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A lmost all nutrients taken up by plants and microbes are taken up in their position of the soil solution, together with knowledge of nutrient turnover rates, can provide valuable insight into soil nutrient availability and into other biogeochemical processes such as rates of weathering and leaching losses. While nutrient pool size per se can be a poor indicator of availability, changes in pool sizes can indicate changes in ecosystem processes that bear closer examination. Moreover, in all soils the potential for significant hydrologic loss of mobile nutrients is directly related to the size of the exchangeable nutrient pool and the proportion in solution at any given time.

In this chapter we present standard methods for the extraction of the major cations and anions from soil, the measurement of exchangeable acidity and soil pH, and cation exchange capacity. Methods for the extraction of dissolved-only nutrients (those ions only in the solution phase as opposed to total exchangeable nutrients that have both solution and surface adsorbed phases) are provided elsewhere (see Chapter 9, this volume), as are methods for available phosphorus (see Chapter 7, this volume) and dissolved organic nitrogen and carbon (see Chapter 5, this volume).

### Exchangeable lons

The determination of exchangeable ions in soil requires that ions on soil exchange sites be forced into a solution in which they can be effectively measured. Generally this involves flooding the exchange sites on clay and organic matter surfaces of a

soil with ions from an extractant, usually a strong salt solution. The extractant, now containing exchangeable soil ions in addition to ions from the added salt, is separated from soil by filtering or centrifugation and is then analyzed for the ions of interest.

Choice of salt for the extractant solution will depend on the target ions. Extractant ions must effectively displace soil ions from exchange sites and must not interfere with subsequent chemical analysis of the extracted solution. For most soils 1.0 mol/ L KCl is a reasonable extractant if K<sup>+</sup> is not the target ion. KCl is the most common extractant for inorganic nitrogen, for example. For total cation analysis, NH<sub>4</sub>OAc is useful because both NH<sub>4</sub><sup>+</sup> and Ac will volatilize and thus not accumulate on spectrometer burners. BaCl<sub>2</sub> provides a reasonable but expensive alternative for simultaneous extractants and precautions are needed for trace metal species (e.g., Pb, Cu), however, and will not be covered here (see various chapters in Sparks et al. 1996). For most major cations (e.g., NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>+2</sup>, Ca<sup>+2</sup>, Al<sup>+3</sup>) and anions (e.g., NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-2</sup>), any of these extractants will work well.

In general, soils should be extracted when fresh from the field, prior to drying. This is especially important for ions that can undergo rapid microbial transformations during storage (e.g.,  $NH_4^+$ ,  $NO_3^-$ ,  $PO_4^{-3}$ ) or undergo volatilization or some other chemical transformation at elevated temperatures (e.g.,  $NH_4^+$ ,  $PO_4^{-3}$ ). Where immediate extraction is not possible, or when the ion of interest is unlikely to undergo significant microbial transformation or precipitation reaction, samples can be dried at low temperature (<45 °C). Prior to extraction, soil should be sieved and mixed as described in Chapter 1, this volume.

### Materials

- 1. 120 mL screw-cap polyethylene extraction cups and lids (e.g., urinalysis cups) or equivalent
- Extractant: For ions other than K<sup>+</sup> and Cl<sup>-</sup>, use 1 mol/L KCl (74.6 g/L). For K<sup>+</sup> and ions other than NH<sub>4</sub><sup>+</sup>, use 1 mol/L NH<sub>4</sub>OAc at pH 7.0 (add 77.1 g NH<sub>4</sub>OAc to 950 mL deionized water, adjust pH to 7.0 with acetic acid or aqueous ammonia, and bring volume to 1.0 L with deionized water).
- Sample vials sufficient to hold extracted sample (e.g., 20 mL screw-cap polyethylene scintillation vials)
- 4. 10 cc Luerlok polyethylene syringes, reusable Gelman syringe filter holders (25 mm diameter), and Gelman Type A/E glass-fiber filter paper (25 mm diameter) or other filter known to be free of target ions. Alternately, use standard glass or plastic funnels, a funnel holding rack, and glass-fiber filter paper to fit the funnel.

### Procedure

1. Weigh triplicate 10.0 g subsamples of fresh sieved soil into each of three extraction cups. Soil should be passed through at least a 4 mm sieve; 2 mm (undried) is preferred if soil is sufficiently dry (see Chapter 1, this volume).

- 2. Weigh separate soil samples for gravimetric moisture analysis (see Chapter 3, this volume).
- 3. Add 100 mL extractant to each cup, cap, and shake vigorously for 1 minute. Also add 100 mL extractant to three cups without soil to serve as blanks. Allow to equilibrate overnight (12–24 hours).
- 4. Reshake extraction cups and allow to settle for 45 minutes.
- 5. Remove 10 mL solution from the extraction cup into a syringe. Place a preloaded filter holder on the syringe and filter the solution directly into a sample vial. Use a separate syringe and filter holder for each replicate sample to avoid cross-contamination. Alternatively, filter each extract through a clean glass fiber filter paper held in a funnel.
- 6. Label vials and store in refrigerator or freezer until analysis.
- 7. Analyze appropriately as per specific instrumentation (see the section "Special Considerations," below).

### Calculations

Gravimetric Basis—Element Mass

 $\mu$ g element/g soil = ( $C \times V$ ) / W

where

C = concentration of ion in extract in mg/L, as provided by standards used for elemental analysis

V = volume of extract (mL), e.g., 100 mL, plus water in soil sample.

W = dry mass of soil, e.g., 10.0 g (as in step 1) less its water content as determined in step 2, above.

Gravimetric Basis—Element Moles of Charge

$$\text{cmol}_{c} \text{ element/kg} = (C_{q} \times n) / (10 \times A)$$

where

 $C_{\rho}$  = element mass on gravimetric basis, as µg element/g soil

n = valence of ion

A =atomic mass of ion

Areal Basis—Element Mass

g element/m<sup>2</sup> =  $C_g \times BD \times SD$ 

where

 $C_a$  = element mass on gravimetric basis as µg element/g soil

BD = bulk density as g soil/cm<sup>3</sup> soil or Mg soil/m<sup>3</sup> soil (see Chapter 4, this volume)

SD = sample depth in m, e.g., 0.2 m for standard Level 1 depth of 20 cm (see Chapter 1, this volume)

### **Special Considerations**

- 1. If a shaker table is available, 1 hour on a shaker table can substitute for the shaking and overnight equilibration described here.
- 2. Filter holders should be loaded using care to avoid touching filters or other surfaces that will contact the extractant; use forceps and wear latex gloves as needed (but beware of glove talc as a potential contaminant). For large numbers of samples it is convenient to have on hand the same number of syringes and reusable preloaded filter holders as extraction cups.
- 3. Centrifugation (e.g., 10 minutes at 1000 g) can substitute for filtration, but take care to avoid floating pieces of organic debris when sampling from the centrifuge tubes.
- 4. Procedures for the analysis of specific ions will depend on available instrumentation and manufacturer-specific protocols. In general, colorimetric techniques are recommended for  $NH_4^+$ ,  $NO_3^-$ , and  $Si^{+4}$ , ion chromatography for  $SO_4^{-2}$ , and atomic absorption (AA) spectrometry or inductively coupled plasma atomic emission spectrometry (ICP-AES) for other cations. Ion-specific electrodes are rarely appropriate due to their general insensitivity and to differential interference from other ions in the soil solution matrix; where used, they should always be calibrated against colorimetric values for each soil examined. Ion chromatography (IC) and high-performance liquid chromatography (HPLC), ideally suited for leachate and rainwater samples, are generally not preferred for soil extracts because of complications introduced by the high concentration of salt in the extractant solution. It is essential to include blanks and check standards as part of the analysis and to make all analytical standards in the extractant solution (see Chapter 1, this volume).
- 5. When preparing NH<sub>4</sub>OAc, add aqueous ammonia under a hood in a room or building not used for the preparation of samples for NH<sub>4</sub><sup>+</sup> analysis; volatilized NH<sub>3</sub> will readily contaminate samples and surfaces exposed to the atmosphere.
- As noted in Chapter 1, values should also be expressed on an areal basis for making ecosystem-level comparisons.

### Soil pH

Soil pH is a measure of hydrogen ion activity in the soil solution. pH is generally measured electrometrically, although chemical means can provide a coarse indication (e.g.,  $\pm$  0.5 pH units for pH strips). The electrometric pH reading is a product of complex interactions between the electrode and the soil suspension; differences in the soil:water extraction ratio, the electrolyte concentration of the soil suspension, and the spatial placement of the electrode can all affect measured pH.

### Materials

- 1. Extraction cups or beakers (50-100 mL)
- 2. Deionized water
- 3. pH meter with standard combination electrode
- 4. Standard pH buffers, available commercially (pH 4.0, 7.0, and 10.0)
- 5. Squirt bottle and beaker for rinsing the electrode between samples

### Procedure

- 1. Calibrate the electrode as per the manufacturer's instructions. Always use two buffers that span the pH range of the sampled soils.
- 2. Weigh duplicate 15.0 g subsamples of fresh (undried), sieved soil into each of two extraction cups. Use a 2 mm sieve if the soil is sufficiently dry; otherwise 4 mm will suffice (see Chapter 1, this volume).
- 3. Add 30 mL deionized water and stir the mixture well.
- 4. Allow the mixture to stand for 30 minutes to equilibrate with atmospheric  $CO_2$ , stir again, then read pH to nearest 0.1 pH unit. The soil slurry should be gently swirled while taking the measurement.
- Check electrode stability every 10–12 samples with a standard buffer solution and recalibrate electrode as needed. Rinse the electrode well between samples, and especially well following immersion in the buffer solution.

### Calculations

No further calculations are necessary for reporting pH. To convert pH to [H<sup>+</sup>], use the equation

### $[H^+] = 10^{-pH}$

### **Special Considerations**

- Depending on the buffer capacity of an individual soil, pH readings may be extremely sensitive to electrode condition. Always store electrodes in recommended salt solution between uses. The electrode needs to be open to air during measurement (there is often a small rubber vent cap near the top of the electrode tube) and closed during storage. Combination electrodes should be kept filled with electrolyte solution as per the manufacturer's instructions. If the pH reading of soil does not stabilize to 0.1 units within a few minutes, consider reconditioning or replacing the electrode.
- 2. Depending on the level of biological activity in a soil, measurement of pH may need to be performed within hours (e.g., tropical sites) or can be postponed indefinitely (e.g., desert sites).
- 3. Use as a check sample a dried soil analyzed previously.
- 4. In some situations it may also be useful to measure pH in a weak CaCl<sub>2</sub> solution, in which case the procedure can be performed as described earlier but substituting 0.01 mol/L CaCl<sub>2</sub> for deionized water. This procedure is useful

chiefly for historical comparisons where earlier measurements may have used a salt extractant to correct for variable salts in soil. It is not the preferred method today even in agricultural soils (Thomas 1996).

### **Exchangeable Acidity and Aluminum**

Aluminum is a predominant cation in many soils and can be a critical variable in establishing effective cation exchange capacity (ECEC) values. In exchange reactions its characterization is complicated by the coexistence of complex multiphase Al components that make its measurement specific to a particular extractant and potentially difficult to interpret (Bertsch and Bloom 1996). In practice, the most common extractant for calculations of ECEC and Al saturation is 1 mol/L KCl. For ECEC determinations it is not necessary to differentiate between exchangeable Al<sup>+3</sup> and H<sup>+</sup>, and analysis can stop after step 4 of the following procedure. Al mobility in soil depends on its speciation in addition to total concentration; see Driscoll et al. (1985, 1989) for appropriate speciation methods.

### Materials

- 1. Extraction cup or beaker (100 mL)
- 2. Buchner funnel with prewashed Whatman no. 42 filter paper (see the section "Special Considerations," below)
- 3. Burrette for titrations
- 4. 1 mol/L potassium chloride (74.6 g KCl/L) stored in plastic carboy (150 mL per soil sample)
- 5. Phenolphalein solution, 1 g phenolphthalein dissolved in 100 mL ethanol
- 6. 0.1 N sodium hydroxide (4.0 g NaOH/L)
- 7. 1 mol/L potassium fluoride (58.1 g KF/L) (for determination of exchangeable Al)
- 8. 0.1 N hydrochloric acid (HCl) (for determination of exchangeable Al)

### Procedure

- . 1. Weigh 10.0 g fresh (undried), sieved soil into a 100 mL extraction cup, add 25 mL KCl, stir or shake well, and let sit for 30 minutes. Use a 2 mm sieve if the soil is sufficiently dry; otherwise 4 mm will do (see Chapter 1, this volume).
- Determine moisture content of a separate subsample as per Chapter 3, this volume.
- 3. Filter through a Buchner funnel and then wash with five successive 25 mL aliquots of KCl, for a total of 150 mL KCl per soil sample.
- 4. To the filtrate add 5 drops of phenolphthalein and titrate with 0.1 N NaOH to the first permanent pink end point. Record the volume of NaOH solution used.
- 5. Repeat step 4 for a blank solution of 150 mL KCl, also washed through a Buchner funnel. Record the volume of NaOH used.

6. For exchangeable aluminum, note the volume of NaOH added in step 4, add to the titrated solution 10 mL of 1 mol/L KF, and titrate with 0.1 N HCl until the pink color disappears. If the solution turns pink again after 30 minutes, add additional HCl and re-evaluate after 30 minutes. Record the volume of HCl used.

### Calculations

Exchangeable acidity (cmol/kg) =  $(NaOH_{dif}/W) \times (0.1 \text{ mmol } \text{H}^+/\text{mL } \text{NaOH}) \times (0.1 \text{ cmol } \text{H}^+/\text{mmol } \text{H}^+) \times (10^3 \text{ g soil/kg soil})$ 

where

 $NaOH_{dif} = mL$  of NaOH added to sample filtrate less mL of NaOH added to blank solution

W = g dry soil (e.g., 10.0 g less its water content as determined in step 2, above)

Exchangeable Al (cmol/kg) =  $(HCl_{sample}/W) \times (0.1 \text{ mmol Al}^{+3}/\text{mL HCl}) \times (0.1 \text{ cmol Al}^{+3}/\text{mmol Al}^{+3}) \times (10^{3}\text{g soil/kg soil})$ 

where

 $HCl_{sample} = mL$  of HCl added to sample W = g dry soil based on moisture determination

Exchangeable  $H^+$  = Exchangeable acidity - Exchangeable Al

### **Special Considerations**

Where exchangeable Al values are low and filter materials could introduce error, use a 0.45  $\mu$ m polycarbonate filter.

### **Cation Exchange Capacity**

The measurement of cation exchange capacity (CEC) is complicated by the fact that CEC is affected by both pH and the ionic strength of the soil solution, especially in highly weathered soils and other soils rich in Al and Fe oxides, hydroxides, and amorphous clays. Traditional methods for measuring CEC include adjustment of soil pH to 7.0, which will misrepresent CEC in soils with variable charge minerals or substantial organic matter. The compulsive exchange method (Gillman 1979) avoids both pH and ionic strength problems but is very laborious. For routine work and comparisons among soils dominated by 2:1 clay minerals, we recommend summing exchangeable cations to provide a measure of ECEC.

Exchangeable cations include both base cations (K<sup>+</sup>, Ca<sup>+2</sup>, Mg<sup>+2</sup>, and Na<sup>+</sup>) and the acidic cations (Al<sup>+3</sup> and H<sup>+</sup>). Other cations such as  $NH_4^+$  and trace metals are usually present in relatively minor amounts and can be effectively ignored. In cal-

careous and saline soils ECEC will overestimate CEC because measured cations will also include those solubilized from mineral deposits. In these soils a more specialized technique is appropriate (e.g., Amrhein and Suarez 1990, described in Sumner and Miller 1996).

### **Materials and Procedure**

- 1. Measure base cations (K<sup>+</sup>, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+</sup>) as described in the section "Exchangeable Ions," above; ammonium acetate is the preferred extractant for AA and ICP analysis.
- 2. Measure exchangeable acidity (Al<sup>+3</sup> and H<sup>+</sup>) as described in the section "Exchangeable Acidity and Aluminum," above. It is not necessary to measure either ion separately.

### Calculation

ECEC  $(\text{cmol}_c/\text{kg}) = exch K^+ + exch Ca^{+2} + exch Mg^{+2} + exch Na^+ + exch acidity$ 

### where

exch  $K^+$  etc. = concentrations of individual ions expressed as cmol<sub>c</sub>/kg dry soil

### **Special Considerations**

Na<sup>+</sup> is likely to be important mainly in arid and coastal soils and can often be ignored in other environments.

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## STANDARD SOIL METHODS

FOR

# LONG-TERM ECOLOGICAL RESEARCH

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