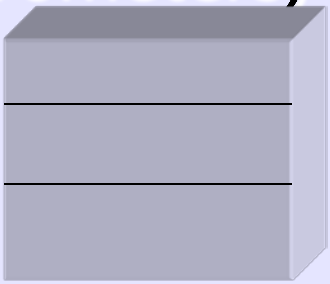
Basic Soil Chemistry

Objectives

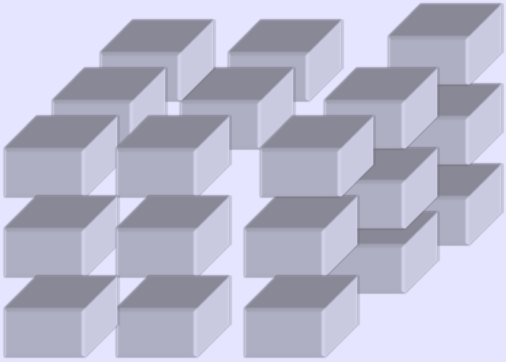
- Properties of colloids
- Properties of soil clays
- Cation Exchange Capacity
- Base Saturation
- The Soil Solution
- Soil pH and acidity in soils
- Effects of Aluminum on soil acidity

Properties of Colloids

- Size affects Reactivity
  - With water
  - With chemicals
  - With biological components
- Surface Area
- Colloids
  - clay sized (< 2 micrometers)
- Charge



0.3 x 0.3 x 6=0.54



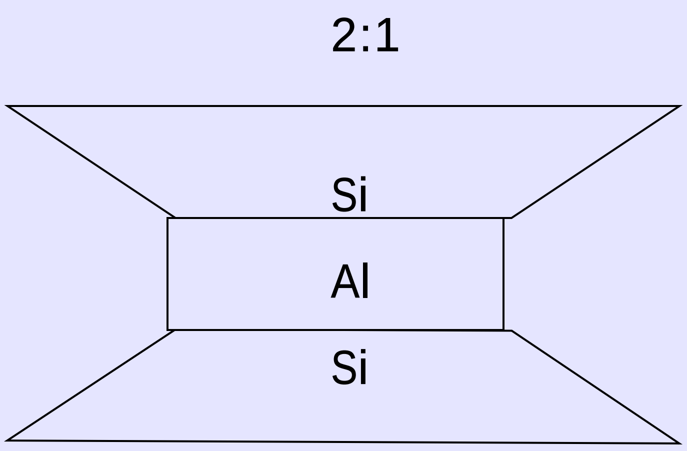
0.1 x 0.1 x 6 x 27=1.62

Sources of Charge

- Permanent Charge
  - Clay (layer silicates) Minerals
- Variable Charge (pH dependent)
  - Mineral Edges
  - Oxides and Hydroxides of Fe and Al
  - Organic Matter

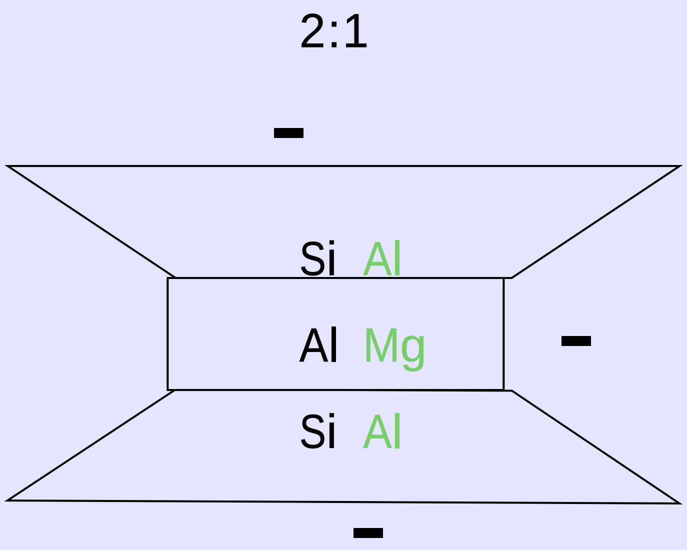
Permanent Charge

- Soils high in primary minerals, Si, Al, Mg, pH
- Layer silicates with 2 Si and 1 Al Layers
- If layers contain only Si and Al
  - Balanced
  - Uncharged
  - Stable
- But .....



Permanent Charge: Ionic Substitution

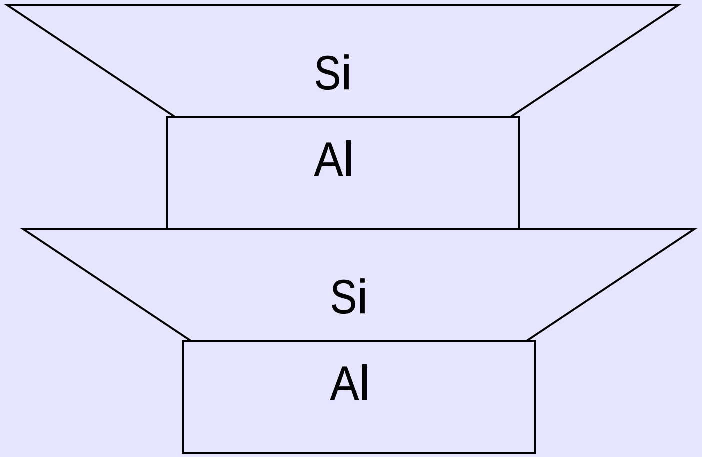
- If some Si^{+4} is replaced by Al^{+3}
- Or some Al^{+3} replaced by Mg^{+2}
  - Creates charged sites (ground)
- With Increasing substitution
  - Increasing charge
  - Decreases stability
- Location of Charge (Si or Al layer)
  - Affects Strength
  - Expandability
  - K Fixation



Permanent Charge

- Soils low in soluble Si, Mg, and primary minerals, lower pH, and high in Al
- Layer silicates with 1 Si and 1 Al
  - "No" substituion
  - Low Charge
  - Highly Stable

1:1

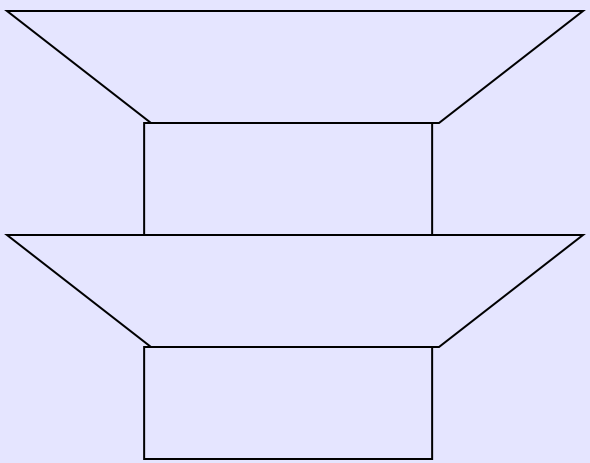


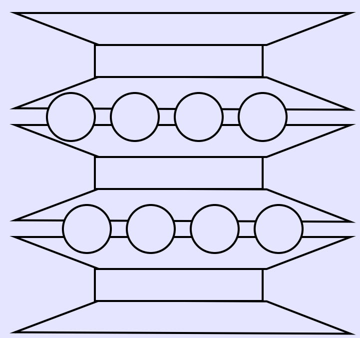
Stacked Plates
Low surface area

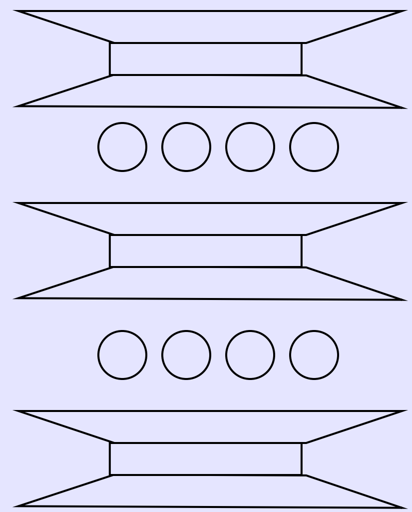
Why is this important?

Silicate Clays

1:1	Layer Silicates	Kaolinite
2:1	Layer Silicates	Micas
2:1	Layer Silicates	Smectites & Vermiculites

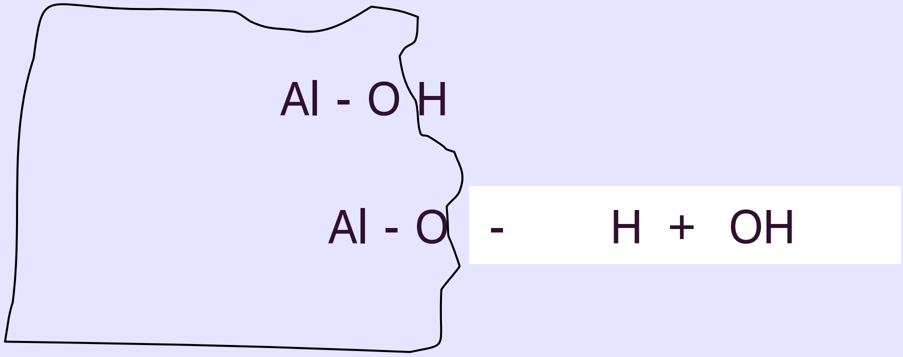






Variable Charge Minerals

- Edges of clay minerals
- Edges of oxides, hydroxides of Fe and Al
- Exposed Edges of amorphous coatings
- Raise pH, increase charge

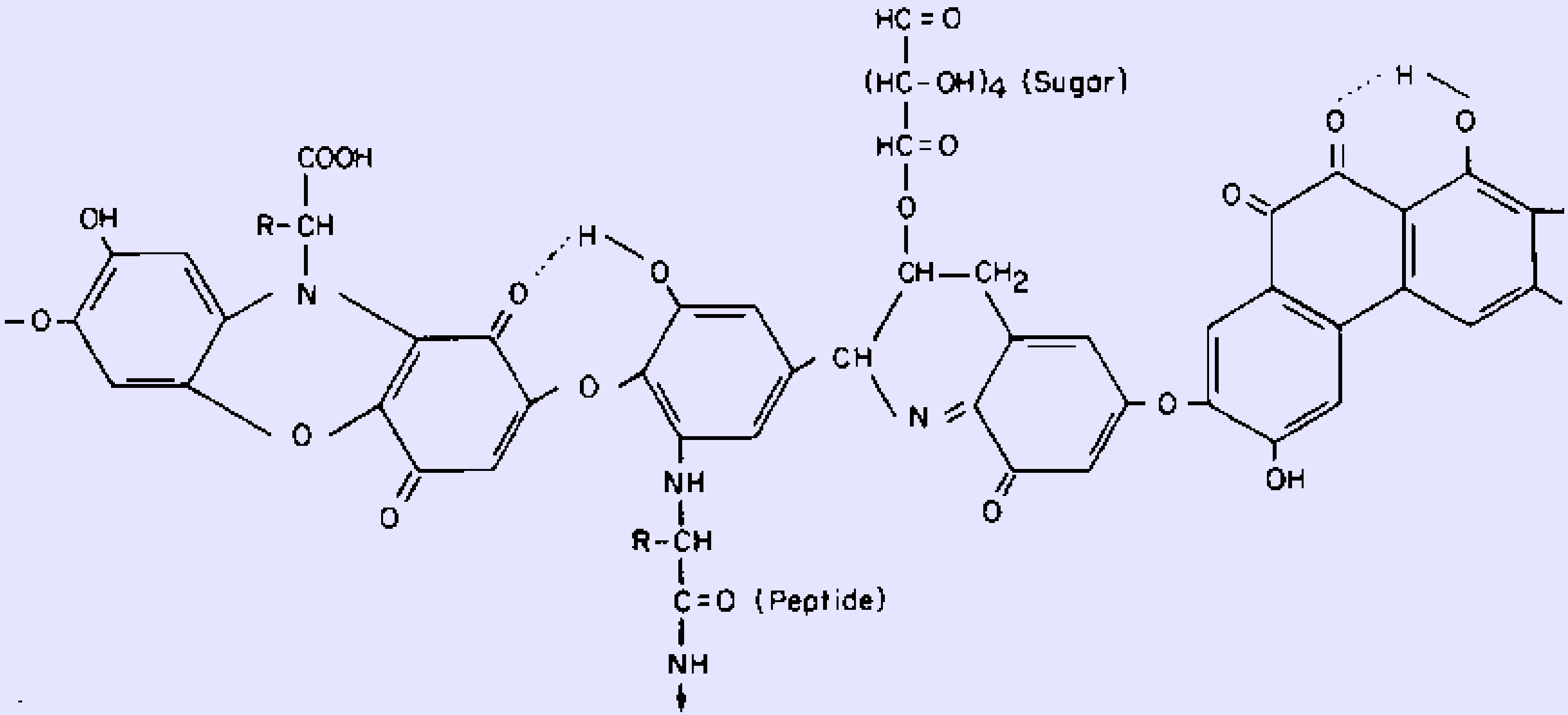


Organic Matter

- What is it?
  - High carbon Leftovers
  - Very high surface area
  - Very complex chemistry

Organic Matter - Humus

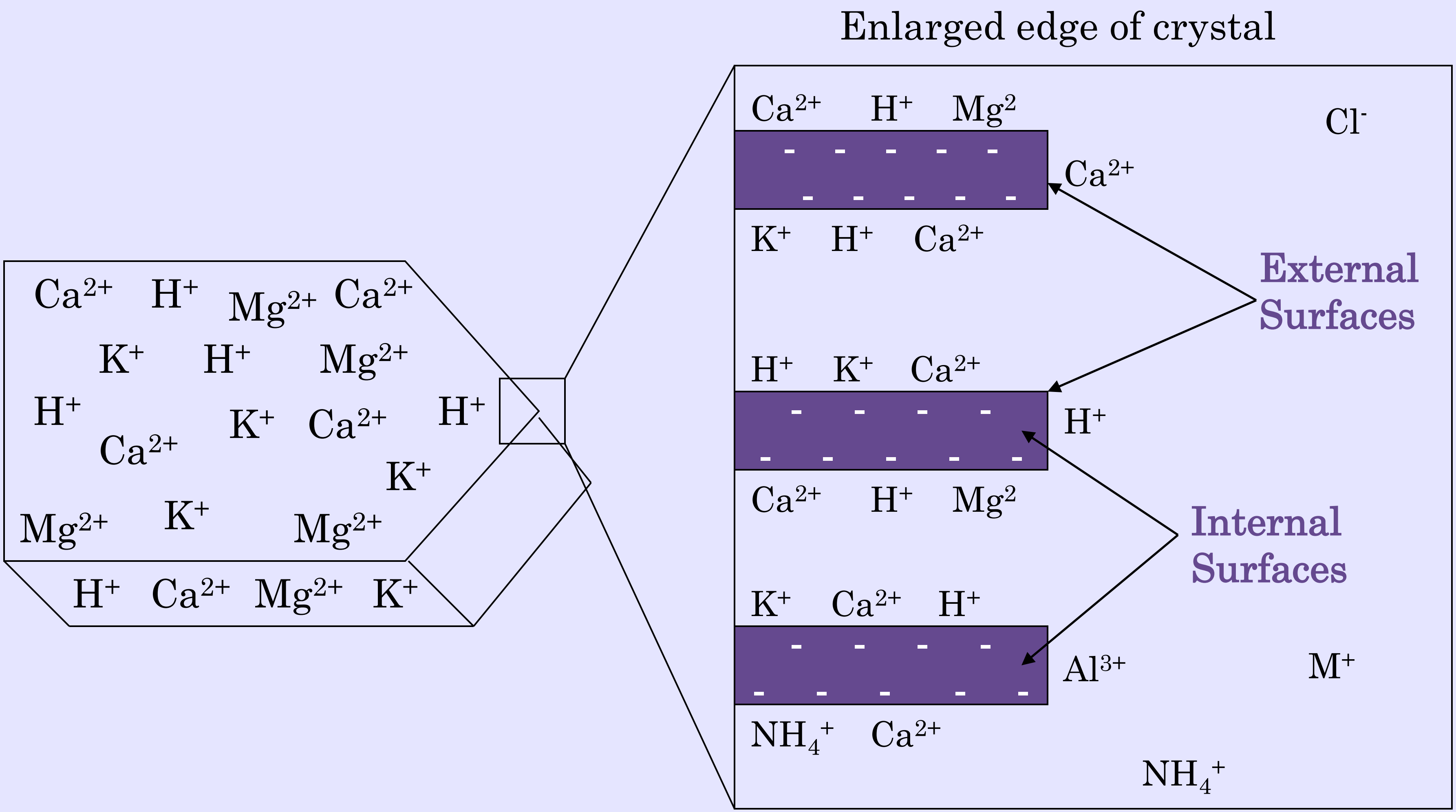
- R-COOH + OH → R-COO $^-$ + HOH



Distribution of Charge

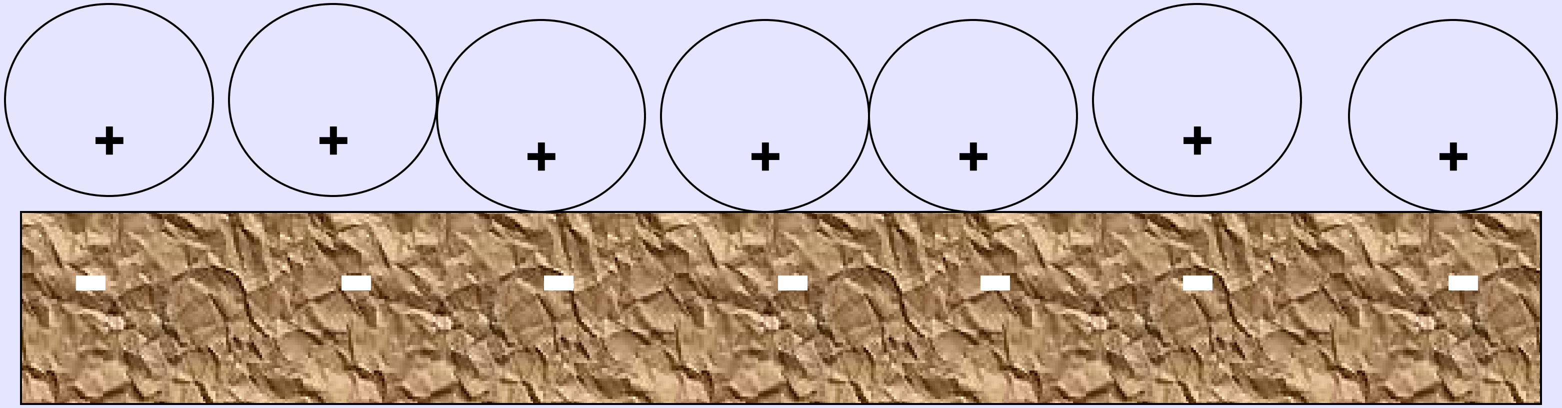
Type Colloid	Charge	Constant	Variable
	cmol/kg	%	%
Organic	200	10	90
Vermiculite	150	95	5
Smectite	100	95	5
Kaolinite	8	5	95
Geothite	4	0	100

Silicate Clays - Crystal



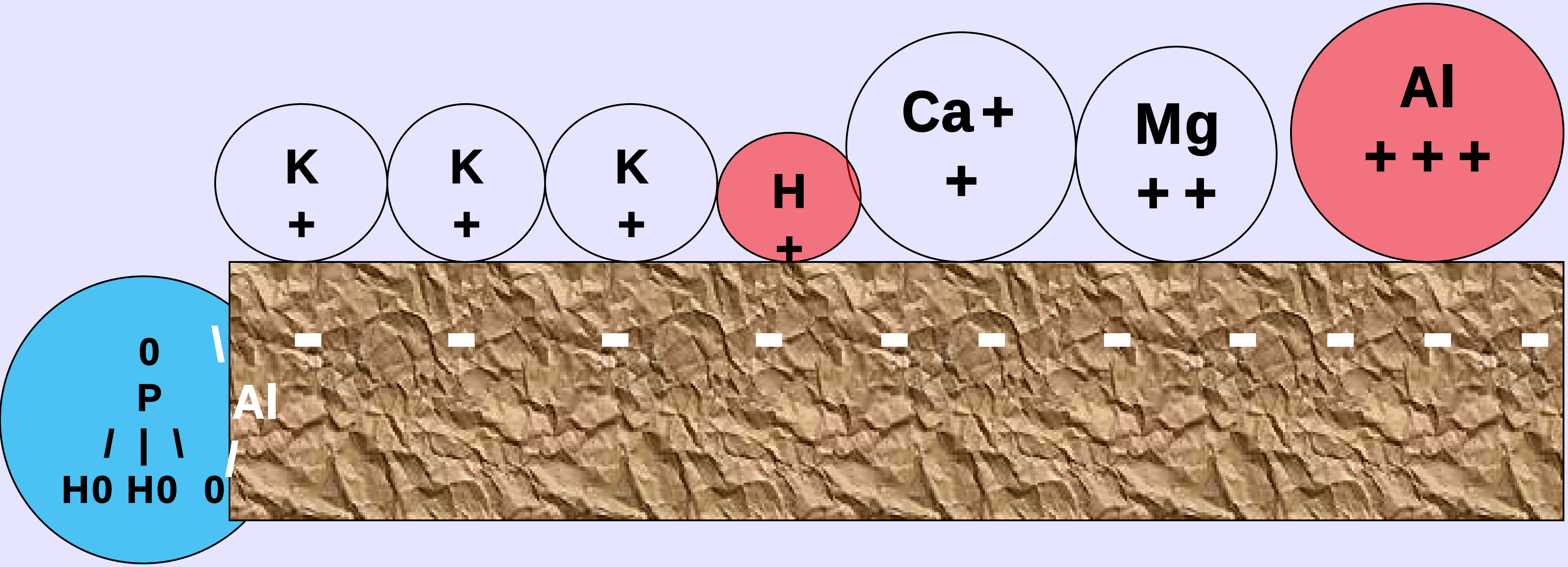
How Nutrients are Held

- Permanent Charge
- pH dependent charge
- Minus Meets Plus



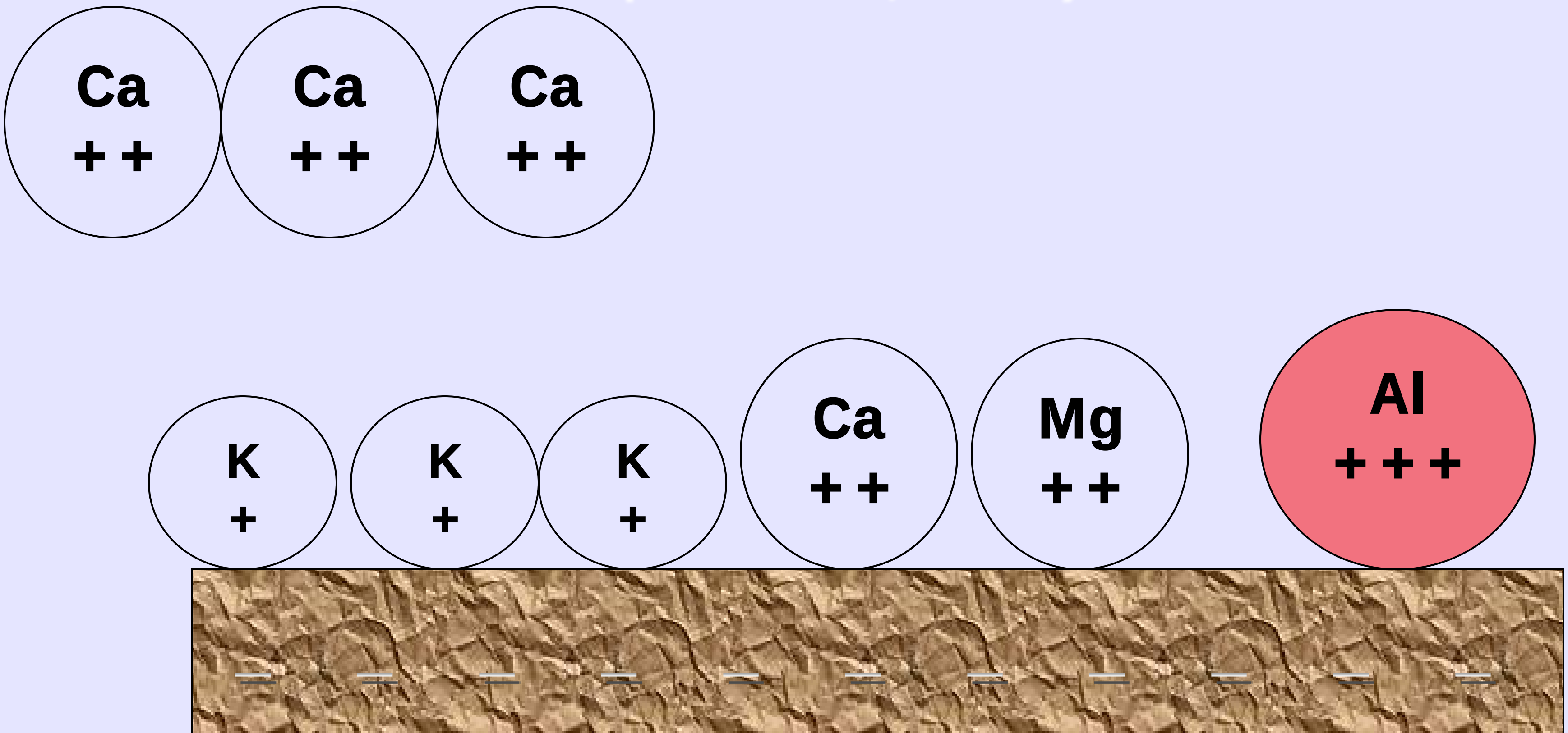
Strength of Retention

- Type of Charge (+ or -)
- Amount of Charge
- Reactivity ($H_2PO_4^-$)



Cation Exchange

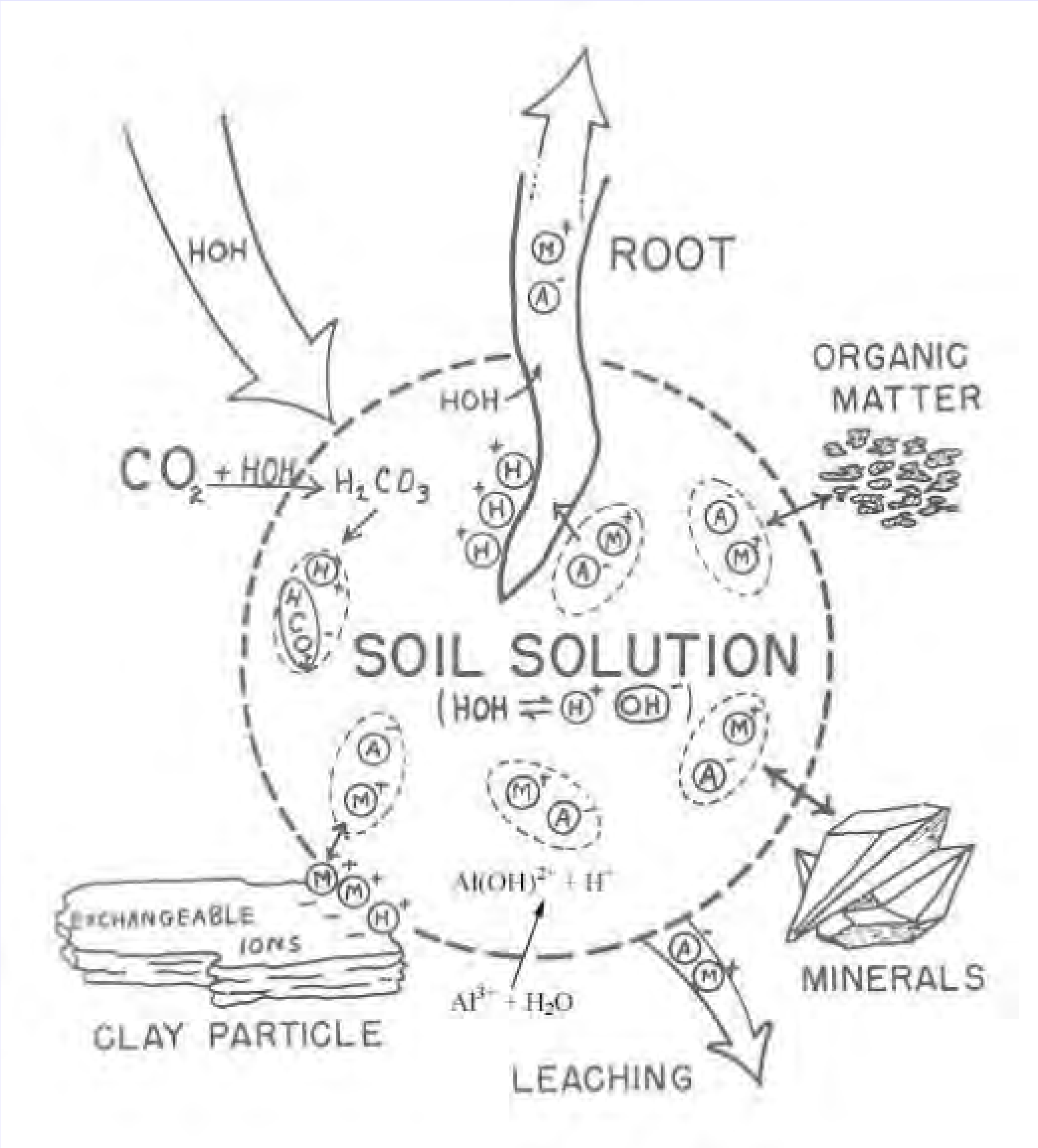
- Add Cations (fertilizers, root exudes, rainfall, decomposition, etc.)



Soil Solution

- Plants depend primarily on what is in solution, not what is on the exchange complex (solids).
- Typical concentrations 4 da to 7 da, readily available
- Change readily
- Mobile (can be lost)
- Must be replenished

The Soil Solution

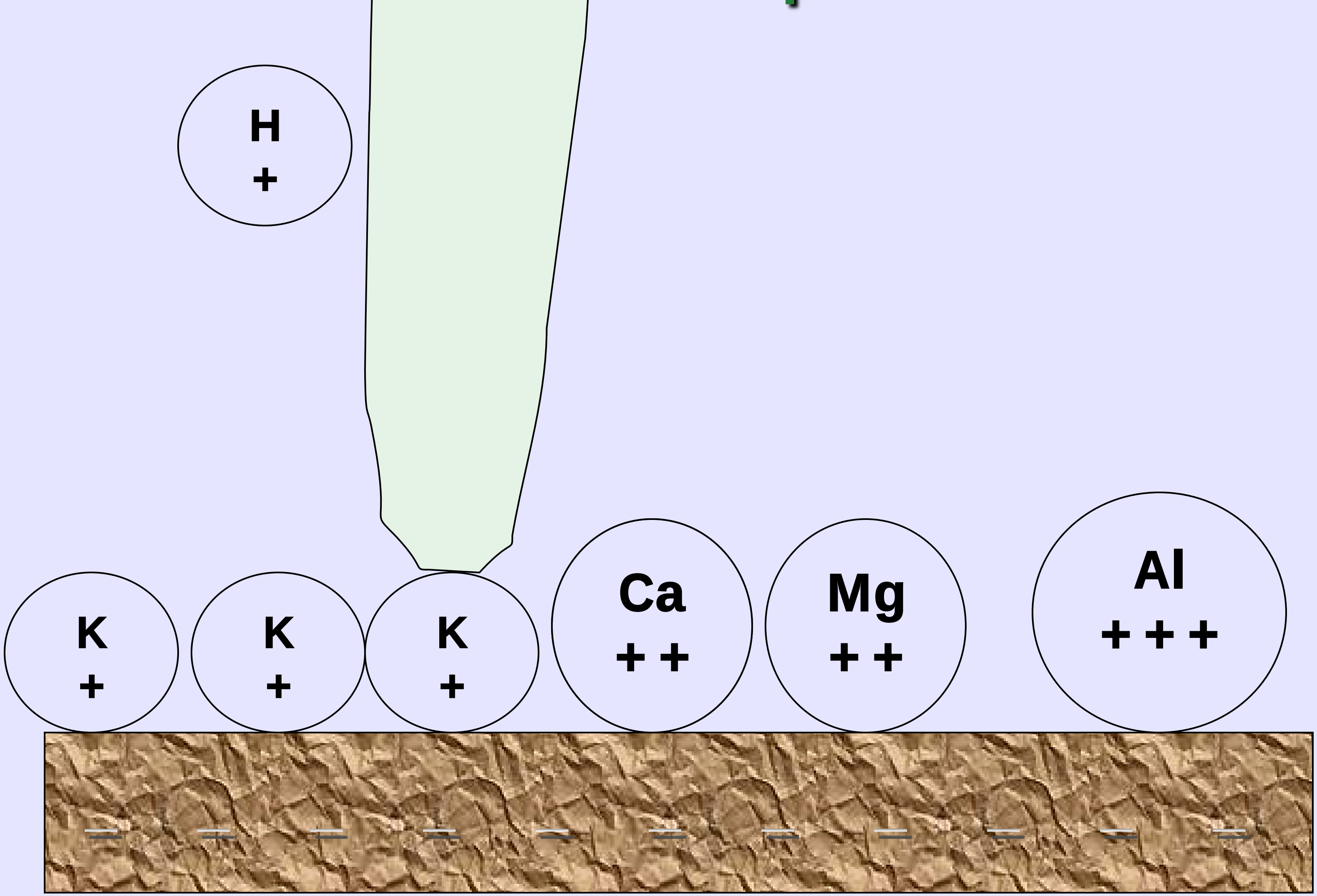


- Weathering of mineral/ organic compounds
- Dissolution of soluble forms into cations and anions
- Hydrolysis reactions- Water with minerals
- Oxidation/Reduction Reactions
- Exchange reactions of "ions" held in an exchangeable form on solid soils

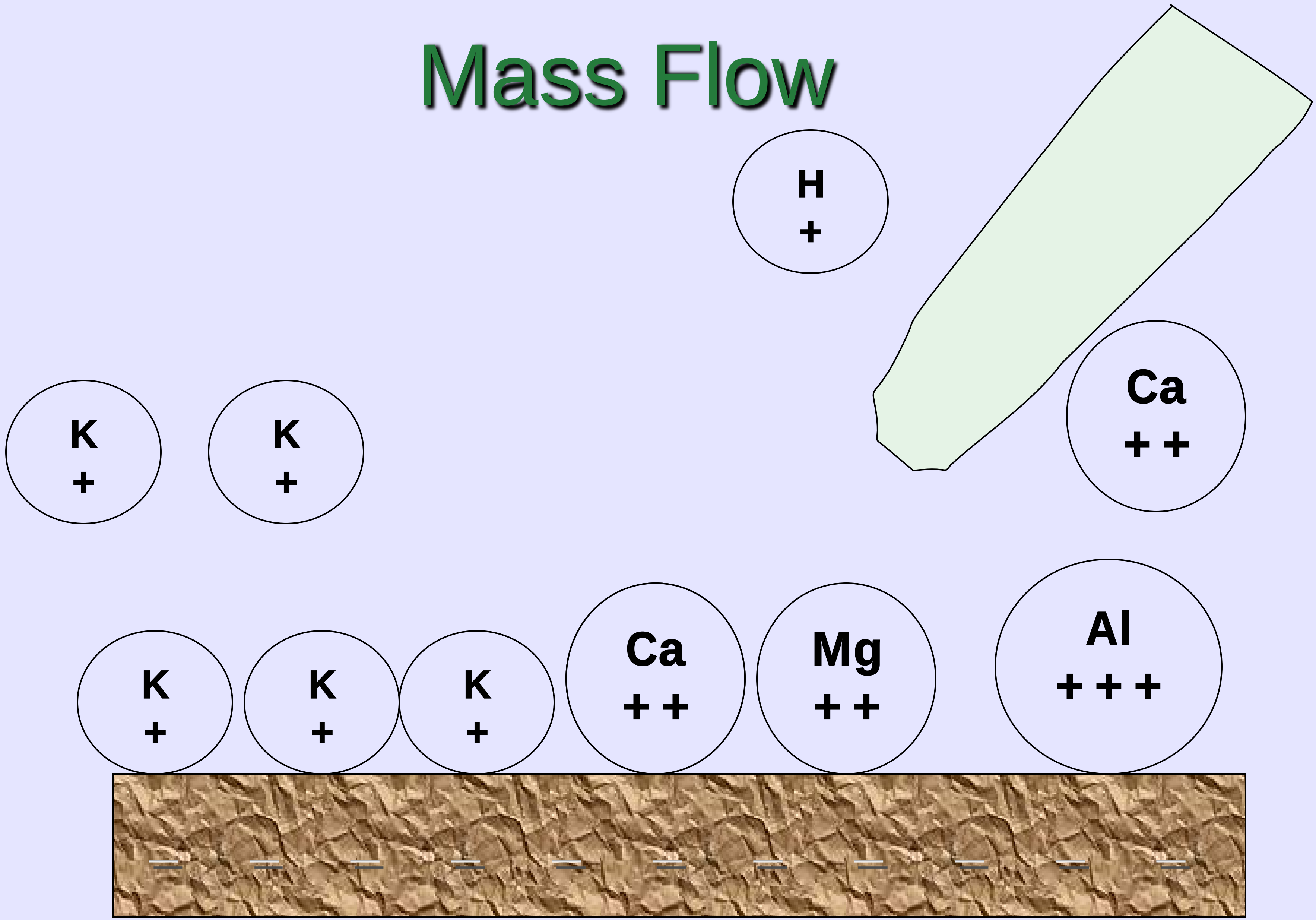
How does Nutrient Uptake Occur?

- Root Interception
- Mass Flow
- Diffusion

Root Interception

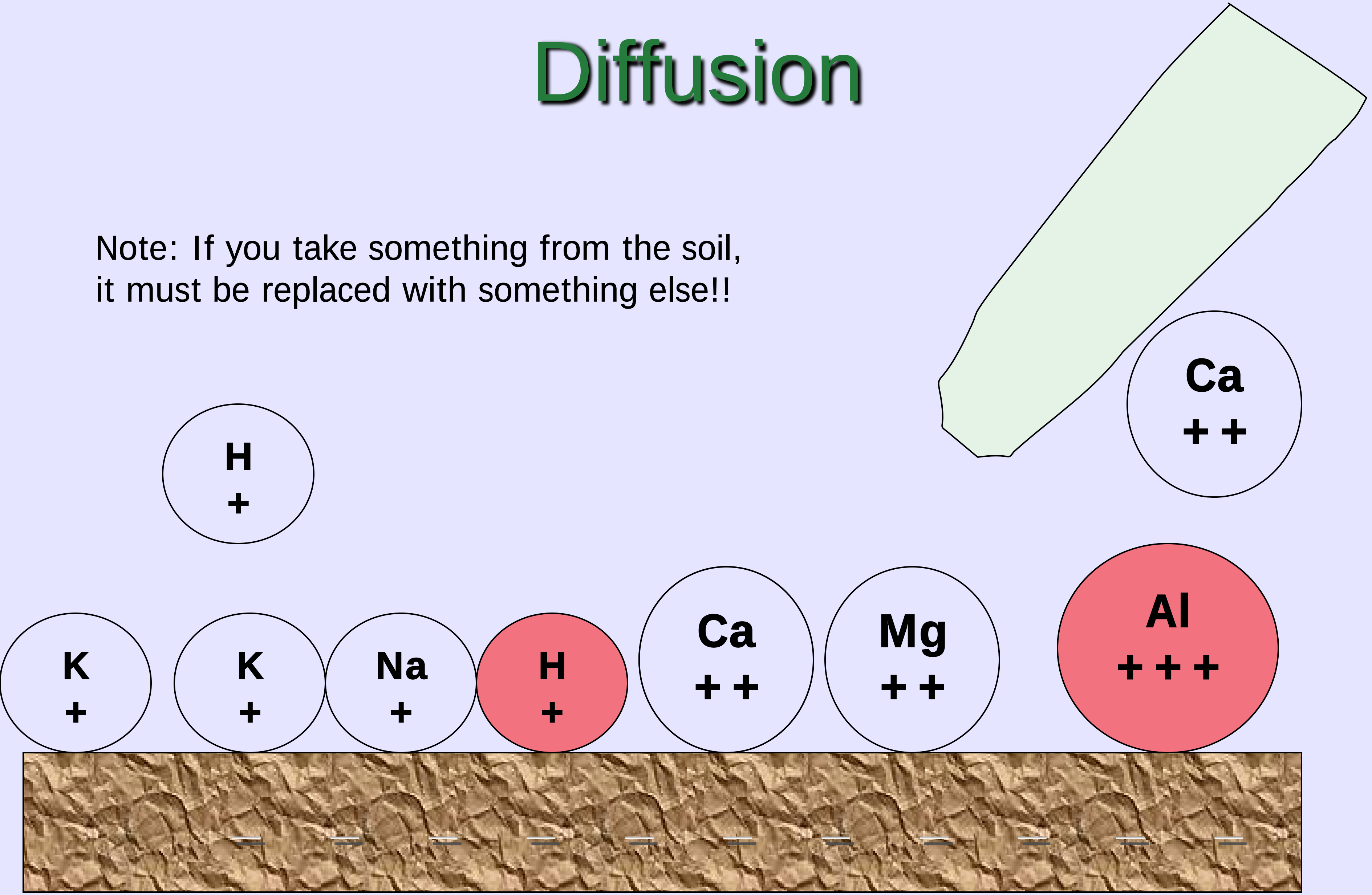


Mass Flow

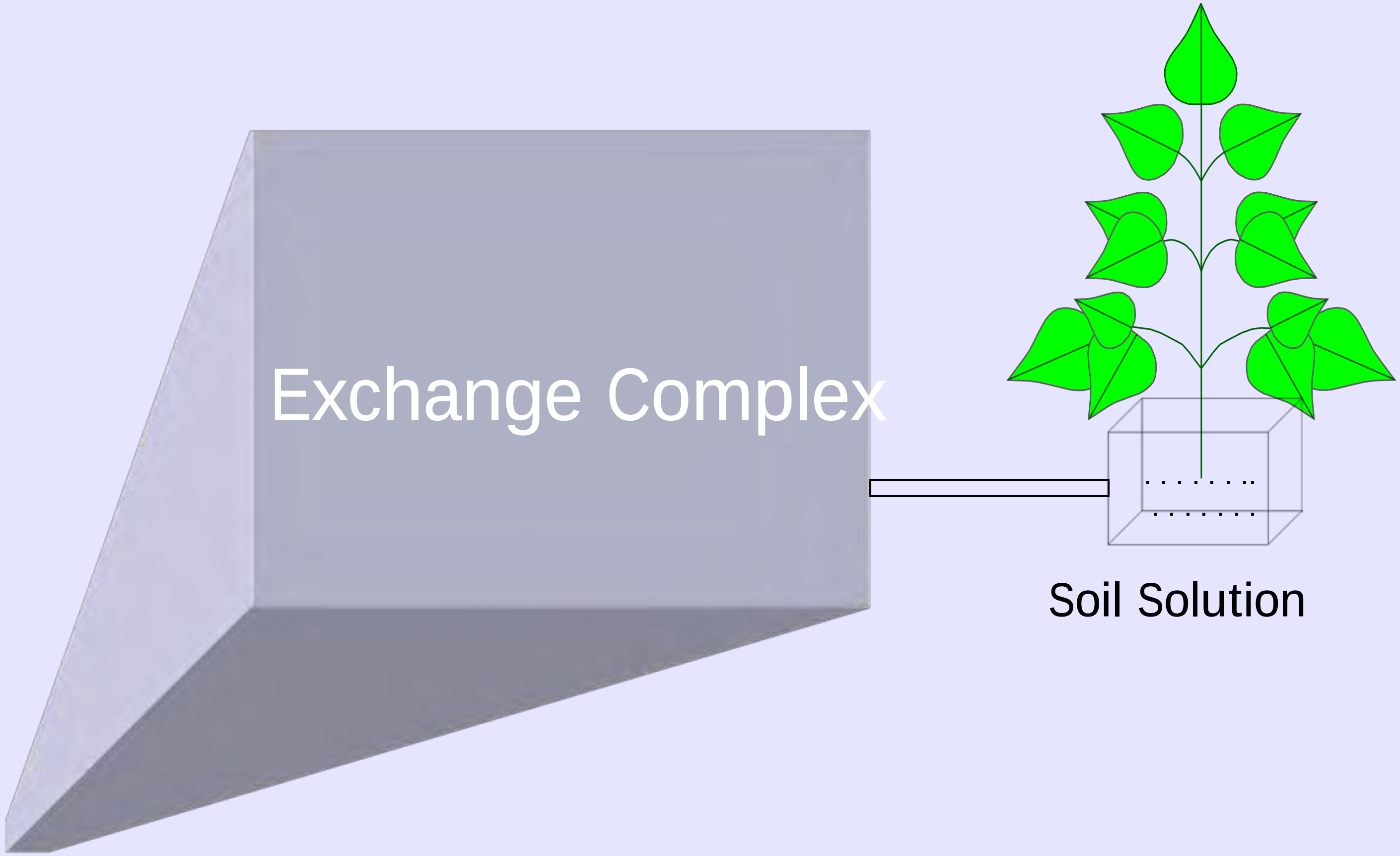


Diffusion

Note: If you take something from the soil, it must be replaced with something else!!

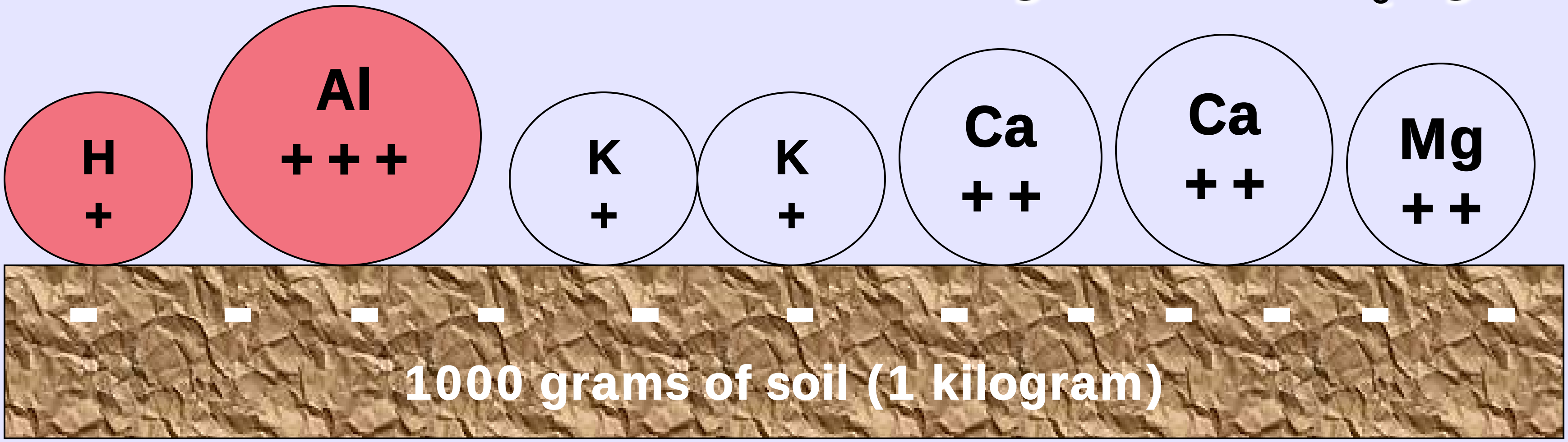


How are soils buffered against change?

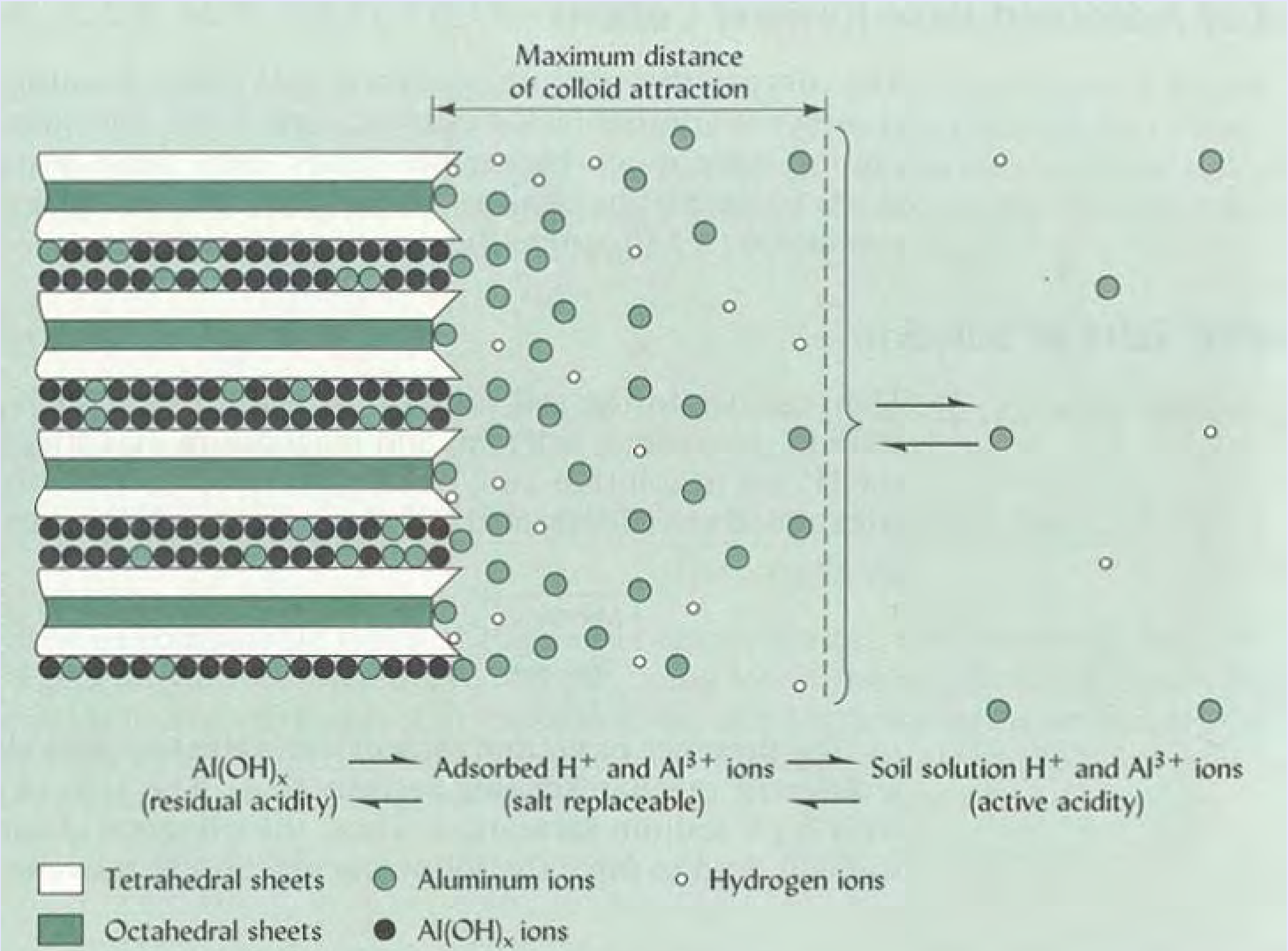


Cation Exchange Capacity (CEC)

- Cation Exchange Capacity $cmol_c\ kg^{-1}$
  - Sum of all cations (H, Na, K, Ca, Mg, Al, etc.) held by soil charges on an equivalent basis (per 1000 g)
  - 1H + 3 Al +2 K + 4 Ca +2 Mg = 12 $cmol_c\ kg^{-1}$



Buffering Capacity

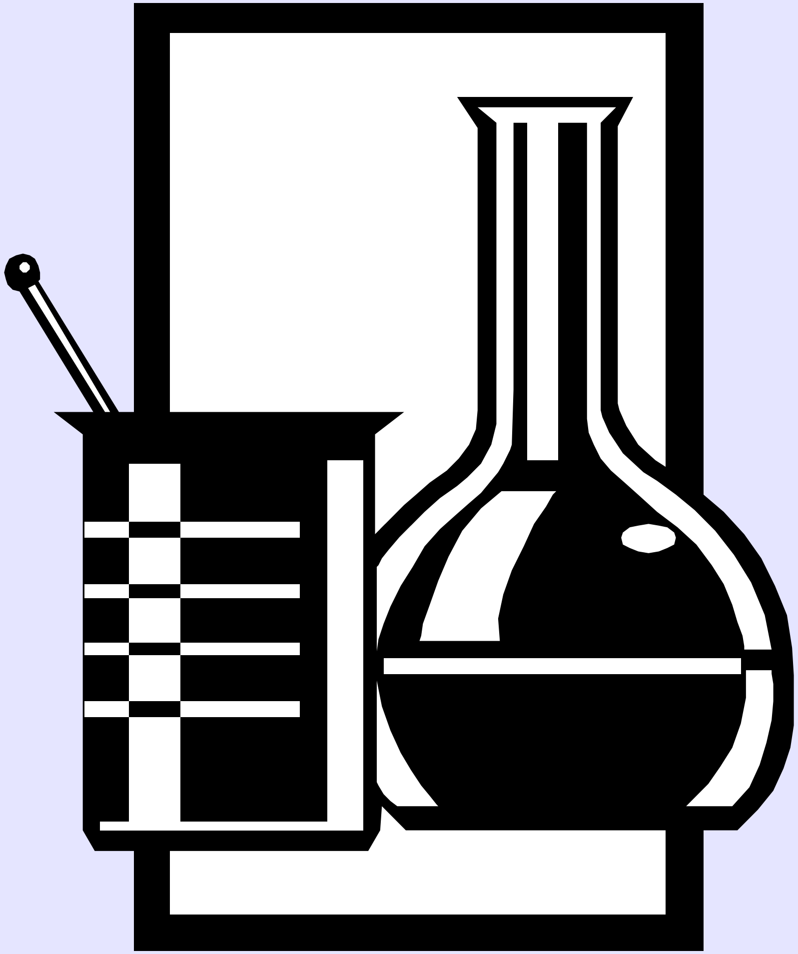


Soil Science

How does CEC Affect Nutrient Availability?

- Solution depletion (uptake or leaching) causes:
  - Exchange
  - Dissolution
- Solution additions cause:
  - Exchange
  - Precipitation
    - Al, Fe Oxides and P
    - $CaCO_3$, P
- Dynamic Equilibrium

Acidity, pH, and Source of Acid in Soils



Definitions

- Acid
  - A substance which gives up hydrogen (H^+)
- Base
  - A substance which accepts hydrogen (H^+)
- pH
  - $pH = -(\log_{10}([H^+]))$
  - measures H^+ in solution

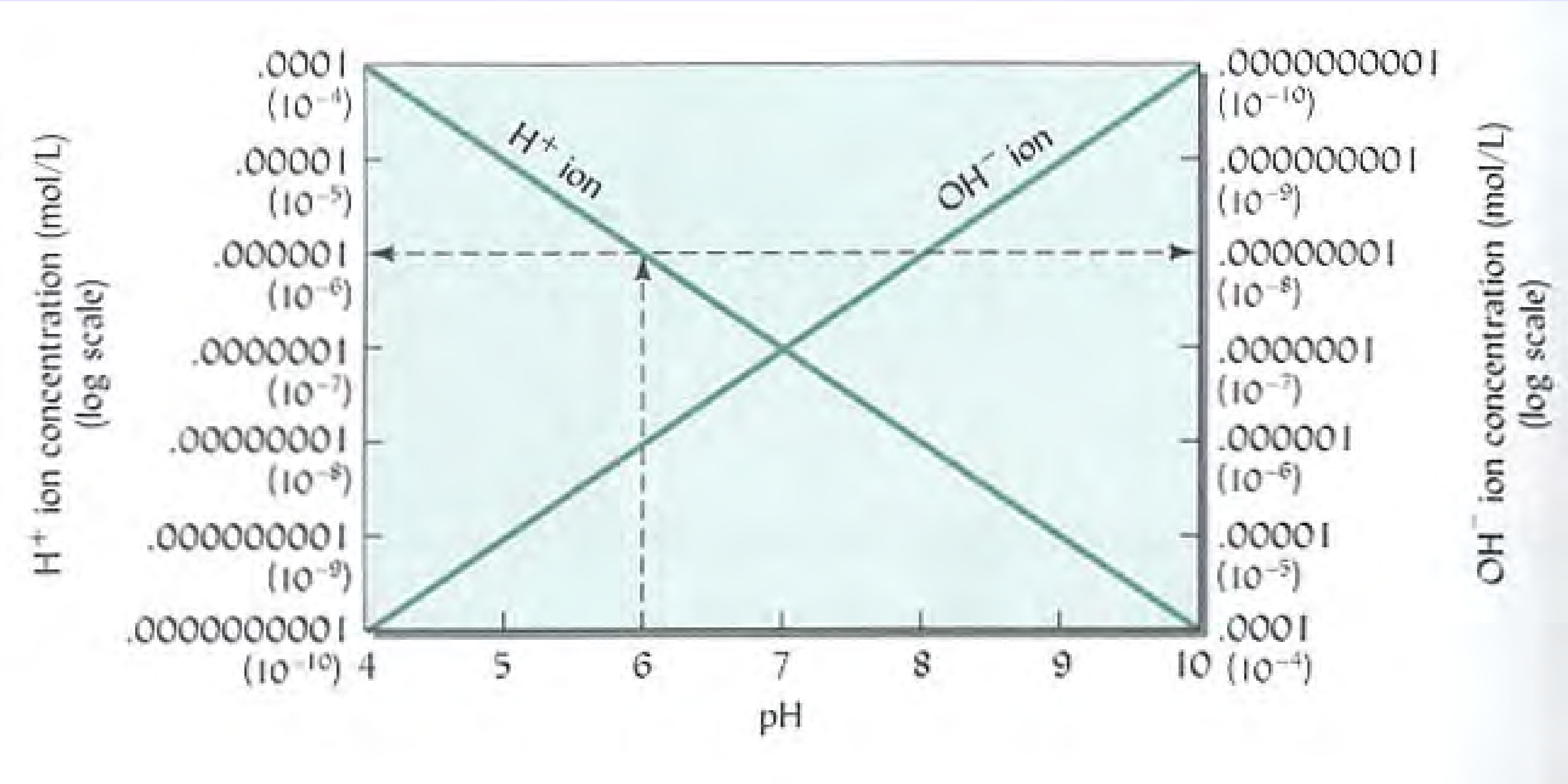
pH Concept
Hydrogen Ion Concentrations

- pH is a way to express very small numbers with a wide range easily
- The activity of Hydrogen (H^+) and Hydroxyl (OH^-) ions ***in solution*** determine if the pH is acid, neutral or alkaline.
- Pure water provides these ions in equal concentration.

$$H_20 \rightleftharpoons H^+ + OH^-$$

- The equilibrium for this reaction is far to the left (meaning most of the molecules occur as water). A tiny amount of H^+ and OH^- ions result from this reaction.
- The ion product of the concentrations of H^+ and OH^- is a constant, (K_{sp}), which at 25 degrees C is known to be **1×10^{-14},** thus
  - pH = - log H   OR   pH = log 1/(H^+)   OR   pH = 7 at neutrality
  - At pH = 7   the molar concentration of Hydrogen is 0.0000001 moles/L
  - At pH = 5   the molar concentration of Hydrogen is 0.00001   moles/L

pH vs. pOH



.0001
(10⁻⁴)
.00001
(10⁻⁵)
.000001
(10⁻⁶)
.0000001
(10⁻⁷)
.00000001
(10⁻⁸)
.000000001
(10⁻⁹)
.0000000001
(10⁻¹⁰)
H+ ion concentration (mol/L)
(log scale)
H+ ion
OH⁻ ion
4
5
6
7
8
9
10
pH
.0000000001
(10⁻¹⁰)
.000000001
(10⁻⁹)
.00000001
(10⁻⁸)
.0000001
(10⁻⁷)
.000001
(10⁻⁶)
.00001
(10⁻⁵)
.0001
(10⁻⁴)
OH⁻ ion concentration (mol/L)
(log scale)

Types of Soils, Based on Soil Reaction

- Acid Soils – Al and H dominated ($pH<7$)
- Neutral Soils – equal mix of acid and alkaline ($pH=7.0$)
- Calcareous soil – Ca dominated (pH 7.1 to 8.2)
- Saline soils – Ca + Sodium (Na) ($pH> 8$, free salts)
- Sodic soils- Sodium dominated (free salts)

How do soils become acid?

- Addition of Hydrogen (H^+)
  - Acid Rain
  - Root exudates
  - Organic matter decay
  - Ammonium-based fertilizers
  - Breakdown of minerals and release of Al
- Removal of Ca, Mg, and K
  - Leaching
  - Crop uptake of basic cations

How does Al affect pH?

- Al^{+3} is bound to the soil or in solution

$-Al^{+3}$

$$\longleftrightarrow Al^{3+} + HOH = Al(OH)^{2+} + H^{+}$$

and,

$$Al(OH)^{2+} + HOH = Al(OH)_2^{+} + H^{+}$$

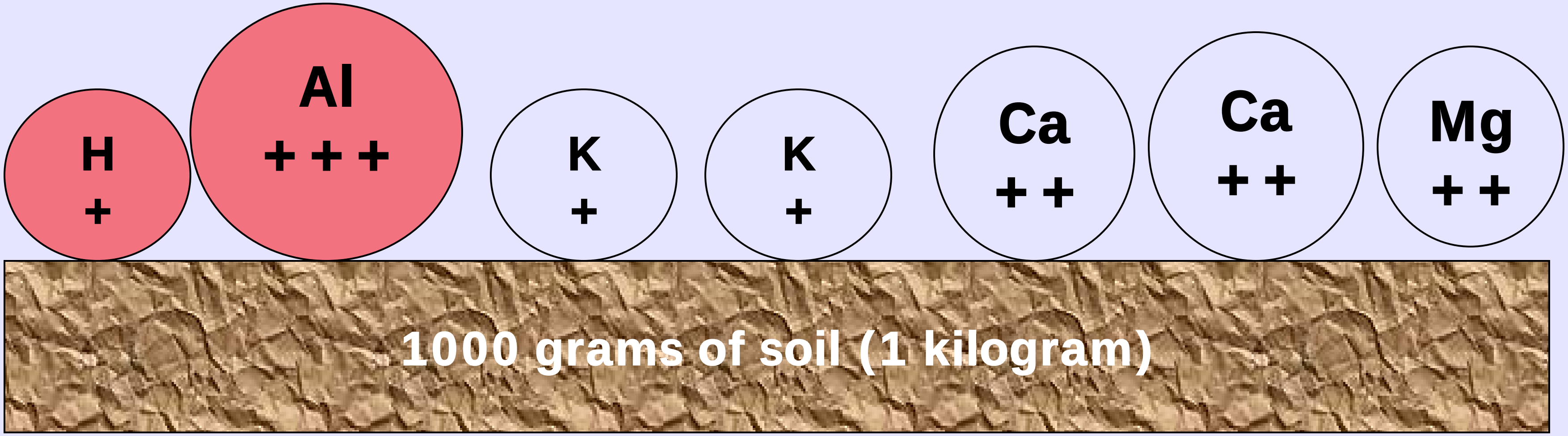
$$Al(OH)_2^{+} + HOH = Al(OH)_{3(s)} + H^{+}$$

Acid Soil Toxicity

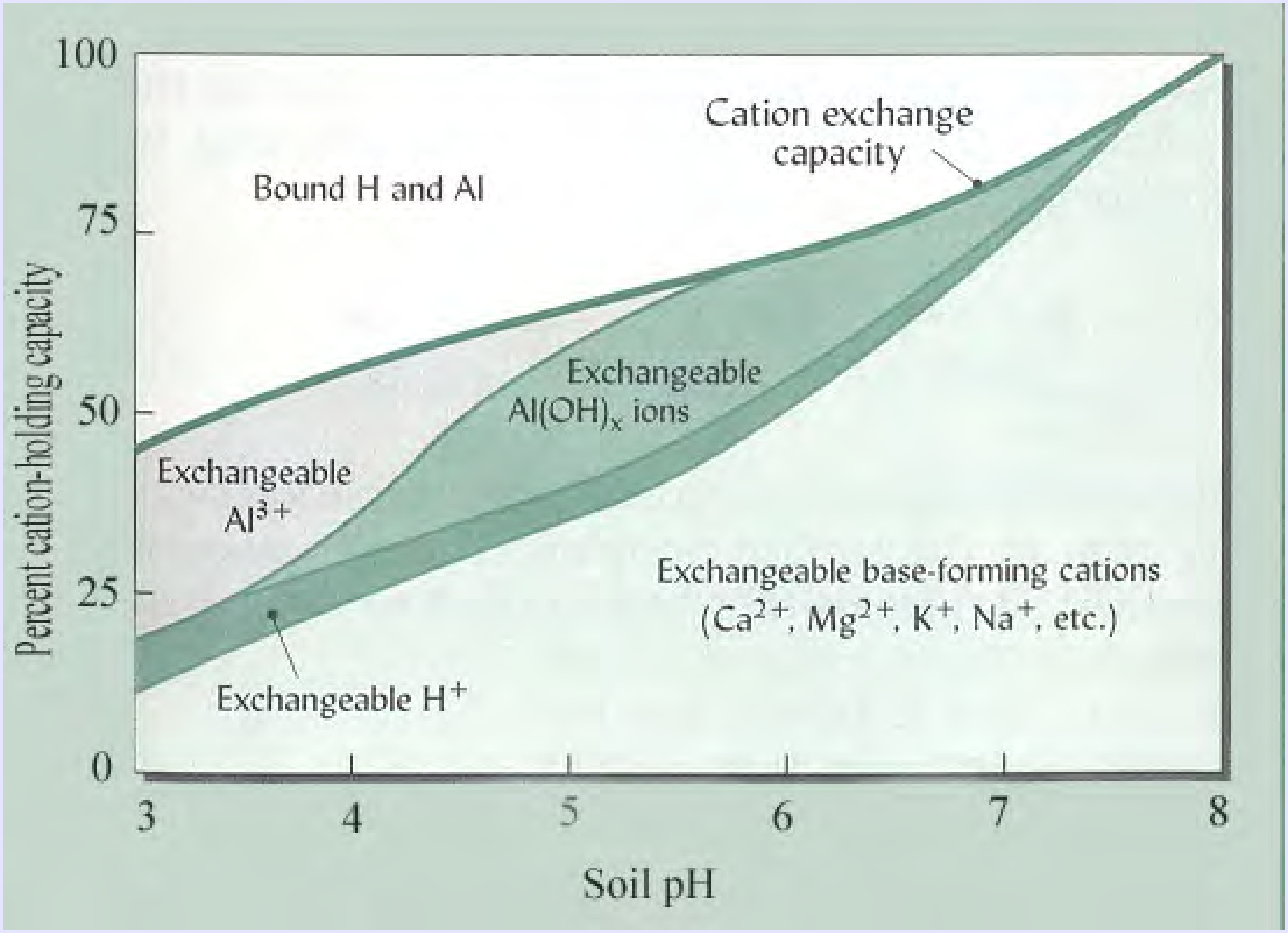
- Hydrogen Toxicity
  - Injury to roots at less than pH 4.0
  - Decrease in uptake of Ca and Mg
- Aluminum Toxicity
  - Decreased root growth
  - Decreased Ca and P uptake
  - Decreased Microbial Activity (Rhizobia)
- Manganese Toxicity
  - pH less than 5.0 with high total manganese

%Base Saturation

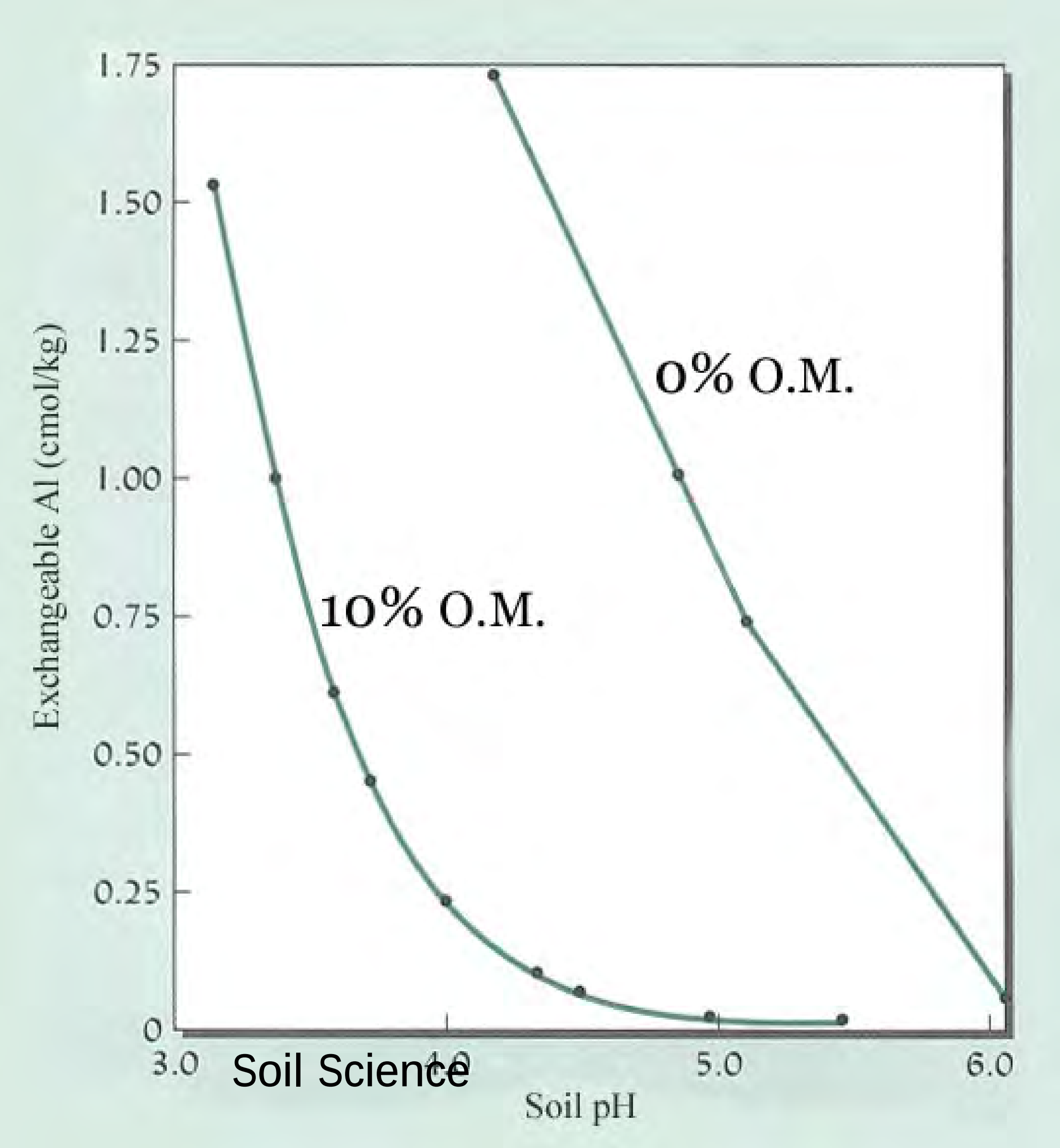
- 100 x (Sum of Bases / CEC)
  - BASIC Cations are Na, K, Ca, and Mg
  - CEC= 1 H + 3 Al +2 K + 4 Ca +2 Mg = 12 cmol/kg
  - Base saturation = 100 x (2 + 4 +2) /12=75%



Relationship of Soil pH and % Cation Holding Capacity



Effect of O.M. on Aluminum and Soil Acidity



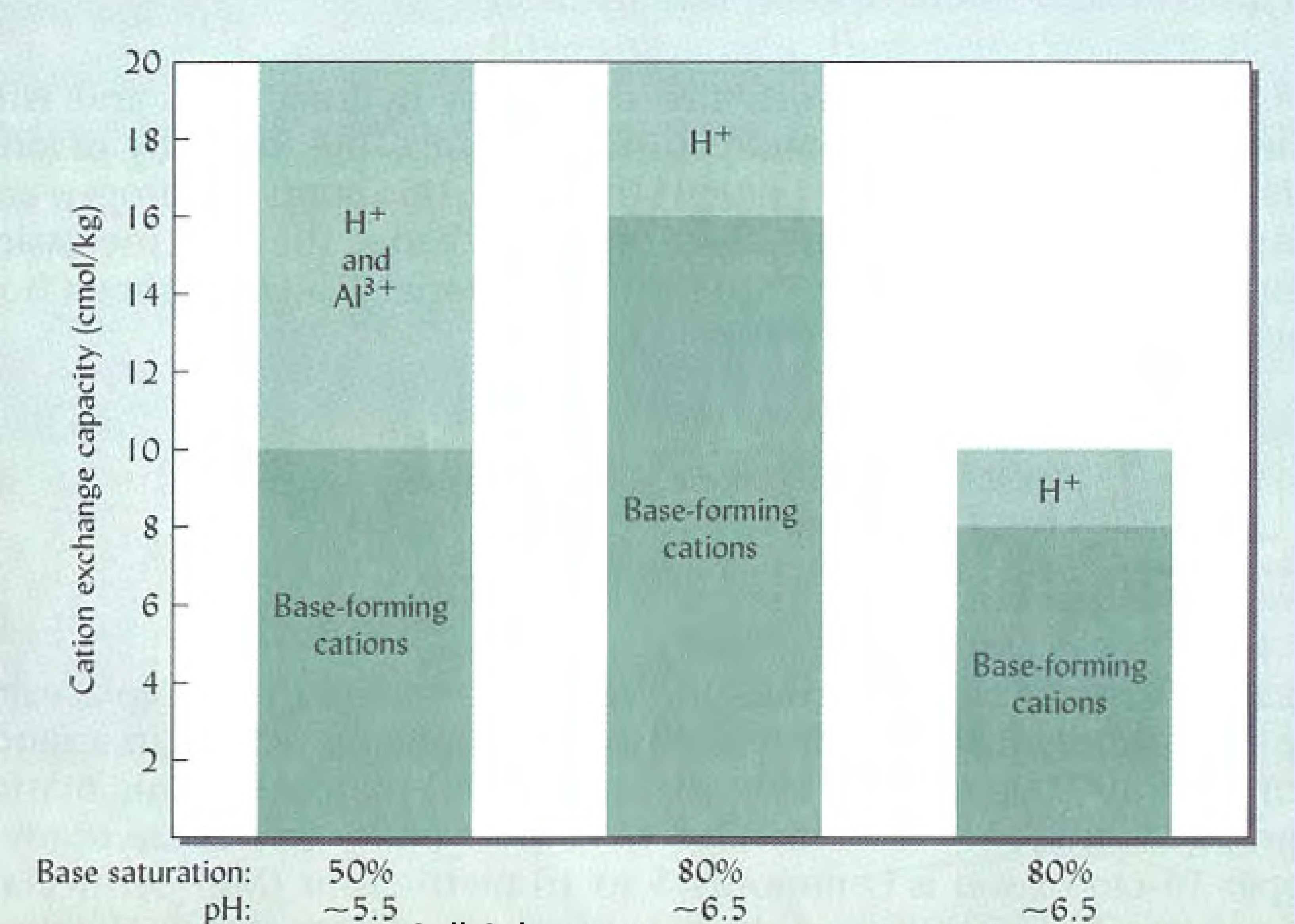
How do liming materials affect pH

- CaCO3 + 2 H_2O = Ca + 2 OH + H2CO3, then

$$\begin{matrix} H^+ \\ H^+ \end{matrix} + 2\,OH^- + Ca^{2+} = 2\,H_2O + Ca^{++}$$

$$\begin{matrix} Al^{3+} \\ Al^{3+} \end{matrix} + 6\,OH^- + 3\,Ca^{2+} = Al(OH)_{3(s)} + H_2O + \begin{matrix} Ca^{++} \\ Ca^{++} \\ Ca^{++} \end{matrix}$$

Limed and Non-Limed Soils



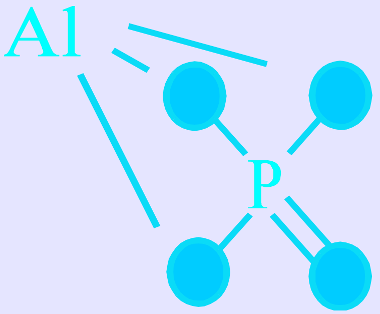
Soil Science

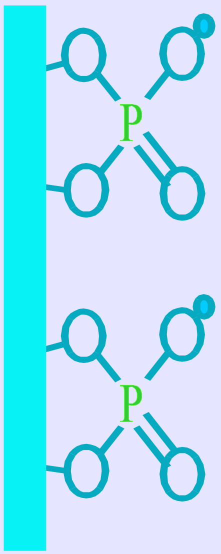
Phosphorus

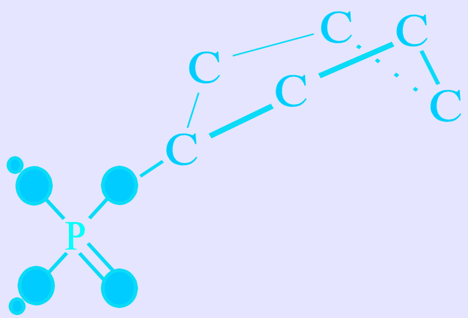
- Generally very low in natural soils
- Exceptions:
  - Alluvial landscapes where O.M. is deposited by water with sediments
  - Where P bearing minerals are abundant in soil parent materials
- Where Phosphorus tests of surface soils are High
  - Due to P that has been added:
    - Manures and or chemical fertilizer
  - Much is tied up in the Organic Fraction
  - Some is tied up as oxides of Al and Fe and as such is relatively unavailable

Forms in Soils

- Acid Soils
  - Al and Fe phosphate
  - Organic P
  - Soil Solution - $H_2PO_4^{-1}$
- Calcareous/Alkaline Soils
  - Ca phosphates
  - Organic P
  - Soil Solution - HPO_4^{-2}

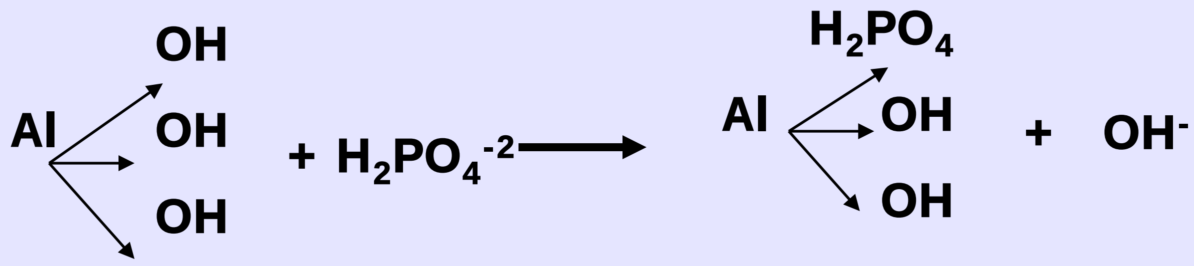






Fertilizer P Reactions

- Acid Soils



- Calcareous/Alkaline Soils

$$Ca^{+2} + HPO_4^{\ -2} \longrightarrow CaHPO4$$

Movement in Soils

- Low Mobility
  - Moves primarily by diffusion
  - Rates are very low - less than 1/4 of an inch
- Factors Affecting Movement
  - Water Content of Soil
  - Clay Content: connection of water films
  - Organic binding - phytate-P in manures more mobile
  - Amount of added P: Capacity to hold P limited

Factors Affecting Availability

- Amount of Available P
- Soil pH:
  - Acid soils: Al inhibits root growth, precipitates P in solution
  - Calcareous soils: Free carbonates precipitate P in solution
- Soil Properties
  - Amounts of Fe and Al oxides, hydroxides; higher in soils with 1:1 clays than 2:1 clays

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