

GEOL 408/508

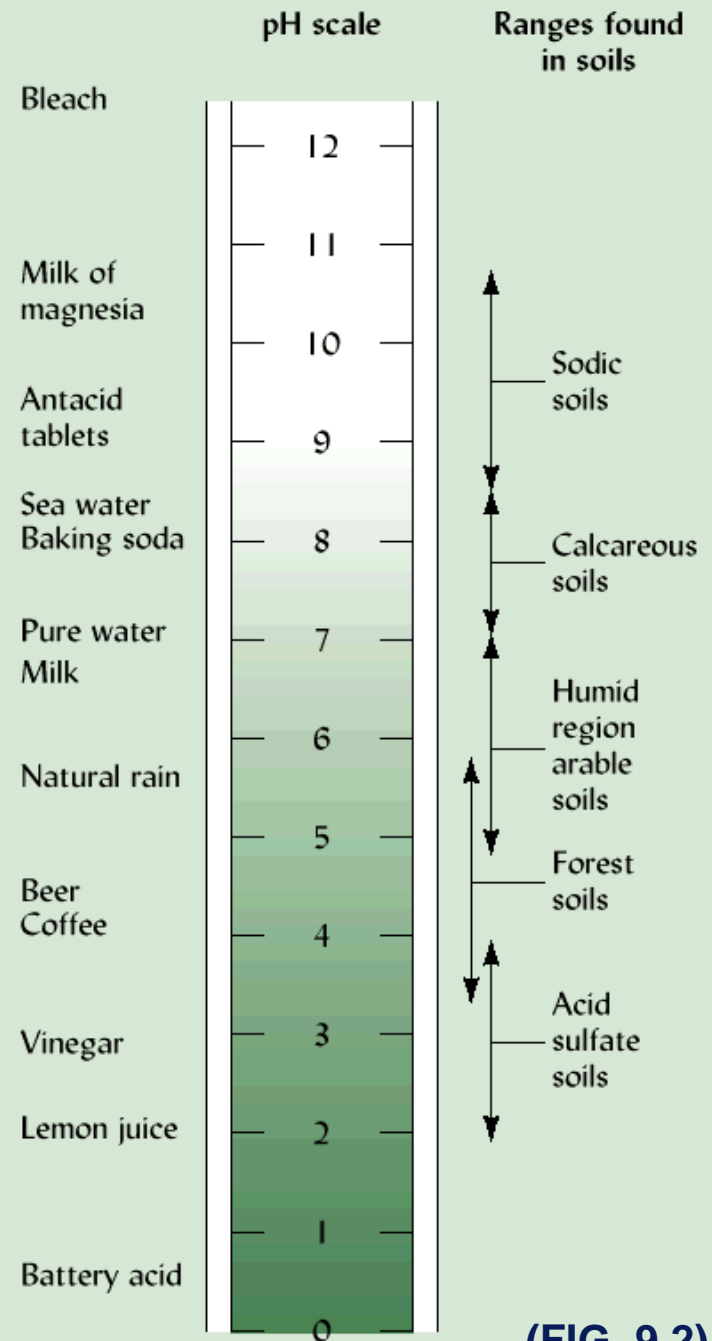
SOIL ACIDITY

Chapter 9

Brady and Weil, Rev. 14th Ed.

THE PROCESS OF SOIL ACIDIFICATION

Chart showing a range of pH from 1 to 12 and the approximate pH of products commonly used in our society every day (left). Comparable pH ranges are shown (right) for soils we will be studying in this text.



(FIG. 9.2)

THE PROCESS OF SOIL ACIDIFICATION

Soil acidification is a normal and on-going soil process

Sources of hydrogen ions:

- Carbonic acid:



- Acids from biological metabolism:



Accumulation of OM:

- OM is a source of H^+
- OM forms soluble complexes with Ca^{+2} , Mg^{+2} , etc thus facilitating their loss via leaching

THE PROCESS OF SOIL ACIDIFICATION

Sources of hydrogen ions (con't):

- Oxidation of nitrogen (nitrification):



- Oxidation of sulfur:



THE PROCESS OF SOIL ACIDIFICATION

Sources of hydrogen ions (con't):

- **Acids in precipitation:**

- primarily H_2SO_4 & HNO_3
- rainfall pH in many industrial areas may be < 4.3

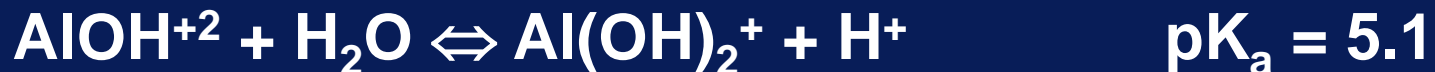
- **Plant uptake of cations:**

- plant roots also must maintain electrical charge balances
- plant roots often exude H^+ when absorbing cations
- plant may uptake both cation & anion

THE PROCESS OF SOIL ACIDIFICATION

Balance between production & consumption of H⁺:

- Several soil & plant processes will consume H⁺:
 - uptake of NO₃⁻ liberates HCO₃⁻ into soil solution
 - weathering of basic cations from minerals
- Hydrolysis of Al will produce H⁺:



POOLS OF SOIL ACIDITY

Principal pools of soil acidity:

- (1) active acidity - Al^{+3} & H^+ in soil solution
- (2) salt replaceable (exchangeable) - Al^{+3} & H^+ that are *easily exchangeable* by other cations in an **unbuffered** salt solution **(100X > active)**
- (3) residual acidity - can be neutralized by limestone or other alkaline material but is not exchangeable **(10^3 - 10^6 X > exchangeable)**

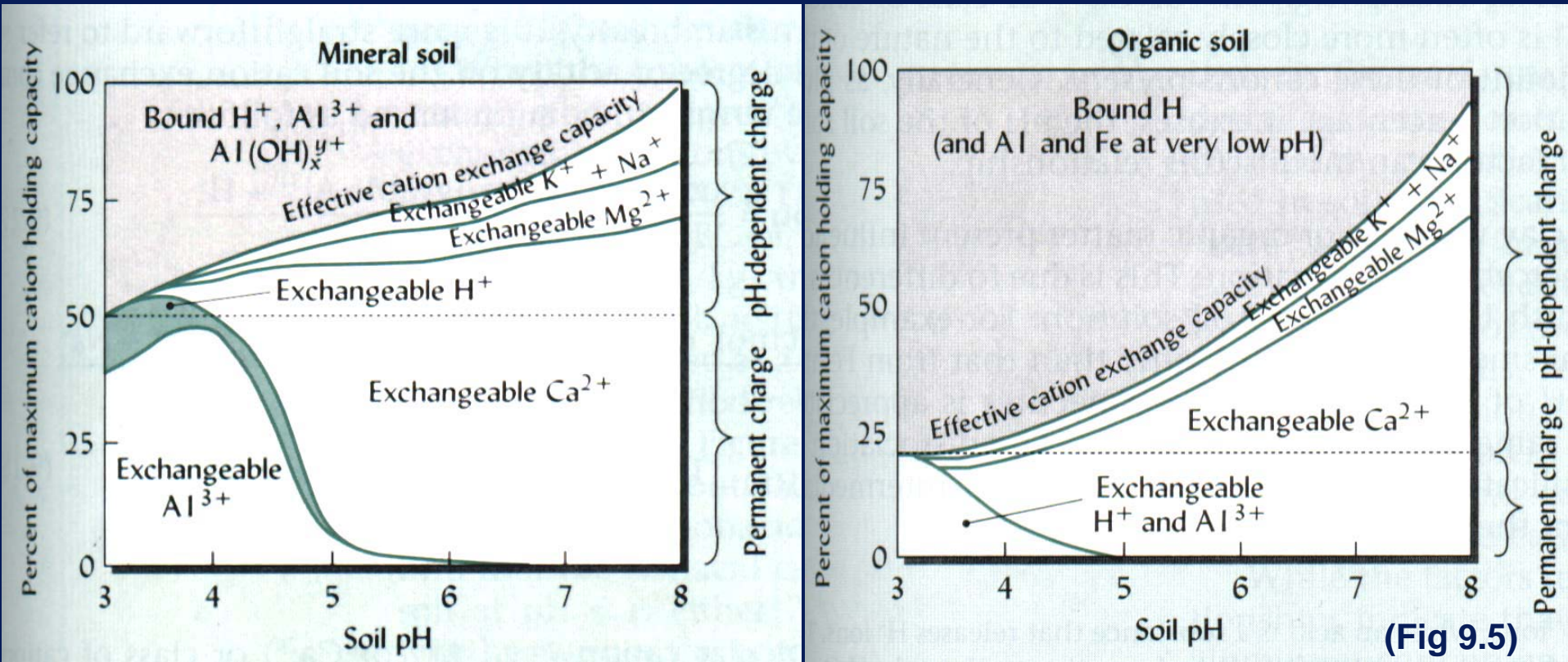
Total acidity = (1) + (2) + (3)

- (last section noted importance of Al^{+3})

POOLS OF SOIL ACIDITY

Soil pH & cation associations:

- Exchangeable & bound cations
- Effective CEC & pH



POOLS OF SOIL ACIDITY

Cation saturation percentages:

$$\% \text{ acid sat'n} = [\text{cmol}_c \text{ of exch Al}^{+3} + \text{H}^+] \div [\text{cmol}_c \text{ of CEC}]$$

$$\% \text{ base sat'n} = [\text{cmol}_c \text{ of exch Ca}^{+2}, \text{Mg}^{+2}, \text{K}^+, \text{Na}^+] \div [\text{cmol}_c \text{ of CEC}]$$

% base sat'n is more correctly termed nonacid saturation

“base” cations do not hydrolyze and increase soil pH

acid cations do increase soil acidity (lower pH)

POOLS OF SOIL ACIDITY

Acid (& nonacid) cation saturation & pH:

- **Effect of type of colloid:**

- at same % acid sat'n, soil pH with higher CEC colloid is lower than colloid of lower CEC (the higher the reservoir of H⁺, the greater amount in solution)

- **Effect of method of measuring CEC:**

- measured at buffered pH (potential CEC) or at pH of soil as collected (effective CEC)

- **Uses of cation saturation percentages:**

- soils that have > 20% acid saturation may have Al toxicity

BUFFERING OF pH IN SOILS

Titration curves:

- the resistance to change in soil pH when an acid or base is added is called buffering and can be depicted by generating a buffer curve (Fig. 9.7)
- soils are most highly buffered at high & low pHs

Mechanisms of buffering:

• Aluminum hydrolysis:

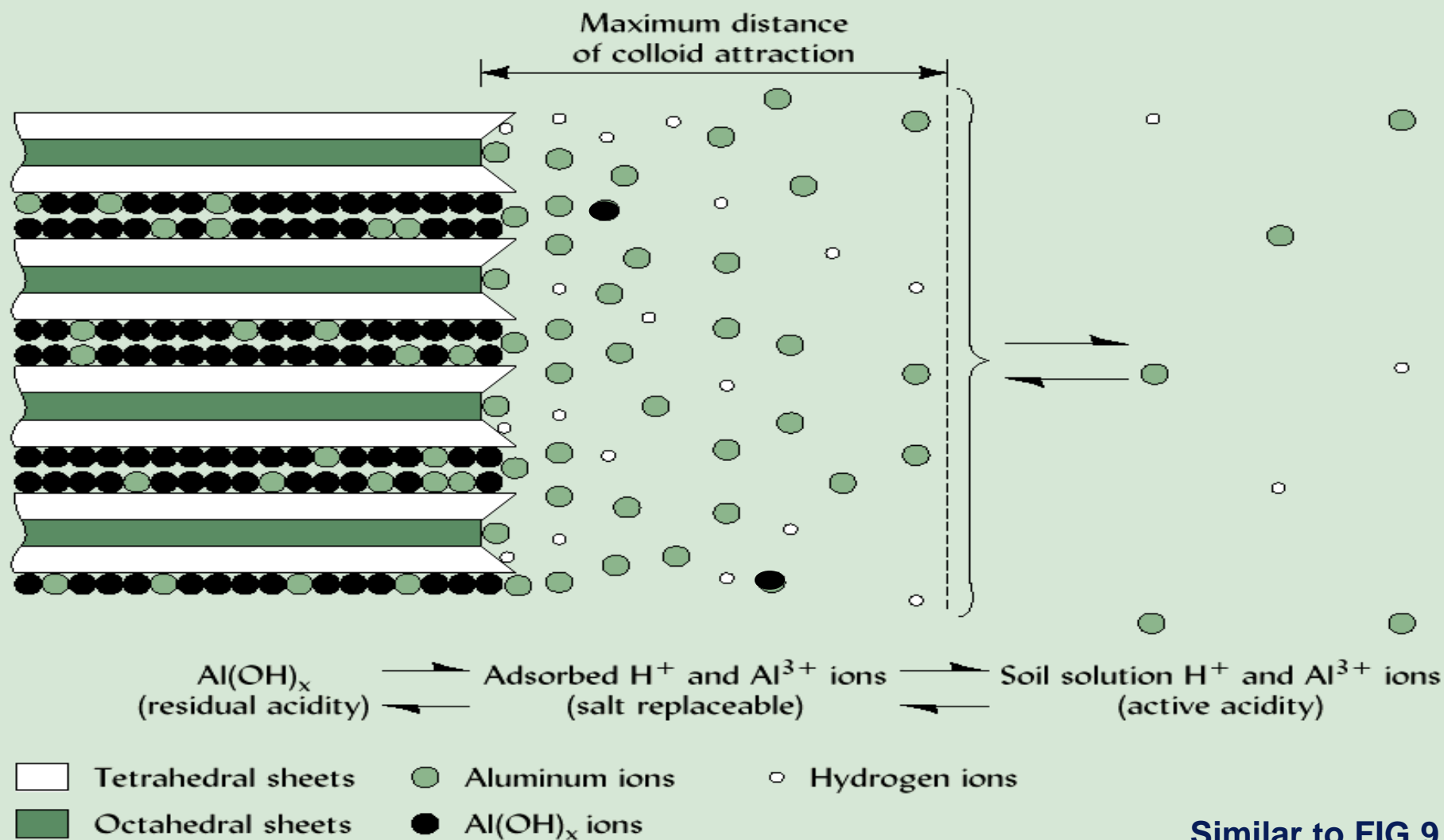


- add H^+ , reaction moves to right
- add OH^- , reacts with H^+

• Organic matter reactions:

- protonation or deprotonation of OM functional groups (R-OH) provides much buffering

Equilibrium relationship among residual, salt-replaceable (exchangeable), and soil solution (active) acidity on a 2:1 colloid.



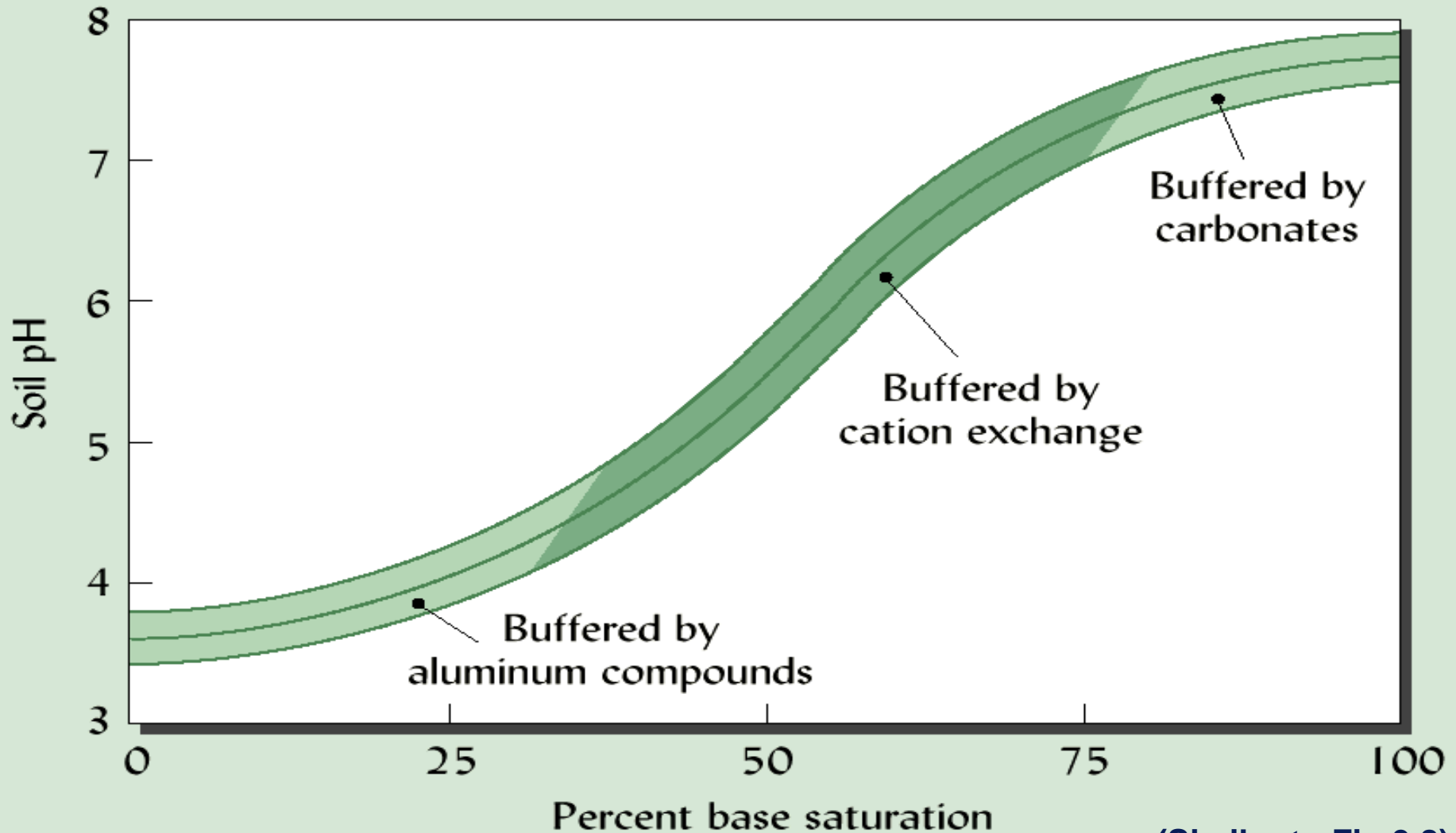
Similar to FIG 9.9

BUFFERING OF pH IN SOILS

Mechanisms of buffering, continued:

- **pH-dependent charge sites on clay:**
 - Si-O and Al-O, Al-OH groups - source and sink for H⁺
- **Cation exchange:**
 - when H⁺ is added to soil solution, will be sorbed by displacing other cations, H⁺ in sol'n changed little
 - when base is added, will react with sol'n H⁺ which will be replaced from sorbed H⁺
- **Carbonate dissolution & precipitation:**
 - carbonates, bicarbonates & carbonic acid reactions - see text

The relationship between percent base saturation and soil pH of Vermont soils.

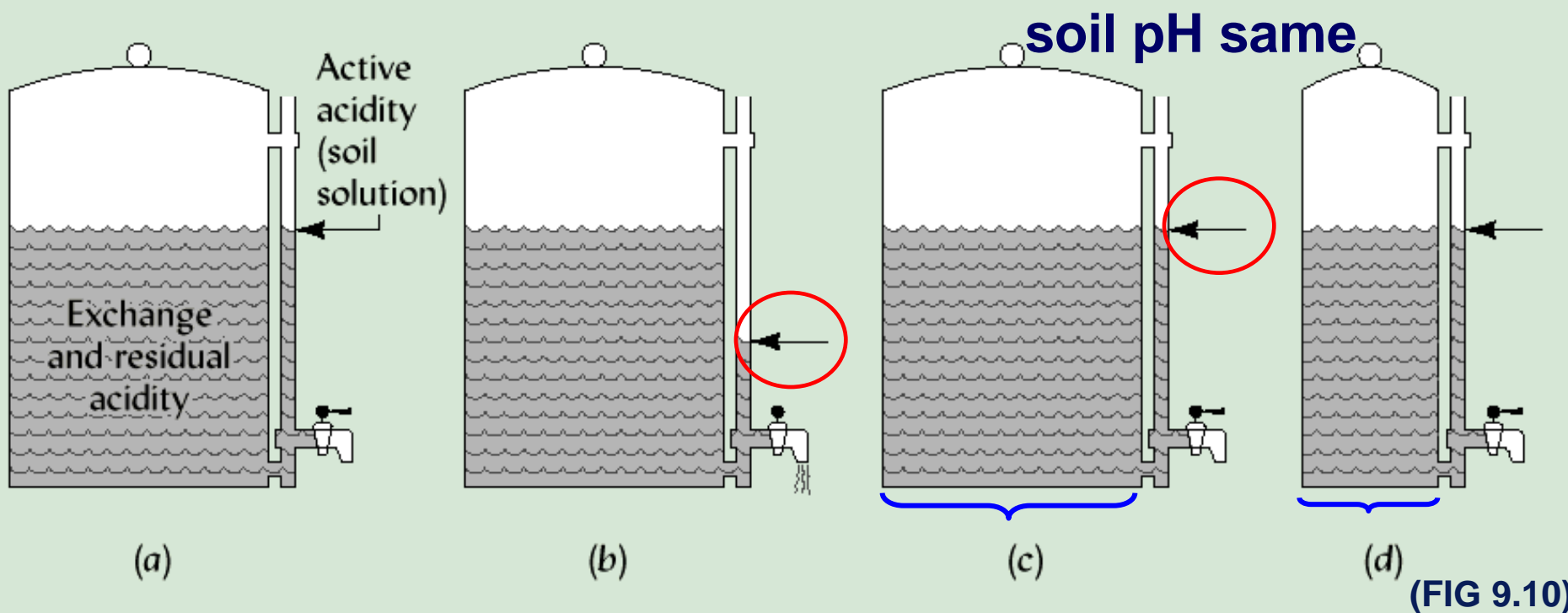


(Similar to Fig 9.8)

BUFFERING OF pH IN SOILS

Importance of soil buffering capacity:

- prevents drastic changes in soil pH
- influences amounts of amendments needed to cause a change in pH
- concept of soil buffering:



DETERMINATION OF SOIL pH

Color dyes:

- solutions often used for field measurements

Potentiometric methods:

- most precise is pH electrode
- use 1:1 or 1:2.5 ratio of soil:water

Variability in the field:

- **Spatial variation:** may occur over small distances; effects of plant roots/ nutrient uptake; uneven placement of fertilizer
- **With soil depth:** liming, fertilization at surface; leaching effects
- **Effects of season & time:** may have salt accumulation in drier seasons; less biotic activity, > pH, in cold temps; most natural changes slow

HUMAN-INFLUENCED SOIL ACIDIFICATION

Nitrogen fertilization:

- **Chemical fertilizers:**

- ammonium-based fertilizers are widely used



- soil is acidified by portion of N not uptaken (Why?)

- **Acid-forming organic materials:**

- many biosolids & animal manures will cause acidification due to release of organic acids & oxid'n of N

- some biosolids are lime-stabilized and have pHs of 7.5 - 8.5 - need to take care not to

overlime

HUMAN-INFLUENCED SOIL ACIDIFICATION

Acid deposition from the atmosphere:

- **Origins of acid rain:**

- nitric & sulfuric acids from combustion of oil, coal; fuel in vehicles; smelting of S-containing ores; forest fires; burning of crop residues

- **Effects of acid rain:**

- damage to buildings & stone monuments
- detrimental effects on forests & aquatic life

- **Soil acidification:**

- H^+ removes nonacid cations & Al^{+3} , H^+ predominate on exchange complex, soil solution & drainage waters

Illustration of the formation of nitrogen and sulfur oxides from the combustion of fuel in sulfide ore processing and from motor vehicles.

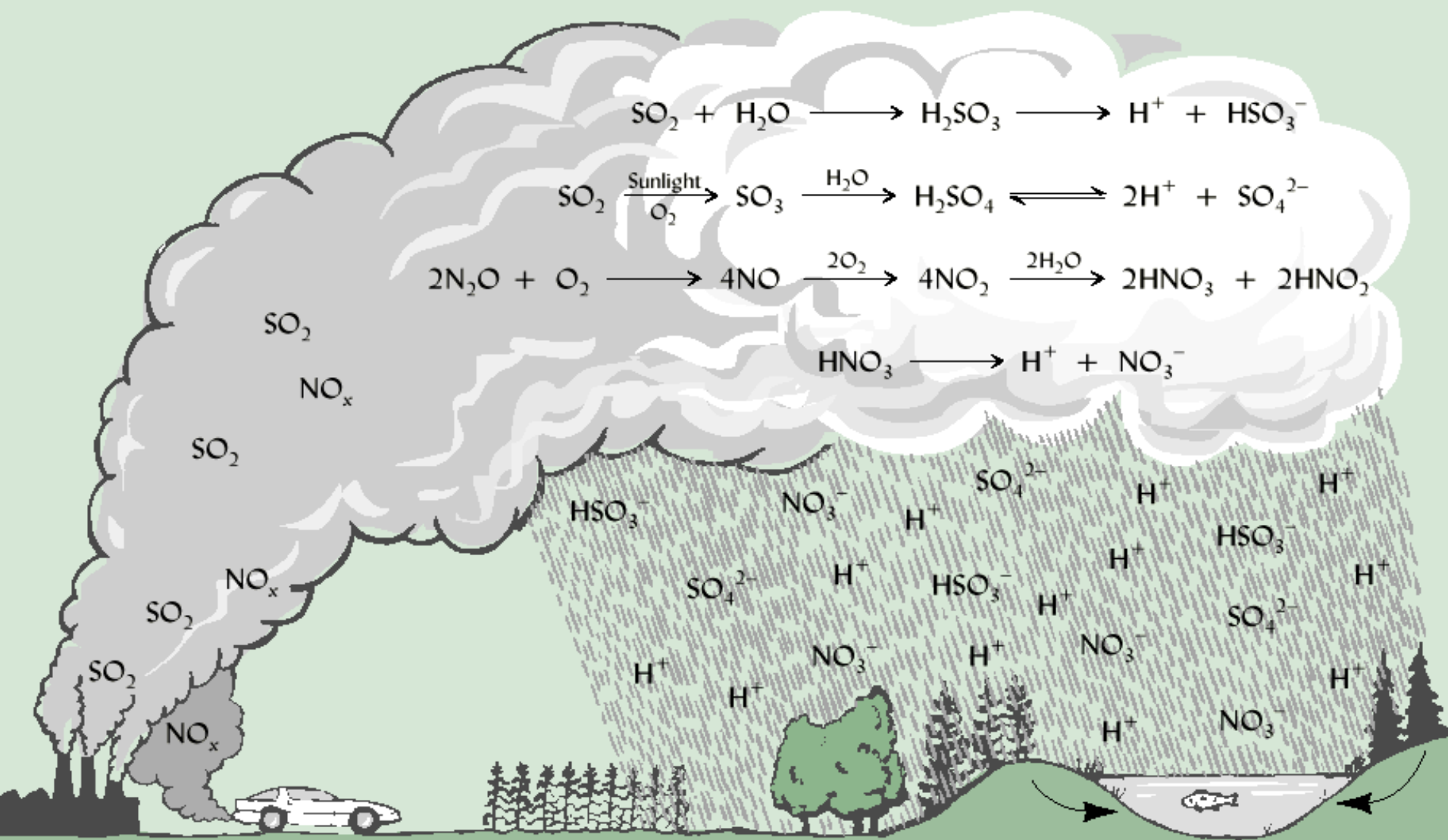
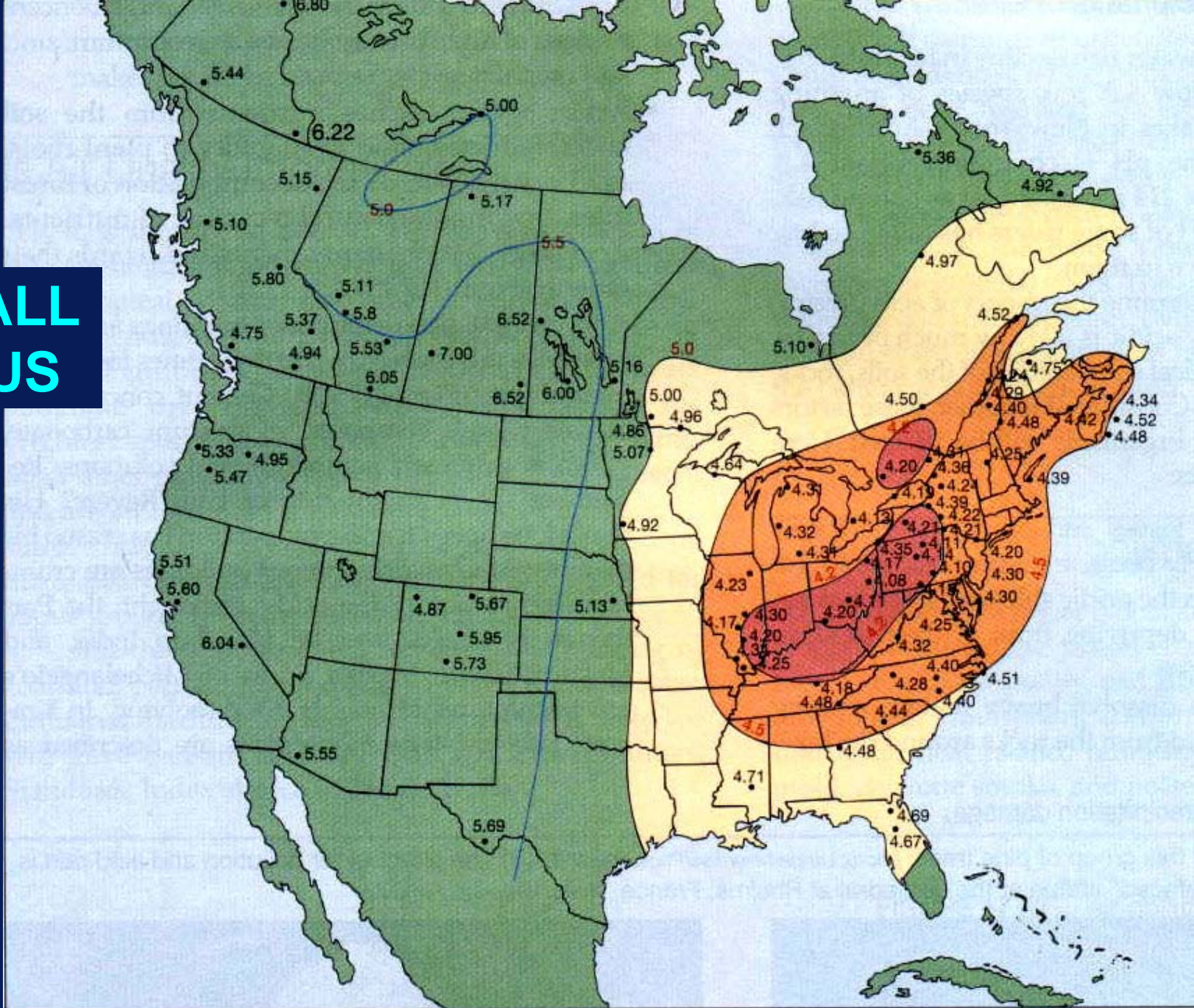


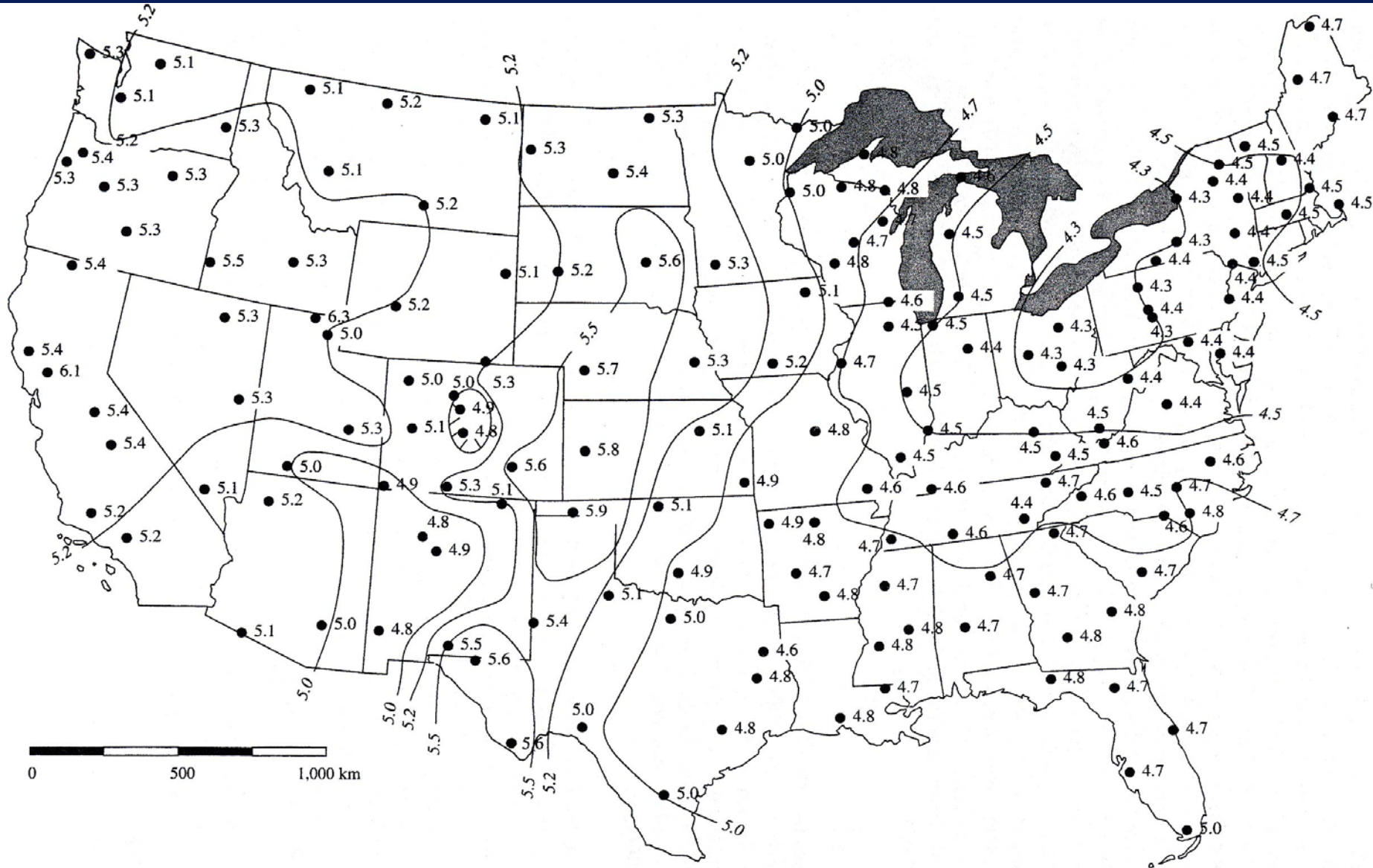
Fig 9.16

RAINFALL pH IN US

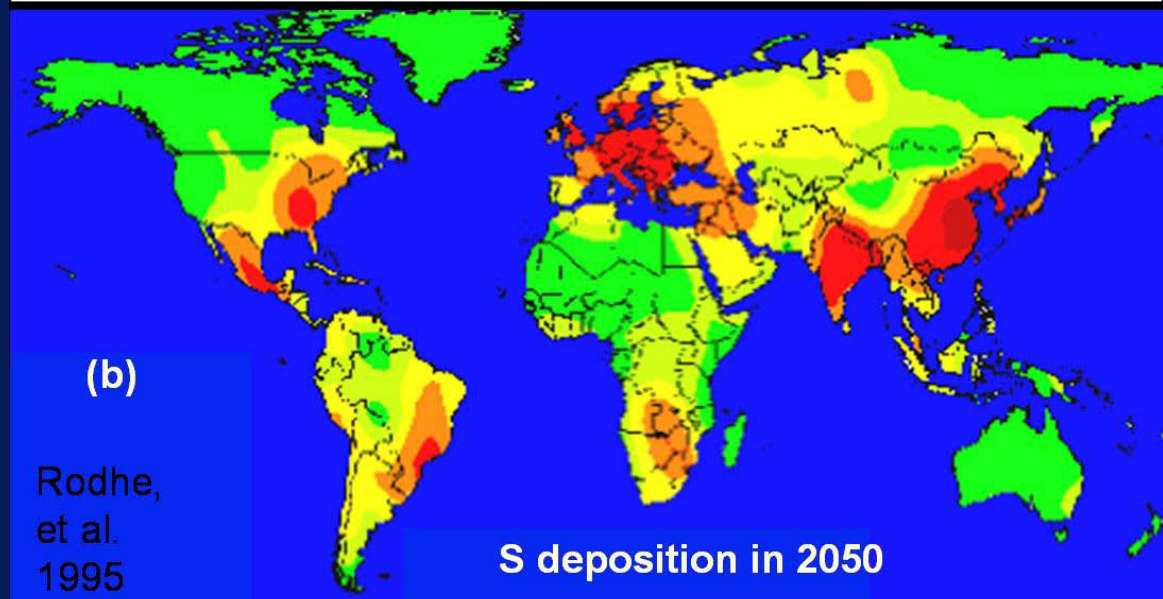
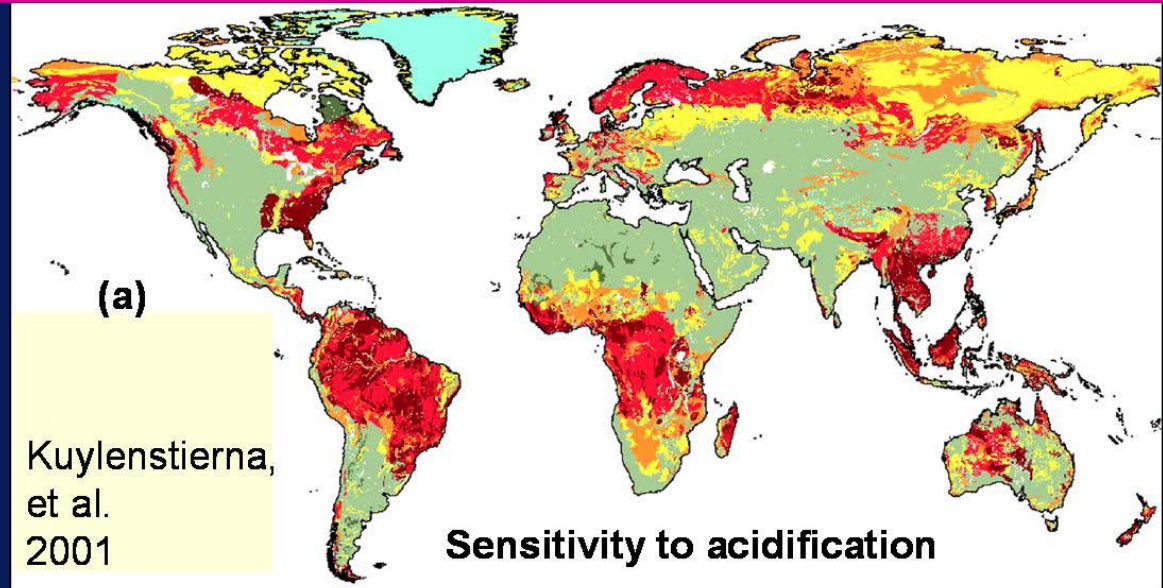


This map of pH reveals a pattern of air pollution. Year - 1980

Avg pH of rainfall in contiguous USA for 1995



Sensitivity of global ecosystems to damage by acid deposition and S deposition



HUMAN-INFLUENCED SOIL ACIDIFICATION

Acid deposition from the atmosphere:

- **Effects on forests:**

- decrease in available Ca^{+2} ; effects unsure
- toxic effects of excess Al^{+3} ; especially at molar ratios of Ca:Al of < 1 , where reduced root growth & Ca uptake occurs

- **Effects on aquatic ecosystems:**

- Al^{+3} is directly toxic to fish & other aquatics
- at pH = 5, virtually all fish are killed

- **Sensitive soils:**

- soils with low buffering and non-carbonate PMs are most susceptible

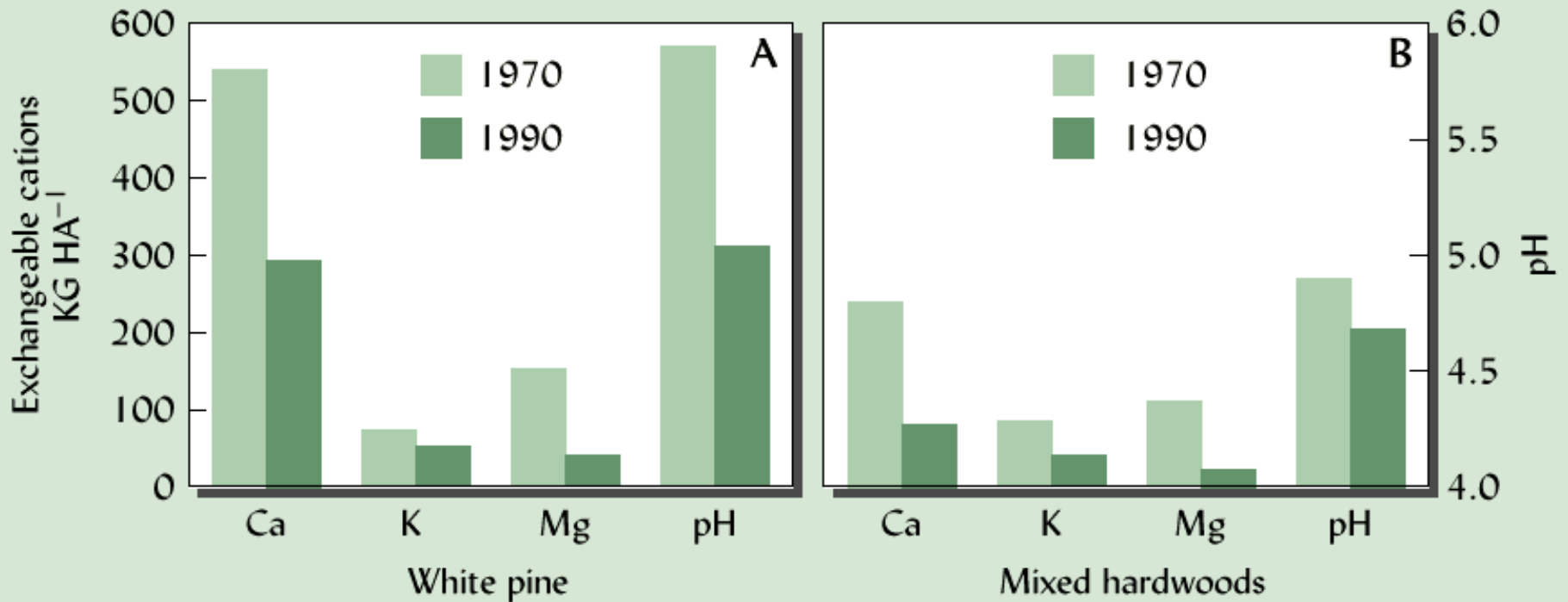
HUMAN-INFLUENCED SOIL ACIDIFICATION

Acid deposition from the atmosphere:

- **Slow progress:**

- deposition of sulfates in North America has decreased since 1970 (US Clean Air Act)
- technologies may also have removed tiny particles that are rich in Ca
- dust from unpaved roads has declined in recent years
- reduced emissions of N- & S- gasses should continue to decline in industrialized countries
- developing countries are facing growing problem

DECLINE IN EXCHANGEABLE CATIONS - ACID RAIN EFFECTS



Exchangeable Ca^{2+} , Mg^{2+} , and K^{+} soil pH declined appreciably from 1970 to 1990 in the A horizon of soils of two forested watersheds in the mountains of North Carolina, one (a) producing white pine, the other (b) mixed hardwood trees.

HUMAN-INFLUENCED SOIL ACIDIFICATION

Exposure of potential acid sulfate minerals:

- **Drainage of certain coastal wetlands:**

- many contain significant amounts of sulfides

- oxidation of S:



- oxidation of Fe:



- hydrolysis of ferric sulfate:



- **Excavation of pyrite-containing materials:**

- shipping-channel dredge spoils, mining activities (coal, sulfide ores, sand, road cuts, buildings)

ACID SULFATE MATERIALS IN WETLAND SOILS



ACID SULFATE MATERIALS IN WETLAND SOILS



BIOLOGICAL EFFECTS OF SOIL pH

Aluminum toxicity:

• Effects on plants:

- Al is absorbed passively by roots and remains in roots
- Al may block sites where Ca is taken into root
- Al binds very strongly with phosphate & interferes with P-metabolism (energy transfers & genetic coding)
- becomes problem at < pH 5.2

• Symptoms:

- stunted root system with short, thick, stubby roots
- root tips & lateral roots often turn brown
- Al toxicity produces P-deficiency symptoms in foliage (stunted, dark-green, purple stems)

BIOLOGICAL EFFECTS OF SOIL pH

Aluminum toxicity, continued:

- **Tolerance:**

- great variety of genetic variability to Al toxicity
- plants that originate in areas dominated by acid soils tend to be less sensitive than those from areas of neutral to alkaline soils
- tolerance mechanisms:
 - exclude Al from roots
 - raise pH in rhizosphere
 - excrete organic mucilage to complex Al & prevent uptake
 - produce organic acids to combine with Al to produce nontoxic compounds

BIOLOGICAL EFFECTS OF SOIL pH

Mn, H & Fe toxicity to plants:

- Mn toxicity:

- problems not as widespread as with Al
- Mn is an essential element but is toxic in high conc
- problems can begin at pH < 5.6
- greater problems in low O₂ soils [Mn(II) is more soluble than Mn(IV)]

- H⁺ toxicity:

- can occur at pH < 4.0-4.5
- primary damage is to root membranes
- may also kill *Rhizobium* bacteria (N-fixing)

- Fe toxicity:

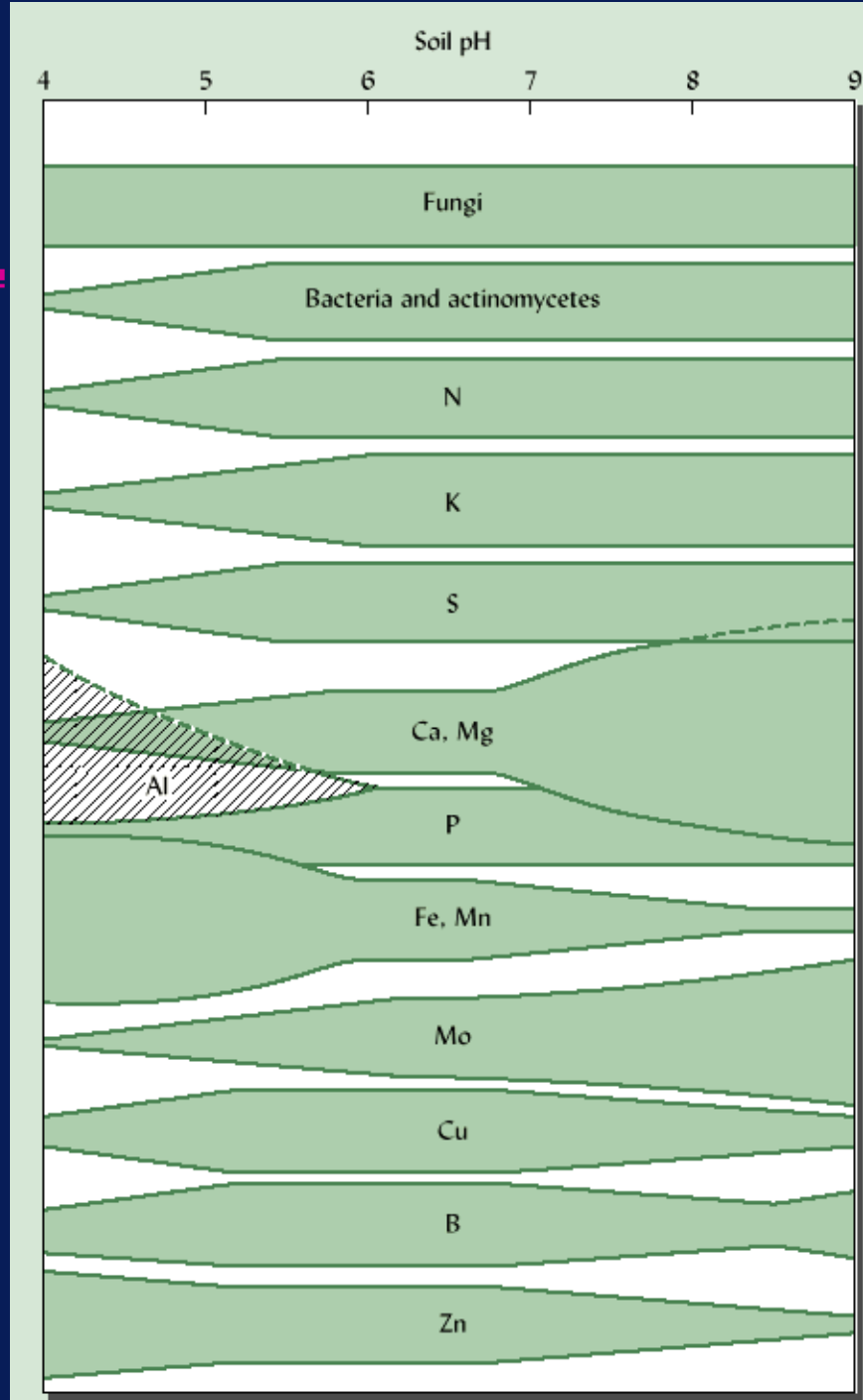
- may become toxic at pH < 4.0
- may become more available & toxic in low O₂ soils

BIOLOGICAL EFFECTS OF SOIL pH

- **Nutrient availability to plants:**
 - major influence of pH on nutrient availability
 - different effects on different elements (**Fig 9.22**)
 - best general pH range is from 5.5 to 6.5
- **Microbial effects:**
 - fungi function well at all pH levels
 - bacteria & actinomycetes function well at intermediate & high pH levels
 - can often use pH to control plant diseases
- **Optimal pH conditions for plant growth:**
 - optimal pH varies widely as a function of species
 - generally is related to availability of nutrients
 - management: lawn - high pH; azaleas - low pH
 - see Text, Figure 9.23

SOIL pH & NUTRIENT AVAILABILITY

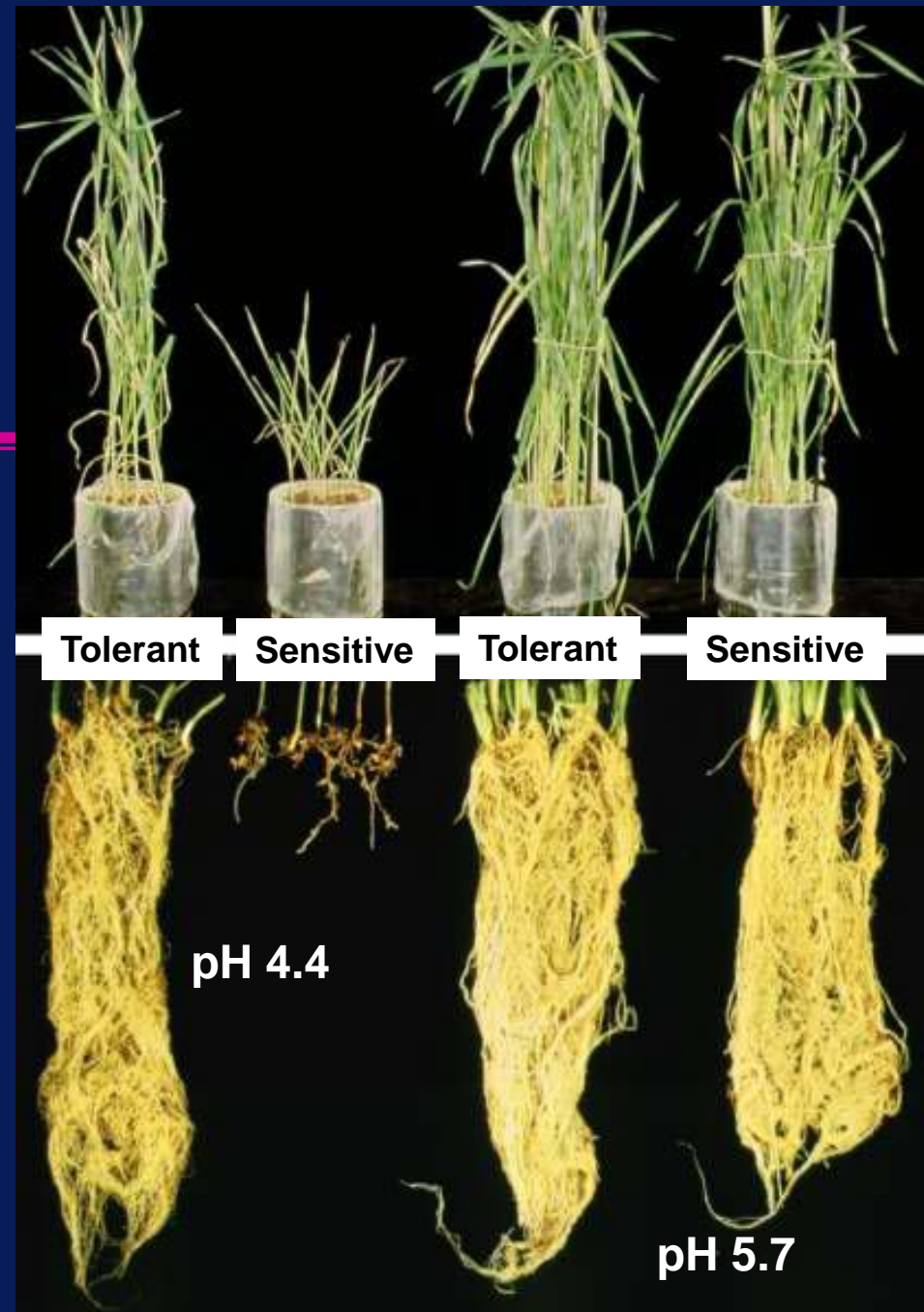
Relationships existing in mineral soils between pH on the one hand and the activity of microorganisms and the availability of plant nutrients on the other. (Fig 9.22)



BIOLOGICAL EFFECTS OF SOIL pH

- **Soil pH & organic molecules:**
 - in low pH soils, ionic herbicides containing -NH_2 & -COO^- groups will protonate (gain H^+)
 - the positively charged molecule will be attracted to negatively charged soil colloids
 - herbicides thus effected will generally be less effective and will have less leaching potential
 - thus, management decision on soil pH level

Influence of pH on the growth of roots and shoots from two wheat varieties



(Figure 9.21)

RAISING SOIL pH BY LIMING

Agricultural materials:

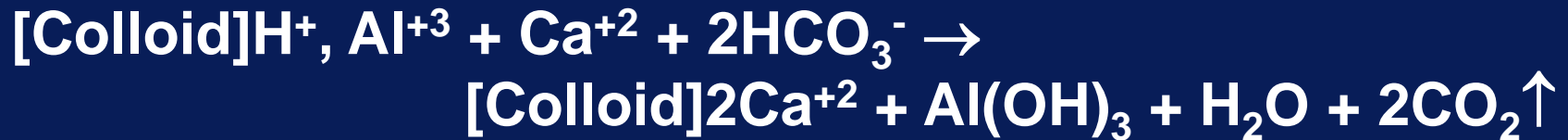
- substances which will supply conjugate base such as (CO_3^-) or (OH^-)
- $\text{CO}_3^- + \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
- generally use agricultural limes, carbonates, oxides or hydroxides of Ca (& Mg)
- also supply Ca & Mg to plants
- *“the purpose of liming is usually to change the chemical makeup of a substantial part of the root zone”*

RAISING SOIL pH BY LIMING

How liming materials react to raise soil pH:



Bicarbonates are soluble & reactive with the active & residual soil acidity



RAISING SOIL pH BY LIMING

Lime requirement: How much lime is needed to do the job?

- **Current and desired pH:**

- generally want to improve growth of acid sensitive plants
- optimal ranges for many plants shown in Fig 9.23
- add to contaminated soil to bind toxic metals or to stimulate bacteria in degrading contaminant

- **Soil buffer capacity:**

- most important parameter; must measure this
- varies with texture; related to clay & OM (CEC)
- see Fig 9.8 and Box 9.4
- can approximate the amount of needed lime

RAISING SOIL pH BY LIMING

Lime requirement: How much lime is needed to do the job?

- **Buffer pH methods for lime requirement:**
 - add specially buffered solution that contains a small amount of a neutral salt
 - change in pH of buffer is quantitatively related to the proportion of acidity released from soil
- **Exchangeable Al:**
 - base lime requirement on amount needed to eliminate the exchangeable Al
 - use the CEC value and % Al saturation (see text)
- **Influence of composition & fineness:**
 - need to know composition & purity
 - need to know particle size range
 - should have >50% particles < 60-mesh (0.25 mm)

RAISING SOIL pH BY LIMING

How lime is applied:

Frequency:

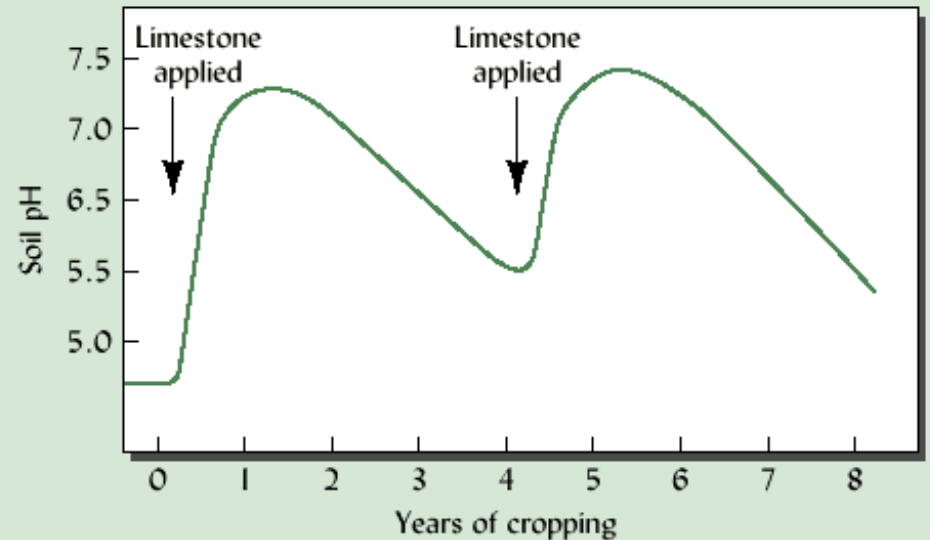
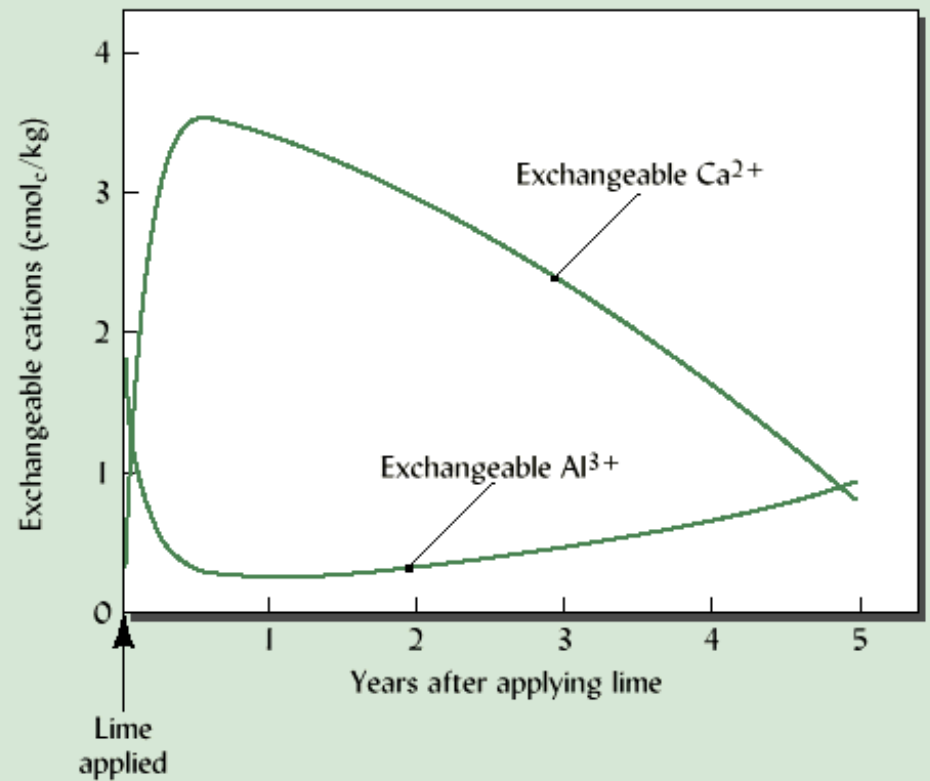
- after lime addition, reactions are slow (few months to one year depending upon liming agent)
- over time soil becomes more acid and lime is again needed (generally each 3-5 years- Fig. 9.25)

Timing:

- addition needed about 6-12 months ahead of critical crop needs
- apply when soil area is in physical condition to be least affected (i.e., in sod or hay crop)

CHANGES IN SOIL pH IN RESPONSE TO LIMING

Diagram to illustrate why repeated applications of limestone are needed to maintain the appropriate chemical balances in the soil. (FIG 9.25)



RAISING SOIL pH BY LIMING

How lime is applied:

- **Depth of incorporation:**

- application would be most beneficial if incorporated within the entire rooting zone
- economically & physically feasible to mix into the upper 15-20 cm of soil
- if subsoils are extremely acid, plant roots will be shallow and not able to utilize water there in summer
- sometimes may use special applicator that cuts deeper narrow slots for lime

- **Overliming:**

- may occur with overapplication, especially on coarse textured soils
- may induce deficiencies of Fe, Mn, Cu, Zn, P

RAISING SOIL pH BY LIMING

Special liming situations:

- **Liming forests:**

- rarely is practical; is very expensive
- must use aerial application
- may be worthwhile for acid, sandy soils

- **Untilled soils:**

- no-till farming, lawns, golf greens, other turf areas
- cannot cultivate these areas
- should be sure to treat severe problems before establishing vegetation
- use small frequent lime applications
- test for lime requirement; test after application

ALTERNATE WAYS TO AMELIORATE THE ILL EFFECTS OF SOIL ACIDITY

Gypsum applications:

- gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, does not raise the soil pH
- the Ca^{+2} and SO_4^{-2} ions leach into subsoil where reactions with Al^{+3} decrease Al toxicity
- in subsoil, the SO_4^{-2} may replace $-\text{OH}^-$ from oxyhydroxides to allow $\text{Ca}(\text{OH})_2$ form'n, which, in turn, may cause $\text{Al}(\text{OH})_3$ form'n

Using organic matter:

- sources such as: biosolids, cover crops, wastes
- Al^{+3} binds tightly with humified OM
- low-MW acids produced in rhizosphere react with Al^{+3} to form non-toxic complexes
- many OM types contain significant amounts of Ca which may cause reductions in Al^{+3} toxicity

ALTERNATE WAYS TO AMELIORATE THE ILL EFFECTS OF SOIL ACIDITY

Selecting adapted plants:

- **Selection of tolerant species:**
 - very often is much more cost effective than attempting to adjust & maintain soil pH
 - see Table 9.3 & Figure 9.23
- **Genetic improvement of acid tolerance:**
 - natural and selected variation of plant cultivars in tolerance to pH & Al effects (Figs. 9.21 & 9.29)
 - especially important for developing countries

LOWERING SOIL pH

Acid organic matter:

- many plants grow poorly or die at high soil pH
- most notable are azalias, rhododendrons & blueberries (see photos)
- OM types that are low in Ca will acidify soil (acid peat moss, pine needles, tanbark, pine sawdust)
- some OM types are alkaline (biosolids, poultry manures, leaf-mould of some deciduous trees)

Inorganic chemicals:

- “alum”, $\text{Al}_2(\text{SO}_4)_3$ or $\text{Fe}^{\text{II}}\text{SO}_4$
- hydrolysis of Al & Fe produces acidity
- elemental S: $2\text{S} + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4$
- pyrite, Fe_2S (“ironite”)

Highbush blueberry leaves with chlorosis, caused by Fe deficiency (bottom row)



Iron-deficient young orange leaves, with green veins and midrib (typical pattern).

