Soil Acidity and pH

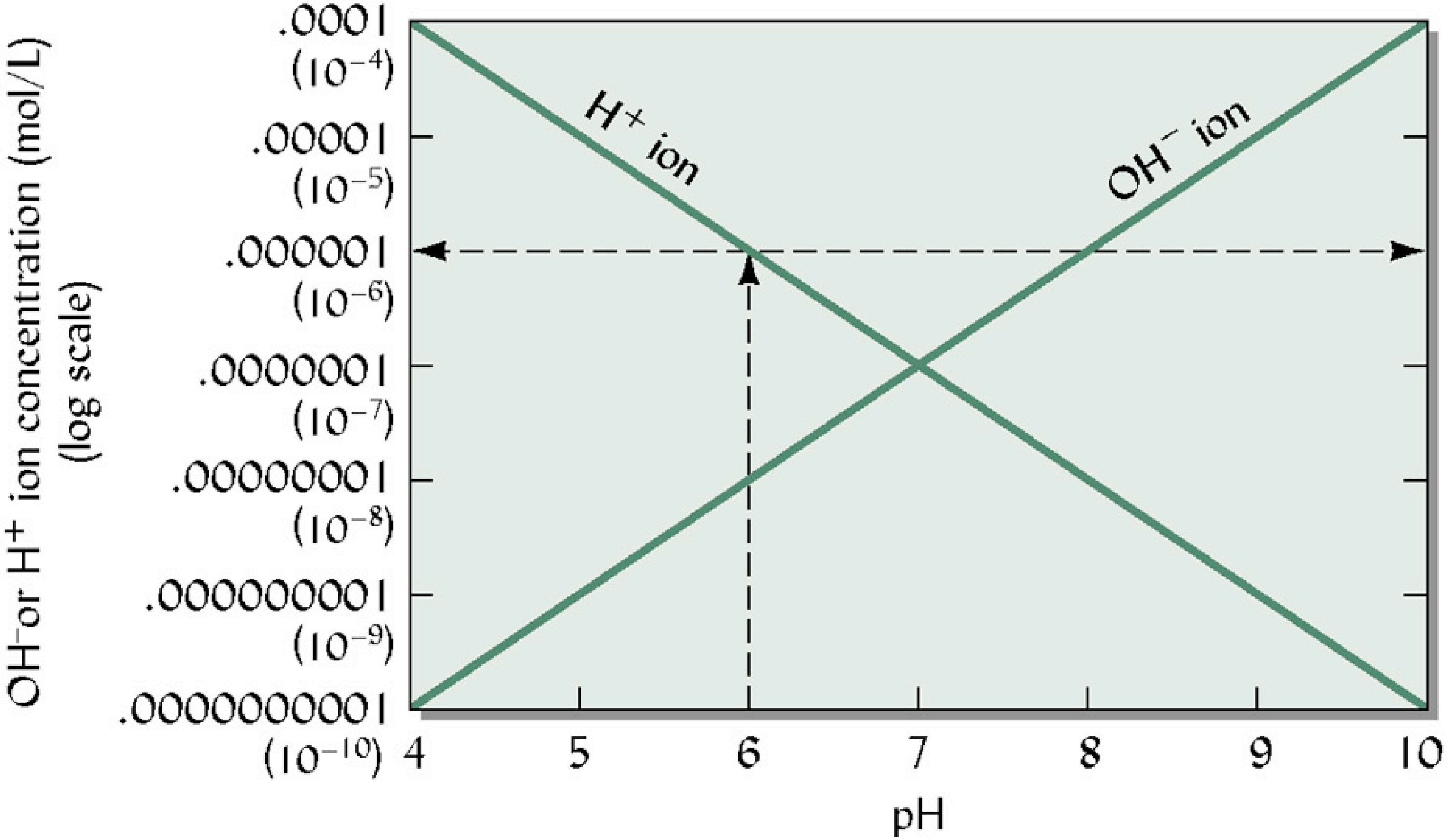
Acid Soil

pH

$pH = -\log(H^+)$

$$H_2O \leftrightarrow H^+ + OH^-$$

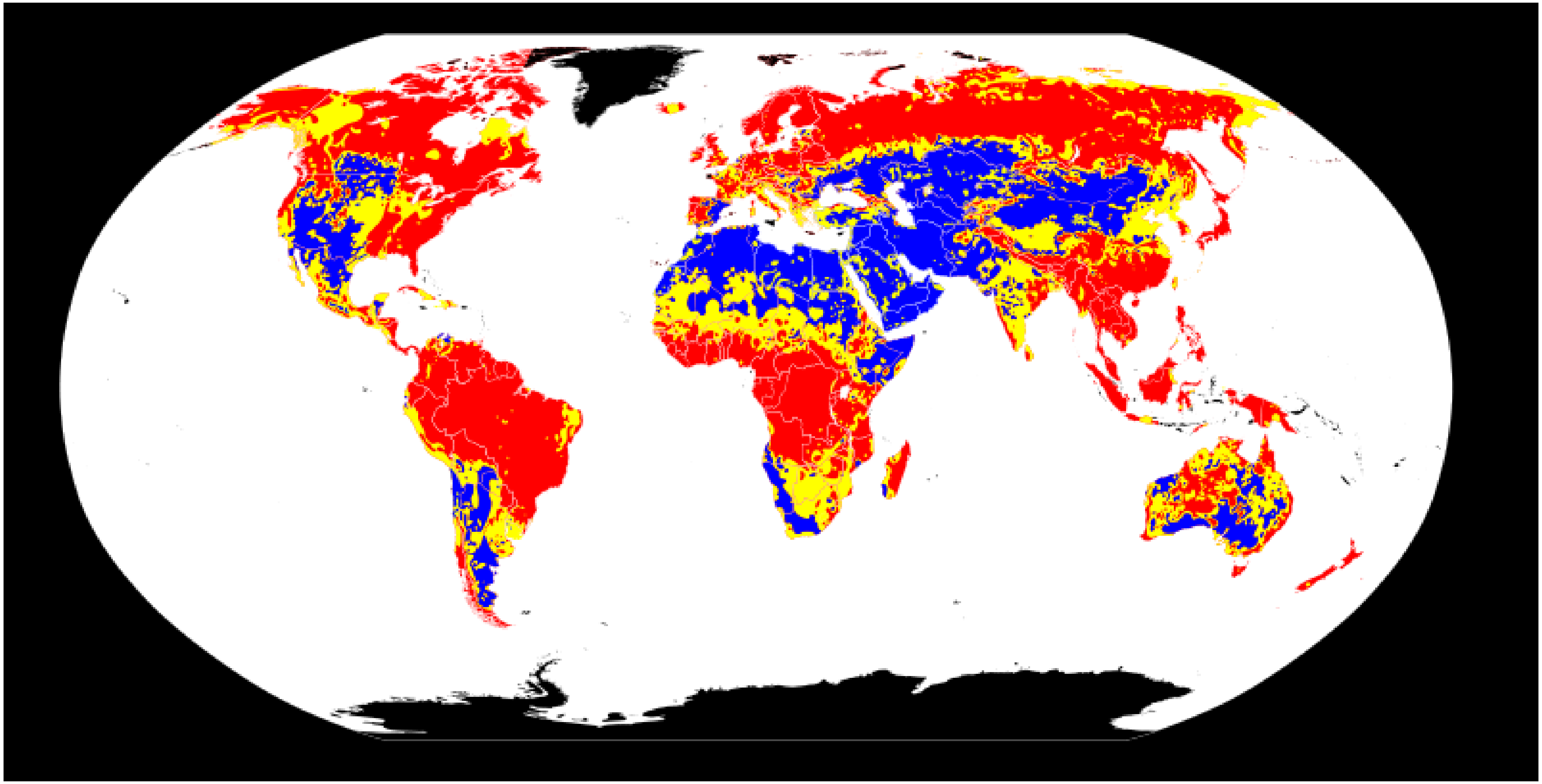
$$(H^+) \times (OH^-) = K_w = 10^{-14}$$



measures H^+ activity with an electrode (in the lab), solutions (in the field)

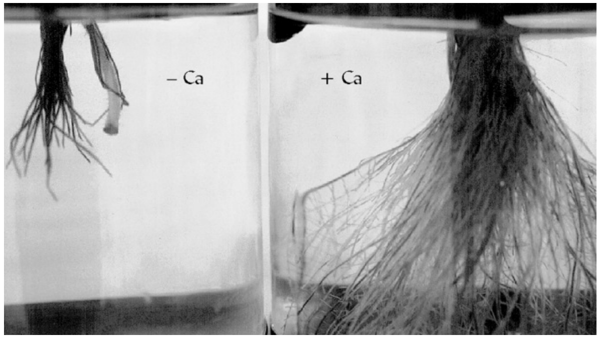
reflects the acid <u>intensity</u>, not total quantity

Soil pH values worldwide



red = acidic yellow = neutral blue = alkaline black = no data

Soil Acidity and pH: why do we care?



Direct effect on plant growth (roots) and microorganisms

- very low (< 3) or very high (>9) pH values

Indirect effects on plants and microorganisms

- low pH (~5 - 5.5):
    - Al and metal (Mn, Zn, Cu) toxicity
    - Ca and P deficiency (tropical soils)

<u>soluble levels</u> might be high enough to be biologically toxic

- high pH (> 7):
    - metal deficiency (Zn, Fe, Cu, Mn)

<u>solubility</u> of micronutrient low enough to reach deficiency values

Indicator of chemical imbalances

- pH > 8.5:
    - Na^+ on exchange sites
- pH < 3:
    - indicates that sulfides are (might be) present

Controls on chemical reactions:

- ion exchange; specific adsorption, precipitation; redox; weathering; solution speciation

Factors affecting Soil pH:

Balance between acid (H^+, Al^{3+}) and non-acid (Ca^{2+}, Mg^{2+}, K^+, Na^+) cations on colloid surfaces

Balance between acid (H^+) and base (OH^-) in the soil solution

Soils resist changes in pH: buffering reactions

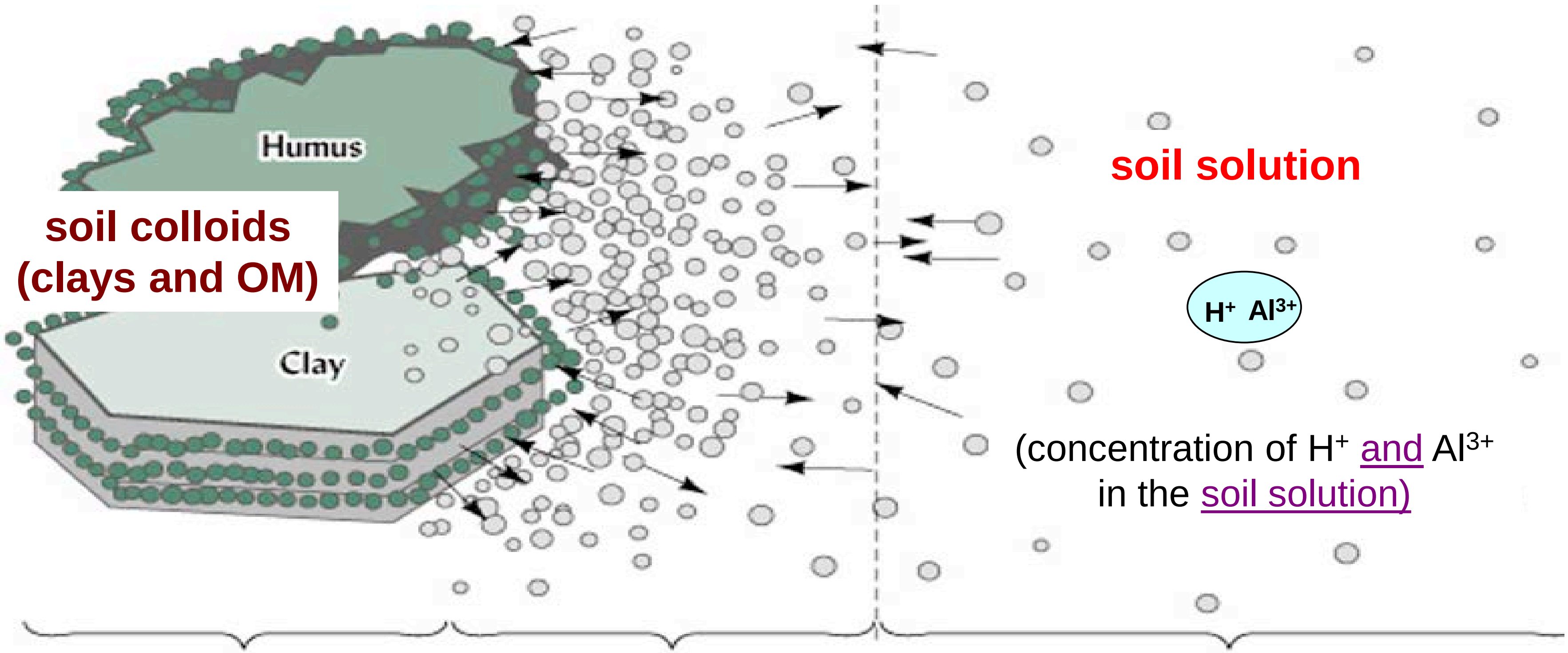
Resist increases in pH: reserve acidity

Resist decreases in pH: buffering capacity

Changes in the chemistry of the soil solution reflect-- or are a consequence of-- changes in the chemistry of the soil solids

Active and Reserve Acidity

total acidity = (residual + exchangeable) + active



residual | exchangeable | **active acidity**

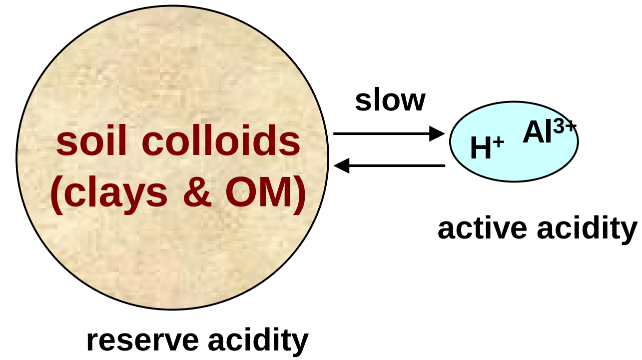
reserve acidity → **quantity that represents the *buffer capacity* of the soil**

- acidity retained on soil solids – surface acidity
- explicit: **proton**; latent: **proton-generating forms**

Active and Reserve Acidity

total acidity = active + (exchangeable + residual)

Forms of reserve acidity:



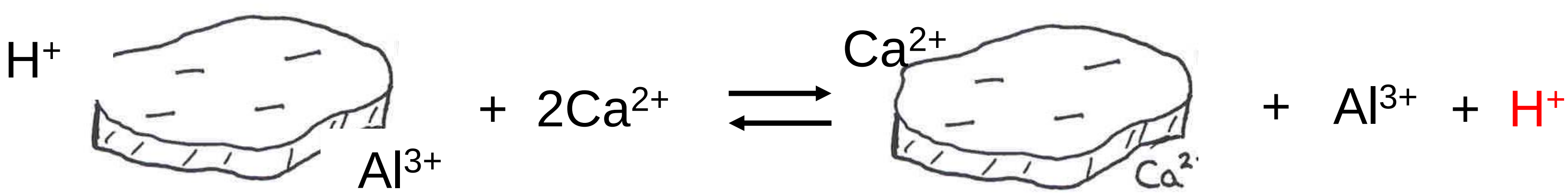
quantity that represents the *buffer capacity* of the soil

Acidity (H^+) release by cation exchange and hydrolysis:
exchangeable H^+ and Al^{3+}

$$Ca^{2+}/K^+ + H^+\text{-smectite} = H^+ + Ca^{2+}/K^+\text{-smectite}$$

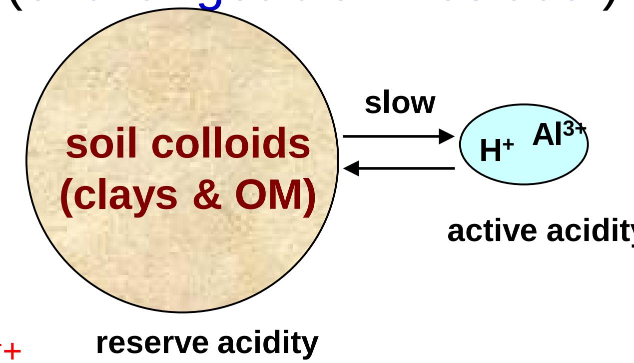
$$Ca^{2+}/K^+ + Al^{3+}\text{-smectite} = AlOH^{2+} + Ca^{2+}/K^+\text{-smectite} + H^+$$

$$\text{Colloid-}Al^{3+}/H^+ \text{ (solid)} + Ca^{2+}/K^+\text{(aq)} = \text{Colloid-}Ca^{2+} \text{ (solid)} + Al^{3+} + H^+$$



Active and Reserve Acidity

total acidity = active + (exchangeable + residual)



Forms of reserve acidity:

residual: -acidity retained on soil solids – surface acidity

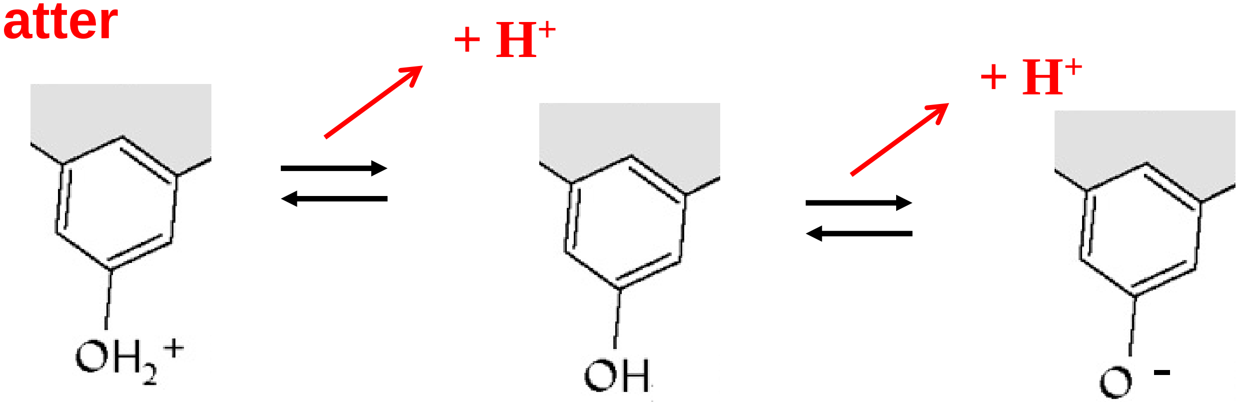
Minerals/clays

$$> Al - OH_2^+ \overset{+\,H^+}{\rightleftharpoons} > Al - OH\,]^0 \overset{+\,H^+}{\rightleftharpoons} > Al - O^-$$

non-exchangeable forms of acidity on minerals

$>Fe\text{-}OH_2]^{+1/2} = >Fe\text{-}OH]^{-1/2} + H^+$

Organic Matter



acidity (H^+) release by dissociation of organic molecules

R-H =

Low pH

positive charge

High pH

negative charge

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Soils resist changes in pH: buffering reactions

Resist increases in pH: reserve acidity

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Mechanisms involved in the soil's ability to buffer pH

Changes in the chemistry of the soil solution reflect-- or are a consequence of-- changes in the chemistry of the soil solids

Mechanisms involved in the soil's ability to buffer pH to acid additions

High pH (>7):

- dissolution of basic minerals (e.g. Ca and Mg carbonates)

$$CaCO_3 + \mathbf{H^+} = \underbrace{HCO_3^- + Ca^{2+}}$$

acid neutralization reaction

carbonic acid, organic acids, acid rain

leaching of bicarbonate salts from soil surface

Low pH (< ~ 5.5):

oxide charging:

$$>Fe\text{-}OH]^{-1/2} + \mathbf{H^+} = >Fe\text{-}OH_2]^{+1/2}$$

increases reserve acidity

weathering rxns:

primary mineral or layer aluminosilicate clay + $\mathbf{H^+}$ = $Si(OH)_4^0$ + $Al(OH)_{3(solid)}$ + base cations

(monosilicic acid)

Very low pH (< ~ 4):

oxide dissolution:

$$Al(OH)_3 + \mathbf{H^+} = Al^{3+} + H_2O$$

part of the acidity accumulates (soluble and exchangeable Al)

$$MnO_2 + \mathbf{H^+} = Mn^{2+} + H_2O \qquad FeOOH + \mathbf{H^+} = Fe^{3+\text{ or }2+} + H_2O$$

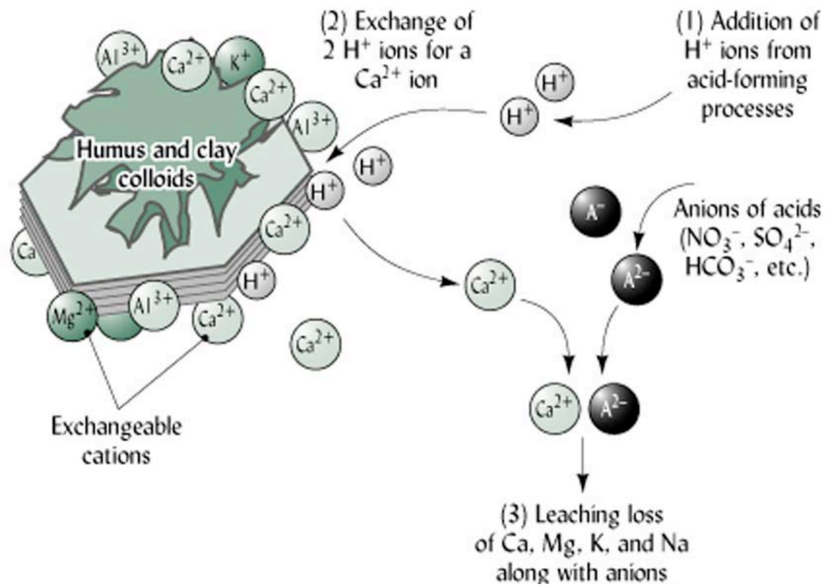
reduction rxns

Acid soils are more sensitive to strong acids since the buffering must be achieved by dissolution reactions

Mechanisms involved in the soil's ability to buffer pH

to acid additions

Moderate pH (5.5 to 7):



- displacement of base cations (exchangeable base cation buffering)

$$2H^+ + \text{Ca-clay} = 2H^+\text{-clay} + Ca^{2+}$$

$$2H^+ + \text{Ca-OM} = 2H^+\text{-OM} + Ca^{2+}$$

reduces acidity

- buffering capacity depends on the quantity of exchangeable base cations in the soil

- not a neutralization reaction; <u>increases the reserve acidity</u> pool of the soil

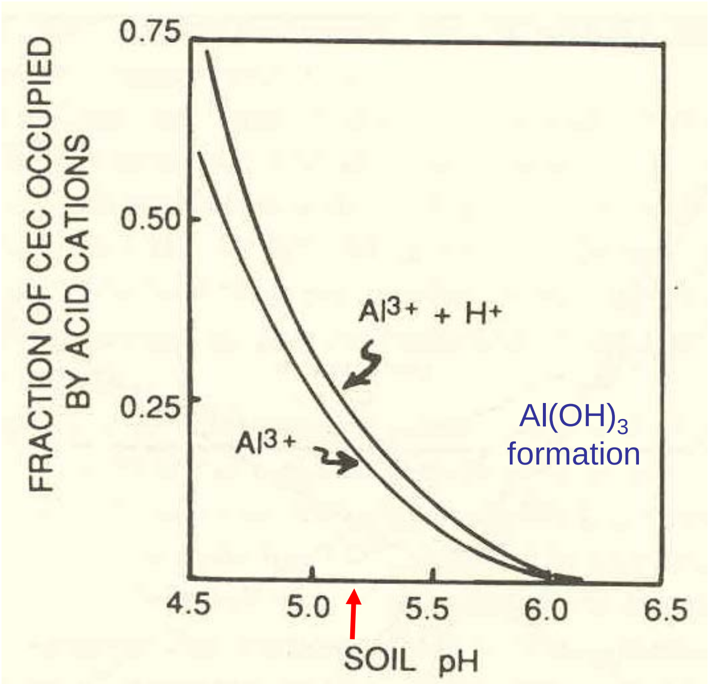
- leaching can result in depletion of exchangeable base cations from the soil

High OM and layer silicate clay content α base cation buffering capacity α CEC (as Σ base cations)

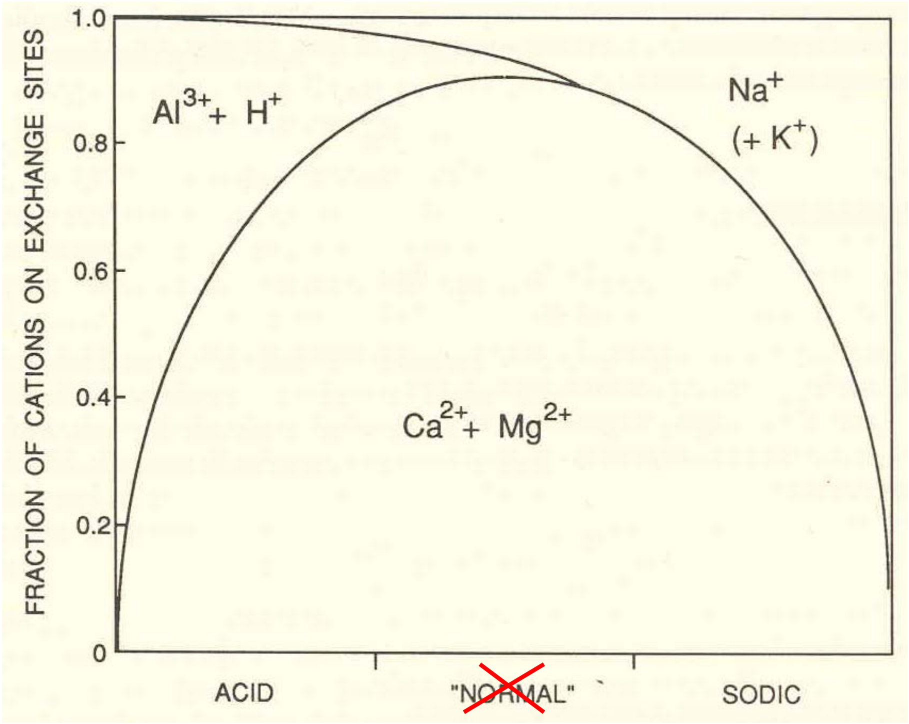
Exchangeable Aluminum (and other cations) in Soils

Unique characteristic of acid soils

Acidic cations (Al^{3+} and H^{+}) on soil exchange sites vs pH



Relative cation composition of exchange sites in sodic, “typical” and acid soils



Aluminum Toxicity

- most common severe problem associated with acid soils

- plant and bacteria populations are affected (plants by (1) blocking Ca entrance into plants, (2) binds with P (in ATP) which inhibits energy transfer and genetic coding, and (3) restricts cell wall expansion)

- rarely a problem above a pH of 5.2

Saturation of Cation Exchange Sites

Base Saturation

$$BS = \frac{\text{number of exchange sites occupied by Ca + Mg + K + Na}}{\text{total number of exchange sites}} \times 100$$

Cation Saturation Percentage (saturation by a given ion)

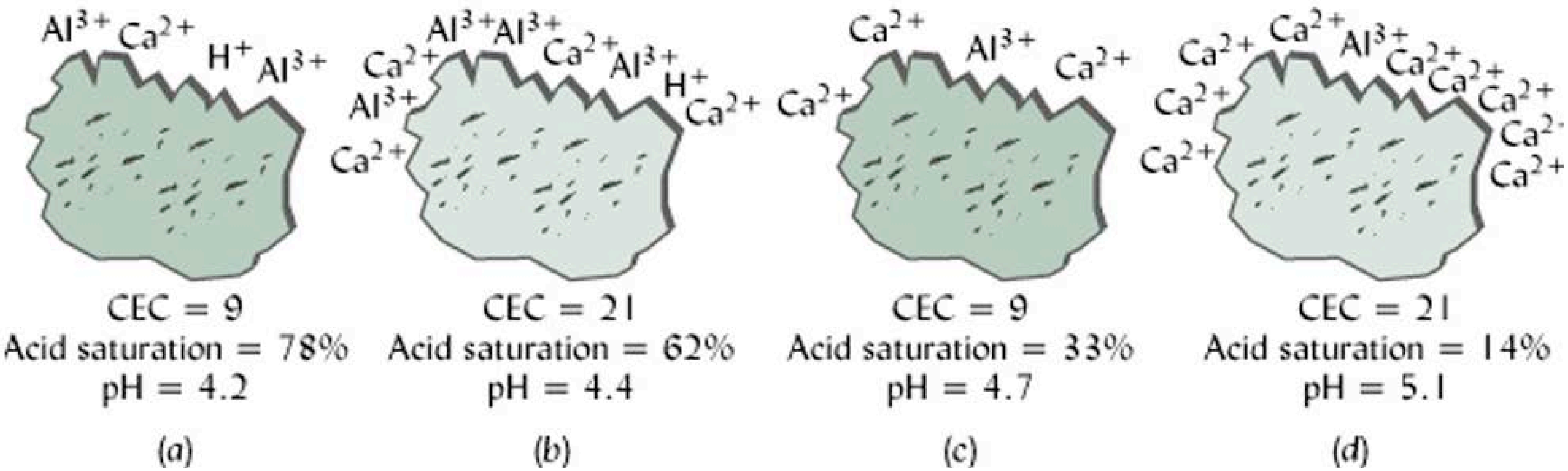
$$\text{“X”S} = \frac{\text{number of exchange sites occupied by cation X}}{\text{total number of exchange sites}} \times 100$$

Acid Cation (Al^{3+} and H^{+}) Saturation Percentage

$$AS = \frac{\text{number of exchange sites occupied by Al + H}}{\text{total number of exchange sites}} \times 100$$

Acid Cation (Al^{3+} and H^+) Saturation Percentage

$$\% \text{ Acid Saturation} = \frac{\text{cmol}_c \text{ of exchangeable } Al^{3+} + H^+}{\text{cmol}_c \text{ of CEC}} \times 100$$



3 acid cations	5 acid cations	1 acid cation	1 acid cation
7 mol_c	13 mol_c	3 mol_c	3 mol_c

pH is more closely related to the % acid saturation than to the absolute amount of acid cations

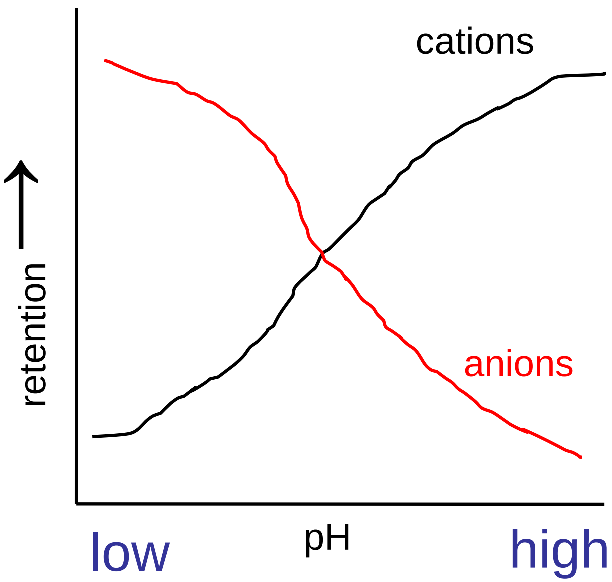
Nutrient Availability

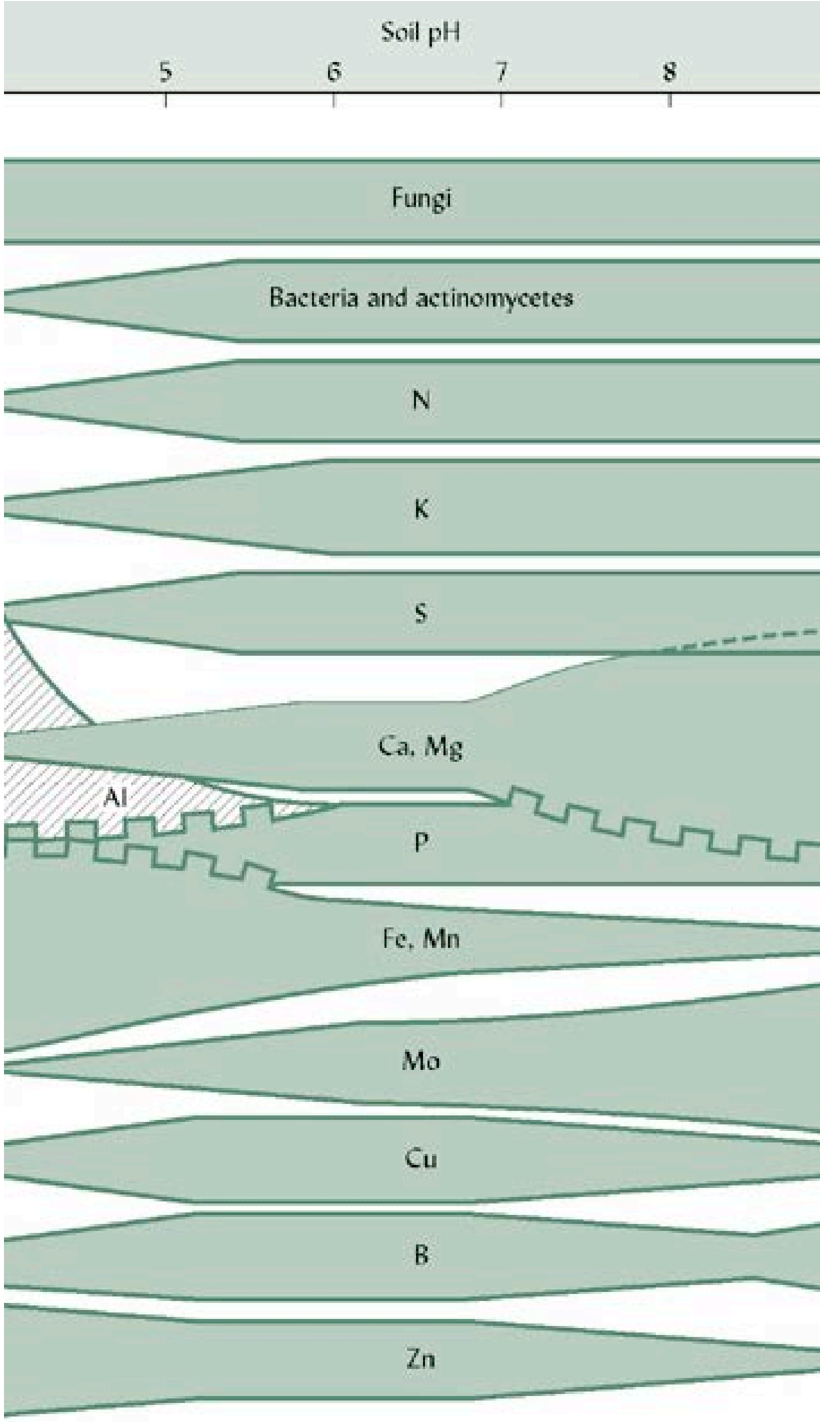
At low pH values (high acidity):

- the availability of macronutrients is limited (e.g., Ca, Mg, K, P, N, and S)

- the availability of most micronutrients increases (e.g., Fe, Mn, Zn, Cu and Co)

(leaching losses, increased solubility, sorption anions)





Optimum pH range for nutrient availability: **5.5-6.5**

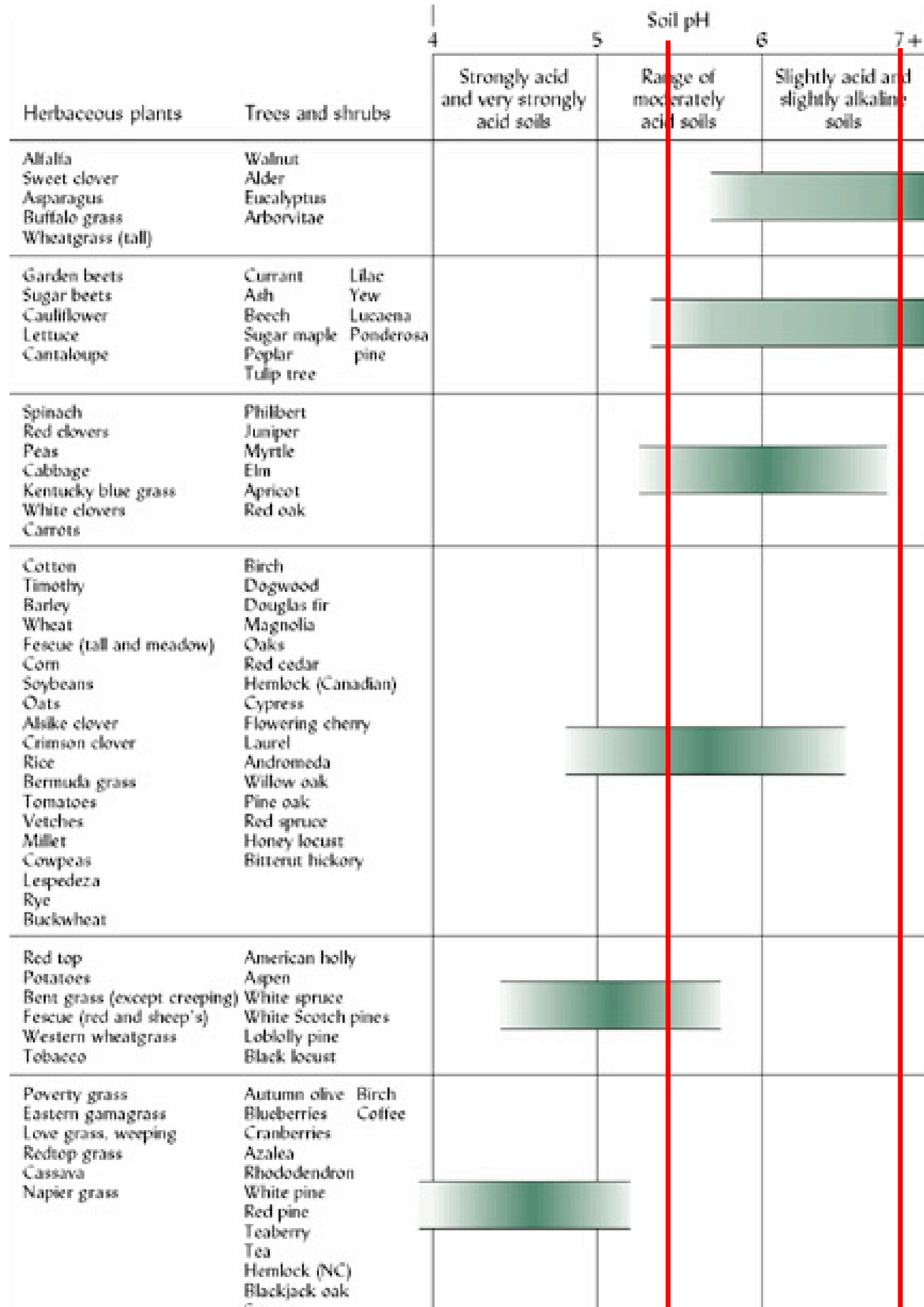
Appropriate pH conditions for optimal growth of various plants

Plants vary considerably in their optimum pH growth range: appear to be based on sensitivity to Al and their requirement for Ca

Species with high Ca nutrient needs require high pH's where more Ca is available

Species that have optimum ranges in the lower pH's, are typically forest species from humid regions and have developed tolerance for high [Al] and often require higher [Fe] which is more available at low pHs

Most cultivated crops grow well in soils with a slight acidity (5.5 to 7)



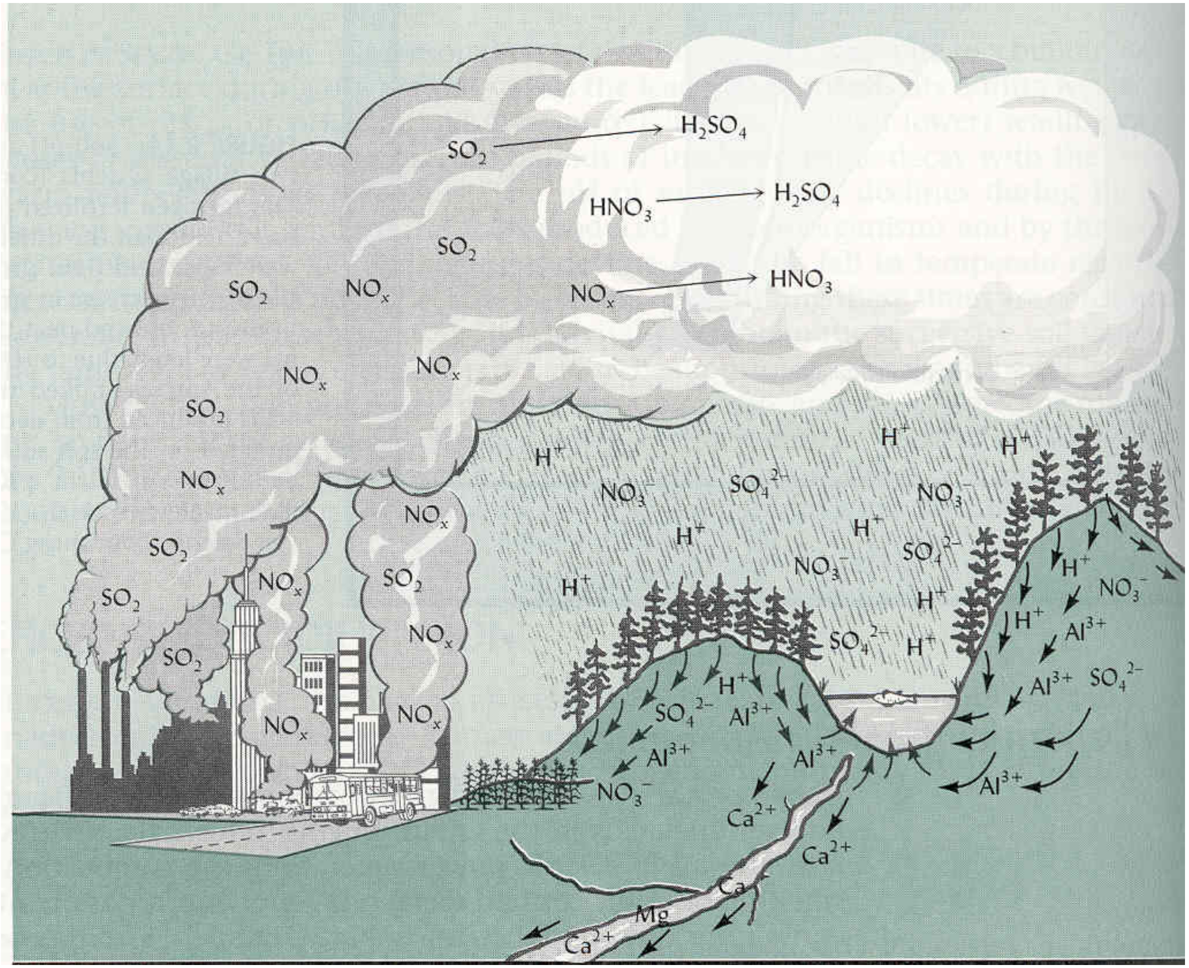
Chemically: What is the result of soil acidification?

decrease in soil pH (eventually)

augment the reserve acidity of soils

decrease buffering capacity of soils

mineral dissolution



Formation of acid rain and its impact on distant watersheds. N and S emissions from combustion of fossil fuels (electric power plants, vehicles). Sulfuric and nitric acids (in clouds) return to earth in precipitation and dry deposition. Soil acidification occurs – accelerate Ca and Mg losses. The principal ecological effects in sensitive watersheds are the decline in forest health and aquatic ecosystems.