentration of CO_2 to rise to levels that have never been experienced during the evolutionary history of most species that now occupy our planet (Pearson and Palmer 2000).

In this chapter, we consider a simple model for the carbon cycle on the Earth and for assessing human impacts on that cycle. We then consider the magnitude of past fluctuations in the carbon cycle to gain some perspective on the current human impact. We look briefly at the

budgets of methane (CH_4) and carbon monoxide (CO) in the atmosphere. Because increasing concentrations of carbon dioxide and methane are associated with global warming through the greenhouse effect (Figure 3.2), the global carbon cycle is directly linked to considerations of global climate change and to international efforts to combat global warming. Finally, we examine the linkage of the carbon and oxygen cycles on Earth as a means of "cross-checking" our estimated budgets for these elements at the global level.

THE MODERN CARBON CYCLE

The Earth contains about 32×10^{23} g of carbon (Marty 2012). About 7×10^{22} g C is found in the upper mantle (Zhang and Zindler 1993). At the crust of the Earth, carbon is found in sedimentary rocks (Table 2.3), where it is held in organic compounds (1.56×10^{22} g C; Des Marais et al. 1992) and carbonates (5.4–6.5×10^{22} g C; Li 1972, Lecuyer et al. 2000; compare Table 2.3). Conventional fossil fuels are estimated to contain 4×10^{18} g C (Sundquist and Visser 2005). Live microbial biomass is a small component of the sedimentary organic carbon, perhaps containing up to 100×10^{15} g C (Lipp et al. 2008; compare to Whitman et al. 1998, who suggest up to 546×10^{15} g C).

The sum of the active pools of carbon at the Earth's surface is about 40×10^{18} g C (Figure 11.1). Dissolved inorganic carbon in the ocean is the largest near-surface pool, which has an enormous
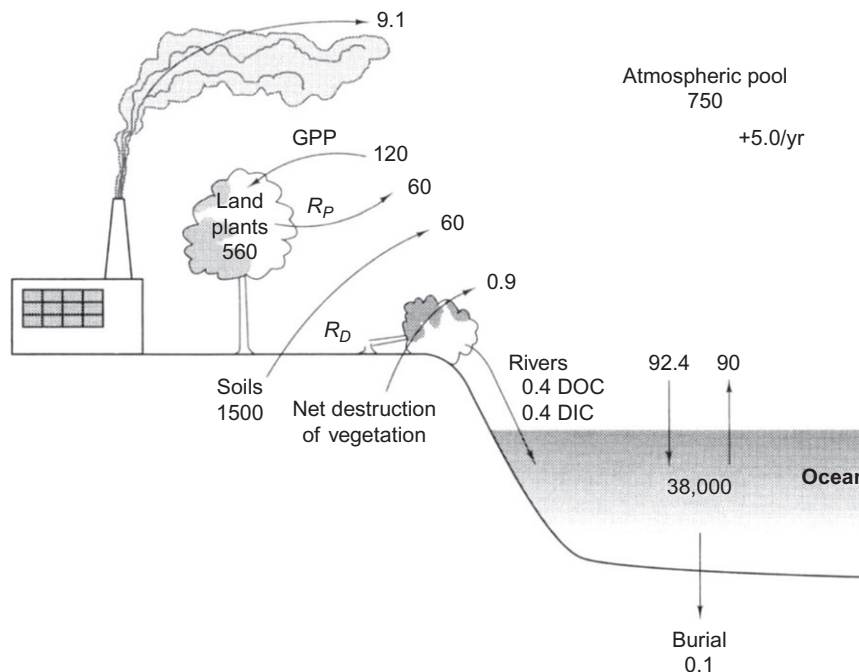

FIGURE 11.1   The global carbon cycle. All pools are expressed in units of 10^{15} g C and all annual fluxes in units of 10^{15} g C/yr, estimated for 2010. Values are taken from the text.

capacity to buffer changes in the atmosphere via Henry's Law (Eq. 2.7). At equilibrium, the sea contains about 50 times as much carbon as the atmosphere (Raven and Falkowski 1999). On land, the largest pool of carbon is contained in soils (Table 5.4). Even though atmospheric CO_2 is measured in parts per million, the atmosphere contains more carbon than all of the Earth's living vegetation (600×10^{15} g C; Table 5.3).

The largest fluxes of the global carbon cycle are those that link atmospheric carbon dioxide to land vegetation and to the sea (Figure 11.1). Global net primary production on land is estimated at 60×10^{15} g C/yr (Chapter 5), which is about half of recent estimates of gross primary production from the MODIS satellite (Beer et al. 2010, Ryu et al. 2011, Jung et al. 2011). Considering land vegetation alone, we find that each molecule of CO_2 in the atmosphere has the potential to be captured in net primary production in about 12.5 years. The annual exchange of CO_2 with the oceans is somewhat greater, so the overall mean residence time of CO_2 in the atmosphere is about 5 years.[1] Because this mean residence time is similar to the mixing time of the atmosphere, CO_2 shows small regional and seasonal variations that are superimposed on its global average concentration of nearly 400 ppm today (Figure 3.6).

The oscillations in the atmospheric content of CO_2 are the result of the seasonal uptake of CO_2 by photosynthesis in each hemisphere and seasonal differences in the use of fossil fuels and in the exchange of CO_2 with the oceans. The role of photosynthesis is indicated inasmuch as the oscillation in CO_2 is mirrored by slight oscillations in atmospheric O_2, which has a much longer mean residence time in the atmosphere and a much larger pool size (Figure 1.1). Globally, about two-thirds of the terrestrial vegetation occurs in regions with seasonal periods of growth, and the remainder occurs in the moist tropics, where growth occurs throughout the year (Box 1988). The seasonal effect of photosynthesis on atmospheric CO_2 is most pronounced in the Northern Hemisphere (Figure 3.6; Hammerling et al. 2012), which contains most of the world's land area. At high northern latitudes, vegetation accounts for about 50% of the seasonal variation in atmospheric CO_2 (D'Arrigo et al. 1987). In the Southern Hemisphere, smaller fluctuations in atmospheric CO_2 are seasonally reversed relative to the Northern Hemisphere, and they appear to be dominated by exchange with ocean waters (Keeling et al. 1984). The oscillation at Mauna Loa, Hawaii, located at 19° N latitude, is about 6 ppm/yr (Figure 1.1), equivalent to a transfer of about 13×10^{15} g C/yr to and from the atmosphere. This value is less than the annual net primary productivity of land plants (Table 5.3) because of the asynchrony of terrestrial photosynthesis and respiration throughout the globe and the buffering of atmospheric CO_2 concentrations by exchange with the oceans.

The release of CO_2 in fossil fuels, currently more than 9×10^{15} g C/yr, is one of the best-known values in the global carbon cycle.[2] If all of this CO_2 accumulated in the atmosphere, the annual increment would be >1.0%/yr. In fact, the atmospheric increase is about 0.4%/yr (2 ppm) because only about 56% of the fossil fuel release remains in the atmosphere (Sabine

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[1] This calculation is based on the traditional definition of mean residence time for a steady-state pool (i.e., mass/input) see footnote 1, Chapter 3. A recent report of the Intergovernmental Panel on Climate Change (Houghton et al. 1995; Table 3, p. 25) indicates a mean residence time of 50 to 200 years for atmospheric CO_2. This is actually the time it would take for the current human perturbation of the atmosphere to disappear into other pools at the Earth's surface (e.g., the ocean) if the use of fossil fuels were to cease. Thus, it would take several centuries to return steady-state conditions to the carbon cycle on Earth.

[2] *www.globalcarbonproject.org/carbonbudget/10/presentation.htm*.

et al. 2004). This is known as the "airborne fraction," which has increased slightly in recent years (Canadell et al. 2007, Le Quere et al. 2009). Where is the rest?

Oceanographers believe that about 32% ($\sim 2 \times 10^{15}$ g C/yr) of the CO_2 released from fossil fuels enters the oceans each year (Sabine et al. 2004, Khatiwala et al. 2009). This estimate is derived from measurements of the simultaneous increase in chloroflurocarbons, ^3H, ^{14}C, $\delta^{13}C$, and total inorganic carbon in seawater as a result of human activities (e.g., McNeil et al. 2003, Sweeney et al. 2007, Quay et al. 2003, Takahashi et al. 1997). Thus, Figure 11.1 shows an annual uptake by the oceans (92×10^{15} g/yr) that is slightly greater than the return of CO_2 to the atmosphere (90×10^{15} g C/yr). Following Henry's Law (Eq. 2.7), the excess CO_2 dissolves in seawater, where it causes ocean acidification and dissolution of marine carbonates (Eqs. 9.3–9.5). The uptake of CO_2 by the oceans shows significant year-to-year variation, amounting to $\sim 20\%$ of the estimated net flux (Gruber et al. 2002, Watson et al. 2009). Most of the uptake occurs in the large areas of downwelling water in the North Atlantic and Southern oceans (Figure 11.2) and in continental shelf areas throughout the world (Thomas et al. 2004a). Owing to the low levels of nutrients in seawater, changes in marine NPP are believed to be relatively unimportant to the current oceanic uptake of anthropogenic CO_2, which is largely determined by the dissolution of CO_2 in the surface waters (Shaffer 1993).

Remembering that the exchange of CO_2 between the atmosphere and the oceans takes place only in the surface waters (Chapter 9), we can calculate the mean residence time of CO_2 in the surface ocean—about 10 years—by dividing the pool of carbon in surface waters
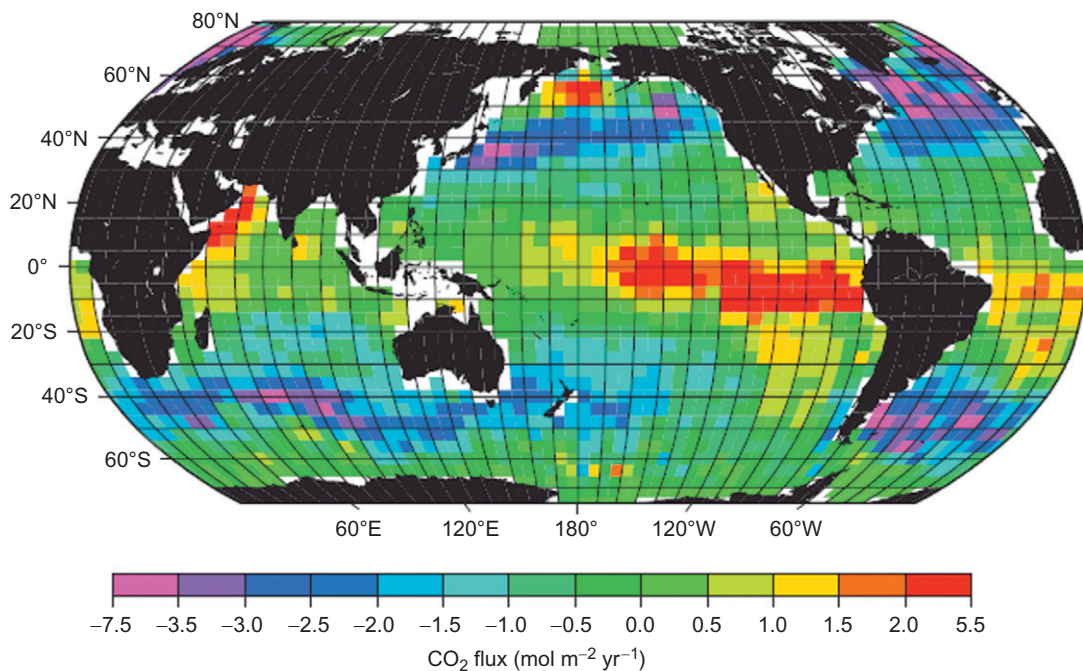

FIGURE 11.2   Estimates of the flux of CO_2 between the atmosphere and the oceans' surface for 1995. *Source: From Denman et al. (2007). Used with permission of Cambridge University Press.*

TABLE 11.1 Global Budget for Anthropogenic CO_2 in Earth's Atmosphere

	Fossil fuel		Biomass destruction[a]	=	Atmospheric increase		Ocean uptake		Terrestrial uptake	References
1990s	6.4	+	1.6	=	3.2	+	2.2	+	2.6	IPCC (2007)
2000–2007			1.1						2.3	Pan et al. (2011)
2010[b]	9.1		0.9		5.0		2.4		2.6	

Note: All data in 10^{15} g C/yr.
[a] Net biomass destruction in the tropics.
[b] Source: www.globalcarbonproject.org/carbonbudget/index.htm.

$(921 \times 10^{15}$ g C) by the rate of influx $(92 \times 10^{15}$ g C/yr). A similar mixing time is calculated from the distribution of ^{14}C in the surface ocean (Chapter 9). Turnover of carbon in the entire ocean is much slower, about 350 years—consistent with the age of deep ocean waters. Thus, the uptake of CO_2 by the oceans is constrained by mixing of surface and deep waters—not by the rate of dissolution of CO_2 across the surface (Chapter 9). Significantly, if the oceans were completely mixed, they might take up as much as 6×10^{15} g C/yr (Keeling 1983), indicating that it is the rate of release from fossil fuels relative to the rate at which the oceans can take up carbon that accounts for the current increase of CO_2 in the atmosphere. If the release of CO_2 from fossil fuels were curtailed, nearly all the CO_2 that has accumulated in the atmosphere would eventually dissolve in the oceans and the global carbon cycle would return to a steady state in a couple of hundred years (Laurmann 1979).

Taken alone, the atmospheric increase and oceanic uptake of CO_2 account for almost 90% of the annual emissions from fossil fuels (Sabine et al. 2004). Considering the errors associated with these global estimates, it would seem that we have a fairly tidy picture of the global carbon cycle. However, many terrestrial ecologists believe that there have also been substantial releases of CO_2 from terrestrial vegetation and soils, caused by the destruction of forest vegetation in favor of agriculture, especially in the tropics (Chapter 5). If their calculations are accurate, then the atmospheric budget is misbalanced, and a large amount of carbon dioxide that ought to be in the atmosphere is "missing" (Table 11.1).

The net release of CO_2 from vegetation is difficult to estimate globally (Chapter 5). At any time, some land is being cleared, while agriculture is abandoned in other areas that are allowed to regrow. For example, the Amazon Basin appears roughly in balance with respect to carbon flux, despite observations of widespread deforestation in the region (Houghton et al. 2000, Hansen et al. 2010). Estimates of carbon flux from the Amazonian rainforest are complicated by significant year-to-year variation, and the region is a net source of CO_2 during droughts (Tian et al. 1998, Phillips et al. 2009, Potter et al. 2011).

Historical changes in the ^{13}C and ^{14}C isotopic ratios in atmospheric CO_2 show unequivocal evidence of a net release from the biosphere early in this century (Wilson 1978).[3] Both are diluted by burning of fossil fuels, whereas only ^{13}C is reduced by burning vegetation.

[3] The changes in $^{14}CO_2$ in the atmosphere were only meaningful until the early 1960s, when the atmospheric signal was overwhelmed by the release of radiocarbon from atmospheric testing of nuclear weapons.

Until about 1960, the release from land clearing may have exceeded the release from fossil fuel combustion (Houghton et al. 1983). For the 1990s, estimates of the net CO_2 released from deforestation in the tropics range from 0.9 to 1.5×10^{15} g C (DeFries et al. 2002, Pan et al. 2011), but recent estimates of the *gross* release of carbon from tropical deforestation is much less—0.81×10^{15} g C/yr (Harris et al. 2012). The release of carbon from tropical deforestation is partially balanced by the carbon captured by the regrowth of forests in temperate and boreal regions, estimated as 0.65 to 1.17×10^{15} g C (Goodale et al. 2002, Myneni et al. 2001, Pan et al. 2011). Forests in the United States—mostly in New England—now appear to accumulate 0.1 to 0.2×10^{15} g C/yr (Birdsey et al. 1993, Turner et al. 1995, Woodbury et al. 2007, Thompson et al. 2011, Zhang et al. 2012a). Similar amounts of forest regrowth are estimated for Europe (0.165×10^{15} g C/yr; Peters et al. 2010), China ($<0.26 \times 10^{15}$ g C/yr; Piao et al. 2009), and Russia ($<0.13 \times 10^{15}$ g C/yr; Beer et al. 2006). Old-growth tropical forests also appear to provide net carbon storage from the atmosphere (Lewis et al. 2009, Davidson et al. 2012), so the global net sink for carbon in vegetation may be about 1.1×10^{15} g C/yr (Pan et al. 2011). Niwa et al. (2012) provide an independent estimate of the gross carbon sequestration in land vegetation (2.22 PgC/yr) using measurements of variations in atmospheric CO_2 obtained from passenger aircraft (compare Table 11.1). Global estimates of changes in the carbon held in vegetation and soils will improve with the application of remote sensing by satellites, which shows a significant flux of carbon from selective logging, not normally considered in estimates of deforestation (Asner et al. 2010). Any net release of carbon from land complicates our ability to balance a carbon dioxide budget for the atmosphere (Table 11.1).

We might reconcile the carbon dioxide budget of the atmosphere if we find evidence that the pool of carbon in land vegetation and soils has increased as a result of a global stimulation of plant growth by higher concentrations of atmospheric CO_2 (Chapter 5). Despite widespread forest destruction, enhanced uptake of CO_2 in areas of undisturbed vegetation could act as a sink for atmospheric CO_2 and add to the pool of carbon on land. The overall stimulation of terrestrial photosynthesis by human activities is informally known as the "beta" factor in models of the global carbon cycle. Beta is usually defined as the change in NPP that would derive from a doubling of atmospheric CO_2 concentration. In controlled experiments with tree seedlings, the beta factor usually lies in a range of 32 to 41% as a result of CO_2 fertilization (Poorter 1993, Curtis and Wang 1998, Wang et al. 2012). Free-Air CO_2 Enrichment (FACE) experiments (Chapter 5) show an average 18% stimulation of net primary production in forests grown at 1.5 times current levels of CO_2 (Norby et al. 2005). Most of the net carbon uptake is stored in woody biomass (McCarthy et al. 2010); changes in soils are less dramatic (van Groenigen et al. 2006, Lichter et al. 2008). Through a reallocation of photosynthate to roots, many trees appear to avoid the nutrient deficiencies that might be expected to develop as a result of faster growth at high CO_2 (Drake et al. 2011). However, soil nitrogen appears to constrain the long-term growth response at the FACE experiment at Oak Ridge, Tennessee (Norby et al. 2010, Garten et al. 2011).

The historical record of CO_2 in the atmosphere offers several indirect approaches for estimating changes in global net primary production and the potential for a significant, positive beta factor. For example, in the record of atmospheric CO_2 in the Northern Hemisphere, the seasonal decline each summer is largely due to photosynthesis, while the seasonal upswing in the autumn derives from decomposition. An increasing *amplitude* of the CO_2 oscillation, after the removal of fossil fuel and El Niño effects, implies a greater activity of the terrestrial
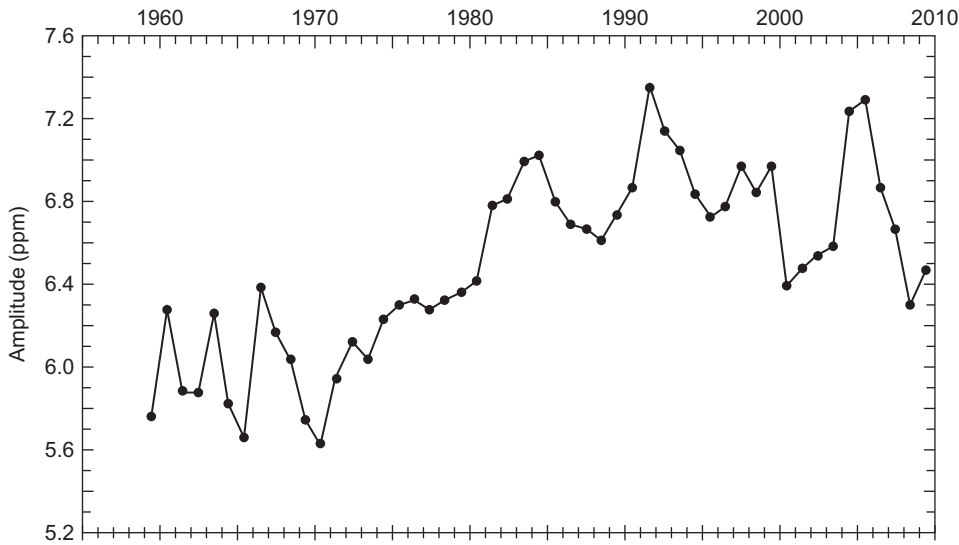
FIGURE 11.3 Increasing amplitude of the seasonal oscillations in atmospheric CO_2 at Mauna Loa, Hawaii. *Source: From Steve Piper, personal communication (2012).*

biosphere outside the tropics, where growth and decomposition occur year-round. Such a trend is evident in an analysis of the Mauna Loa record of CO_2 (Figure 11.3), in which the amplitude has increased by about 0.54%/yr from 1958 until the mid 1990s (Bacastow et al. 1985, Keeling 1993). The increase of amplitude at high northern latitudes has been about 0.66%/yr since 1960, perhaps as a result of climatic warming in this region over the same period (Keeling et al. 1996, Randerson et al. 1997). Although an increasing annual oscillation in the concentration of atmospheric CO_2 suggests that biospheric processes have been stimulated, we should not necessarily assume that a greater amount of carbon is being stored on land. Greater rates of decomposition may simply balance increased rates of photosynthesis (Houghton 1987, Keeling et al. 1996, Piao et al. 2008).

There is a small difference (about 4 ppm) in the concentration of atmospheric CO_2 between the Northern and the Southern Hemispheres, owing to the greater use of fossil fuel in the Northern Hemisphere (Keeling 1993). This observed latitudinal gradient in atmospheric CO_2 can be compared to the concentrations of CO_2 that would be expected due to the rate of mixing of the atmosphere, as calculated from general circulation models (Chapter 3). In fact, many of these models suggest that the concentration in the Northern Hemisphere, particularly at temperate latitudes, should be even greater than what is actually observed in the atmosphere, implying that there is significant uptake, perhaps by land plants (Tans et al. 1990, Denning et al. 1995, Fan et al. 1998b). The relative importance of land plants (versus uptake by the ocean) is also indicated by a latitudinal gradient in the isotopic ratio of atmospheric CO_2 (i.e., $\delta^{13}C$), which is fractionated by photosynthesis but not by dissolution in seawater (Ciais et al. 1995). These *inverse* models suggest a net uptake of carbon dioxide in vegetation worldwide—largely in forests, which contain most of the world's biomass.

Despite substantial theoretical and indirect evidence that it *should* occur, the direct evidence that an enhanced growth of land plants (e.g., changes in tree-ring thickness) currently acts as a large sink for atmospheric CO_2 is equivocal (Chapter 5). Our knowledge of the overall response of the terrestrial biosphere to future conditions is limited to a few studies that have examined changes in both CO_2 and temperature. Whereas plant uptake of CO_2 might increase as a result of longer growing seasons, one might expect substantial carbon losses from warmer soils. Oechel et al. (1994) found that wet tundra ecosystems in Alaska showed a complete physiological adjustment and no net carbon storage in response to a 3-year exposure to elevated CO_2. However, carbon storage in these ecosystems increased when both CO_2 and temperature were maintained at elevated levels. It is possible that the warmer soil temperatures enhanced decomposition, improving the supply of nutrients for plant growth (Van Cleve et al. 1990). Because the C/N ratio of soil organic matter (12–15) is lower than the C/N ratio of plant tissues (about 160; Table 6.5), a small amount of additional nitrogen mineralization in soils could yield a large enhancement of NPP and carbon sequestration in plants (Rastetter et al. 1992, McGuire et al. 1992). In a soil-warming experiment at the Harvard Forest in Massachusetts. Melillo et al. (2011) found that the mobilization of nitrogen from decomposing soil organic matter stimulated carbon uptake by the trees, so that changes in net carbon storage in the entire ecosystem were relatively minor.

Many areas of the world receive an excess atmospheric deposition of nitrogen derived from anthropogenic emissions of NO_x and NH_3 (Chapters 3 and 12). In some areas the N input is so extreme that symptoms of forest decline are observed (Chapter 6), but in other areas the added nitrogen has the potential to act as a fertilizer, stimulating plant growth (Townsend et al. 1996). If the global human production of fixed N ($\sim 100 \times 10^{12}$ g/yr; Chapter 12) were all stored in the woody tissues of plants with a C/N ratio of ~ 160 (Table 6.5), then as much as 16×10^{15} g C/yr might be stored in terrestrial ecosystems. Such a large storage is unlikely because not all nitrogen falls on forests and some nitrogen is removed from the land by runoff and denitrification (Schlesinger 2009). In some areas, the fate of the excess nitrogen deposited from the atmosphere is unclear—some may accumulate in soil organic matter, leading to greater carbon storage (Hyvonen et al. 2008, Nave et al. 2009, Liu and Greaver 2010; but see Mack et al. 2004). In European forests, the change in carbon storage per unit nitrogen deposition is about 40 ± 20 (Hogberg 2012). Using a slightly higher value, Thomas et al. (2010) indicate that forests may accumulate 0.31×10^{15} g C/yr as a result of inadvertent nitrogen fertilization worldwide.

Over longer periods of time, changes in the distribution of vegetation as a result of global climate change could also affect the concentration of atmospheric CO_2 (Chapter 5). Coupled to models of climate change, most models of the global carbon cycle suggest an increase in the carbon content of vegetation and soils when vegetation is in equilibrium with a warmer and wetter world of the future (Smith et al. 1992b). If the adjustment of vegetation to climate occurs over 100 years, these models suggest that the net uptake by the terrestrial biosphere could be as high as 1.8×10^{15} g C/yr—mostly in vegetation. However, other models suggest that changes in vegetation and soils during the transition in climate may yield the opposite effect. Smith and Shugart (1993) estimate large losses of carbon from vegetation during the transient period of drought that is likely to accompany global warming over the next century.

In sum, whole-ecosystem response will be determined by various factors—CO_2, nutrient availability, and global patterns of temperature and rainfall, which are all affected by human activities. Although it seems unlikely that enhanced growth by terrestrial vegetation will ultimately stem the rise of CO_2 that is derived from fossil fuels (see Idso and Kimball 1993), the response of the terrestrial biosphere could have a dramatic impact on the future composition of the atmosphere.

In our view of the global carbon cycle, it is important to recognize that the annual movements of carbon, rather than the amount stored in various reservoirs, are most important. Desert soil carbonates contain more carbon (930×10^{15} g) than land vegetation, but the exchange between desert soils and the atmosphere is tiny (0.023×10^{15} g C/yr), yielding a turnover time of 85,000 years in that pool (Schlesinger 1985). In the global carbon cycle, a flux that has not changed in recent times, no matter how large, is not likely to affect the concentration of atmospheric CO_2 (Houghton et al. 1983). For example, the release of CO_2 in forest fires is of no consequence to changes in atmospheric CO_2 unless the frequency or area of forest fires has changed in recent times (Adams et al. 1977, Auclair and Carter 1993, Kasischke et al. 1995). The carbon flux in rivers or sinking pteropods cannot serve as a net sink for anthropogenic CO_2 in the ocean, unless the flux in these pathways is greater as a result of human activities. Similarly, the storage of carbon in peatland soils is not a sink for fossil fuel CO_2, unless the rate of storage in these areas has increased significantly during the Industrial Revolution. These peatlands have accumulated carbon throughout the Holocene when atmospheric CO_2 has been relatively constant (Harden et al. 1992).[4] On the other hand, landfills (0.12×10^{15} g/yr; Barlaz 1998) and wood products (0.03×10^{15} g/yr for the United States; Pacala et al. 2001) are sinks for CO_2 released from fossil fuel combustion during the past century.

Relatively small changes in large pools of carbon can have a dramatic impact on the carbon dioxide content of the atmosphere, especially if they are not balanced by simultaneous changes in other components of the carbon cycle. A 1% increase in the rate of decomposition on land, as a result of global warming, would release nearly 0.6×10^{15} g C/yr to the atmosphere. Schimel et al. (1994) estimated that the soil carbon pool could lose 0.7% of its content (11×10^{15} g C) for every degree of global warming during the next century (compare to Kirschbaum 1995, Trumbore et al. 1996). Recent losses of carbon from soils throughout England are attributed to a warming climate (Bellamy et al. 2005). Losses of carbon from the large pool of soil organic matter frozen in permafrost have the potential to release large amounts of CO_2 to the atmosphere and exacerbate global warming (Dorrepaal et al. 2009, Schuur et al. 2009, Tarnocai et al. 2009, Ping et al. 2008, Schaefer et al. 2011).

Similarly, a 1%/yr increment to the biomass of carbon on land, as a result of a greater storage of NPP, could balance the CO_2 budget in the atmosphere and stem the rise of CO_2 (Table 11.1). We can speculate that this increment should be first realized in vegetation, which has a faster turnover time than soils; only a small percentage of NPP that enters the soil survives to become a component of soil organic matter (Schlesinger 1990; Chapter 5).

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[4] Many who deny the potential impact of humans on climate argue that the flux from fossil fuels is so small compared to CO_2 from natural sources that it couldn't possibly have much effect on the concentration of atmospheric CO_2. This argument is easily dismissed, since the flux to and from the land and sea must have been balanced when CO_2 concentrations were relatively constant before the Industrial Revolution. The flux from fossil fuels is new to the carbon cycle and not balanced by other large human-induced sinks for carbon.

At the surface of the Earth, the largest global pool of carbon is found in sedimentary rocks, including fossil fuels (Table 2.3). Storage of organic carbon in these deposits accounts for the accumulation of O_2 in the atmosphere through geologic time (Chapter 2). In the absence of human perturbations, the exchange between the fossil pool and the atmosphere could be ignored in global models. Only a small amount of buried sedimentary organic matter is exposed to uplift, erosion, and oxidation each year—0.043 to 0.097×10^{15} g C/yr (Di-Giovanni et al. 2002, Copard et al. 2007). In extracting fossil fuels from the Earth's crust, humans affect the global system by creating a large biogeochemical flux, $\sim 9 \times 10^{15}$ g C/yr, where essentially none existed before. Carbon dioxide emission from fossil fuel combustion dwarfs the CO_2 exhaled by the human population worldwide, 0.6×10^{15} g C/yr (Prairie and Duarte 2006). The rise in atmospheric CO_2 is closely correlated with the rise in human population (Hofmann et al. 2009), economic activity, and the "carbon-intensity" of the modern economy (Canadell et al. 2007).

TEMPORAL PERSPECTIVES ON THE CARBON CYCLE

Studies of the biogeochemistry of carbon on Earth must begin with a consideration of the origin of carbon as an element and with theories that explain its differential abundance on the planets of our solar system (Chapter 2). During the early development of Earth, the carbon cycle was decidedly non-steady-state: The carbon content of the planet grew with the receipt of planetesimals and meteorites—especially carbonaceous chondrites—and the atmospheric content increased as volcanoes released CO_2 trapped in Earth's mantle. Today, the Earth's mantle appears to release about 0.03×10^{15} g C to the atmosphere each year (Kerrick 2001, Wallace 2005, Dasgupta and Hirschmann 2010). The oldest geologic sediments suggest that atmospheric CO_2 may have been as high as 3% on primitive Earth, contributing to a greenhouse effect during a time of low solar output (Walker 1985, Rye et al. 1995). Today small amounts of water vapor and CO_2 in our atmosphere maintain the surface temperature of the Earth above freezing—obviously an essential condition for the persistence of the biosphere (Ramanathan 1988, Lacis et al. 2010, Schmidt et al. 2010a).

As discussed in Chapter 4, CO_2 in the atmosphere interacts with the crust of the Earth, causing rock weathering (Eq. 4.3). Carbon dioxide is removed from the atmosphere and transferred via rivers to the oceans, where it is eventually deposited on the seafloor in carbonate rocks, adding to the Earth's crust (Figure 1.3). Along with carbonates, undecomposed organic materials also accumulate in marine sediments from photosynthesis on land and in the sea. As early as 1918, Arrhenius (1918, p. 177) speculated that the consumption of CO_2 by rock weathering might eventually cool the planet through a loss of its natural "greenhouse effect":

> As the crust grew thicker, the supply of this gas [CO_2] diminished and was further used up in the process of disintegration [weathering]. As a consequence the temperature slowly decreased, although decided fluctuations occurred with the changing volcanic activity during different periods. Supply and consumption of carbon dioxide fairly balanced as disintegration ran parallel with the proportion of this gas in the air.

Fortunately, CO_2 is returned to the atmosphere as a result of tectonic activity. In the complete geochemical cycle of carbon (Figure 1.3), subduction of the oceanic crust carries carbon deposited on the seafloor to the interior of the Earth, where CO_2 and other volatile elements are once again released by hydrothermal and volcanic emissions. Alt et al. (2012) estimate that 0.07×10^{15} g C/yr are subducted worldwide. Mixing of the subducted oceanic crust may extend to

1000-km depth in the mantle (Walter et al. 2011). Total volcanic emanation of volatile carbon from the Earth's surface, including both degassing of the mantle and of recycled sedimentary materials, is estimated at about 0.10×10^{15} g C/yr (Morner and Etiope 2002)—similar to estimates of carbon accumulation in ocean sediments. At these rates, the entire mass of carbon in the upper mantle, 7×10^{22} g, would recycle in less than a billion years (Dasgupta and Hirschmann 2010); thus, it is likely that much of the carbon in the mantle has spent some time in the biosphere in the geologic past. If this cycle were not complete, rock weathering would deplete CO_2 in the atmosphere and oceans in $\sim$500,000 years, and all carbon would be stored in sedimentary rocks.

On Earth, this geochemical cycle has helped to maintain the concentration of atmospheric CO_2 below 1% (10,000 ppm) for the last 100 million years (Berner and Lasaga 1989). On Mars, where this cycle has slowed or stopped, the atmosphere contains a small amount of CO_2, and the planet is very cold (Chapter 2). On Venus, which is too hot for CO_2 to react with crustal minerals, the atmosphere contains a large amount of CO_2, reinforcing its greenhouse effect (Walker 1977, Nozette and Lewis 1982). During periods of extensive volcanism, the atmospheric concentration of CO_2 on Earth may have been greater than today's, leading to warmer climates (Owen and Rea 1985); however, a continuous geologic record of liquid oceans on Earth indicates that CO_2 and other greenhouse gases have always remained at levels that produce relatively moderate surface temperatures. Deposition of carbon in ocean sediments by various biotic activities is one way that life may help promote long-term stability in Earth's climate, favorable to the persistence of life.

Despite their long-term significance in buffering atmospheric CO_2, the annual transfers of carbon in the geochemical cycle are relatively small. The massive quantities of CO_2 that are now tied up in the carbonate minerals of the Earth's crust are the result of a slow accumulation of these materials over long periods of Earth's history. Today rivers carry about 500×10^{12} g/yr of Ca^{2+} (Milliman 1993) and 0.40×10^{15} g/yr of carbon as HCO_3^- to the sea (Sarmiento and Sundquist 1992), with about 65% derived from the atmosphere and the rest from carbonate minerals (Gaillardet et al. 1999, Suchet et al. 2003, Hartmann et al. 2009). For seawater to maintain fairly constant concentrations of calcium, an equivalent amount of Ca must be deposited as $CaCO_3$ in ocean sediments, carrying 0.15×10^{15} g C/yr to the oceanic crust. Dividing the mass of carbonate rocks by their annual rate of formation, we find that each atom of carbon sequestered in marine carbonate spends more than 400 million years in that reservoir.

With the appearance of life, a *bio*geochemical cycle was added on top of the underlying geochemical cycle of carbon on Earth. Models of the modern biogeochemical cycle of carbon focus on the large annual transfer of CO_2 from the atmosphere to plants as a result of photosynthesis and the large return of CO_2 to the atmosphere as a result of decomposition (Figure 11.1). Today, the fluxes of carbon in the biogeochemical cycle of carbon, mostly expressed in units of 10^{15} to 10^{17} g C/yr, dwarf the fluxes of the underlying geochemical cycle of carbon, where the movements are typically 10^{13} to 10^{14} g C/yr.

During Earth's history, at times when the production of organic carbon by photosynthesis has exceeded its decomposition, organic carbon has accumulated in geologic sediments. The earliest organic carbon is present in rocks from 3.8 bya, with the pool increasing to 1.56×10^{22} g by about 540 mya (Des Marais et al. 1992). During that interval, about 20% of all the carbon buried in marine sediments was organic—similar to the ratio found in modern marine sediments (Li 1972; Holser et al. 1988; Dobrovolsky 1994, p. 163). During the Carboniferous Period (300 mya), large deposits of organic carbon were stored in freshwater environments, leading to modern economic deposits of coal.
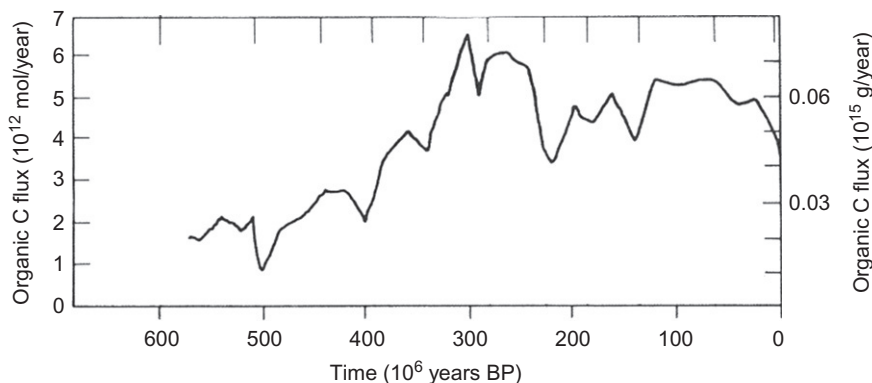
FIGURE 11.4 Burial of organic carbon on Earth during the past 600 million years. *Source: From Olson et al. (1985).*

During the Tertiary Epoch, the precursors to modern deposits of petroleum were added to marine sediments. Net storage of organic carbon in sediments has varied between about 0.04 and 0.07×10^{15} g C/yr during the last 300 million years (Figure 11.4; Berner and Raiswell 1983); a rate of 0.10×10^{15} g C/yr is estimated for the present (Chapter 9). Today, about 10 to 20% of the global organic burial occurs in the Bengal Fan as a result of rapid burial by Himalayan sediment (Galy et al. 2007, France-Lanord and Derry 1997).

Life also stimulated some of the reactions in the underlying geochemical cycle of carbon. Various marine organisms enhance the deposition of calcareous sediments, which now cover more than half of the oceans' seafloor (Kennett 1982). Land plants, by maintaining high concentrations of CO_2 in the soil pore space, raise the rate of carbonation weathering, speeding the reaction of CO_2 with the Earth's crust (Moulton et al. 2000; Chapter 4). Land plants and soil microbes also excrete a variety of organic compounds, byproducts of photosynthesis, which enhance rock weathering. Various models developed and summarized by Robert Berner of Yale University suggest that the atmospheric concentration of CO_2 declined precipitously as land plants gained dominance about 350 mya (Berner 1992, Berner and Kothavala 2001, Royer et al. 2001, Rothman 2002). The record of CO_2 in Earth's atmosphere suggests that concentrations have remained between 150 and 500 ppm for the past 24 million years (Pearson and Palmer 2000) and below 1500 ppm for the past 50 million years (Pagani et al. 2005, Zachos et al. 2008). Calcium levels in seawater were higher, atmospheric CO_2 levels were lower, and the Earth's climate was colder during the Miocene, 13,000,000 years ago (Griffith et al. 2008). Indeed, atmospheric CO_2 concentrations and global temperature are well correlated, especially for the last 20 million years (Came et al. 2007, Tripati et al. 2009).

Collections of gas trapped in ice cores from the Antarctic provide a historical record of atmospheric CO_2 for the last 800,000 years (Figure 1.2). The cyclic fluctuations of CO_2 in Earth's atmosphere imply non-steady-state conditions of the carbon cycle, with a periodicity of 100,000 years. Concentrations varied between 180 and 280 ppm, with the lowest values found in layers of ice that were deposited during glacial periods.[5] CO_2 concentrations and global

[5] The consistent minimum at $\sim$200 ppm and maximum at $\sim$280 ppm during glacial-interglacial intervals (Figure 1.2) is striking. Holland (1965) suggests that the minimum may be related to the onset of gypsum precipitation in ocean sediments, which raises the pH of seawater and leads to the precipitation of calcite (Lindsay 1979, p. 49).

temperatures have been well correlated for the past 160,000 years (Cuffey and Vimeux 2001). The lowest concentrations of CO_2 were likely to invoke significant physiological effects on land plants, reducing their photosynthesis (Gerhart and Ward 2010). Although the exact magnitude is controversial, the mass of carbon stored in vegetation and soils was also lower during the last glacial, as a result of the advance of continental ice sheets and widespread desertification of land habitats (Adams et al. 1990, Servant 1994, Bird et al. 1994, Beerling 1999). Thus, glacial conditions must have produced changes in the oceans that allowed a large uptake of CO_2 (Faure 1990, Sundquist 1993); this carbon dioxide was returned to the atmosphere at the end of the glacial epoch (Yu et al. 2010, Burke and Robinson 2012, Schmitt et al. 2012).

Increased marine NPP or an increased efficiency of the marine "biotic pump" (Chapter 9) seem unlikely mechanisms for CO_2 uptake during glacial conditions (Leuenberger et al. 1992), but a decrease in the amount of carbon stored as carbonates could lead to a greater retention of CO_2 in the oceans, following Eqs. 9.3 and 9.4. Most of the $CaCO_3$ dissolution in marine sediments is driven by CO_2 released during the decomposition of organic matter (Berelson et al. 1990), so Archer and Maier-Reimer (1994) suggest that an increase in the ratio of organic carbon to carbonate in sinking particles could lead to a greater dissolution of carbonate in marine sediments. Sanyal et al. (1995) report evidence for a higher pH of the glacial ocean, consistent with a greater dissolution of carbonates in the deep sea.

At the end of the last glacial, 17,000 years ago, atmospheric CO_2 rose to about 280 ppm, where it remained with minor variations until the beginning of the Industrial Revolution (Figure 11.5; Indermuhle et al. 1999, Meure et al. 2006, Alm et al. 2006). The increase in concentration from 280 ppm to today's value of about 400 ppm represents a global change of 43% in less than 200 years! Although the current level of CO_2 is not unprecedented in the geologic record, our concern is the speed at which a basic characteristic of the planet has changed to levels not previously experienced during human history or during the evolution of current ecosystems. Since global temperature and atmospheric CO_2 are related, we are destined for significant global warming during the near future (Shakun et al. 2012; Figure 1.2).
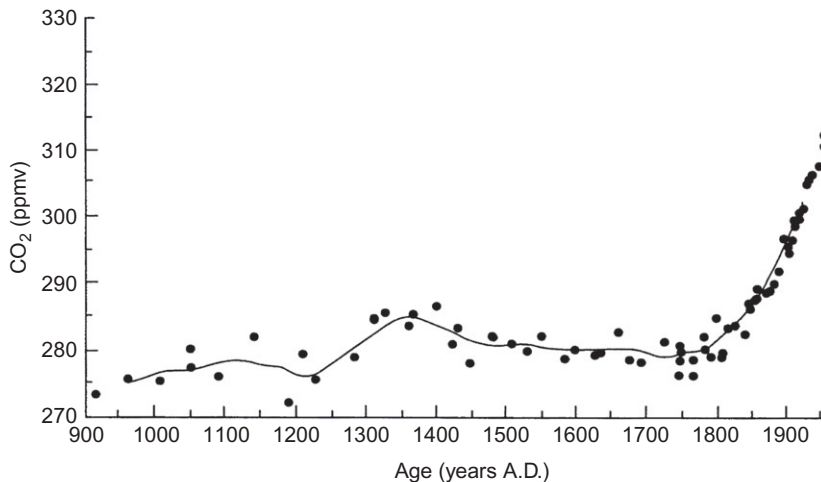

FIGURE 11.5 Concentrations of atmospheric CO_2 estimated from bubbles of gas trapped in ice cores from Antarctica. *Source: From Barnola et al. (1995).*

These perspectives on the global carbon cycle extend from processes that occur on a time scale of 10^9 years to those that occur annually. The global carbon cycle is composed of large, rapid transfers in the *bio*geochemical cycle superimposed on the underlying, small, slow transfers of the geologic cycle. Buffering of atmospheric CO_2 over geologic time involves small net changes in carbon storage that occur relatively slowly. Thus, an increase in the natural rate of rock weathering (which consumes $\sim 0.25 \times 10^{15}$ g C/yr) as a result of high CO_2 and rising global temperature is not likely to be an effective buffer to the rapid release of CO_2 from fossil fuels (9×10^{15} g C/yr). In contrast, the current net exchange of CO_2 between the atmosphere and the biosphere is about 150×10^{15} g C/yr, so the biosphere is more likely to buffer the rise of CO_2 due to human activities. The current increase in atmospheric CO_2 results from our ability to change the flux of CO_2 to the atmosphere by an amount that is significant relative to the biogeochemical reactions that buffer the system over long periods of time.

ATMOSPHERIC METHANE

At first glance, the annual flux of methane (CH_4) would seem to be only a minor component of the global carbon cycle. All sources of methane in the atmosphere are in the range of 10^{12} to 10^{14} g C/yr, which is several orders of magnitude lower than the flux for CO_2 shown in Figure 11.1. Globally, the atmospheric methane concentration is about 1.83 ppm, versus 400 ppm for CO_2 (Table 3.1). However, at the beginning of the Industrial Revolution, the concentration of methane in the atmosphere began to increase at an average rate of about 1%/yr (Figure 11.6), which was much faster than the rate of CO_2 increase over the same interval
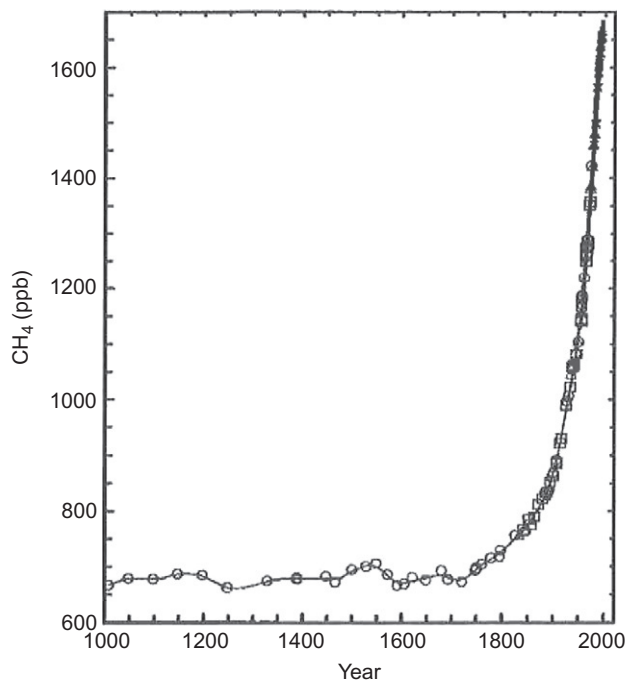

FIGURE 11.6   Concentrations of CH_4 in air extracted from Antarctic ice cores. *Source: From Etheridge et al. (1998). Used with permission of the American Geophysical Union.*

(Figure 11.5). The methane concentration in Earth's atmosphere has more than doubled since the beginning of the Industrial Revolution. Strangely, the rise in methane concentration slowed in the early 1990s, but an upward trend now seems to have commenced again (Dlugokencky et al. 2011, Terao et al. 2011). Over the next century each molecule of methane in the atmosphere has the potential to contribute 25 to $35\times$ or more to the human-induced greenhouse effect compared to each molecule of CO_2 (Lashof and Ahuja 1990, Shindell et al. 2009). Substantial progress in mitigating global warming could accompany a reduction in methane emissions (Montzka et al. 2011a, Shindell et al. 2012).

The cause of the increase in methane in Earth's atmosphere is not obvious, because a wide variety of sources contribute to the total annual production of about 600×10^{12} g/yr (Table 11.2). The sum of anthropogenic sources is about twice the sum of natural sources, so it is perhaps surprising that the annual increase of methane in the atmosphere is not larger. The estimate of total flux is fairly well constrained because it yields a mean residence time for atmospheric CH_4 of about 9 years, which is consistent with independent calculations based on methane consumption (Khalil and Rasmussen 1990, Prinn et al. 1995, Dentener et al. 2003) and with the spatial variation in CH_4 concentration in the atmosphere (Figure 3.5). The concentration of CH_4 is slightly higher in the Northern Hemisphere, suggesting that it is the location of major emissions (Figure 3.4).

Like CO_2, the concentration of methane in the atmosphere oscillates, showing a minimum concentration in midsummer in the Northern Hemisphere (Steele et al. 1987, Khalil et al. 1993a, Dlugokencky et al. 1994). While methane emissions from wetlands are greatest during warm periods, the summer is also the time of the most rapid destruction of atmospheric methane by OH radicals (Khalil et al. 1993b).

In 2006, do Carmo et al. reported anomalously high methane concentrations above the canopy of tropical rainforest in Brazil, also seen in satellite observations of atmospheric methane over tropical rainforests (Frankenberg et al. 2005). At about the same time, Keppler et al. (2006) suggested a large global flux of methane ($62–236 \times 10^{12}$ g/yr) from upland vegetation from an unknown, but aerobic, biochemical pathway. This conclusion has now been tempered by the failure of laboratory measurements to confirm the observation and by more cautious extrapolation to a global estimate (Kirschbaum et al. 2006, Megonigal and Guenther 2008, Dueck et al. 2007, Nisbet et al. 2009). Methane is produced in hollow trees (Covey et al. 2012), but a large flux of methane from upland vegetation cannot be accommodated in the current budget for atmospheric methane (refer to Table 11.2) without yielding a mean residence time that is incompatible with atmospheric measurements and conflicting with the observed midsummer minimum for methane concentrations in the atmosphere. The observations of methane flux from tropical rainforests are likely due to the extensive areas of flooded soils within them.

Methanogenesis in wetland habitats is widely acknowledged as the dominant natural source of atmospheric methane (Chapter 7). Matthews and Fung (1987) estimated that 110×10^{12} g/yr stem from anaerobic decomposition in natural wetlands globally. The rate of methane release would undoubtedly be much higher if it were not for high rates of methanotrophy by bacteria in wetland soils (Megonigal and Schlesinger 2002). The rate of production is higher in tropical wetlands than in boreal wetlands (Schütz et al. 1991, Bartlett and Harriss 1993, Cao et al. 1996), reflecting the positive relationship between temperature, net ecosystem production, and the rate of methanogenesis in many wetland

TABLE 11.2 Estimated Sources and Sinks of Methane in the Atmosphere in 2010

Natural sources	Flux (10^{12} g CH_4/yr)		References
Wetlands	143		Neef et al. 2010
Tropics		46	Bloom et al. 2010
Northern latitude		20	Christensen et al. 1996
Upland vegetation	10 (estimate)		Megonigal and Guenther 2008; Kirschbaum et al. 2006
Termites	19		Sanderson 1996
Oceans	10		Reeburgh 2007
Geological seepage[a]	33		Etiope et al. 2008
Anthropogenic sources			
Fossil fuel related			
Coal mines	30		Prather et al. 1995
Coal combustion	15		Prather et al. 1995
Oil and gas	72		Neef et al. 2010
Waste and waste management			
Landfills	18		Bogner and Matthews 2003
Animal waste	25		Prather et al. 1995
Sewage treatment	25		Prather et al. 1995
Ruminants	116		Neef et al. 2010
Reservoirs	70		St. Louis et al. 2000
Biomass burning	19		Kaiser et al. 2012
Rice cultivation	40		Sass and Fisher 1997, Bloom et al. 2010
Total sources	**645**		
Sinks			
Reaction with OH radicals	522		Neef et al. 2010
Removal in the stratosphere	34		Neef et al. 2010
Removal by soils	25		Curry 2007 Dutaur and Verchot 2007
Total sinks	**581**		
Atmospheric increase (2007)	23		Dlugokencky et al. 2009

Note: All data in 10^{12} g CH_4/yr from various sources as cited here and in the text.
[a] *Total geological seepage less marine.*

ecosystems (Chapter 7). Because tropical wetlands cover a large area of the world, they dominate the methane flux from wetlands globally (Aselmann and Crutzen 1989, Fung et al. 1991, Bartlett and Harriss 1993).

A large portion of the current increase in atmospheric methane may derive from an increase in the worldwide cultivation of rice (Sass and Fisher 1997). Because most rice paddies are found in warm climates, they often yield a large CH_4 flux, which is enhanced by the upward transport of CH_4 through the hollow stems of rice (Chapter 7). Matthews et al.

(1991) provide maps of the global distribution of CH_4 production from rice cultivation, which is likely to increase by more than 1%/yr during the next several decades (Anastasi et al. 1992). Better management of rice cultivation may be responsible for a reduced flux of CH_4 to the atmosphere in recent years (Kai et al. 2011).

Many grazing animals and termites maintain a population of anaerobic microbes that conduct fermentation at low redox potentials in their digestive tract. Digestion in these animals provides the functional equivalent of a mobile wetland soil! The belches[6] of grazing animals make a significant contribution to the global sources of methane (Table 11.2). In the early 1980s, about 78×10^{12} g/yr of CH_4 were derived from domestic and wild animals, with humans contributing 1×10^{12} g/yr (Crutzen et al. 1986, Lerner et al. 1988). Anastasi and Simpson (1993) suggest that larger herds of grazing animals may increase the global flux of methane from animals by about 1×10^{12} g/yr during the next several decades (compare to Table 11.2). Some termites and other insects also make a small but significant contribution to atmospheric methane as a result of anaerobic decomposition in their hindgut (Khalil et al. 1990, Brauman et al. 1992, Hackstein and Stumm 1994). It is not likely, however, that the flux of CH_4 from termites has increased significantly in recent years.

Forest fires produce methane as a product of incomplete combustion. We know little about the annual area of burning in the preindustrial world, but it is likely that the current release of CH_4 from forest fires has increased as a result of high, recent rates of biomass burning in the tropics (Andreae 1991). Kaufman et al. (1990) used remote sensing of fires in Brazil to calculate a loss of 7×10^{12} g CH_4/yr in that region in 1987, and Delmas et al. (1991) found a flux of 9.2×10^{12} g CH_4 from burning of African savannas. CH_4 typically accounts for 1% of the total carbon lost by fire (Levine et al. 1993), so the estimate of methane flux from forest fires (19 Tg CH_4/yr; Table 11.2) is compatible with a range of global estimates of the carbon released in forest fires (1.4 to 3.6×10^{15} g C/yr; Chapter 5).

Humans contribute directly to atmospheric methane during the production and use of fossil fuels and due to the disposal of wastes. The flux of methane from landfills increases linearly with the amount of material buried, which presumably decomposes under anoxic conditions (Thorneloe et al. 1993). The global flux from landfills is estimated at 16 to 20 Tg CH_4/yr (Bogner and Matthews 2003). Inadvertent releases of fossil CH_4 during the mining and use of coal and natural gas must account for about 20 to 30% of the total annual flux of CH_4 to the atmosphere, based on the ^{14}C age of atmospheric methane (Ehhalt 1974; Wahlen et al. 1989; Quay et al. 1991, 1999; Etiope et al. 2008).

Biomass burning and releases of natural gas appear to have increased the $\delta^{13}C$ of atmospheric methane from a preindustrial value of around -50‰ to the value of -47‰ that is observed today (Craig et al. 1988, Quay 1988). Increasing emissions from wetlands cannot be responsible, because methanogenesis by acetate or CO_2 reduction yields CH_4 that is more depleted in ^{13}C (Chapter 7). Indeed, an increased release of CH_4 by biomass burning would seem to be the only single source that is consistent with observed changes in both atmospheric $^{13}CH_4$ (Craig et al. 1988, Sowers et al. 2005) and $^{14}CH_4$ (Wahlen et al. 1989) in recent years.

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[6] Although many believe that farts are the major pathway for methane release from cattle, about 90 to 95% of the methane is released from digestive burps from the rumen (Hayhoe and Farley 2009, p. 33). Wilkinson et al. (2012) suggest that similar methane emissions from dinosaurs may have warmed Earth in the Mesozoic.

However, a combination of changing contributions from various source and sink reactions is also possible (Whiticar 1993).

The major sink for atmospheric methane is reaction with hydroxyl radicals in the atmosphere (Chapter 3). Each year about 522×10^{12} g is removed from the troposphere by this process (Neef et al. 2010). As a result of its mean atmospheric lifetime of 9 years, a large portion of the tropospheric CH_4 mixes into the stratosphere, where about 30×10^{12} g is destroyed by reaction with OH, producing CO_2 and water vapor. Some workers have suggested that the rise in atmospheric methane during the Industrial Revolution was derived from a reduction in the sink strength offered by hydroxyl radicals, which react more rapidly with CO, which is also increasing in the atmosphere (Khalil and Rasmussen 1985). Although this mechanism cannot be dismissed, it is inconsistent with indirect observations that the concentration of hydroxyl radicals has not decreased, and may even have increased, in the atmosphere in recent years (Dentener et al. 2003, Prinn et al. 2005; Chapter 3).

A small amount of methane diffuses from the atmosphere into upland soils, where it is oxidized by methanotrophic bacteria (King 1992). In Mojave Desert soils, where the supply of labile organic matter is limited, soil bacteria consume an average of 0.66 mg CH_4 m^{-2} day^{-1}, with the greatest rates observed after rainstorms (Striegl et al. 1992). Consumption of CH_4 in temperate and tropical forest soils typically ranges from 1.0 to 5.0 mg CH_4 m^{-2} day^{-1} (Crill 1991, Adamsen and King 1993, Ishizuka et al. 2000, Smith et al. 2000, Price et al. 2004), with lower values after rainstorms, which tend to retard the diffusion of O_2 and CH_4 into clay-rich soils (Koschorreck and Conrad 1993; Castro et al. 1994, 1995). Methanotrophic bacteria remain active at extremely low CH_4 concentrations (Conrad 1994), so the global significance of soil methanotrophy appears limited by the rate of diffusion of methane into the soil (Born et al. 1990, King and Adamsen 1992).

Some of the methanotrophic activity in soils derives from the activities of nitrifying bacteria, which can use CH_4 as an alternative substrate to NH_4^+ (Jones and Morita 1983, Hyman and Wood 1983, Bédard and Knowles 1989). Steudler et al. (1989) suggested that the consumption of CH_4 by nitrifying bacteria may be lower in forests that currently receive a large atmospheric deposition of NH_4^+, because the NH_4^+/CH_4 ratio in soils has greatly increased in these regions. A number of workers reported reduced methane uptake when forest and grassland soils were fertilized with nitrogen, with the threshold being about 100 kg N ha^{-1} yr^{-1} (Aronson and Helliker 2010, Kim et al. 2012). Methane uptake by soils is also lower after land clearing, which stimulates nitrification (Hütsch et al. 1994, Keller and Reiners 1994). With fertilization or land clearing, ammonium oxidation produces small amounts of nitrite (NO_2), which may cause a persistent inhibition of methanotrophic bacteria in soils (King and Schnell 1994, Schnell and King 1994). Atmospheric deposition of nitrate is also known to reduce CH_4 uptake by forest soils (Steudler et al. 1984, Mochiguki et al. 2012).

Over large regions, the sink for methane in upland soils consumes only a small fraction of the production of methane in adjacent, wet lowland soils (e.g., Whalen et al. 1991, Delmas et al. 1992, Yavitt and Fahey 1993, Ullah and Moore 2011). The global estimate of the sink for atmospheric methane in soils is about 20 to 30×10^{12} g/yr (Curry 2007, Dutaur and Verchot 2007). Given this relatively small value, it is unlikely that changes in this process by human activities can account for the current increase in atmospheric CH_4 globally (e.g., Willison et al. 1995).
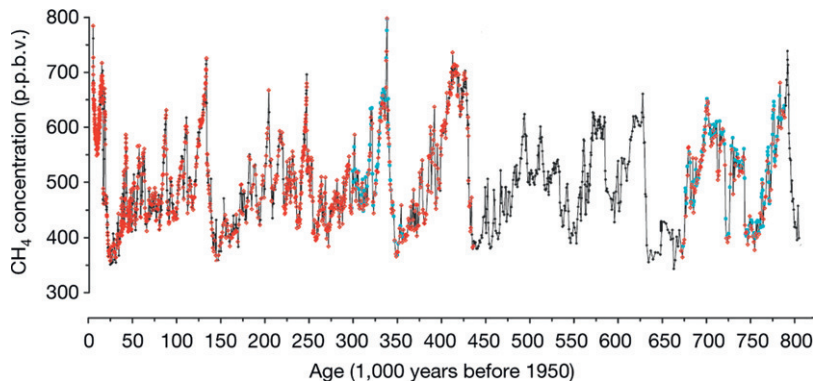
FIGURE 11.7 Concentrations of CH_4 in air that is extracted from ice cores in Antarctica dating to 800,000 years before present. *Source: From Loulergue et al. (2008). Compare to Figure 1.2.*

Ice-core records of atmospheric methane show that concentrations were about 400 ppb during the last glacial period, increasing abruptly to the preindustrial value of 700 ppb as the glaciers melted (Chappellaz et al. 1990, Loulergue et al. 2008; Figure 11.7). The increase during deglaciation seems to have occurred while many northern wetlands were still covered with ice, suggesting that changes in tropical wetlands may have caused the initial methane increase, which reinforced the global warming during deglaciation (Chappellaz et al. 1993). However, high-latitude, northern wetlands may have also contributed to the accumulation of methane in the atmosphere during the Holocene (Zimov et al. 1997, Walter et al. 2007, Smith et al. 2004).

Concentrations of atmospheric methane showed minor variation during the Holocene ($\pm 15\%$; Blunier et al. 1995, Mitchell et al. 2011a), but beginning about 200 years ago the concentration began to increase rapidly (Figure 11.7). The atmospheric concentration of methane has doubled during this period. The rise in atmospheric methane is paralleled by a rise in formaldehyde—a methane oxidation product (Eq. 3.21)—in polar ice cores (Staffelbach et al. 1991). Recently measured increases in stratospheric water vapor are also linked to an increasing transport of CH_4 to the stratosphere, where it is oxidized (Thomas et al. 1989, Oltmans and Hofmann 1995).

Although the annual increase in methane in the atmosphere averaged about 1%/yr during the 1980s, the rate of increase slowed in the 1990s and was minimal during the early 2000s (Figure 11.8). A variety of explanations have been offered: Some workers suggest that less natural gas was leaking from gas fields of the former Soviet Union as a result of slower economic growth and of efforts to patch pipeline leaks (Law and Nisbet 1996, Aydin et al. 2011). Leakage was estimated at 40 Tg CH_4/yr in 1990 (Reshetnikov et al. 2000). Alternatively, Bekki et al. (1994) suggest that an increasing depletion of stratospheric ozone allowed greater amounts of uvB radiation to penetrate to the troposphere, where it produces OH radicals that oxidize CH_4. As the ozone hole has stabilized, so too has the production of OH radicals.

Future changes in the global methane budget as a result of rising CO_2 and global temperatures are difficult to predict. Warmer conditions may shift the balance between aerobic and anaerobic decomposition in wetlands and increase the ratio of CO_2 to CH_4 emitted from these ecosystems (Whalen and Reeburgh 1990, Funk et al. 1994, Moore and Dalva 1993). On the
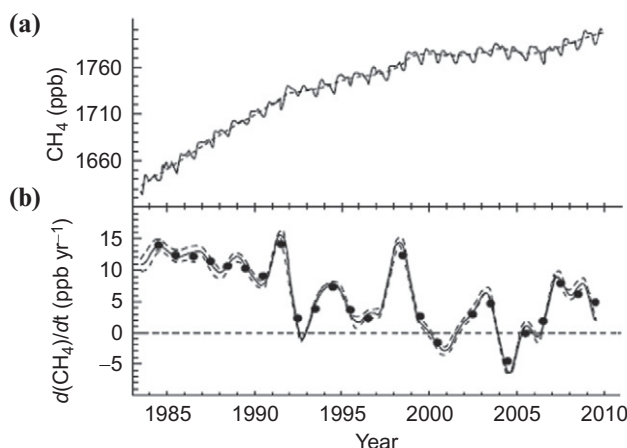
(a)

FIGURE 11.8   Concentration of methane (a) and its annual change (b) in Earth's atmosphere during the past three decades. *Source: From Dlugokencky et al. (2011). Used with permission of The Royal Society.*

other hand, methanogenic bacteria show a greater positive response to temperature than methane-oxidizing bacteria, suggesting that the flux of methane from wetland soils could increase with global warming (King and Adamsen 1992, Dunfield et al. 1993, Megonigal and Schlesinger 2002). An increasing flux of CH_4 may also accompany a CO_2-induced stimulation of wetland plants, which leak excess carbohydrate from their roots fueling methanogenesis in wetland soils (Dacey et al. 1994, Hutchin et al. 1995, Megonigal and Schlesinger 1997, van Groenigen et al. 2011). In contrast, methane consumption in upland soils appears to decline when forests are grown at high CO_2 (Phillips et al. 2001a, McLain et al. 2002).

Catastrophic release of methane from marine sediments, where it is held as methane hydrate (clathrate) could also yield a large increase in atmospheric methane and greenhouse warming in the future (MacDonald 1990). Burwicz et al. (2011) estimate the global pool in clathrates may be as large as 995×10^{15} g CH_4-C—more than $1000\times$ current annual emissions (refer to Table 11.2). The geologic record indicates release of methane from hydrates in the past (Jahren et al. 2001, Katz et al. 1999), although evidence for such degassing at the end of the last glacial epoch is equivocal (Kennett et al. 2000, Sowers 2006, Petrenko et al. 2009). Given methane's potential as a greenhouse gas and indications that increasing concentrations of CH_4 may have preceded the global warming 10,000 years ago, a better understanding of the global methane budget is paramount if biogeochemists are to contribute to the development of effective international policy to combat global warming (Nisbet and Ingham 1995).

CARBON MONOXIDE

Carbon monoxide has a low concentration (45 to 250 ppb) and a short lifetime (2 months) in the atmosphere (Table 3.5). The short lifetime is consistent with wide regional and seasonal variations in its concentration (Figure 3.5); the concentration of CO in the Northern Hemisphere is typically three times larger than that in the Southern Hemisphere (Dianov-Klokov et al. 1989, Novelli et al. 2003). The budget for CO is dominated by anthropogenic sources (Table 11.3), especially fossil fuel combustion and biomass burning, which are

TABLE 11.3 Budget for Major Sources and Sinks for CO in the Atmosphere

Sources	Flux
Fossil fuel combustion	400
Biofuel combustion	160
Biomass burning	460[a]
Oxidation of methane	820
Oxidation of other volatile carbon compounds	521
Total	**2361**
Sinks	
Uptake by soils (Sanhueza et al. 1998)	115–230
Oxidation by OH reactions (Prather et al. 1995)	1400–2600
Stratospheric destruction	100
Total	**1615–3030**

Note: All units are 10^{12} g CO/yr; from Duncan et al. (2007) unless otherwise noted.
[a] *Kaiser et al. (2012), Jain (2007), and Mieville et al. (2010) give alternative estimates of 351, 372, and 500 × 10^{12} g CO/yr, respectively.*

concentrated in the Northern Hemisphere. Year-to-year variations in the occurrence of forest fires account for much of the variation in CO concentrations in downwind regions (Wotawa et al. 2001, Novelli et al. 2003, Vasileva et al. 2011). Variations in the concentration of CO and its isotopic composition (i.e., $\delta^{13}C$) in the Antarctic icepack have been used to trace biomass burning in the Southern Hemisphere for the past 650 years (Wang et al. 2010c).

Until recently, the concentration of CO was increasing at a rate of >1%/yr (Khalil and Rasmussen 1988, Dianov-Klokov et al. 1989), presumably as a result of increasing emissions from fossil fuel combustion and an increasing production of CO as a methane-oxidation product (Chapter 3). Surprisingly, CO concentrations began to decline slightly during the early 1990s (Novelli et al. 1994, Khalil and Rasmussen 1994), reflecting a greater emphasis on the control of air pollution in the United States and Europe (Novelli et al. 2003, Hudman et al. 2008). The decline in CO may also be related to the slower growth rate of atmospheric CH_4, inasmuch as methane oxidation to CO accounts for 28 to 35% of the inputs of CO to the troposphere (Granier et al. 2000b; Table 11.3).

A small amount of CO is taken up by vegetation and soils, but the dominant sink for CO is oxidation by hydroxyl radicals in the atmosphere (Eqs. 3.30–3.35). Because it is oxidized to CO_2 so rapidly, carbon monoxide is normally included as a component of the CO_2 flux in most accounts of the global carbon cycle (e.g., Figure 11.1). Actually, the direct release of CO may account for about 5% of the total carbon emitted during fossil fuel combustion and perhaps as much as 15% of the carbon released during biomass burning (Andreae 1991).

Carbon monoxide shows limited absorption of infrared radiation. Its main effect on the greenhouse warming of Earth is probably indirect—by slowing the destruction of methane in the atmosphere (Lashof and Ahuja 1990). More important, carbon monoxide plays a major

role in atmospheric chemistry by controlling levels of tropospheric ozone (Chapter 3). High concentrations of atmospheric ozone over the tropical regions of South America and Africa appear to be related to the production of CO by forest burning (Figure 3.9), followed by the reaction of CO with OH radicals to produce ozone. About 2% of net primary production on land may be lost as CO or as volatile hydrocarbons that are oxidized to CO in the atmosphere (Chapter 5).

SYNTHESIS: LINKING THE CARBON AND OXYGEN CYCLES

Even on a lifeless Earth, photolysis of water vapor in the atmosphere would produce small amounts of O_2, as it has on planets such as Mars (Chapter 2). Early in its history, Earth may have lost up to 35% of the water degassed from the mantle by photolysis (Chapter 10). The process is now limited by cold temperatures and the ozone layer in the stratosphere, which minimize the amount of water vapor exposed to ultraviolet light. During the geologic history of Earth, significant amounts of atmospheric O_2 appeared only about 2.4 billion years ago, well after the advent of autotrophic photosynthesis. O_2 began to accumulate to its present level when the annual production exceeded the reaction of O_2 with reduced minerals in the Earth's crust.

The current atmospheric pool of O_2 is only a small fraction of the total O_2 produced over geologic time; most of the rest has been consumed in the oxidation of Fe and S (refer to Figure 2.8). The total net production of O_2 over geologic time is balanced stoichiometrically by the storage of reduced organic carbon (1.56×10^{22} g) and sedimentary pyrite (4.97×10^{21} gS; refer to Table 13.1) in the Earth's crust. Today, the content of oxygen in Earth's atmosphere is determined by the balance between the burial of organic carbon in sediments and the subsequent weathering of ancient sedimentary rocks, which have been uplifted to form the continents (Petsch et al. 2001). Oxygen is likely to have accumulated most rapidly during periods when large amounts of organic sediments were buried (Des Marais et al. 1992, France-Lanord and Derry 1997).

Today, the uplift and weathering of sedimentary rocks expose about 0.1 to 0.2×10^{15} g/yr of organic carbon to oxidation (Di-Giovanni et al. 2002; Figure 11.9). Much of the organic matter in exposed sedimentary rocks is labile (Schillawski and Petsch 2008, Galy et al. 2008). For instance, the biomass of microbes degrading organic matter in 365-million-year-old shales exposed to weathering in Kentucky is almost entirely derived from the shale (Petsch et al. 2001).

We have little evidence of historical variations in atmospheric O_2, but geochemical models suggest that the concentrations may have ranged from 15 to 35% during the past 500 million years (Berner and Canfield 1989, Berner 2001). The highest values would be expected in the Carboniferous and Permian periods, when a large amount of organic matter was buried in sediments (Berner et al. 2000; Figure 11.4). High concentrations of O_2 would have dramatic implications for the physiology, morphology, and evolution of most organisms (Graham et al. 1995). Giant insects are known to have been common during this period of high O_2 concentrations (Harrison et al. 2010). Fortunately, the pool of atmospheric O_2 is well buffered over geologic time because increases in O_2 expand the area and depth of aerobic respiration in marine sediments, leading to a greater consumption of O_2 and lower storage of organic carbon (Chapters 7 and 9). High levels of oxygen also reduce the rate of photosynthesis by causing increasing amounts of photorespiration (Tolbert et al. 1995; Chapter 5). The geologic record of sedimentary charcoal suggests that higher levels of O_2 may increase the occurrence
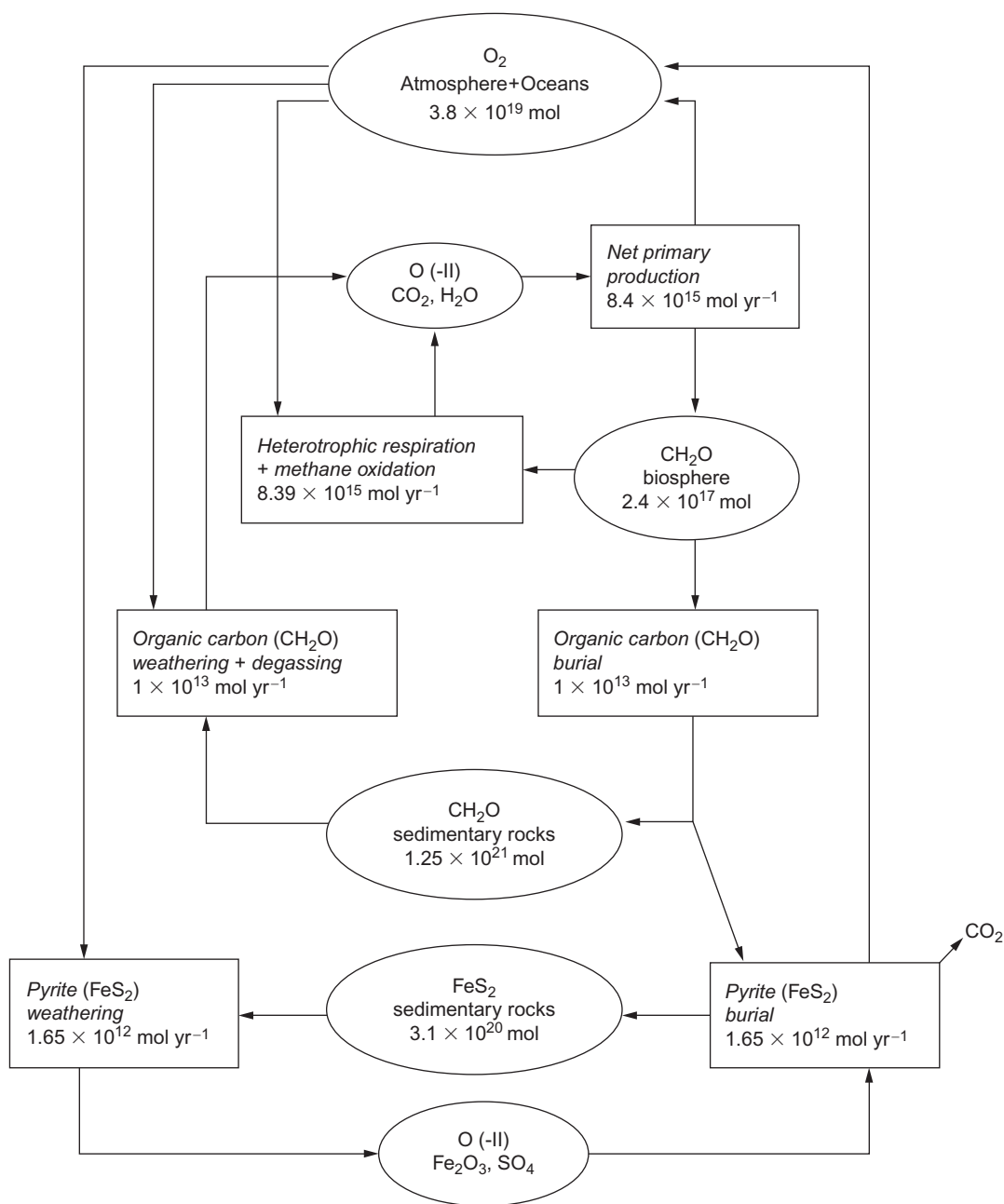
FIGURE 11.9   Linkage of the global carbon and oxygen cycles. Ovals contain estimates of the reservoirs of O_2 or the equivalent amount of reduced molecules that could be oxidized by O_2. Boxes indicate fluxes of O_2 or reduced molecules in moles/year. *Source: Modified from Lenton (2001).*

of forest fires (Scott and Glasspool 2006) and suppress the release of P by rock weathering (Lenton 2001). Finally, high dissolved O_2 in seawater would increase the adsorption of P to iron minerals in marine sediments, subsequently lowering nutrient availability and NPP in the sea (Van Cappellen and Ingall 1996). These interactions between the carbon, oxygen, and phosphorus cycles buffer the concentration of O_2 in Earth's atmosphere. Unlike geologic uplift and weathering, these processes are directly responsive to changes in the Earth's oxygen concentration.

Like the carbon cycle, the modern oxygen cycle is composed of a set of large, annual fluxes superimposed on the smaller, slow fluxes of the geologic cycle (Walker 1980). The current atmospheric pool of O_2 is maintained in a dynamic equilibrium between the production of O_2 by photosynthesis and its consumption in respiration, including fires (Figure 11.9). The annual fluctuation of O_2 in the atmosphere due to photosynthesis and respiration is about $\pm 0.0020\%$ in an average background concentration of 20.946% (Keeling and Shertz 1992). The mean residence time of O_2 in the atmosphere is about 4000 years—significantly shorter than what would be predicted merely by the reaction of O_2 with the Earth's crust, about 100,000,000 years (Figure 11.9).

Measured changes in the concentration of atmospheric O_2 provide a check on current estimates of CO_2 uptake by the terrestrial and marine biosphere (Bender et al. 1998). Photosynthesis on land produces O_2 and consumes CO_2 on an equal molar basis; the reverse is true when biomass and fossil fuels are burned. In contrast, uptake of CO_2 by the oceans, largely driven by Henry's Law, is not accompanied by a significant flux of O_2 to the atmosphere; the O_2 from marine photosynthesis remains dissolved in seawater and is consumed in the oceans during the degradation of organic matter. Thus, with fossil fuel combustion, the molar content of CO_2 should increase in Earth's atmosphere less rapidly than the molar decrease of O_2; the difference will reflect the dissolution of CO_2 in the oceans.

This method, developed by Ralph Keeling and Stephen Shertz (1992), in conjunction with precise measurements of changes in O_2 in the atmosphere, confirms a sink for about 1.7×10^{15} g C in the world's oceans and thus, an apparent net sink of 1.0×10^{15} g C in the terrestrial biosphere for the 1990s (compare to Bender et al. 2005; Table 11.1). This net sink for carbon in vegetation is relatively recent; the same methods show relatively little carbon accumulation on land during the 1980s (Langenfelds et al. 1999, Battle et al. 2000, Bopp et al. 2002). The sink for CO_2 in the oceans, increasing ocean acidification, is projected to exceed what is observed in sedimentary records for the past 300,000,000 years (Hönisch et al. 2012).

An examination of the isotopic composition of atmospheric O_2 (i.e., $\delta^{18}O$) also allows us to constrain the atmospheric CO_2 budget within certain limits. Photosynthesis does not discriminate among the oxygen isotopes of water—the O_2 released has an isotopic composition that is identical to that in the seawater or the soil water in which the plant is growing. Respiration discriminates among oxygen isotopes, consuming $^{16}O_2$ in preference to $^{18}O_2$; as a result $^{18}O_2$ is enriched in the atmosphere—known as the Dole effect (Luz and Barkan 2011). The $\delta^{18}O$ of atmospheric O_2 (+23.5‰) suggests that gross primary production must be $>170 \times 10^{15}$ g C/yr on land and about 140×10^{15} g C/yr in the oceans (Bender et al. 1994).[7] Assuming that

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[7] This calculation is based on the amount of GPP, evolving O_2 identical to that in soil or seawater (i.e., $\delta^{18}O = 0$), that is necessary to maintain a constant level of $\delta^{18}O$ in the atmosphere in the face of preferential respiratory consumption of the light isotope.

net primary production is one-half of gross primary production, in both cases, these values would seem to indicate that NPP is somewhat higher than what we have estimated independently for land (Table 5.3; Beer et al. 2010) and marine (Table 9.2) habitats globally. Nevertheless, these values offer an upper limit for NPP, which helps constrain our estimates for the global carbon cycle (Figure 11.1).

The oxygen cycle is directly linked to other biogeochemical cycles. For example, assuming that NO_3 accounts for about half the plant uptake of N on land (1200×10^{12} g) and about 10% of the N cycle in the oceans (8000×10^{12} g; Figure 9.21), then about 2% of the annual production of O_2 by photosynthesis is used to oxidize NH_4 in the nitrification reactions (compare to Ciais et al. 2007).

The formation and oxidation of sedimentary pyrite, through sulfate reduction, also affects the concentration of O_2 in the atmosphere. For every mole of pyrite-S oxidized, nearly 2 moles of O_2 are consumed from the atmosphere (Eq. 9.2). Currently, the annual burial of pyrite in marine sediments accounts for about 20% of the oxygen in our atmosphere (Chapter 9).

Methanogenesis in freshwater sediments returns CH_4 to the atmosphere, where it is oxidized (Henrichs and Reeburgh 1987). Methane oxidation in the atmosphere accounts for about 1% of the total consumption of atmospheric O_2 each year. In the absence of methanogenesis, the burial of organic carbon in freshwater sediments might be greater and the atmospheric content of O_2 might be slightly higher. Thus, methanogenesis acts as a negative feedback in the regulation of atmospheric O_2 (Watson et al. 1978, Kump and Garrels 1986).

It is perhaps entertaining to speculate whether the carbon cycle on Earth drives the oxygen cycle, or vice versa. Over geologic time, the answer is obvious: The conditions on our neighboring planets provide ample evidence that O_2 is derived from life. Now, however, the carbon and oxygen cycles are inextricably linked, and the metabolism of eukaryotic organisms, including humans, depends on the flow of electrons from reduced organic molecules to oxygen.

SUMMARY

Humans harvest about 20% of the annual production of organic carbon on land (i.e., NPP; Imhoff et al. 2004b, Haberl et al. 2007). In many areas we have destroyed land vegetation, while in other areas we have planted productive crops and forests and perhaps stimulated NPP by raising levels of atmospheric CO_2 and nitrogen deposition. At the moment, it appears that humans have created a net sink for carbon in the terrestrial biosphere, which mitigates some of the anticipated rise in atmospheric CO_2 from fossil fuel combustion (Table 11.1). With the use of fossil fuels, humans have, of course, supplemented the energy available to power modern society, including vast supplements to the agricultural systems that feed us. Dukes (2003) calculates that each year we burn the equivalent of the organic matter stored during 400 years of primary production in the geologic past. Accelerating use of fossil fuels is destined to lead to large changes in the Earth's conditions, which have otherwise been relatively stable during the 8000-year history of organized human society.

Recommended Readings

Archer, D. 2010. *The Global Carbon Cycle.* Princeton University Press.
Field, C.B., and M.R. Raupach (Eds.). 2004. *The Global Carbon Cycle: Integrating Humans, Climate, and the Natural World.* Island Press.
Solomon, S., D. Qin, M. Manning, M. Marquis, K. Averyt, M.M.B. Tignor, H.L. Miller, and Z. Chen. 2007. *Climate Change 2007: The Physical Science Basis.* Cambridge University Press.

PROBLEMS

1. How does the annual human extraction of fossil carbon (in grams) from the Earth's crust compare to the chemical and mechanical denudation of the continents (Chapter 4) by wind and water?

2. If wood has a density of 0.8 g/cm^3 and a carbon content of 50% by mass, what is the size of a cube of wood that contains 10^{15} g of carbon?

3. Calculate the pool of carbon in the global biomass of the human species, making and stating reasonable assumptions about the mass of individual humans and the abundance of their number globally.

4. Each molecule of methane contributes about $25\times$ as much to the Earth's greenhouse effect as each molecule of CO_2. If we were interested in preventing global warming, what would be the effect, versus reducing CO_2 emissions, if we were to eliminate all anthropogenic inputs of methane to the atmosphere (Table 11.2)?