



# **Availability of nutrients**

#### Soil particles as nutrient stores

Most nutrients are present in soil water as cations. They are bonded to negatively charged sites on soil particles. How strongly a cation is held depends on:

- the soil particle, for example whether it is inorganic (and whether these are sand, silt or clay) or organic;
- the cation, for example its size and charge.

The surfaces of inorganic particles are often negatively charged as a result of the following types of reaction:

Inorganic-OH(s) + 
$$H_2O(I) \rightleftharpoons Inorganic-O^-(s) + H_3O^+(aq)$$
  
Organic-COOH(s) +  $H_2O(I) \rightleftharpoons Organic-COO^-(s) + H_3O^+(aq)$ 



**Figure 1** Clay soils and soils rich in organic material contain higher levels of nutrients than sandy soils.

Cations in soil water are attracted to the negative sites and equilibria exist between cations in solution and bonded to the surfaces of soil particles, both inorganic and organic:

Inorganic
$$-O^-(s) + M^+(aq) \rightleftharpoons Inorganic $-O^-M^+(s)$   
Organic $-COO^-(s) + M^+(aq) \rightleftharpoons Organic $-COO^-M^+(s)$$$$

A few nutrients are present as anions. Anions are held less strongly to soil particles because there are few positively charged sites on soil particles.

### Availability of cations from inorganic soil particles

The strength of attraction to soil particles affects their availability to plants.

Cations bound to inorganic particles can exchange with other cations. For example:

Inorganic
$$-O^-M^+(s) + H_3O^+(aq) \rightleftharpoons Inorganic $-O^-H^+(s) + M^+(aq) + H_2O(l)$$$

Increasing the acidity of soil water (lowering the pH) moves the position of equilibrium to the right, releasing metal ions.

Inorganic
$$-O^-M^+(s) + NH_4^+(aq) \rightleftharpoons Inorganic $-O^-NH_4^+(s) + M^+(aq)$$$

NH<sub>4</sub><sup>+</sup> has a similar strength of attraction as K<sup>+</sup>.

2 Inorganic
$$-O^-M^+(s) + M^{\ell+}(aq) \rightleftharpoons [Inorganic $-O^-]_2M^{\ell+}(s) + 2M^+(aq)$$$

The position of equilibrium depends upon the charge on the ion and the hydrated radius of the ion. For example, calcium ions,  $Ca^{2+}$ , are held more strongly than sodium ions,  $Na^{+}$ .

The higher the positive charge on a metal ion, the more strongly it will be attracted to the soil particle.

#### Availability of cations from organic soil particles

Similar exchanges can happen with organic soil particles, especially if it contains carboxylic acid groups. For example:

Organic-COO<sup>-</sup>
$$M^{\dagger}$$
(s) + H<sub>3</sub>O<sup>+</sup>(aq)  $\rightleftharpoons$  Organic-COOH(s) +  $M^{\dagger}$ (aq) + H<sub>2</sub>O(l)

This is the equivalent of forming a simple metal salt.





However, organic compounds, including carboxylic acids, can form complexes with metal ions. This happens when the metal ion is able to form coordinate (dative covalent) bonds. Various

Figure 2 An example of a metal complex formed from organic matter in soil and a metal ion.

organic groups can act as ligands, donating one or more lone pairs of electrons to form coordinate bonds.

Again an equilibrium reaction is established:

Organic-
$$L + M^{x+}(aq) \rightleftharpoons ML^{x+}$$

where *L* represents an organic group that can act as a ligand.

For example:

Organic
$$-(COO^-)_2 + Cu^{2+}(aq) \rightleftharpoons$$
  
Organic $-(COO)_2Cu$ 

The strength of the coordinate bond determines the position of equilibrium. It is the equivalent of a stability constant for a metal complex.

## **Cation exchange capacity**

Cation exchange capacity (CEC) is a measure of the number of negatively charged binding sites in the soil. Since these sites bind most of the nutrient ions, CEC is also a measure of the nutrient holding capacity of the soil.

CEC is measured in milliequivalents (meq). This means that a cation with a 2+ charge is equivalent to two cations with a 1+ charge.

CEC depends on the nature of particles (sand, silt and clay), particle size (surface area to volume ratio) and organic matter content. In general, the more clay particles and organic matter in the soil the higher is the CEC.

Soil type	Sands (light coloured)	Sands (dark coloured)	Loams	Silt loams	Clay and clay loams	Organic soils
CEC	3 - 5	10 - 20	10 - 15	15 - 25	20 - 50	50 - 100

## **Precipitation**

Another factor that affects nutrient availability is that some metal ions released into soil water may precipitate as a hydroxide, hydrated oxide or carbonate depending on other ions in the water. For example, if the water is alkaline this type of reaction may happen:

In alkaline soil water:  $M^{x+}(aq) + xOH^{-}(aq) \rightleftharpoons M(OH)_{x}(s)$ 

In soil water containing carbonate ions:  $M^{2+}(ag) + CO_3^{2-}(ag) \rightleftharpoons MCO_3(s)$ 

Phosphate ions, for example from some fertilisers, also form insoluble salts with some metal ions.

Although many ionic compounds are 'insoluble', they do dissolve very slightly and equilibrium is established between the dissolved ions and solid.

#### **Finding out**

Why does the strength of binding of metal ions on clays vary as shown below?

$$AI^{3+} > Ca^{2+} > Mg^{2+} > K^{+} \approx NH_{4}^{+} > Na^{+}$$