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External Quality-Assurance Programs Managed by the U.S. Geological Survey in Support of the National Atmospheric Deposition Program/National Trends Network

Open-File Report 2005–1024

U.S. Department of the Interior
U.S. Geological Survey

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By Natalie E. Latysh and Gregory A. Wetherbee

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Conversion Factors, Abbreviations, and Datum

Multiply	By	To obtain
centimeter (cm)	0.3937	inch (in.)
foot (ft)	1.609	meter (m)
inch (in.)	2.54	centimeter (cm)
liter (L)	1.057	quart (qt)
meter (m)	3.281	foot (ft)
milliliter (mL)	0.03381	ounce, fluid (oz)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

°F = (1.8 x °C) + 32.

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

°C = (°F - 32) / 1.8.

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

centimeter per ohm (cm/ohm)
gram (g)
gram per milliliter (g/mL)
gram per mole (g/mol)
kilogram (kg)
kilogram per hectare (kg/ha)
kilohm (kΩ)
megaohm (MΩ)
microgram (μg)
microequivalent per liter (μeq/L)
milligrams per liter (mg/L)
mole per liter (mol/L)

Absolute value of x=|x|, where x takes the form of numerical values or algebraic expressions.

Maximum probability of rejecting the null hypothesis when it is true (α).

Water year is the 12-month period October 1 through September 30 and is designated by the calendar in which it ends.

Abbreviation	Full name
ACM	Aerochem Metrics
ADORC	Acid Deposition and Oxidant Research Center (Niigata-shi, Japan)
AES	Atmospheric Environment Service, Environment Canada (Ontario, Canada)
ATL	USGS National Water Quality Laboratory (Atlanta, Georgia)
BQS	Branch of Quality Systems
CAL	Central Analytical Laboratory (Champaign, Illinois)
DEN	USGS National Water Quality Laboratory (Lakewood, Colorado)
DI	Ultrapure (>16.7 megohm, MΩ) deionized water
ESE	ESE, Hunter, Environmental Services, Inc., (1989–93) (Gainesville, Florida); Environmental Science and Engineering, Inc., (1994–2001)
EMSI	Environmental Monitoring and Services (Camarillo, California)
FORF	Field observer report form
GGC	Global Geochemistry Corporation (Canoga Park, California)
H^+	Hydrogen ion
HDPE	High-density polyethylene
HNO_3	Nitric acid
HPS	High Purity Standards, Inc. (Charleston, South Carolina)
IWD	Inland Waters Directorate (Ontario, Canada)
KCl	Potassium chloride
MACTEC	MACTEC, Inc. (Gainesville, Florida)
MOEE	Ministry of Environment and Energy (Dorset, Ontario, Canada)
MPV	Most probable value
MRL	Minimum reporting limit
MSC	Meteorological Service of Canada (Toronto, Ontario, Canada)
NADP	National Atmospheric Deposition Program
NILU	Norwegian Institute for Air Research (Kjeller, Norway)
NIST	National Institute of Standards and Technology
NOS	Network Operations Subcommittee
NTN	National Trends Network
NWQL	USGS National Water Quality Laboratory (Denver, Colorado)
NYSDEC	New York State Department of Environmental Conservation (Albany, New York)
SA	Shepard Analytical Service (Simi Valley, California)
SAS	SAS Institute Inc.
SC	Specific conductance
SHE	Sample-handling evaluation
SRWS	Standard reference water samples
URL	Universal resource locator
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

Horizontal coordinate information is referenced to the *North American Datum of 1983 (NAVD 83).*

External Quality-Assurance Programs Managed by the U.S. Geological Survey in Support of the National Atmospheric Deposition Program/National Trends Network

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Abstract

The U.S. Geological Survey, Branch of Quality Systems, operates the external quality-assurance programs for the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Beginning in 1978, six different programs have been implemented—the intersite-comparison program, the blind-audit program, the sample-handling evaluation program, the field-audit program, the interlaboratory-comparison program, and the collocated-sampler program. Each program was designed to measure error contributed by specific components in the data-collection process. The intersite-comparison program, which was discontinued in 2004, was designed to assess the accuracy and reliability of field pH and specific-conductance measurements made by site operators. The blind-audit and sample-handling evaluation programs, which also were discontinued in 2002 and 2004, respectively, assessed contamination that may result from sampling equipment and routine handling and processing of the wet-deposition samples. The field-audit program assesses the effects of sample handling, processing, and field exposure. The interlaboratory-comparison program evaluates bias and precision of analytical results produced by the contract laboratory for NADP, the Illinois State Water Survey, Central Analytical Laboratory, and compares its performance with the performance of international laboratories. The collocated-sampler program assesses the overall precision of wet-deposition data collected by NADP/NTN.

This report documents historical operations and the operating procedures for each of these external quality-assurance programs. USGS quality-assurance information allows NADP/NTN data users to discern between actual environmental trends and inherent measurement variability.

Introduction

The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) was initiated in 1978 by the Association of State Agricultural Experiment Stations to monitor long-term atmospheric chemistry and the effects pollutants have on aquatic and terrestrial systems (National Atmospheric Deposition Program, 1985; Nilles, 2000). As of fall 2004, precipitation was being collected at 261 sites in the United States, including Puerto Rico and the Virgin Islands (fig. 1). The U.S. Geological Survey Branch of Quality Systems (USGS-BQS) began quality-assurance monitoring for NADP/NTN in 1978. From 1997 through 2004, USGS operated six external quality-assurance programs for NADP/NTN. The quality-assurance programs were intended to assess and document the quality of wet-deposition data for NADP/NTN. The Illinois State Water Survey, Central Analytical Laboratory (CAL), located in Champaign, Illinois, is the contract laboratory for NADP/NTN, analyzing all weekly precipitation samples collected by NADP/NTN. USGS-BQS works closely with CAL in designing, implementing, and monitoring the quality-assurance programs.

Three external quality-assurance programs operated by USGS have been discontinued. The intersite-comparison and the sample-handling evaluation programs were discontinued in 2004. The intersite-comparison program was designed to assess the accuracy and reliability of field pH and specific-conductance (SC) measurements performed by site operators. Chemical changes between field and laboratory measurements render the initial assessment of precipitation chemistry important (Latysh and Gordon, 2004). In January 2003, the blind-audit program was replaced by the sample-handling evaluation program. The blind-audit and sample-handling evaluation programs assessed the effects of sampling equipment, sample handling, shipping, and processing on sample chemistry. The two programs were intended to monitor processes that may introduce contamination to precipitation samples.

Beginning in 1997, the field-audit program, similar to the sample-handling evaluation program, has assessed the effects of sample handling, shipping, and processing but has also considered the effects of field exposure on sample chemistry. Beginning in 1982, the interlaboratory-comparison program has evaluated the performance of CAL and provided a comparability of wet-deposition data collected around the

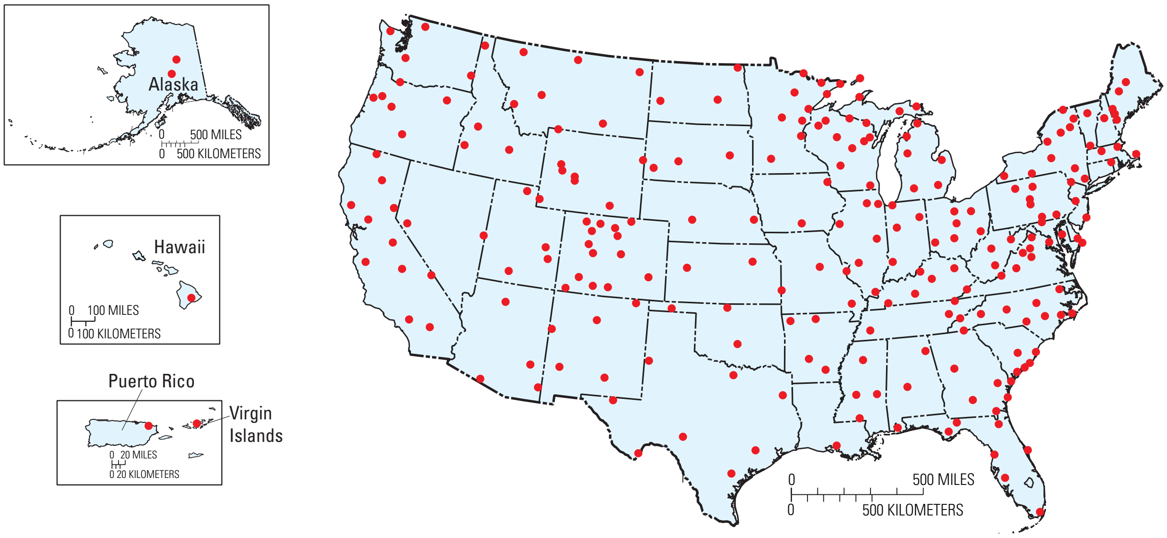


Figure 1. Location of National Atmospheric Deposition Program/National Trends Network sites, fall 2004 (from URL http://nadp.sws.uiuc.edu/).

world. Beginning in 1988, the collocated-sampler program has provided a measure of NADP/NTN's overall variability by comparing data collected from two sets of identical precipitation monitoring instruments situated at an NADP/NTN site. The aim of these programs is to evaluate most of the possible sources of variability in data collected by NADP/NTN. USGS quality-assurance information allows NADP/NTN data users to discern between actual environmental trends and inherent measurement variability.

This report documents procedures used by USGS in external quality-assurance programs in support of NADP/NTN. This report supersedes USGS Water-Resources Investigations Report 90-4029, "Programs and analytical methods for the U.S. Geological Survey acid rain quality-assurance project" (See and others, 1990). Quality-assurance programs are continually evolving, and many changes have occurred since the 1990 publication for evaluating data quality. The procedures outlined in this report have been relevant to the programs since 1997, when the field-audit program was added.

Intersite-Comparison Program

The intersite-comparison program was initiated in 1978 and conducted through December 2004. The intersite-comparison program was conducted on a semiannual basis, during the spring and fall. The program assessed the accuracy of field pH and SC measurements, which NADP/NTN site operators performed when total weekly rainfall exceeded 0.04 in. The program was intended to identify poor field-measurement techniques and defective equipment and to describe the performance of NADP/NTN's pH and SC field measurements. Elimination of the intersite-comparison program was prompted by the discontinuance of field chemistry measurements at NTN sites effective January 4, 2005. NADP members decided that financial resources allocated toward field measurements could be better spent on other aspects of data collection by the network (Lehmann and others, 2004). Laboratory pH and SC measurements continue for all NTN weekly samples.

A flowchart describing the program is provided in figure 2, and a summary of modifications made to the program during its tenure is provided in table 1. In each intersite-comparison study, site operators were asked to determine the pH and SC of a synthetic low-ionic-strength intersite-comparison solution formulated by USGS. USGS made solutions targeting pH and SC values within the interquartile range for precipitation samples collected by NADP/NTN. The pH and SC target values of the solutions used in the program initially were unknown to the site operators. In each study, the median values for pH and SC calculated from all responding site operators were designated as the most probable values (MPVs) of the intersite-comparison solutions. MPVs were revealed to the operators at the end of each study. In each intersite-comparison study, accuracy goals for pH and SC measurements were determined according to MPVs of the intersite-comparison solution. A followup to each intersite-comparison study was conducted for sites whose analyses did not meet the accuracy goals for pH and SC, requiring measurements of additional solutions to help the site operators improve their techniques and (or) identify defective equipment.

Sample Preparation

The diverse pH and SC values of intersite-comparison solutions reflect the varying values of these constituents in natural precipitation collected by NADP/NTN. At the beginning of each intersite-comparison study, target pH and SC values were selected. A spreadsheet was used to calculate the amount of nitric acid (HNO_3) and potassium chloride (KCl) required to achieve the desired target pH and SC values for each study. All

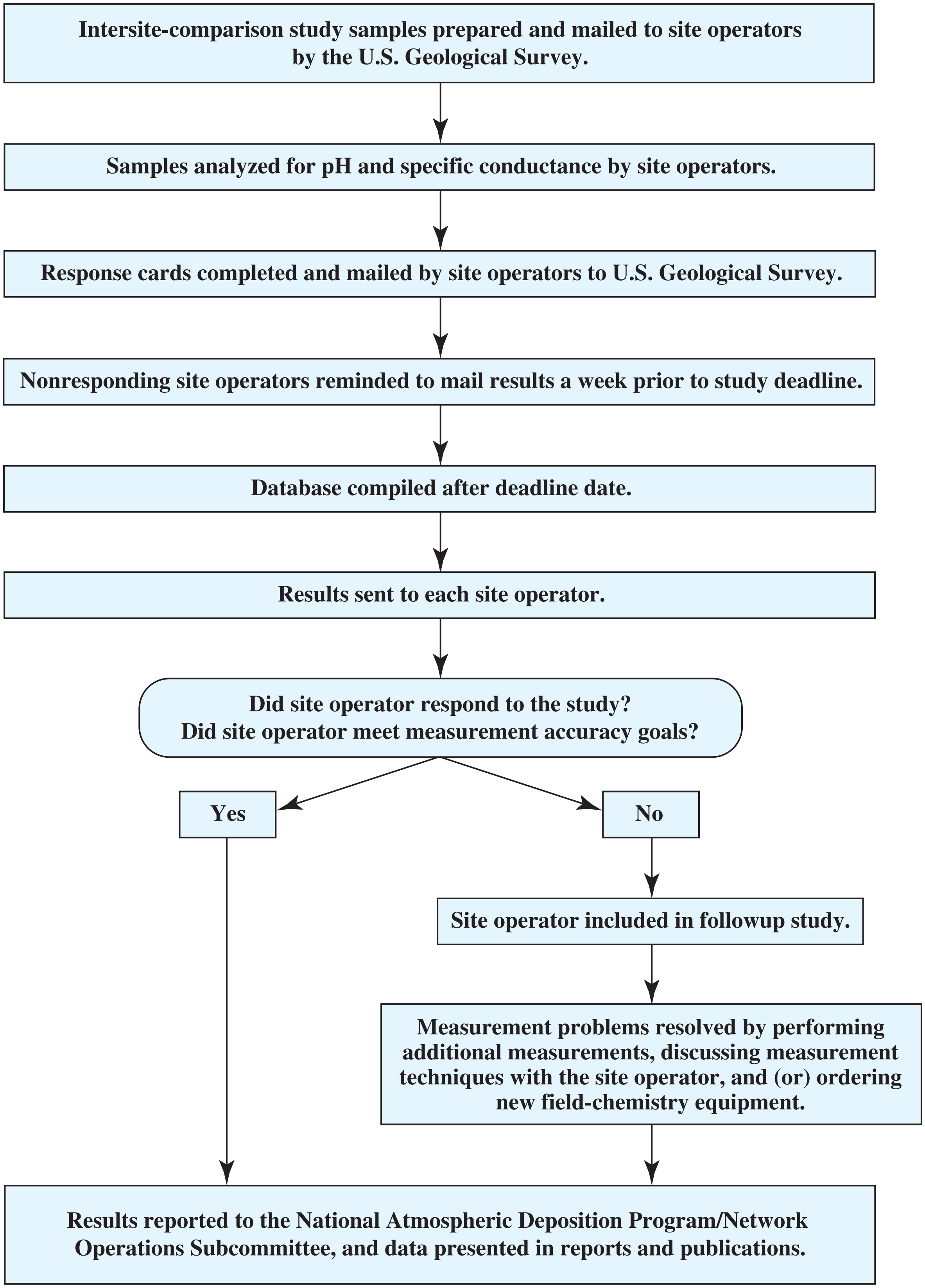


Figure 2. Flowchart describing intersite-comparison program.

Table 1. Procedural changes and additions made to the intersite-comparison program.

[CAL, Illinois State Water Survey, Central Analytical Laboratory; HNO_3, nitric acid; USGS, U.S. Geological Survey; µS/cm, microsiemens per centimeter at 25 degrees Celsius; SC, specific conductance; USGS-BQS, U.S. Geological Survey Branch of Quality Systems; SAS, SAS Institute Inc.]

Date	Modification
November 1978	First intersite-comarison study completed by CAL using a dilute HNO_3 solution.
June 1980	Semiannual site operator training initiated at CAL.
October 1981	USGS assumes responsibility for the intersite-comparison program and begins conducting studies on a semiannual basis.
October 1981 to May 1988	USGS reanalyzes aliquots of test samples when site operaators fail to meet acceptance criteria.
February 1983	USGS completes pH and SC stability experiments confirming that dilute HNO_3 solutions used in intersite-comparison studies are stable for at least 10 weeks.
December 1983	CAL begins supplying pH electrodes to site operators.
October 1984	Majority of site operators using pH electrodes supplied by CAL.
December 1984	Site visitation program initiated. Sites are visited by designated quality-assurance personnel to examine data-collection techniques.
February 1985	Frequency of intersite-comparison studies increases from twice per year to four times per year.
July 1987	Semiannual intersite-comparison studies resumed.
January 1995	Accuracy goals for SC measurements changes from $\pm$4 µS/cm for all target SC values to $\pm$2 µS/cm for SC values of 10 µS/cm or less, $\pm$4 µS/cm for SC values greater than 10 µS/cm and less than 60 µS/cm, and $\pm$6 µS/cm for SC values greater than 60 µS/cm.
May 2000	Site operators able to submit results electronically, not having to mail the response postcards to USGS.
January 2002	Four intersite-comparison solutions no longer submitted for each intersite-comparison study to USGS National Water Quality Laboratory for nitrate analysis, which was used to confirm the pH target value.
June 2003	Four most-recent intersite-comparison solutions are stored in the cooler at USGS-BQS Laboratory. Older solutions are discarded because they are likely to undergo chemical changes.
June 2004	Intersite-comparison program data are stored in Microsoft Access instead of SAS datasets.
December 2004	The intersite-comparison program is eliminated after study 53 is completed.

calculations, sample preparation procedures, and a synopsis of the submitted results were recorded in the intersite-comparison program notebook by USGS for reference and permanent record.

Intersite-comparison solutions were formulated by USGS and consisted of a mixture of HNO_3 and ultrapure (>16.7 megohm, MΩ) deionized (DI) water. KCl was added to the solution when needed to adjust the SC to the target value. Figures 3 and 4 display the median and target pH and SC values, respectively, for intersite-comparison solutions used in studies 20 through 53, conducted from fall 1987 through fall 2004. Median pH and SC values in these studies ranged from 4.01 to 5.64 standard units and 0.5 to 43.2 µS/cm, respectively.

Prior to assembling an intersite-comparison solution, concentrated HNO_3 was diluted 1 to 50 with DI water to minimize error associated with pipetting small volumes. The following equation was used to calculate the amount of dilute HNO_3 required for mixing with DI water in a 51-L carboy to achieve the pH target value:

$$HNO_3(mL) = \frac{100wMVu}{pd}, \qquad (1)$$

where

w = atomic weight of HNO_3 (63.0128 g/mol);
M = hydrogen ion (H^+) concentration (moles per liter) = 10^{-pH};
V = volume of solution being prepared (51 L);
u = dilution factor used to dilute concentrated HNO_3 (50);
p = weight percentage of HNO_3 (70.4 percent); and
d = density of concentrated HNO_3 (1.41 g/mL).

The following equation was used to calculate the SC of the HNO_3 and DI water mixture in the 51-L carboy:

$$K = 1{,}000\,(M{*}C_1 + M{*}C_2), \qquad (2)$$

where

K = SC (microsiemens per centimeter at 25 °Celsius);
M = H^+ concentration (equivalents per liter);
C_1 = SC of NO_3^- (71.44 cm/ohm); and
C_2 = SC of H^+ (349.8 cm/ohm).

If the target SC value was greater than that produced solely by dilution of HNO_3, KCl was added to the solution. The following equation was used to determine the amount of KCl required to increase the SC:

$$W_{KCl} = \{[T - (M * 4.21{*}10^5) - (2.228{*}10^{-7}/M)]/1.9837\} * V, \qquad (3)$$

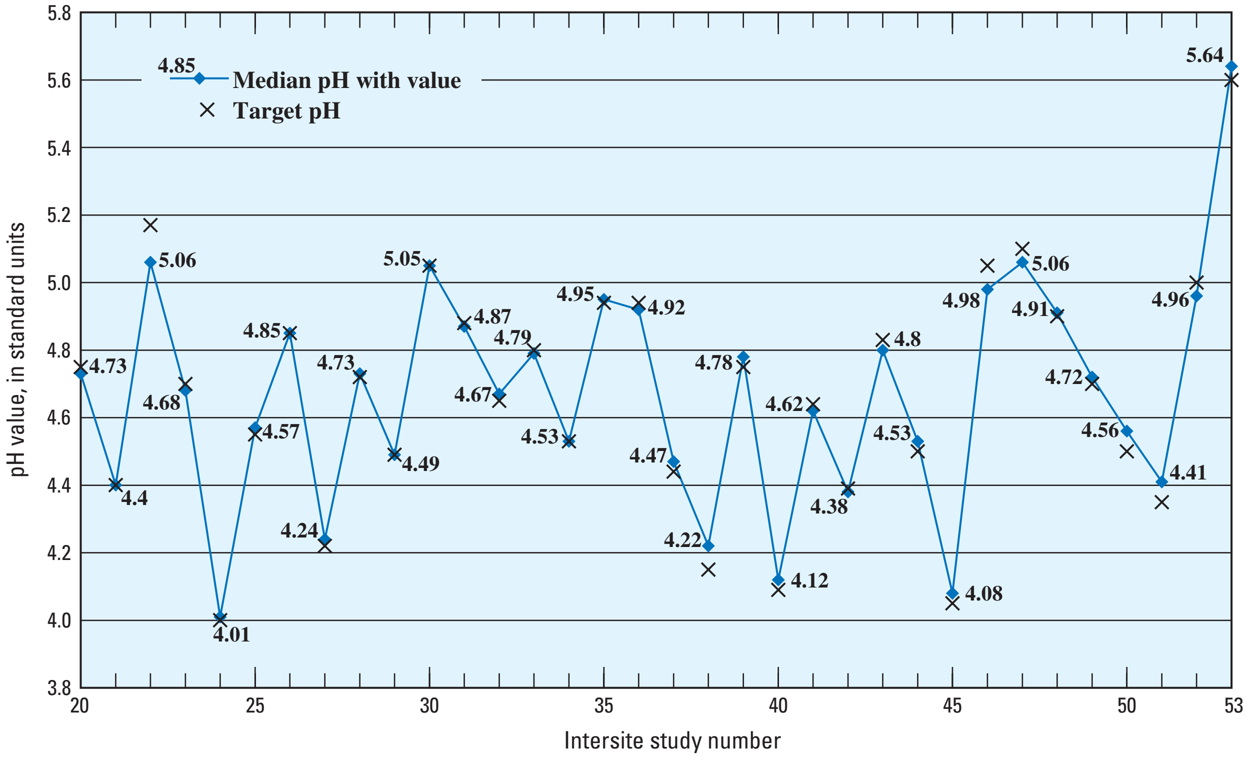


Figure 3. Distribution of median and target pH values for solutions used in intersite-comparison studies 20 through 53, completed fall 1987 through fall 2004.

where

W_{KCl} = weight of KCl required for the desired SC (milligrams);

T = target SC (microsiemens per centimeter at 25 °C);

M = H^+ concentration (moles per liter) = 10^{-pH}; and

V = volume of solution being prepared (51 L).

Prior to solution preparation, KCl was dried in an oven at 110 °F for 24 hours. The carboy was filled with DI water for a minimum of 48 hours prior to sample preparation and stored to leach contamination from the carboy. Then, the stored DI water was discarded. This ensured a clean container for sample preparation and reduced the chemical effects of the plastic container on the solution. Once the diluted HNO_3 and KCl were combined with DI water, the carboy was placed on a magnetic stirrer, a Teflon-coated magnetic stir bar was added, the carboy lid was sealed, and the solution was mixed for 48 hours.

Sample Bottling and Distribution

The intersite-comparison solution was bottled in 125-mL high-density polyethylene bottles (HDPE) that had been filled and stored with DI water for a minimum of 1 week. The bottles were rinsed several times with DI water and conditioned with the intersite-comparison solution prior to bottling. Approximately 160 mL of solution were required to condition and fill each bottle. The bottles were filled with the intersite-comparison solution, capped, and labeled. The labels identified the intersite-comparison study number, the date the solution was bottled, and the last name of the person preparing the solution.

Every 50th bottle was removed from the sample group, and pH and SC were measured by USGS prior to shipment to site operators. Consistency in measurement results for the target analytes among the approximately six separated samples indicated thorough mixing. Discrepancies of greater than 0.05 standard unit for pH measurements and greater than 3 percent for SC measurements required the solution to be remade. Approximately 8 L of solution were retained by USGS to use for intersite-comparison followup studies and quality control for the laboratory pH meters and SC probes. These samples were stored refrigerated by USGS for 2 years. Older solutions were discarded because they may have been prone to chemical changes.

The median pH and median SC values calculated from all measurements submitted by site operators prior to the study deadline were considered to be MPVs of the intersite-comparison solutions. The target and median pH and SC values calculated from all submitted results were typically in close agreement. Median absolute differences between the target and the median values calculated from all submitted results for intersite-comparison studies 6 through 53, conducted from

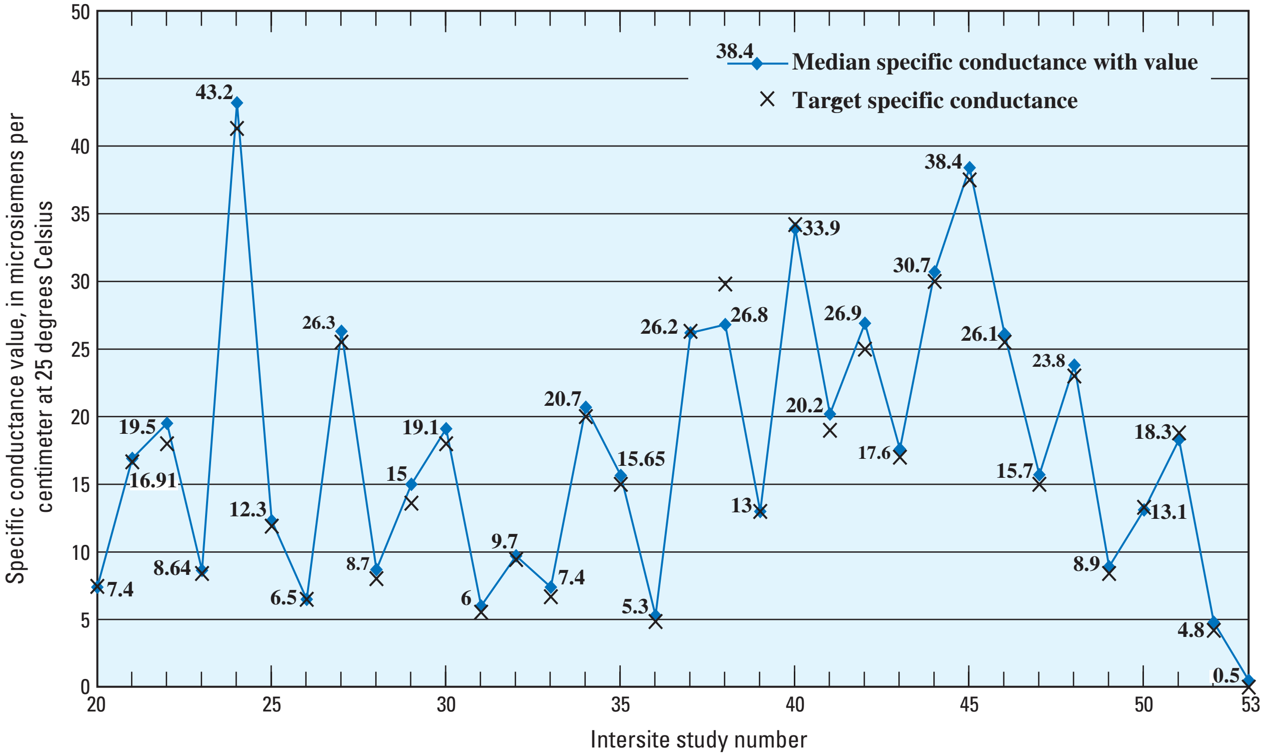


Figure 4. Distribution of median and target specific-conductance values for solutions used in intersite-comparison studies 20 through 53, completed fall 1987 through fall 2004.

1982 through 2004, were 0.02 standard unit for pH and 0.6 µS/cm for SC.

Once the solution was bottled and the pH and SC values were verified to be comparable to the target values, the bottles were mailed to participating site operators. Prior to each intersite-comparison study, CAL provided USGS with an updated list of contact and address information for each participating site. In each intersite-comparison study, each NADP/NTN site that routinely performed field chemistry measurements received a box containing the intersite-comparison solution, instructions for completing the intersite-comparison study (Attachment 1), and an addressed postcard to USGS for recording the measured pH and SC values (Attachment 2). Site operators who collected precipitation from two sites were mailed only one intersite-comparison sample because they used the same equipment for the separate field measurements.

The site operator was asked to retain the remaining intersite-comparison solution after performing the required pH and SC measurements until notified of the results. If the site operator did not meet the accuracy goals, the remaining intersite-comparison solution was used for additional measurements during the followup portion of the study. Due to the high employee turnover and seasonal nature of employment at some sites, a set of detailed instructions, modified from CAL's documents, was mailed annually with the intersite-comparison sample. The instructions included guidelines for making successful pH (Attachment 3) and SC (Attachment 4) measurements. These guidelines also were available on the precipitation chemistry project Web site (http://bqs.usgs.gov/). Most site operators were trained in performing field measurements either through CAL's annual training course, use of NADP/NTN site operation manual, a training video "Every Tuesday Morning" issued by the NADP Program Office, or by other personnel in the office. Therefore, the instructions were intended as reminders and helpful references for troubleshooting potential problems.

As of spring 2003, approximately 75 percent of the site operators had completed CAL's site operator training course (Kathy Douglas, Illinois State Water Survey, written commun., 2003). The 3-day course, conducted annually, covers all aspects of site operation including sample collection, field measurement techniques, participation in the external quality-assurance programs conducted by USGS, and equipment maintenance. In addition, external site auditors visit each NADP/NTN site approximately every 3.5 years. Among other evaluations, they assessed field chemistry measurement techniques and resolved potential problems until field chemistry was discontinued in January 2005.

Data Analysis

Results submitted prior to the study's deadline were entered into a spreadsheet and imported into a database where they were formatted and are archived. Intersite-comparison data are stored in Microsoft Access, and SAS Institute Inc. (SAS) is the principal software package used to analyze intersite-comparison data.

Site operators were given a deadline of 45 days following sample mailing to report their results. Ten days prior to the deadline, a reminder letter was mailed to operators who had not yet responded. The median pH and SC values, calculated from all results submitted prior to the study's deadline, were used to establish a range of acceptable values. Equations derived from multiple regression analysis that was based on the median pH value were used to establish the acceptable pH range (upper and lower bounds) for each intersite-comparison study. The following equations, developed by Mark Wotawa (Colorado State University) and John Gordon (USGS) in 1995 (John Gordon, USGS, written commun., 2003), were used to establish the acceptable pH range:

The median pH value was converted to H^+ ion activity (microequivalents per liter, µeq/L):

$$[H^+_{median}] = (10^6 \mu eqL^{-1}/eqL^{-1}) \text{ x } 10(^{-1 \text{ x median pH}}) . \quad (4)$$

The upper bounds and lower bounds defining the accuracy goals for the median pH value were determined:

$$[H^+_{upper}] = [H^+_{median}] - 1.68 \text{ x } 10^{(2.80 - 0.492 \text{ x median pH})} ,$$
and (5)

$$[H^+_{lower}] = [H^+_{median}] + 2.72 \text{ x } 10^{(2.80 - 0.492 \text{ x median pH})} . \quad (6)$$

The hydrogen ion activity values were converted back to pH units:

$$\text{Upper bound pH} = [-\log_{10}(H^+_{upper}) \text{ x } (eqL^{-1}/10^6 \mu eqL^{-1})], \text{ and} \quad (7)$$

$$\text{Lower bound pH} = [-\log_{10}(H^+_{lower}) \text{ x } (eqL^{-1}/10^6 \mu eqL^{-1})]. \quad (8)$$

The analysis used data obtained from intersite-comparison program studies numbered 5 through 32, conducted between 1981 and 1993. Equations 4 through 8 yielded larger acceptable pH ranges for solutions with higher pH target values than for solutions with lower pH target values. The pH of low-ionic-strength solutions is more difficult to measure accurately than the pH of solutions with higher hydrogen-ion concentrations.

The SC goals for each study were based on the median value calculated from SC determinations submitted by site participants. Once the median SC was computed, the upper and lower limits of the accuracy goals for the SC measurements were determined by the algorithm in table 2.

Late responses were recorded but were not included in statistical calculations. Within 3 weeks of an intersite-comparison study completion, site operators were mailed a letter stating their results with the study's descriptive statistics (Attachment 5) and a scatterplot of pH in relation to SC (Attachment 6), which included the range of accuracy goals for both measurements. This information allowed site operators to gage their performance and compare their measurements with those submitted by all NADP/NTN site operators. Results from each study were provided to the NADP Program Office, which considered performance in the intersite-comparison studies prior to using the site's field chemistry measurements in the annual summary reports. The data were presented to the NADP/Network Operations Subcommittee (NADP/NOS) annually.

Intersite-Comparison Followup Study

Site operators who did not meet the accuracy goals for pH and (or) SC measurements or who did not respond to the intersite-comparison study were included in the followup study. Measurement accuracy of pH and SC was evaluated for each site operator participating in the followup study by calculating standardized z-values, which are similar to z-scores described by Iman and Conover (1983). A z-score was used to indicate how far the value deviated from the distribution's mean. To eliminate the need for normally distributed data, z-scores described by Iman and Conover (1983) were modified into z-values by replacing the parametric standard deviation value with the nonparametric f-pseudosigma value as the statistical reference (Hoaglin and others, 1983). Use of f-pseudosigma values eliminated effects from outlying data points. Z-scores and z-values are calculated using the following equations:

$$\text{Z-score} = \frac{x - x_1}{S}, \text{ and} \quad (9)$$

$$\text{Z-value} = \frac{x - x_2}{\text{fps}}, \quad (10)$$

where

x = an individual observation;
x_1 = mean of all observations;
x_2 = median of all observations;
S = standard deviation of all observations; and
fps = f-pseudosigma of all observations is computed with the equation:

$$\frac{\text{75th} - \text{25th percentile}}{1.349} . \quad (11)$$

Table 2. Algorithm for specific-conductance accuracy goals for the intersite-comparison program.

[µS/cm, microsiemens per centimeter at 25 degrees Celsius; <, less than; >, greater than]

Median specific-conductance range	Specific-conductance accuracy goals
Median value < 10 µS/cm	Median value ± 2 µS/cm
10 µS/cm < Median value < 60 µS/cm	Median value ± 4 µS/cm
Median value > 60 µS/cm	Median value ± 6 µS/cm

The use of z-values allowed an objective comparison of a site operator's performance with the rest of the population and provided the degree of deviation from the median value. The z-value incorporated the difficulty of measuring lower hydrogen-ion concentrations by incorporating the f-pseudosigma, which is calculated using the interquartile range of all observations. The interquartile range for intersite-comparison solutions increased with increasing pH values due to the greater difficulty in accurately measuring higher pH solutions (Latysh and Gordon, 2004).

In the followup study, absolute z-values were calculated for results submitted by site operators that did not meet the accuracy goals for the intersite-comparison study. Proxy numbers were assigned to the absolute z-values according to the algorithm in table 3. A proxy number of 1 was not used in these calculations to enhance the differentiation between site operators whose performance was consistently unacceptable and site operators who occasionally failed to meet the accuracy goals for the intersite-comparison studies. Results from each site operator in the three most-recent intersite studies were evaluated to identify consistent performance and to determine which of the four followup levels the site was assigned. The proxy numbers for the three most-recent intersite-comparison studies were summed and used to determine the corresponding followup level for the site, outlined in table 4.

The followup level requirements were:

Level 1—Site operators received a letter (Attachment 7) stating that they did not meet the accuracy goals for the intersite-comparison study. They were advised to review their measuring techniques and were encouraged to voluntarily remeasure their intersite-comparison solution.

Level 2—Site operators received a letter (Attachment 8) stating that because they did not meet the accuracy goals for the intersite-comparison study, they should remeasure their intersite-comparison solution, complete the enclosed postcard for recording their measurements, and return it to USGS. Site operators who did not participate in the initial phase of the intersite-comparison study were categorized in level 2 of the followup study. They were mailed a cover letter (Attachment 9), the study's intersite-comparison solution, and a postcard for reporting results. Once more, these site operators were asked to determine the pH and SC.

Level 3—Site operators received a letter (Attachment 10) stating that because they did not meet the accuracy goals for the intersite-comparison study, they should remeasure the intersite-comparison solution along with an additional solution that was mailed to them. Two postcards addressed to USGS were provided for recording results for both of the solutions each operator was asked to measure.

Level 4—Site operators received a letter (Attachment 11) stating that because they did not meet the accuracy goals for the intersite-comparison study, they should remeasure the intersite-comparison solution along with two additional solutions that were mailed to them. Three postcards addressed to USGS were provided for recording results for each of the solutions each operator was asked to measure.

Additional solutions that were used for evaluating site operators' performance in levels 3 and 4 of the intersite-comparison followup studies were derived from two of the four most-recent intersite-comparison studies. The acceptable pH and SC ranges, determined for these solutions in each intersite-comparison study, were recorded in the intersite-comparison notebook. To ensure sample stability, BQS personnel verified the pH and SC values prior to including a solution in the followup evaluation.

All site operators participating in the intersite-comparison followup evaluation were provided with guidelines to improve measurement accuracy (Attachments 3, 4). Site operators were allowed approximately 21 days to submit their followup results. The results were evaluated individually, and a letter was mailed to each site operator describing their performance. Their reported values for the followup evaluation were compared with the accuracy goals for the solutions that were recorded in the intersite-comparison notebook. If followup measurements were unacceptable, the site operator was contacted by phone to discuss potential problems. Often the operator was encouraged to purchase new equipment.

Site operators who did not respond to an intersite-comparison followup study were contacted to determine the reason for the lack of participation in this mandatory program. Due to seasonality of many outdoor jobs and employment of student apprentices, approximately 25 percent of the sites annually change operators (Kathy Douglas, Illinois State Water Survey, written commun., 2003). A change in operators may have affected a site's participation in the quality-assurance studies. However, most operators recognized the importance of these studies and were willing to participate or make up

Table 3. Algorithm for assigning proxy numbers to absolute z-values.

[<, less than; >, greater than]

Z-value for individual intersite-comparison studies	Proxy number
< 1.5	0
1.5 – 2.5	2
> 2.5	3

Table 4. Algorithm for assigning followup levels to summed proxy numbers for three most-recent intersite-comparison studies.

[>, greater than]

Summed proxy numbers for three most-recent intersite-comparison studies	Followup level
0 – 2	1
3 – 4	2
5 – 6	3
> 7	4

measurements that they had missed. Data for each followup study are archived by USGS, and a synopsis of the followup results are recorded in the intersite-comparison program notebook and summarized in USGS reports (Gordon, 1999; Wetherbee and others, 2004).

Blind-Audit and Sample-Handling Evaluation Programs

The sample-handling evaluation (SHE) program was initiated in January 2003, replacing the blind-audit program, which was conducted since 1982. The SHE program evaluated the effects that sampling equipment, sample handling, processing, and shipping procedures had on reference solution chemistry to detect bias in weekly precipitation samples collected by NADP/NTN. A flowchart outlining the program is illustrated in figure 5.

Sample Processing

For processing the SHE sample, the site operator was asked to use a clean field bucket, a clean 1-L HDPE sample bottle, and a field observer report form (FORF) from their supplies provided by CAL. To begin sample processing, the site operator removed the bucket and lid from the plastic bags in which they were shipped. The operator poured 75 percent of the SHE solution into the clean field bucket. A line on the solution bottle marked the 25 percent of the solution that should have remained in the bottle. The operator swirled the solution, which made contact with the bucket surface, and placed the lid on the bucket. After a minimum of 24 hours, the operator transferred the SHE sample from the bucket into a clean 1-L HDPE sample bottle that was routinely used to ship samples to CAL. Site operators who received a 2-L SHE sample were asked to discard excess solution that did not fit into the 1-L sample bottle after the processing steps were completed. The residence time of the solution in the sample-collection bucket could have varied from a minimum of 24 hours to 6 days, replicating the duration a natural precipitation sample may spend in a field bucket. The operator extracted four aliquots of the solution and conducted field pH and SC measurements. Sites that did not perform field chemistry measurements were exempt from performing these analyses.

A postcard addressed to USGS was provided for recording the field chemistry measurements and the times and dates the solution was added to and removed from the bucket. The site operator completed a FORF, listing similar information that was included in the postcard. The FORF, the 75 percent of the solution that resided in the bucket and was transferred to a 1-L sample-collection bottle, the 25 percent of the solution remaining in the original bottle, and the bucket and lid used to process the SHE sample were placed into a shipping mailer that was routinely used to ship precipitation samples and mailed to CAL. The postcard was mailed to USGS, indicating the sample had been processed and sent to CAL. Prior to the third quarter of 2003, the site operator was provided with an additional postcard for reporting results to the NADP Program Office, in addition to USGS. However, this information had little benefit; therefore, postcards addressed to the NADP Program Office were no longer provided with SHE and field-audit samples.

Similar to the SHE program, the blind-audit program also assessed bias due to sampling equipment and sample processing, but it required the bucket samples, the 75 percent of the solution poured into a collection bucket, to be disguised as actual precipitation samples. The identity of the bucket samples was concealed to avoid special care by CAL personnel. The bottle sample, the 25 percent of the solution remaining in the original bottle, was shipped to CAL separate from the bucket samples. Therefore, the bucket and bottle samples often were introduced to the laboratory analysis train on different days. This introduced an additional source of laboratory variability, making it difficult to separate sample-handling, processing, and shipping effects. To isolate the effects of sampling equipment, sample handling, processing, and shipping from laboratory variability, the quality-assurance samples shipped to CAL were no longer disguised and were analyzed in sequence in the SHE program.

Each annual quarter, 25 sites were randomly selected from all regions of the country to participate in the SHE program. Every site in NADP/NTN participated in the SHE program once before a site was asked to participate again. A site participated in the program approximately once every 2.5 years. Prior to sample mailing, the NADP Quality Assurance Manager from the NADP Program Office reviewed the sites selected by USGS to ensure every site was adequately represented in the program.

Site operators were assigned a specific date when they should process their SHE sample, which was on a Tuesday, to coincide with the weekly site visit when they collected the previous week's precipitation sample and replaced the sample-collection bucket. The SHE samples were mailed weekly, arriving at the sites 1 week prior to their scheduled processing date. Along with the SHE sample, the site operator received a cover letter (Attachment 12), instructions for processing the SHE sample (Attachment 13), a FORF (Attachment 14), and a postcard for reporting the residence time of the SHE sample in the clean bucket and the field chemistry measurements to USGS (Attachment 15). A week prior to the submission date, the NADP Quality Assurance Manager sent a postcard to the sites scheduled to submit a SHE sample, providing a short description of sample processing and reminding them to process the sample. Each site was assigned a dummy number, ranging from 1 to 25 (DU01, DU02, and so forth), which identified the sequence of the sites scheduled to participate during the quarter.

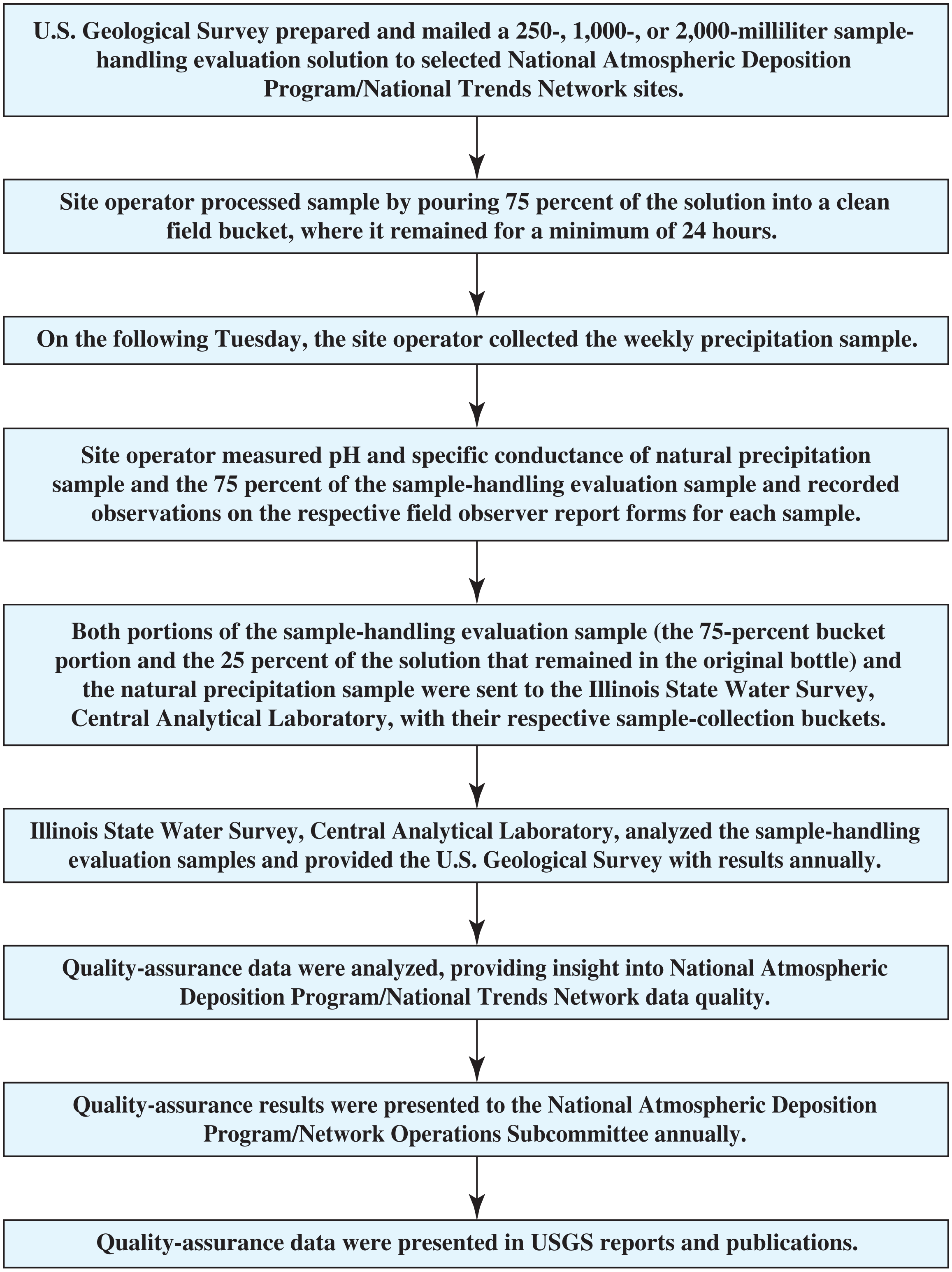


Figure 5. Flowchart describing sample-handling evaluation program.

Sample Preparation

Samples used in the SHE program included DI water samples prepared by USGS and five standard reference samples with certified U.S. National Institute of Standards and Technology (NIST) traceable concentration values. The standard reference samples were prepared by High Purity Standards, Inc. (HPS) located in Charleston, South Carolina, and diluted by USGS.

Stock solutions used in the SHE, field-audit, and interlaboratory-comparison programs were diluted using the same protocols. Prewashed and prerinsed 2,000-, 4,000- or 6,000-mL volumetric flasks were used to make the dilutions. These flasks were stored filled with diluted HNO_3 when not in use. The sample bottles were stored filled with DI water for a minimum of 1 week and rinsed three times with DI water prior to sample preparation. The required volume of the stock solution was pipetted into the volumetric flask and diluted 1 to 500 with DI water. The solutions were mixed for approximately 15 minutes on a magnetic stirrer with a Teflon-coated magnetic stir bar. HDPE sample bottles were conditioned with approximately 40 mL of the solution prior to bottling.

Samples for the SHE program were prepared several weeks prior to the beginning of each quarter. The solution bottles were sealed and labeled with the solution identification, manufacturer-assigned lot number, expiration date, dummy identification, identification of site assigned to process the sample, name of USGS employee making the solution, and the scheduled bucket off-date, a Tuesday, when the sample was scheduled to be processed by the site operator. The solution bottles also were labeled with a synoptic description of sample processing, instructing the site operator to pour 75 percent of the solution into a clean collection bucket.

The analyte concentrations in the solutions used in the SHE program were intended to represent the range of concentrations measured in precipitation samples collected by NADP/NTN. With the advent of the SHE program in January 2003, precipitation sample volumes collected by NADP/NTN were evaluated to determine if the quality-assurance sample volumes used in the blind-audit and field-audit programs adequately represented the precipitation volume distribution. Larger sample volumes were found to be underrepresented, prompting USGS to replace the 250-, 500-, and 1,000-mL volumes with 250-, 1,000-, and 2,000-mL volumes, respectively, for samples used in the blind-audit, SHE, and field-audit programs. Six solutions, with different analyte concentrations, and three sample volumes were used in the SHE program to assess how sample handling affected sample chemistry in solutions with different concentrations and volumes. A description of the solutions and a summary of target values for the standard reference solutions used in USGS quality-assurance programs, including the SHE program, are provided in tables 5 and 6, respectively.

The distribution of solution types and volumes for SHE samples mailed to site operators was consistent each quarter. The sites were randomly assigned a specific solution type and volume. The distribution of the solution types and their respective volumes used in the SHE program are listed in table 7.

Data Records

The site operator mailed the preaddressed postcard to USGS after processing the SHE sample. USGS personnel transferred information from the postcard to the SHE program database and filed the postcard for record. Card submission

Table 5. Solutions used in the sample-handling evaluation, field-audit, and interlaboratory-comparison programs.

Solution	Agency preparing the solution	Description
Natural precipitation[1]	Illinois State Water Survey, Central Analytical Laboratory	Natural wet-deposition samples collected at National Atmospheric Deposition Program/National Trends Network sites and bottled by the Illinois State Water Survey, Central Analytical Laboratory.
Ultrapure[1, 2, 3]	U.S. Geological Survey	Deionized water with a measured resistivity greater than 16.7 megohm.
SP-1[1, 2] SP-2[1, 2, 3] SP-3[3] SP-5[1, 2] SP-97[1, 2] SP-98[1, 2]	High Purity Standards, Inc. U.S. Geological Survey	National Institute of Standards and Technology certified reference solutions prepared by High Purity Standards, Inc. and diluted by the U.S. Geological Survey.

[1] Solution used in the interlaboratory-comparison program.

[2] Solution used in the sample-handling evaluation program.

[3] Solution used in the field-audit program.

Table 6. Target values for solutions used in the sample-handling evaluation, field-audit, and interlaboratory-comparison programs.

[Significant figures vary due to differences in laboratory precision. Ca^{2+}, calcium; Mg^{2+}, magnesium; Na^{+}, sodium; K^{+}, potassium; NH_4^{+}, ammonium; Cl^{-}, chloride; NO_3^{-}, nitrate; SO_4^{2-}, sulfate; pH, in standard units; specific conductance, in microsiemens per centimeter at 25 degrees Celsius; < MRL indicates value less than minimum reporting limit]

Solution	[1]Ca^{2+}	[1]Mg^{2+}	[1]Na^{+}	[1]K^{+}	[1]NH_4^{+}	[1]Cl^{-}	[1]NO^{3-}	[1]SO_4^{2-}	[2]pH	[2,3]Specific conductance
Ultrapure[4, 5, 6]	< MRL	< MRL	< MRL	< MRL	< MRL	< MRL	< MRL	< MRL	5.55	1.3
SP–1[4, 6]	0.460	0.092	0.420	0.076	0.68	0.590	2.10	3.85	4.42	30
SP–2[4, 5, 6]	.460	.070	.360	.060	.56	.450	3.00	2.33	4.51	25
SP–3[5]	.159	.049	.111	.023	.14	.170	1.08	.960	4.78	11
SP–5[4, 6]	.575	.168	.454	.083	.71	.720	2.55	4.51	4.33	36
SP–97[4, 6]	.130	.019	.024	.019	.29	.056	1.18	1.14	4.22	16
SP–98[4, 6]	.016	.038	.208	.061	.12	.234	.570	2.43	4.16	18

[1] Concentration certified by the National Institute of Standards and Technology.

[2] Concentration not certified by the National Institute of Standards and Technology. Value was obtained as the median of all the blind-audit, field-audit, and interlaboratory-comparison samples analyzed in 2001.

[3] At 25 degrees Celsius and 1 atmosphere pressure (Hem, 1985).

[4] Used in the sample-handling evaluation program.

[5] Used in the field-audit program.

[6] Used in the interlaboratory-comparison program.

Table 7. Solution names, sample volumes, and number of samples used in the sample-handling evaluation program each annual quarter.

[mL, milliliters]

Solution name	Sample volume (mL)	Number of samples
Ultrapure deionized water	250	4
SP–1	250	3
SP–2	250	3
SP–5	250	3
SP–5	1,000	3
SP–5	2,000	3
SP–97	250	3
SP–98	250	3

was evidence that the SHE sample had been submitted. When CAL did not receive a scheduled SHE sample from a site, the NADP Quality Assurance Manager contacted the site and USGS. Sites that could not process the sample on the designated date were rescheduled, preferably within the same quarter.

CAL supplied USGS with analytical results from the SHE program on a yearly basis. USGS made statistical interpretations of analytical data, which were published in annual reports and presented to NADP/NOS. All SHE data are archived in SAS and Microsoft Access databases, which are stored and backed up on a file server.

Two sets of analyses were produced for each SHE sample—one for 75 percent of the solution that was transferred to the sample-collection bucket, known as the bucket portion, and one for the 25 percent of the solution that remained in the original bottle mailed to the site operator, known as the bottle portion. Analyte concentrations from the bucket portion, which was subject to all the same field and laboratory handling and processing steps as an environmental precipitation sample, were compared with those from the minimally handled bottle portion. Paired concentration differences between the bucket and bottle portions may have indicated network bias due to possible contamination introduced during standard handling and processing.

Selected statistics (from SAS software) used for reporting the paired bucket-bottle differences included median and other quartile values, the f-pseudosigma, and relative and absolute percentage differences. Boxplots commonly were presented to illustrate the distribution of the differences for different sample volumes and concentrations. A Wilcoxon signed-ranks test and a paired t-test were used to determine if there were statistically significant relations between bucket-minus-bottle differences and analyte concentrations. A Kruskal-Wallis test was performed for determining if statistically significant differences due to sample handling existed for paired bucket-bottle concentrations by sample volume. These statistical methods are explained in Ott (1993), and examples of these statistics are presented in the annual reports for USGS quality-assurance programs (Gordon, 1999).

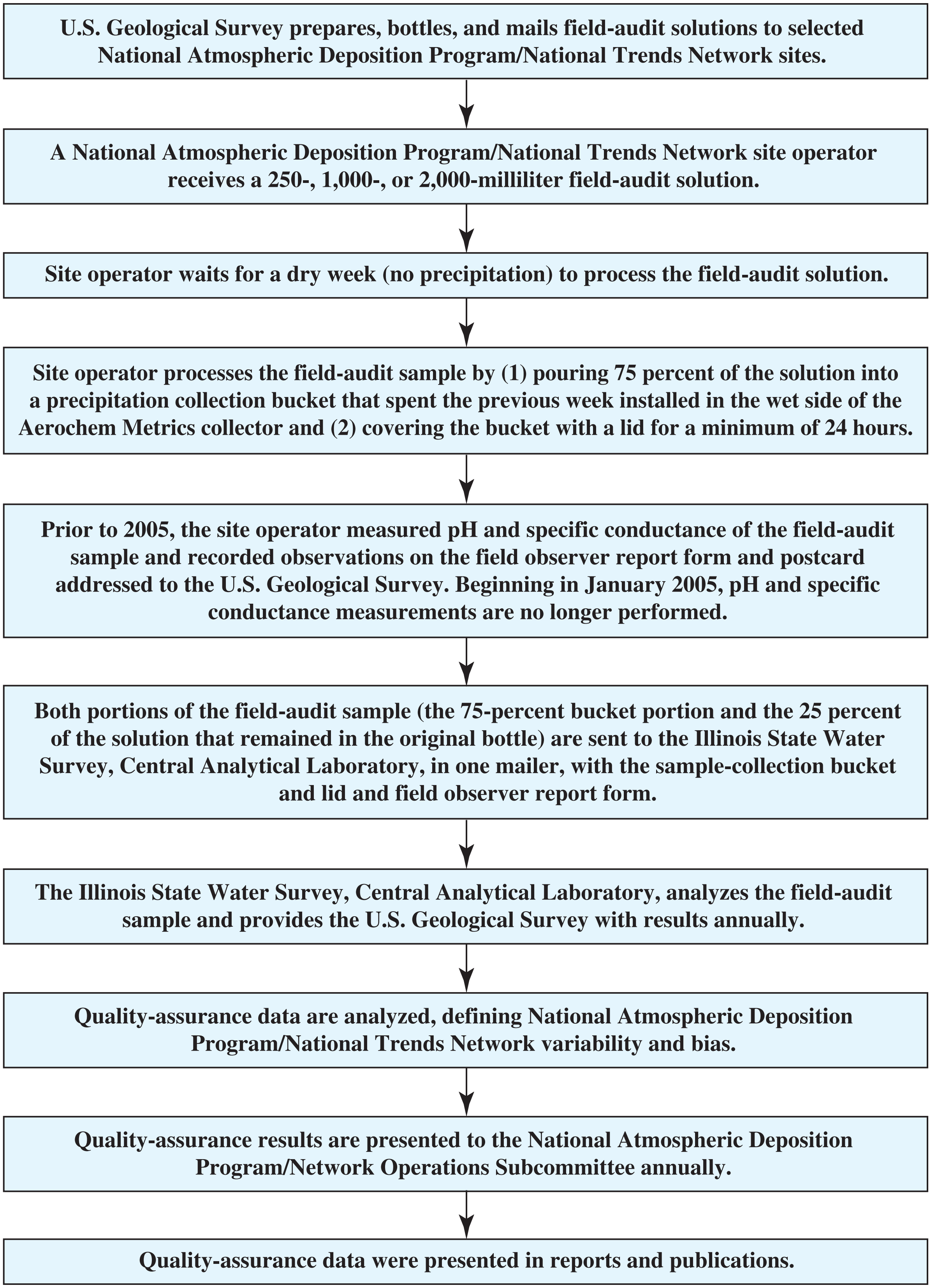
Changes in NADP/NTN sampling equipment and in other materials used for sample collection may affect sample chemistry, which the blind-audit and SHE programs were designed to help identify. Prior to 1994, large analytical differences between the bucket and bottle portions in the blind-audit program helped to identify contamination contributed by the bucket lid o-ring, which was used to seal the bucket lids during sample shipment. Other studies conducted by CAL supported these findings and resulted in changes to the sample shipping protocol (Lynch and others, 1996). Sample contamination resulting from handling and processing is still monitored by the field-audit program (discussed in the next section)—a program that also incorporates variability that field exposure contributes to weekly NTN samples. The SHE program was discontinued in July 2004 because it was determined to be providing information that was not substantially different from the field-audit program. Moreover, CAL regularly analyzes blank samples exposed to the collection buckets and plastic bags, used to protect the buckets and lids during transport, to ensure they are not a source of contamination to NTN samples.

Field-Audit Program

The purpose of the field-audit program (also referred to as the field-blank program) is to evaluate the effects of field exposure, sample handling, and processing on precipitation chemistry. The field-audit program was initiated in August 1996 as a pilot study. The program began full operation in July 1997, replacing the weekly analysis of dry-side buckets. A flowchart describing the field-audit program is provided in figure 6.

Sample Processing

For processing the field-audit sample, the site operator uses a bucket that was installed on the NADP-Aerochem Metrics (ACM) precipitation collector for 1 full week when no precipitation occurred. The site operator is asked to verify that no precipitation occurred by checking the rain-gage chart to make sure the collector lid did not open during the preceding week. Exceptions are allowed for sites in humid areas, where lid openings occur without precipitation due to the sensitivity of the ACM precipitation sensor. If these exceptions were not granted, field-audit solutions might not have been processed by sites located in areas prone to high humidity. The operator verifies that these lid openings were not accompanied by precipitation, indicated by a flat pen trace on the rain-gage chart. The bucket also is inspected for moisture. DI rinse water from CAL may have been present in the bucket when it arrived at the site. The site operator is advised to check if rinse water is present prior to installing the bucket in the field to ensure the water's presence at the end of the week does not signify precipitation.



U.S. Geological Survey prepares, bottles, and mails field-audit solutions to selected National Atmospheric Deposition Program/National Trends Network sites.

A National Atmospheric Deposition Program/National Trends Network site operator receives a 250-, 1,000-, or 2,000-milliliter field-audit solution.

Site operator waits for a dry week (no precipitation) to process the field-audit solution.

Site operator processes the field-audit sample by (1) pouring 75 percent of the solution into a precipitation collection bucket that spent the previous week installed in the wet side of the Aerochem Metrics collector and (2) covering the bucket with a lid for a minimum of 24 hours.

Prior to 2005, the site operator measured pH and specific conductance of the field-audit sample and recorded observations on the field observer report form and postcard addressed to the U.S. Geological Survey. Beginning in January 2005, pH and specific conductance measurements are no longer performed.

Both portions of the field-audit sample (the 75-percent bucket portion and the 25 percent of the solution that remained in the original bottle) are sent to the Illinois State Water Survey, Central Analytical Laboratory, in one mailer, with the sample-collection bucket and lid and field observer report form.

The Illinois State Water Survey, Central Analytical Laboratory, analyzes the field-audit sample and provides the U.S. Geological Survey with results annually.

Quality-assurance data are analyzed, defining National Atmospheric Deposition Program/National Trends Network variability and bias.

Quality-assurance results are presented to the National Atmospheric Deposition Program/Network Operations Subcommittee annually.

Quality-assurance data were presented in reports and publications.

Figure 6. Flowchart describing field-audit program.

The bucket that was installed in the ACM collector for 1 week is removed from the field and brought into the laboratory. Once the operator verifies that all criteria for a dry week have been met, 75 percent of the field-audit solution is poured into the bucket. The amount of solution to be poured into the bucket is marked on the solution bottle. The operator swirls the solution in the bucket and places the lid on the bucket. After a minimum of 24 hours, the operator transfers the field-audit sample from the bucket into a clean 1-L HDPE sample bottle that is routinely used to ship precipitation samples to CAL. The residence time of the solution in the sample-collection bucket can vary from a minimum of 24 hours to 6 days, replicating the duration a natural precipitation sample may spend in a sample-collection bucket.

During 1997-2004, the operator poured four aliquots of the solution and conducted field pH and SC measurements. Sites that did not perform field chemistry measurements were exempt from performing these analyses. Beginning in 2005, aliquots of the solution for field pH and SC measurements are no longer removed.

A postcard, addressed to USGS, is provided for recording the field measurements and the times and dates the solution was added to and removed from the bucket. The site operator completes a FORF, listing similar information that is included in the postcard. The FORF, the 1-L HDPE sample bottle, the 25 percent of the solution remaining in the original bottle, and the bucket and lid used to process the field-audit solution are placed into a mailer that is routinely used to ship natural precipitation samples, and the package is mailed to CAL.

Data Records

The site operator mails the preaddressed postcard to USGS after processing the field-audit sample. USGS enters information from the card into the field-audit program database, and the card is filed for archive. Card receipt by USGS indicates the field-audit sample was submitted to CAL. USGS and CAL jointly track field-audit sample submission and invalidate samples that are not submitted within 1 year of mailing.

CAL supplies USGS with analytical results from the field-audit program on a yearly basis. The data are interpreted by USGS and published in annual reports and presented to NADP/NOS. Similar to the SHE program, analyte concentrations from the bucket portion, which was subject to field exposure and all of the handling and processing steps of an environmental precipitation sample, are compared with those from the minimally handled bottle portion, the 25 percent of the solution that remained in the original field-audit bottle. Paired concentration differences between the bottle and bucket portions indicate possible contamination introduced during standard field residence of the bucket in the ACM collector, as well as during handling and processing of the samples. Presence of windblown particulates in the sample-collection bucket, improper bucket cleaning, sample-handling contamination, and changes in manufactured equipment used for sample collection are examples of causes of statistically significant differences between the bucket and bottle portions in the field-audit program.

Similar to the SHE program, sites are randomly selected to participate in the field-audit program from diverse regions of the country. Every site in NADP/NTN participates in the program once before a site is asked to participate again. During 1997 through 2004, a site participated in the program approximately once every 2.5 years. This frequency increased in 2005, as described later in the "2005 Field-Audit Program Modifications" section of this report. Twenty-five field-audit samples consisting of a DI water or a synthetic precipitation solution were distributed to site operators each annual quarter. Because this program requires an entire week with no precipitation, a submission date for the field-audit sample is not specified. During 1997-2004, the site operator was asked to submit the solution during the same quarter as when the field-audit solution was mailed. If a dry week did not occur within the scheduled quarter, the site operator was asked to process the field-audit solution during the following three quarters, as soon as a full dry week occurred. If a dry week did not occur within a year of the originally scheduled quarter, the site operator was asked to notify USGS, and the field-audit solution was invalidated.

Each site operator chosen to participate in the field-audit program received a cover letter (Attachment 16), a set of instructions for processing the solution (Attachment 17), one postcard addressed to USGS for reporting field measurements and confirming solution submittal to CAL (Attachment 18), and a field-audit solution. Prior to choosing the final sites for participation in the field-audit program each quarter, a list of the sites was sent to the NADP Program Office. The sites were reviewed by the NADP Quality Assurance Manager to check for participation discrepancies and ensure sites were adequately represented. USGS mailed the field-audit solutions to all participating sites 2 weeks prior to the beginning of each quarter.

Sample Preparation

As with the SHE program, the analyte concentrations in the synthetic precipitation solutions used in the field-audit program are intended to represent the range of concentrations in precipitation samples collected by NADP/NTN. Three solutions, with different analyte concentrations, and three sample volumes are used in the field-audit program to assess how sample handling and field exposure affect sample chemistry in solutions with different concentrations and volumes. A description of the solutions and a summary of target values for the synthetic precipitation solutions used in the field-audit program are provided in tables 5 and 6, respectively. The distribution of solution types and sample volumes was consistent each quarter. The sites were randomly assigned a specific solution type and volume. The distribution of the solution types and their respective volumes used in the field-audit program during 1997–2004 are listed in table 8.

Table 8. Solution names, sample volumes, and number of samples used in the field-audit program each annual quarter during 1997–2004.

[mL, milliliters]

Solution name	Sample volume (mL)	Number of samples
Ultrapure deionized water	250	3
Ultrapure deionized water	1,000	3
Ultrapure deionized water	2,000	3
SP–2	250	3
SP–2	1,000	2
SP–2	2,000	3
SP–3	250	3
SP–3	1,000	2
SP–3	2,000	3

2005 Field-Audit Program Modifications

The discontinuance of the SHE program prompted the expansion of the field-audit program, requiring all sites to process a quality-assurance sample annually. Beginning January 2005, the field-audit program began to be conducted on a semiannual basis. Half of all NTN sites are randomly chosen to receive a synthetic or DI water sample, in a 250-, 1,000-, or 2,000-mL volume, during the first half of the year. The remaining sites receive the same samples during the second half of the year. Prior to 2005, three solutions were used in the field-audit program, whereas six solutions are used in the field-audit program in 2005. Solutions SP-5 and SP-98 have been added to the modified field-audit program. Table 9 lists the distribution of the solutions and their respective volumes used in the modified field-audit program beginning January 2005.

Table 9. Solution names, sample volumes, and number of samples used in the field-audit program semiannually beginning January 2005.

[mL, milliliters]

Solution name	Sample volume (mL)	Number of samples of each solution
Ultrapure deionized water, SP–2, SP–3, SP–5, SP–98	250	9
Ultrapure deionized water, SP–2, SP–3, SP–5, SP–98	1,000	9
Ultrapure deionized water, SP–2, SP–3, SP–5, SP–98	2,000	8

Interlaboratory-Comparison Program

The purpose of the interlaboratory-comparison program is (1) to evaluate the analytical precision and accuracy of data produced by participating laboratories and (2) to quantify the uncertainty of chemical analyses determined by CAL. Participating laboratories analyze four synthetic or natural precipitation samples that are mailed to them every 2 weeks, except Shepard Analytical Service (SA), which analyzes 52 samples annually. A flowchart of the program is provided in figure 7. The interlaboratory-comparison program was initiated in 1982 with three participating laboratories. During the subsequent years, many laboratories have participated in the program. A history of laboratory participation in the interlaboratory-comparison program is provided in table 10. Results submitted by the participating laboratories are compiled, analyzed, posted on the Internet (http://bqs.usgs.gov/), and published in annual reports.

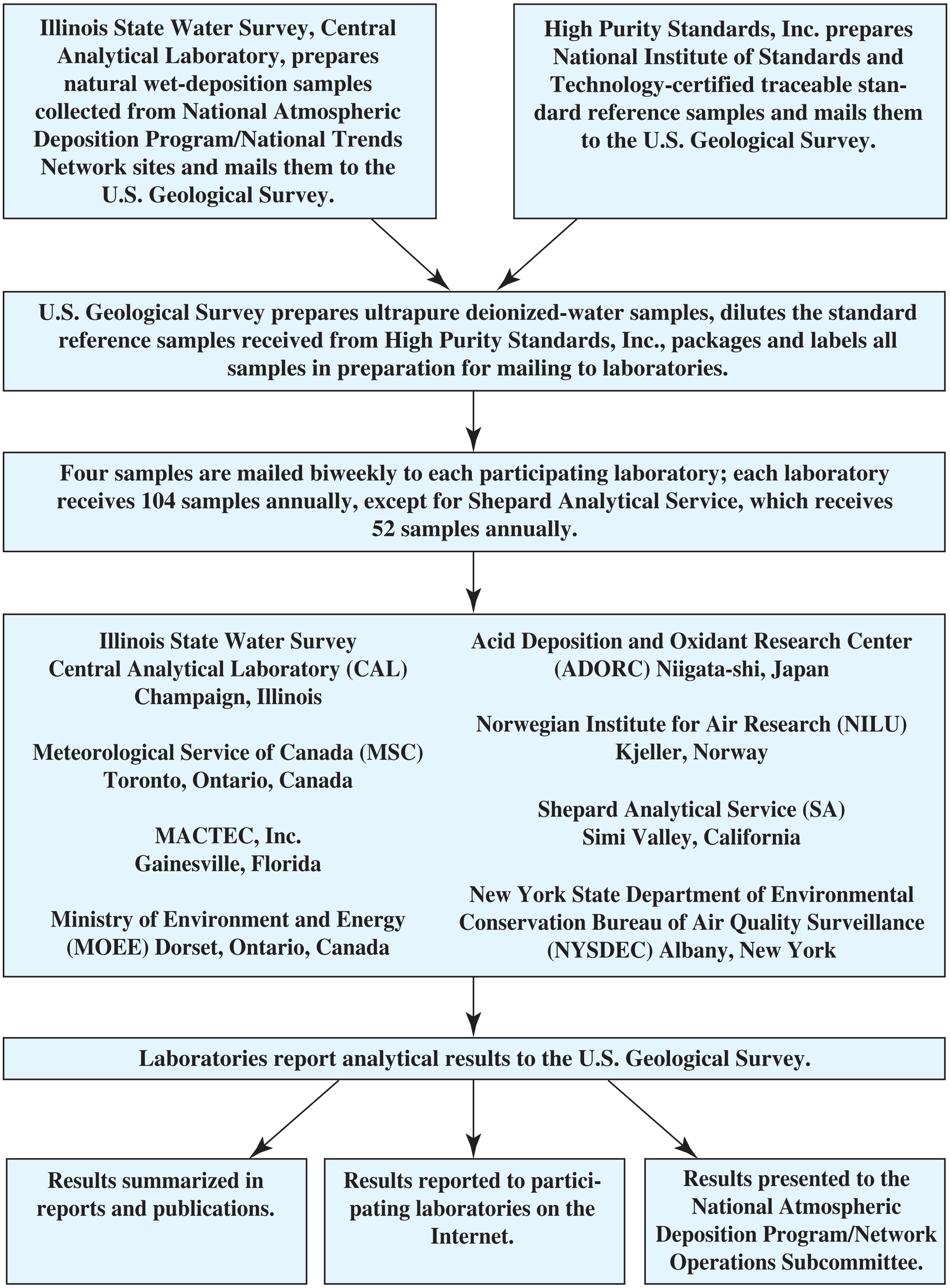
Sample Preparation

Samples for the interlaboratory-comparison program are shipped by USGS to the participating laboratories every 2 weeks. Each laboratory receives four samples derived from the same source solutions in a mailing. Shipments to laboratories consist of either:

- triplicate synthetic wet-deposition samples and a single sample of DI water;
- four replicates of synthetic wet-deposition samples;
- two duplicate synthetic wet-deposition samples along with two different synthetic wet-deposition samples;
- two duplicate synthetic wet-deposition samples along with two DI water samples;
- two duplicate sets of synthetic wet-deposition samples; or
- two duplicate sets of natural wet-deposition samples.

A random schedule of the biweekly solution distribution is generated. Annually, CAL is notified of the approximate mailing schedule for the natural precipitation samples so that these samples can be prepared by CAL staff and shipped to USGS in time to be mailed to the program participants on the scheduled dates.

All samples are labeled with a unique 10-digit sample number assigned by USGS to ensure the participating laboratories can not determine the sample type (natural or synthetic) or the target analyte concentrations until the chemical analyses are performed. The 10-digit sample identification is assigned as follows: the first 4 digits of the 10-digit sample number represent the year during which the study is conducted, followed by the 3-digit Julian date of sample mailing, and the unique 3-digit identification of the sample, ranging from 001 to 032. The unique 3-digit identification is randomly assigned to the samples. For example, the 16th interlaboratory-comparison sample



Illinois State Water Survey, Central Analytical Laboratory, prepares natural wet-deposition samples collected from National Atmospheric Deposition Program/National Trends Network sites and mails them to the U.S. Geological Survey.

High Purity Standards, Inc. prepares National Institute of Standards and Technology-certified traceable standard reference samples and mails them to the U.S. Geological Survey.

U.S. Geological Survey prepares ultrapure deionized-water samples, dilutes the standard reference samples received from High Purity Standards, Inc., packages and labels all samples in preparation for mailing to laboratories.

Four samples are mailed biweekly to each participating laboratory; each laboratory receives 104 samples annually, except for Shepard Analytical Service, which receives 52 samples annually.

Illinois State Water Survey
Central Analytical Laboratory (CAL)
Champaign, Illinois

Meteorological Service of Canada (MSC)
Toronto, Ontario, Canada

MACTEC, Inc.
Gainesville, Florida

Ministry of Environment and Energy
(MOEE) Dorset, Ontario, Canada

Acid Deposition and Oxidant Research Center
(ADORC) Niigata-shi, Japan

Norwegian Institute for Air Research (NILU)
Kjeller, Norway

Shepard Analytical Service (SA)
Simi Valley, California

New York State Department of Environmental
Conservation Bureau of Air Quality Surveillance
(NYSDEC) Albany, New York

Laboratories report analytical results to the U.S. Geological Survey.

Results summarized in reports and publications.

Results reported to participating laboratories on the Internet.

Results presented to the National Atmospheric Deposition Program/Network Operations Subcommittee.

Figure 7. Flowchart describing interlaboratory-comparison program.

Table 10. Laboratory participants in the interlaboratory-comparison program.

[ATL, USGS National Water Quality Laboratory, Atlanta, Ga.; DEN, USGS National Water Quality Laboratory, Lakewood, Colo.; CAL, Illinois State Water Survey, Champaign, Ill.; IWD, Inland Waters Directorate, Ontario, Canada; EMSI, Environmental Monitoring and Services, Camarillo, Calif.; ESE, Hunter, Environmental Services, Inc., Gainesville, Fla. (1989–93); ESE, Environmental Science and Engineering, Inc., Gainesville, Fla. (1994–2001); MACTEC, MACTEC, Inc., Gainesville, Fla. (formerly ESE); GGC, Global Geochemistry Corporation, Canoga Park, Calif.; MOEE, Ontario Ministry of the Environment and Energy, Ontario, Canada; AES, Atmospheric Environment Service, Environment Canada, Ontario, Canada; SA, Shepard Analytical Service, Simi Valley, Calif.; NILU, Norwegian Institute for Air Research, Kjeller, Norway; MSC, Meteorological Services of Canada, Ontario, Canada; ADORC, Acid Deposition and Oxidant Research Center, Niigata-shi, Japan; NYSDEC, New York State Department of Environmental Conservation Bureau of Air Quality Surveillance, Albany, N.Y.]

Participating laboratories	Year of participation
Interlaboratory-comparison program began with three initial laboratories: ATL, CAL, DEN	November 1982
ATL, DEN, CAL, IWD	1983–85
CAL, DEN, EMSI, IWD ATL consolidated with DEN in October 1985 DEN dropped out of the program December 1987	1986–87
CAL, EMSI, IWD	1988
CAL, ESE, IWD	1989
CAL, ESE, IWD	1990
CAL, ESE, IWD, MOEE	1991
CAL, ESE, GGC, IWD, MOEE	1992
AES, CAL, ESE, GGC, MOEE	1993–96
AES, CAL, ESE, MOEE, SA	1997
AES, CAL, ESE, MOEE, SA	1998
AES, CAL, ESE, ADORC, MOEE, NILU, SA	1999
ADORC, CAL, ESE, MOEE, MSC, NILU, SA	2000–01
ADORC, CAL, MACTEC, MOEE, MSC, NILU, SA, NYSDEC	2002–04

in the sequence, mailed to a participating laboratory on December 6, 2004, would have had the following identification: 2004341016.

A maximum of 104 samples are distributed to each laboratory on an annual basis, as part of the interlaboratory-comparison program. Of the 104 samples, 52 are aliquots of natural wet-deposition samples collected at NADP/NTN sites and blended by CAL, 44 are standard reference samples with certified NIST traceable values, prepared by HPS and diluted by USGS, and 8 are DI water samples prepared by USGS. SA chooses not to analyze the natural wet-deposition samples and receives only 52 samples per year. Table 11 lists solutions that were used in the program during 1982–2004. Information for the solutions used in USGS quality-assurance programs, including the interlaboratory-comparison program, is provided in table 5. Target values for the standard reference solutions are listed in table 6.

Natural Precipitation Samples

CAL randomly selects natural precipitation samples collected at NADP/NTN sites that have volumes greater than 750 mL for use in the interlaboratory-comparison program. Each natural wet-deposition sample is a composite of precipitation collected from two NADP/NTN sites. The two precipitation samples are filtered and combined in a 2-L container. Prior to 1999, a deca-splitter was used to divide the precipitation samples into 10 aliquots. Beginning in 1999, the deca-splitter is no longer used to divide the precipitation samples. Instead, the bottle containing the natural precipitation is thoroughly mixed by being manually inverted and vigorously shaken. The composite solution is allowed to sit for 24 hours. The sample is shaken again, an aliquot is removed, and pH and SC are measured. CAL bottles the precipitation aliquots in 60-mL and 125-mL HDPE containers that are rinsed with DI water prior to bottling. Between pouring the solution into each sample container, the 2-L sample container is inverted and shaken (Jane Rothert, Illinois State Water Survey, written commun., 2003).

Two composite solutions are made and bottled for each natural precipitation sample mailing. Bottled samples are shipped in chilled, insulated containers to USGS in Denver, Colorado. With the exception of pH and SC, CAL does not analyze the samples for target values prior to shipping the samples to USGS. CAL notifies USGS of sample shipment. Natural samples are kept refrigerated, and USGS ships them to participating laboratories within 10 days of receipt. Laboratories that analyze natural wet-deposition solutions receive four natural wet-deposition samples consisting of two pairs of duplicates in a sample mailing.

Table 11. Solutions used in the interlaboratory-comparison program.

[CAL, Central Analytical Laboratory; NIST, U.S. National Institute of Standards and Technology; HPS, High Purity Standards, Inc.; SRWS, USGS standard reference water samples; DI, ultrapure (greater than 16.7 megohm, MΩ) deionized water; USEPA, U.S. Environmental Protection Agency; USGS, U.S. Geological Survey]

Solutions	Date
Natural precipitation samples prepared by CAL Diluted SRWS DI prepared by the USGS	1982–84
Natural precipitation samples prepared by CAL	1985
DI prepared by USGS Dilute, pH 4.3 standard units, nitric acid prepared by CAL for use as blank samples Natural precipitation samples prepared by CAL NIST standard reference material 2694, levels I and II	1986
DI prepared by USGS Synthetic precipitation samples prepared by USGS Natural precipitation samples prepared by CAL NIST standard reference material 2694, levels I and II	1987
DI prepared by USGS Synthetic wet-deposition samples prepared by USGS NIST standard reference material 2694, levels I and II Synthetic wet-deposition samples prepared by CAL Natural wet-deposition samples prepared by CAL	1988–89
DI prepared by USGS Synthetic wet-deposition samples prepared by USGS NIST standard reference material 2694, levels I and II Synthetic wet-deposition stock solutions supplied by USEPA and diluted by USGS Natural wet-deposition samples prepared by CAL	1990–91
DI prepared by USGS Synthetic wet-deposition samples prepared by USGS NIST standard reference material 2694A, levels I and II Synthetic wet-deposition stock solutions supplied by USEPA and diluted by USGS Natural wet-deposition samples prepared by CAL	1992–93
DI prepared by USGS Synthetic wet-deposition samples prepared by USGS NIST standard reference material 2694A, levels I and II Natural wet-deposition samples prepared by CAL	1994–96
DI prepared by USGS Synthetic wet-deposition samples prepared by USGS NIST standard reference material 2694A, levels I and II NIST-traceable standard reference solution samples prepared by HPS Natural wet-deposition samples prepared by CAL	1997
DI prepared by USGS Synthetic wet-deposition stock solutions supplied by HPS and diluted by USGS NIST-traceable standard reference solution samples prepared by HPS Natural wet-deposition samples prepared by CAL	1998–2002
DI prepared by USGS Synthetic wet-deposition stock solutions supplied by HPS and diluted by USGS Natural wet-deposition samples prepared by CAL	2003–04

Standard Reference Solution Samples

Between 1982 and 1984, standard reference water samples (SRWS) were used in the interlaboratory-comparison program (table 11). These samples were diluted by BQS personnel to produce solutions with approximate analyte concentrations found in precipitation. Deionized water was used for the dilutions, and the hydrogen-ion concentration was increased with perchloric acid to a pH between 4.0 and 6.5 standard units. Most-probable analyte concentrations were established for these solutions in the standard reference sample project-laboratory performance comparison studies (Brooks and others, 1985).

Synthetic wet-deposition matrices prepared by USEPA, known as the Performance Audit Solutions, were used in the interlaboratory-comparison program from 1990 through 1993 (table 11). BQS personnel diluted these solutions prior to sample mailing (See and others, 1990).

Between 1986 and 1997, standard reference samples prepared and certified by NIST were used in the interlaboratory-comparison program (table 11). Median laboratory values were compared to the certified values reported by NIST. Laboratory values outside of the certified values plus or minus the estimated uncertainty reported by NIST indicated potential bias. Analyte concentrations in NIST-certified sample 2694A-II were much higher than values typically measured in natural precipitation and required dilution prior to sample mailing (Gordon, 1999).

As of 1998, NIST-traceable standard reference solutions manufactured by HPS have been used in the interlaboratory-comparison program (table 11). These solutions are formulated to replicate the chemical properties of actual precipitation collected at NADP/NTN sites. USGS receives stock solutions from HPS during the fall and dilutes them in December for use in the interlaboratory-comparison program during the following year. Sample preparation for the interlaboratory-comparison program is performed once during the year to reduce variability. However, there is some question that evaporation may occur despite chilling of the samples and that solutions should be diluted more frequently. HPS provides NIST-traceable certified values for the major ions measured in the standard reference stock solutions. However, certified values are not available for pH and SC.

Ultrapure Deionized-Water Samples

DI water samples are included in the interlaboratory-comparison program to detect low-level laboratory contamination. Prior to sample mailing, USGS fills HDPE bottles, which are stored with DI water for a minimum of 1 week, with fresh DI water.

Sample Mailing to Laboratory Participants

Interlaboratory-comparison samples are mailed biweekly to participating laboratories on a Monday morning. Preparation for the mailing begins the previous week. Sample bottles are filled and stored with DI water for a minimum of 1 week prior to mailing. Gel-filled ice packs, used for cooling samples during shipment to laboratories within the United States, are wrapped in aluminum foil, sealed inside ziploc bags, and frozen. DI water frozen in large ziploc bags is used for cooling samples during shipment to laboratories located outside of the United States.

USGS personnel remove the natural precipitation samples from refrigeration during the day of mailing. The 12-character identification labels assigned by CAL are recorded and replaced by a USGS-assigned label so the samples are not identified as natural precipitation solutions. The natural precipitation solutions remain in the original bottles prepared by CAL. For bottling the synthetic and DI water samples, bottles are rinsed three times with DI water and conditioned twice with the appropriate solution prior to bottling and labeling. MOEE laboratory receives 125-mL volume samples; other laboratories receive 60-mL volume samples. A USGS label is affixed to each sample, identifying the sample as an interlaboratory-comparison solution, listing the laboratory recipient name and the assigned 10-digit USGS identification number. Four samples are sealed in one ziploc bag and placed into a shipping container. The shipping containers are lined with plastic bags supplied to USGS by CAL. These bags also are used by CAL to store precipitation collection buckets and lids and are analyzed weekly to ensure they are not a source of contamination. A cover letter is included with each set of samples, listing the sample identification numbers and the requested analyte determinations (Attachment 19).

Laboratories located in the United States and MSC in Canada receive coolers chilled with ice packs, shipped by the U.S. Postal Service. Laboratories return these coolers and ice packs to USGS. With the exception of CAL, laboratories within the United States receive postage-paid merchandise return labels for mailing the coolers back to USGS. CAL pays the shipping cost of returning their coolers to USGS. The international laboratories receive styrofoam-lined cardboard coolers, chilled with frozen DI water packs, which are shipped to them by contract carrier. To avoid return shipping costs, disposable shipping materials are used for mailing samples to international laboratories.

Data Records

Participating laboratories provide analytical results to USGS in electronic format including Microsoft Excel, ASCII, and Quattro Pro. Data are compiled, processed, and graphically displayed using SAS software. The data are presented in control charts and tables on the Internet (http://bqs.usgs.gov/precip_2/), examples of which are included in Attachments 20 and 21, respectively. Each laboratory's data are only accessible by the individual laboratory and USGS. The control charts are used to identify potential systematic error that might affect the quality of a laboratory's data.

Interlaboratory and intralaboratory bias are investigated in the interlaboratory-comparison program. Interlaboratory bias (bias among participating laboratories) is determined by systematic difference of reported values from the median values determined from all participating laboratories. Interlaboratory results are available for final annual data, when all data from the participants have been received. As a preliminary indication, intralaboratory bias (bias within a single laboratory) is identified by a systematic difference between the reported and expected values. These expected values include NIST-certified target values for the synthetic wet-deposition samples and individual laboratory minimum reporting limits (MRL) for each analyte, which when exceeded for DI water analyses identify contamination.

Final results for all laboratories are posted on the Internet (http://bqs.usgs.gov/) when analyses for all samples mailed during the year are received. Acceptance criteria for final data are based on median values derived from all submitted results for each analyte. Differences between the reported and median analyte concentrations are graphically presented for individual analytes on control charts. Consistent, acceptable laboratory performance is indicated when the data remain within the control limits on the control charts. Warning limits are positioned at ± 2 f-pseudosigma from the zero difference line, and the control limits are placed at ± 3 f-pseudosigma from the zero difference line.

The frequency of data reporting throughout the year varies for the individual laboratories. The data are posted on the Internet within 1 week of receipt of the data. Data that are received from laboratories throughout the year are considered preliminary and are posted on the Internet using the previous year's warning and control limits. However, the preliminary results are evaluated against the NIST-certified target values for the solutions, not the median values, which are not available until all annual data have been submitted.

Laboratory precision is determined by the agreement between measurements of duplicate samples. Final annual results for each laboratory include statistical analysis (50th and 90th percentile) of absolute error between the duplicate samples. These results are posted on the precipitation chemistry project Web site (http://bqs.usgs.gov/).

Results for detected constituents in the eight DI water samples are posted in a table showing the number of times each laboratory reported a concentration greater than the MRL for each analyte (Attachment 22). Prior to 2003, the largest MRL used by the participating laboratories was assigned as the MRL for all laboratories for analysis of DI water results to facilitate the intercomparison among laboratories. It was thought that laboratories with lower reporting limits would have a higher number of analyses exceeding the MRL for the DI water samples than laboratories with higher reporting limits. The purpose of providing DI water samples to participating laboratories is not to compare the possibility of contamination amongst the laboratories based on the highest MRL but to evaluate potential contamination that may be affecting each laboratory's reported data. As of 2003, individual MRLs for each laboratory are used to evaluate DI water results to assess contamination.

2005 Modifications to the Interlaboratory-Comparison Program

The interlaboratory-comparison program continues to be a valuable monitoring tool in assessing the accuracy and precision of laboratory analyses of weekly precipitation samples and providing comparability among participating laboratories. Beginning January 2005, data reporting to the participating laboratories have included plots for each analyte showing the relative percentage differences between the calculated median concentrations for each solution and reported values for all participants.

Collocated-Sampler Program

The collocated-sampler program was preceded by an 18-month study, beginning in fall 1978, at site NC41 at Finley Farm, North Carolina. This study, involving USGS personnel, included 10 collocated samplers to assess collection efficiency, evaporation loss, and variation in pH and SC measurements (Schroder and others, 1984). USGS supported and participated in other subsequent collocated-sampler studies associated with NADP/NTN (See and others, 1990). In 1988, USGS established the collocated-sampler program to assess overall variability in NADP/NTN data, on an annual basis, in different parts of the United States.

The purpose of the collocated-sampler program is to evaluate the overall error associated with collecting, handling, processing, and analyzing NADP/NTN wet-deposition samples. The overall error is estimated by comparing data collected by duplicate sets of equipment installed at NADP/NTN sites. From 1988 through 1996, four sites participated in the collocated-sampler program each water year (October 1 through September 30), with the exception of 1994, when sites were operated on a calendar year basis (Gordon and others, 1997). In 1997, the number of sites collocated each water year was reduced to two, primarily to apply resources to the new field-audit program. Site NH02, at Hubbard Brook in New Hampshire, was the first collocated-sampler site to operate for 2 consecutive years, during water years 2000 and 2001. Site WI98, at Wildcat Mountain State Park in Wisconsin, was the second site to host collocated sampling equipment for 2 consecutive years, during water years 2002 and 2003. Meteorological monitoring equipment, including an anemometer (for measuring wind speed and direction) and an air-temperature thermometer also were installed at site WI98 to determine if variability in collocated data was affected by weather. Photographs of collocated equipment installed at sites NH02 and WI98 are provided in figures 8 and 9, respectively.

Figure 8. Collocated sampling equipment at site NH02 at Hubbard Brook in New Hampshire, August 1999.

Figure 9. Collocated sampling equipment at site WI98 at Wildcat Mountain State Park in Wisconsin, August 2001.

Sites for the collocated-sampler program are chosen approximately 6 months prior to equipment installation. Several criteria have to be satisfied for a site to become a candidate for the program:

1. The site must have ample space for a duplicate set of monitoring equipment, while adhering to the siting protocols required by NADP/NTN.
2. The site operator must be reliable, demonstrating acceptable performance in the intersite-comparison studies.
3. The site must be willing to host the additional equipment and process the extra precipitation samples for an additional fee.
4. Equipment setup must be reasonable, eliminating sites that are remote or sites that would require building additional equipment to replicate the original site, such as towers to support the collection equipment.

One of the aims of the program is to achieve an understanding of variability throughout NADP/NTN. Hence, collocated sampler sites are chosen to achieve a regionally representative distribution throughout the United States. A map showing the location of collocated sites operated during water years 1988 through 2004 is provided in figure 10.

Equipment Preparation and Testing

Prior to equipment installation at NADP/NTN sites, sample-collection equipment is assembled at the USGS-BQS laboratory in Denver, Colorado, cleaned, and tested. Parts that are prone to malfunction, especially the precipitation sensor, motor box, and rain-gage tower, often are exchanged at the NADP Program Office's equipment depot for refurbished equipment. Several tests are used in the laboratory to guarantee proper function of the ACM collector and Belfort rain gage in the field. All test results are recorded in the collocated sampler's logbook. These tests are described as follows:

1. Check the sensor gap with a gap thickness tool to ensure the grill plate is evenly spaced above the sensor and is not bent or misaligned.
2. Check the sensor's temperature when the wet-side bucket lid is open and closed. The sensor's heating plate should be at a consistent temperature at the top, middle, and bottom. Three temperature readings are recorded at these locations. The temperature of the heating plate should be approximately 120 ^{o}F when the lid is open and at ambient temperature when the lid is closed.
3. Check the lid seal on the wet-side bucket to ensure it is snug and that windblown debris cannot enter the bucket when the lid is closed. The height of the lid is measured at its four corners while it covers the wet-side bucket.

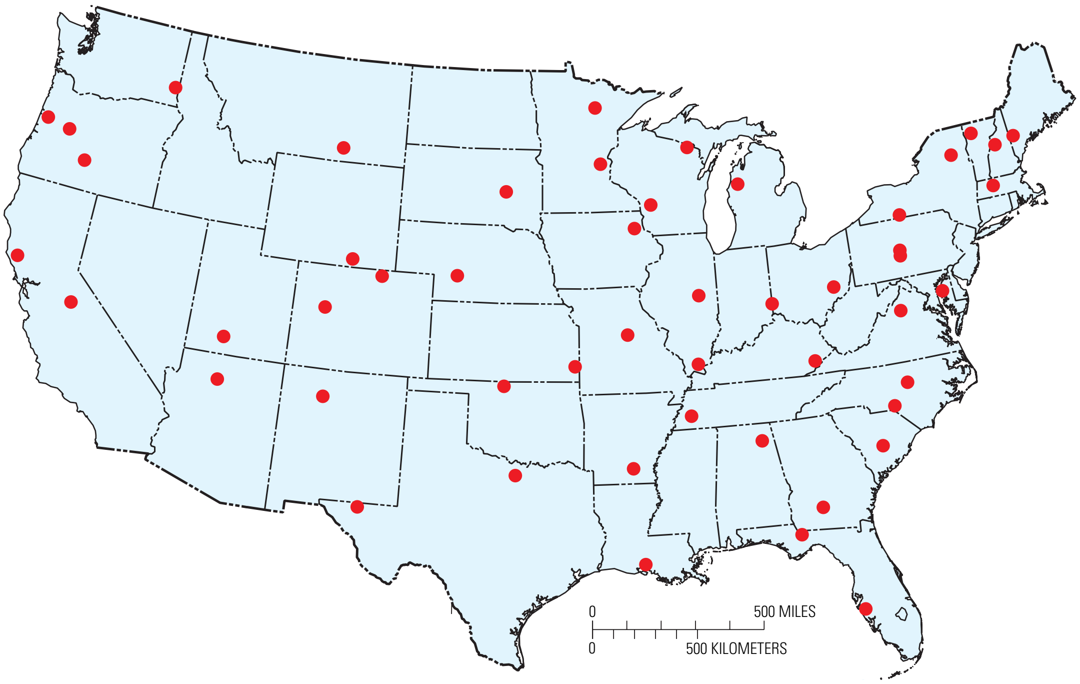


Figure 10. Location of collocated samplers at National Atmospheric Deposition Program/National Trends Network sites operated during water years 1988 through 2004 (from URL http://nadp.sws.uiuc.edu/).

These same measurements are recorded with the wet-side bucket removed from the collector. The differences in height between the two measurements at each corner of the lid provide an indication of the tightness of the seal and should be approximately 1 in.

4. Check the minimum resistance required for the sensor to activate the lid opening. A minimum resistance device is attached to the sensor of the ACM collector. A load is applied until the wet-side bucket lid is triggered to open. A voltage meter reads the resistance from the loading device, which should be approximately 70 to 90 KΩ.
5. Check the voltage delivered to the event recorder on the Belfort rain gage from the ACM collector's motor box. The ACM collector activates the event recorder on the Belfort rain gage when the dry-side bucket is closed. Precipitation is recorded on the Belfort's chart. The voltage should be zero when there is no activity and approximately 12 volts when triggered by the collector's sensor.
6. Check the strength of the ACM collector's motor box, which mechanically moves the collector lid. The motor box should be able to move the lid with two rain-gage calibration weights resting on top of the lid (approximately 1.4 kg).
7. Calibrate the Belfort rain gage with standard Belfort calibration weights at an interval equivalent to 1 in. of precipitation. The calibration should be within 0.1 in. for the entire calibration range of 12 in. If the calibration difference exceeds 0.1 in., adjustments must be made to calibrate the rain gage.
8. Check the operation of the rain-gage clock and pen trace by operating the Belfort mechanism for several weeks. The pen should mark a legible trace, and the clock should keep accurate time.

The equipment is thoroughly inspected and parts are replaced as needed. Extra hardware, fuses, parts, and equipment are brought to the field. Most NADP/NTN sites are located in rural regions. Therefore, preparation for unforeseen circumstances during site setup saves valuable time. Backup batteries are purchased near the sites because shipping batteries is often cost-prohibitive. However, sealed gel-filled solar batteries are shipped because they are expensive and have a life guarantee of 5 years. All tests, observations, and a summary of the equipment installation are recorded in the collocated-sampler's logbook.

Equipment Shipment and Installation

The precipitation collection equipment is shipped to host sites in plywood boxes. Great care is taken to securely fit the fragile equipment in the boxes. The equipment is typically shipped to the site 1 week prior to installation. The USGS personnel, often with a CAL representative, visit the site in early to mid-September to install the collocated equipment. Site operators routinely help with the installation. The newly installed equipment replicates the original set of equipment. For example, if a heated roof for snow is installed on the original collector, then a heated roof is installed on the newly collocated equipment. Collocated equipment placement adheres to the NTN siting rules as much as possible, which include some of the following criteria:

1. All equipment must be a minimum of 5 m from the nearest object that is higher than 1 m and can deflect wind.
2. Angle from the ACM collector's and Belfort's wet-deposition collection orifices to any object must be less than 45 degrees, except that the angle to a house must be less than 30 degrees.
3. The Belfort rain gage should be located within 5 to 30 m of the ACM collector.
4. The top of the Belfort rain-gage orifice must be within 1 ft of the level of the top of the ACM collector's bucket opening.

Both sets of collection equipment—the newly installed collocated equipment and the original equipment—are field-tested, and both Belfort rain gages are checked for calibration. The field tests involve the same procedures conducted in the laboratory to test the collocated equipment. The collocated site is regarded as a unique NADP/NTN site and assumes a four-character code that is based on the original site code. For instance, a site collocated at site CA99, Yosemite National Park, California, assumes the identity of 99CA in the NADP/NTN's database. Both sets of equipment are labeled with their respective site identifications (CA99 and 99CA), and photographs are taken.

The collocated sites are operated as independent NADP/NTN sites. The site operator collects the precipitation samples from both collectors, conducts field chemistry measurements (if the site routinely performs these measurements), and mails both samples to CAL. CAL analyzes both samples as routine weekly samples. At the end of the collocation period, the site operator disassembles and returns the collocated equipment to USGS. A manual sent to the site operators, with instructions on disassembling and packing the Belfort rain gage and ACM collector, is included in Attachment 23.

Data Records

CAL provides the collocated data to USGS on an annual basis. To characterize the wet-deposition at a collocated site, data from the collocated and original site are combined for analysis. Median sample chemistry varies substantially between NADP/NTN sites, reflecting the diverse climatic and human-related effects around the United States. Weekly deposition values for each analyte at collocated sites are calculated by using the precipitation depth determined by the Belfort rain gages. Concentration, reported in milligrams per liter, is multiplied by 10^{-1} times the precipitation depth reported in centimeters, to yield deposition, in kilograms per hectare. Measured deposition differences are due to natural variability in precipitation chemistry and instrumentation differences. Median differences are calculated for data collected by the original and collocated sets of equipment in terms of concentration and deposition. These differences between the two sets of collocated equipment provide an estimate of the overall NADP/NTN error, from the point of sample collection to data reporting of weekly precipitation analyses. Smaller analyte concentrations generally are more prone to larger differences on a percentage basis (Wetherbee and others, 2004).

Nonparametric statistics are used for analysis of collocated data to describe the overall sampling precision because nonparametric methods are robust against extreme outlying values. Analysis of collocated data at each site, for each analyte, involves the calculation of the median absolute percentage differences for concentration and deposition. These collocated-sampler data are interpreted by USGS, published in annual reports, and presented to NADP/NOS.

Long-Term Benchmark Collocated-Sampler Sites

Starting in water year 2005, three long-term benchmark collocated sites have been established at site WI98, Wildcat Mountain State Park, Wisconsin; AZ03, Grand Canyon National Park, Arizona; and VT99, Underhill at Proctor Maple Research Center, Vermont. These sites will be used to collect data for assessment of overall error during NADP/NTN's transition to updated, modern field instrumentation. Yearly changes in site collocation will be discontinued in favor of these long-term sites, situated in different regions of the country with varying climatic regimes. Long-term collocated monitoring, using both current-day and modern instruments, will generate data for identification of potential "step-function" changes in NADP/NTN data resulting from the equipment differences so that such data shifts may not be inappropriately interpreted as environmental changes.

Summary

The external quality-assurance programs conducted by USGS in support of NADP/NTN have provided an assessment of data quality for more than 25 years. Since 1978, six different programs have been implemented—the intersite-comparison program, the blind-audit program, the sample-handling evaluation program, the field-audit program, the interlaboratory-comparison program, and the collocated-sampler program. The programs gage the effects of numerous variables that affect precipitation chemistry such as sample handling, processing and shipping, field equipment and sampling techniques, laboratory analyses, field exposure, precipitation variability, and data reporting. The programs provide useful information for interpretation of NADP/NTN data and continue to evolve to help answer new questions.

The intersite-comparison, blind-audit, and sample-handling evaluation programs have been discontinued and augmented by revised field-audit and long-term collocated-sampler programs. In 2005, the field-audit program began on a semiannual basis, with all NTN sites receiving a quality-assurance solution during a calendar year. In the collocated-sampler program, yearly changes in site collocation have been discontinued in favor of three long-term sites established in different regions of the country with varying climatic regimes. As of January 2005, three quality-assurance programs are managed by USGS in support of NADP/NTN, the interlaboratory-comparison program, the field-audit program, and the collocated-sampler program. These programs continue to allow NADP/NTN data users to discern between actual environmental trends and inherent measurement variability.

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Attachments

Attachment 1. Sample-processing instructions mailed to site operators participating in the intersite-comparison program. Highlighted text indicates customized fields for each intersite-comparison study.

United States Department of the Interior
U.S. GEOLOGICAL SURVEY
Box 25046 M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

IN REPLY REFER TO:

INSTRUCTIONS FOR NADP/NTN INTERSITE COMPARISON STUDY NO. --

Sample Mailing Date

RESPONSE CARD SHOULD BE RETURNED BY 45 days following the sample mailing date

Enclosed please find the following materials:

- One 125-mL bottle of intersite comparison study no. -- solution.
- One intersite comparison study no. -- response card for recording measurements, electrode information and remarks.

1. Please 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 response card.

- If either meter/electrode is inoperable or if you are experiencing problems with the equipment, please note this in the “remarks” section and perform the measurement for which you have a working meter/electrode.
- If BOTH the pH and conductance meters/electrodes are inoperable, please note this on the response card and return it. Sites that do not submit data because of equipment problems are coded differently in the database than sites which do not respond at all.
- If you know the date your current pH electrode was put into service, please record this date in the “REMARKS” section. If you are unsure of the service date, use the date written on the electrode.
- If you are unable to participate in the study, for whatever reason, please let us know.

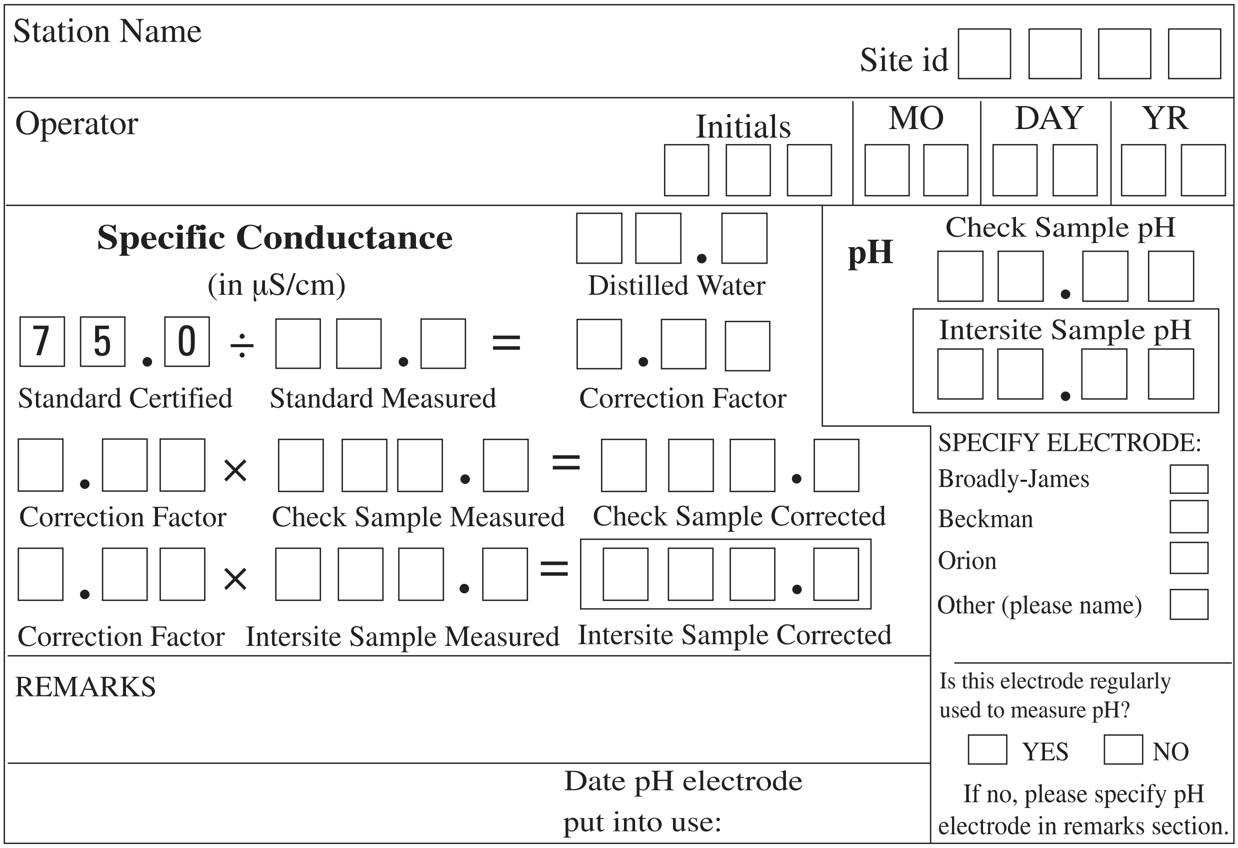
2. Please photocopy the response card for your records and return the card to the U.S. Geological Survey.

3. Retain the remaining intersite comparison solution until you receive a report discussing your results. Store the remaining portion in a cool, dark place. If the report indicates you have met the accuracy goals for study no. --, you may discard the remaining solution. If you do not meet the goals, you may receive further instructions requesting you remeasure the remaining portion of the solution.

Please analyze the enclosed sample and return your response card promptly. At the very latest, your response card **must be in the mail by the deadline.** You may also submit your results on line at: http://btdqs.usgs.gov/precip/project_overview/intersite_forms/form_2.htm. A report describing your results will be mailed to you. Description of previous intersite-comparison studies, along with instructions and helpful hints for making successful field pH and specific-conductance measurements, links and useful information pertinent to the NADP/NTN are posted on the Web site: http://btdqs.usgs.gov/precip/projecfst_overview/intersite_forms/is_intro.htm. If this package was addressed to the wrong person, or if your site address needs to be updated, please call or e-mail Natalie Latysh at: (303)236-1874, nlatysh@usgs.gov.

Thank you very much for your participation!

Attachment 2. Postcard mailed to site operators for reporting pH and specific-conductance measurements for the intersite-comparison solutions.



Station Name

Site id ☐ ☐ ☐ ☐

Operator

Initials ☐ ☐ ☐

MO ☐ ☐

DAY ☐ ☐

YR ☐ ☐

Specific Conductance

(in µS/cm)

☐ ☐ . ☐

Distilled Water

7 5 . 0 ÷ ☐ ☐ . ☐ = ☐ . ☐ ☐

Standard Certified Standard Measured Correction Factor

☐ . ☐ ☐ × ☐ ☐ ☐ . ☐ = ☐ ☐ ☐ . ☐

Correction Factor Check Sample Measured Check Sample Corrected

☐ . ☐ ☐ × ☐ ☐ ☐ . ☐ = ☐ ☐ ☐ . ☐

Correction Factor Intersite Sample Measured Intersite Sample Corrected

pH

Check Sample pH

☐ ☐ . ☐ ☐

Intersite Sample pH

☐ ☐ . ☐ ☐

SPECIFY ELECTRODE:

Broadly-James ☐

Beckman ☐

Orion ☐

Other (please name) ☐

Is this electrode regularly used to measure pH?

☐ YES ☐ NO

If no, please specify pH electrode in remarks section.

REMARKS

Date pH electrode put into use:

Attachment 3. Guidelines for performing successful pH measurements, provided annually to site operators participating in the intersite-comparison program.

MARCH 3, 1849

IN REPLY REFER TO:

United States Department of the Interior
U.S. GEOLOGICAL SURVEY
Box 25046 M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

Guidelines for Performing pH Measurements

These instructions are general guidelines for helping with common problems that may occur while measuring pH of precipitation samples collected by the NADP. Please read these instructions carefully to ensure that you are measuring pH properly and obtaining optimum performance from your electrode. If you have problems with the pH electrode, please call Tracie Patten ([217] 333-3936) or Scott Dossett ([800] 952-7353) at the CAL.

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1. Each electrode has its own individual characteristics, working slightly differently than its counterpart. Electrode performance changes with age and usage and each electrode may work differently with various meters in different settings. You will need to “get to know your electrode” and understand its individual working pattern so that you will be able to recognize problems or less than optimal performance. To familiarize yourself with the electrode and to help keep the electrode in working condition, the CAL recommends calibrating the electrode and measuring the pH of the check solution each week.
2. Electrodes typically respond quickly but can be sensitive to movement. Therefore, when performing measurements, you may need to stand still or stand away from the electrode to give it a chance to stabilize.
3. Please use the appropriate filling solution for your electrode. Do not use filling solution brands that are not approved for your electrode; they will damage it. Top the filling solution in the pH electrode to just below the fill hole, if needed. If filling solution is added, carefully flick the electrode (as you would a fever thermometer) to remove potential air bubbles. Hold the electrode near the filling port when you flick it.
4. The fill hole of the electrode should be uncovered during measurements and covered during storage of the electrode.
5. If using a Broadley-James electrode:
    A. Please use the AUTO READ function on the pH meter, which is available on later models. This will provide the fastest and most accurate reading. The AUTO READ function indicates when the stable pH endpoint is reached.

Attachment 3. Guidelines for performing successful pH measurements, provided annually to site operators participating in the intersite-comparison program—Continued.

B. Remove the soaking bottle from the electrode tip by unscrewing the bottle from the cap and gently pulling the bottle off the electrode while leaving the cap and o-ring on the electrode barrel. Be sure there are no salt crystals or large drops of storage solution adhering to the cap, which can contaminate the calibration and rainwater samples during pH measurements. Rinse the electrode and the underside of the cap with copious amounts of deionized or distilled water, which should dissolve the crystals and prevent contamination. Alternately, you may remove the cap, the o-ring, and the bottle simultaneously by slowly pulling the electrode out of the bottle with a gentle back and forth twisting motion. Whichever method you use, please be careful when removing and replacing the soaking bottle. Handle the electrode gently and carefully so that the fragile electrode barrel does not crack during the process.

C. Agitate the solution to speed up electrode response, but take the pH reading when the solution is still.

6. **If using a Beckman electrode**:

    A. When not in use, the electrode should be stored dry and suspended vertically. Protect the tip from dust settling on it by covering with parafilm or the green rubber tip included with the electrode.

7. **If using an Orion Sure-Flow electrode:**

    A. The electrode should be stored in the Orion #91001 storage solution sent with the electrode.

8. Rinse the electrode bulb and junction area with copious amounts of deionized or distilled water before measuring pH.
9. Always condition the sample vial and electrode by rinsing with the solution you are about to analyze before measuring the pH.
10. Never return a solution to its storage bottle after removal. Discard unused solutions removed from its storage bottle to prevent contamination.
11. Inspect all solutions prior to analysis for foreign material. Please replace solution if contamination is present.
12. Store all solutions out of the sun, preferably in a cool, dark place.
13. Make certain prior to any measurement that all samples, including the precipitation sample, are at the same room temperature.
14. Please refer to Section 3.3.8 - Field Laboratory Analysis in the NTN Site Operation Manual for detailed instructions to:

- calibrate the pH meter
- measure the quality-control check sample
- measure pH of the precipitation samples

Attachment 4. Guidelines for performing specific-conductance measurements, provided annually to site operators participating in the intersite-comparison program.

MARCH 3, 1849

IN REPLY REFER TO:

United States Department of the Interior
U.S. GEOLOGICAL SURVEY
Box 25046 M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

Guidelines for Performing Specific-Conductance Measurements

These instructions are general guidelines for helping with common problems that may occur while measuring specific-conductance of precipitation samples collected by the NADP. Please read these instructions carefully to ensure that you are measuring specific-conductance properly. If you have problems, please call Tracie Patten ([217] 333-3936) or Scott Dossett ([800] 952-7353) at the CAL.

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1. Ensure the specific-conductance cell is clean. The cell can be cleaned with a mild detergent solution and warm water. Rinse several times with deionized or distilled water after cleaning.
2. 2. Rinse the cell several times with generous amounts of deionized or distilled water prior to measurement.
3. Deionized or distilled water measurement readings should be less than 5 µS/cm. If measurements are higher, clean or replace the deionized or distilled water supply.
4. Condition the cell by rinsing it at least once with the calibration standard or the sample prior to measuring the specific-conductance to ensure all rinse water is removed from the cell.
5. While performing a specific-conductance measurement, immerse the cell completely in the sample (trying to avoid air bubbles).
6. Do not use the same aliquot of sample for a specific-conductance measurement that has been used for a pH measurement, as this may introduce contamination from the pH electrode or buffer solutions. If you have to use the same aliquot, measure the conductance first.
7. If the dip method is used, please make sure that the container used for the measurement is properly cleaned and conditioned.
8. During storage of the conductance cell, change the storage water weekly even if analyses are not performed.

Attachment 4. Guidelines for performing specific-conductance measurements, provided annually to site operators participating in the intersite comparison program—Continued.

Specific-Conductance Meter Calibration

1. Measure the specific-conductance of the 75 µS/cm standard. Calculate the correction factor by dividing the standard certified value (75 µS/cm) by your measured value of the standard solution. If the specific-conductance reading of the certified standard or check sample is not reasonable, corrective action must be taken prior to recording the correction factor (check the expiration dates of the standard and stock solutions).
2. Avoid high correction factors and large meter adjustments. Keep a log documenting previous correction factors and meter adjustments to recognize abnormalities.
3. Ensure proper storage of the calibration standard solution and allow the solution to adjust to room temperature prior to performing a measurement.
4. Do not return unused portions of the standard to the original container. Discard the solution to avoid contamination.

Attachment 5. Letter mailed to site operators describing their intersite-comparison results. Highlighted text indicates customized fields for a NADP/NTN site participating in an intersite-comparison study.

United States Department of the Interior
U.S. GEOLOGICAL SURVEY
Box 25046 M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

IN REPLY REFER TO:

Date

To: Site operator name, Site identification

From: Natalie Latysh, USGS External Quality Assurance Project for the NADP/NTN

Subject: Intersite-Comparison Study Number

The intersite-comparison results for site identification are:

	REPORTED VALUE	MET NADP/NTN GOALS?
pH	--	**YES/NO**
Specific Conductance	--	**YES/NO**

Please note: reported values of -9 = missing value; -6 = equipment problems

Please check your records to confirm the values for your site.

Sites that missed the accuracy goals may be asked to participate in a followup evaluation to investigate the source of error. The following line graph along with the scatter plot of pH versus specific conductance on the back of this page can be used to determine where your reported values fall within the distribution of all reported values for intersite-comparison study number:

	Most Probable Values				
Percentiles	10%	25%*	50%	75%	90%
pH	--	--	--	--	--
Specific conductance	--	--	--	--	--

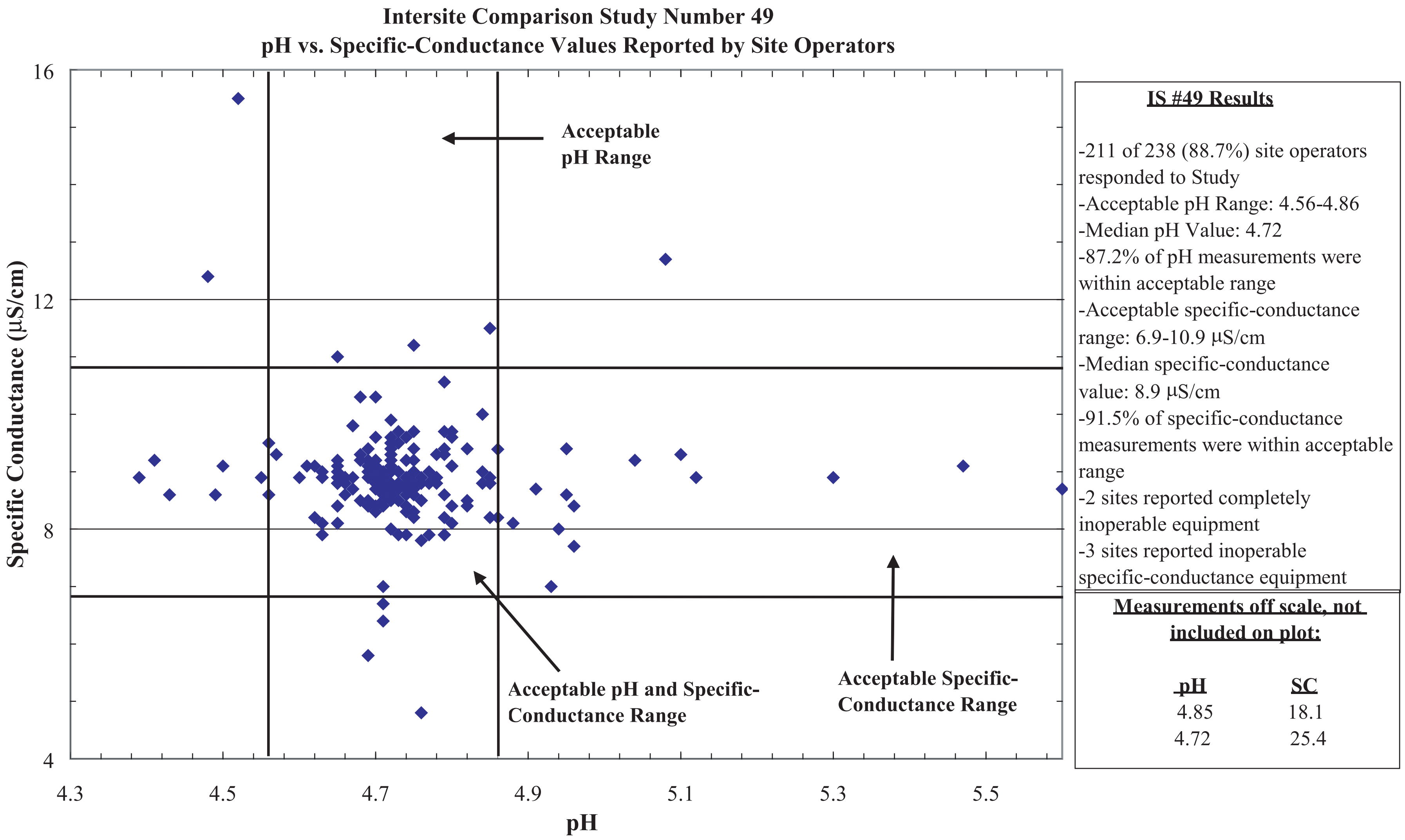
(25% of all reported values were less than this value; 75% were greater)

Thank you for participating in this study. If you have questions regarding your results, please contact me at: **(303) 236-1874** or, e-mail: nlatysh@usgs.gov. Please refer to our Web site: http://bqssun/precip/project_ overview/intersite_forms/is_intro.htm, for helpful hints and informative links.

Best regards,

Natalie Latysh

Attachment 6. Scatter plot of pH and specific-conductance values showing site operators' performance, mailed with intersite-comparison results for study 49.



Intersite Comparison Study Number 49
pH vs. Specific-Conductance Values Reported by Site Operators

IS #49 Results

-211 of 238 (88.7%) site operators responded to Study
-Acceptable pH Range: 4.56-4.86
-Median pH Value: 4.72
-87.2% of pH measurements were within acceptable range
-Acceptable specific-conductance range: 6.9-10.9 µS/cm
-Median specific-conductance value: 8.9 µS/cm
-91.5% of specific-conductance measurements were within acceptable range
-2 sites reported completely inoperable equipment
-3 sites reported inoperable specific-conductance equipment

Measurements off scale, not included on plot:

pH	SC
4.85	18.1
4.72	25.4

Attachment 7. Letter mailed to site operators qualifying for level 1 of the followup evaluation for the intersite-comparison program. Highlighted text indicates customized fields for a NADP/NTN site participating in an intersite-comparison study.

United States Department of the Interior
U.S. GEOLOGICAL SURVEY
Box 25046 M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

IN REPLY REFER TO:

Date

To: Site Operator Name, Site Id
From: Natalie Latysh, USGS External Quality Assurance Project for the NADP/NTN
Subject: Intersite-Comparison Study Number

Dear Site Operator Name:

The pH value of -- pH units reported by your NADP/NTN site for intersite-comparison study number was not within the acceptable range.

Measuring the pH of low-ionic strength solutions (like wet-deposition or, intersite-comparison solutions) can be difficult. The following problems may be sources of difficulties when measuring pH at site id:

1. pH electrode/meter problems
2. Systematic measuring technique errors
3. Calibrating pH meter with contaminated buffer solutions

Seeing how you have submitted acceptable results in previous studies, we ask that you review your techniques, check the expiration dates on the buffer solutions, and ensure the fluids are at room temperature when taking pH measurements (sample temperature can affect results). Please review the guidelines for performing pH measurements on our Web site: http://bqssun/precip/project_overview/intersite_forms/is_intro.htm, for helpful information. You may wish to remeasure the remaining portion of the intersite comparison solution and e-mail or phone in your new results (optional). If you are still unable to obtain a value in the acceptable range of -- to -- pH units, or if you have questions, please contact me at: nlatysh@usgs.gov, (303)236-1874. Thank you for participating in the intersite-comparison program.

Best regards,

Natalie Latysh

Attachment 8. Letter mailed to site operators qualifying for level 2 of the followup evaluation for the intersite-comparison program. Highlighted text indicates customized fields for a NADP/NTN site participating in an intersite-comparison study.

United States Department of the Interior
U.S. GEOLOGICAL SURVEY
Box 25046 M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

IN REPLY REFER TO:

Date

To: Site Operator Name, Site Id
From: Natalie Latysh, USGS External Quality Assurance Project for the NADP/NTN
Subject: Intersite-Comparison Study Number

Dear Site Operator Name:

The pH value of -- pH units reported by your NADP/NTN site for intersite-comparison study number was not within the acceptable range. Measuring the pH of low-ionic strength solutions (like wet-deposition or intersite-comparison solutions) can be difficult. The following problems may be sources of difficulties when measuring pH at site id:

1. pH electrode/meter problems
2. Systematic measuring technique errors
3. Calibrating meter with contaminated buffer solutions

Please review your techniques, check the expiration dates on the buffer solutions, ensure the fluids are at ambient room temperature when taking pH measurements (sample temperature can affect results), and replace the electrode filling solution if you have not done so recently. Please review the guidelines for performing pH measurements on our web site: http://bqssun/precip/project_overview/intersite_forms/is_intro.htm, for helpful information. Please remeasure the pH of the remaining portion of the intersite number solution and complete the enclosed card to report your new pH value. You do not need to remeasure specific conductance. Please mail your response by date. If you have any questions, please e-mail me at: nlatysh@usgs.gov or call: (303)236-1874.

Thank you for participating in the intersite-comparison program.

Best regards,

Natalie Latysh

Attachment 9. Letter mailed to site operators who do not respond to the original intersite-comparison study qualifying for level 2 of the followup evaluation for the intersite-comparison program. Highlighted text indicates customized fields for a NADP/NTN site participating in an intersite-comparison study.

United States Department of the Interior
U.S. GEOLOGICAL SURVEY
Box 25046 M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

IN REPLY REFER TO:

Date

To: Site Operator Name, Site Id
From: Natalie Latysh, USGS External Quality Assurance Project for the NADP/NTN
Subject: Intersite-Comparison Study Number

Dear Site Operator Name:

Results were not received for intersite-comparison study number from site id. The intersite-comparison program is a mandatory quality-assurance program for NADP/NTN sites, which assesses the accuracy of field pH and specific-conductance measurements. Field measurements provide the most accurate gage of precipitation chemistry because samples can change prior to laboratory analysis. The intention of this program is to ensure field measurements are accurate by identifying possible problems; therefore the accuracy and precision of field measurements must be evaluated for all sites in the NADP/NTN.

Because site id did not participate in study number, we are requesting the following:

1. Please measure the pH and specific conductance of the enclosed sample, and
2. Return the enclosed response card by date.

A report describing the results will be sent to you. IF YOU ARE NOT ABLE TO PERFORM THE REQUESTED MEASUREMENTS PLEASE LET US KNOW. You can direct questions and concerns to Natalie Latysh at: (303)236-1874, nlatysh@usgs.gov, or fax: (303) 236-1880. Thank you!

Best regards,

Natalie Latysh

Attachment 10. Letter mailed to site operators qualifying for level 3 of the followup evaluation for the intersite-comparison program. Highlighted text indicates customized fields for a NADP/NTN site participating in an intersite-comparison study.

MARCH 3, 1849

IN REPLY REFER TO:

United States Department of the Interior
U.S. GEOLOGICAL SURVEY
Box 25046 M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

Date

To: Site Operator Name, Site Id
From: Natalie Latysh, USGS External Quality Assurance Project for the NADP/NTN
Subject: Intersite-Comparison Study Number

Dear Site Operator Name:

The pH value of -- pH units reported by your NADP/NTN site for intersite-comparison study number was not within the acceptable range. Measuring the pH of low-ionic-strength solutions (like wet-deposition or intersite-comparison solutions) can be difficult. The following problems may be sources of difficulties when measuring pH at site id:

1. pH electrode/meter problems
2. Systematic measuring technique errors
3. Calibrating meter with contaminated buffer solutions
4. Solutions not being at room temperature (>23°C/65°F) during analysis

To help isolate the problem(s) we are requesting that you:

1. Measure the pH of the enclosed aliquot;
2. Remeasure the remaining portion of the intersite number solution;
3. Report your pH values on the enclosed response cards and mail them to the USGS.

Note: <u>You do not need to measure specific conductance.</u>

Please review your techniques, check the expiration dates on the buffer solutions, ensure the fluids are at ambient room temperature when taking pH measurements (sample temperature can affect results), and replace the electrode filling solution if you have not done so recently. Please review the guidelines for performing pH measurements on our Web site: http://bqssun/precip/project_overview/intersite_forms/is_intro.htm. Please mail your response by date. If you have any questions, please e-mail me at: nlatysh@usgs.gov or call: (303)236-1874. Thank you for participating in the intersite comparison program.

Best regards,

Natalie Latysh

Attachment 11. Letter mailed to site operators qualifying for level 4 of the followup evaluation for the intersite-comparison program. Highlighted text indicates customized fields for a NADP/NTN site participating in an intersite-comparison study.

United States Department of the Interior
U.S. GEOLOGICAL SURVEY
Box 25046 M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

IN REPLY REFER TO:

Date

To: Site Operator Name, Site Id

From: Natalie Latysh, USGS External Quality Assurance Project for the NADP/NTN

Subject: Intersite-Comparison Study Number

Dear Site Operator Name:

The pH value of -- pH units reported by your NADP/NTN site for intersite-comparison study number was not within the acceptable range. Measuring the pH of low-ionic-strength solutions (like wet-deposition or intersite-comparison solutions) can be difficult. The following problems may be sources of difficulties when measuring pH at site id:

1. pH electrode/meter problems
2. Systematic measuring technique errors
3. Calibrating meter with contaminated buffer solutions
4. Solutions not being at room temperature (>23^{o}C/65^{o}F) during analysis

To help isolate the problem(s) we are requesting that you:

1. Please measure the pH of the TWO enclosed aliquots;
2. Remeasure the remaining portion of intersite number solution;
3. Report your values on the appropriate response cards.

Note: You do not need to measure specific conductance.

Please review your techniques, check the expiration dates on the buffer solutions, ensure the fluids are at ambient room temperature when taking pH measurements (sample temperature can affect results), and replace the electrode filling solution if you have not done so recently. Please review the guidelines for performing pH measurements on our Web site: http://bqssun/precip/project_overview/intersite_forms/ is_intro.htm. Please mail your response by date. If you have any questions, please e-mail me at: nlatysh@usgs.gov or call: (303) 236-1874. Thank you for participating in the intersite-comparison program.

Best regards,

Natalie Latysh

Attachment 12. Cover letter mailed to site operators participating in the sample-handling evaluation program. Highlighted text indicates customized fields for a NADP/NTN site participating in a sample-handling evaluation study.

MARCH 3, 1849
IN REPLY REFER TO:

United States Department of the Interior
U.S. GEOLOGICAL SURVEY
Box 25046 M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

Date

Site Operator Address

Dear Site Operator Name,

Your site has been chosen to participate in the NADP/NTN sample-handling evaluation (SHE) program during the first quarter of 2004. This quality-assurance program is intended to measure the effects of bucket residence time, routine handling, and processing on the chemistry of NADP/NTN precipitation samples. We appreciate your participation in this mandatory NADP/NTN quality-assurance program.

Enclosed please find the quality-assurance sample, instructions, and a Field Observer Report Form (FORF) for your participation in the SHE Program. Please read the enclosed instructions carefully and verify in advance that all of the supplies necessary to process the sample are available. The SHE sample sent to you should be submitted to the CAL along with the wet-deposition sample collected on date. If the pre-assigned date presents a scheduling conflict, please call me and we will reschedule your submission date. Please follow the steps outlined in the enclosed procedures and process the SHE sample accordingly.

If you have any questions, please call me at (303) 236-1874 or e-mail: nlatysh@usgs.gov. Thank you in advance for your participation in the sample-handling evaluation program.

Sincerely,

Natalie Latysh

Attachment 13. Sample-processing instructions mailed to site operators participating in the sample-handling evaluation program.

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK SAMPLE-HANDLING EVALUATION PROGRAM

INSTRUCTIONS FOR SUBMITTING A QUALITY-ASSURANCE SAMPLE FOR THE SAMPLE-HANDLING EVALUATION PROGRAM

Your site has been selected to participate in the Sample-Handling Evaluation (SHE) Program. The SHE Program is one of the external quality-assurance programs operated by the U.S. Geological Survey for the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). It is designed to measure the effects of handling, processing, and shipping on the chemistry of NADP/NTN precipitation samples.

PLEASE READ ALL INSTRUCTIONS BEFORE PROCEEDING

Please verify ahead of time that you have all necessary supplies

****** DO NOT SUBMIT THE SAMPLE UNTIL YOUR ASSIGNED DATE ******

(Please refer to the attached cover letter for the assigned date)

ENCLOSED PLEASE FIND THE FOLLOWING SUPPLIES:

- Sample Handling Evaluation sample
- Postage paid "Sample Handling Evaluation Record" card for sample transfer and decanting times addressed to the USGS
- Field Observer Report Form (FORF)

If you did not receive any of these items, please call: (303) 236-1874 or e-mail: nlatysh@usgs.gov.

ADDITIONAL SUPPLIES THAT YOU WILL NEED (from the supply cache provided to you by the CAL):

- A clean field bucket and snap-on lid (bagged)
- Clean 1-liter High-Density Polyethylene (HDPE) sample bottle (bagged)
- Clean 4-milliliter vials for field chemistry measurements*
- Equipment for performing pH and specific-conductance measurements*
- A standard mailer for shipping samples to the CAL

* If your site does not perform chemistry measurements, please note this on the enclosed postcard and complete the other sample-processing steps according to the instructions.

****

OVERVIEW: 75% of the sample-handling evaluation (referred to as SHE from this point) sample will be poured into a clean sample-collection bucket where it will remain for a minimum of 24 hours. The sample will then be transferred into a standard 1-liter sample-collection bottle in your laboratory and field chemistry measurements will be determined. The two SHE samples (25% remaining in original bottle and 75% of the sample that resided in the bucket) will be sent to the CAL in one mailer, along with the sample-collection bucket and lid used to process the SHE sample. There are many detailed steps that need to be correctly completed; so please read all of the instructions carefully before you begin, then follow all instructions in the order they are listed.

****

Attachment 13. Sample-processing instructions mailed to site operators participating in the sample-handling evaluation program—Continued.

As you go through the following steps, please keep in mind that one of your goals is to handle the SHE sample in the same manner that you would an actual precipitation sample. Take the same care with the SHE sample that you exercise with the weekly precipitation sample.

B. Initial processing of the SHE sample

On the morning of the day before you go to the field (typically Monday) to collect the wet-side bucket from your site (the day before the assigned bucket-off date listed on the SHE bottle and the enclosed cover letter), you will need to do some initial processing of the SHE sample:

Pour 75% of the SHE sample (down to the line on the bottle) into a clean, unused NADP/NTN field bucket. Tightly recap the bottle containing the remaining 25% of the SHE solution and place it into the ziploc bag in which it was sent. Using the bag as a glove, cover the bucket with a clean snap-on lid. Record on the "Sample Handling Evaluation - Card 1" postcard, under "Step A", the date and time you transferred 75% of the sample into the bucket.

Note: the SHE sample must reside in the bucket for a minimum of 24 hours and no more than 6 days.

C. Collecting the SHE sample

After a minimum 24-hour residence time, transfer the SHE sample from the bucket into a clean 1-liter sample bottle following standard NADP protocols. Be sure that the lip of the bucket does not touch the lip of the bottle while pouring the contents of the bucket into the bottle. **If you received a 2-liter sized SHE sample, please discard excess sample that does not fit into the 1-liter bottle after all processing is complete.**

Fill 4-mL vials and measure the pH and specific conductance following standard procedures; record your measurements on the enclosed postcard and on the provided FORF (if you do not perform chemistry measurements, please note this on the enclosed postcard). Please place the 1-liter bottle containing the SHE sample into the ziploc bag labeled "SHE Sample Bucket Portion." The two SHE samples (1-liter bottle containing the bucket portion; original bottle containing 25% of the solution) should be placed into a shipping mailer.

Record on the "Sample Handling Evaluation" postcard, under "Step B," the date and time that you transferred the SHE sample from the bucket to the 1-liter bottle. Under "Step C," record the sample pH and specific conductance.

D. Procedures for submitting the precipitation sample from your site to the CAL

Please follow standard procedures for submitting the weekly precipitation sample to the CAL: 1) collect the wet-side bucket; 2) measure the pH and specific conductance; 3) fill out the FORF accordingly; 4) place the precipitation sample bottle into a ziploc bag; and 5) mail all materials to the CAL, as you normally do each Tuesday. The SHE sample should be processed whether or not precipitation occurred at your site.

Attachment 13. Sample-processing instructions mailed to site operators participating in the sample-handling evaluation program—Continued.

E. Filling out the FORF for the SHE sample

Please fill out the enclosed FORF with information regarding the SHE sample. Several fields have already been filled out by the USGS. Please fill in the following fields: (1) Site Name; (2) Observer, initials; (3) Bucket on date and time when you poured the SHE sample into the bucket, and the bucket off date and time when you transferred the sample to a 1-liter bottle for shipment to the CAL (these values should correspond with the values on the postcard); (5) Sample Condition; (6) Bucket sample weight; (8) Sample chemistry; and (10) Remarks. Do not fill out the precipitation record. The sample depth and total raingage depth values will not agree.

F. Packing and shipping the SHE sample to the CAL

The two SHE samples (75% bucket portion, 25% remaining in original bottle), FORF, the bucket lid, and bucket in which the SHE sample was stored should be packed together in a shipping mailer. Please place the bucket and lid into a plastic bag and tuck the two SHE samples into the corners, around the bucket.

The 2-liter SHE sample does not fit in a corner by the bucket. In this case, please place the bucket lid under the bucket and package them both in a plastic bag. Push the plastic bag inside, conforming it to the inside shape of the bucket and place the two SHE sample bottles inside. The sample bottles should not touch the bucket surfaces because the bucket is completely enclosed in the plastic bag.

On the bag containing the bucket and lid that was used to store the SHE sample, please write your site identification, the date when you transferred the SHE sample from the bucket to the 1-liter bottle and indicate that it is a SHE sample. If you accidentally introduced any contamination into the sample, please write this on the bag. Otherwise, write "no contamination" for the contamination summary on the bag. Retain the pink copy of the FORF for your records.

G. Please mail the postcard addressed to the USGS promptly.

SUMMARY

On the scheduled date for processing the SHE sample you will mail two mailers to the CAL:

Mailer 1 will contain: (1) 25% of the minimally handled SHE sample in its original container; (2) 75% of the SHE sample that resided in the sample collection bucket and was transferred to a 1-liter bottle; (3) the FORF that was mailed to you with the SHE sample; and (4) the bagged bucket and lid used for processing the SHE sample, labeled with site id, SHE sample identification, contamination summary and the bucket off date.

Mailer 2 will contain: (1) the weekly precipitation sample; (2) field bucket and lid; (3) FORF; and (4) raingage chart-the standard materials that you typically mail to the CAL each week.

Special Notes:

For the 2-liter SHE samples, please discard excess sample that does not fit into the 1-liter bottle after all processing is complete.
If you do not perform field chemistry measurements, please note this on the enclosed postcard.
If you cannot process the SHE sample on the scheduled date, please contact the USGS and we will reschedule.

Attachment 13. Sample-processing instructions mailed to site operators participating in the sample-handling evaluation program—Continued.

Answers to Frequently Asked Questions:

1. **Q** If there wasn't any precipitation at my site during the past week, do I still submit the SHE sample?

   A Yes, you will still submit the SHE sample. The SHE sample and the weekly precipitation sample are processed completely separately from each other.

2. **Q** Do I need to write anything on the 1-L shipping bottle that contains my actual sample or on the 1-L shipping bottle containing 75% of the SHE sample for identification purposes?

   A No, process the weekly precipitation sample as you do each week and the SHE sample according to the instructions. Please make sure that the correct samples are placed in the correct mailers. Please never write on the sample bottles.

3. **Q** Which sample information should go on the enclosed postcards?

   A Please only enter the information about the SHE sample on the postcards.

4. **Q** The instructions are to decant 75% of the SHE sample on the morning of the day before the regular precipitation sample is collected. If this Monday is a holiday and I hadn't planned to come into the office that day can I decant 75% of the SHE sample on Friday and process it the following Tuesday?

   A The sample can reside in the clean bucket for up to 6 days before the scheduled processing date. Be sure to record the dates and times the sample was transferred into and out of the bucket on the postcard. A range of residence times varying from 1 to 7 days replicates what happens with actual precipitation at the site.

5. **Q** With submission of the SHE sample, what do I need to do differently with my weekly precipitation sample?

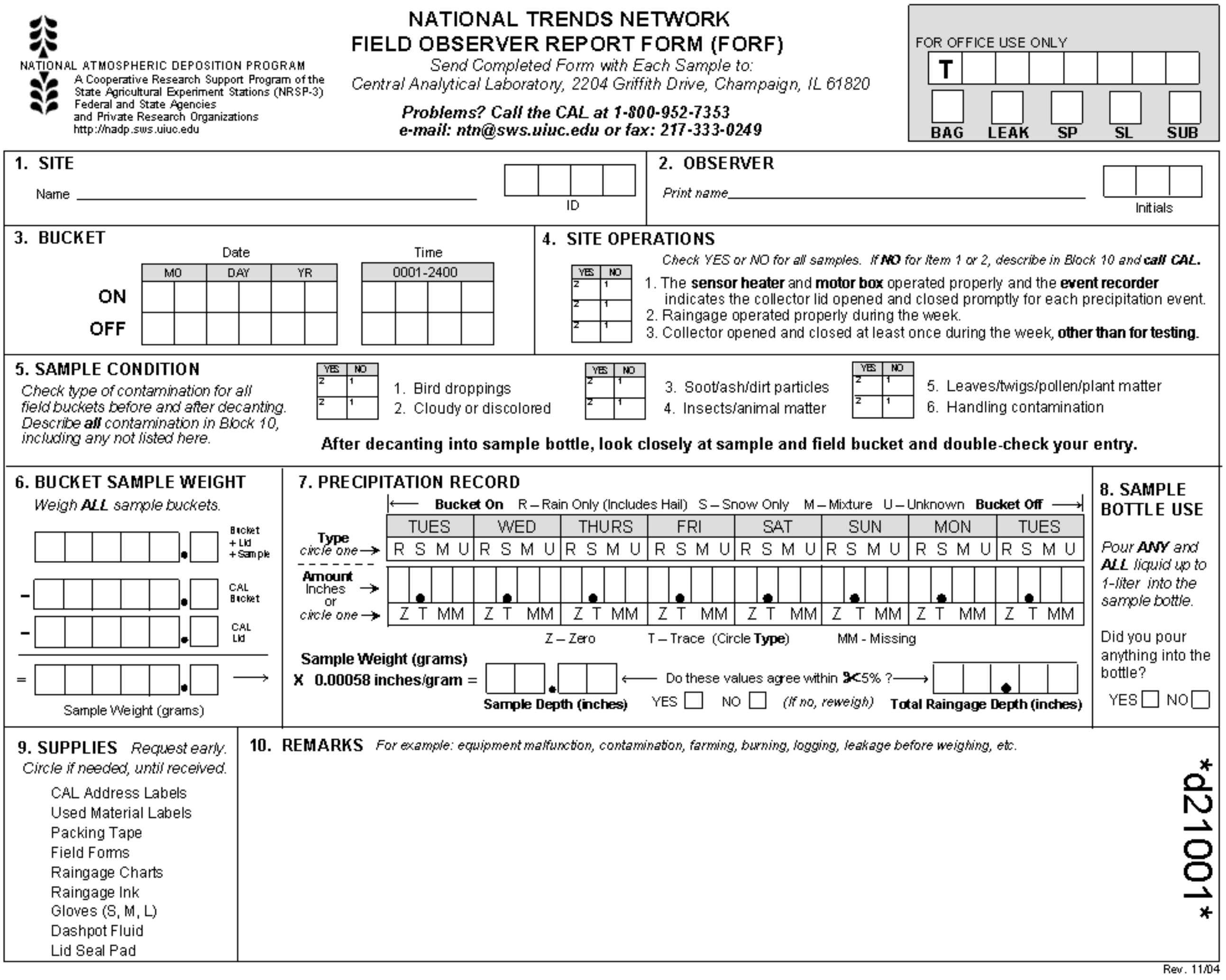
   A Nothing differently needs to be done when submitting the weekly precipitation sample. Please fill out the FORF the same way you do each week, include the raingage chart, and mail everything to the CAL in a separate mailer from the SHE sample. You are basically processing two separate samples that have nothing to do with each other.

Please contact the USGS if you have questions or concerns:

Natalie Latysh - (303) 236-1874, e-mail: nlatysh@usgs.gov

Thank you for your participation in the Sample-Handling Evaluation Program. Your time is greatly appreciated.

Attachment 14. Field observer report form used by NADP/NTN site operators for recording sample information.



NATIONAL ATMOSPHERIC DEPOSITION PROGRAM
A Cooperative Research Support Program of the State Agricultural Experiment Stations (NRSP-3)
Federal and State Agencies
and Private Research Organizations
http://nadp.sws.uiuc.edu

NATIONAL TRENDS NETWORK
FIELD OBSERVER REPORT FORM (FORF)
Send Completed Form with Each Sample to:
Central Analytical Laboratory, 2204 Griffith Drive, Champaign, IL 61820
Problems? Call the CAL at 1-800-952-7353
e-mail: ntn@sws.uiuc.edu or fax: 217-333-0249

FOR OFFICE USE ONLY
T ☐☐☐☐☐☐☐
☐ BAG ☐ LEAK ☐ SP ☐ SL ☐ SUB

1. SITE
Name ____________________ ☐☐☐☐ ID

2. OBSERVER
*Print name*____________________ ☐☐☐ Initials

3. BUCKET

	Date MO	Date DAY	Date YR	Time 0001-2400
ON				
OFF				

4. SITE OPERATIONS
*Check YES or NO for all samples. If **NO** for Item 1 or 2, describe in Block 10 and **call CAL.***

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

5. SAMPLE CONDITION
*Check type of contamination for all field buckets before and after decanting. Describe **all** contamination in Block 10, including any not listed here.*

YES	NO	
☐	☐	1. Bird droppings
☐	☐	2. Cloudy or discolored
☐	☐	3. Soot/ash/dirt particles
☐	☐	4. Insects/animal matter
☐	☐	5. Leaves/twigs/pollen/plant matter
☐	☐	6. Handling contamination

After decanting into sample bottle, look closely at sample and field bucket and double-check your entry.

6. BUCKET SAMPLE WEIGHT
*Weigh **ALL** sample buckets.*

	☐☐☐☐☐.☐	Bucket + Lid + Sample
–	☐☐☐☐☐.☐	CAL Bucket
–	☐☐☐☐☐.☐	CAL Lid
=	☐☐☐☐☐.☐ →	Sample Weight (grams)

7. PRECIPITATION RECORD
← **Bucket On** R – Rain Only (Includes Hail) S – Snow Only M – Mixture U – Unknown **Bucket Off** →

	TUES	WED	THURS	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
Amount 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

Z – Zero T – Trace (Circle **Type**) MM - Missing

Sample Weight (grams)
X 0.00058 inches/gram = ☐☐.☐☐ **Sample Depth (inches)** ← Do these values agree within ✂5% ? → ☐☐.☐☐☐ **Total Raingage Depth (inches)**
YES ☐ NO ☐ *(If no, reweigh)*

8. SAMPLE BOTTLE USE
*Pour **ANY** and **ALL** liquid up to 1-liter into the sample bottle.*
Did you pour anything into the bottle?
YES ☐ NO ☐

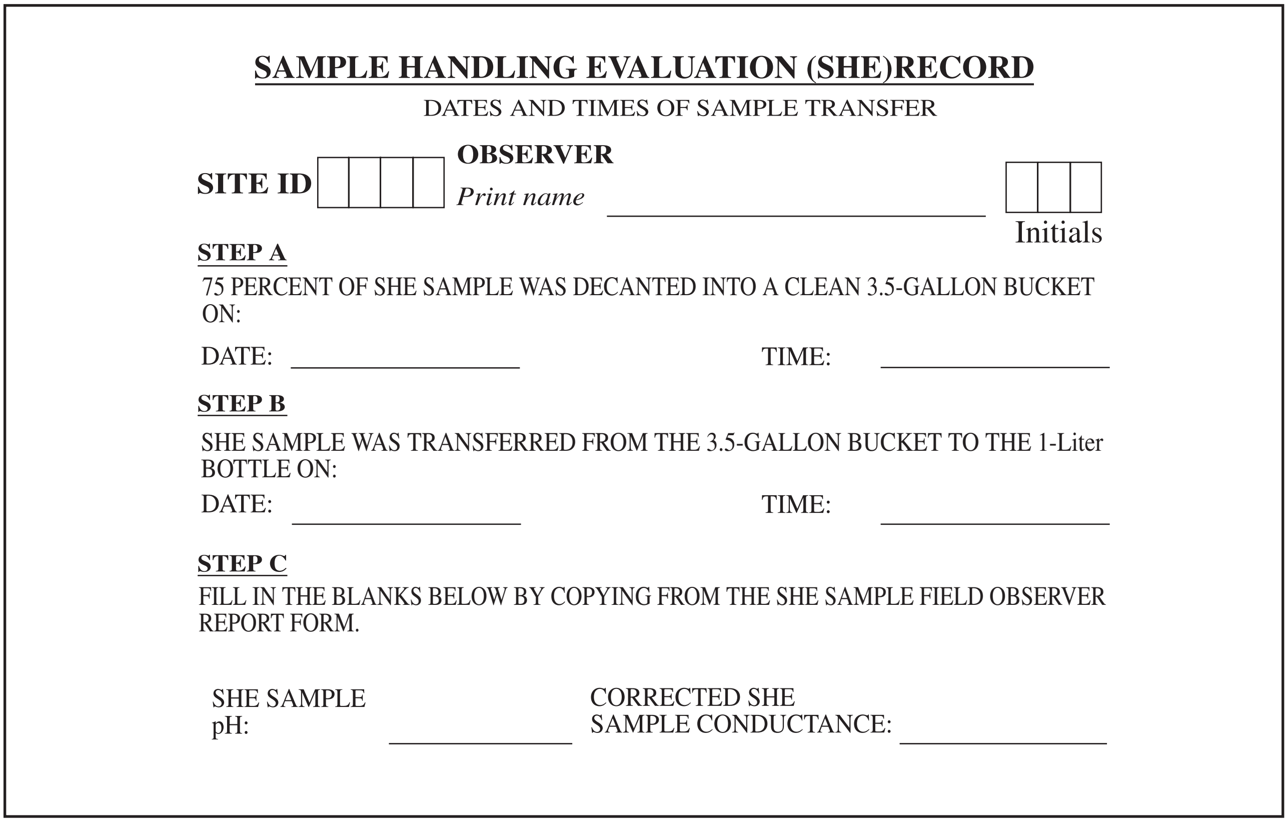
9. SUPPLIES *Request early.*
Circle if needed, until received.
CAL Address Labels
Used Material Labels
Packing Tape
Field Forms
Raingage Charts
Raingage Ink
Gloves (S, M, L)
Dashpot Fluid
Lid Seal Pad

10. REMARKS *For example: equipment malfunction, contamination, farming, burning, logging, leakage before weighing, etc.*

d21001

Rev. 11/04

Attachment 15. Postcard mailed to site operators for reporting processing information to the U.S. Geological Survey for the sample-handling evaluation sample.



SAMPLE HANDLING EVALUATION (SHE)RECORD

DATES AND TIMES OF SAMPLE TRANSFER

SITE ID ☐☐☐☐ **OBSERVER**
Print name ____________________ ☐☐☐
Initials

STEP A

75 PERCENT OF SHE SAMPLE WAS DECANTED INTO A CLEAN 3.5-GALLON BUCKET ON:

DATE: ______________ TIME: ______________

STEP B

SHE SAMPLE WAS TRANSFERRED FROM THE 3.5-GALLON BUCKET TO THE 1-Liter BOTTLE ON:

DATE: ______________ TIME: ______________

STEP C

FILL IN THE BLANKS BELOW BY COPYING FROM THE SHE SAMPLE FIELD OBSERVER REPORT FORM.

SHE SAMPLE pH: ____________ CORRECTED SHE SAMPLE CONDUCTANCE: ____________

Attachment 16. Cover letter mailed to site operators participating in the field-audit program. Highlighted text indicates customized fields for a NADP/NTN site participating in a field-audit study.

MARCH 3, 1849

IN REPLY REFER TO:

United States Department of the Interior
U.S. GEOLOGICAL SURVEY
Box 25046 M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

Date

Site Operator Address

Dear Site Operator Name,

Your site has been chosen to participate in the NADP/NTN field-audit program. This quality-assurance program is designed to measure the effects of field exposure, handling, and processing on the chemistry of NADP/NTN precipitation samples. We appreciate your participation in this mandatory NADP/NTN quality-assurance program.

Enclosed please find the sample, instructions, and forms for your participation in the NADP/NTN field-audit program. Please read the enclosed instructions carefully and verify in advance that all of the supplies necessary to process the sample are available. A portion of the field-audit solution must be poured into the Aerochem wet-side collection bucket that was installed in the field for an entire week with no precipitation. Because we cannot predict when your site will have a dry week, we cannot specify a submission date. Rather, you should try to submit the sample to the CAL between date (first Tuesday of the quarter) and date (last Tuesday of the quarter). If a dry week does not occur during this period, retain the sample until a full dry week occurs. If you do not have a dry week before deadline date (one year from quarter when sample is mailed), the sample will be invalidated.

A postcard is enclosed for recording sample-processing information. This information is needed to keep track of sample residence time in the bucket, notify the USGS of site participation, and ensure the data are correctly coded in the database. Because there is no specified submission date, it is important that you contact Scott Dossett, the CAL NADP/NTN site liaison, immediately after the sample is submitted, at (800) 952-7353, or e-mail: scottd@uiuc.edu. If you have any questions or concerns regarding the submission of the field-audit sample please call me at (303) 236-1874, or e-mail: nlatysh@usgs.gov. Thank you in advance for your participation in the field-audit program.

Sincerely,

Natalie Latysh

Attachment 17. Sample-processing instructions mailed to site operators participating in the field-audit program. Highlighted text indicates customized fields for a specific quarter during which a field-audit study is being conducted.

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK FIELD-AUDIT PROGRAM

INSTRUCTIONS FOR SUBMISSION OF THE FIELD-AUDIT SAMPLE

PLEASE READ ALL INSTRUCTIONS CAREFULLY BEFORE PROCEEDING

Your site has been selected to participate in the Field-Audit Program. The Field-Audit Program is one of the external quality-assurance programs operated by the U.S. Geological Survey for the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). The field-audit program is designed to measure the effects of field exposure, handling, and processing on the chemistry of NADP/NTN precipitation samples.

****** PLEASE DO NOT SUBMIT A FIELD-AUDIT SAMPLE UNTIL A WEEK ******
****** WITHOUT PRECIPITATION OCCURS AT YOUR SITE ******

The sample you have been sent should be submitted during the quarter of year (dates of specified quarter), after the first standard Tuesday-to-Tuesday sampling week without precipitation.

If you do not have a full dry week during this quarter, please retain the sample and process it after a dry week occurs during the following quarter. Continue to carry over to the following quarter until a year from the end of your originally assigned quarter passes (the label on the field audit sample indicates the last date for sample submission – deadline date). If your site does not have a dry week during this time period, enter “no dry week between dates (first date of assigned quarter-last date of quarter a year from the originally assigned quarter)” on the enclosed postcard. Return the pre-addressed postcard promptly and discard the sample.

ENCLOSED PLEASE FIND THE FOLLOWING SUPPLIES:

- One - field audit sample
- One - postage paid ‘FIELD AUDIT RECORD’ postcard for recording sample transfer information, decanting times, presence of rinse water, sample pH, and specific-conductance measurements

If you did not receive any of these items or these instructions are unclear, please call Natalie Latysh: (303)236-1874.

OTHER SUPPLIES YOU WILL NEED (ITEMS PROVIDED BY THE CAL THAT YOU NORMALLY USE TO PROCESS WEEKLY PRECIPITATION SAMPLES):

- A clean field bucket and snap-on lid (bagged)
- A clean 1-liter high-density polyethylene (HDPE) wide-mouth sample bottle (bagged)
- Four clean 4-milliliter vials for field chemistry measurements*
- Equipment for performing pH and specific-conductance measurements*
- Field Observer Report Form (FORF)
- A standard mailer for shipping samples to the CAL

* If your site does not perform chemistry measurements, please note this on the enclosed postcard and process the field-audit sample according to the instructions.

Attachment 17. Sample-processing instructions mailed to site operators participating in the field-audit program. Highlighted text indicates customized fields for a specific quarter during which a field-audit study is being conducted–Continued.

****

OVERVIEW: After verifying that no precipitation occurred during the preceding week, 75% of the field-audit sample is to be poured into the bucket that spent the previous week installed in the ìwet sideî of the collector. The field-audit solution should be allowed to equilibrate in the bucket for at least 24 hours. After a minimum of 24 hours, the sample must be processed and submitted to the CAL in the same manner as an actual precipitation sample. The remaining 25% of the field-audit sample should be shipped to the CAL in its original container. There are many detailed steps that need to be correctly completed, so please read the instructions carefully and follow them in the order listed.

****

STEP BY STEP INSTRUCTIONS

Procedures for submitting the field-audit sample from your site to the CAL:

A. Remove collection bucket from the field

Remove the wet-side collection bucket and snap the lid on the bucket, using the plastic bag as a glove. Install the new bucket as usual. Remove the raingage chart and install a new one. Transport the sealed bucket in a labeled plastic bag to where you perform field analysis and sample mailing.

B. **Verify that no precipitation occurred**

Process and submit a field-audit sample only if you have a standard Tuesday-to-Tuesday period when no precipitation occurred. Check the raingage chart, making sure the AeroChem collector lid did not open and uncover the wet-side bucket. Verify that no precipitation occurred; any event pen marks indicating that the sensor was activated must not have been accompanied by even the slightest rise on the precipitation record pen trace. If you are in an area with high humidity that results in lid openings during the week without precipitation, please note this in the comments section of the FORF (example: ìcollector opened due to heavy fog/humidity, but no precipitation occurredî). Verify the record is complete and there were no clock stoppages or pen skips on the event recorder chart. Inspect the wet-side bucket to ensure that it is at least as dry as it was when you installed it the previous week. If there were a few drops of rinse water in the bucket when you installed it the previous week, then there may still be a few drops of rinse water present in the bucket. THE KEY INDICATOR IS THAT THE PRECIPITATION TRACE WAS ABSOLUTELY FLAT EVEN IF THERE WERE LID OPENINGS IN RESPONSE TO PERIODS OF HIGH HUMIDITY. Once you have verified that (1) the wet deposition collector was working properly for the week; (2) there was no precipitation; (3) and any lid openings were caused by high humidity, proceed to step C to begin processing the field-audit sample. (If you cannot decide whether the criteria for submitting the field-audit sample have been met, please call Natalie Latysh at (303)236-1874.)

C. **Pour the field-audit sample into the wet-side bucket removed from the field**

During the transfer of the sample, please wear laboratory gloves and be careful not to contaminate the sample in any way. Pour 75% of the field-audit sample (down to the line marked on the bottle) into the bucket removed from the field. Tightly recap the bottle and place it in the plastic bag in which the field-audit sample was shipped. You will send this bottle containing 25% of the field-audit sample to the CAL for analysis. Cover the bucket securely with its snap-on lid. Swirl and shake the sample in the bucket several times to make sure that it has good contact with the bucket walls and lid, then set the bucket aside for at least 24 hours (but no longer than 6 days).

Attachment 17. Sample-processing instructions mailed to site operators participating in the field-audit program. Highlighted text indicates customized fields for a specific quarter during which a field-audit study is being conducted—Continued.

D. Transfer the sample from bucket to bottle and measure pH and specific conductance

After a minimum 24-hour equilibration period, transfer the field-audit sample from the field bucket into a clean 1-liter sample bottle provided by the CAL. Follow standard NADP protocols and keep in mind that the goal is to handle the field audit sample in the same manner, with the same care, as an actual precipitation sample. During sample transfer, be sure that the lip of the bucket does not touch the lip of the bottle. Record on the "FIELD AUDIT RECORD" postcard, under "Part A," the date and time that you transferred the sample into the bucket. Under "Part B" of the postcard, check the appropriate box, either "rinse water present in bucket" or "bucket was dry," depending on what you found. **THIS IS VERY IMPORTANT SINCE IT CAN INFLUENCE LABORATORY ANALYSIS. THE ONLY WATER PRESENT IN THE BUCKET BEFORE YOU ADD THE 75% OF THE SAMPLE SHOULD BE RINSE WATER.** In "Part C" please record your pH and corrected specific-conductance measurements.

E. Complete the Field Observer Report Form (FORF)

Use a normal FORF from the supply of forms sent to you by the CAL. PLEASE FILL OUT THE FORF FOLLOWING THESE INSTRUCTIONS:

1. STATION	Enter your site name and site id
2. OBSERVER	Print your name and initials
3. BUCKET ON/BUCKET OFF	Record the length of time the bucket spent in the field, as you do for a standard weekly precipitation sample
4. SITE OPERATIONS	Check appropriate boxes for items 1, 2 and 3
5. SAMPLE CONDITION	If you observed any contamination, check the appropriate box and be sure to note if any contamination is accidentally introduced
6. BUCKET SAMPLE WEIGHT	Weigh the (bucket+lid+sample) and record the weight, calculate the appropriate sample depth. NOTE: This value will not agree with the total raingage depth value because no precipitation was recorded, leave the box: ìDo these values agree within ± 5%?î blank
7. PRECIPITATION RECORD	Record the precipitation record off the raingage chart. NOTE: If conditions specified in Section B for submission of the field-audit sample were met, these values should be zero for the week. Check 'Yes' under BOTTLE USE for the question "Did you pour sample into the bottle?"
8. SAMPLE CHEMISTRY	Pour sample from the 1-liter HDPE bottle into clean vials and measure the pH and specific conductance following standard procedures and record your measurements
9. SUPPLIES	Request any supplies needed
10. REMARKS	Please write in the remarks that this is a 'FIELD AUDIT SAMPLE' and record any other remarks as you normally would

Attachment 17. Sample-processing instructions mailed to site operators participating in the field-audit program. Highlighted text indicates customized fields for a specific quarter during which a field-audit study is being conducted—Continued.

F. Fill out postcards and notify the NADP/NTN

Please mail the the postcard promptly to the USGS. The date you will be submitting the sample depends on a dry week occurring and is not known ahead of time. Therefore, it is important that you promptly call Scott Dossett, the NADP/NTN CAL site liaison, at 800-952-7353 or send an e-mail to sdossett@uiuc.edu upon sending the sample to alert the CAL of its arrival.

G. Mail both portions of the field-audit sample to the CAL in the shipping mailer

Use the shipping mailer to ship the 1-liter bottle to the CAL in the same manner as if it were the actual wet-deposition sample for your site. Be sure to include the original bottle with the remaining 25% of the field-audit sample. Enclose the raingage chart and the white and yellow copies of the field-audit sample Field Observer Report Form. Retain the pink copy for your records.

As a final checklist, please make sure the following items are in the shipping mailer:

1. The 1-liter sample bottle sealed in a plastic ziploc shipping bag, with site id, off date, and time written on the bag
2. The remaining 25% of sample in the original field-audit sample bottle, sealed in the original plastic ziploc shipping bag
3. The raingage chart
4. White and yellow copies of the FORF, with **“FIELD AUDIT SAMPLE”** written in the remarks field
5. Bagged bucket and lid, with site id, off date, and time written on the bag

Attachment 17. Sample-processing instructions mailed to site operators participating in the field-audit program. Highlighted text indicates customized fields for a specific quarter during which a field-audit study is being conducted—Continued.

ANSWERS TO FREQUENTLY ASKED QUESTIONS:

1. **Q** If there was some precipitation at my site during the past week, do I still submit the sample?

   A No, you will not submit the field-audit sample in this case. The field-audit sample is to be poured into the bucket which was installed in the collector only if there was a week with no precipitation and no water (other than rinse water) present in the collector bucket.

2. **Q** There was some precipitation at my site during the past week, but the collector malfunctioned and never opened. Do I still submit the field audit sample?

   A No, you will not submit the field-audit sample in this case. If the collector did not open due to a malfunction, please wait to submit the field-audit sample until a dry week occurs when all the equipment operates correctly.

3. **Q** There was no precipitation during the week, but the bucket has a few drops of water in it. I'm sure it is either condensation or water that was in the bucket when it arrived from the CAL. Do I submit the field-audit sample in this case?

   A Yes, you will submit the field-audit sample in this case. However, if any water other than CAL rinse water gets into the collection bucket, the field-audit sample should not be submitted. If, after reviewing the sensor activation pen marks, you are still not sure if the water in the bucket is only CAL rinse water, do not process the field audit sample.

4. **Q** Do I need to write anything on the 1-L shipping bottle for identification purposes?

   A No, send the sample to the CAL as if it were a regular sample from your site. Note the site id, off date, and time on the plastic bag.

5. **Q** The collector opened during the preceding week, but I am sure it was due to high humidity. Should I submit the field-audit sample?

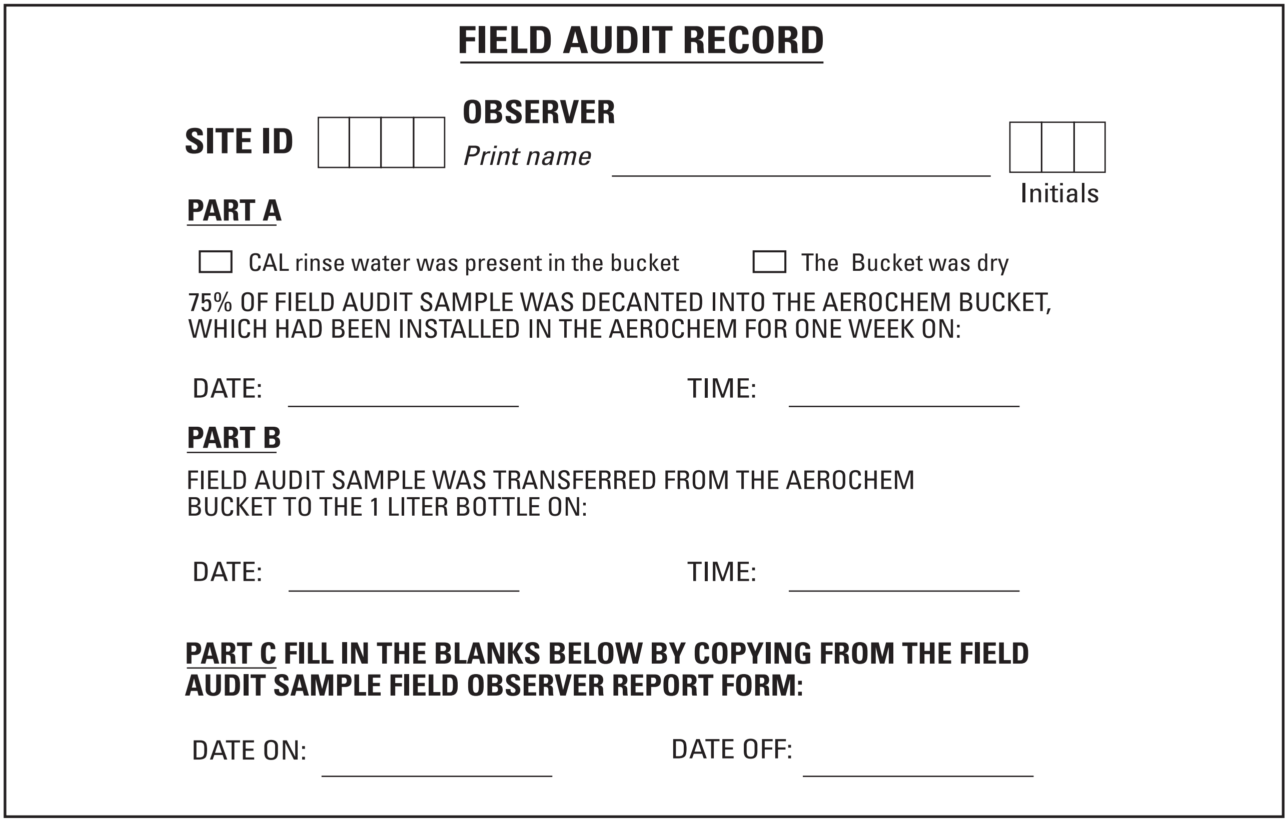
   A Yes, you should submit the sample after checking the raingage chart, making sure the pen marks did not record wet deposition. Please note in the comments why you think the collector opened (in this case please note the high humidity). This is very important since the CAL might not know the reason for the opening and hence invalidate the sample.

Thank you for your time and participation in the Field-Audit Program.

If you have any questions please contact:

Natalie Latysh
(303) 236-1874
E-mail address: nlatysh@usgs.gov

Attachment 18. Postcard mailed to site operators for reporting processing information for the field-audit solution.



FIELD AUDIT RECORD

SITE ID ☐☐☐☐

OBSERVER

Print name ____________________ ☐☐☐ Initials

PART A

☐ CAL rinse water was present in the bucket ☐ The Bucket was dry

75% OF FIELD AUDIT SAMPLE WAS DECANTED INTO THE AEROCHEM BUCKET, WHICH HAD BEEN INSTALLED IN THE AEROCHEM FOR ONE WEEK ON:

DATE: ____________ TIME: ____________

PART B

FIELD AUDIT SAMPLE WAS TRANSFERRED FROM THE AEROCHEM BUCKET TO THE 1 LITER BOTTLE ON:

DATE: ____________ TIME: ____________

PART C FILL IN THE BLANKS BELOW BY COPYING FROM THE FIELD AUDIT SAMPLE FIELD OBSERVER REPORT FORM:

DATE ON: ____________ DATE OFF: ____________

Attachment 19. Cover letter mailed to laboratories participating in the interlaboratory-comparison program. Highlighted text indicates customized fields for each participating laboratory.

MARCH 3, 1849

United States Department of the Interior
U.S. GEOLOGICAL SURVEY
Box 25046 M.S. 401
Denver Federal Center
Denver, Colorado 80225
Office of Water Quality
Branch of Quality Systems

IN REPLY REFER TO:

Date

Laboratory address

Dear Lab Participant:

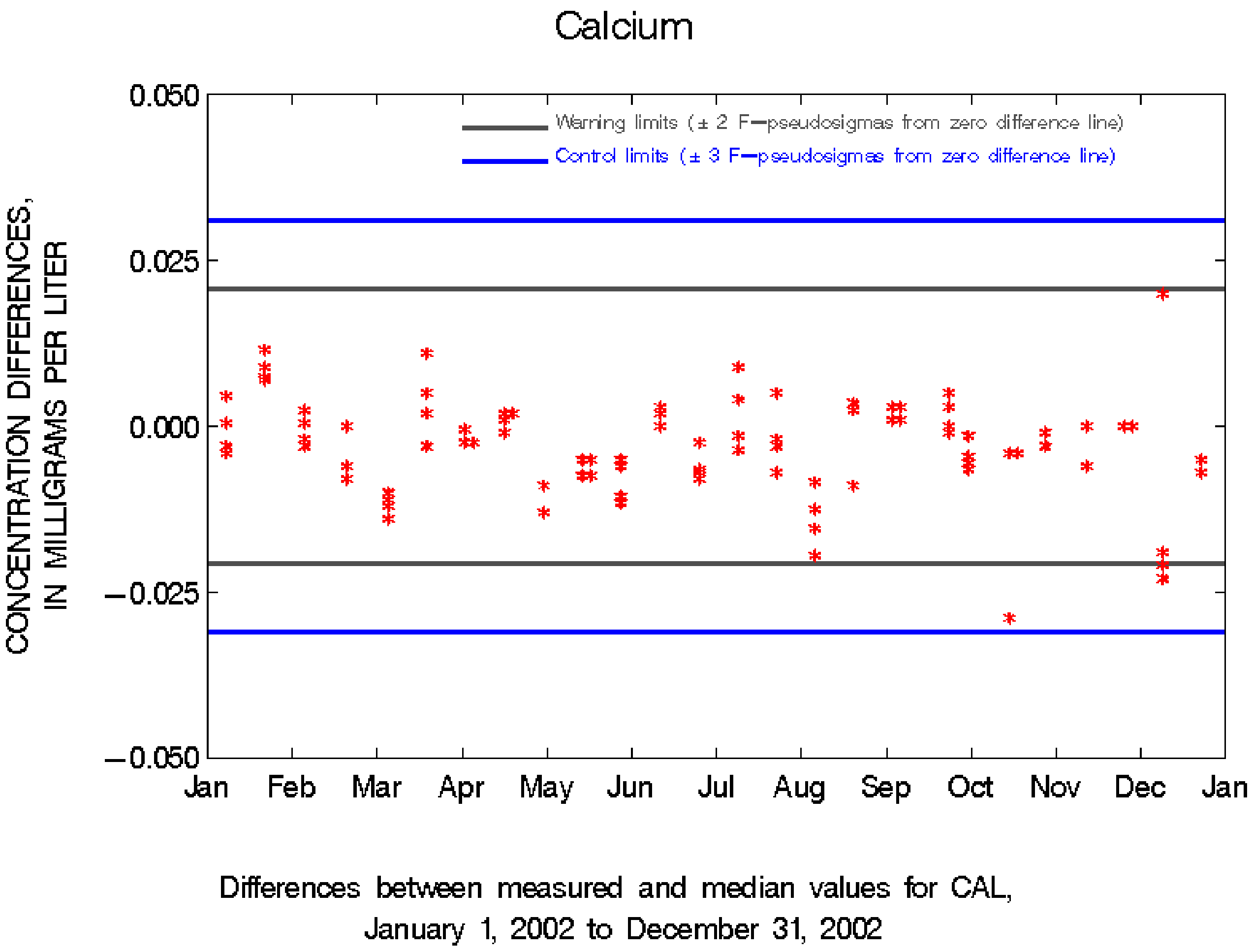
Enclosed are four samples for the interlaboratory-comparison program conducted by the U.S. Geological Survey in support of the National Atmospheric Deposition Program (NADP). The identification numbers for the enclosed samples are:

Please include the sample-identification numbers with your results. Please process these samples as soon as possible, to ensure sample stability. Each sample should be analyzed for pH, specific conductance, Ca^{2+}, Mg^{2+}, Na^{+}, NH_4^{+}, K^{+}, Cl^{-}, SO_4^{2-}, NO_3^{-}, and PO_4^{3-}. Please indicate the concentration units for your data, and indicate if NH_4, NO_3, and PO_4 values are reported as elements or species. Please include your precision values and detection limits. Please contact the USGS if you have questions ([303] 236-1874; nlatysh@usgs.gov).

Sincerely,

Natalie Latysh

Attachment 20. Control chart posted on the Internet (http://bqs.usgs.gov/precip_2/) displaying a participating laboratory’s results for the interlaboratory-comparison program.



Attachment 21. Data table displaying a final annual statistical summary for a solution analyzed by laboratories participating in the interlaboratory-comparison program.

Attachment B—Median values, 75th percentile values, 25th percentile values, number of samples analyzed, and f-pseudosigma values for the National Institute of Standards and Technology (NIST) certified sample SP1 submitted to the laboratories participating in the Interlaboratory Comparison Program during 2002.

SAMPLE NAME	LAB NAME	STAT	pH units	COND (mS/cm)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	NH4 (mg/L)	Cl (mg/L)	NO3 (mg/L)	SO4 (mg/L)
SP1	**ADORC**	Median	4.45	29.2	0.453	0.098	0.411	0.068	0.678	0.556	2.020	3.882
		25th Percentile	4.47	29.4	0.457	0.100	0.412	0.092	0.679	0.586	2.022	3.886
		75th Percentile	4.44	28.7	0.450	0.093	0.410	0.065	0.673	0.551	2.017	3.818
		F-pseudosigma	0.023	0.519	0.005	0.005	0.002	0.020	0.004	0.026	0.004	0.051
		N	9	9	9	9	9	9	9	9	9	9
	CAL	Median	4.429999828	30.4	0.439	0.095	0.419	0.078	0.634	0.586	2.111	3.891
		25th Percentile	4.43	30.7	0.445	0.097	0.427	0.081	0.638	0.593	2.124	3.920
		75th Percentile	4.420000076	30.2	0.436	0.093	0.418	0.078	0.632	0.584	2.103	3.856
		F-pseudosigma	0.007	0.363	0.007	0.003	0.007	0.002	0.004	0.007	0.016	0.047
		N	9	9	9	9	9	9	9	9	9	9
	MACTEC	Median	4.43	28.0	0.465	0.097	0.410	0.075	0.686	0.584	2.036	3.830
		25th Percentile	4.45	30.6	0.467	0.099	0.415	0.076	0.693	0.590	2.063	3.880
		75th Percentile	4.42	27.6	0.465	0.096	0.397	0.073	0.685	0.578	2.014	3.830
		F-pseudosigma	0.022	2.224	0.002	0.002	0.014	0.002	0.006	0.009	0.036	0.037
		N	9	9	9	9	9	9	9	9	9	9
	MOE	Median	4.41	27.4	0.440	0.095	0.395	0.075	0.686	0.590	2.095	3.900
		25th Percentile	4.42	27.9	0.440	0.100	0.400	0.075	0.686	0.590	2.135	3.925
		75th Percentile	4.37	27.0	0.440	0.095	0.390	0.070	0.682	0.585	2.009	3.875
		F-pseudosigma	0.037	0.702	0.000	0.004	0.007	0.004	0.003	0.004	0.094	0.037
		N	9	8	9	9	9	9	6	3	6	3
	MSC	Median	4.42		0.443	0.099	0.418	0.079	0.669	0.596	2.050	3.762
		25th Percentile	4.44		0.448	0.099	0.420	0.082	0.670	0.601	2.069	3.778
		75th Percentile	4.41		0.439	0.098	0.416	0.076	0.666	0.593	2.033	3.734
		F-pseudosigma	0.022		0.007	0.001	0.003	0.004	0.003	0.006	0.027	0.033
		N	9		9	9	9	9	9	9	9	9
	NILU	Median	4.42	30.6	0.450	0.100	0.417	0.080	0.670	0.580	2.081	3.865
		25th Percentile	4.46	30.9	0.480	0.100	0.420	0.090	0.676	0.593	2.081	3.984
		75th Percentile	4.41	30.4	0.430	0.100	0.410	0.077	0.670	0.570	2.036	3.805
		F-pseudosigma	0.040	0.371	0.037	0.000	0.007	0.010	0.005	0.017	0.033	0.133
		N	9	9	9	9	9	9	9	9	9	9
	NYSDEC	Median	4.41	23.0	0.502	0.104	0.406	0.097	0.671	0.558	2.042	3.342
		25th Percentile	4.42	27.0	0.531	0.106	0.410	0.107	0.695	0.562	2.084	3.844
		75th Percentile	4.40	23.0	0.481	0.099	0.382	0.085	0.669	0.554	2.007	3.320
		F-pseudosigma	0.015	2.965	0.037	0.005	0.021	0.017	0.019	0.006	0.057	0.388
		N	9	9	9	9	9	9	9	9	9	9
	SA	Median	4.36	26.0	0.424	0.094	0.411	0.074	0.678	0.585	2.066	3.767
		25th Percentile	4.38	26.1	0.434	0.097	0.412	0.074	0.680	0.586	2.079	3.774
		75th Percentile	4.36	25.8	0.418	0.093	0.399	0.070	0.673	0.581	2.061	3.753
		F-pseudosigma	0.015	0.222	0.012	0.003	0.010	0.003	0.005	0.004	0.013	0.016
		N	9	9	9	9	9	9	9	9	9	9

Median of all participating laboratories regarded as target values	4.42	28.3	0.448	0.098	0.411	0.076	0.673	0.585	2.063	3.828
25th percentile	4.38	26.5	0.437	0.095	0.400	0.072	0.667	0.571	2.023	3.767
75th percentile	4.44	30.2	0.465	0.100	0.419	0.082	0.686	0.592	2.090	3.883
NIST-certified concentrations reported by solution manufacturer (High Purity Standards)			0.460	0.092	0.420	0.076	0.680	0.590	2.100	3.850

Attachment 22. Data table displaying the number of times each participating laboratory reported a concentration greater than the minimum reporting limit for each analyte in the ultrapure deionized-water samples during 2003.

Laboratory	n[1]	NH4	Ca	Cl	Mg	NO3	K	Na	SO4
CAL	8						1[2]	1[3]	
Lab 2	8								
Lab 3	8								
Lab 4	8					4			
Lab 5	8	2	3			1	2	1	1
Lab 6	8								
Lab 7	8							1	
Lab 8	8								

[1] Represents the number of deionized water analyses submitted by each laboratory. Each laboratory receives eight ultrapure deionized-water samples annually.

[2] Sample identification: 2003147032.

[3] Sample identification: 2003062029.

Attachment 23. Instructions mailed to sites participating in the collocated-sampler program for disassembling and shipping the Belfort rain gage and Aerochem Metrics collector to the U.S. Geological Survey.

INSTRUCTIONS FOR PREPARING THE BELFORT RAINGAGE AND THE AEROCHEM METRICS WET/DRY SAMPLER FOR SHIPPING

Please take the Belfort Raingage Instruction Manual and NADP/NTN Site Operations Manual to the site during the disassembly, because the figures and text may be helpful.

Please do not attempt the disassembly of the tower if there is a chance of precipitation or blowing dust. The linkages of the tower are sensitive to corrosion and debris. The disassembly of the collocated site should take 3 to 5 hours to complete, depending on complexity of the site and the number of participants. An assistant is recommended.

Items included in this shipping mailer:

- Shipping stand for raingage tower
- USGS/NADP raingage disassembly instructions manual
- Twist ties for securing raingage pen arms during shipment
- Orange-handled screwdriver

You will need the following supplies:

- Two or three standard screwdrivers with small- to medium-sized blades for dismantling the equipment
- Original shipping crates with packing material (packing peanuts, shredded foam rubber, shredded newspaper or package tissue)
- Strapping tape, scissors, and a small plastic bag for loose hardware

Attachment 23. Instructions mailed to sites participating in the collocated-sampler program for disassembling and shipping the Belfort rain gage and Aerochem Metrics collector to the U.S. Geological Survey—Continued.

I. **Prepare the Belfort Raingage for shipment as follows:**

A. Remove the collector top (figure 1, #1) by rotating it sufficiently clockwise to disengage the bayonet lock and pulling it up and off of the raingage housing. Remove the catch bucket (figure 1, #4).

Figure 1

B. Remove the screw, washer, and bucket platform (figure 1, #5).

C. Unscrew the bottom five screws of the raingage housing (figure 2). Lift the case carefully off to expose the interior mechanism of the gage.

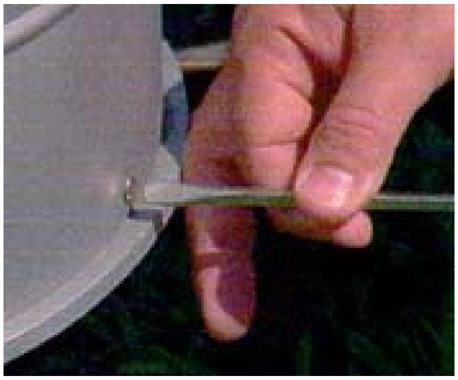


Figure 2

D. Move the mechanism’s chart pens out of the way with the supporting lever. If present, remove thumbnut from chart drive mechanism spindle (located inside the top of the chart cylinder). Remove chart cylinder (with chart clip) from the spindle and replace the thumbnut. Tape the chart clip to the chart cylinder so it is not lost during shipping.

Attachment 23. Instructions mailed to sites participating in the collocated-sampler program for disassembling and shipping the Belfort rain gage and Aerochem Metrics collector to the U.S. Geological Survey—Continued.

E. Spin the clock counterclockwise to remove it.

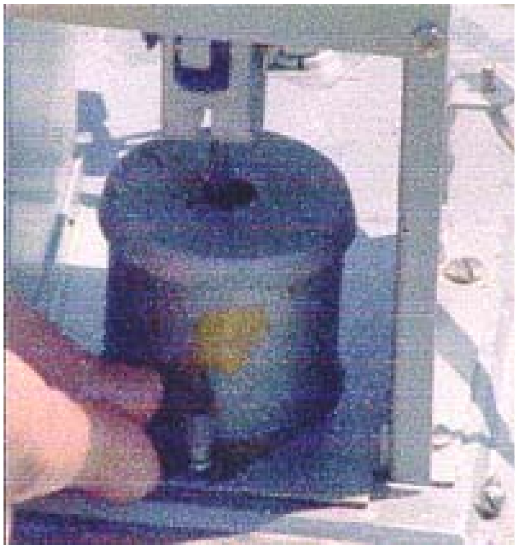


Figure 3.

F. To remove the dashpot, reach inside the bottom of the tower, remove both thumb screws that hold the dashpot in place, push up the dashpot cover and gently slide the dashpot forward (figure 3). Be careful not to spill the dashpot oil on your clothes. The dashpot top and connecting rod will stay in place as the dashpot is moved out from under the tower. PLEASE DO NOT FORCE this removal. With a little pressure the dashpot should slide right out. Empty the dashpot oil into a container. Dab the recording ink from the pens with a napkin.

G. Disconnect the event recorder cable from the Belfort and Aerochem Metrics terminals, replacing the screws on the terminals of both instruments. Pull up the event recorder cable and place it in the Belfort bucket, along with the bottle of recording ink and the dashpot. Please surround the items with packing peanuts or other packing material (shredded newspaper, tissue shredded foam rubber).

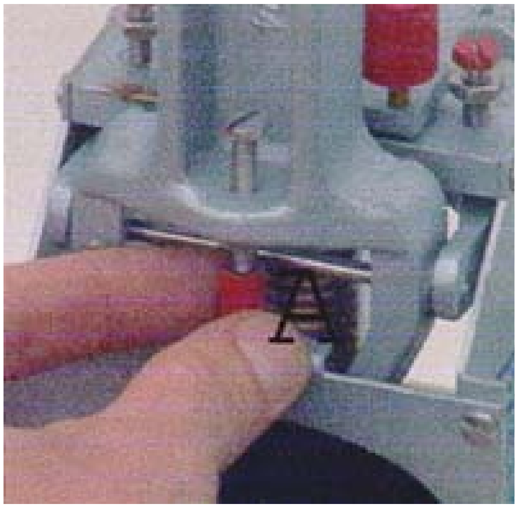


Figure 4.

H. Place the red shipping stop sleeve to stabilize the mechanism (figure 4, A; noted by red arrow in figure 7). As the limit screws are tightened (described in next step) the bolt should come down until it clears the inside of the sleeve and locks the whole mechanism in place. **IMPORTANT: DO NOT tighten the bolt (at point A, figure 4) or change its setting in any way!!!**

Attachment 23. Instructions mailed to sites participating in the collocated-sampler program for disassembling and shipping the Belfort rain gage and Aerochem Metrics collector to the U.S. Geological Survey—Continued.

I. Tighten the two limit screws equally, alternating between the two screws as you tighten them all the way down (figure 5, two small red screws) to stabilize the tower during transport. The lock nuts on the limit screws should be tightened and the limit screws should be lowered (turned clockwise) until they are firmly set against the top lever (U-shaped piece at Point B in figure 5). The tightening procedure will cause the pen level to be at about the 3-inch level. Tie the pen arms to the pen shifter using the enclosed twist ties. The shaft that supports the bucket platform should now be completely immobilized.

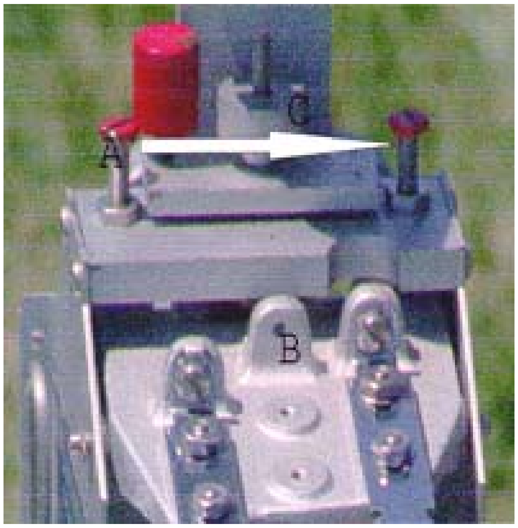


Figure 5

J. Using the orange-handled screwdriver, separate the tower from the mechanism base by removing the 4 small screws at each corner (figure 6). Please handle the tower and screws with care; the tower is fragile and the screws are easy to lose. Pick up the tower by holding it in the middle, on the left side. Do not put pressure on the backside of the mechanism where the fragile stick-like “links” are located.

Figure 6

Attachment 23. Instructions mailed to sites participating in the collocated-sampler program for disassembling and shipping the Belfort rain gage and Aerochem Metrics collector to the U.S. Geological Survey—Continued.

J. Using the orange-handled screwdriver, separate the tower from the mechanism base by removing the 4 small screws at each corner (figure 6). Please handle the tower and screws with care; the tower is fragile and the screws are easy to lose. Pick up the tower by holding it in the middle, on the left side. Do not put pressure on the backside of the mechanism where the fragile stick-like “links” are located.

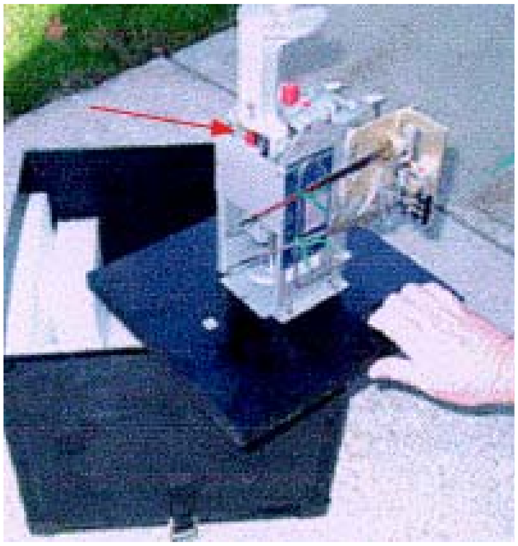


Figure 7

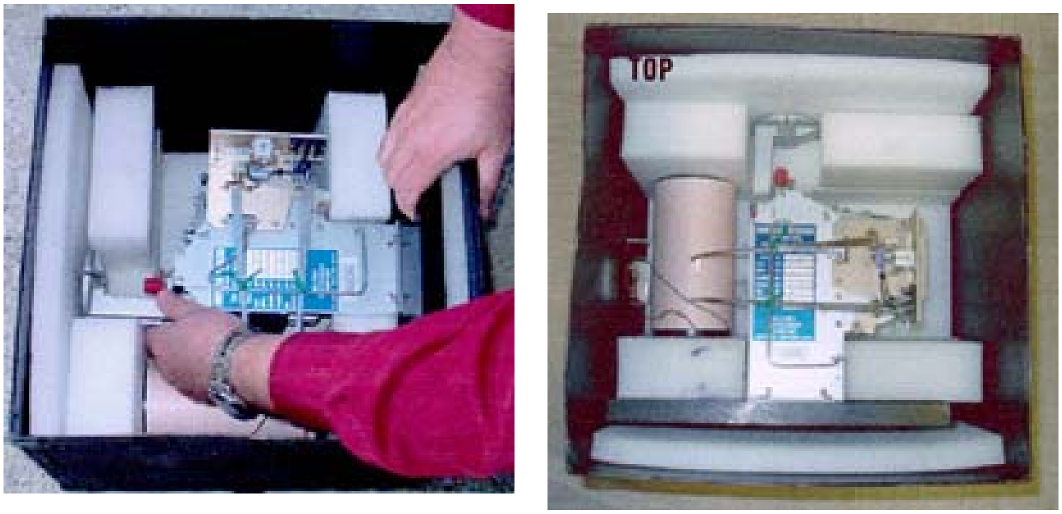


Figure 8

L. Place the raingage clock and drum into the corner of the packing as shown (figure 8). Grasp the top of the tower (mounted on the black base) with your left hand and the black plastic shipping base with your right hand and carefully lower the tower into the mailer.

Attachment 23. Instructions mailed to sites participating in the collocated-sampler program for disassembling and shipping the Belfort rain gage and Aerochem Metrics collector to the U.S. Geological Survey—Continued.

M. Insert the bucket-retaining platform and screw the washer into the top of the white foam packing. Place the foam block on top of the mailer (figure 9). Place lid on the mailer. Run each strap through the small, loose metal clasp, cinching it down between the small metal clasp and the larger buckle.

Figure 9

N. Remove the heavy aluminum base of the raingage from the platform (the three-legged T-bar stand that supports the base of the raingage) by unscrewing the large bolts. Replace the raingage housing, correctly positioning it on the mechanism base (reversing Step B). Fasten the housing in place with the five screws. Please include the bucket in the housing and support it with packing material to prevent damage during transport.

O. Pull/dig up the Belfort platform. Disassemble the platform by removing the 3 bolts holding the 3 stakes onto the cross-piece (T-bar) base. Tape the stakes together and wrap with padding material. Place the stakes and base in the Belfort shipping crate. Make sure that the stakes and platform are well padded and will not move during shipment.

P. Replace the collector top on the raingage housing, reversing the procedure of Step A. You may have to position the collector top upside-down on the raingage housing in order for the collector to fit in the shipping crate. Place the raingage housing in the shipping crate and secure it with packing material so that it will not shift during transit.

Attachment 23. Instructions mailed to sites participating in the collocated-sampler program for disassembling and shipping the Belfort rain gage and Aerochem Metrics collector to the U.S. Geological Survey—Continued.

II. <u>Prepare the Aerochem Metrics Wet/Dry Collector for shipping as follows</u>:

A. Remove the bolts or rebar stakes that secure the Aerochem Metrics Wet/Dry (ACM) collector. The stakes or rebar should be taped together and padded for shipping in the ACM collector crate.

B. Set the ACM Wet/Dry Collector on its side and remove the aluminum legs and cross supports. Tape the 6 legs and cross supports together for shipping. Put the nuts and bolts in a plastic bag and tape the bag to the underside of the ACM collector.

C. Remove the sensor, wrap with bubblewrap or other soft, protective material, and secure it to the underside of the frame of the collector, using heavy-duty packing tape. The sensor is fragile. Please secure it away from the motorbox and counterweight. Secure the bucket spring clips. You can tape them to the collector deck or remove them (if they come off easily), put them in a plastic bag, and tape the bag to the underside of the collector.

D. Secure all other loose bolts and parts in a plastic bag and tape to the underside of the collector.

Pack the raingage and collector in the same crates used to ship the equipment to your site. Install sufficient packing material under, around, and above the equipment to prevent shifting and damage during transit.

Attachment 23. Instructions mailed to sites participating in the collocated-sampler program for disassembling and shipping the Belfort rain gage and Aerochem Metrics collector to the U.S. Geological Survey—Continued.

PLEASE SHIP THE FOLLOWING ITEMS TO THE USGS:

- A black shipping mailer containing
  - Belfort tower mechanism with event recorder
  - Bucket retaining platform with screw and washer
  - Clock drive with chart drum and clip
  - Orange-handled screwdriver
- Belfort raingage housing, including top catchment
- Raingage bucket
- ACM collector, rebar stakes, 6 legs, sensor, bucket clips, extension cord, nuts and bolts
- This instruction manual

PLEASE SHIP THE EQUIPMENT TO:

Natalie Latysh, MS 401
US Geological Survey
Denver Federal Center
Bldg. 53, Entrance S-1
Denver, CO 80225

Please notify the USGS when the equipment is shipped ([303]236-1874; nlatysh@usgs.gov).

We realize the extra effort involved in running a collocated site. We greatly appreciate the extra time you have invested in this Program!!!

Thank you for your work on this project!

USGS

Latysh and Wetherbee—**External Quality-Assurance Programs Managed by the U.S. Geological Survey in Support of the National Atmospheric Deposition Program/National Trends Network**—USGS/OFR 2005–1024

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