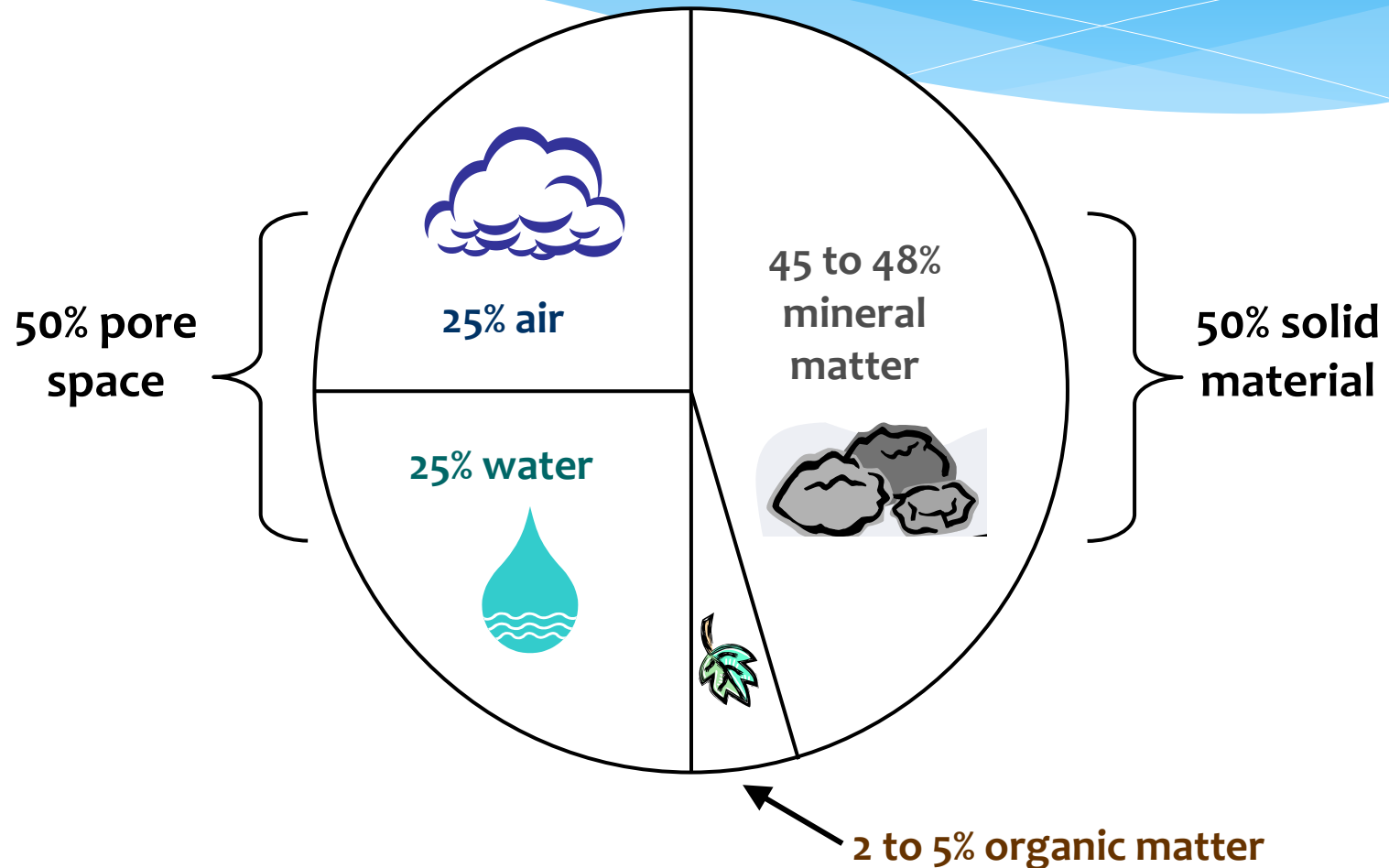


# Soil Chemistry



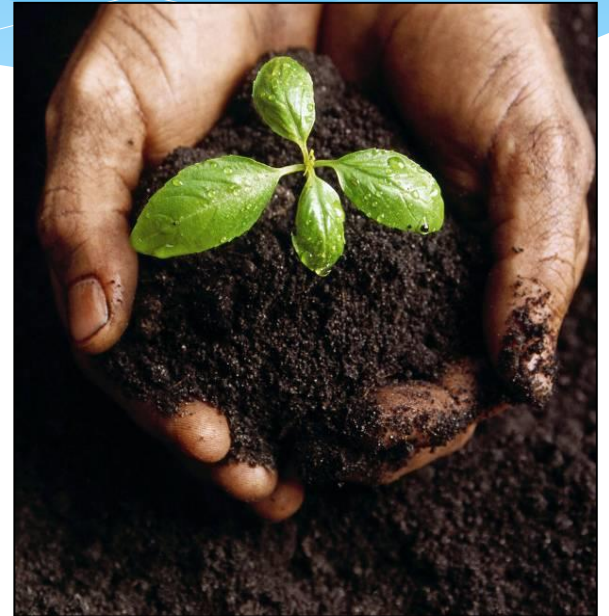
# Volume Composition of a Desirable Surface Soil



# Soil Organic Matter

## ❖ *Soil organic matter:*

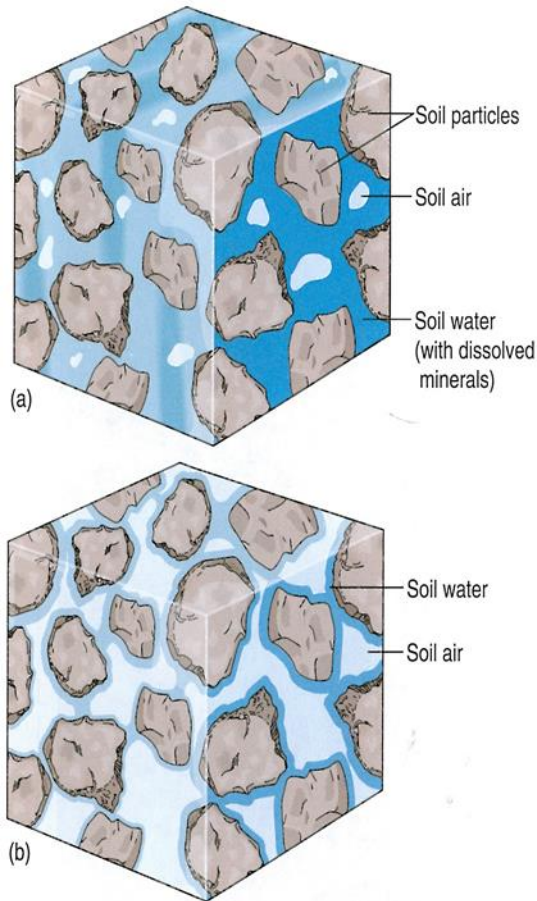
- Plant and animal residues in various stages of decay.
- Sources: dead roots, litter and leaf drop, and the bodies of soil animals such as insects and worms.
- Primary energy and nutrient source for insects, bacteria, fungi, and other soil organisms.
- After decomposition, nutrients released from the residues available for use by growing plants.



## ❖ *Soil humus:*

- Fully decomposed and stable organic matter.
- Most reactive and important component of soil organic matter.
- Form of soil organic material that is typically reported as “organic matter” on soil testing reports.

# Soil Composition- Soil Water



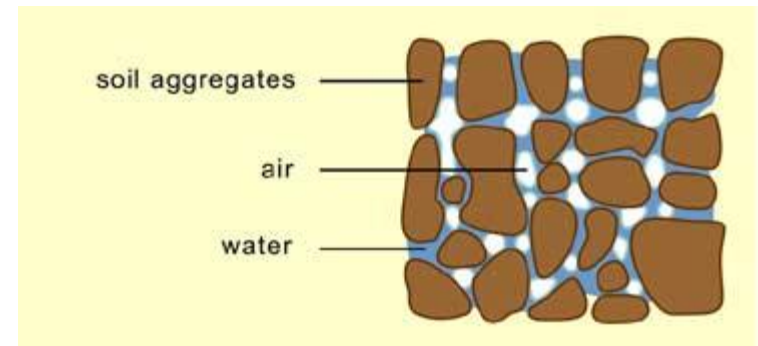
- Not all water in soils is available to plants.
- Water is held within soil pores with varying degrees of tenacity.
- When soil moisture is abundant, plants can readily absorb water, mostly from large to intermediate pore spaces between soil particles.
- When soil moisture becomes limiting, the remaining moisture is present in small pores and as thin films around soil particles.

**Figure 15.3 Pore space.** (a) In a wet soil, most of the pore space is filled with water. (b) In a dry soil, a thin film of water is tightly bound to soil particles, and soil air occupies most of the pore space.

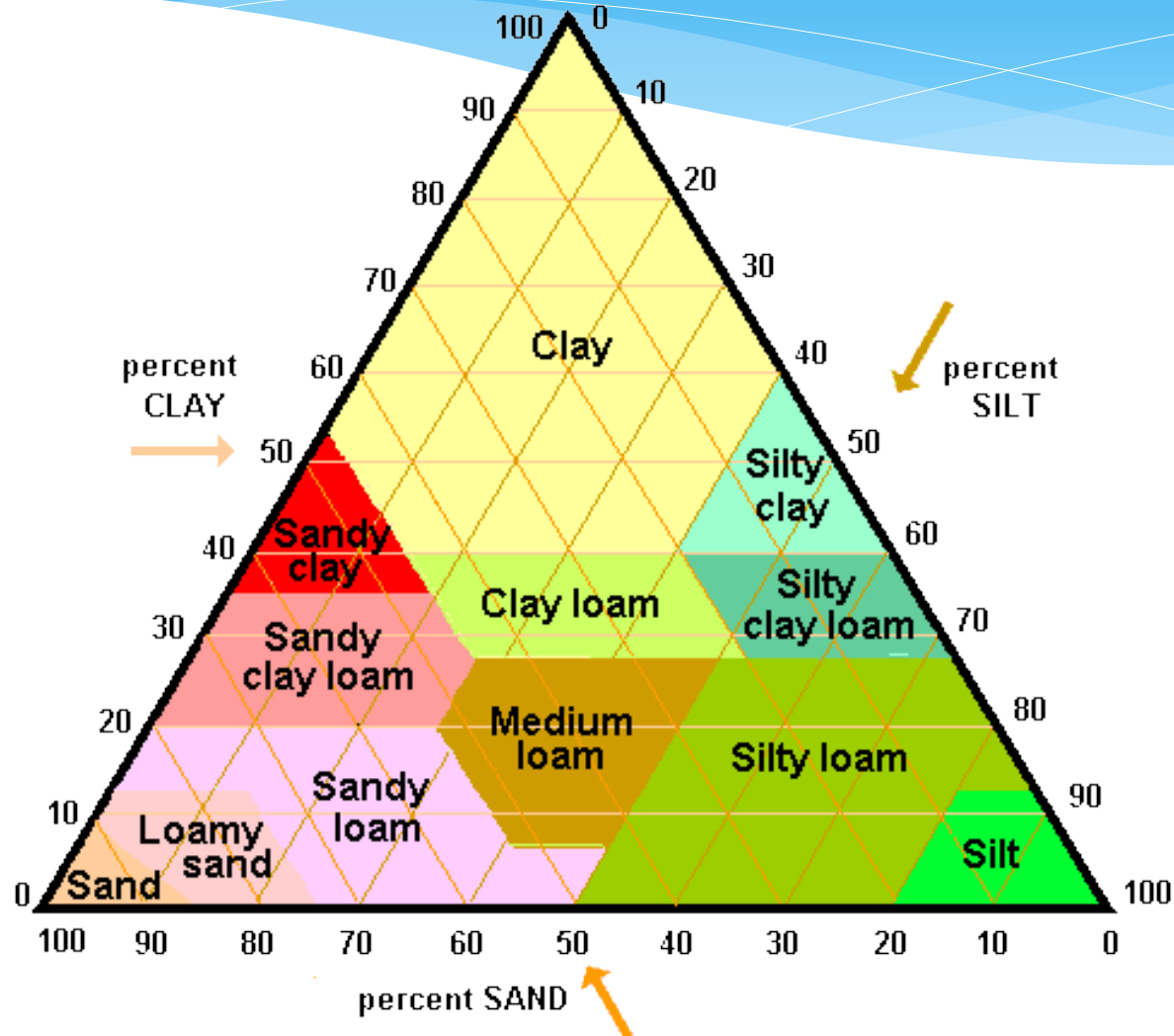
# Soil Composition- Soil Air

is different than atmospheric air.

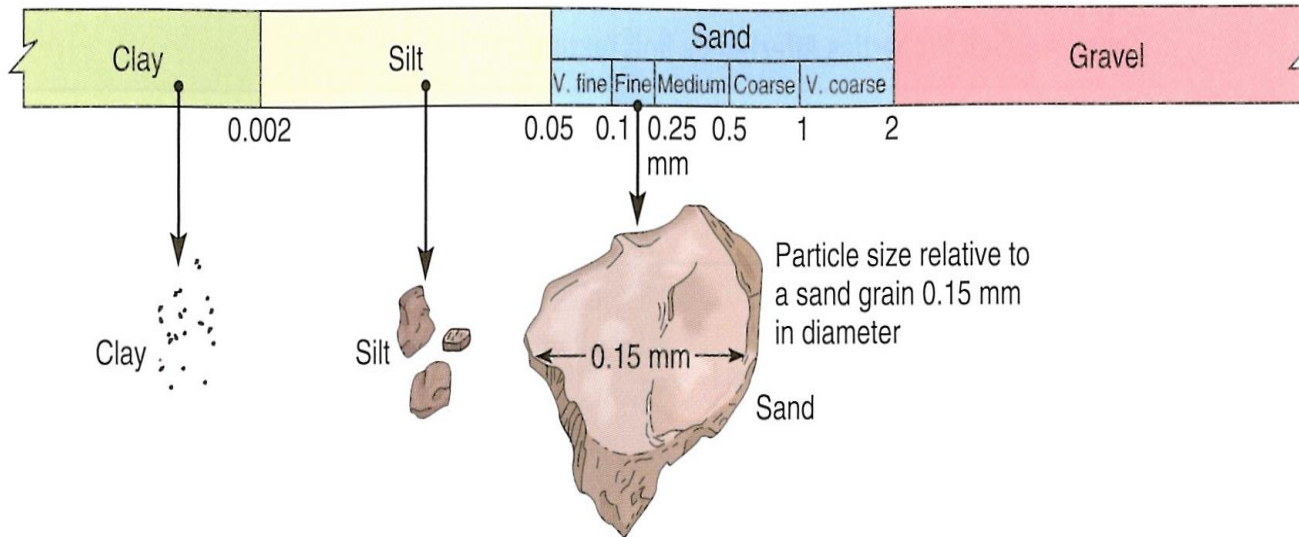
- a. Has a higher moisture content than the atmosphere – up to 100% under optimal soil moisture.
- b. CO<sub>2</sub> concentration much higher (from root respiration). O<sub>2</sub> conc. may only be 10-12%.
- c. The larger the pore size of the soil, the better aerated the soil is.
- d. Compacted soils, or soils made of small particles are not as well aerated.



# Soil Texture Triangle



# Soil Particles



**Figure 15.7** Relative sizes of soil particles.

# Soil Particles

## ❖ Sand:

- Particles range in size from very fine (0.05 mm) to very coarse (2.0 mm) in average diameter.
- Most particles can be seen without a magnifying glass.
- Feel coarse and gritty when rubbed between the thumb and fingers.



**Sand texture**

(Photo by Jim Baker, Virginia Tech)



# Soil Particles

## ❖ *Silt:*

- Particles range in size from **0.05 mm to 0.002 mm.**
- Cannot usually be seen by the unaided eye
- When moistened, silt feels smooth but is not slick or sticky. When dry, it is smooth and floury



**Silt loam texture**

(photo by Jim Baker, Virginia Tech)

# Soil Particles

## ❖ Clay:

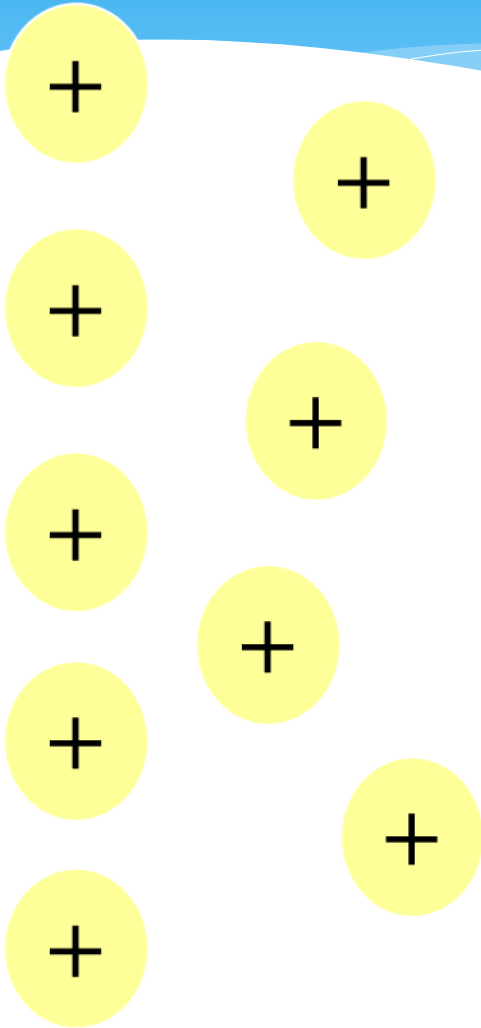
- Particles are *finer than 0.002 mm*.
- Can be seen only with the aid of an electron microscope.
- Feels extremely smooth or powdery when dry, and becomes plastic and sticky when wet.



**Clay texture**

(Photo by Jim Baker, Virginia Tech)

# Ion Exchange



- \* Ions adsorbed to soil surfaces can be exchanged with ions in soil solution.
- \* Cations and anions
  - \* Cation exchange (e.g.,  $\text{Ca}^{2+}$  for  $\text{K}^+$ )
  - \* Anion exchange (e.g.,  $\text{H}_2\text{PO}_4^-$  for  $\text{NO}_3^-$ )

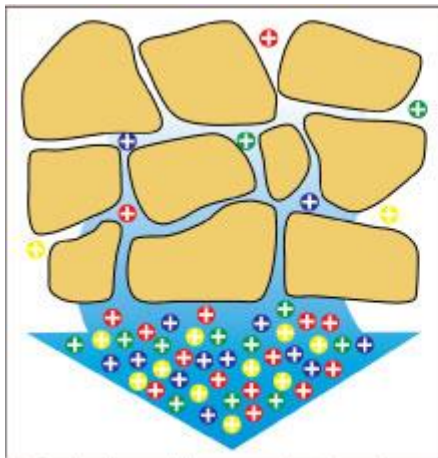
# Ion exchange

- \* Where do ions in soil come from?
  - \* Release from organic matter
  - \* Rain
  - \* Weathering of parent material

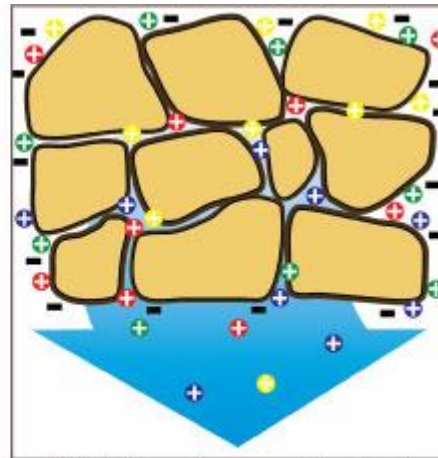
# Why do soils exchange ions?

- \* Clay particles
- \* Organic matter in soil

..... are negatively charged



Sandy soils poor in humus can't retain nutrients.



Effect of cation exchange capacity to soils with the addition of humic acid.

Mineral Soil Particles	
Sand	Clay
$\text{Si}_2\text{O}_4$	$\text{SiAlO}_4^-$
No charge. Does not retain cations.	Negative charge. Attracts and retains cations.

# What's so great about ion exchange?

- \* Retards the release of pollutants to groundwater
- \* Affects permeability, with implications for landfills, ponds, etc.
- \* Plant nutrients Ca, Mg, K are supplied to plants mainly from exchangeable forms
- \* necessary for soil fertility

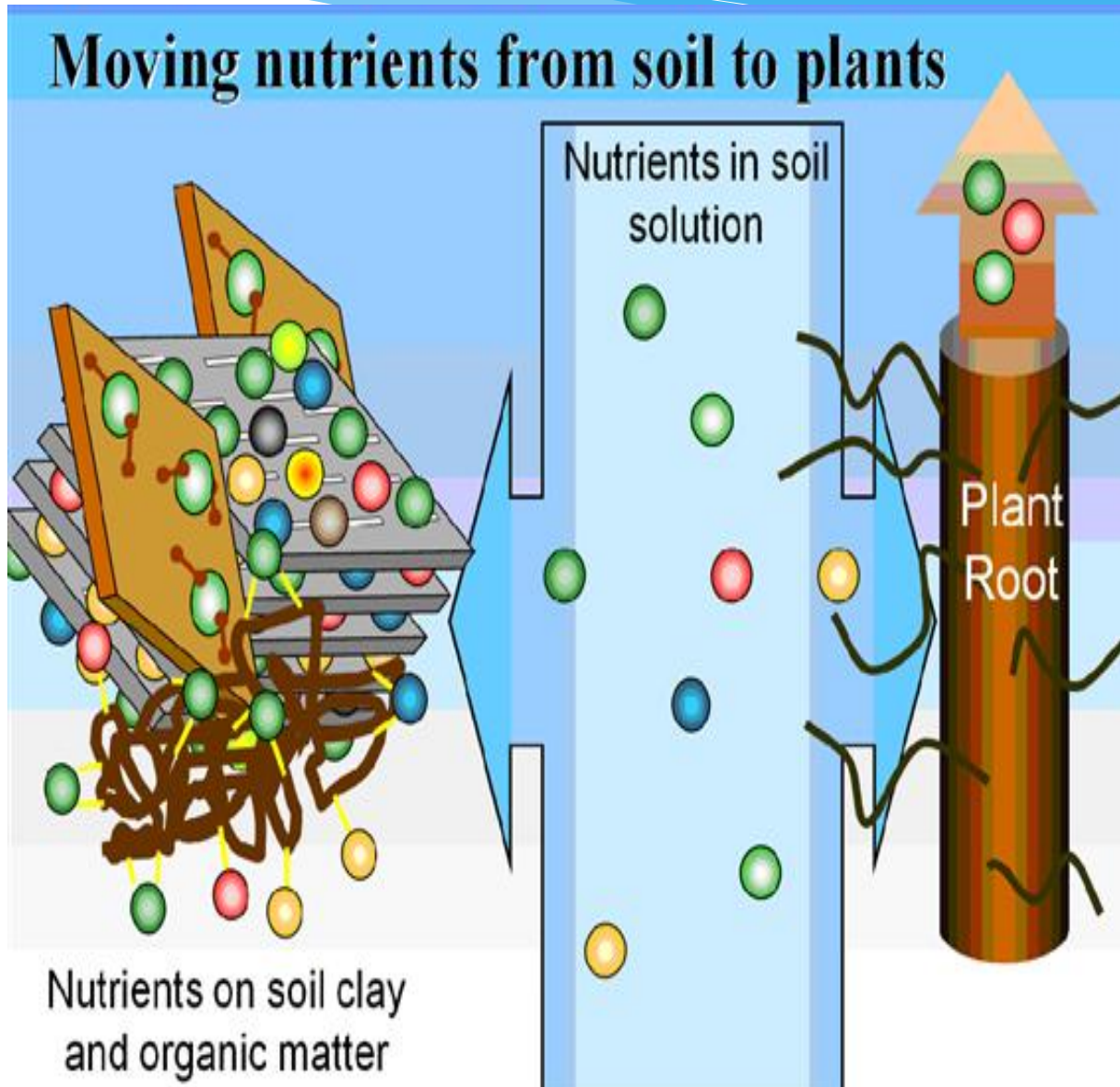
“Next to photosynthesis and respiration, probably no process in nature is as vital to plant and animal life as the exchange of ions between soil particles and growing plant roots.”

Nyle C. Brady

# Definitions

- \* cation exchange: A process - cations in solution exchanged with cations on exchange sites of minerals and OM
- \* cation exchange capacity (CEC): The total amount of exchangeable cations that a particular material or soil can adsorb at a given pH

# Cation Exchange Capacity

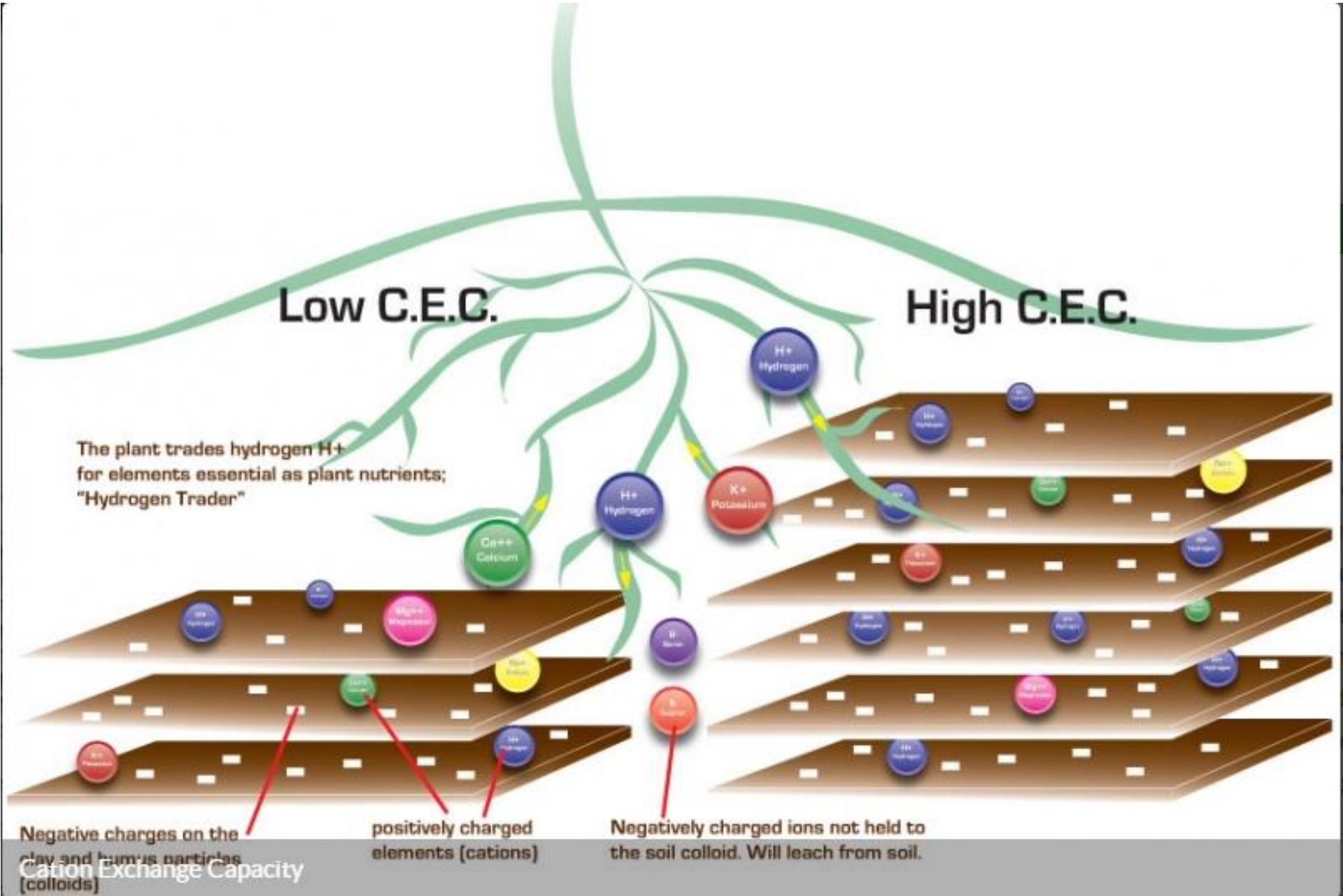




**Low C.E.C.**

**High C.E.C.**

The plant trades hydrogen  $H^+$  for elements essential as plant nutrients; "Hydrogen Trader"

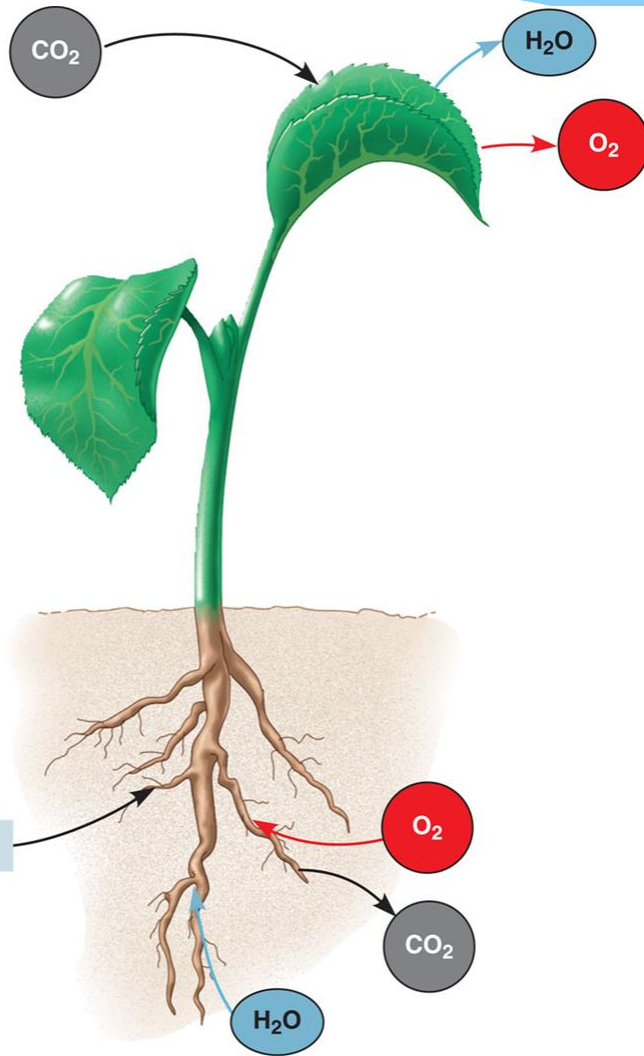


Negative charges on the clay and humus particles (colloids)  
**Cation Exchange Capacity**

positively charged elements (cations)

Negatively charged ions not held to the soil colloid. Will leach from soil.

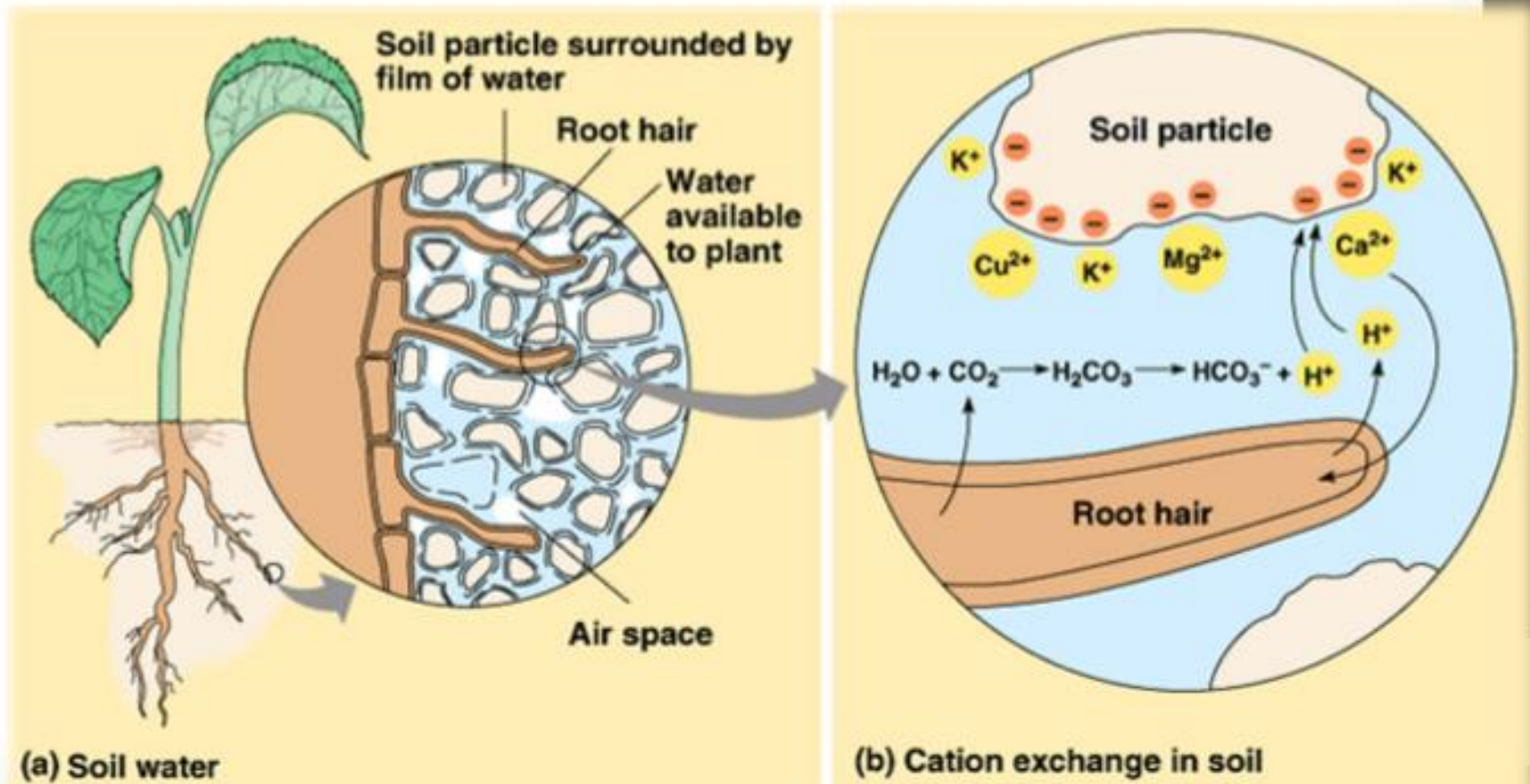
# Significance of CEC



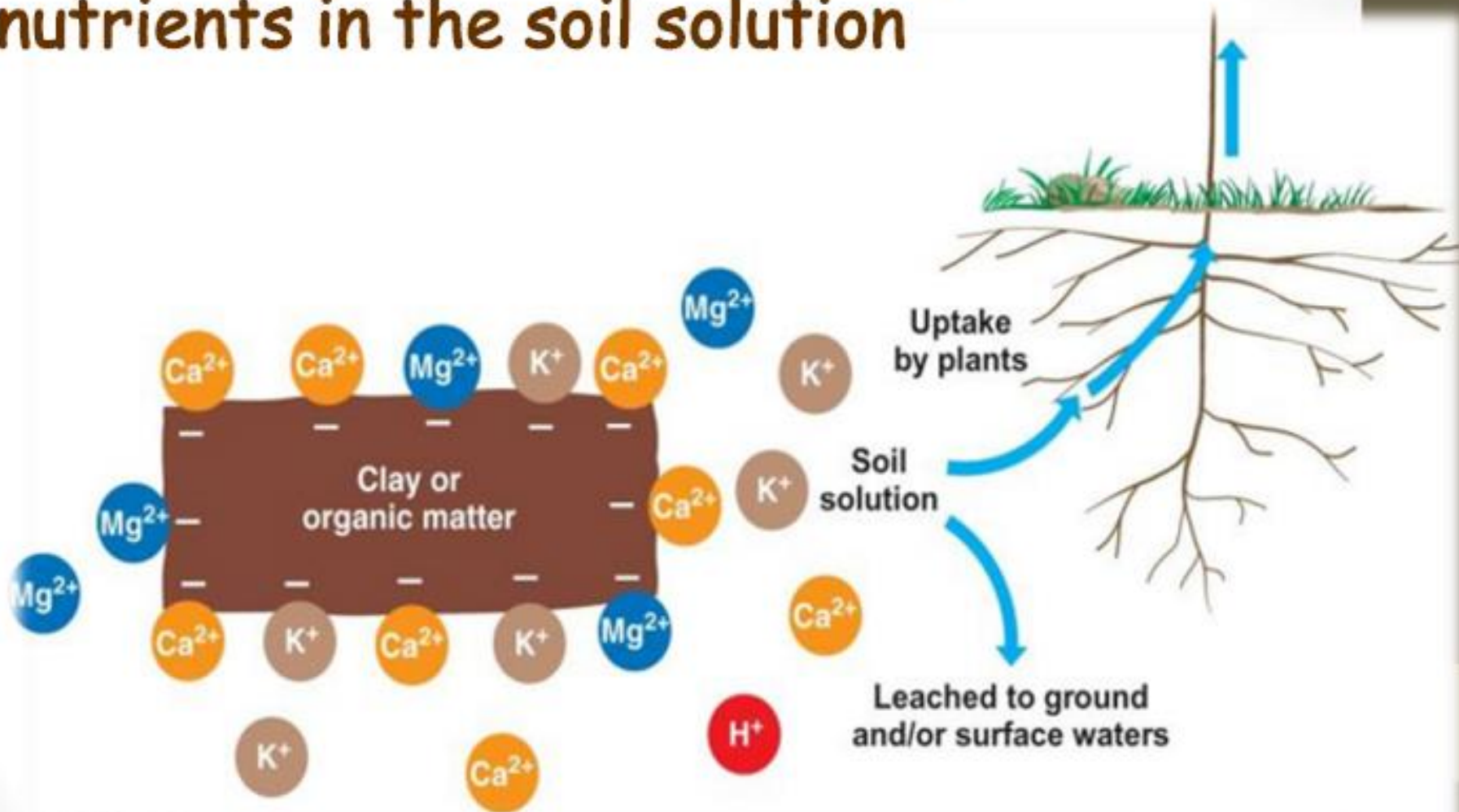
- \* uptake of nutrient ions from plant roots occurs from solution only
- \* as cations are absorbed into the roots, they are replaced in the soil solution by H<sup>+</sup> ions
- \* when the exchange equilibrium is disturbed, some of that ion will desorb from the soil particles
- \* replaced by another ion
- \* if the nutrient is a weakly adsorbed one, such as K, there may not be enough adsorbed to replenish the soil, presenting a fertility problem
- \* K is the most likely cation to be in short supply

# Plant roots use cation exchange to assist in nutrient uptake from the soil—

- (a) Soil moisture surrounding the roots
- (b) Absorption of soil mineral nutrients by cation exchange



# Absorption and leaching of soil nutrients in the soil solution



# Cation Exchange Capacity

- \* Expressed in terms of positive charge adsorbed per unit mass

usually mmole/100g or cmole/kg (the same value)

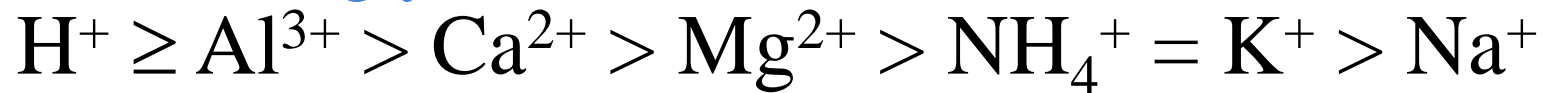
$\text{cmol}_c$  = centimole of unbalanced charge

- \* If  $\text{CEC} = 10 \text{ cmol}_c/\text{kg}$ 
  - soil adsorbs 10 cmol of  $\text{H}^+$
  - can exchange it with 10 cmol  $\text{K}^+$ , or 5 cmol  $\text{Ca}^{2+}$
  - ✓ number of charges, not number of ions, what matters

# Exchange affinity

Held more strongly

Held more weakly



This is referred to as the “Lyotropic series”

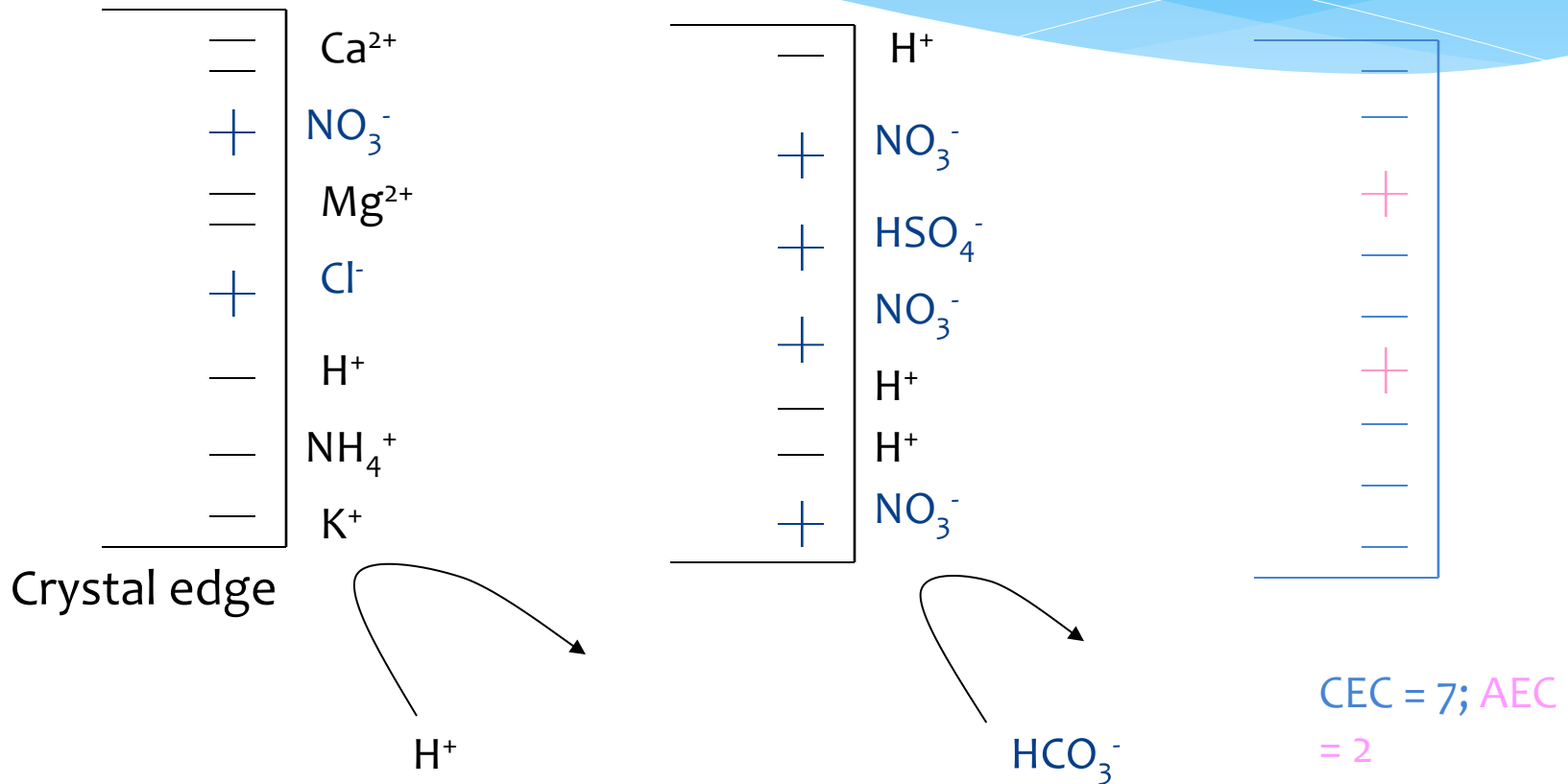
Strength of adsorption proportional to valence  $\div$   
hydrated radius

# Ion exchange vs. CEC

How many charges are there to fill???

Sandy loam

VERY acidic soil



# CEC depends upon

- \* Amount of clay and organic matter
- \* Type of clay minerals present

Organic matter can have a 4 to 50 times higher CEC per given weight than clay.

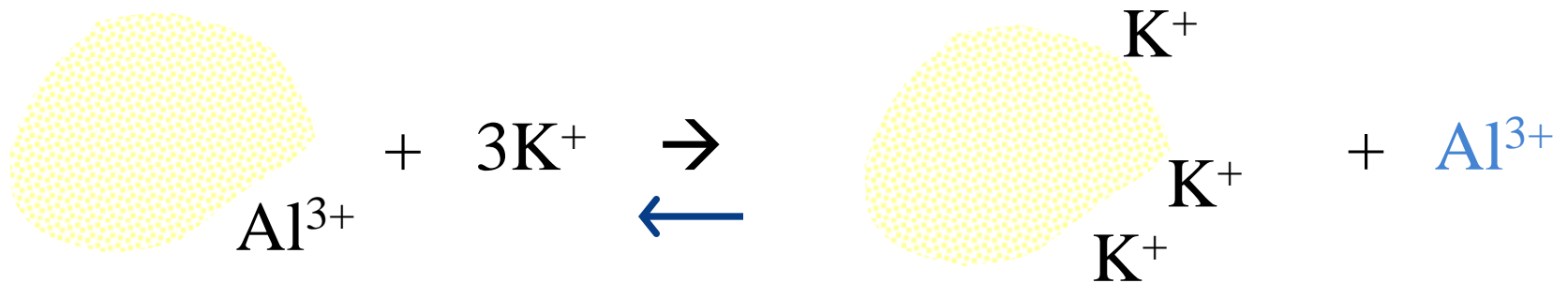
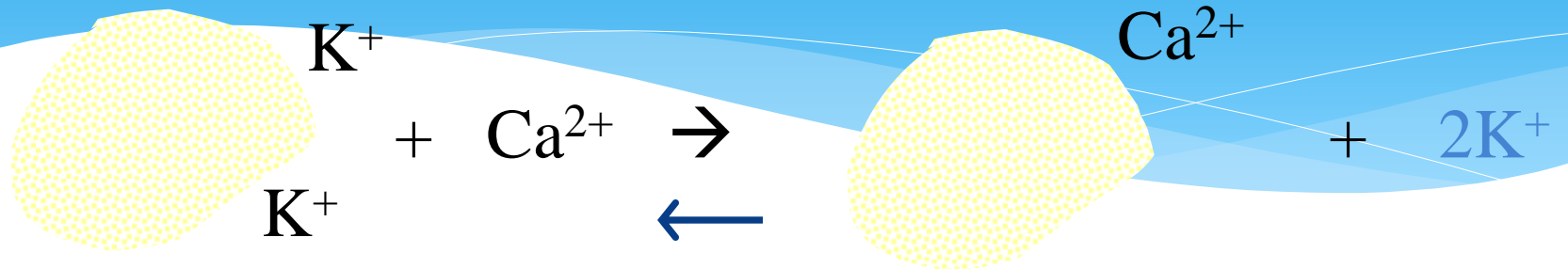


## Cation exchange capacity: Sources of negative charge

### ❖ Negative charge sources related to *mineralogy of the clay fraction*:

- **Isomorphous substitution:** the replacement of a  $\text{Si}^{4+}$  or  $\text{Al}^{3+}$  cation in the mineral structure with a cation with a lower charge.
- Clay minerals with a repeating layer structure of two silica sheets sandwiched around an aluminum sheet (2:1 clays, such as vermiculite or smectite), typically have a higher total negative charge than clay minerals with one silica sheet and one aluminum sheet (1:1 clays, such as kaolinite).

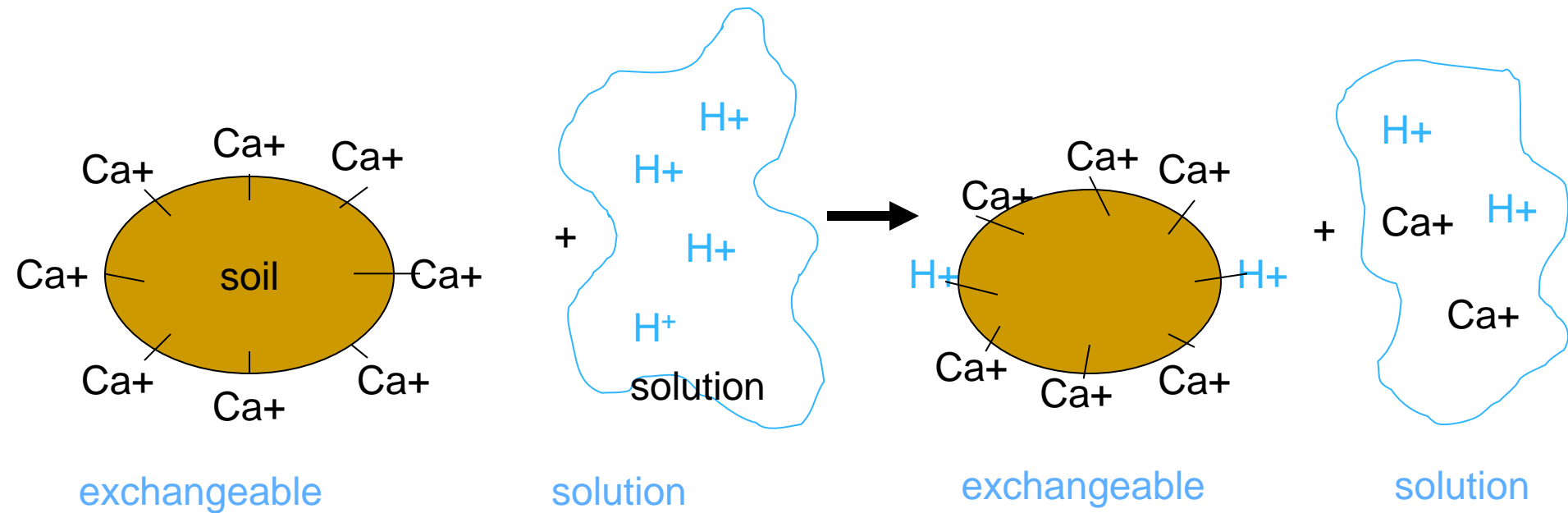
# Examples of cation exchange



The interchange between a cation in solution and one on a colloid must be **CHARGE** balanced.

The reactions are **reversible**, unless...

# Ion exchange example: Add $H^+$ ions to soil



# Cation Exchange Capacity of different soils

Table 1

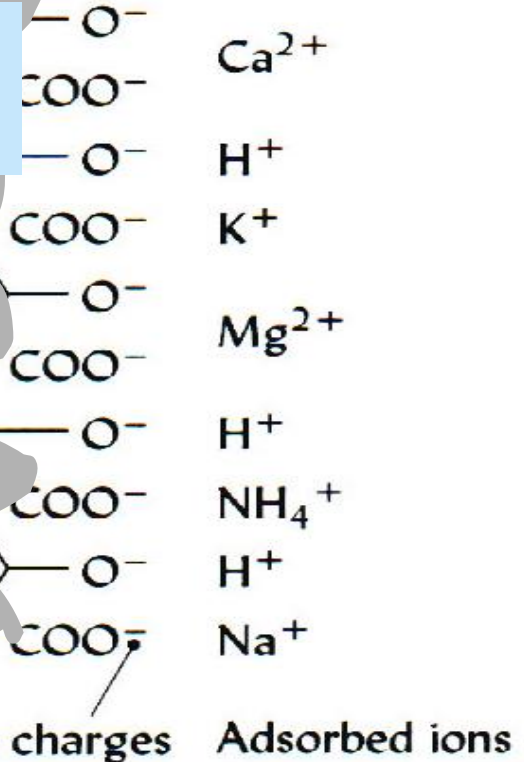
Values of cation exchange capacity for different materials  
(from Rowell, 1993)

Material	CEC, meq/100 g
Organic matter	130-500
Vermiculite	100-150
Montmorillonite	29-150
Hydro mica	10-40
Kaolin	3-15
Fine sand	0.8
Sand	1 -4
Loamy sand	2 - 12
Sandy loam	7 - 16
Clay	4 - 60

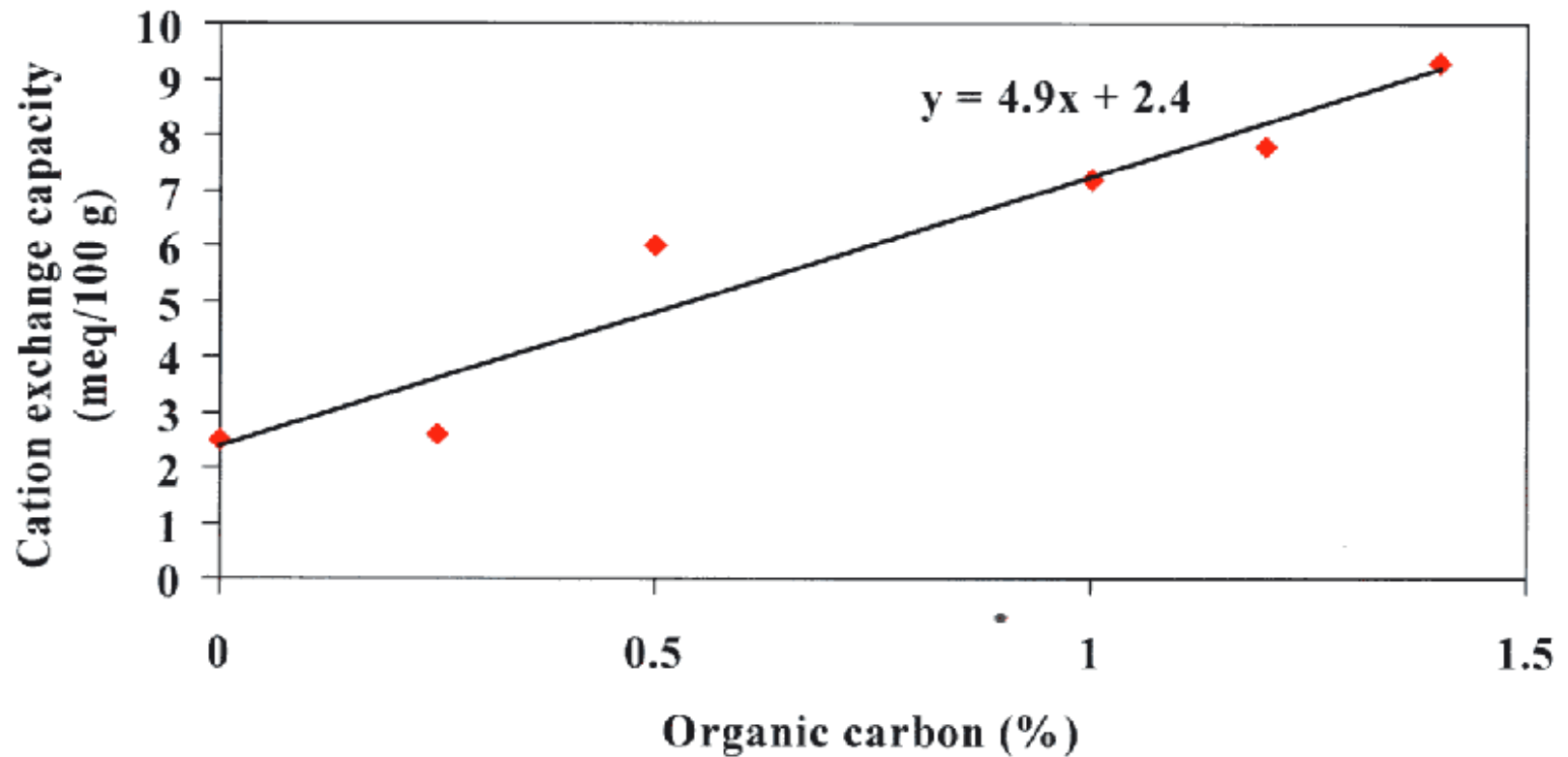
# Negative charges on humus

ENORMOUS external surface area! (but no internal surface – all edges)

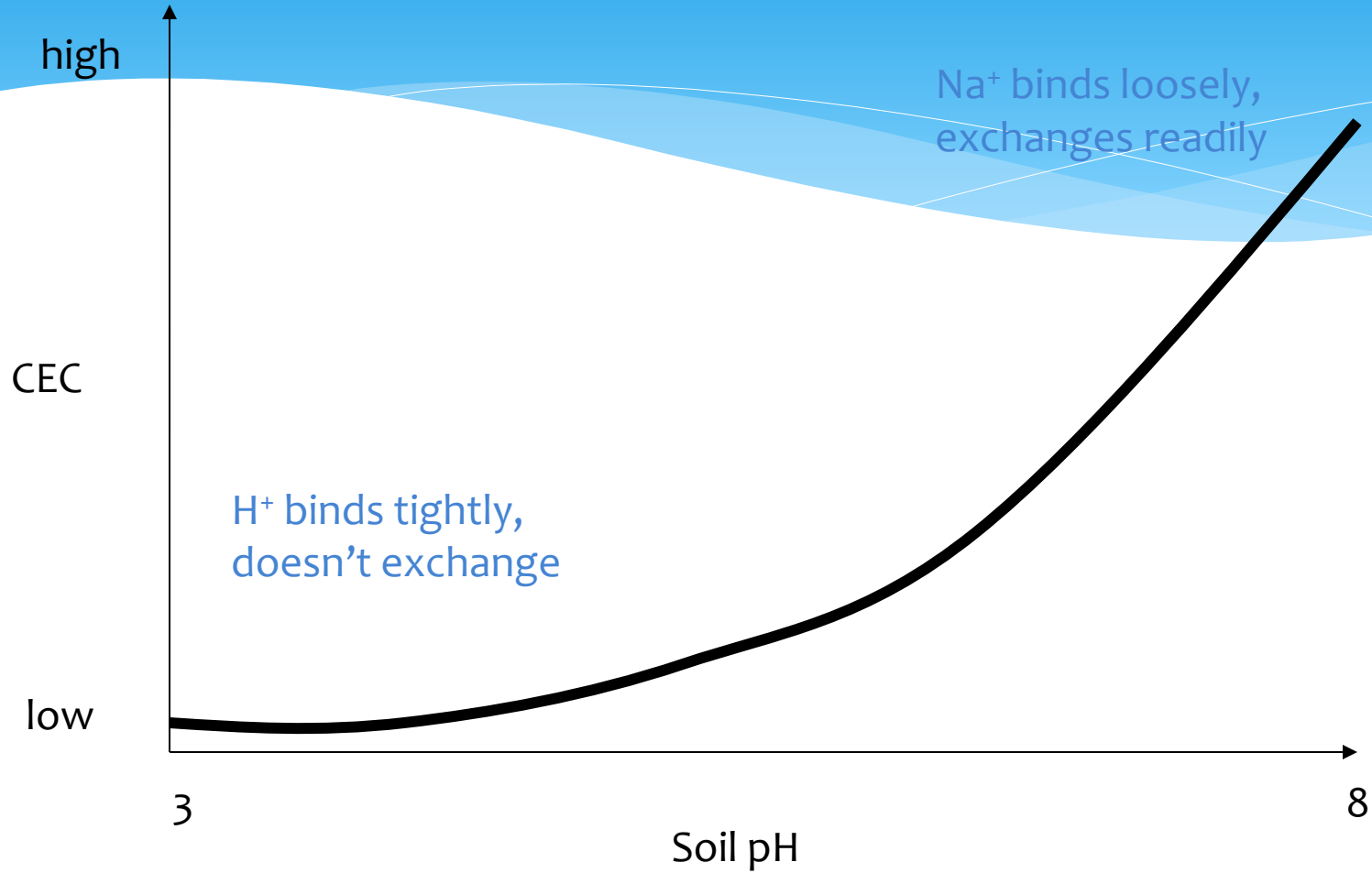
Central unit of a humus colloid (mostly C and H)



# Organic matter and CEC



# CEC and pH



# A real-life application:

How lime raises pH --





# Base saturation

- \* Of the common soil-bound cations,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  are considered to be *basic cations*.
- \* A measure of the proportion of basic cations occupying the exchange sites
- \* Base cations are those that do not form acids
  - \*  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$  . . . ,
  - \* ions OTHER THAN  $\text{H}^+$  and  $\text{Al}^{3+}$
- ❖ **High base saturation (>50%) enhances Ca, Mg, and K availability and prevents soil pH decline.**
- ❖ **Low base saturation (<25%) is indicative of a strongly acid soil that may maintain  $\text{Al}^{3+}$  activity high enough to cause phytotoxicity.**

# Equation for base saturation

$$\text{Base Saturation} = \sum \frac{Ca^{2+}, Mg^{2+}, K^+, NH_4^+, \dots}{CEC} \times 100$$

# Soil pH

## Indication of the acidity/basicity of the soil

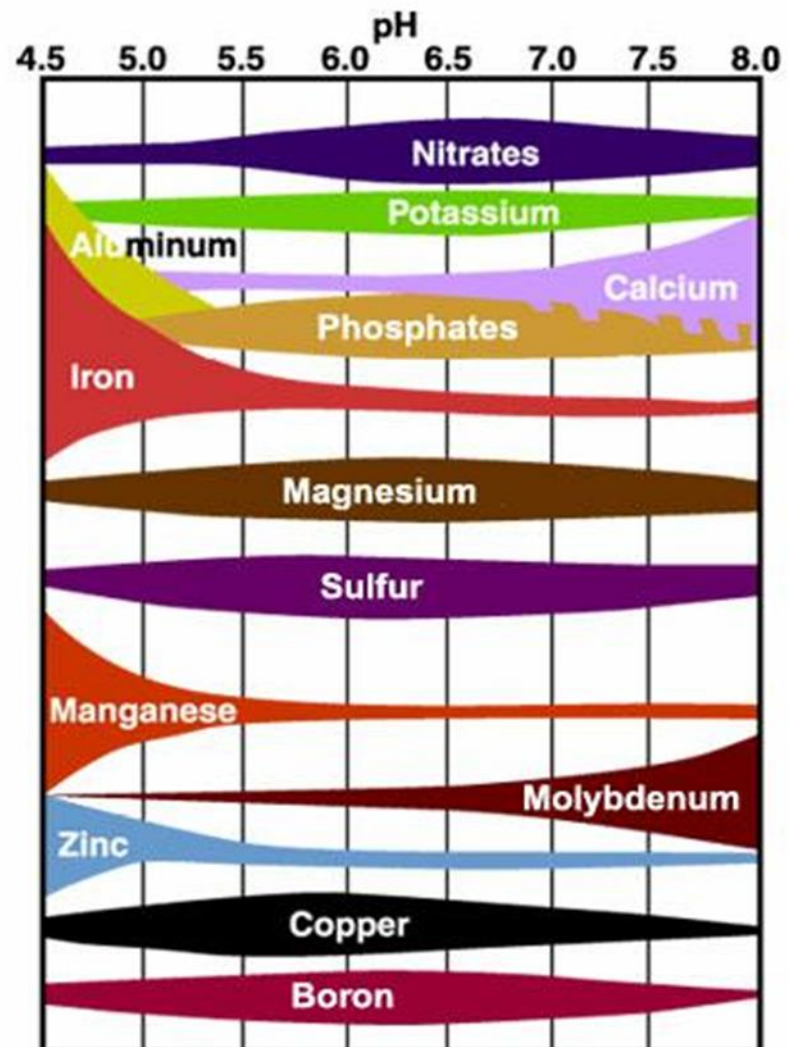
- \* At pH 7.0 –  $H^+$  ions equal  $OH^-$  ions
- \* 10x change between each whole pH number
  - \* pH 5.0 is 10x more acidic than pH 6.0
- \* Typical soil pH ranges from 4.0 to 10
  - \* Most plants grow well from 5.5 to 8.5
    - \* Strongly acidic soils undesirable – develop toxic levels of Al & Mn, microbe activity greatly reduced
    - \* Strongly alkaline soils have low micronutrient availability, P may be deficient

# Soil pH

- \* Importance of Soil pH
  - \* Affects solubility of minerals
    - \* More soluble in slightly acidic soils
    - \* Most crops do best at pH – 6.5
  - \* Plants preferring acid soils
    - \* Azaleas, rhododendrons, blueberries, pineapple
  - \* Plants preferring basic soils
    - \* Barley, sugar beets
      - \* High Ca demand
  - \* Alfalfa – neutral/slightly basic pH

# Significance of soil pH

- \* *nutrient availability*  
– the ability of plants to take up nutrients is very much dependent on the soil pH



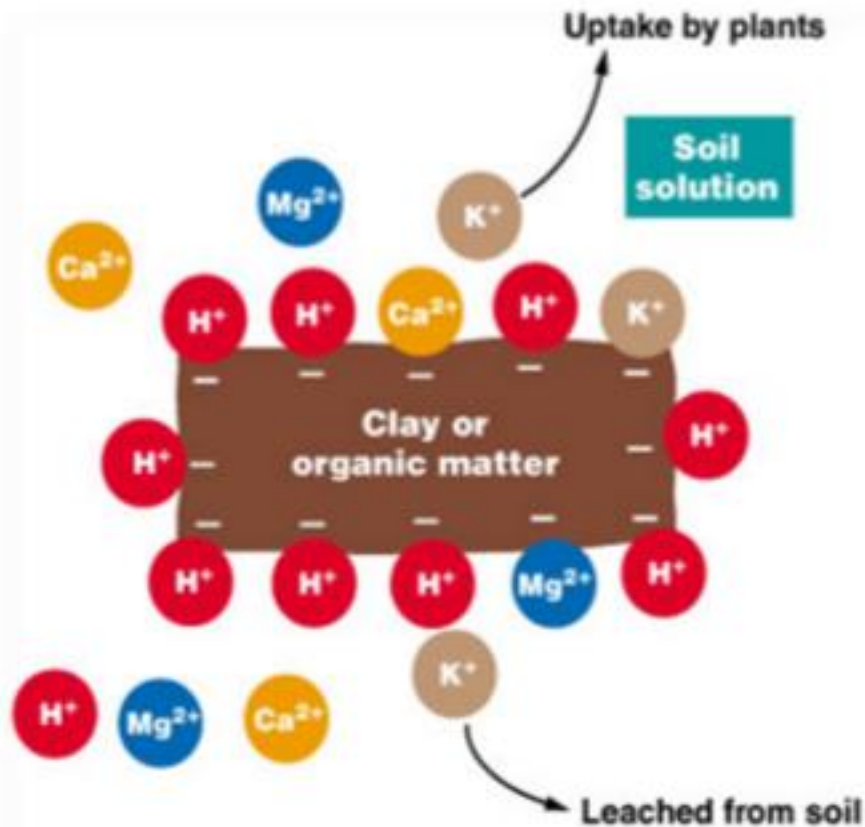
# Soil pH

- \* Also affects soil microbes
  - \* Decreased soil microbe activity w/ acidic soils
  - \* Slow/stop decomposition of beneficial materials
  - \* Decreased N availability
- \* Basic Cation Saturation Percentage
  - \* *Base Saturation Percentage* – proportion of basic cations to the total cations
    - \* More acidic the soil, the lower the BSP
    - \* At pH 7.0, BSP is essentially 100%
    - \* Aids in the decision on how much lime to add

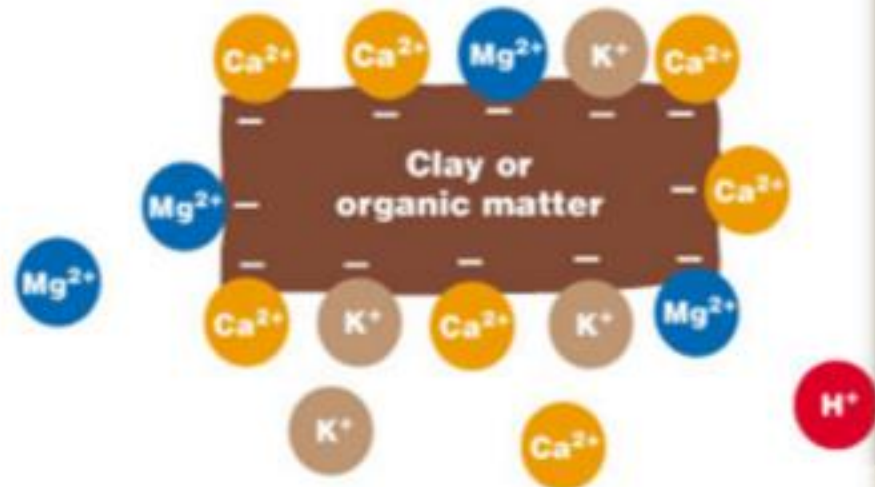
# Sources of soil acidity

- \* *rain* - polluted or fresh will be slightly acidic due to dissolved gases
- \* *microbial and root respiration* → produces CO<sub>2</sub>
- \* *oxidation of organic matter* → produces organic acids known as humic acids, together with nitric and sulfuric acids

# Cation exchange on soil particles — effects of soil pH



**(a) Acidic soil (low pH)**

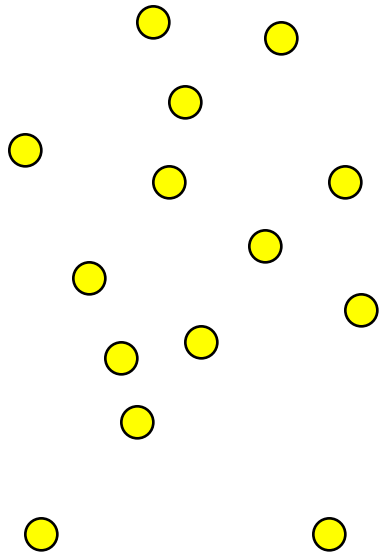


**(b) Neutral to basic soil (higher pH)**

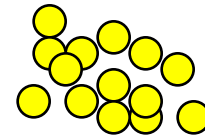


Soil clay particles can be unattached to one another (*dispersed*) or clumped together (*flocculated*) in aggregates. Soil aggregates are cemented clusters of sand, silt, and clay

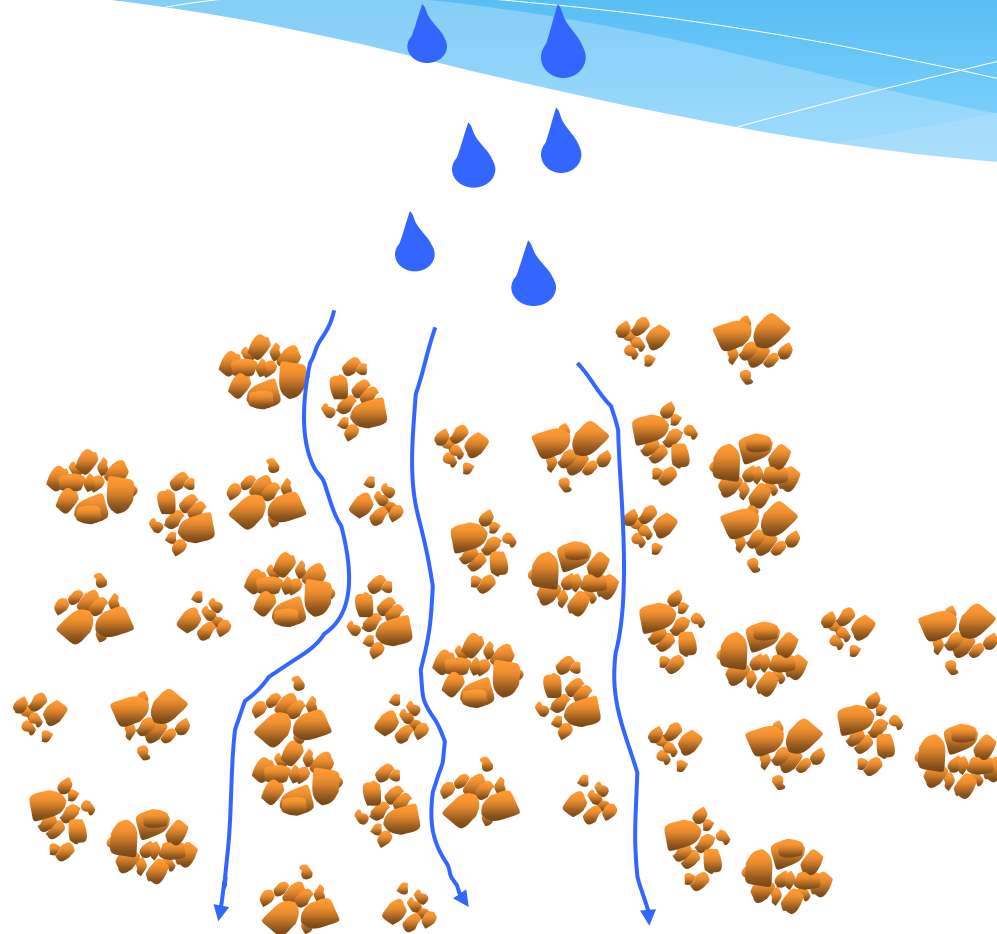
Dispersed Particles



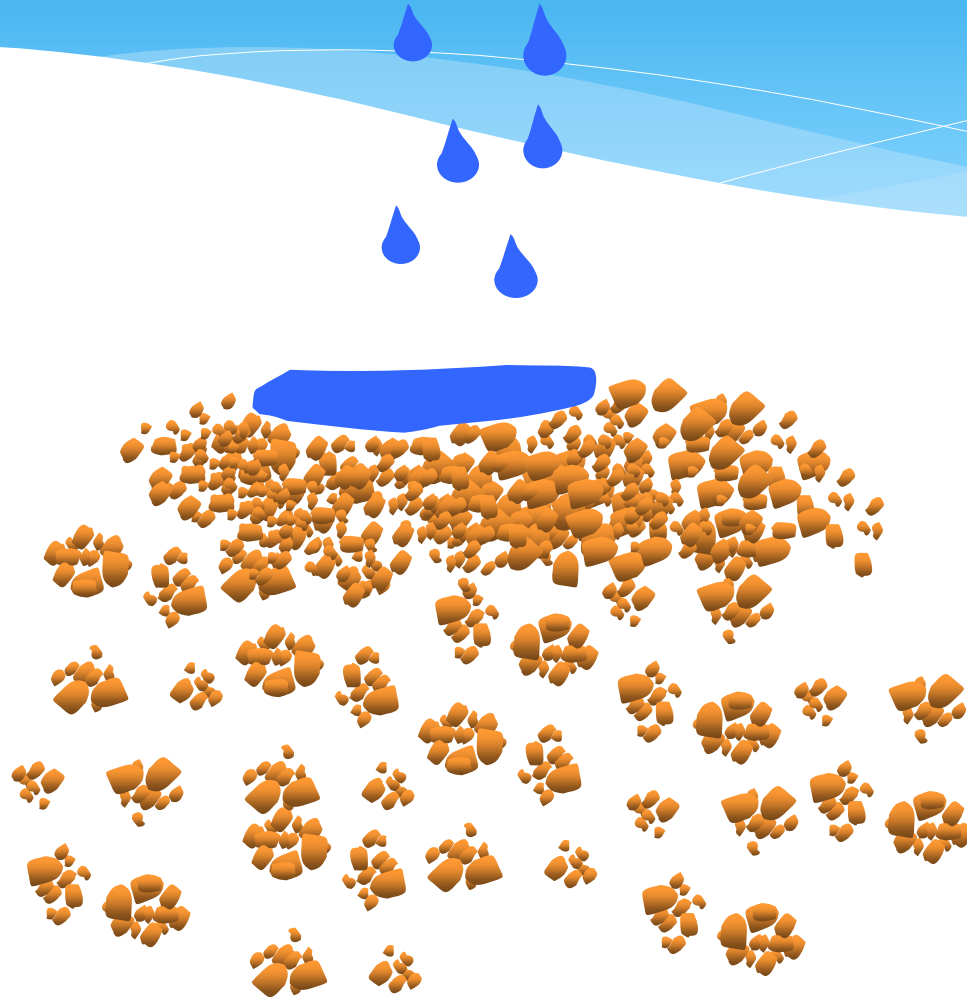
Flocculated Particles



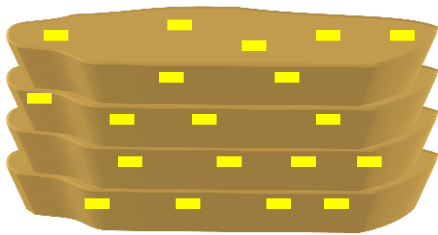
Flocculation is important because water moves mostly in large pores between aggregates. Also, plant roots grow mainly between aggregates.



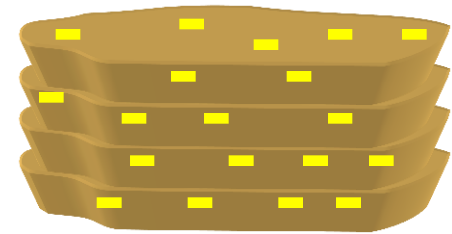
In all but the sandiest soils, dispersed clays plug soil pores and impede water infiltration and soil drainage.



Most clay particles have a negative electrical charge. Like charges repel, so clay particles repel one another.

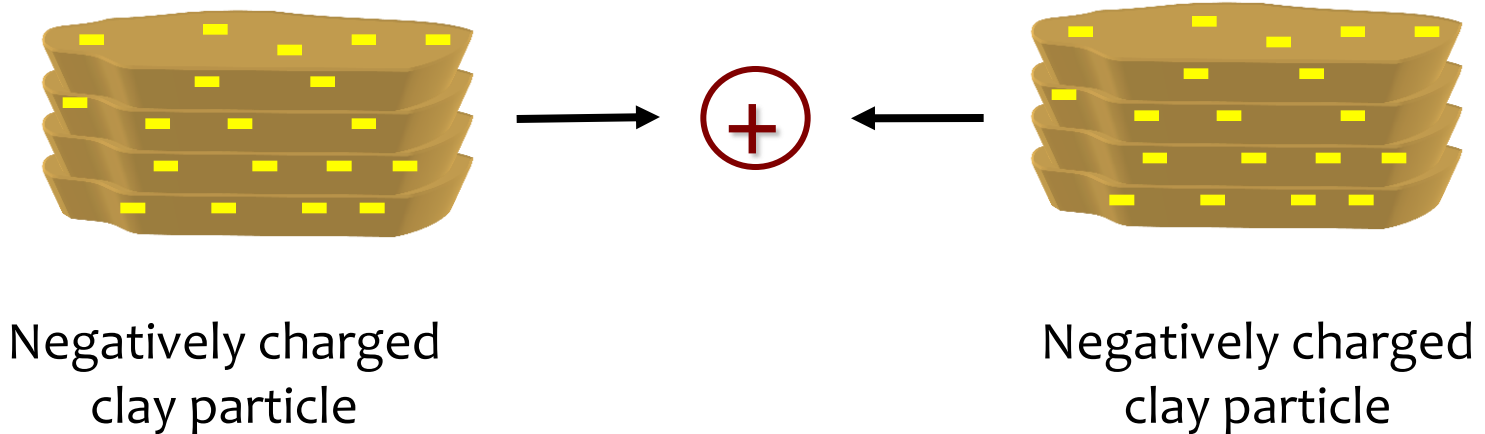


Negatively charged  
clay particle



Negatively charged  
clay particle

Cations can make clay particles stick together (flocculate).



# Flocculating Cations

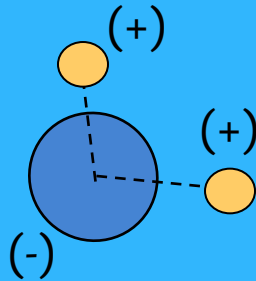
- \* We can divide cations into two categories
  - \* Poor flocculators
    - \* Sodium
  - \* Good flocculators
    - \* Calcium
    - \* Magnesium

Ion		Relative Flocculating Power
Sodium	Na <sup>+</sup>	1.0
Potassium	K <sup>+</sup>	1.7
Magnesium	Mg <sup>2+</sup>	27.0
Calcium	Ca <sup>2+</sup>	43.0

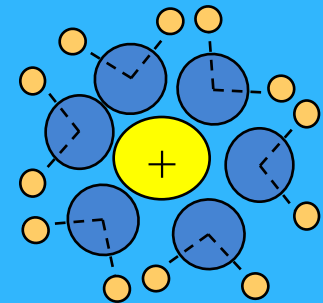
# Flocculating Power of Cations

Cations in water attract water molecules because of their charge, and become hydrated.

Water molecule is polar:  
(+) on one end, (-) on the other end



Hydrated cation

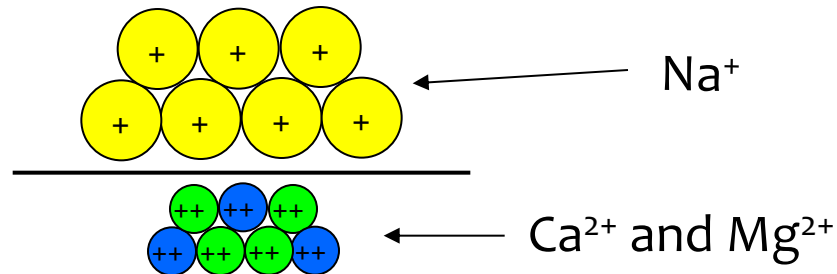


Cations with a single charge and large hydrated radii are the poorest flocculators.

Cation	Charges per molecule	Hydrated radius (nm)	Relative flocculating power
Sodium	1	0.79	1.0
Potassium	1	0.53	1.7
Magnesium	2	1.08	27.0
Calcium	2	0.96	43.0

# Sodium Adsorption Ratio

The ratio of 'bad' to 'good' flocculators gives an indication of the relative status of these cations:



Mathematically, this is expressed as the 'sodium adsorption ratio' or SAR:

$$SAR = \frac{[Na^+]}{\sqrt{[Ca^{2+}] + [Mg^{2+}]}}$$

where concentrations are expressed in mmoles/L



# Electrical Conductivity

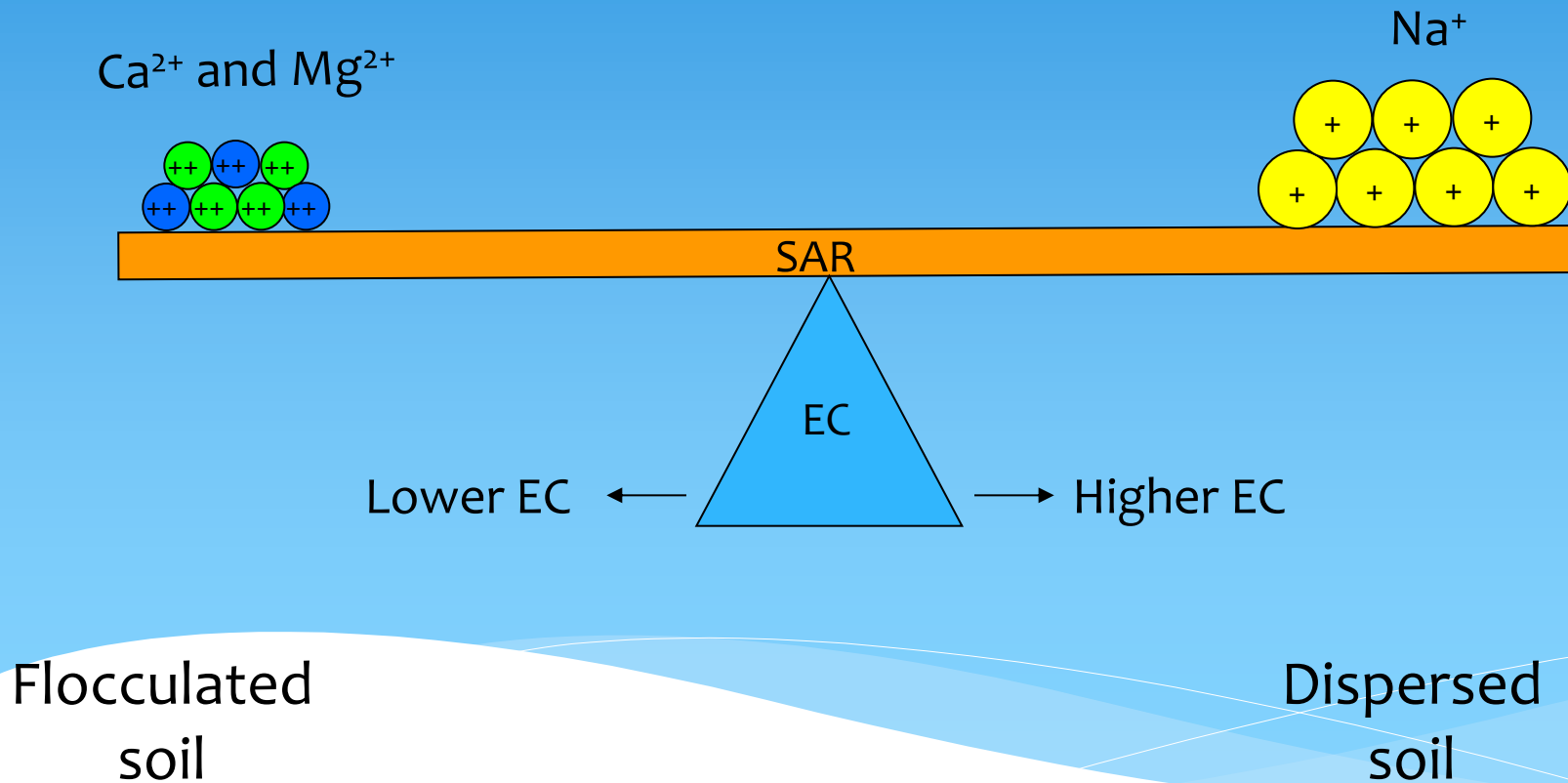
Ions in solution conduct electricity, so the total amount of soluble soil ions can be estimated by measuring the electrical conductivity (EC) of a soil water extract.

EC is measured in units of conductance over a known distance:

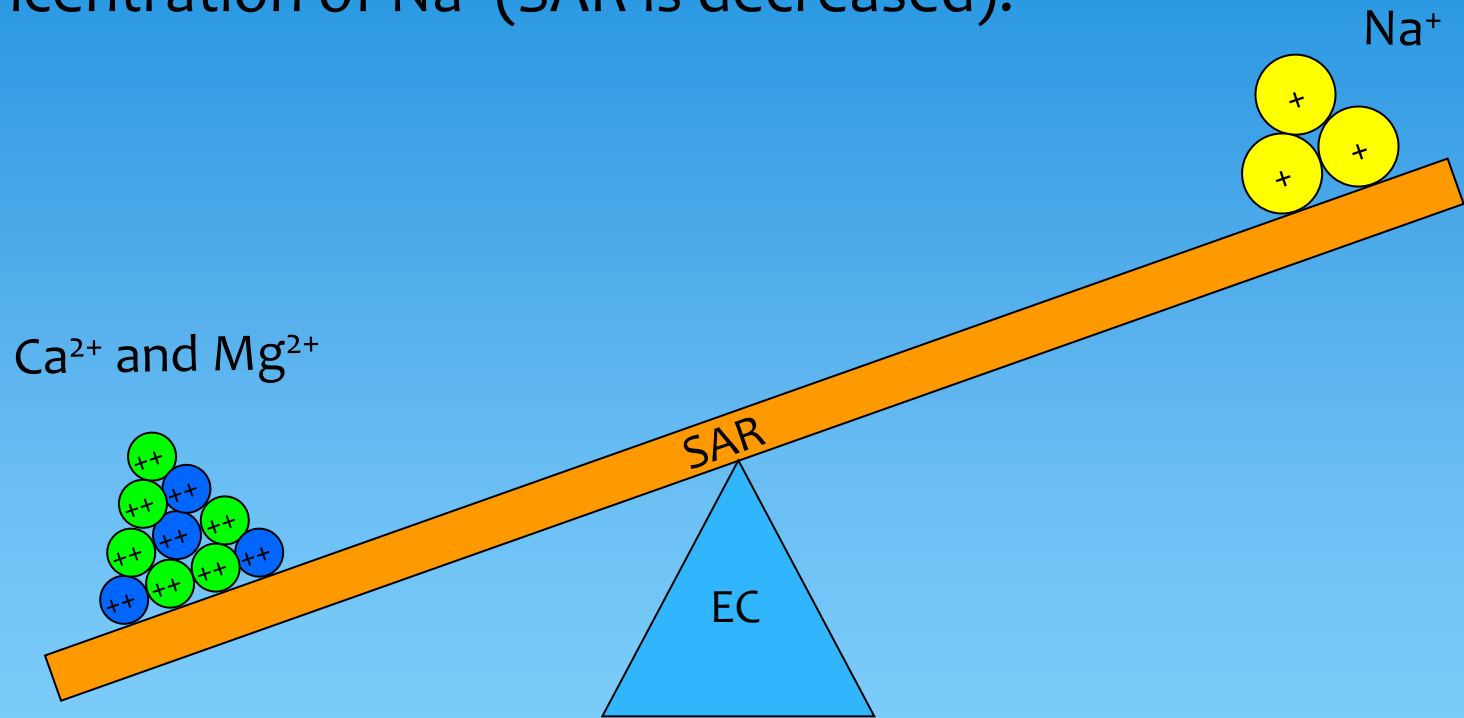
deci-Siemens per meter or dS/m

Soil with a high EC is salty; soil with a low EC is not.

Aggregate stability (dispersion and flocculation) depends on the balance (SAR) between ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and  $\text{Na}^+$  as well as the amount of soluble salts (EC) in the soil.



Soil particles will flocculate if concentrations of ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) are increased relative to the concentration of  $\text{Na}^+$  (SAR is decreased).

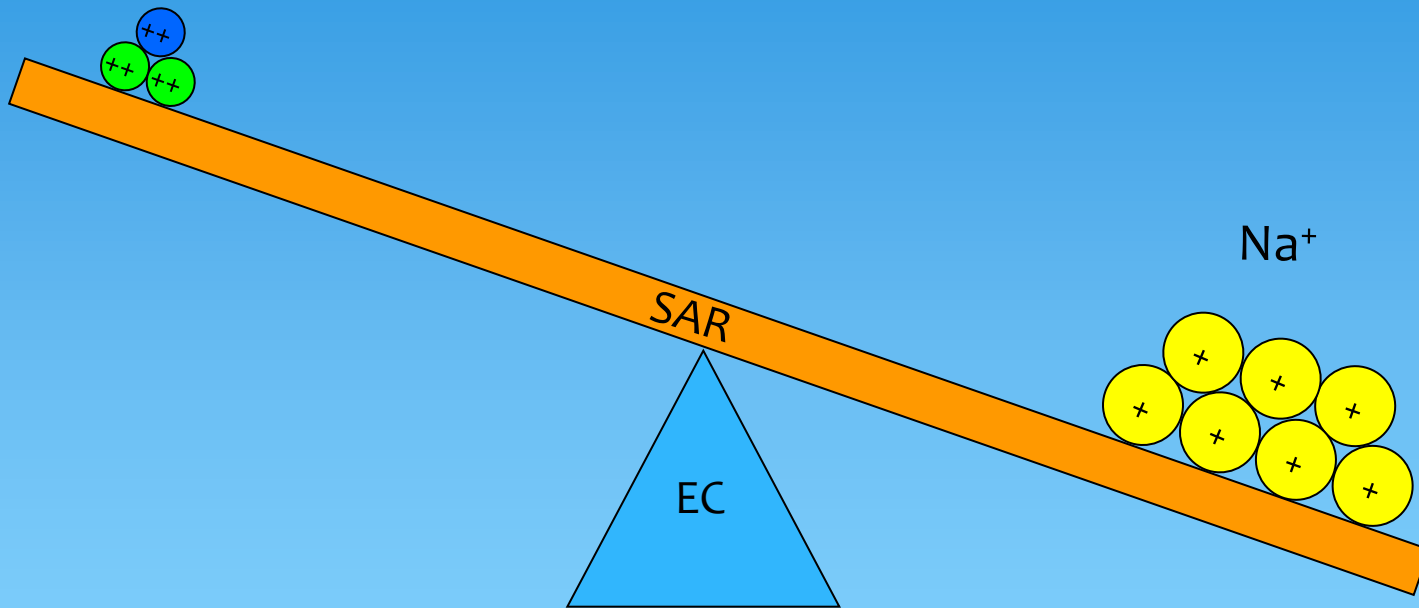


**Flocculated  
soil**

Dispersed  
soil

Soil particles will disperse if concentrations of ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) are decreased relative to the concentration of  $\text{Na}^+$  (SAR is increased).

$\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$



$\text{Na}^+$

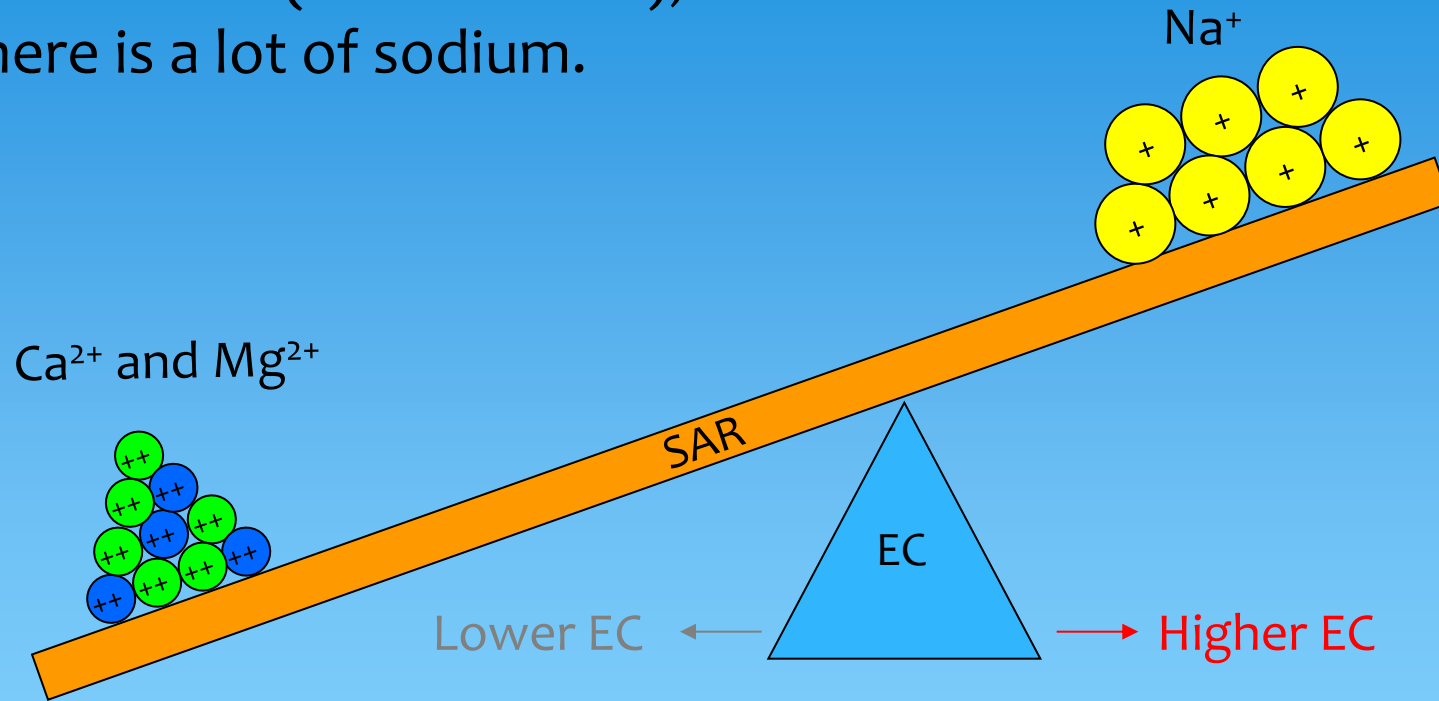
SAR

EC

Flocculated  
soil

Dispersed  
soil

Soil particles will flocculate if the amount of soluble salts in the soil is increased (increased EC), even if there is a lot of sodium.

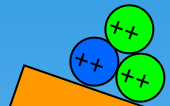


**Flocculated soil**

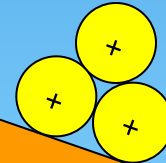
Dispersed soil

Soil particles may disperse if the amount of soluble salts in the soil is decreased (i.e. if EC is decreased).

$\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$



$\text{Na}^{+}$



SAR

EC

Lower EC



Higher EC

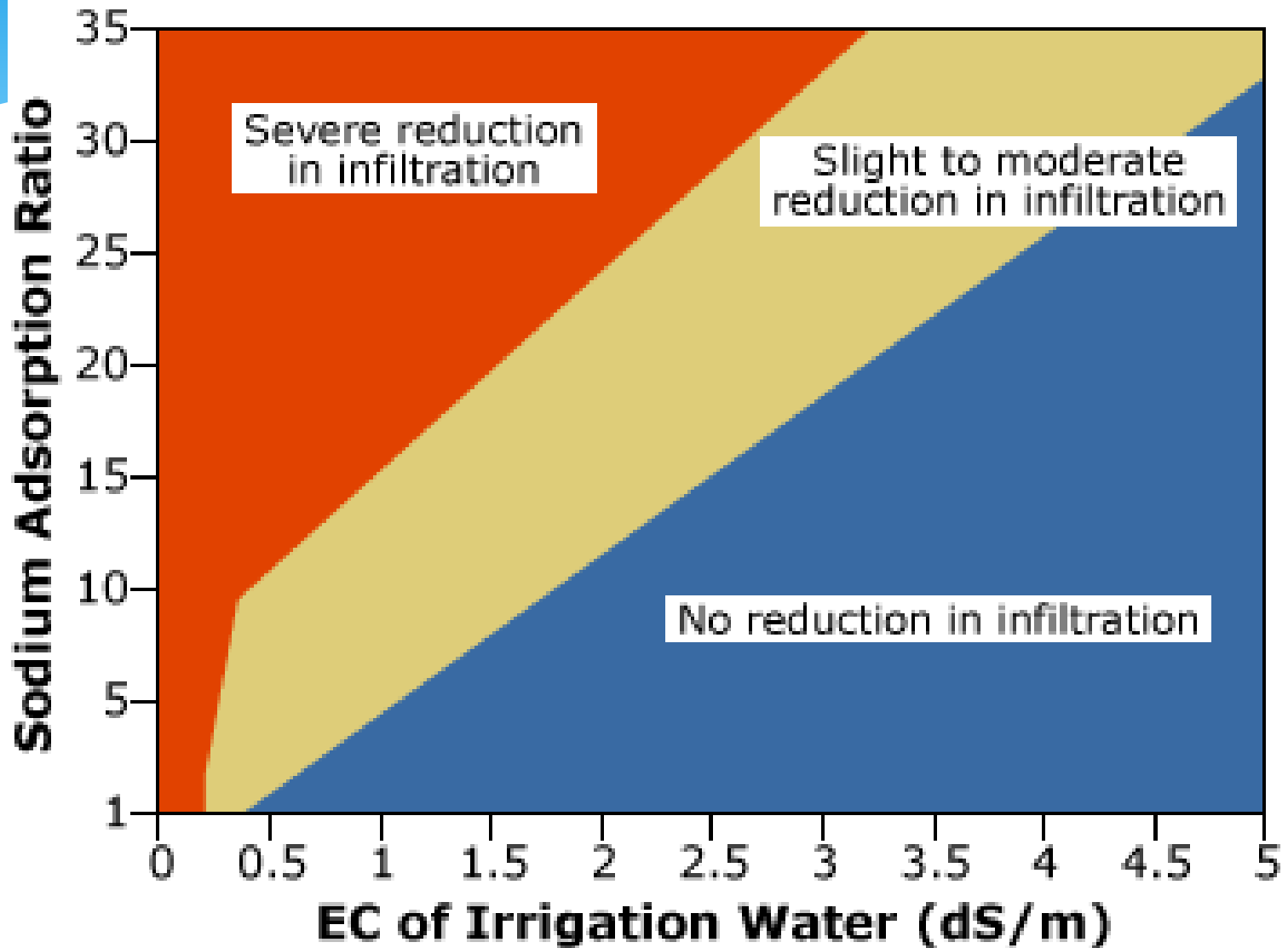
Flocculated  
soil

Dispersed  
soil



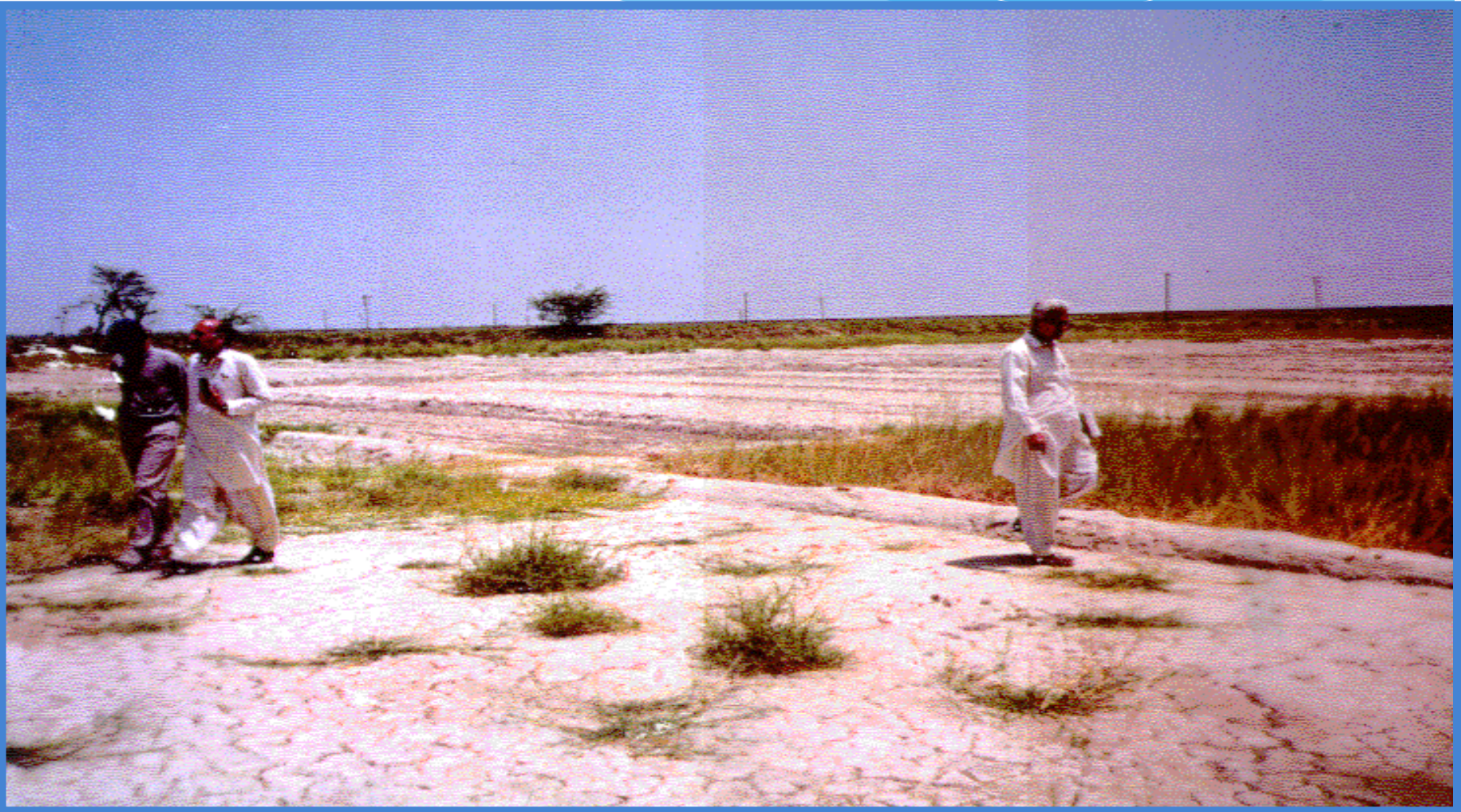
Soils can be classified by the amount of soluble salts (EC) and sodium status (SAR). This classification can tell us something about soil structure.

Soil Classification	EC	SAR	Condition
Normal	<4	<13	Flocculated
Saline	>4	<13	Flocculated
Sodic	<4	>13	Dispersed
Saline-Sodic	>4	>13	Flocculated





# Saline-Sodic Soils



**before rainfall**



**after rainfall**