

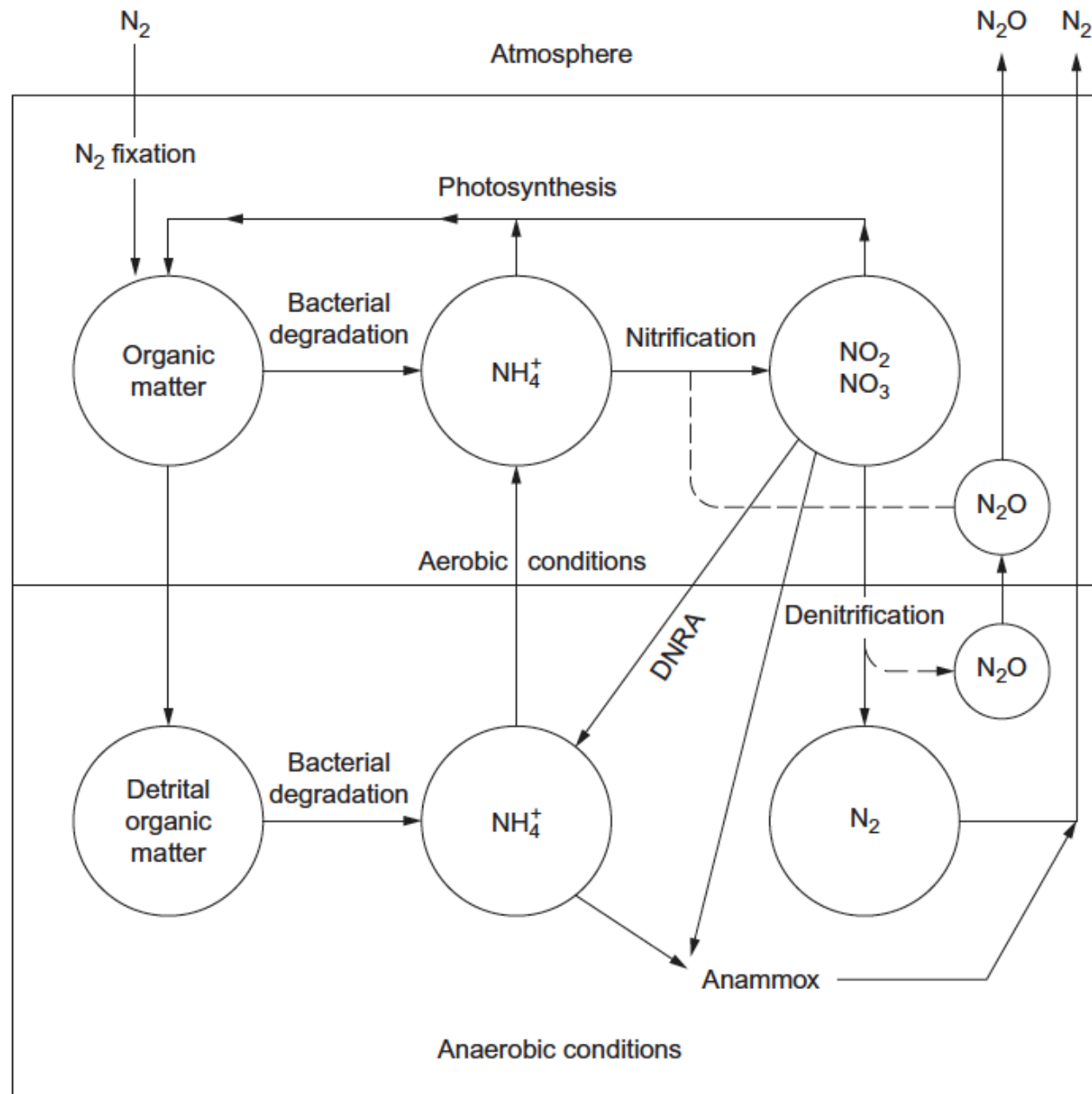
# The Global Cycles of Nitrogen and Phosphorus

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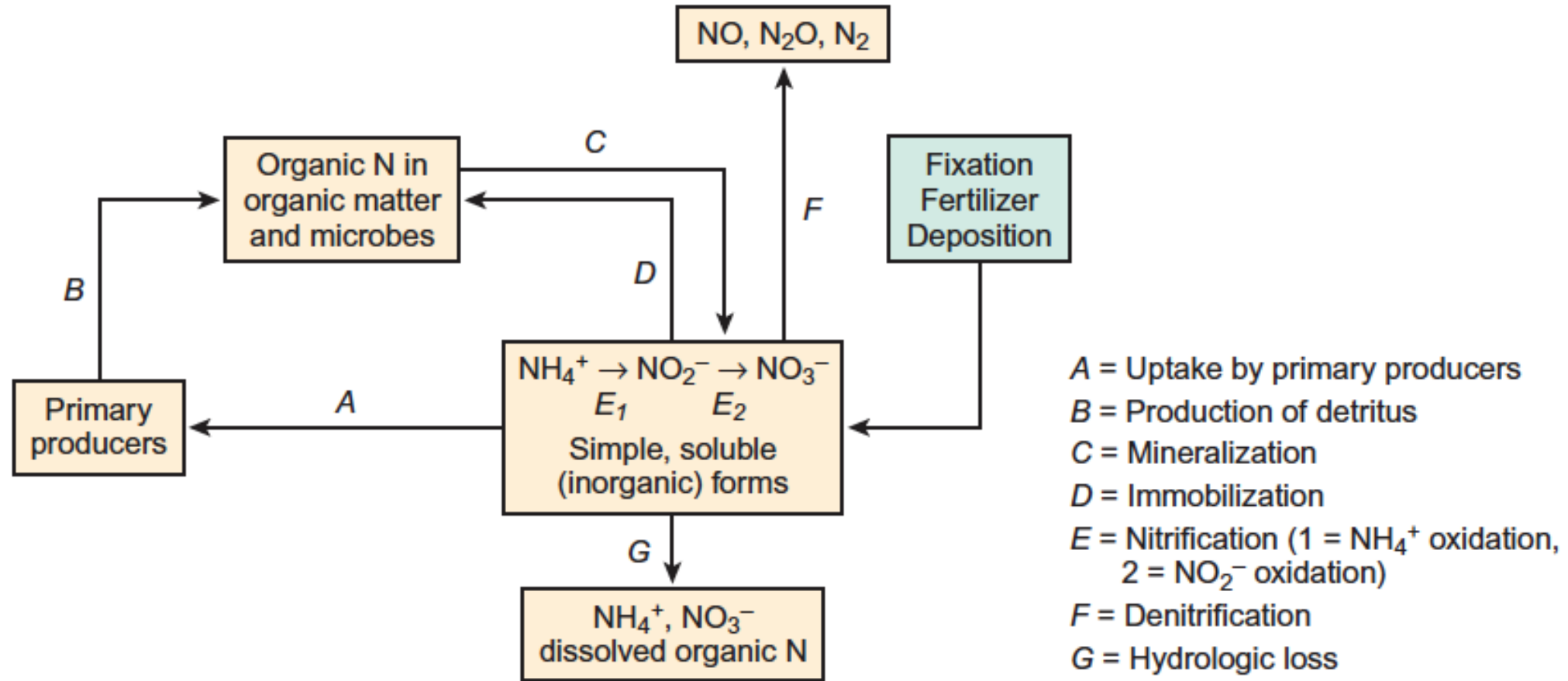
## OUTLINE

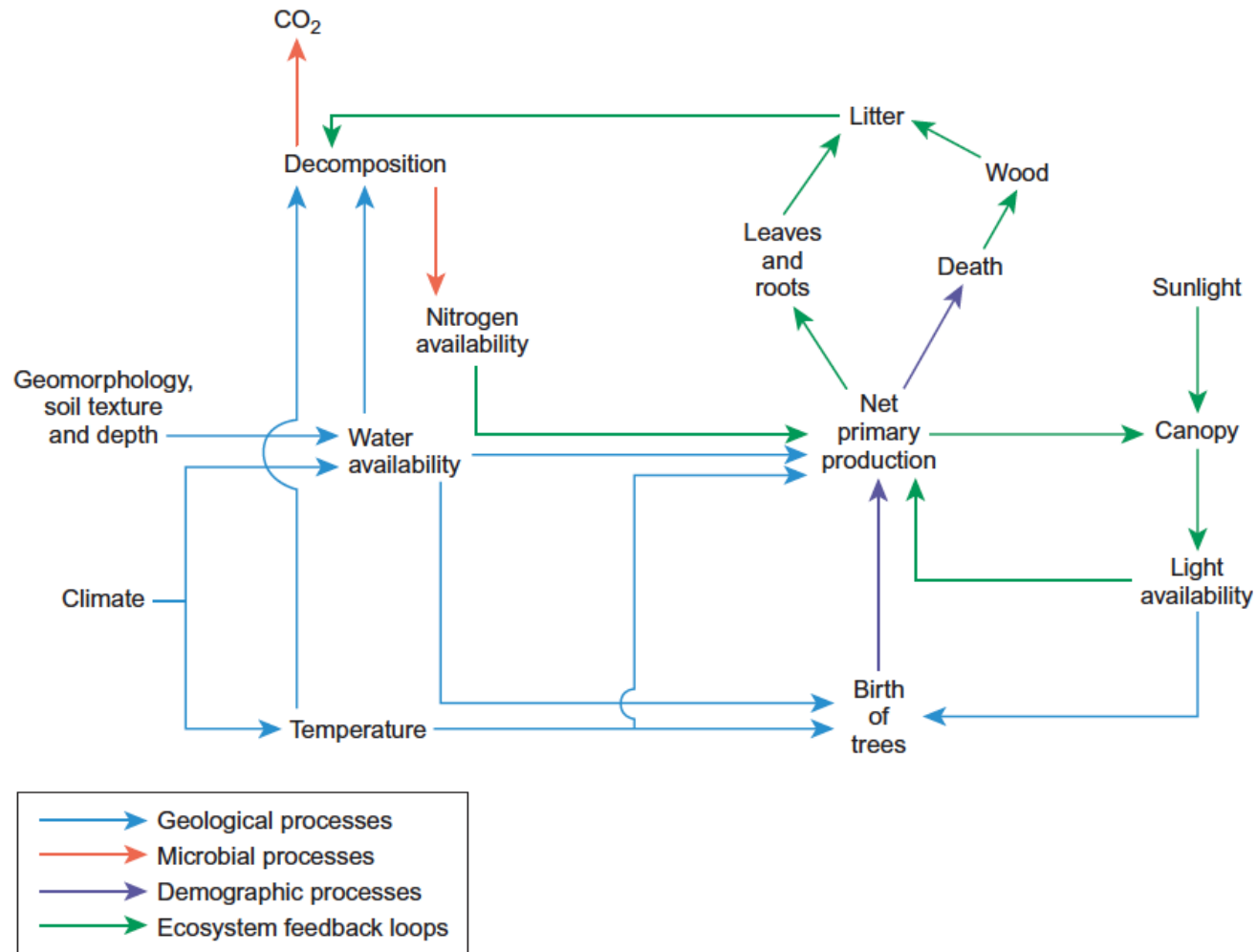
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Pools/Chemical Forms		Importance
<i>Gases</i>		
$N_2$	Dinitrogen	Dominant global pool, 79% of atmosphere.
$N_2O$	Nitrous oxide	Greenhouse gas, destroys stratospheric ozone.
$NO$	Nitric oxide	Toxic, precursor of tropospheric ozone.
$NH_3$	Ammonia	Plant available (soluble), can be toxic, rapidly deposited.
$NO_y$	Diverse reactive forms of N in the atmosphere produced by combustion of fossil fuels and/or atmospheric chemical reactions	Plant available (soluble), component of acid rain, rapidly deposited.
<i>Ions/Soluble Forms</i>		
$NH_4^+$	Ammonium	Available to plants.
$NO_2^-$	Nitrite	Toxic, rarely found at high levels in nature.
$NO_3^-$	Nitrate	Available to plants, highly leachable.
DON	Dissolved organic nitrogen	Mixture of many different chemical forms.
<i>Processes</i>		
$N_2 \rightarrow NH_3$	Biological N fixation	See text.
$N_2 \rightarrow NO_y$	Abiotic N fixation	See text.
Organic N $\rightarrow NH_4^+$	Mineralization	See text.
$NH_4^+$ or $NO_3^- \rightarrow$ Organic N	Immobilization	See text.
$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$	Nitrification	See text.
$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$	Denitrification	See text.
$NO_3^- \rightarrow NH_3$	Dissimilatory nitrate reduction to ammonia (DNRA)	See text.
$NH_4^+ + NO_2^- \rightarrow N_2$	Anaerobic oxidation of ammonium (anammox)	See text.

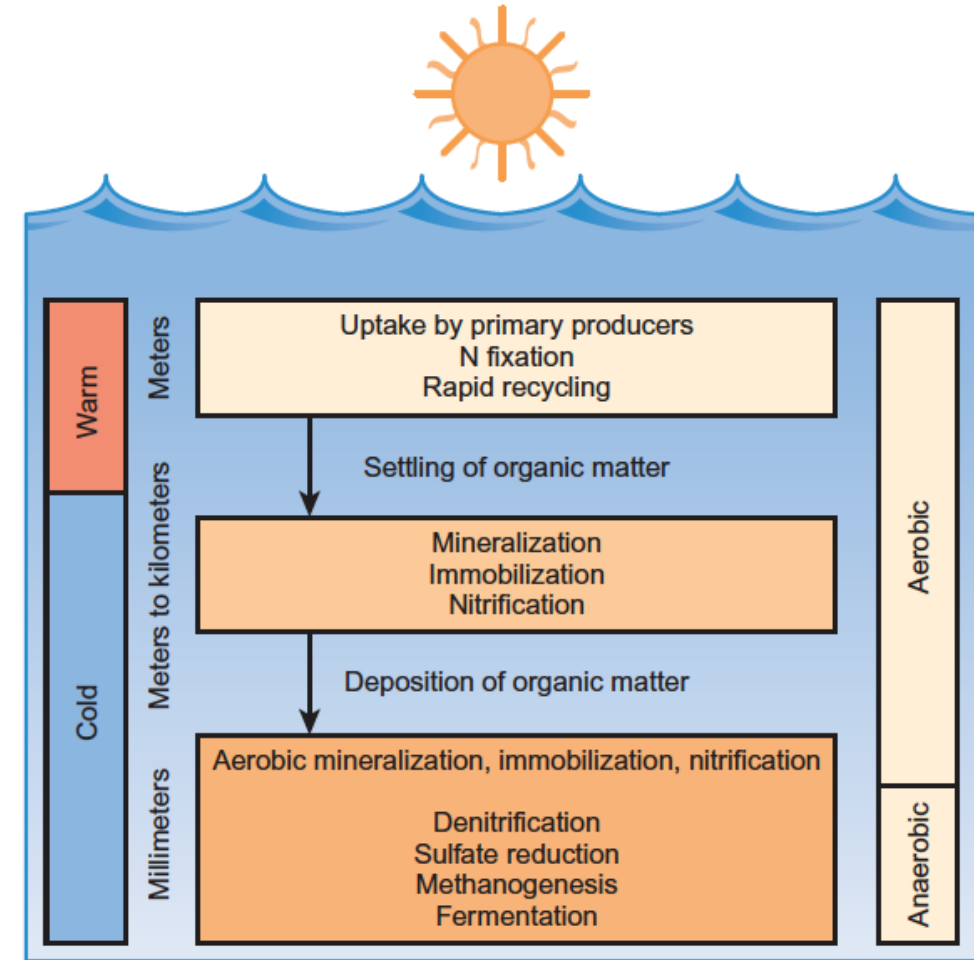


**FIGURE 12.1** Microbial transformations in the nitrogen cycle (DNRA = Dissimilatory Nitrate Reduction to Ammonium). *Source: Modified from Wollast (1981).*





**FIGURE 7.7** Conceptual model showing how site characteristics (geomorphology, soil texture, and depth) influence water availability, which in turn influences litter quality and nitrogen availability in temperate forests. (From Pastor and Post 1986.)

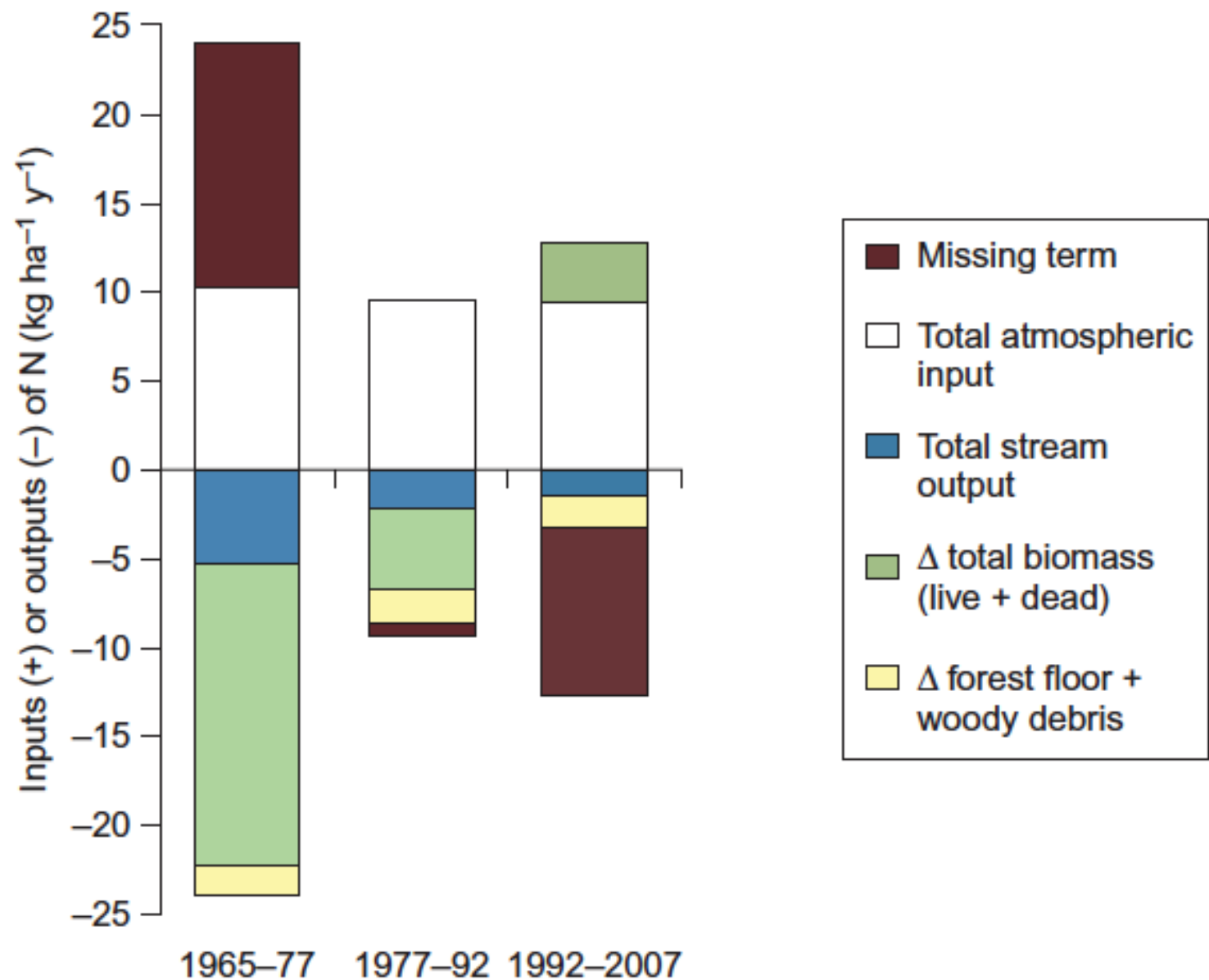


**TABLE 7.3** Pools and fluxes of N in an aggrading (55-year-old) northern hardwood forest (Hubbard Brook, New Hampshire) and an ungrazed tallgrass prairie (Konza Prairie, Kansas)

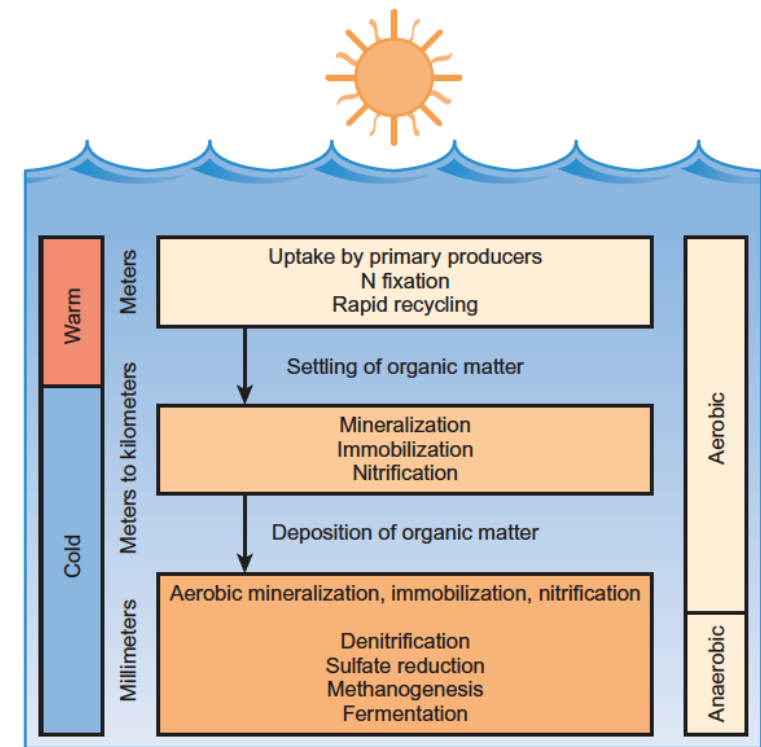
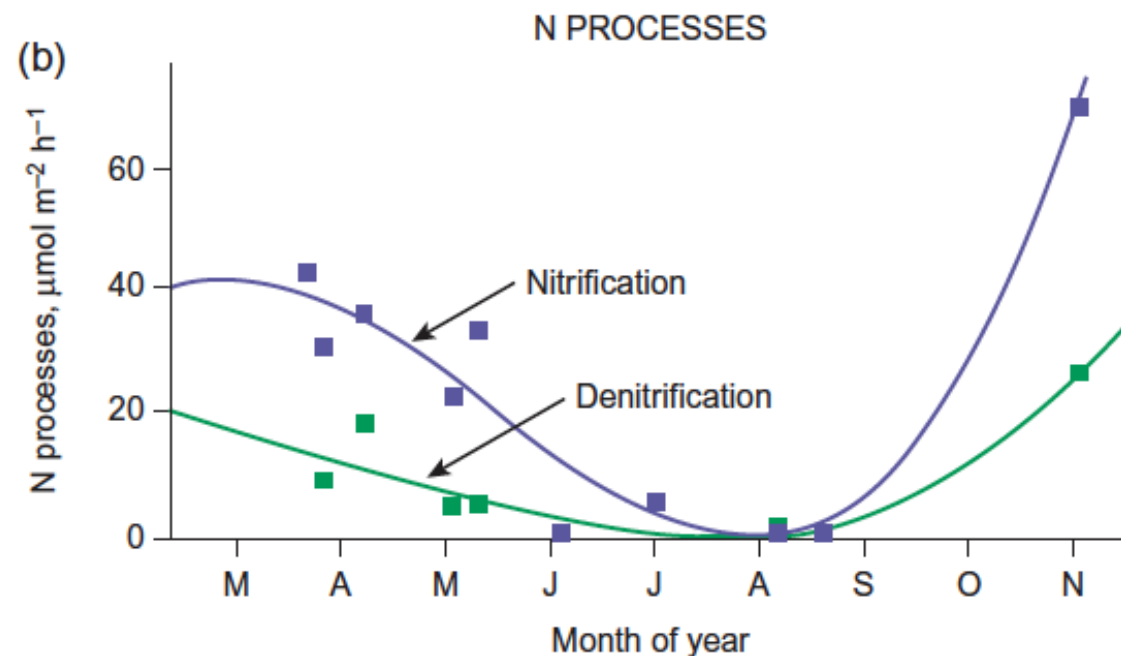
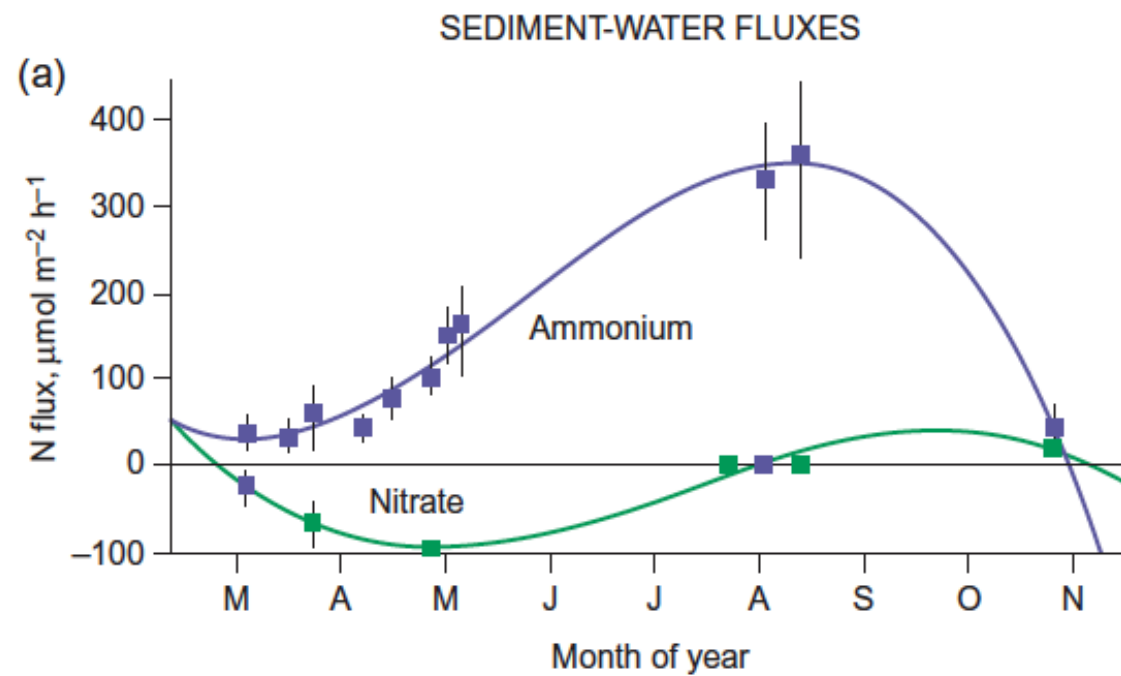
Pools (kg N/ha)	Hubbard Brook <sup>1</sup>	Konza Prairie <sup>2</sup>
Soil organic matter	4700	6250
Inorganic N pool in soil	26	2–6
Plant biomass	532	60–250
Fluxes (kg N ha <sup>-1</sup> y <sup>-1</sup> )		
Atmospheric deposition	10	10–20
N fixation	1	1–5
Net mineralization	70	10–40
Net nitrification	15	?
Hydrologic losses	4	0.1–0.3
Denitrification	0–10	0–10
Plant uptake	80	40–50
Litterfall	54	5–20

<sup>1</sup>Values from *Bormann et al. (1977)*, *Likens and Bormann (1995)*, and *Melillo (1977)*.

<sup>2</sup>From *Blair et al. (1998)*.

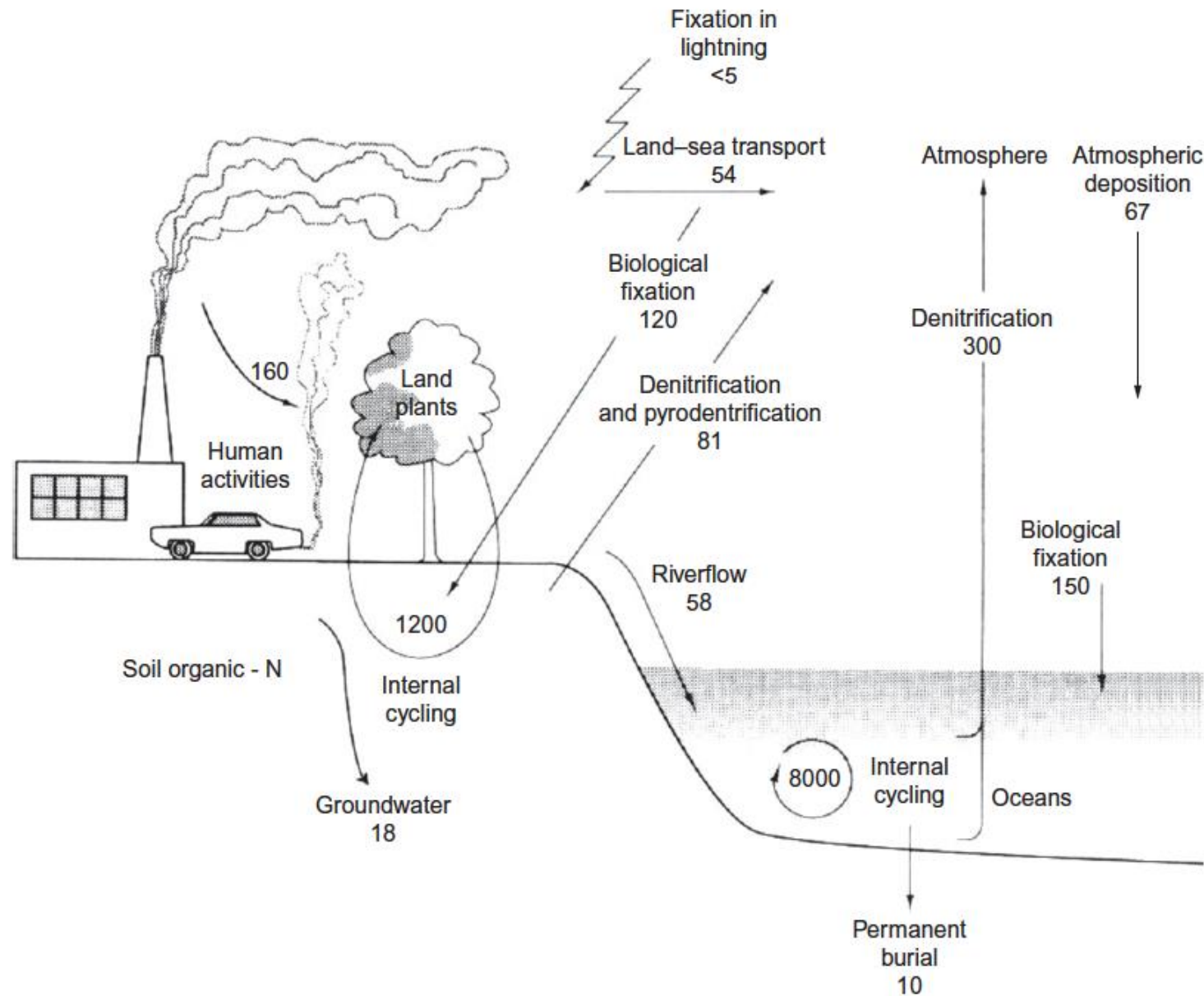


**FIGURE 7.6** The watershed-scale mass balance of nitrogen at Hubbard Brook Experimental Forest Watershed 6 (New Hampshire) is shown for a 37-year period. This northern hardwood forest was aggrading (building up) biomass until about 1982. During the aggrading period, there were “missing inputs” to support the large accumulation in biomass, and in the nonaggrading period, there were “missing outputs” as stream output, which is measured very accurately at Hubbard Brook, and is much lower than atmospheric input. These missing outputs must be either to gases or accumulation in soil organic matter. (From Yanai, R.D., S.P. Hamburg, M.A. Arthur, M.A. Vadeboncoeur, C.B. Fuss, and T.G. Siccama, unpublished.)

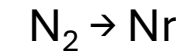


**FIGURE 7.8** Sediment N dynamics in the mesohaline portion of the Chesapeake Bay. (a) Seasonal variation in net fluxes of ammonium and nitrate across the sediment–water interface. (b) Seasonal variation in net nitrification and denitrification in sediments. Nitrogen dynamics are driven by oxygen availability, which is low in summer. (From *Kemp et al. 1990*.)





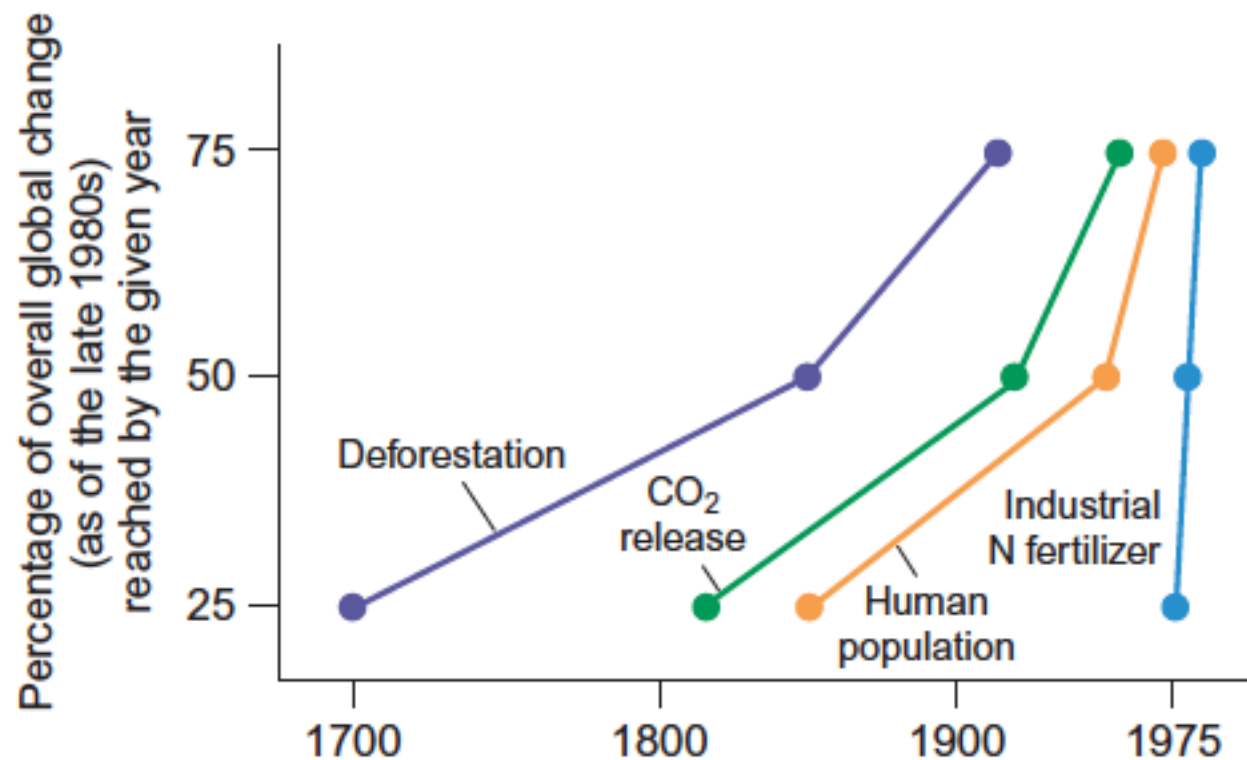
## Reactive Nitrogen



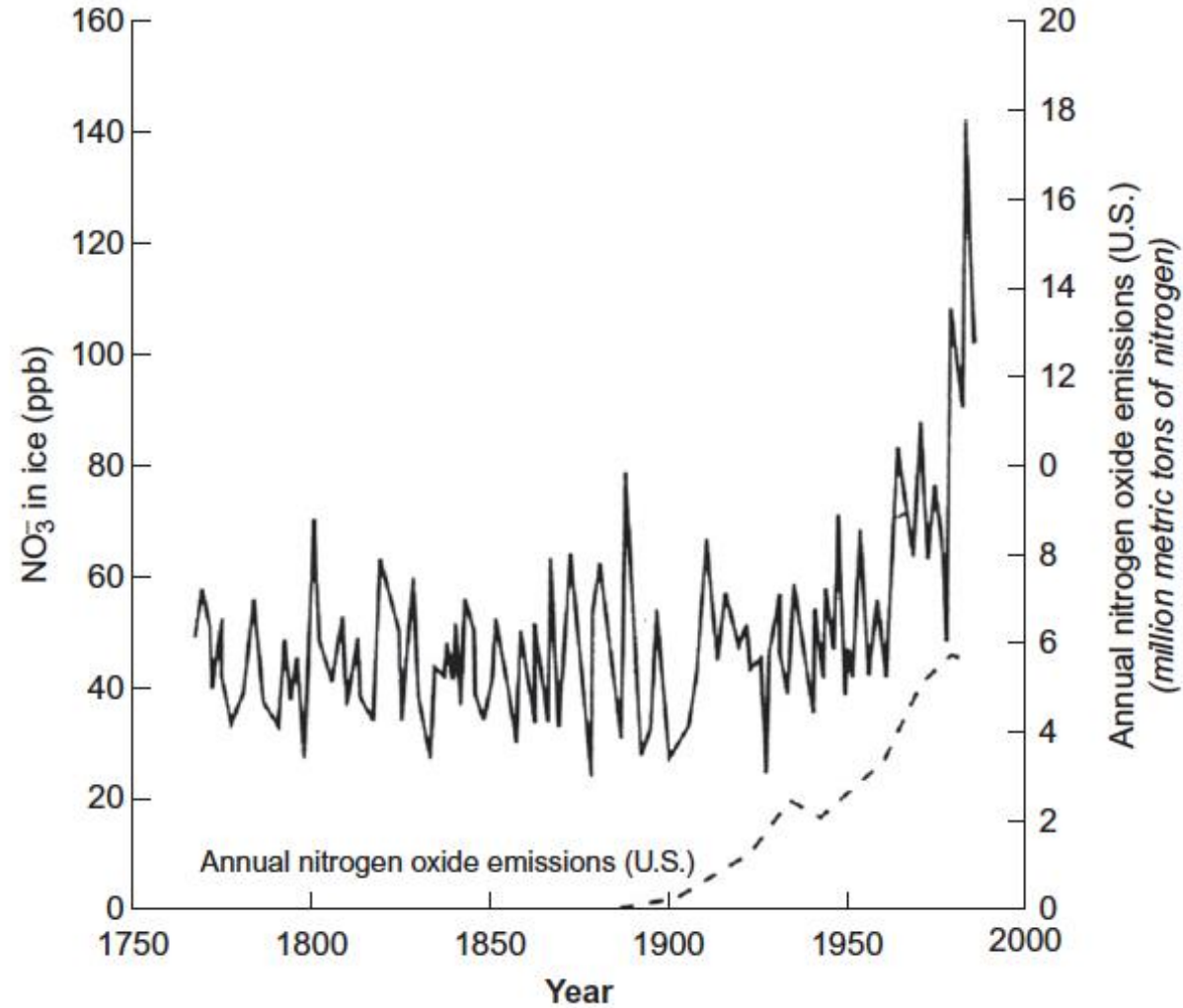
## Common Forms

- Nitrogen Oxides -  $\text{NO}_x$
- Ammonia -  $\text{NH}_3/\text{NH}_4$
- Nitrous Oxide -  $\text{N}_2\text{O}$
- Nitrate -  $\text{NO}_3^-$

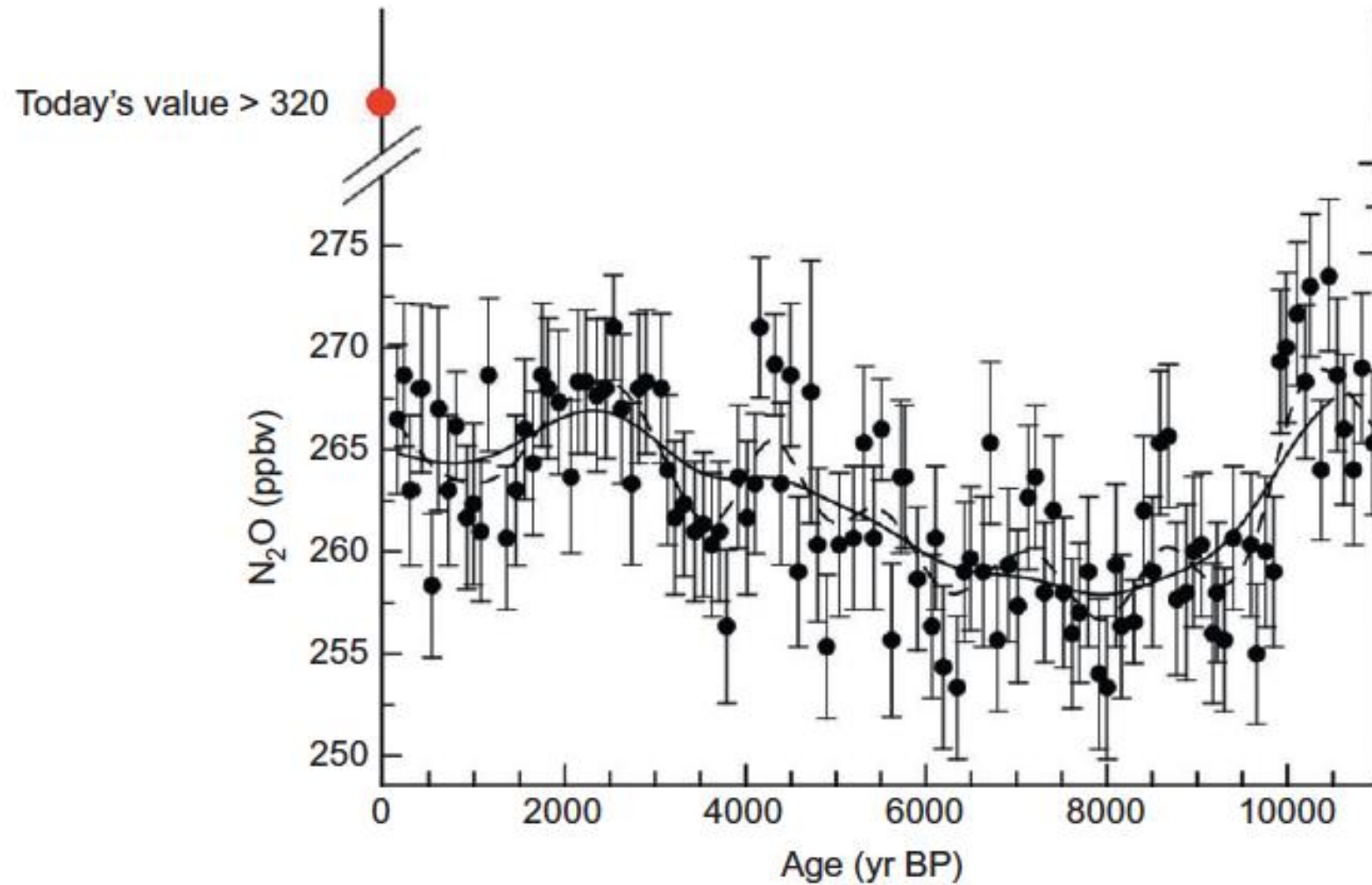
**FIGURE 12.2** The global nitrogen cycle. Each flux is shown in units of  $10^{12}$  g N/yr. Values as derived in the text. See also Table 12.3.



**FIGURE 7.1** The time course of selected human actions that have effects at the global scale. Note that human manipulation of the global N cycle has been the most recent and drastic component of global change. (From Vitousek *et al.* 1997.)

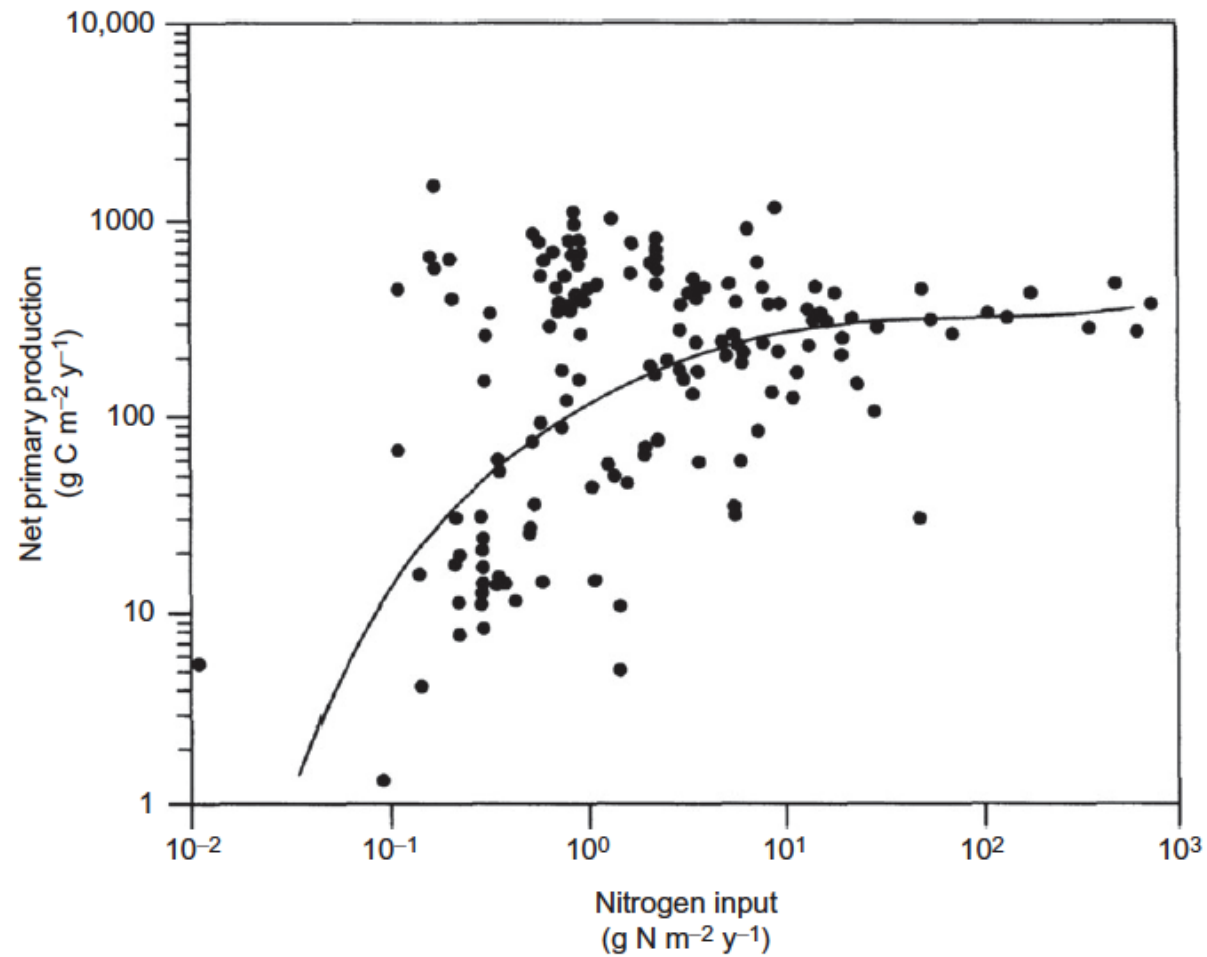


**FIGURE 12.4** The 200-year record of nitrate in layers of the Greenland ice pack and the annual production of nitric oxides by fossil fuel combustion in the United States. *Source: Modified from Mayewski et al. (1990).*

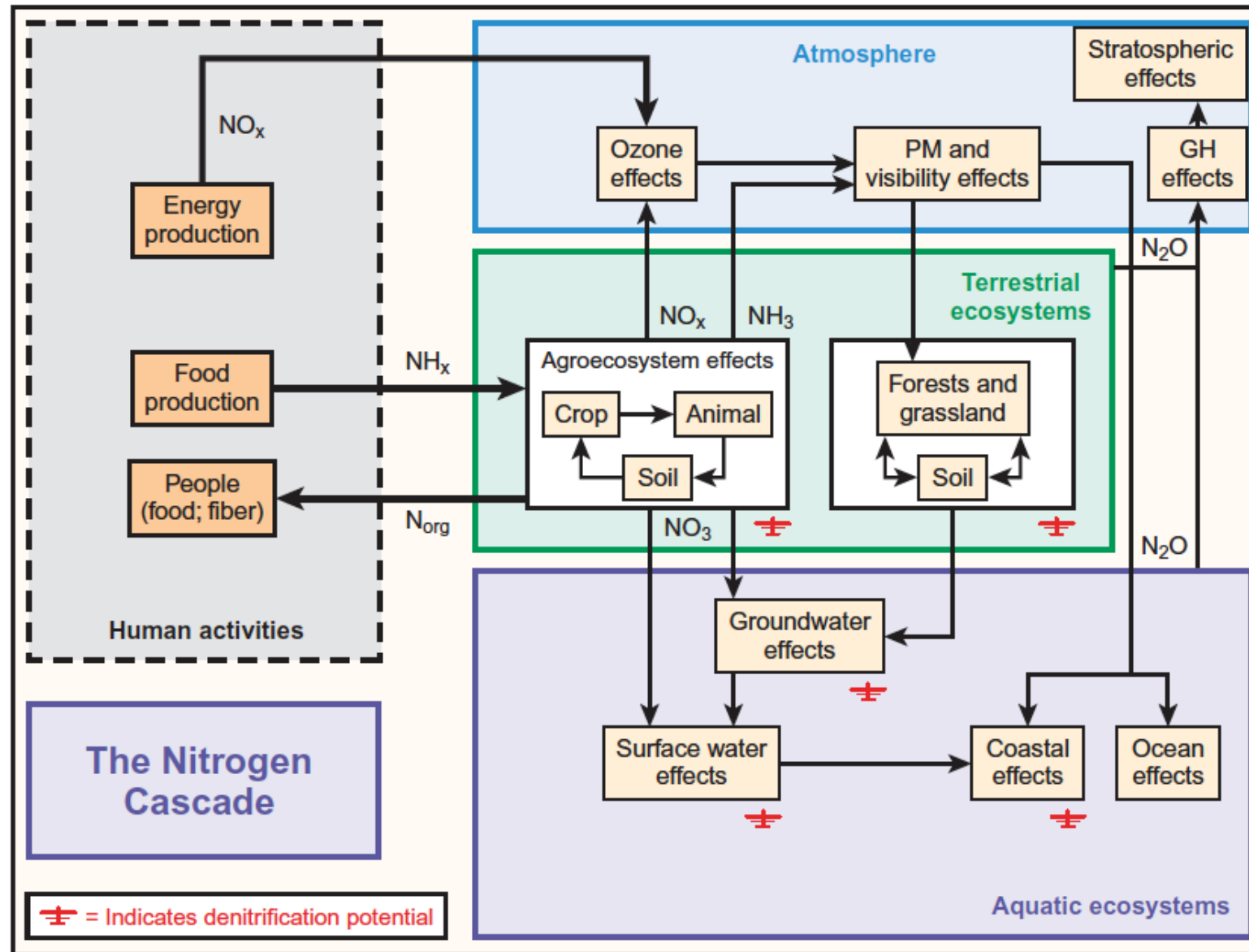


- $O_3$
- Greenhouse Gas

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



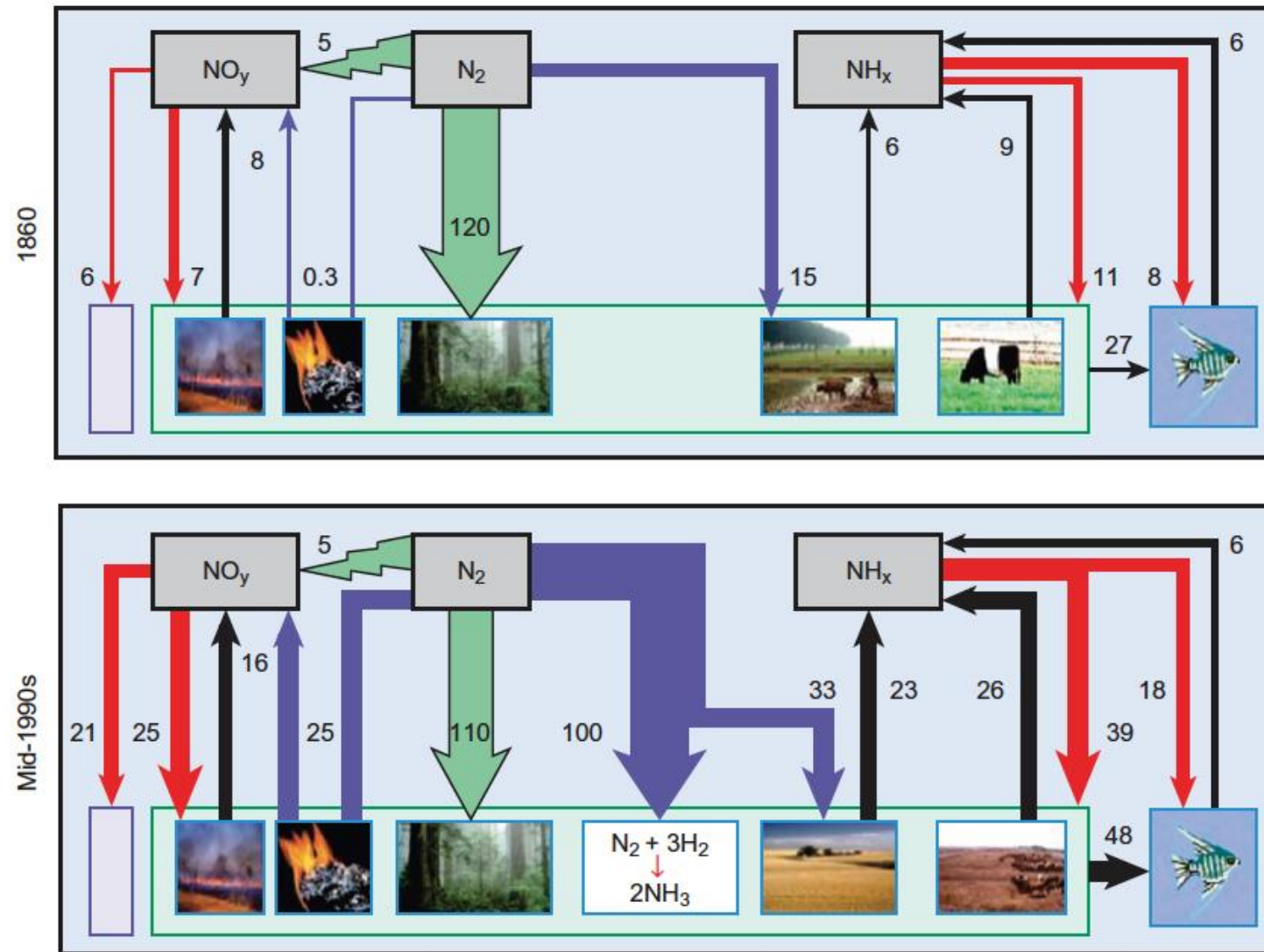
**FIGURE 12.8** Net primary production versus nitrogen inputs to terrestrial, aquatic, and marine ecosystems. Net primary production increases in direct response to added nitrogen up to inputs of about  $10 \text{ g N m}^{-2} \text{ yr}^{-1}$  (100 kg/ha). Inputs in excess of that level are rarely found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



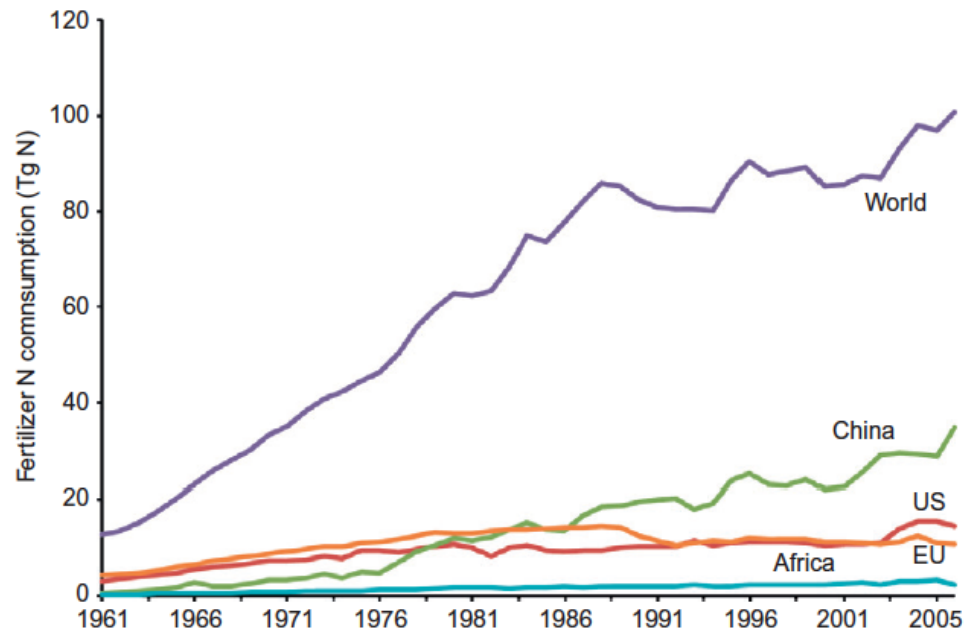
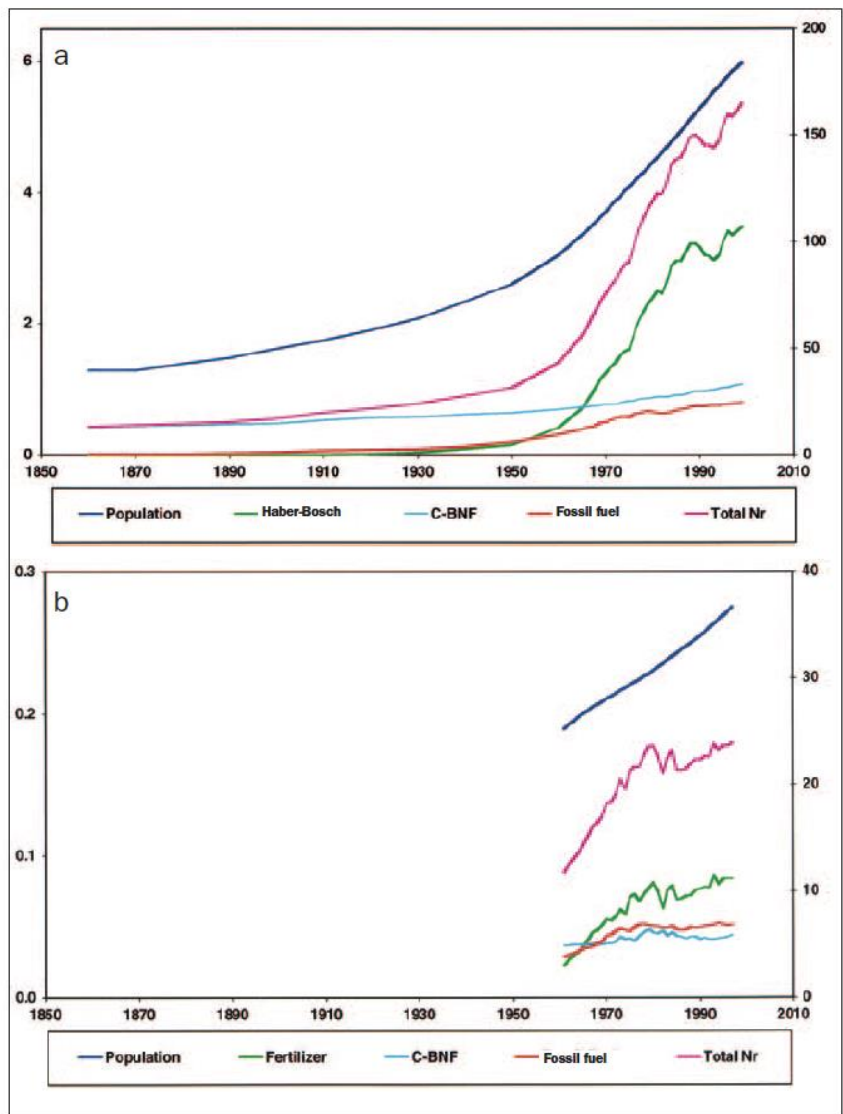
**FIGURE 7.3** The nitrogen cascade. Nitrogen added to the environment by human activity “cascades” through the atmosphere and terrestrial and aquatic ecosystems causing a series of air- and water-quality problems. (From Galloway 2003.)



THE GLOBAL NITROGEN BUDGET IN 1860 AND MID-1990s, TgN/yr



**FIGURE 7.2** Global nitrogen budget for 1860 and mid-1990s. Data in Tg N/yr. The emissions to the  $\text{NO}_y$  box from the coal reflect fossil-fuel combustion. Those from the vegetation include agricultural and natural soil emissions, and combustion of biofuel, biomass (savannah and forests), and agricultural waste. The emissions to the  $\text{NH}_x$  box from the agricultural field include emissions from agricultural land and combustion of biofuel, biomass (savannah and forests), and agricultural waste. The  $\text{NH}_x$  emissions from the cow and feedlot reflect emissions from animal waste. (From Galloway and Cowling 2002.)



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



**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).

**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	Kaiser et al. 2012
Biomass burning	7.7	
Human excrement	2.6	
Coal combustion and industry	0.3	
Automobiles	0.2	
<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	Duce et al. 2008; Dentener et al. 2006
Deposition on the ocean surface	24.0	
Reaction with OH radicals	1.0	
<b>Total sinks</b>	<b>63.7</b>	Schlesinger and Hartley 1992

*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).

**TABLE 12.5** A Global Budget for Nitrous Oxide (N<sub>2</sub>O) in the Atmosphere (all values are Tg N/yr (10<sup>12</sup> g/yr) nitrogen, as N<sub>2</sub>O)

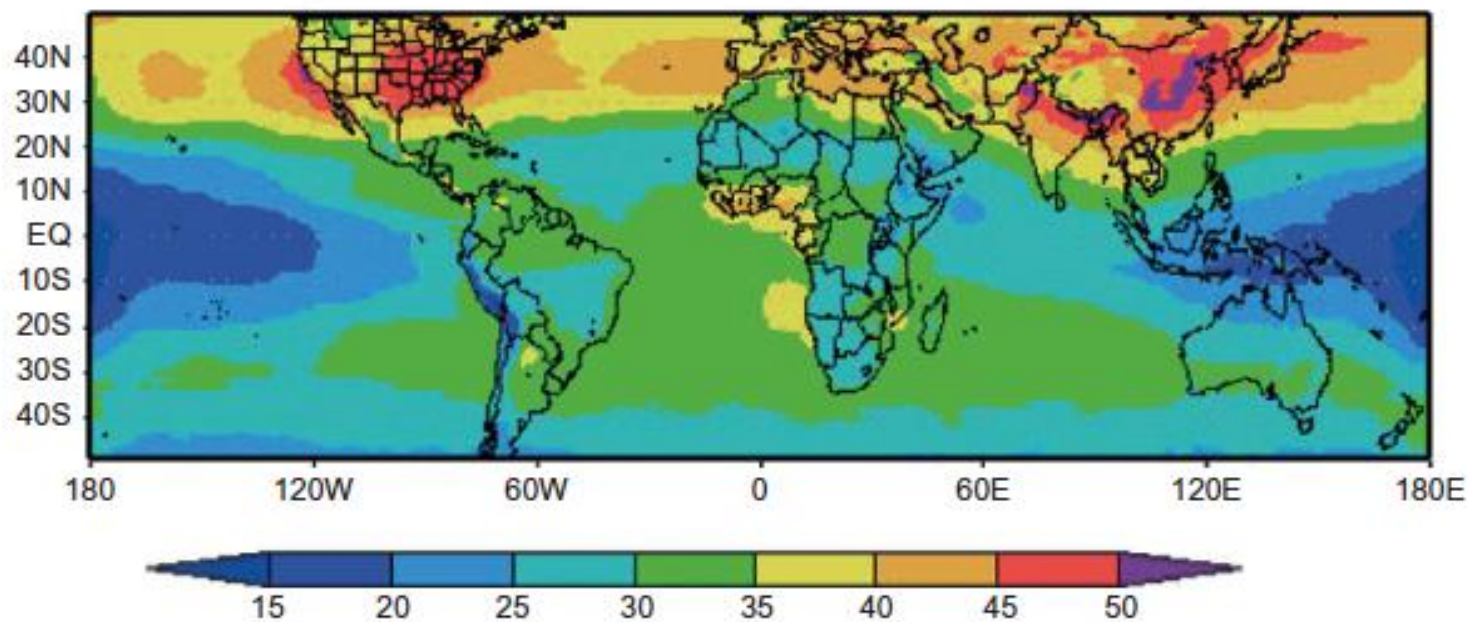
Natural sources	Annual flux	References
Soils	3.4 ± 1.3	Zhuang et al. 2012 <sup>a</sup>
Ocean surface	6.2 ± 3.2	Bianchi et al. 2012
Total natural	9.6	
<b>Anthropogenic sources</b>		
Agricultural soils	2.8	Bouwman et al. 2002b <sup>b</sup>
Cattle and feed lots	2.8	Davidson 2009
Biomass burning	0.9	Kaiser 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 N<sub>2</sub>O from natural soils includes 6.1 Tg N/yr (Potter et al. 1996) and 6.6 Tg N/yr (Bouwman et al. 1995).

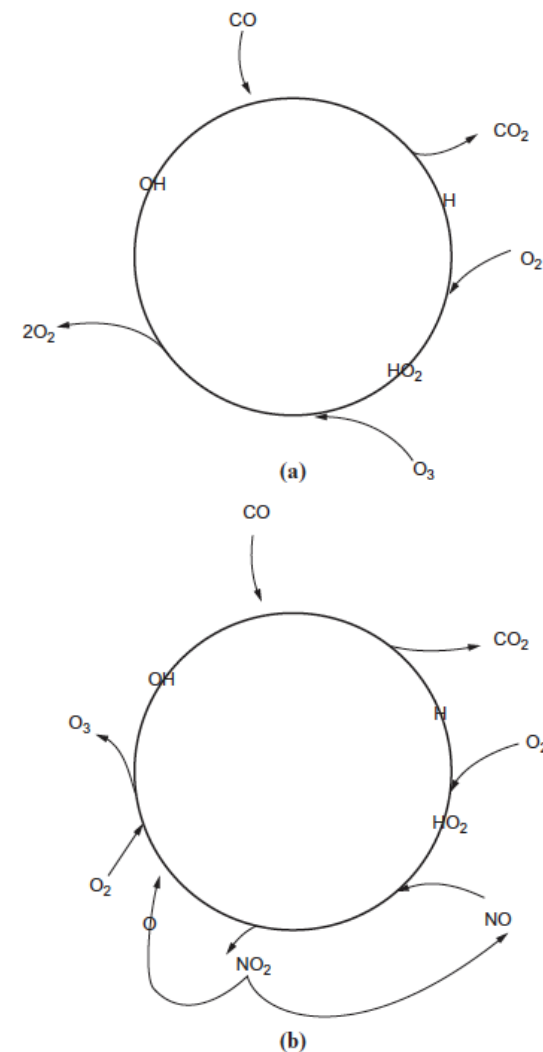
<sup>b</sup> The sum of emissions from agriculture and domestic animals given here, 5.6 Tg N/yr, is in close agreement with the value of 5.0 Tg N/yr estimated by Syakila and Kroeze (2011). These estimates of N<sub>2</sub>O flux from agricultural activities include emissions of N<sub>2</sub>O from downstream ecosystems and groundwaters impacted by agricultural inputs in these regions.

**TABLE 12.1** A Global Budget for Atmospheric NO<sub>x</sub> (values are Tg N (10<sup>12</sup> 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 ~ 21 Tg N/yr; Davidson and Kinglerlee 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>	

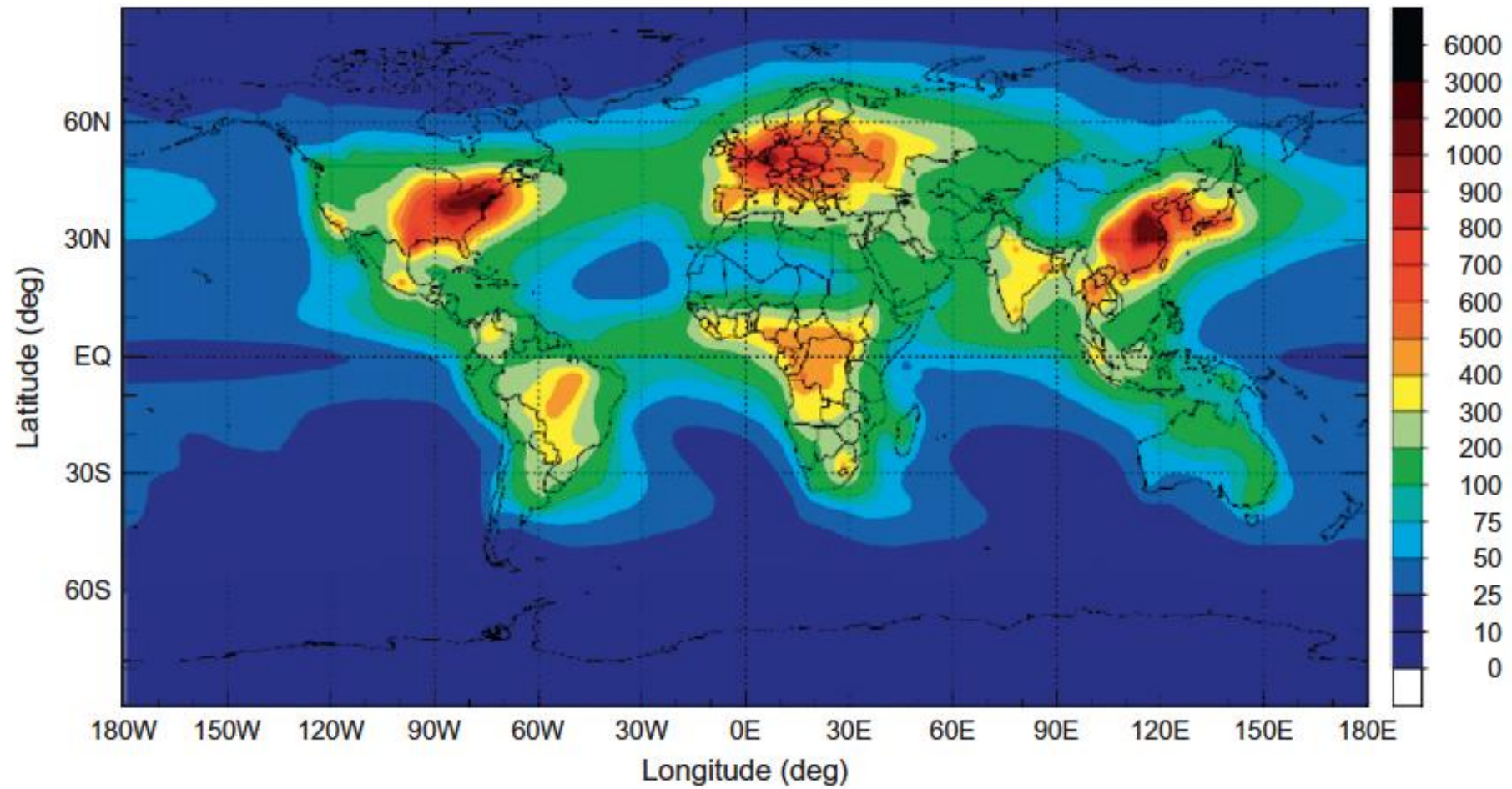


**FIGURE 3.9** Distribution of ozone in Earth's atmosphere, for summer months, averaged over 1979–1991. Note high ozone concentrations over the eastern United States and China. Data are in Dobson units (see page 83). *Source: From Fishman et al. (2003). Used with permission of European Geosciences Union.*



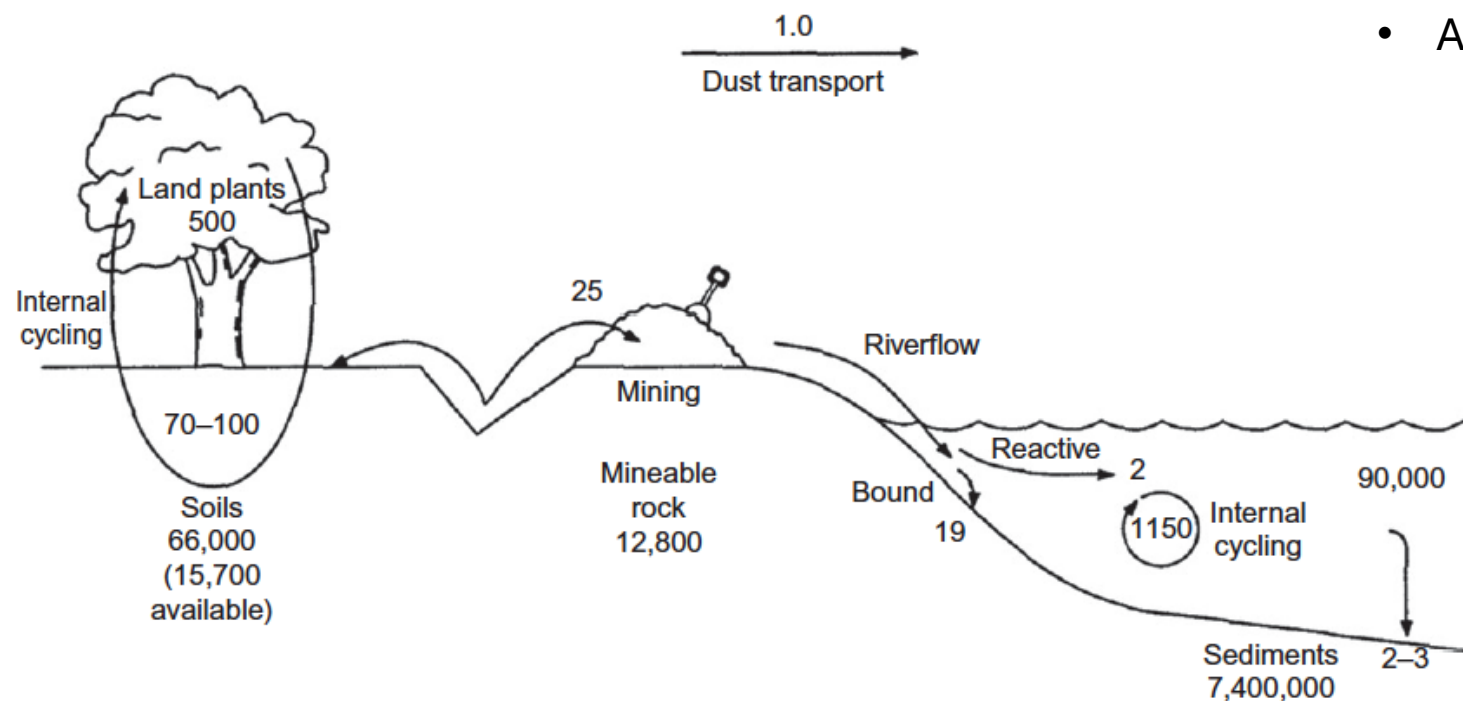
**FIGURE 3.8** Reaction chain for the oxidation of CO in (a) clean and (b) dirty atmospheric conditions.





**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).

- Minimal Gaseous emissions
- Weathering of Calcium Phosphate minerals
- Mycorrhizae
- Autochthonous cycling of organic forms



**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.