

# FOREST INVENTORY & ANALYSIS MANUAL OF SOIL ANALYSIS METHODS

2003 Edition

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## INTRODUCTION

This manual contains the methods used to prepare and analyze soil samples collected as part of the Forest Inventory and Analysis (FIA) and Forest Health Monitoring (FHM) soil monitoring programs. This includes all soil samples collected from FIA P3 base grid Detection Monitoring plots (formerly FHM plots) as well as any sampling intensifications or special projects such as FHM Evaluation Monitoring and Intensive Site Monitoring (ISM) plots and USEPA EMAP plots.

The physical and chemical properties that are measured and the methods used are summarized in Table 1. For some analyses, more than one method can be used, but the preferred method is indicated in Table 1. For the results to be included as part of the FIA database, the procedures documented in this manual must be followed explicitly, particularly with regard to extraction conditions such as solution to soil ratios, extraction times, and shaking rates. All of these variables directly influence the results and must not be varied. However, some adaptation of the methods to different analytical laboratory environments may be necessary. Allowable modifications include such things as instrument manufacturers, types of supplies, and equipment.

### Method Development

There have been numerous changes to the soil indicator field measurement, sample collection, and laboratory analysis protocols during development of the indicator in the FHM program and, later, during the transition of the Detection Monitoring plots from FHM to FIA. Additional laboratory analyses have been added to the program since the transition and modification of previous laboratory methods were implemented. These changes are summarized in Table 2.

#### *Exchangeable Cations and Aluminum*

During development of the soil indicator in the FHM program, exchangeable cations (Na, K, Mg, and Ca) were extracted with the pH 7, 1 M ammonium acetate method using a mechanical vacuum extractor and extracts were analyzed by atomic absorption spectroscopy (AAS). Because of the need to add Al, trace metals (Mn, Fe, Ni, Cu, Zn, Cd, and Pb), and S to list of exchangeable elements, the extractant was changed to unbuffered, 1 M ammonium chloride (NH<sub>4</sub>Cl). The extraction method was also modified to a batch shaking and filtering procedure which greatly increased sample throughput speed and efficiency. The 1 M NH<sub>4</sub>Cl extracts are now analyzed by inductively coupled plasma - atomic emission spectroscopy (ICP-AES), which permits the simultaneous determination of several elements (e.g., Na, K, Mg, Ca, Al, Mn, Fe, Ni, Cu, Zn, Cd, Pb, and S).

The pH 7, 1 M ammonium acetate method is still included in the manual as a reference method, but is no longer preferred for extracting exchangeable cations analysis because it cannot be used to determine exchangeable Al. The classical unbuffered salt method for exchangeable Al is the 1 M KCl extraction method (Bertsch and Bloom, 1996) and is included in the manual for reference purposes. However, the only extractant that will allow for the simultaneous extraction and determination of all the elements of interest in the FIA soil indicator program is 1 M NH<sub>4</sub>Cl. Both batch and mechanical vacuum extractor versions of all the exchangeable cation methods are

included in the manual, but for reasons of sample throughput speed and efficiency, the batch extraction method with shaking and filtering is preferred.

### *Extractable P*

In the FHM program, extractable P for all soil samples was determined using the Bray 1 (0.03 M  $\text{NH}_4\text{F}$  + 0.025 M HCl) method. This method was developed for plant available P associated with Fe and Al oxides in acidic, weathered soils and is not suitable for near-neutral and alkaline soils where most inorganic P is in Ca phosphate minerals. The dilute HCl in the Bray-1 extractant dissolves excessive levels of Ca phosphates that are not bioavailable to plants. In addition, reactive carbonate minerals in calcareous soils will neutralize the dilute HCl and other secondary minerals such as  $\text{CaF}_2$  can form during extraction (Kuo, 1996) leading to extractable P results that cannot be interpreted and bear no relation to plant available P. For this reason, we included the Olsen (pH 8.5, 0.5 M ammonium bicarbonate) method in the FIA program for extraction of plant available P from near-neutral and alkaline soils. Both methods overlap in slightly acid soils, but the Bray 1 method should not be used for soils above pH 6.8 (Soil and Plant Analysis Council, 1999). The Olsen method is suitable for slightly to moderately acid soils. We have selected pH 6.0 as the dividing line between the Bray 1 and Olsen methods for extractable P to be used in the FIA program. Soils with a pH equal to or less than 6.0 are extracted by the Bray 1 method and those with a pH of greater than 6.0 are extracted with the Olsen method.

### *Carbon and Nitrogen*

Combustion methods are preferred for determining total, organic, and inorganic C and total N in the FIA soil indicator program. The classic combustion method for total C in soils (Nelson and Sommers, 1996) cannot distinguish between organic and inorganic (carbonate) forms of C, but is suitable for forest floor samples and noncalcareous mineral soil samples because virtually all the C is in the organic form. Both total organic C and total N can be determined in forest floor and noncalcareous mineral soil samples using the LECO CHN-2000 analyzer. Because of the need to determine both organic and inorganic forms of C in calcareous soils in the FIA program, the new multi-carbon analyzer (e.g., RC-412) from LECO is now the preferred combustion method for calcareous mineral soils. This instrument allows for the determination of multiple forms of C in the same sample in one analytical run.

The classic dichromate oxidation with heating method for the determination of organic C in soils is also provided in the manual as a reference method (Nelson and Sommers, 1996). A new, relatively simple pressure calcimeter method for soil carbonates is also included (Sherrod et al., 2002) for reference purposes. If the classic combustion method is used to determine total C in calcareous soils, then organic C by the dichromate oxidation with heating method or inorganic C by the pressure calcimeter method must also be measured to determine the other form of C by difference. Analyzing a calcareous soil by all three methods (combustion for total C, dichromate oxidation with heating for organic C, and pressure calcimeter for inorganic C) can provide a check on completeness and accuracy of the analysis of the major forms of soil C. This is a suitable protocol for lab quality control checks of selected samples, but for routine processing of calcareous mineral soil samples we recommend the multi-carbon analyzer.

The combustion method is also preferred for total soil N. The classic Kjeldahl method for total soil N (Bremner, 1996) is included for reference purposes and can serve as a check of the combustion method.

References:

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Table 1. Methods used and soil physical and chemical properties measured in the FIA program.

Physical soil properties	Units	Methods
Whole-sample field-moist soil weight	g	Gravimetric
Whole-sample air-dry soil weight	g	Gravimetric after air-drying
Subsample oven-dry soil weight	g	Gravimetric with oven-drying
Water content (total, field-moist to air-dry, air-dry to oven-dry)	%	Calculated from soil sample weights
Bulk density	g/cm <sup>3</sup>	Calculated from oven-dry soil weight and soil core volume
Coarse fragment (> 2-mm) content	%	Gravimetric after sieving

Table 1. Methods used and soil physical and chemical properties measured in the FIA program (continued).

Chemical soil properties	Units	Methods	Preferred or reference method
Soil pH		Measurement with a combination pH electrode in a 1:1 soil-water suspension (1:2 soil-water suspension for high organic matter samples)	Preferred
Salt pH		Measurement with a combination pH electrode in a 1:1 soil - 0.01 M CaCl <sub>2</sub> suspension	Preferred
Exchangeable Na, K, Mg, Ca only	mg/kg	pH 7, 1 M NH <sub>4</sub> acetate extraction - AAS analysis	Reference
Exchangeable Al and Mn only	mg/kg	1 M KCl extraction - AAS analysis	Reference
Exchangeable cations (Na, K, Mg, Ca, Al), trace metals (Mn, Fe, Ni, Cu, Zn, Cd, and Pb), and S	mg/kg	1 M NH <sub>4</sub> Cl extraction - ICP-AES analysis (preferred method)	Preferred
Extractable P for soils with pH < 6.0	mg/kg	Bray 1 (0.03 M NH <sub>4</sub> F + 0.025 M HCl) extraction - colorimetric analysis by ascorbic acid method	Preferred
Extractable P for soils with pH > 6.0	mg/kg	Olsen (pH 8.5, 0.5 M NaHCO <sub>3</sub> ) extraction - colorimetric analysis by ascorbic acid method	Preferred
Total C	%	Combustion analyzer (e.g., LECO CHN-2000) for total C (preferred for forest floor and noncalcareous mineral soil samples)	Preferred
Organic and inorganic C	%	Combustion analyzer (e.g. LECO RC-412) for multiple forms of C (preferred for calcareous mineral soil samples)	Preferred
Organic C only	%	Dichromate oxidation with heating	Reference
Inorganic C (carbonates) only	%	Pressure calcimeter	Reference
Total N	%	Combustion analyzer (e.g., LECO CHN-2000 or FP-528) (preferred)  Kjeldahl digestion followed by NH <sub>4</sub> -N analysis by the automated phenate method	Preferred

Table 2. Changes to the soil indicator during development in the FHM program (1998 - 2000) and transition to the FIA program (2001 to present).

Variable	Year implemented	Method
Soil erosion:		
Cover estimates	1998 - 2001	Visual % cover estimates of bare soil, litter, and vegetation (< 6 ft tall) on all subplots
	2002 - present	Visual % cover estimates of bare soil only on all subplots
Forest floor thickness	1998 - 2000	Measurement at center of each soil erosion plot
	2001	Median of 5 measurements at center and N, S, E, and W edges of each soil erosion plot
	2002 - present	Variable dropped from soil indicator because it overlapped measurements made as part of the down woody material and vegetation structure and diversity indicators



Table 2. Changes to the soil indicator during development in the FHM program (1998 - 2000) and transition to the FIA program (2001 to present) (continued).

Soil erosion (continued):		
Vegetation height	1998 - 2000	Three 12-ft diameter soil erosion plots established on each subplot centered 12 ft N, S, and W of each subplot center. If forest floor thickness < 5 cm, mean height to lowest overhanging vegetation estimated for each soil erosion plot
	2001	If forest floor thickness < 5 cm, height to lowest overhanging vegetation measured at center and N, S, E, and W edges of each soil erosion plot measured and median value recorded
	2002 - present	Variable dropped from soil indicator because it overlapped measurements made as part of the vegetation structure and diversity data
Slope length	1998 - 2001	Estimated from the center of each subplot to break in the slope
	2002 - present	Variable dropped because slope length changed to plot dimensions for modeling of soil erosion

Table 2. Changes to the soil indicator during development in the FHM program (1998 - 2000) and transition to the FIA program (2001 to present) (continued).

Soil compaction:		
Evidences for compaction	1998 - 2001	Visual evidences of soil compaction including change in soil penetration resistance, platy structure, loss of structure, and mottling were recorded
	2002 - present	Variables dropped because they were non-quantitative
Types of compaction	1998 - present	Types of compaction (compacted trail, rutted trail, compacted area) are recorded
Area of compaction	1998 - present	Visual estimate of % compacted area of each subplot

Table 2. Changes to the soil indicator during development in the FHM program (1998 - 2000) and transition to the FIA program (2001 to present) (continued).

Soil sampling:		
Types and numbers of soil samples	1998 - 1999	One forest floor sample collected per plot from subplot 2 (litter and humus layers sampled separately if humus > 5 cm thick), mineral soils sampled by horizon (A and sub A) using excavation method from subplots 2, 3, and 4 and were composited if forest condition class and soil texture were the same in each subplot
	2000	Mineral soils sampled by depth (0-10 cm and 10-20 cm) using impact-driven soil-core sampler to obtain bulk density data, mineral soil core from subplot 2 only was analyzed
	2001 - present	Three forest floor samples collected per plot (subplots 2, 3, and 4), entire forest floor was sampled (litter and humus layers not sampled separately), one mineral soil core per plot was collected (subplot 2 only)
Depth to restrictive horizon	1998 - 2000	Mean value within forest floor sampling frame measured by soil probe
	2001 - present	Measured at center and N, S, E, and W edges of forest floor sampling frame with soil probe and median value recorded

Table 2. Changes to the soil indicator during development in the FHM program (1998 - 2000) and transition to the FIA program (2001 to present) (continued).

Soil properties:		
Sample preparation and water content	1998 - 1999	Samples frozen for pest control and oven-dried prior to analysis
	2000 - present	Samples air-dried after being logged in and field-moist sample weights recorded, short term storage at < 4°C prior to log-in, subsample used for oven-dry water content determination
Bulk density	1998 - 1999	Not measured
	2000 - present	Calculated from soil core volume and oven-dry sample weight
Coarse fragments	1998 - 1999	Not measured
	2000 - present	2-mm sieve method
Soil pH	1998-1999	Solid state electrode
	2000 - present	Glass bulb electrode
Exchangeable Na, K, Mg, Ca	1998 - 1999	Extraction with pH 7, 1 M ammonium acetate using mechanical vacuum extractor, analysis by AAS
	2000 - present	Extraction with 1 M NH <sub>4</sub> Cl by batch method, analysis by ICP-AES
Exchangeable Al, trace metals (Mn, Fe, Ni, Cu, Zn, Cd, Pb), and S	1998 - 1999	Not measured
	2000 - present	Extraction with 1 M NH <sub>4</sub> Cl, analysis by ICP-AES
Extractable P	1998 -1999	Bray 1 method used for all soils regardless of pH
	2000 - present	Bray 1 method used for pH < 6 soils, Olsen method used for pH > 6 soils

## SOIL SAMPLE PREPARATION AND BULK DENSITY, WATER CONTENT, AND COARSE FRAGMENT CONTENT DETERMINATIONS

### I. Method:

- A. Soil sample preparation: Air-drying, crushing aggregates, and sieving (<2-mm) to remove coarse fragments
- B. Bulk density determinations: Gravimetric determination of oven-dry equivalent soil weight of soil core of known volume
- C. Water content: Gravimetric with oven-drying of subsample at 105 °C.

### II. Supplies and Equipment:

- A. Top-loading balance ( $\pm 0.01$  g accuracy)
- B. Plastic trays for air-drying and weighing soil samples
- C. 0.5 or 1-oz soil moisture cans
- D. Forced-air drying oven capable of maintaining a constant temperature of 105 °C.
- E. Desiccator
- F. Large ceramic mortar and pestle or mechanical jaw crusher to break up stable aggregates
- G. Vibrating or Ro-tap sieve shaker
- H. 2-mm stainless steel sieve
- I. Soil grinder with ceramic revolving and stationary plates
- J. Wiley mill with 20-mesh screen
- K. Scintillation vial rotator with steel tumblers for pulverizing small volumes of soil for total carbon and nitrogen analysis
- L. Soil sample storage containers:
  - 1. Plastic-lined bags or screw-cap or snap-cap wide-mouth plastic jars
  - 2. 20-mL glass scintillation vials

III. Standards: None

IV. Reagents: None

V. Procedure:

A. Initial soil sample preparation, weighing, and air-drying:

1. Log in soil samples, assign a laboratory tracking number to each individual forest floor (litter + organic) or mineral soil sample, and complete any necessary paperwork, soil sample information data entry, or other required documentation.
2. For each day's operation, calibrate the top-loading balance and record any information needed for quality assurance documentation.
3. Zero balance, place plastic tray on balance pan, and record tray tare weight.
4. Open soil sample bag and quantitatively transfer the entire field-moist soil sample to the plastic drying tray. Once the balance reading stabilizes, record the weight of the field-moist soil sample plus plastic tray.
5. Repeat steps 3 and 4 for each soil sample.
6. Place the trays containing the field-moist soil samples on the drying racks in the soil drying room.
7. Allow samples to dry to a constant weight. The time required to attain this depends on the drying environment (air temperature, humidity, air circulation). To test, weigh a few test soil samples ranging in texture from sandy to clayey each day until a constant weight is obtained (less than 5 % weight change per day). Use this drying time for all subsequent samples. Well-aggregated (high clay) soils benefit from having the clods lightly crushed during the drying process.
8. After the samples have air-dried, remove the trays from the drying room, calibrate and zero the balance, and re-weigh the air-dried soil plus tray.

9. Save the air-dried soil samples for water content analysis, sieving to remove coarse fragments, texture analysis, and other chemical analyses.

B. Oven-drying for water content determination:

1. Assign a pre-numbered, pre-weighed soil moisture can to each soil sample and record the can numbers associated with each soil sample laboratory tracking number.
2. Transfer a representative 10 to 15-g subsample of air-dried soil sample into the assigned, pre-numbered, pre-weighed soil moisture can. Repeat for each soil sample.
3. Weigh the air-dried soil sample plus can on the calibrated and zeroed balance and record the soil plus can weight. Repeat for each sample.
4. Dry the soil samples in open cans overnight in a forced-air drying oven set to maintain a constant temperature of 105 °C.
5. Transfer the cans containing the oven-dry soil samples into a desiccator to cool.
6. Once the soil samples and cans have cooled to room temperature, re-weigh each oven-dry soil plus can on the calibrated and zeroed balance and record the weights.
7. Discard the oven-dry soil subsamples, and wash the cans for re-use.
8. Enter all soil sample identification and weight data into a spreadsheet and calculate soil water contents and bulk densities using the formulas given below.

C. Sieving to remove coarse fragments from mineral soil samples:

1. After a subsample has been removed for oven-drying, sieve the remainder of each air-dried mineral soil sample through a 2-mm stainless steel sieve to remove coarse fragments. Stable soil aggregates should be crushed with a ceramic mortar and pestle or mechanical jaw crusher before sieving. The purpose of the aggregate crushing step is to avoid discarding these as part of the coarse fragments (e.g., stones and rock chips). However, the soil should not be ground at this point to avoid changing particle size

distribution (sand, silt, clay) until after soil texture is determined. Sieving may be done by hand or using a mechanical vibrating or Ro-tap sieve shaker.

2. Weigh the < 2-mm (sand + silt + clay) and > 2-mm (coarse fragments) size fractions on a calibrated and zeroed top-loading balance and record the weights. For convenience, samples should be weighed using tared plastic weighing trays.
3. Discard the coarse fragments (> 2-mm fraction). These should consist entirely of stones and rock fragments.
4. Store the air-dried and sieved (< 2-mm size fraction) mineral soil samples in labeled plastic-lined bags or screw-capped or snap-cap wide-mouth plastic jars.
5. Enter the > 2 and < 2-mm size fraction weights into a spreadsheet and calculate the coarse fragment contents using the formula given below.

D. Grinding forest floor (litter + organic) and organic soil samples:

1. Carefully check the air-dried forest floor or organic soil samples for mineral coarse fragments and discard these to avoid damaging the Wiley mill. If necessary, these samples can be sieved through a 2-mm sieve to make it easier to separate any mineral coarse fragments from large pieces of woody debris.
2. After a subsample has been removed for oven-drying, grind a representative subsample of the forest floor or organic sample in a Wiley mill to <20-mesh.
3. Store a subsample of the forest floor or organic soil sample in a labeled 20-mL glass scintillation vial and the remainder in labeled plastic-lined bags or screw-capped or snap-cap wide-mouth plastic jars.

E. Grinding mineral soil samples:

1. If necessary, mineral soil samples may be further ground in a soil grinder with stationary and revolving ceramic plates.
2. For convenience, small quantities of mineral soil samples may be ground for total carbon and nitrogen analysis by filling a 20-mL glass scintillation vial about half-full of soil sample, adding a steel



tumbler, and rotating the vial on a vial rotator for 1 to 2 days to pulverize the sample. This method produces uniformly ground mineral soil samples (< 100 mesh) suitable for instruments that use small sample weights (e.g., carbon and nitrogen analysis). It is less effective with organic soil samples.

VI. Calculations:

A. Soil water content:

1. Enter the tare weights (plastic drying trays, soil moisture cans), field-moist and air-dry whole soil sample + tare weights, and oven-dry soil subsample + tare weights into a spreadsheet.
2. Subtract the tare weights from the oven and air dry soil sample + tare weights to obtain field-moist and air-dry whole soil sample weights and oven-dry soil subsample weights.
3. Compute the water content of the original field-moist whole soil sample on an air-dry basis:

$$\theta_{ad} = \frac{\text{weight of moist soil sample, g}}{\text{weight of air dry soil sample, g}} - 1$$

where  $\theta_{ad}$  is the soil water content on an air-dry basis. Multiply by 100 to report  $\theta_{ad}$  as a %.

4. Compute the residual water content of the air-dry soil sample on an oven-dry basis:

$$\theta_{od} = \frac{\text{weight of air dry soil subsample, g}}{\text{weight of oven dry soil subsample, g}} - 1$$

where  $\theta_{od}$  is the residual water content of the air-dry soil on an oven-dry basis. Multiply by 100 to report  $\theta_{od}$  as a %.

5. The residual water content of the air-dry soil sample may be used to calculate the oven-dry weight of a soil sample which can then be used to express bulk density and any or all of the chemical analysis of the air-dry soil samples on an oven-dry basis:

$$\text{Weight of soil sample (oven dry basis), g} = \frac{\text{weight of air dry soil sample, g}}{\theta_{od} + 1}$$

For example, 10 g of air-dry soil with a residual water content of 0.02 (2 %) is equivalent to 9.80 g of oven-dry soil.

B. Bulk density:

1. Correct the air-dry weight of each whole soil core sample to an oven-dry basis using the equation in part IV.A.5 above.
2. Divide the dry weight (oven-dry basis) of each whole soil core sample by the volume of the core (202.68 cm<sup>3</sup>) to obtain the bulk density of the soil core:

$$\rho_b = \frac{\text{Whole soil core dry weight (oven dry basis), g}}{\text{Soil core volume, cm}^3}$$

where  $\rho_b$  is the soil core bulk density, g/cm<sup>3</sup>

C. Coarse fragment content:

$$\text{Coarse fragments, \%} = \frac{\text{Weight of } > 2 \text{ mm size fraction, g}}{\text{Weight of } > 2 \text{ mm } & < 2 \text{ mm size fractions, g}} \times 100$$

VII. References:

- A. Soil Survey Laboratory. 1996. Soil survey laboratory methods manual. Soil survey investigations report no. 42. Ver. 3.0. USDA-NRCS, Lincoln, NE.
- B. Soil and Plant Analysis Council. 1999. Soil analysis handbook of reference methods. CRC Press, Boca Raton, FL.

## SOIL pH (Water and Salt Methods)

### I. Method:

- A. Water pH: 1:1 soil-water suspension for mineral soil samples, 1:2 soil-water suspension for organic soil samples
- B. Salt pH: 0.01 M CaCl<sub>2</sub>

### II. Supplies and Equipment:

- A. Top-loading balance
- B. 50-mL disposable plastic beakers or cups
- C. 25-mL adjustable-volume bottle-top dispenser
- D. Stirring rod, mechanical stirrer, or platform shaker
- E. 1-mL adjustable-volume repipet and tips
- F. pH meter and combination pH electrode

### III. Standards:

pH 4, 7, and 10 buffers

### IV. Reagents:

- A. Deionized water
- B. 1 M CaCl<sub>2</sub>: Dissolve 147 g of CaCl<sub>2</sub>·2H<sub>2</sub>O in deionized water and dilute to 1 L.

### V. Procedure:

- A. Water pH:
  - 1. Add 20.0 g of prepared mineral soil sample or 10.0 g of prepared organic soil sample to a 50-mL disposable plastic beaker or cup.
  - 2. Add 20.0 mL of deionized water.

3. Mix the soil-water suspension thoroughly with a stirring rod. Wipe off the stirring rod between samples to avoid cross contamination. Alternatively, use a mechanical stirrer to mix the soil-water suspension.
4. Allow the soil-water suspension to sit for 30 min. Alternatively, shake for 30 min on a platform shaker.
5. Calibrate the pH meter and combination pH electrode according to the manufacturer's instruction manual using pH 4, 7, and 10 buffers.
6. While stirring, measure the pH of the soil-water suspension. When a stable reading is obtained, record the pH to the nearest 0.1 pH unit.

B. Salt pH:

1. Pipet 200  $\mu\text{L}$  of 1 M  $\text{CaCl}_2$  into the soil-water suspension.
2. Mix the soil-water suspension with a stirring rod or mechanical stirrer.
3. Allow the soil-water suspension to sit for 30 min. Re-stir at 10 min intervals. Alternatively, shake for 30 min on a platform shaker.
4. While stirring, measure the pH of the soil-water suspension. When a stable reading is obtained, record the pH to the nearest 0.1 pH unit.

VI. Calculations: None

VII. References:

- A. Thomas, G. W. 1996. Soil pH and soil acidity. p. 475-490. In: D.L. Sparks et al. (eds.) Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI.
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- C. Soil and Plant Analysis Council. 1999. Soil analysis handbook of reference methods. CRC Press, Boca Raton, FL.

- D. Western States Laboratory Proficiency Testing Program. 1996. Soil and plant analytical methods. Western States Laboratory Proficiency Testing Program, Utah State Univ., Logan, UT.

## EXCHANGEABLE Na, K, Mg, and Ca (pH 7, 1 M NH<sub>4</sub> Acetate Method)

### I. Method:

Extraction of exchangeable Na, K, Mg, and Ca from acid soils with pH 7, 1 M NH<sub>4</sub> acetate, analysis by AAS or ICP-AES. This is a reference method.

### II. Supplies and Equipment:

#### A. Batch method:

1. Top-loading balance
2. 125-mL (4-oz) wide-mouth, screw-cap, plastic bottles or jars
3. 25-mL adjustable-volume bottle-top dispenser
4. Orbital shaker
5. 125-mm quantitative filter paper, plastic filter funnels, and filtering racks
6. 30-mL (1-oz) plastic storage bottles

#### B. Mechanical vacuum extractor method:

1. Top-loading balance
2. Analytical filter pulp
3. 60-mL plastic syringes to serve as extraction tubes, reservoir tubes, and receiving tubes on the mechanical vacuum extractor
4. Modified syringe plunger to pack filter pulp into extraction tube: Remove the rubber tip from a syringe plunger and cut off the plastic protrusion.
5. 1/8 ID x 1/4 OD x 1 in long rubber tubing pieces to connect extraction and receiving tubes
6. Centurion or Mavco mechanical vacuum extractor
7. 60-mL (2-oz) plastic storage bottles

III. Standards: None

IV. Reagents:

pH 7, 1 M NH<sub>4</sub> acetate: Add 57 mL of glacial acetic acid and 68 mL of conc. NH<sub>4</sub>OH to 800 mL of deionized water. Allow to cool, adjust the pH to 7.0 using 3 M acetic acid or 3 M NH<sub>4</sub>OH, and dilute to volume with deionized water. Prepare larger volumes as needed.

V. Procedure:

A. Batch method:

1. Add 2.50 g of prepared soil sample to a 125-mL wide-mouth jar.
2. Add 25.0 mL of pH 7, 1 M NH<sub>4</sub> acetate.
3. Shake for 30 min at 150 rpm.
4. Filter through quantitative filter paper and store at < 4 C pending analysis.
5. Analyze the extract for Na, K, Mg and Ca by AAS or ICP-AES.

B. Mechanical vacuum extractor method:

1. Weigh a receiving syringe to the nearest 0.01 g.
2. Prepare the extraction tube by tightly compressing a 1-g ball of analytical filter pulp into the bottom of a syringe barrel using the modified syringe plunger.
3. Place 2.50 g of prepared soil sample on top of the filter pulp.
4. Place the extraction tube containing the soil sample on the upper disk of the extractor and connect a weighed receiving syringe to the extraction tube using a 1-in length of 1/8 ID rubber tubing. Insert the plunger of the receiving syringe into the slot on the bottom disk of the extractor.
5. Add 10 mL of pH 7, 1 M NH<sub>4</sub> acetate to the extraction tube and allow to sit for 30 min to wet the sample.

6. Operate the extractor according to the manufacturer's instruction manual to rapidly leach the soil until the NH<sub>4</sub> acetate solution is about 0.5 to 1 cm above the top of the soil.
7. Connect a reservoir tube (another syringe barrel) to the top of the extraction tube and add 45 mL of pH 7, 1 M NH<sub>4</sub> acetate to the reservoir tube.
8. Operate the extractor according to the manufacturer's instruction manual to leach the soil overnight (16 h).
9. Remove the receiving syringe from the extractor and weigh to the nearest 0.01 g.
10. Store the extract at < 4 °C pending analysis.
11. Analyze the extract for Na, K, Mg and Ca by AAS or ICP-AES

VI. Calculations:

$$M_{\text{exch}} = (C \cdot V) / (EW \cdot W / 10)$$

where  $M_{\text{exch}}$  = exchangeable cation concentration,  $\text{cmol}_c \cdot \text{kg}^{-1}$

C = extract cation concentration,  $\text{mg} \cdot \text{L}^{-1}$

V = extract volume, L

EW = cation equivalent weight,  $\text{g} \cdot \text{mol}_c^{-1}$  (Na: 22.99, K: 39.1, Mg: 12.16, Ca: 20.04)

W = sample weight, kg

VII. References:

- A. Sumner, M.E., and W.P. Miller. 1996. Cation exchange capacity and exchange coefficients. p. 1201-1229. In: D.L. Sparks et al. (eds.) Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI.
- B. Soil Survey Laboratory. 1996. Soil survey laboratory methods manual. Soil survey investigations report no. 42. Ver. 3.0. USDA-NRCS, Lincoln, NE.
- C. Soil and Plant Analysis Council. 1999. Soil analysis handbook of reference methods. CRC Press, Boca Raton, FL.
- D. Western States Laboratory Proficiency Testing Program. 1996. Soil and plant analytical methods. Western States Laboratory Proficiency Testing Program, Utah State Univ., Logan, UT.



## EXCHANGEABLE Al AND Mn (1 M KCl Method)

### I. Method:

Extraction of exchangeable Al and Mn from acid soils with 1 M KCl, analysis by AAS or ICP-AES. This is a reference method.

### II. Supplies and Equipment:

#### A. Batch method:

1. Top-loading balance
2. 125-mL (4-oz) wide-mouth, screw-cap, plastic bottles or jars
3. 25-mL adjustable-volume bottle-top dispenser
4. Orbital shaker
5. 125-mm quantitative filter paper, plastic filter funnels, and filtering racks
6. 30-mL (1-oz) plastic storage bottles

#### B. Mechanical vacuum extractor method:

1. Top-loading balance
2. Analytical filter pulp
3. 60-mL plastic syringes to serve as extraction tubes, reservoir tubes, and receiving tubes on the mechanical vacuum extractor
4. Modified syringe plunger to pack filter pulp into extraction tube: Remove the rubber tip from a syringe plunger and cut off the plastic protrusion.
5. 1/8 ID x 1/4 OD x 1 in long rubber tubing pieces to connect extraction and receiving tubes
6. Centurion or Mavco mechanical vacuum extractor
7. 60-mL (2-oz) plastic storage bottles

III. Standards: None

IV. Reagents:

1 M KCl: Dissolve 74.56 g of KCl in deionized water and dilute to 1 L.

V. Procedure:

A. Batch method:

1. Add 2.50 g of prepared soil sample to a 125-mL wide-mouth jar.
2. Add 25.0 mL of 1 M KCl.
3. Shake for 30 min at 150 rpm.
4. Filter through quantitative filter paper and store at  $< 4^{\circ}\text{C}$  pending analysis.
5. Analyze the extract for Al and Mn by AAS or ICP-AES.

B. Mechanical vacuum extractor method:

1. Weigh a receiving syringe to the nearest 0.01 g.
2. Prepare the extraction tube by tightly compressing a 1-g ball of analytical filter pulp into the bottom of a syringe barrel using the modified syringe plunger.
3. Place 2.50 g of prepared soil sample on top of the filter pulp.
4. Place the extraction tube containing the soil sample on the upper disk of the extractor and connect a weighed receiving syringe to the extraction tube using a 1-in length of 1/8 ID rubber tubing. Insert the plunger of the receiving syringe into the slot on the bottom disk of the extractor.
5. Add 10 mL of 1 M KCl to the extraction tube and allow to sit for 30 min to wet the sample.
6. Operate the extractor according to the manufacturer's instruction manual to rapidly leach the soil until the KCl solution is about 0.5 to 1 cm above the top of the soil.

7. Connect a reservoir tube (another syringe barrel) to the top of the extraction tube and add 45 mL of 1 M KCl to the reservoir tube.
8. Operate the extractor according to the manufacturer's instruction manual to leach the soil for 45 min.
9. Remove the receiving syringe from the extractor and weigh to the nearest 0.01 g.
10. Store the extract at  $< 4^{\circ}\text{C}$  pending analysis.
11. Analyze the extract for Al and Mn by AAS or ICP-AES

VI. Calculations:

$$M_{\text{exch}} = (C \cdot V) / (EW \cdot W / 10)$$

where  $M_{\text{exch}}$  = exchangeable cation concentration,  $\text{cmol}_c \cdot \text{kg}^{-1}$

C = extract cation concentration,  $\text{mg} \cdot \text{L}^{-1}$

V = extract volume, L

EW = cation equivalent weight,  $\text{g} \cdot \text{mol}_c^{-1}$  (Mn: 27.47, Al: 8.99)

W = sample weight, kg

VII. References:

- A. Bertsch, P.M., and P.R. Bloom. 1996. Aluminum. p. 517-550. In: D.L. Sparks et al. (eds.) Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI.
- B. Soil Survey Laboratory. 1996. Soil survey laboratory methods manual. Soil survey investigations report no. 42. Ver. 3.0. USDA-NRCS, Lincoln, NE.

EXCHANGEABLE CATIONS (Na, K, Mg, Ca, Al),  
TRACE METALS (Mn, Fe, Ni, Cu, Zn, Cd, Pb), AND S (1 M NH<sub>4</sub>Cl Method)

I. Method:

Extraction of exchangeable cations (Na, K, Mg, Ca, Al), trace elements (Mn, Fe, Ni, Cu, Zn, Cd, Pb), and S from acid or alkaline soils with 1 M NH<sub>4</sub>Cl, analysis by ICP-AES. This is the preferred method.

II. Supplies and Equipment:

A. Batch method:

1. Top-loading balance
2. 125-mL (4-oz) wide-mouth, screw-cap, plastic bottles or jars
3. 25-mL adjustable-volume bottle-top dispenser
4. Orbital shaker
5. 125-mm quantitative filter paper, plastic filter funnels, and filtering racks
6. 30-mL (1-oz) plastic storage bottles

B. Mechanical vacuum extractor method:

1. Top-loading balance
2. Analytical filter pulp
3. 60-mL plastic syringes to serve as extraction tubes, reservoir tubes, and receiving tubes on the mechanical vacuum extractor
4. Modified syringe plunger to pack filter pulp into extraction tube: Remove the rubber tip from a syringe plunger and cut off the plastic protrusion.
5. 1/8 ID x 1/4 OD x 1 in long rubber tubing pieces to connect extraction and receiving tubes
6. Centurion or Mavco mechanical vacuum extractor

7. 60-mL (2-oz) plastic storage bottles

III. Standards: None

IV. Reagents:

1 M NH<sub>4</sub>Cl: Dissolve 53.49 g of NH<sub>4</sub>Cl in deionized water and dilute to 1 L. Prepare larger volumes as needed.

V. Procedure:

A. Batch method:

1. Add 2.50 g of prepared soil sample to a 125-mL wide-mouth jar.
2. Add 25.0 mL of 1 M NH<sub>4</sub>Cl.
3. Shake for 30 min at 150 rpm.
4. Filter through quantitative filter paper and store at < 4 °C pending analysis.
5. Analyze the extract for Na, K, Mg, Ca, Al, trace elements if needed, and S by ICP-AES.

B. Mechanical vacuum extractor method:

1. Weigh a receiving syringe to the nearest 0.01 g.
2. Prepare the extraction tube by tightly compressing a 1-g ball of analytical filter pulp into the bottom of a syringe barrel using the modified syringe plunger.
3. Place 2.50 g of prepared soil sample on top of the filter pulp.
4. Place the extraction tube containing the soil sample on the upper disk of the extractor and connect a weighed receiving syringe to the extraction tube using a 1-in length of 1/8 ID rubber tubing. Insert the plunger of the receiving syringe into the slot on the bottom disk of the extractor.
5. Add 10 mL of 1 M NH<sub>4</sub>Cl to the extraction tube and allow to sit for 30 min to wet the sample.

6. Operate the extractor according to the manufacturer's instruction manual to rapidly leach the soil until the NH<sub>4</sub>Cl solution is about 0.5 to 1 cm above the top of the soil.
7. Connect a reservoir tube (another syringe barrel) to the top of the extraction tube and add 45 mL of 1 M NH<sub>4</sub>Cl to the reservoir tube.
8. Operate the extractor according to the manufacturer's instruction manual to leach the soil overnight (16 h).
9. Remove the receiving syringe from the extractor and weigh to the nearest 0.01 g.
10. Store the extract at < 4 °C pending analysis.
11. Analyze the extract for Na, K, Mg, Ca, Al, trace elements if needed, and S by ICP-AES.

VI. Calculations:

A.  $M_{\text{exch}} = (C \cdot V) / (EW \cdot W / 10)$

where  $M_{\text{exch}}$  = exchangeable cation concentration,  $\text{cmol}_c \cdot \text{kg}^{-1}$

C = extract cation concentration,  $\text{mg} \cdot \text{L}^{-1}$

V = extract volume, L

EW = cation equivalent weight,  $\text{g} \cdot \text{mol}_c^{-1}$  (Na: 22.99, K: 39.1, Mg: 12.16, Ca: 20.04, Sr: 43.82, Ba: 68.68, Mn: 27.47, Al: 8.99)

W = sample weight, kg

To calculate trace element (e.g., Ni, Cu, Zn, Cd, Pb) and S concentrations in the soil in  $\text{mg} \cdot \text{kg}^{-1}$ , omit the equivalent weight and value of 10 from the denominator of the above equation.

B.  $\text{ECEC} = \sum M$

where ECEC = effective cation exchange capacity,  $\text{cmol}_c \cdot \text{kg}^{-1}$

$\sum M$  = summation of exchangeable cations,  $\text{cmol}_c \cdot \text{kg}^{-1}$

VII. References:

- A. Amacher, M.C., R.E. Henderson, M.D. Breithaupt, C.L. Seale, and J.M. LaBauve. 1990. Unbuffered and buffered salt methods for exchangeable cations and effective cation-exchange capacity. Soil Sci. Soc. Am. J. 54:1036-1042.

- B. Suarez, D.L. 1996. Beryllium, magnesium, calcium, strontium, and barium. p. 575-601. In: D.L. Sparks et al. (eds.) Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI.
- C. Sumner, M.E., and W.P. Miller. 1996. Cation exchange capacity and exchange coefficients. p. 1201-1229. In: D.L. Sparks et al. (eds.) Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI.
- D. Soil Survey Laboratory. 1996. Soil survey laboratory methods manual. Soil survey investigations report no. 42. Ver. 3.0. USDA-NRCS, Lincoln, NE.

## EXTRACTABLE PHOSPHORUS (Bray 1 Method)

### I. Method:

Extraction of P from acid (pH = 6.0) soils with 0.03 M  $\text{NH}_4\text{F}$  + 0.025 M HCl

### II. Supplies and Equipment:

- A. Top-loading balance
- B. 125-mL (4-oz) wide-mouth, screw-cap, plastic bottles or jars
- C. 25-mL adjustable-volume bottle-top dispenser
- D. Orbital shaker
- E. 125-mm quantitative filter paper, plastic filter funnels, and filtering racks
- F. 30-mL (1-oz) plastic storage bottles

### III. Standards: None

### IV. Reagents:

- A. 1 M  $\text{NH}_4\text{F}$ : Dissolve 37.0 g of  $\text{NH}_4\text{F}$  in deionized water and dilute to 1 L.
- B. 0.5 M HCl: Dilute 41.6 mL of conc. HCl to 1 L with deionized water.
- C. 0.03 M  $\text{NH}_4\text{F}$  + 0.025 M HCl: Dilute 30 mL of 1 M  $\text{NH}_4\text{F}$  and 50 mL of 0.5 M HCl to 1 L with deionized water. Prepare larger volumes as needed and store in a plastic container.

### V. Procedure:

- A. Add 2.50 g of prepared soil sample to a 125-mL wide-mouth jar.
- B. Add 25.0 mL of 0.03 M  $\text{NH}_4\text{F}$  + 0.025 M HCl.
- C. Shake for 5 min at 150 rpm.
- D. Filter through quantitative filter paper and store at  $< 4^\circ\text{C}$  pending analysis. Analyze for inorganic P using the ascorbic acid colorimetric method.



VI. Calculations:

$$C_s = C_{\text{extr}} V / W$$

where  $C_s$  = soil P concentration,  $\text{mg} \cdot \text{kg}^{-1}$

$C_{\text{extr}}$  = extract P concentration,  $\text{mg} \cdot \text{L}^{-1}$

$V$  = extract volume, L

$W$  = sample weight, kg

VII. References:

- A. Kuo, S. 1996. Phosphorus. p. 869-919. In: D.L. Sparks et al. (eds.) Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI.
- B. Soil and Plant Analysis Council. 1999. Soil analysis handbook of reference methods. CRC Press, Boca Raton, FL.
- C. Western States Laboratory Proficiency Testing Program. 1996. Soil and plant analytical methods. Western States Laboratory Proficiency Testing Program, Utah State Univ., Logan, UT.

## EXTRACTABLE PHOSPHORUS (Olsen Method)

### I. Method:

Extraction of P from near-neutral (pH > 6.0) and alkaline soils with pH 8.5, 0.5 M NaHCO<sub>3</sub>

### II. Supplies and Equipment:

- A. Top-loading balance
- B. 125-mL (4-oz) wide-mouth, screw-cap, plastic bottles or jars
- C. 50-mL adjustable-volume bottle-top dispenser
- D. Orbital shaker
- E. 125-mm quantitative filter paper, plastic filter funnels, and filtering racks
- F. 60-mL (2-oz) plastic storage bottles

### III. Standards: None

### IV. Reagents:

pH 8.5, 0.5 M NaHCO<sub>3</sub>: Dissolve 42.00 g of NaHCO<sub>3</sub> in about 800 mL of deionized water, adjust to pH 8.5 with 1 M NaOH, and dilute to 1 L. Prepare larger volumes as needed. Protect reagent against absorption of atmospheric CO<sub>2</sub> and prepare new reagent if the pH increases.

### V. Procedure:

- A. Add 2.00 g of prepared soil sample to a 125-mL wide-mouth jar.
- B. Add 40.0 mL of pH 8.5, 0.5 M NaHCO<sub>3</sub>.
- C. Shake for 30 min at 150 rpm.
- D. Filter through quantitative filter paper and store at < 4 °C pending analysis. Analyze for inorganic P using the ascorbic acid colorimetric method.

VI. Calculations:

$$C_s = C_{\text{extr}} V / W$$

where  $C_s$  = soil P concentration,  $\text{mg} \cdot \text{kg}^{-1}$

$C_{\text{extr}}$  = extract P concentration,  $\text{mg} \cdot \text{L}^{-1}$

$V$  = extract volume, L

$W$  = sample weight, kg

VII. References:

- A. Kuo, S. 1996. Phosphorus. p. 869-919. In: D.L. Sparks et al. (eds.) Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI.
- B. Soil and Plant Analysis Council. 1999. Soil analysis handbook of reference methods. CRC Press, Boca Raton, FL.
- C. Western States Laboratory Proficiency Testing Program. 1996. Soil and plant analytical methods. Western States Laboratory Proficiency Testing Program, Utah State Univ., Logan, UT.

COLORIMETRIC ANALYSIS OF PHOSPHORUS IN SOIL EXTRACTS  
(Ascorbic Acid Method)

- I. Method: Ascorbic acid reduction of phosphomolybdate
- II. Supplies and Equipment:
  - A. 50-mL Erlenmeyer flasks
  - B. 1-mL and 10 mL adjustable-volume repipets and tips
  - C. 25-mL adjustable-volume bottle-top dispenser
  - D. Colorimeter and cuvettes
- III. Standards:
  - A. 1000 mg•L<sup>-1</sup> P: Available from a commercial source.
  - B. 100 mg•L<sup>-1</sup> P: Dilute 10 mL of the 1000 mg•L<sup>-1</sup> P standard to 100 mL with deionized water in a volumetric flask.
  - C. P standards in 0.03 M NH<sub>4</sub>F + 0.025 M HCl: Pipet 0.2, 0.4, 0.8, 1.6, 2.4, 3.2, 4.0 mL of the 100 mg•L<sup>-1</sup> P standard into a series of 100 mL volumetric flasks and dilute to volume with 0.03 M NH<sub>4</sub>F + 0.025 M HCl. The P concentrations are 0.2, 0.4, 0.8, 1.6, 2.4, 3.2, and 4.0 mg•L<sup>-1</sup>.
  - D. P standards in pH 8.5, 0.5 M NaHCO<sub>3</sub>: Pipet 0.2, 0.4, 0.8, 1.6, 2.4, 3.2, 4.0 mL of the 100 mg•L<sup>-1</sup> P standard into a series of 100 mL volumetric flasks and dilute to volume with pH 8.5, 0.5 M NaHCO<sub>3</sub>. The P concentrations are 0.2, 0.4, 0.8, 1.6, 2.4, 3.2, and 4.0 mg•L<sup>-1</sup>.
- IV. Reagents:
  - A. Molybdate-tartrate solution: Add 69 mL of conc. (18 M) H<sub>2</sub>SO<sub>4</sub> to about 500 mL of deionized water in a 1-L volumetric flask and allow to cool to room temperature before proceeding. Dissolve 6 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O in about 100 mL of deionized water and quantitatively transfer to the sulfuric acid solution. Dissolve 0.1454 g K(SBO)C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> in about 50 mL of deionized water and quantitatively transfer to the sulfuric acid solution. Dilute to volume and store in an amber glass bottle in a refrigerator.
  - B. Combined reagent: Dissolve 1.056 g of ascorbic acid in 200 mL of the molybdate-tartrate solution. Prepare fresh solution daily as needed.

- C. 1.25 M H<sub>2</sub>SO<sub>4</sub>: Add 69 mL of conc. (18 M) H<sub>2</sub>SO<sub>4</sub> to about 500 mL of deionized water in a 1-L volumetric flask. Allow to cool and dilute to volume with deionized water.

V. Procedure:

A. Bray 1 (0.03 M NH<sub>4</sub>F + 0.025 M HCl) extracts:

1. Pipet 5.0 mL of 0.03 M NH<sub>4</sub>F + 0.025 M HCl (reagent blank), each standard, and each sample extract into a series of 50-mL Erlenmeyer flasks.
2. Add 16.0 mL of deionized water to each flask.
3. Add 4.0 mL of combined reagent to each flask and swirl to mix.
4. After 30 min of color development, measure the absorbencies at 880 nm.
5. Samples with absorbencies above the range of the standard curve need to be diluted and re-analyzed. In such cases, pipet 1.0 mL of sample and 4.0 mL of 0.03 M NH<sub>4</sub>F + 0.025 M HCl into a 50-mL Erlenmeyer flask and follow steps 2 through 4 above.

B. Olsen (pH 8.5, 0.5 M NaHCO<sub>3</sub>) extracts:

1. Pipet 5.0 mL of pH 8.5, 0.5 M NaHCO<sub>3</sub> (reagent blank), each standard, and each sample extract into a series of 50-mL Erlenmeyer flasks.
2. Add 15.0 mL of deionized water to each flask.
3. Add 1.0 mL of 1.25 M H<sub>2</sub>SO<sub>4</sub> to each flask and swirl to mix. Allow the flasks to stand for at least one hour to dissipate the CO<sub>2</sub> produced when the carbonate in the extract reacts with the acid.
4. Add 4.0 mL of combined reagent to each flask and swirl to mix.
5. After 30 min of color development, measure the absorbencies at 880 nm.
6. Samples with absorbencies above the range of the standard curve need to be diluted and re-analyzed. In such cases, pipet 1.0 mL of sample and 4.0 mL of pH 8.5, 0.5 M NaHCO<sub>3</sub> into a 50-mL Erlenmeyer flask and follow steps 2 through 5 above.

VI. Calculations:

$$C_s = C_{\text{extr}} V / W$$

where  $C_s$  = soil P concentration,  $\text{mg? kg}^{-1}$

$C_{\text{extr}}$  = extract P concentration,  $\text{mg? L}^{-1}$

$V$  = extract volume, L

$W$  = sample weight, kg

VII. References:

Kuo, S. 1996. Phosphorus. p. 869-919. In: D.L. Sparks et al. (eds.) Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI.

TOTAL CARBON (TC), TOTAL ORGANIC CARBON (TOC),  
AND TOTAL INORGANIC CARBON (TIC) (Combustion Methods)

I. Method:

Dry combustion at controlled heating rates and temperatures to release CO<sub>2</sub> from organic and carbonate phases measured by an infrared detector on an automated C analyzer. This is the preferred method.

II. Supplies and Equipment:

A. LECO model RC-412 multi-carbon analyzer

B. O<sub>2</sub> regulator

C. Operating supplies:

1. Quartz boats (LECO 781-335)

2. Nickel liner boats (LECO 782-059)

3. Combustion tube (LECO 783-299)

D. Analytical balance

E. Muffle oven

III. Standards:

A. Low-C cell calibration: Use a low-C synthetic C standard (e.g., LECO 502-029).

B. High-C cell calibration: Use reagent-grade CaCO<sub>3</sub> (12.0 % C).

IV. Reagents:

A. Carrier gases: 99.5 % O<sub>2</sub> and 99.5 % N<sub>2</sub>

B. Copper oxide (LECO 501-170)

C. Lecosorb, 20-30 mesh (NaOH on inert base) (LECO 502-174)

D. Anhydron (anhydrous magnesium perchlorate) (LECO 501-171)

V. Procedure:

- A. Prepare nickel boat liners by baking them in a muffle oven at 1000 °C for 1 h.
- B. Set up C analyzer according to the operating manual. Operating conditions for calibration are

Furnace idle temperature: 500<sup>b</sup>C  
Afterburner temperature: 800<sup>b</sup>C  
Catalyst temperature: 750<sup>b</sup>C  
Carrier gas: O<sub>2</sub>  
Mass flow: 750 mL

C. Determine blank:

- 1. Enter 0.500 g weight into weight stack.
- 2. Press analyze key.
- 3. Slide empty quartz boat into furnace on “Load furnace” command.
- 4. Complete steps C1 through C3 a minimum of three times.
- 5. Enter the average blank value by following the blank procedure outlined in the operating manual.

D. Calibrate instrument:

- 1. To calibrate the low-C cell, weigh 0.2 g of LECO synthetic C standard into a prepared and tared nickel boat liner and enter exact weight of standard (to nearest 0.0001 g) into weight stack.

Low-C cell operating conditions:

Cell	Start °C	End °C	Ramp	Hold sec
Low C	500	900	100	60

- 2. Press analyze key.
- 3. Slide quartz boat with nickel liner containing the standard into furnace on “Load furnace” command.



4. Do steps D1 through D3 a minimum of three times.
5. To calibrate the high-C cell, weigh 0.1 g of reagent-grade CaCO<sub>3</sub> into a prepared and tared nickel boat liner and enter exact weight of standard (to nearest 0.0001 g) into weight stack.

High-C cell operating conditions:

Cell	Start	End	Ramp	Hold
	°C	°C		sec
High C	500	900	100	120

6. Press analyze key.
7. Slide quartz boat with nickel liner containing the standard into furnace on "Load furnace" command.
8. Complete steps D5 to D7 a minimum of three times.
9. Calibrate the C analyzer by following the procedure outlined in the operating manual.
10. Verify the calibration by analyzing the standard again. Repeat calibration steps if the measured value is not within tolerance limits for the standard.

E. Analyze prepared soil samples for TOC and TIC content using the following operating conditions:

Phase	Start	End	Ramp	Hold
	°C	°C		sec
TOC	500	500	0	300
TIC	500	800	200	240

1. Weigh 0.05 to 0.20 g of prepared sample into a prepared nickel boat liner and enter exact sample weight (to nearest 0.0001 g) into weight stack.
2. Press analyze key.
3. Slide quartz boat with nickel liner containing the sample into furnace on "Load furnace" command.
4. Repeat steps E1 through E3 for each sample.

V. Calculations: None

VII. References:

LECO CR-412 multi-carbon analyzer operating manual

## TOTAL ORGANIC CARBON (Dichromate Oxidation with Heating Method)

### I. Method:

Oxidation of TOC in a mixture of dichromate and sulfuric acid using a heated block digester followed by measurement of remaining dichromate by titration with ferrous ammonium sulfate. This method serves as an independent check of the combustion method for measuring TOC and is a reference method.

### II. Supplies and Equipment:

- A. Analytical balance
- B. 100-mL digestion tubes
- C. 10 and 25-mL adjustable -volume bottle-top dispensers
- D. Block digester
- E. 250-mL glass Erlenmeyer flasks
- F. Titration stir plate with fluorescent lighted top
- G. Teflon stir bars
- H. 25-mL digital buret

### III. Reagents:

- A. 0.5 N  $K_2Cr_2O_7$ : Dissolve 24.5125 g of  $K_2Cr_2O_7$  in deionized water and dilute to 1 L.
- B. 0.2 N  $Fe(NH_4)_2(SO_4)_2$ : Dissolve 78.390 g of  $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$  in deionized water and dilute to 1 L.
- C. Conc.  $H_2SO_4$
- D. Indicator solution: Dissolve 14.85 g of o-phenanthroline monohydrate and 6.95 g of  $FeSO_4 \cdot 7H_2O$  in deionized water and dilute to 1 L.

### IV. Procedure:

- A. Add 0.500 g of prepared sample to a digestion tube.

- B. Add 10.00 mL of 0.5 N  $K_2Cr_2O_7$  and 15.0 mL of conc.  $H_2SO_4$  to the sample tube, an empty tube to serve as the digested blank, and a 250-mL Erlenmeyer flask to serve as an undigested blank for standardizing the 0.2 N  $Fe(NH_4)_2(SO_4)_2$ .
- C. Heat the tubes in the block digester to 200 °C, digest for 30 min at 200 °C, remove the tubes from the block digester, and allow to cool.
- D. Transfer the contents of each tube to a 250-mL Erlenmeyer flask by thorough rinsing with deionized water and dilute the contents in each flask to about 100 mL.
- E. Add a stir bar and five drops of indicator solution to each flask.
- F. Titrate the undigested and digested blanks and sample to the endpoint with 0.2 N  $Fe(NH_4)_2(SO_4)_2$ . The color changes from yellow to green to blue-green to blue-gray to red at the endpoint.

V. Calculations:

A. 
$$A = (V_{DB} - V_{samp}) [ (V_{UB} - V_{DB}) / V_{UB} ] + (V_{DB} - V_{samp})$$

where A = correction factor, mL

$V_{UB}$  = volume of titrant used on undigested blank, mL

$V_{DB}$  = volume of titrant used on digested blank, mL

$V_{samp}$  = volume of titrant used on sample, mL

B. 
$$\% \text{ organic C} = A N ( 0.003 ) ( 100 ) / W$$

where N = normality of  $Fe(NH_4)_2(SO_4)_2$  titrant

W = sample weight, g

VI. References:

Nelson, D.W., and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. p. 961-1010. In: D.L. Sparks et al. (eds.) Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI.

## CARBONATES (Modified Pressure Calcimeter Method)

### I. Method:

Soil samples containing carbonate minerals are reacted with HCl in a sealed reactor. The resulting CO<sub>2</sub> released is measured with a pressure transducer. This method serves as an independent check of the combustion method for measuring TIC and is a reference method.

### II. Supplies and Equipment:

- A. Pressure transducer (Setra model 280E, 0-105 kPa, 0.03-5.03 VDC output)
- B. Power supply (SR Components DC-24-600-2.1 transformer, model ddu240060; input: 120 VAC, 60 Hz, 21 W; output: 24 VDC, 600 mA)
- C. Digital voltmeter (Wavetek model 5XL)
- D. 14-gauge copper wire to connect pressure transducer to power supply
- E. 20-cm of 9.5-mm ID Tygon R-3603 tubing
- F. 18-gauge Luer-Lok hypodermic needle
- G. 0.6-um particle filter (LECO 768-980)
- H. 20-mL (no. 223742) and 100-mL (no. 223747) Wheaton serum bottles
- I. 13-20-mm Wheaton no. 224100-194 gray butyl serum bottle stoppers with flange and slotted plug
- J. 20-mm Wheaton no. 224208 aluminum tear-off seals
- K. 20-mm Wheaton no. 224303 crimper
- L. 20-mm Wheaton no. 224353 decapper
- M. 2-mL auto-sampler vials
- N. 5-mL adjustable-volume bottle-top dispenser

III. Standards:

- A. Reagent grade  $\text{CaCO}_3$
- B. 80-mesh  $\text{SiO}_2$
- C. 0.25, 0.50, 1.0, 2.0, 5.0, 10.0, 15.0, 20.0, 30.0, 40.0, and 50.0 %  $\text{CaCO}_3$  standards: Prepare 100 g of each standard by mixing 0.250, 0.500, 1.00, 2.00, 5.00, 10.00, 15.00, 20.00, 30.00, 40.00, and 50.00 g of  $\text{CaCO}_3$  with 99.75, 99.50, 99.00, 98.00, 95.00, 90.00, 85.00, 80.00, 70.00, 60.00, and 50.00 g of 80-mesh  $\text{SiO}_2$ .

IV. Reagents:

6 m HCl with 3 %  $\text{FeCl}_2$ : Mix 500 mL of conc. HCl with 500 mL of deionized water. Add 30 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and mix until it dissolves.

V. Procedure:

- A. Assemble the pressure calcimeter by wiring the pressure transducer and voltmeter to the power supply. Connect the filter to the pressure transducer using a short piece of tubing and connect the filter to the hypodermic needle using the remaining tubing.
- B. Soils with < 15 %  $\text{CaCO}_3$ :
  1. Add 1.00 g of prepared soil sample to a 20-mL serum bottle.
  2. Dispense 1.8 mL of 6 M HCl reagent into a 2-mL vial.
  3. Carefully place the vial into the serum bottle without spilling the HCl.
  4. Seal the bottle with a serum bottle stopper and crimp closed with an aluminum tear-off cap seal using the hand crimper.
  5. Vigorously shake the bottle so that the HCl comes into contact with the soil to begin the release of  $\text{CO}_2$ .
  6. Allow the bottle to sit for 5 h.
  7. Remove the tear-off cap, puncture the stopper with the hypodermic needle, and record the voltage output after 3 to 5 s.

8. Run a blank and standard curve by carrying 1.00 g of SiO<sub>2</sub> (blank) and 1.00 g of the 0.25, 0.50, 1.0, 2.0, 5.0, 10.0, and 15.0 % CaCO<sub>3</sub> standards through steps 2 through 7.

C. Soils with > 15 % CaCO<sub>3</sub>:

1. Add 1.00 g of prepared soil sample to a 100-mL serum bottle. Use 0.50 g if the soil is > 50 % CaCO<sub>3</sub>.
2. Follow steps B2 through B7 above.
3. Run a blank and standard curve by carrying 1.00 g of SiO<sub>2</sub>(blank) and 1.00 g of the 0.50, 1.0, 5.0, 10.0, 20.0, 30.0, 40.0 and 50.0 % CaCO<sub>3</sub> standards through steps B2 through B7 above.

VI. Calculations:

- A. Calculate a linear regression equation for % CaCO<sub>3</sub> versus voltage for the blank and standards. Use the equation to calculate the % CaCO<sub>3</sub> content of the sample.
- B. % TIC = % CaCO<sub>3</sub> \*12/100

VII. References:

Sherrod, L.A., G. Dunn, G.A. Peterson, and R.L. Kolberg. 2002. Inorganic carbon analysis by modified pressure calcimeter method. Soil Sci. Soc. Am. J. 66:299-305.

## TOTAL NITROGEN (COMBUSTION METHOD)

### I. Method:

Dry combustion at high temperature to release N measured by a thermal conductivity detector on an automated N analyzer. This is the preferred method.

### II. Supplies and Equipment:

- A. LECO model FP-528 N analyzer
- B. Compressed air, carrier gas (He or Ar), and O<sub>2</sub> regulators
- C. External computer for data processing
- D. Operating supplies:
  - 1. Tin foil sample cups (LECO 502-186)
  - 2. Sample cup holder (LECO 604-398)
  - 3. Quartz wool strips (LECO 608-379)
  - 4. Porous crucibles (LECO 614-961-110)
  - 5. Quartz lance tube (LECO 614-962)
  - 6. Combustion tube (LECO 616-108)
  - 7. Crucible extractor tool (LECO 616-152)
- E. Analytical balance

### III. Standards:

- A. Forest floor samples: Use EDTA (9.52-9.60 % N)
- B. Mineral soil samples with > 0.25 % N: Use EDTA.
- C. Mineral soil samples with < 0.25 % N: Use mineral soil samples with a range of total N values as determined by Kjeldahl digestion and analysis



IV. Reagents:

- A. Carrier gas: 99.99 % He or Ar
- B. Combustion gas: 99.99 % O<sub>2</sub>
- C. Pneumatic gas: compressed air
- D. Lecosorb, 20-30 mesh (NaOH on an inert base) (LECO 502-174)
- E. Anhydron (anhydrous magnesium perchlorate) (LECO 501-171)
- F. Copper sticks (LECO 502-189)
- G. Furnace reagent (LECO 501-609)
- H. Reagent N catalyst (LECO 502-049)
- I. Tube catalyst (LECO 601-437)
- J. Lubricating grease (LECO 616-529)

V. Procedure:

- A. Place a tin foil sample cup in a suitable holder on an analytical balance and zero the balance. For convenience, a screw cap from a small glass vial may be used as a holder for the tin foil sample cup during weighing.
- B. For forest floor samples, add about 0.1 g of prepared sample to the tin foil sample cup and record the exact sample weight to the nearest 0.0001 g. For mineral soil samples, add about 0.2 g of prepared sample to the tin foil sample cup and record the exact sample weight to the nearest 0.0001 g.
- C. Secure the sample in the foil cup by twisting the top closed. Be sure the sample packet is the right size to drop into the combustion chamber during analysis.
- D. Place the prepared and weighed sample packets into the autoloader tray.
- E. Calibrate and operate the LECO FP-528 N analyzer according to the instrument operating manual.

VI. Calculations: None

VII. References:

- A. Soil Survey Laboratory. 1996. Soil survey laboratory methods manual. Soil survey investigations report no. 42. Ver. 3.0. USDA-NRCS, Lincoln, NE.
- B. LECO FP-528 N analyzer operating manual

## TOTAL NITROGEN (Kjeldahl Digestion Method)

### I. Method:

Kjeldahl digestion followed by analysis of  $\text{NH}_4$  in digest using LACHAT QuikChem Method 13-107-06-2-D. This method serves as an independent check of the combustion method for measuring total N and is a reference method.

### II. Supplies and Equipment:

- A. Analytical balance
- B. 100-mL digestion tubes
- C. 10-mL adjustable-volume bottle-top dispenser
- D. Block digester

### III. Standards: None

### IV. Reagents:

- A. Digestion tablets: 3.5 g  $\text{K}_2\text{SO}_4$  + 0.035 g Se or 1.5 g  $\text{K}_2\text{SO}_4$  + 0.015 g Se
- B. Conc.  $\text{H}_2\text{SO}_4$

### V. Procedure:

- A. Add 0.500 g of prepared sample to a digestion tube.
- B. Add a digestion tablet.
- C. Add 10 mL of conc.  $\text{H}_2\text{SO}_4$  if a 3.5-g tablet is used and 4 mL of conc.  $\text{H}_2\text{SO}_4$  if a 1.5-g tablet is used.
- D. Heat the tube slowly in the block digester to 375 C. After the digest clears, continue heating at 375 C for an additional 2.5 h, remove the tube from digester, and allow to cool.
- E. Slowly add deionized water to the tube, dilute to 100 mL, stopper, mix, and save the solution for analysis.

- F. Analyze the digest for  $\text{NH}_4$  by the automated phenate method (LACHAT QuikChem Method 13-107-06-2-D).

VI. Calculations:

$$C_s = C_{\text{extr}} V / W$$

where  $C_s$  = solid phase N concentration,  $\text{mg}\cdot\text{kg}^{-1}$

$C_{\text{extr}}$  = digest N concentration,  $\text{mg}\cdot\text{L}^{-1}$

$V$  = digest volume, L

$W$  = sample weight, kg

VII. References:

Bremner, J.M. 1996. Nitrogen - total. p. 1085-1121. In: D.L. Sparks et al. (eds.) Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI.

COLORIMETRIC ANALYSIS OF AMMONIA NITROGEN IN KJELDAHL DIGESTS  
(Automated Phenate Method)

I. Method: LACHAT QuikChem Method 13-107-06-2-D

II. Supplies and Equipment:

LACHAT flow injection analyzer (FIA)

III. Standards:

A. 1000 mg•L<sup>-1</sup> NH<sub>4</sub>-N: Available from a commercial source.

B. Matrix solution: Carefully add 40 mL of conc. H<sub>2</sub>SO<sub>4</sub> to about 700 mL of deionized water in a 1-L volumetric flask. Add 10 digestion tablets, stir until dissolved, cool, dilute to volume, and mix.

C. 100, 75, 50, 25 mg•L<sup>-1</sup> NH<sub>4</sub>-N: Dilute 10, 7.5, 5, and 2.5 mL of the 1000 mg•L<sup>-1</sup> NH<sub>4</sub>-N standard to 100 mL with matrix solution in a series of volumetric flasks.

IV. Reagents:

A. Buffer solution: Dissolve 65 g of NaOH, 50.0 g of sodium potassium tartrate, and 26.8 g of Na<sub>2</sub>HPO<sub>4</sub>•7H<sub>2</sub>O in deionized water and dilute to 1-L in a volumetric flask.

B. Salicylate + nitroprusside solution: Dissolve 150.0 g of sodium salicylate and 1.00 g of sodium nitroprusside in deionized water and dilute to 1-L in a volumetric flask. Store in an amber glass bottle and prepare fresh monthly.

C. Hypochlorite solution: Dilute 60.0 mL of 5.25 % NaOCl to 1 L in a volumetric flask.

V. Procedure:

Follow the instructions for the automated determination of NH<sub>4</sub>-N in soil and plant digests by LACHAT QuikChem Method 13-107-06-2-D.

VI. Calculations:

$$C_s = C_{\text{extr}} V / W$$

where  $C_s$  = solid phase N concentration,  $\text{mg}\cdot\text{kg}^{-1}$

$C_{\text{extr}}$  = digest N concentration,  $\text{mg}\cdot\text{L}^{-1}$

$V$  = digest volume, L

$W$  = sample weight, kg

VII. References:

Zellweger Analytics. 1996. Total nitrogen in Kjeldahl digests of soils and plants (QuikChem Method 13-107-06-2-D). Zellweger Analytics, Milwaukee, WI.

## LABORATORY QUALITY CONTROL/QUALITY ASSURANCE

Quality control is the set of protocols that lab personnel follow to help maximize the accuracy of all soil preparation, extraction, and analysis procedures. Quality assurance is the documentation of those quality control results. Quality control protocols utilized by the FIA regional labs include the use of blanks, calibration standards, independent check standards, and check samples analyzed by other labs participating in a sample exchange program. Details of these quality control procedures are outlined below. Currently, the FIA labs do not have a central database to automatically monitor quality assurance performance by automatically checking results against independent check standards and sample exchange results. However, the development of a lab information management system is in progress. At present, FIA laboratory personnel and directors monitor lab performance by manually checking results against independent check standards and sample exchange results.

### Balance accuracy:

All balances are serviced annually by a contractor who performs a multipoint service check of balance performance and accuracy and corrects any problems. In addition, lab personnel are required to check the accuracy of older top-loading balances using certified weights for each day of use. The newer electronic analytical balances have automatic calibration and performance checks built into the balance operating systems.

### Drying oven temperatures for oven-dry water content:

Drying oven temperature is checked each day of operation and adjusted if necessary. Microprocessor controlled ovens maintain the drying temperature at  $105 \pm 1$  °C.

### pH buffer standards:

pH meters and combination pH electrodes are calibrated using pH 4.00 and pH 7.00 certified buffer standards before each group of samples is run and after every six samples. For example, at the Logan FIA Lab, a sample group for 1:1 soil/water pH analysis will consist of 12 samples. Thus, the buffers are checked a total of 3 times for each group of samples (before the 1<sup>st</sup> sample, after the 6<sup>th</sup> sample, after the 12<sup>th</sup> sample). The same buffer check sequence is used for the salt pH measurements. pH meters are re-calibrated if the measured pH differs from the buffer pH by more than 0.02 pH units at each buffer check.

## Blanks:

Two types of blanks are used in most soil extraction and analysis methods: reagent blanks and method blanks. Reagent blanks are used in the calibration of instruments such as the ICP-AES used for the cation, trace metals, and S analysis and the colorimeter used for the extractable P analysis. Extraction solutions are used as reagent blanks (e.g., 1 M  $\text{NH}_4\text{Cl}$  for exchangeable elements, Bray 1 or Olsen extractants for P). A reagent blank is included with every set of standards used to calibrate the analytical instruments. Method blanks are used to check for contamination in the extraction steps. As with reagent blanks, extraction solutions are used as method blanks except that the method blanks are carried through all the extraction procedure steps including shaking and filtering. More details on the various reagent and method blanks can be found in the individual analysis sections of this manual. As an example, the Logan FIA lab generally extracts groups of soil samples in multiples of 12. Method blanks are included with every batch of 24 samples extracted for P analysis and with every batch of 48 samples extracted for cation, trace metal, and S analysis.

## Calibration standards:

Prepared or commercially available certified standards are used to calibrate all analytical instruments used to measure the element concentrations in the soil samples or extracts. We recommend using commercially available certified standards to prepare working standards for calibrating the ICP-AES. These should be prepared in 1 M  $\text{NH}_4\text{Cl}$  to match the extraction solution. We recommend using reagent-grade  $\text{KH}_2\text{PO}_4$  to prepare a stock P standard, which is then used to prepare the P calibration standards in the extraction solution. We recommend using LECO standards to calibrate the C and N analyzers.

The Logan FIA lab uses a LECO 1 % C synthetic standard and reagent grade  $\text{CaCO}_3$  to calibrate the LECO RC-412 multi-carbon analyzer for mineral soil sample analysis. We use EDTA to calibrate the LECO CHN-2000 analyzer for C and N analysis of forest floor samples. We use EDTA or mineral soil samples with a range of total N values as determined by Kjeldahl digestion and analysis to calibrate the LECO FP-528 N analyzer for N analysis of mineral soil samples depending on the organic matter content of the sample. We use EDTA to calibrate the N analyzer for soil samples with total N levels above 0.25 % and mineral soil samples with a range of N values to calibrate the instrument for soil samples with total N levels less than 0.25 %.

The ICP-AES and C and N analyzers instruments are calibrated for each day's run and are re-calibrated when independent check standards (see below) differ from their certified reference values by more than 10 %. A P standard curve with reagent blank is run with every group of 24 samples. Additional details on calibration standards can be found in the individual analysis sections of this manual.



### Independent check standards:

As an independent check of instrument calibration and performance over time, commercially available certified check or reference standards should be analyzed after every 10 samples. In the case of ICP-AES analysis of the 1 M NH<sub>4</sub>Cl extracts and the colorimetric analysis of the P extracts, working check standards should be prepared in the extractant solutions by diluting the certified stock reference standards.

### Spiked samples:

Spiked samples contain a known added amount of the analyte being measured. They are useful for measuring % recovery of added analytes to test for the presence of interferences. Spiked samples are not routinely used in the FIA program, but if interference problems are suspected, the use of spiked samples can help confirm their presence or absence.

### Check samples:

Check samples differ from the check standards in that they are soil samples representing a range of soil property values that are not certified, but have been analyzed by numerous other laboratories and thus serve as a check of overall lab performance. The FIA regional labs participate in the North American Proficiency Testing (NAPT) program sponsored by the Soil Science Society of America. The NAPT is a sample exchange program designed to monitor interlaboratory differences and assess overall lab performance. More than 100 soil analysis labs participate in this program. Six soil samples are sent to each participating lab quarterly (four times per year). One of these soil samples is the same sample each quarter. Labs submit their results to the NAPT program director who compiles the results, computes population statistics, and issues quarterly reports. Because data are often distributed non-normally, a median value and median average deviation (MAD) are calculated for each analysis. Because the soil properties measured in this program are not certifiable, warning limits are established at 2.5 times the MAD value for each analysis. Control limits are 4 times the MAD value for each analysis. Soil samples to the NAPT program are contributed from throughout the continental U.S. and thus represent a wide range of soil types. Because of the large number of labs participating in the program and the wide range of soil types included, this program is a robust measure of overall lab performance.

## MISSING AND MINIMUM REPORTABLE VALUES

### Missing data:

#### Forest floor:

For various reasons, samples may have missing values for some variables. One of the primary causes of missing variables is that there is an insufficient amount sample to complete all the analyses. For example, some forest soils have little, if any, forest floor (litter + humus). Field crews are trained to collect the entire forest floor within a sampling frame of known area, but for soils with a sparse forest floor, this method will result in an extremely small sample amount. In such cases, there is not enough sample to determine oven-dry water content. For those samples, the total water content is reported as the air-dry water content and the oven-dry water content data will be missing. In rare cases, there may not be enough sample to determine the total organic carbon and total nitrogen contents of the forest floor.

An additional source of missing values may result from problems with sample integrity that occur during shipment. On occasion, bags may become unsealed or punctured, resulting in sample loss. Although there may be sufficient sample for chemical analysis, the initial weight of the sample does not reflect field conditions and the sample can not be used for determination of forest floor density.

#### Mineral soils:

Bulk density values are calculated only if a mineral soil sample is collected using the bulk density sampler. Because soil samples collected by the excavation method have an unknown sample volume, bulk density values are not calculated for these soil samples. Thus, not all soil samples will have an associated bulk density value.

On rare occasions, there will not be enough mineral soil to take a subsample to determine oven-dry water content. Soil samples are sieved after air-drying and the coarse fragments are discarded. If the coarse fragment content of the soil sample is very high, there may not be enough soil sample in the <2-mm size fraction to complete all of the analyses. In such cases, analyses are prioritized on the basis of the amount of soil in the <2-mm size fraction. When there is insufficient sample to complete all the mineral soil analyses, the analysis priorities are: (1) carbon and nitrogen, (2) exchangeable cations, trace metals and S, (3) extractable phosphorus, and (4) pH. Soil pH has the lowest priority since it requires the largest amount of sample.

Although an insufficient amount of sample is the major reason for missing data, samples may occasionally be lost because of spillage. The samples are handled many times during sample preparation, extraction, and analysis, and although precautions are taken, some occasional sample loss is unavoidable. In addition, analyses are re-run in those cases where check samples and standards do not pass quality control checks. In some cases, there is not enough of a sample remaining when re-analysis is required and results are not reported for these analyses.

Statistically, missing sample analyses should be treated as missing data. The data fields in the database should be left blank in such cases. Alternatively, a numeric code could be used to indicate missing analyses, but great care must be taken to not allow the missing data numeric code to be included in the data analysis.

Minimum values:

*Soil wet, air-dry, and oven-dry weights:*

These should be reported to the nearest 0.01 g. Because air-drying is temperature and humidity dependent, soil samples from arid states (e.g., Arizona and Nevada) may increase in weight while air-drying on benches if the humidity at the drying facility is higher than ambient humidity when and where the sample was collected. For this reason, calculated air-dry water contents can be negative for some samples. This usually only occurs for forest floor samples where the sample amount is very small. Negative water content values should be reported as zero values.

*Organic, inorganic, and total carbon; total nitrogen; exchangeable cations, sulfur, and trace metals; extractable phosphorus:*

The detection, determination, or reporting limits of each of these analyses depend on the methods used. The instruments used to obtain these data are capable of reporting numeric values below the method detection limits. The actual analytical results (including zero level and positive non-zero numbers) should be reported rather than non-numeric reporting values with less than (<) symbols. Less-than results (i.e., censored values) cannot be included in statistical analyses without deleting the data, substituting numeric values for the censored data, or using distributional or robust methods to estimate summary statistics of datasets containing censored data. Many of the instrumental methods of analysis use regression techniques to calculate calibration curves that are then used to convert raw instrument readings to final concentration results. In some cases, readings below calibration blanks will result in calculation of negative results. In such cases, results should be reported as zero values.

Table 4. Summary of minimum values and reporting precision for FIA soil analysis parameters

Missing values for any parameter: leave data field blank in database

Parameter	Minimum reporting value
Forest floor:	
Wet, air-dry, and oven-dry weights	0.01 g
Total water content	0.00 %
Total organic carbon	0.00 %
Total nitrogen	0.000 %
Mineral soils:	
Wet, air-dry, and oven-dry weights	0.01 g
Bulk density	0.01 g/cm <sup>3</sup>
Water content	0.00 %
Coarse fragments	0.00 %
Water and salt pH	Not applicable, report value to 2 decimal places (e.g., 5.50)
Organic, inorganic, and total carbon	0.00 %
Total nitrogen	0.000 %
Exchangeable cations (Na, K, Mg, Ca, Al)	0 mg/kg
Effective cation exchange capacity (ECEC)	0.00 cmol(+)/kg
Exchangeable trace metals (Mn, Fe, Ni, Cu, Zn, Cd, Pb)	0.0 mg/kg
Exchangeable sulfur	0 mg/kg
Extractable phosphorus	0.0 mg/kg

## SPECIAL INSTRUCTIONS FOR PREPARING AND STORING REGULATED SOILS

To prevent transmission of plant pests and pathogens, the shipment of soils from certain states is regulated by the U.S. Department of Agriculture. Only those laboratories that hold a permit granted by the Plant Protection and Quarantine (PPQ) division of the USDA's Animal and Plant Health Protection Service (APHIS) are authorized to receive shipments of soils from regulated states. Answers to questions regarding permitting procedures or specific regulations may be found by contacting the PPQ permit office at 1-877-770-5990 or accessing the PPQ web site at <http://www.aphis.usda.gov/ppq/>.

### **Regulated States:**

Soils from selected counties in the following states have been found to contain plant pests or pathogens and are currently regulated by the USDA.

Alabama	Florida	New Mexico	Puerto Rico
Arkansas	Georgia	New York	South Carolina
Arizona	Louisiana	North Carolina	Tennessee
California	Mississippi	Oklahoma	Texas

A map of regulated areas may be found at  
<http://www.aphis.usda.gov/ppq/maps/soilmap.html>

### **Preparation and Storage of Regulated Soils:**

1. Regulated soils can be kept only within the laboratory or designated area at the permittee's address.
2. All shipping materials that come into contact with the soils (including bags and cardboard boxes) must be sterilized prior to discarding.
3. There are no special sample preparation procedures necessary for regulated soils. However, regulated soils must be clearly labeled and stored separately from other soils throughout the analysis process. Note: Designating a separate shelf or area within a common storage room is acceptable.
4. Authorized PPQ and state regulator officials have the right to inspect permitted labs without prior notice and during reasonable hours.

### **Shipping Samples to Another Lab:**

1. Individual sample bags must be double-bagged or grouped together and enclosed within a larger plastic or unbreakable container (e.g. trash bag, rubbermaid container).
2. A copy of the soil permit for the receiving lab must be attached to the outside of the box. If the soil permit is not available, then the permit number and the name of the responsible party at the receiving lab must be indicated.
3. Both the shipping label and the outside of the box should clearly state that the shipment contains regulated soils.

### **Discarding Samples:**

All soil materials from regulated states (including samples used for analysis) must be sterilized prior to being discarded.