EXTERNAL QUALITY-ASSURANCE RESULTS FOR THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/ NATIONAL TRENDS NETWORK DURING 1994

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CONVERSION FACTORS

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
liter (L)	1.057	quart
milliliter (mL)	0.03381	ounce, fluid

Temperature can be converted from degree Celsius (°C) to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5(°C) + 32$$

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

microsiemens per centimeter at 25 degrees Celsius (µS/cm)
megohms (MΩ)
microequivalents per liter (µeq/L)
milligrams per liter (mg/L)
kilograms per hectare (kg/ha)
microgram (µg)

External Quality-Assurance Results for the National Atmospheric Deposition Program/National Trends Network During 1994

By John D. Gordon, Mark A. Nilles, Dana K. Polacsek, *and* Melanie E. Ratcliff

ABSTRACT

Four distinct quality-assurance (QA) programs were used by the U.S. Geological Survey to provide external QA for the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). To assess the pH and specific-conductance determinations made by NADP/NTN site operators, an intersite-comparison program was used. The analytical bias introduced during routine handling, processing, and shipping of wet-deposition samples and precision of analyte values were estimated using a blind-audit program. An interlaboratory-comparison program was used to evaluate differences between analytical results and to estimate the analytical precision of five laboratories that routinely analyzed wet deposition in 1994. The precision of the overall precipitation collection and analysis system was estimated by a collocated-sampler program.

Results of two intersite-comparison studies completed in 1994 indicated 85 and 88 percent of the onsite pH determinations met the NADP/NTN accuracy goals, whereas 95 and 96 percent of the specific-conductance determinations were within the established limits.

The Wilcoxon signed-rank test of data collected as part of the blind-audit program indicated that routine sample handling, processing, and shipping introduced positive bias (α=0.05) for calcium and sulfate. Statistically significant negative bias (α=0.05) was introduced for ammonium, sodium, chloride, and hydrogen ion. The median paired differences between the bucket and bottle portions ranged from -0.02 milligram per liter for ammonium to +0.004 milligram per liter for calcium. For hydrogen ion, the median paired difference between the bucket and bottle portions was -1.00 microequivalent per liter.

Surface chemistry effects due to different amounts of precipitation contacting the sample collection and shipping container surfaces were studied in the blind audit program using 3 different sample volumes. The results of a hypothesis test of the relation between hydrogen ion differences and sample volume were not statistically significant in 1994, supporting the premise that the chemical reactions between the 13-L bucket shipping container and the sample that resulted in an increasing loss of hydrogen ion with increasing volume in every year of the study prior to 1994 have been eliminated by the new 1-L bottle sample shipping protocol.

Among the five laboratories participating in the interlaboratory-comparison program, a Friedman test indicated significant bias (α=0.01) in analyte concentrations for calcium, magnesium, sodium, ammonium, chloride, nitrate, sulfate, hydrogen ion, and specific conductance. Intralaboratory bias was indicated for most laboratories in tests of certified analyte concentrations from standard reference material samples and from ultrapure deionized-water samples. Precision estimates for the cations at the 50th percentile exhibited less variability than precision estimates at the 50th percentile for the anions, pH, and specific conductance.

Results from the collocated-sampler program indicated the median relative error for cation concentration exceeded 7 percent at most sites, whereas the median relative error for sulfate and nitrate concentration and sample volume was less than 7 percent at all sites. The median relative error for hydrogen-ion concentration and deposition ranged from 4.6 to 13.0 percent at the four sites and, as indicated in previous years of the study, was inversely proportional to the acidity of the precipitation at a given site. Overall,

collocated-sampling error typically was five times that of laboratory error estimates for most analytes.

INTRODUCTION

The National Atmospheric Deposition Program/ National Trends Network (NADP/NTN) investigates the occurrence and effects of wet deposition across the United States. NADP/NTN data are used to monitor spatial and temporal trends in the chemical composition of wet deposition (Robertson and Wilson, 1985; Peden, 1986). Research scientists use NADP/NTN data to study the effects of acidic deposition on human health and the environment. All operators of NADP/ NTN sites used the same type of wet-deposition collectors, which are described by Bigelow and Dossett (1988). Sample-handling and shipping protocols were extensively revised in 1994 in an effort to reduce sample contamination. These protocol changes have been delineated in a revised edition of the NADP/NTN instruction manual, which is currently available to site operators but has not been published as such (Scott Dossett, Illinois State Water Survey, oral commun., 1996). All site operators used the same sample-handling protocols and sent their samples for chemical analysis to the Illinois State Water Survey, Central Analytical Laboratory (CAL).

This report describes the results of the external quality-assurance (QA) programs operated by the U.S. Geological Survey (USGS) in support of the NADP/ NTN during 1994. These programs are designed to: (1) Assess the precision and accuracy of onsite determinations of pH and specific conductance (intersite-comparison program); (2) evaluate potential contamination of samples due to handling, processing, and shipping of samples collected within the NADP/NTN (blind-audit program); (3) estimate the comparability, bias, and precision of analytical results obtained by separate laboratories routinely measuring wet deposition when portions of common samples are sent to the participating laboratories (interlaboratory-comparison program); and (4) estimate the overall precision of the monitoring network, from the point of sample collection through storage of the data in the NADP/NTN data base, by the analysis of paired samples from collocated samplers at selected sites in the network (collocated-sampler program). A protocol report providing detailed information on the procedures and analytical methods used in these four QA programs is available (See and others, 1990).

STATISTICAL APPROACH

Hypothesis testing for paired differences using rank-based alternatives to traditional hypothesis testing (which assume a normal distribution) were used extensively in this report, including the Wilcoxon signed-ranks test, the Kruskal-Wallis test, and the Friedman test. Nonparametric statistical tests were used because none of the data sets for these QA programs satisfy the normal distribution requirements essential to traditional statistics. The use of non-parametric tests also avoided the problems inherent in the use of transformations commonly used to compensate for non-normal data, such as the difficulty of converting the results of statistical tests back to the original scale (Berthouex and Brown, 1994). Concise graphical displays such as boxplots were used to depict data distributions and provide visual representations of NADP/NTN data quality. The magnitude of measurement bias was quantified in many different ways for the convenience of the reader, including units of concentration, mass, and percent differences.

INTERSITE-COMPARISON PROGRAM

On a weekly basis, NADP/NTN site operators remove the precipitation samples from their AeroChem collectors and measure the pH and specific conductance before shipping the samples to the CAL for analysis. The importance of these onsite measurements is underscored by the fact that under certain conditions, changes in the chemical composition of precipitation will occur between the time a sample is collected in the field and the time it is analyzed at a central laboratory (Bigelow and Dossett, 1988). Hem (1985) found that onsite determinations of pH and specific conductance are much more likely to represent conditions in precipitation when it occurred than are subsequent laboratory determinations.

Intersite-comparison studies assess the accuracy and precision of pH and specific-conductance measurements made by NADP/NTN site operators (Gordon and others, 1991). All site operators were mailed intersite-comparison samples and asked to determine pH and specific conductance during each intersite-comparison study. Intersite-comparison samples consisted of synthetic precipitation with pH formulated to be within a range of 3.9 to 5.3, the approximate range for natural wet-deposition samples collected by the NADP/NTN. Because the reference solutions were formulated from dilute nitric acid, the specific conductance was a predictable function of the pH of the solution.

Results for Intersite-Comparison Studies 33 and 34

The sample mailings for intersite-comparison studies 33 and 34 were completed in April and September 1994, respectively. Site-operators were allowed 45 days to accomplish the requested analyses. Table 1 summarizes the statistics and site-operator participation in 1994. Site-operator results were assessed using the NADP/NTN measurement-accuracy criterion (Aubertin and others, 1990). The NADP/NTN accuracy goals for onsite pH determinations used in 1994 were ±0.10 pH unit of the actual pH. This criterion increases to ±0.30 pH unit when the actual pH exceeds 5.0. The NADP/NTN goal for onsite specific-conductance measurements was ±4.0 µS/cm. A flowchart depicting the intersite-comparison program is shown in figure 1.

The target pH of the intersite study 33 reference solution was 4.80; the calculated specific conductance corresponding to this target pH was 6.68 µS/cm. The median pH of those values reported by the study 33 deadline was 4.79, and the median specific conductance of those values reported by the deadline was 7.40 µS/cm. A total of 182 site operators submitted pH results on time in study 33, and 85 percent of these pH values met the established NADP/NTN accuracy requirements (± 0.10 pH unit of the overall median pH). Using the median value of all on time responses as the best estimate of the actual specific conductance, 95 percent of the site operators' reported values that were submitted by the deadline met the NADP/NTN accuracy goal for specific conductance (± 4.0 µS/cm of the median value).

The reference solution used in study 34 had a target pH of 4.54 and a calculated specific conductance of 20.0 µS/cm. The median pH of those values reported by the closing date for study 34 was 4.54, and the median specific conductance of those values reported by the deadline for study 34 was 20.7 µS/cm. Of the pH values reported by the deadline for study 34, 88 percent were within the acceptable range of 4.54 ± 0.10 pH. In study 34, 96 percent of the specific-conductance values reported on time were within the NADP/NTN accuracy goal of ± 4.0 µS/cm.

Figure 2 depicts scatterplots of the distribution of pH and specific-conductance values for all of the participating site operators in studies 33 and 34. Superimposed on the scatterplots in figure 2 are boundaries defining NADP/NTN accuracy goals for pH and specific-conductance measurements. Boundaries delineating the pH and specific-conductance values for those site operators successfully meeting the goals for one, both, or none of the measurements are also depicted. The percentile distributions for the reported pH and specific-conductance values in studies 33 and 34 are provided in figure 3.

Intersite-Comparison Study Followup Program

After the data from the intersite-comparison study were tabulated, the results from sites whose operators did not meet the pH accuracy goals were examined further. Prior to further evaluation, the reported values were converted into standardized z-values. Z-values are analogous to z-scores, which are described by Iman and Conover (1983). By using standardized z-values, each site operator's performance relative to the performance of all other site operators can be evaluated objectively. The standardized z-values take into account the amount by which the pH measurement accuracy goals were missed, given the relative difficulty of measuring the pH of the solution on the basis of its hydrogen-ion concentration. Using a cumulative z-value total for the three most recent studies, each site operator was placed into one of five categories. Category 0 sites were judged to have a very minor problem with their performance and thus received no followup. Sites in categories 1-4 each received different levels of followup. The followup for each successive category was additive, building on the followup for the preceding category of site operators. Category 1 operators receive a letter discussing the problem with the recent measurements reported for their site with suggestions for improving measurement quality. Category 2 operators are asked to remeasure the intersite sample. Category 3 operators receive one additional aliquot to measure, and category 4 operators receive two additional aliquots to measure.

Additional aliquots of synthetic rain samples with pH and specific-conductance values within the normal range for precipitation collected at NADP/NTN sites were distributed to site operators asked to participate in followup levels 3 and 4. Thirty-three site operators either did not participate or did not meet the pH measurement accuracy goals in the initial phase of intersite study number 33 and were included in the fol-

Table 1. *Site-operator responses and summary statistics for the 1994 intersite-comparison program*

	Intersite-comparison study	
Site-operator responses	**33**	**34**
Number of site operators receiving samples	189	189
Number of site operators submitting pH values by closing date of study	182	180
Number of site operators submitting specific conductance values by closing date of study	183	182
Site operators responding late	1	3
Number of nonresponding site operators	6	2
Sites that were not in operation	0	0
Site operators reporting equipment problems:		
pH meter/electrode completely inoperable	0	4
pH meter/electrode problems	0	4
Specific-conductance probe/meter completely inoperable	0	2
Specific-conductance probe/meter problems	0	0
Median pH[1]	4.79	4.54
F-pseudosigma for pH[1]	.067	.044
Median specific conductance, in microsiemens per centimeter at 25 degrees Celsius[1]	7.40	20.7
F-pseudosigma for specific conductance[1]	.371	.667
Number of responding sites that met the pH accuracy goals (±0.10)[1]	155	159
Percentage of responding sites that met the pH accuracy goals (±0.10)[1]	85	88
Number of responding sites that met the specific-conductance accuracy goals (±4.0 µS/cm)[1] goals (±4 µS/cm)	173	177
Percentage of responding sites that met the specific-conductance accuracy goals(±4.0 µs/cm)[1] goals (±4 µS/cm)	95	96

[1] Late responses not included.

lowup study. Of these 33 sites, 10 received the least serious form of followup, a letter describing common causes of measurement error. The remaining 23 sites included in the followup study were asked to complete additional pH measurements. Fifteen of the 23 operators asked to make additional pH measurements as part of the intersite-comparison study 33 followup procedure met the NADP/NTN accuracy goals for those measurements which they completed, indicating apparent successful resolution of the cause of their initial measurement difficulties. The followup portion of study 34 involved 30 site operators, all of whom were asked to complete additional pH measurements. Of the 26 operators that participated in the intersite-comparison study 34 followup procedure, 19 met the accuracy goals for all additional measurements. Figure 4 summarizes the followup results for 1994.

BLIND-AUDIT PROGRAM

Description of program

A blind-audit program is used to estimate the effects of routine sample handling, processing, and shipping of wet-deposition samples on analyte bias and precision. Site operators disguise a portion of the blind-audit sample as an actual precipitation sample and submit it to the CAL for analysis. The remaining portion of the blind-audit sample is sent to the CAL in a separate mailer and analyzed independently of the portion disguised as an actual precipitation sample. Figure 5 records all components of the blind-audit program, from sample preparation to distribution of interpretive reports.

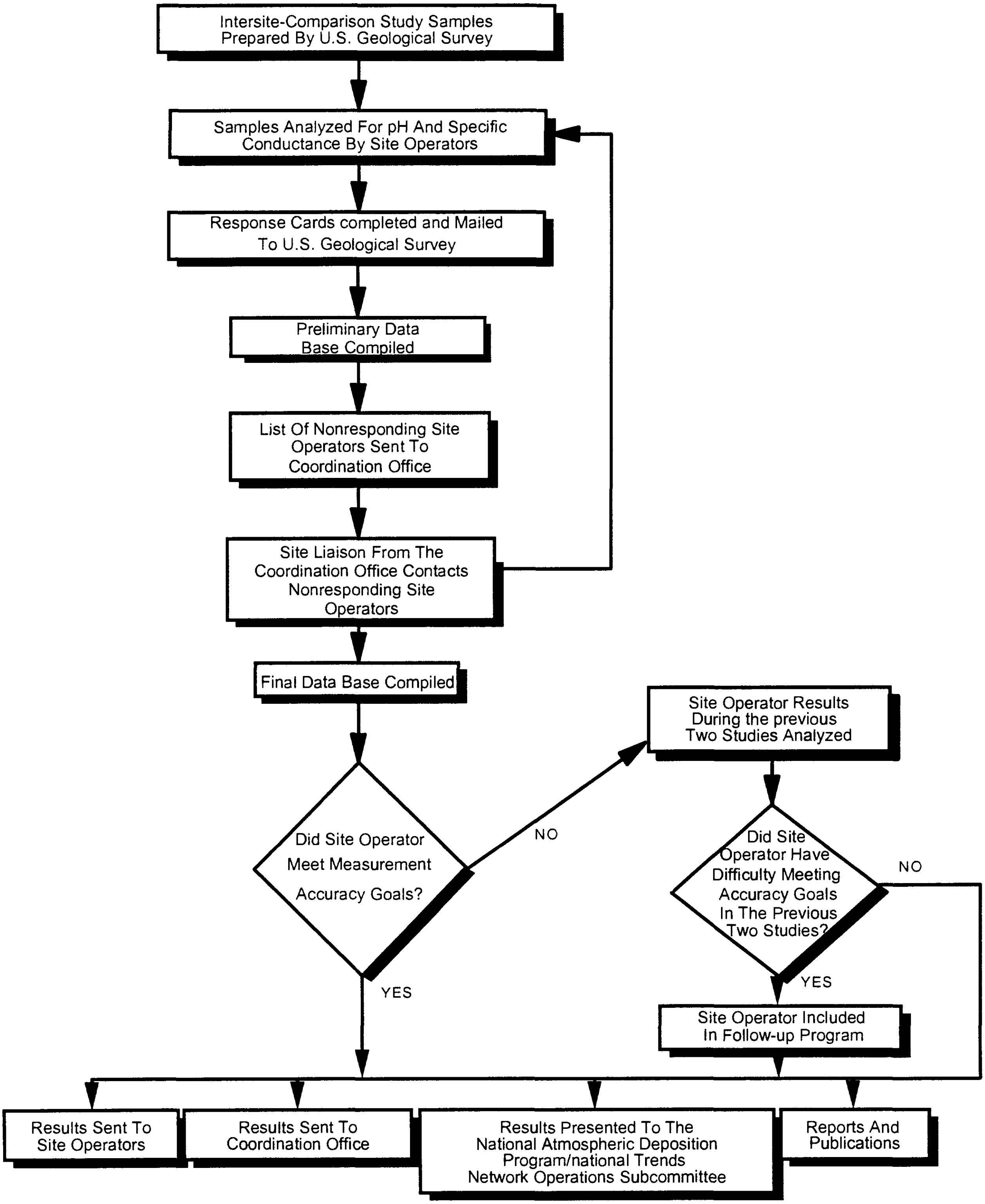
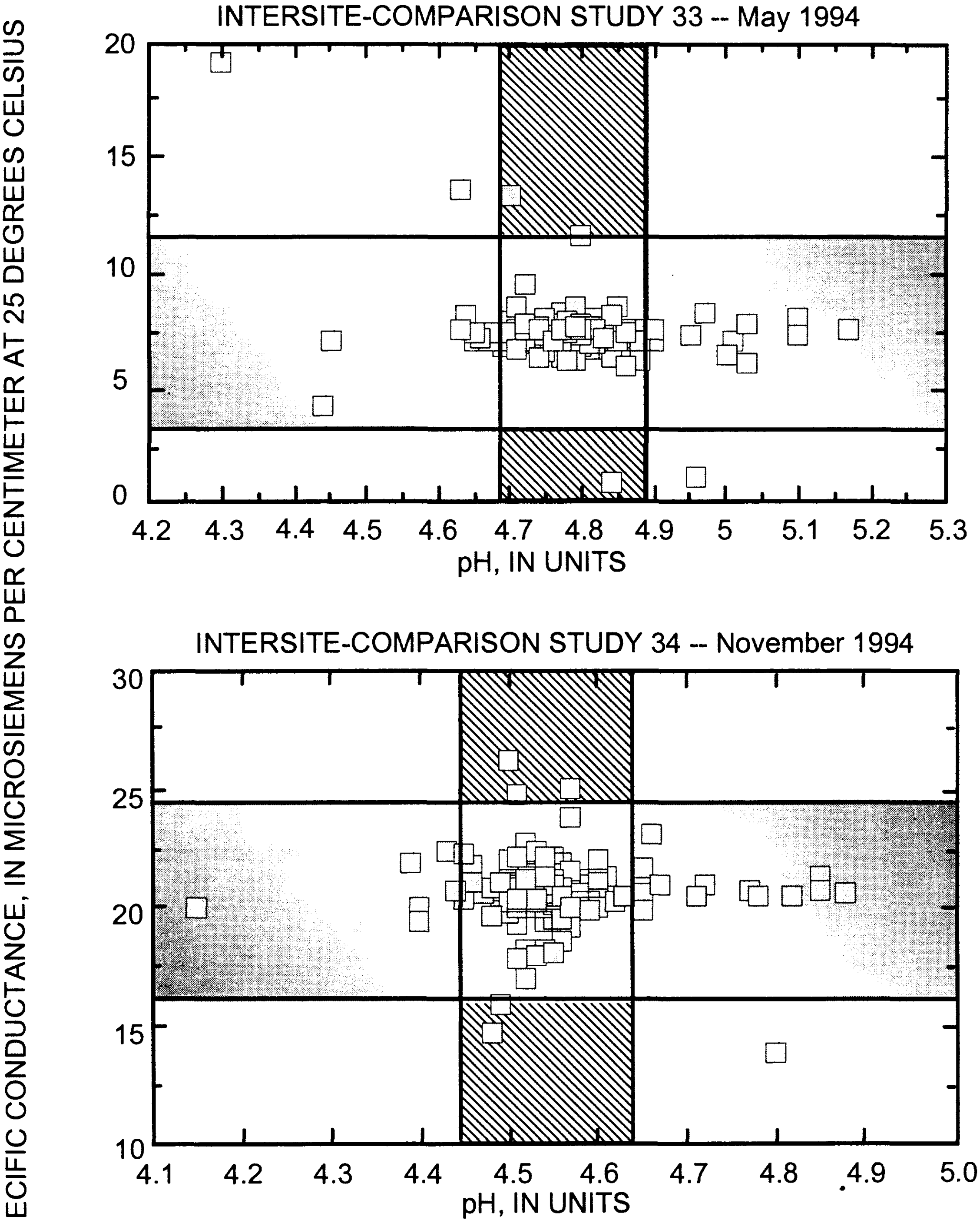


Figure 1. Intersite-comparison program.



EXPLANATION

▨ **Met National Atmospheric Deposition Program/ National Trends Network (NADP/NTN) goals for pH only**

☐ **Met NADP/NTN goals for pH and specific-conductance**

▧ **Met NADP/NTN goals for Specific Conductance only**

Note: These data pairs were off-scale in study 33:

pH, Specific Conductance	
4.48, 78.9	4.79, 31.5
4.70, 28.9	4.86, 69.0
4.72, 71.9	5.33, 5.50

No data pairs were off-scale in study 34.

Figure 2. Distribution of pH and specific-conductance values for intersite-comparison studies 33 and 34.

PERCENTILES

FOR pH MEASUREMENTS

INTERSITE-COMPARISON STUDY NUMBER	5	10	25	50	75	90	95
33	4.64	4.70	4.74	4.79	4.83	4.80	4.97
34	4.46	4.49	4.51	4.54	4.57	4.63	4.69

pH, IN UNITS

FOR SPECIFIC CONDUCTANCE MEASUREMENTS

	5	10	25	50	75	90	95
33	6.30	6.70	7.10	7.40	7.60	8.2	8.60
34	18.3	19.6	20.3	20.7	21.2	22.0	22.3

SPECIFIC CONDUCTANCE, IN MICROSIEMENS PER CENTIMETER

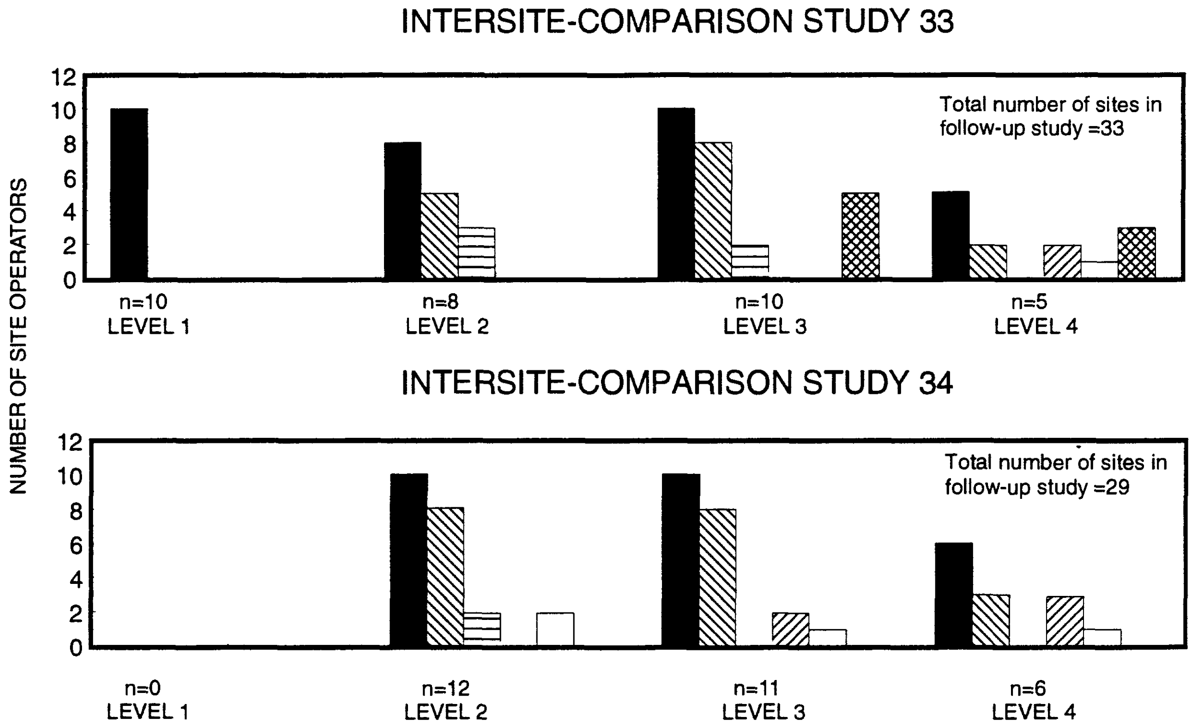
EXPLANATION

▨ MEDIAN VALUES OF THOSE REPORTED BY ALL SITE OPERATORS RESPONDING BY THE CLOSING DATE OF THE STUDY ARE USED FOR DEFINING NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK ACCURACY CRITERIA

ACCURACY CRITERIA ON pH MEASUREMENTS IN STUDIES 33 AND 34 WAS THE MEDIAN VALUE ± 0.10 pH UNIT

ACCURACY CRITERIA ON SPECIFIC CONDUCTANCE MEASUREMENTS IN STUDIES 33 AND 34 WAS THE MEDIAN VALUE ± 4.0 µS/cm

Figure 3. Percentiles for pH and specific conductance from intersite-comparison studies 33 and 34.



EXPLANATION

Number of site operators that:

■ Participated in the follow-up study

▧ Met NADP/NTN goals for pH measurements in the follow-up study*

▤ Did not meet NADP/NTN goals for pH measurements in the follow-up study

▨ Had mixed success meeting NADP/NTN goals for pH measurements in the follow-up study*

□ Did not participate in the follow-up study

▩ Did not complete all of the follow-up analysis

*For those measurements which the site operator completed. Site operators in levels 2-4 were asked to perform 1-3 additional measurements as explained below, and sometimes did not complete all of the requested analysis.

LEVEL 1 follow-up:
(1) Letter discussing common sources of measurement errors

LEVEL 2 follow-up:
(1) Letter discussing common sources measurement errors
(2) Request that site operator reanalyze the remaining portion of the test solution

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

LEVEL 4 follow-up:
(1) Letter discussing common sources of measurement errors
(2) Request that site operator reanalyze the remaining portion of the test solution
(3) Two additional aliquots of test solution

Figure 4. Followup study results for intersite-comparison studies 33 and 34.

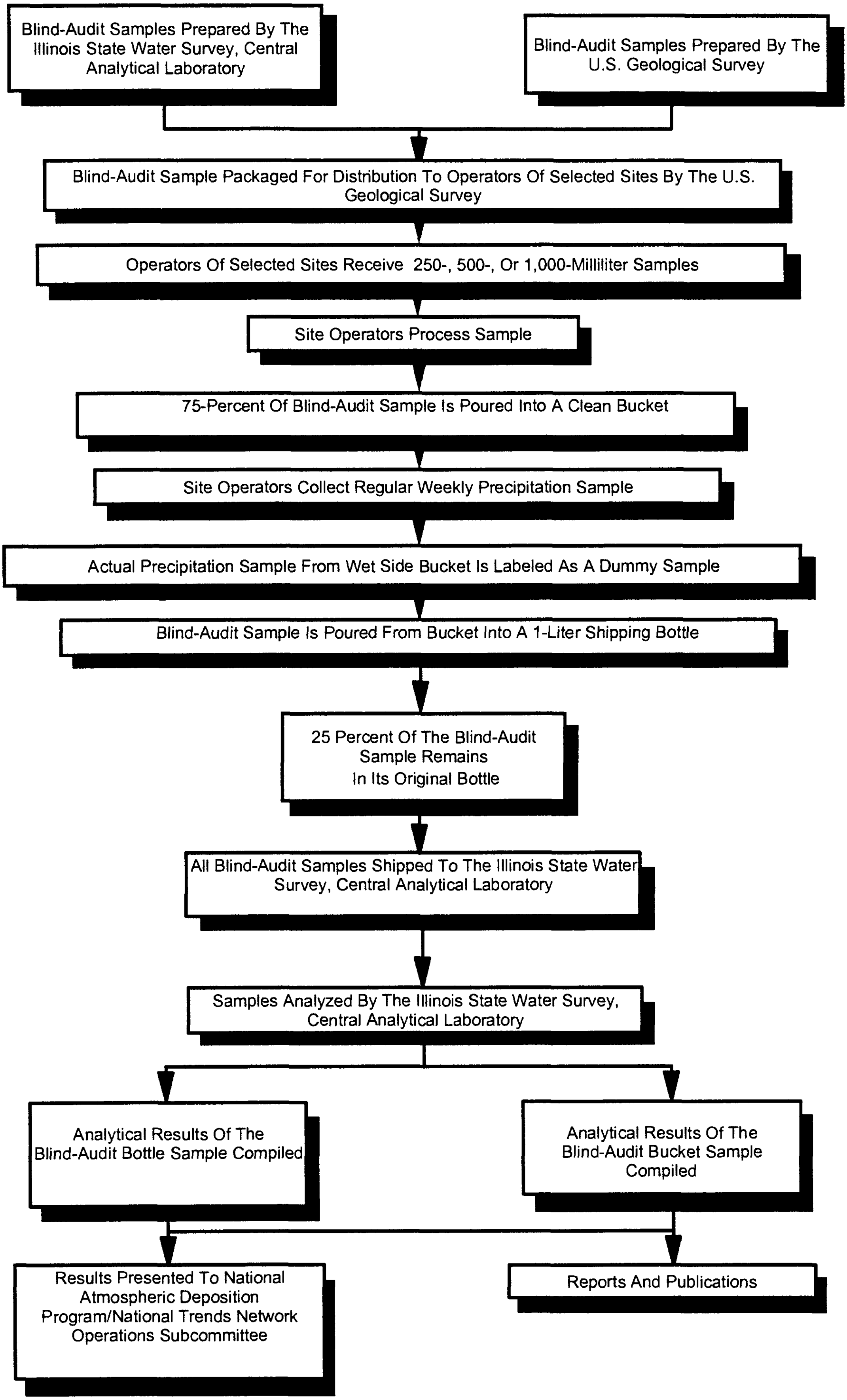


Figure 5. Blind-audit program.

On a quarterly basis, blind-audit samples are sent to a group of randomly selected NADP/NTN sites. Thirty-two sites are selected each quarter by using a computer program that ensures uniform geographic distribution throughout the United States. After a site has been selected for the blind-audit program and the operator of the selected site has successfully participated, the site is not selected again until the operators of all NADP/NTN sites have participated.

Biased analytical data result if contamination is introduced during the shipping, handling, or processing of samples. Contact with the sample-collection container and the routine handling of wet-deposition samples have been identified as sources of wet-deposition sample contamination (Nilles and others, 1995; See and others, 1989). To provide the most accurate estimates of the precision and bias associated with onsite processing steps, the solutions used in the blind-audit program are selected to replicate the chemical and physical properties of actual precipitation collected at NADP/NTN sites. The median analyte-concentration values for bottle samples approximated the 50th percentile of actual precipitation samples collected at NADP/NTN sites for most analytes. With the exception of the ultrapure deionized-water samples, which are used as a type of system blank, all of the median analyte-concentration values for the solutions used in the blind-audit program were between the 25th and 75th percentile of actual precipitation samples collected at NADP/NTN sites. The solutions used in the 1994 blind-audit program included: (1) Synthetic wet-deposition samples (USGS, SP-1 and SP-2) and ultrapure deionized-water samples (Ultrapure) prepared by the U.S. Geological Survey Acid Rain Project, (2) synthetic wet-deposition samples prepared by the Illinois State Water Survey Central Analytical Laboratory (CAL 4.3), and (3) natural wet-deposition samples collected and bottled by the U.S. Geological Survey Standard Water Reference Program (P-17). Table 2 contains information on the preparation of these solutions, as well as the solution names of NIST certified samples used in the interlaboratory comparison program. The target values of these solutions are listed in table 3.

The protocol that site operators adhere to for submitting blind-audit samples was revised in 1994. The new protocol is designed to mirror as closely as possible the new sample-shipping procedure implemented by the NADP/NTN on January 11, 1994. Prior to 1994, samples were shipped in the 13-L polyethylene buckets in which they were collected to the CAL for laboratory analysis. Since January 11, 1994, site operators have been instructed to decant precipitation samples from the 13-L polyethylene collection buckets into 1-L high-density polyethylene (HDPE) bottles for shipment to the laboratory.

Table 2. *Solutions used in the 1994 blind-audit program and interlaboratory-comparison program*

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; USGS, U.S. Geological Survey, Denver, Colo.; MΩ, megaohms]

Solution name	Agency that prepared the solution	Remarks
CAL 4.3	Illinois State Water Survey Central Analytical Laboratory	Dilute acid solution
Ultrapure	U.S. Geological Survey	Deionized water with a measured resistivity greater than 16.7 MΩ.
USGS SP-1 SP-2	U.S. Geological Survey	Prepared from dissolved salts and deionized water.
P-17	U.S. Geological Survey	Quality assurance sample prepared from natural precipitation by the standard reference water sample project.
2694A-I 2694A-II	National Institute of Standards and Technology	Supplied as certified reference solutions.

To duplicate this new shipping procedure, on an assigned date the site operators poured 75 percent of the blind-audit sample into a clean 13-L polyethylene collection bucket, secured the lid, and set the bucket aside while they proceeded to collect and process the regular weekly precipitation sample collected at their sites. After a period ranging from several minutes to 30 or more hours, the portion of the blind-audit sample decanted into a clean bucket was then poured into a clean 1-L HDPE shipping bottle.

Before transferring the sample from the bucket to the shipping bottle, the operators determined the weight of the bucket containing 75 percent of the blind-audit sample and removed a 20-mL aliquot for measuring the pH and specific conductance. The 75-percent

Table 3. *Target values for solutions used in the 1994 U.S. Geological Survey blind-audit program and interlaboratory-comparison program*

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; USGS, U.S. Geological Survey, Denver, Colo.; pH, in units; specific conductance, in microsiemens per centimeters at 25 degrees Celsius; <dl, indicates value less than method detection limit; significant figures vary because of differences in laboratory precision]

Solution	Milligrams per liter								pH	Specific conductance
	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}		
[1]CAL	<dl	<dl	<dl	<dl	<dl	<dl	3.14	<dl	4.3	21.8
[1]p-17	0.30	0.045	0.283	0.057	0.10	0.416	1.12	0.50	5.55	7.00
[1,2]USGS	.14	.029	.113	.024	.160	.160	1.05	.88	4.80	8.0
[1,2]Ultrapure	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl	[3]5.65	[3].064
[1,2]SP-1	.460	.092	.420	.076	.680	.590	2.100	3.850	4.36	30.27
[1,2]SP-2	.460	.070	.360	.060	.560	.450	3.000	2.334	4.51	23.47
[2]2694A-I	.0126	.0242	.208	.056	[4].12	[4].23	[4].53	2.69	4.30	25.4
[2]2694A-II	.0364	.0484	.423	.108	[4]1.06	[4].94	7.19	10.6	3.60	129.3

[1] Solution used in the 1994 blind-audit program.

[2] Solution used in the 1994 interlaboratory-comparison program.

[3] At 25°C and 1 Atmosphere (Hem, 1985; Dean, 1979).

[4] Concentration not certified by the National Institute of Standards and Technology.

portion of the blind-audit sample was submitted to the CAL disguised as the actual precipitation sample collected at the site, while the actual sample collected at the site was submitted disguised as a quality assurance (QA) sample with a "Dummy Field Observer Report Form." The portion of the blind-audit sample remaining in the bottle in which it was originally shipped to the site operators was concurrently submitted to the CAL under separate cover and was analyzed independent of the other portion of the blind-audit sample. The portion of the blind-audit sample decanted into a 13-L bucket and shipped in a 1-L bottle is referred to as the "bucket sample." The portion remaining in the original container and subject to minimal handling is referred to as the "bottle sample."

All of the handling and processing steps that a regular weekly precipitation sample is subject to were duplicated with the bucket sample as closely as possible. The operator filled out a fictitious NADP/NTN field-observer report form and submitted the bucket to the CAL for analysis.

Analytical chemists at the CAL could not identify individual samples as being from an external QA program. When the bottle portion of the blind-audit sample was submitted to the CAL, only the sample processing group of the laboratory staff knew that it was not an actual NADP/NTN sample. At the time the analyses were performed, the samples appeared to be regular network precipitation samples. When the analyses for the bucket and bottle portions of the blind-audit samples and actual precipitation samples were complete, the identities of each sample were disclosed to the CAL Data QA Officer. The NADP/NTN data base was then corrected by matching the proper analytical data with each sample. Information concerning sample chemical composition was not provided to the CAL staff performing the analyses or to the site operators that did the processing.

Data Analysis

To estimate analytical bias, differences between the results from the bucket and bottle portions are evaluated. Both the bucket and bottle portions are analyzed by the same laboratory at approximately the same time; bias due to field processing can therefore be isolated from other sources of error, such as bias related to laboratory analysis methods. In 1994, the CAL analyzed all paired bucket and bottle samples within 21 days of each other; except for a small number of sample pairs, most were analyzed within 1 week of each other.

The portion of the blind-audit sample remaining in the original bottle in which it was sent to the site operator did not undergo the onsite processing and handling to which the bucket portion was subjected. For this reason, it was expected that analyte concentrations in the bottle portion would not change significantly since it was subject to only minimal handling and processing by the site operator. Furthermore, sample stability studies have indicated that the analytes in full, unopened quality-assurance samples similar in composition to those currently used in the blind-audit program are stable for at least 45 days (Gordon and others, 1995; Peden and Skowron, 1978; Willoughby and others, 1991). Complete bucket and bottle analyses were available for 121 of the 128 blind-audit samples sent to participating site operators in 1994. Four site operators failed to submit the blind-audit sample. Three site operators failed to follow the specified protocol and thus invalidated the blind-audit samples they submitted.

Contamination codes ("C" codes) are assigned at the CAL on the basis of site-operator observations in the field and any physical evidence of contamination observed when the samples arrive for analysis. Due to the shipping protocol change in 1994, the CAL can no longer observe the entire precipitation sample in the container in which it was collected and must rely extensively on observations concerning contamination made by the site operator. The CAL assigns "C" codes to actual precipitation samples on the basis of recorded observations, physical evidence of contamination, and anomalous chemistry results (James, 1996). Regardless of the sample chemistry, bucket and bottle portions of the blind-audit samples containing foreign material are also assigned a "C" code. The "C" codes are only assigned after the CAL Data Quality-Assurance Officer has been informed of the true identities of the bucket and bottle portions of the blind-audit sample. Because prior investigations have indicated no significant differences in analytical results among bottle samples coded as "uncontaminated" and bucket samples coded as "contaminated" (See and others, 1989), data from samples assigned as "C" code were included in the statistical analysis.

Prior to determining paired bucket minus bottle differences, bucket and bottle values reported as less than the minimum detection limit were first set equal to the minimum detection limit. After all of the laboratory analyses were completed, values reported as less than the detection limit were alternatively set equal to one-half the detection limit, and then they were set equal to zero. It was determined that the treatment of values reported as less than the detection limit had no discernible effect on the robust nonparametric statistics and graphical analysis methods used to evaluate and depict this data set.

The median paired bucket minus bottle differences for all analytes are presented in table 4, along with the upper and lower quartiles and the interquartile range of the paired blind-audit sample differences. The median and interquartile values represent the central location and spread in the data, respectively. Calcium was the only analyte where the median bucket-sample concentration was larger than the median bottle-sample concentration (indicated by the fact that the median paired bucket minus bottle difference for calcium was positive). The median bucket-sample values were smaller than the median bottle-sample determinations for sodium, ammonium, hydrogen ion, and specific conductance. The median bucket minus bottle differences ranged from -0.02 mg/L for ammonium to 0.004 mg/L for calcium. Median differences for hydrogen ion and specific conductance were -1.002 µeq/L and -0.10 µS/cm, respectively.

Table 4. *Selected statistics for the paired bucket-sample concentration minus bottle-sample concentration differences in the blind-audit program*

[All units in milligrams per liter except: hydrogen ion, in microequivalents per liter, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius; Q1, the lower quartile in the data distribution; Q3, the upper quartile in the data distribution]

		Quartiles		Inter-quartile range
Analyte	**Median**	**Q1**	**Q3**	
Calcium	0.004	-0.001	0.011	0.012
Magnesium	.000	-.001	.002	.003
Sodium	-.019	-.041	-.002	.039
Potassium	.000	-.001	.002	.003
Chloride	.000	-.038	.010	.048
Sulfate	.000	.000	.030	.030
Ammonium	-.020	-.050	.000	.050
Nitrate	-.010	-.040	.025	.065
Hydrogen ion	-1.002	-2.612	.000	2.612
Specific conductance	-.100	-.825	.400	1.225

A Wilcoxon signed-rank test (Conover, 1980) was used to determine if statistically significant differences existed between the analyte concentrations measured for the paired bucket and bottle portions of the blind-audit samples submitted in 1994. All blind-audit samples that had paired analyte determinations were included in the statistical analyses. The Wilcoxon signed-rank test indicated that the paired bucket minus bottle differences were statistically significant at the $\alpha=0.05$ level (based on a two-sided test) for calcium, sodium, chloride, sulfate, ammonium, and hydrogen ion. Side-by-side boxplots are used to present the paired blind-audit differences for each analyte in figure 6. The upper and lower lines defining the "box" portions of the graphs depict the interquartile range of the differences for each analyte. The "whisker" portions of the boxplots were defined by the most distant value within a limit defined by 1.5 times the interquartile range (Conover, 1980). The complete results of the Wilcoxon signed-rank test for bias with values that were less than the minimum reporting limit set equal to the minimum reporting limit are listed in table 5.

Boxplots in figures 7 and 8 depict the paired blind-audit sample differences for all the major ions by solution type. Visual inspection of the boxplots in figures 7 and 8 reveal that for most analytes, no relation between the variance in paired blind-audit sample differences and target concentration is readily apparent. A Kruskal-Wallis test was used to determine if the distributions of paired bucket minus bottle differences were statistically different for the various solutions used in the blind-audit program in 1994. The Kruskal-Wallis test is a rank-based method of evaluating differences in the distributions for two or more groups of data. Differences between the distributions implies the probability of the concentration in the bucket portion equaling the concentration in the bottle portion no longer approximates 0.50 (Conover, 1980). A statistically significant ($\alpha=0.05$) relation between paired blind-audit sample differences and the original target concentration of the sample was detected for ammonium, sulfate, nitrate, hydrogen ion, and specific-conductance (table 6).

A total of 17 ultrapure deionized-water samples were included in the 1994 blind-audit program. The analytical results for the ultrapure sample were evaluated for evidence of systematic bias. Using the Wilcoxon signed-rank test, no statistically significant ($\alpha=0.05$) differences were found between the minimally handled bottle portions and field-exposed bucket portions of the ultrapure deionized-water samples. The total number of determinations exceeding the method detection limit was also determined. In all 17 ultrapure samples, sodium was detected at levels greater than the method detection limit for both the minimally handled and field-exposed portions of the blind-audit sample. The results for sodium are consistent with internal QA results at the CAL that consistently showed increased sodium concentrations in filtered blind-audit and ultra

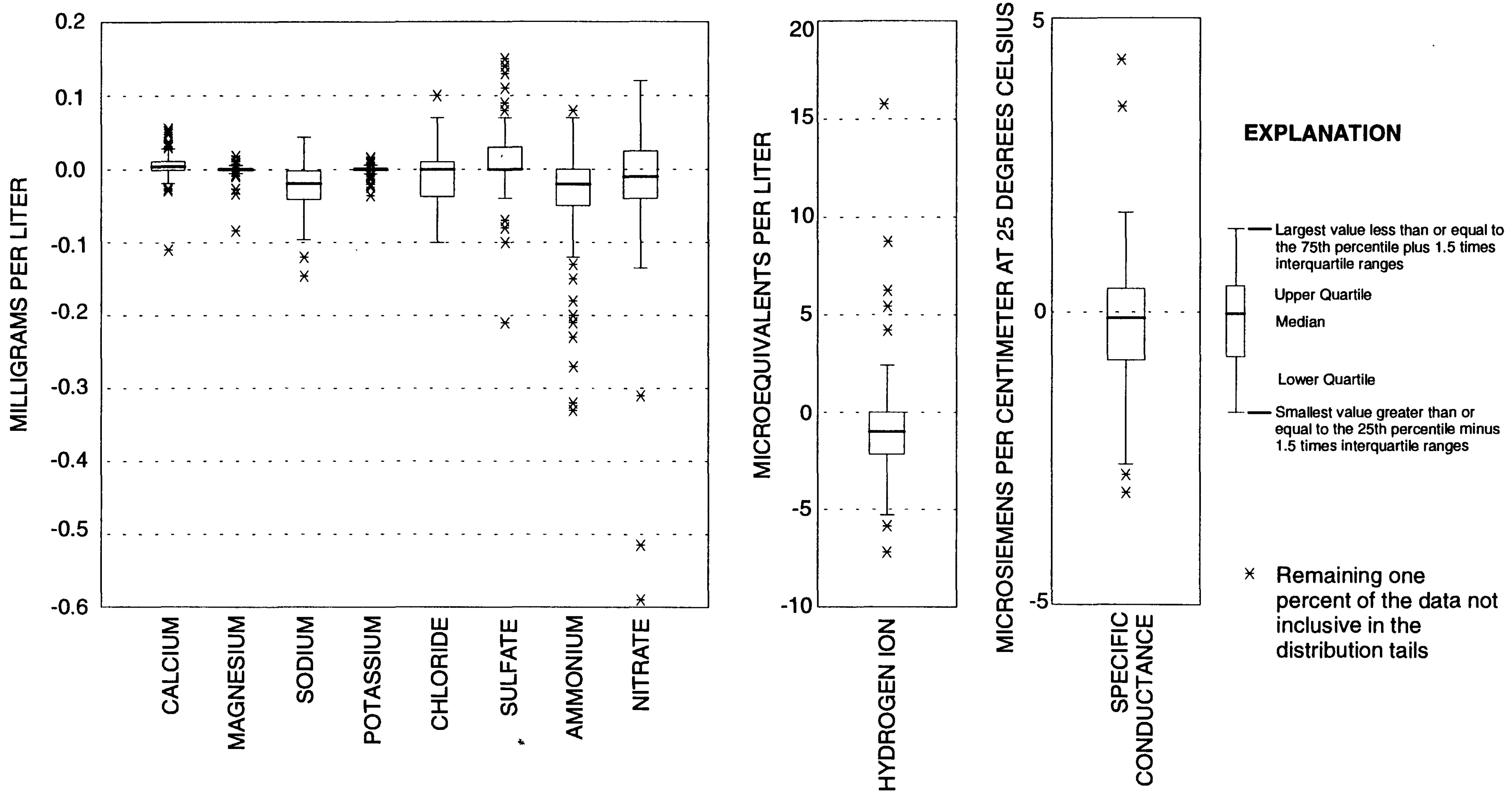


Figure 6. Paired bucket sample concentrations minus bottle sample concentrations in the blind-audit program.

Table 5. *Results of the tests for bias in the blind-audit program, using a Wilcoxon signed-rank test*

[Bucket and bottle values less than the minimum reporting limit set equal to the minimum reporting limit]

Analyte	The number of times the concentration in the bucket portion exceeded the concentration in the bottle portion	The number of times the concentration in the bottle portion exceeded the concentration in the bucket portion	The number of times the concentration in the bottle portion equaled the concentration in the bucket portion	Determined to be biased ($\alpha = 0.05$)?
Calcium	71	31	19	YES
Magnesium	50	36	35	NO
Sodium	26	93	2	YES
Potassium	48	37	36	NO
Chloride	36	60	25	YES
Sulfate	59	21	41	YES
Ammonium	21	82	18	YES
Nitrate	48	61	12	NO
Hydrogen ion	28	79	14	YES
Specific conductance	48	65	8	NO

pure samples in 1994 (James, 1996). All NADP/NTN samples (including external QA samples submitted by the USGS) are filtered upon arrival at the CAL in the same manner as the internal QA samples described by James (1996). Ammonium, nitrate, and chloride were detected in about one-half the ultrapure samples (the number of reported values exceeding the MDL ranged from 7 to 11), with a roughly equal number of occurrences in the minimally handled and field-exposed portions of the blind-audit sample. Three or fewer occurrences when the reported values exceeded the MDL were observed for calcium, magnesium, and sulfate (table 7).

Percent bias was determined for all of the bucket minus bottle paired differences by calculating both the relative (signed) and absolute paired difference as a percentage of the concentration measured in the bottle portion (table 8). Bucket-bottle data pairs were excluded if the target concentration was less than the MDL for a given analyte. The median relative percent bias ranged from -16.67 percent for ammonium to +3.61 percent for calcium. When compared to 1993 blind-audit results, the median percent bias decreased in 1994 for all analytes except sodium, ammonium, and chloride. The median percent bias for hydrogen ion decreased from -42.5 percent in 1993 to -4.50 percent in 1994. This marked decrease in the amount of hydrogen ion lost during normal onsite processing indicates that the significant loss of hydrogen ion attributed to the old shipping protocol no longer occurs since the new protocol was implemented in 1994. The median relative percent biases for specific conductance also improved substantially in 1994, decreasing to -0.92 percent from -17.4 percent in 1993. On the other hand, the magnitude of the median relative percent bias for sodium increased from 1.82 percent in 1993 to -10.86 percent in 1994. The relative percent bias for calcium, magnesium, and sulfate was fairly small, ranging from 1.48 to 3.61 percent, whereas the median relative percent differences for nitrate and potassium were both 0.00. Large differences in the magnitude of the percent bias compared to the magnitude of the absolute paired differences were observed for chloride, sodium, and ammonium. Large differences in the magnitude of the percent bias compared to the magnitude of the absolute paired differences indicates large amounts of scatter in the paired differences. For example, paired ammonium differences displayed a large amount of scatter about the zero difference line, and the median absolute percent difference was 20.0 percent, compared to a median relative percent difference of -16.67 percent.

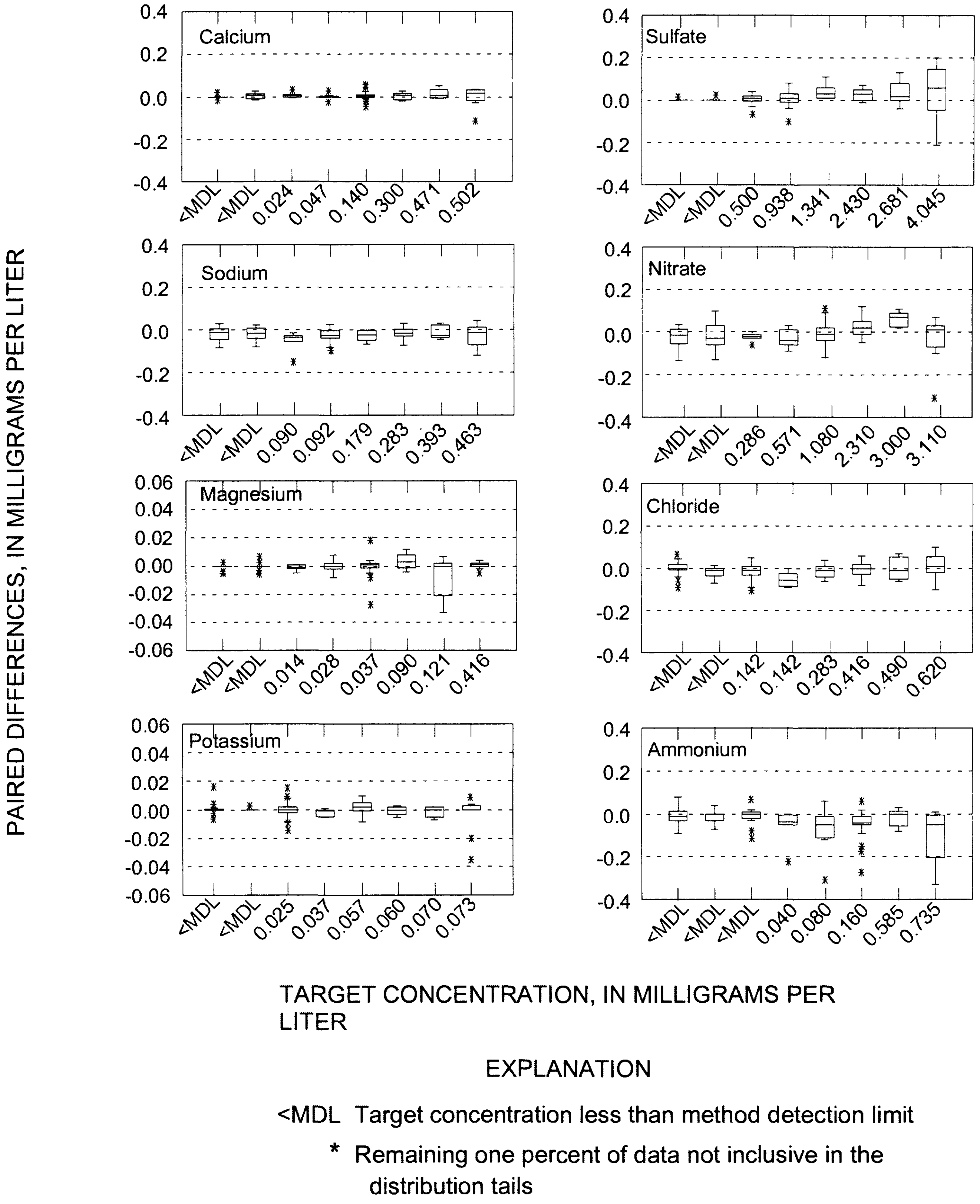
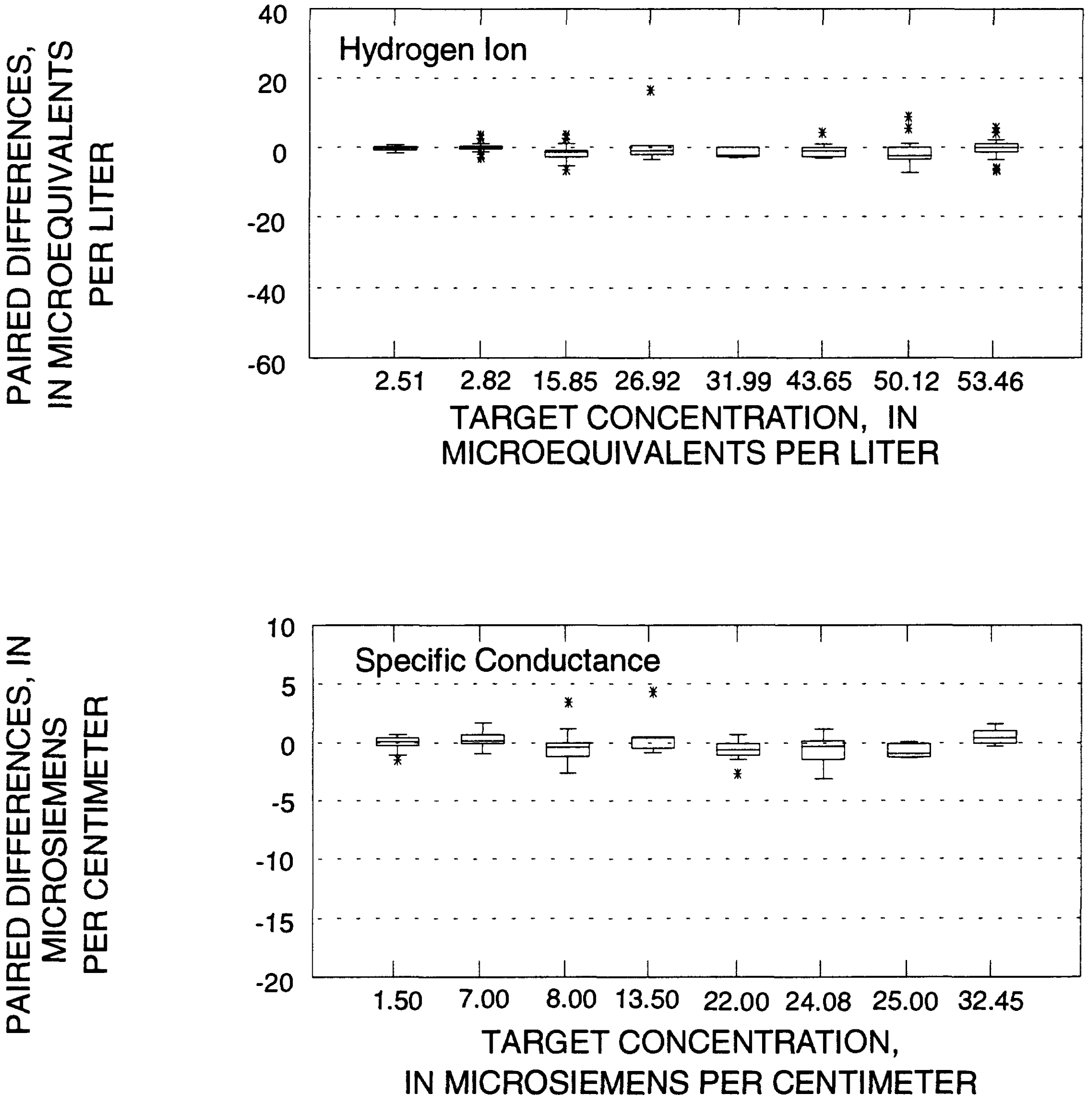


Figure 7. Relation between paired blind-audit differences for major ions and the analyte concentrations of solutions used in the blind-audit program.



EXPLANATION

<MDL Target concentration less than method detection limit

* Remaining one percent of data not inclusive in the distribution tails

Figure 8. Relation between paired blind-audit differences for hydrogen-ion and specific conductance and the analyte concentrations of solutions used in the blind-audit program.

Table 6. *Results of the Kruskal-Wallis analysis of variance test to determine the relation between paired blind-audit sample differences and the target concentrations used in the blind-audit program*

Analyte	Bucket minus bottle differences significance levels (p-values) by sample target concentration	Statistically significant (α=0.05) differences by concentration?
Calcium	0.482	NO
Magnesium	.124	NO
Sodium	.366	NO
Potassium	.180	NO
Chloride	.319	NO
Sulfate	.006	YES
Ammonium	.006	YES
Nitrate	.019	YES
Hydrogen ion	.006	YES
Specific conductance	.000	YES

Table 7. *Number of determinations exceeding the method detection limit for the 17 ultrapure deionized-water sample submitted as part of the 1994 blind-audit program*

Analyte	Field-exposed bucket portion	Minimally handled bottle portion
Calcium	3	1
Magnesium	1	2
Sodium	17	17
Potassium	5	3
Ammonium	8	9
Sulfate	1	0
Nitrate	9	11
Chloride	9	7

Table 8. *Median relative and median absolute bucket minus bottle differences calculated as a percentage of the target bottle concentration for each analyte*

[All units in percent]

	Median relative bucket minus bottle differences expressed as a percentage of the corresponding target bottle concentration; selected data pairs only[1]			Median absolute bucket minus bottle differences expressed as a percentage of the corresponding target bottle concentration; selected data pairs only[1]		
	Percentiles			Percentiles		
Analyte	25th	50th	75th	25th	50th	75th
Calcium	-0.93	3.61	7.32	2.34	5.30	9.53
Magnesium	-4.67	2.17	6.67	3.14	5.88	10.20
Sodium	-28.05	-10.86	-1.19	7.02	16.77	35.10
Potassium	-7.69	.00	6.53	2.94	7.41	12.50
Ammonium	-33.33	-16.67	-1.35	9.09	20.00	35.83
Chloride	-13.42	-3.12	5.98	3.96	9.09	17.65
Nitrate	-5.70	.00	1.81	.95	2.87	6.34
Sulfate	.00	1.48	3.42	1.10	2.22	4.28
Hydrogen ion	-10.87	-4.50	.00	2.33	6.67	14.83
Specific conductance	-5.34	-.92	3.77	1.86	4.71	11.51

[1] Bucket minus bottle data pairs were excluded if the target value for the blind-audit solution was less than the minimum detection limit established by the Illinois State Water Survey, Central Analytical Laboratory for a given analyte.

A range of sample volumes was used in 1994 to assess if there was a relation between sample volume and the differences between the analyte mass in the bucket and bottle portions of the blind-audit samples. Sixteen each of 250-mL, 500-mL, and 1,000-mL bottles of the same solution (USGS) were sent to the operators of selected sites. To prepare the "bucket portion" of the sample, the site operators poured about 75 percent of each USGS blind-audit sample into a clean 13-L polyethylene bucket, processed it as if it were the wet-deposition sample from the previous week, and shipped it to the CAL in a clean 1-L shipping bottle. The remaining 25 percent of the USGS samples was sent to the CAL under separate cover as the "bottle portion" of the blind-audit sample. To analyze the differences for the major ions on a mass basis, the differences between the measured concentration in the bucket and bottle portions of the blind-audit samples in milligrams per liter were multiplied by the milliliters of blind-audit sample volume that the site operator poured into a 13-L bucket during the processing of the sample. This converts the differences between the bucket and bottle portions of the blind-audit sample from milligrams per liter to micrograms(µg). Hydrogen ion differences were converted from microequivalents per liter to microequivalents; specific-conductance differences were left in the original units of microsiemens per centimeter.

A Kruskal-Wallis test (Iman and Conover, 1983) was used to determine if there was a statistically significant relation between paired blind-audit sample differences and sample volume. A statistically significant (α=0.05) relation between analyte bias and sample volume was found for sodium, ammonium, and sulfate. Results of the Kruskal-Wallis test (table 9) indicate no significant difference in bucket minus bottle values on a mass per bucket basis for calcium, magnesium, potassium, chloride, nitrate, hydrogen ion, or specific conductance. For many of the analytes, the effect of sample volume on mass differences has been relatively small and somewhat variable during the past few years. In contrast, a consistent relation between sample volume and the paired differences in microequivalents for hydrogen ion was observed for many years prior to 1994. As a direct result of the change in sample-shipping protocol to 1-L HDPE bottles, the relation between hydrogen ion differences and sample volume was markedly reduced in 1994 to a level that was no longer statistically significant. These results support the hypothesis that the chemical reactions between the 13-L bucket shipping container and the sample that resulted in an increasing loss of hydrogen ion with increasing volume have been effectively eliminated by the new protocol.

Table 9. *Results of the Kruskal-Wallis analysis of variance tests to determine if bucket minus bottle differences for the 250-, 500-, and 1,000-milliliter samples of the USGS solution used in the blind-audit program have equivalent distributions*

Analyte	Bucket minus bottle differences significance levels (p-values) by sample target concentration	Statistically significant (α=0.05) differences by solution type?
Calcium	0.796	NO
Magnesium	.594	NO
Sodium	.019	YES
Potassium	.069	NO
Ammonium	.003	YES
Chloride	.588	NO
Nitrate	.512	NO
Sulfate	.017	YES
Hydrogen ion	.843	NO
Specific conductance	.122	NO

As in 1993, this 1994 study found a negative relation between sample volume and analyte bias for sodium, indicating the concentration measured in the sample portion subject to all onsite handling steps was actually less than the concentration measured in the bottle portion, which was subject only to minimal handling. The relation between bias and sample volume was similar for sodium and ammonium. For both sodium and ammonium, much larger median differences were determined for the 1,000-mL samples. For sodium, the median difference was -24.8 µg for 1,000-mL samples compared to median differences of -3.14 and -6.87 µg for 250- or 500-mL samples, respectively. For ammonium, the median difference was -30.5 µg for the 1,000-mL samples, -15.58 µg for the 500-mL samples, and -4.29 µg for the 250-mL samples. The results for sodium and ammonium indicate complex surface chemistry reactions may be occurring which bind these positively charged ions to the negatively charged surfaces of the sample collection and shipping containers. The results for sodium and ammonium contrast sharply with the results for sulfate, which were positively biased, indicating the possible addition of sulfate from the container surfaces. The median difference for sulfate was +15.54 µg for the 1,000-mL samples, +5.59 µg for the 500-mL samples, and 0.00 µg for the 250-mL samples. Boxplots in figure 9 depict the differences between the bucket and bottle portions by sample volume for all of the major ions as well as for hydrogen ion and specific conductance.

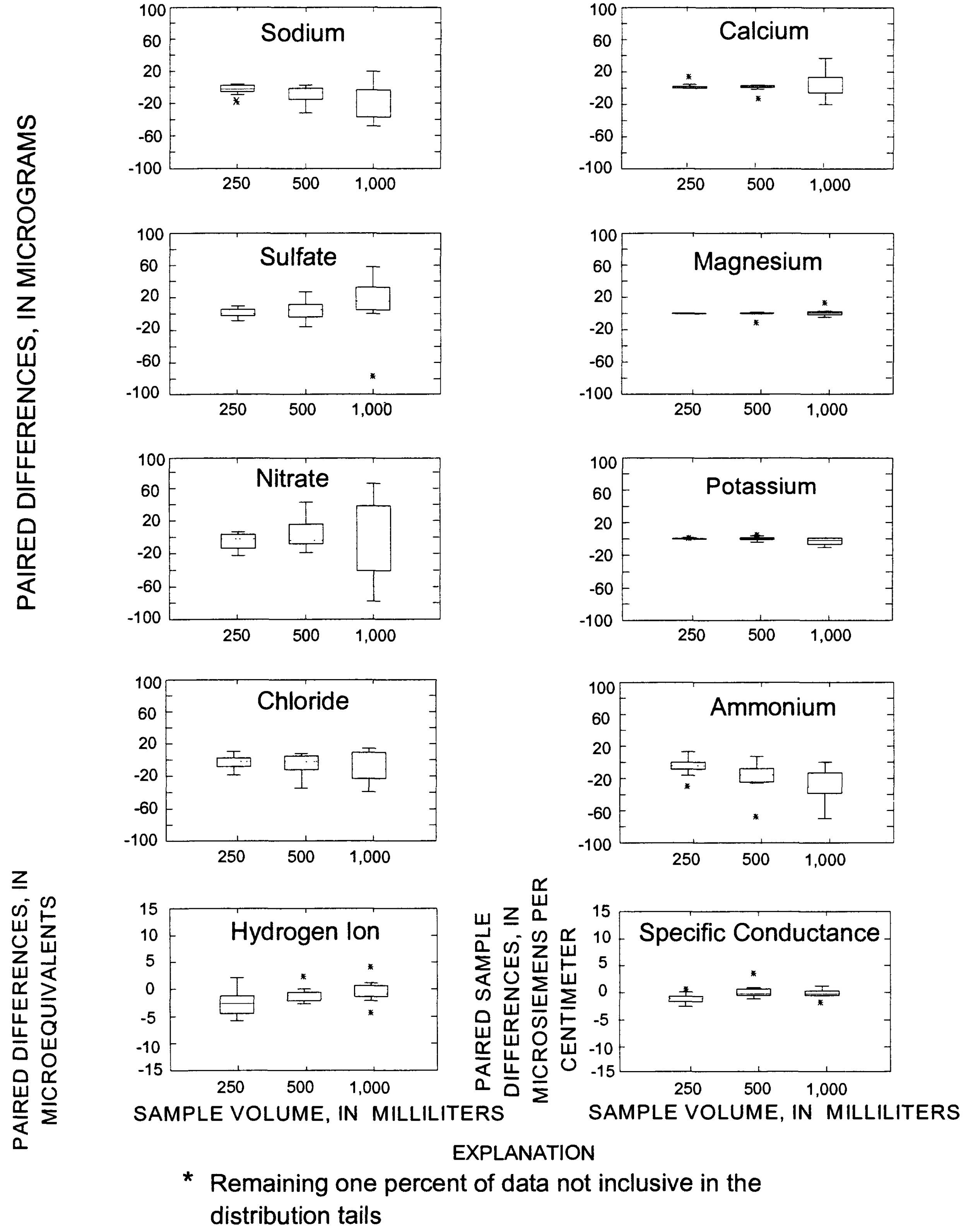


Figure 9. Relation between paired blind-audit differences and sample volume for the 250-, 500-, and 1,000- milliliter USGS solution samples.

INTERLABORATORY-COMPARISON PROGRAM

The two objectives of the interlaboratory-comparison program in 1994 were: (1) To estimate the analytical precision of participating laboratories, and (2) to determine if statistically significant differences existed among the analytical results of participating laboratories. Five laboratories routinely measured the chemistry of wet-deposition samples in the interlaboratory-comparison program in 1994: (1) Illinois State Water Survey, Central Analytical Laboratory (CAL) in Champaign, Illinois; (2) Atmospheric Environment Service, Environment Canada (AES) in Ontario, Canada; (3) Environmental Science and Engineering, Inc. (ESE) in Gainesville, Florida; (4) Ontario Ministry of the Environment, Water Quality Section (MOE) in Ontario, Canada; and (5) Global Geochemistry Corporation (GGC) in Canoga Park, California.

Samples from three sources were used in the 1994 interlaboratory-comparison program: (1) synthetic wet-deposition samples (USGS) and ultrapure deionized-water samples (Ultrapure) prepared by the U.S. Geological Survey, (2) standard reference samples (2694A-I, and 2694A-II) prepared and certified by the U.S. National Institute of Standards and Technology (NIST), and (3) natural wet-deposition samples collected at NADP/NTN sites and bottled by the CAL. Table 2 contains information on the preparation of the synthetic solutions made by the U.S. Geological Survey or CAL, as well as the solution names of the NIST certified samples. Target values for all of the synthetic wet-deposition solutions used in the interlaboratory-comparison program are listed in table 3. Of the 104 samples distributed to each laboratory as part of the 1994 interlaboratory-comparison program, 52 were aliquots of natural precipitation bottled by the CAL, 12 were synthetic samples made by the U.S. Geological Survey and known as "USGS solution", 18 were NIST certified samples, eight were synthetic samples made by the U.S. Geological Survey and known as "SP-1 solution", eight were synthetic samples made by the U.S. Geological Survey and known as "SP-2 solution", and six were Ultrapure samples bottled by the U.S. Geological Survey.

Natural wet-deposition samples collected at NADP/NTN sites that had volumes greater than 750 mL were selected randomly by the CAL for use in the interlaboratory-comparison program.

These natural wet-deposition samples were divided into 10 aliquots by using a deca-splitter. The aliquots were bottled in 125-mL polyethylene bottles and shipped in chilled, insulated containers to the USGS in Denver, Colorado. Natural samples were kept refrigerated and were reshipped to participating laboratories within 10 days of receipt by the USGS. In 1994, synthetic wet-deposition samples prepared by the USGS replaced two synthetic wet-deposition matrices from the U.S. Environmental Protection Agency that were used in previous years. Target values for synthetic wet-deposition solutions used in the interlaboratory-comparison program are listed in table 3.

Samples used for the 1994 interlaboratory-comparison program were relabeled and shipped by the USGS to the five participating laboratories approximately every 2 weeks. Each laboratory received four samples per shipment, and each laboratory received the same type of samples for a given mailing. Specifically, the first shipment for all laboratories in a 4-week period consisted of triplicate synthetic wet-deposition samples prepared by NIST and a single aliquot of ultrapure deionized water or four replicates of synthetic wet-deposition samples. The second shipment consisted of two natural wet-deposition samples, in duplicate. All samples were relabeled with a sample number to ensure that laboratory personnel could not determine the type of sample (natural or synthetic) or the actual analyte concentrations in the samples until the chemical analyses were performed. A flowchart of the interlaboratory-comparison program is shown in figure 10.

Laboratory Precision

Laboratory precision was estimated for each analyte by calculating the 50th and 90th percentile of the absolute differences for the results reported for the replicate natural and synthetic wet-deposition samples (table 10). Differences were calculated from 90 sample pairs for each laboratory in 1994. Ultrapure samples were excluded from this evaluation. Analyte concentrations reported as less than the minimum reporting limit were set equal to the minimum reporting limit.

Cation precision estimates at the 50th percentile were quite similar among laboratories. All participating laboratories had median absolute differences that were less than or equal to 0.004 mg/L for the cations. Some differences between laboratories were apparent for precision estimates at the 90th percentile for calcium, sodium, potassium, and ammonium.

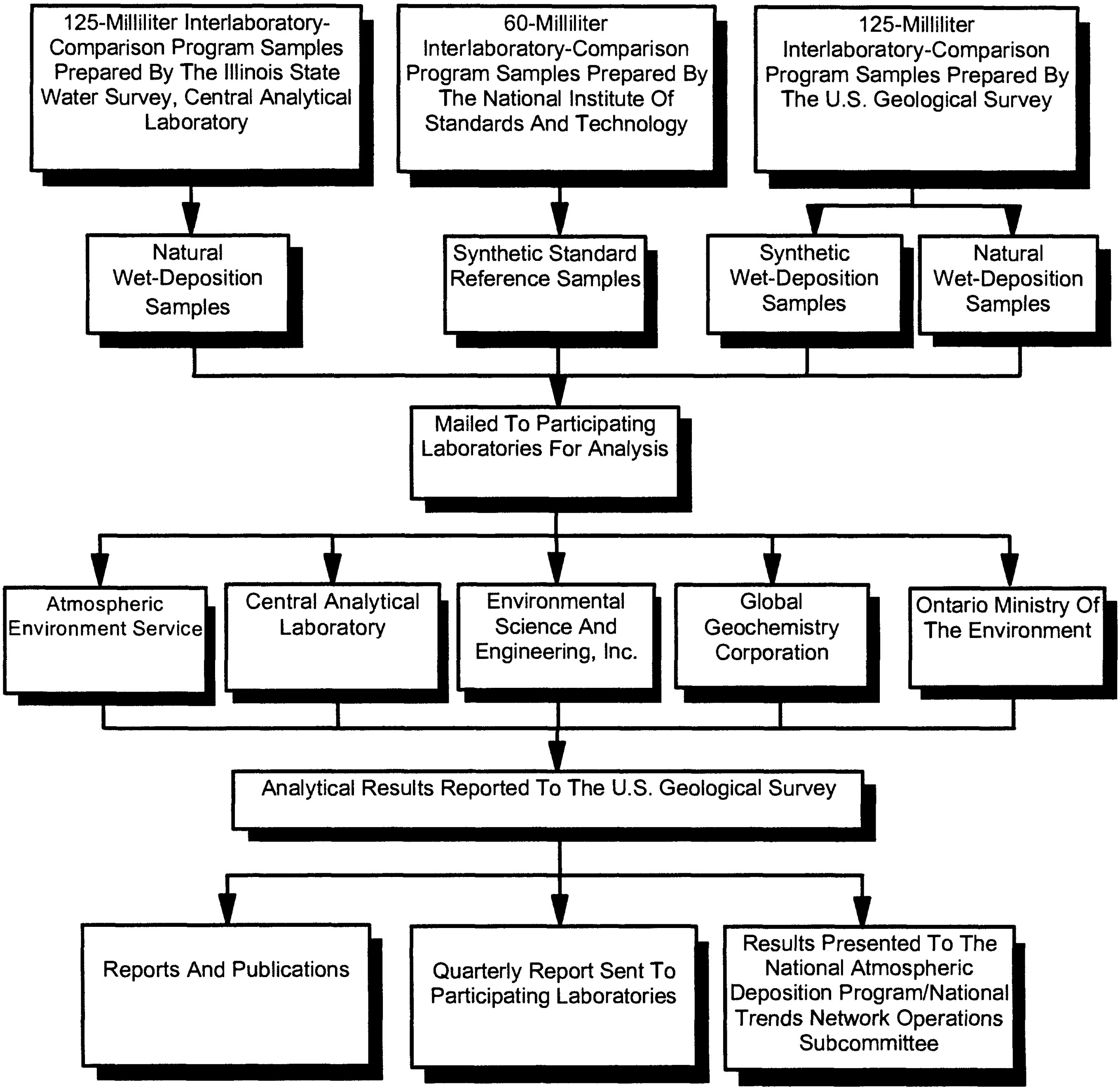


Figure 10. Interlaboratory-comparison program.

Table 10. *Fiftieth- and 90th-percentile absolute differences for analyses of replicate samples determined by five laboratories participating in the 1994 interlaboratory-comparison program*

[All units in milligrams per liter except: hydrogen ion, in microequivalents per liter, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius. CAL, Illinois State Water Survey Central Analytical Laboratory; AES, Atmospheric Environment Service; ESE, Environmental Science and Engineering, Inc.; GGC, Global Geochemistry Corporation; MOE, Ontario Ministry of the Environment; --, Not Calculated]

	CAL		AES		ESE		GGC		MOE	
Analyte	**50th**	**90th**	**50th**	**90th**	**50th**	**90th**	**50th**	**90th**	**50th**	**90th**
Calcium	0.000	0.000	0.000	0.010	0.001	0.004	0.002	0.011	0.002	0.010
Magnesium	.001	.001	.000	.000	.000	.001	.001	.002	.001	.005
Sodium	.001	.004	.000	.010	.003	.009	.002	.005	.003	.007
Potassium	.001	.009	.000	.010	.001	.004	.001	.016	.001	.022
Ammonium	.000	.010	.003	.015	.004	.017	.003	.010	.001	.008
Chloride	.000	.010	.010	.020	.003	.009	.003	.023	.000	.030
Nitrate	.010	.020	.010	.040	.004	.022	.013	.029	.000	.027
Sulfate	.000	.030	.010	.110	.006	.020	.014	.038	.010	.150
Hydrogen ion	.23	4.16	.72	1.76	1.80	8.71	1.02	5.45	.39	3.58
Specific conductance	.15	1.20	--	--	.20	.80	.12	.80	.30	1.30

Anion precision estimates at the 50th percentile exhibited greater variability among laboratories. Participating laboratories had median absolute differences that were less than or equal to 0.014 mg/L for the anions. Greater differences among laboratories were apparent for precision estimates at the 90th percentile for all anions. For example, 90th percentile differences for sulfate were less than 0.04 mg/L for CAL, ESE, and GGC, while the differences exceeded 0.10 mg/L for AES and MOE.

The pH (expressed as hydrogen ion concentration) precision estimates at both the 50th and 90th percentile exhibited variability among laboratories. Median absolute differences ranged from 0.23 microequivalents per liter (μeq/L) to 1.80 μeq/L; precision estimates at the 90th percentile ranged from 1.76 μeq/L to 8.71 μeq/L.

Four laboratories routinely reported specific-conductance results. MOE's absolute difference results for specific-conductance were not as consistent as the absolute difference results reported for CAL, ESE, and GGC. AES does not routinely report specific-conductance measurements.

Interlaboratory Bias

Interlaboratory bias (bias between multiple laboratories) is defined as a systematic difference in reported values for a given laboratory observed when the results from several laboratories are compared to each other. To examine potential bias in the analytical results between the laboratories, a Friedman test (SAS Institute Inc., 1989) was performed. A Friedman test is a nonparametric test used to compare differences in response for multiple treatments for more than two subjects (Kanji, 1993). In this application, the test allows the comparison of paired data from the five laboratories while controlling for the different sample matrices sent in different mailings. Results of the Friedman test indicate significant (α=0.01) differences in analyte measurements for calcium, magnesium, sodium, ammonium, chloride, nitrate, sulfate, hydrogen ion, and specific conductance among the five laboratories. In order to facilitate a visual comparison of interlaboratory differences, graphs of each laboratory's analyte concentrations minus the analyte medians calculated for all laboratories are presented in figures 11 through 15.

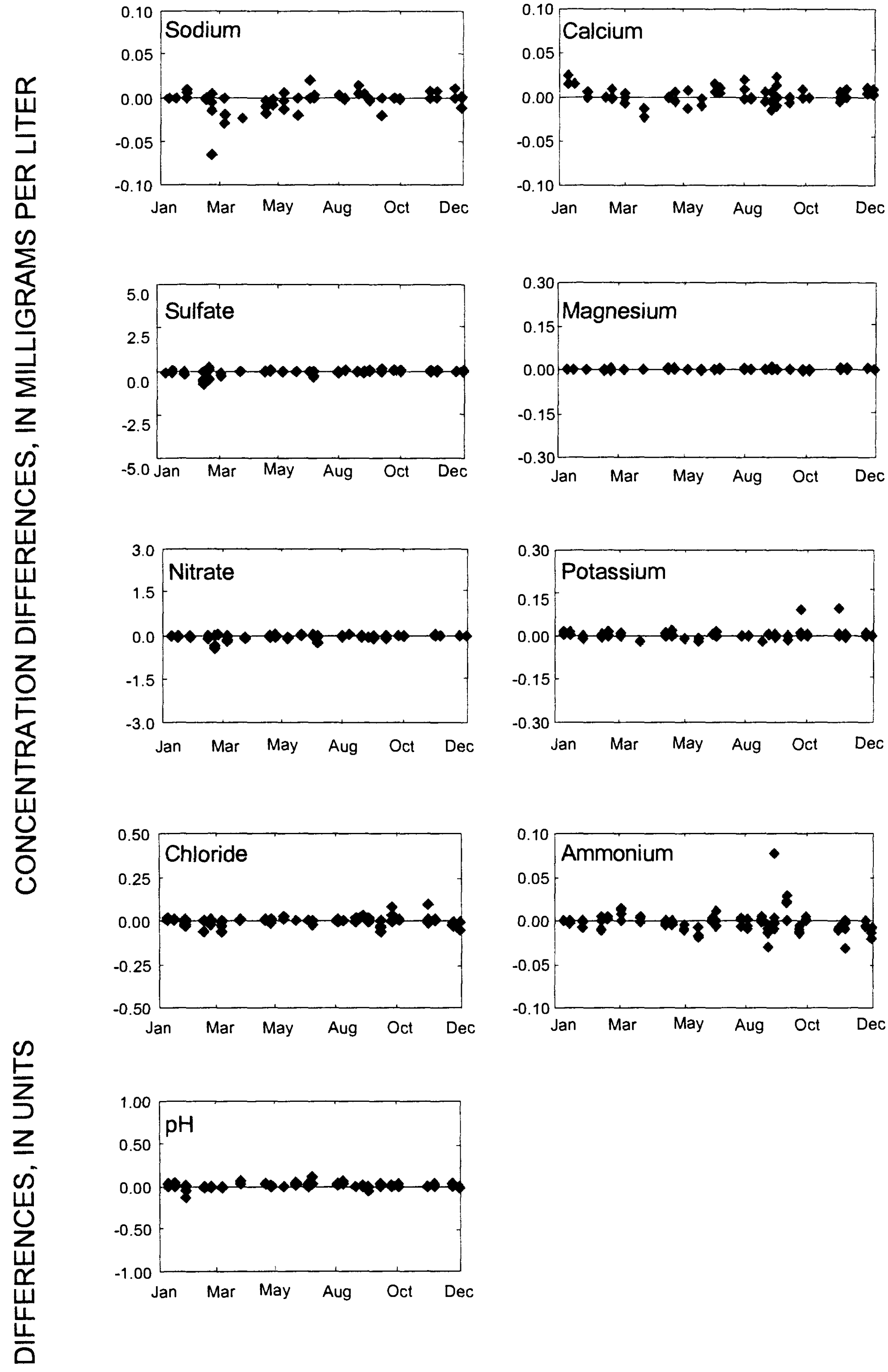


Figure 11. Difference between the measured value reported by the Atmospheric Environment Service and the median value calculated for all participating laboratories in the interlaboratory-comparison program during 1994. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.

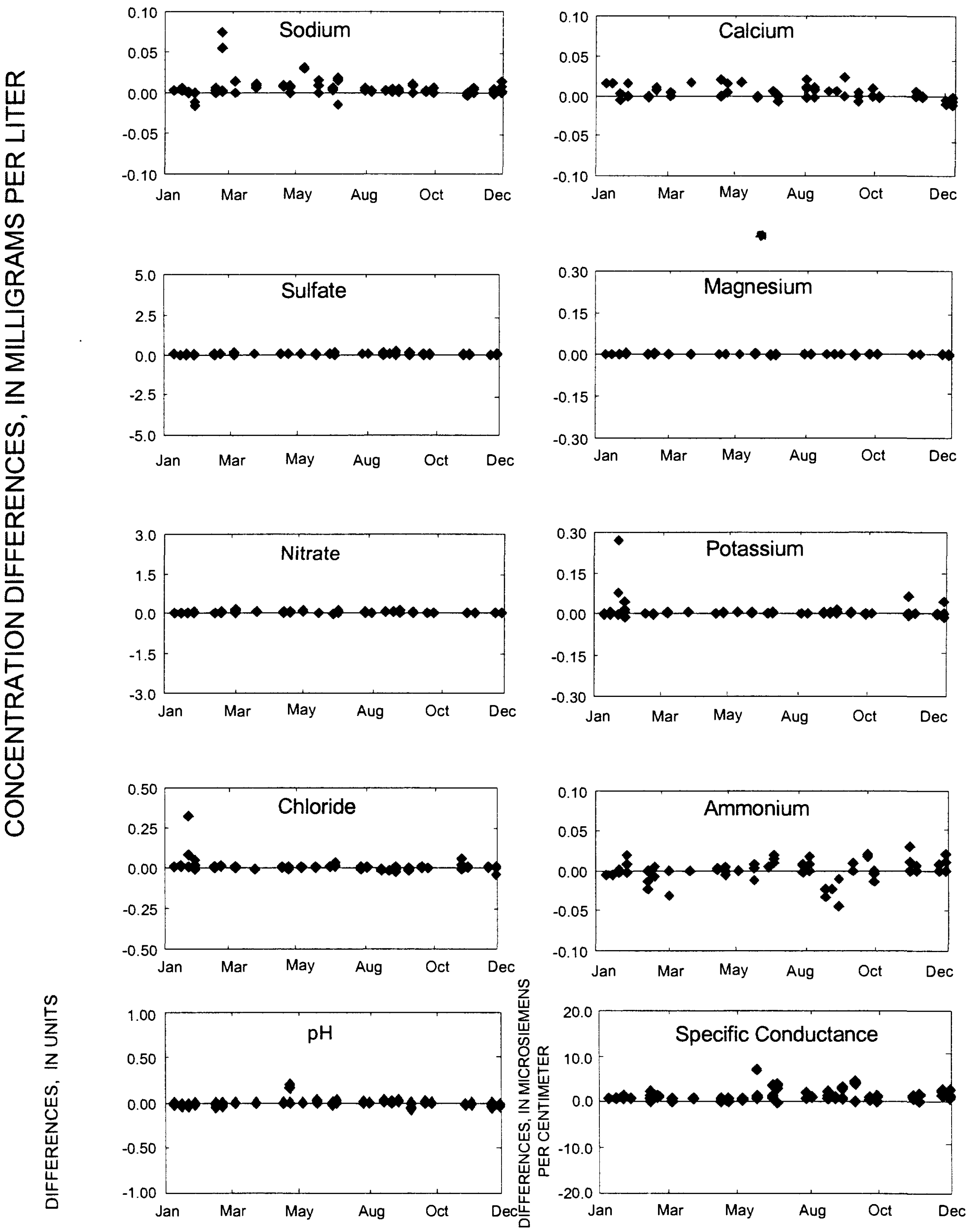


Figure 12. Difference between the measured value reported by the Illinois State Water Survey Central Analytical Laboratory and the median value calculated for all participating laboratories in the interlaboratory-comparison program during 1994. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.

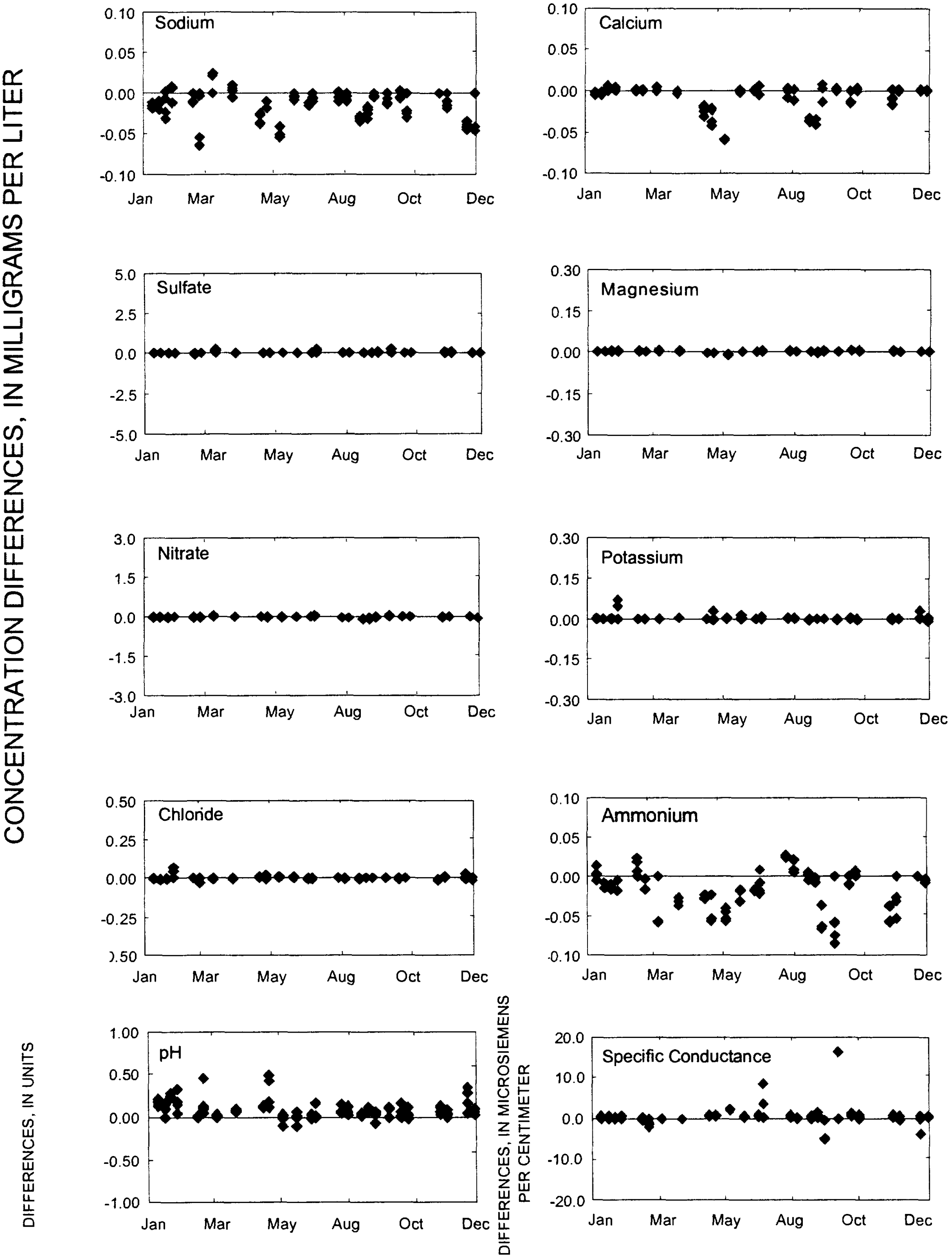


Figure 13. Difference between the measured value reported by the Environmental Science and Engineering, Incorporated, and the median value calculated for all participating laboratories in the interlaboratory-comparison program during 1994. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.

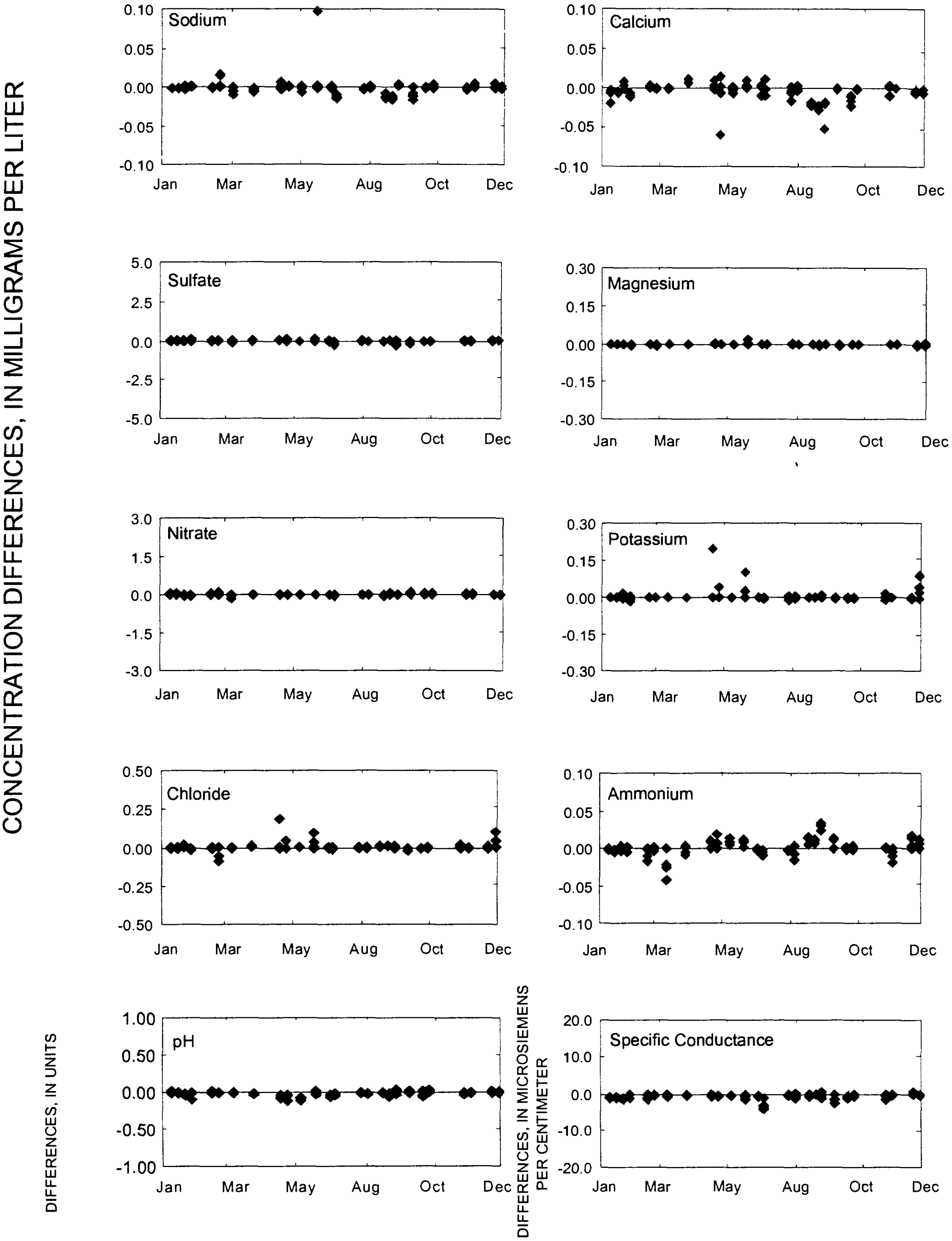


Figure 14. Difference between the measured value reported by the Global Geochemistry Corporation and the median value calculated for all participating laboratories in the interlaboratory-comparison program during 1994. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.

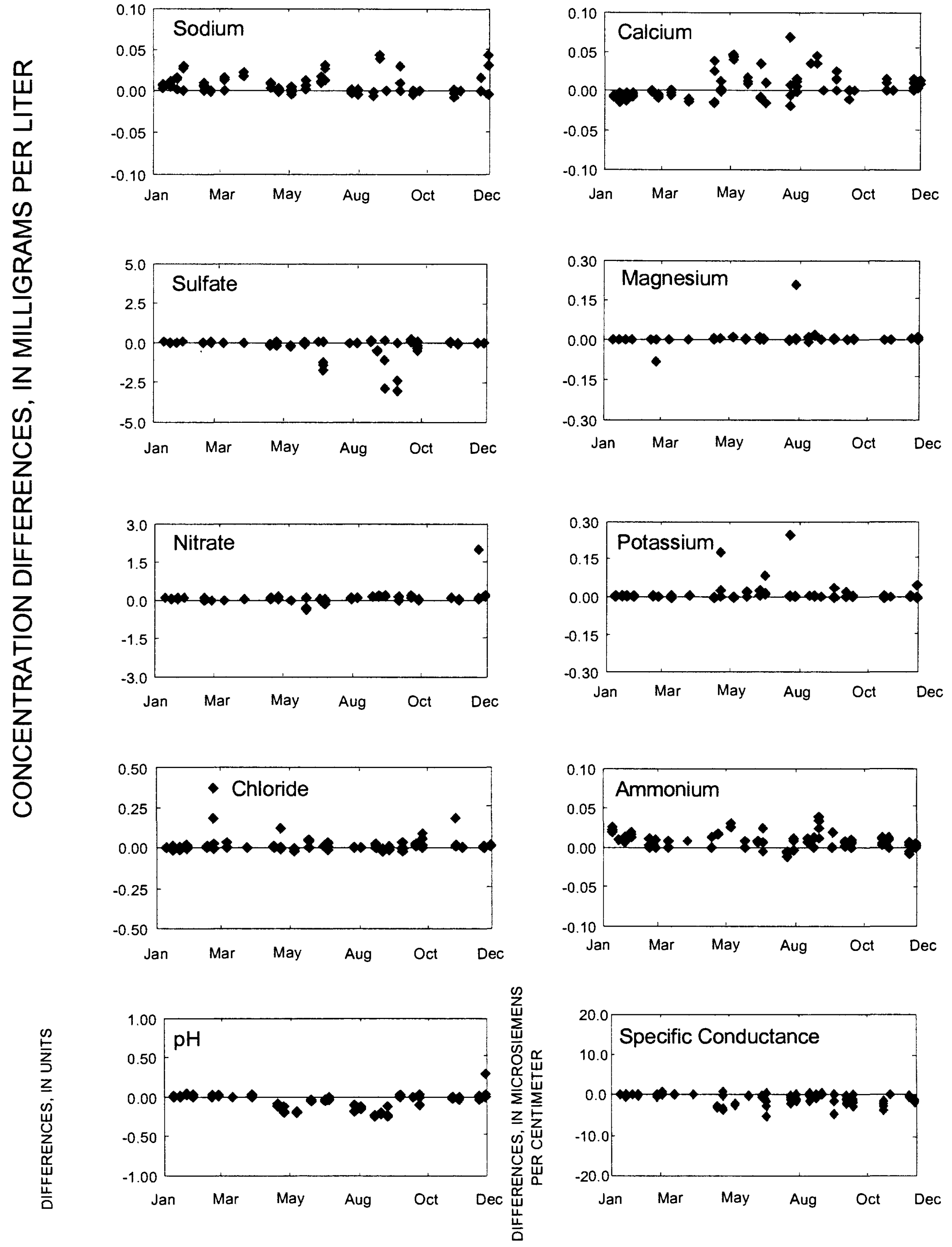


Figure 15. Difference between the measured value reported by the Ontario Ministry of the Environment and the median value calculated for all participating laboratories in the interlaboratory-comparison program during 1994. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.

Intralaboratory Bias

Intralaboratory bias (bias within a single laboratory) is defined as a systematic difference between the measured and expected values due to laboratory sample handling and analysis procedures and is detected when each laboratory is reviewed independently. Potential bias for laboratories participating in the interlaboratory-comparison program was evaluated by two methods: (1) comparison of laboratory results with the certified values and the estimated uncertainties reported by NIST for standard reference material 2694A, Level I and Level II; and (2) comparison of laboratory results with expected values (less than the detection limit) for ultrapure deionized-water samples.

National Institute of Standards and Technology Standard Reference Samples

Potential bias was examined by comparing the median laboratory-reported values to the certified values reported by the NIST. The NIST certifies values for seven measurements from standard reference sample 2694A - Level I samples and eight measurements from standard reference sample 2694A - Level II samples. Bias was indicated when the laboratory-reported median values were outside the NIST-certified values, plus or minus the estimated uncertainty reported by NIST (table 11). A summary of the estimated uncertainty ranges for the NIST standard-reference materials 2694A-I and 2694A-II and the median-analysis values for each laboratory is also presented in table 11.

Each laboratory was sent 18 NIST samples in 1994, 9 samples of Level I and 9 samples of Level II. AES did not report results for one Level II sample in one of the mailings. MOE did not report results for specific conductance, calcium, and magnesium from one Level I mailing or for sodium and potassium from two Level I mailings. ESE, GGC, and MOE each failed to report results for specific-conductance from one Level II mailing.

Out of 15 measurements certified by NIST, CAL and MOE reported 9 median analyses that were within the NIST range of uncertainty for the certified samples. Similarly, AES reported 3 median analyses, ESE reported 5 median analyses, and GGC reported 7 median analyses that were within the NIST range of uncertainty.

Ultrapure Deionized-Water Samples

In order to detect possible low-level sample contamination resulting from laboratory analyses, six Ultrapure samples were included among the samples submitted to the participating laboratories throughout 1994. Table 12 shows the number of times that each laboratory reported a concentration greater than the minimum reporting limit in a solution not expected to contain detectable analyte concentrations. Measured concentrations greater than the minimum reporting limit for the Ultrapure samples indicate possible contamination.

The CAL was the only laboratory that did not detect concentrations greater than reporting limits for the six Ultrapure samples. AES reported one concentration for calcium greater than the analyte minimum reporting limit. ESE reported six concentrations greater than the minimum reporting limit, two for calcium and four for ammonium. However, ESE's reporting limit for calcium is an order of magnitude lower compared to the other participating laboratories; all calcium concentrations reported by ESE as above their detection limit were below the minimum reporting limits of the other four participating laboratories. GGC reported two sodium concentrations and one nitrate concentration greater than the minimum reporting limits for the respective analytes. MOE reported one calcium concentration, three sodium concentrations, three potassium concentrations, two ammonium concentrations, one nitrate concentration, and one sulfate concentration above the minimum reporting limit.

Of these reported concentrations exceeding the minimum reporting limits, AES, ESE, GGC, and MOE reported concentrations which also exceeded the 5th percentile of concentration values measured in natural precipitation by the NADP/NTN in 1994 (James, 1996). AES reported one calcium concentration that approximated the 25th percentile for calcium. ESE reported one ammonium concentration that approximated the 10th percentile for ammonium. MOE reported one potassium concentration that approximated the 95th percentile for potassium. MOE also reported one sodium concentration that approximated the 25th percentile for sodium.

COLLOCATED-SAMPLER PROGRAM

Description of Program

The collocated-sampler program was established in October 1988 to provide an estimate of the overall precision of the precipitation-monitoring system. This esti-mate of precision includes variability in the data-collection system from the point of sample collection through storage of the data in the NADP/NTN data base. Additional details of the collocated-sampler program along with precision estimates based upon the

Table 11. *Comparison of laboratory median values with analyte range reported by the National Institute of Standards and Technology (NIST) for standard reference materials 2694A-I and 2694A-II*

[All units in milligrams per liter except: hydrogenion, in microequivalents per liter, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius. AES, Atmospheric Environment Service; CAL, Central Analytical Laboratory, Illinois State Water Survey; ESE, Environmental Science and Engineering, Inc.; GGC, Global Geochemistry Corporation; MOE, Ontario Ministry of Environment. Shading indicates median values outside NIST range; NIST ranges from NIST Certificate for Standard Reference Material 2694A, dated June 10, 1991; boxed areas indicate median value was calculated from less than nine (maximum possible) reported values]

	pH	Specific conductance	Calcium	Magnesium	Sodium	Potassium	Ammonium	Chloride	Nitrate	Sulfate
	NIST RANGE, 2694A-I									
Lower	4.27	24.2	0.011	0.024	0.206	0.054	[1]0.12	[1]0.23	[1]0.53	2.66
Upper	4.33	26.6	.014	.024	.210	.058	[1].12	[1].23	[1].53	2.72
	LABORATORY MEDIAN, 2694A-I									
AES	4.27	[2]	.020	.020	.200	.060	.12	.23	.52	2.70
CAL	4.24	28.3	.010	.024	.208	.055	.12	.22	.54	2.73
ESE	4.29	27.2	.013	.026	.187	.051	.13	.22	.52	2.72
GGC	4.27	26.0	.012	.021	.203	.053	.12	.23	.58	2.69
MOE	4.27	26.1	.016	.024	.209	.056	.13	.22	.58	2.60

	pH	Specific conductance	Calcium	Magnesium	Sodium	Potassium	Ammonium	Chloride	Nitrate	Sulfate
	NIST RANGE, 2694A-II									
Lower	3.57	128.0	0.036	0.047	0.411	0.105	[1]1.06	[1]0.94	7.03	10.5
Upper	3.63	130.6	.037	.049	.435	.111	[1]1.06	[1].94	7.35	10.7
	LABORATORY MEDIAN, 2694-II									
AES	3.59	[2]	.035	.050	.390	.100	1.06	.92	7.00	10.4
CAL	3.57	133.3	.040	.047	.423	.107	1.05	.95	7.20	10.7
ESE	3.59	142.0	.040	.052	.403	.101	.99	.95	7.17	10.8
GGC	3.56	125.7	.036	.047	.400	.101	1.04	.95	7.09	10.4
MOE	3.57	127.4	.031	.054	.425	.107	1.07	.98	7.08	9.2

[1] Value not certified by NIST.

[2] Data not available.

Table 12. *Number of analyte determinations greater than reporting limits for the ultrapure deionized-water samples for each laboratory participating in the interlaboratory-comparison program during 1994*

[CAL, Illinois State Water Survey Central Analytical Laboratory; AES, Atmospheric Environment Service; ESE, Environmental Science and Engineering, Inc.; MOE, Ontario Ministry of the Environment; GGC, Global Geochemistry Corporation; N, None]

Analyte	CAL	AES	ESE	MOE	GGC
Calcium	N	1	2	N	N
Magnesium	N	N	N	N	N
Sodium	N	N	N	N	2
Potassium	N	N	N	1	N
Ammonium	N	N	4	1	N
Chloride	N	N	N	N	N
Nitrate	N	N	N	N	N
Sulfate	N	N	N	N	N

first two years of the study are provided by Nilles and others (1991). In every year prior to 1994, collocated sites were operated on a water year basis (October 1 to September 30). Estimates of intrasite precision are provided in this report for four sites participating on a calendar year basis (January 4, 1994 to January 3, 1995). The commencement of collocated sampling was delayed from the usual first week of October start up date to a January start up date to coincide with the January 1994 NADP/NTN sample shipping protocol change. Estimates of network precision that include several years of collocated sampling and provide estimates for precision on a network wide basis are given in Nilles and others (1993).

Sites that meet prerequisite criteria are selected for each year of the collocated-sampler study. NADP/NTN guidelines for site selection and installation (Bigelow, 1984) are used in the establishment of each collocated site. A distribution of sites among diverse regional locations and among a range of precipitation regimes is needed. Only those sites with stable operational histories are considered to minimize data loss due to changes in personnel. Lack of room for collocated equipment is a common reason for eliminating fenced sites from consideration. The locations of sites participating in the collocated-sampler study in 1994 are shown in figure 16.

After the sites for the collocated-sampler program were selected, equipment was shipped by the USGS to each site, and installed by USGS personnel with assistance from site supervisors or operators. The site operator processed samples from each pair of collectors using standard NADP/NTN procedures (Bigelow and Dossett, 1988). Onsite pH and specific-conductance measurements on the samples from the newly installed collocated samplers were not required; however, a 20-mL aliquot was removed from samples of 70 mL or larger to provide equivalent treatments to both samples from the collocated-sampler site. All samples were analyzed as routine weekly NADP/NTN samples by the CAL, and all sites selected for the collocated-sampler study were inspected by USGS personnel. The sites were inspected by the principal investigator for the collocated-sampler study in November 1993 after equipment installation and before collection of the first sample in January 1994.

For wet-deposition samples, only data from samples with volume greater than 35 mL (lab type "W") that did not require dilution were used in the statistical summaries. Samples requiring dilution are inherently prone to a greater error component. Median concentrations for selected analytes in weekly samples collected at the 1994 collocated sites are depicted in figure 17. Figure 18 depicts the median hydrogen ion concentration, median specific conductance, median sample volume, and median precipitation depth for the 1994 collocated sites.

Median sample chemistry varied widely among sites. The differences in the chemistry of analytes associated with significant anthropogenic sources (for example, sulfate, nitrate, and hydrogen ion concentration) are notable when comparing Ohio site 49OH with the sites in less industrialized areas. Hydrogen-ion concentrations for 49OH are nearly 15 times higher than the hydrogen-ion concentrations from a site in northern Minnesota (16MN).

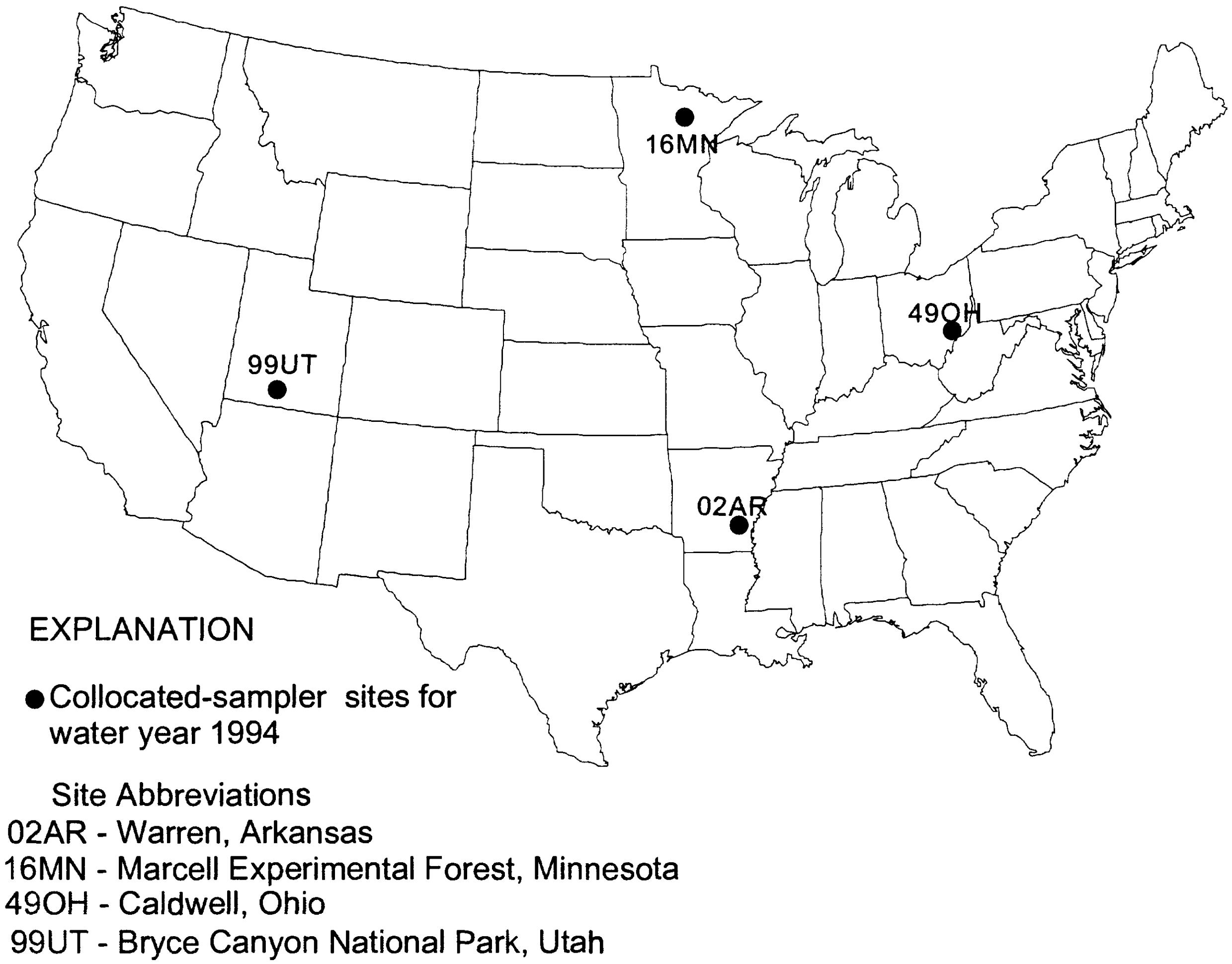


Figure 16. Location of National Atmospheric Deposition Program/National Trends Network sites with collocated samplers in 1994.

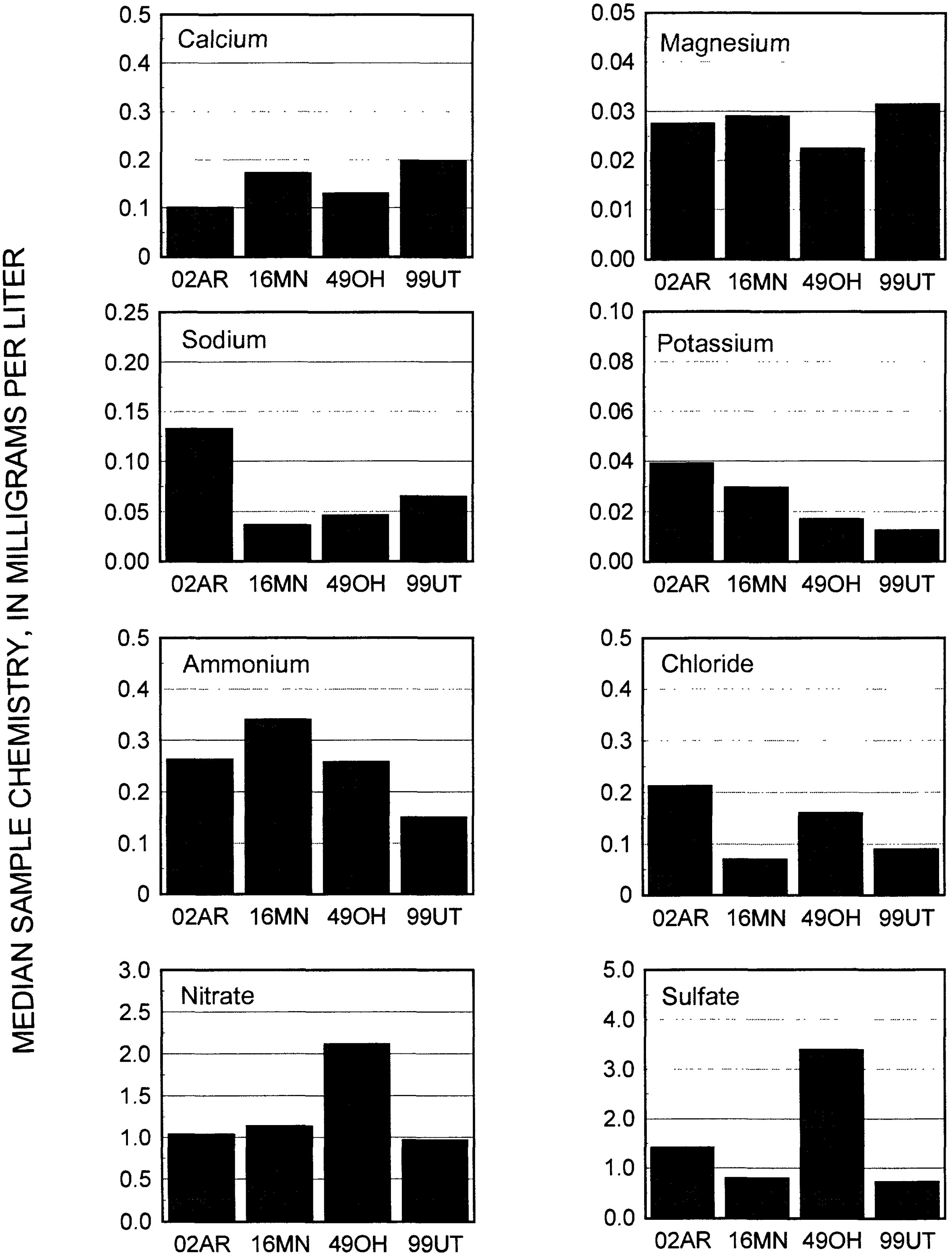


Figure 17. Median sample chemistry for selected analytes at four National Atmospheric Deposition Program/National Trends Network sites with collocated samplers.

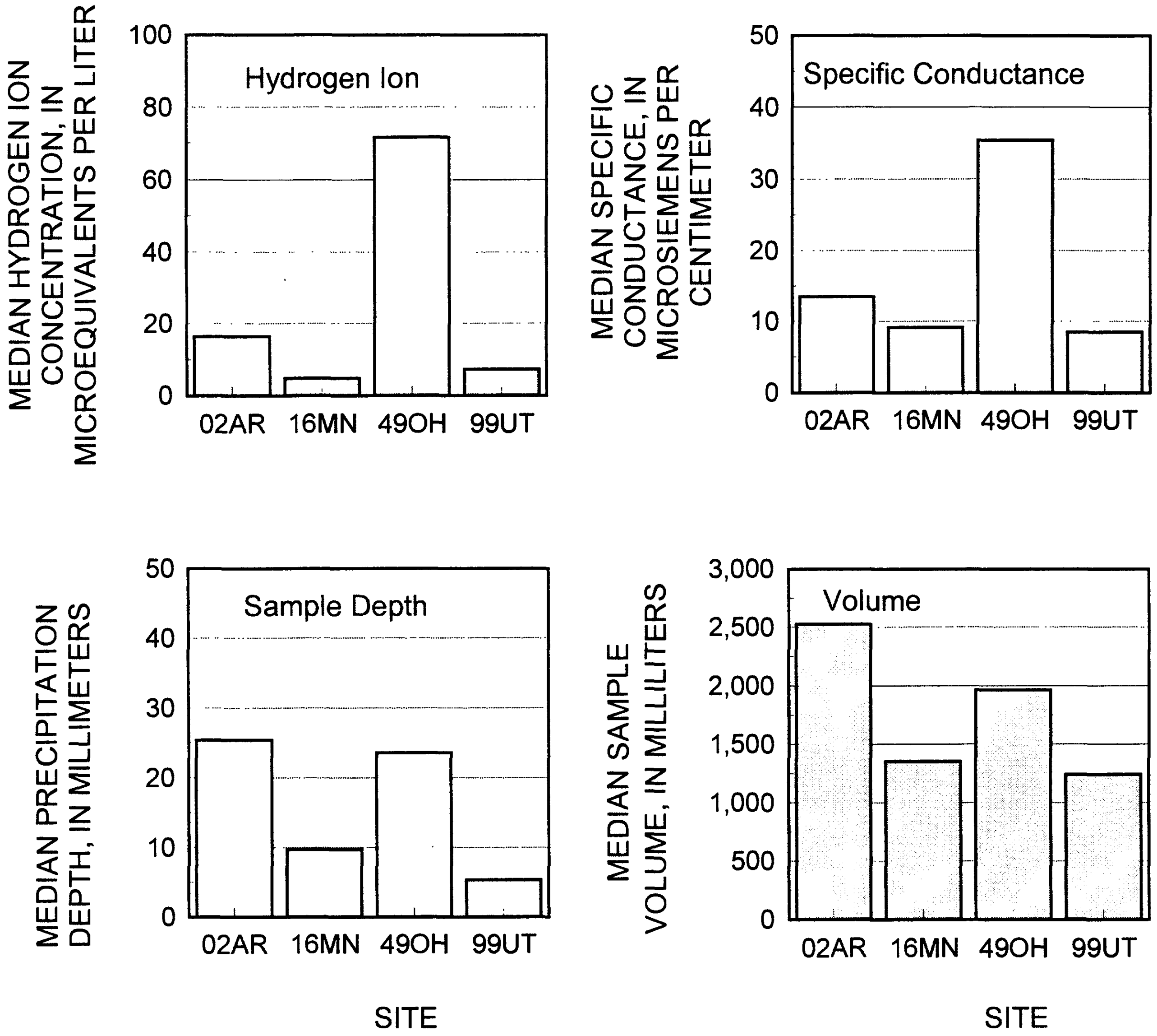


Figure 18. Median hydrogen ion concentration, specific conductance, sample volume, and precipitation depth for four National Atmospheric Deposition Program/National Trends Network sites with collocated samplers.

Annual summaries of NADP/NTN data describe precipitation chemistry in units of concentration and deposition for ionic constituents (National Atmospheric Deposition Program, 1996). Statistical summaries for both concentration and deposition of ionic constituents are therefore included in this report. The weekly precipitation depth associated with each Belfort recording rain-gage was used to calculate deposition values at the collocated sites. Concentration in mg/L is converted to mg/1000 cm^3 and then multiplied by 10^{-1} times the rainfall depth in centimeters to yield deposition in kg/ha. This approach accounts for the variability due to differences in rain gage collection efficiency in the precision estimates for deposition. Care was taken to select statistics that were meaningful in describing overall sampling precision and that were not overly sensitive to a few extreme outliers.

Precision estimates for each site are calculated from the relative and absolute differences between the pairs of collocated samples and are expressed as median relative and median absolute error for a given site and analyte. The equations used to estimate median relative and absolute error from collocated data are:

$$\text{Median relative error} = M\left|\frac{C_1 - C_2}{(C_1 + C_2)/2}\right| * 100$$
(in percent)

and

$$\text{Median absolute error} = M|C_1 - C_2|$$
(in mg/L or kg/ha)

where

M = Median of all paired differences;
C_1 = Sample concentration(mg/L) from the original precipitation sampler, or deposition(kg/ha) from the original precipitation sampler and rain-gage; and
C_2 = Sample concentration(mg/L) from the collocated precipitation sampler, or deposition(kg/ha) from the collocated precipitation sampler and rain-gage.

Precision estimates defined by the median of the unsigned absolute or relative percent difference are fairly insensitive to a few extreme values. For sample pairs with low concentrations of ionic constituents, the relative percent error can be very large, although the absolute difference between the samples is small. In 1994, site 16MN had 48 valid sample pairs that were used to calculate precision estimates. Sites 02AR and 49OH had 44 and 41 valid sample pairs, respectively. Fewer pairs (35) were available from site 99UT, reflecting the semiarid climate in southern Utah.

Median relative error (MRE) for chemical determinations was the smallest for sulfate concentration, ranging from 2.9 percent to 5.2 percent among the sites, and were consistent with the magnitude of MRE's calculated in previous years of the study. The same characterization of precision is observed for nitrate concentration, specific conductance, collected sample volume from the AeroChem collectors, and precipitation depth from the Belfort rain-gages. MRE's for these properties were uniformly small (less than 10 percent) and fairly consistent at all four sites despite differences in typical sample chemistry and precipitation amounts between the sites. MRE's for the sample chemistry in terms of concentration, deposition and for the physical measurements of sample volume and precipitation depth are provided in figure 19.

The MRE's were larger and more variable from site to site for all cations and particularly for cations whose concentrations typically were near laboratory detection limits. The MRE's for cations exceeded 7 percent at most sites. Assuming that random contamination is independent of sample concentration and laboratory error increases with lower concentration samples, an increase in relative error at sites with lower concentrations would be expected. For example, the MRE for potassium concentration, an analyte found in very low levels in precipitation, ranged from 18.0 percent to 37.5 percent at the four collocated sites in 1994.

As in previous years, the precision for hydrogen ion concentration and deposition varied in absolute and in relative terms among the sites, depending upon the acidity of the precipitation at a given collocated site. The MRE's for hydrogen-ion concentration ranged from 12 to 13 percent at 02AR, 16MN, and 99UT, three sites with relatively low levels of hydrogen-ion concentration, to 4.6 percent at 49OH, a site with significantly higher levels of hydrogen-ion in weekly samples. The difference in precision estimates for hydrogen ion between 49OH and the other three sites can be accounted for by differences in median concentration. Median hydrogen-ion concentration at 49OH was at least four times greater than that of the other three sites (fig. 18).

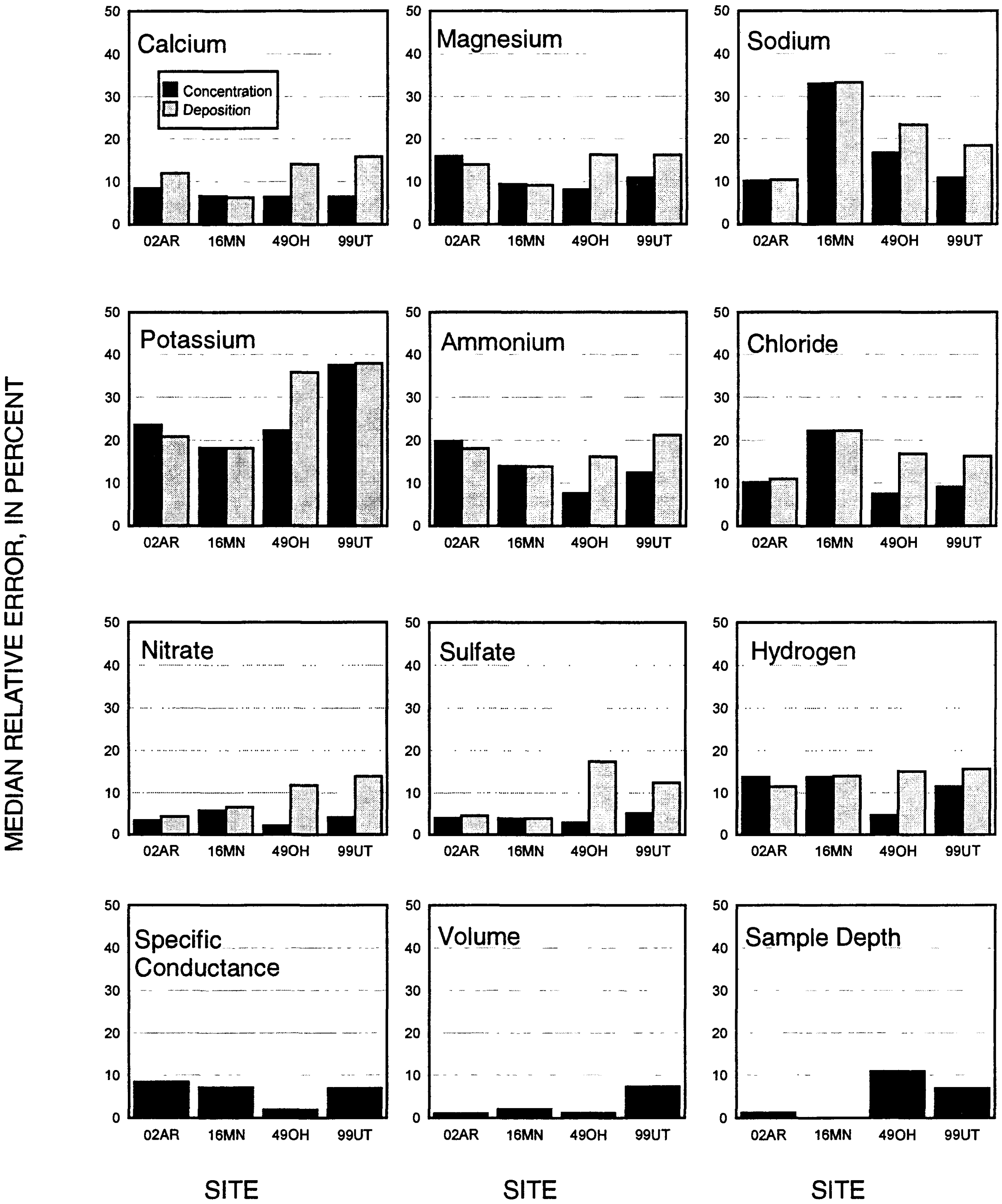


Figure 19. Median relative error for analyte concentration, deposition, and other physical parameters for weekly samples from collocated wet-dry precipitation collectors and precipitation depth from collocated rain gages. All data is in percent.

The MRE's calculated for weekly analyte deposition at the four sites incorporate variability due to differences in sample depth between the original and collocated Belfort recording rain gages as well as chemistry differences. Although not consistent among sites or analytes, MRE's were only slightly greater when calculated using deposition data rather than concentration data for sites 02AR, 16MN and 99UT (fig. 18). The MRE's for deposition were elevated when compared to concentration for site 49OH. Error in deposition incorporates systematic and random error associated with the Belfort rain-gage. The original and collocated Belfort gages at OH49 and 49OH were not in as close agreement as were the collocated rain gages at other sites. The MRE's for precipitation depth were 7 percent or less at 02AR, 16MN, and 99UT, while the MRE for site 49OH exceeded 10 percent.

In table 13, collocated-analyte precision estimates are compared to analytical precision estimates calculated in the same manner from 90 sample pairs submitted to the CAL in 1994 as part of the interlaboratory-comparison program described in the preceding section of this report. Aliquots of natural, weekly, wet-deposition samples with volumes greater than 750 mL are used in the USGS interlaboratory-comparison programs as well as synthetic precipitation samples. The natural interlaboratory samples had slightly lower specific conductance and median concentrations of analytes when compared to the median values for all NADP/NTN samples analyzed at the CAL.

Comparison of Laboratory and Network Error

A comparison of the laboratory random error to the overall network error estimated from the collocated-sampler program indirectly provides a method to apportion the relative amount of error attributable to laboratory operations. Laboratory random error, as calculated from replicate samples submitted to the CAL for analysis, is estimated typically to account for one-fifth of the overall collocated-sampling error, although the fraction of sampling error attributable to laboratory random error varies with site and with analyte. Comparisons of laboratory random error to sampling error from specific NADP/NTN sites has limitations because sampling error is site-specific for some analytes such as hydrogen ion. Specific partitioning of error at a given site would only be valid if the laboratory error term was calculated from a number of replicate samples collected at sites with similar hydrogen-ion concentration values.

Table 13. *Median absolute error for analyte concentrations from weekly collocated wet-dry precipitation samples and replicate samples*

[All units in milligrams per liter except: hydrogen ion, in microequivalents per liter, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius. CAL, Illinois State Water Survey Central Analytical Laboratory; <, less than]

	Sampling site				
Analyte	**02AR**	**16MN**	**49OH**	**99UT**	**CAL**
Calcium	0.009	0.013	0.008	0.014	<0.001
Magnesium	.003	.003	.001	.003	.001
Sodium	.013	.011	.007	.008	.001
Potassium	.005	.004	.004	.003	.001
Ammonium	.05	.03	.02	.02	<.01
Chloride	.02	.01	.01	.01	<.01
Nitrate	.04	.07	.05	.04	.01
Sulfate	.04	.03	.08	.03	<.01
Hydrogen ion	2.31	.45	2.57	.82	.23
Specific conductance	1.35	.75	.75	.70	.15

Bias was evaluated for each site and analyte by using the median signed difference between collocated-sample concentrations (fig. 20). Bias estimates for sample volume from the precipitation collectors and precipitation depth from the recording rain gages also were calculated. Because the collocated paired samples were shipped from the sites weekly to the same laboratory at the same time, the authors attribute bias in the data-set pairs to systematic differences in: (1) sampler response, (2) sample collection, and (3) sample handling prior to shipment. Bias for analytes accounted for less than 20 percent of the overall relative error in collocated measurements. The absence of bias as a significant contributor to overall variability in NADP/NTN wet-chemistry measurements from the four sites was not surprising due to the good precision and low bias associated with the AeroChem collectors in 1994. The small amount of bias that was associated with Aerochem collectors was usually due to small differences in lid opening and closing rates due to sensor differences. Bias in sample volume between collectors did not exceed ± 1.5 percent at any collocated site operated during 1994. The results for 1994 are somewhat better than the results from prior years in the collocated program when bias in sample volume was as large as -7.0 percent and frequently exceeded ± 1.5 percent.

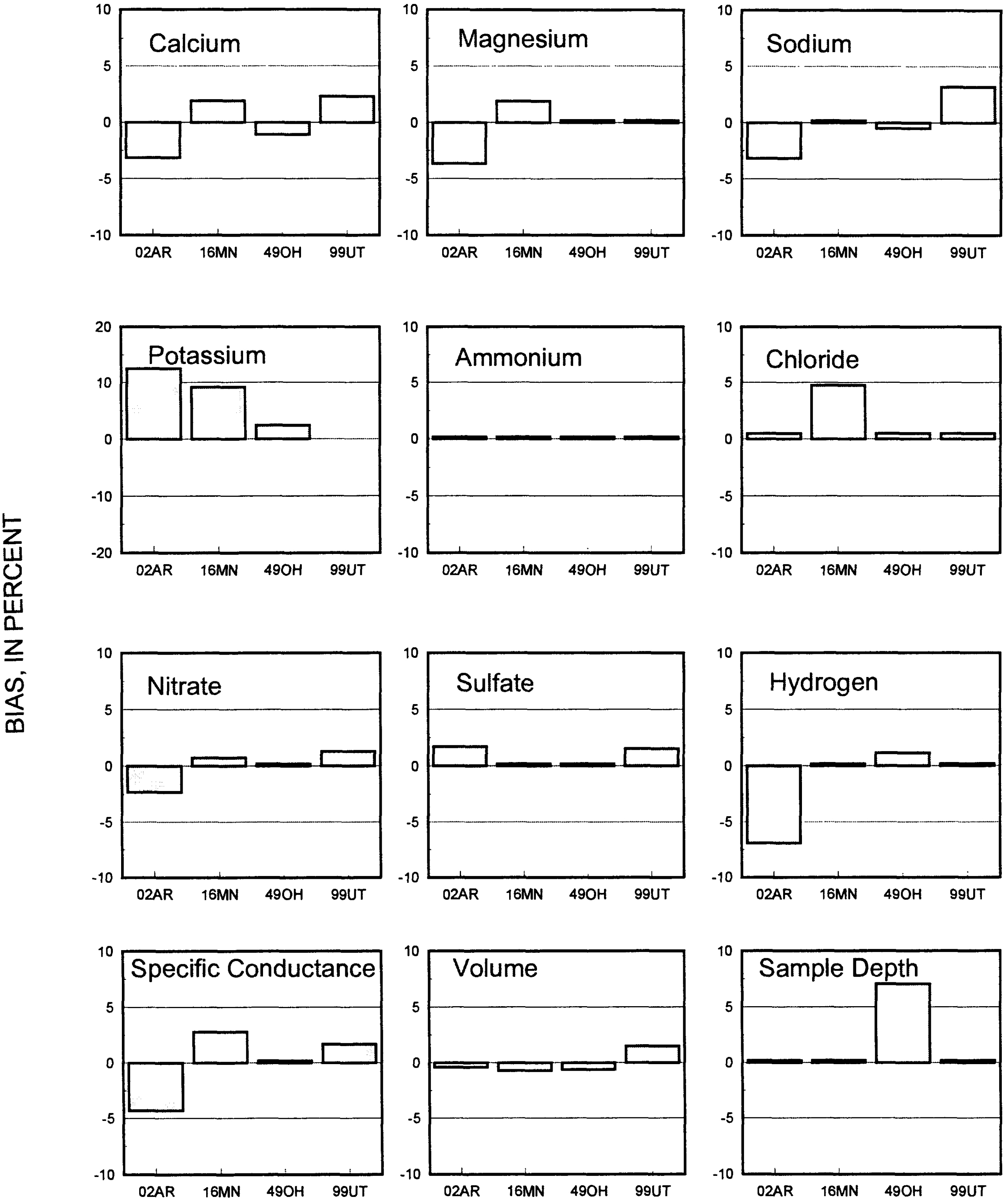


Figure 20. Bias for analyte concentrations, deposition, and other physical parameters for weekly samples from collocated wet-dry precipitation collectors and precipitation depth from collocated rain gages. All data is in percent.

SUMMARY

During 1994, the U.S. Geological Survey used four programs designed to provide external quality-assurance monitoring for the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). An intersite-comparison program was used to estimate the accuracy and precision of onsite pH and specific-conductance determinations. A blind-audit program was used to assess the effects of routine sample handling, processing, and shipping of wet-deposition samples on the precision and bias of NADP/NTN wet-deposition data. As part of the interlaboratory-comparison program, analytical results from five laboratories that routinely analyze wet-deposition samples were examined to determine estimates of analytical bias and precision for major constituents in wet deposition from each laboratory. A collocated-sampler program was used to determine the overall precision of NADP/NTN wet-deposition data at selected sites in the network.

Intersite-Comparison Program

The median pH of the intersite comparison study 33 reference solution was 4.79. Of the site operators responding by the deadline for study 33, 85 percent met the accuracy goals of ± 0.10 pH unit of the overall median. The median specific-conductance for study 33 was 7.40 µS/cm; 95 percent of the specific-conductance values reported by the deadline met the NADP/NTN accuracy goals of ± 4.0 µS/cm of the median value. In study 34 a reference solution was used with a median pH 4.54; the median specific conductance was 20.7 µS/cm. In study 34, 88 percent of the site operators reporting by the deadline met the accuracy goals for pH, and 96 percent of the site operators reporting by the deadline met the accuracy goals for specific conductance. Site operators who either did not meet the accuracy goals or did not participate were evaluated for inclusion in an additional followup study. Followup ranged from a letter discussing common sources of measurement error to requests that the site operator complete one or more additional measurements. Ten of the 33 site operators included in the followup study for intersite 33 were evaluated as having minor problems with their pH measurements and only received a letter describing common causes of measurement error. Fifteen of the remaining 23 operators asked to do additional pH measurements as part of the intersite 33 followup study met the NADP/NTN accuracy goals for the measurements they completed, indicating they apparently were able to resolve the cause of their initial measurement difficulties. The followup portion of study 34 involved 30 site operators, all of whom were asked to complete extra pH measurements. Of the 26 operators that participated in the intersite 34 followup study, 19 met the accuracy goals for all additional measurements.

Blind-Audit Program

A Wilcoxon signed-rank test was used to determine if significant differences existed between the analyte concentrations measured in paired blind-audit samples. One part of the blind-audit sample was subject to all of the normal onsite handling and processing steps that a regular weekly precipitation sample is subject to, whereas the other portion received only minimal handling. The change in network sample shipping protocol from 13.5-L buckets to 1-L bottles (and the corresponding change in the blind audit procedures) have strongly affected the 1994 results relative to preceding years. Results of the Wilcoxon signed-rank test for bias indicated significant ($\alpha=0.05$) positive bias for only two analytes, calcium and sulfate. Significant ($\alpha=0.05$) negative bias was determined for sodium, ammonium, chloride, and hydrogen ion. The median paired differences between the bucket and bottle portions ranged from -0.02 mg/L for ammonium to +0.004 mg/L for calcium. The median relative and absolute percent bias values were determined for all of the paired blind-audit sample differences by calculating each signed and unsigned paired difference, respectively, as a percentage of the concentration measured in the bottle portion of the bucket-bottle data pair. The median relative percent bias for hydrogen ion decreased from -42.5 percent in 1993 to -4.50 percent in 1994, indicating a substantial reduction in the amount of hydrogen ion lost as a result of routine shipping and handling procedures. The median relative percent bias for specific conductance also improved substantially, decreasing to -0.92 percent in 1994 compared to -17.4 percent in 1993. However, the magnitude of the median relative percent bias for sodium increased sharply in 1994 to -10.86 percent from a nominal 1.82 percent in 1993.

The median relative percent bias for ammonium was -16.7 percent, whereas for chloride it was -3.12 percent. The median relative percent bias was between 0 and 5 percent for calcium, magnesium, potassium, nitrate, and sulfate. The absolute percent bias values were similar in magnitude to the relative percent bias values for calcium, magnesium, nitrate, sulfate and specific conductance. The absolute percent bias was much larger than the relative percent bias for ammonium, chloride, potassium, sodium and hydrogen ion.

Surface chemistry effects due to different amounts of precipitation contacting the sample collection and shipping container surfaces were studied in the blind audit program using three different sample volumes. To determine if a relation existed between the volume collected in the bucket and the differences between the analyte concentrations in the bucket and bottle portions of the blind-audit sample, sixteen 250-mL, sixteen 500-mL, and sixteen 1,000-mL bottles of the same solution (USGS) were sent to the operators of selected sites in 1994. Results of a Kruskal-Wallis test indicated no significant (α=0.05) difference in bucket minus bottle differences on a mass per bucket basis for calcium, magnesium, potassium, chloride, nitrate, hydrogen ion, or specific conductance, whereas statistically significant (α=0.05) differences were determined for sodium, ammonium, and sulfate. The results for sodium and ammonium indicate negative bias which may be caused by complex surface chemistry reactions that bind these positively charged ions to the negative surfaces of the sample collection and shipping containers. The magnitude of the negative bias of sodium and ammonium in units of mass increased with increasing sample volume. The results for sodium and ammonium contrast sharply with the results for sulfate, which were positively biased, indicating the addition of sulfate from the container surfaces. Sulfate had an increasing positive bias in units of mass with increasing sample volume. The results of a hypothesis test of the relation between hydrogen ion differences and sample volume were, for the first time since studies of volume effects began in 1988, not statistically significant. This supports the premise that the chemical reactions between the 13-L bucket shipping container and the sample that resulted in an increasing loss of hydrogen ion with increasing volume in every year of the study prior to 1994 have been effectively reduced to a level that is not chemically significant by the new 1-L bottle sample shipping protocol.

In all 17 Ultrapure deionized-water samples, (Ultrapure) sodium was detected at levels greater than the method detection limit. The results for sodium are consistent with internal QA results at the CAL that consistently showed increased sodium concentrations in filtered blind-audit and Ultrapure samples in 1994.

Interlaboratory-Comparison Program

A Friedman test indicated significant bias (α=0.01) in analyte concentrations for calcium, magnesium, sodium, ammonium, chloride, nitrate, sulfate, hydrogen ion, and specific-conductance among the laboratories participating in the interlaboratory-comparison program. Cation precision estimates at the 50th percentile exhibited less variability than anion, pH (expressed as hydrogen ion concentration), and specific-conductance precision estimates at the 50th percentile. Precision estimates at the 90th percentile exhibited some variability among the laboratories for the cations, anions, pH, and specific conductance.

Analytical results from National Institute of Standards and Technology reference solutions indicated that the CAL and MOE each had six median analyses that were significantly different from certified values. AES and ESE each had ten median analyses that were significantly different from certified values, and GGC had eight median analyses that were significantly different from certified values.

All of the determinations by the CAL for the analyses of Ultrapure samples were below the minimum reporting limit. AES reported one determination exceeding the minimum reporting limit, whereas ESE, MOE, and GGC reported 6, 2, and 2 determinations, respectively, which exceeded the minimum reporting limit for the analyses of Ultrapure samples. Two determinations reported by ESE as exceeding minimum reporting limits were below the minimum reporting limits for the other laboratories. The results for all of the analytes for the five laboratories are within the same range of variability that was determined in the 1993 interlaboratory comparison study.

Collocated Sample Program

A collocated-sampler program was used to estimate the overall variability of chemical measurements of wet-deposition data collected for the NADP/NTN. The estimates of precision include all variability in the data-collection system, from the point of sample collection through storage in the NADP/NTN data base. Weekly wet-deposition samples and precipitation measurements from collocated NADP/NTN sites were compared. Estimates of precision were calculated in terms of median relative and median absolute difference for both concentration and deposition of ionic constituents of wet deposition. The median relative error for sulfate and nitrate concentrations and for collected sample volumes was typically less than the median relative error calculated for the other analytes examined. Relative error typically was greater for cations, with median relative error exceeding 7 percent at most sites. As in previous years the precision for hydrogen concentration and deposition varied greatly in absolute and relative terms among the sites, depending upon the acidity of the precipitation at a given collocated site. Laboratory error typically is estimated to account for one-fifth of the overall collocated-sampling error on the basis of data from replicate natural samples analyzed at the CAL. Bias in collocated measurements typically accounted for less than 20 percent of the overall error in collocated measurements.

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