



Project Summary

Analytical Methods Manual for the Direct/Delayed Response Project Soil Survey

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The U.S. Environmental Protection Agency, in conjunction with the National Acid Precipitation Assessment Program, has designed and implemented a research program to predict the long-term response of watersheds and surface waters in the United States to acidic deposition. On the basis of this research, each watershed system studied will be classified according to the time scale in which it will reach an acidic steady state, assuming current levels of acidic deposition.

The U.S. Environmental Protection Agency requires that data collection activities be based on a program which ensures that the resulting data are of known quality and are suitable for the purpose for which they are intended. In addition, it is necessary that the data obtained be consistent and comparable throughout the survey. For these reasons, the same detailed analytical methodology must be available to and must be used by all analysts participating in the study.

The manual specifies the analytical methods and internal quality control used to process and analyze samples for the Direct/Delayed Response Project Soil Survey. This document was submitted in partial fulfillment of contract number 68-03-3249 by Lockheed Engineering and Management Services Company, Inc. under sponsorship of the U.S. Environmental Protection Agency. Work on this document spanned a period from February 1985 to March 1987.

This Project Summary was developed by EPA's Environmental Monitoring

Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The U.S. Environmental Protection Agency (EPA), in conjunction with the National Acid Precipitation Assessment Program (NAPAP), has designed and implemented a research program to predict the long-term response of watersheds and surface waters in the United States to acidic deposition. On the basis of this research, each watershed system studied will be classified according to the time scale in which it will reach an acidic steady state, assuming current levels of acidic deposition.

As an element of NAPAP, the National Surface Water Survey (NSWS) was initiated to evaluate the water chemistry of lakes and streams, to determine the status of fisheries and other biotic resources, and to select regionally representative surface waters for a long-term monitoring program that will study future changes in aquatic resources. Subsequently, the Direct/Delayed Response Project (DDRP) was designed as the soil study complement to NSWS. DDRP, like NSWS, focuses on areas of the United States that have been identified as potentially sensitive to surface-water acidification.

Specific goals of the DDRP soil survey are (1) to define physical, chemical, and mineralogical characteristics of the soils and to define other watershed characteristics across these regions, (2) to assess

the variability of these characteristics, and (3) to determine which of these characteristics are most strongly related to surface-water chemistry. Additional DDRP goals are (4) to estimate the relative importance of key watershed processes in controlling surface-water chemistry across the regions of concern, and (5) to classify the sample of watersheds as direct response, delayed response, or capacity protected (to the degree that is scientifically defensible) and to extrapolate the results from the sample of watershed to the regions of concern.

The three classes of watersheds are defined as follows:

- **Direct response systems** — Watersheds in which surface waters are presently acidic (i.e., alkalinity < 0 $\mu\text{eq/L}$) or will become acidic within 3 to 4 mean water residence times (i.e., within 10 years). A mean water residence time is the average time period required to replenish totally the water contained in a lake.
- **Delayed response systems** — Watersheds in which surface waters will become acidic in the time frame of a few mean residence times to several decades (i.e., 10 to 100 years).
- **Capacity Protected Systems** — Watersheds in which surface waters will not become acidic for centuries to millennia.

The proposed methods of data analysis fall into three levels of complexity: (1) system description, (2) single-factor response time estimates, and (3) dynamic systems modeling. Each level of analysis involves decision criteria that are used to classify watersheds as direct response, delayed response, or capacity protected. After the representative watersheds are classified, the results will be extrapolated to classify the response time of each watershed in a given region. This manual defines the physical, chemical, and mineralogical procedures used to analyze the soils from these watersheds.

Procedures

The manual describes the analytical methods and quality assurance/quality control procedures utilized during the collection, preparation, and analysis of soil samples. Included are sections on sample handling and shipping, labware cleanliness standards, calibration procedures, and quality control samples.

The detailed procedures for physical and chemical parameters are described in 17 separate sections of the manual, according to the analysis being conducted.

Each section addresses the following:

- Scope and Application
- Summary of Method
- Interferences
- Safety
- Apparatus and Equipment
- Reagents and Consumable Materials
- Sample Collection, Preservation, and Storage
- Calibration and Standardization
- Quality Control
- Procedure
- Calculations
- Precision and Accuracy
- References

The physical, chemical, and mineralogical procedures presented in the manual are briefly summarized below:

Physical Parameters

- **Moisture Content** — A standard soil testing method is used to determine soil moisture content on a dry weight basis. Air-dry soil is weighed, dried in an oven, then reweighed. The moisture content is then used to place all measurements on an over-dry basis.
- **Particle Size** — Soil textural analysis is routinely determined for soil characterization and classification purposes. Rock fragments greater than 20 mm are determined by field sieving and weighing. Rock fragments 2 to 20 mm are determined at the preparation laboratory, and soil particles less than 2 mm are determined at the analytical laboratory by the standard sieve/pipet method.
- **Specific Surface** — A gravimetric method that employs saturation with ethylene glycol monoethyl ether (EGME) is used to measure specific surface. Specific surface is highly correlated to cation exchange capacity, sulfate adsorption, analyte adsorption/desorption, and the type of clay minerals.

Physical/Chemical Parameters

- **pH** — pH is an indication of free hydrogen ion activity. pH measurements are determined in three soil suspensions: deionized water, 0.01 M CaCl_2 , and 0.002 M CaCl_2 .
- **Cation Exchange Capacity** — Cation exchange capacity (CEC) is a standard soil characterization parameter. CEC indicates the ability of a soil to adsorb cations, especially the exchangeable basic cations, Ca^{2+} , Mg^{2+} , K^+ , and Na^+ . CEC is highly correlated with

the buffering capacity of the soil. Two saturating solutions are used: buffered ammonium acetate (NH_4OAc) solution to measure total CEC and neutral ammonium chloride (NH_4Cl) solution to measure effective CEC. Analysis is by titration or by flow injection analysis.

- **Exchangeable Basic Cations** — The exchangeable basic cations, Ca^{2+} , Mg^{2+} , K^+ , and Na^+ extracted during the CEC determinations, are determined by atomic absorption (AA) or by inductively coupled plasma (ICP). Measurement of the level of exchangeable basic cations indicates the base saturation of the soil.
- **Exchangeable Acidity** — Exchangeable acidity is a measure of the exchangeable cations that are not part of the base saturation. Two methods of analysis are used. One employs a buffered BaCl_2 -TEA extraction; the other, a neutral 1.0 N KCl extraction. The BaCl_2 -TEA method is a back-titration method which indicates total exchangeable acidity. The KCl method is a direct titration method which estimates effective exchangeable acidity. KCl-extractable Al is determined by AA or by ICP.

Chemical Parameters

- **Lime and Aluminum Potential** — Lime potential is used in place of base saturation as an input for certain models. Lime potential is defined as $[\text{pH} - 1/2 \text{ pCa}]$. Another characteristic important to watershed modeling is the relationship of pH to solution Al^{3+} levels. This is defined as aluminum potential (K_A) which is equal to $[3\text{pH} - \text{pAl}]$. This method involves extracting soil with 0.002 M CaCl_2 and determining Ca^{2+} and Al^{3+} in the extract. The cations, Na^+ , K^+ and Mg^{2+} , and exchangeable Fe^{3+} are also determined in this extract for comparison to cation concentrations in other extracts.
- **Extractable Iron and Aluminum** — Iron and aluminum oxides are highly correlated to sulfate adsorption and are important in standard soil characterization. Extractable Fe and Al are determined by AA or by ICP in three different extracts. Each extract yields an estimate of a specific Al or Fe fraction. The three fractions of extractable iron and aluminum include those extracted by: sodium pyrophosphate which estimates organic Fe and Al, ammonium oxalate

which measures organic Fe and Al plus sesquioxides, and citrate-dithionite which indicates nonsilicate Fe and Al. Analysis is performed by AA or by ICP.

- **Extractable Sulfate and Nitrate** — The amount of extractable sulfate and nitrate indicates the sulfate and nitrate saturation of the anion exchange sites. Sulfate is determined in two different extracts: deionized water and 500 mg P/L sodium phosphate. Nitrate is determined only in the deionized water extract. Analysis is by ion chromatography.
- **Sulfate Adsorption Isotherms** — The ability of soil to adsorb sulfate is related to soil buffering capacity. Isotherms are developed by placing soil samples in six magnesium sulfate solutions of different concentrations: 0, 2, 4, 8, 16, and 32 mg S/L. Subsequently the amount of sulfate remaining in solution after contact with the soil is determined. Subtraction yields the amount of sulfate adsorbed by the soil. These isotherms represent the maximum sulfate adsorption capacity of the soil under laboratory conditions.
- **Total Carbon and Total Nitrogen** — These two parameters are closely related to soil organic matter type and quantity. The method of analysis is rapid oxidation followed by thermal conductivity detection using an automated CHN analyzer.
- **Inorganic Carbon** — Inorganic carbon is quantified because of the inherent ability of carbonates to buffer acidic input. In soils with a water pH greater than or equal to 6.0, carbonates are determined by coulometric detection of evolved CO₂ after decomposition with a strong acid.
- **Total Sulfur** — Total sulfur is measured to inventory existing sulfur levels in order to monitor future input of anthropogenic sulfur. An automated method involving sample combustion followed by infrared detection or titration of evolved sulfur dioxide is specified.

Mineralogical Parameters

- **Semiquantitative X-Ray Diffraction** — The mineral content is quantified by X-rating the samples selected for mineralogical study. To determine the mineral content, the samples are X-rayed and are compared against mineral standards for quantification. Physical separations

of the <0.002-mm fraction and the 2-mm to 0.002-mm fractions are required.

- **X-ray Fluorescence** — This method gives the general chemistry of the bulk sample and of the clay fraction. The samples are pulverized, pressed into pellets, and analyzed. These data combined with data from X-ray diffraction identify the distribution of the elements.
- **Scanning Electron Microscopy/Energy Dispersive XRF** — With these two methods, topographic features are examined, and local chemistry of discrete particles is analyzed. These results give information concerning type and degree of mineral weathering.

Conclusion

The Analytical Methods Manual will be of interest to those involved in environmental research and analysis. The methods are innovative in their utilization of state-of-the-art instrumentation and procedures, including the Centurion mechanical extractor, coulometric techniques, and quantitative clay mineralogy. The application of QA/QC criteria is more extensive than in other soils investigations of this magnitude.

This manual is a key document in a series of reports concerning various facets of the DDRP soil survey. Other recommended DDRP documents include the following:

- Direct/Delayed Response Project: Quality Assurance Plan for Soil Sampling, Preparation, and Analysis by Bartz, Drouse, Papp, Cappo, Raab, Blume, Stapanian, Garner, and Coffey (1987).
- Direct/Delayed Response Project: Field Operations and Quality Assurance Report for Soil Sampling and Preparation in the Northeastern United States, Volume I: Sampling (in preparation).
- Direct/Delayed Response Project: Field Operations and Quality Assurance Report for Soil Sampling and Preparation in the Southern Blue Ridge Province of the United States, Volume II: Preparation (in preparation).
- Direct/Delayed Response Project: Quality Assurance Report for Physical and Chemical Analyses of Soils from the Northeastern United States (in preparation).
- Direct/Delayed Response Project: Quality Assurance Report for Miner-

alogy of Soils from the Northeastern United States (in preparation).

- Direct/Delayed Response Project: Field Operations and Quality Assurance Report for Soil Sampling and Preparation in the Southern Blue Ridge Province of the United States, Volume I: Sampling (in preparation).
- Direct/Delayed Response Project: Field Operations and Quality Assurance Report for Soil Sampling and Preparation in the Southern Blue Ridge Province of the United States, Volume II: Preparation (in preparation).
- Direct/Delayed Response Project: Quality Assurance Report for Physical and Chemical Analyses of Soils from the Southern Blue Ridge Province of the United States (in preparation).
- Direct/Delayed Response Project: Quality Assurance Report for Mineralogy of Soils from the Southern Blue Ridge Province of the United States (in preparation).

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*National Technical Information Service
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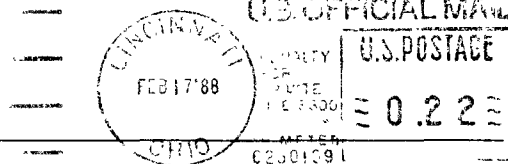
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