LABORATORY 6

ION EXCHANGE AND CATION EXCHANGE CAPACITY

I   Objectives

Demonstrate the phenomenon of ion exchange.   Learn standard methods used to determine the cation exchange capacity of soils.

II   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 $cmol_c$ / kg). The sum of adsorbed negative charge per kg is the **anion exchange capacity** (**AEC**, units of $cmol_c$ / 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 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 a 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 $\blacksquare\ 2K^+$ represent a negatively charged colloidal particle with 2 adsorbed potassium ions (the net charge on this unit is zero) and $\blacksquare\ Ca^{2+}$, the same situation but with adsorbed divalent calcium, then

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

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 but 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.

In this laboratory, you will prove to yourself that cation exchange is a real phenomenon. Furthermore, you will determine the CEC of a soil.

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, filter the soil solution from the soil solids and measure the concentration of the various cations desorbed from the exchange complex. It's almost that simple but not quite.

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 ($Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+$). All others are **basic cations**. Ca^{2+}, Mg^{2+}, K^+ and Na^+ are the most common basic cations in soil.

As it turns out, soil colloids have an especially great affinity for acidic cations so that acidic cations are not nearly as exchangeable as are most basic cations. To overcome this problem, different salt solutions are used for extraction of acidic and basic cations. Each extractant is pH-buffered but extraction of acidic cations is carried out at a basic, rather than neutral or somewhat acidic, pH. Basic cations are quantified by measuring concentrations in the extract. However, acidic cations are measured indirectly by titrating residual OH^- that did not react with H^+, Al^{3+} and other acidic cations displaced from the exchange complex during extraction.

The total CEC is equal to the sum of extracted acidic and basic cationic charges per unit mass of soil ($cmol_c$ / kg). For example, if a soil contained

Ca^{2+}	Mg^{2+}	K^+	Na^+	H^+	Al^{3+}
---------------------- $cmol_c$ / kg ---------------------				--- $cmol_c$ / kg —	
4.0	2.0	0.8	0.2	1.0	2.0

the CEC would be 7.0 $cmol_c$ / kg (bases) + 3.0 $cmol_c$ / kg (acids) = 10.0 $cmol_c$ / kg. The fraction of the CEC composed of basic cations is called the **base saturation (BS)**. It is usually expressed as a percentage. In the above example,

% BS = (7.0 $cmol_c$ / kg) x 100 % / (10.0 $cmol_c$ / kg) = 70 %

III   Procedures

A   Cation Adsorption and Ion Exchange

Extraction of Cations from Soil

1.   Weigh 6 g of an acid soil into a clean test tube.

2.   Add 15 mL of neutral 1 $\underline{mM}$ $Mg(NO_3)_2$.

3.   Stopper the tube and shake vigorously for 1 minute.

4.   Allow the sample to stand at least 5 minutes while you fit a funnel with Whatman No. 2 filter paper and put it in a clean test tube.

5.   Shake the sample again and filter. The filtrate is used in the next two exercises.

Exchange of Mg^{+2} for H^+

6.   Put 2 mL of filtrate into a clean test tube.

7.   Put 2 mL of the Mg $(NO_3)_2$ solution into a second clean tube.

8.   Add 1 drop of Duplex indicator to each tube. Color indicates H^+ concentration.

Color	Green	Greenish Yellow	Yellow	Orange Yellow	Orange	Pink
pH	7.0	6.5	6.0	5.5	5.0	4.0

9.   Answer question # 1.

Exchange of Mg^{+2} for Ca^{+2}

10.   Put 2 mL of filtrate into a clean test tube.

11.   Put 2 mL of Mg$(NO_3)_2$ into a second clean tube.

12.   Add 10 drops of ammonium oxalate to each tube.

13.   Shake each tube and allow to stand a few minutes. A white, cloudy precipitate indicates the presence of Ca^{2+} as Ca oxalate.

14.   Answer question # 2.

B   Cation Exchange Capacity

This exercise defines CEC as the sum of exchangeable bases and extractable acidity. Different methods are used for each. You will do extraction of bases and be given data for extractable acidity. The procedure for extractable acidity is briefly described below.

Extractable Acidity

A sample of soil is extracted with a salt in the presence of base. The salt is $BaCl_2$ and the Ba^{2+} replaces all adsorbed cations, though not quantitatively for the acids, H^+ and Al^{3+} in the absence of a base. Presence of base, however, consumes H^+, forming water, and precipitates Al^{3+} as the hydroxide, keeping their solution concentrations very low, allowing Ba^{2+} to quantitatively extract H^+ and Al^{3+}. These, of course, cannot be directly measured. Instead, the filtered extract is titrated with standard acid and the difference in concentration of OH^- between input solution and extract is a direct measure of OH^- consumed and an indirect measure of charge on combined H^+ and Al^{3+} extracted.

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Exchangeable Bases

1. Put 10 g (oven-dry equivalent) soil in a 125 mL Erlenmeyer flask and add 40 mL of 1 N NH$_4$OAc. Swirl and let stand ½ h.   Record mass of air-dry soil (Table 1).

2. Set up a 5.5 cm Büchner funnel fitted with Whatman # 42 filter paper and connected to a 250 mL vacuum flask attached to vacuum source.

3. Moisten filter paper using 1 N NH$_4$OAc from a wash bottle and apply vacuum, then transfer soil and solution to funnel.   Transfer last traces of soil from Erlenmeyer flask to funnel using 10 mL increments of 1 N NH$_4$OAc. Use no more than 5 such amounts (50 mL). *Make sure filter paper is flush against the funnel. Pour slowly at first, keeping the filter paper moist. If soil bypasses the filter paper around the edges, you will have to re-filter.*

4. Carefully transfer to a 100 mL volumetric flask. Wash down inside of vacuum flask with a minimum of 1 N NH$_4$OAc and transfer to volumetric flask. Bring to 100 mL volume.

5. Stopper securely, invert several times to mix well and transfer about 20 mL to a polyethylene vial. Label vial with lab group number. Analysis for concentration of Ca^{2+}, Mg^{2+}, K^+ and Na^+ will be done in the Soil Testing and Plant AnalysisLaboratory using ICP spectrometry. Results will be available next lab.

6. Calculations (Table 2).

    a) Convert concentration data from ppm (mg / L) to meq / L by dividing by the milliequivalent weight of each basic cation, then express concentration of each basic cation in terms of cmol$_c$ / kg. First, find the cmol$_c$ extracted from the soil sample

        cmol$_c$ = (meq / L) x (0.1 cmol$_c$ / meq) X 0.1 L

    b) Then divide by the number of kgs in the soil sample

        cmol$_c$ / kg = [cmol$_c$ x 1000 g / kg] / g oven-dry soil

IV   Worksheet and Questions

A   Cation Adsorption and Ion Exchange

1.   What does the difference in color (pH indicator) between the $Mg(NO_3)_2$ solution and the soil filtrate solution tell you about exchange of Mg^{+2} for H^+ ?

Write an equation depicting the exchange of Mg^{+2} for H^+ on exchange sites.

2.   What was the source of the Ca^{2+}?

Would you expect Ca^{2+}, Mg^{+2} and H^+ ions to leach out of the soil rapidly?

B   Cation Exchange Capacity

Air-dry Mass Soil	Air-dry Moisture %	Oven-Dry Mass Soil

	Ca^{2+}	Mg^{2+}	K^+	Na^+	Total
mg / L					
$cmol_c$ / kg					

Acids	Bases	CEC	% BS