Chapter 9

Recommended Methods for Determining Soil Cation Exchange Capacity

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The cation exchange capacity (CEC) of a soil is a measure of the quantity of negatively charged sites on soil surfaces that can retain positively charged ions (cations) such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+), by electrostatic forces. Cations retained electrostatically are easily exchangeable with cations in the soil solution so a soil with a higher CEC has a greater capacity to maintain adequate quantities of Ca^{2+}, Mg^{2+} and K^+ than a soil with a low CEC. A soil with a higher CEC may not necessarily be more fertile because a soil's CEC can also be occupied by acid cations such as hydrogen (H^+) and aluminum (Al^{3+}). However, 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 minerals and organic matter (OM) surfaces. Soil OM will develop a greater CEC at near-neutral pH than under acidic conditions (pH-dependent CEC). Thus, addition of an organic material will likely increase a soil's CEC over time. On the other hand, a soil's CEC can decrease with time as well, through e.g. natural or fertilizer-induced acidification and/or OM decomposition.

Soil CEC is normally expressed in one of two numerically equivalent sets of units: meq/100 g (milliequivalents of charge per 100 g of dry soil) or $cmol_c/kg$ (centimoles of charge per kilogram of dry soil).

Because of the differing methods to estimate CEC, it is important to know the intended use of the data. For soil classification purposes, a soil's CEC is often measured at a standard pH value. Examples are the ammonium acetate method of Schollenberger and Dreibelbis (1930) which is buffered at pH 7, and the barium chloride-triethanolamine method of Mehlich (1938) which is buffered at pH 8.2. Such CEC measures can result in values very different from the CEC of the soil at its field pH (effective CEC or CEC_e), especially in acidic soils with pH-dependent CEC. If a pH-buffered CEC measurement is needed (e.g. for regulatory and/or soil classification purposes), ammonium acetate buffered at pH 7 is the recommended procedure. In the Northeastern USA, the CEC as determined by this method tends to range from less than 3 $cmol_c/kg$ for sandy soils low in OM to greater than 25 $cmol_c/kg$ for soils high in certain types of clay minerals or OM.

For an accurate measure of the CEC of a soil under field conditions, the $BaCl_2$-compulsive exchange procedure (Gillman, 1979, Gillman and Sumpter, 1986; Rhoades, 1982) is suggested. This method gives an estimate of the soil's capacity to retain nonacid cations (CEC_b) under field conditions. For an estimate of the CEC_e, exchangeable Al obtained by extraction with 1 *M* KCl (Bertsch and Bloom, 1996) needs to be added.

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Soil testing laboratories do not usually provide a direct measure of CEC_e. Instead, often the CEC is estimated (calculated, CEC_{sum}) based on the quantities of Ca^{2+}, Mg^{2+}, and K^+ extracted in the standard agronomic soil test (e.g. Mehlich 3 or (modified) Morgan's extraction solution and methods). Sodium is not often present in large quantities in soils in the Northeast but if present in appreciable quantities, extractable Na^+ should be added to the calculation too. If soil pH is <6, exchangeable acidity is added to the sum of extractable Ca^{2+}, Mg^{2+} and K^+, reflecting that significant quantities of exchangeable Al^{3+} may be present. Exchangeable acidity is often estimated from a regression equation between 1 *M* KCl exchangeable acidity (an actual measure of exchangeable Al^{3+} unless the soil is extremely acid or very high in OM) and a buffer pH measurement as used to determine lime requirements.

When soil pH is 7.5 or less and the soil has not been limed within the past 6 months or received recent additions of K, Ca or Mg containing fertilizer, CEC_{sum} can be a reasonable estimate of the CEC_e. Above pH 7.5, significant quantities of unreacted lime ($CaCO_3$) or other free salts may be dissolved in the extracting solution, leading to overestimation of the CEC_e of the soil.

Methods for Measuring Cation Exchange Capacity

CEC at pH 7 with Ammonium Acetate
(Chapman, 1965)

Advantages of pH 7 Ammonium Acetate CEC:

Many state agencies have traditionally required CEC to be measured by this procedure and a large database exists for soil CEC by this method. This method can readily and cost-effectively be implemented by most soil testing laboratories.

Disadvantages of pH 7 Ammonium Acetate CEC:

The main problem with this method is that it buffers soil pH at 7.0. Thus, this method will only approximate CEC_e if a soil's pH is 7.0 and can result in large overestimates of CEC_e for the many 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 H_2O in a 1 L volumetric flask. Add 68 mL of concentrated NH_4OH, mix and cool. Adjust pH to 7.0 with NH_4OH 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 NH_4OAc, 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 NH_4-N in the KCl extract by distillation or colorimetry. Also determine NH_4-N in the original KCl extracting solution (blank) to adjust for possible NH_4-N contamination in this reagent.

Calculations:

Where NH_4-N is reported in mg N/L:

$$CEC \text{ (cmol}_c\text{/kg)} = (NH_4\text{-N}_{in\ extract} - NH_4\text{-N}_{in\ blank}) / 14$$

Where NH_4-N is reported in mg NH_4/L:

$$CEC \text{ (cmol}_c\text{/kg)} = (NH_4\text{-N}_{in\ extract} - NH_4\text{-N}_{in\ blank}) / 18$$

CEC$_b$ Determination by the BaCl$_2$ Compulsive Exchange Method
(Gillman and Sumpter, 1986)

Advantages of CEC by Compulsive Exchange:

The compulsive exchange method of Gillman and Sumpter (1986) 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$_b$. This method determines CEC$_b$ at the pH and ionic strength of the soil. For an estimate of the CEC$_e$, exchangeable Al obtained by extraction with 1 *M* KCl (Bertsch and Bloom, 1996) needs to be added. However, for soils with a pH of 6 or greater, exchangeable Al will be negligible and the CEC$_b$ estimate of the compulsive exchange method can be equated to CEC$_e$.

Disadvantages of Compulsive Exchange CEC:

This method is very time-consuming and generates a hazardous waste (BaCl$_2$·2H$_2$O). This method is unlikely to be well-suited for most routine soil testing laboratories and might only be offered by University laboratories.

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* BaCl$_2$·2H$_2$O extracting solution:** Dissolve 24.428 g of barium chloride (BaCl$_2$·2H$_2$O) 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* BaCl$_2$·2H$_2$O equilibrating solution:** Dilute 20 mL of the 0.1 *M* BaCl$_2$ solution to 1 L with distilled water.

3. **0.1 *M* MgSO$_4$·7H$_2$O:** Dissolve 24.648 g of magnesium sulfate (MgSO$_4$·7H$_2$O) 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* MgSO$_4$·7H$_2$O**: Dilute 15 and 50 mL of the 0.1 *M* MgSO$_4$ solution, respectively, each to 1 L with distilled water and mix well.

5. **0.05 *M* H$_2$SO$_4$:** Add 2.8 mL of concentrated H$_2$SO$_4$ 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 BaCl$_2$ 2H$_2$O, cap, and shake for 2 hours.

3. Centrifuge at about 10,000 rpm and decant carefully.

    Note 1: 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). For ICP or AA results in mg/L: CEC (cmol$_c$/kg soil) = [Ca/20 + Mg/12 + K/39 + Al/9].

    *Note 2: For a safer method, substitute 1 M NH$_4$Cl for BaCl$_2$ and determine the cations in the NH$_4$Cl extract. Ammonium chloride **cannot** be substituted for BaCl$_2$ in the full CEC procedure.*

4. Add 20 mL of 2 mM BaCl$_2$ 2H$_2$O, cap, and shake for 1 hour. If needed, shake vigorously at first to disperse soil pellet.

5. Centrifuge and discard supernatant.

6. Repeat steps 4 and 5 twice. Before the third centrifugation, obtain slurry pH.

7. After the third decantation of 2 mM BaCl$_2$ 2H$_2$O, add 10.00 mL of 5 mM MgSO$_4$ and shake gently for one hour.

8. Determine conductivity of the 1.5 mM MgSO$_4$ solution (it should be ~300 µS or µmhos). If the conductivity of the sample solution is not 1.5x this value, add 0.100 mL increments of 0.1 M MgSO$_4$ until it is (keep track of the amount of 0.1 M MgSO$_4$ added).

9. Determine the pH of the solution. If it is not within 0.1 units of the previous measure, add 0.05 M H$_2$SO$_4$ drop-wise until pH is in appropriate range.

10. Add distilled water, with mixing, until the solution conductivity is that of the 1.5 mM MgSO$_4$. Adjust solution pH and conductivity alternately until the endpoints are reached.

11. Wipe outside of the tube dry and weigh.

Calculations for CEC$_e$:

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 MgSO$_4$ has 0.003 meq/mL]

c. **Total Mg added (meq) =**
   0.1 meq [meq in 10 mLs of 5 mM MgSO$_4$] + meq added in 0.1 M MgSO$_4$
   [mLs of 0.1 M MgSO$_4$ x 0.2 meq/mL (0.1 M MgSO$_4$ 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 weight: 49.743 g; added 0.1 M MgSO$_4$: 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 MgSO$_4$] = **0.0837 meq**

c. **Total Mg added (meq) =**
   0.1 meq [10mL of 5 mM MgSO$_4$]+(0.3 mLx0.2 meq/mL) [0.1 M MgSO$_4$]=**0.16meq**

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 BaCl$_2$·2H$_2$O allowing each addition to soak into the soil before adding more.

3. Leach the soil with 60 mL of 2 mM BaCl$_2$·2H$_2$O 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 MgSO$_4$.

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 BaCl$_2$·2H$_2$O 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 BaCl$_2$·2H$_2$O and the 1.5 mM MgSO$_4$.

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.

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Calculation of CEC from Agronomic Soil Tests (CEC$_{sum}$)

Advantages of CEC$_{sum}$

CEC$_{sum}$ is a simple, rapid means to estimate a CEC. It does not require additional tests beyond the routine agronomic (Mehlich 3 or (modified) Morgan) soil test and therefore can easily be done for large numbers of soils without additional analytical costs.

Disadvantages of CEC$_{sum}$

CEC$_{sum}$ is not a direct measurement of a soil's CEC$_e$, rather it is an estimate based on soil test extractable Ca, K, and Mg and some rapid measure of exchangeable acidity. Common extracting solutions such as Mehlich 3, Morgan, and 1 *M* NH$_4$OAc have a higher ionic strength and a different pH than are found in soil solution. Thus, direct measures of CEC may be preferred because they will be more accurate, especially for calcareous soils and soils that have recently been amended with lime or fertilizer.

Procedure:

1. Calculate CEC$_{sum}$ from values of Ca, Mg, and K obtained with routine soil test:

   For agronomic soil test results in ppm or mg/dm^3:

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

   For agronomic soil test results in lbs/acre:

   CEC$_{sum}$ (meq/100 g or cmol$_c$ kg^{-1}) =
   $\qquad$ (lbs/A Ca / 400) + (lbs/A Mg / 240) + (lbs/A K / 780)

2. Calculations in step 1 assume 100% base saturation. For soils with a pH of 6 or lower, exchangeable acidity should be taken into account. Most states estimate exchangeable acidity from a regression equation between 1 *M* 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$_{sum}$ from step 1. For example, Maine has experimentally derived the following equation:

Exch. acidity (meq/100g) = 20.1 – (0.88 x pH in water) – (2.46 x pH in Mehlich buffer)

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

Notes on CEC_{sum} Method:

1. If soil pH is >7.5 or if the soil has been recently limed or fertilized do not use this method. For soils with a pH<6, exchangeable acidity should be taken into account.

2. A bulk density of 1 g/cm^3 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/cm^3. If this is done, simply multiply final result by the assumed bulk density. More accurately, measure the weight per volume of the sample and use this value for adjustment.

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References

1. Chapman, H.D. 1965. Cation-exchange capacity. *In:* C.A. Black (ed.). Methods of soil analysis - Chemical and microbiological properties. Agronomy 9:891-901.

2. Gillman, G.P. 1979. A proposed method for the measurement of exchange properties of highly weathered soils. Aust. J. Soil. Res. 17:129-139.

3. Gillman, G.P. and E.A. Sumpter. 1986. Modification to the compulsive exchange method for measuring exchange characteristics of soils. Aust. J. Soil Res. 24:61-66.

4. Hendershot, W.H. and M. Duquette. 1986. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. Soil Sci. Soc. Am. J. 50:605-608.

5. Magdoff, F.R. and R.J. Bartlett. 1985. Soil pH buffering revisited. Soil Sci. Soc. Am. J. 49:145-148.

6. Mehlich, A. 1938. Use of triethanolamine acetate-barium hydroxide buffer for the determination of some base exchange properties and lime requirement of soil. Soil Sci. Soc. Am. Proc. 29:374-378.

7. Rhoades, J.D. 1982. Cation exchange capacity. *In:* A.L. Page (ed.) Methods of soil analysis. Part 2: Chemical and microbiological properties (2nd ed.) Agronomy 9:149-157.

8. Schollenberger,C.J. 1927. Exchangeable hydrogen and soil reaction. Sci. 35:552-553

9. Sumner, M.E. and W.P. Miller. 1996. Cation exchange capacity, and exchange coefficients. *In:* D.L. Sparks (ed.) Methods of soil analysis. Part 2: Chemical properties (3rd ed.). ASA, SSSA, CSSA, Madison, WI.

10. Thomas, G.W. 1982. Exchangeable cations. *In:* A.L. Page (ed.). Methods of soil analysis. Part 2: Chemical and microbiological properties (2nd ed.) Agronomy 9:159-165.

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