

# The Global Cycles of Nitrogen and Phosphorus

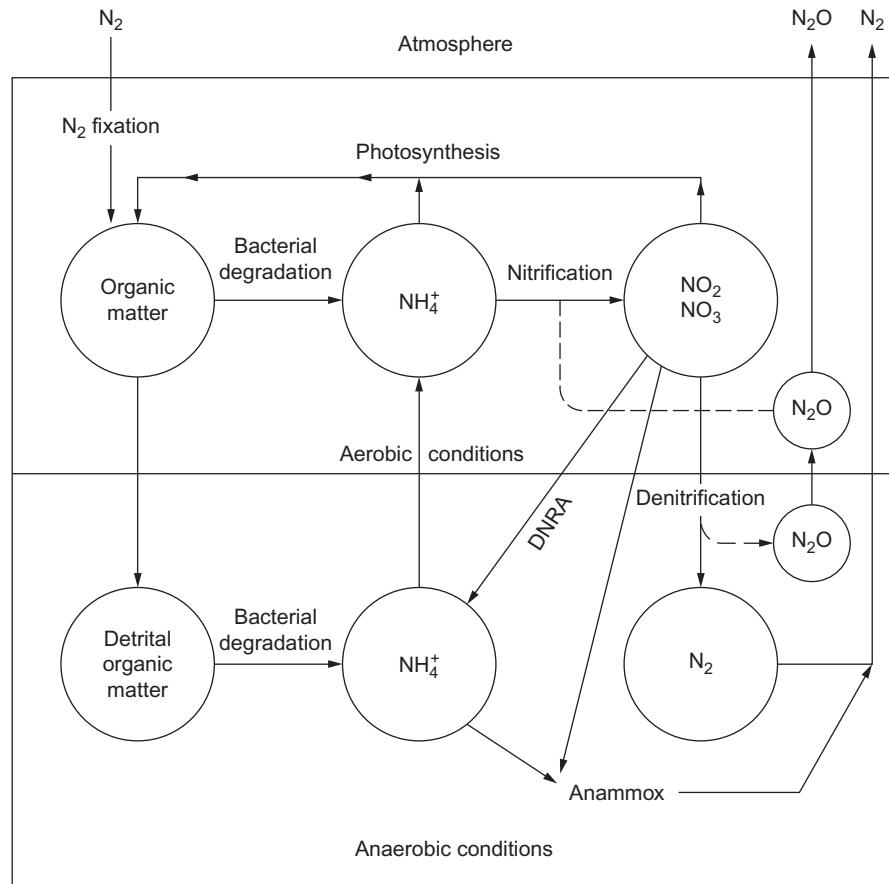
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## INTRODUCTION

The availability of nitrogen and phosphorus controls many aspects of ecosystem function and global biogeochemistry. Nitrogen often limits the rate of net primary production on land and in the sea (Chapters 6 and 9). In living tissues, nitrogen is an integral part of enzymes, which mediate the biochemical reactions in which carbon is reduced (e.g., photosynthesis) or oxidized (e.g., respiration). Nearly all of the nitrogen in biomass is first assimilated by the attachment of an amine group ( $-\text{NH}_2$ ) to the 5-carbon sugar oxoglutarate, linking the C and N cycles at the level of cellular biochemistry (Williams 1996, p. 158). Phosphorus is an essential component of DNA, ATP, and the phospholipid molecules of cell membranes. The ratio of N to P in plant tissues, about 16, finds its basis in the ratio of protein to RNA in protoplasm (Loladze and Elser 2011). Changes in the availability of N and P and their relative abundance are likely to have controlled the size and activity of the biosphere through geologic time.

A large number of biochemical transformations of nitrogen are possible, since nitrogen is found at valence states ranging from  $-3$  (in  $\text{NH}_3$ ) to  $+5$  (in  $\text{NO}_3^-$ ). A variety of microbes capitalize on the potential for transformations of N among these states and use the energy released by the changes in redox potential to maintain their life processes (Rosswall 1982).



**FIGURE 12.1** Microbial transformations in the nitrogen cycle (DNRA = Dissimilatory Nitrate Reduction to Ammonium). *Source: Modified from Wollast (1981).*

Collectively, these microbial reactions drive the cycle of nitrogen (Figure 12.1). In contrast, whether it occurs in soils or in biochemistry, phosphorus is almost always found in combination with oxygen (i.e., as  $PO_4^{3-}$ ). Most metabolic activity is associated with the synthesis or destruction of high-energy bonds between a phosphate ion and various organic molecules, but in nearly all cases the phosphorus atom remains at a valence of +5 in these reactions.

The most abundant form of nitrogen at the surface of the Earth,  $N_2$ , is the least reactive species. Nitrogen fixation converts atmospheric  $N_2$  to one of the forms of reactive nitrogen ("fixed" or "odd"; Chapter 3) that can be used by biota. Nitrogen-fixing species are most abundant in nitrogen-poor habitats, where their activity increases the availability of nitrogen for the biosphere (Eq. 2.10). At the same time, denitrifying bacteria return  $N_2$  to the atmosphere (Eq. 2.20), lowering the overall stock of nitrogen available for life on Earth.

Rocks of the continental crust hold the reservoir of phosphorus that becomes available to the biosphere through rock weathering. Land plants can increase the rate of rock weathering in P-deficient habitats (Chapter 4), but in nearly all cases the phosphorus content of rocks is

relatively low. Subsequent reactions between dissolved P and other minerals reduce the availability of P in soil solutions or seawater (Figure 4.10). Thus, in most habitats—both on land and in the sea—the availability of P is controlled by the degradation of organic forms of P (e.g., Figure 6.19). This biogeochemical cycle temporarily retains and recycles some P from the unrelenting flow of P from weathered rock to ocean sediments. The global P cycle is complete only when sedimentary rocks are lifted above sea level and the weathering begins again.

Because supplies of nitrogen and phosphorus often define soil fertility, humans have added enormous quantities of these elements to soils to enhance crop production. The production of fertilizer has more than doubled the supply of N and P on the land surface, altering biogeochemical cycling and leading to inadvertent enrichments of ecosystems downwind or downstream of the point of application.

In this chapter, we examine our current understanding of the global cycles of N and P. We attempt to balance N and P budgets for the world's land area and for the sea. For N, the balance between N fixation and denitrification through geologic time determines the nitrogen available to biota and the global nitrogen cycle. One of the byproducts of nitrification and denitrification is  $\text{N}_2\text{O}$  (nitrous oxide), which is both a greenhouse gas and a cause of ozone destruction in the stratosphere (Chapter 3). We present a budget for  $\text{N}_2\text{O}$  based on our current understanding of the sources of this gas in the atmosphere.

## THE GLOBAL NITROGEN CYCLE

### Land

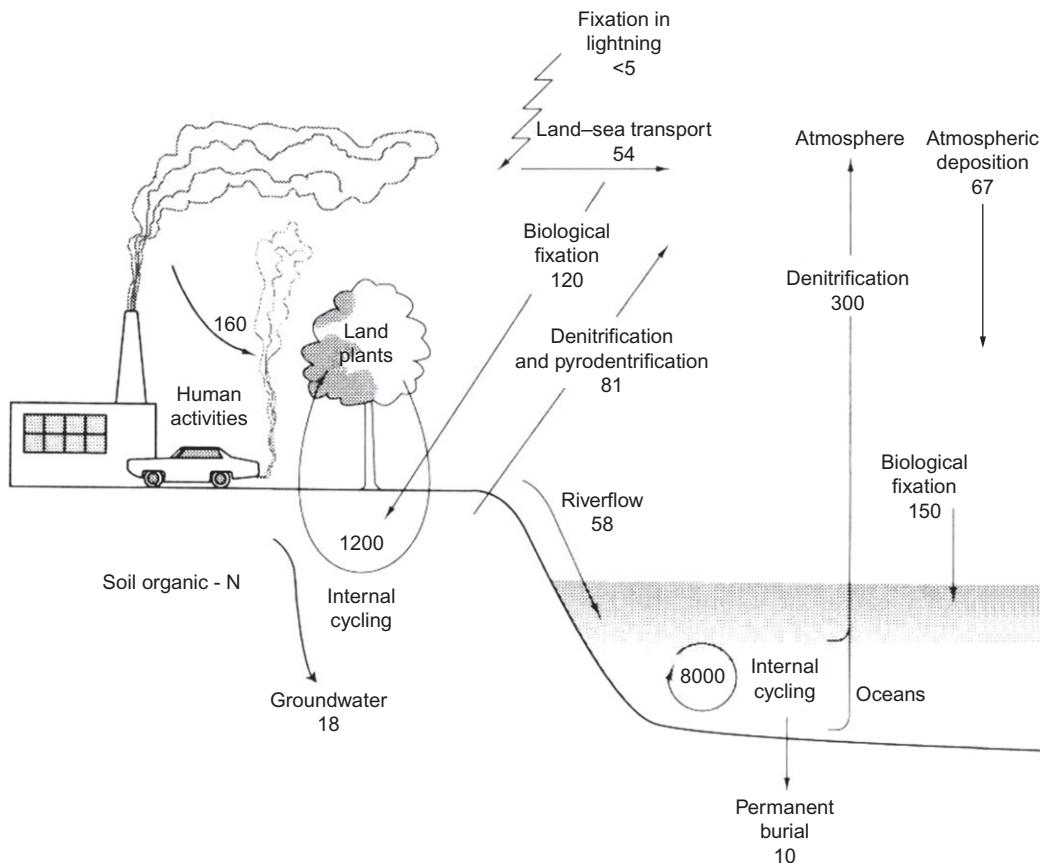
Figure 12.2 presents the global nitrogen cycle, showing the linkage between the atmosphere, the land, and the oceans. The atmosphere contains the largest pool ( $3.9 \times 10^{21}$  g N; Table 3.1). Relatively small amounts of N are found in terrestrial biomass ( $3.8 \times 10^{15}$  g<sup>1</sup>) and in soil organic matter ( $95\text{--}140 \times 10^{15}$  g to 1-m depth; Post et al. 1985, Batjes et al. 1996). The mean C/N ratios for terrestrial biomass and soil organic matter are about 160 and 12, respectively. At any time, the pool of inorganic nitrogen,  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , in soils is very small. The uptake of N by organisms is so rapid that little nitrogen remains in inorganic forms, despite the large annual flux through this pool (Chapter 6).<sup>2</sup> Since most N in soils is held in organic forms, soil organic matter is a good predictor of total nitrogen content in most circumstances (Glendining et al. 2011).

The nitrogen in the atmosphere is not available to most organisms because the great strength of the triple bond in  $\text{N}_2$  makes this molecule practically inert.<sup>3</sup> All nitrogen that is

<sup>1</sup> This value is derived from an estimate of  $600 \times 10^{15}$  g C in terrestrial biomass (Table 5.3) and a C/N ratio of 160 in forest biomass (Table 6.4). Given the convergence of estimates for the carbon pool in biomass, higher estimates for the N pool in vegetation would require a lower estimate of the C/N ratio in biomass, which seems unlikely.

<sup>2</sup> Typically the C/N ratio in desert soils is very low (Post et al. 1985). In deserts, where soil biotic activity is limited, a large amount of nitrate may accumulate in the soil profile below the rooting zone of plants, perhaps amounting to  $3\text{--}15 \times 10^{15}$  g N globally (Walvoord et al. 2003).

<sup>3</sup> The mean bond energy in  $\text{N}_2$  is 226 kcal/mole, versus N-H (93), N-C (70), or N-O (48) (Davies 1972).



**FIGURE 12.2** The global nitrogen cycle. Each flux is shown in units of  $10^{12}$  g N/yr. Values as derived in the text. See also Table 12.3.

available to biota was originally derived from nitrogen fixation—either by lightning or by a few specialized species of microbes, which convert  $N_2$  to forms of reactive nitrogen (Chapter 6). The rate of nitrogen fixation by lightning, which produces momentary conditions of high pressure and temperature allowing  $N_2$  and  $O_2$  to form  $NO_x$ , is relatively small. Most recent global estimates are in the range of 2 to  $6 \times 10^{12}$  g N/yr (Borucki and Chameides 1984, Kumar et al. 1995b, Ridley et al. 1996, Levy et al. 1996, Nesbitt et al. 2000, Martin et al. 2007, Schumann and Huntrieser 2007), and the estimated total annual deposition of oxidized N ( $NO_y$ ) from the preindustrial atmosphere precludes an estimate higher than about  $12 \times 10^{12}$  g N/yr (Galloway et al. 2004). Assuming that lightning is distributed uniformly over land and sea, a liberal estimate for the deposition of N fixed by lightning over land would be  $2 \times 10^{12}$  g N/yr. The present-day deposition of oxidized nitrogen on land is about  $25 \times 10^{12}$  g/yr, owing to the additional  $NO_x$  that is emitted from soils, biomass burning, and human activities (Table 12.1).

**TABLE 12.1** A Global Budget for Atmospheric NO<sub>x</sub> (values are Tg N ( $10^{12}$  g N)/yr as NO)

Process	Annual Flux	References
<b>Sources</b>		
Fossil fuel combustion	25	Galloway et al. 2004
Net emissions from soils	12	Ganzeveld et al. 2002 (Gross flux $\sim$ 21 Tg N/yr; Davidson and Kingerlee 1997)
Biomass burning	9.6	Andreae and Merlet 2001, Kaiser et al. 2012 (compare 9.8 Tg N/yr, Mieville et al. 2010)
Lightning	5	See text references
NH <sub>3</sub> oxidation	1	Compare to <a href="#">Table 12.2</a> (Warneck 2000)
Aircraft	0.4	Prather et al. 1995
Transport from the stratosphere	0.6	For total NO <sub>y</sub> (Prather et al. 1995)
<b>Total sources</b>	<b>53.6</b>	Compare 37 Tg N/yr from satellite measurements (Martin et al. 2003; 46 Tg N/yr (Galloway et al. 2004))
<b>Sinks</b>		
Deposition on land	24.8	Galloway et al. 2004
Deposition on the ocean surface	23.0	Duce et al. 2008, Dentener et al. 2006
<b>Total sinks</b>	<b>47.8</b>	

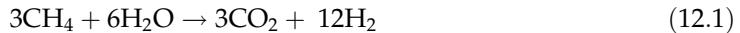
Biological nitrogen fixation is performed by several species of microbes, which are either free-living in lake waters, soils, and sediments or found in symbiotic association with the roots of plants ([Chapter 6](#)). Prior to widespread human activities, total biological nitrogen fixation on land is likely to have been  $60$  to  $195 \times 10^{12}$  g N/yr (Cleveland et al. 1999, Vitousek et al. in press). The current rate of biological nitrogen fixation is estimated at  $120$  to  $180 \times 10^{12}$  g N/yr for the sum of natural and agricultural ecosystems (Burns and Hardy 1975, Wang and Houlton 2009). As natural lands have given way to cultivation, the nitrogen fixation in agricultural systems has replaced (and even exceeded) the nitrogen fixation that was lost from natural ecosystems (Galloway et al. 2004). Estimates of N fixation in agriculture are as high as  $50$  to  $70 \times 10^{12}$  g N/yr, or nearly half of the land total (Herridge et al. 2008; compare to  $21 \times 10^{12}$  g N/yr, Liu et al. 2010).

These estimates of N fixation on land are equivalent to about 10 kg N/yr for each hectare of the Earth's land surface. Most studies of nitrogen fixation in free-living soil bacteria report values ranging from 1 to 5 kg ha<sup>-1</sup> yr<sup>-1</sup> ([Chapter 6](#)). A value of 3 kg N ha<sup>-1</sup> yr<sup>-1</sup> multiplied by the world's land area suggests that asymbiotic fixation contributes about one-third of the global total. The remainder is assumed to come from symbiotic association of bacteria with higher plants. This flux is not distributed uniformly among natural ecosystems; the greatest values are often found in tropical forests and in areas of disturbed or successional vegetation (Vitousek and Howarth 1991). In any case, biotic N fixation dwarfs abiotic fixation by lightning as the source of fixed N. The evolution of life and of nitrogen fixation on Earth greatly speeded the movement of nitrogen in a biogeochemical cycle. Taking all forms of N fixation as

the only source, the mean residence time of nitrogen in the terrestrial biosphere is about 700 years (i.e., pool/input). This calculation is not altered significantly by considering the small amount of fixed nitrogen that is contained in sedimentary and metasedimentary rocks, which may contribute more than  $20 \times 10^{12}$  g N/yr to the terrestrial biosphere by chemical weathering (Holloway and Dahlgren 2002; Houlton, personal communication, 2011).

Assuming that the estimate of terrestrial net primary production,  $60 \times 10^{15}$  g C/yr, is roughly correct and that the mean C/N ratio of net primary production is about 50, the nitrogen requirement of land plants is about  $1200 \times 10^{12}$  g/yr (Chapter 6).<sup>4</sup> Thus, nitrogen fixation supplies only about 15% of the nitrogen that is assimilated by land plants each year. The remaining nitrogen must be derived from internal recycling and the decomposition of dead materials in the soil (Chapter 6). When the turnover in the soil is calculated with respect to the input of dead plant materials, the mean residence time of nitrogen in soil organic matter is >100 years. Thus, the mean residence time of N exceeds that of C in both land vegetation and soils (5 and 25 years, respectively; Chapter 5).

Humans have a dramatic impact on the global N cycle. In addition to planting N-fixing species for crops, humans produce nitrogen fertilizers through the Haber process; namely:



in which natural gas is burned to produce hydrogen, which is combined with N<sub>2</sub> to form ammonia under conditions of high temperature and pressure (Smil 2001). The industrial production of reactive N by these reactions supplies  $>136 \times 10^{12}$  g N/yr for agricultural and chemical uses<sup>5</sup>—roughly matching the natural rate of nitrogen fixation on land.

A substantial fraction, perhaps half, of the annual application of nitrogen fertilizer to agricultural lands is lost to the atmosphere and to runoff waters (Erisman et al. 2007). Some NH<sub>3</sub> is volatilized directly to the atmosphere from cultivated soils (Figure 6.14), while some fertilizer N is lost indirectly from the excrement of domestic livestock that are fed forage crops (Table 12.2). The loss of NH<sub>3</sub> from agricultural lands to the atmosphere carries fixed N to adjacent natural ecosystems where it is deposited and enters biogeochemical cycles (Draaijers et al. 1989, Hesterberg et al. 1996).

Fossil fuel combustion also produces about  $25 \times 10^{12}$  g of fixed N (namely, NO<sub>x</sub>) annually (Galloway et al. 2004). Some of this is derived from the organic nitrogen contained in fuels (Bowman 1991), but it is best regarded as a source of new, fixed N for the biosphere because in the absence of human activities, this N would remain inaccessible in the Earth's crust. NO<sub>x</sub> also forms directly from N<sub>2</sub> and O<sub>2</sub> during the combustion of fossil fuels, especially in automobiles and coal-fired power plants (Bowman 1992, Davidson et al. 1998, Marufu et al. 2004,

<sup>4</sup> Most primary production consists of short-lived tissues with a C/N ratio that is much lower than that of wood (160), which composes most of the terrestrial biomass. Mineralization of  $\sim 1000 \times 10^{12}$  g N/yr is consistent with experimental observations suggesting 1 to 3% turnover of nitrogen in soils annually (Chapter 6). Raven et al. (1993) give an alternative estimate of  $2338 \times 10^{12}$  g/yr for the nitrogen uptake by land plants. Another recent global model for the N cycle assumes a C/N ratio of about 10 and uptake of  $6207 \times 10^{12}$  g N/yr by terrestrial NPP, which seems unlikely (Lin et al. 2000).

<sup>5</sup> <http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/mcs-2012-nitro.pdf>.

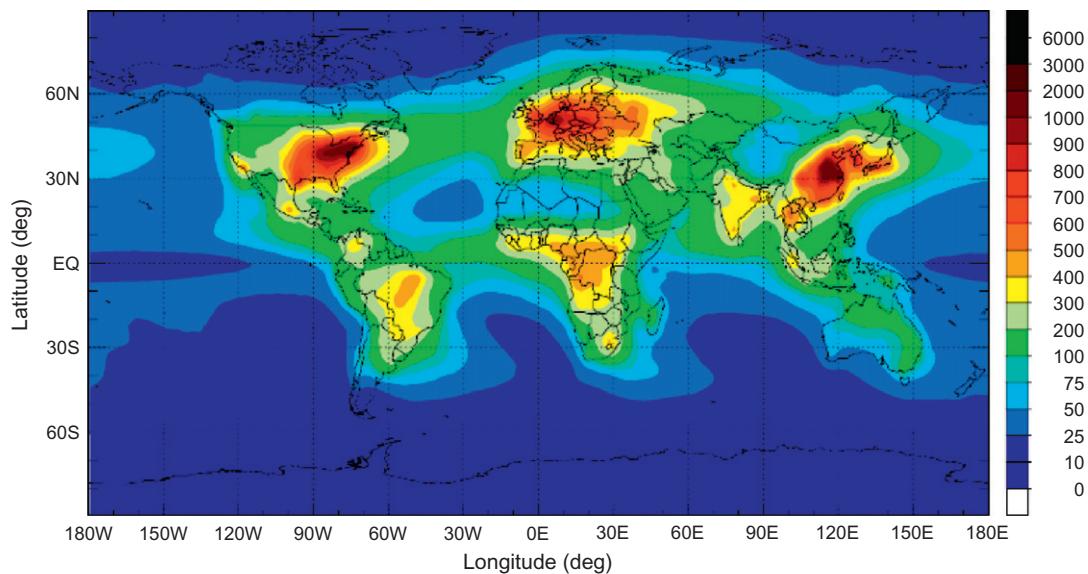
**TABLE 12.2** A Global Budget for Atmospheric Ammonia

Process	Annual flux	References
<b>Sources</b>		
Domestic animals	18.5	Bouwman et al. 2002
Wild animals	0.1	
Sea surface	8.2	
Undisturbed soils	2.4	
Agricultural soils	3.6	
Fertilizers	9.0	
Biomass burning	7.7	Kaiser et al. 2012
Human excrement	2.6	
Coal combustion and industry	0.3	
Automobiles	0.2	Schlesinger and Hartley 1992
<b>Total sources</b>	<b>52.6</b>	Compare 58.2 Tg N/yr; Galloway et al. 2004
<b>Sinks</b>		
Deposition on land	38.7	
Deposition on the ocean surface	24.0	Duce et al. 2008; Dentener et al. 2006
Reaction with OH radicals	1.0	Schlesinger and Hartley 1992
<b>Total sinks</b>	<b>63.7</b>	

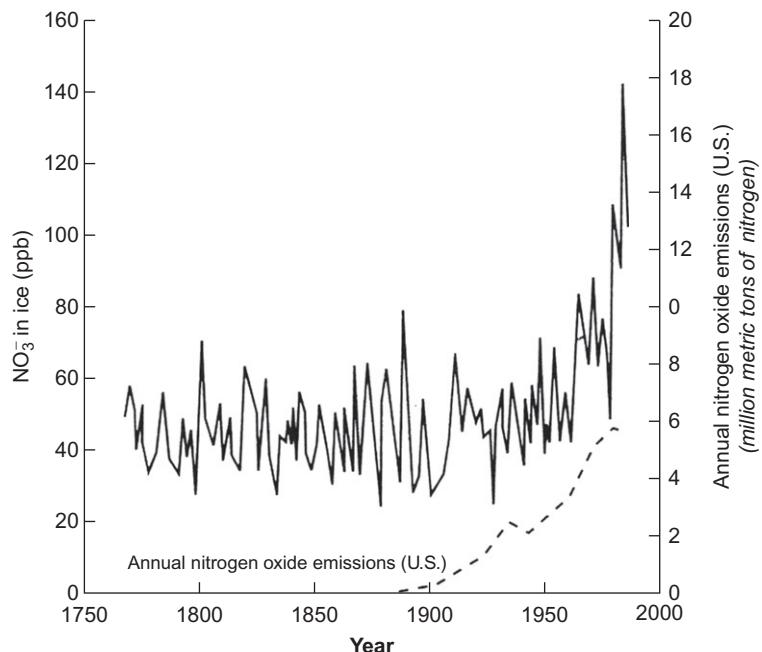
*Note:* Unless noted otherwise, sources are derived from Bouwman et al. (1997) and sinks from Galloway et al. (2004). All values are Tg N ( $10^{12}$  g N)/yr as  $\text{NH}_3$  or  $\text{NH}_4^+$  (in deposition).

Kim et al. 2006). In automobiles, some  $\text{NO}_x$  is converted to  $\text{NH}_3$  by catalytic converters (Bhattacharyya and Das 1999, Emmenegger et al. 2004). Owing to the short residence time of  $\text{NO}_x$  and  $\text{NH}_3$  in the atmosphere (Eq. 3.26; Table 3.5), most of this nitrogen is deposited by precipitation over land, where it enters biogeochemical cycles (Figure 12.3). A small portion of  $\text{NO}_x$  undergoes long-distance transport in the troposphere, accounting for excess nitrogen deposition in the oceans (Duce et al. 2008, Kim et al. 2011) and the rising levels of  $\text{NO}_3^-$  deposited in Greenland snow (Fischer et al. 1998, Burkhart et al. 2006; Figure 12.4).

Evidence for anthropogenic emissions of nitrogen to the atmosphere dates to about 1900 (Hastings et al. 2009, Holtgrieve et al. 2011). In some areas, the atmospheric deposition of N may fertilize plant growth (Chapter 6), leading to an increment in the sink for carbon in vegetation (Chapter 11). However, some high-elevation forests downwind of major population centers now receive enormous nitrogen inputs, both  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , which may be related to forest decline (Chapter 6). Various workers have tried to define the “critical load”—the level of nitrogen deposition that can be expected to cause changes in ecosystem properties—for example, increased nitrification and leaching. In many ecosystems, noticeable effects begin at nitrogen depositions of  $1 \text{ kg ha}^{-1} \text{ yr}^{-1}$  (Pardo et al. 2011, Liu et al. 2011). As a



**FIGURE 12.3** Deposition of  $\text{NO}_y$  on Earth's surface. All values are  $\text{mg N m}^{-2} \text{yr}^{-1}$ . Source: From Dentener et al. (2006).



**FIGURE 12.4** The 200-year record of nitrate in layers of the Greenland ice pack and the annual production of nitric oxides by fossil fuel combustion in the United States. Source: Modified from Mayewski et al. (1990).

result of air-pollution control legislation, deposition of nitrogen from the atmosphere is now declining in North America (Zbieranowski and Aherne 2011).

In total, about  $300 \times 10^{12}$  g of newly fixed N is delivered from the atmosphere to the Earth's land surface each year—28% from natural and 72% from human-derived sources (Table 12.3). Some of this nitrogen remains sequestered in the terrestrial biosphere, primarily in forests and in agricultural soils, which store about 30 to 40% of the applied nitrogen (Schindler and Knighton 1999, Fritsch et al. 2004, Stevens et al. 2005, Gardner and Drinkwater 2009). In the absence of processes removing nitrogen, a very large pool of nitrogen would be found on land in a relatively short time. About 23% of the nitrogen deposited on the land surface is lost to runoff (Howarth 1998, van Breemen et al. 2002), especially during periods of peak flow (Chapter 8). Runoff of nitrogen into Lake Michigan is well correlated to fertilizer and land-use changes in its basin (Han and Allan 2011). Globally, rivers carry nearly  $60 \times 10^{12}$  g N/yr from land to the sea (Boyer et al. 2006, Van Drecht et al. 2003), and humans may account for more than half of the present-day transport of N in rivers (Schlesinger 2009).

TABLE 12.3 Mass Balance for Nitrogen on the Earth's Land Surface

Inputs	Preindustrial	Human derived	Total
Biological N fixation	60 <sup>a</sup>	60 <sup>b</sup>	120
Lightning	5	0	5
Rock weathering	20 <sup>c</sup>	0	20
Industrial N fixation	0	136 <sup>d</sup>	136
Fossil fuel combustion	0	25	25
<b>Total</b>	<b>85</b>	<b>221</b>	<b>306</b>
<b>Fates</b>			
Biospheric increment	0	9	9
Soil accumulation	0	48	48
Riverflow	27	31	58
Groundwater	0	18	18
Denitrification	27 <sup>e</sup>	17	44
Pyrodenitrification	25 <sup>f</sup>	12	37
Atmospheric land-sea transport <sup>g</sup>	6	48	54
<b>Total</b>	<b>85</b>	<b>183</b>	<b>268</b>

Note: Updated from Schlesinger (2009), with permission from the National Academy of Sciences. Unless otherwise indicated, preindustrial values and human-derived inputs are from Galloway et al. (2004). Fates of anthropogenic nitrogen are derived in this chapter.

Note: All values are in Tg N/yr ( $=10^{12}$  g N/yr).

<sup>a</sup> Vitousek et al. *in press*

<sup>b</sup> Herridge et al. (2008); value is the net from human activities.

<sup>c</sup> B.Z. Houlton, personal communication (2011).

<sup>d</sup> <http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/mcs-2012-nitro.pdf>.

<sup>e</sup> To balance.

<sup>f</sup> See derivation in the text.

<sup>g</sup> Duce et al. (2008).

Human additions of fixed nitrogen to the terrestrial biosphere have also resulted in marked increases in the nitrogen content of groundwaters, especially in many agricultural areas (Spalding and Exner 1993, Rupert 2008, Kroeger and Charette 2008, Scanlon et al. 2010). For example, the loss of nitrate to groundwater was the largest single fate of nitrogen added to the fields of a dairy farm in Ontario (Barry et al. 1993). Nitrogen and other biochemical elements are also enriched in the drainage from cemeteries (Zychowski 2012). The global transport of N to groundwaters may approach  $18 \times 10^{12}$  g N/yr—calculated from an estimate of the annual flux of groundwater ( $12,666 \text{ km}^3/\text{yr}$ ; Doll and Fiedler 2008) and the median concentration of 1.9 mg N/liter in groundwaters of the United States (Nolan et al. 2002, Schlesinger 2009).

Despite these large transports, riverflow and groundwater cannot account for all of the nitrogen that is lost from land. The remaining nitrogen is assumed to be lost by denitrification and other gaseous pathways in terrestrial soils (Chapter 6), in wetlands (Chapter 7), and during forest fires (Chapter 6). Seitzinger et al. (2006) have compiled rates of denitrification showing that roughly  $124 \times 10^{12}$  g N/yr occur in soils and  $110 \times 10^{12}$  g/yr in freshwater environments (Table 12.4). If N fixation and denitrification were once in balance, then a terrestrial denitrification rate of  $\sim 100 \times 10^{12}$  g N/yr was most likely in the preindustrial world (i.e., fixation minus riverflow; Schlesinger 2009). Most of the loss occurs as  $\text{N}_2$ , but the small fraction that is lost as  $\text{N}_2\text{O}$  during nitrification and denitrification (Chapter 6) contributes significantly to the global budget of this gas.

Indeed, the current rise in atmospheric  $\text{N}_2\text{O}$  can be used to estimate the overall increase in global denitrification as a result of human activities (Schlesinger 2009). If we assume that the  $(\text{N}_2 + \text{N}_2\text{O})/\text{N}_2\text{O}$  ratio for denitrification is about 4.0 and that the recent increase of  $\text{N}_2\text{O}$  in

**TABLE 12.4** A Global Estimate of Denitrification of Nitrogen on or Applied to Land

System	Denitrification (Tg N/yr)
<b>Terrestrial</b>	
Soils	124 (65–175)
<b>Freshwater</b>	
Groundwater	44 (>0–138)
Lakes and reservoirs	31 (19–43)
Rivers	35 (20–35)
Subtotal	110 (39–216)
<b>Marine</b>	
Estuaries	8 (3–10)
Continental shelves	46 (>0–70)
Oxygen minimum zones	25 (>0–30?)
Subtotal	79 (3–145)

Source: From Seitzinger et al. (2006).

the atmosphere (nearly  $4 \times 10^{12}$  g N/yr) all derives from increased denitrification, then it is possible that the overall loss of N<sub>2</sub> from denitrification has increased by as much as  $17 \times 10^{12}$  g N/yr, helping to balance the present-day N budget on land (Figure 12.2).<sup>6</sup> Denitrification leaves soils enriched in δ<sup>15</sup>N globally (Amundson et al. 2003, Houlton and Bai 2009); especially high rates of denitrification and high soil δ<sup>15</sup>N are reported in the tropics (Houlton et al. 2006, Koba et al. 2012).

Nitrogen in biomass is volatilized as NH<sub>3</sub>, NO<sub>x</sub>, and N<sub>2</sub> during fires—the last constituting a form of *pyrodenitrification* (Chapter 6). About 30% of the nitrogen in fuel is converted to N<sub>2</sub>, so globally biomass burning may return about  $37 \times 10^{12}$  g N/yr to the atmosphere as N<sub>2</sub> (Kuhlbusch et al. 1991). The rate of biomass burning has increased by about 1.5× in recent years (Mouillet et al. 2006), so this form of denitrification may have increased from a preindustrial level of  $\sim 25 \times 10^{12}$  g N/yr.

In balancing the terrestrial N cycle, we concentrate on processes that affect the net production or loss of fixed nitrogen (Table 12.3). We do not include processes that recycle N that was fixed at an earlier time. Thus, NH<sub>3</sub> volatilization from biomass burning (Table 12.2) and the natural emission of NO<sub>x</sub> from soils (Table 12.1) can be ignored to the extent that these forms are redeposited on land in precipitation. Ammonia and NO<sub>x</sub> have relatively short atmospheric lifetimes, so they are usually deposited in precipitation and dryfall near their point of origin (Chapter 3). Indeed, some have suggested that nitrogen “hop-scotches” across the landscape, where losses from one area result in increased deposition and local cycling in other areas. The cycle is complete only when nitrogen is returned to the atmosphere as N<sub>2</sub>. By focusing on the new sources of available nitrogen from the atmosphere, we find that nearly all of the human perturbation of the global nitrogen cycle has occurred in the past 150 years.

## Sea

The world’s oceans receive about  $60 \times 10^{12}$  g N/yr in dissolved forms from rivers (Chapter 8), about  $150 \times 10^{12}$  g N/yr via biological N fixation (Chapter 9), and about  $67 \times 10^{12}$  g N in precipitation (Duce et al. 2008). Some of the precipitation flux is NH<sub>4</sub><sup>+</sup> that is derived from NH<sub>3</sub> volatilized from the sea (Quinn et al. 1988), but about 80% of the atmospheric deposition of N in the oceans derives from human activities on land (Duce et al. 2008). A significant fraction of the deposition of atmospheric nitrogen on the oceans is found in various types of organic compounds (Cornell et al. 2003). Through their various activities, humans have created a large flux of nitrogen through the atmosphere, from land to sea.

As we have shown for terrestrial ecosystems, most of the net primary production in the sea is supported by nitrogen recycling in the water column (Table 9.3). Nitrogen inputs from the atmosphere have the greatest influence in the open oceans, where the pool of inorganic nitrogen is very small. The riverflux of N assumes its greatest importance in coastal seas and estuaries. Here, runoff of excess nitrogen has caused significant changes in the productivity of coastal ecosystems, leading to eutrophication and hypoxia (Beman et al. 2005, Goolsby et al. 2001, Kim et al. 2011).

<sup>6</sup> The ratio ranges from 2.0 in upland soils to >12 in wetlands (Schlesinger 2009), so the total increase in denitrification caused by human inputs may range from 8 to  $68 \times 10^{12}$  g N/yr.

The deep ocean contains a large pool of inorganic nitrogen ( $720 \times 10^{15}$  g N)<sup>7</sup> derived from the decomposition of sinking organic debris and mineralization from dissolved organic compounds. Permanent burial of organic nitrogen in sediments is small, so most of the nitrogen input to the oceans must be returned to the atmosphere as N<sub>2</sub> by denitrification and the anammox reaction (Figures 9.21 and 12.2). Important areas of denitrification are found in the anaerobic deep waters of the eastern tropical Pacific Ocean and the Arabian Sea (Chapter 9). Seitzinger et al. (2006) estimate denitrification of up to  $145 \times 10^{12}$  g N/yr in near-shore waters. Globally, coastal and marine denitrification may account for the return of  $270$  to  $400 \times 10^{12}$  g N/yr to the atmosphere as N<sub>2</sub>, yielding an overall mean residence time for N in the oceans of <2000 years (Brandes and Devol 2002, Codispoti 2007, Bianchi et al. 2012).

Although the estimates are subject to large uncertainty, the model of Figure 12.2 indicates a net loss of nitrogen from the oceans. The overall gaseous losses of nitrogen from the ocean exceed the inputs from rivers and the atmosphere, so that the oceans may be declining in nitrogen content (McElroy 1983, Codispoti 2007). Various workers have suggested that, in the absence of denitrification, higher concentrations of NO<sub>3</sub> would be found in the ocean and lower concentrations of N<sub>2</sub> in the atmosphere. The balance of nitrogen fixation and denitrification has probably controlled marine NPP through past glacial cycles (Ganeshram et al. 1995). Globally, suboxic waters, in which available nitrogen is depleted by denitrification, are also sites of N fixation, providing long-term self-regulation to the nitrogen cycle of the oceans (Deutsch et al. 2007).

## TEMPORAL VARIATIONS IN THE GLOBAL NITROGEN CYCLE

The earliest atmosphere on Earth is thought to have been dominated by nitrogen, since N is abundant in volcanic emissions and only sparingly soluble in seawater (Chapter 2). The early rate of degassing of N<sub>2</sub> from the Earth's mantle must have been much greater than today. The present-day flux of N<sub>2</sub> from the mantle is about  $78 \times 10^9$  g N/yr (Sano et al. 2001) to  $123 \times 10^9$  g N/yr (Tajika 1998), which could not result in the observed accumulations of nitrogen at the Earth's surface (refer to Table 2.3), even after 4.5 billion years of Earth's history.<sup>8</sup>

Before the origin of life, nitrogen was fixed by lightning and in the shock waves of meteors, which create local conditions of high temperature and pressure in the atmosphere (Mancinelli and McKay 1988). The rate of N fixation was very low, perhaps about 6% of the present-day rate, because abiotic fixation in an atmosphere dominated by N<sub>2</sub> and CO<sub>2</sub> is much slower than in an atmosphere of N<sub>2</sub> and O<sub>2</sub> (Kasting and Walker 1981). The limited supply of fixed nitrogen in the primitive oceans on Earth is likely to have led to the early evolution of N fixation in marine biota (Chapter 2).

<sup>7</sup> Volume of the deep oceans ( $0.95 \times 1.335 \times 10^{24}$  g; Figure 10.1) multiplied by the NO<sub>3</sub><sup>-</sup> in the deep ocean (40 µmol NO<sub>3</sub>/kg; Figures 9.18 and 9.27) multiplied by 14 g/mole.

<sup>8</sup> Some nitrogen degassed to the Earth's surface is carried back to the mantle by subduction of sediments ( $760 \times 10^9$  g N/yr; Busigny et al. 2003), with the contemporary net flux to the mantle perhaps amounting to  $330 \times 10^9$  g/yr to  $960 \times 10^9$  g N/yr (Goldblatt et al. 2009, Busigny et al. 2011). Thus the pool of nitrogen at the Earth's surface is decreasing slightly each year by net entrainment in the mantle.

The best estimates of abiotic N fixation on the primitive Earth suggest that it had a limited effect on the content of atmospheric nitrogen but provided a small though important supply of fixed nitrogen, largely  $\text{NO}_3^-$ , to the ocean's waters (Kasting and Walker 1981, Mancinelli and McKay 1988). Similar abiotic N fixation on Mars is postulated to have resulted in accumulations of nitrate or cyanide (HCN) on its surface (Segura and Navarro-Gonzalez 2005, Manning et al. 2008). Nitrate also accumulates in extremely arid soils on Earth, although here it is likely derived from distant biogenic sources (Michalski et al. 2004a).

With respect to N fixation by lightning, the mean residence time of  $\text{N}_2$  in the atmosphere is about 1 billion years. The mean residence time of atmospheric nitrogen decreases to about 14,000,000 years when biological nitrogen fixation is included. This is much shorter than the history of life on Earth, and it speaks strongly to the importance of denitrification in returning  $\text{N}_2$  to the atmosphere over geologic time. Denitrification closes the global biogeochemical cycle of nitrogen, but it also means that nitrogen remains in short supply for the biosphere. In the absence of denitrification, most nitrogen on Earth would be found as  $\text{NO}_3^-$  in seawater and the oceans would be quite acidic (Sillén 1966).

It is likely that denitrification appeared later than the other major metabolic pathways; denitrifying bacteria are facultative anaerobes, switching from simple heterotrophic respiration to  $\text{NO}_3^-$  respiration under anaerobic conditions (Broda 1975, Betlach 1982). Denitrification enzymes are somewhat tolerant of low concentrations of  $\text{O}_2$ , allowing denitrifying bacteria to persist in environments with fluctuations in redox potential (Bonin et al. 1989, McKenney et al. 1994, Carter et al. 1995). The geologic record offers some insight regarding the origin of denitrification. Sedimentary rocks with enrichments of  $\delta^{15}\text{N}$ , indicating denitrification, date only to 2.7 bya—well after the origin of oxygenic photosynthesis (Beaumont and Robert 1999, Godfrey and Falkowski 2009, Thomazo et al. 2011).

Requiring oxygen as a reactant, nitrification clearly arose after photosynthesis and the development of an  $\text{O}_2$ -rich atmosphere (Eqs. 2.17 and 2.18). Some of the earliest nitrifying organisms may have been archaea, which are found in many soils (Leininger et al. 2006). Today, the rate of denitrification is controlled by the rate of nitrification, which supplies  $\text{NO}_3^-$  as a substrate (Eq. 2.20; Figure 6.13). In any case, the major microbial reactions in the nitrogen cycle (Figure 12.1) are all likely to have been in place at least 2 billion years ago.

Because  $\text{NO}_3^-$  is very soluble, there is little reliable record of changes in the content of  $\text{NO}_3^-$  in seawater through geologic time. Only changes in the deposition of organic nitrogen are recorded in sediments. Altabet and Curry (1989) show that the  $^{15}\text{N}/^{14}\text{N}$  record in sedimentary foraminifera is useful in reconstructing the past record of ocean N chemistry. The isotope ratio in sedimentary organic matter increases when high rates of denitrification remove  $\text{NO}_3^-$  from the oceans, leaving the residual pool of nitrate enriched in  $^{15}\text{N}$  (Altabet et al. 1995, Ganeshram et al. 1995).

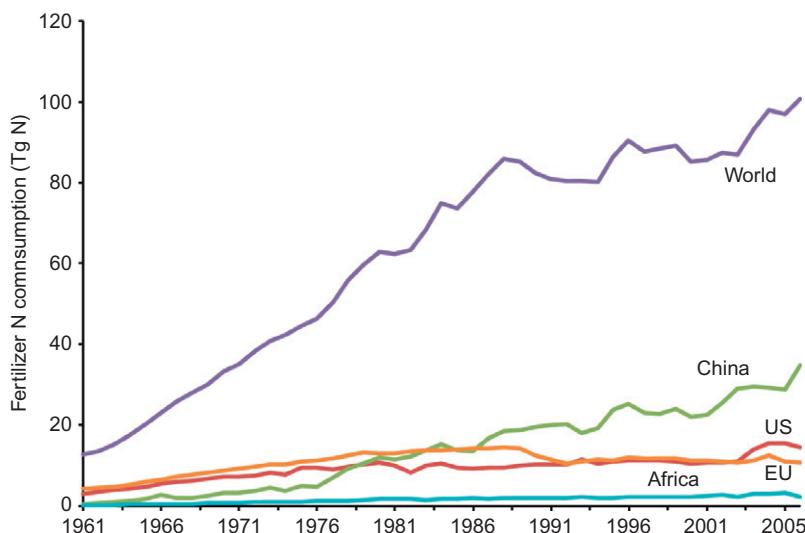
Assuming a steady state in the ocean nitrogen cycle, the mean residence time for an atom of fixed N in the sea is <2000 years. During this time, this atom will make several trips through the deep ocean, each lasting 200 to 500 years (Chapter 9). Because the turnover of N is much longer than the mixing time for ocean water,  $\text{NO}_3^-$  shows a relatively uniform distribution in deep ocean water. The nitrogen budget in the oceans appears not in steady state; current estimates of the rate of denitrification exceed known inputs (compare to Figure 12.2). McElroy (1983) suggests that the oceans received a large input of nitrogen during the continental glaciation 20,000 years ago, and they have been recovering from this input ever since

(Christensen et al. 1987). This suggestion is consistent with sedimentary evidence of greater net primary production in the oceans during the last ice age (Broecker 1982), and with the low ratio of  $^{15}\text{N}/^{14}\text{N}$  in sedimentary organic matter of glacial age implying low rates of denitrification (Ganeshram et al. 1995, Altabet et al. 2002, Gruber and Galloway 2008).

McElroy's paper should remind us to question the assumption of steady-state conditions when we construct global models of Earth's biogeochemistry, such as Figure 12.2. Earth has experienced large fluctuations in its biogeochemical function through geologic time. Changes in the global distribution and circulation of nitrogen may have accompanied climatic changes—just as the rise in CO<sub>2</sub> concentrations at the end of the last glacial epoch indicates a period of non-steady-state conditions in the global carbon cycle (Chapter 11).

At present, human activities have certainly disrupted the potential for steady-state conditions in the nitrogen cycle on land (Galloway et al. 2004, Liu et al. 2010). Humans have greatly accelerated the natural rate of N fixation; the production of N fertilizers and the cultivation of leguminous crops have increased dramatically since World War II, allowing higher crop yields to feed the world's growing human population (Figure 12.5). Archival collections show decreasing  $\delta^{15}\text{N}$  in plant tissues, consistent with greater anthropogenic nitrogen inputs in recent years (Peñuelas and Filella 2001; compare to Hastings et al. 2009 and Holtgrieve et al. 2011).

Enrichments of nitrogen in terrestrial ecosystems, stimulating the rates of nitrification and denitrification, are likely to account for the rapid rise in the atmospheric content of N<sub>2</sub>O, contributing to global climate change (Vitousek 1994). Changes in the global nitrogen cycle have important implications for human health (Townsend et al. 2003), carbon storage in the biosphere (Townsend et al. 1996), and the persistence of species diversity in nature (Bobbink et al. 2010, Stevens et al. 2010). Controls on N<sub>2</sub>O emissions may be one of the most effective ways to reduce the threat of global climate change (Montzka et al. 2011a).



**FIGURE 12.5** The production history of nitrogen fertilizer. Source: From Robertson et al. (2009). Used with permission of the Annual Review.

## NITROUS OXIDE

Nitrous oxide, N<sub>2</sub>O, has a mean concentration of 320 ppb in Earth's atmosphere, which indicates a global pool of  $2.5 \times 10^{15}$  g N<sub>2</sub>O or  $1.6 \times 10^{15}$  g N (Table 3.1). The concentration of N<sub>2</sub>O is increasing at a rate of 0.3%/yr (IPCC 2007). Each molecule of N<sub>2</sub>O has the potential to contribute about 300× to the greenhouse effect relative to each molecule of CO<sub>2</sub>, so the current increase in the atmosphere has the potential to impact global climate over the next century (Shindell et al. 2009). Also, nitrous oxide is now the dominant human emission that causes ozone depletion in Earth's stratosphere (Ravishankara et al. 2009).

The only significant sink for N<sub>2</sub>O—stratospheric destruction (Eqs. 3.47–3.49)—consumes about  $12.2 \times 10^{12}$  g N as N<sub>2</sub>O per year (Minschwaner et al. 1993). A few soils also appear to consume N<sub>2</sub>O, but the global sink in soils is probably very small (Chapuis-Lardy et al. 2007, Syakila and Kroeze 2011). The mean residence time for N<sub>2</sub>O in the atmosphere is about 120 years, consistent with observations of a relatively uniform ( $320 \pm 1$  ppb) concentration of atmospheric N<sub>2</sub>O around the world (Ishijima et al. 2009; see Figure 3.5). Nitrous oxide shows minor seasonal variation in the atmosphere, with greater amplitude at high northern latitudes ( $\pm 1.15$  ppb) than at the South Pole ( $\pm 0.29$  ppb; Jiang et al. 2007; compare to Ishijima et al. 2009). Unfortunately, estimates of sources—particularly sources that have changed greatly in recent years—are poorly constrained (Table 12.5).

The oceans appear to be a source of N<sub>2</sub>O to the atmosphere as a result of nitrification in the deep sea (Cohen and Gordon 1979, Oudot et al. 1990). The isotopic content of N<sub>2</sub>O from the marine environment is consistent with a source from nitrifying archaea in seawater (Santoro et al. 2011). Some of this N<sub>2</sub>O may subsequently be *consumed* by denitrification as it passes upward through zones of low O<sub>2</sub> (Cohen and Gordon 1978, Kim and Craig 1990).

In many areas, surface waters are supersaturated in N<sub>2</sub>O with respect to the atmosphere (Walter et al. 2004b). Specifically, the waters of the northwest Indian Ocean, a local zone of upwelling, may account for 20% of the total flux of N<sub>2</sub>O from the oceans to the atmosphere (Law and Owens 1990). Based on the belief that the N<sub>2</sub>O supersaturation of seawater was worldwide, calculated emissions from the ocean dominated the earliest global estimates of N<sub>2</sub>O sources (Liss and Slater 1974, Hahn 1974). When more extensive sampling showed that the areas of supersaturation were regional, these workers substantially lowered their estimate of N<sub>2</sub>O production in marine ecosystems. The most extensive survey of ocean waters suggests a flux of about 4 to  $6 \times 10^{12}$  g N/yr, emitted as N<sub>2</sub>O to the atmosphere (Nevison et al. 1995, Bianchi et al. 2012). A large portion of this may derive from coastal waters, where increasing N<sub>2</sub>O flux may derive from seawater enriched with NO<sub>3</sub><sup>-</sup> from terrestrial runoff (Bange et al. 1996, Nevison et al. 2004, Naqvi et al. 2000).

Soil emissions from nitrification and denitrification (Chapter 6) are now thought to compose the largest global source of N<sub>2</sub>O (Table 12.5). Particularly large emissions of N<sub>2</sub>O are found from tropical soils (Bouwman et al. 1993, Kort et al. 2011). Conversion of tropical forests to cultivated lands and pasture results in greater N<sub>2</sub>O emissions (Matson and Vitousek 1990, Keller and Reiners 1994), and the flux of N<sub>2</sub>O increases when agricultural lands and forests are fertilized or manured (Chapter 6). Typically about 1% of the application of nitrogen fertilizer is lost to the atmosphere as N<sub>2</sub>O (Bouwman et al. 2002b, Lesschen et al. 2011), and N<sub>2</sub>O emissions have increased in parallel with fertilizer applications during the past century (Gao et al. 2011). Presumably the increased flux of N<sub>2</sub>O from disturbed and fertilized soils stems

**TABLE 12.5** A Global Budget for Nitrous Oxide ( $\text{N}_2\text{O}$ ) in the Atmosphere (all values are Tg N/yr ( $10^{12}$  g/yr) nitrogen, as  $\text{N}_2\text{O}$ )

Natural sources	Annual flux	References
Soils	$3.4 \pm 1.3$	Zhuang et al. 2012 <sup>a</sup>
Ocean surface	$6.2 \pm 3.2$	Bianchi et al. 2012
Total natural	9.6	
<b>Anthropogenic sources</b>		
Agricultural soils	2.8	Bouwman et al. 2002b <sup>b</sup>
Cattle and feed lots	2.8	Davidson 2009
Biomass burning	0.9	Kaiser et al. 2012
Industry and transportation	0.8	Davidson 2009
Human sewage	0.2	Mosier et al. 1998
Total anthropogenic	7.5	
<b>Total sources</b>	<b>17.1</b>	
<b>Sinks</b>		
Stratospheric destruction	12.3	Prather et al. 1995
Uptake by soils	<0.1	Syakila and Kroeze 2011
Atmospheric increase	4.0	IPCC 2007
<b>Total identified sinks</b>	<b>16.4</b>	

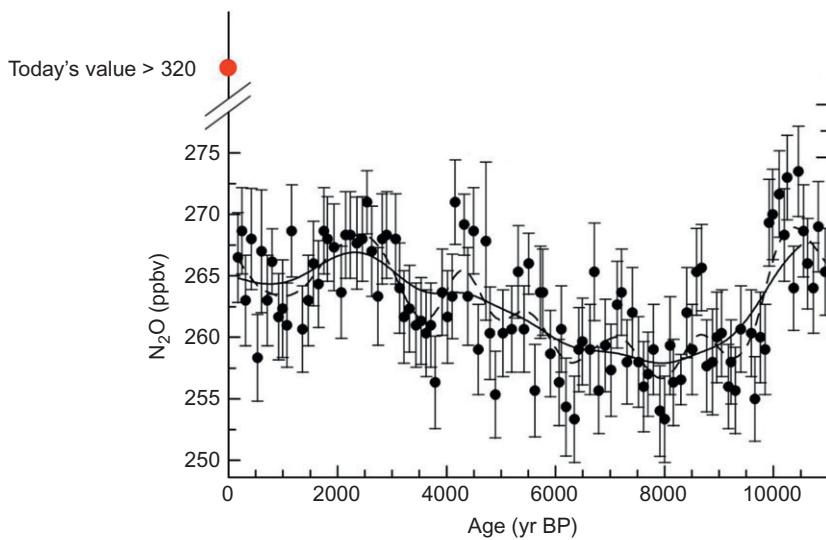
<sup>a</sup> Alternative estimates for the flux of  $\text{N}_2\text{O}$  from natural soils includes 6.1 Tg N/yr (Potter et al. 1996) and 6.6 Tg N/yr (Bouwman et al. 1995).

<sup>b</sup> The sum of emissions from agriculture and domestic animals given here, 5.6 Tg N/yr, is in close agreement with the value of 5.0 Tg N/yr estimated by Syakila and Kroeze (2011). These estimates of  $\text{N}_2\text{O}$  flux from agricultural activities include emissions of  $\text{N}_2\text{O}$  from downstream ecosystems and groundwaters impacted by agricultural inputs in these regions.

from higher rates of nitrification and greater availability of  $\text{NO}_3^-$  to denitrifying bacteria. Globally the flux of  $\text{N}_2\text{O}$  from agricultural soils is about  $2.2$  to  $2.8 \times 10^{12}$  g N/yr (Bouwman et al. 2002b, Davidson 2009), and the total production of  $\text{N}_2\text{O}$  from all soils is likely to be  $<10 \times 10^{12}$  g N/yr (Table 12.5). In most ecosystems, soil  $\text{CO}_2$  and  $\text{N}_2\text{O}$  losses are correlated, and a  $\text{N}_2\text{O}$  flux of  $13.3 \times 10^{12}$  g N/yr from soils is indicated from current estimates of  $\text{CO}_2$  efflux (Xu et al. 2008b).

Downward leaching of fertilizer nitrate also has the potential to stimulate denitrification in groundwaters. Ronen et al. (1988) suggest that groundwater may be an important source of  $\text{N}_2\text{O}$  to the atmosphere—up to  $1 \times 10^{12}$  g N/yr, but most recent assessments suggest significantly lower values (Bottcher et al. 2011, Keuskamp et al. 2012). Excess nitrogen in surface runoff also causes a significant flux of  $\text{N}_2\text{O}$  from streams and rivers (Beaulieu et al. 2011), as does the disposal of human sewage (Kaplan et al. 1978, McElroy and Wang 2005).

Relatively small emissions of  $\text{N}_2\text{O}$  result from the combustion of fossil fuels or biomass (Table 12.5), but the industrial production of nylon and industrial chemicals results in



**FIGURE 12.6** Nitrous oxide measurements from ice-core samples in Antarctica. *Source:* From Flückiger et al. (2002).

significant emissions of  $\text{N}_2\text{O}$  to the atmosphere (Thiemens and Trogler 1991). Total anthropogenic sources of  $\text{N}_2\text{O}$  are more than enough to explain its rate of increase in the atmosphere, and the total compilation of sources—both natural and anthropogenic—is slightly more than the known sinks, including the rate of  $\text{N}_2\text{O}$  accumulation in the atmosphere (Table 12.5).

Some constraints on the global budget for  $\text{N}_2\text{O}$  in Earth’s atmosphere are set by studies of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  in the gas. The flux of  $\text{N}_2\text{O}$  from soils is depleted in  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ , since denitrifiers discriminate against the heavy isotopes in the pool of available  $\text{NO}_3^-$  (Chapter 6). Conversely, the “backflux” of  $\text{N}_2\text{O}$  from the stratosphere is enriched in both  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ , since the photochemical destruction of  $\text{N}_2\text{O}$  in the stratosphere also discriminates against the heavy isotopes (Morgan et al. 2004). Estimates of changes in the sources of  $\text{N}_2\text{O}$  in the troposphere are constrained by its isotopic content, which is determined by  $\text{N}_2\text{O}$  from the stratosphere mixing with the weighted average of the isotopic content in various sources of  $\text{N}_2\text{O}$  at the Earth’s surface (Kim and Craig 1993). In the past few decades, both  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  in atmospheric  $\text{N}_2\text{O}$  have declined—consistent with an increasing flux from soils to the atmosphere (Ishijima et al. 2007, Rockmann and Levin 2005, Park et al. 2012).<sup>9</sup>

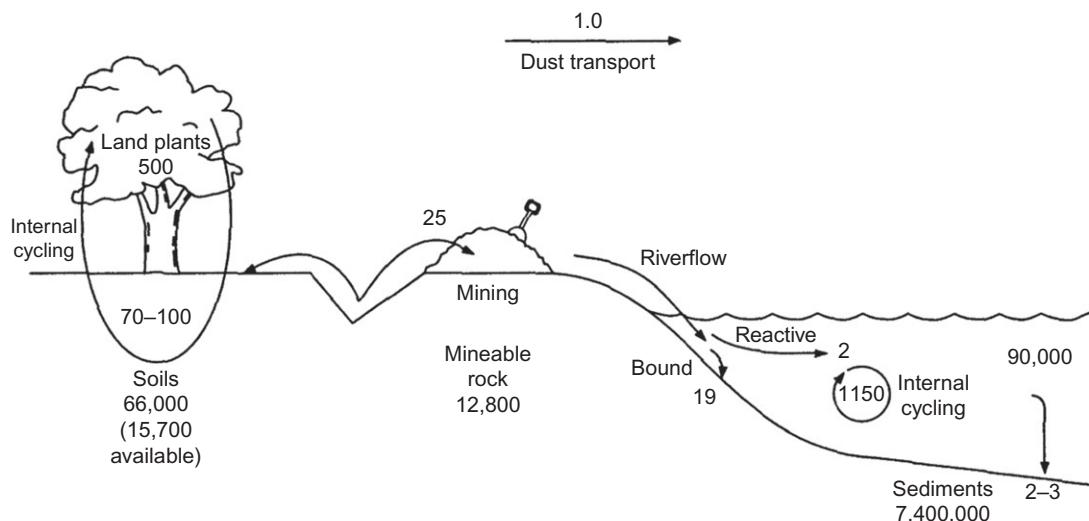
Cores extracted from the Antarctic ice cap show that the concentration of  $\text{N}_2\text{O}$  was much lower (180 ppb) during the last glacial period (Leuenberger and Siegenthaler 1992, Sowers et al. 2003, Schilt et al. 2010). At the end of the Pleistocene, concentrations rose to ~265 ppb and remained fairly constant until the Industrial Revolution, when they increased to the present value of about 320 ppb (Figure 12.6; Flückiger et al. 2002, Sowers et al. 2003). Anticipating

<sup>9</sup>  $\text{N}_2\text{O}$  is a linear molecule (NNO). Analyses of the isotopic composition of the nitrogen atoms at the central (alpha) and end positions show promise to distinguish among various sources of  $\text{N}_2\text{O}$ , including nitrification and denitrification contributing to  $\text{N}_2\text{O}$  flux (Yoshida and Toyoda 2000, Sutka et al. 2006, Koba et al. 2009, Toyoda et al. 2011, Snider et al. 2012).

the future, field experiments show that rising CO<sub>2</sub> in Earth's atmosphere, excess N deposition in precipitation, and additions of Fe to ocean waters are all likely to increase the flux of N<sub>2</sub>O to Earth's atmosphere and exacerbate global warming (Kammann et al. 2008, Liu and Greaver 2009, Law and Ling 2001, van Groenigen et al. 2011, Kim et al. 2012). Indeed, increasing N<sub>2</sub>O emissions from soils may negate some of the benefits seen in the use of fertilizer to enhance crop growth for biofuels and soil carbon sequestration (Adler et al. 2007, Melillo et al. 2009).

## THE GLOBAL PHOSPHORUS CYCLE

The global cycle of P is unique among the cycles of the major biogeochemical elements in having no significant gaseous component (Figure 12.7). The redox potential of most soils is too high to allow for the production of phosphine gas (PH<sub>3</sub>), except under very specialized, local conditions (Bartlett 1986). Phosphine emissions are reported for sewage treatment ponds in Hungary (Dévai et al. 1988), marshes in Louisiana and Florida (Dévai and DeLaune 1995), and a lake in China (Geng et al. 2005). Phosphine is also found in the marine atmosphere over the Atlantic and Pacific oceans, where it may be derived from the impact of lightning on P-containing soil dusts (Glindemann et al. 2003, Zhu et al. 2007). The global flux of P in phosphine is probably  $<0.04 \times 10^{12}$  g P/yr (Gassmann and Glindemann 1993).



**FIGURE 12.7** The global phosphorus cycle. Each flux is shown in units of  $10^{12}$  g P/yr. Values for P production and reserves are taken from the U.S. Geological Survey. Estimate for sediments is from Van Cappellen et al. (1996), and estimates for other pools and flux are derived from the text.

The flux of P through the atmosphere in soil dust and seaspray ( $1 \times 10^{12}$  g P/yr; Graham and Duce 1979, Mahowald et al. 2008) is also much smaller than other transfers in the global P cycle, which are largely derived from chemical weathering in soils. However, the atmospheric deposition of P is known to make a critical contribution to the supply of available P when it is deposited in some tropical forests on highly weathered soils (Swap et al. 1992, Chadwick et al. 1999, Okin et al. 2004) and in the open ocean (Talbot et al. 1986, Bristow et al. 2010). Newman (1995) reports P deposition from the atmosphere ( $0.07$  to  $1.7$  kg ha $^{-1}$  yr $^{-1}$ ) that rivals P derived from rock weathering ( $0.05$  to  $1.0$  kg ha $^{-1}$  yr $^{-1}$ ) in various terrestrial ecosystems. The Bodélé depression in Chad is thought to be the source of  $0.12 \times 10^{12}$  g P/yr in soil dusts that blow eastward over the Atlantic Ocean and into the Amazon Basin (Bristow et al. 2010, Ben-Ami et al. 2010).

Unlike transfers in the global nitrogen cycle, the major source of reactive P in the global P cycle is not provided by microbial reactions. Nearly all the phosphorus in terrestrial ecosystems is originally derived from the weathering of calcium phosphate minerals, especially apatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ; Eq. 4.7). The phosphorus content of most rocks is not large, and in most soils only a small fraction of the total P is available to biota (Chapter 4). Land vegetation appears to contain about  $0.5 \times 10^{15}$  g P (Smil 2000), while soils, to 50-cm depth, hold about  $46 \times 10^{15}$  g P, of which only  $13.8 \times 10^{15}$  g P is in labile or organic forms (X. Yang, personal communication, 2012). Estimated plant uptake on land,  $70$  to  $100 \times 10^{12}$  g P/yr (Smil 2000), implies a turnover of  $0.5\%/\text{yr}$  in soils. Root exudates and mycorrhizae may increase the rate of rock weathering on land (Chapter 4), but there is no process, equivalent to N fixation, that can produce dramatic increases in phosphorus availability for plants in P-deficient habitats. Thus, on both land and at sea, biota persist as a result of a well-developed recycling of phosphorus in organic forms (Figures 6.19 and 9.22).

The main flux of P in the global cycle is carried by rivers, which transport about  $21 \times 10^{12}$  g P/yr to the sea (Meybeck 1982, Smil 2000)—about twice as much as 300 years ago (Wallmann 2010, Liu et al. 2008). Only about 10% of this flux is potentially available to marine biota; the remainder is strongly bound to soil particles that are rapidly sedimented on the continental shelf (Chapter 9). The solubility product of apatite is only about  $10^{-58}$  (Lindsay and Vlek 1977). At a seawater pH of 8.3, the phosphorus concentration in equilibrium with apatite is about  $1.3 \times 10^{-7}$  molar ( $\sim 4$   $\mu\text{g P/l}$ ; Atlas and Pytkowicz 1977; compare to Figure 4.10). In seawater, organic and colloidal forms maintain the concentration of P in excess of that in equilibrium with respect to apatite; the average content of P in deep ocean water is about  $3 \times 10^{-6}$  molar ( $\sim 93$   $\mu\text{g/l}$ ; compare to Figures 9.18 and 9.27). The concentration of  $\text{PO}_4^{3-}$  in the surface oceans is low, but the large volume of the deep sea accounts for a substantial pool of P (Figure 12.6). The overall mean residence time for reactive P in the sea is about 25,000 years (Chapter 9).

The turnover of P through the organic pools in the surface ocean occurs in a few days. Nearly 90% of the phosphorus taken up by marine biota is regenerated in the surface ocean, and most of the rest is mineralized in the deep sea (Figure 9.22). Eventually, however, phosphorus is deposited in ocean sediments, which contain the largest phosphorus pool near the surface of the Earth (Van Cappellen and Ingall 1996). About  $2$  to  $3 \times 10^{12}$  g P/yr are added to sediments of the open ocean—roughly equivalent to the delivery of reactive P to the oceans by rivers (Wallmann 2010, Baturin 2007; Figure 9.22). On a time scale of hundreds of millions of years, these sediments are uplifted and subject to rock weathering, completing the global

cycle. Today, most of the phosphorus in rivers is derived from the weathering of sedimentary rocks, and it represents P that has made at least one complete journey through the global cycle (Griffith et al. 1977).

It is likely that  $\text{PO}_4$  has always been the dominant form of P available to biota. Students of Earth's earliest life have speculated on mechanisms by which  $\text{PO}_4$  could be polymerized and condensed so it could be incorporated into biochemical molecules. It is possible that lightning, volcanic eruptions, and other local high-energy environments may have been involved in the production of phosphite and polyphosphates (Yamagata et al. 1991, Pasek and Block 2009). Griffith et al. (1977) calculates that it took about 3 billion years for the weathering of igneous rocks to saturate seawater with  $\text{PO}_4$ , allowing the development of phosphorite skeletons in organisms (Cook and Shergold 1984) and the precipitation of authigenic apatites in sediments (Chapter 9). Today, these minerals are carried by subduction to the mantle, completing the global phosphorus cycle following tectonic uplift that returns rocks to the surface (Guidry et al. 2000, Buendia et al. 2010). Although the present-day burial of phosphorus appears similar to the rate during much of Earth's history (Filippelli and Delaney 1992), periods of massive uplift and erosion may have fueled high net primary productivity in the oceans (Filippelli and Delaney 1994, Filippelli 2008).

Van Cappellen and Ingall (1996) suggest a negative-feedback mechanism by which changes in the concentration of  $\text{O}_2$  in Earth's atmosphere determine the availability of P in the deep sea, where the net mineralization of P is affected by its adsorption on Fe minerals in oxic sediments. This cycle stabilizes the level of  $\text{O}_2$  in Earth's atmosphere through geologic time. For instance, if the concentration of  $\text{O}_2$  in the atmosphere were to fall to low levels, available P would become more plentiful in waters upwelling from the deep sea, marine NPP would increase, and more  $\text{O}_2$  would be released to the atmosphere from the oceans. Ocean productivity may have been first limited by P adsorption to Fe oxides shortly after the evolution of oxygenic photosynthesis, 3.5 to 3.8 bya (Bjerrum and Canfield 2002). Kump (1988) and Lenton (2001) offer analogous models centered on the terrestrial biosphere, in which the frequency of fire modulates changes in phosphorus availability, primary productivity, and changes in the levels of  $\text{O}_2$  in the atmosphere.

In many areas, humans have enhanced the availability of P by mining phosphate rocks— $25 \times 10^{12}$  g P/yr—that can be used as fertilizer.<sup>10</sup> Most of the economic deposits of phosphate are found in sedimentary rocks of marine origin, so the mining activity directly enhances the turnover of the global P cycle. The largest deposits are found in Morocco (Cooper et al. 2011); in the United States, deposits of phosphate rock are found in Florida and North Carolina. In many areas, the flux of P in rivers is significantly higher than it was in prehistoric times as a result of erosion, pollution, and fertilizer runoff (Bennett et al. 2001, Liu et al. 2008, Yuan et al. 2011). By mining phosphate rock, humans impact the global P cycle at a rate that rivals their impact on the global N cycle. The ratio of industrial nitrogen fixation to the mining of phosphate rock is about 14.3 (molar), somewhat less than the ratio in the uptake of these elements by land plants (31.3) but similar to the Redfield ratio for the uptake by marine phytoplankton (16). Indeed, the extensive mining of phosphate rock, a nonrenewable resource, may lead to

<sup>10</sup> [http://minerals.usgs.gov/minerals/pubs/commodity/phosphate\\_rock/](http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/).

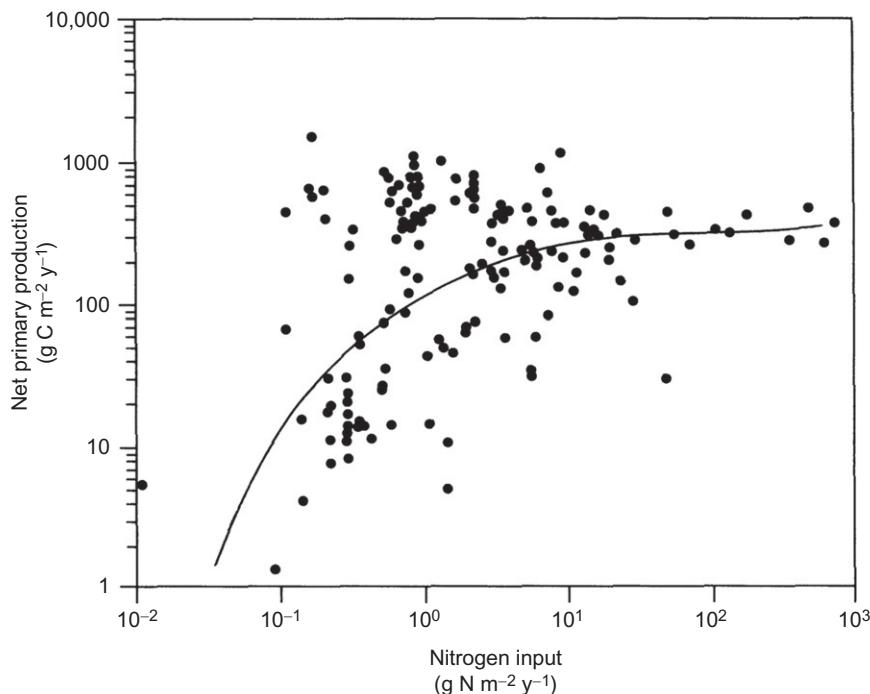
phosphorus shortages for agriculture. At current rates of use, the global estimate of phosphorus reserves will last about 370 years (Cooper et al. 2011).

## LINKING GLOBAL BIOGEOCHEMICAL CYCLES

The cycles of important biogeochemical elements are linked at many levels. Stock et al. (1990) describe how P is used to activate a transcriptional protein, stimulating nitrogen fixation in bacteria when nitrogen is in short supply. In this case, an understanding of the interaction between these elements is gained through the study of molecular biology. In [Chapter 5](#), we saw that the photosynthetic rate of land plants is related to the N and P content of their leaves, linking the net production of organic carbon to the availability of these elements in plant cells. In marine ecosystems, net primary productivity is often calculated from the Redfield ratio of C:N:P in phytoplankton biomass ([Chapter 9](#)). The molar N/P ratio of 16 may reflect fundamental relationships between the requirements for protein and RNA synthesis common to all plants (Loladze and Elser 2011). Whatever our viewpoint—from molecules to whole ecosystems—the movements of N, P, and C are strongly linked in biogeochemistry (Reiners 1986).

Nitrogen fixation by free-living bacteria appears inversely related to the N/P ratio in soil ([Figure 6.4](#)), and the rate of accumulation of N is greatest in soils with high P content (Walker and Adams 1958). Similarly, N/P ratios  $< 29$  appear to stimulate N fixation in freshwater ecosystems ([Chapter 7](#)). One might speculate that the high demand for P by N-fixing organisms links the global cycles of N and P, with P being the ultimate limit on nitrogen availability and net primary production. Indeed, in many soils the accumulation of organic carbon is correlated to available P ([Chapter 6](#)). N fixation in ocean waters is stimulated by P and Fe deposition from soil dusts (Falkowski et al. 1998). Despite these theoretical arguments for a phosphorus limitation of the biosphere through geologic time, net primary production in most terrestrial and marine ecosystems usually shows an immediate response to additions of N ([Figure 12.8](#)). Denitrification appears to maintain small supplies of N in most ecosystems, and colimitation by N and P is commonplace (Harpole et al. 2011).

It is urgent that biogeochemists offer improved predictions of the response of the biosphere to ongoing changes in the availability of N and P, which may allow a sustained increase in plant growth in response to rising CO<sub>2</sub> in Earth's atmosphere. Theoretical considerations based on stoichiometry indicate that the sink for CO<sub>2</sub> in land plants will be limited (van Groenigen et al. 2006, Reay et al. 2008), but changes in soil nutrient turnover and plant uptake may provide enhanced nutrient supplies (Finzi et al. 2007, Drake et al. 2011, Dieleman et al. 2010). Similarly, changes in the supply of N and P to the surface oceans of the world, as determined by changes in circulation and nutrient turnover, may determine the long-term sink for carbon in the sea. Such changes in biogeochemistry are likely to have affected the concentration of CO<sub>2</sub> in the atmosphere and Earth's climate during glacial-interglacial cycles, implying that the marine biosphere could respond rapidly to future climate change (Falkowski et al. 1998, Altabet et al. 2002, Gruber and Galloway 2008).



**FIGURE 12.8** Net primary production versus nitrogen inputs to terrestrial, aquatic, and marine ecosystems. Net primary production increases in direct response to added nitrogen up to inputs of about  $10 \text{ g N m}^{-2} \text{ yr}^{-1}$  (100 kg/ha). Inputs in excess of that level are rarely found in natural ecosystems, but are seen in polluted environments and agricultural soils. *Source: Modified, with permission from Princeton University Press, from Levin (1989).*

## SUMMARY

For both N and P, a small biogeochemical cycle with relatively rapid turnover is coupled to a large global pool with relatively slow turnover. For N, the major pool is found in the atmosphere. For P, the large pool is found in unweathered rock and soil.

The biogeochemical cycle of N begins with the fixation of atmospheric nitrogen, which transfers a small amount of inert  $\text{N}_2$  to the biosphere. This transfer is balanced by denitrification, which returns  $\text{N}_2$  to the atmosphere. The balance of these processes maintains a steady-state concentration of  $\text{N}_2$  in the atmosphere with a turnover time of  $10^7$  years. In the absence of denitrification, most of the N inventory on Earth would eventually be sequestered in the ocean and in organic sediments. Denitrification closes the global nitrogen cycle, and it causes nitrogen to cycle more rapidly than phosphorus, which has no gaseous phase. The mean residence time of phosphorus in sedimentary rocks is measured in  $10^8$  yr, and the phosphorus cycle is complete only as a result of tectonic movements of the Earth's crust.

Once within the biosphere, the movements of N and P are more rapid than in their global cycles, showing turnover times ranging from hours (for soluble P in seawater) to hundreds of

years (for N in biomass). In response to nutrient limitations, biotic recycling in terrestrial and marine habitats allows much greater rates of net primary production than rates of N fixation and rock weathering alone would otherwise support (Tables 6.1 and 9.3). The high efficiency of nutrient recycling may explain why, in the face of widespread nitrogen limitation, only about 2.5% of global net primary production is diverted to nitrogen fixation (Gutschick 1981).

Human perturbations of the global nitrogen and phosphorus cycles are widespread and dramatic. Through the production of fertilizers, humans have doubled the rate at which nitrogen enters the biogeochemical cycle on land. It is unclear how rapidly denitrification will respond to this global increase in nitrogen availability, but the rising concentrations of atmospheric  $\text{N}_2\text{O}$  are perhaps one indication of an ongoing biotic response (Vitousek 1994). Increasing nitrogen availability has led to the local extinction of species from polluted ecosystems and has shifted the limitation of net primary production in some systems from N to P (e.g., Mohren et al. 1986, Elser et al. 2007, Peñuelas et al. 2012). Increasing transport of N and P in rivers has shifted many estuarine and coastal ecosystems to a condition of Si deficiency (Justic et al. 1995). All of these changes indicate the effect of a single species—the human—in upsetting previous steady-state conditions in global nutrient cycling.

## Recommended Readings

- Melillo, J.M., C.B. Field, and B. Moldan. 2003. *Interactions of the Major Biogeochemical Cycles*. Island Press.  
Smil, V. 2001. *Enriching the Earth*. MIT Press.  
Schlesinger, W.H. (Ed.). 2004. *Biogeochemistry. Treatise on Geochemistry*, Volume 8. Elsevier.  
Tiessen, H. (Ed.). 1995. *Phosphorus Cycling in Terrestrial and Aquatic Ecosystems*. Wiley.

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## PROBLEMS

- Assuming that the concentration of P in crustal materials is 0.76 mg/g (Table 4.1), how much P is transported through the atmosphere by soil dust (Table 3.3)? How does this compare to the annual transport of P in rivers?
  - Assuming 100% efficiency in the industrial production of  $\text{NH}_3$ , compare the  $\text{CO}_2$  “cost” in the production of ammonia fertilizer to the potential carbon sink that might be realized by higher NPP and soil organic matter in areas that receive this fertilizer.
  - Human pollution of the world’s rivers has potentially doubled the transport of N and tripled the transport of P to the world’s coastal seas. Assuming the Redfield ratio applies to NPP, what is the potential increase in NPP in coastal waters globally?
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