PROGRAMS AND ANALYTICAL METHODS FOR THE U.S. GEOLOGICAL SURVEY ACID RAIN QUALITY-ASSURANCE PROJECT

By Randolph B. See, Timothy C. Willoughby, Myron H. Brooks, and John D. Gordon

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CONTENTS

FIGURES

ATTACHMENTS

CONVERSION FACTORS

Metric units (International System) in this report may be converted to inch-pound units by using the following conversion factors:

Multiply metric unit	*By*	*To obtain inch-pound unit*
liter (L)	1.057	quart, liquid
milliliter (mL)	0.03381	ounce, fluid
gram (g)	0.03527	ounce, avoirdupois
centimeter (cm)	0.3937	inch (in.)
kilometer	0.6214	mile
milligrams (mg)	35.27	ounce, avoirdupois
liter	0.2642	gallon (gal)

The following terms and abbreviations also were used in this report:

microsiemens per centimeter at 25 degrees Celsius (µS/cm)
mole (mol)
equivalent (equiv.)
minute (min)
megohm (MΩ)
high density polyethylene (HDPE)

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ABSTRACT

The U.S. Geological Survey operates four programs to provide external quality-assurance of wet deposition monitoring by the National Atmospheric Deposition Program and the National Trends Network. An intersite-comparison program assesses the precision and bias of onsite determinations of pH and specific conductance made by site operators. A blind-audit program is used to assess the effect of routine sample-handling procedures and transportation on the precision and bias of wet-deposition data. An interlaboratory-comparison program is used to assess analytical results from three or more laboratories, which routinely analyze wet-deposition samples from the major North American networks, to determine if comparability exists between laboratory analytical results and to provide estimates of the analytical precision of each laboratory. A collocated-sampler program is used to estimate the precision of wet/dry precipitation sampling throughout the National Atmospheric Deposition Program and the National Trends Network, to assess the variability of diverse spatial arrays, and to evaluate the impact of violations of specific site criteria. This report documents the procedures and analytical methods used in these four quality-assurance programs.

INTRODUCTION

The National Atmospheric Deposition Program (NADP) and the National Trends Network (NTN) were established to monitor spatial and temporal trends in the chemical composition of wet-atmospheric deposition. Wet-deposition samples are collected at about 200 sites in the United States and Canada. The purpose of this report is to describe the operating procedures in four external quality-assurance programs operated by the U.S. Geological Survey on behalf of the NADP and NTN monitoring programs. The quality-assurance programs are designed to decrease uncertainties in the data base and to provide an assessment of the quality of the data base produced by the NADP and NTN programs.

An intersite-comparison program evaluates the precision and bias of onsite pH and specific-conductance measurements made by NADP and NTN site operators. A blind-audit program assesses the variations in laboratory measurements caused by routine sample-handling and shipping procedures. An interlaboratory-comparison program determines the comparability of the laboratories performing analyses of wet deposition for major North American

networks. It determines independent precision and bias data for each laboratory. A collocated-sampler program is used to evaluate the overall network precision, to evaluate the importance of siting criteria, and to provide points of comparison with other networks.

INTERSITE-COMPARISON PROGRAM

The intersite-comparison program is a semiannual check of the precision and bias of pH and specific-conductance measurements made by NADP and NTN site operators. This section describes the preparation and distribution of samples and the recording and reporting of results. A flow chart of the intersite-comparison program is presented in figure 1.

Sample Preparation

Intersite-comparison samples are solutions of dilute nitric acid or dilute nitric acid with potassium chloride added. The total volume of sample required depends on the number of active NADP/NTN sites and is determined by the following equation:

$$(\text{Number of sites} + 20) \times 140 \text{ mL} + 5{,}000 \text{ mL} = \text{TOTAL VOLUME (mL)} \qquad (1)$$

To compensate for spills, additional determinations, and bottle rinsing, extra solution is prepared. Twenty extra bottles are prepared for pH and specific conductance determinations by the U.S. Geological Survey during each intersite comparison. The 140-mL volume includes 15 mL for rinsing of each 125-mL sample bottle during the bottling operation. The 5,000-mL excess is bottled for use as a pH and specific-conductance check solution for the acid rain project.

When the sample volume has been calculated, a target value for pH is selected and the volume of dilute nitric acid needed to result in the target value of pH is calculated. The target value of pH is based on past comparison results and varies between 3.5 and 5.5 pH units.

The sample is prepared in a 50-L polyethylene carboy, which is marked with volume graduations. The volume of concentrated nitric acid required is:

$$HNO_3 \text{ in milliliters} = \frac{100\ wM \cdot v}{pd} \qquad (2)$$

where w = atomic weight of HNO_3 (63.0128 g/mol);
M = desired NO_3^- concentration (mol/L) = H^+ concentration (in moles per liter) = 10^{-pH};
v = volume of solution being prepared (in liters);
p = weight percentage of HNO_3 (70.4 percent); and
d = density of concentrated HNO_3 (1.42 g/mL).

For the constants stated:

$$HNO_3 \text{ (mL)} = \frac{100 \times 53.0128 \times M \times v}{70.4 \times 1.42} = 63.033\ v \cdot M$$

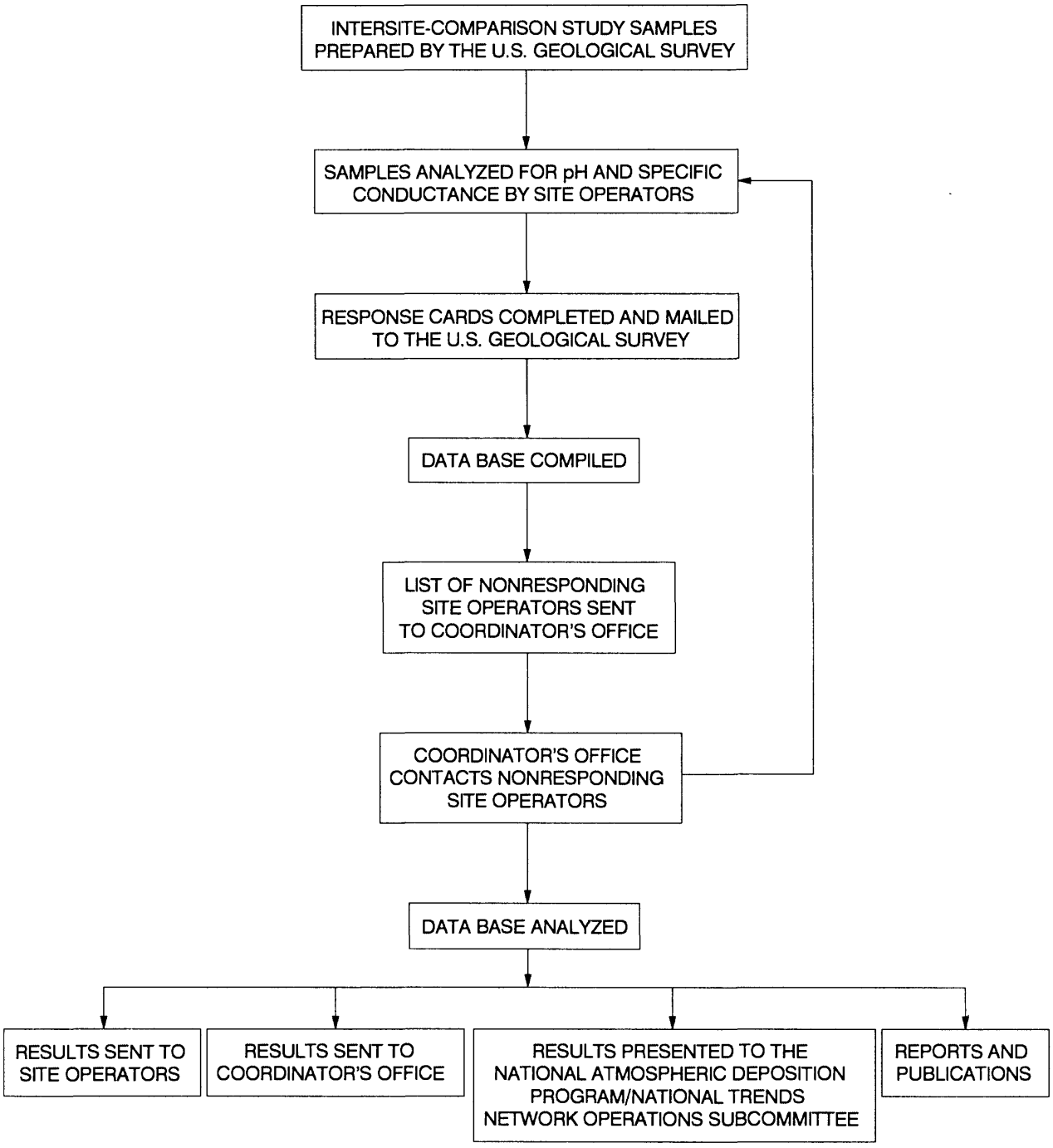

Figure 1.--Intersite-comparison program

To minimize the error associated with pipetting small volumes, a stock solution of nitric acid is prepared by diluting the concentrated nitric acid 1 to 100 for a 45-L solution with a target pH less than 5.0, or 1 to 1,000 for a 45-L solution with a target pH greater than 5.0. This solution enables pipetting a larger volume. The sample is prepared by adding the calculated volume of stock nitric acid solution to the required volume of ultrapure (>16.7-MΩ) water in the 50-L polyethylene carboy. Once the dilution has been made, a Teflon[1]-coated magnetic stir bar is added and a lid is placed on the carboy. The carboy is placed on a magnetic stirrer and the solution is stirred for 48 hours. All related information and calculations for the preparation of each intersite-comparison solution are recorded in the intersite-comparison record book.

Sample Bottling

When the solution is thoroughly stirred, it is bottled in 125-mL high-density polyethylene bottles (HDPE) that are rinsed once (using 15 mL of solution), filled with solution, and then tightly capped. Each bottle is labeled to identify the intersite-comparison number. Labels are prepared using a FORTRAN program located on the project personal computer (attachment 1 at the end of the report).

Sample Verification

Bottles are placed on a laboratory bench in the order they were filled. Four bottles, which are spaced evenly throughout the entire bottling, are set aside to test the homogeneity of the solution. The pH and specific conductance of the samples in these four bottles are measured. Discrepancies of greater than ±0.05 unit for pH or greater than ±3 percent for specific-conductance measurements indicate that the solution must be prepared again.

A second confirmation of pH is an ion-chromatographic (IC) determination of nitrate. In a solution prepared by using only nitric acid, nitrate-ion concentration, in moles per liter, is equal to the hydrogen-ion concentration, in moles per liter $\{[NO_3^-] = [H^+]\}$. To convert the measured nitrate, in grams per liter, to nitrate, in moles per liter, the measured nitrate concentration is divided by the atomic weight of nitrate (62.005 g/mol). The pH is determined by using the equation:

$$pH = -\log(H^+) = -\log(NO_3^-) \tag{3}$$

To determine the specific conductance of the solution from the nitrate determination, the following equation (Castellan, 1971, p. 729-730) is used:

$$K = \frac{1}{1{,}000} \Sigma\, C_i z_i \tag{4}$$

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[1]The use of brand, firm, or trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

where: K = conductivity (microsiemens per centimeter)
C_i = concentration of ions, i, in the solution (equivalents per liter); and
z_i = the equivalent conductivity of the ion, i (H^+ = 349.8 and NO_3^- = 71.44 centimeter per ohm equivalent).

These calculated pH and specific-conductance values should be within ±0.05 unit for pH and ±3 percent for specific conductance to the measured values for the bottled samples.

During the intersite-comparison study, at least 10 bottles are set aside to test the stability of the sample. One bottle per week is opened and the pH and specific conductance are measured. Results of these analyses are recorded. Also, five 1-L bottles are filled in 250-mL increments at intervals throughout the bottling process. These aliquots are check samples for quality control of the laboratory meters for measuring pH and specific conductance.

Sample Mailing

After verification of pH and specific conductance, bottled and labeled samples are ready for mailing. A complete list of active NADP/NTN sites is acquired from a data clerk at the Central Analytical Laboratory (CAL) of the Illinois State Water Survey (attachment 2) about 2 weeks prior to the planned mailing date. Two sets of mailing labels are requested for mailing the samples and, later, for mailing the results to the site operators. An instruction letter (attachment 3) and two response cards (attachments 4 and 5) accompany each sample. The instruction letter is in the computer files for the quality-assurance project (attachment 1) and may be printed as needed. The response cards are preprinted, pre-addressed cards on which the site operators record their results. Beginning with intersite study 25, site operators are also asked to record the type of pH electrode used to measure the intersite solution, and to indicate if this electrode is routinely used at the site (attachment 5). Site operators analyze the intersite-comparison solution and return the completed response cards to the U.S. Geological Survey. The site operators are requested to retain the remaining portion of the solution until they receive further instructions. After their results are evaluated, site operators will be instructed to either discard or remeasure the remaining test solution.

Data Records

A summary of responses from all sites is mailed to each site operator. Data from the analyses done by site operators are archived in: (1) Computer files for the quality-assurance project, (2) intersite-comparison notebooks, (3) original response cards, and (4) copies of the response cards stored at the NADP/NTN Coordinator's Office.

Single and double dash marks (- and --) in the data records are indicators of missing data. If a site operator responds, but does not return a result for one or both analytes [if the meter(s) is(are) inoperable, for example], then single dashes are used for pH or specific conductance, or both. Double dashes indicate that the site operator has not responded at all.

Forty-five days after the samples are mailed, the data set is closed and data analysis done. Late response cards continue to be recorded, but they are not included in the summary statistics that are mailed to all site operators. Data analyses consist of a determination of the central tendencies of pH and specific-conductance results and of the spread (F-pseudosigma) of the results. The cover letter for the data summary (attachment 6) includes the summary statistics, the site name, and the results reported by that site. This letter is produced by using files on the project computer. Instructions for creating and using form letters and associated data files are in the Microsoft Word Manual (Zager and Chase, 1987). The scatterplot of pH versus specific conductance is a visual display of the data, which can by used by the site operators in evaluating their own responses (attachment 7).

The ratio known as F-pseudosigma (Hoaglin, 1983) is calculated as a resistant analogue to a standard deviation. Using the F-pseudosigma is advantageous because it is less affected by a few outlying observations. Site operators can use the F-pseudosigma as an additional guide to their performance. If operators feel their results are accurate and yet outside the NADP/NTN goals or F-pseudosigma range, they may return the sample to the U.S. Geological Survey for further analysis and confirmation of their results.

Because the NADP/NTN consists of more than 200 sites, no follow-up protocol existed for sites that failed to meet measurement accuracy criteria until May 1990. In May 1990 a follow-up program based on statistical quality-control procedures was implemented. A screening procedure using statistical quality-control techniques was used to select a subset of the sites that failed to meet the accuracy goals for pH determinations for inclusion in the follow-up program. Using statistical quality-control screening techniques, site performance in recent intersite-comparison studies is evaluated before deciding to include a site in the follow-up program. The follow-up program includes four different levels of follow-up. The follow-up that a site receives depends on a quality-control chart analysis of their results in the last three intersite-comparison studies. A description of the four levels of follow-up is contained in attachment 8.

An archive copy of the intersite-comparison results is maintained in a computer file for the project. This copy is a PSTAT library file (attachment 1) and contains data from intersite-comparisons 1-25.

Copies of the final data files also are stored in the intersite-comparison notebook. The original response cards are stored in alphabetical order by site name in project files.

Copies of the computer file (on 5-1/4-in. floppy disk) that contain the intersite-comparison results, summary statistics, graphics, and response cards are mailed to the NADP/NTN Coordinator's Office, Fort Collins, Colo., for inclusion into the NADP/NTN data base. Any late results from previous intersite comparisons are also sent at this time so the data base can be updated.

BLIND-AUDIT PROGRAM

The blind-audit program is designed to assess the variations in analyte concentrations caused by the routine sample-handling and shipping procedures to determine if they are possible sources of bias in the NADP/NTN data. A total of 128 blind-audit samples per year are distributed at quarterly intervals (32 per quarter) to active NADP/NTN sites. The site operator submits the simulated wet-deposition sample to the CAL for analysis in a clean network sample container (13-L polyethylene bucket). The blind-audit sample is disguised as an actual wet-deposition sample and, therefore, is blind to the CAL. Blind-audit samples are submitted at a rate of two or three per week. Submissions of blind-audit samples are distributed within each quarterly interval among four geographic regions of the country (attachment 9).

The 32 sites for each quarter, for the entire year, are selected based upon the list of active NADP/NTN sites. All active NADP/NTN sites participate in the blind-audit program before a site is asked to participate again. Attachment 10 is a current (1990) listing of active sites, which are randomly selected within each region. A record of participants for each quarter is maintained.

Each site is assigned one of the standard sampling periods for submitting the blind-audit sample. The actual wet-deposition sample is submitted to the CAL, using a dummy-site identification number, DU01 through DU32. A flow chart depicting the blind-audit program is presented in figure 2.

Sample Preparation and Verification

Simulated wet deposition, CAL pH-4.30 check solution, and ultrapure water samples are used as blind-audit solutions. Because contamination is a problem, latex gloves are worn at all times during preparation and analysis of the solutions.

Blind-audit samples are bottled in 250-, 500-, or 1,000-mL HDPE bottles. The sample type, the site receiving the blind-audit sample, and the dates of the sampling period for which the sample will be substituted for the actual wet-deposition sample are written on the bottle. Every sample bottle has a line that indicates the 75-mL remaining mark. The word "SAVE" is written below this mark, and an arrow points from SAVE to the line. A label which identifies the sample as a NADP/NTN blind-audit sample is placed on the bottle. Black indelible ink is used for all bottle labeling.

CAL pH-4.30 check solution is obtained from CAL, Illinois State Water Survey (attachment 2) in 250-mL bottles suitable for immediate use. Ultrapure deionized-water samples are bottled by the U.S. Geological Survey, using clean 250-mL bottles.

Simulated wet-deposition samples are U.S. Geological Survey Standard Reference Water Samples (SRWS), National Institute of Standards and Technology (NIST), Environmental Protection Agency (EPA) reference water samples and additional solutions prepared by the U.S. Geological Survey and CAL, Illinois State Water Survey. Some of the reference water samples have very large

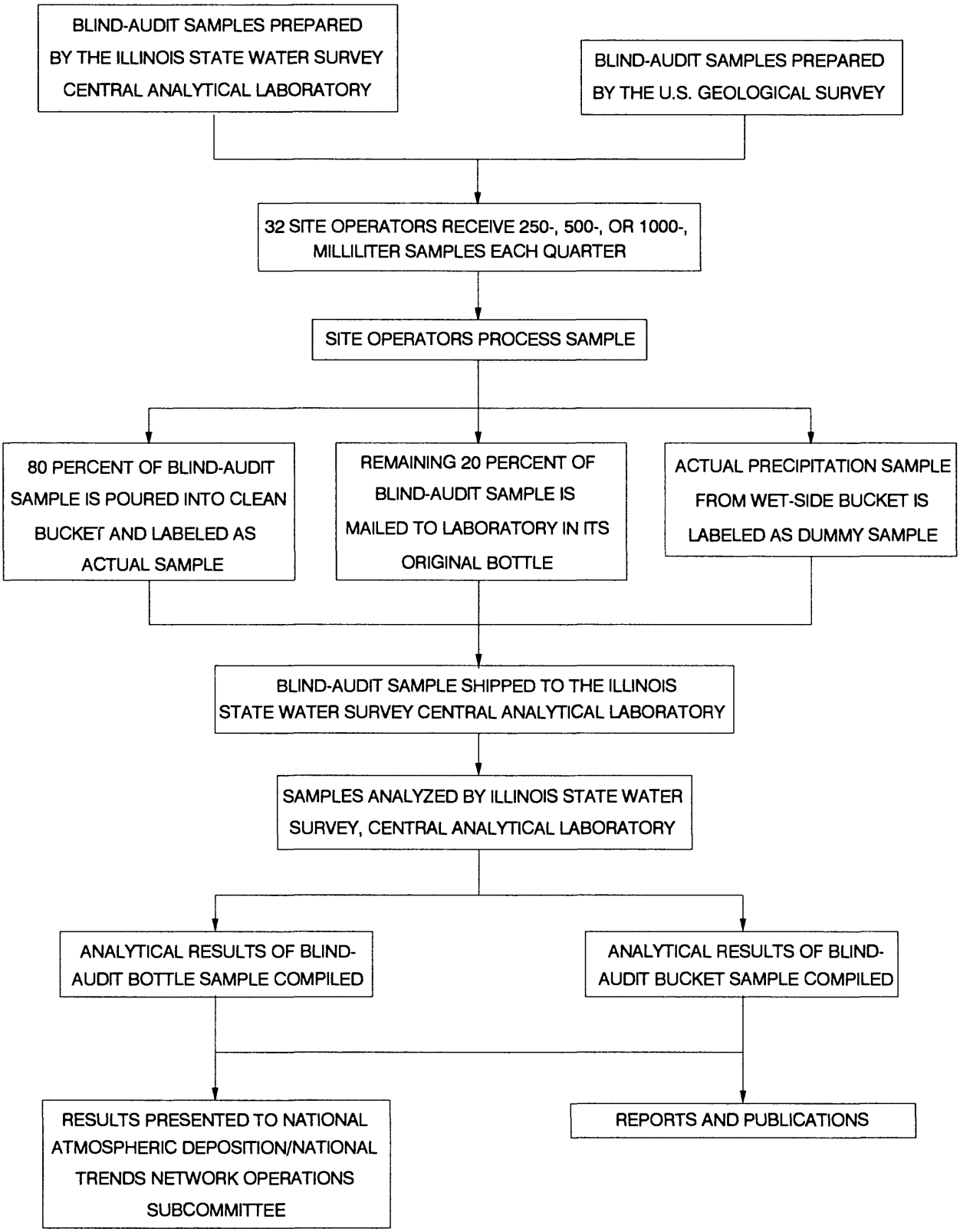

Figure 2.--Blind-audit program.

standard deviations for some analytes; therefore, the solution selected must have relative standard deviations that are less than 10 percent for most analytes. Some simulated wet-deposition samples may be prepared by diluting the original reference solution with deionized water. Samples chosen for the stock solution should not be diluted by a ratio greater than 1:200. This simplifies verification and decreases errors caused by serial dilutions. The analytical concentrations and relative standard deviations for solutions that were used during 1989 are listed in attachment 11.

For dilution of SRWS, NIST, or EPA reference waters, eight or sixteen 250-mL HDPE bottles and one 2,000- or 4,000-mL volumetric flask are cleaned. The bottles and the volumetric flasks are rinsed three times, using >16.7-MΩ water, and then are filled with water 1 day before preparing the dilutions. Bottles are capped, using prewashed caps, and allowed to stand for 24 hours; all bottles, flasks, and caps are rinsed, using >16.7-MΩ water, three more times before use.

Simulated precipitation solutions are prepared in a prewashed and rinsed 2,000- or 4,000-mL volumetric flask. The pipet is rinsed three times, using >16.7-MΩ water, and once, using the stock solution. The required volume of stock solution then is pipetted into the volumetric flask and diluted using the >16.7-MΩ water. The prewashed polyethylene bottles are rinsed once, using 20 mL of the simulated precipitation solution. The solution then is immediately transferred from the volumetric flask to the bottles, and the bottles are sealed and labeled using the solution identification number and the date.

Before the diluted reference water samples are used in the blind-audit program, the accuracy of the dilution is verified by ion chromatography (IC) and flame atomic absorption spectroscopy (AA). To verify the sample, the measured mean must be within the range of the calculated mean plus or minus the estimated error. The following equation is used for estimating the error:

$$\text{Estimated error (percent)} = \text{relative standard deviation} + \text{pipetting error} + \text{Survey analytical error} \quad (5)$$

where relative standard deviation = standard deviation/mean × 100 percent
pipetting error = 2.5 percent, and
Survey analytical error = (see attachment 12).

The relative standard deviation is calculated by dividing the standard deviations by the blind-audit solution means, which are listed in attachment 11. The error in pipetting the solution is estimated to be 2.5 percent. The analytical error is determined for each analyte in sample type P12 from the data stored in a project computer file (attachment 1). The analytical error is recalculated quarterly by determining the standard deviation for the analyses of P12. The current estimated values for the analytical error for each analyte are listed in attachment 12.

As an example, the acceptable range for calcium has been calculated for Standard Reference Water Sample M4 with a 100 to 1 dilution. The reported mean for calcium in M4 is 11.4 mg/L, and the standard deviation is 0.8 mg/L.

The relative standard deviation is:

$$(0.8/11.4) \times 100 \text{ percent} = \pm 7.0 \text{ percent}.$$

Adding the ±2.5 percent for estimated pipetting errors and 6.1 percent for analytical error gives a total estimated error of ±15.6 percent.

A sample will not be accepted if all measured analyte values obtained from the IC and flame AA analysis are biased--that is, all are greater than or all are less than the reported means. The analytical results for the IC and flame AA are recorded.

Sample Mailing

A package is prepared for each selected site which contains a cover letter to the operator, a blind-audit sample, an instruction sheet, two pre-addressed post cards, a field observer report form, and a pre-addressed mailing envelope. An example of the cover letter to the site operators is shown in attachment 13). It includes a request for the submittal of a blind-audit sample to the CAL. An example of the cover letter that the site supervisor receives, which includes a request that their site participate in the blind-audit program, is in attachment 14. Site name and address information for both letters are obtained from the current NADP/NTN site listing supplied by CAL for the intersite-comparison program.

The instruction sheet sent with each blind-audit sample is shown in attachment 15. The instruction sheet lists each item that the site operator receives and details the procedures that should be followed in processing the blind-audit sample. The instruction sheet is dated, so only the most recent copies are mailed to the site operators.

An example of the field observer report form that is used to submit the actual wet-deposition sample for the assigned Tuesday-Tuesday time period is shown in attachment 16. Sections 1 and 2, and part of section 4, are already filled in with information appropriate for the particular site and dates.

The front and back of the two response cards that will be completed and mailed by the site operator on submission of the blind-audit sample are shown in attachment 17. One card is addressed to the NADP/NTN Coordinator's Office; the other is addressed to the U.S. Geological Survey. The dates of the Tuesday-Tuesday sampling period, the identification number for blind-audit sample solution, and the identification number for the dummy site are written on the bottom of each card before the blind-audit sample package is mailed to the site operator.

An example of the letter that is sent to the NADP/NTN Coordinator's Office, which includes the sites, the identification numbers of the dummy sites, and the sampling periods for samples from each quarter is shown in attachment 18. The NADP/NTN Coordinator's Office uses this information to contact the operator at each participating site about 1 week before the scheduled submission date. The CAL is provided similar information concerning the dates of submission. The letter to CAL (attachment 19) does not list the site identifications. Those identifications are provided to CAL by the NADP/NTN Coordinator's Office about 4 weeks after the site has submitted the blind-audit sample to CAL.

The site operator pours 75 percent of the blind-audit sample into a clean NADP/NTN sample collection bucket and mails the sample to CAL as if it were an actual wet-deposition sample. The site operator mails the remaining 25 percent of the blind-audit sample to CAL in a separate package. The sample remaining in the bottle is also analyzed by CAL. A Wilcoxon signed ranks test is used to determine if significant differences exist between bucket and bottle samples.

Data Records

The NADP/NTN Coordinator's Office sends copies of the response cards received from site operators to the U.S. Geological Survey. Receipt of the card from the site operator and the copy from the Coordinator's Office are recorded and the card is filed for later use. Receipt of this card is evidence that a blind-audit sample has been submitted. Cards that are not received within 10 days after the scheduled submission date are an indication that the blind-audit sample was not submitted to the CAL. Usually, the lack of submission will be noticed by the CAL staff or by the NADP/NTN Coordinator's Office. The site operator or supervisor is contacted to determine whether the sample was submitted as instructed.

Preliminary analytical results from the blind-audit samples are mailed to the U.S. Geological Survey about 2 to 3 months after the samples were submitted to the CAL. The NADP/NTN Coordinator's Office periodically notifies CAL personnel regarding the actual identity of the dummy-site samples. The true identities of the samples are corrected in the data base by the CAL. Analytical results for the blind-audit sample are reassigned to the dummy-site identification number that was used for the actual wet-deposition sample from that site.

An example of the two preliminary data sheets that are periodically sent to the U.S. Geological Survey by the CAL is shown in attachment 20. In the Sample ID column, the last four places in the entries are the site identification numbers. Actual wet-deposition samples are submitted, using the dummy-site identification numbers, DU01 to DU32. Blind-audit samples are confirmed by comparing the field pH and specific-conductance values written on the submission card by the site operator with those on the preliminary data sheet. After the analyses are completed, the NADP/NTN Coordinator's Office notifies the CAL of the actual identification numbers for the sites for each dummy site.

The final versions of the data are sent by the CAL to the U.S. Geological Survey at 2-month intervals. The time lag between preliminary and final data is 3 months. The CAL also provides the data from analyses of the contents remaining in the sample bottles. These data are paired with data for the blind-audit sample (bucket analyses) to assess the biases resulting from field-sample handling. An archive PSTAT library file of the blind-audit results is maintained in a computer file for the project (attachment 1).

Summary of Revisions

This section acknowledges the additions and changes in NADP/NTN blind-audit program protocols. The following additions and changes in NADP/NTN blind-audit program have been recorded:

Revisions	Date
The partial blind-audit sample remaining in the bottle was mailed by the site operator to the U.S. Geological Survey, who then mailed it to CAL for analysis (Reference 19). To avoid unnecessary handling, the bottle sample is now sent directly from the site to the CAL.	Jan 84
Rather than sending the real precipitation sample with a dummy Field Operator's Report Form to CAL, the site operator sent the bucket containing actual wet-deposition to the U.S. Geological Survey, who forwarded the bucket on to CAL and sent a clean bucket to the site operator.	Jan 84
The blind-audit samples were sent out in 250-mL volumes. Previously 250-mL and 500-mL volumes were used.	Apr 85
Blind-audit sample is submitted to CAL regardless of whether the site received wet deposition or not. Prior to this date, the blind-audit sample was only submitted if no wet deposition occurred.	Oct 85
The two dummy site ids submitted each week will be numbered DU01 and DU02, alternately, for the 25 blind-audit samples sent out each quarter.	Jan 86
The number of sample solutions used in the blind-audit program will be limited to 6-8 different solutions. As solutions are used up, new solutions must be added to the program.	Oct 88
Include samples with larger volumes, to investigate potential dilution effects on blind-audit samples. Included in the additional 25 samples each year will be samples of U.S. Geological Survey solution in 250, 500, and 1,000-mL sample volumes.	Jan 89
A total of 128 blind-audit samples per year will be distributed (32 per quarter).	Jan 89

INTERLABORATORY-COMPARISON PROGRAM

The purpose of the interlaboratory-comparison program is to determine the comparability of data produced by the laboratories providing chemical analyses for the major North American wet-deposition networks. The laboratories analyze identical samples of three types: (1) Natural wet deposition, (2) simulated wet deposition, and (3) ultrapure deionized water. The data are analyzed to provide a statistical estimate of comparability and an independent assessment of the precision and bias of the participating laboratories. Currently (1989) the interlaboratory-comparison program includes three laboratories: Central Analytical Laboratory (CAL), Illinois State Water Survey, Champaign, Illinois; Inland Waters Directorate (IWD), Burlington, Ontario; and Hunter, Environmental Science and Engineering, Inc., Gainesville, Florida (ESE). In the past the program has included: The U.S. Geological Survey National Water Quality Laboratories in Atlanta, Georgia, and Arvada, Colorado, and Environmental Monitoring & Services, Inc., Camarillo, California, during periods of involvement in monitoring programs. A flow chart of the interlaboratory-comparison program is presented in figure 3.

Sample Preparation

Interlaboratory-comparison samples are assigned unique eight-digit numbers (U.S. Geological Survey project identification numbers). The first two digits are the year of submission. The third, fourth, and fifth digits are the Julian date. The last three digits are unique, beginning at 001 and ending with 016. Any original numbers or labels are removed from each bottle, and the appropriate U.S. Geological Survey project identification number is written on each bottle. Samples are assigned to each laboratory in a randomized block design (Little and Hills, 1978).

Natural Wet-Deposition Samples

The natural wet-deposition samples are aliquots of wet-deposition samples collected by the NADP/NTN. Natural wet-deposition samples received at the CAL that have a volume larger than 750 mL are randomly selected for use as interlaboratory-comparison samples. The sample is filtered and split into 10 aliquots. Each aliquot is collected in a 125-mL HDPE bottle, and labeled, using a four-digit number that is a part of the CAL laboratory code for the original NADP/NTN sample. Two sets of 10 chilled, natural wet-deposition samples are shipped from the CAL in an insulated container to the U.S. Geological Survey every 4 weeks. The samples are removed from the cooler and refrigerated upon receipt. The sample bottles are relabeled using U.S. Geological Survey project identification numbers before they are distributed to the participating laboratories. The use of 10 bottles could allow up to 5 laboratories to analyze the 2 natural wet-deposition samples in duplicate.

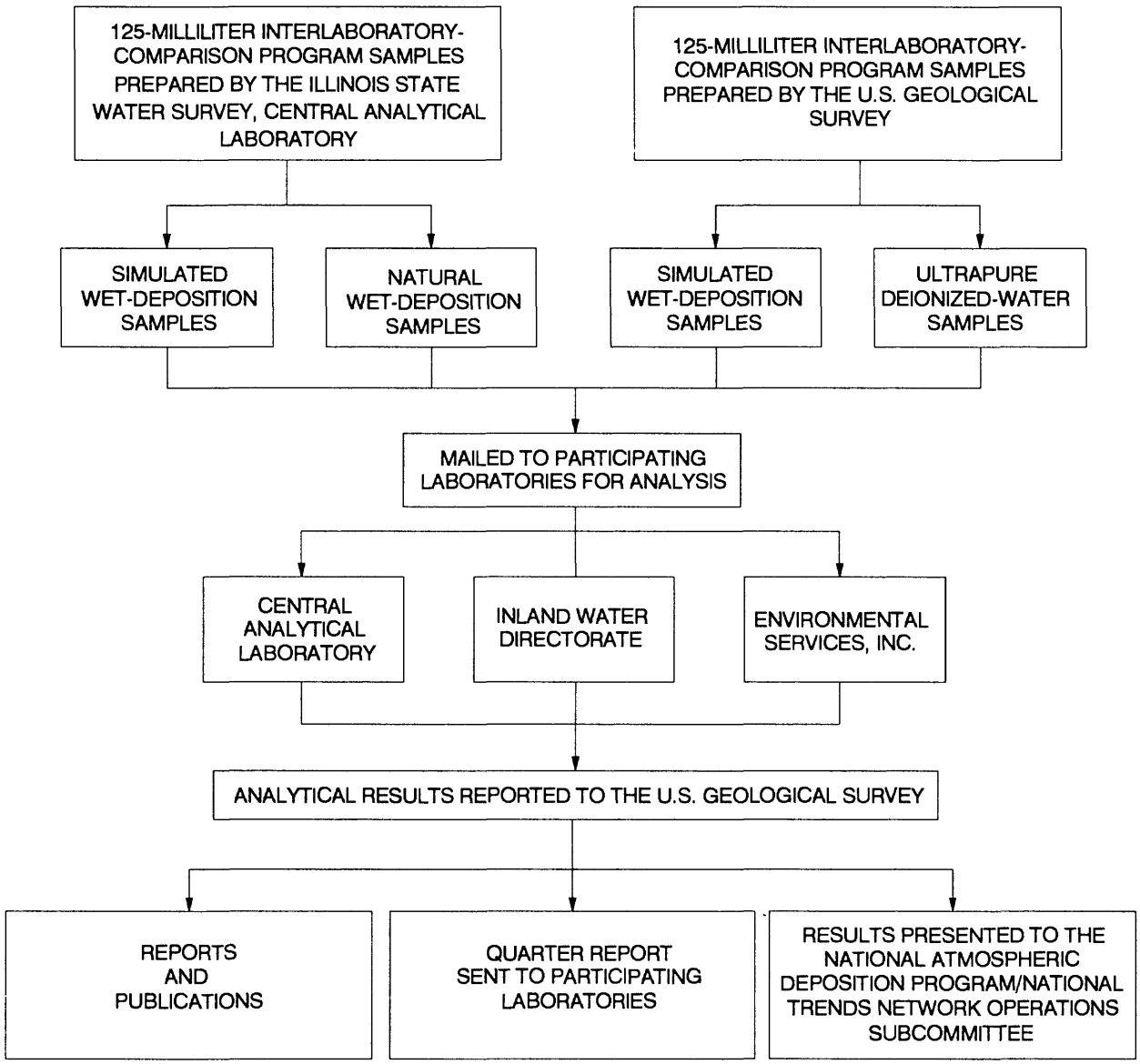

Figure 3.--Interlaboratory-comparison program.

Simulated Wet-Deposition Samples

Each participating laboratory receives two simulated wet-deposition samples in duplicate or one simulated wet-deposition sample in triplicate and one deionized water sample in every other 2-week mailing. The simulated wet-deposition samples are dilutions of a simulated precipitation sample from SRWS, EPA Performance Audit Solutions, simulated precipitation samples that are prepared by the CAL, or are undiluted NIST standard reference materials. The preparation and verification of simulated wet-deposition samples are the same as the proceduress described for blind-audit samples, which is detailed in the "Sample Preparation and Verification" subsection of the "Blind-Audit Program" section. The sample bottles are labeled with a unique eight-digit U.S. Geological Survey project identification number.

Ultrapure Deionized-Water Samples

Each participating laboratory receives approximately seven of ultrapure deionized water samples every year, accompanying the simulated wet-deposition samples which are sent to participating laboratories in triplicate. The sample bottles are pre-conditioned by leaching each bottle for 24 hours using deionized water; rinsing each bottle three times using deionized water; and then filling each bottle with deionized water. All deionized water is >16.7-MΩ. Each sample bottle is assigned a unique eight-digit U.S. Geological Survey project identification number.

Sample Mailing

Interlaboratory-comparison samples are shipped to each laboratory in chilled containers every 2 weeks. Natural wet-deposition samples are received from the CAL and distributed by the U.S. Geological Survey every 4 weeks. Simulated wet-deposition and ultrapure deionized-water samples are distributed 2 weeks later. A schedule for the distribution of samples for 1989 is in the interlaboratory-comparison notebook. Samples are packed with ice and mailed in coolers. One 3-gal cooler is used to ship the samples to the CAL to provide a shipping container large enough to hold 20 natural samples. The other laboratories receive their samples in 1-gal coolers. The ice must be sealed in a plastic bag to keep moisture from the sample bottles and accompanying forms.

Records of sample mailings for the interlaboratory-comparison program are kept in the interlaboratory-comparison notebook. A page from this notebook is shown in attachment 21. The CAL number and the U.S. Geological Survey project identification number are important keys for matching samples when the analyses are complete. The CAL number for natural wet-deposition samples is the four-digit sequential number assigned by CAL to the original sample. For simulated wet-deposition samples, the CAL number is a descriptive code that identifies the type of simulated wet-deposition sample (2694-I or USGS-1, for example). Ultrapure deionized-water samples are numbered sequentially, starting with DI0001. The Date received column has the date that natural wet-deposition samples were received by the U.S. Geological Survey. The Project ID column has the eight-digit number assigned to each sample before it is mailed to the participating laboratories. The Lab code column contains a

one-letter code that identifies which laboratory was sent that particular sample bottle. A key to the one-letter laboratory codes is in the interlaboratory-comparison notebook. Mailing addresses for the participating laboratories are listed in attachment 2. The Date shipped column has the date that samples were shipped by the U.S. Geological Survey. Samples are mailed to participating laboratories before 12 p.m. on Tuesday. Samples that are mailed later than 12 p.m. on Tuesday may not reach their destination before the end of the week and will not remain chilled. The Data received column is checked when a laboratory has reported all of the data that was requested for a particular sample. The Data punched column indicates that the data for a particular sample have been entered into project computer files.

As reported in the preceding paragraph, samples are mailed to the participating laboratories on or before Tuesday noon. Samples that arrive from CAL later than noon Tuesday should remain chilled and be mailed the following Monday morning. Each laboratory receives a letter listing the eight-digit U.S. Geological Survey project identification number and the analytes to determine for the samples (attachment 22). In addition, the IWD laboratory requires a form (attachment 23) to log the samples into the IWD analytical system.

Data Records

The analytical results from each laboratory arrive in different formats, and procedures for handling data from each laboratory are described in this section. Results from some laboratories arrive in hard-copy form, which must be keypunched; the remainder is supplied on floppy disks. The goal is to produce a data set that will enable a comparison of the laboratory results. This comparison is done by using a personal computer and PSTAT statistical-analysis software.

Data from the CAL arrives every 2 months on a 3½-in. floppy diskette. The contents of the diskette can be loaded into any of the project computers. A PSTAT editor has been written to read the CAL data into PSTAT (attachment 24). When the diskette has been successfully read, the appropriate columns in the interlaboratory-comparison notebook are checked for each sample analysis received. An archive PSTAT library file of the interlaboratory-comparison results is maintained in a computer file for the project (attachment 1).

Examples of the analytical results from ESE and IWD are shown in attachments 25 and 26. The Data received column and the Data punched column in the notebook (attachment 21) are checked when data are received and entered into the data base.

For laboratory values that are reported as less than the limit of detection, a negative value for the detection limit is entered in the data file. Values that are missing (deleted because of insufficient sample volume, for example) are entered as two dashes (--).

A quarterly report is sent to the participating laboratories. This report lists the samples that were submitted for the previous quarter, the reported results from the laboratories, and the U.S. Geological Survey's reported values for simulated wet-deposition samples.

COLLOCATED-SAMPLER PROGRAM

Data were collected from an array of Aerochem Metrics samplers at Finley Farm, North Carolina, for 18 months at the beginning of the NADP/NTN and were reported on by Schroder, et al. (1984). This first study evaluated collection efficiency, evaporation loss, and variation in pH and specific conductance among the data derived from 10 closely located samplers. Subsequently, the U.S. Geological Survey has used or supported collocated-sampler studies in association with the NADP/NTN for a variety of purposes. The most common and continuing study is performed to determine the precision of the wet-deposition data-collection system from the point of sample collection through storage in the Network's data base. Collocated studies also have been conducted to assess the variability of sample collection over relatively short distances, tens of meters, and somewhat greater distances, 5 to 20 km, (Richard Graham, U.S. Department of the Army, written commun., 1988); and to compare the performance of sampling equipment of differing manufacturers.

Finally, collocated studies are used to assess data comparability between two or more networks. One such study is underway involving NADP/NTN and Canadian Acid Precipitation Monitoring Network (CAPMoN) at one site in the United States and one site in Canada. Each site is equipped fully according to the protocols of each network and operated appropriately. The data collected at collocated sites over several years can be used to combine multiple sources for improved spatial and temporal coverage. The details of the current study which follows are exemplary of preceding studies with similar objectives. This study further expands the geographic and climatological coverage of the data on sampling precision for NADP/NTN.

The objectives of the current study are: (1) To provide an estimate of sampler precision at selected NADP/NTN sites, and (2) to evaluate the differences among Aerochem Metrics samplers that affect the sampling precision of these collection devices.

The study includes several elements. The U.S. Geological Survey installed additional Aerochem Metrics samplers at four sites where Aerochem Metrics samplers currently are in operation. The sites were selected using the following criteria:

1. Sites should be distributed among diverse regional locations.
2. Sites should be distributed among high, medium, and low rainfall regions.
3. Stable site operational histories must be maintained to ensure that data are not lost due to changes in operators.

The sites selected for the first year of study were:

1. Tifton, Ga.
2. Huntington Forest, N.Y.
3. LBJ Grasslands, Texas.
4. Oxford, Ohio.

The four pairs of Aerochem Metrics samplers will be operated at each set of sites for 1 year. Samples will be processed, using standard NADP/NTN procedures, by the site operator (except that field chemistry will not be done) and will be analyzed by the CAL. In addition:

1. Sensors will be set at manufacturer specifications.
2. An Aerochem Metrics sampler and a Belfort rain gage that has an event recorder will be installed at each site.
3. Alterations to the wet/dry samplers, such as pad heaters and peaked roofs, are duplicated at individual sites.
4. The CAL provides copies of the rain-gage charts to the U.S. Geological Survey; the chemistry data are obtained from the NADP/NTN Coordinator's Office (attachment 2).

Several investigators have estimated the precision for Aerochem Metrics collectors using different equations. Bigelow (1986) has summarized precision estimates from Topol (1982), de Pena (1980) and a 'traditional' estimate of pooled standard deviation. A fourth estimate of precision is provided by Taylor (1987).

A statistical evaluation will be prepared, which estimates the precision of the Aerochem Metrics collectors for all data determined by using standard NADP/NTN procedures. Precision estimates will be calculated by using the previously listed methods.

ANALYTICAL METHODS

The Acid Rain Quality Assurance Project of the U.S. Geological Survey performs all of its own analytical work in association with the Analytical Chemistry of Inorganic Constituents Project at the NWQL. The analytical instruments used for determining the concentration of simulated precipitation water samples are ion chromatography for anions and flame atomic absorption for cations. Contamination can be a major problem in obtaining good analytical results. All glassware and equipment is scrupulously cleaned and latex gloves are worn during the preparation and sampling handling.

The methods used for the analysis of anions in wet deposition samples for chloride, nitrate, and sulfate are American Society for Testing and Materials (ASTM) method D4327-84; for sodium, ASTM method D4191-82; for magnesium, ASTM method D858-84; for potassium, ASTM method D41192-82; and for calcium, ASTM method D511-84 (ASTM, 1986). One modification has been made to ASTM method D4327-84: samples analyzed by ion chromatography for chloride, nitrate, and sulfate are not spiked with a concentrated eluent to resolve the water dip because chloride elutes after the water dip. If fluoride is analyzed, the samples must be spiked with a concentrated eluent to resolve the water dip. Attachment 27 lists the detection limit and precision results for the Acid Rain project.

SUMMARY

This report describes: (1) The operation of four quality-assurance programs managed by the U.S. Geological Survey for the National Atmospheric Deposition Program and the National Trends Network; (2) the analytical method used by the U.S. Geological Survey. The data collected in these programs are used to analyze the precision of onsite pH and specific-conductance measurements; the precision and bias associated with onsite and laboratory handling of samples; the precision associated with laboratory analyses of precipitation samples; and estimates of precision for the sample collection system. These four programs contribute quality-assurance data which may be used in the estimates of performance within the National Atmospheric Deposition Program and National Trends Network and among the major North American wet-deposition monitoring networks.

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ATTACHMENTS

to

PROGRAMS AND ANALYTICAL METHODS FOR THE U.S. GEOLOGICAL SURVEY ACID RAIN QUALITY-ASSURANCE PROJECT

Attachment 1.--Computer directories and files for the U.S. Geological Survey's Acid Rain Quality-Assurance Project

Directory of D:\SITE_LST

DOCUMENT	file describing the files located in this directory
LIST0490.DOC	ASCII copy of the site addresses received from CAL in April 1990
SITE_ADD.EXE	FORTRAN program used to convert the file LIST0490.DOC into a format that can be read by Word

Directory of D:\ARCHIVE\INTERSIT

DOCUMENT	file describing the files located in this directory
INTERSITE.LIB	PSTAT library of all available intersite data

Directory of D:\INTERSIT\LETTERS\INSTRUCT

INST26.DOC	instructions for intersite comparison 26

Directory of D:\INTERSIT\LETTERS\STATS

STATS25.DOC	response letter and statistics for intersite-comparison 25

Directory of D:\INTERSIT\GRAPHICS

SCAT25.DRW	scatter plot for intersite-comparison 25

Directory of D:\INTERSIT\DATA\RAW_DATA

INST25.DAT	data for intersite-comparison 25

Directory of D:\INTERSIT\PROGRAMS

DOCUMENT	file describing the files located in this directory
INTLABEL.EXE	FORTRAN program to prepare bottle labels

Attachment 1.--Computer directories and files for the U.S. Geological Survey's Acid Rain Quality-Assurance Project--Continued

Directory of D:\ARCHIVE\BLIND

DOCUMENT	file describing the files located in this directory
BLIND.LIB	PSTAT library of all available blind-audit data and all available bucket and bottle matches
NOTMAT.LIB	PSTAT library of all blind-audit results that no bucket and bottle matches were found
MATCHTOT.ED	PSTAT editor file to match all bucket and bottle results from the file contained in BLIND.LIB

Directory of D:\BLIND\DATA\RAW_DATA

DOCUMENT	file describing the files located in this directory
JANMAR89.DAT	data for January to March 1989
DATAREAD.ED	PSTAT editor file to read data received from CAL
MATCH.ED	PSTAT editor file to match bucket and bottle results

Directory of D:\BLIND\LETTERS\INSTRUCT

DOCUMENT	file describing the files located in this directory
BAI250.DOC	instructions for submitting the 250-mL blind-audit samples
BAI500.DOC	instructions for submitting the 500-mL blind-audit samples
BAI1000.DOC	instructions for submitting the 1000-mL blind-audit samples

Directory of D:\BLIND\LETTERS\SUB_SITE

DOCUMENT	file describing the files located in this directory
CHOOSE.ED	PSTAT editor to choose the 32 blind-audit sites each quarter
SUBSITE.DOC	list of sites and when they submitted blind-audit samples
SUBSITE.ASC	ASCII copy of SUBSITE.DOC
NEWSITES.DOC	file built by CHOOSE.ED, file contains the 32 sites for the next quarterly mailing

Attachment 1.--Computer directories and files for the U.S. Geological Survey's Acid Rain Quality-Assurance Project--Continued

Directory of D:\BLIND\LETTERS\LTRS1990\QUARTER4

DOCUMENT	file describing the files located in this directory
ANDREA4.DOC	cover letter to Andrea Morden-Moore for the fourth quarter, 1990 blind-audit program
OLSSON4.DOC	cover letter to Cindy Olsson for the fourth quarter, 1990 blind-audit program
SUPER4.DOC	cover letter for site supervisors participating in the fourth quarter, 1990 blind-audit program
SUPLBLS4.DOC	file used to prepare mailing labels for the site supervisors participating in the fourth quarter, 1990 blind-audit program
SUPER4.DAT	data file for the file SUPER4.DOC and the file SUPLBLS4.DOC
OPERA4.DOC	cover letter for site operators participating in the fourth quarter, 1990 blind-audit program
OPRLBLS4.DOC	file used to prepare mailing labels for the site operators participating in the fourth quarter, 1990 blind-audit program
OPERA4.DAT	data file for the file OPERA4.DOC and the file OPRLBLS4.DOC

Directory of D:\ARCHIVE\INTERLAB

DOCUMENT	file describing the files located in this directory
INTERLAB.LIB	PSTAT library of all available interlaboratory-comparison data

Directory of D:\INTERLAB\LETTERS\INSTRUCT

DOCUMENT	file describing the files located in this directory
CAL_INS.DOC	instruction letter for CAL
IWD_INS.DOC	instruction letter for IWD
ESE_INS.DOC	instruction letter for ESE

Attachment 1.--Computer directories and files for the U.S. Geological Survey's Acid Rain Quality-Assurance Project--Continued

Directory of D:\INTERLAB\LETTERS\QUARTER\JULY_90

DOCUMENT	file describing the files located in this directory
ATTACHA.ED	PSTAT editor file to prepare attachment A of the July, 1990 quarterly report
ATTACHB.ED	PSTAT editor file to prepare attachment B of the July, 1990 quarterly report
ATTACHC.ED	PSTAT editor file to prepare attachment C of the July, 1990 quarterly report
CAL.DOC	cover letter for CAL of the July, 1990 quarterly report
IWD.DOC	cover letter for IWD of the July, 1990 quarterly report
ESE.DOC	cover letter for ESE of the July, 1990 quarterly report
MALO.DOC	cover letter for Bernie Malo of the July, 1990 quarterly report
QUARTER.CAL	attachment A for CAL of the July, 1990 quarterly report
QUARTER.ESE	attachment A for ESE of the July, 1990 quarterly report
QUARTER.IWD	attachment A for IWD of the July, 1990 quarterly report
QUARTER.PER	attachment B of the July, 1990 quarterly report

Directory of D:\INTERLAB\DATA\RAW_DATA\CAL

DOCUMENT	file describing the files located in this directory
CAL.ED	PSTAT editor file to read diskettes received from CAL
CAL1.DAT	data contained in first diskette received from CAL

Directory of D:\INTERLAB\DATA\RAW_DATA\IWD

DOCUMENT	file describing the files located in this directory
IWD1.DAT	data contained in the first correspondence received from IWD

Attachment 1.--Computer directories and files for the U.S. Geological Survey's Acid Rain Quality-Assurance Project--Continued

Directory of D:\INTERLAB\DATA\RAW_DATA\ESE

DOCUMENT	file describing the files located in this directory
ESE1.DAT	data contained in the first correspondence received from ESE

Directory of D:\ANALYTIC

DOCUMENT	file describing the files located in this directory
ANALERR.DOC	data file for SRWS solution P12 and the USGS solution

Attachment 2.--Directory of organizations associated with the U.S. Geological Survey Acid Rain Quality-Assurance Project

Central Analytical Laboratory Illinois State Water Survey 2204 Griffith Drive Champaign, Illinois 61820	Bowersox, Van 217-333-7871 Dossett, Scotty R. 217-333-7871 Douglas, Kathy 217-333-7871 James, Kenni 217-333-7871 Morden-Moore, Andrea 217-333-7871 Peden, Mark E. 217-333-7871 Sauer, Jackie 217-333-7871 Stensland, Gary 217-333-7871
Inland Waters Directorate (IWD) Water Quality Branch 867 Lakeshore Road, Box 5050 Burlington, Ontario L7R 4A6 Canada	Agemian, Haig 416-336-4679 Carrier, Sharon 416-336-4679 Sampson, R.C.J. 416-336-6404
Hunter, Environmental Science & Engineering, Inc. P.O. Box 1703 Gainesville, Florida 32602-1703	Prentice, Hugh S. 904-332-3318 Ryals, Selina 904-332-3318
NADP/NTN Coordinator's Office Natural Resources Ecology Laboratory Colorado State University Fort Collins, Colorado 80523	Bandhaur, Linda 303-491-1977 Bigelow, David S. 303-491-5574 Gibson, James 303-491-1978 Klahn, Sarah 303-491-1989 Scott, Gwen 303-491-1465 Simmons, Carol 303-491-1978

Attachment 2.--Directory of organizations associated with the U.S. Geological Survey Acid Rain Quality-Assurance Project--Continued

U.S. Geological Survey
Mail Stop 401, Box 25046
Denver Federal Center
Denver, Colorado 80225

Gordon, John D.
303-236-1495
FTS 776-1495
Schroder, LeRoy J.
303-236-3605
FTS 776-3605
Nilles, Mark A.
303-236-9278
FTS 776-9278
Willoughby, Timothy C.
303-236-9278
FTS 776-9278

U.S. Geological Survey
Mail Stop 416 National Center
12201 Sunrise Valley Drive
Reston, Virginia 22092

Kapinos, F. Paul
703-648-6876
FTS 959-6876
Malo, Bernard A.
703-648-6866
FTS 959-6866

Attachment 3.--Example of letter of instruction to active-site operators participating in intersite-comparison study #26 (to be printed on U.S. Geological Survey letterhead)

401

INSTRUCTIONS FOR NADP/NTN INTERSITE-COMPARISON 26

The Network Operations Subcommittee has modified the Intersite Program:

NEW INSTRUCTIONS--PLEASE READ CAREFULLY

Enclosed please find the following materials:

* one 125 mL bottle of intersite-comparison 26 sample

* one intersite-comparison 26 response card for recording your measurements

* one intersite-comparison 26 response card for recording pH electrode information

New Instructions for Intersite 26

Measure the pH and specific conductance of the enclosed sample exactly as you do each week for the contents of the NADP/NTN wet-side bucket. Please complete all requested information on the enclosed, self-addressed cards. Be sure to complete the response card concerning pH electrodes.

If EITHER of your field meters is inoperable, please note this in the remarks section and perform the measurement for which you do have a working meter.

If BOTH of your field meters are inoperable, note this on the response card and return it. Sites which do not submit data because of equipment problems are coded differently in the data base from sites which do not respond at all.

When you have completed your measurements, return your response cards to the U.S. Geological Survey. Retain the remaining intersite-comparison solution and the shipping box until you receive confirmation of your results along with further instructions. Sites that do not return all of the intersite-comparison 26 response cards will be contacted by the NADP/NTN coordinator's office.

Please analyze the enclosed sample and return your response cards promptly. At the very latest your response must be received by November 12, 1990, or data from your site will not be included in the summary report. A report describing your results will be mailed to you by November 16, 1990. Please direct any questions to John Gordon at (303) 236-1495 or FTS 776-1495.

Attachment 4.--Example of an intersite-comparison response card

9-1887D
UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
MS 401
Box 25046, Federal Center
DENVER, COLORADO 80225

OFFICIAL BUSINESS
Penalty For Private Use, $300

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF THE INTERIOR
INT-413

U.S. Geological Survey
Branch of Quality Assurance
NADP/NTN Intersite Comparison Program
Mail Stop 401
Box 25046, Denver Federal Center
Lakewood, Colorado 80225

STATION Name _____ SITE ID ☐☐☐☐

OBSERVER _____ Initials ☐☐☐ MO ☐☐ DAY ☐☐ YR ☐☐

Conductance in µS/cm = ☐☐.☐ Distilled Water

75.0 Standard Certified ÷ ☐☐.☐ Standard Measured = ☐☐.☐ Correction Factor

☐.☐☐ Correction Factor X ☐☐☐☐.☐ Check Sample Measured = ☐☐☐☐.☐ Check Sample Corrected

☐.☐☐ Correction Factor X ☐☐☐☐.☐ Intersite Sample Measured = ☐☐☐☐.☐ Intersite Sample Corrected

pH ☐☐.☐☐ Intersite Sample ☐☐.☐☐ Check Sample

REMARKS:

Attachment 5.--Example of a pH electrode questionnaire

9-16
UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, $300

...ID FEES PAID
U.S. DEPARTMENT OF THE INTERIOR
INT 413

INTERSITE 26

SITE ID _____ OPERATORS INITIALS _____

Please indicate the type of pH electrode used to measure this intersite solution

__ Beckman __ Orion __ Broadly-James
__ Other Specify Manufacturer_____

Is this electode routinely used at your site?

__ YES __ NO

If no specify electrode used_____

(May 1989)
UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
MS_____
Box 25046 FEDERAL CENTER
DENVER, COLORADO 80225-0046

OFFICIAL BUSINESS
Penalty For Private Use, $300

POSTAGE AND FEES PAID
U. S. DEPARTMENT OF THE INTERIOR
INT 413

U.S. Geological Survey,WRD,BQA
Fed. Center,PO 25046,MS 401
Denver, CO 80225
ATTN: John Gordon

Attachment 6.--Example of a form cover letter for statistical summary for intersite-comparison study #25

«DATA IS25D.doc»

401

TO: NADP/NTN Site Operator, Site «site»

FROM: John D. Gordon, U.S. Geological Survey Acid Rain Quality Assurance Project

SUBJECT: Intersite-comparison study #25

Enclosed is a scatterplot of pH versus specific conductance for the NADP/NTN sites that participated in intersite-comparison study #25. The results for your site for intersite-comparison #25 were as follows:

	REPORTED VALUE	MET NADP/NTN GOALS?*
pH	«IF pHIS="-"»Not Reported«ELSE»«IF pHIS="--"»Not Reported«ELSE»«pHIS»«ENDIF»«ENDIF»	«IF pHIS="-"» «ELSE»«IF pHIS="--"» «ELSE» «MGOLPH»«ENDIF»«ENDIF»
Specific Conductance	«IF SCIS="-"»Not Reported«ELSE»«IF SCIS="--"»Not Reported«ELSE»«SCIS»«ENDIF»«ENDIF»	«IF SCIS="-"» «ELSE»«IF SCIS="--"» «ELSE» «MGOLSC»«ENDIF»«ENDIF»

*pH values between 4.47 and 4.67 met the accuracy goals
*conductance values between 8.3 - 16.3 met the accuracy goals

Check your records to confirm these values.

Use the following line graph and the enclosed scatterplot to help determine where your reported values fall within the distribution of all reported values:

			MOST PROBABLE VALUES		
PERCENTILES	5%	25%*	50%	75%	95%
pH	4.39	4.53	4.57	4.61	4.70
Specific Conductance	10.8	11.8	12.3	12.7	14.2

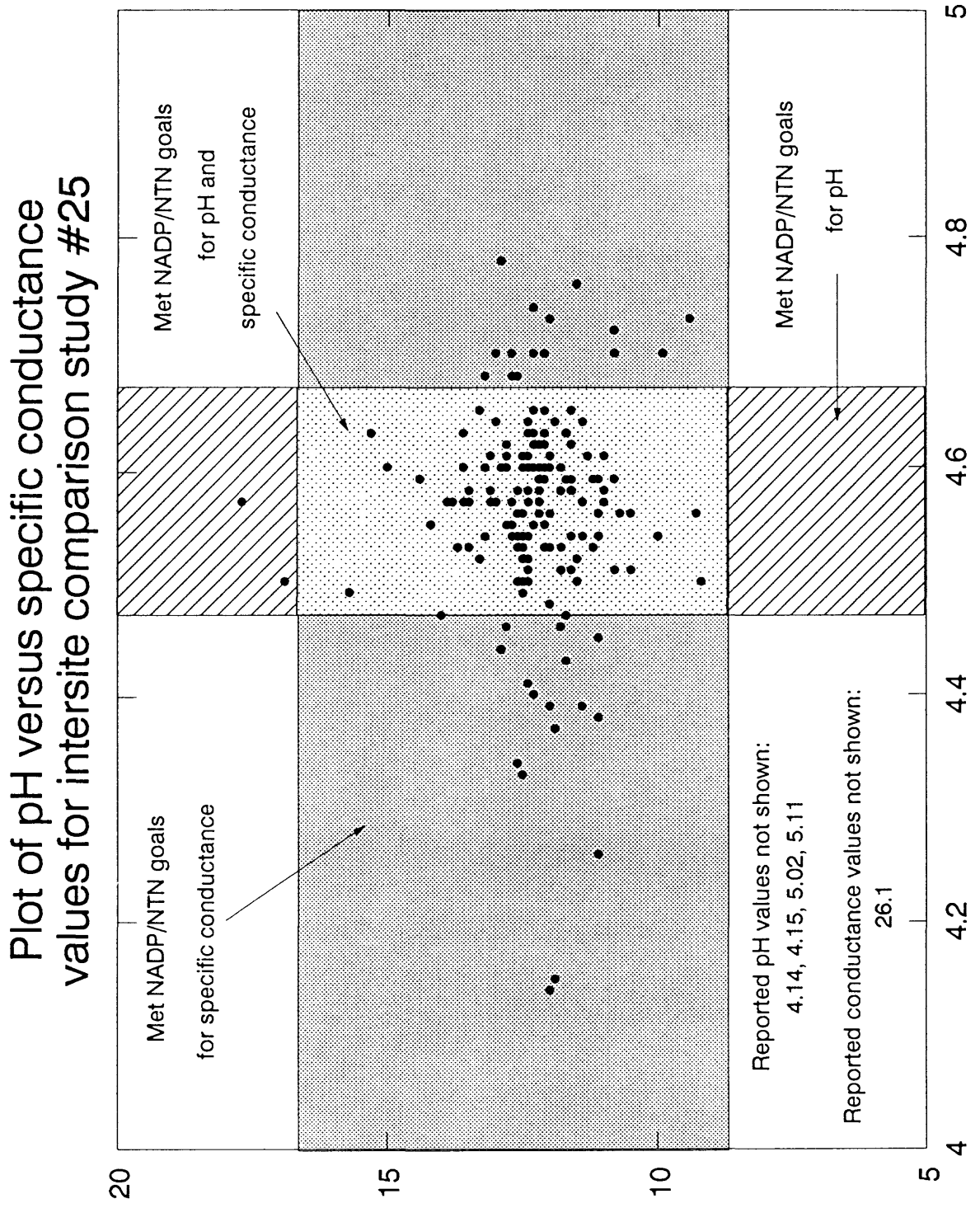
*e.g. 25% of all reported values were less than this value; 75% were greater.

If you have any questions regarding your results, please contact me at (303) 236-1495 or FTS 776-1495.

Sincerely,

John Gordon

Attachment 7.--Plot of pH versus specific conductance values for intersite-comparison study #25



Attachment 8.--Description of the four levels of follow-up in the intersite-comparison program.

LEVEL 1 FOLLOW-UP:

1) Letter discussing common sources of measurement errors

LEVEL 2 FOLLOW-UP

1) Letter discussing common sources of measurement errors
2) Request that site operator reanalyze the remaining portion of the test solution

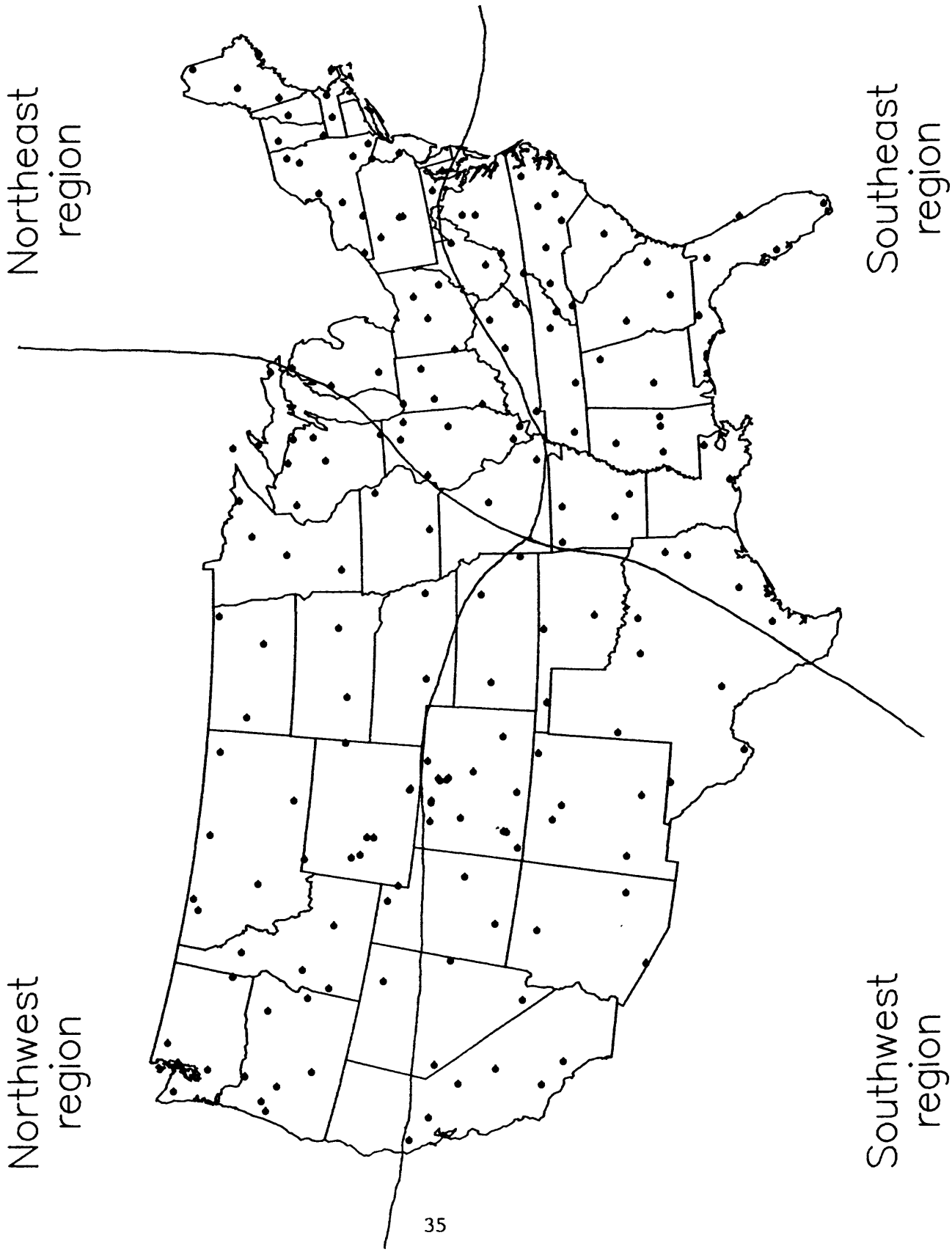
LEVEL 3 FOLLOW-UP:

1) Letter discussing common sources of measurement errors
2) Request that site operator reanalyze the remaining portion of the test solution
3) One additional aliquot of test solution

LEVEL 4 FOLLOW-UP:

1) Letter discussing common sources of measurement errors
2) Request that site operator reanalyze the remaining portion of the test solution
3) Two additional aliquots of test solution

Attachment 9.--Geographical distribution of sites in the blind-audit program



Attachment 10.--Randomized listing of sites for the blind-audit program

Northeast Region	Northwest Region	Southeast Region	Southwest Region
WY08	NY10	NC45	CO21
WA21	NY65	NC36	TX02
WY00	IL11	FL11	TX56
WA19	IN41	PR20	AZ99
MN16	ME00	AL10	CO93
WA24	CAN4	MS30	UT98
OR02	IN22	NC41	TX04
WY99	MI98	NC34	CO00
WY98	IL19	NC03	OK00
OR98	NH02	TX21	CO99
WA14	WI99	AR02	CO97
OR09	VT01	AR27	NM07
NE99	ME02	TN11	OK29
MT05	IL63	TN14	CO96
MT13	WI28	LA30	CA99
ID15	IL99	MS19	NM01
OH49	KY38	AR16	CA88
ID04	MA13	MS10	AZ03
SD08	IL78	LA12	CO01
WY97	IL35	VA00	CA42
WY96	NY68	TX10	KS32
MT00	WI37	KY03	NV05
OH71	MA01	KY22	CO19
OR97	MI97	TX38	NV01
ID11	NY52	GA50	OK17
ND07	MI26	FL03	KS07
UT08	MD13	TN99	NV00
HI00	MI53	WV18	TX51
ID03	NY08	VA29	CA76
ND11	IN34	NC35	NM09
MO03	PA42	WV04	CA98
IA08	MD03	AR03	KS31
MT07	WI36	GA41	CO22
ND08	ME09	FL14	UT99
MN18	PA72	FL99	TX16
MO05	NY99	TX03	NM12
SD99	NY20	VA28	CO02
OH09	PA29	FL41	CO94
IA23	NJ99	KY35	CO92
MN27	MI09	SC06	CO08
OH17	IL18	AL99	TX22
NE15	WI98	TN00	AZ06
OR11	IN20	NC25	CA45
OR18	MI99	GA20	CA75
OR10	WI09	--	AS01
UT01	PA15	--	NV03
WY06	MA08	--	CO15
AK03	ME98	--	NM08
MN23	NY98	--	CO98
MT98	WI25	--	--
WY02	VT99	--	--

Attachment 11.--Analytical mean concentrations and standard deviations for solutions used in the blind-audit or interlaboratory-comparison programs during 1989

[All units, in milligrams per liter, except pH, which is in units, and specific conductance, which is in microsiemens per centimeter at 25 degrees Celsius; -- indicates data are unavailable]

Solution	Target values									
	pH	Specific conductance	Ca	Mg	Na	K	Cl	NO_3	SO_4	NH_4
1085-1-1:1	4.27	24.9	0.065	0.021	0.182	0.079	0.289	0.610	2.75	0.117
Standard deviation	.07	3.0	.045	.008	.034	.029	.102	.155	.10	.050
2694-I	4.27	26	.014	.024	.205	.052	.24	--	2.75	--
Standard deviation	.03	2	.003	.002	.009	.007	--	--	.05	--
2694-II	3.59	130	.049	.051	.419	.106	1.0	7.06	10.9	--
Standard deviation	.02	2	.011	.003	.015	.008	--	.15	.2	--
CAL-4.3	4.3	22	--	--	--	--	--	3.11	--	--
Standard deviation	.1	2	--	--	--	--	--	--	--	--
CAL-A	4.84	7.5	.069	.017	.050	.016	.12	.50	.67	--
Standard deviation	.04	.2	.003	.001	.003	.001	.02	.03	.03	--
CAL-B	4.31	27.6	.282	.070	.187	.051	.51	1.98	2.66	--
Standard deviation	.04	.6	.005	.002	.004	.003	.03	.10	.07	--
P12	6.58	10.0	.91	.06	.71	.05	.66	--	.65	--
Standard deviation	.31	.6	.06	.01	.05	.01	.04	--	.13	--
P8	5.97	3.77	.23	.03	.07	.05	.17	.27	.45	.04
Standard deviation	.27	.76	.04	.01	.04	.02	.15	.04	.23	.01
USGS-1	4.80	8.0	.14	.037	.092	.025	.142	1.08	.938	.160
Standard deviation	.01	.1	.008	.006	.008	.009	.006	.02	.009	--
USGS-2	4.80	8.0	.14	.037	.092	.025	.142	1.08	.938	.160
Standard deviation	.01	.1	.008	.006	.008	.009	.006	.02	.009	--

Attachment 12.--Estimated analytical error of the Illinois State Water Survey, Central Analytical Laboratory, and U.S. Geological Survey Acid Rain Quality-Assurance Project for 1989

Analyte	Analytical error (percent)	
	Illinois State Water Survey	U.S. Geological Survey
Calcium	3.9	6.1
Magnesium	5.9	8.6
Sodium	1.2	5.1
Potassium	5.0	19.9
Chloride	10.5	3.3
Nitrate	2.5	3.0
Sulfate	4.2	1.4

Attachment 13.--Example of a form cover letter to site operators participating in the first quarter, 1990, blind-audit program (to be printed on U.S. Geological Survey letterhead)

«data OPERA1.DAT»

401

Mark A. Nilles
U.S. Geological Survey
Mail Stop 401, Box 25046
Denver Federal Center
Denver, Colorado 80225

December 15, 1989

«FIRSTO» «LASTO»
«if OPR2»«OPR2»
«endif
«if OPR3»«OPR3»
«endif
«if OPR4»«OPR4»
«endif
«if OPR5»«OPR5»
«endif

Enclosed please find the necessary sample, instructions, and forms for your participation in the **NADP/NTN Blind-Audit Sample Program.** The purpose of the Blind-Audit Sample Program is to objectively test the network sample handling procedures for possible bias.

The blind-audit sample you have received should be submitted to CAL in place of the wet-deposition sample collected on **«date», 1990,** for site **«COD».** The actual wet-deposition sample from this sampling period should be submitted to CAL using the enclosed partially completed site observer report form. Details for the submission of the blind-audit and actual wet-deposition samples are found in the enclosed instruction sheet.

You will be contacted by the NADP/NTN Coordinator's Office approximately one week before your scheduled submission date. If you are not contacted, or have any questions, please call me at (303) 236-9278 or FTS 776-9278.

Thank you for your participation.

Sincerely,

Mark A. Nilles

Attachment 14.--Example of form cover letter to site supervisors participating in the first quarter, 1989, blind-audit program (to be printed on U.S. Geological Survey letterhead)

«data super1.dat»

401

Mark A. Nilles
U.S. Geological Survey
Mail Stop 401, Box 25046
Denver Federal Center
Denver, Colorado 80225

December 15, 1989

«firsts» «lasts»
«if sup2»«sup2»
«endif
«if sup3»«sup3»
«endif
«if sup4»«sup4»
«endif
«if sup5»«sup5»
«endif

I am writing to notify you that site «cod» has been asked to submit a blind-audit sample to the Illinois State Water Survey, Central Analytical Lab (CAL). The blind-audit sample has been mailed directly to the site operator. The blind-audit sample should be submitted to CAL in place of the wet-deposition sample collected on «date», **1990**.

The site operator will be contacted by the NADP/NTN Coordinator's Office approximately one week before the scheduled submission date for the blind-audit sample. Your help in assuring that the blind-audit sample is submitted to CAL as directed will be greatly appreciated. If you have any questions please feel free to call me at (303) 236-9278 or FTS 776-9278.

Thank you for your participation.

Sincerely,

Mark A. Nilles

Attachment 15.--Instruction sheet for the submission of blind-audit samples

NATIONAL ATMOSPHERIC DEPOSITION NETWORK
AND NATIONAL TRENDS NETWORK

******* INSTRUCTIONS FOR SUBMISSION OF THE BLIND-AUDIT SAMPLE *******

-New Instructions prepared September 1, 1990-
PLEASE READ CAREFULLY BEFORE PROCEEDING

DO NOT SUBMIT THE SAMPLE UNTIL YOUR ASSIGNED DAY
(indicated by the collection date reported on the cover letter)

PLEASE FIND ENCLOSED:

one - 250 mL polyethylene blind-audit sample bottle
two - pre-addressed notification cards
one - pre-addressed mailing envelope
one - dummy-site Field Observer Report Form

If you did not receive any of the above items, please call Mark Nilles immediately.

PROCEDURES:

Submission of the Wet-Side Bucket

On the "bucket off" date indicated on the enclosed dummy-site Field Observer Report Form, collect the wet-side bucket as you normally do each Tuesday; HOWEVER, USE THE DUMMY-SITE FIELD OBSERVER REPORT FORM FOR SUBMISSION OF THE WET-SIDE BUCKET TO CAL. Notice that the sections labeled STATION, OBSERVER, BUCKET ON, and BUCKET OFF are already filled in for you.

Complete the remaining sections of the dummy-site Field Observer Report Form as you normally do for a wet-side bucket.

Do not include the actual rain-gage chart, and do not make up a dummy rain-gage chart. (Instructions for the rain-gage chart are included in step D of the "submission of the blind-audit sample" section.)

Seal the wet-side bucket and send it to CAL as you normally do. Enclose the white and yellow copies of the dummy-site Field Observer Report Form in the bucket mailer. Retain the pink copy for your records.

NOTE: YOU ARE SUBMITTING YOUR WET-SIDE BUCKET SAMPLE
DISGUISED AS THE DUMMY SAMPLE

****

Attachment 15.--Instruction sheet for the submission of blind-audit samples--Continued

YOU WILL NOW SUBMIT PART OF THE BLIND-AUDIT SAMPLE
DISGUISED AS YOUR WET SIDE BUCKET SAMPLE

PLEASE FOLLOW ALL INSTRUCTIONS CAREFULLY

Submission of the blind-audit sample

A) Use a new, clean bucket for this sample. You will only use 70 percent of the blind-audit sample. All precautions should be taken to avoid contamination of the sample.

B) Pour 70 percent of the blind-audit sample (down to the line on the bottle) into the bucket. DO THIS REGARDLESS OF THE BOTTLE SIZE. SEVERAL DIFFERENT BOTTLE SIZES ARE NOW USED IN THE BLIND-AUDIT PROGRAM TO SIMULATE A RANGE OF RAINFALL AMOUNTS. Tightly recap the bottle; you will send the bottle back to CAL (instructions for this are included in step E).

C) The bucket containing the blind-audit sample should be treated as if it were the wet-side bucket from the previous week. Prepare a Field Observer Report Form. (NOT THE DUMMY FORM SENT WITH THE BLIND-AUDIT PACKET). Do not indicate in any way on the report form that this is a blind audit or the sample will be invalidated. FILL OUT A FIELD OBSERVER REPORT FORM FOR THE BLIND-AUDIT SAMPLE FOLLOWING THESE INSTRUCTIONS:

1.	STATION	Enter your site name and site ID
2.	OBSERVER	Enter your name and initials
3.	SAMPLE BUCKET	Check wet-side
4.	BUCKET ON/BUCKET OFF	Record the same dates and times that were used for the actual wet-side sample submitted using the Dummy-Site name and ID.
5.	SITE OPERATIONS	Check YES for all items
6.	SAMPLE CONDITION	Check NO for all items
7.	SAMPLE WEIGHT	Weigh the blind-audit sample and record your measurements
8.	PRECIPITATION RECORD	Create a seven day precipitation record. For your 250-mL blind-audit sample, make up and record daily values that add up to 0.12 inches.

Attachment 15.--Instruction sheet for the submission of blind-audit samples--Continued

9.	SAMPLE CHEMISTRY	Remove your normal aliquot from the blind-audit sample bucket and determine pH and specific conductance; record your measurements.
10.	SUPPLIES	Request any supplies you may need.
11.	REMARKS	Make any appropriate remarks, but DO NOT indicate in any way that this is a blind-audit sample.

D) Seal the blind-audit sample bucket and place it in a bucket mailer. Enclose the rain-gage chart from your site, and the white and yellow copies of the blind-audit sample Field Observer Report Form in the bucket mailer. Retain the pink copy for your records. Ship the blind-audit sample bucket to CAL as if it were the actual wet-side bucket.

E) Fill in the requested information, about the blind-audit sample, on the back of the two inclosed postcards and mail the postcards.

F) PROCESSING INSTRUCTIONS FOR THE SOLUTION REMAINING IN THE BLIND-AUDIT SAMPLE BOTTLE:

Use the enclosed, mailing envelope addressed to Andrea Morden-Moore to ship the remaining contents of the blind-audit sample bottle.

Attachment 15.--Instruction sheet for the submission of blind-audit samples--Continued

ANSWERS TO FREQUENTLY ASKED QUESTIONS:

1. Do I mail the blind-audit sample bottle with the bucket?

   No. Use the mailing envelope provided.

2. Do I need to make up a dummy rain-gage chart? After all, my rain-gage chart looks a lot different from the precipitation record I made up.

   No, do not make up a dummy rain-gage chart. The chart and bucket get separated immediately once they reach CAL--no one will notice (at least for several weeks).

3. In which mailer should I put the rain-gage chart?

   Put the rain-gage chart in the mailer with the blind-audit sample bucket.

4. Won't CAL know they received two buckets from my site (therefore compromising the "blindness" of the audit)?

   No. They won't notice until all of the analyses are done, because of the order in which things are processed and compiled.

5. The precipitation record on the rain-gage chart is very different from what is recorded on the field form. Won't CAL notice?

   No. Remember, the rain-gage charts are removed from the mailers and processed separately. No one will notice until all of the data are compiled.

6. Will I lose the data for my actual wet-side bucket sample, since I am submitting it to CAL disguised as a dummy sample?

   No. After all the analyses are completed and the results are tabulated, the data base is corrected and site ID's are carefully matched to the correct data.

7. Which sample information should go on the enclosed postcards?

   Enter the information about the blind-audit sample on the postcards.

Please direct any further questions regarding the blind-audit sample program to:

Mark A. Nilles
(303) 236-9278
FTS 776-9278

Attachment 16.--Example of report form for use by field observers for the National Atmospheric Deposition Program and the National Trends Network

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM
A Cooperative Research Program of the State Agricultural Experiment Stations and other Federal, State and Private Research Organizations • IR-7

NADP/NTN FIELD OBSERVER REPORT FORM

Send Completed Form With Each Bucket To
The Central Analytical Laboratory

CAL/NREL Use Only
N
BAG ☐ LEAK ☐
SP ☐ SL ☐

1. STATION Name Dummy Site
ID D U 0 1

2. OBSERVER Initials X X X
Signature

3. SAMPLE BUCKET *Check One* ☐ Wet-Side ☐ Dry-Side

4.

BUCKET ON Date MO 01 DAY 03 YR 89 Time 0000-2400

BUCKET OFF Date MO 11 DAY 08 YR 89 Time 0000-2400

5. SITE OPERATIONS *Check* Yes *or* No *for all* Wet-Side *samples.* If No, explain in data Block II, Remarks

YES	NO	
2	1	1. The **sensor heater** and **motor box** operated properly and the **event recorder** indicates the collector lid closed promptly at the end of each precipitation event.
2	1	2. Rain gage appears to have operated properly during the week.
2	1	3. Collector opened and closed at least once during the week, **other than for testing.**

6. SAMPLE CONDITION *Check* Yes *or* No *for all samples containing precipitation* Describe all else in Data Block 11, Remarks

YES	NO	
2	1	1. Bird Droppings
2	1	2. Cloudy or Discolored
2	1	3. Unusual amounts of soot or dirt for this site

7. SAMPLE WEIGHT *For all buckets containing precipitation*

Bucket + Lid + Sample
− Bucket + Lid
= Sample Weight in grams

8. PRECIPITATION RECORD *For* Wet-Side *Samples Only*

R - Rain Only
S - Snow Only
M - Mixture
U - Unknown
Z - Zero
T - Trace
MM - Missing

Bucket On				To				Bucket Off →															
TUES				WED				THUR				FRI				SAT				SUN				MON				TUES			
Type Circle one	R	S	M	U	R	S	M	U	R	S	M	U	R	S	M	U	R	S	M	U	R	S	M	U	R	S	M	U	R	S	M	U
Inches or circle one	Z	T	MM		Z	T	MM		Z	T	MM		Z	T	MM		Z	T	MM		Z	T	MM		Z	T	MM		Z	T	MM	

Total sampling period precipitation from rain gage ____ Inches
Total precipitation from sampler = Sample Weight × 0.00058 inches/gram ____ Inches

9. SAMPLE CHEMISTRY *Only for* Wet-Side *buckets with a Sample Weight of more than 70 grams.*

MO DAY YR

Conductance in μS/cm

7 5 ● 0 Standard Certified	÷	Standard Measured	= Correction Factor
Correction Factor	×	Check Sample Measured	= Check Sample Corrected
Correction Factor	×	Precipitation Sample Measured	= Precipitation Sample Corrected

Distilled Water

pH
Precipitation Sample
Check Sample

Aliquot Removed in mls

10. SUPPLIES
Circle if needed
pH 4 Buffer
pH 7 Buffer
Check Sample
75 μS/cm Standard
Field Forms
Vials
pH electrode
Rain gage chart
Rain gage ink

11. REMARKS *For example: Insect contamination, contamination by operator, equipment malfunction, harvesting in area, etc.*

REVISED 5/86

Attachment 17.--Example of blind-audit submission cards

9-160a
UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, $300

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF THE INTERIOR
INT 413

RECORD OF BLIND-AUDIT SAMPLE SUBMISSION
FILL IN THE BLANKS BELOW BY COPYING FROM THE
BLIND-AUDIT SAMPLE FIELD OBSERVER REPORT FORM

STATION ID _____ STATION NAME _____

DATE ON _____ DATE OFF _____

FIELD PH _____ CORRECTED FLD COND. ___

9-1887D
UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
MS _____
Box 25046, Federal Center
DENVER, COLORADO 80225

OFFICIAL BUSINESS
Penalty For Private Use, $300

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF THE INTERIOR
INT-413

JAMES GIBSON
NATURAL RESOURCES ECOLOGY LAB
COLORADO STATE UNIVERSITY
FORT COLLINS, CO 80523

9-1887D
UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
MS _____
Box 25046, Federal Center
DENVER, COLORADO 80225

OFFICIAL BUSINESS
Penalty For Private Use, $300

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF THE INTERIOR
INT-413

U.S. Geological Survey, WRD, BQA
Den. Fed. Center, PO 25046, MS 401
Lakewood, CO 80225
ATTN: Randolph See

Attachment 18.--Example of a notification letter for the quarterly blind-audit program

401

December 15, 1989

Mark A. Nilles
U.S. Geological Survey
Mail Stop 401, Box 25046
Denver Federal Center
Denver, Colorado 80225

Cindy Olsson
NADP Coordinator's Office
Natural Resources Ecology Laboratory
Colorado State University
Fort Collins, Colorado 80523

Dear Cindy,

The following is a list of the sites, Dummy ID's and sample off dates for the first quarter of the 1990 blind-audit sample program:

Site	Dummy ID	Date sample off	Solution
ND08	DU01	January 9	P12
FL11	DU02	January 9	1085-1-1:1
NY68	DU03	January 9	USGS-3 (500)
UT99	DU04	January 16	ULTRAPURE
MT99	DU05	January 16	USGS-3 (250)
TN11	DU06	January 23	CAL 4.3
MN18	DU07	January 23	1085-1-2:1
WI28	DU08	January 23	USGS-3 (1000)
OK29	DU09	January 30	1085-1-2:1
CA45	DU10	January 30	CAL 4.3
WA14	DU11	February 6	USGS-3 (250)
SC06	DU12	February 6	1085-1-2:1
OH49	DU13	February 6	P12
TX51	DU14	February 13	USGS-3 (500)
NC45	DU15	February 13	1085-1-1:1
ID11	DU16	February 20	1085-1-1:1
NY99	DU17	February 20	USGS-3 (250)
NM12	DU18	February 20	1085-1-2:1
TN99	DU19	February 27	USGS-3 (1000)
MS14	DU20	February 27	CAL 4.3
ME09	DU21	March 6	ULTRAPURE
CO01	DU22	March 6	1085-1-1:1
IL19	DU23	March 6	P12
IN41	DU24	March 13	USGS-3 (500)

Attachment 18.--Example of a notification letter for the quarterly blind-audit program-continued

NY08	DU25	March 13	ULTRAPURE
IN22	DU26	March 20	USGS-3 (1000)
OR98	DU27	March 20	USGS-3 (250)
VA28	DU28	March 20	USGS-3 (500)
CA99	DU29	March 27	CAL 4.3
NV01	DU30	March 27	ULTRAPURE
AR02	DU31	April 3	P12
MI09	DU32	April 3	USGS-3 (1000)

Sincerely,

Mark A. Nilles
Hydrologist

Attachment 19.--Example of a notification letter for the quarterly blind-audit program

401

December 15, 1989

Mark A. Nilles
U.S. Geological Survey
Mail Stop 401, Box 25046
Denver Federal Center
Denver, Colorado 80225

Andrea Morden-Moore
Central Analytical Laboratory
Illinois State Water Survey
2204 Griffith Drive
Champaign, Illinois 61820

Dear Andrea,

The first quarter 1989 blind-audit samples have been mailed. Two to three samples per week will be submitted during the period 01/90 to 04/90. The samples will be numbered consecutively DU01 to DU32. I have mailed this information to Dave Bigelow and he will supply any additional information to you at the appropriate intervals. Please call me if you have any questions regarding the external quality-assurance program.

Sincerely,

Mark A. Nilles
Hydrologist

Attachment 20.--Example of preliminary data sheet from the Illinois State Water Survey, Champaign, Illinois

NADP/NTN CENTRAL ANALYTICAL LABORATORY - ILLINOIS STATE WATER SURVEY

FIELD PRINTOUT
PRINTOUT DATE: 9-DEC-88

PLEASE NOTE - DATA WITH A SAMPLE ID LESS THAN NG79000W (MARKED WITH AN ASTERISK) HAS BEEN REVIEWED BY THE CAL FOR THIS REPORT

SAMPLE ID	LAB TYPE	DATE ON	TIME ON	DATE OFF	TIME OFF	TIME ZONE	PH LAB	PH FLD	CONDUCTIVITY LAB	CONDUCTIVITY FLD	SAMPLE VOLUME (ML)	SAMPLE DEPTH (IN.)	PRECIP. DEPTH (IN.)	LEAKAGE
NG87330WDU02	W	092788	0700	100488	0700	LT	4.52	4.25	15.5	21.3	172.8	0.10	0.11	NONE

PRELIMINARY PRINTOUT
DATE: 12-DEC-88

NADP/NTN CENTRAL ANALYTICAL LABORATORY - ILLINOIS STATE WATER SURVEY

PLEASE NOTE - DATA WITH A SAMPLE ID LESS THAN NG79010W (MARKED WITH AN ASTERISK) HAS BEEN REVIEWED BY THE CAL FOR THIS REPORT

SAMPLE ID	LAB TYPE	DATE ON	TIME ON	DATE OFF	TIME OFF	CONCENTRATIONS (MG/L) CA	MG	K	NA	NH4	NO3	CL	SO4	PO4	FIELD COND. (MICROMHOS/CM)	LAB COND.	FIELD PH	LAB PH
NG87330DU02	W	092788	0700	100488	0700	0.050	0.014	0.008	0.085	0.02	3.25	<0.03	0.05	<0.020	21.3	15.5	4.25	4.52

SAMPLE ID	LAB TYPE	DEPOSITION(MILLIGRAMS/SQUARE METER) CA	MG	K	NA	NH4	NO3	CL	SO4	PO4	H	SAMPLE VOL(ML)	MEAS ANIONS	MEAS CATIONS (MICROEQUIV/L)
NG87330DU02	W	0.13	0.04	0.02	0.22	0.05	8.27	<0.08	0.13	<0.05	0.08	172.8	54.2	38.9

Attachment 21.--Example page from the 1989 notebook of the interlaboratory-comparison program

CAL #	DATE RECEIVED	PROJECT ID	LAB CODE	DATE SHIP	DATA RECEIVED	DATA ENTERED
2694-II		89128001	O	5/8/89		
2694-II		89128002	S			
2694-II		89128003	C			
2694-II		89128004	C			
2694-II		89128005	S			
2694-II		89128006	O			
2694-II		89128007	S	5/8/89		
2694-II		89128008	C			
2694-II		89128009	O			
DI0033		89128010	C			
DI0033		89128011	O			
DI0033		89128012	S	5/8/89		

DI0033 IS USGS OLTRAPURE WATER

STANDARD REFERENCE MATERIAL

NBS

2694-II

Simulated Rainwater

DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
GAITHERSBURG, MD 20899

Attachment 22.--Example of a cover letter to participants in the interlaboratory-comparison program
(to be printed on U.S. Geological Survey letterhead)

401

Central Analytical Laboratory
Illinois State Water Survey
2204 Griffith Drive
Champaign, Illinois 61820

Enclosed are four samples for the interlaboratory-comparison program managed by the U.S. Geological Survey. The identification numbers for the enclosed samples are:

_____

_____

_____

_____

When reporting your data, please include the above sample identification numbers. If possible, these samples should be processed immediately. Each sample should be analyzed for Ca, Mg, Na, K, Cl, SO_4, NO_3, PO_4, pH, and specific conductance. Please indicate the concentration units for your data, and indicate if the nitrogen and phosphorus results are reported as the element or species. Please direct any questions regarding the program to:

Mark A. Nilles
U.S. Geological Survey
Box 25046, MS 401
Denver Federal Center
Denver, Colorado 80225
(303) 236-9278

Sincerely,

Mark A. Nilles

Attachment 23.--Example of submission form for samples sent to the Inland Waters Directorate, Burlington, Ontario

WATER QUALITY PROJECT _____

PROJECT LEADER: _____

WATER QUALITY LABORATORY, IWD

SAMPLE SUBMISSION FORM

SAMPLE SUBMITTER: _____

PHONE _____

NAQUADAT SUBMITTER ID.

LAB #	SCHEMA(S)	# PARM	# CTRS	NAQUADAT STN. ID.	SAMPLE ID	ANALYSES REQUIRED	DATE/TIME COLLECTED	SMPL TYPE	REMARKS

SHADED AREAS FOR WATER QUALITY USE ONLY

SMPL TYPE W:WATER F:FISH S:SEDIMENT
O:OTHER (PLEASE SPECIFY)

Attachment 24.--PSTAT editor file for reading interlaboratory data received from the Central Analytical Laboratory, Illinois State Water Survey, Champaign, Ill.

```
DATA CAL.RAW,

   NV 14,

   FILE CAL.all;

*FMT( T2,C6,T16,C6,T30,C2,T37,N5.2,T42,3N6.3,T61,N5.2,T67,N5.2 /

T14, N5.2,T20,N5.2, N6.3,T37,N6.1,T49,N4.2 )

*LAB STATION, DATE, YEAR, CA, MG, K, NA, N4, NO3, CL, SO4, PO4,

COND, PH

*READ

return$
```

Attachment 25.--Example of analytical results from Hunter, Environmental Science and Engineering, Inc., Gainesville, Florida

ENVIRONMENTAL SCIENCE AND ENGINEERING INC. MAY 1, 1990
USGS INTERLABORATORY STUDY SAMPLES, RECEIVED QUARTER 4, 1989

FIELD GROUP	SEQ #	SAMPLE ID	PH STD. UNITS	COND UMHOS/CM	CA MG/L	MG MG/L	NA MG/L	K MG/L	NH4-N MG/L	SO4 MG/L	NO3-N MG/L	CL MG/L	NO2-N MG/L	TOTAL CATIONS	TOTAL ANIONS	H ION PREDICTED	H ION FOUND	COND PREDICTED	COND DIFF	ION DIFF
W89-40	20	290004	4.63	14.6	0.033	0.053	0.343	0.028	0.099	1.34	0.150	0.743	<0.004	52.2	59.5	30	23.4	14.4	0.91	-10
W89-40	21	290008	4.63	14.6	0.032	0.053	0.350	0.018	0.099	1.34	0.150	0.693	<0.004	52.2	58.2	30	23.4	14.3	1.6	-10
W89-40	22	290012	4.88	6.60	0.012	<0.009	0.035	0.011	0.037	0.587	0.087	0.127	<0.004	18.6	22.0	20	13.2	6.65	-.71	-20
W89-40	23	290016	4.88	6.76	0.009	<0.009	0.041	0.013	0.029	0.575	0.077	0.115	<0.004	18.2	20.8	20	13.2	6.52	3.6	-10
W89-42	20	304002	4.27	24.5	0.012	0.022	0.172	0.045	<0.010	2.93	<0.008	0.293	<0.004	65.1	69.6	60	53.7	24.9	-1.6	-7
W89-42	21	304008	4.24	26.5	0.012	0.022	0.168	0.046	<0.010	2.93	0.074	0.242	<0.004	68.8	73.1	60	57.5	26.5	0.03	-6
W89-42	22	304010	4.23	26.5	0.013	0.021	0.172	0.045	<0.010	2.94	<0.008	0.279	<0.004	70.3	69.3	60	58.9	26.7	-.94	1
W89-42	23	304013	5.60	1.51	<0.003	<0.009	<0.018	<0.005	<0.010	<0.040	<0.008	<0.020	<0.004	3.8	0.98	-.3	2.51	<3.00	0.66	100
W89-46	20	332003	4.73	10.6	0.118	0.027	0.081	0.023	0.125	0.928	0.228	0.152	<0.004	39.8	39.9	20	18.6	10.9	-2.7	-.4
W89-46	21	332009	4.74	10.8	0.116	0.029	0.076	0.022	0.124	0.924	0.228	0.149	<0.004	39.1	39.8	20	18.2	10.7	0.89	-2
W89-46	22	332010	4.74	10.8	0.117	0.028	0.082	0.023	0.123	0.929	0.228	0.145	<0.004	39.3	39.7	20	18.2	10.7	0.84	-1
W89-46	23	332014	4.74	10.6	0.116	0.027	0.084	0.022	0.127	0.927	0.229	0.141	<0.004	39.5	39.6	20	18.2	10.7	-1.2	-.4
W89-50	20	352005	5.46	5.41	0.028	0.046	0.373	0.015	0.040	0.277	0.023	0.706	<0.004	28.1	27.3	3	3.47	4.64	15	3
W89-50	21	352007	5.49	5.41	0.028	0.044	0.379	0.031	0.041	0.266	0.023	0.722	<0.004	28.5	27.5	2	3.24	4.61	16	3
W89-50	22	352009	4.73	9.75	0.018	<0.009	0.019	0.005	0.037	0.910	0.089	0.051	<0.004	23.5	26.7	20	18.6	8.90	9.1	-10
W89-50	23	352013	4.73	9.96	0.017	<0.009	0.022	0.005	0.035	0.914	0.087	0.049	<0.004	23.4	26.6	20	18.6	8.89	11	-10

Note: NH4, NO3, and NO2 are reported as N.

Attachment 26.--Example of analytical results from Inland Waters Directorate, Burlington, Ontario

NATIONAL WATER QUALITY LABORATORY

FINAL SAMPLE ANALYSIS REPORT - MISCELLANEOUS 19-Jul-90
PROJECT ID: 778-89 PAGE: 1
PROJECT TITLE: USGS NETWORK

PROJECT LEADER: T.WILLOUGHBY

Sample		8996123	8996124	8996125	8996126
Field id		90058002	90058008	90058012	90058016
Sampling date		19-Mar-90	19-Mar-90	19-Mar-90	19-Mar-90
Date last analyzed		17-May-90	17-May-90	17-May-90	12-Jun-90
No. containers		01	01	01	01
Date received		19-Mar-90	19-Mar-90	19-Mar-90	19-Mar-90
Exp.completion		14-May-90	14-May-90	14-May-90	14-May-90
Acceptance status		Accpt **	Accpt **	Accpt **	Accpt **
	AWQU CODE				
CA(MG/L)	0019	.04 Y	.05 Y	.04 Y	L.01 Y
MG(MG/L)	0023	.05 Y	.05 Y	.05 Y	L.01 Y
NA(MG/L)	0030	.42 Y	.43 Y	.42 Y	.06 Y1
K(MG/L)	0027	.11 Y	.11 Y	.11 Y	.02 Y1
NH4-[N](MG/L)	0063	*NSSMP* Y1	.824 Y1	*NSSMP* Y	.001 Y
NO3-N/IC(MG/L)	0650	1.53 Y	1.54 Y	1.54 Y	L.01 Y
CL/IC(MG/L)	0649	.99 Y	1.00 Y	1.00 Y	L.01 Y
SO4/IC(MG/L)	0651	10.47 Y	10.53 Y	10.58 Y	L.01 Y
SIO2(MG/L)	0039	*NAPPL* Y	*NAPPL* Y	*NAPPL* Y	*NAPPL* Y
PH(PHUNITS)	0003	3.60 Y	3.58 Y	3.58 Y	5.28 Y
SP.COND.(MUS/C)	0005	*NAPPL* Y	*NAPPL* Y	*NAPPL* Y	*NAPPL* Y
ACDCACO3(MG/L)	0652	*NAPPL* Y	*NAPPL* Y	*NAPPL* Y	*NAPPL* Y
ALKCACO3(MG/L)	0653	*NAPPL* Y	*NAPPL* Y	*NAPPL* Y	*NAPPL* Y

Attachment 27.--Detection limits and precision values for analytes determined by the U.S. Geological Survey, Acid Rain Quality-Assurance Project

Analyte	Detection Limit (mg/L)	Precision (mg/L)
Calcium	0.013	0.053
Magnesium	.010	.005
Sodium	.024	.035
Potassium	.014	.010
Chloride	.052	.022
Nitrate	.048	.015
Sulfate	.009	.027

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