Soil Nitrogen and Sulfur Dynamics

Ecological Agriculture TESC 2-7-06

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Biological Importance of Nitrogen and Sulfur

- Essential elements in amino acids, building blocks of all proteins
- Nitrogen – nucleic acids, chlorophyll, carbohydrate utilization, makes up 2-4% plant dry matter
- Sulfur – B vitamins, aromatic oils, S-S disulfide bonds affect protein tertiary and quanternary folding structure, makes up 0.15 – 0.45% plant dry matter

Why consider Nitrogen and Sulfur together?

Why consider Nitrogen and Sulfur together?

- Cycle through soil-plant-animal-atmosphere system
- In the surface horizons of most soils, both N and S are largely found in organic forms
- Can enter and leave the soil in gaseous forms
- Anionic forms (nitrate and sulfate) are subject to leaching from the soil
- Transformation and availability are largely functions of soil microorganisms
  - Mineralization from organic compounds and immobilization into organic compounds (microbial biomass)
  - Oxidation – reduction reactions

Why consider Nitrogen and Sulfur together?

- Air pollution issues
- Sulfur – sulfur dioxide forms sulfuric acid, precipitates as acid rain, pH = 4
- Nitrogen
  - N oxide gases form nitric acid – acid rain
  - N oxide gases react with VOP's = ozone smog
  - NO is greenhouse gas = 300X carbon dioxide
  - N_2O in stratosphere depletes ozone layer

Nitrogen Cycle

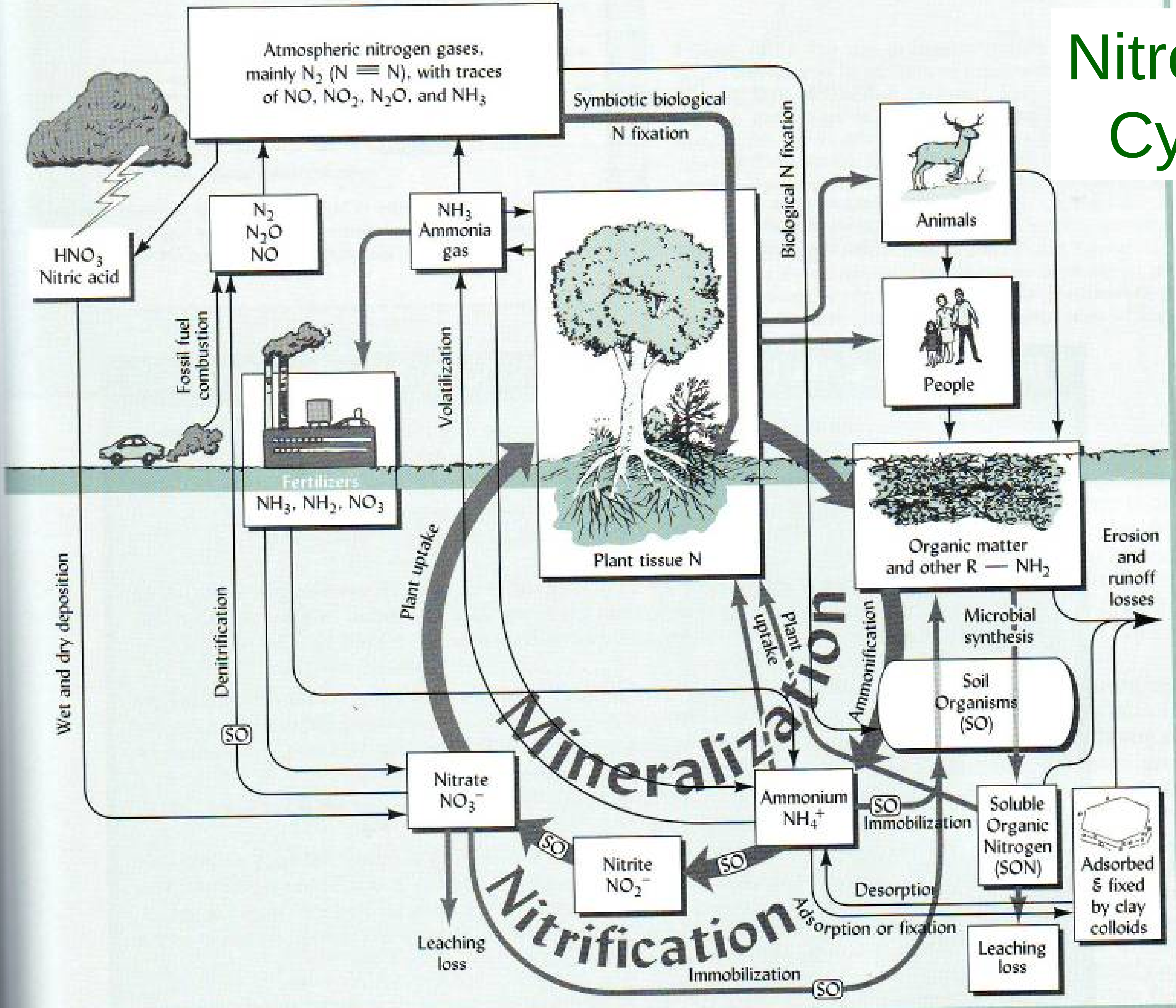


FIGURE 13.2 The nitrogen cycle, emphasizing the primary cycle (heavy, dark arrows) in which organic nitrogen is mineralized, plants take up the mineral nitrogen, and eventually organic nitrogen is returned to the soil as plant residues. Note also the pathways by which

Sulfur Cycle

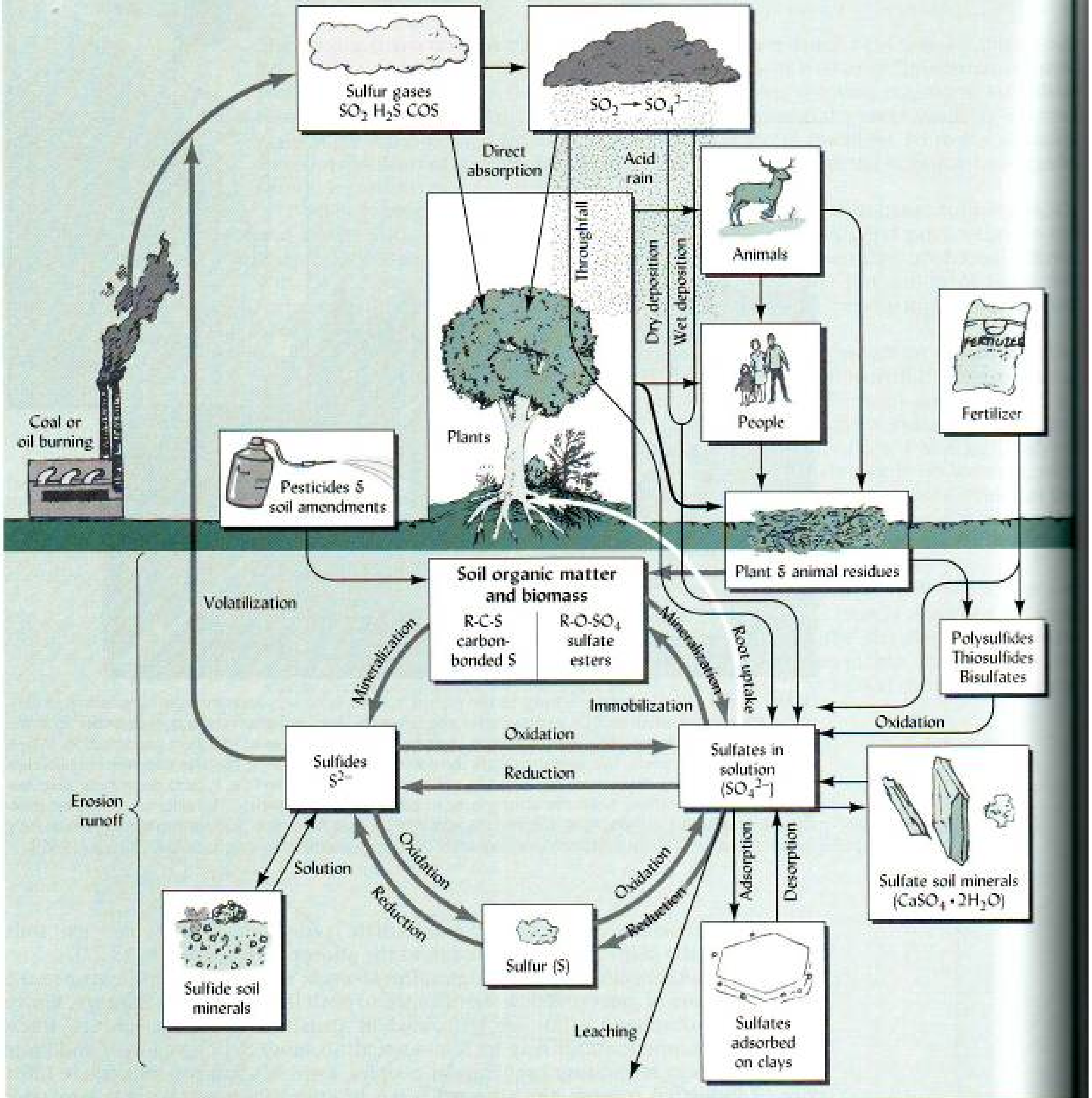


FIGURE 13.29 The sulfur cycle, showing some of the transformations that occur as this element is cycled through the soil–plant–animal–atmosphere system. In the surface horizons of all but a few types of arid-region soils, the great bulk of sulfur is in organic forms. However, in deeper horizons or in excavated soil materials, various inorganic forms may dominate. The oxidation and reduction reactions that transform sulfur from one form to another are mainly mediated by soil microorganisms.

Nitrogen budgeting on a state-wide level, 1000 Mg

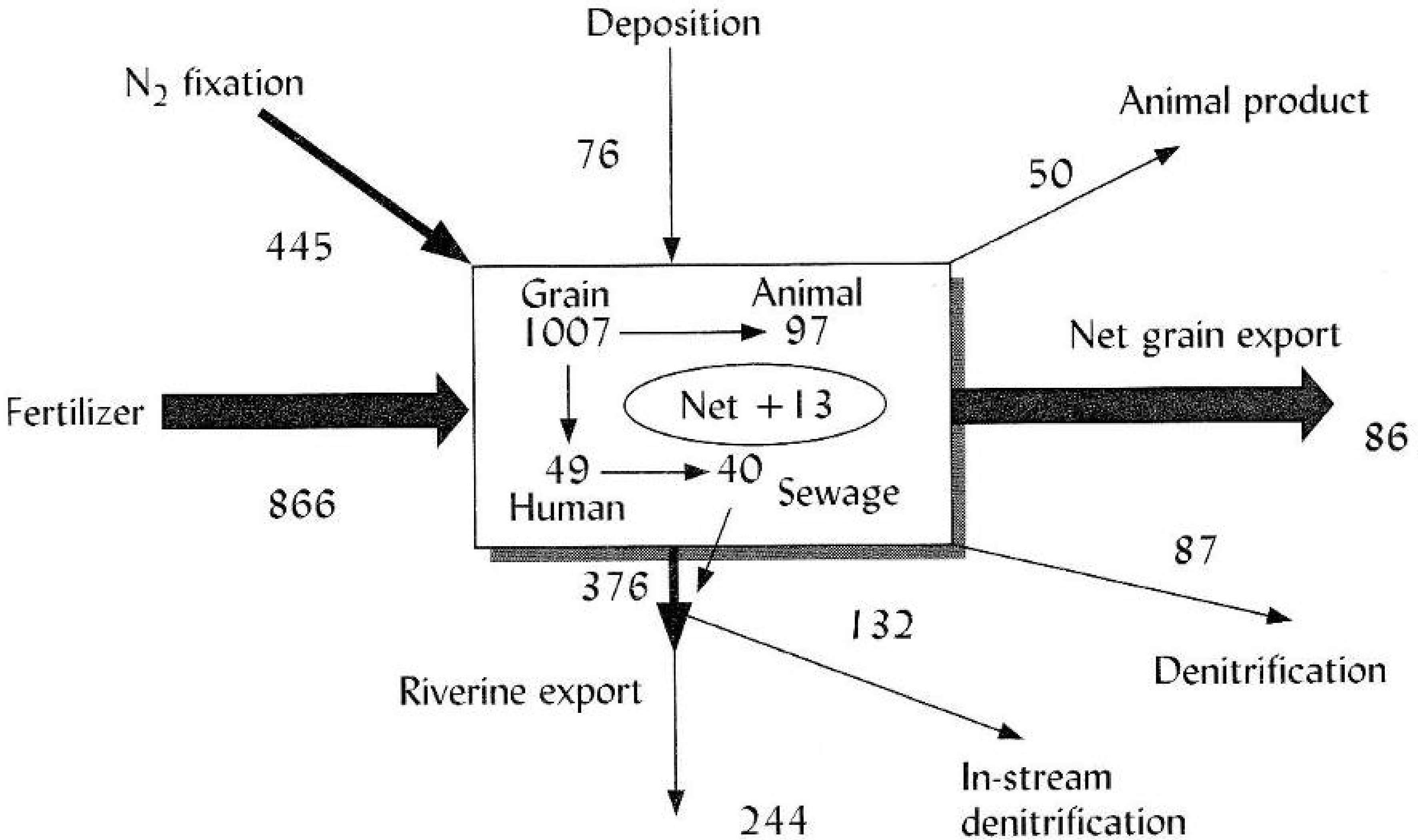


FIGURE 13.24 Diagram showing the annual inputs and outputs of nitrogen for the state of Illinois, averaged for 18 years (1979–96 for terrestrial fluxes

Pools/Sources of Nitrogen

- Atmosphere 78% N_2, traces of N oxide gases and NH_3
- Soils range from 0.02 – 0.5% N
  - Average soil N = 0.15%
  - Hectare contains 7000 kg N
  - 95-99% of soil N is in organic compounds
- Fertilizers
  - Based on Urea, Ammonia, and Nitrate
  - Haber-Bosch process for converting N_2 to NH_3
    - High temperature and pressure reaction uses natural gas

Nitrogen deficiency
verses
excessive N fertilizer

PLATE 50 Nitrogen-deficient corn on Udolls in central Illinois. Ponded water after heavy rains resulted in nitrogen loss by denitrification and leaching.

PLATE 44 Leaves from near the bottom of nitrogen-deficient (yellow tip and midrib), potassium-deficient (necrotic leaf edges), and normal corn plants. All the leaves came from the same field.

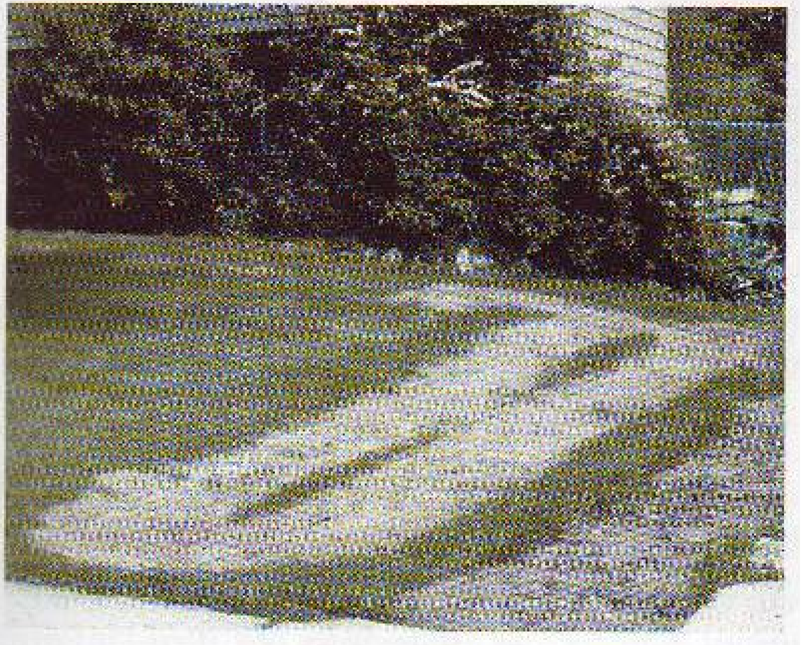
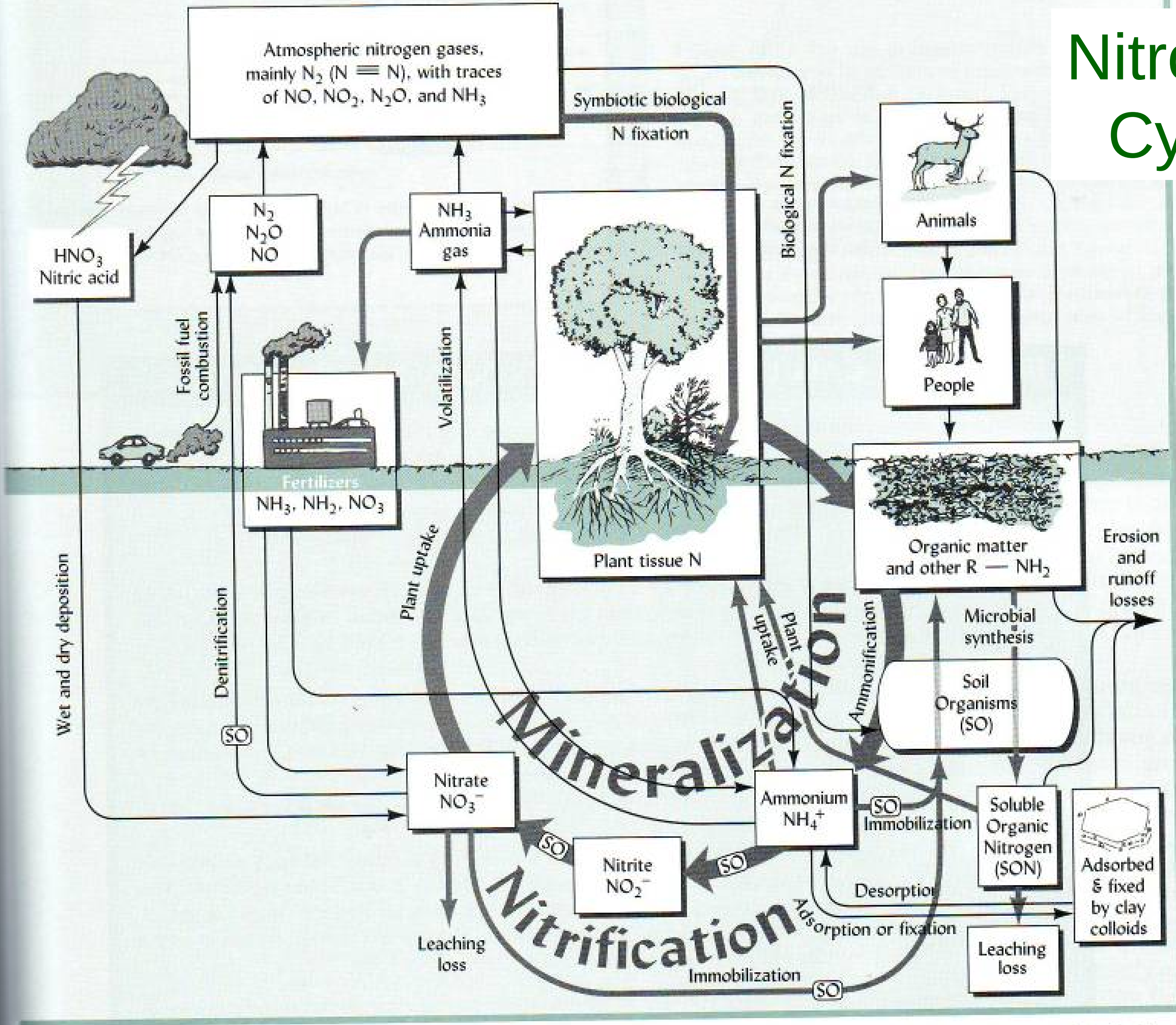


PLATE 62 It's a good thing this homeowner readjusted his spreader before he finished fertilizing the lawn. Salt "burn" from too much nitrogen fertilizer.

Nitrogen Cycle



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Nitrogen Mineralization

- Microbial decomposition of organic matter releases amine compounds
- *Ammonification*
- Amines are hydrolyzed to ammonium
- $R\text{-}NH_2 + 2H_2O \rightarrow OH^- + R\text{-}OH + NH_4^+$
- Reverse reaction is microbes immobilizing ammonium to build biomass

Ammonium and Ammonia
NH_4^+ and NH_3

$$NH_4^+ + OH^- \rightleftharpoons H_2O + NH_3\uparrow$$

Dissolved ions — Gas

- Environmental conditions favoring loss of NH_3
  - pH > 7
  - High temperatures
  - Drying soil
- Ammonium fixation by 2:1-type clay minerals

Nitrification by aerobic bacteria

Requires oxygen, carbon source, neutral pH and available water

Produces protons = acidification of the soil

anion molecule leaches with mass flow of water

Step 1

$$NH_4^+ + 1\,{}^1/{}_2O_2 \xrightarrow[\text{bacteria}]{\textit{Nitrosomonas}} NO_2^- + 2H^+ + H_2O + 275 \text{ kJ energy}$$

Ammonium — Nitrite

Step 2

$$NO_2^- + {}^1/{}_2O_2 \xrightarrow[\text{bacteria}]{\textit{Nitrobacter}} NO_3^- + 76 \text{ kJ energy}$$

Nitrite — Nitrite

Nitrate, page 552

Urea and ammonium fertilizers cause soil acidification

Soil acidification from long-term use of ammonium containing fertilizers

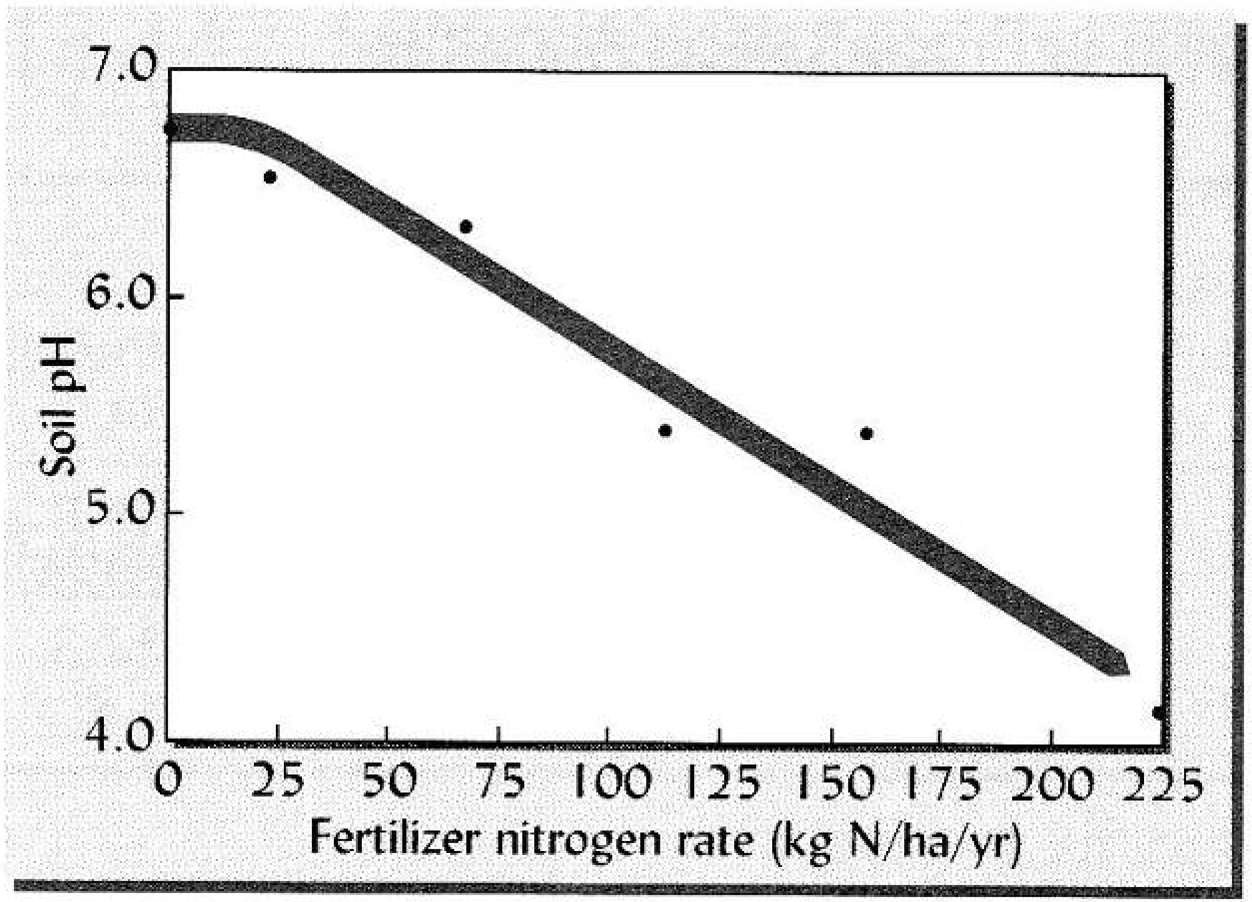

FIGURE 13.23
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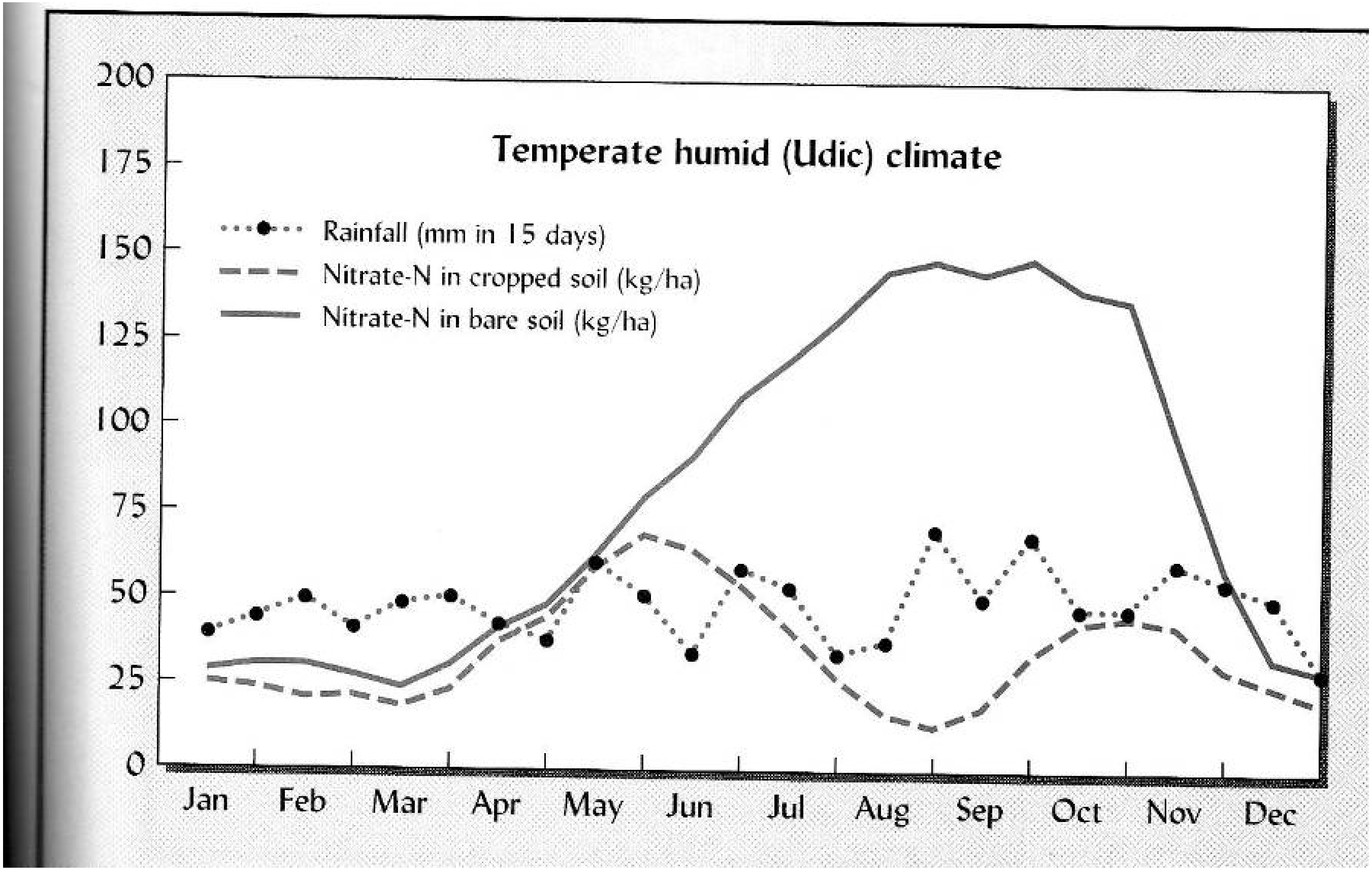
Influence of soil water and seasonal soil temperatures on nitrification rates and accumulation of soil nitrate



Water saturation of soil pores stops aerobic mineralization and enhances anaerobic denitrification

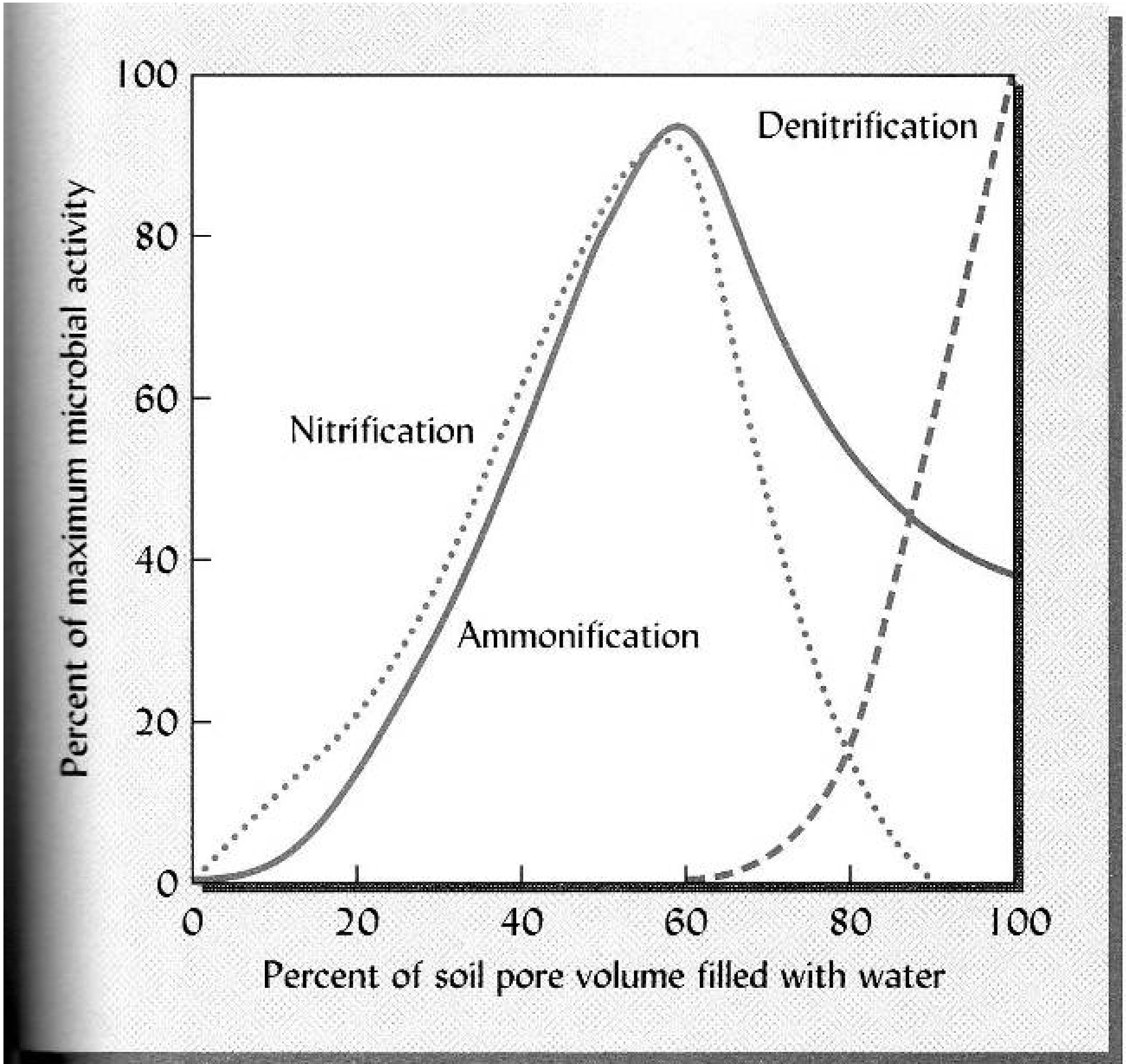


FIGURE 13.5
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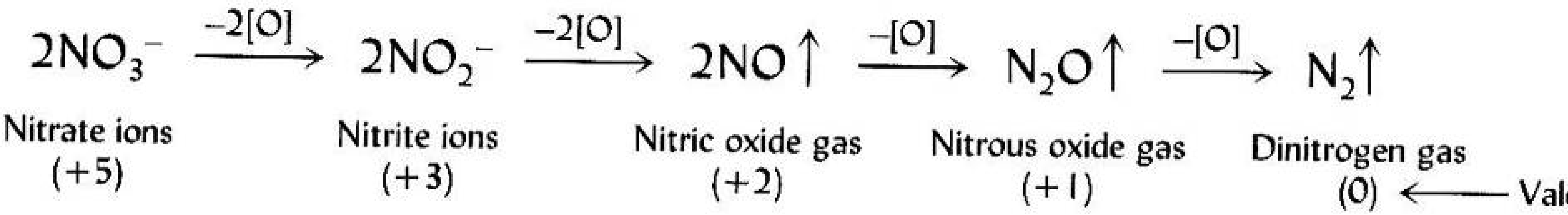
Denitrification by heterotrophic, facultative anaerobic or anaerobic bacteria require carbon source and reduced oxygen



Valence state of nitrogen

Denitrification Process
Relative production of Nitrogenous gases

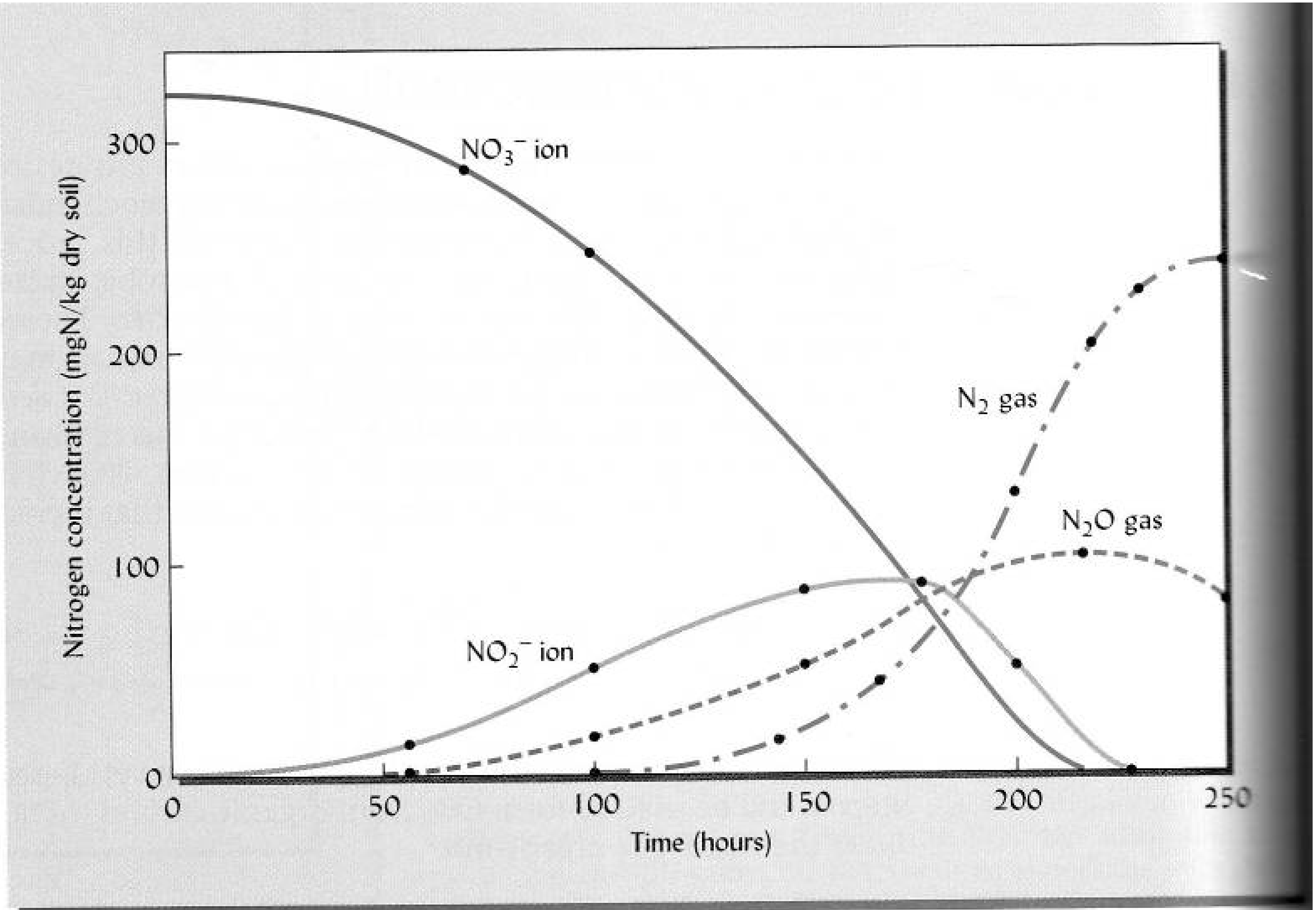


FIGURE 13.10 Changes in various forms of nitrogen during the process of denitrification in a moist soil incubated in the absence of atmospheric oxygen. [From Leffelaar and Wessel (1988)]

Reducing denitrification in paddy soils by deep fertilizer placement

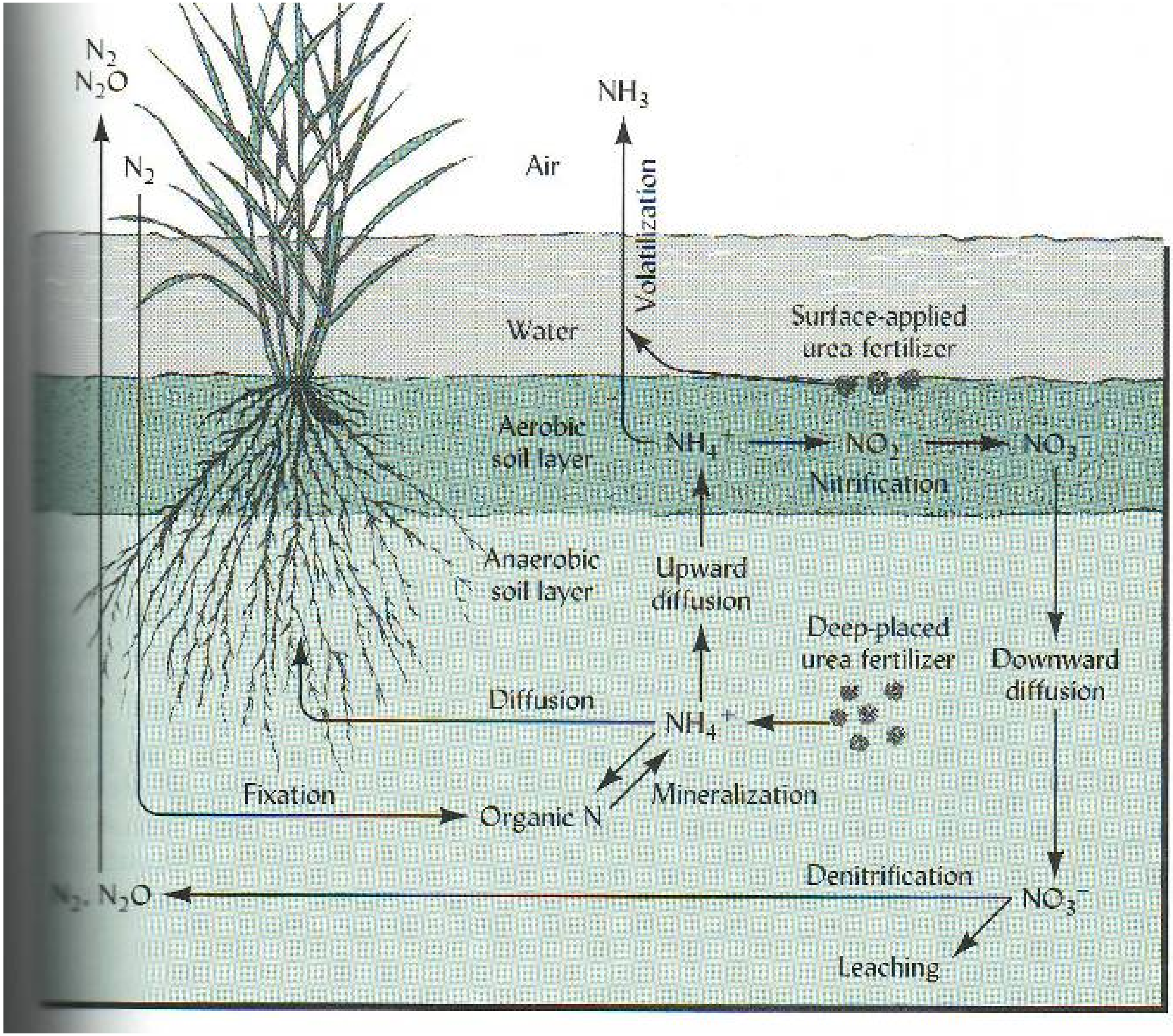


FIGURE 13.13
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Can plants use organic N sources?

- Until recently only believed that plants take up inorganic N – NH_4^+ and NO_3^-
- Soluble Organic Nitrogen (SON)
  - SON can be at same quantity in soil as inorganic forms of N
  - Plant uptake mechanisms not well understood
  - SON can leach out of soil profile, causing pollution problem

USA Nitrogen input greatly exceeds plant uptake potential

Nitrogen output or input	Millions of Mg 1987[a]	1977[b]
Outputs		
Harvested crops	10.60	8.9
Crop residues	2.89	3.0
Total outputs	13.50	11.9
Inputs to cropland		
As commercial fertilizer	9.39	9.5
As legume N fixation	6.87	7.2
In crop residues returned	2.89	3.0
Recoverable manure	1.73	1.4
Total inputs	20.9	21.1
Balance = inputs – outputs	7.42	9.2

[a] Data from Table 6-3 in National Research Council (1993).
[b] Data abstracted from Power (1981) as cited in NRC (1993).

Note that this doesn't estimate losses due to nitrate leaching, denitrification, or soil accumulation

Managing fertilizer application based on available soil nitrate level, Pre-sidedress Nitrate Test (PSNT) for Corn in the Midwest

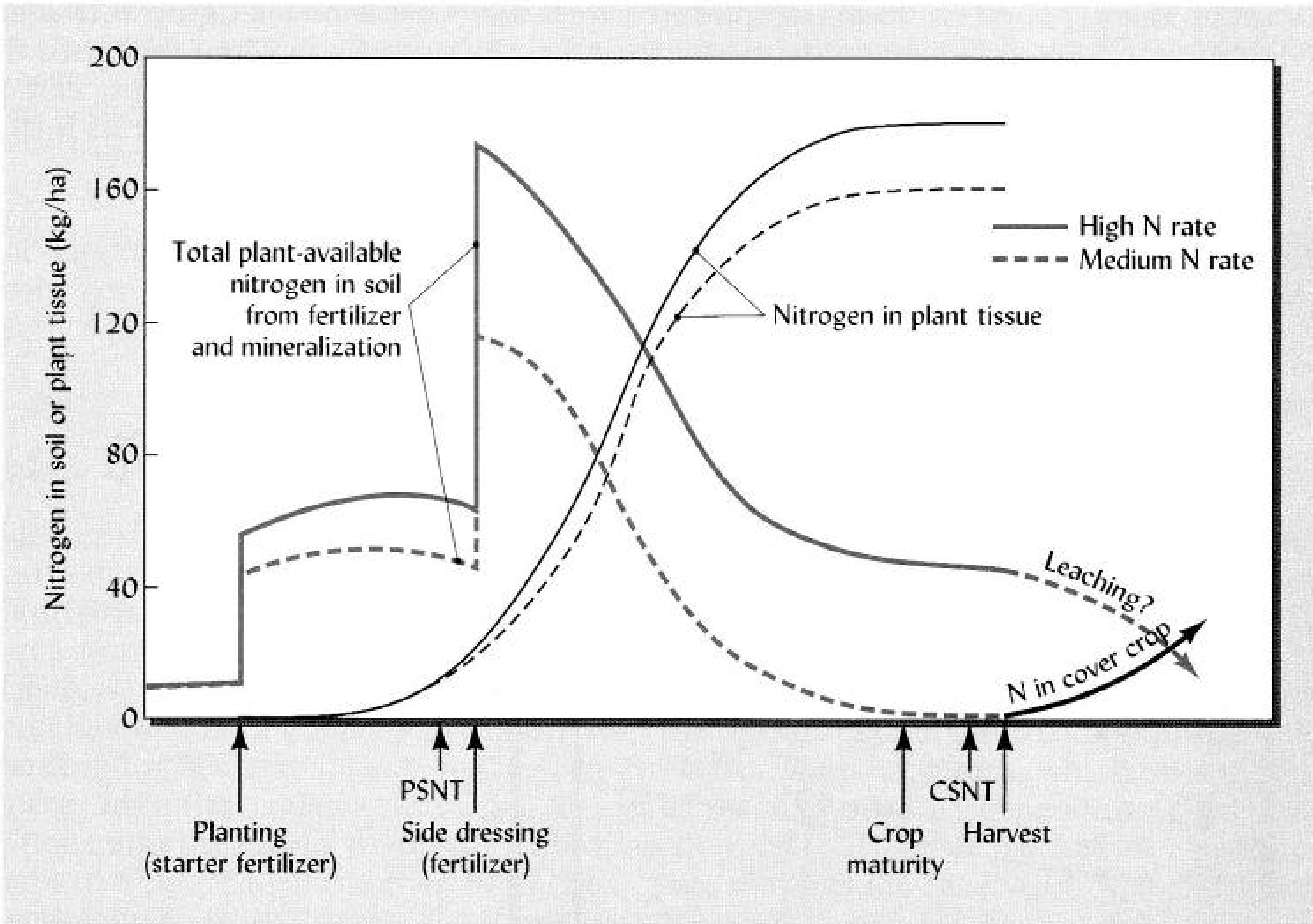
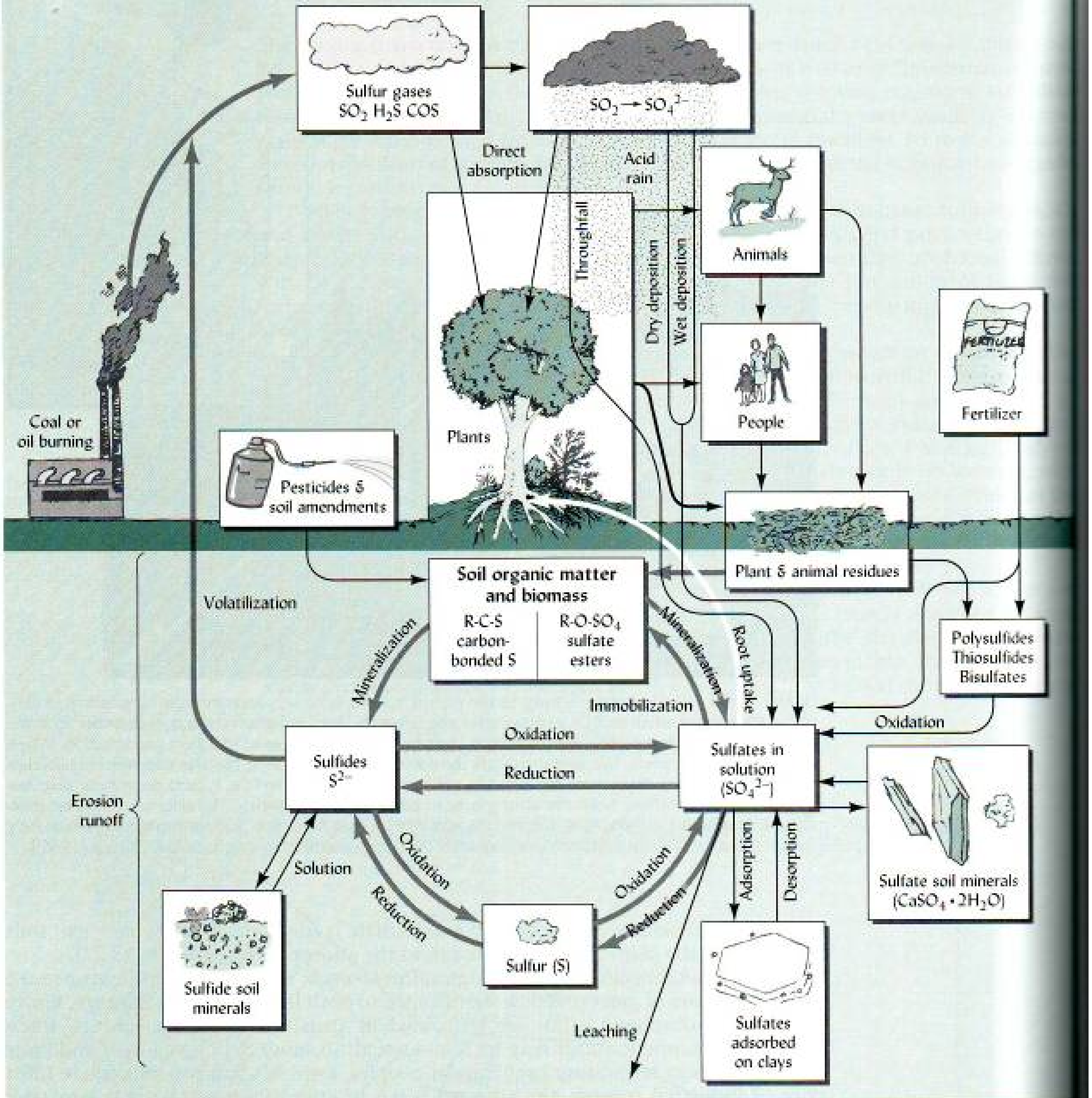


FIGURE 13.7 Two nitrogen fertilizer systems for corn production in the Midwest. The system that has been dominant in the past (solid lines) involves very high nitrogen applications and continuous corn cul-

Sulfur cycle, elemental forms, and transformation reactions

- Elemental sulfur – S
- Organic sulfur – carbon-based compounds
- Sulfides
- Sulfates

Sulfur Cycle



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Sulfur deficiency symptoms

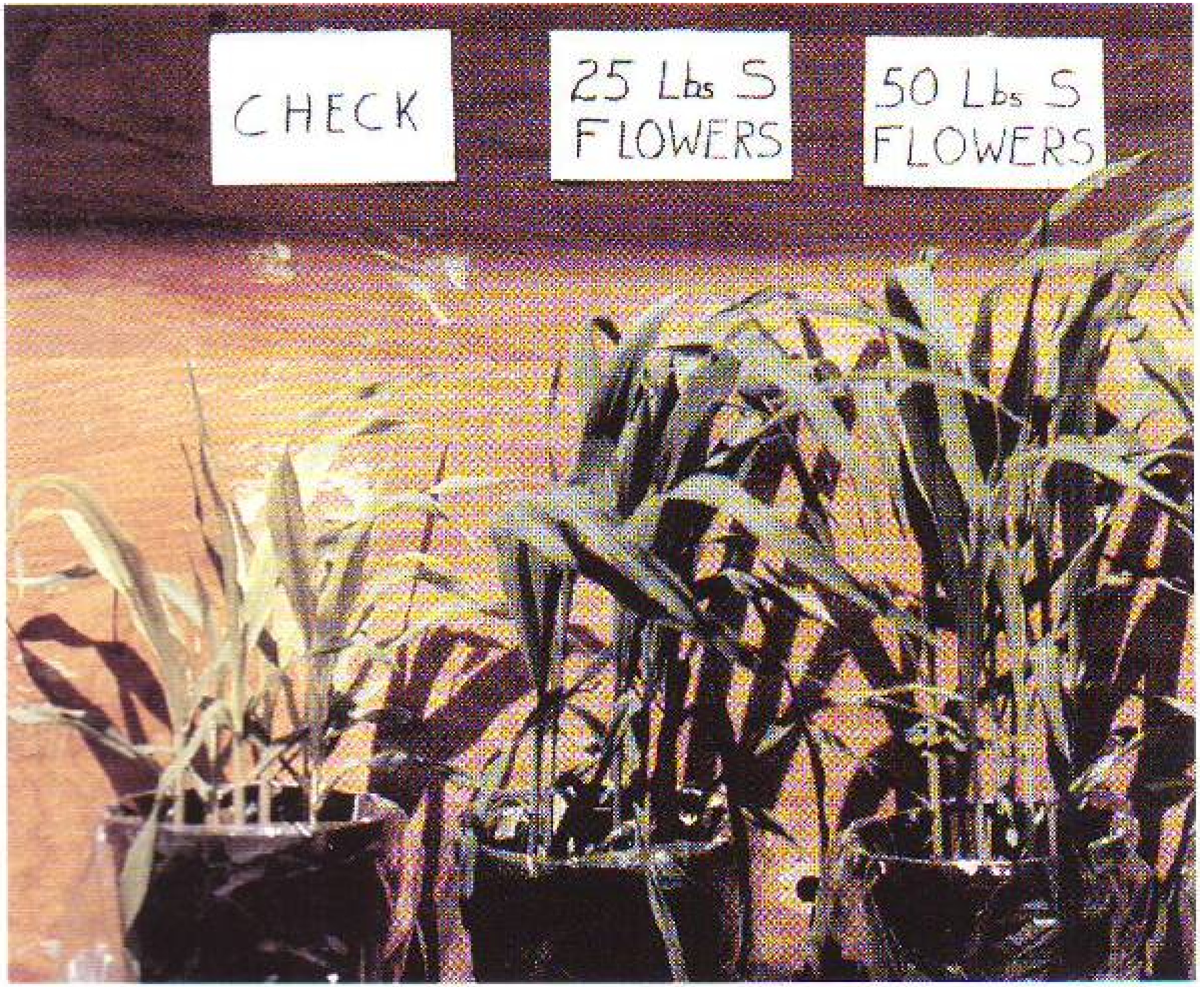


PLATE 49 Sulfur deficiency typically causes chlorosis (yellowing) on the *youngest* leaves first, or on all the foliage, as in the sorghum plant on the left. This contrasts with nitrogen deficiency, which causes chlorosis first on the *oldest* leaves. Plants growing on low-sulfur soil responded to sulfur addition.

Major gains and losses of available soil sulfur

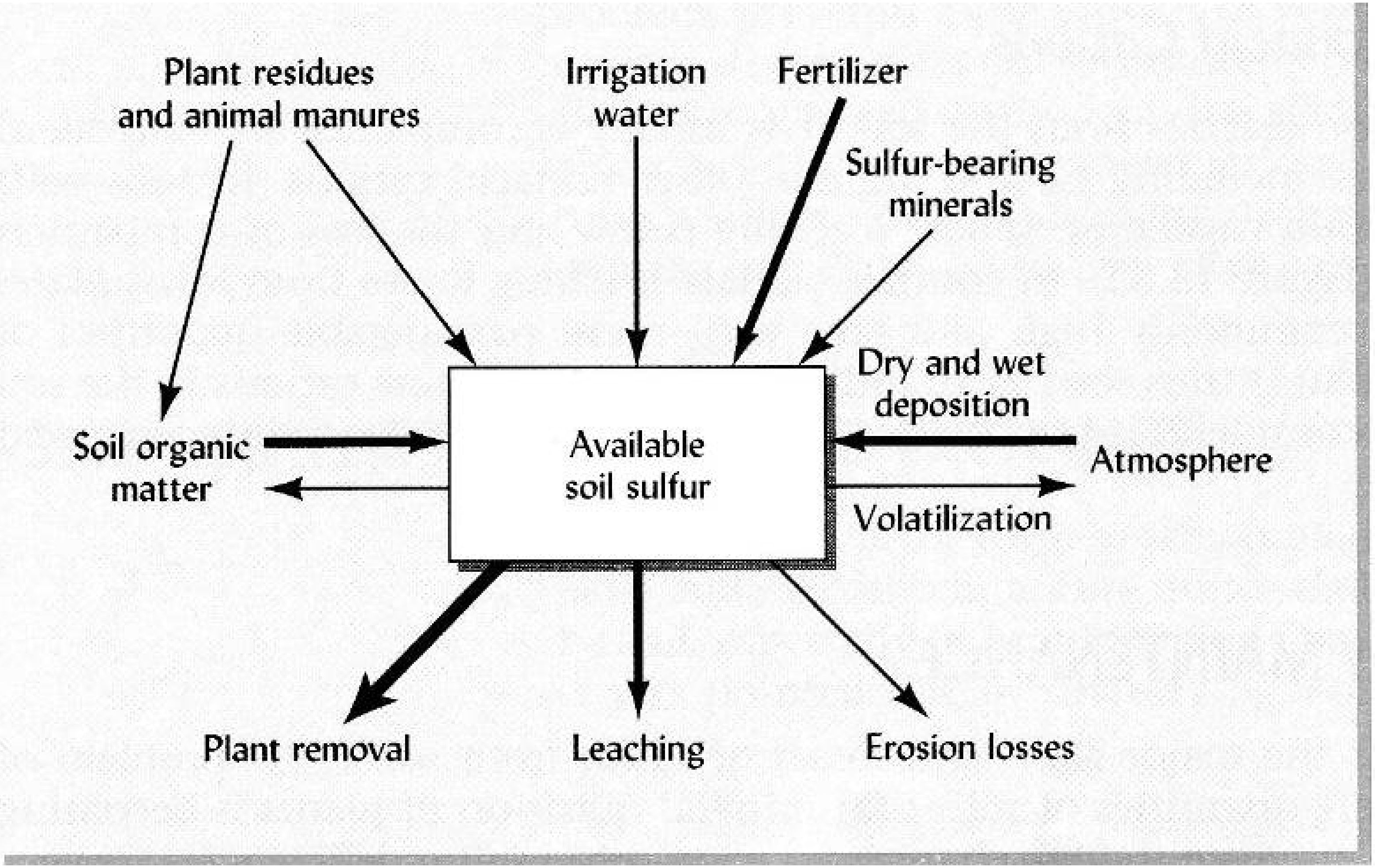
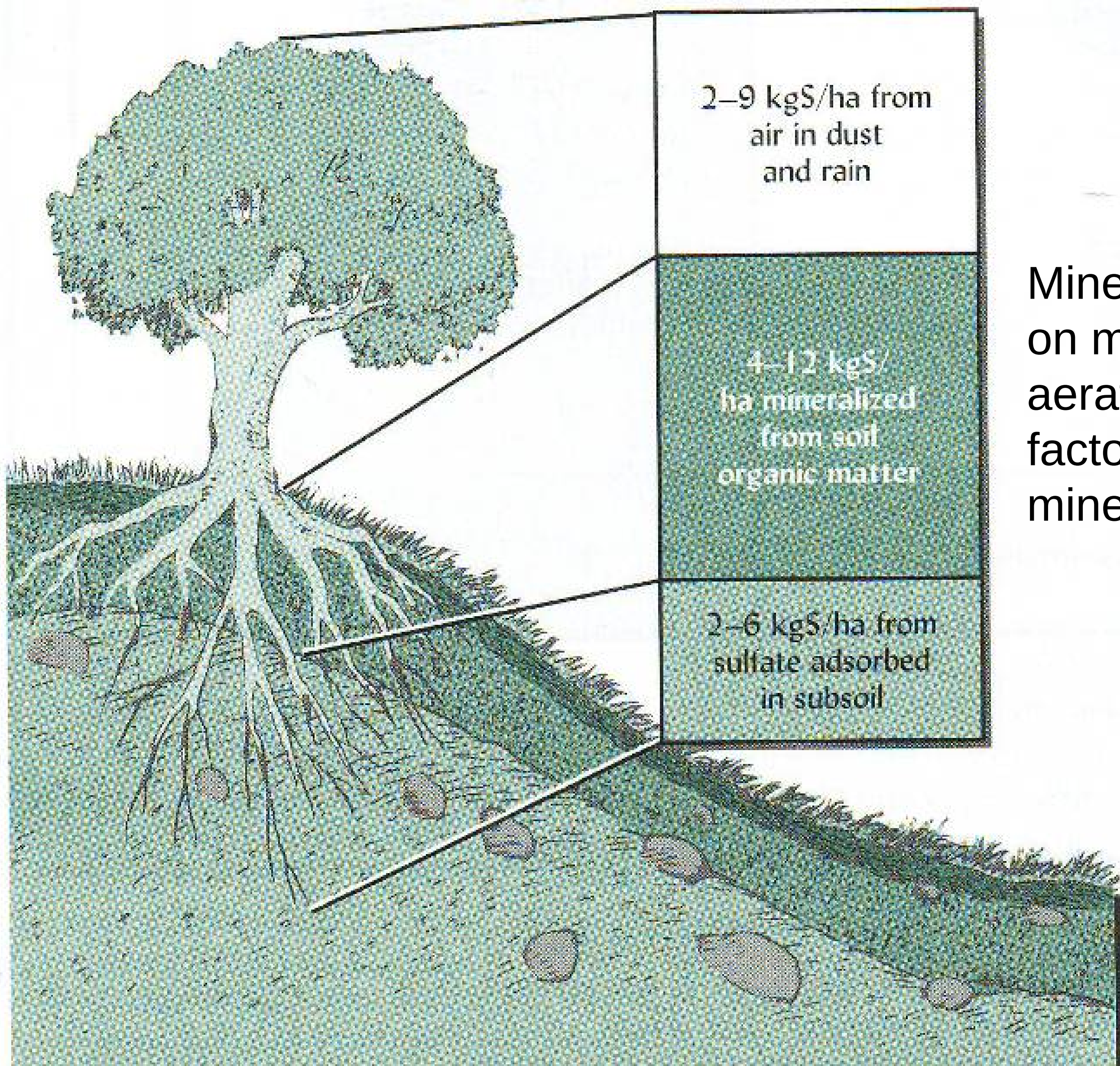


FIGURE 13.34
soil sulfur. The
relative amoun
under average
occurs in the fi

Sulfur acquisition by plants – airborne, soil organic matter, inorganic sulfate in the subsoil



Mineralization rate depends on moisture, temperature, aeration, and pH – same factors as for Nitrogen mineralization.

FIGURE 13.26
three sources: su
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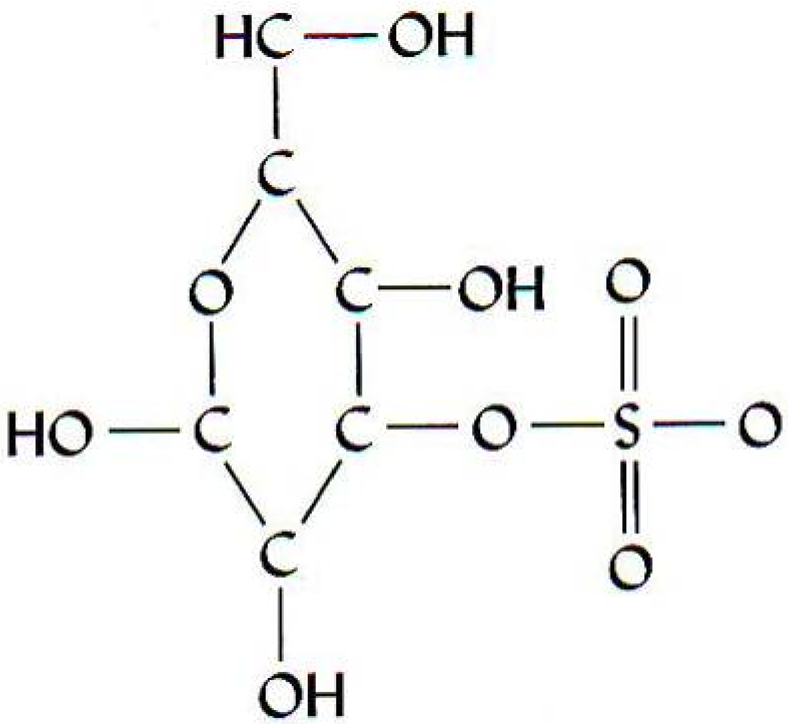
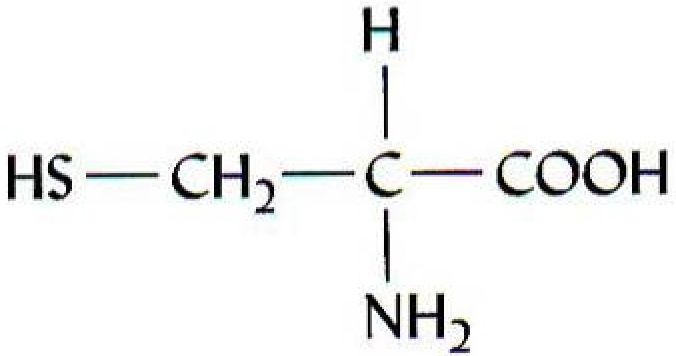
Organic Sulfur Compounds in the Soil



Ester sulfate (glucose sulfate)



Carbon-bonded sulfur (cysteine)

microbes can mineralize SO_4 directly from esters

Sulfur Oxidation – produces protons = acidification

$$\text{Organic sulfur} \longrightarrow \text{decay products} \xrightarrow{O_2} SO_4^{2-} + 2H^+$$

Proteins and other organic combinations

H_2S and other sulfides are simple examples

Sulfates

Sulfur Reduction

$$H_2S + 2O_2 \longrightarrow H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$

$$2S + 3O_2 + 2H_2O \longrightarrow 2H_2SO_4 \longrightarrow 4H^+ + SO_4^{2-}$$

2

Page 584

Deposition of airborne Sulfur as function of distance from industrial air polluter

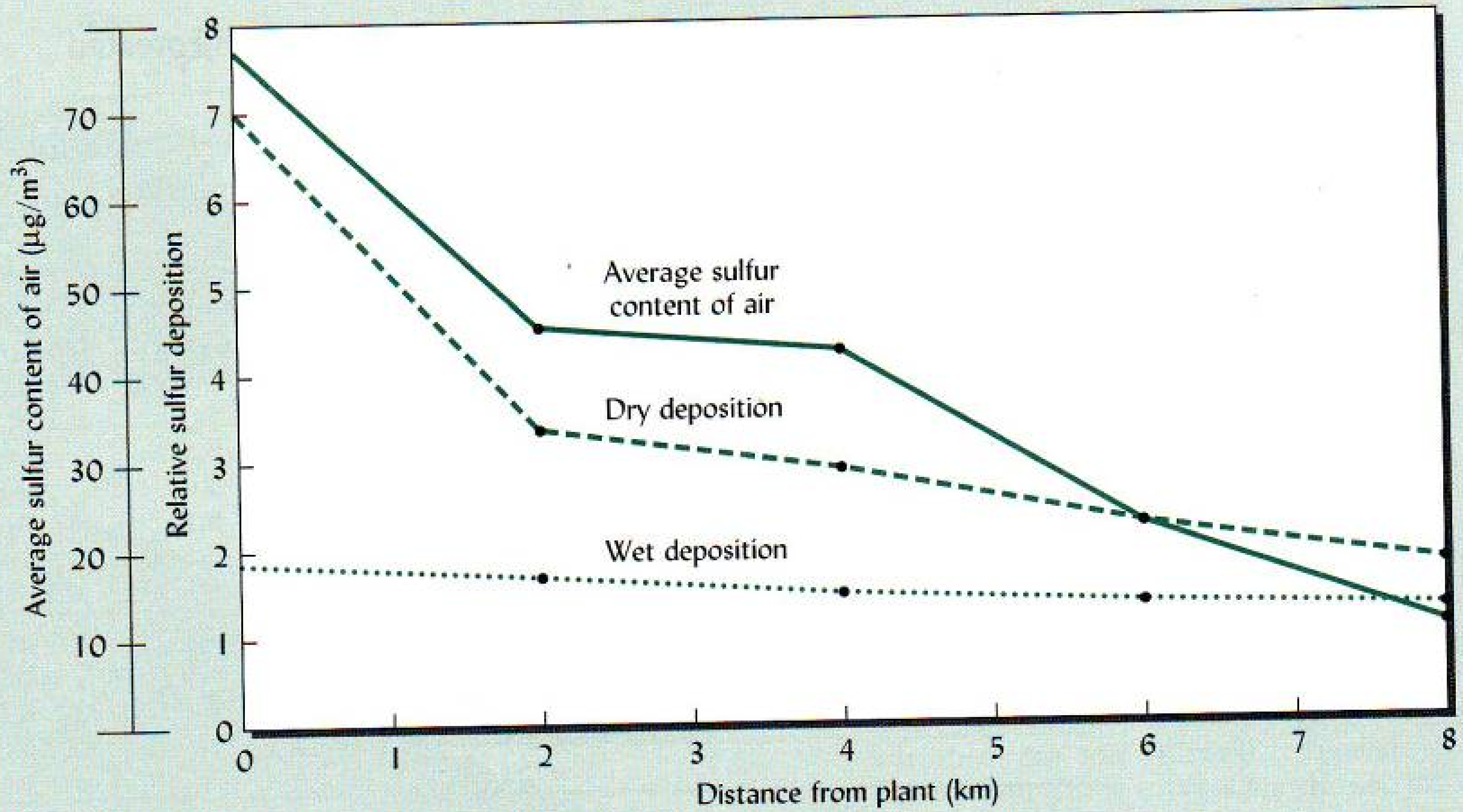
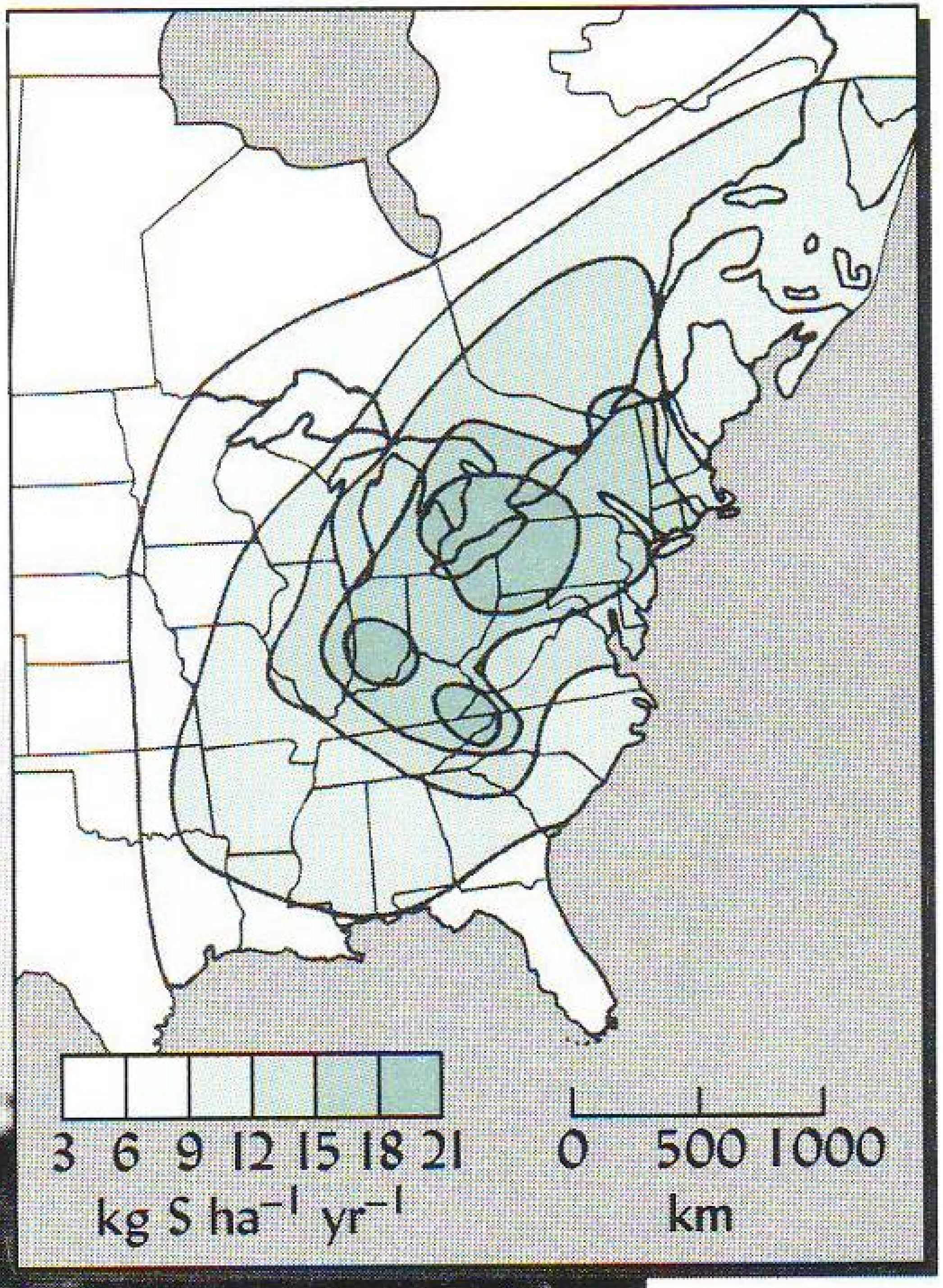


FIGURE 13.27 Industrial facilities such as coal- or oil-burning power plants or metal smelters can provide large inputs of sulfur to nearby soils. Note the rapid drop-off in sulfur deposition at increasing distances from the source of sulfur emissions. Dry deposition of sulfur from the atmosphere is dominant at locations very close to the source, but at greater distances dry and wet deposition are nearly equal. Regulations in many countries would today require that such a power plant greatly reduce its sulfur emissions. [From Johannson (1960)]

Industrial Sulfur Deposition in Eastern USA



pH dependent adsorption of sulfate to 1:1 clays and oxides reduces cation leaching

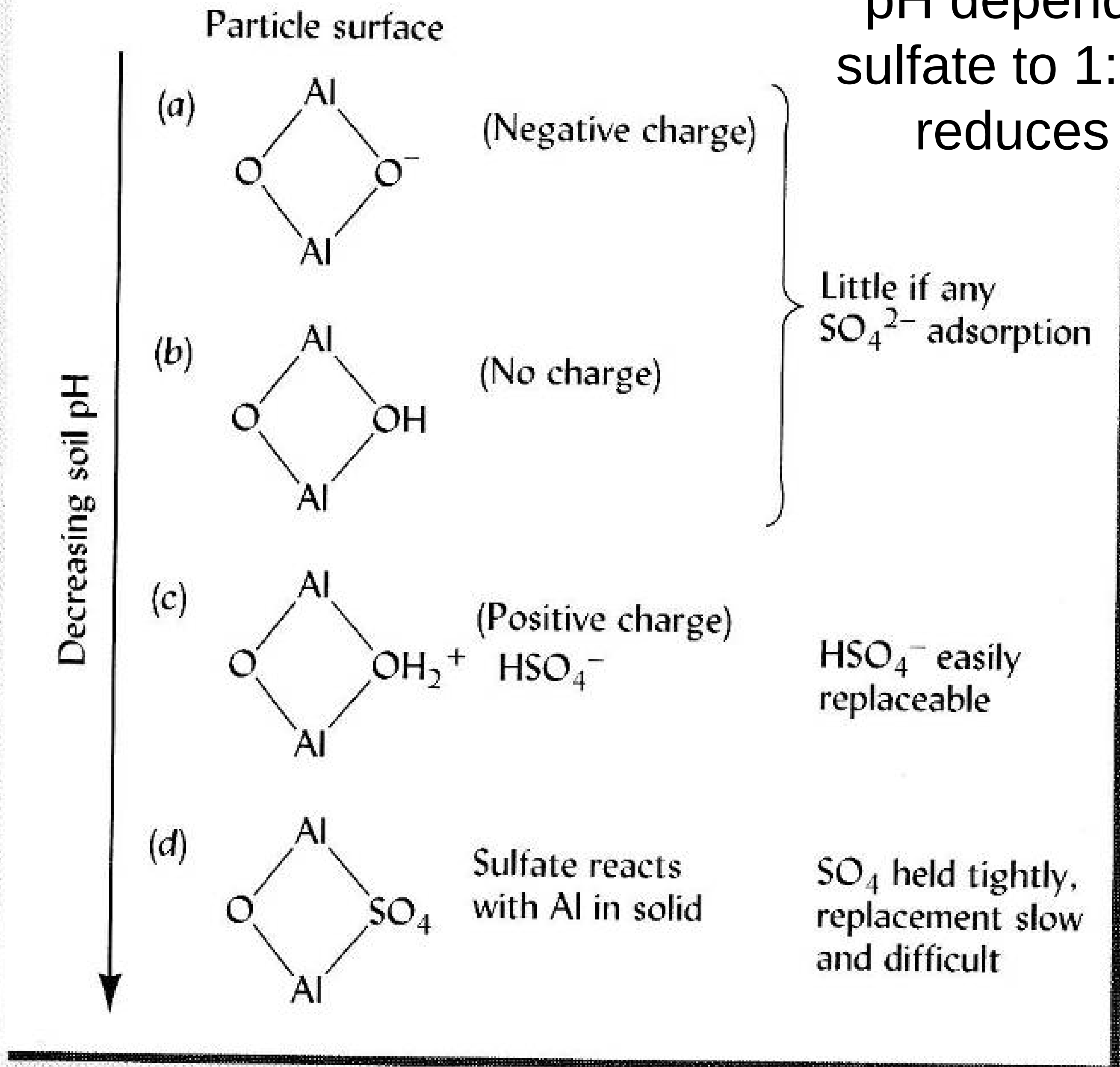


FIGURE 13.32
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high pH levels (
cation exchange
are adsorbed. Su
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SO_4^{2-} ions are sti
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the SO_4^{2-} reacts
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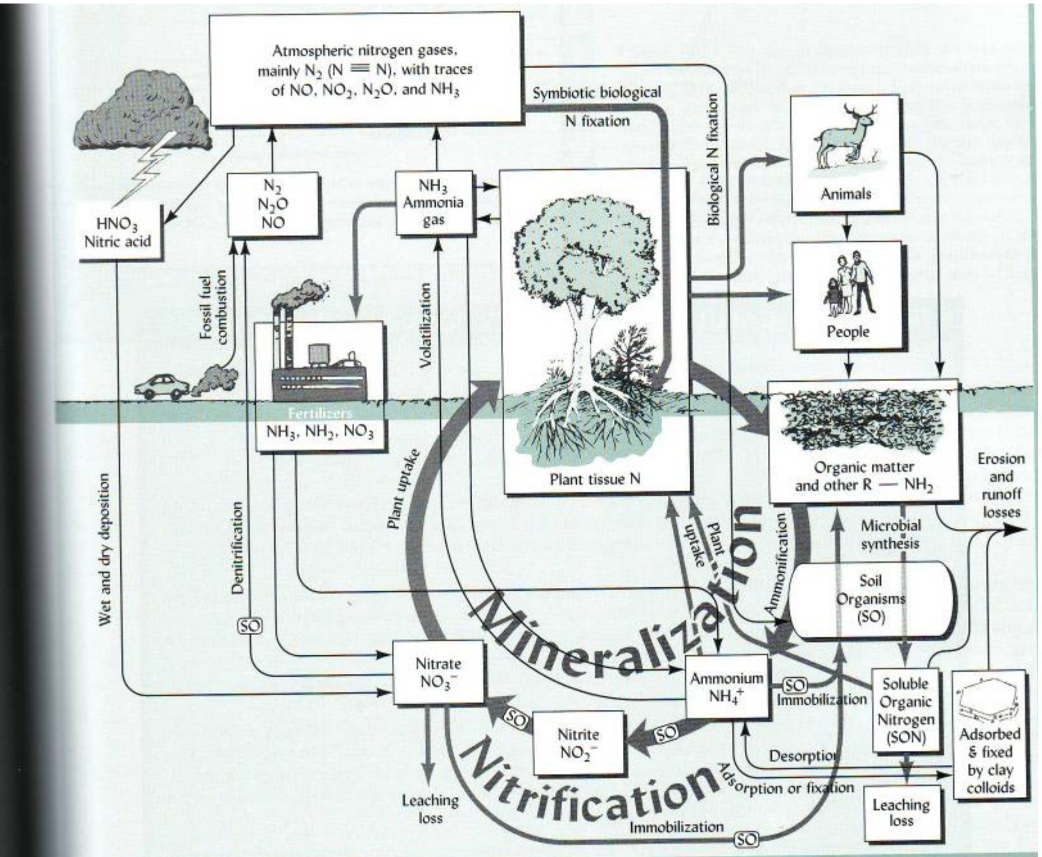
Understanding the big picture
Compare and contrast N and S cycles



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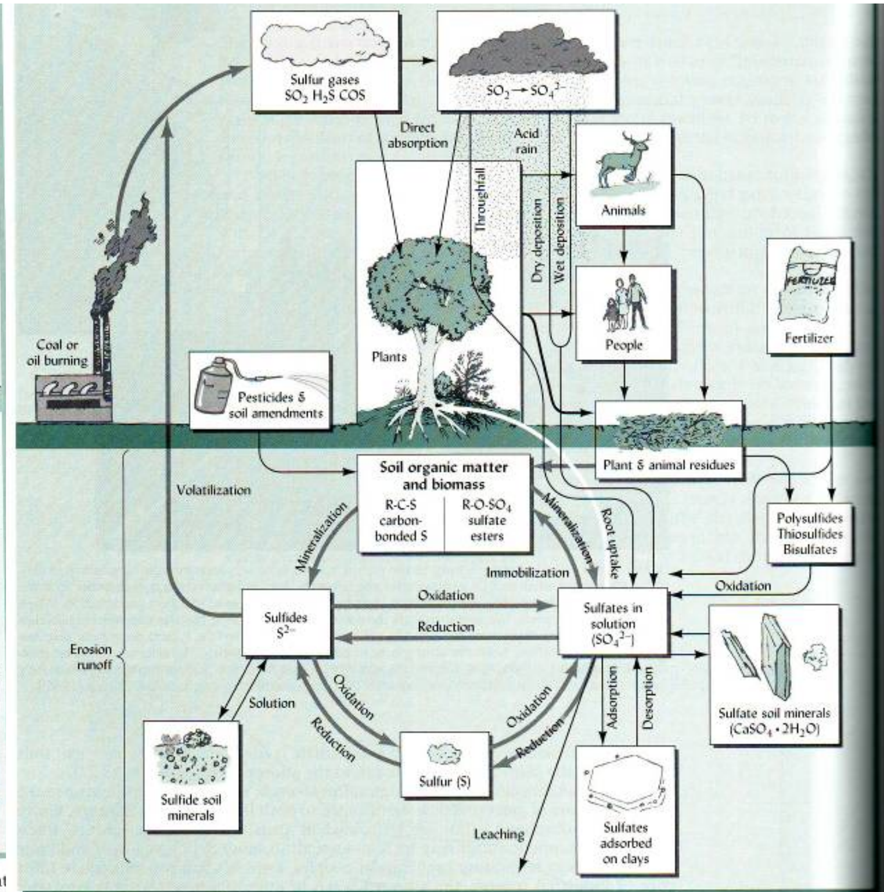

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Calculation of N mineralization

- Box 13.1 on page 548
- Gives an idea of how much N will become available from the soil organic matter
- This is a good preview for Thursday exercise in the CAL
- Think about this in terms of adding organic fertilizers for supplying Nitrogen to plants
  - Repeated applications over years requires accounting for previous years application

Study Questions

- Chapter 13 all questions