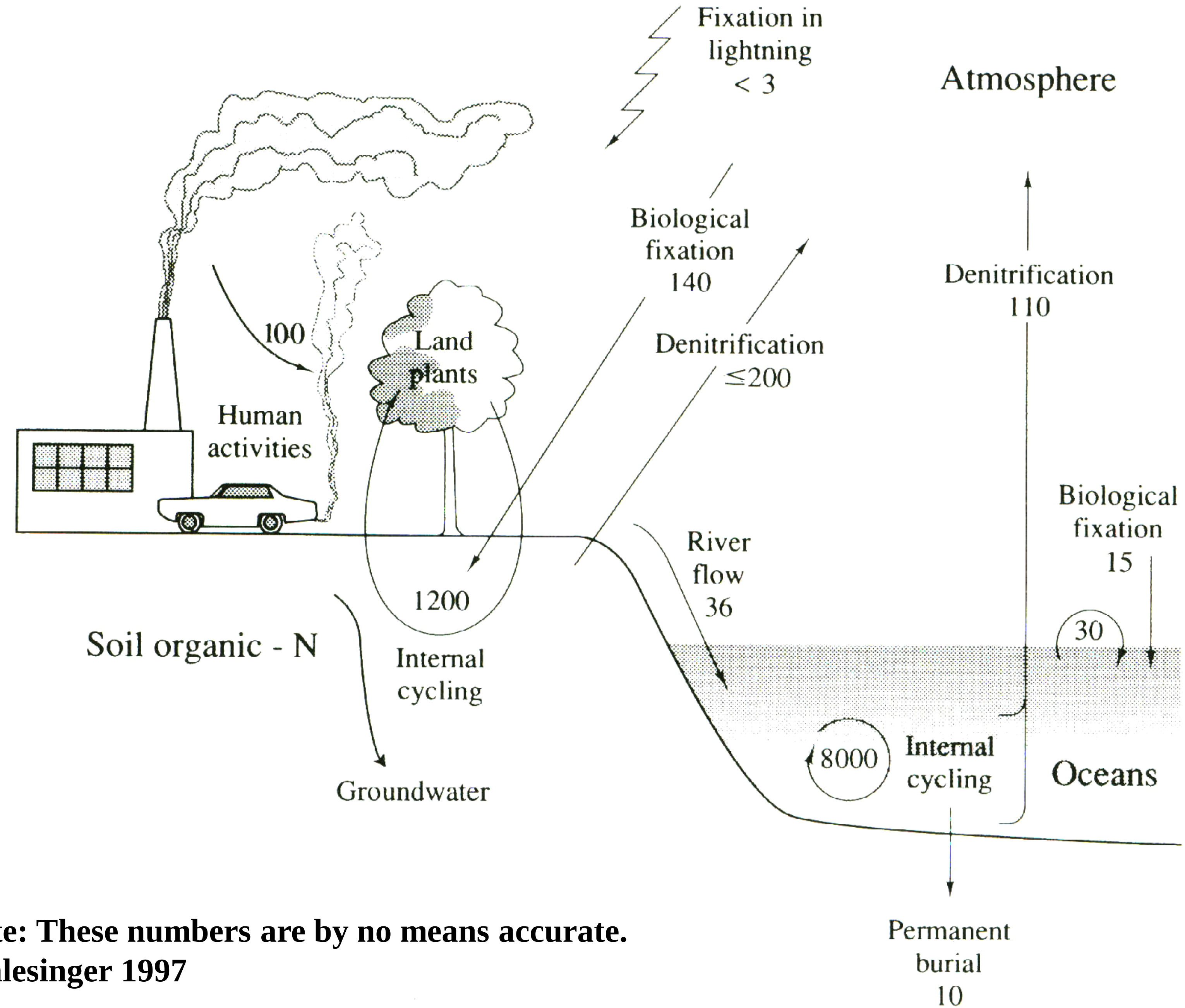
The Global Nitrogen Cycle



Note: These numbers are by no means accurate.
Schlesinger 1997

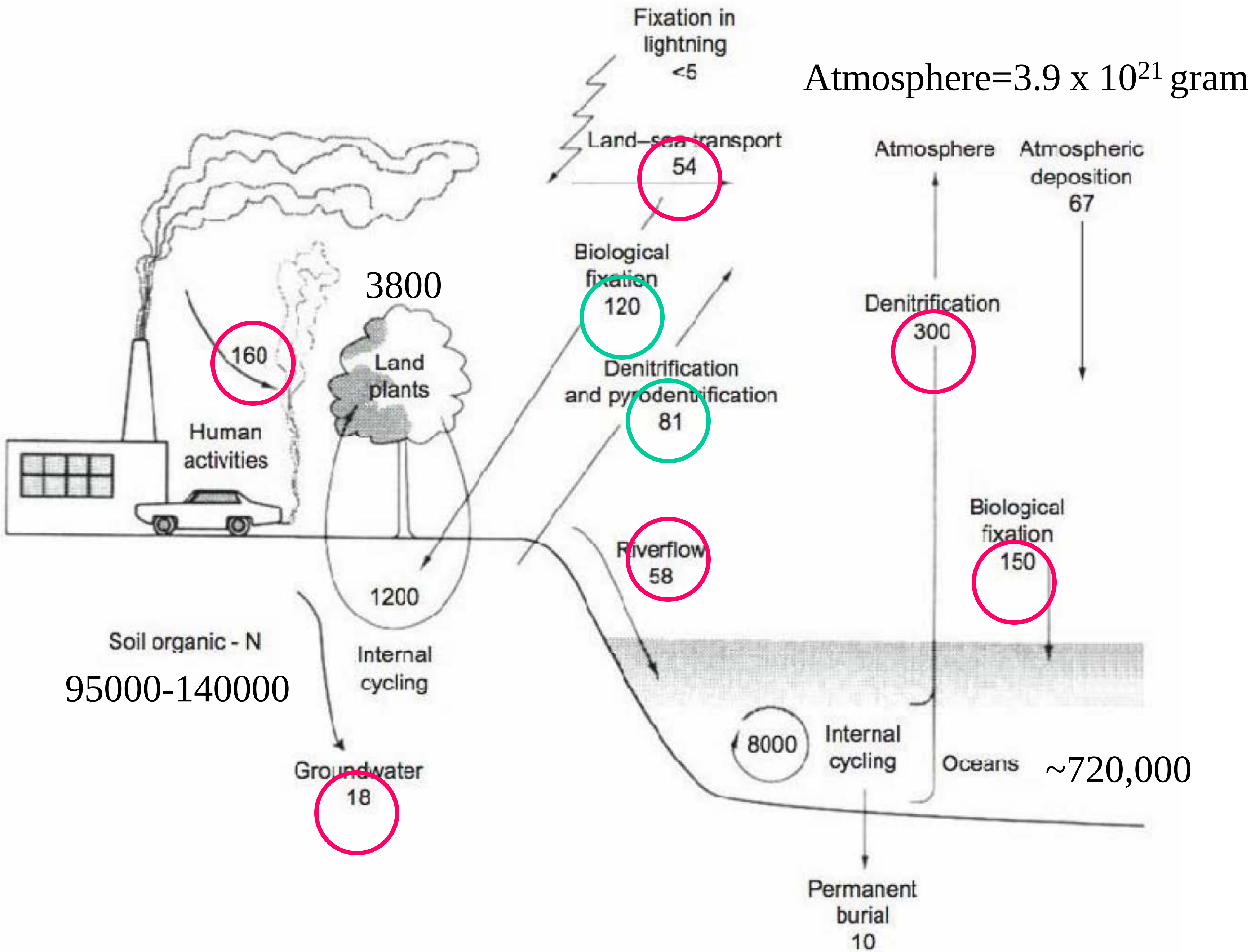


FIGURE 12.2 The global nitrogen cycle. Each flux is shown in units of 10^{12} g N/yr. Values as derived in the text. See also Table 12.3.

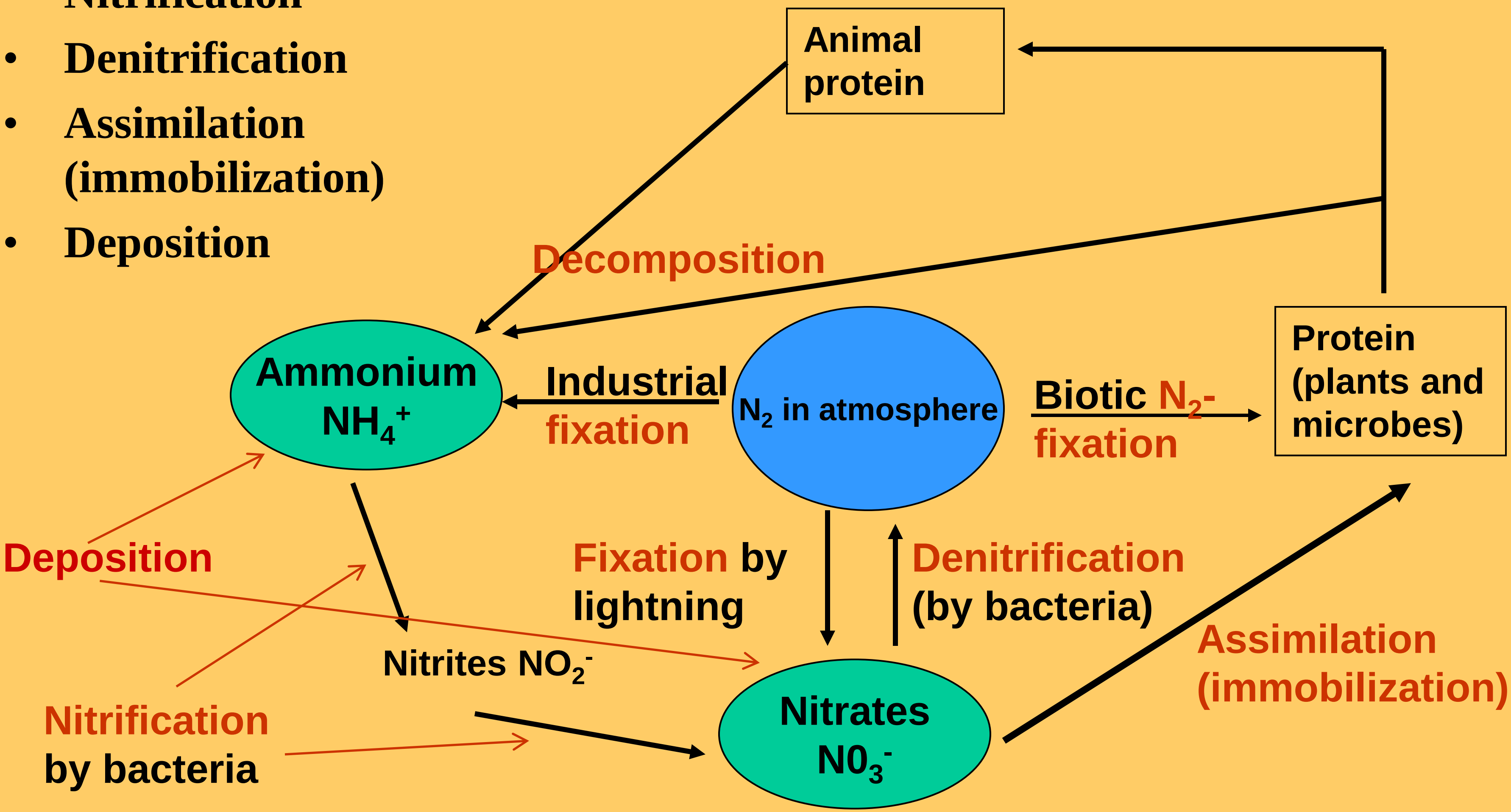
TABLE 12.3 Mass Balance for Nitrogen on the Earth's Land Surface

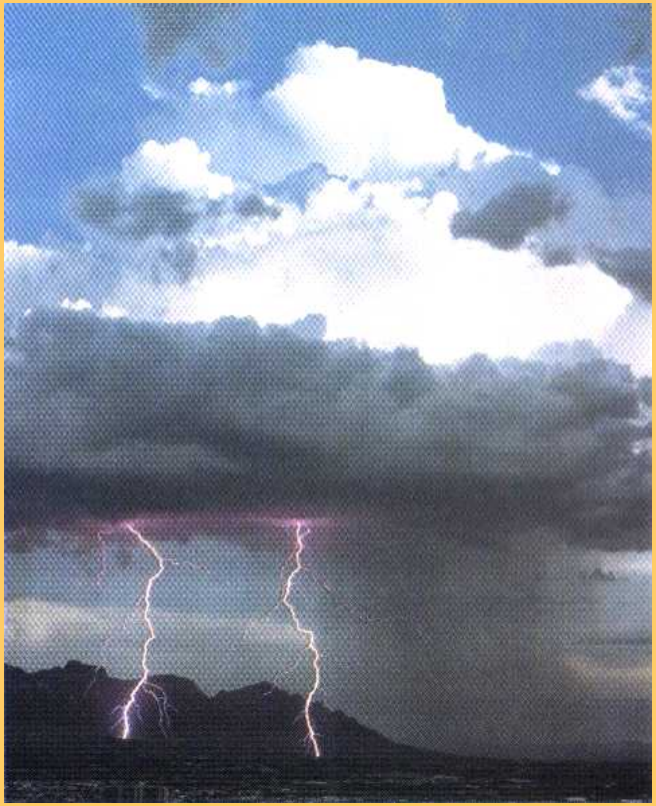
Inputs	Preindustrial	Human derived	Total
Biological N fixation	60[a]	60[b]	120
Lightning	5	0	5
Rock weathering	20[c]	0	20
Industrial N fixation	0	136[d]	136
Fossil fuel combustion	0	25	25
Total	**85**	**221**	**306**
Fates			
Biospheric increment	0	9	9
Soil accumulation	0	48	48
Riverflow	27	31	58
Groundwater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

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

Six processes in cycling nitrogen through the biosphere

- N_2 fixation
- Ammonification (decomposition)
- Nitrification
- Denitrification
- Assimilation (immobilization)
- Deposition





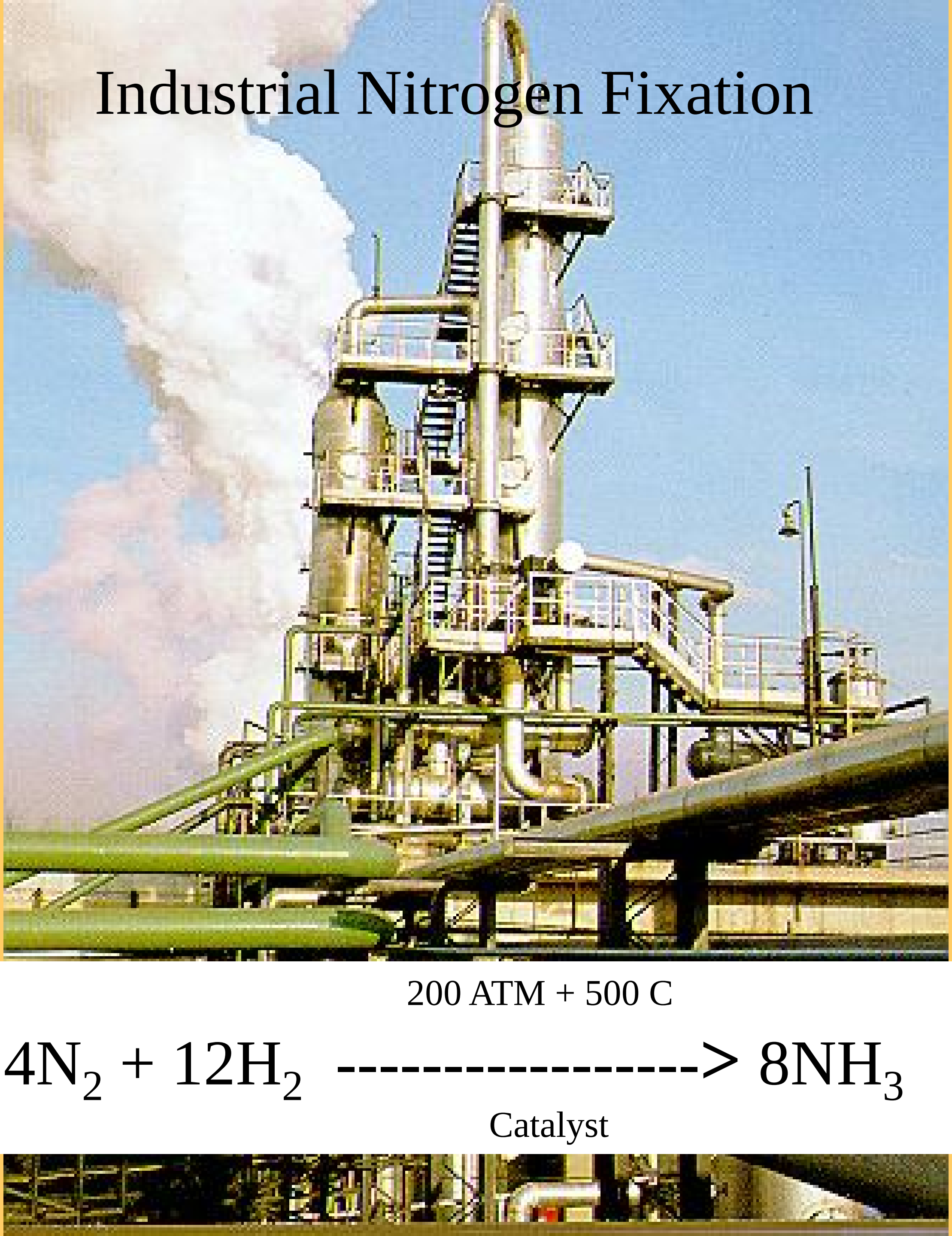
High-voltage electrical discharges, such as lightning, can oxidize N_2.

$$N_2 \text{ ---> } NO_x \text{ ---> } NO_3^-$$

Internal combustion engines produce NO and NO_2 because the high internal temperatures and pressures cause atmospheric N_2 and O_2 to react.

Industrial Nitrogen Fixation

Total N fertilizer use in the world: ~130 million metric tons per year as of 2010.



$$4N_2 + 12H_2 \xrightarrow[\text{Catalyst}]{\text{200 ATM + 500 C}} 8NH_3$$

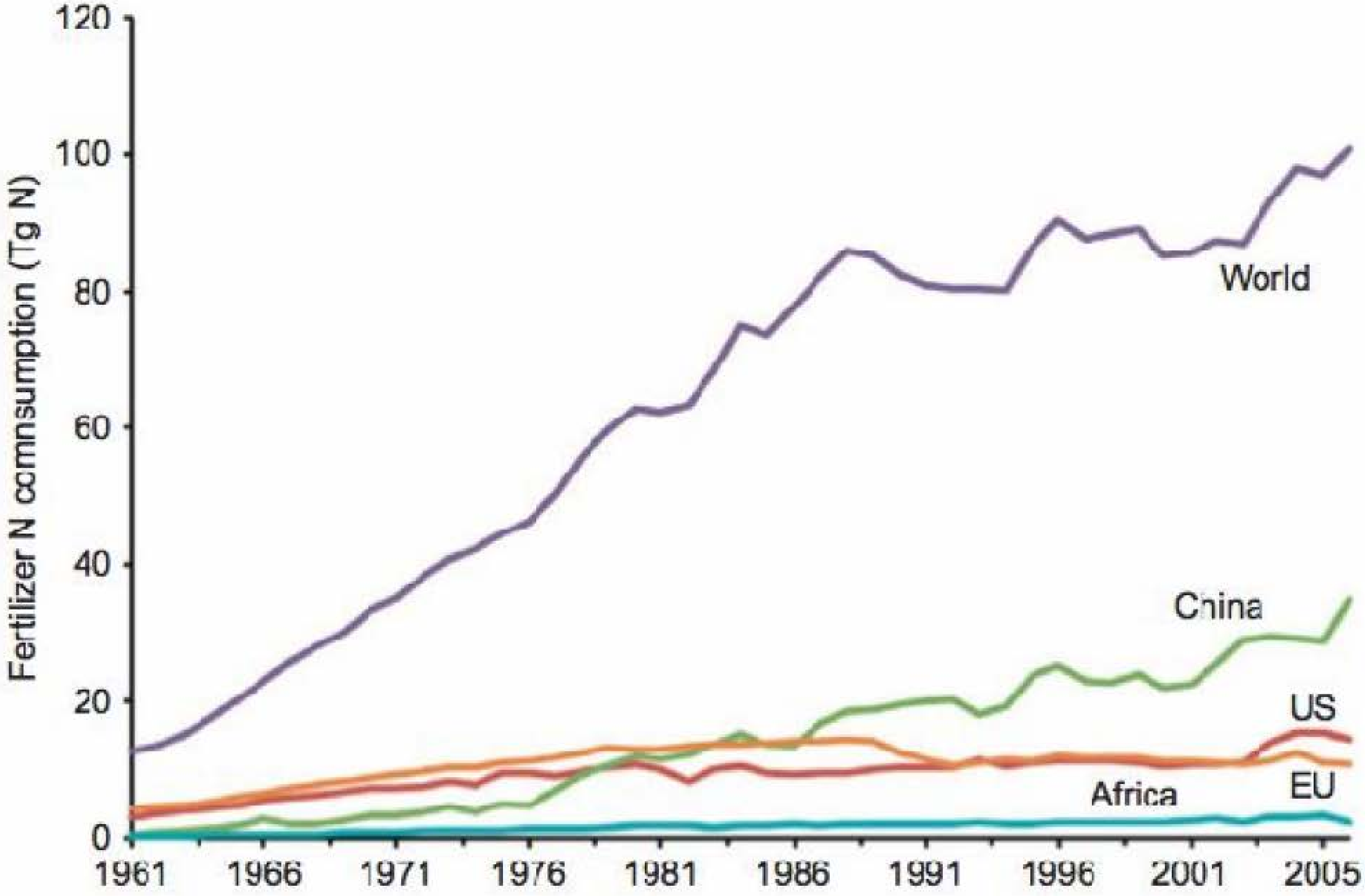
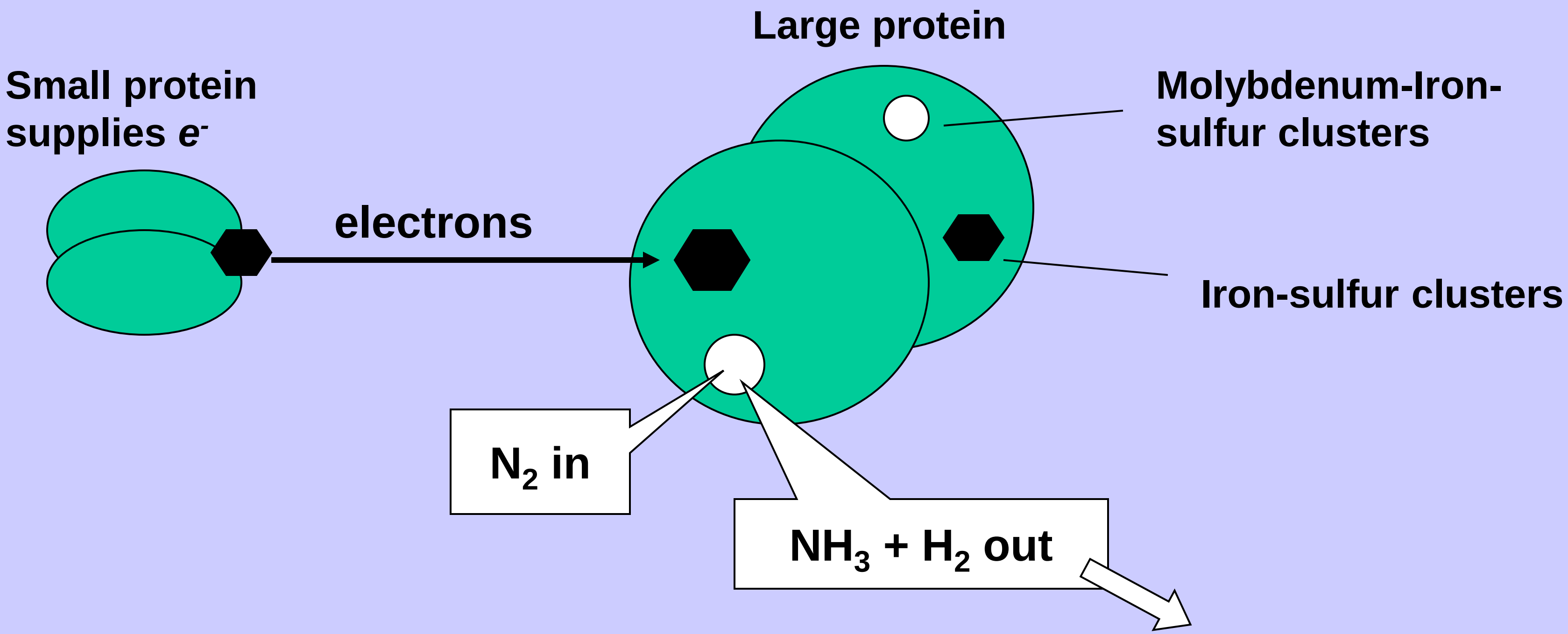


FIGURE 12.5 The production history of nitrogen fertilizer. *Source: From Robertson et al. (2009). Used with permission of the Annual Review.*

Mechanism of Biological N-fixation

$$N_2 + 8H^+ + 6e^- + 16ATP \xrightarrow[\text{(Fe, Mo)}]{\text{(Nitrogenase)}} 2NH_3 + H_2 + 16ADP + 16P_i$$

- This reaction is performed exclusively by **prokaryotes** (the bacteria and related organisms), using an enzyme complex termed **nitrogenase**.
- Nitrogenase consists of two proteins - an iron protein and a molybdenum-iron protein, as shown below



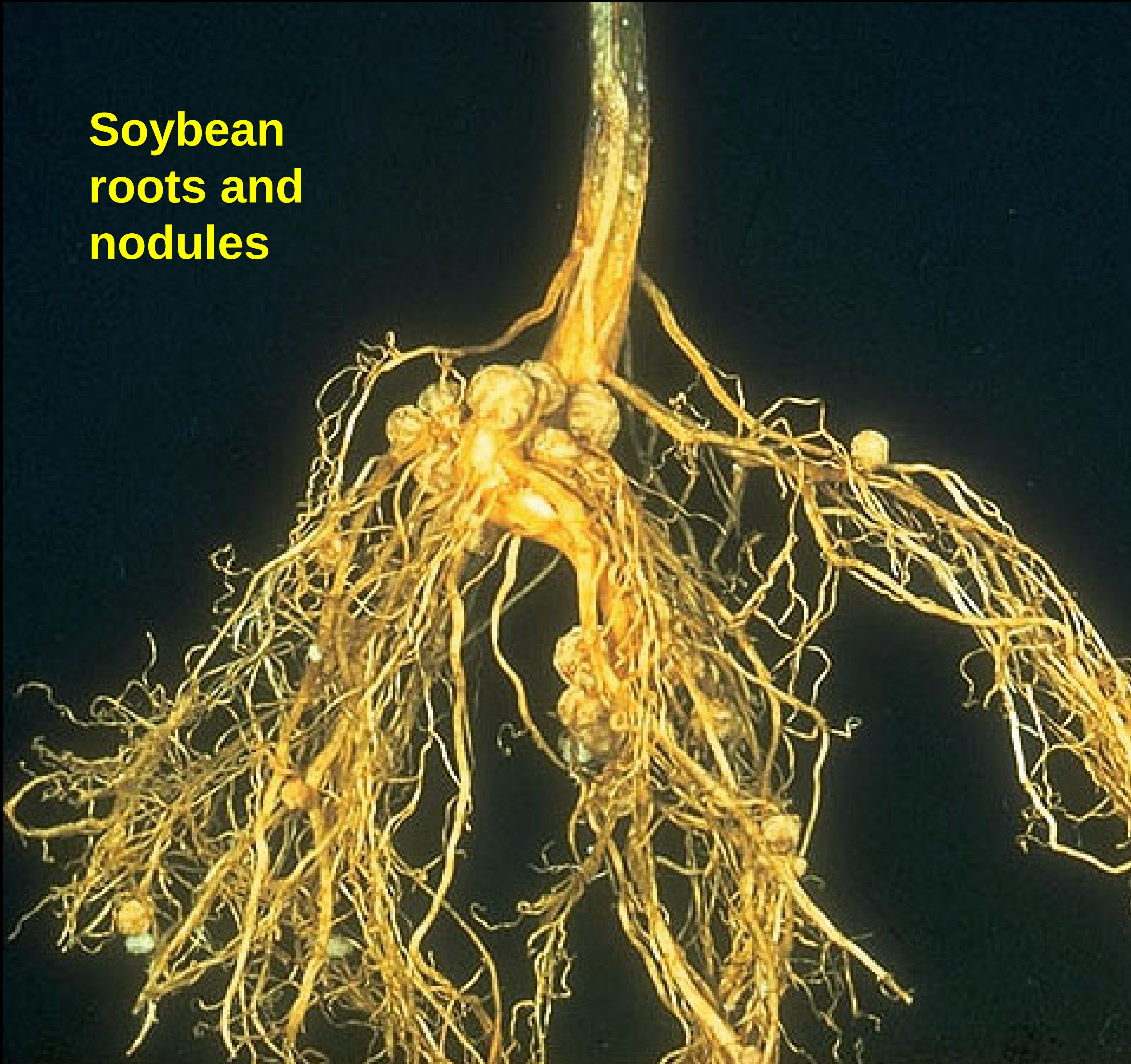
Facts about Biological N_2-fixation

- Reduction of N_2 to NH_3 requires a lot of energy to break triple bond.
- Nitrogenase is destroyed by free O_2.
- The reduction reaction is end-product inhibited -- an accumulation of ammonia will inhibit nitrogen fixation.
- Nitrogen fixing organisms have a relatively high requirement for Mo, Fe, P, and S, because these nutrients are either part of the nitrogenase molecule or are needed for its synthesis and use.

Legumes

- Bacteria: Rhizobium and Bradyrhizobium
- Legume plants (examples): peas, lentils, beans, alfalfa, lupine, peanuts, clover

Pea root system


Soybean
roots and
nodules

Leghemoglobin

Soybean and alfalfa nodules

Nitrogenase is destroyed by free O_2. N fixing organisms must protect the enzyme from exposure. One means of protecting the enzyme from free O_2 is the formation of leghemoglobin, which binds O_2 to protect nitrogenase while making oxygen available for respiration in other parts of nodule tissue.

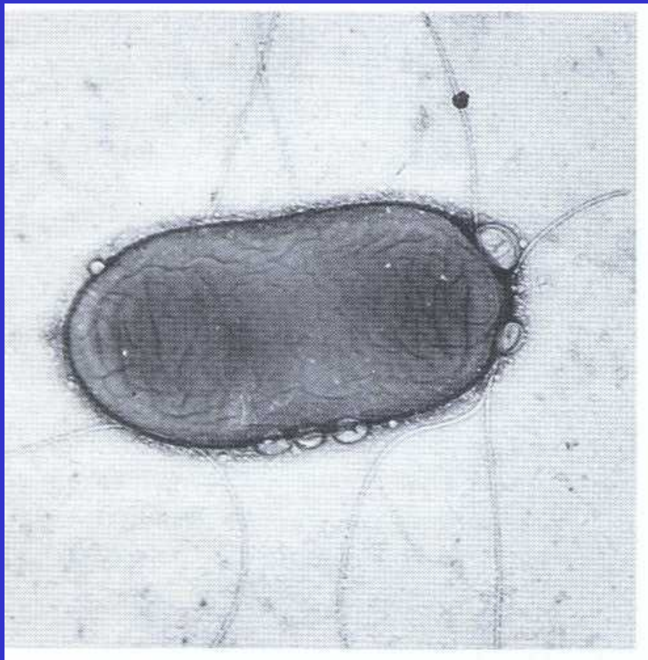
Nonlegumes

- Cyanobacteria
- Bacteria
- Actinomycetes (*Frankia*) associated with angiosperms

Red Alder (*Alnus rubra*) forms a symbiotic association with an actinomycete of the genus *Frankia*.

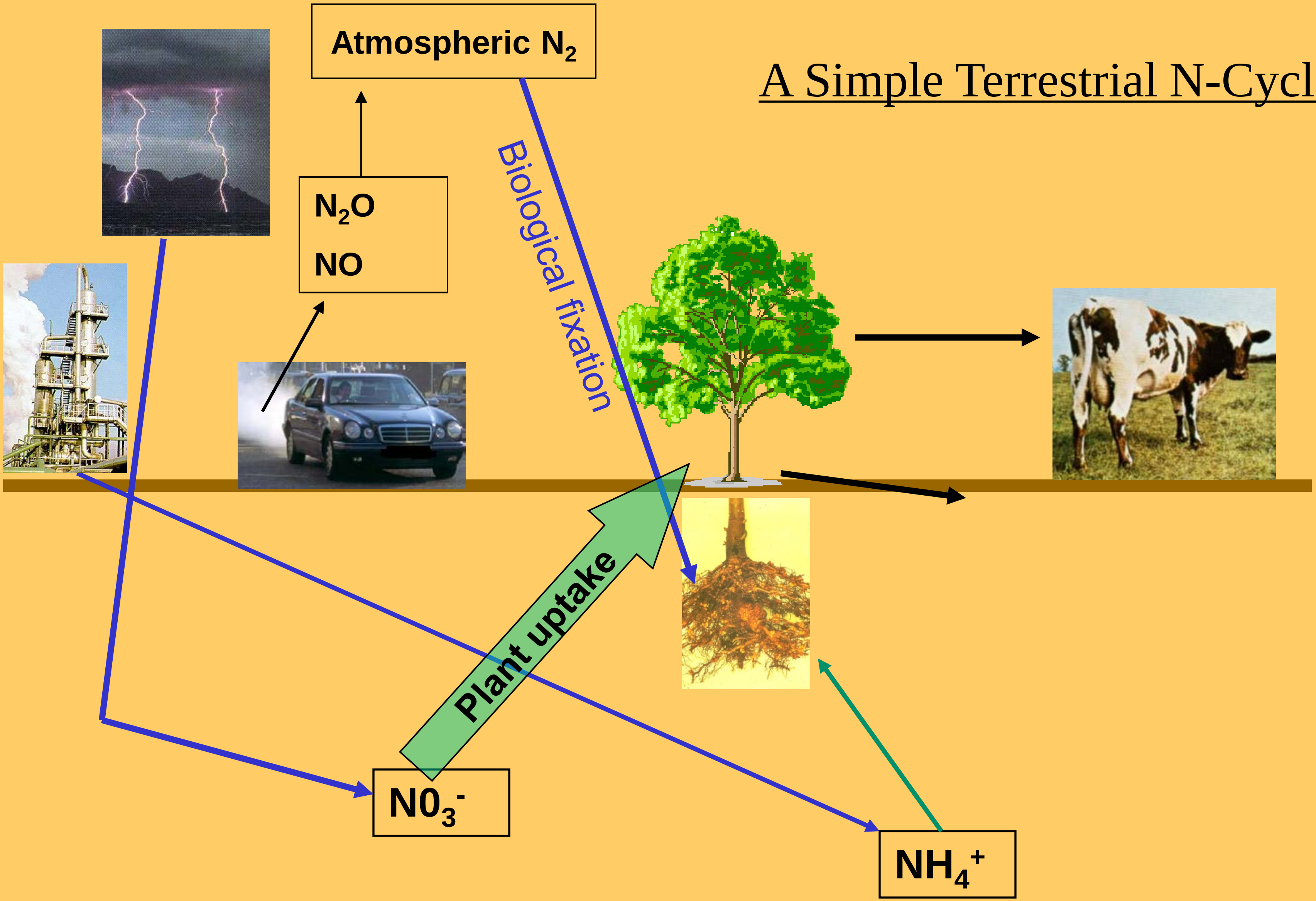
"Free-living" N-fixers: e.g., *Azotobacter*, *Azospirillum*, *Beijerinckia*, and cyanobacteria

A microbial mat at a hot spring in eastern Oregon. Some of the organisms in the mat are **cyanobacteria** that can fix nitrogen.



A transmission electron micrograph of *Acetobacter diazotrophicus*. These bacteria live and grow inside sugarcane plants and fix N_2 for both the plant and themselves.

A Simple Terrestrial N-Cycle



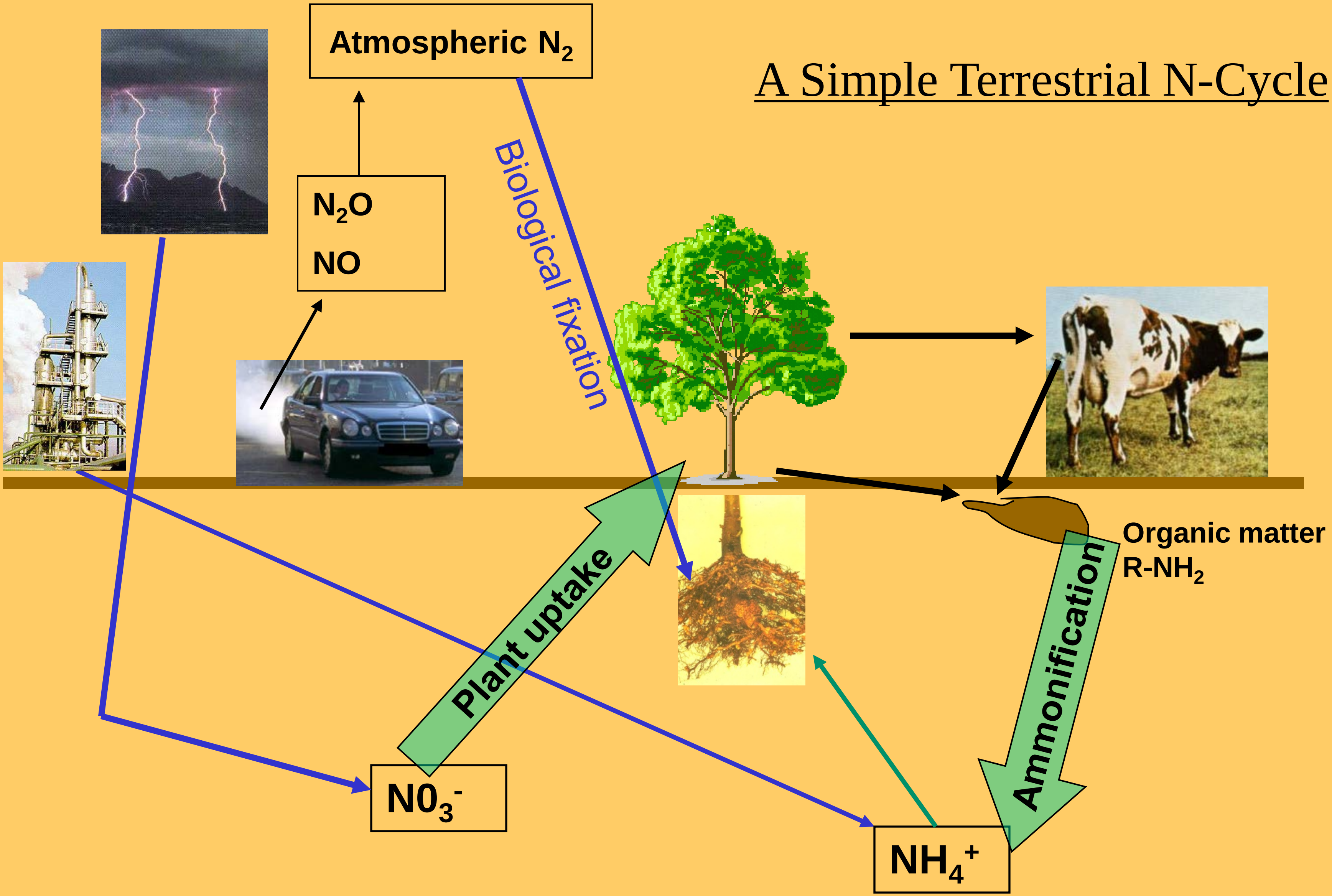
Assimilation

- Nitrogen assimilation is the process in which inorganic nitrogen (NH_4^+ or NO_3^-) is converted into organic nitrogen forms.
- A typical one:

  NO_3^- (NH_4^+) ----> $R\text{-}NH_2$

  (Amine group)

- This process happens only within biological systems (or living cells).
- N assimilation by soil microorganisms is also called "**N immobilization**."

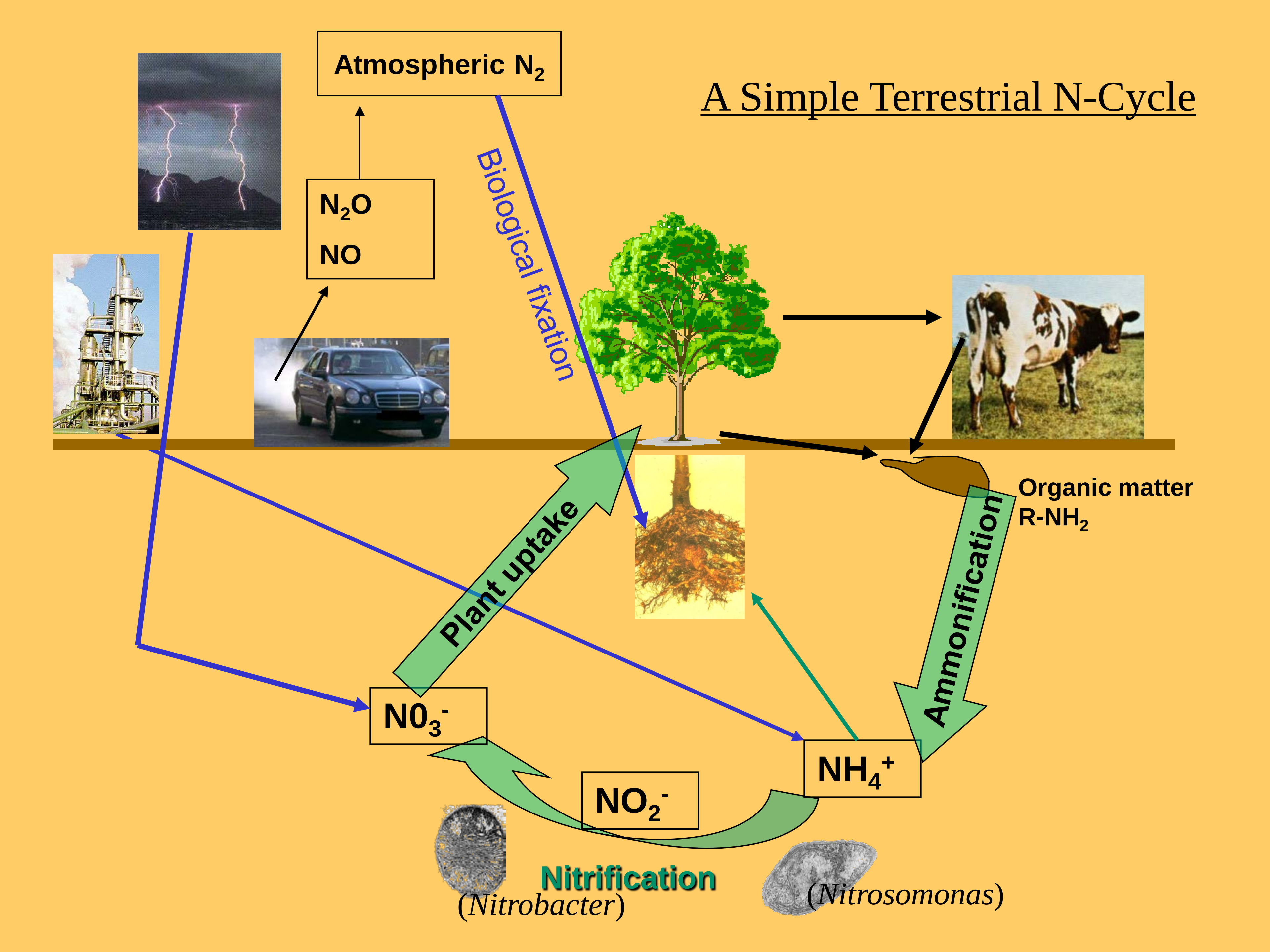

A Simple Terrestrial N-Cycle
Atmospheric N_2
N_2O
NO
Biological fixation
Plant uptake
Ammonification
Organic matter
R-NH_2
$N0_3^-$
NH_4^+

Ammonification

- Ammonification is the biological conversion from organic nitrogen to inorganic nitrogen--ammonium.

$$R\text{-}NH_2 \text{ ----> } NH_4^+ \ (NH_3)$$

- Many microorganisms are capable of ammonification. Most decomposers do it.


A Simple Terrestrial N-Cycle
Atmospheric N_2
N_2O
NO
Biological fixation
Organic matter
$R-NH_2$
Plant uptake
Ammonification
$N0_3^-$
NH_4^+
NO_2^-
Nitrification
(*Nitrobacter*)
(*Nitrosomonas*)

Nitrification

Nitrosomonas *Nitrobacter*

$NH_4^+ \rightarrow \{N_2O \rightarrow NO_x \rightarrow\} NO_2^- \rightarrow NO_3^-$

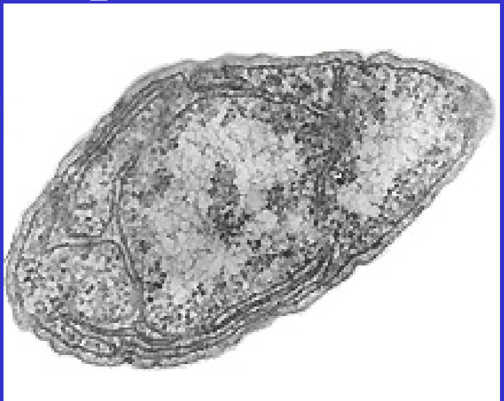
Both *Nitrosomonas* and *Nitrobacter* are chemolithotrophs, both can be active under low pH since nitrification lowers the pH of the environment. There are many kinds of ammonium-oxidizing bacteria and archaebacteria living in the soil.

Nitrification

Step 1:

Nitrosomonas

$\mathbf{NH_4^+} + 1.5\ 0_2$ -------------> $\mathbf{N0_2^-} + 2H^+ + H_2O + 275$ kJ energy



Nitrosomonas

Ammonium to Nitrite

Step 2:

Nitrobacter

$\mathbf{N0_2^-} + 1.5\ 0_2$ -------------> $\mathbf{NO_3^-} + 76$ kJ energy

Nitrite to Nitrate

Nitrobacter

Nitrification

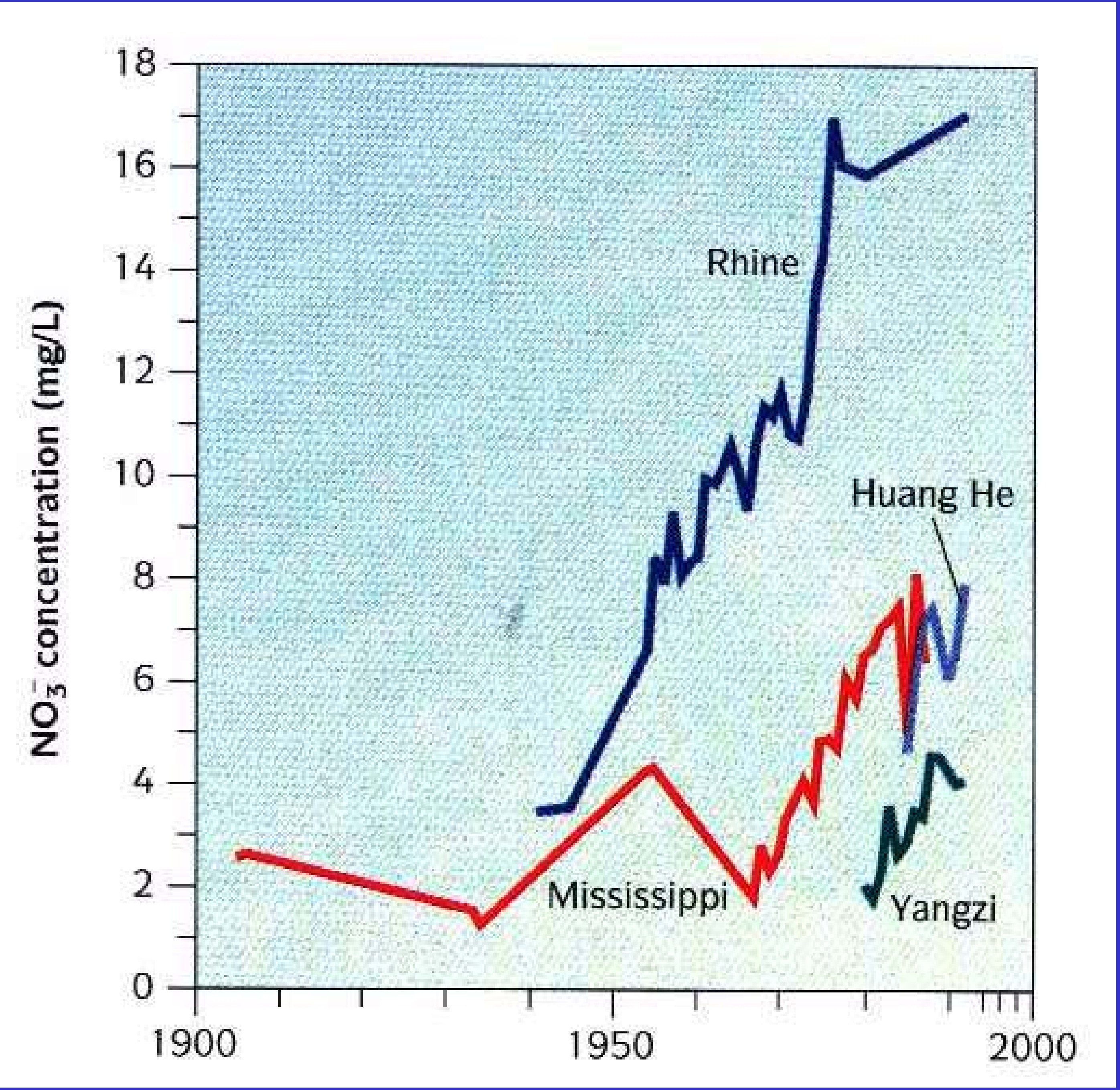
From NH_4^+ to NO_3^- is a very significant change, especially in soil. NH_4^+ is absorbed on soil surface (cation exchange), while NO_3^- is free moving.

Nitrate in ground water is a serious problem:

1. Nitrate + amino compounds ---nitrosamines (highly carcinogenic)

2. Nitrate can be reduced in gastrointestinal tract of infants into toxic nitrite, which combines with hemoglobin of the blood, causing respiratory distress or the so-called blue baby syndrome.

3. Nitrate reduction to nitrite may also occur in the rumen of live stock, causing animal disease.



18
16
14
12
10
8
6
4
2
0
NO_3^- concentration (mg/L)
1900
1950
2000
Rhine
Huang He
Mississippi
Yangzi

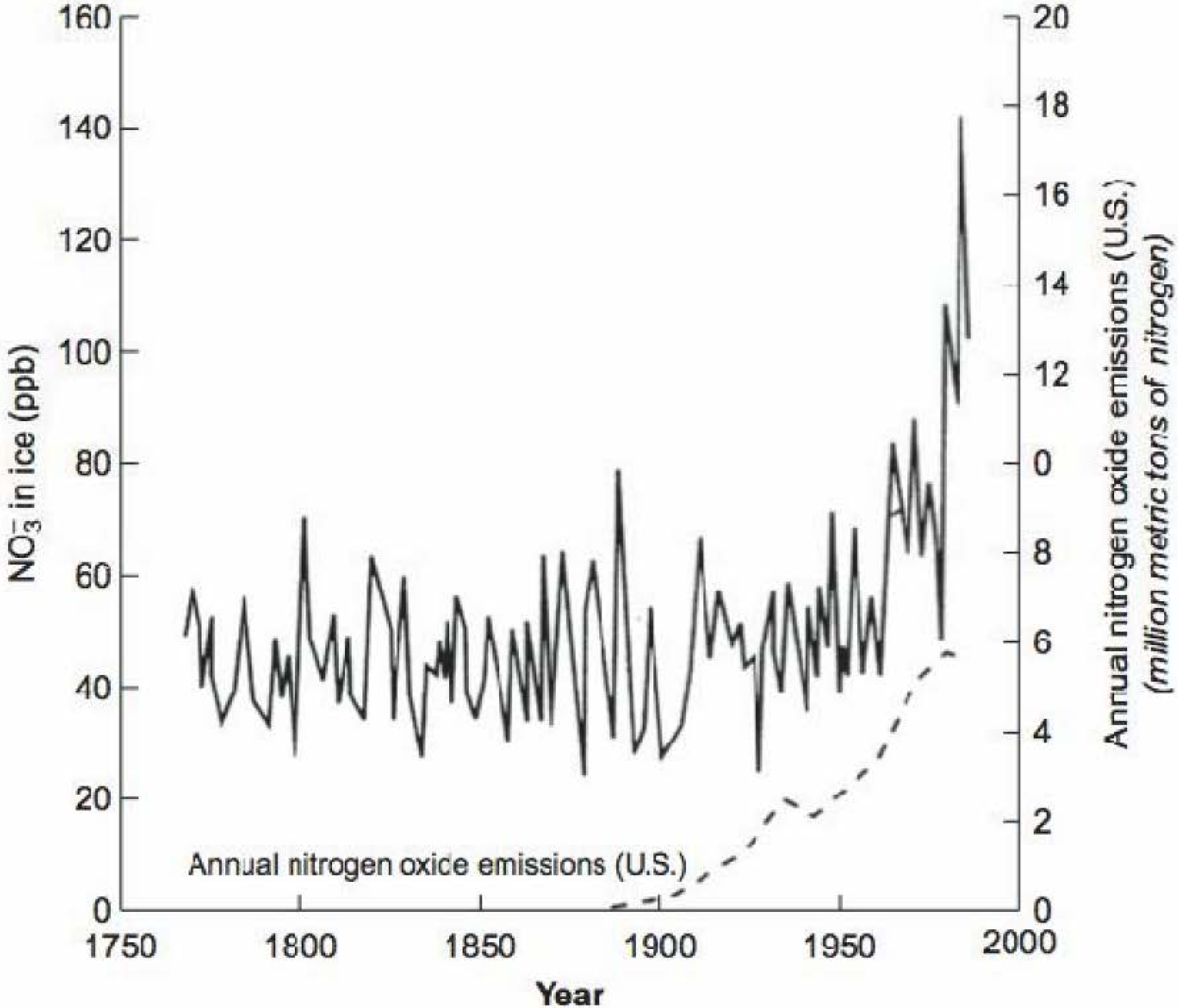
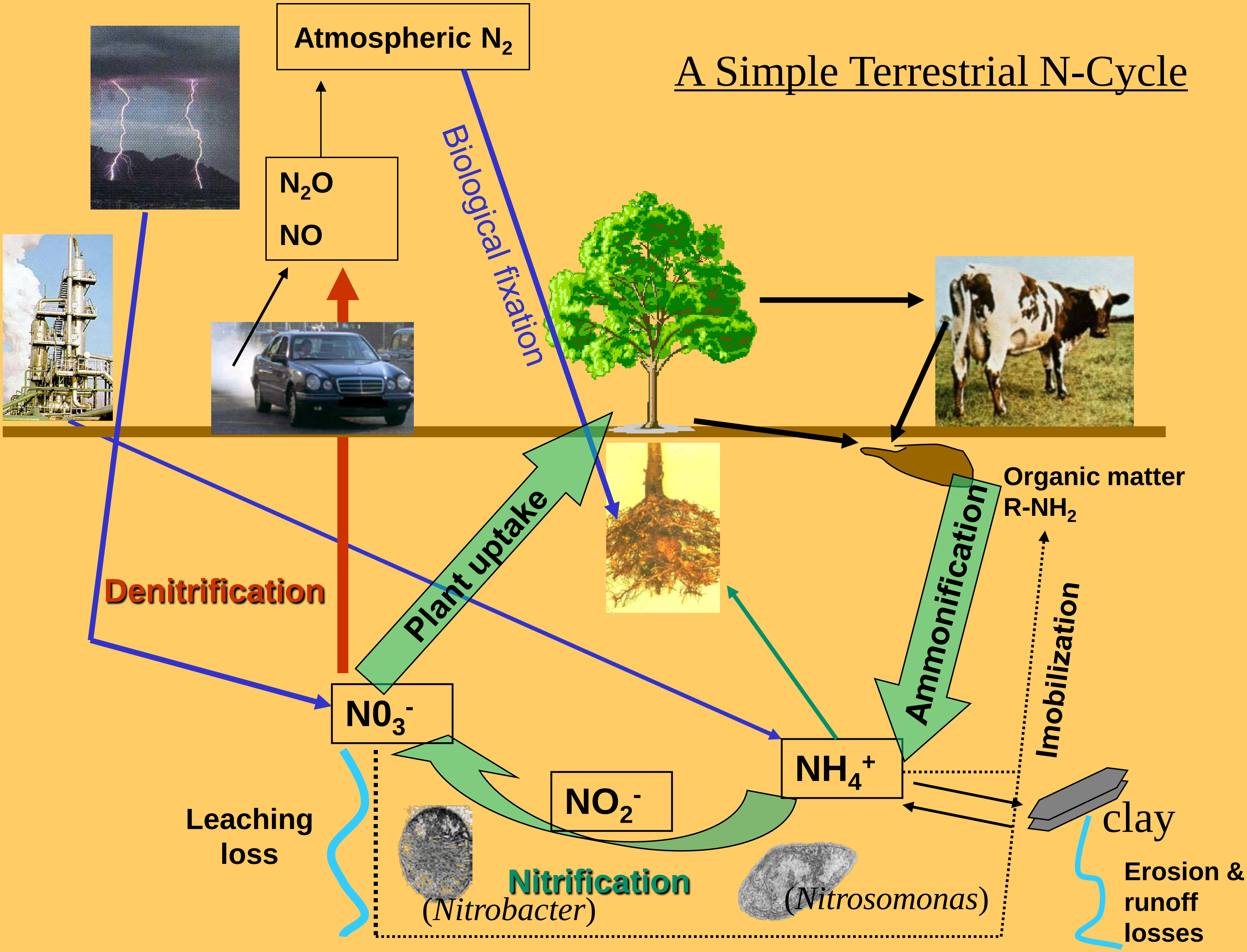


FIGURE 12.4 The 200-year record of nitrate in layers of the Greenland ice pack and the annual production of nitric oxides by fossil fuel combustion in the United States. *Source: Modified from Mayewski et al. (1990).*

TABLE 12.1 A Global Budget for Atmospheric NO_x (values are Tg N (10^{12} g N)/yr as NO)

Process	Annual Flux	References
Sources		
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 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_3 oxidation	1	Compare to Table 12.2 (Warneck 2000)
Aircraft	0.4	Prather et al. 1995
Transport from the stratosphere	0.6	For total NO_y (Prather et al. 1995)
Total sources	**53.6**	Compare 37 Tg N/yr from satellite measurements (Martin et al. 2003; 46 Tg N/yr (Galloway et al. 2004)
Sinks		
Deposition on land	24.8	Galloway et al. 2004
Deposition on the ocean surface	23.0	Duce et al. 2008, Dentener et al. 2006
Total sinks	**47.8**	

A Simple Terrestrial N-Cycle



Denitrification

- Denitrification is a series of processes starting from nitrate (NO_3^-) and ending with N_2.

  NO_3^- ---> NO_2^- ---> (NO_x) ---> N_2O ---> N_2
- Some microbial species capable of denitrification: (*Paracoccus denitrificans*, *Thiobacillus denitrificans*, *Pseudomonans spp*.), Bacillus licheniformis, and others.

Denitrification

- 1. Denitrifying microbes use NO_3^- or NO_2^- as electron acceptors.
- 2. Denitrification only occurs under anaerobic condition.
- 3. Denitrification needs reducing substrates as energy source.
- 4. The enzyme system is totally inhibited by free oxygen, but not ammonia.
- 5. acetylene can block the N_2O (nitrous oxide) reductase (Balderson et al.1976), so now this is used for measuring denitrification rate, since N_2 is very hard to measure due to the high background in the air. When adding 0.01 atm acetylene gas to the incubation atmosphere, the final product of denitrification is N_2O.

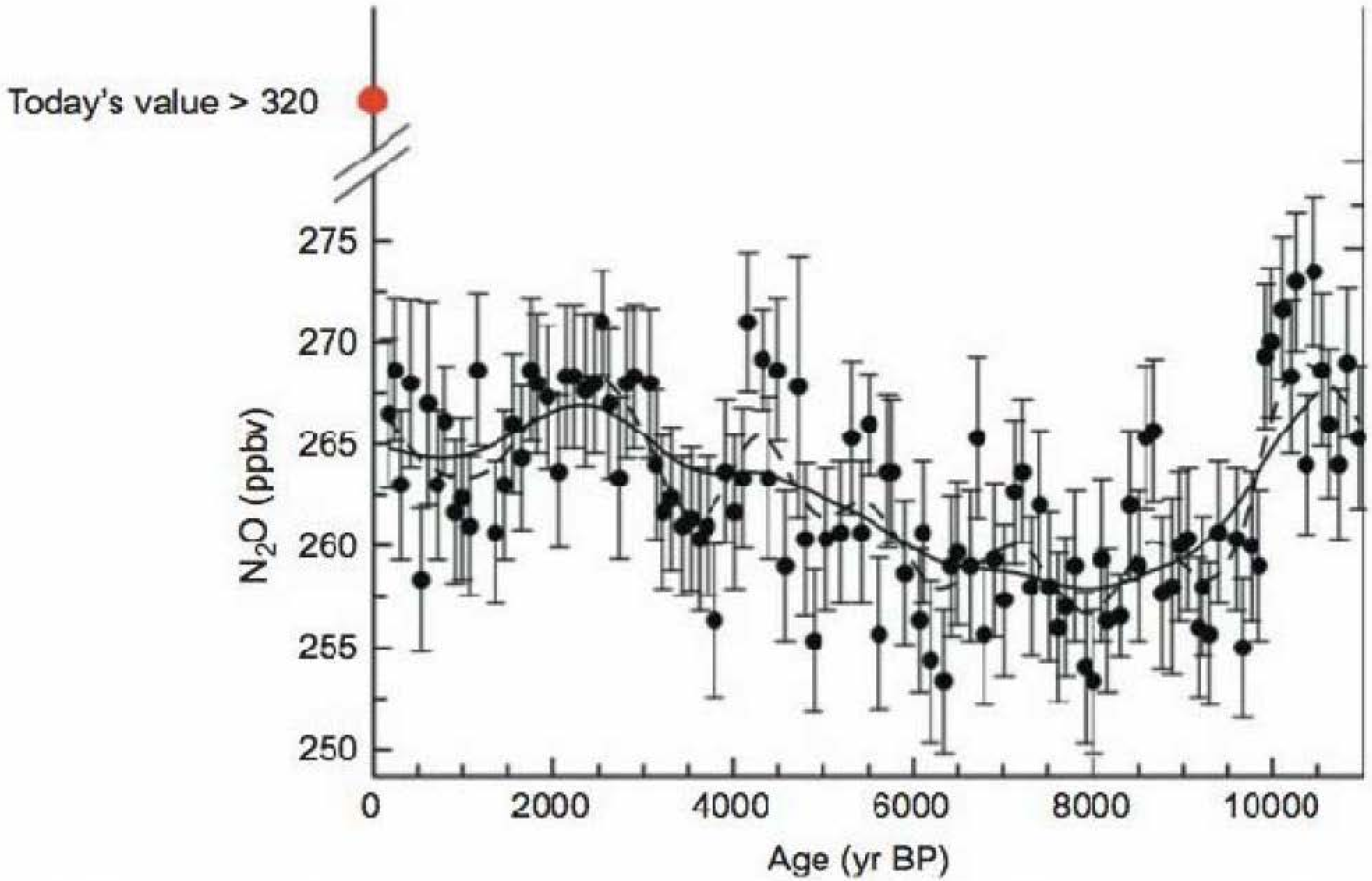


FIGURE 12.6 Nitrous oxide measurements from ice-core samples in Antarctica. *Source: From Flückiger et al. (2002).*

TABLE 12.5 A Global Budget for Nitrous Oxide (N_2O) in the Atmosphere (all values are Tg N/yr (10^{12} g/yr) nitrogen, as N_2O)

Natural sources	Annual flux	References
Soils	3.4 ± 1.3	Zhuang et al. 2012[a]
Ocean surface	6.2 ± 3.2	Bianchi et al. 2012
Total natural	9.6	
Anthropogenic sources		
Agricultural soils	2.8	Bouwman et al. 2002b[b]
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	
Total sources	**17.1**	
Sinks		
Stratospheric destruction	12.3	Prather et al. 1995
Uptake by soils	<0.1	Syakila and Kroeze 2011
Atmospheric increase	4.0	IPCC 2007
Total identified sinks	**16.4**	

[a] *Alternative estimates for the flux of N_2O from natural soils includes 6.1 Tg N/yr (Potter et al. 1996) and 6.6 Tg N/yr (Bouwman et al. 1995).*

[b] *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_2O flux from agricultural activities include emissions of N_2O from downstream ecosystems and groundwaters impacted by agricultural inputs in these regions.*

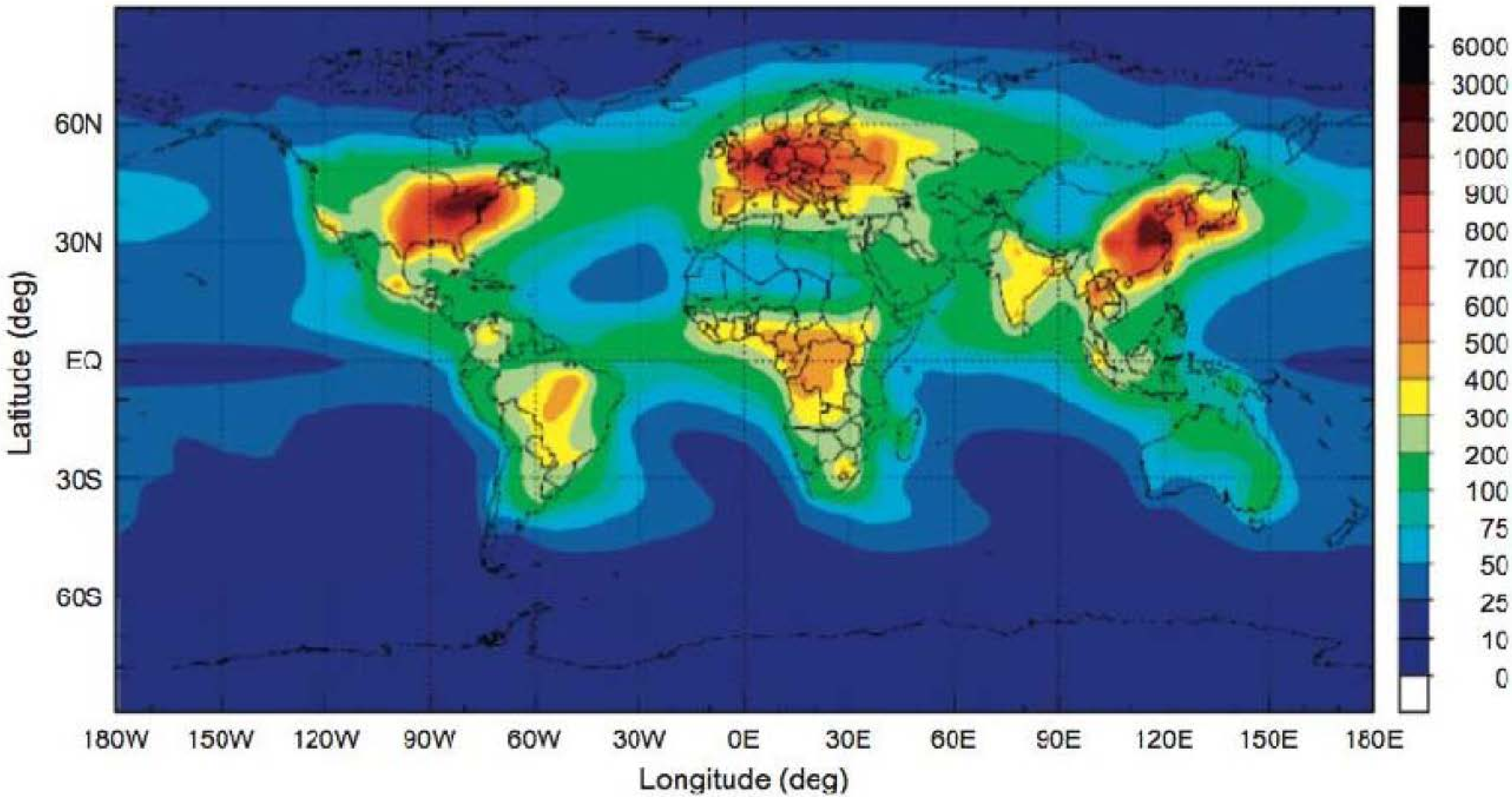
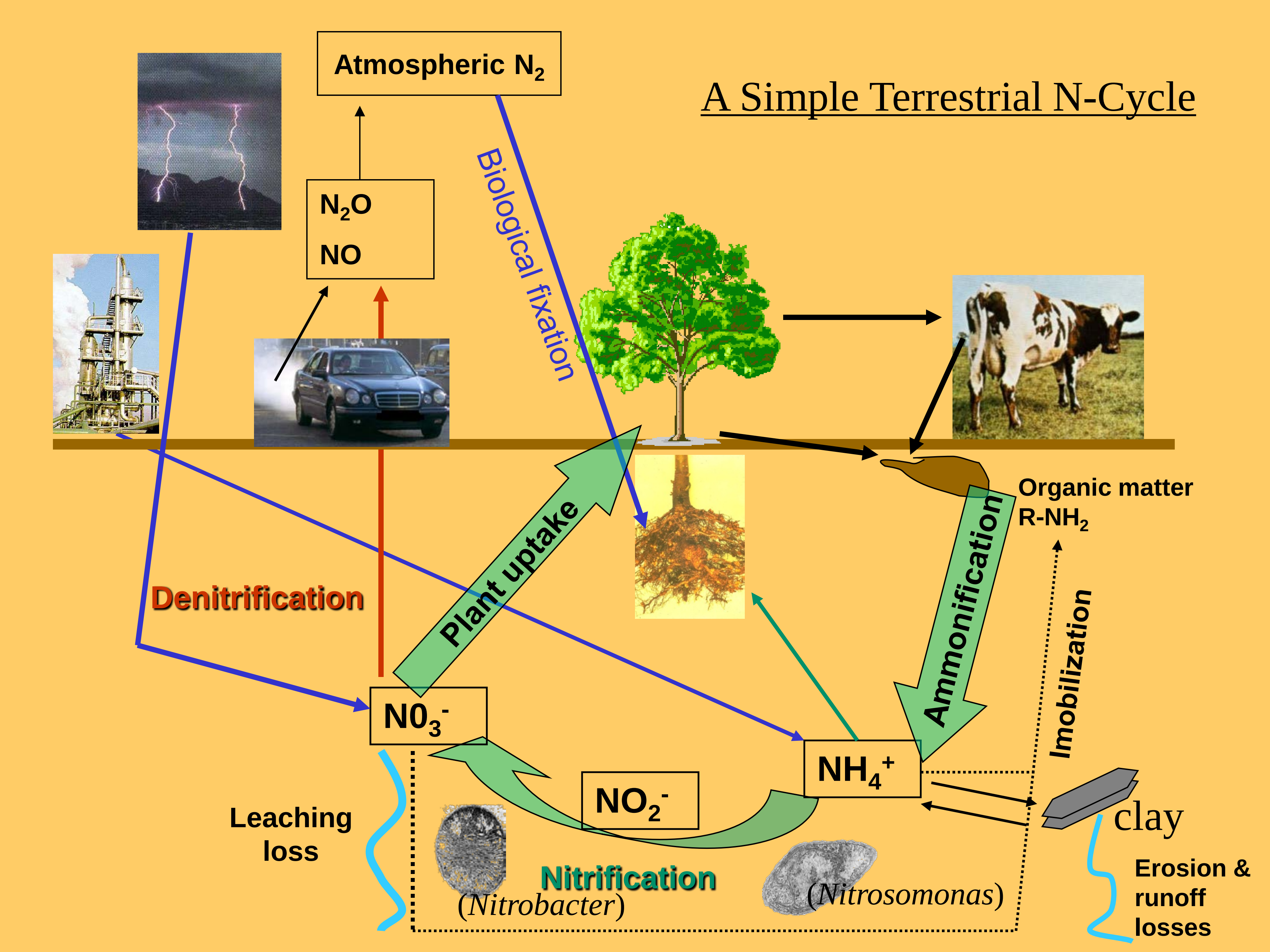
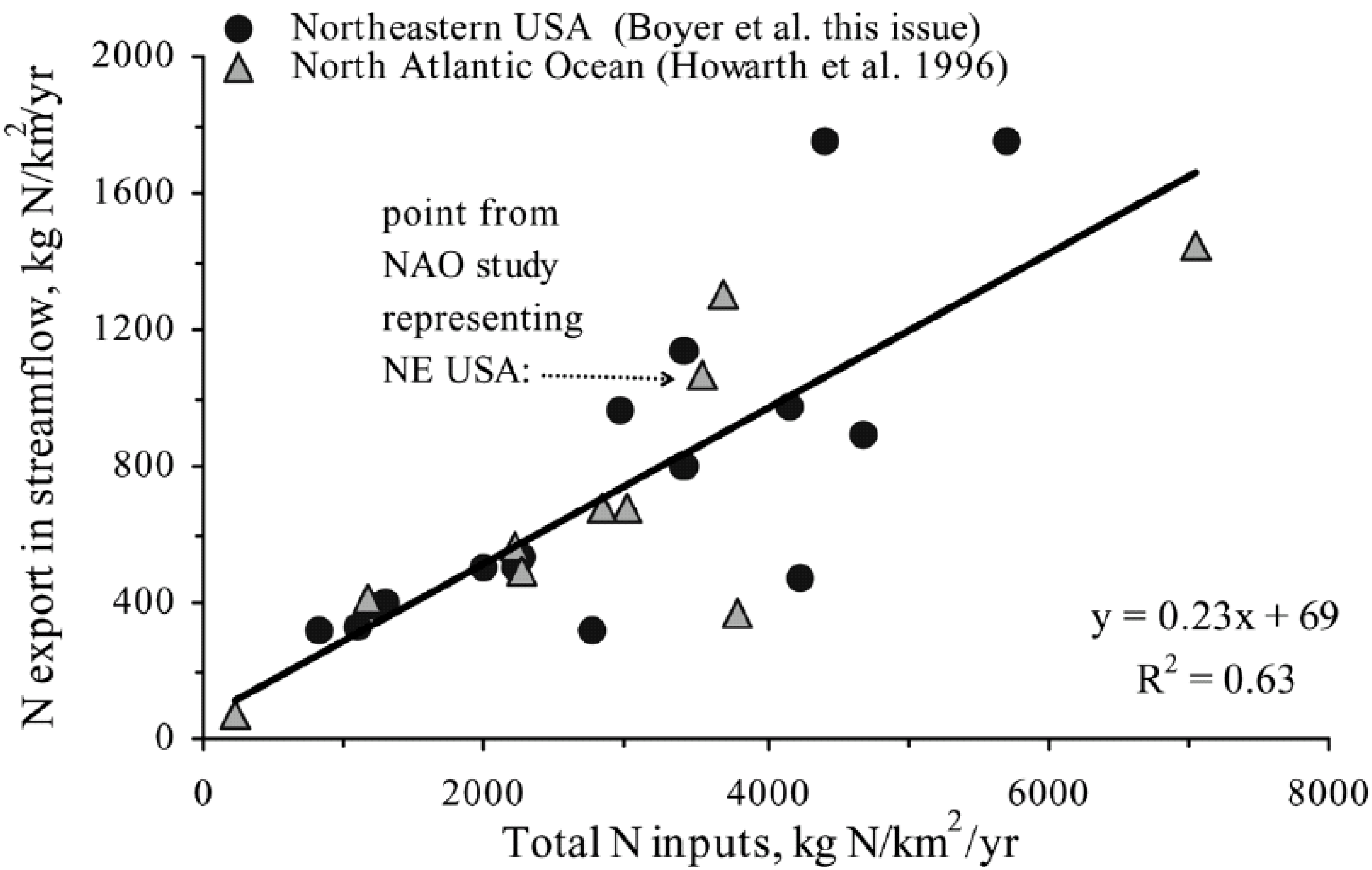


FIGURE 12.3 Deposition of NO_y on Earth's surface. All values are mg N m^{-2} yr^{-1}. *Source: From Dentener et al. (2006).*


A Simple Terrestrial N-Cycle
Atmospheric N_2
N_2O
NO
Biological fixation
Denitrification
Plant uptake
Organic matter
$R\text{-}NH_2$
Ammonification
Imobilization
NO_3^-
NH_4^+
NO_2^-
clay
Leaching loss
Nitrification
(Nitrobacter)
(Nitrosomonas)
Erosion & runoff losses

Nitrogen Cycling in Watersheds



From: Van Breemen et al. 2002. Biogeochemistry 57/58:267-293

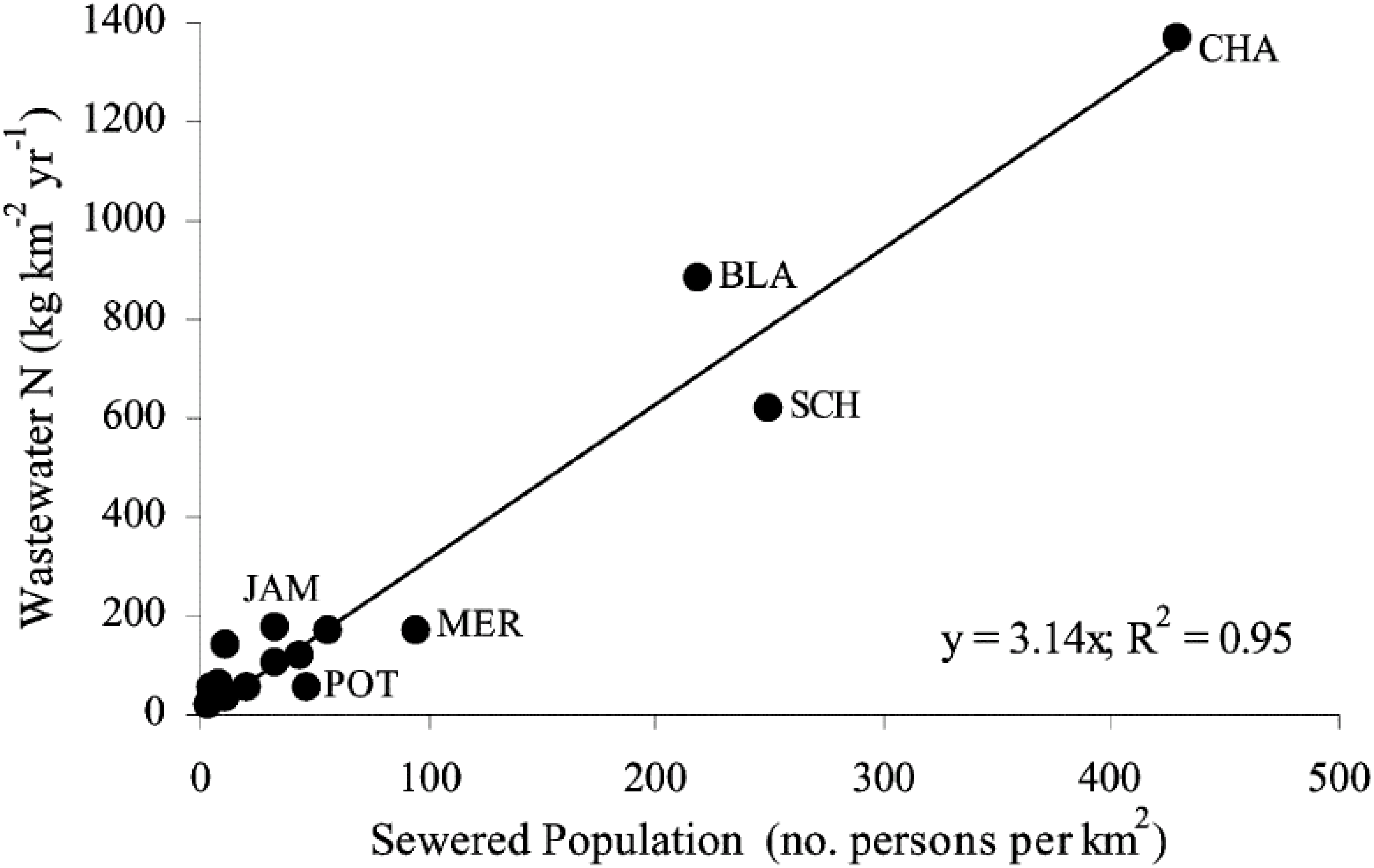


Figure 4. Relationship between sewered population and nitrogen fluxes due to sewage wastewater. The regression line indicates a per capita load in wastewater of 3.1 kg N yr^{-1} per person.

From: Van Breemen et al. 2002. Biogeochemistry 57/58:267-293

Hypoxia and Eutrophication

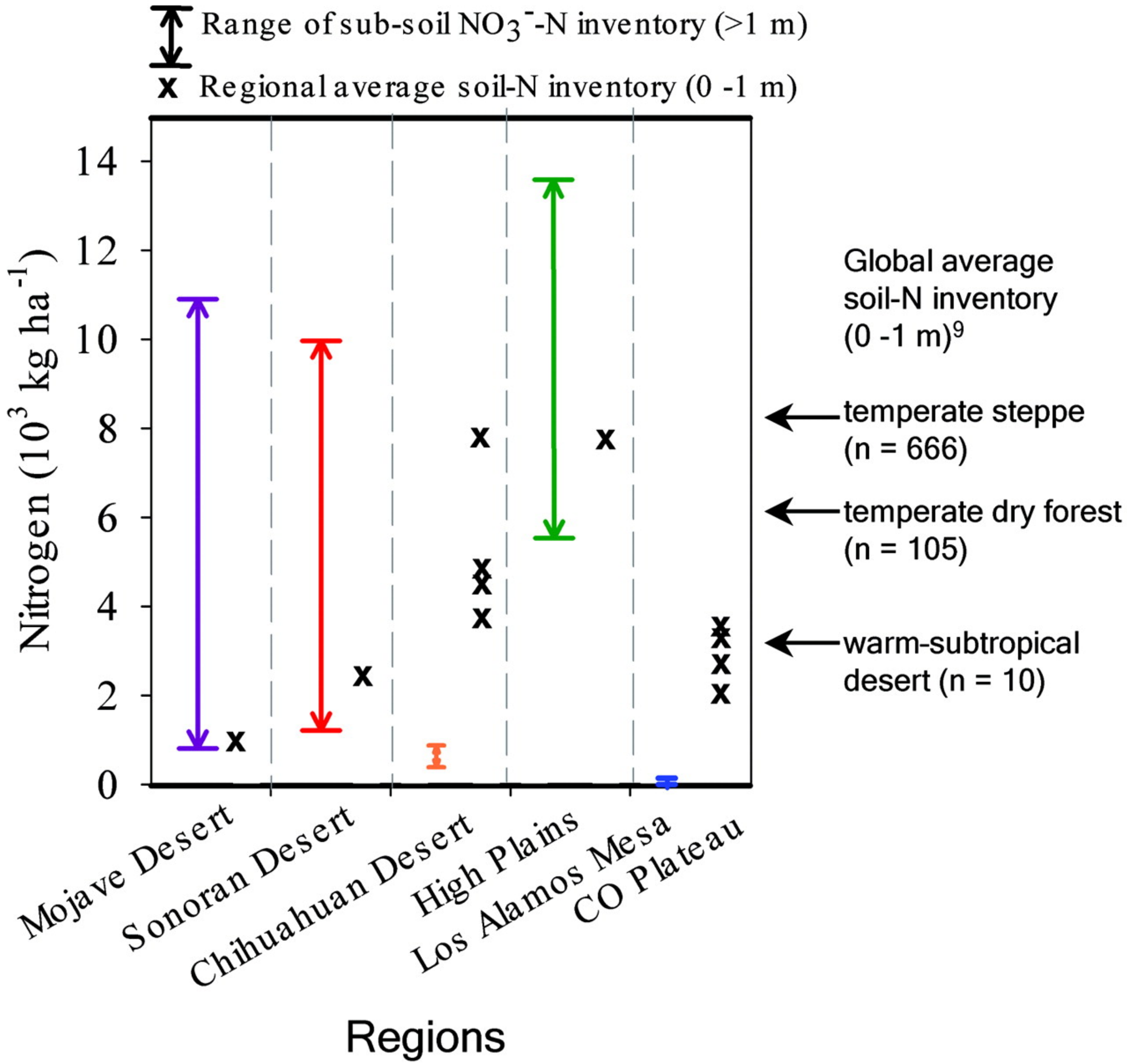
Increased nutrient input to aquatic ecosystems may cause eutrophication. **Eutrophication** leads to excessive growth of algae and cyanobacteria. Later after death of these excessive biomass, much increased decomposition by bacteria depletes oxygen in the water, which causes fish kills and other detrimental effects –the Dead Zone.

Summary

1. Comprehend the global N budget (pools and fluxes)
2. Articulate the interconversions of several different forms of nitrogen.
3. Clearly understand all the concepts (processes) about nitrogen transformation.
4. Clearly distinguish different types of N_2-fixation, both biotic and abiotic.
5. Understand the inputs and the outputs of N at the watershed level.
6. Capable of making the connection between the human-enhanced N-cycle and the issue of eutrophication.

Abstract of Walvoord et al. 2003 (Science 302:1021)

A large reservoir of bioavailable nitrogen (**up to ~104 kilograms of nitrogen per hectare, as nitrate**) has been previously overlooked in studies of global nitrogen distribution. The reservoir has been accumulating in subsoil zones of arid regions throughout the Holocene. Consideration of the subsoil reservoir raises estimates of vadose-zone nitrogen inventories by 14 to 71% for warm deserts and arid shrub lands worldwide and by 3 to 16% globally. Subsoil nitrate accumulation indicates long-term leaching from desert soils, impelling further evaluation of nutrient dynamics in xeric ecosystems. Evidence that subsoil accumulations are readily mobilized raises concern about groundwater contamination after land-use or climate change.



Range of sub-soil NO3⁻-N inventory (>1 m)
x Regional average soil-N inventory (0 -1 m)
Nitrogen (10^3 kg ha^-1)
14
12
10
8
6
4
2
0
Global average soil-N inventory (0 -1 m)9
temperate steppe (n = 666)
temperate dry forest (n = 105)
warm-subtropical desert (n = 10)
Mojave Desert
Sonoran Desert
Chihuahuan Desert
High Plains
Los Alamos Mesa
CO Plateau
Regions

TABLE 12.2 A Global Budget for Atmospheric Ammonia

Process	Annual flux	References
Sources		
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
Total sources	**52.6**	Compare 58.2 Tg N/yr; Galloway et al. 2004
Sinks		
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
Total sinks	**63.7**	

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 NH_3 or NH_4^+ (in deposition).