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Project Summary

Direct/Delayed Response Project: Quality Assurance Plan for Preparation and Analysis of Soils from the Mid-Appalachian Region of the United States

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The quality assurance (QA) policy of the U.S. Environmental Protection Agency (EPA) requires every monitoring and measurement project to have a written and approved quality assurance project plan. The purpose of this quality assurance plan is to specify the policies, organization, objectives, and the quality evaluation and quality control activities needed to achieve the data quality requirements of the Direct/Delayed Response Project (DDRP), Mid-Appalachian Soil Survey (MASS). These specifications are used to assess and control measurement errors that may enter the system at various phases of the project, e.g., during soil sampling, preparation, and analysis.

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).

Project Description

The DDRP is conducted as part of the interagency, federally mandated National Acid Precipitation Assessment Program which addresses the concern over potential acidification of surface waters by atmospheric deposition within the United States. The overall purpose of the project is to characterize geographic regions of the United States by predicting the long-term response of watersheds and surface waters to acidic deposition.

The EPA is assessing the role that atmospheric deposition of sulfur plays in controlling long-term acidification of surface waters. Recent trend analyses have indicated that the rate of sulfur deposition is either unchanging or slowly declining in the Northeastern United States, but is increasing in the Southeastern United States. If a "direct" response exists between sulfur deposition and surface water alkalinity, then the extent of current effects on surface water probably would not change much at current levels of deposition, and conditions would improve as the levels of deposition decline. If surface water chemistry changes in a "delayed" manner, e.g., due to chemical changes in the watershed, then future changes in water chemistry (even with level or declining rates of deposition) become difficult to predict. This range of potential effects has clear and significant implications to public policy decisions on sulfur emissions control strategies.

The DDRP focuses on regions of the United States that have been identified as potentially sensitive to surface water acidification. The MASS is the third of three DDRP regional surveys and includes portions of Pennsylvania, Virginia, and West Virginia. Surface water acidification in the Mid-Appalachian region was studied during the Eastern Lakes Survey in 1984 and in the National Stream Survey, Phase I, in 1985. Information gained during these and other surveys has been used to optimize the quality assurance program in the MASS.

Field and laboratory data collected in the DDRP are included in the system description modeling and are then used to assess the key processes that regulate the dynamics of base cation supply and sulfur retention within watersheds. Integrated watershed data are used to calibrate three dynamic simulation models that predict future regional responses to acidic deposition. Uncertainty and error propagation estimates are an important part of all levels of analysis.

The DDRP staff at the EPA Environmental Research Laboratory in Corvallis, Oregon, is involved in all aspects of the MASS. Responsibilities of this laboratory include the development of an experimental design, QA oversight for soil mapping and sampling, and data analysis and interpretation. The DDRP staff at the EPA Environmental Monitoring Systems Laboratory in Las Vegas, Nevada, is involved in matters relating to QA implementation, logistics, and analytical services. The responsibilities of this laboratory include the development and implementation of operational procedures and quality evaluation/control criteria for soil sample preparation and analysis, and the development of data verification procedures for field and laboratory data.

The use of interagency agreements by EPA has allowed the DDRP to engage support from several groups that have expertise in areas of importance to the project. The DDRP staff at Oak Ridge National Laboratory is involved in structuring and managing large data bases to satisfy DDRP data analysis requirements. The soil survey staff of the United States Department of Agriculture, Soil Conservation Service is involved in DDRP soil mapping and sampling. Laboratory analysis support is solicited through competitive bid by independent contract laboratories.

Field and Laboratory Operations

Field mapping and sampling operations in the MASS are conducted by Soil Conservation Service soil scientists under the supervision of EPA representatives. Approximately five sampling crews, each composed of three to four qualified persons, are selected. These crews are responsible for the description of soil and site characteristics, sample collection, and shipment of samples to the preparation laboratory. Members of each crew are soil scientists that are experienced with the universally recognized National Cooperative Soil Survey characterization procedures. The crew leader is responsible for selecting sampling sites and documenting all field data.

The sampling protocols specify the procedures for ensuring the integrity of the samples. Specific instructions on excavating and draining (if necessary) soil pits are given. Crews are provided with standard containers for sample collection. Samples are kept as cool as possible in the field and during transport to the preparation laboratory. In order to maintain their integrity and to reduce the possibility of biological degradation, samples are stored at a temperature of 4°C within 24 hours of sampling. It is anticipated that 150 pedons are to be sampled during the MASS, with each pedon yielding an average of six routine samples from its component horizons.

To allow the determination of bulk density, natural soil clods are collected in triplicate, where possible from each soil horizon. Where clods cannot be collected, known volumes of soil are collected in duplicate. Using a volume replacement method, the volume of soil is estimated by replacing a small excavated soil cavity with a known volume of foam beads. If this method does not yield satisfactory samples, a volume filling method is attempted by filling a container of known volume with soil and attempting to pack it to the same density normally encountered in the horizon being sampled.

The preparation laboratory is the intermediate link between the sampling crews and the analytical laboratories. The laboratory is located at the EPA Environmental Monitoring Systems Laboratory in Las Vegas, Nevada, although previous DDRP surveys utilized the services of multiple university laboratories for sample preparation. It was thought that consolidating t
preparation activities at a single labc
tory might result in better samp
handling, improved sample integrity, a
higher data quality. The laboratory serv
as a central location for soil processi
and for introducing double-bli
measurement quality samples into t
sample flow. The soil samples collect
by the sampling crews are sent v
overnight courier to the preparati
laboratory, where the laboratory st
processes the samples and prepar
homogeneous, anonymous subsampl
that are shipped to the analytic
laboratories. To accomplish these tas
successfully, the preparation laborato
must uniformly track, process, and sto
all samples.

After a bulk soil sample is air dried, t
soil is carefully disaggregated a
sieved. The less than 2-mm soil
retained in a labeled plastic bottle a
placed in cold storage when not und
going processing. The rock fragments a
retained for gravimetric analysis. In orc
to obtain representative volumes of soil
is necessary to prepare homogeneo
subsamples from the less than 2-mm s
fraction using a riffle splitter. T
subsamples are placed in labeled plas
bottles and are organized in batches t
are shipped to separate contra
analytical laboratories for general a
elemental analyses. Each batch norma
contains 40 samples but may have
many as 42 samples. With the excepti
of a quality control audit sample,
samples are randomly placed within
batch and cannot be distinguished by t
recipient laboratory. The unused portio
of the bulk soil samples are archived
cold storage.

All raw data obtained are recorded or
series of preparation laboratory raw d
forms and are immediately entered into
personal computer to ensure prop
tracking, processing, and evaluation
the samples. The computer is direc
linked to the QA staff and allows real-tir
data evaluation and tracking of samp
by both parties. The precision a
accuracy criteria for measurement qua
samples are checked while the samp
are being processed, permitting t
prompt identification of any discre
ancies.

During shipment, the samples receiv
by the analytical laboratories c
undergo segregation both by particle s
and by density; therefore, each sam
must be re-homogenized by thorou
mixing prior to the removal of aliquots

analysis. The raw data generated during sample analysis are entered on a personal computer using a specially designed entry and verification system. Data reports are then generated to assist in the evaluation of data quality. Before a batch of analytical data is accepted all completeness and quality control requirements must be met. In addition, the following documents must be updated constantly at the analytical laboratory and must be available, upon request, to the analysts and the supervisor involved in the project: standard operating procedures, laboratory QA plan, list of in-house samples, instrument performance data, control charts for all check samples and detection limit check samples, and quality control data reports.

Frequent communications, i.e., two or three contacts each week, are maintained with each analytical laboratory in order to obtain current sample status and to discuss any problems that may occur during analyses. These discussions are to be recorded in a logbook by the QA staff and the laboratory staff. Preliminary and final data are available for access via electronic transfer. The preliminary data are reviewed for anomalies and if a problem is identified, the laboratory is notified. Corrective action or reanalysis may be suggested.

Legal chain-of-custody procedures are not required for this study; however, sample custody must be documented. The sampling crew leader is responsible for all samples in the field as well as the sample shipments. As soil shipments are received in the preparation laboratory, they are immediately logged in and checked against the packing slip and the pedon description forms for proper labeling and quantity. If any discrepancies are found, the soil sampling task leader and the field crew leader are notified. Following the receipt of samples, the appropriate laboratory managers are responsible for sample integrity until the samples are archived.

Quality Assurance Program

The data collection criteria provide a balance between constraints of time and cost and the quality of data necessary to achieve the DDRP research objectives. The MASS QA Plan is designed to accomplish the following general objectives:

- establish the QA criteria used to control and assess data collected in the survey,
- provide standardized sampling, preparation, and analytical methods and procedures,
- utilize assessment samples and procedures to verify the quality of the data,
- perform field and laboratory on-site audits to ensure that all activities are properly performed and that discrepancies are identified and resolved,
- evaluate the data and document the results in QA reports to EPA management.

The raw soil characterization data for the DDRP surveys are collected during four major operational phases consisting of mapping, sampling, preparation, and analysis. A certain amount of data measurement uncertainty is expected to enter the system at each phase. Grouping of the data, e.g., by sampling class/horizon configurations, also increases uncertainty. The sampling population itself is a source of confounded uncertainty that is extremely difficult to quantify.

Generally, the data quality objectives for the MASS encompass the overall allowable uncertainty from sample measurement and from the sampling population that the data users are willing to accept in the analytical results. Because of the many possible confounded sources of uncertainty and the data collection focus of this QA plan, overall data quality objectives for the survey are not described herein. Rather, the plan focuses on the definition, implementation, and assessment of measurement quality objectives (MQOs) that are specified for the entire sample preparation and analysis phases of data collection and portions of the field sampling phase. The MQOs are more or less specific goals defined by the data users that clearly describe the data quality that is sought for each of the measurement phases. The MQOs are defined according to the following six attributes:

- Detectability—the lowest concentration of an analyte that a specific analytical procedure can reliably detect,
- Precision—the level of agreement among multiple measurements of the same characteristic,
- Accuracy—the difference between an observed value and the true value of the parameter being estimated,
- Representativeness—the degree to which the data collected accurately represent the population of interest,
- Completeness—the quantity of data that is successfully collected with respect to the amount intended in the experimental design,
- Comparability—the similarity of data from different sources included within individual or multiple data sets; the similarity of analytical methods and data from related projects across regions of concern.

An attempt has been made to define each quality attribute individually for each measurement phase of the program (sampling, preparation, analysis) or collectively for overall measurement system uncertainty on a parameter-by-parameter basis. The term "uncertainty" is used as a generic term to describe the sum of all sources of error associated with a given portion of the measurement system. In order to reduce measurement uncertainty in the final data values, error occurring in each phase must be identified and rectified during that phase of the survey. Measurement uncertainty for the MASS is controlled through well-defined protocols, system audits, and the introduction of measurement quality samples at each measurement phase.

Initial MQOs were established on the basis of the requirements of EPA data users and on the selection of appropriate methods to obtain the data. The MQOs were reviewed by persons familiar with analytical methods and soil characterization techniques, including soil chemists and laboratory personnel. Modifications to the MQOs and protocols were implemented based on information gained from the DDRP Northeastern region and Southern Blue Ridge Province surveys, from peer review comments, or according to a particular analytical procedure or instrument.

Measurement quality samples are placed at a rate of about one sample in four in each batch of analytical samples to determine measurement uncertainty. The measurement quality samples are used during various phases of the survey and allow the QA staff to control and assess the quality of the data collection process. Included in each batch of samples are: audit samples that have known ranges of analyte concentration (detectability, precision, and accuracy), duplicates of routine samples introduced at each measurement phase (precision and representativeness), and an audit sample for use in laboratory quality control (accuracy). There are separate analytical within-batch precision and accuracy MQOs for organic and mineral soils because of differences in methodology and the expected wide variability in analyte concentrations. For this reason, mineral and organic samples are organized and analyzed in separate batches (see below)

The quality evaluation samples are those samples which are known to the QA staff but are either blind or double blind to the sampling crews, preparation laboratory, or analytical laboratory. A blind sample has a concentration range that is unknown to the analysts, whereas a double blind sample cannot be distinguished from routine sample and has a concentration range that is unknown to the analyst. These samples provide an independent check on the analytical process and can be used to evaluate whether the MQOs have been met for any given run or batch, or for all batches, i.e., overall measurement uncertainty. Important characteristics of the audit samples include their similarity to routine samples in matrix type and concentration level, their homogeneity and stability, and their defined accuracy windows. Every quality evaluation sample has a specific purpose in the data assessment scheme.

In order to produce data of consistently high quality, the contract laboratories are required to analyze certain types of quality control samples that are known to the laboratory staff and that can be used by the analysts to identify and control analytical measurement uncertainty. Each of these samples has certain specifications that must be met before data for the parameter or batch are accepted. The control samples are non-blind samples procured under contract to assist the laboratories in meeting laboratory MQOs and include soil samples, e.g., analytical duplicates, and non-soil samples, e.g., reagent blanks. The samples allow the laboratory manager and the QA staff to assess whether the physical and chemical analysis is under control.

Quality Assurance Implementation

The quality assurance program is implemented through training, on-site systems audits, independent assessments, and other procedures used to control and assure the quality of the data being collected. Verification of these data is accomplished through a series of computer and manual checks of data quality.

Corrective action for errors made at the preparation and analytical laboratories is accomplished primarily through the application of a QA reanalysis template for each analysis of interest. The templates provide a precision and accuracy checklist of the measurement quality samples for each batch and a useful in deciding whether to reanalyze particular parameter.

The analytical data verification is multi-faceted, computerized approach provide a concise and consiste assessment of the data. The over process if highlighted by the Laborato Entry and Verification Information Syste (LEVIS). The LEVIS programs a implemented on personal computers a facilitate the data entry and qual control sample evaluation at the analyti laboratories as well as the evaluation laboratory performance by the QA st The system is a menu-driven prod that is designed as a two-pha operation, where phase one is analytical laboratory system and pha two is a quality assessment system. T LEVIS initiative was pursued becau previous surveys had shown that man verification of the data was both lab and time-intensive, and allowed only limited amount of real-time correcti action on the part of the laboratories.

An internal consistency program used to generate routine data outliers each sample batch. Analytical data fr each parameter are correlated agai corresponding data from all oth analytical parameters measured in t MASS. For each parameter, t parameter pair with the strongest line relationship is identified and evaluate Soil chemistry relationships are anot tool used to examine the intern consistency of the routine sample data is expected that approximately

Status and Assessment of Measurement Quality Samples

		Status of Sample[a]				Assessment Purpose[b]			
Sample Type	# Per Batch	QA Staff	Sampling Crew	Preparation Laboratory	Analytical Laboratory	System	Sampling	Preparation	Analysi
Low-range field audit*	1	K	B	B	DB	D,A	D,A	D,A	A
Field audit pair**	2	K	B	B	DB	P,A	P,A	P,A	P,A
Field duplicate	1	--	B	B	DB	P	P,R	P	P
Low-range lab audit*	1	K	--	--	DB	--	--	--	D
Lab audit pair**	2	K	--	--	DB	--	--	--	P,A
Preparation duplicate	2	--	--	B	DB	--	--	P,R	P
Quality control audit	1	K	--	--	B	--	--	--	A
Manager's sample	--	K	--	B	--	--	--	A	--

[a] K = known concentration, B = blind, DB = double blind.
[b] D = detectability/contamination, P = precision, A = accuracy, R = representativeness.
* Not placed in organic soil batches.
** Triplicate in organic soil batches.

percent of the data will not comply with the relationships; these anomalous data are examined by a staff soil chemist who either qualifies them or assigns appropriate flags signifying the discrepancy.

Data Quality Assessment and Reporting

The assessment of detectability is accomplished on a parameter basis at four levels: (1) compliance with contract-required detection limits; (2) calculation of actual instrument detection limits; (3) calculation of estimated system detection limits; and (4) identification of routine samples having concentrations below the system detection limits. The results can be grouped in tabular form to allow comparisons among the values for any parameter of interest.

A statistical evaluation procedure that has been developed by the QA staff and data users is applied to the data in order to assess precision as a function of confounded data collection uncertainty. An additive step-function model is used, where an observed value of any soil characteristic is considered as the sum of the "true" or accepted value and an error term. Precision is evaluated for each variance segment of the range of concentration for a given analyte.

The accuracy windows for the laboratory audit samples are based on previous interlaboratory analyses of the same sample material by the same protocols. The objective of setting windows is to specify a range of acceptable single values based on a mean and standard deviation computed from a number of previously observed values. The prediction intervals used for the accuracy windows are generally determined with confidence intervals constructed around the mean of these values, using appropriate weighting factors.

The sampling aspect of representativeness is assessed by comparing the individual site and pedon classifications with the component sampling classes to which the soils are assigned. Representativeness of the measurement quality samples is assessed by comparing the concentration ranges of data from the duplicate samples to the overall concentration range of the routine sample data. Representativeness of the analytical samples is identified by assessing the homogenization and subsampling procedures at the preparation and analytical laboratories using precision estimates form the duplicate samples.

Sampling completeness is assessed by comparing the actual number of soil pedons and associated horizons sampled to that number specified in the MASS design. Completeness of the sample collection, preparation, and analysis is calculated using data from the verified data base, while completeness of the data form a data user's perspective, i.e., amount of usable data, is determined using the validated data base.

Following completion of the MASS, a comparison is made across the Northeastern, Southern Blue Ridge, and Mid-Appalachian regions that focuses on method differences, audit sample results, laboratory effects, and other QA features of the surveys. Comparison of the DDRP data bases to other similar data bases may also be undertaken. Summary statistics are used to collate individual values into groups that enable the data users to discern trends of interest among the surveys.

Task leaders for the various stages of the MASS provide a written summary of operations to the project managers on a quarterly basis. These reports describe the kinds of data collected as well as summarize the QA activities associated with the data. The summary of QA activities includes the following:

- Overview of QA activities,
- List of changes to the QA program,
- Results of system and performance audits,
- Assessment of data quality based on the verified data bases,
- Documentation of unfavorable incidents and corrective actions,
- Distribution of updated control charts,
- Results of special studies.

Reports relating to data quality assessment are also prepared by QA staff. These reports include interpretation of performance audits and replicate sample data, estimates of measurement error, and identification of any major discrepancies found during the assessment. In addition to this QA Plan, the QA staff produces laboratory operations manuals for use in the preparation and analysis of soil samples. Upon completion of the data verification activities, summary QA reports of the sample preparation and sample analysis data are produced and distributed to all cooperating DDRP staff and data users.

Data Management System

The purpose of data base management for the MASS is to facilitate the collection, entry, review, modification, and distribution of all data associated with the survey. Additional tasks include the data analysis for report generation, statistical analysis, verification, and data file security. The MASS final data base contains three progressive versions of the data gathered: (1) raw data base, (2) verified data base, and (3) validated data base.

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The complete report, entitled "Direct/Delayed Response Project: Quality Assurance Plan for Preparation and Analysis of Soils from the Mid-Appalachian Region of the United States," (Order No. PB 90-116 971/AS; Cost: $31.00, subject to change) will be available only from:
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