Bioecology
Module: Soil Science

Lecture 9.
Adsorption of ions: Ion exchange, CEC& AEC

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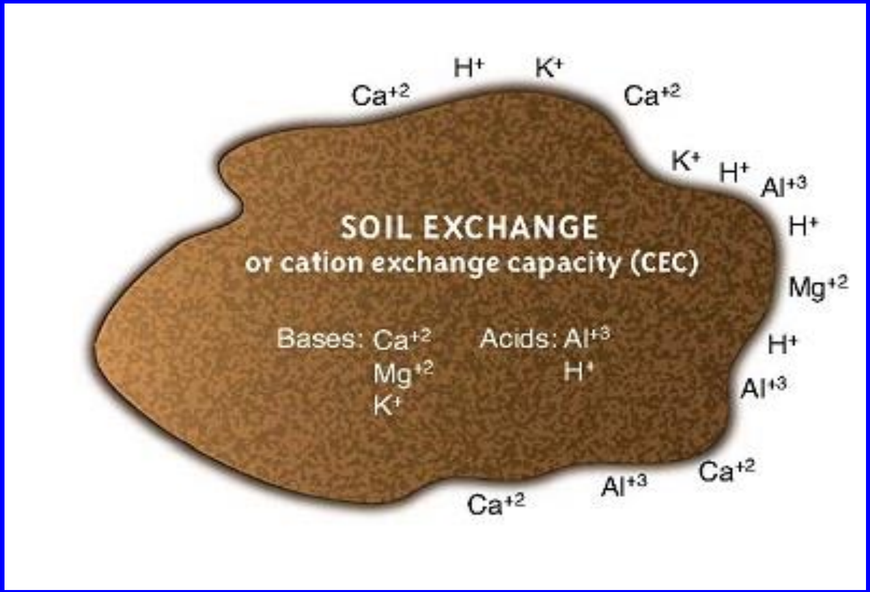
Adsorption of ions

Ion adsorption and subsequent exchange are important processes that take place between soil colloidal particles (clays, organic matter, sesquioxides, and amorphous minerals) and various ions. Soil colloids are the sites within the soil where ions of essential plant nutrients are held and protected from excessive loss by leaching. Subsequently, the nutrients can be "withdrawn" from the colloidal "bank" sites and taken up by plant roots. In turn, these elements can be "deposited" or returned to the colloids through the addition of fertilizers, lime, manures, and plant residues.

The charges associated with soil particles attract ions of opposite charge. In temperate region soils, negative charges generally predominate on the soil particles (colloids), hence adsorbed cations are present in larger quantities than anions.



Ion exchange reactions – Cation exchange, anion exchange and base saturation

The process by which ions are exchanged between solid and liquid phases and /or between solid phases if in close contact with each other is called ***ion exchange.*** The Ion Exchange phenomenon was first identified by Harry Stephen Thompson (1850).

The common exchangeable cations are Ca^{2+}, Mg^{2+}, H^+, K^+, NH_4^+ and Na^+. The common anions are SO_4^{2-}, Cl^-, PO_4^{-3} and NO_3^-.

Exchange of cation is called ***cation exchange*** and exchange of anion is called ***anion exchange***. The cation exchange phenomenon was first discovered by Thomasway (1850)

Ion exchange is the second most important reaction is nature.

The capacity of the soil to hold cation is called ***cation exchange capacity (CEC)***. The unit is C mol (P^+)/ kg.

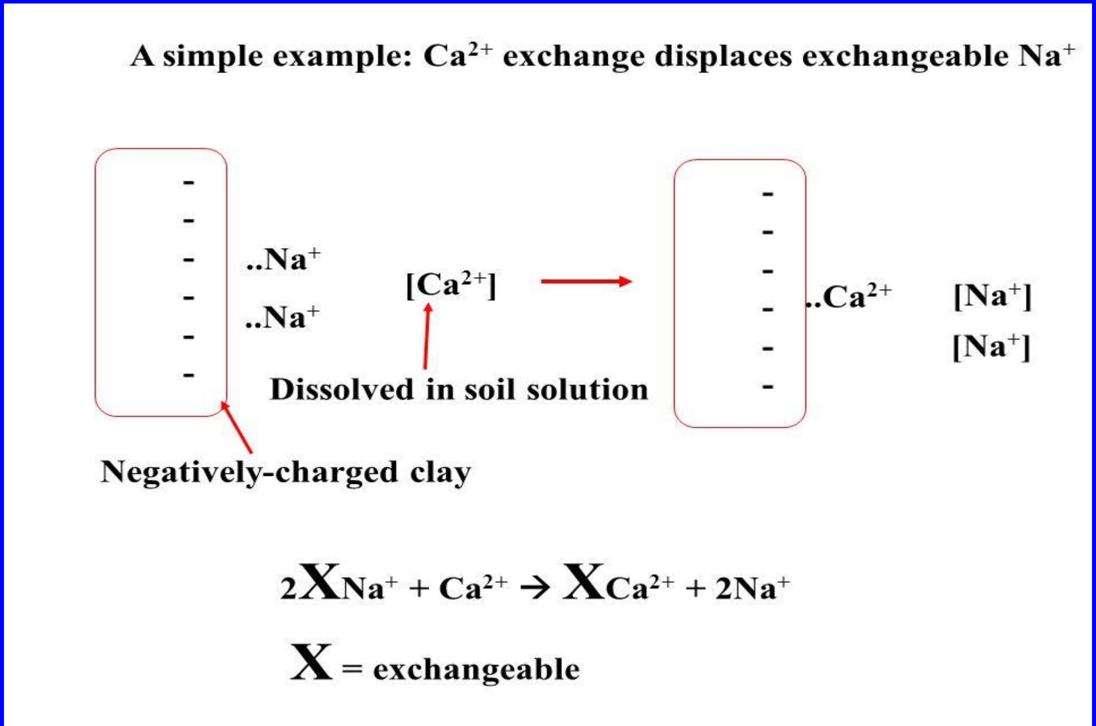
The capacity to hold anion is called ***Anion exchange capacity*** (AEC). The unit of expression is C mol(e^-)/kg

Mechanism of cation exchange

Clay colloids have negative charges. Cations are attracted to the clay particles. These cations are held on the held on the clay surfaces electro statistically. They are held by small particles of clay and organic matter (Micelle (Micro cell).

The cations that can be replaced on exchange site by other cations are called **exchangeable cations**. They are weekly held and they are in direct contact with the soil solution.

Ions that are held very lightly with the colloid may be traped between layers of clay micelle. They do not pass to the soil solution very easily. They are called **non-exchangeable cations**.



Cation exchange capacity (CEC)

The ***cation exchange capacity*** (CEC) is the sum total of the exchangeable cations that a soil can adsorb. It is also defined as “the amount of cationic species bound at pH 7.0”. Some authors consider pH 4.0 as the appropriate point.

Principles governing cation exchange reaction

Reversibility

$$\boxed{\text{Micelle}}\,Na^{+} + H^{+} \rightleftharpoons \boxed{\text{Micelle}}\,H^{+} + Na^{+}$$

(soil colloid) (soil solution) (soil colloid) (soil solution)

Charge equivalence

$$\boxed{\text{Micelle}}\,Ca^{2+} + 2H^{+} \rightleftharpoons \boxed{\text{Micelle}}\begin{matrix}H^{+}\\H^{+}\end{matrix} + Ca^{2+}$$

(soil colloid) (soil solution) (soil colloid) (soil solution)

Principles governing cation exchange reaction

Ratio law

$$\boxed{\text{Micelle}}\ 20\,Ca^{2+} + 5\,Mg^{2+} \rightleftharpoons \boxed{\text{Micelle}}\begin{matrix}16\,Ca^{2+}\\ 4\,Mg^{2+}\end{matrix} + 1\,Mg^{2+} + 4\,Ca^{2+}$$

(colloid) (soil solution) (colloid) (soil solution)

Ratio: 4Ca:1Mg

Anion effects on mass action

$$\boxed{\text{Micelle}}\begin{matrix}H^{+}\\ H^{+}\end{matrix} + CaCO_3 \rightleftharpoons \boxed{\text{Micelle}}\,Ca^{2+} + H_2O + CO_2\uparrow$$

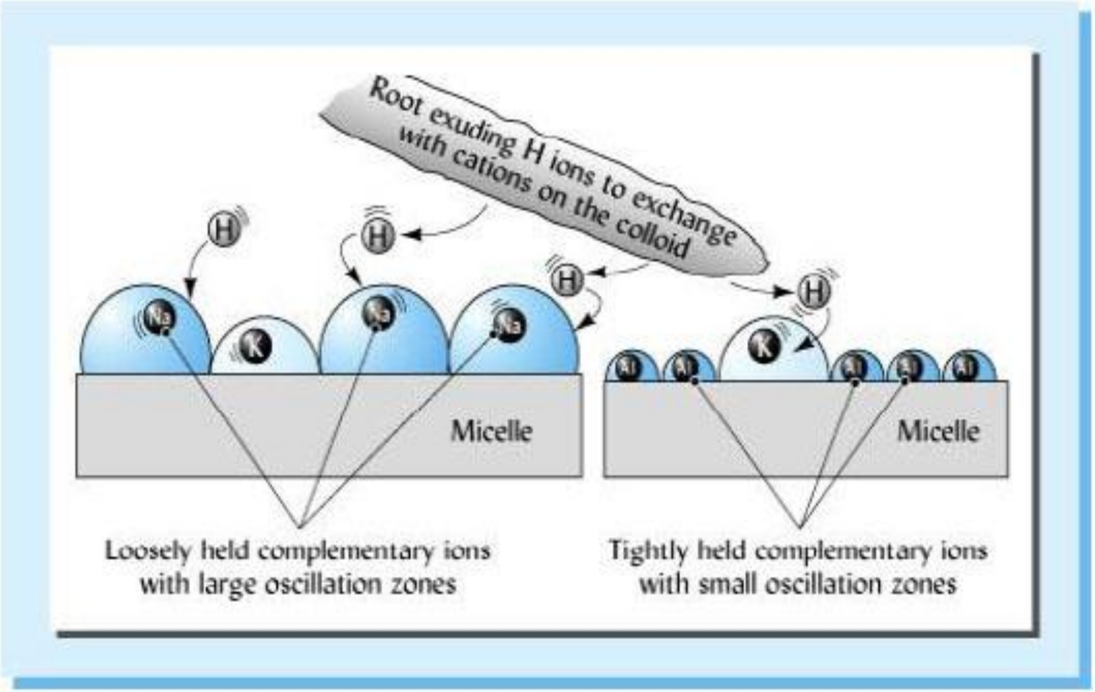
(added) Water (gas)

Cation selectivity

$$Al^{3+} > Ca^{2+} > Mg^{2+} > K^{+} = NH_4^{+} > Na^{+}$$

Principles governing cation exchange reaction

Complementary ion effect



CEC of different textural classes.

Sand	0-5 C mol (P^+) / Kg.
Sandy loam	5-10 "
Loam	10-15 "
Clay loam	15-30
Clay	30.0

CEC of important clay minerals

Kaolinite	7-10 C mol (P^+) / Kg
Montmorillonite	80-100 "
Vermiculite	100-150 "
Illite	25-30 "
Chlorite	25-30 "
Fe & Al oxides	5.0 "
Humus	200-400 "

Replacing power of ions

Replacing power of ions increases with atomic weight. Divalent cations have more replacing power than monovalent ions. Hydrogen is an exemption. H ions are adsorbed more strongly than other monovalent or divalent ions. The replacing power of cations varies with the **type of ion, size, degree of hydration, valence, concentration and the kind of clay mineral** involved. As it is controlled by number of factors no single order of replacement can be given.

All other factors being equal the replacing power of monovalent cations increases in the following order:

$$Li < Na < K < Cs < H$$

for divalent cations:

$$Mg < Ca < Sr < Ba.$$

In case of mixture of monovalent and divalent cations as they exist in normal soils the replacing power increases in the following order:

$$Na < K < NH_4 < Mg < Ca < H.$$

This means Na is more easily replaced than K and K more easily than NH_4.

Base saturation

The ***base saturation percentage*** is the percentage of CEC that is satisfied by the base forming cations

% Base saturation = (Exchangeable base forming cations/CEC) x 100

Al and H_2 are considered as *acid forming ions (**acidoids**)*. Ca, Mg, K and Na are considered as *base forming ions (**besoids**)*.

The ***Exchangeable sodium percentage (ESP)*** is the percentage of Na in the total CEC:

[(Na/CEC) x 100]

A knowledge of base saturation percentage is useful:

1. It helps in determining the quantity of lime required to raise the pH of acid soils.
2. It indicates the proportion of plant nutrients in CEC. It is an index of soil fertility.
3. Degree of saturation of a particular cation in CEC indicates the ease with which the cation can be released for plant nutrition. For example if calcium saturation is more Ca can be very easily replaced from the exchange complex.
4. For a fertile soil it is considered that the base saturation percentage should be more than 80.

Anion exchange

The anion exchange is replacement of one anion by another anion on the positively charged colloids. Positive charges are due to OH of iron and aluminium, 1:1 clays and allophone (amorphous clays).

Anion exchange is pH dependent. Lower the pH greater is the anion exchange. Soils with Kaolinite dominant clay have higher anion exchange capacity than montmorillonite or illite.

The relative order of anion exchange is

$$OH > H_2PO_4 > SO_4 > NO_3 > Cl.$$

Importance of anion exchange:

1. The phenomenon of anion exchange is important for the release of fixed P in the soil. In acid soils the phosphorus is fixed as insoluble Al-Phosphate. Liming the acid soils release fixed P. Here the OH ion replaces H_2PO_4 from $(Al(OH)_2)(H_2PO_4)$.

$$(Al(OH)_2)(H_2PO_4) + OH \rightarrow Al(OH)_3 + H_2\,PO_4.$$

2. Similarly the availability of other nutrients like NO_3, SO_4 and Cl are influenced by anion exchange.

$$(\text{Soil colloid})\text{-}NO_3 + Cl \rightarrow (\text{Soil colloid})\text{-}Cl + NO_3$$

Thank you for attention!