What is going on in the environment to produce a specific pH at one “place” and a different pH at another “place”?

What are the consequences of pH?

So what is it about the environment?

large and small scale

1. Pools of Soil Acidity
    1. active
    2. exchangeable
    3. residual

Total Acidity = active + exchangeable + residual

2. Buffering of pH in Soils

1. Active Acidity

The $[H^+]$ ion concentration in the soil solution

While this pool is a relatively small pool of the total acidity…

it is extremely important as it determines the solubility of substances in the soil

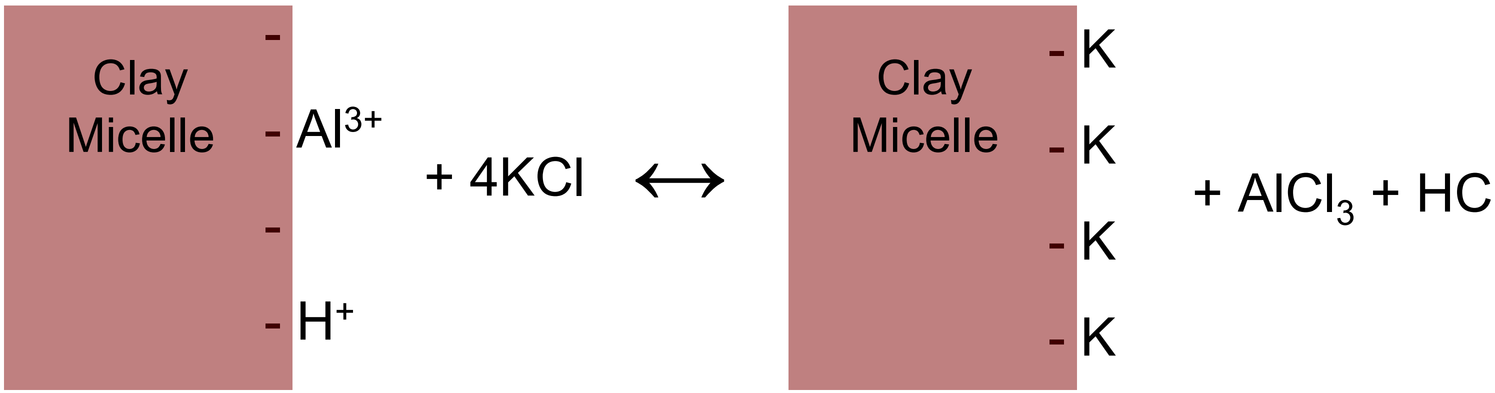
NB: this is the acidity that you are measuring when you do standard pH testing – e.g. what you did in the field

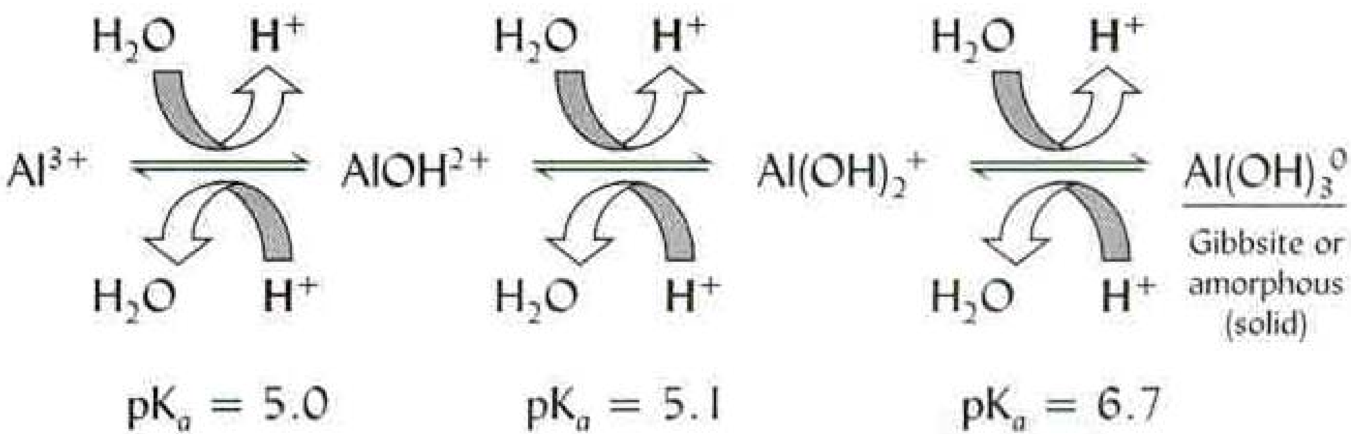
2. Exchangeable Acidity

- often termed salt replaceable

Primarily associated with exchangeable Al and H ions

- ions associated with the cation exchange sites

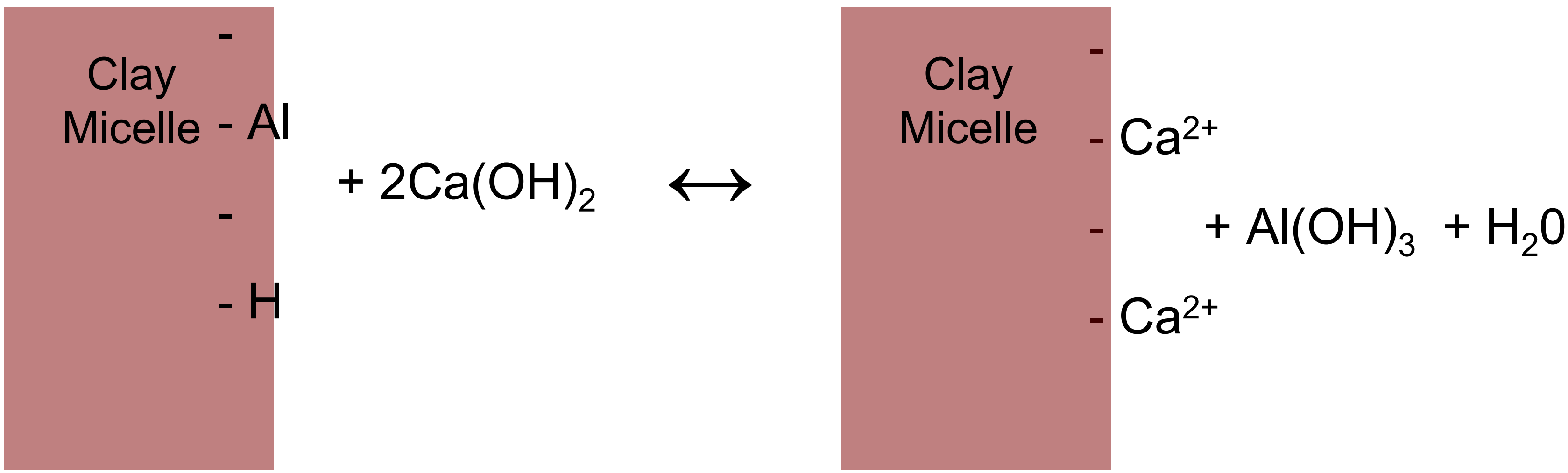




NB: The Al can then hydrolyze H_2O and increase the active acidity

3. Residual Acidity

Primarily associated with non-exchangeable Al and H ions within the phylosilicate crystal structure or organic matter



3.5 Reduced Sulfur

Sulfuricization

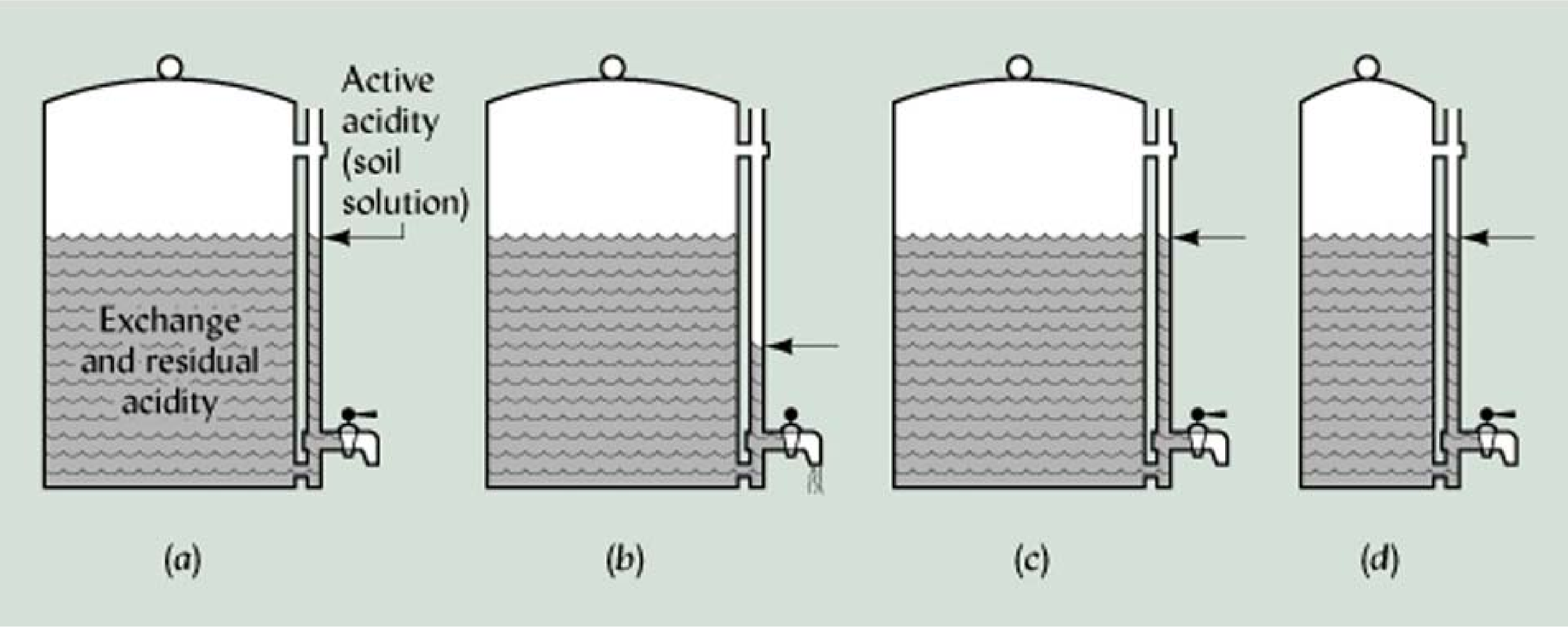
$$FeS_2 + 3.5\ O_2 + H_2O \leftrightarrow FeSO_4 + 2H^+ + SO4^{2-}$$

Total Acidity = active + exchangeable + residual

So if our pH measurements are only accounting for the active acidity…

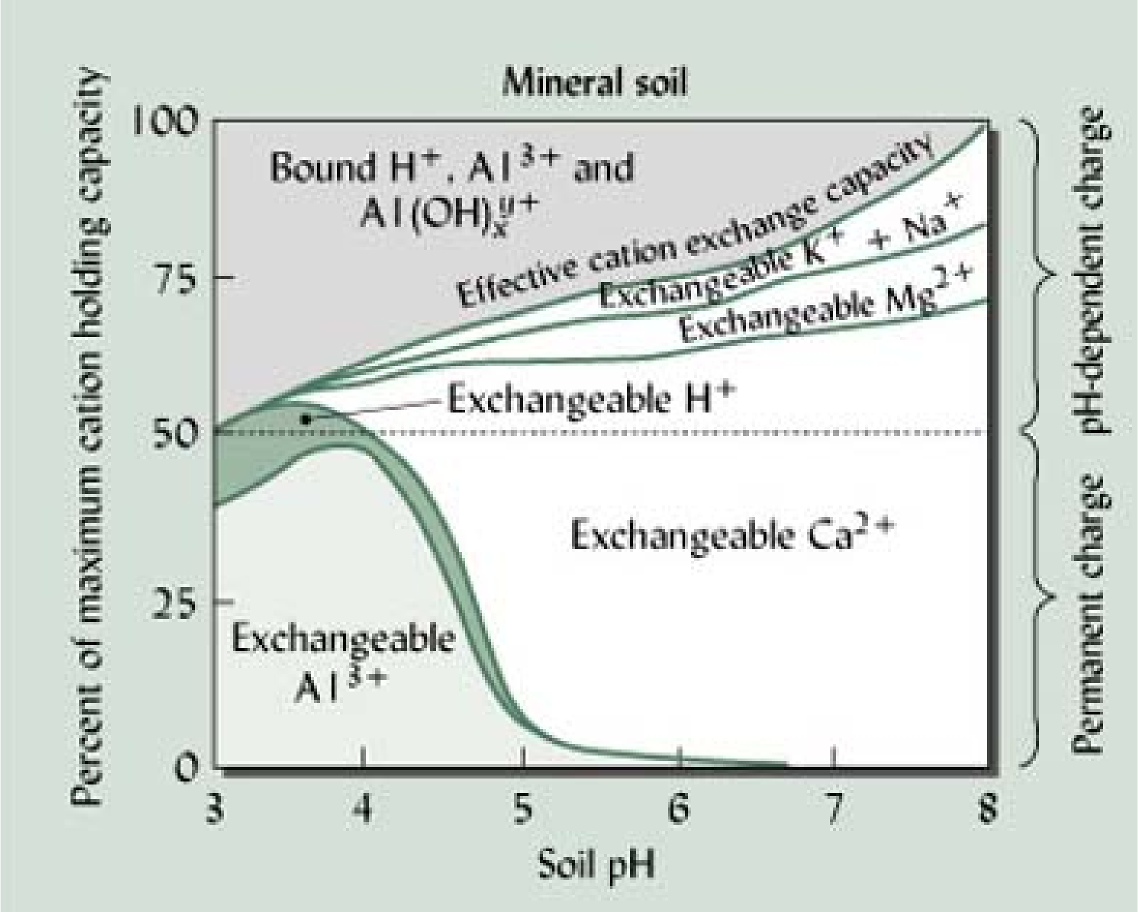
we need to account for total acidity when

we are managing the pH's of the soil

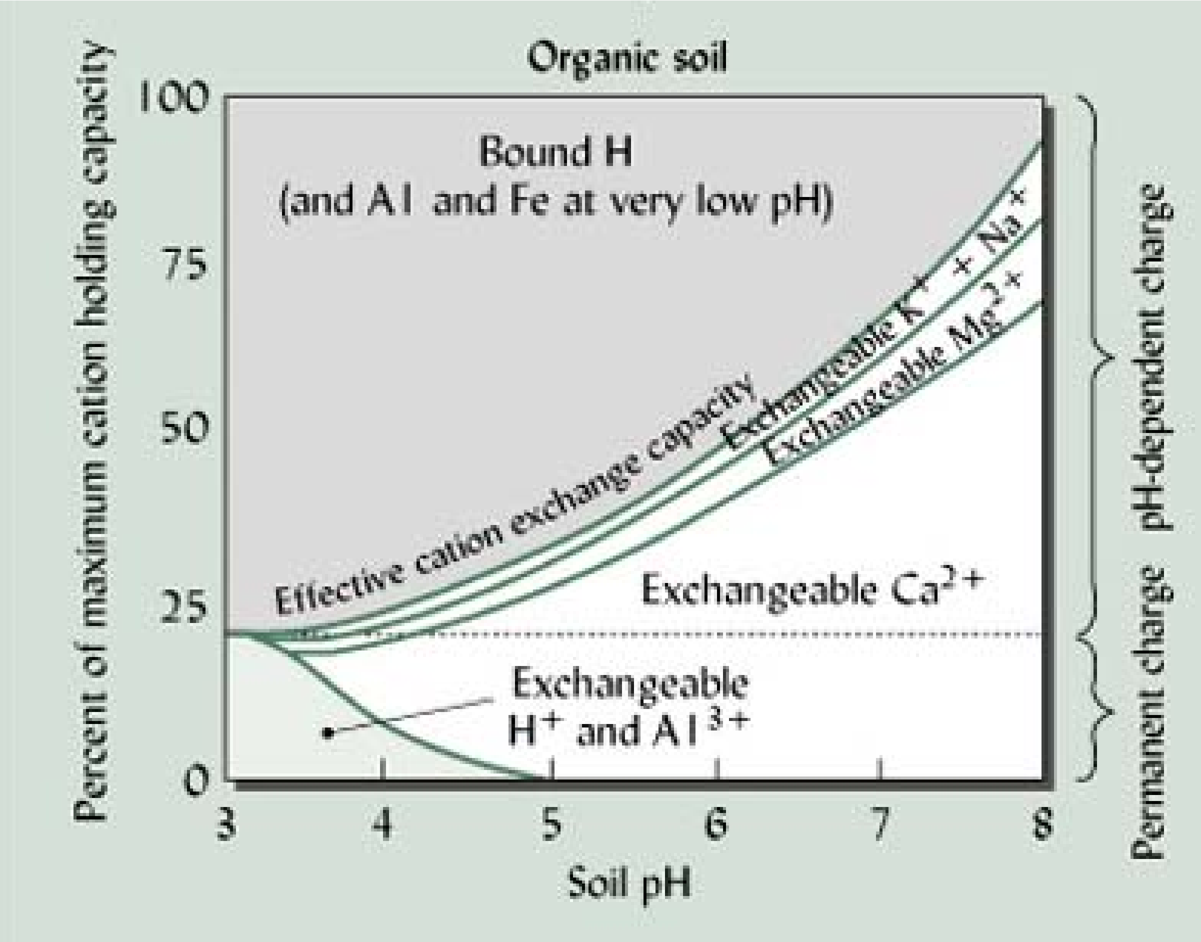


The exchange and residual acidity pools are associated with exchange and structural cations

What about this relationship between pH and exchangeable cations



This same relationship occurs with Organic Soils, but…



MANAGEMENT OF SOIL ACIDITY

ACID	5.5	8.5	ALKALINE
USUALLY REQUIRES LIME	MINIMAL MANAGEMENT		MAY NEED ACIDIFICATION (MICRONUTRIENT DEFICIENCIES)

Soil pH may shift on this scale:

- cropping in humid climates slowly decreases pH

- pH in arid climates may increase due to alkalinity in incoming water

LIME = an alkaline substance (base) that neutralizes H^+

LIMING MATERIALS -

$CaCO_3$ (limestone)
$CaMg(CO_3)_2$ (dolomitic limestone)
$Ca(OH)_2$, $Mg(OH)_2$ costly
Ca silicate costly

CEC only measures the capacity of a soil to hold exchangeable cations

Base Saturation is a measure of base cations located on the exchange sites.

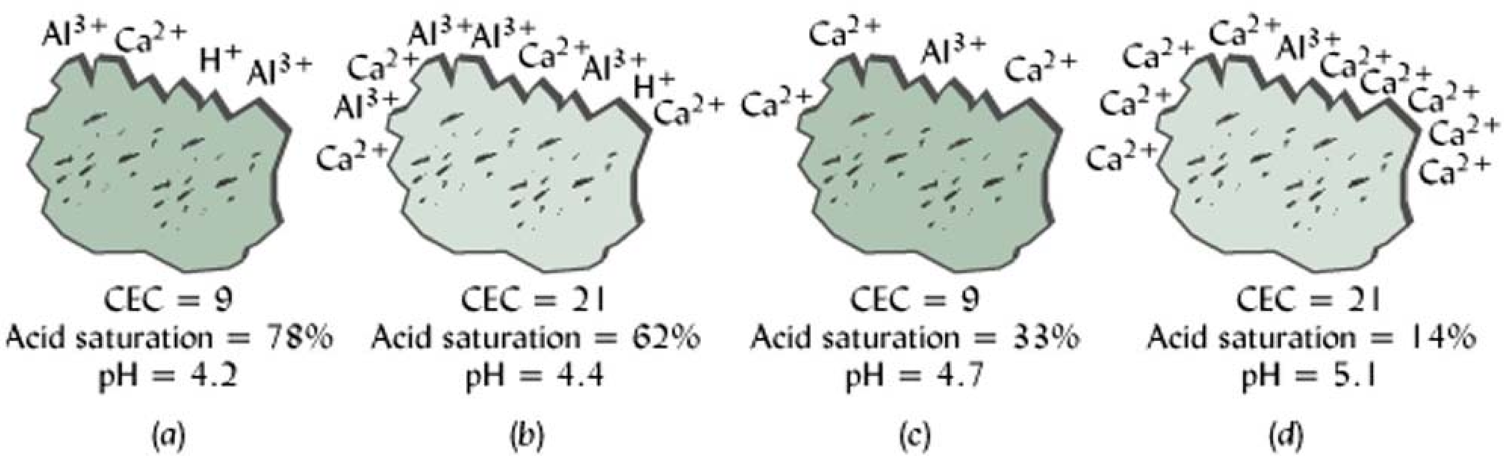
Base Cations* (Ca, Mg, K and Na) or non-acid cations
vs.
Acid Cations (Al^{3+} and H^{+})

Base Saturation = the percentage of CEC sites occupied by bases

*Technically these non-acid base cations are not bases, but they do serve to reduce acidity and increase the pH in the soil solution – hence the term “base”

1. Nonacid (Base) Saturation
2. Cation Saturation Percentage (saturation by a given ion)
3. Acid Cation (Al^{3+} and H^{+}) Saturation Percentage

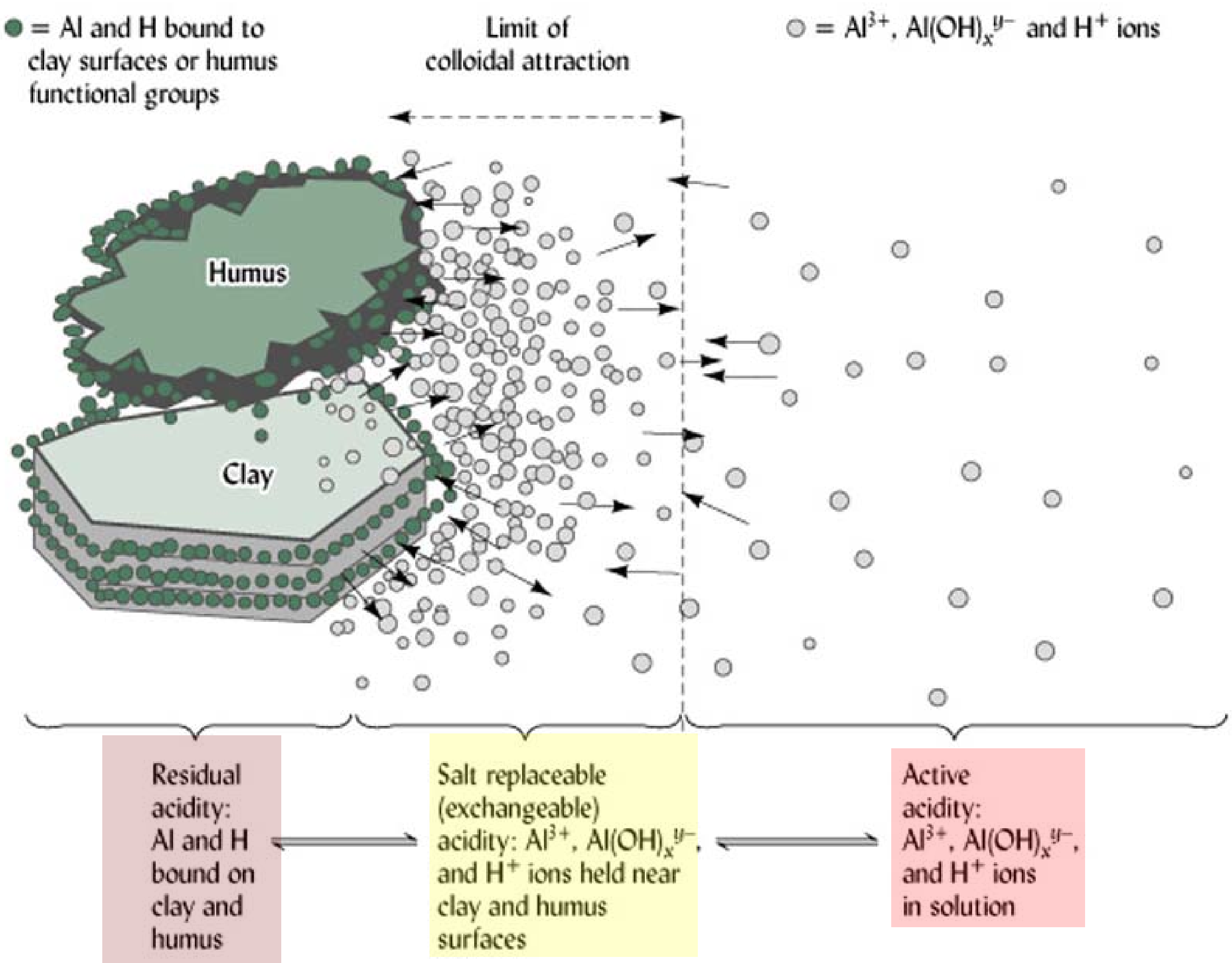
$$\% \text{ Acid Saturation} = \frac{\text{cmol}_c \text{ of exchangeable } Al^{3+} + H^{+}}{\text{cmol}_c \text{ of CEC}}$$



Buffering of pH in Soils

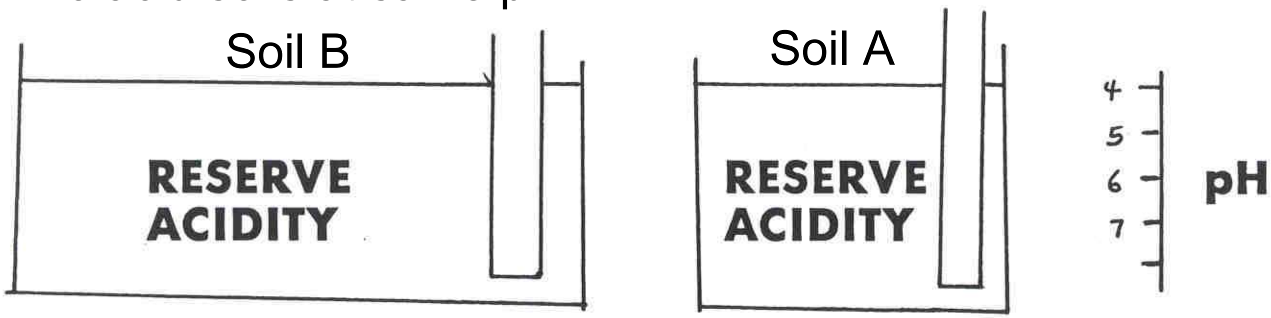
Soils tend to resist changes in pH

– this is termed a soil's buffering capacity (buffering for short)



$$Al(OH)_3,\ H_2O \xleftarrow[+\text{ lime}]{\text{fast}} \boxed{\text{ACTIVE ACIDITY}} \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}} \boxed{\text{RESERVE ACIDITY } (Al^{3+},\ H^{+} \text{ on colloids})}$$

Two acid soils at same pH



WELL-BUFFERED | **WEAKLY BUFFERED**

BUFFER CAPACITY OF SOIL

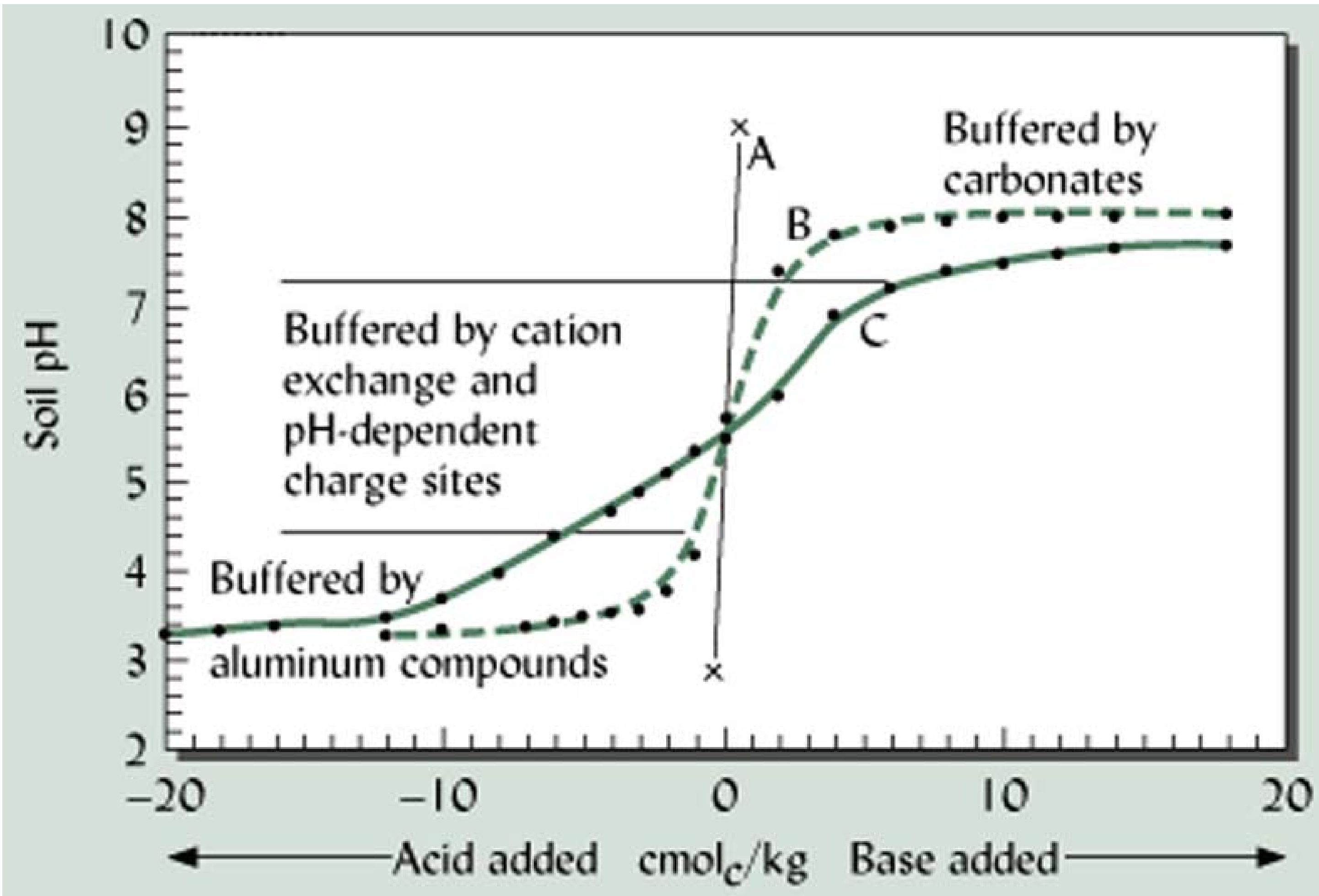
= capacity to release or neutralize Al, H

= amount of acid/base needed to bring about a specific shift in pH

A —— water

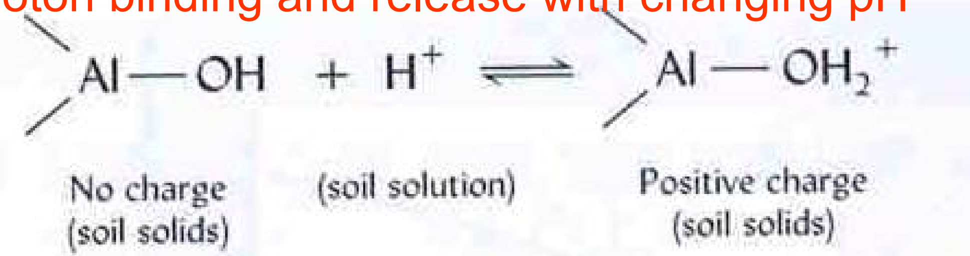
B - - - moderately buffered soil

C —— well buffered soil

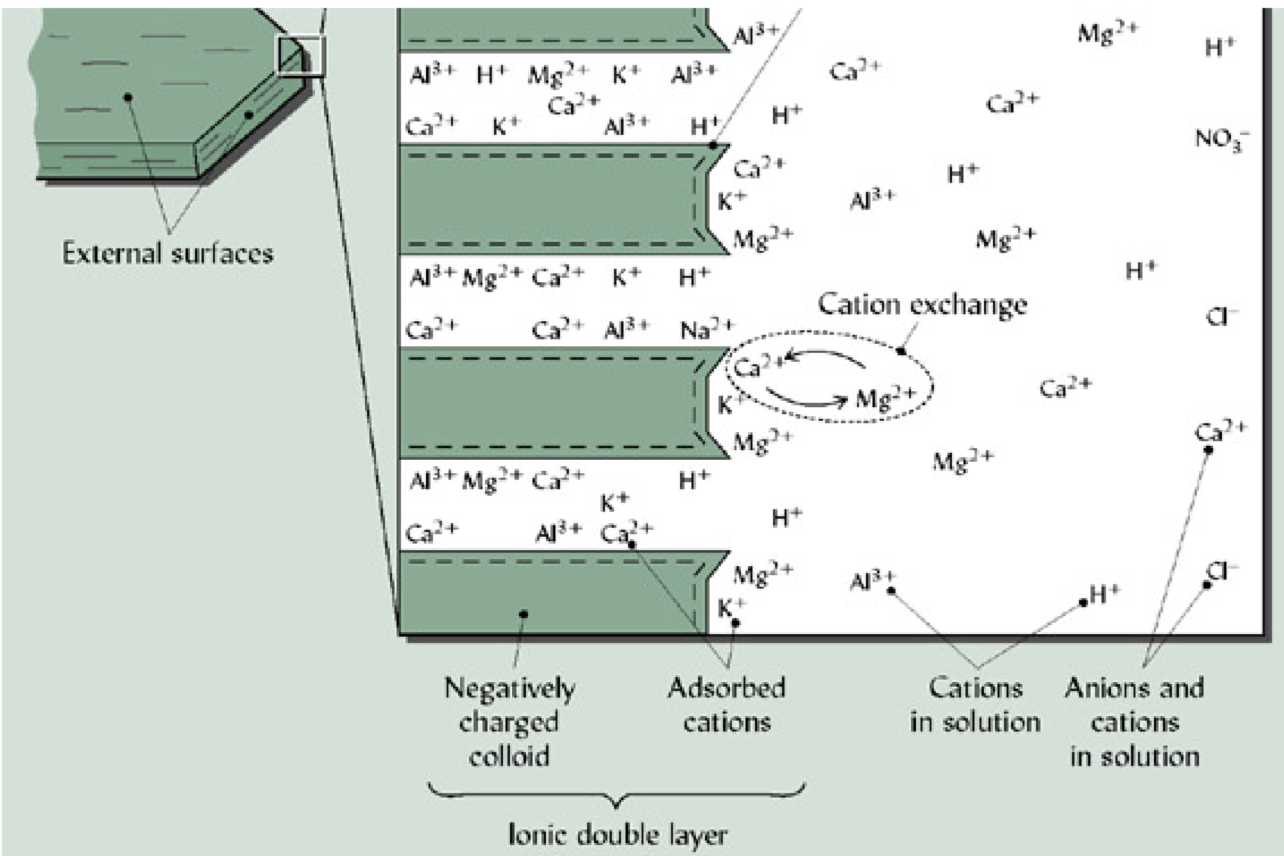


Buffering in the middle – pH’s 4.5 to 7.5

Proton binding and release with changing pH



Proton binding and release with changing pH



Remember

Mass Action Rule – where any one cation can replace another if its concentration is high enough

and

with decreasing pH there is an increasing $[H^+]$

Buffering at the edges – pH > 7.5 and < 4.5

At **high** pH's buffering is through carbonate formation

$$CO_2 + H_2O \leftrightarrow H_2CO_3\ (H^+ + HCO_3^-)$$

$$Ca^{2+} + 2(H^+ + HCO_3^-) \leftrightarrow 2H^+ + CaCO_3 + H_2O + CO_2$$

At **low** pH's, buffering is via Al hydrolysis

$$Al(OH)_2^+ + H_2O \leftrightarrow Al(OH)_3 + H^+$$

Base reacts with soil acid:

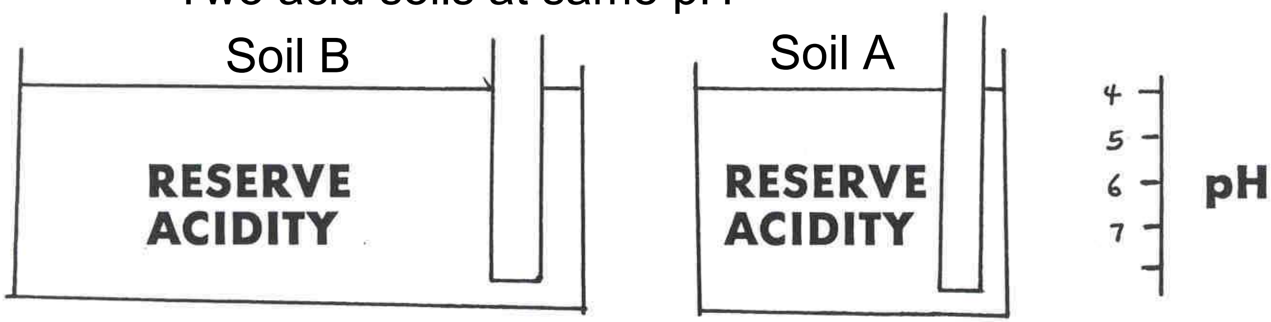
$$CaCO_3 + 2H^+ \dashrightarrow Ca^{2+} + CO_2\uparrow + H_2O$$
$$Ca(OH)_2 + 2H^+ \dashrightarrow Ca^{2+} + 2H_2O$$

As H^+ is consumed, pH rises,
Al^{3+} precipitates:

$$Al^{3+} + 3OH^- \dashrightarrow Al(OH)_3\downarrow$$

Result: Each mole of Al^{3+} consumes 3 moles of base (OH^-).

Two acid soils at same pH

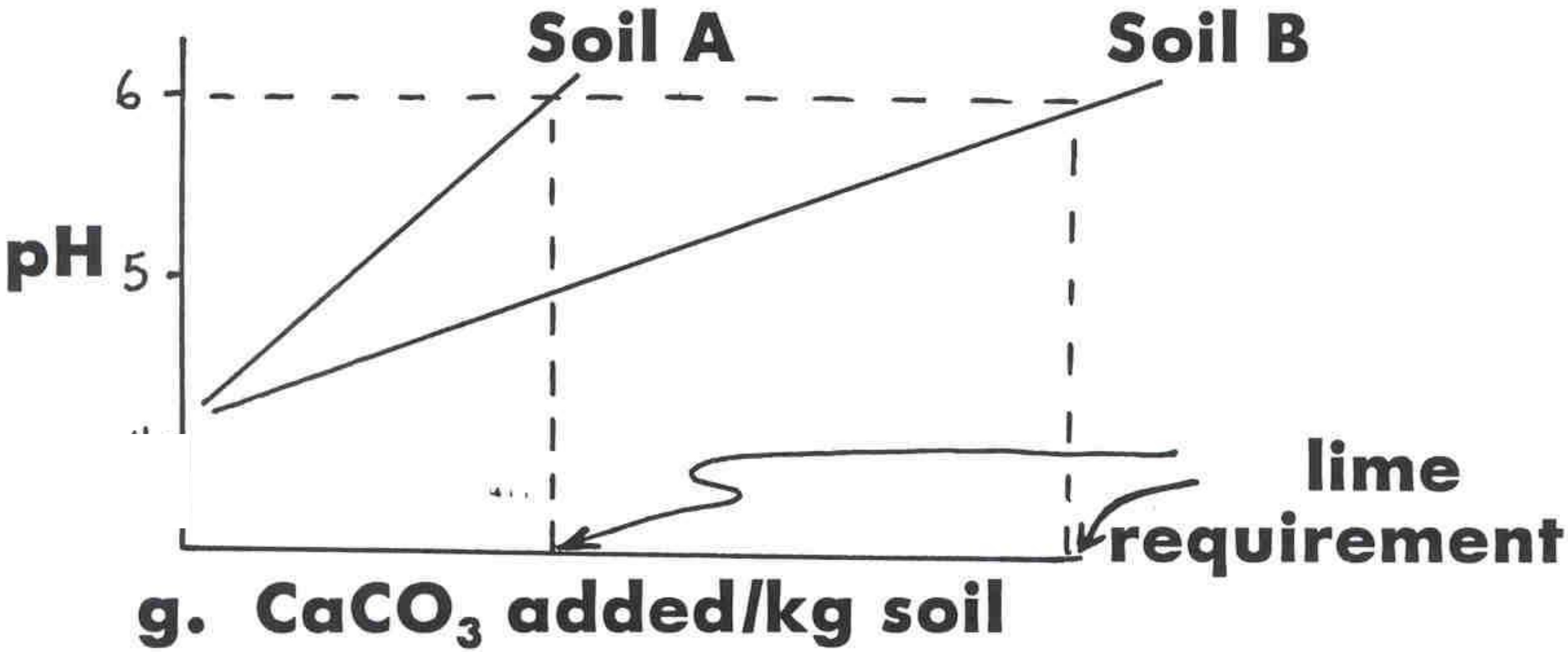


WELL-BUFFERED | **WEAKLY BUFFERED**

BUFFER CAPACITY OF SOIL

= capacity to release or neutralize Al, H

= amount of acid/base needed to bring about a specific shift in pH



Soil A
Soil B
6
5
pH
lime
requirement
g. $CaCO_3$ added/kg soil

While at high pH calcification acts as a buffering reaction to prevent high pH

At low pH it acts to raise the pH!

Liming Reaction

$$Ca^{2+} + 2(H^+ + HCO_3^-) \leftrightarrow 2H^+ + CaCO_3 + H_2O + CO_2$$

Remember all reactions are reversible

DIAGNOSIS OF LIME NEEDS

1. **LABORATORY -**

   Titrate soil to several pH values with lime. Interpolate lime requirement based on desired pH (usually 5-6).

2. **RULE OF THUMB**

   Based on soil texture, color (organic content)

Soil Texture	Amt. of Lime to Raise pH 4.5->5.5
Sand	1,000 kg/ha
Sandy loam	2,000
Clay loam	4,000
Organic soil (peat)	8,000

TABLE 9.4 Common Liming Materials: Their Composition and Use

The two limestones are by far the most commonly used. Use of the other materials is largely dependent on the need for fast reaction, cost, and local availability. The relative amounts needed of the different materials can be judged by comparing the respective $CaCO_3$ equivalent values.

Common name of liming material	*Chemical formula (of pure materials)*	*% $CaCO_3$ equivalent*	*Comments on manufacture and use*
Calcitic limestone	$CaCO_3$	100	Natural rock ground to a fine powder. Low solubility; may be stored outdoors uncovered. Noncaustic, slow to react.
Dolomitic limestone	$CaMg(CO_3)_2$	95–108	Natural rock ground to a fine powder; somewhat slower reacting than calcitic limestone. Supplies Mg to plants.
Burned lime (oxide of lime)	CaO (+ MgO)[a]	178	Caustic, difficult to handle, fast acting, can burn foliage, expensive. Made by heating limestone. Protect from moisture.
Hydrated lime (hydroxide of lime)	$Ca(OH)_2$ (+ $Mg(OH)_2$)[a]	134	Even more caustic and more difficult to handle than CaO. Fast acting, can burn foliage, expensive. Made by slaking hot CaO with water. Protect from moisture.
Basic slag	$CaSiO_3$	70	By-product of pig-iron industry. Must be finely ground. Also contains 1–7%P.
Marl	$CaCO_3$	40–70	Usually mined from shallow coastal beds, dried, and ground before use. May be mixed with soil or peat.
Wood ashes	CaO, MgO, K_2O, $K(OH)$, etc.	40	Caustic, largely water-soluble, must be protected from water.
Misc. lime-containing by-products	Usually $CaCO_3$ with various impurities	20–100	Variable composition; test for toxic impurities.

[a] If made from dolomitic limestone.