

Chapter 9

Recommended Methods for Determining Soil Cation Exchange Capacity

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The cation exchange capacity (CEC) of a soil is simply a measure of the quantity of sites on soil surfaces that can retain positively charged ions (cations) by electrostatic forces. Cations retained electrostatically are easily exchangeable with other cations in the soil solution and are thus readily available for plant uptake. Thus, CEC is important for maintaining adequate quantities of plant available calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+) in soils. Under acid conditions ($\text{pH} < 5.5$), aluminum (Al^{3+}) may also be present as an exchangeable cation. 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 charge per 100 g of dry soil) or cmol_c/kg (centimoles of charge per kilogram of dry soil). While a soil with a higher CEC may not necessarily be more fertile, when combined with other measures of soil fertility, CEC is a good indicator of soil quality and productivity.

Cation exchange sites are found primarily on clay and organic matter (OM) surfaces. Normal CEC ranges in soils would be from < 3 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.

There are numerous methods for determining CEC and many will give quite different results. A brief history of their development may be helpful. Researchers in the 1920's and 30's did not recognize either the existence of exchangeable Al^{3+} or the increase in CEC with increasing pH (pH dependent charge). It was believed that the basic cations (Ca^{2+} , Mg^{2+} , and K^+) could be easily extracted and measured but that a significant portion of the CEC was occupied by hydrogen (H^+) and this portion was difficult to fully extract. For this reason, initial CEC tests used extractants buffered at high pH, e.g. pH 7 ammonium acetate (Schollenberger, 1927) and pH 8.2 barium chloride-triethanolamine (Mehlich, 1938). "Exchangeable acidity" measured in this fashion was really a measure of pH buffering capacity. It is now well accepted that to measure the actual CEC of a soil, pH must not be changed during the procedure. In interpreting results, it is vital to know what type of CEC measurement was performed. Older, buffered methods will almost always give higher results, especially for acid soils.

The problem with replacing older CEC methods with newer, unbuffered tests is that the older methods have been widely used to regulate land application of woodash and

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biosolids. They are also used to calculate base saturation (BS) ratios (the quantity of Ca^{2+} , Mg^{2+} , and K^{+} , in meq/100 g, divided by the measured CEC). In reality, soils above pH 5.5 are close to 100% BS (Magdoff and Bartlett, 1986). If buffered CEC methods are replaced with those that measure CEC at the pH of the soil, education of end users on the proper interpretation of all CEC methods will be critical.

Soil testing laboratories do not usually provide a direct measure of CEC but, rather, an estimate based on the quantities of Ca^{2+} , Mg^{2+} , and K^{+} extracted by their normal soil test solution, (e.g. Mehlich 3, Morgan's). If soil pH is <5.5, significant quantities of exchangeable Al^{3+} may be present but not able to be accurately measured with these extractants, causing an underestimate of the CEC. To overcome this, many labs add exchangeable acidity to soil test K, Ca and Mg. Exchangeable acidity is often estimated from a regression equation between 1 M KCl exchangeable acidity (actually a measure of exchangeable Al^{3+} unless the soil is extremely acid or very high in OM) and the lime requirement buffer measurement. These types of measurements, termed "effective" CEC and often abbreviated as CEC_e , will be reasonably accurate when soil values are below 7.5 (or unless the soil has been recently limed). Above this pH, significant quantities of unreacted lime (CaCO_3) or other free salts may be dissolved in the extracting solution, causing an overestimate of the CEC.

Because of the differing methods to estimate CEC, it is important to know the intended use of the data. If a pH-buffered CEC measurement is needed (e.g. for regulatory purposes), the pH 7.0 ammonium acetate procedure of Chapman (1965) is recommended. To estimate the actual CEC (at the pH of the soil), the sum of cations

extracted by a routine soil test (CEC_e) should suffice. For a very precise measure of CEC, the BaCl_2 -compulsive exchange procedure (Gillman, 1979, Gillman and Sumpter, 1986; Rhoades, 1982) is suggested. All three methods are described below.

Calculation of Effective CEC (CEC_e: With or without Exchangeable Acidity)

Advantages of CEC_e

CEC_e is a simple, rapid means to estimate the CEC of most soils at the current soil pH. It does not require additional tests beyond the routine soil test hence it can be easily done for large numbers of soils at low cost.

Disadvantages of CEC_e

CEC_e is not a direct measurement of a soil's CEC, rather it is an estimate based on soil test extractable Ca, K, and Mg and some rapid measure of exchangeable acidity. Direct measures of CEC may be preferred because they will be more accurate.

Procedure:

1. Calculate CEC_e from values of Ca, Mg, and K obtained with routine soil test:

For results expressed in ppm or mg/dm³:

$$\text{CEC}_e \text{ (meq/100 g or cmol}_c \text{ kg}^{-1}) = \\ (\text{ppm Ca} \div 200) + (\text{ppm Mg} \div 120) + (\text{ppm K} \div 390)$$

For results in units of lbs/acre:

$$\text{CEC}_e \text{ (meq/100 g or cmol}_c \text{ kg}^{-1}) = \\ \text{ppm Ca} \div 400 + \text{ppm Mg} \div 240 + \text{ppm K} \div 780$$

2. Most states estimate exchangeable acidity from a regression equation between KCl exchangeable acidity (Thomas, 1982) and the lime requirement buffer pH (see Table A-1 in the appendix). This value is added to the CEC_e from step 1. For example, Maine has experimentally derived the following equation:

$$\text{Exch. acidity (meq/100g)} =$$

$$12.6 - (1.64 \times \text{pH in water}) - (0.48 \times \text{pH in SMP buffer})$$

Contact the soil testing laboratory in your state for the appropriate equation to estimate exchangeable acidity from soil buffer pH.

Notes on CEC_e Method:

If soil pH is >7.5 or if the soil has been recently limed do not use this method. Determine the CEC directly by the methods described below. If soil pH is >5.5, the exchangeable acidity should be quite low and its omission should not create a significant error in estimation of CEC. A bulk density of 1 g/cm³ is assumed for the conversion from volume to weight. For some soils it may be more appropriate to assume a higher bulk density, such as a value of 1.25 g/cm³. If this is done, simply multiply your final result by the assumed bulk density. Alternatively, measure the weight per volume of the sample in question and use this value for adjustment.

CEC Determination by the BaCl₂ Compulsive Exchange Method

(Gillman and Sumpter, 1986)

Advantages of CEC by Compulsive Exchange:

Determining CEC by compulsive exchange is the method recommended by the Soil Science Society of America (Sumner and Miller, 1996) because it is a highly repeatable, precise, direct measure of a soil's CEC.

Disadvantages of Compulsive Exchange CEC:

The compulsive exchange method for CEC is a very time-consuming approach that can require specialized equipment. It is unlikely to be well suited for most routine soil testing laboratories where rapid estimates of CEC for many soils are required. This method also generates a hazardous waste (BaCl₂·2H₂O).

Equipment:

1. Centrifuge and 30 mL centrifuge tubes
2. Reciprocating shaker.
3. Scale capable of weighing to nearest mg.
4. Conductivity and pH meters.

Reagents:

1. 0.1 M BaCl₂·2H₂O extracting solution
Dissolve 24.428 g of barium chloride (BaCl₂·2H₂O) in a 1 L volumetric flask containing ~800 mL of distilled water. Dilute to volume with distilled water and mix. [Caution: Barium is toxic if ingested].
2. 2 mM BaCl₂·2H₂O equilibrating solution:
Dilute 20 mL of the 0.1 M BaCl₂ solution to 1 L with distilled water.

3. 0.1 M MgSO₄·7H₂O: Dissolve 24.648 g of magnesium sulfate (MgSO₄·7H₂O) in a 1 L volumetric flask that contains about 800 mL of distilled water. Dilute to volume with distilled water and mix.
4. 1.5 mM and 5 mM MgSO₄·7H₂O: Dilute 15 and 50 mL of the 0.1 M MgSO₄ solution, respectively, each to 1 L with distilled water and mix well.
6. 0.05 M sulfuric acid: Add 2.8 mL of concentrated H₂SO₄ to a 1 L volumetric flask almost filled with distilled water, make to volume, and mix thoroughly.

Procedure:

1. Weigh each 30 mL centrifuge tube to the nearest mg.
2. Add 2.00 g of soil, 20 mL of 0.1 M BaCl₂·2H₂O, cap, and shake for 2 hours.
3. Centrifuge at about 10,000 rpm and decant carefully.

Note: A good direct measure for CEC_e can be obtained at this point by measuring Ca, Mg, K, and Al in this extract by ICP or AA (Hendershot and Duquette, 1986). If results are in mg/L:

$$\text{CEC} = [\text{Ca} \div 20 + \text{Mg} \div 12 + \text{K} \div 39 + \text{Al} \div 9]$$

For a safer method, substitute 1 M NH₄Cl for BaCl₂ and then determine the cations in the NH₄Cl extract. Ammonium chloride cannot be substituted for BaCl₂ in the full CEC procedure.

4. Add 20 mL of 2 mM BaCl₂·2H₂O, cap and shake for 1 hour. If needed, shake vigorously at first to disperse soil pellet.
5. Centrifuge and discard supernatant.

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| <p>6. Repeat steps 4 and 5 twice. Before the third centrifugation, obtain slurry pH.</p> <p>7. After the third decantation of 2 mM BaCl₂·2H₂O, add 10.00 mL of 5 mM MgSO₄ and shake gently for one hour.</p> <p>8. Determine conductivity of the 1.5 mM MgSO₄ solution (it should be ~300 μS or μmhos). If conductivity of the sample solution is not 1.5x this value, add 0.100 mL increments of 0.1 M MgSO₄ until it is (keep track of amount added).</p> | <p>9. Determine the pH of the solution. If it is not within 0.1 units of the previous measure, add 0.05 M H₂SO₄ dropwise until pH is in appropriate range.</p> <p>10. Add distilled water, with mixing, until the solution conductivity is that of the 1.5 mM MgSO₄. Adjust solution pH and conductivity alternately until the endpoints are reached.</p> <p>11. Wipe outside of the tube dry and weigh.</p> |
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12. Calculations for CEC:

- a. *Total solution (mLs) [assumes 1 mL weighs 1 g] =*
 final tube weight (g) - tube tare weight (g) - 2 g [weight of soil used]
- b. *Mg in solution, not on CEC (meq)=*
 total solution (mLs) x 0.003 (meq/mL) [1.5 mM MgSO₄ has 0.003 meq/mL]
- c. *Total Mg added (meq) =*
 0.1 meq [meq in 10 mLs of 5 mM MgSO₄] + meq added in 0.1 M MgSO₄
 [mLs of 0.1 M MgSO₄ x 0.2 meq/mL (0.1 M MgSO₄ has 0.2 meq/mL)]
- d. *CEC (meq/100g) = (c - b) x 50*
 [Total Mg added - Mg in final solution; 50 is to convert from 2 g of soil to 100 g]

Example: Tube tare: 19.858 g; final wt.: 49.743 g; added 0.1 M MgSO₄: 0.3 mL.

- a. *Total solution (mLs) = 49.743 [final tube wt.] - 19.858 [tare wt.] - 2.00 [soil wt.] = 27.885*
- b. *Mg in solution (meq) = 27.885 mLs x 0.003 meq/mL [1.5 mM MgSO₄] = 0.0837 meq*
- c. *Total Mg added (meq) =*
 0.1 meq [10 mLs of 5 mM MgSO₄] + (0.3 mLs x 0.2 meq/mL) [0.1 M MgSO₄] = 0.16 meq
- d. *CEC (meq/100g) = (0.16 meq [added] - 0.0837 meq [final]) x (50) = 3.8 meq/100 g*
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Alternate Procedure Without Centrifuge

1. Measure 2.00 g soil into a funnel containing medium grade filter paper.
2. Slowly leach the soil with 20 mL of the 0.1 M BaCl₂·2H₂O allowing each addition to soak into the soil before adding more.
3. Leach the soil with 60 mL of 2 mM BaCl₂·2H₂O in six 10 mL portions, again allowing each addition to soak into the soil. Save the last 10 mL of leachate separately for pH determination.
4. After leaching, carefully transfer the filter plus soil to a pre-weighed 125 mL flask and add 10.0 mL of 5 mM MgSO₄.
5. After 1 hour of occasional swirling, perform steps 8 to 12 above, weighing the flask for a final solution weight.

Notes on the Compulsive Exchange CEC Method:

1. The 0.1 M BaCl₂·2H₂O extractant should be treated as hazardous waste after use.
2. Final pH in the procedure can be adjusted to give a CEC at any desired pH.
3. Final ionic strength can be adjusted by changing the concentrations of the 2 mM BaCl₂·2H₂O and the 1.5 mM MgSO₄.
4. A more accurate result will be obtained if the final Mg concentration is measured by ICP or AA instead of assumed to be 1.5 mM. If this is done, substitute twice the measured molarity of Mg for 0.003 in the calculation for Mg in solution.

Determination of CEC at pH 7 with Ammonium Acetate

(Chapman, 1965)

Advantages of pH 7 Ammonium Acetate CEC:

The pH 7.0 ammonium acetate CEC method has been widely used in the U.S. for decades. Consequently, a large data base exists for soil CEC by this method. Many state agencies have traditionally required CEC to be measured by this procedure.

Disadvantages of pH 7 Ammonium Acetate CEC:

The pH 7.0 ammonium acetate CEC method is more time-consuming than effective CEC but can be readily adapted by most soil testing laboratories. The main problem with this method is that it buffers soil pH at 7.0 causing large overestimates of CEC for many of the acid soils common to the northeast.

Equipment:

1. Buchner funnel filtration apparatus.
2. Balance.
3. 250 and 500 mL Erlenmeyer flasks.
4. Apparatus for ammonium determination (steam distillation or colorimetric).

Reagents:

1. 1 M ammonium acetate (NH₄OAc) saturating solution: Dilute, in a chemical hood, 57 mLs glacial acetic acid (99.5%) with ~800 mL of distilled H₂O in a 1 L volumetric flask. Add 68 mL of concentrated NH₄OH, mix and cool. Adjust pH to 7.0 with NH₄OH if needed and dilute to 1 L.

2. 1 M KCl replacing solution: Completely dissolve 74.5 g KCl in distilled water and dilute to a final volume of 1 L.

3. Ethanol, 95%

Procedure:

1. Add 25.0 g of soil to a 500 mL Erlenmeyer flask.
2. Add 125 mL of the 1 M NH₄OAc, shake thoroughly, and allow to stand 16 hours (or overnight).
3. Fit a 5.5 cm Buchner funnel with retentive filter paper, moisten the paper, apply light suction, and transfer the soil. If the filtrate is not clear, refilter through the soil.
4. Gently wash the soil four times with 25 mL additions of the NH₄OAc, allowing each addition to filter through but not allowing the soil to crack or dry. Apply suction only as needed to ensure slow filtering. Discard the leachate, unless exchangeable cations are to be determined.
Note: Exchangeable cations can be determined on the leachate after diluting it to 250 mL.
5. Wash the soil with eight separate additions of 95% ethanol to remove excess saturating solution. Only add enough to cover the soil surface, and allow each addition to filter through before adding more. Discard the leachate and clean the receiving flask.

6. Extract the adsorbed NH_4 by leaching the soil with eight separate 25 mL additions of 1 M KCl, leaching slowly and completely as above. Discard the soil and transfer the leachate to a 250 mL volumetric. Dilute to volume with additional KCl.
7. Determine the concentration of $\text{NH}_4\text{-N}$ in the KCl extract by distillation or colorimetry. Also determine $\text{NH}_4\text{-N}$ in the original KCl extracting solution (blank) to adjust for possible $\text{NH}_4\text{-N}$ contamination in this reagent.

8. Calculations:

$$\text{CEC (meq/100g)} = \text{NH}_4\text{-N}^+ \text{ (mg/L as N)} \div 14$$

$$^+(\text{NH}_4\text{-N in extract} - \text{NH}_4\text{-N in blank})$$

Note:

If $\text{NH}_4\text{-N}$ is expressed as mg/L of NH_4 , not $\text{NH}_4\text{-N}$, divide the result by 18 instead of 14 to obtain CEC.

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