**SOIL 4234 Laboratory #4**

**Nutrient Mobility and Cation Exchange Capacity (20 points)**

 Student

 Lab

 TA

**Objectives**

1. Understand the relationship between units commonly used to express cation exchange capacity (CEC) and be able to show that meq/100g equals cmoles(c)/kg.
2. Learn the CEC of common clays and organic matter.
3. Explain how ions exchange in clays and organic matter and how we can use it to measure cation exchange capacity.
4. Explain why we use Ba2+ as the exchanging ion for exchangeable H+.
5. Explain why ammonium acetate and Mehlich 3 can be used as extracting solutions for exchangeable bases.
6. Calculate percent base saturation, given the total cmoles(c)/kg (or total CEC) and the number of cmoles(c)/kg of basic cations.
7. List the steps, reagents, and analytical instruments used to measure CEC by summation.
8. List the steps, reagents, and analytical instruments used to measure CEC by one alternate method.

**Introduction**

 Cation exchange capacity (CEC) is the measure of the capacity of the soil to hold positively charged ions (cations) at a given pH. The CEC of a soil is one of its most important chemical properties and influences either directly or indirectly many other chemical properties. CEC is a measure of the net negative charge of a soil, and is related to the organic matter content and kind and amount of clay present in the soil. Organic matter is often the greatest source of charge in soil. The charge contributed by organic matter is termed “variable charge” because it can change with soil pH due to protonation or deprotonation of reactive functional groups such as phenols and carboxylic acids. Clay minerals also have some variable charge associated with broken edges of the mineral structure. However, most of the charge contributed by clay minerals is associated with isomorphic substitution (atoms of lower valence substituting for atoms of higher valence) in the tetrahedral and/or octahedral layers. Table 1 gives some examples of the CEC of some common clay minerals and soil organic matter.

Table 1. CEC of Clays and Organic Matter

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

 Type of Material Typical Exchange Capacity, pH dependent

 cmoles(c)/kg charge

 Kaolinite 3-5 high

 Illite 20-40 low

 Montmorillonite 80-120 low

 Vermiculite 120-150 low

 Chlorite 20-40 high

 Organic Matter 100-300 high

 Most soil test reports and environmental regulations are written using meq/100g. However some confusion arises from the fact that the scientific community uses the SI system of measurement in which CEC is expressed as cmoles(c)/kg. Both sets of units define the same number of charges or quantity of exchanged ions per unit of soil. Thus a soil with a CEC of 10 meq/100g has a CEC of 10 cmoles(c)/kg. In this class, and in your text, CEC will be expressed as cmoles(c)/kg or as meq/100g.

Remember:

 1 equivalent = 1 mole (6.023 x 1023)of charge

 1 cmole+ = cmole(c)

 1 cmole+ = 1/100 mole of charge or 100 cmole+ = 1 mole of charge

 1 meq = 1/1000 mole of charge or 1000 meq = 1 mole of charge

 or

 1 equivalent = 1 mole(c) = 100 cmole(c) = 1000 meq

Therefore,



Meaning:

 1 cmole(c) = 10 meq and…

 1 meq/100 g soil = 1 cmole(c)/ kg soil

 In this exercise barium acetate, Ba(CH3COO)2, is used to displace the hydrogen and aluminum ions from the exchange sites. The quantity of acidity removed is measured by titration of the leachate with sodium hydroxide of known normality. Barium is a cation commonly used in these types of procedures since H+ and Al3+ are held very tightly on the clay particles and Ba2+ has a strong enough attraction for the soil exchange sites to pull off the H+.

The exchangeable basic cations will be measured by displacing them from a second soil sample using Mehlich 3 extractant which has been adopted by many laboratories as a near-universal extractant (Mehlich, 1984). The procedure provides a simple and accurate determination of Potassium, Calcium, Sodium, Magnesium, Iron, Manganese, Copper, Zinc, Boron, Sulphur, and Phosphorus. Research has shown that Mehlich 3 is a satisfactory extractant for K and for Ca and Mg on non-calcareous soils (Warncke & Brown, 1998). They also indicate that either Mehlich 3 or ammonium acetate may be used to extract K. However, Mehlich 3 is **not** recommended as a substitute for ammonium acetate as an extractant for Ca and Mg from calcareous soils. The Mehlich 3 extractant solution contains 0.2 N CH3COOH (acetic acid), 0.25 N NH4NO3 (ammonium nitrate), 0.015 N NH4F (ammonium fluoride), 0.013 N HNO3 (nitric acid), 0.001 M EDTA [(HOOCH2)2NCH2NCCH2COOH)2, ethylenediaminetetraacetic acid].

The quantities of Mg2+, Ca2+, and K+ are measured because they constitute almost all of the basic cations found in our soils. Thus, summation of these three ions estimates the total basic cations present in the soil. However, in areas where saline/sodic soils may occur, Na+ may also be measured as a basic cation. The chemical nature of the soils associated with Na+ does not lend itself to use with Mehlich 3 extractant and another extractant must be used. This will be discussed further in the saline/sodic lab. Unlike the procedure for determining the exchangeable hydrogen, barium acetate is not used to determine the exchangeable bases. Impurities associated with the barium might interfere with the extraction procedure.

 The CEC of the soil will be estimated by summing the cmoles+ of acidic cations and the cmoles+ of basic cations found on the soil. This is commonly referred to as CEC by summation. Other procedures are used which involve replacing all the cations on the exchange complex by a cation such as ammonium. The ammonium is then replaced with potassium and the quantity of ammonium displaced is measured. Generally these procedures involve a number of sequential treatments to ensure saturation of the exchange complex followed by sequential treatments with the extracting solution to ensure that all of the saturating cation has been removed. The CEC values obtained from these more exhaustive procedures are generally 10 to 20% higher than CEC estimated by summation. However, since the cost of running these more exhaustive tests is many times higher, they are not used for routine, management oriented, soil tests.

**Impact on Nutrient Mobility**

Leaching is the downward movement of fertilizers through the soil with percolating water. A vast majority of mineral soils in Oklahoma have a particle surface that has a net negative charge, and thus, absorb cations and repel anions. This property is termed cation exchange capacity (CEC). Therefore, negatively charged ions are much more mobile in the soil solution than are cations. The magnitude of fertilizer leaching is a concern for both general society and the agricultural community. Applying the right rate of fertilizer, at the right time, in the right source, and at the right place are all critical criteria to minimize fertilizer leaching.

 When fertilizers leach through the soil they may reach groundwater aquifers and degrade the quality of public drinking water sources. If the nutrients in the drinking water are a health hazard and the level exceeds established standards (e.g. nitrate-N in excess of 10 ppm), then society may wish to limit fertilizer use, or at least have input to how the fertilizer is managed. The agricultural community is interested in knowing if fertilizers leach because this could decrease the effectiveness in relation to plant growth and crop production. If the fertilizer leaches easily, more fertilizer may need to be applied to meet the needs of the crop.

 Bray’s nutrient ‘Mobility Concept’ indicates that management of nutrient inputs to correct deficiencies, or project deficiencies, is closely linked to whether the nutrient is mobile in the soil or not. Fertilizers that are subject to leaching must contain nutrient forms that are relatively mobile in the soil.

Nutrient Mobility

 High rates of N, P, and K fertilizers are applied in the field to the surface of a relatively level, permeable soil in advance of a normal rainy period or irrigation. High rates are used to assure nutrient accumulation levels can be detected by common nutrient extraction methods and that the levels will be much higher than that found in unfertilized (control) soil.

 Amounts of each nutrient extracted from fertilized areas are first adjusted by subtracting the amounts found in similar soil layers of the control soil. A second adjustment may be made for soil-changes to the nutrient that causes it to be “non-extractable”. The amount found in each layer of soil extracted is summed and the sum divided into the total added to obtain an “adjustment” factor for that nutrient. This factor is used to adjust the amount of that nutrient found in each layer before comparisons among nutrients are made. Step-wise calculations are made by completing indicated tables.

Fertilizer Leaching

 Fertilizer leaching is estimated by calculating changes in the water-soluble forms of the nutrients found in subsoil of fertilized areas.

Exchangeable Basic Cations (Group activity 3-4 students per group)

 1. Place 2.0 g of the air-dried soil provided into a plastic cup (record weight
 to the nearest 0.01 g).

 2. Add 20 ml of Mehlich 3 extracting solution to each plastic cup and shake for 5 minutes.

 3. Decant the liquid portion through a Whatman #42 filter, saving the filtrate in a clean

container (another plastic cup). **Be careful not to get too much soil onto your filter paper as this will greatly slow the rate of filtration (**refilter if extract is not clear).

Exchangeable Acidity (Conducted by TAs)

1. Weigh 2.0 g of air dried soil provided into a 125 ml Erlenmeyer flask (record weight to

 nearest 0.001 g).

1. Add 20 ml of 1 N Ba(CH3COO)2, shake vigorously.
2. Decant the liquid portion into a Whatman #42 filter paper, collecting the filtrate in a clean 250 ml beaker.
3. Add 10 ml additional 1 N Ba(CH3COO)2 to the soil in the flask, shake vigorously and decant the liquid through the filter, adding this filtrate to the beaker containing the first filtrate.
4. Add 3 drops of phenolphthalein to the collected filtrate and titrate to a faint pink color with standardized NaOH, which should be approximately 0.1 N. Record the exact normality of the NaOH for use in the calculations.
5. Calculate the cmoles of exchangeable acidity per kilogram of soil.

**Results**

A. Calculating Exchangeable Acidity

The barium acetate removes all of the cations from the exchange sites of the 2 g of soil. However, in the titration we measure only the acidic cations in the filtered solution:

1. 

1. 

 3)

#### B. Calculating Exchangeable Basic Cations

The NH4(CH3COO) or Mehlich 3 extractant removes all of the basic cations and some of the acidic cations from the exchange sites of the 2 g of soil. We then measure the three most common basic cations (Ca, Mg, and K) either directly from the filtered solution or from a diluted portion of that solution. The following calculations can be used to convert from the concentration in the final dilution read on the AA/ICP to cmoles of cation per 1000 g of soil. The Ca calculations are used as an example.

1. μg cation/ kg of soil



1. 

 \*\***To determine cmoles of charge, you need to multiply by the valence charge of the cation (Ca2+, Mg2+ or K1+)**

C. Calculating CEC by summation

 1)

#### D. Calculating percent base saturation

 1)



Exchangeable Basic Cations (0.5 pt each)

 Volume: **20 mL** Sample wt: **2.005 g**

Absorbance of K from ICP (abs.) \_**0.1470**\_\_\_\_\_\_\_

Concentration of K extract from standard curve (µg/ml) \_\_\_\_\_\_\_\_\_\_\_

Absorbance of Ca from ICP (abs.) \_\_**0.0625**\_\_\_\_\_

Concentration of Ca extract from standard curve (µg/ml) \_\_\_\_\_\_\_\_\_\_\_\_

Absorbance of Mg from ICP (abs.) \_\_\_**0.4384**\_\_\_\_

Concentration of Mg extract from standard curve (µg/ml) \_\_\_\_\_\_\_\_\_\_\_\_

Exchangeable K (cmoles(c)/kg of soil) \_\_\_\_\_\_\_\_\_\_\_\_

Exchangeable Ca (cmoles(c)/kg of soil) \_\_\_\_\_\_\_\_\_\_\_\_

Exchangeable Mg (cmoles(c)/kg of soil) \_\_\_\_\_\_\_\_\_\_\_\_

Exch. Basic cations: (cmoles(c)/kg soil) \_\_\_\_\_\_\_\_\_\_\_\_

Exchangeable Acidity

 Rep 1 Rep 2

Wt. of sample (g) \_\_\_\_2.02\_\_\_\_ \_\_\_\_\_2.01\_\_\_\_

Concentration of base used (N) \_\_\_\_0.1\_\_\_\_\_ \_\_\_\_\_0.1\_\_\_ \_\_

Vol. of base used (ml) \_\_\_\_5.1\_\_\_\_\_ \_\_\_\_\_4.9 \_\_\_\_

cmole of base used (cmoles(c)) \_\_\_\_\_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_\_\_\_\_

Exchangeable Hydrogen (cmoles(c)/ kg soil) \_\_\_\_\_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_\_\_\_\_

 Mean \_\_\_\_\_\_\_\_\_\_\_\_\_

Cation Exchange Capacity

Cation exchange capacity by summation (cmoles(c)/kg) \_\_\_\_\_\_\_\_\_\_\_\_\_

Percent Base Saturation \_\_\_\_\_\_\_\_\_\_\_\_\_

***Show calculations to receive full credit!***

***You may use the back. Calculation: 4 points!***

**Data** (12 pts). Include Page 7 with all raw data and calculations.

 ***Show all calculations to receive full credit!***

**Questions**

1. (2 pt.) How does texture affect CEC? Which soil would have a higher CEC? Silt Loam or Sand?
2. (2 pt.) Define anion exchange capacity (AEC) and discuss what soil and environmental
 conditions result in anion exchange capacity.
3. (4 pts.) A producer calls you (an agronomist), and talks about wanting to manage two locations on site-by-site basis. One field has a low CEC, low pH (4.6), and a texture of sandy loam. His other location, has a higher CEC, a slightly acidic pH (5.5), and a silty clay loam texture. Based on the information given, and combination of lab and class thus far, how do agronomic recommendations differ between these fields. Be specific in your answer.