LAB 7

DETERMINATION OF CATION EXCHANGE CAPACITY (CEC) AND BASE SATURATION

Learning outcomes

The student is able to:
1. measure the cation exchange capacity of soil
2. calculate the base saturation of soil

Introduction

Soil particles (primarily clay and humus particles) have negative and positive surface charges. In temperate regions of the world, layer silicates are the most common type of clay. Negative charges predominate in layer silicates. However, in tropical regions soils are more highly weathered and acidic. Hydrous oxides of Fe and Al are the most common type of clay. In these minerals, positive charges exceed negative charges.

Electrostatic charges on clay and humus particles are balanced by adsorbed cations and anions. The sum of adsorbed positive charge per kg is called the cation exchange capacity (CEC, units of cmolc / kg). The sum of adsorbed negative charge per kg is the anion exchange capacity (AEC, units of cmolc / kg). These ion exchange capacities are not fixed quantities but vary with soil solution pH because the relative number of negatively charged sites increases, and number of positively charged sites decreases, with increasing soil pH (and visa-versa). This phenomenon is less pronounced in soils having an exchange complex dominated by layer silicates because most of the exchange capacity of these minerals is due to isomorphic substitution -substitution of a cation of lower valance for one of higher valence in
the crystal lattice during mineral formation. This type of charge is called **permanent charge** to distinguish it from **pH-dependent charge**.

Adsorbed cations and anions are in equilibrium with like cations and anions in solution. This is a complex equilibrium that involves many different types of cations and anions in the solution and adsorbed phases. Concentrations in solution and on the exchange complex are constantly changing due to inputs (such as atmospheric deposition and fertilizer application) and losses (especially, leaching and plant uptake). Yet equilibrium is maintained. For example, plants absorb nearly all required nutrients from the soil solution. As uptake of a particular ion occurs, these ions are largely replaced by those previously adsorbed on soil particles. Such desorption of ions from the exchange complex is accompanied by the adsorption of an equal charge of ions from the soil solution, a process known as **ion exchange**. Such exchange involving cations is called **cation exchange** and exchange involving anions, **anion exchange**.

Anion and cation exchange are similar and can be illustrated with a cation exchange equation. These will help clarify cation exchange and the dynamic equilibrium between solution and adsorbed cations. Let $2K^+$ represent a negatively charged colloidal particle with 2 adsorbed potassium ions (the net charge on this unit is zero) and $Ca^{2+}$ the same situation but with adsorbed divalent calcium, then

$$2K^+ + Ca^{2+} (aq) \rightarrow Ca^{2+} + 2 K^+ (aq)$$

shows the stoichiometric exchange of 2 positive charges of calcium initially in solution for 2 positive charges of potassium initially adsorbed. Exchange of solution calcium for adsorbed potassium doesn’t go to completion. Instead, it goes only so far and an equilibrium is reached with calcium and potassium both in solution and adsorbed.

Since the cation exchange complex is a storehouse of plant nutrients, the greater the CEC, the more exchangeable nutrients a soil holds. At a given pH, the CEC of a soil depends on the separate CECs of different colloidal substances and how much of each is present. Humus, the amorphous and colloidal fraction of soil organic matter, has a very high CEC (pH-dependent about 200 cmol$_c$ / kg at neutral pH. This is one reason why high fertility is associated with high levels of soil organic matter). Certain 2:1 type layer silicate clays may have CECs nearly as great, however, 1:1 layer silicates and Al and Fe oxides have much lower CECs.
Perhaps a simpler statement is that the CEC of a soil is determined by four factors: the amount of organic matter, the amount of clay, the type of clay and the pH. The first three factors generally have the greatest influence on CEC and are also fairly constant for a given soil. However, the influence of pH on CEC is especially important in soils with high levels of organic matter and highly weathered clays because the CEC of these components decreases as pH decreases and increases as pH increases.

The CEC of a soil is satisfied (negative charge balanced) by adsorption of many different types of cations. In principle, all one has to do to measure the CEC of a soil is to add a sufficiently high concentration of a foreign (one other than commonly found in soil) cation and essentially all initially adsorbed cations will be forced into solution by exchange with the added cation. Next, the foreign cation that saturates the soil is forced into solution by another cation. The foreign cation is measured to determine the CEC.

Some of the cations found in soil are called acidic cations. This is because these are either actually H\(^+\) or react with water to produce H\(^+\). Al\(^{3+}\) is a prime example of the latter \(\text{Al}^{3+} + \text{H}_2\text{O} \rightarrow \text{Al(OH)}^{2+} + \text{H}^+\). All others are basic cations. Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\) and Na\(^+\) are the most common basic cations in soil.

### Materials

- Leaching columns
- Conical flask
- 1 N NH\(_4\)OAc
- 1 M K\(_2\)SO\(_4\)
- Distillation Unit
- Titration unit
- Boric acid (2%)
- Ethyl alcohol
- Strontium chloride (10,000 \(\mu\)g/ml)
- Atomic Absorption Spectrometer
- Stock solution (Na, K, Ca and Mg)
Activities

A. Leaching

1. Weigh 10g soil and put it in a leaching tube.
2. Pour in 1 N NH₄OAc buffered at pH 7.0 in the leaching tube to leach the soil (5 – 7 hours of leaching). Keep this leachate and mark it as Leachate I for determining basic (Na, K, Ca and Mg) and, if needed, acidic (Al and H) cations.
3. NH₄⁺ saturated soil in the leaching tube is then washed with 150 ml 50% ethyl alcohol followed by 30 ml 90% ethyl alcohol to remove the excess NH₄⁺.
4. The washed NH₄⁺ saturated soil is leached with K₂SO₄ solution for about 5-6 hours and the leachate (marked as Leachate II) is used to determine the cation exchange capacity.

B. Determination of CEC by Distillation and Titration

1. Pipette 10 ml of aliquot from Leachate II and put it into the distillation unit.
2. Distilled NH₃ is put into conical flask containing 10 ml 30% NaOH solution in 2% boric acid with an indicator. Keep distilling until the receiving solution raise to 50 ml in volume.
3. Titrate the distillate with 0.1 M HCl until the colour just about to change from green to light red as the end point.

C. Determination of Exchangeable Basic Cations

Use the aliquot from Leachate I for this determination.
1. Determine the content of Na and K directly from the aliquot with AAS.
2. For Mg and Ca, the leachate is diluted at least 10 times with strontium chloride solution before determining their content with AAS.
Worksheet and Questions

Worksheet

Cation Exchange Capacity can be expressed in two ways:

1) the number of cation adsorption sites per unit weight of soil or,
2) the sum total of exchangeable cations that a soil can adsorb.

Soil CEC is normally expressed in units of charge per weight of soil. Two different, but numerically equivalent sets of units are used: meq/100 g (milliequivalents of element per 100 g of dry soil) or cmolc/kg (centimoles of charge per kilogram of dry soil).

The unit of milliequivalents (meq) per 100 g of oven dry soil is used to better reflect it is the charge in the soil that determines how many cations can be attracted. The equivalent weight of an element is the molecular or atomic wt (g) ÷ valence; or charges per formula milliequivalent (MEQ). One meq wt. of CEC has $6.02 \times 10^{20}$ adsorption sites. Cation exchange sites are found primarily on clay and organic matter (OM) surfaces.

<table>
<thead>
<tr>
<th>meq Weight of Common Cations</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K⁺</td>
</tr>
<tr>
<td>Valence</td>
<td>1</td>
</tr>
<tr>
<td>Atomic Wt. (g)</td>
<td>39</td>
</tr>
<tr>
<td>meq Wt. (g)</td>
<td>0.039</td>
</tr>
</tbody>
</table>

The unit of centimoles of charge (cmolc) per kg of oven dry soil is the charge (positive or negative) of one centimole of an ion with either +1 or -1 charge. An ion such as Ca²⁺ has 2 centimole of charge for each centimole of calcium atoms because it has two positive charges. One mole of charge of any ion will always be equivalent to 1 mole of charge of any other ion.
Normal CEC ranges in soils would be from < 1 cmol_c/kg, for sandy soils low in OM, to >25 cmol_c/kg for soils high in certain types of clay or OM. Soil OM will develop a greater CEC at near-neutral pH than under acidic conditions. Additions of an organic material will likely increase a soil's CEC. Soil CEC may also decrease with time through acidification and OM decomposition.

*Calculate the CEC, the individual basic cations and Base Saturation of your soil sample.*

**A. Calculating the CEC**

\[
\text{CEC} = \frac{\text{ml. HCl} \times \text{Conc. HCl}}{10 \text{ g soil}} \times \frac{100 \text{ ml}}{10 \text{ ml}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ cmol}}{10 \text{ mmol}}
\]

= ……. cmol_(c+) /kg soil

**B. Calculating mol of Na and K cations**

For Na:
Suppose that the reading of Na concentration from AAS is 1.32 mg/L (=1.32 µg/ml).
Then, the content of Na in 100 ml of leachate I is:

\[
= (1.32 \, \mu g / ml) \times \frac{\text{volume of leachate}}{\text{weight of soil (g)}}
\]

\[
= (1.32 \, \mu g / ml) \times \frac{100 \, ml}{10 \, g}
\]

= 13.2 µg/g soil

= 13.2 µg x 1000 g

= 13.2 mg/kg
Since Na is a unit charge, 1 cmol Na\(^+\) = 23 23 cg Na

\[= 1.32 \text{ cg Na}^+\]

\[= 0.057 \text{ cmol}_{(+)}/\text{kg soil.}\]

Similarly, calculate for K and 1 cmol K\(^+\) = 39 cg.

**C. Calculating mol of Ca and Mg cations**

For Ca\(^{2+}\):

Suppose that the reading of Ca concentration from AAS is 2.13 mg/L (=2.13 µg/ml). Then, the content of Ca in 100 ml of Leachate I is:

\[= 2.13 \mu g \times \text{volume of leachate} \times \text{dilution factor}\]

\[= 2.13 \mu g \times 100 \text{ ml} \times 10 \text{ (if the dilution factor is 10)}\]

\[= 213 \mu g/\text{g soil}\]

\[= 213 \text{ mg/kg soil}\]

\[= 21.3 \text{ cg/kg soil}\]

(1 mol Ca\(^{2+}\) = 40 g; 1 cmol \(\frac{1}{2}\)Ca\(^{2+}\) = 20 cg)

Then,

21.3 cg Ca/kg soil has a cmol\(_{(+)}\) of 21.3/20

\[= 1.065 \text{ cmol}_{(+)}/\text{kg soil.}\]

Similarly, calculate for Mg, where 1 cmol \(\frac{1}{2}\)Mg\(^{2+}\) = 12 cg.

**D. Base Saturation calculation**

Base saturation (%) = \[\frac{\sum \text{Base cations cmol}}{\text{CEC cmol}}\] x 100
E. Questions

1. Change the following weights to cmol of the element.
   a. 120 mg Ca
   b. 75 mg Mg
   c. 125 mg K
   d. 1 g Ca
   e. 0.08 g Na
   f. 0.027 g Al
   g. 11.6 mg H

2. A soil has 20% clay and CEC of 10 cmol_c/kg soil. Suppose that the soil has one type of clay and no organic matter, calculate the CEC of this clay in cmol_c/kg clay.

3. Can a sandy loam soil have higher CEC than a clay loam soil? Explain. Give at least two different ways how this is possible.

4. If 1 kg of soil sample can adsorb 0.60 g Ca^{2+}, 0.78 g K^+, 0.36 g Mg^{2+}, 0.02 g H^+ and 0.18 g Al^{3+}.
   a. Calculate cmol of each cation
   b. What is the CEC of this soil considering that these are the cations adsorbed onto the soil?
   c. What is the base saturation of this soil?

5. If a soil has a CEC of 10 cmol_c/kg:
   a. How many gram of K^+ can be held by a kg of this soil?
   b. How many kg of K can be held by an hectare-15 cm thick of this soil?