

The magnitude of biotic and human impacts on ecosystem processes becomes clear when summed at the global scale. This chapter describes changes in the biogeochemical cycles of the Earth System that have occurred during the Anthropocene.

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## Introduction

**Human activities have altered biogeochemical cycles at global scales in ways that change the functioning of Earth as an ecosystem.** Human activities have dramatically altered element cycles since the beginning of the industrial revolution. Burning of fossil fuels in particular has increased emissions of CO<sub>2</sub>, nitric oxides, and several sulfur gases. Mining and agriculture have also altered the availability and mobility of carbon, nitrogen, phosphorus, and sulfur. Changes in these biogeochemical cycles have altered Earth's climate, speeding up the global hydrologic cycle, which in turn feeds back to other biogeochemical cycles. Together these changes alter ecosystems at all scales, ranging from individual organisms to the entire biosphere. In this chapter, we summarize at the global scale the pools and fluxes in key biogeochemical cycles and the factors responsible for change.

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## A Focal Issue

**The aggregate effects of human activities have altered biogeochemical cycles at global scales.** Fossil fuel emissions have increased atmospheric CO<sub>2</sub> concentration by 35% and increased ocean acidity by a similar proportion. Ocean acidity is the “other CO<sub>2</sub> problem” that is invisible to most people but it has potentially profound effects by dissolving the calcium carbonate structures of marine organisms as diverse as reef-forming corals, marine invertebrates such as mussels and crabs, and microscopic foraminifera that are an important base to marine food chains. Many marine coral reefs are already threatened by rising temperatures, warming-induced coral bleaching, and nutrient and sediment runoff from land. How do these multiple human impacts interact to affect reef development and the diverse ecosystems that they support (Fig. 14.1)? What are the potential consequences of altering the food base of the world oceans? How might changes in ocean productivity feedback to affect the CO<sub>2</sub> concentration and climate of Earth? Are these effects large or small compared to the changes in the capacity of terrestrial biosphere to influence climate? Understanding of global biogeochemical cycles places these important questions in an integrated context that can inform society of the interactive consequences of human actions.



**Fig. 14.1** Coral reefs are the rainforests of the ocean in the sense of being hot spots of biodiversity. Reefs also provide important food resources and storm protection to local

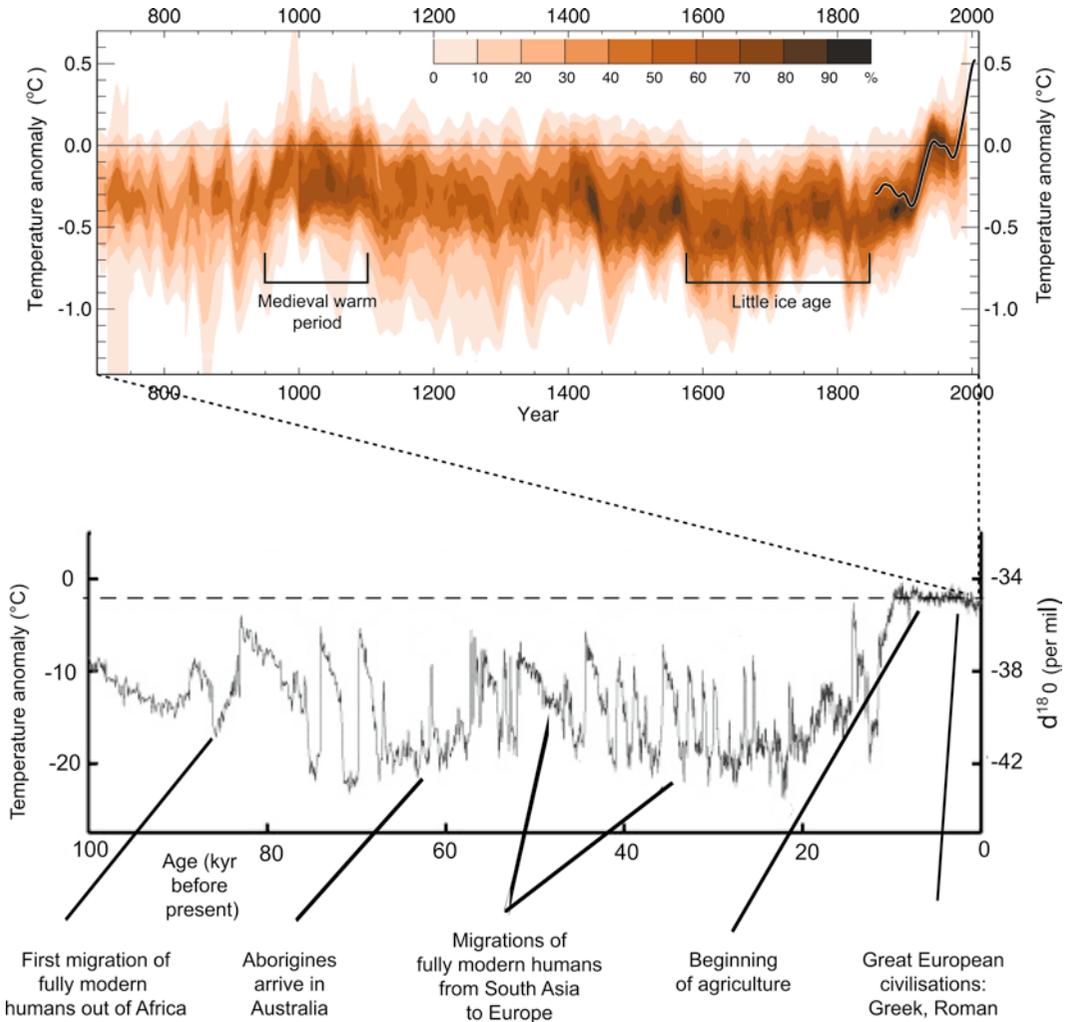
residents and are an important cultural, recreational, and aesthetic resources that benefit society broadly. Photograph of corals near Key Largo, Florida (istockphoto)

## Human Drivers of Change

**The rising human population and its consumption of resources account for many recent changes in the Earth System.** The last 10,000 years (**Holocene** interglacial period), since the end of the last ice advance, constitute a remarkably stable and benign period in Earth's climate history (Fig. 14.2). This stability contributed to the initiation of agriculture that provided people with a more stable food supply, the formation of sedentary communities to tend and use this food, and the founding of diverse civilizations around the globe. Human population increased about 100-fold (from 5 million to 700 million) from the end of the last ice age to the beginning of the industrial revolution in 1750. It increased another 10-fold over the next 250 years to seven billion people in 2010. Throughout human history people have affected their environment, just as all organisms do (see Chap. 11). This included human hunting that

contributed to the extinction of the Pleistocene megafauna (Flannery 1994, Zimov et al. 1995, Gill et al. 2009) and the spread of agriculture and grazing by domestic livestock that have altered land cover on about half of the terrestrial surface (see Chap. 13; Ellis and Ramankutty 2008). However, prior to the industrial revolution, these changes were small enough in scale that they had had only modest effects on the global environment. Since 1750, however, human population and its consumption of resources have had a dramatic impact on the Earth System. These changes have been particularly pronounced since 1950 (the **Great Acceleration**), with projections of even more rapid changes in the first half of the twenty-first century, if human use of resources is not substantially reduced (Steffen et al. 2004, Young and Steffen 2009).

Even modest temperature variations during the Holocene, such as the Medieval Warm Period and the Little Ice Age (Fig. 14.2), had



**Fig. 14.2** Temperature trends of the last 1,300 and last 100,000 years. Temperatures for the last 1,300 years have been estimated from 10 proxy records collected throughout the world; the percentage of records that show a given temperature ( $\pm 1$  standard error) is shown by the degree of shad-

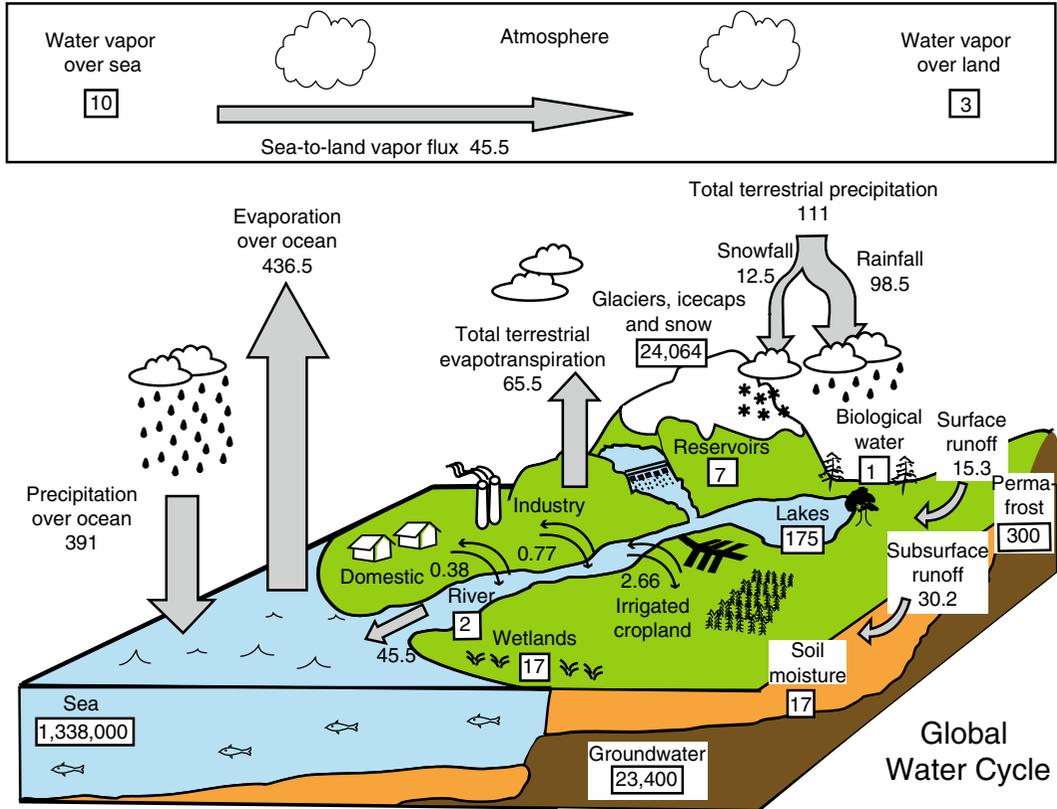
ing. The solid line shows the temperatures estimated from direct temperature records (IPCC 2007). Temperatures for the last 100,000 years are estimated from  $^{18}\text{O}$  concentrations in ice cores; also shown are selected events in human history. Redrawn from IPCC (2007) and Young and Steffen (2009)

major impacts on food production and human migration. The sharp increase in global temperature since 1800 is unprecedented in the last 1,000 years. This raises the distinct possibility that human impacts on the Earth System could push it beyond a threshold to a new state that might be less favorable to human well-being (see Chap. 15; MEA 2005; Rockström et al. 2009).

## The Global Water Cycle

### Water Pools and Fluxes

**Only a tiny fraction of Earth’s water (0.01%) is in soils, where it is accessible to plants and available to support the activities of terrestrial organisms. Most of Earth’s water is in the ocean**



**Fig. 14.3** The global water cycle, showing approximate magnitudes of the major pools (1,000 km<sup>3</sup>; boxes) and fluxes (1,000 km<sup>3</sup> year<sup>-1</sup>; arrows). Most water is in the ocean, ice, and groundwater, where it is not directly

accessible to terrestrial organisms. The major water fluxes are precipitation, evapotranspiration, and runoff. Modified from Carpenter and Biggs (2009)

(96.5%), ice caps and glaciers (2.4%), and groundwater (1%; Fig. 14.3; Oki and Kanae 2006, Carpenter and Biggs 2009). About 90% of the water that evaporates from the ocean returns there as precipitation. Another 10% of ocean evaporation (45,000 km<sup>3</sup> year<sup>-1</sup>) moves over the land, where it falls as precipitation and returns to the ocean as river runoff. The evaporation from land (65,000 km<sup>3</sup> year<sup>-1</sup>) is about 15% of global evaporation, although land occupies about 30% of Earth’s surface; this indicates that average evapotranspiration rates are about half as great on land as over the ocean. There are large regional variations in evaporation rate over both land and ocean related to climate and, in the case of land, in water availability and transpiration rates of vegetation. Of the terrestrial precipitation (110,000 km<sup>3</sup> year<sup>-1</sup>), about 40% comes from the

ocean (45,000 km<sup>3</sup> year<sup>-1</sup>), and 60% (65,000 km<sup>3</sup> year<sup>-1</sup>) is evaporated from land and recycled. Evaporation and precipitation are highly variable, both regionally and seasonally.

The quantity of water in the atmosphere is only 2.6% of that which annually cycles through the atmosphere in evaporation and transpiration, giving an average **turnover time** (i.e., time required to replenish this pool) of about 10 days. Precipitation is therefore tightly linked to evapotranspiration from upwind ecosystems over time scales of hours to weeks. Soil moisture has an average turnover time of about 2 months, with substantial regional variability, so plant water use is quite sensitive to seasonal variations in precipitation. Groundwater has an average turnover time of about 200 years (Fig. 14.3). This makes it a more dependable water source than surface

moisture but also implies that replenishment of groundwater takes a long time, if it is overexploited for irrigation or other uses. In some cases, **fossil groundwater** accumulated in the past, when climate may have been different. In these cases, replenishment of groundwater may not occur in the current climate or may take much longer than its calculated turnover time implies.

## Anthropogenic Changes in the Water Cycle

**Human-induced climate warming has accelerated the global hydrologic cycle through increases in both evapotranspiration and precipitation.** As Earth's air warms, it holds more moisture, driving greater evaporation and increasing the potential for precipitation. Precipitation over land, for example, increased north of 30°N during the twentieth century (IPCC 2007). With continued warming, wet areas are projected to become wetter, with more frequent large floods, and dry areas may become drier.

Land-use changes also alter the hydrologic cycle by changing (1) the quantity of energy absorbed, (2) the pathway of energy loss, and (3) the moisture content and temperature of the atmosphere. Conversion from tropical rainforest to pasture, for example, leads to less energy absorption because of increased albedo and a larger proportion of energy dissipated to the atmosphere as sensible rather than latent heat (Foley et al. 2003b). The warmer drier atmosphere allows less precipitation, favoring the persistence of pastures rather than succession to rainforests (see Fig. 2.14). When land-use changes are extensive, they can have continental-scale effects on temperature and precipitation, often at locations remote from the region of land-cover change, as a result of large-scale adjustments in atmospheric circulation (Chase et al. 2000). Land-cover changes in Southeast Asia, for example, have particularly large effects on global-scale climate through atmospheric teleconnections.

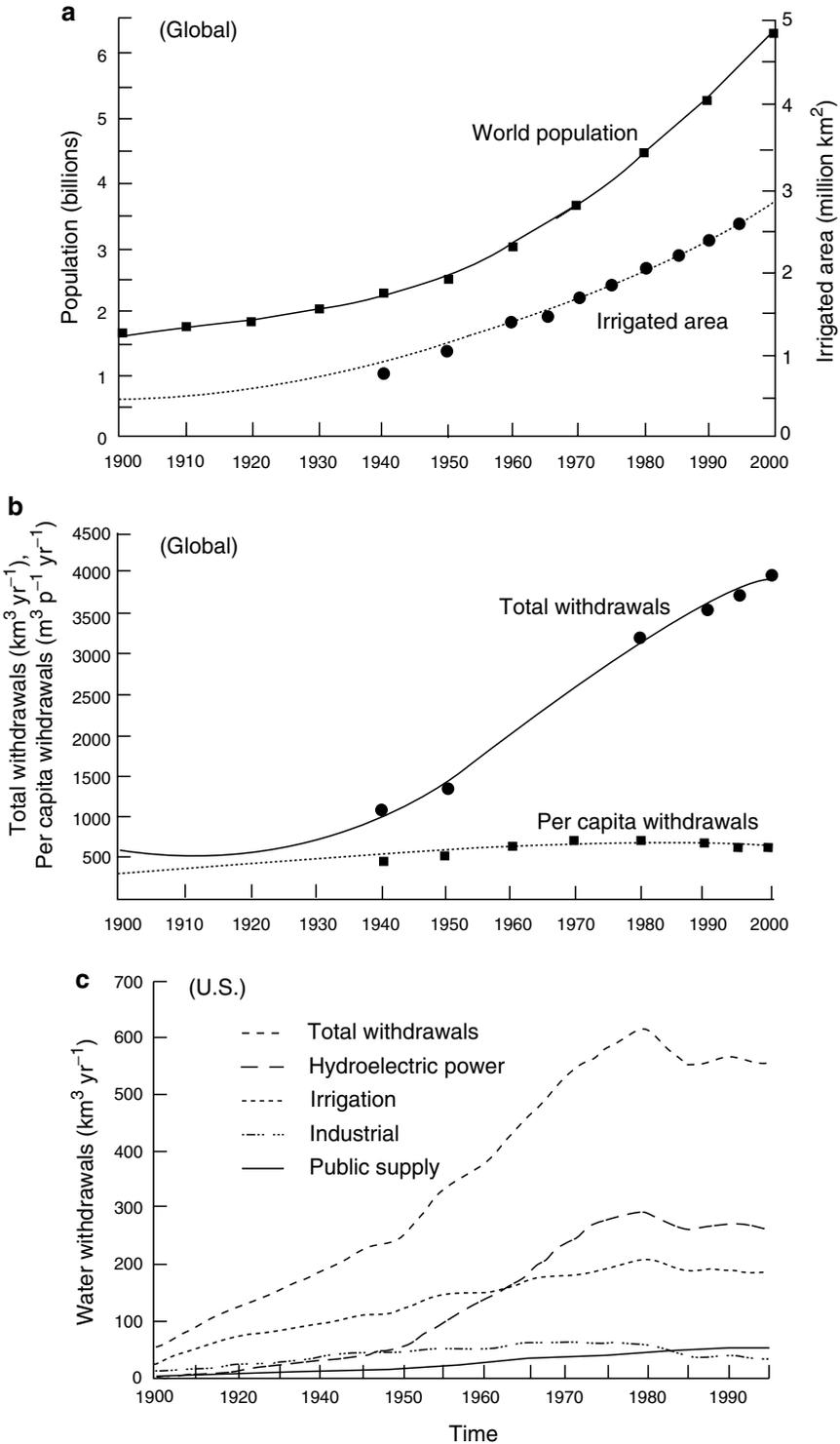
Terrestrial ecosystems are generally more sensitive to soil moisture than to precipitation. Soil moisture will probably decline in areas with

reduced precipitation and in regions where evaporation increases more than precipitation. Models generally project increased soil moisture at high latitudes and oceanic islands and reduced summer soil moisture in the interiors of continents due to higher temperatures and insufficient increases (or reductions) of rainfall. Many continental areas that are currently important for agriculture, such as the Ukraine and the mid-western U.S., may be particularly prone to future drought, and grain-producing areas may migrate poleward to areas that are currently too cold to support intensive agriculture. These changes in location of soil moisture suitable for agriculture will have major regional and national economic and societal impacts.

## Consequences of Changes in the Water Cycle

**Society depends most directly on some of the smallest and most vulnerable pools in the global hydrologic cycle.** Nonirrigated agriculture, for example, relies on soil water derived from precipitation, a relatively small pool that responds rapidly to changes in the balance between precipitation and evapotranspiration. In some areas, soil moisture derived from precipitation is supplemented by irrigation, which withdraws water from lakes, rivers, and groundwater. Irrigated croplands have increased fivefold during the twentieth century and support 40% of global crop production (Fig. 14.4; Gleick 1998, Carpenter and Biggs 2009). During the past century, there was an eightfold increase in the water used to support human activities, which paralleled a fourfold increase in human population and a 50% increase in per capita water consumption. People now use 25% of the continental runoff (see Chap. 4). Most of this water is used for hydroelectric power and irrigation. Selective expansion of irrigated agriculture in very poor regions of the world represents an important opportunity to alleviate hunger and poverty (Carpenter and Biggs 2009).

The scarcity of water is only part of the hydrologic challenges facing society. Forty percent of the world's population had no access to adequate



**Fig. 14.4** Trends in (a) world population and global land area under irrigation, (b) water withdrawals to support human activities expressed as a global total and on a per capita (p<sup>-1</sup>) basis, and (c) water withdrawal in the U.S. separated by economic sector. Redrawn from Gleick (1998)

sanitation in 2004, and 17% had no clean drinking water (Vörösmarty et al. 2005). The shortage of clean water is particularly severe in the developing nations of the world, where future population growth and water requirements are likely to be greatest (Postel and Richter 2003).

The projected increases in human demands for fresh water will have strong impacts on aquatic ecosystems through diversion of fresh water for irrigation and modification of flow regimes by dams and reservoirs. These impacts can be minimized by increasing the efficiency with which society uses water and nutrients.

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## The Global Carbon Cycle

### Carbon Pools and Fluxes

**Photosynthetic uptake of carbon from the atmosphere and ocean provides the fuel for most biological processes.** This reduced carbon comprises about half of the mass of Earth's organic matter. Biological systems, in turn, respire CO<sub>2</sub> when they use organic carbon as an energy source to support maintenance and growth. The controls over the carbon cycle depend on time scale, ranging from seconds, where cycling is controlled by photosynthetic rate and surface–air exchange, to millions of years, where cycling is controlled by movements of Earth's crust (see Chaps. 5–7).

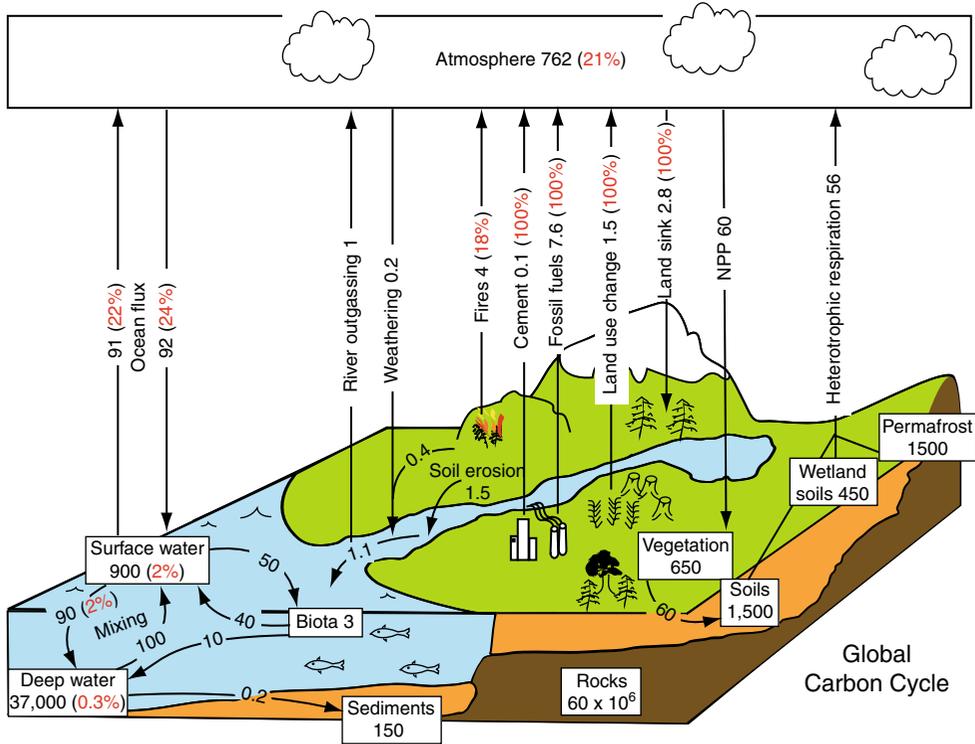
Carbon is distributed among four major pools: the atmosphere, ocean, land (soils and vegetation), and sediments and rocks (Fig. 14.5; Reeburgh 1997, Sarmiento and Gruber 2006, IPCC 2007). Atmospheric carbon, which consists primarily of CO<sub>2</sub>, is the smallest but most dynamic of these pools. It turns over about every 5 years, primarily through its removal by photosynthesis and return by respiration. The metabolism of organisms therefore constitutes the engine that drives the global carbon cycle on time scales of seconds to centuries.

Carbon is present in the ocean as dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and particulate organic carbon (POC), which consists of both live organisms and dead

material. Most (98%) of this carbon is in inorganic form, primarily as bicarbonate (90%), with most of the rest as carbonate. Free CO<sub>2</sub>, the form that is directly used by most marine primary producers, accounts for less than 1% of this inorganic pool. These three forms of DIC are in a pH-dependent equilibrium (see Chap. 5). The marine biota account for only 3 Pg ( $3 \times 10^{15}$  g) of carbon, although they cycle almost as much carbon annually as does terrestrial vegetation. The carbon in marine biota turns over about every 3 weeks.

The ocean's surface waters that interact with the atmosphere contain about 920 Pg of carbon, similar to the quantity in the atmosphere (Fig. 14.5). The capacity of the ocean to take up carbon is constrained by three categories of processes that operate at different time scales (Schlesinger 1997). In the short term, surface exchange rate depends on wind speed, surface temperature, and the CO<sub>2</sub> concentration of surface waters. On daily to monthly time scales, the CO<sub>2</sub> concentration in surface water depends on photosynthesis and pH-dependent buffering reactions. Finally, the surface waters are a relatively small pool (only 75–200 m deep) of water that exchanges relatively slowly with deeper ocean layers because the warm, low-salinity surface water is less dense than deeper layers (see Fig. 2.10). Carbon that enters surface waters is transported slowly to depth by two major mechanisms. First, organic detritus and its CaCO<sub>3</sub> skeletal content, which form in the euphotic zone, sink to deeper waters, a process termed the **biological pump** (see Chap. 7). Second, bottom-water formation in the polar seas transports dissolved carbon to depth, a process termed the **solubility pump** (see Chap. 2). Once carbon reaches intermediate and deep waters, it is stored for hundreds to thousands of years before returning to the surface through upwelling. Most (97%) of the ocean carbon is in the intermediate and deep waters (Fig. 14.5).

The terrestrial biosphere contains the largest biological reservoir of carbon. There is nearly as much carbon in terrestrial vegetation as in the atmosphere, with 2–3 times more organic carbon in soils than in the atmosphere (Fig. 14.5; Jobbágy



**Fig. 14.5** The global carbon cycle, showing approximate magnitudes of the major pools (boxes) and fluxes (arrows) in units of  $\text{Pg year}^{-1}$  for the 1990s. A petagram (Pg) is  $10^{15}$  g. Red numbers in parenthesis are the anthropogenic contributions to these pools and fluxes relative to preindustrial times (1750). Data are from Sabine et al. (2004), Sarmiento and Gruber (2006), and IPCC (2007), and anthropogenic fluxes for 2000–2006 from Canadell et al. (2007). The carbon pools that contribute to carbon cycling over decades to centuries are the atmosphere, land (vegetation and soils), and surface ocean water. On land, the carbon gain by vegetation due to “fertilization” by elevated  $\text{CO}_2$  and nitrogen deposition (i.e., the land sink) is slightly greater than the carbon loss due to land-use

change, leading to net carbon transfer to land. A similar quantity of land carbon is eroded into rivers, with half being outgassed to the atmosphere and half transported to the ocean. The carbon input from the atmosphere to the ocean is also slightly greater than the carbon returned to the atmosphere. These terrestrial and ocean sinks are less than half of the carbon emitted to the atmosphere from burning of fossil fuels, leading to  $\text{CO}_2$  accumulation in the atmosphere. The terrestrial biosphere accounts for 50–60% of global NPP. Most (80%) of the marine NPP is released to the environment by heterotrophic respiration, with the remaining 20% going to the deep ocean by the biological pump. Ocean upwelling returns most of this carbon to the surface ocean waters

and Jackson 2000, Sabine et al. 2004, IPCC 2007). Permafrost (permanently frozen ground) also contains a large carbon pool that, until recently, turned over very slowly (Zimov et al. 2006, Schuur et al. 2008, Tarnocai et al. 2009). Terrestrial NPP is slightly greater than that in the ocean, but, due to the much larger plant biomass on land, terrestrial plant carbon has a turnover time of about 11 years, compared to 3 weeks in the ocean. NPP

is about half of GPP (i.e., photosynthetic carbon gain) on land ( $60 \text{ Pg year}^{-1}$  out of  $120 \text{ Pg year}^{-1}$ ) and in the ocean ( $45 \text{ Pg year}^{-1}$  out of  $103 \text{ Pg year}^{-1}$ ; Prentice et al. 2001, IPCC 2007). Soil carbon turns over on average every 25 years. These average turnover times mask large differences in turnover time among components of the terrestrial carbon cycle. Photosynthetically fixed carbon in chloroplasts turns over on time scales of seconds

**Table 14.1** Average (2000–2006) annual emissions and fate of anthropogenic carbon. Adapted from Canadell et al. (2007) and Le Quéré et al. (2009)

Sources and sinks of anthropogenic carbon	Annual net flux (Pg C year <sup>-1</sup> )
Anthropogenic carbon sources	9.1
Fossil fuel and cement production (8.7 in 2008)	7.6
Land-use change	1.5
Carbon sinks (1990–2000)	9.1
Storage in the atmosphere	4.1
Oceanic uptake	2.2
Terrestrial uptake	2.8

through photorespiration (see Chap. 5). Leaves and roots are replaced over weeks to years, and wood is replaced over decades to centuries. Components of soil organic matter also have quite different turnover times, with labile forms turning over in minutes and humus having turnover times of decades to thousands of years (see Chap. 7).

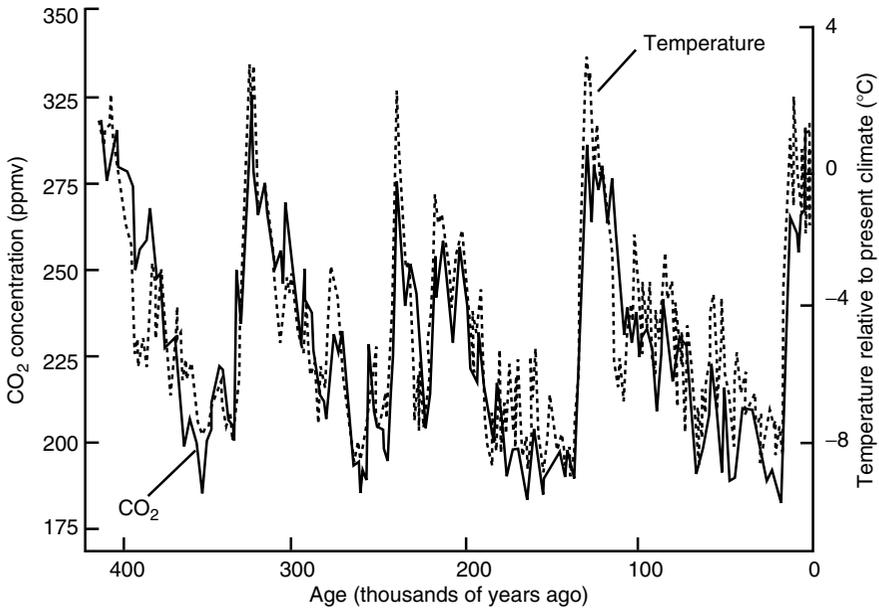
Carbon in rocks and sediments accounts for well over 99% of Earth's carbon ( $10^7$  Pg; Reeburgh 1997, Schlesinger 1997). This carbon pool cycles extremely slowly, with turnover times of millions of years. Factors governing the turnover of these pools are geologic processes associated with the rock cycle, including the movement of continental plates, volcanism, uplift, and weathering (see Chap. 3).

Human activities are now a significant component of the global carbon cycle. Human carbon emissions from combustion of fossil fuels increased 40% from 1990 to 2008 (to 8.7 Pg year<sup>-1</sup>; Canadell et al. 2007, IPCC 2007, Le Quéré et al. 2009). Land-use conversion releases an additional 1.5 Pg year<sup>-1</sup> of carbon by biomass burning and enhanced decomposition (Table 14.1; Canadell et al. 2007). Together these anthropogenic fluxes are about 15% of the carbon cycled by terrestrial or by marine production, making human carbon emissions the third largest biologically controlled flux of carbon to the atmosphere. Moreover, unlike primary production, human carbon fluxes represent net additions to the atmosphere.

## Changes in Atmospheric CO<sub>2</sub>

**Critical processes in the carbon cycle respond to environment at multiple time scales.** The critical controls over carbon cycling are photosynthesis and respiration on time scales of seconds to years; NPP, SOM turnover, and disturbance on time scales of years to centuries; and uplift, weathering, and ocean sedimentation over thousands to millions of years. Atmospheric CO<sub>2</sub> concentration has varied at least 10-fold through Earth's history, from the preindustrial concentration of 280 ppmv to greater than 3,000 ppmv. Geochemical processes determine variation in atmospheric CO<sub>2</sub> on geological time scales. These include the weathering of silicate rocks (which consumes CO<sub>2</sub> and releases bicarbonate), burial of organic carbon in sediments, and volcanism (which releases CO<sub>2</sub>) (Berner 1997, Sundquist and Visser 2004). Biological processes influence geochemical cycling in many ways, for example by increasing weathering rates (see Chap. 3). Although critical on long time scales, the rates of these geochemical processes are so slow compared to anthropogenic changes that they do not influence current trajectories of change in atmospheric CO<sub>2</sub>.

Over the last 650,000 years, changes in solar input associated with variations in Earth's orbit (see Chap. 2) caused cyclic variation in atmospheric CO<sub>2</sub> concentrations associated with glacial–interglacial cycles (Fig. 14.6; Petit et al. 1999, Sigman and Boyle 2000, IPCC 2007). CO<sub>2</sub> concentration declined during glacial periods and increased during interglacials. These changes in CO<sub>2</sub> concentration are much larger than can be explained simply by changes in light intensity and temperature in response to altered solar input. The large biospheric changes must result from amplification by biogeochemical feedbacks in the Earth System. Several feedbacks could contribute to these atmospheric changes (Sigman and Boyle 2000, IPCC 2007). (1) Increased transport of dust off the less-vegetated continents during glacial periods may have increased iron, phosphorus, and silica transport and enhanced NPP in high-latitude ocean basins, leading to increased CO<sub>2</sub> uptake and transport to depth via the biological pump

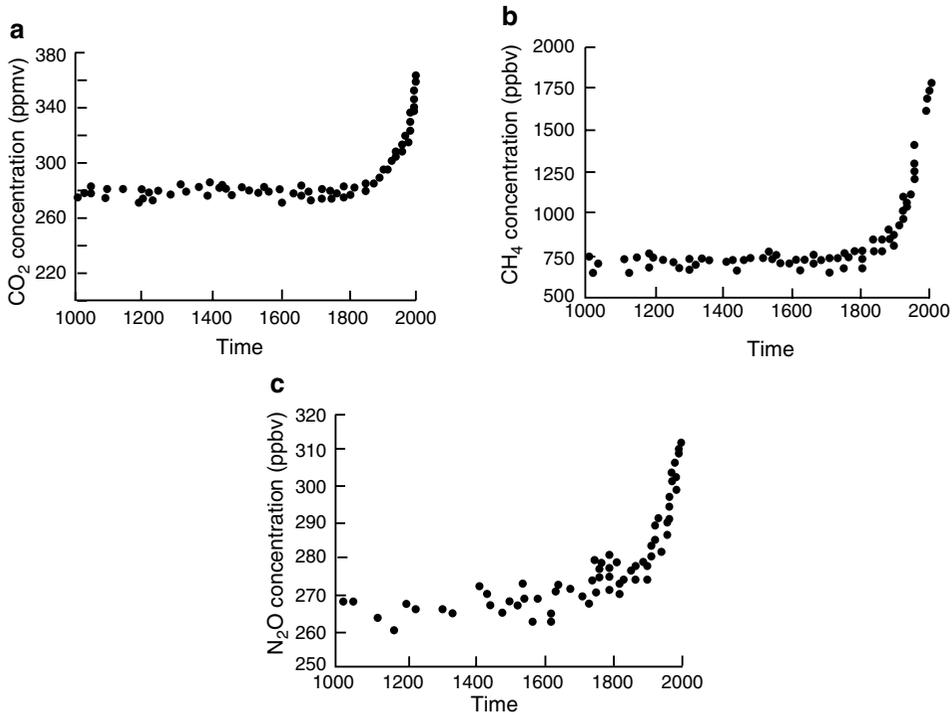


**Fig. 14.6** Variations in temperature and atmospheric CO<sub>2</sub> concentrations derived from air trapped in Antarctic ice cores. Redrawn from Folland et al. (2001)

(see Fig. 7.26). (2) Extensive winter sea ice around Antarctica may have reduced out-gassing of CO<sub>2</sub> in locations of upwelling of CO<sub>2</sub>-rich deep waters (Stephens and Keeling 2000). (3) Additional carbon may have been stored on land during glacial periods – both on continental shelves exposed by the drop in sea level and in permafrost at high latitudes (Zimov et al. 2006). However, terrestrial systems also lost carbon during glacial periods, due to the replacement of forests by grasslands, deserts, tundra, and ice sheets. Although the net effect of all these changes is uncertain (IPCC 2007), there have been large redistributions of carbon between land, atmosphere, and ocean over the course of glacial cycles (Bird et al. 1994, Crowley 1995). An improved understanding of controls over carbon redistribution among global pools could indicate how the Earth System will respond to current trends of increasing temperature and atmospheric CO<sub>2</sub>.

Like air temperature (Fig. 14.2), atmospheric CO<sub>2</sub> concentration has been relatively stable over

the last 12,000 years, ranging from about 260 to 280 ppmv in preindustrial times (Fig. 14.7). During the past century, however, CO<sub>2</sub> concentration has risen 10-fold more rapidly than at any time in the previous 20,000 years (Petit et al. 1999). Its concentration of 390 ppmv in 2011 is the highest in at least 650,000 years and probably the last 20 million years (Pearson and Palmer 2000, Canadell et al. 2007). Despite recent efforts to reduce emissions, atmospheric CO<sub>2</sub> continues to rise at an ever-increasing rate (Canadell et al. 2007, IPCC 2007, Solomon et al. 2009). This occurs primarily because of increasing emissions, especially in rapidly developing nations like China and India, and continued high emission rates by developed nations, such as the U.S., Japan, and Europe. These recent changes in the global cycles of carbon and other elements caused by human activities are large enough to indicate that Earth has entered a new geologic epoch, the **Anthropocene** (see Fig. 2.15; Crutzen 2002).



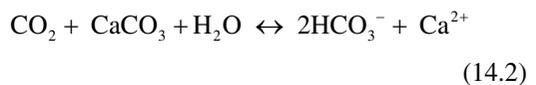
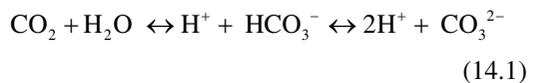
**Fig. 14.7** Changes over the last millennium in the atmospheric concentrations of three radiatively active gases that are influenced by human activities. Data shown are a

composite of time series from air trapped in Antarctic ice cores and from direct atmospheric measurements. Redrawn from Prentice et al. (2001)

### Marine Sinks for CO<sub>2</sub>

**The ocean removes CO<sub>2</sub> from the atmosphere through dissolution in seawater and photosynthesis by marine organisms.** The dissolution of CO<sub>2</sub> in the ocean, which accounts for most movement of CO<sub>2</sub> to the ocean, produces acidity (H<sup>+</sup>), as it equilibrates with bicarbonate and carbonate ions (Eq. 14.1; Doney et al. 2009). The rising dissolved CO<sub>2</sub> concentration and resulting 30% increase in ocean acidity have at least two important consequences (Feely et al. 2004, Orr et al. 2005). It tends to dissolve the carbonate (e.g., CaCO<sub>3</sub>) shells of marine invertebrates (e.g., lobsters, oysters, and corals; Fig. 14.1; Eq. 14.2) and

diatoms, altering the functioning of marine ecosystems. In addition, it reduces the rate at which CO<sub>2</sub> dissolves in the ocean – i.e., makes the ocean a weaker sink for CO<sub>2</sub>. This contributes to an increasing proportion of fossil-fuel carbon that remains as a greenhouse gas in the atmosphere (see Fig. 7.28, Box 14.1; Canadell et al. 2007).



### Box 14.1 Partitioning of Carbon Uptake Between the Land and Ocean

Only about half of the anthropogenic CO<sub>2</sub> that enters the atmosphere remains there. The land or ocean takes up the remainder (Table 14.1). Changes in the oxygen content of the atmosphere provide a measure of relative importance of land and ocean uptake. Net terrestrial uptake of CO<sub>2</sub> is accompanied by a net release of oxygen, with a 1:1 ratio of moles of CO<sub>2</sub> absorbed to moles of O<sub>2</sub> released. When CO<sub>2</sub> dissolves in ocean water, however, this causes no net release of oxygen. This difference in exchange processes can be used to partition the total CO<sub>2</sub> uptake between terrestrial and ocean components (Keeling et al. 1996b).

The relative abundance of the two stable isotopes of carbon (<sup>13</sup>C and <sup>12</sup>C) in the atmosphere provides a second measure of the relative activity of the terrestrial and oceanic components of the global carbon cycle (Ciais et al. 1995). Fractionation during photosynthesis by C<sub>3</sub> plants discriminates

against <sup>13</sup>C, causing biospheric carbon to be depleted in <sup>13</sup>C by about 18‰ relative to the atmosphere. Exchanges with the ocean, however, involve relatively small fractionation effects. Changes in the <sup>13</sup>C/<sup>12</sup>C ratio of atmospheric CO<sub>2</sub> therefore indicate the relative magnitude of terrestrial and oceanic CO<sub>2</sub> uptake.

Measurement of the global pattern and temporal changes in oxygen concentration and the <sup>13</sup>C/<sup>12</sup>C ratio of atmospheric CO<sub>2</sub> suggest that the land and ocean contribute about equally to the removal of anthropogenic CO<sub>2</sub> from the atmosphere (IPCC 2007). There are, however, many assumptions and complications in using either of these approaches to estimate the relative magnitudes of terrestrial and oceanic carbon uptake. The advantage of atmospheric measurements is that they give an integrated estimate of all uptake processes on Earth because of the relatively rapid rate at which the atmosphere mixes.

## Terrestrial Sinks for CO<sub>2</sub>

**Land-use change, CO<sub>2</sub> fertilization, nitrogen deposition, and various climate effects contribute to the terrestrial sink for CO<sub>2</sub>** (Schimel 1995, Reich et al. 2006, Luo 2007). The conversion of forests to agricultural lands dominated land-use change in the middle and high latitudes until the mid-twentieth century. Today, forest regrowth in abandoned agricultural lands has enhanced carbon storage, particularly in Europe and North America. The widespread suppression of wildfire also enhances the mid-latitude carbon sink because it reduces fire emissions and allows woody plants to encroach into grasslands (Houghton 2004). These are probably the most important reasons why north-temperate terrestrial ecosystems are a net carbon sink (IPCC 2007). Meanwhile, increasing rates of deforestation in the tropics reduce the low-latitude sink for CO<sub>2</sub> (Field et al. 2007).

CO<sub>2</sub> enhancement of photosynthesis also contributes to carbon storage (Norby et al. 2005, Long et al. 2006), although not as much as the short-term CO<sub>2</sub> response of photosynthesis might suggest. Over the longer term, CO<sub>2</sub> uptake becomes nutrient-limited, as nutrients become sequestered in live and dead organic matter (see Chap. 6; Shaver et al. 1992, Norby et al. 2010). The effect of CO<sub>2</sub> fertilization on carbon storage appears to be smaller than that due to reforestation in the temperate zone, but in the tropics, CO<sub>2</sub> fertilization appears sufficient to offset the loss to deforestation of carbon-fixation capacity (Field et al. 2007).

Nitrogen additions through fertilizer applications or atmospheric deposition of air pollutants like NO<sub>x</sub> from fossil-fuel burning have stimulated photosynthesis and reduced respiration, leading to greater carbon sequestration in some places (see Chap. 7; Magnani et al. 2007, de Vries et al. 2009, Janssens et al. 2010).

Finally, climate changes (including changes in temperature, moisture, and radiation) affect carbon storage through their effects on carbon inputs (photosynthesis) and outputs (respiration). These effects vary regionally and are difficult to generalize because direct climatic effects (e.g., stimulation of respiratory carbon loss by warmer temperatures) are often offset by indirect effects (e.g., stimulation of NPP by the nutrients released during decomposition; Shaver et al. 2000). Vegetation generally has a much higher C:N ratio (160:1) than does soil organic matter (14:1), so the transfer of a given quantity of nitrogen from the soil to plants enhances carbon storage (Vukicevic et al. 2001). In addition, plant respiration acclimatizes to temperature, so ecosystem respiration increases less in response to warming than might be expected from short-term measurements (Luo et al. 2001).

The relative importance of the various mechanisms of enhanced carbon storage in the terrestrial biosphere is uncertain (Schimel et al. 2001), but together they are probably sufficient to account for the observed movement of a fraction of anthropogenic CO<sub>2</sub> from the atmosphere to land. Just as described for the ocean, the strength of the terrestrial carbon sink appears to be weakening (see Fig. 7.28; Le Quéré et al. 2007), suggesting that the various sink mechanisms (forest regrowth, CO<sub>2</sub> fertilization, nitrogen addition, and climate effects) are beginning to saturate and may remove less CO<sub>2</sub> from the atmosphere in the future. The most effective mechanism of stabilizing atmospheric CO<sub>2</sub> concentration is therefore to reduce anthropogenic emissions.

## CO<sub>2</sub> Effects on Climate

**Much of the increased concentration of fossil-fuel CO<sub>2</sub> will remain in the atmosphere for hundreds to thousands of years.** If all anthropogenic emissions ceased today, about half would be absorbed by lands and the ocean within 30 years, about 30% of it would remain in the atmosphere for several centuries, and the remaining 20% for thousands of years (IPCC 2007, Archer et al. 2009, Solomon et al. 2009). There

are at least four reasons why CO<sub>2</sub> disappears slowly from the atmosphere: (1) the efficiency of the land and ocean sinks is weakening, as described previously; (2) the deep ocean, which is the major long-term sink for CO<sub>2</sub>, equilibrates very slowly with the surface ocean and the atmosphere; (3) stabilizing feedbacks minimize changes in ecosystem carbon pools – for example, the increase in decomposition that occurs in response to increased photosynthesis and litter inputs (see Chap. 7); and (4) weathering of silicate rocks, which is the largest long-term sink for CO<sub>2</sub> on land, occurs very slowly. Because CO<sub>2</sub> is the largest anthropogenic contributor to climate warming (see Fig. 2.18), past CO<sub>2</sub> emissions already commit us to a warmer planet, and decisions about future emissions will strongly influence the magnitude of continued climate warming. In addition, much of the heat absorbed as a result of increased concentrations of greenhouse gases has gone into the ocean and will return to the atmosphere, even if natural cycles or some (as yet unknown) technological solution instantly removed all fossil-fuel carbon from the atmosphere (Solomon et al. 2009). This long-term commitment to future warming enhances concerns that Earth has approached, or perhaps exceeded, a threshold of “dangerous climate change” that warrants rapid and vigorous efforts to reduce carbon emissions to the atmosphere (Stern 2007, Rockström et al. 2009).

## The Global Methane Budget

**Human activities are responsible for increasing methane concentrations in the atmosphere.**

Although the methane (CH<sub>4</sub>) concentration of the atmosphere (1.8 ppmv) is much less than that of CO<sub>2</sub> (390 ppmv), CH<sub>4</sub> is about 23 times more efficient per molecule as a greenhouse gas than is CO<sub>2</sub>. Like CO<sub>2</sub>, the CH<sub>4</sub> concentration of the atmosphere has increased exponentially since the beginning of the industrial revolution (Fig. 14.7). The CH<sub>4</sub> increase accounts for 20% of the increased greenhouse warming potential of the atmosphere (see Fig. 2.18; Bousquet et al. 2006, IPCC 2007). Documenting the major global

**Table 14.2** Global sources and sinks of methane. Data from Wang et al. (2004), Chen and Prinn (2006), and IPCC (2007)

Methane sources and sinks	Annual flux (Tg CH <sub>4</sub> year <sup>-1</sup> )
Natural sources	168
Wetlands	145
Termites and ruminants	23
Anthropogenic sources	428
Coal combustion	48
Oil and gas combustion	36
Landfills and waste	70
Fermentation by cattle	119
Rice agriculture	112
Biomass burning	43
Total sources	596
Sinks	581
Reaction with OH	511
Removal in stratosphere	40
Removal by soils	30
Atmospheric increase	1–22 <sup>a</sup>

<sup>a</sup> Annual atmospheric increase declined from about 22 Tg CH<sub>4</sub> year<sup>-1</sup> in the 1990s to about 1 Tg CH<sub>4</sub> year<sup>-1</sup> in 2000–2004

sources and sinks of atmospheric CH<sub>4</sub> is therefore important to understanding the recent increases in global temperature and the potential for future climate warming.

Methane is produced only under anaerobic conditions (see Chap. 7). Wetlands account for 85% of the naturally produced CH<sub>4</sub>, with the remainder coming primarily from freshwater sediments, fermentation in the guts of animals (e.g., termites and ruminants), and various geological sources (Table 14.2). Anthropogenic methane sources are 2.5 times larger than the natural sources, showing why CH<sub>4</sub> accumulates in the atmosphere despite its high reactivity and rapid turnover (9 years). Fossil-fuel extraction and refining; waste management (landfills, animal wastes, and domestic sewage treatment); and agricultural sources (rice paddies, biomass burning, and fermentation in guts of domestic ruminants like cattle) are each important CH<sub>4</sub> sources. The concentration and rate of accumulation in the atmosphere are known quite precisely, but the relative contributions of different sources and sinks are still topics of active debate. Important new sources are still being identified, including

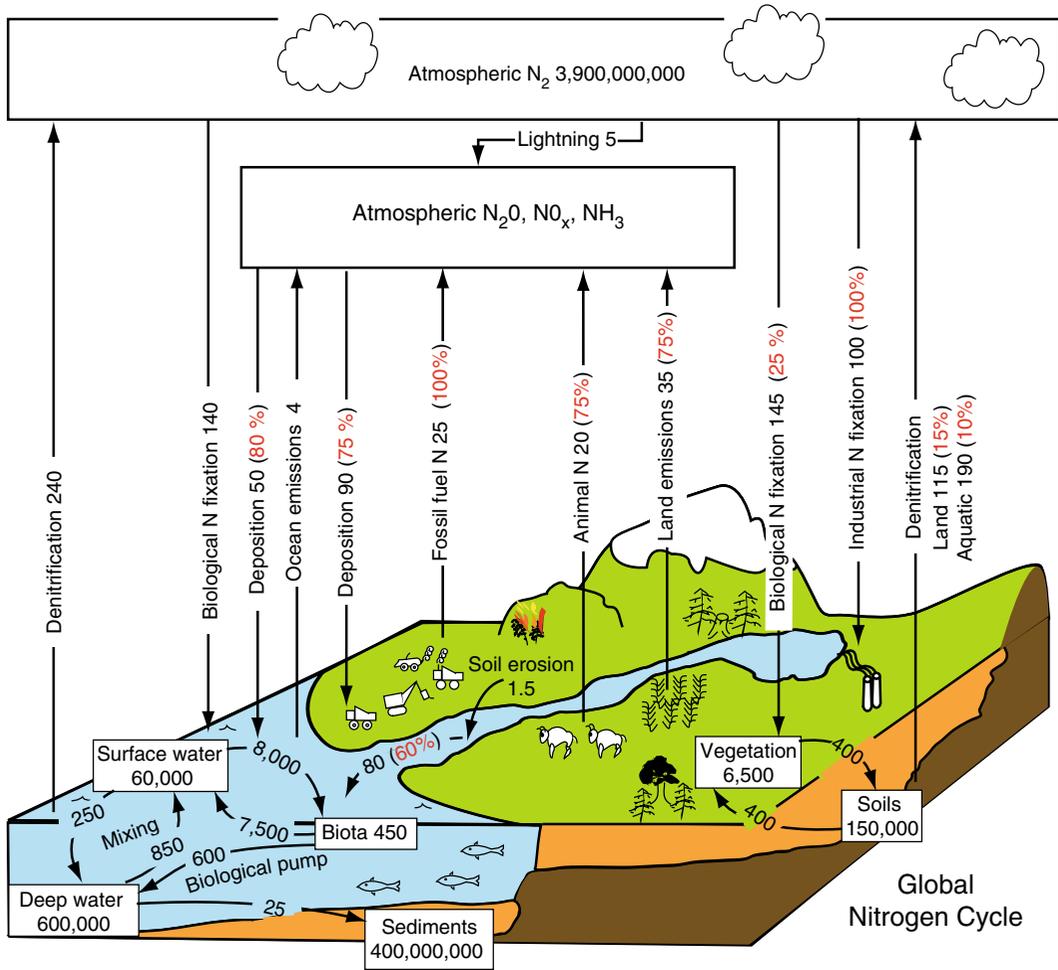
high-latitude thaw lakes and reservoirs with organic-rich substrates (St. Louis et al. 2000, Friedl and Wüest 2002, Walter et al. 2007).

CH<sub>4</sub> reacts readily with OH radicals in the atmosphere in the presence of sunlight. This photochemical process is the major sink for atmospheric CH<sub>4</sub>, accounting for 85% of the CH<sub>4</sub> consumption (Table 14.2). Additional CH<sub>4</sub> mixes into the stratosphere, where it reacts with ozone (see Chap. 2) or is removed by methanotrophs in soils (see Chap. 7). The annual atmospheric accumulation of CH<sub>4</sub> is about 10% of the annual anthropogenic flux, as compared to 50% for CO<sub>2</sub>.

## The Global Nitrogen Cycle

### Nitrogen Pools and Fluxes

**The productivity of many ecosystems on both land and sea is limited in part by the supply of available nitrogen.** Almost all of the nitrogen that is relevant to biogeochemistry is in a single pool (the atmosphere) with comparatively small quantities in the ocean, rocks, and sediments (Fig. 14.8). Organic nitrogen pools are minuscule relative to the atmospheric pool and occur primarily in soils and terrestrial vegetation. Although nitrogen makes up 78% of the atmosphere, it is nearly all N<sub>2</sub> and is unavailable to most organisms. N<sub>2</sub> is transformed to biologically available forms via nitrogen fixation by bacteria in soils and aquatic systems, or living in association with plants. The global quantity of nitrogen fixed annually by natural ecosystems is quite uncertain, with estimates near 100 Tg year<sup>-1</sup> for terrestrial ecosystems and between 40 and 200 Tg year<sup>-1</sup> for marine ecosystems. Lightning probably adds an additional 3–10 Tg year<sup>-1</sup> of nitrogen to the available pool. Prior to human alteration, the amount of nitrogen entering the biosphere via nitrogen fixation was approximately balanced by return to the unavailable pools via denitrification and burial in sediments. During glacial periods, the input of iron and other micronutrients may have caused nitrogen fixation to exceed denitrification, reducing the degree of nitrogen limitation in the ocean. In interglacial periods such as the present, denitrification may exceed nitrogen fixation. There is



**Fig. 14.8** The global nitrogen cycle, showing approximate magnitudes of the major pools (*boxes*) and fluxes (*arrows*) in units of Tg year<sup>-1</sup>. A teragram (Tg) is 10<sup>12</sup> g. *Numbers in parenthesis* are the anthropogenic contributions to these pools and fluxes. Data are from Reeburgh (1997), Chapin et al. (2002), Galloway et al. (2004), and Gruber and Galloway (2008). To ensure consistency among global cycles of different elements, pools and fluxes of biota were calculated from the global carbon budget (Fig. 14.5) assuming mass-based C:N ratios (Serner and Elser 2002) of marine biota (6.6), terrestrial vegetation (100), and terrestrial litter (150) and are close to published estimates for global nitrogen budgets. The

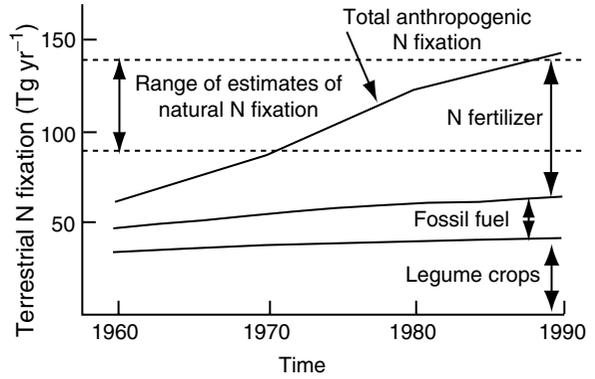
atmosphere contains the vast majority of Earth’s nitrogen. The amount of nitrogen that annually cycles through terrestrial non-crop vegetation is fourfold greater than inputs by nitrogen fixation. In the ocean, the annual cycling of nitrogen through the biota is 60-fold greater than inputs by nitrogen fixation. Denitrification is the major output of nitrogen to the atmosphere. Human activities increase nitrogen inputs through fertilizer production, planting of nitrogen-fixing crops, and combustion of fossil fuels. Human activities also increase emissions of nitrogen trace gases (NO<sub>x</sub>, N<sub>2</sub>O, NH<sub>3</sub>) through fossil fuel emissions, land emissions (agriculture, fire, land-use change), and animal husbandry

considerable debate about the current degree of balance or imbalance between marine nitrogen fixation and denitrification (Falkowski et al. 1998). In contrast to carbon, nitrogen is cycled quite tightly within terrestrial ecosystems, with the annual throughput often being at least four-fold greater than inputs and losses.

### Anthropogenic Changes in the Nitrogen Cycle

**In the past century, human activities have approximately doubled the quantity of nitrogen fixed from the atmosphere into terrestrial systems.** The Haber process, which uses energy

**Fig. 14.9** Anthropogenic fixation of nitrogen in terrestrial ecosystems over time, in comparison with the range of estimates of natural biological nitrogen fixation on land. Redrawn from Vitousek et al. (1997a)



from fossil fuels to convert  $N_2$  to  $NH_3$  to produce fertilizers, fixes more nitrogen than any other anthropogenic process. Industrial fixation of nitrogen by the Haber process began increasing substantially in the 1940s, reaching  $30 \text{ Tg year}^{-1}$  by 1970 and  $100 \text{ Tg year}^{-1}$  by 2000 (Fig. 14.9). It is projected to be  $165 \text{ Tg year}^{-1}$  by 2050 (Galloway et al. 2004). Initially, most nitrogen fertilizer was applied in developed nations, but from 2000 to 2009 about 80% of the global increase in use of nitrogen fertilizer occurred in China and India. Much of the projected increase in fertilizer use is expected to occur in developing nations.

Cultivation of nitrogen-fixing crops such as soybeans, alfalfa, and peas adds fixed nitrogen over and above that which is added via biological fixation in natural ecosystems. Agricultural crops account for about 25% of terrestrial nitrogen fixation (Fig. 14.8). Some nitrogen fixation is also carried out by free-living and associative nitrogen fixers like *Azolla* that commonly occur in rice paddies.

**Human activities account for most of the nitrogen trace gases transferred from Earth to the atmosphere.** In addition to the large pool of relatively unreactive  $N_2$ , the atmosphere contains several nitrogen trace gases, including  $NO_x$  ( $NO$  and  $NO_2$ ),  $N_2O$ , and  $NH_3$ . Although the pools and fluxes of these nitrogen trace gases are much smaller than those of  $N_2$  (Fig. 14.8), they play a very active role in atmospheric chemistry and have been more strongly affected by human activities (see Chap. 9).

Nitrous oxide ( $N_2O$ ), which is increasing at the rate of  $0.2\text{--}0.3\% \text{ year}^{-1}$  (Fig. 14.7), is an

inert gas that is 200-fold more efficient than  $CO_2$  as a greenhouse gas and contributes about 6% of the greenhouse warming (IPCC 2007). Nitrification and denitrification in the ocean and in tropical soils are the major natural sources of  $N_2O$  (Schlesinger 1997, Galloway et al. 2004). Human activities have nearly doubled  $N_2O$  flux from Earth to the atmosphere, primarily through agricultural fertilization. Other anthropogenic  $N_2O$  sources include cattle and feedlots, biomass burning, and various industrial sources.  $N_2O$  is broken down in the stratosphere, where it catalyzes the destruction of stratospheric ozone.

Human activities have tripled the flux of ammonia ( $NH_3$ ) from land to the atmosphere (Galloway et al. 2004). Domestic animals are now the single largest global source of ammonia; agricultural fertilization, biomass burning, and human sewage are other important sources. Cultivated soils, which account for only 10% of the ice-free land area (see Table 6.6), account for about half of the ammonia flux from soils to the atmosphere. In summary, activities associated with agriculture (animal husbandry, fertilizer addition, and biomass burning) are the major cause for increased ammonia transport to the atmosphere and account for 60% of the global flux. Ammonia is a reactant in many atmospheric reactions that form aerosols and generate air pollution. Ammonia is also the main acid-neutralizing agent in the atmosphere, raising the pH of rainfall, cloud water, and aerosols. Most of the ammonia emitted to the atmosphere returns to Earth in precipitation.

Human activities have increased  $\text{NO}_x$  flux to the atmosphere six- to sevenfold, primarily through the combustion of fossil fuels. Nitrification is the largest natural terrestrial source of NO (see Chap. 9). Fertilizer addition has increased the magnitude of this source, with additional NO coming from biomass burning. Preindustrial  $\text{NO}_x$  fluxes were greater in tropical than temperate ecosystems, due to frequent burning of tropical savannas, soil emissions, and production by lightning (Holland et al. 1999). Most  $\text{NO}_x$  deposition now occurs in the temperate zone, where deposition rates have increased fourfold since preindustrial times.

**Nitrogen deposition affects many ecosystem processes.** The widespread nitrogen limitation or co-limitation of plant production in nontropical ecosystems results in retention of a large proportion of anthropogenic nitrogen that is deposited in ecosystems, particularly in young, actively growing forests that are accumulating nutrients in vegetation (see Fig. 12.18). Nitrogen deposition often stimulates carbon storage, by stimulating production in nitrogen-limited sites and reducing heterotrophic respiration in nitrogen-rich sites (Magnani et al. 2007, de Vries et al. 2009, Janssens et al. 2010). Nonetheless, the overall role of nitrogen deposition in explaining the terrestrial land sink for carbon is quite uncertain.

Nitrogen accumulation in production and organic matter storage cannot increase indefinitely. After long-term chronic nitrogen inputs, nitrogen supply may exceed plant and microbial demands, resulting in **nitrogen saturation** (Aber et al. 1998, Driscoll et al. 2001). When ecosystems become nitrogen saturated, nitrogen losses to stream water, groundwater, and the atmosphere increase and should eventually approach nitrogen inputs. Nitrogen saturation is often associated with declines in forest productivity and increased tree mortality in coniferous forests in Europe (Schulze 1989) and the U.S. (Aber et al. 1995, Fahey et al. 2005).

Temperate forests vary regionally in the rate at which they approach nitrogen saturation, depending on rates of nitrogen inputs and the capacity of soils to buffer these inputs (Aber et al. 1995, Fahey et al. 2005, Juice et al. 2006). In tropical

forests, where nitrogen availability is typically high relative to plant and microbial demands, anthropogenic nitrogen deposition may lead to immediate nitrogen losses (Hall and Matson 1998), which could have potentially negative effects on plant and soil processes (Matson et al. 1999). In general, the capacity of a forest ecosystem to retain nitrogen is linked to its productive potential and its degree of nitrogen limitation (Aber et al. 1995, Magill et al. 1997, Magnani et al. 2007).

The addition of limiting nutrients can alter species dominance and reduce the diversity of ecosystems. Nitrogen addition to grasslands or heathlands, for example, increases the dominance of nitrogen-demanding grasses, which then suppress other plant species (Berendse et al. 1993). These species changes can convert nutrient-poor, diverse heathlands to species-poor forests and grasslands (Aerts and Berendse 1988, Tilman and Wedin 1991).

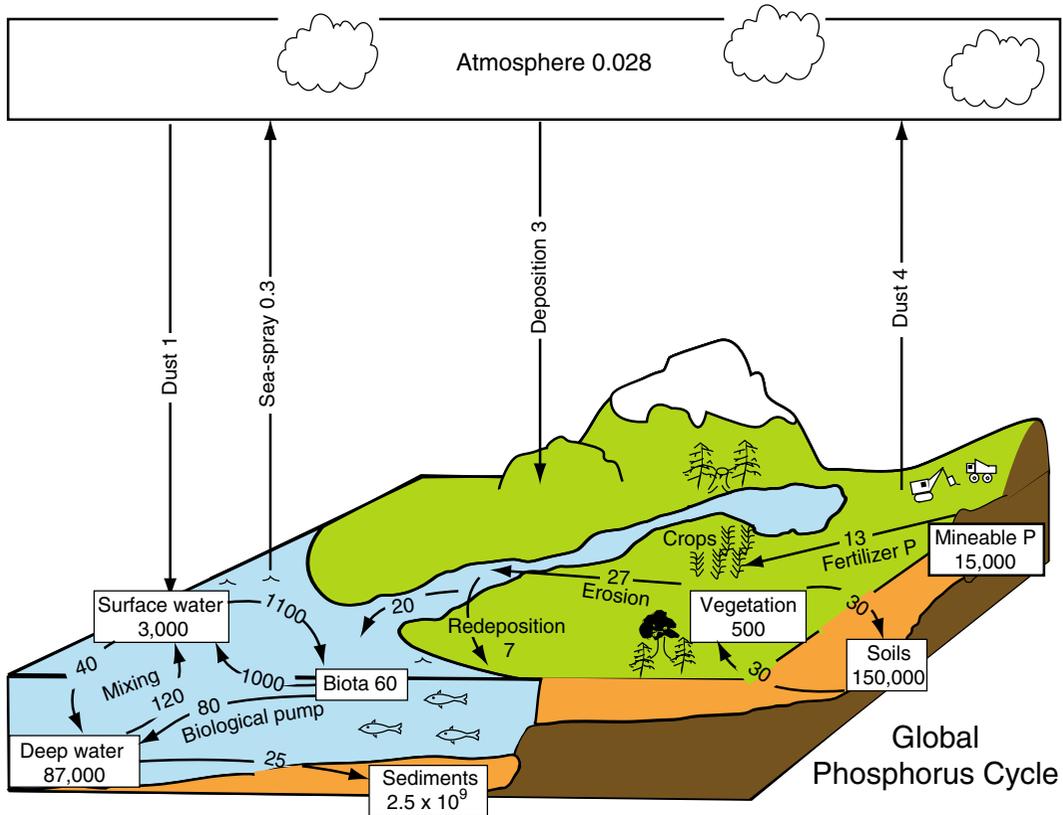
**Human activities increase the nitrogen transfer from terrestrial to aquatic ecosystems.** The massive nitrogen additions to terrestrial ecosystems, in the form of deposition, fertilization, food imports, and growth of nitrogen-fixing crops, have led to a dramatic increase in nitrogen concentrations in surface and ground waters over the past century (see Chap. 9).

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## The Global Phosphorus Cycle

### Phosphorus Pools and Fluxes

**Unlike carbon and nitrogen, phosphorus has only a tiny gaseous component and no biotic pathway that brings new phosphorus into ecosystems.** Ecosystems, until recently, therefore derived most available phosphorus from organic forms, and phosphorus cycled quite tightly within terrestrial ecosystems. Like nitrogen, phosphorus is an essential nutrient that is often in short supply. Marine and freshwater sediments and terrestrial soils account for most phosphorus on Earth's surface (Fig. 14.10). Most of this store is not directly accessible to the biota but occurs primarily in insoluble forms such as calcium or iron



**Fig. 14.10** The global phosphorus cycle, showing approximate magnitudes of the major pools (*boxes*) and fluxes (*arrows*) in units of  $\text{Tg year}^{-1}$ . A teragram (Tg) is  $10^{12}$  g. Data are from Smil (2000) and Ruttenberg (2004). To ensure consistency among global cycles of different elements, pools and fluxes of biota were calculated from the global carbon and nitrogen budgets (Figs. 14.5, 14.8) assuming mass-based N:P ratios (Sterner and Elser 2002) of marine biota (7.2) and terrestrial vegetation and litter (12.6), and are close to published estimates for global phosphorus

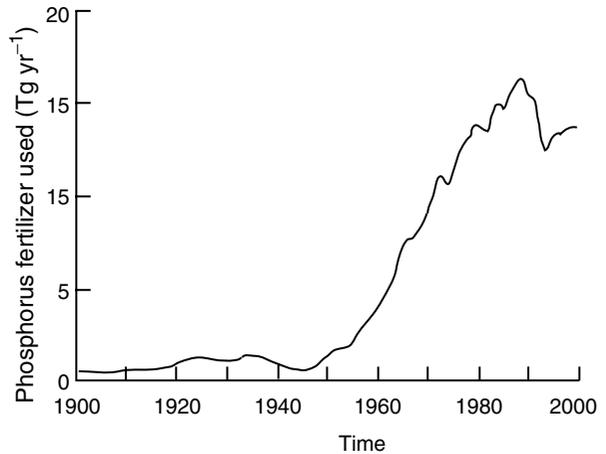
budgets for marine biota but smaller than published estimates for terrestrial biota (Ruttenberg 2004). Most phosphorus that participates in biogeochemical cycles over decades to centuries is present in soils, sediments, and the ocean. Phosphorus cycles tightly between vegetation and soils on land and between marine biota and surface waters in the ocean. The major human impact on the global phosphorus cycle has been application of fertilizers (equivalent to about a third of that which cycles naturally through vegetation) and erosional loss from crop and grazing lands

phosphate. Most organic phosphorus is in plant or microbial biomass. Recycling of that organic matter when it dies is the major source of phosphorus that is directly available to organisms.

The physical transfers of phosphorus around the global system are constrained by the lack of a major atmospheric gaseous component. Leaching losses in natural ecosystems are also low due to the low solubility of phosphorus. Instead, phosphorus moves around the globe primarily through wind erosion and runoff of particulates in rivers and streams to the ocean. The major flux in the

global phosphorus cycle (excluding human activities) is via hydrologic transport from land to the ocean. In the ocean, some of those phosphorus-containing particulates are recycled by marine biota and the rest is buried in sediments. Because there is no atmospheric link from the ocean to land, the flow is one-way on short time scales (Smil 2000). On geological time scales (tens to hundreds of millions of years), phosphorus-containing sedimentary rocks are exposed and weathered, resupplying phosphorus to the biosphere (Ruttenberg 2004).

**Fig. 14.11** Changes in the global use of inorganic phosphorus fertilizers during the twentieth century. Redrawn from Smil (2000)



## Anthropogenic Changes in the Phosphorus Cycle

**Human activities have enhanced the mobility of phosphorus and altered its natural cycling by mining of phosphorus-rich deposits, which accelerates the rate at which phosphorus weathers from rocks, and also by accelerating erosion and wind- and waterborne transport.** Inorganic phosphorus fertilizers have been produced since the mid-1800s, but the amount produced and applied has increased dramatically since the mid-twentieth century (Fig. 14.11), coincident with the intensification of agriculture that accompanied the “Green Revolution” (Smil 2000). Between 1850 and 2000, agricultural systems received about 550 Tg of new phosphorus. The annual application of phosphorus to agricultural ecosystems (10–15 Tg year<sup>-1</sup>) is about a third of that which cycles naturally through all terrestrial ecosystems (Fig. 14.10).

Human land-use change has also increased phosphorus losses from ecosystems. Water and wind erosion cause a 15 Tg year<sup>-1</sup> phosphorus loss from the world’s croplands, an amount similar to the annual fertilizer inputs. Overgrazing has also increased erosional losses, mobilizing about 12 Tg year<sup>-1</sup> of phosphorus from grazing lands (Smil 2000). About 25% of this is redeposited in floodplains or deposited in reservoirs. The production of human and animal wastes have led to point and nonpoint sources of phosphorus. The total phosphorus transfer from land to the ocean

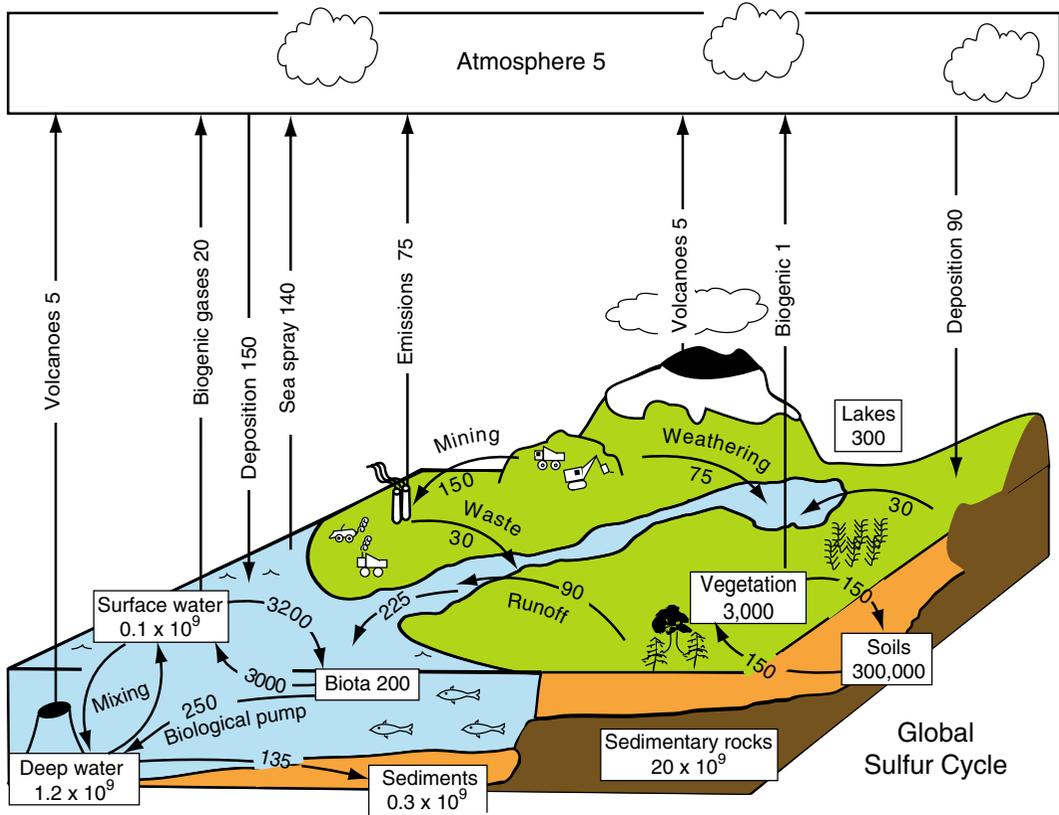
has increased 50–300% due to human activities (Ruttenberg 2004).

Together, these changes have increased the transport of phosphorus around the world (Howarth et al. 1995). Because phosphorus commonly limits production in lakes, the inadvertent phosphorus fertilization of freshwater ecosystems can lead to eutrophication and associated negative consequences for aquatic organisms and society (see Chap. 9). Phosphorus transport by windblown dust can also affect downwind ecosystems such as the Southern Ocean.

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## The Global Sulfur Cycle

**The global cycle of sulfur shares characteristics with the global cycles of nitrogen and phosphorus.** The sulfur cycle, like the nitrogen cycle, has a significant atmospheric component. The gaseous forms in the atmosphere have low concentrations but play important roles. Like phosphorus, sulfur is primarily rock derived. Seawater, sediments, and rocks are the largest reservoirs of sulfur (Fig. 14.12). The atmosphere contains little sulfur. Prior to human activities of the past several centuries, sulfur became available to the biosphere primarily through the weathering of sedimentary pyrite. Once weathered, sulfur moves through the global system by hydrologic transport or emission to the atmosphere as a reduced sulfur gas or sulfur-containing particles. About 100 Tg year<sup>-1</sup> of sulfur, moving mostly as



**Fig. 14.12** The global sulfur cycle, showing approximate magnitudes of the major pools (*boxes*) and fluxes (*arrows*) in units of  $\text{Tg year}^{-1}$ . A teragram (Tg) is  $10^{12}$  g. Data are from Galloway (1996), Reeburgh (1997), Schlesinger (1997), and Brimblecombe (2004). To ensure consistency among global cycles of different elements, pools and fluxes of biota were calculated from the global

carbon and nitrogen budgets (Figs. 14.5, 14.8) assuming mass-based N:S ratio of 7.4 (Bolin et al. 1983). Most sulfur is in rocks, sediments, and ocean waters. The major fluxes in the sulfur are through the biota and various trace gas fluxes. Human activities have doubled the global fluxes of sulfur through mining and increased gas emissions

dissolved sulfate, was transported through rivers to the coastal margins or open ocean in the preindustrial world (Galloway 1996).

Sulfur can be reduced to sulfide or to other trace sulfur gases in anaerobic environments such as wetlands and coastal sediments. The emission of sulfate from seawater (sea spray) and sulfur trace gases from the ocean ( $160 \text{ Tg year}^{-1}$ ) is about 100-fold greater than that from continents (Fig. 14.12). Marine biogenic emissions include dimethylsulfide (DMS), one of the primary sources of atmospheric sulfate; emissions of  $\text{SO}_2$  from volcanic eruptions are the other major natural source.

Sulfur emitted to the atmosphere typically has a short residence time. It is oxidized to sulfate by reaction with OH radicals. Sulfate rains out

downwind within a few days, generally as sulfuric acid. Sulfuric acid quickly condenses to form sulfate in cloud droplets, which readily evaporate to form sulfate aerosols. These aerosols have both direct and indirect effects on Earth's energy budget. Their direct effect is to backscatter (reflect) incoming shortwave radiation, thus reducing solar inputs and tending to reduce global temperature (see Fig. 2.18). Their indirect effects are more complicated and difficult to predict. As particulates, they act as cloud condensation nuclei by providing a surface on which water can condense, thereby influencing cloud formation, cloud lifetimes, cloud droplet size, and therefore cloud albedo. The uncertainty of the direction and magnitude of the multiple effects of sulfate aerosols

on climate is a key reason for concern about the anthropogenic changes in the global sulfur cycle.

Human activities now transfer about  $135 \text{ Tg year}^{-1}$  of sulfur to the atmosphere and ocean, increasing the natural cycling rate by about 50% (Fig. 14.12). Half of this sulfur arises from fossil-fuel combustion and ore refining, and the rest comes from mobilization of sulfur in dust from farming, animal husbandry, erosion of exposed sediments, and other sources. Much of the anthropogenic sulfur moves through the atmosphere and is deposited on land, where it can accumulate in soils or biota, or is discharged to the ocean in solution.

Reconstruction of global temperature records from ice cores shows that sulfur dioxide from volcanic emissions is a major cause of interannual climate variation over long time scales. Consequently, the dramatic increase in sulfur aerosols due to anthropogenic emissions will undoubtedly play an important role in future climate changes. The cooling effects of sulfur emissions and their associated direct and indirect effects could range from 0 to  $1.5 \text{ W m}^2$ , partially offsetting the warming due to greenhouse gases (IPCC 2007).

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## Summary

Ecological processes and human activities play major roles in most biogeochemical cycles. The magnitude of biotic and human impacts on ecosystem processes is substantial when summed at the global scale.

Most water is in the ocean, ice, and groundwater, where it is not directly accessible to terrestrial organisms. The major water fluxes are precipitation, evapotranspiration, and runoff. Human activities have speeded up the global hydrologic cycle by increasing global temperature, which enhances evapotranspiration and therefore precipitation, and by diverting much of the accessible fresh water for human use. Availability of adequate fresh water will be an increasingly scarce resource for society, if current human population trends continue.

Biotic processes (photosynthesis and respiration) constitute the engine that drives the global

carbon cycle. The four major carbon pools that contribute to carbon cycling over decades to centuries are the atmosphere, land, ocean, and surface sediments. On land, the carbon gain by vegetation is slightly greater than the carbon loss in respiration, leading to net carbon storage on land. The net carbon input to the ocean is also slightly greater than the net carbon return to the atmosphere. Marine primary production is about the same as that on land. Most (80%) of this marine NPP is released to the environment by respiration, with the remaining 20% going to the deep ocean by the biological pump. Ocean upwelling returns most of this carbon to the surface ocean waters; only small quantities are deposited in sediments. Human activities cause a net carbon flux to the atmosphere through combustion of fossil fuels, cement production, and land-use change. This flux is equivalent to 14% of terrestrial heterotrophic respiration.

The atmosphere contains the vast majority of Earth's nitrogen. The amount of nitrogen that annually cycles through terrestrial vegetation is ninefold greater than inputs by nitrogen fixation. In the ocean, the annual cycling of nitrogen through the biota is 70-fold greater than inputs by nitrogen fixation. Denitrification is the major output of nitrogen to the atmosphere. Human activities have doubled the quantity of nitrogen fixed by the terrestrial biosphere through fertilizer production, planting of nitrogen-fixing crops, and combustion of fossil fuels.

Most phosphorus that participates in biogeochemical cycles over decades to centuries is present in soils, sediments, and the ocean. Phosphorus cycles tightly between vegetation and soils on land and between marine biota and surface waters in the ocean. The major human impact on the global phosphorus cycle has been application of fertilizers (equivalent to about 40% of that which naturally cycles through vegetation) and erosional loss from crop and grazing lands (equivalent to about half of that which annually cycles through vegetation). Most sulfur is in rocks, sediments, and ocean waters. The major fluxes in the sulfur are through the biota and various trace gas fluxes. Human activities have substantially increased global fluxes of sulfur through mining and increased gas emissions.

## Review Questions

1. How do the major global cycles (carbon, nitrogen, phosphorus, sulfur, and water) differ from one another in terms of (1) the major pools and (2) the major fluxes? In which cycles are soil pools and fluxes largest? In which cycles are atmospheric pools and fluxes largest?
2. How have human activities changed the global water cycle? If the world has so much water, and this water is replenished so frequently by precipitation, why are people concerned about changes in the global water cycle? In what regions of the world will changes in the quantity and quality of water have greatest societal impact? Why?
3. How do the controls over the global carbon cycle differ between time scales of months, decades, and millennia? How has atmospheric CO<sub>2</sub> varied on each of these time scales, and what has caused this variation?
4. How have human activities altered the global carbon cycle? What are the mechanisms that explain why some of the CO<sub>2</sub> generated by human activities becomes sequestered on land and in the ocean?
5. What are the major causes and the climatic consequences of increased atmospheric concentrations of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O? What changes in human activities would be required to reduce the rate of increase of these gases, and what would be the societal consequences of these policy changes?
6. What are the major natural sources and sinks of atmospheric methane? How might these be changed by recent changes in climate and atmospheric composition?
7. What are the major natural sources and sinks of atmospheric N<sub>2</sub>O? How might these be changed by recent changes in climate and land use?
8. How have human activities changed the global nitrogen cycle? How have these

changes affected the nitrogen cycle in unmanaged ecosystems?

9. How do changes in the nitrogen cycle affect the global carbon cycle? How does soil fertility affect the mechanism by which nitrogen affects the carbon cycle?
10. How have human activities changed the global phosphorus and sulfur cycles? How do changes in these cycles affect the global cycles of other elements?

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