



Project Summary

Handbook of Methods for Acid Deposition Studies, Laboratory Analyses for Soil Chemistry

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This handbook describes methods used to process and analyze soil samples. It is intended as a guidance document for groups involved in acid deposition monitoring activities similar to those implemented by the U.S. Environmental Protection Agency's Aquatic Effects Research Program, a part of the National Acid Precipitation Assessment Program. Much of the methodology presented in this handbook is based on existing soil survey protocols; however, most of the methods were modified to meet the particular needs of the Direct/Delayed Response Project. These modifications include specifications for sample size, quality assurance and quality control samples, soil-to-solution ratios, extraction times, extraction apparatus, and holding times. The handbook also delineates methods that were used to make the following laboratory determinations: rock fragments, bulk density, pH, organic matter, air-dry moisture, particle size analysis, cation exchange capacity, exchangeable cations in ammonium acetate, exchangeable cations in calcium chloride for lime and aluminum potential, exchangeable acidity, extractable iron, aluminum, silicon, and sulfate, sulfate adsorption isotherms, and total carbon, nitrogen, and sulfur.

This Project Summary was developed by the EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the handbook that is fully documented in a separate handbook of the same title (see Handbook ordering information at back).

Introduction

Concern about the effects of acidic deposition on the Nation's surface water resources led the U.S. Environmental Protection Agency (EPA) to initiate research in the field in the late 1970s. Early research, focusing on a diversity of potential effects, provided insight into those research areas which were considered central to key policy questions. Recognizing the need for an integrated, stepwise approach to resolve the issues, EPA implemented the Aquatic Effects Research Program (AERP) in 1983 with its present structure, focus, and approach. The AERP is a major component of the National Acid Precipitation Assessment Program's (NAPAP) Aquatic Effects Research Task Group 6, a cooperative effort of nine federal agencies tasked with addressing important policy and assessment questions relating to the acidic deposition phenomenon and its effects.

The Direct/Delayed Response Project (DDRP) is one of the major component projects within the AERP. Its principal mandate is to make regional projections of future effects of sulfur deposition on long-term surface water chemistry based on the best available data and most widely accepted hypothesis of the acidification process (Church et al., 1989). Specific objectives of the DDRP are:

- To describe the regional variability of soil and watershed characteristics.
- To determine which soil and watershed characteristics are most strongly related to surface water chemistry.
- To estimate the relative importance of key watershed processes in moderating regional effects of acidic deposition.

- To classify a sample of watersheds with regard to their response characteristics to inputs of acidic deposition and to extrapolate the results from this sample of watersheds to the DDRP study regions.

Scope of Handbook

The *Handbook of Methods for Acid Deposition Studies, Laboratory Analyses for Soil Chemistry* describes methods used to process and analyze soil samples. These procedures are based on methods used during the three soil surveys comprising the DDRP. Most of the methods were based originally on methodologies employed by the U.S. Department of Agriculture/Soil Conservation Service (USDA/SCS), including methods described in the *National Soils Handbook* (USDA/SCS, 1983), *Soil Survey Manual* (USDA/SCS, 1951; supplement 1962), *Field Study Program Elements to Assess the Sensitivity of Soils to Acid Deposition Induced Alterations in Forest Productivity* (Fernandez, 1983), *Procedures for Collecting Soil Samples and Methods of Analysis for Soil Surveys* (USDA/SCS, 1972), *Methods of Soil Analysis, Part 1* (Klute, 1986) and *Part 2* (Page et al., 1982), *Soil Taxonomy* (USDA/SCS, 1975), *Keys to Soil Taxonomy* (USDA/SCS, 1988), and *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples* (USDA/SCS, 1984). These original methodologies were modified to meet the particular needs of the DDRP. Modifications included specifications for sample sizes, quality assurance and quality control samples, soil-to-solution ratios, extraction times, extraction apparatus, holding times, standard internal quality control procedures, and standard or automated equipment.

The handbook also delineates methods for making the following laboratory analyses:

- Rock fragment determination.
- Bulk density determination.
- Field moist pH determination.
- Organic matter determination.
- Air-dry moisture determination.
- Particle size analysis.
- pH determination.
- Cation exchange capacity.
- Exchangeable cations in ammonium acetate.
- Exchangeable cations in calcium chloride for lime and aluminum potential.
- Exchangeable acidity.
- Extractable iron, aluminum, and silicon.
- Extractable sulfate.
- Sulfate adsorption isotherms.

- Total carbon and nitrogen.
- Total sulfur.

Methods Described In Handbook

Sample Processing and Rock Fragment Determination

The procedures presented here are specific to bulk sample preparation methods employed in the DDRP. Alternatives to these procedures are available in the published literature (e.g., USDA/SCS, 1972).

Sample processing includes sample drying, disaggregation, sieving, homogenization, and subsampling. Each of these is performed as sample processing steps in the preparation laboratory. Homogenization and subsampling are completed at the analytical laboratory. The objective of these procedures is to produce homogeneous subsamples for subsequent analyses of physical and chemical parameter. Also included in this section is the procedure used for determination of percent rock fragments.

Bulk Density Determination

In the DDRP surveys, the clod method is the primary method for determining bulk density. Where possible, three replicate clod samples are extracted from each horizon. The average bulk density of the replicates is assumed to be the bulk density of that particular horizon. Analysis of the clods is based on the method described in the USDA/SCS (1984), Kern and Lee (1989), and Kern et al. (in preparation).

Two alternate methods are also presented for soil horizons that fail to yield satisfactory clods. One method is volume replacement (VR), a method similar to one described by Flint and Childs (1984), which utilizes a known volume of small foam beads packed into a cylinder to replace a selected volume of soil excavated from a given horizon. Subtracting the initial from the final volume yields the estimated volume of sample collected. The other method is a volume filling (VF) method that is used if the clod or VR methods do not produce representative samples. The volume of this type of sample is based on the absolute height of a 250-mL beaker, which is a constant 300 cm³. The known volume samples are processed in a manner similar to the method described in Blake (1965).

Field-Moist pH Determination

This method is applicable to the determination of pH in soil samples. For the DDRP, field-moist pH is determined in the preparation laboratory using an Orion Model 611 pH meter and an Orion Ross combination pH electrode. The method has been written

assuming that the Orion meter and electrode are used (Orion, 1983); however, it can be modified for use with other instrumentation.

Organic Matter Determination

Loss-on-ignition (LOI) is the method used to determine an approximation of percent organic matter of soil samples. Because organic samples are oxidized at high temperatures, percent organic matter can be calculated on a weight-loss basis. From the percent organic matter, the percent organic carbon can be estimated. In the DDRP, LOI was used to classify samples as mineral or organic for subsequent analysis purposes. Oven-dried soil samples are ashed in a muffle furnace to remove organic material. The difference in pre- and post-ashing weights is used to calculate percent organic content. A modified version of the method described in MacDonald (1977) is used.

Air-Dry Moisture Content

Air-dry moisture determination is done both at the preparation laboratory and at the analytical laboratory. In the preparation laboratory, the process is used to ensure that each sample is at an acceptable moisture level for further processing. In the analytical laboratory, the air-dry moisture is determined on all samples to convert all results to an oven-dry basis, and if specified in a procedure, to calculate the weight of sample equivalent to a given weight of oven-dry soil (Brady, 1974).

A subsample of the air-dried bulk soil sample is weighed, oven-dried for approximately 24 hours, and reweighed. The initial and final weights are used to calculate a percent weight loss.

Particle Size Analysis

Particle size analysis is determined on the less than 2-mm fraction from mineral horizons only. The sieve/pipet/gravimetric method described in (USDA/SCS 1984) is used. Organic matter is removed from the sample by digestion with hydrogen peroxide. The sand fractions are separated from the silt and clay fractions by wet sieving. The silt and clay fractions are suspended in water; aliquots taken from the suspension under specified conditions are dried and then weighed. The sand fractions are sieved and each fraction is weighed. The resulting gravimetric data allow calculation of the percentage of each particle size class.

pH Determination

The following procedure was developed to standardize the measurement of pH in soils. The method has been written assuming that the Orion Model 611 pH meter and an Orion Ross combination pH electrode

are used (Orion, 1983); however, it can be modified for use with other instrumentation. The applicable pH range for soil solutions is 3.0 to 11.0.

Two suspensions of each soil sample are prepared, one in deionized (DI) water and one in 0.01 M calcium chloride (CaCl_2) pH. The pH of each suspension is measured with a pH meter and a combination electrode. This method is modified from USDA/SCS (1984). The DI water pH is generally higher than the 0.01 M CaCl_2 pH.

Cation Exchange Capacity

Two saturating solutions are used for cation exchange capacity (CEC) determination. Ammonium acetate (1.0 N NH_4OAc) buffered at pH 7.0 yields a CEC which is close to the total cation exchange capacity for a specific soil. This saturating solution is commonly used for soil comparisons. In acid soils, this estimate results in a high CEC value because of adsorption of NH_4^+ ions to the pH-dependent exchange sites that exist above the soil's natural pH level. The overestimation will not occur when an unbuffered saturating solution of ammonium chloride (1.0 N NH_4Cl) is used. The NH_4Cl CEC has been termed "effective" CEC (i.e., that which occurs at field pH and is of greater importance because it is a more realistic estimate of CEC than the total CEC by NH_4OAc). The two saturating solutions are retained for the exchangeable cation determinations. This method has been written assuming use of a mechanical extractor.

The soil sample is saturated with NH_4^+ from a solution of NH_4OAc or NH_4Cl . Excess NH_4^+ is removed by ethanol rinses. The NH_4^+ is displaced by Na^+ and is analyzed by one of three methods: automated distillation-titration, manual distillation-automated titration, or ammonium displacement-flow injection analysis. The entire procedure is repeated with a fresh aliquot sample and a solution of NH_4Cl as the NH_4^+ source. These methods are based on Doxsee (1985), Rhoades (1982), and USDA/SCS (1984).

Exchangeable Cations in Ammonium Acetate

The exchangeable cations (Ca^{2+} , Mg^{2+} , K^+ , and Na^+) in the soil can be used to estimate the ability of a soil to buffer acidic deposition. Ammonium chloride and buffered ammonium acetate are used to extract exchangeable base cations at pH values near the soil pH and at the buffered pH of 7.0, respectively. Base saturation is defined as the sum of exchangeable base cations divided by the cation exchange capacity (CEC) and is expressed as a percentage.

Previously prepared extracts from the CEC procedure are analyzed for calcium, magnesium, potassium, and sodium. Once the concentration of each cation in the soil extract is determined, the cation concentration in the original soil sample may be calculated. Atomic absorption spectroscopy can be used to measure calcium, magnesium, potassium, and sodium. Inductively coupled plasma spectroscopy can be used to measure cadmium, magnesium, and sodium. Emission spectroscopy can be used to measure potassium and sodium.

Exchangeable Cations in Ammonium Chloride

The exchangeable cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ and Al^{3+}) obtained in unbuffered 1.0 N NH_4Cl represent the effective exchange that occurs at field pH. Values of the exchangeable cations determined by this procedure are theoretically equal to those determined by the buffered NH_4OAc exchange. The concentrations (meq/100 g) of the exchangeable cations plus acidity should approximate the CEC.

Base saturation is given as the total amount of exchangeable base cations divided by the CEC. Exchangeable acidity is a measure of the amount of exchangeable acidic cations on the soil cation exchange complex.

Previously prepared extracts from the CEC procedure are analyzed for aluminum, calcium, magnesium, potassium, and sodium. Once the concentration of each cation in the soil extract is determined, the cation concentrations in the original soil sample can be measured by using atomic absorption spectroscopy, inductively coupled plasma spectroscopy, or emission spectroscopy.

Exchangeable Cations in CaCl_2 for Lime and Aluminum Potential

Lime and aluminum potential are related to the concentrations of calcium (Ca^{2+}) and aluminum (Al^{3+}), respectively, that are extracted from a soil sample by dilute calcium chloride (CaCl_2) solution. Lime potential is defined as $\text{pH} - 1/2 \text{ pCa}$. The p-function is defined as the negative logarithm (base 10) of the molar concentration of that species, or: $\text{pX} = -\log [\text{X}]$. The advantage of using the p-function is that concentration information is available in terms of small positive numbers. Aluminum potential, K_A is defined as: $K_A = 3\text{pH} - \text{pAl}$.

The pH value determined in this method should be between the two pH values determined for each soil sample. Extractable Mg^{2+} , K^+ , and Na^+ are also determined for comparison to amounts determined in the

CEC extracts. Fe^{3+} and Al^{3+} are determined for comparison to amounts obtained by the extractable iron and aluminum procedures.

The procedure involves extraction of soil with 0.002 M CaCl_2 . The soil-to-solution ratio is 1:2 for mineral soils and 1:10 for organic soils. The pH is determined using a pH meter and a combination electrode.

Exchangeable Acidity

The method most frequently used to determine exchangeable acidity involves treatment of the soil sample with a barium chloride triethanolamine (BaCl_2 -TEA) solution buffered to pH 8.2 followed by titration of the extracted solution. This method measures total potential acidity (Thomas, 1982).

Exchangeable acidic ions are extracted from a soil sample using a mechanical extractor with a BaCl_2 -TEA extracting solution. The excess reagent in the extract is back-titrated with HCl. Results are expressed as milliequivalents (meq) exchangeable acidity per 100 g soil.

Extractable Iron, Aluminum, and Silicon

Iron and aluminum are extracted from soil by sodium pyrophosphate, citrate-dithionite, and acid-oxalate solutions. According to the Johnson and Todd (1983) iron and aluminum speciation scheme, the pyrophosphate extract contains organically bound iron and aluminum; the citrate-dithionite extract contains non-silicate Fe^{3+} and Al^{3+} , and the acid-oxalate extract contains organic and amorphous oxides of Fe^{3+} and Al^{3+} . The exchangeable Al^{3+} from the unbuffered NH_4Cl extract is more indicative of readily available Al^{3+} under field conditions. The Fe^{3+} and Al^{3+} values from the pyrophosphate, acid-oxalate, and citrate-dithionite extracts relate directly to the sulfate adsorption capacity and have been used as an indication of this property (Fernandez, 1983). Silicon is extracted with the acid oxalate.

Each of three portions of a soil sample is treated with a different solution to extract iron and aluminum. The three extracting solutions are 0.1 M sodium pyrophosphate, a sodium citrate-sodium dithionite solution, and an oxalic ammonium oxalate solution. After extraction, the three solutions are analyzed for iron, aluminum, and silicon by inductively coupled plasma spectroscopy.

Extractable Sulfate

The ability of soils to adsorb sulfate (SO_4^{2-}) is one of the principal factors affecting the rate and extent of soil and watershed response to acidic deposition. Quantification of existing pools of adsorbed sulfate on a soil, concurrent with measure-

ments of sulfate adsorption capacity of that soil, provide useful information for understanding the status and for predicting the future response of the soil to acidic deposition.

This method requires the extraction of two aliquots of a soil sample. Deionized water is the extracting matrix for readily available sulfate. The extracting matrix for sulfate that is more difficult to dislocate is 0.016 M sodium phosphate (containing 500 mg P/L). After the extractions are completed, the analytes are determined by ion chromatography.

Sulfate Adsorption Isotherms

The most direct and effective way to determine sulfate-adsorption capacity utilizes sulfate adsorption isotherms. In this method, sulfate adsorption isotherms are developed by measuring the amount of sulfate remaining in solution after contact with a soil sample. These sulfate adsorption isotherms allow comparisons to be made between horizons or between pedons.

Six aliquots of the same soil sample are shaken with solution containing 0,2,4,8,16, and 32 mg sulfur per liter, respectively. The mixtures are centrifuged and filtered, and the resulting filtrate is analyzed for sulfate by ion chromatography. The difference between the original concentrations of the sulfur solutions and the final concentrations after this procedure indicates the sulfur uptake or release by the soil.

Total Carbon and Nitrogen

Quantification of carbon and nitrogen provides information about the amount and nature of organic material in the soil. Characterization of organic C and N also provides insight about the potential for uptake or release of nitrogen and/or sulfur by the soil organic matter due to microbial activity. Analyses of total carbon and nitrogen were conducted using automated elemental analyzers.

After sample processing and analysis for moisture content, a soil sample is oxidized at temperatures greater than 1,000°C with catalysts as specified by the instrument manufacturer. The evolved gases (CO₂ and N₂) are determined by thermal conductivity or infrared spectroscopy.

Total Sulfur

The determination of total sulfur is useful for characterizing relationships between inputs of sulfur from acidic deposition and soil sulfur pools. In this method, total sulfur in soil samples is determined by an automated sulfur analyzer by combustion of the sample at approximately 1,370°C. This procedure is based on the operating instructions for a LECO SC-132 sulfur analyzer

(LECO Corporation, 1983), adapted to permit analysis of very low levels of total S (as low as 10 mg/L) in soils.

The sample is placed in a ceramic crucible with combustion accelerators and heated to a maximum of 1,370°C in a resistance furnace. The combustion of the sample liberates SO₂, which is determined by an infrared detector. A microprocessor calculates results by combining the outputs of the infrared detector and system ambient sensors with preprogrammed calibration, linearization, and mass compensation factors. This method is based on research by David et al. (1989).

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D. T. Heggem is the EPA Project Office (see below).

The complete report, entitled "Handbook of Methods for Acid Deposition Studies, Laboratory Analyses for Soil Chemistry," (Order No. PB91-218 016/AS; Cost: \$39.00, subject to change) will be available only from:

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