

External Quality-Assurance Results for the National Atmospheric Deposition Program/ National Trends Network, 1995-96

Water-Resources Investigations Report 99-4072



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*Front cover photographs are of selected National Atmospheric Deposition Program/National Trends Network Sites used in the
collocated project, 1995-96 (clockwise from top right):*

Little Bighorn Battlefield National Monument, Montana, site MT00/00MT

Dixon Springs Agricultural Research Center, Illinois, site IL63/63IL

Dixon Springs Agricultural Research Center, Illinois, site IL63/63IL

Underhill, Vermont, site VT99/99VT

Little Bighorn Battlefield National Monument, Montana, site MT00/00MT

All photographs were taken by the U.S. Geological Survey.

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By John D. Gordon

U.S. GEOLOGICAL SURVEY

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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:

$$^{\circ}\text{F} = 9/5(^{\circ}\text{C}) + 32$$

ADDITIONAL TERMS AND ABBREVIATIONS

- microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$)
- megohm ($\text{M}\Omega$)
- microequivalent per liter ($\mu\text{eq}/\text{L}$)
- milligram per liter (mg/L)
- kilogram per hectare (kg/ha)
- microgram (μg)
- absolute value of $x = |x|$, where x takes the form of numerical values or algebraic expressions
- maximum probability of rejecting the null hypothesis when it is true (α)

External Quality-Assurance Results for the National Atmospheric Deposition Program/National Trends Network, 1995-96

By John D. Gordon

Abstract

The U.S. Geological Survey operated four external quality-assurance programs for the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) in 1995 and 1996: the intersite-comparison program, the blind-audit program, the interlaboratory-comparison program, and the collocated-sampler program. The intersite-comparison program assessed the precision and bias of pH and specific-conductance determinations made by NADP/NTN site operators. The analytical bias introduced during routine handling, processing, and shipping of wet-deposition samples and precision of analyte values was estimated by 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 North American laboratories that routinely analyzed wet deposition. A collocated-sampler program was used to estimate the precision of the overall precipitation collection and analysis system from initial sample collection through final storage of the data.

Results of two intersite-comparison studies completed in 1995 indicated that about 95 and 94 percent of the onsite pH determina-

tions met the NADP/NTN accuracy goals, whereas about 97 and 98 percent of the specific-conductance determinations were within the established limits. The percentages of onsite determinations that met the accuracy goals in 1996 were slightly less for pH and specific-conductance than in 1995. In 1996, about 94 and 88 percent of onsite pH determinations met the accuracy goals, whereas the percentage of onsite specific-conductance measurements that met the goals was about 94 and 95 percent.

The blind-audit program requires a paired-sample design to evaluate the effects of routine sample handling, processing, and shipping on the chemistry of weekly precipitation samples. The portion of the blind-audit sample subject to all of the normal onsite handling and processing steps of a regular weekly precipitation sample is referred to as the bucket portion, whereas the portion receiving only minimal handling is referred to as the bottle portion. Throughout the report, the term positive bias in regard to blind-audit results indicates that the bucket portion had a higher concentration than the bottle portion. The paired t-test of 1995 blind-audit data indicated that routine sample handling, processing, and shipping introduced a very small positive bias [probability level

($\alpha=0.05$) for hydrogen ion and specific conductance and a slight negative bias ($\alpha=0.05$) for ammonium and sodium. In 1995, the median paired differences between the bucket and bottle portions ranged from -0.02 milligram per liter for both ammonium and nitrate to +0.002 milligram per liter for calcium. Although the paired t-test indicated a very small positive bias for hydrogen ion, the median paired difference between the bucket and bottle portions was 0.00 microequivalent per liter, whereas for specific conductance, the median paired difference between the bucket and bottle portions was 0.200 microsiemens per centimeter in 1995. The paired t-test of blind-audit results in 1996 indicated statistically significant bias for 6 of the 10 analytes. Only chloride, nitrate, hydrogen ion, and specific conductance did not show bias in 1996. The magnitude of the bias in 1996, however, was small and only of limited importance from the viewpoint of an analytical chemist or data use. The median paired differences between the bucket and bottle portions ranged from -0.02 milligram per liter for both ammonium and chloride to +0.006 milligram per liter for calcium. For hydrogen ion, the median paired difference between the bucket and bottle portions was -0.357 microequivalent per liter; for specific conductance, the median paired difference between the bucket and bottle portions was 0.00 microsiemens per centimeter in 1996.

Surface-chemistry effects due to different amounts of precipitation contacting the sample-collection and shipping-container surfaces were studied in the blind-audit program by using three different sample volumes. The results of a hypothesis test of the relation between hydrogen-ion differences and sample volume were not statistically significant in either 1995 or 1996. This supports the premise that the chemical reactions between the 13-liter bucket shipping container and the sample, which resulted in an increasing loss of hydrogen ion with increasing volume before 1994, have been eliminated by the new 1-liter bottle sample-shipping protocol.

In the interlaboratory-comparison program in 1995, results of the Friedman test indicated significant ($\alpha=0.05$) differences in analyte measurements for calcium, potassium, nitrate, sulfate, and hydrogen ion among the five laboratories. In 1996, the Friedman test indicated significant ($\alpha=0.05$) differences in analyte measurements for potassium, ammonium, chloride, nitrate, sulfate, and hydrogen ion. Intralaboratory bias was indicated for most laboratories in tests of certified analyte concentrations from standard reference material samples and from Ultrapure deionized water samples. Variability among laboratories was assessed by comparing precision estimates. 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 for the five laboratories that participated in the interlaboratory comparison program.

Results from the collocated-sampler program indicated the median relative error calculated from deposition amounts exceeded 20 percent for sodium and potassium at all of the 1995 collocated sites. In 1996, the median relative error calculated from deposition amounts also exceeded 20 percent at two of the four sites for sodium and potassium. In contrast, the median relative error for sulfate and nitrate deposition was less than 20 percent at all sites in 1995 and 1996; and at four of the eight sites, sulfate and nitrate median relative error was less than 10 percent. The median relative error for hydrogen-ion concentration and deposition ranged from 4.6 to 26.3 percent at the eight sites and was inversely proportional to the acidity of the precipitation at a given site. In those cases where the median laboratory error was greater than zero, median collocated-sampling error estimates, in units of concentration, were typically at two to four times larger than median laboratory error estimates for most analytes. The median laboratory error estimates for the laboratory that analyzes the samples for the NADP/NTN was 0.00 milligram per liter for 4 of 10 analytes.

INTRODUCTION

The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) investigates the occurrence and effects of wet deposition across the United States. The 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 use the same type of wet-deposition collectors, which are described by Bigelow and Dossett (1988). Sample-handling and shipping protocols were extensively revised in January of 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 in a draft form but has yet to be published (Scott Dossett, Illinois State Water Survey, written commun., 1999). 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 1995 and 1996. 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 that routinely measure 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 fifth external QA program, the field-blank and reference-sample program, was begun in late 1996 as a pilot study on a limited basis. A protocol

report providing detailed information on the procedures and analytical methods used in these four QA programs is available (See and others, 1990). For the purposes of this report, the term “major ions” refers to calcium, magnesium, sodium, potassium, ammonium, chloride, nitrate, and sulfate.

STATISTICAL APPROACH

Nonparametric hypothesis-testing techniques (for a non-normal data distribution) for differences in external QA results were used extensively instead of traditional parametric hypothesis-testing techniques for a normal data distribution in this report. The nonparametric techniques included the Wilcoxon signed-ranks test, the Kruskal-Wallis test, and the Friedman test. The paired t-test (parametric) was included in this report in the analysis of paired blind-audit results. The paired t-test is based on blind-audit samples that are paired analyses, whereas the *nonparametric* alternative to the paired t-test, the Wilcoxon signed-rank test, is based on ranks instead of the actual data (avoiding the requirement of a normal distribution) but has the limitation of assuming that the data consist of random, independent samples (Conover, 1980). The Wilcoxon signed-ranks test is, therefore, less powerful for paired samples than the paired t-test (Kanji, 1993). Nonparametric statistical tests were commonly used in the analyses for this report because the data sets (and all water-quality data sets for that matter) do not satisfy normal distribution requirements of parametric statistical techniques. The use of nonparametric tests also eliminated problems associated with data transformations that commonly are used to compensate for non-normal data, such as the difficulty of converting the results of statistical tests on transformed data back to the original scale of the data (Berthouex and Brown, 1995). All of the hypothesis tests were based on two-tailed rather than one-tailed alternatives. The reader should refer to any introductory statistics text for an in-depth discussion of the difference between two-tailed and one-tailed hypothesis testing. Huntsberger and Billingsley (1981) for example, devote several chapters of their text to a detailed explanation of two-tailed and one-tailed hypothesis testing. Concise graphical displays, such as boxplots, were used to depict data distribu-

tions and to provide visual representations of NADP/NTN data quality. Tukey's "schematic plot" version of the notched boxplot (Chambers and others, 1983) was used in this report. Boxplots with notches in their sides help guide the assessment of relative locations. The notches provide an informal 95-percent test of the null hypotheses that the true medians of side by side boxplots are equal: if the notches overlap, the null hypothesis is not rejected with approximate 95-percent confidence (Chambers and others, 1983). If the length of the notch exceeds the length of the box portion of the boxplot, the plot will have the appearance of doubling back on itself. Therefore, the notch was not displayed when the notch length exceeded the length of the box portion of the boxplot. Extending from the box portion of the boxplot are thin lines called "whiskers." Using Tukey's definition, the whiskers extend only to the last observation within a distance of 1.5 times the interquartile range from the top or bottom of the box. For all of the boxplots, values outside the whiskers are shown individually as an asterisk (Helsel and Hirsch, 1992). The magnitude of measurement bias was quantified in several different ways for the convenience of the reader, including units of concentration, mass, and percent differences.

EXTERNAL QUALITY-ASSURANCE RESULTS

Intersite-Comparison Program

NADP/NTN site operators measure pH and specific conductance on weekly precipitation samples, as long as sample volume considerations are satisfied. These measurements are performed on precipitation collected at sampling sites. These onsite measurements are useful and provide the most accurate assessment of pH and specific conductance. Because of the low ionic strength of precipitation, minor changes in pH may occur between the sample collection and laboratory analysis (Bigelow and others, 1989). Many authors have determined that onsite measurements (of pH in particular) are more representative of precipitation than subsequent laboratory determinations (Hem, 1985). To assess the accuracy of onsite measurements, an intersite-comparison study is performed on a semiannual basis. If measurements are not accurate, the site operators are notified of their results in order to troubleshoot their methods and equipment.

Intersite-comparison studies require NADP/NTN site operators to determine the pH and specific conductance of synthetic precipitation-check samples by using standard protocols that are identical to those used on weekly sample measurements (Gordon and others, 1991; Bigelow and Dossett, 1988). The synthetic precipitation-check samples that are prepared by the USGS have ranges of pH and specific conductance similar to natural wet deposition samples that are collected in the NADP/NTN network. The pH is adjusted to a specific value within the range of 3.9 to 5.3 by adding a small amount of nitric acid. The final specific conductance of the solution is either just a function of the nitric acid that was added, or it is increased with small amounts of potassium chloride (KCl). The target values of the solutions are validated through nitrate analysis and pH and specific-conductance measurements.

Results for Intersite-Comparison Study Numbers 35-38

A flowchart that depicts the chronological order of the intersite-comparison program is shown in figure 1. Samples for intersite study numbers 35 and 36 were mailed to the site operators in May and October 1995, respectively. The samples for study numbers 37 and 38 were mailed in April and November 1996. Site operators are allowed 45 days to perform the field measurements. Sites are not included in the percentage of sites that achieved the specified goals if: (1) they respond late; (2) the field equipment is completely inoperable; (3) the site is not in operation at the time of the study; or (4) no field chemistry determinations are made at the site. (Beginning in 1995, accuracy goals that take into consideration the fact that the difficulty of measuring pH increases as the hydrogen-ion concentration decreases were used.) Accuracy goals are based on a multiple-regression equation that incorporates the solution's hydrogenion concentration and the results from past intersite studies. The accuracy goals are symmetrical in units of hydrogen ion and, therefore, are asymmetrical in units of pH. A summary of the results for study numbers 35 and 36 is given in table 1, and the results for study numbers 37 and 38 are summarized in table 2. The accuracy goals used in each study also are listed in tables 1 and 2.

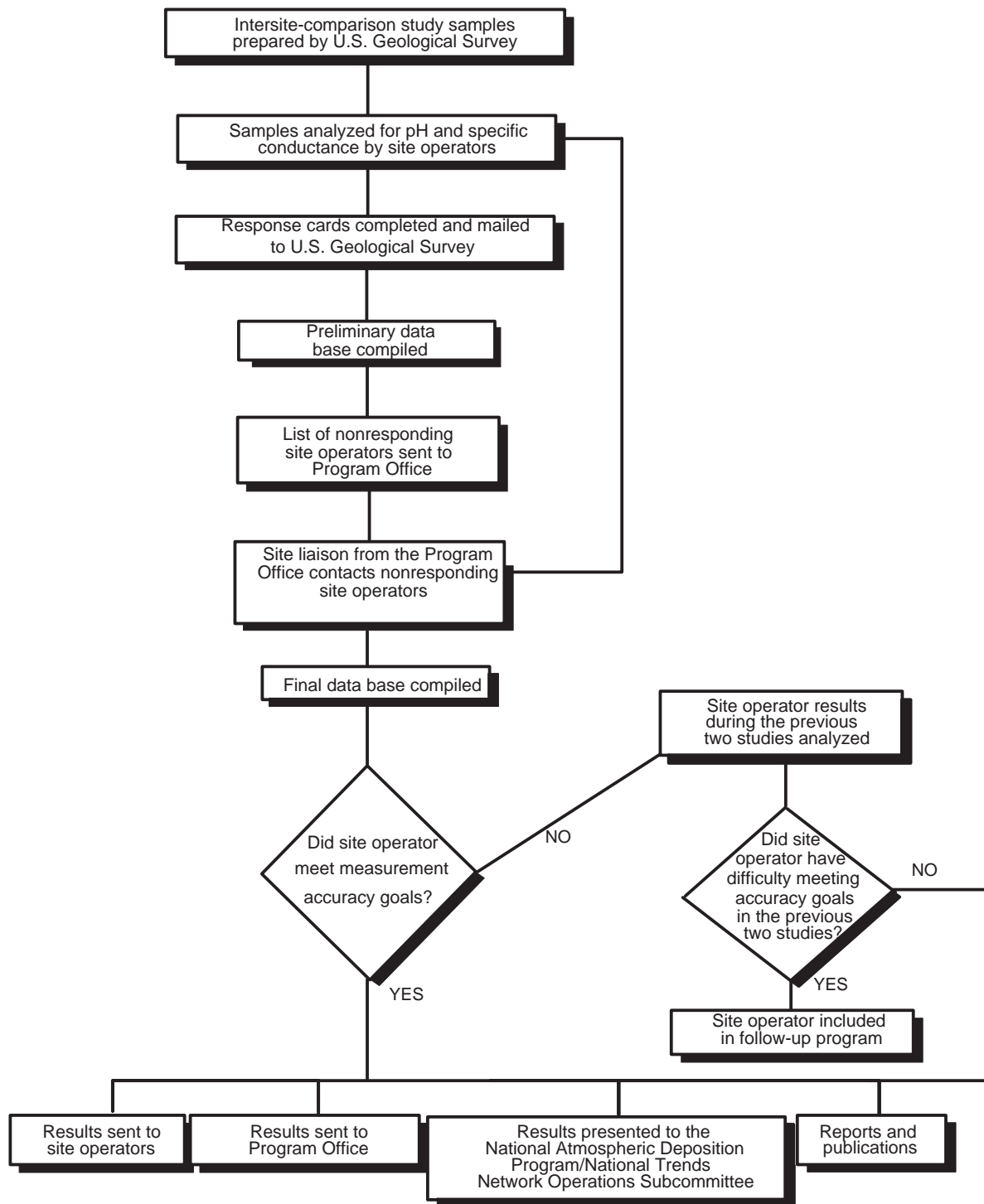


Figure 1. Intersite-comparison program of the U.S. Geological Survey Quality-Assurance Program.

Table 1. Site-operator responses and summary statistics for the 1995 intersite-comparison program

Site-operator responses	Intersite-comparison study number	
	35	36
Number of site operators receiving samples	189	190
Number of site operators submitting pH values by closing date of study	186	180
Number of site operators submitting specific-conductance values by closing date of study	184	181
Site operators responding late	0	0
Number of nonresponding site operators	3	6
Sites that were not in operation	0	2
Site operators reporting equipment problems:		
pH meter/electrode completely inoperable	0	2
pH meter/electrode problems	5	1
Specific-conductance probe/meter completely inoperable	2	1
Specific-conductance probe/meter problems	3	0
Median pH, target pH	4.95, 4.94	4.92, 4.94
Number of responding sites that met the pH accuracy goals	176	170
Accuracy goals for pH: lower and upper acceptable values	4.76, 5.14	4.73, 5.10
Percentage of responding sites that met the pH accuracy goals	94.6	94.4
F-pseudostigma for pH	0.074	0.082
Median specific conductance, target specific conductance, in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$)	15.7, 15.0 ¹	5.3, 4.9
Number of responding sites that met the specific-conductance accuracy goals	179	178
Accuracy goals for specific conductance: lower and upper acceptable values	11.7, 19.7	3.3, 7.3
Percentage of responding sites that met the specific-conductance accuracy goals.	97.2	98.3
F-pseudostigma for specific conductance	0.519	0.297

¹Sample was spiked with potassium chloride to increase the target specific conductance from 5.3 to 15.0 microsiemens per centimeter at 25 degrees Celsius.

Table 2. Site-operator responses and summary statistics for the 1996 intersite-comparison program

Site-operator responses	Intersite-comparison study number	
	37	38
Number of site operators receiving samples	190	187
Number of site operators submitting pH values by closing date of study	179	176
Number of site operators submitting specific-conductance values by closing date of study	181	177
Site operators responding late	1	0
Number of nonresponding site operators	3	2
Sites that were not in operation	5	7
Site operators reporting equipment problems:		
pH meter/electrode completely inoperable	2	2
pH meter/electrode problems	7	5
Specific-conductance probe/meter completely inoperable	0	1
Specific-conductance probe/meter problems	6	1
Median pH, target pH	4.47, 4.47	4.22, 4.22
Number of responding sites that met the pH accuracy goals	167	154
Accuracy goals for pH: lower and upper acceptable values	4.35, 4.57	4.12, 4.29
Percentage of responding sites that met the pH accuracy goals	93.2	87.5
F-pseudostigma for pH	0.037	0.037
Median specific conductance, in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$)	26.3, 26.3 ¹	26.8, 26.8
Number of responding sites that met the specific-conductance accuracy goals	170	168
Accuracy goals for specific conductance: lower and upper acceptable values	22.3, 30.3	22.8, 30.8
Percentage of responding sites that met the specific-conductance accuracy goals.	93.9	94.9
F-pseudostigma for specific conductance	0.889	1.07

¹Sample was spiked with potassium chloride to increase the target specific conductance from 15.3 to 26.3 microsiemens per centimeter at 25 degrees Celsius.

The target pH for the 1995 intersite-comparison study number 35 was 4.94; the resulting median pH produced by site operators responding by the closing date of the study was 4.95. The target specific conductance of study number 35 was increased by the addition of KCl to 15.0 $\mu\text{S}/\text{cm}$; the median value determined from all site-operator measurements was 15.7 $\mu\text{S}/\text{cm}$. As in past years (Gordon and others, 1997; See and others, 1989), the median values from all responding site operators were used as the most probable value for the intersite solutions in 1995 and 1996 on the premise that the median values from about 200 site-operator measurements were a better representation of the most likely values for the intersite-comparison study solutions than either a few in-house measurements or the theoretical values. Previous studies have found no appreciable deterioration of intersite solutions over the length of the studies, further supporting the use of the median site-operator values as the most probable values. The stability of hydrogen ion and specific conductance in filtered wet-deposition samples that are stored at ambient temperatures was investigated (Gordon and others, 1995) and found to be satisfactory for short-term (45-60 days) studies, such as intersite-comparison studies. More than 94 percent (176 out of 186) of the site operators met the pH upper and lower accuracy goals of 4.76 to 5.14 (table 1). The NADP/NTN accuracy goals for specific conductance for study number 35 was $\pm 4 \mu\text{S}/\text{cm}$ of the median value of 15.7. By use of this criterion, 97.2 percent of responding site operators met the goals for specific-conductance measurements. The criterion for specific conductance used in 1995 and 1996 varied with the specific conductance. If the most probable specific conductance was 10 $\mu\text{S}/\text{cm}$ or less, the criterion was $\pm 2 \mu\text{S}/\text{cm}$. If the most probable specific conductance was greater than 10 $\mu\text{S}/\text{cm}$ but less than or equal to 60 $\mu\text{S}/\text{cm}$, the criterion was $\pm 4 \mu\text{S}/\text{cm}$.

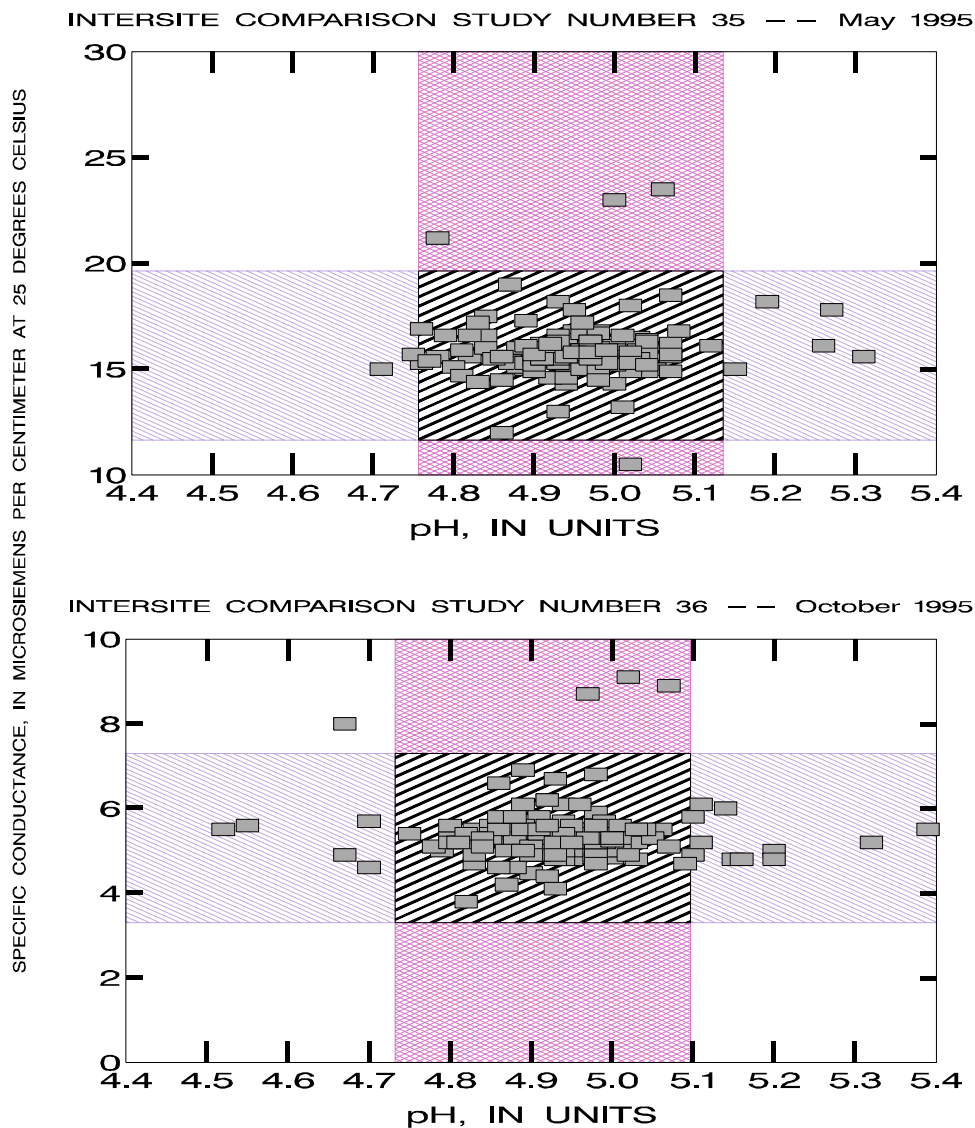
The reference solution used in intersite-comparison study number 36 had a target pH of 4.94 and a target specific conductance of 4.9 $\mu\text{S}/\text{cm}$

(table 1). A total of 170 of the site operators, or 94.4 percent, submitting pH values by the closing date of the study met the pH accuracy goals of 4.73 to 5.10. The median specific conductance was 5.3, with 98.3 percent of site operators that reported on time achieving the $\pm 2 \mu\text{S}/\text{cm}$ of the median value accuracy goal.

For intersite-comparison study number 37, the reference solution target pH was 4.47, and the target specific conductance was 26.3 $\mu\text{S}/\text{cm}$ after the solution was spiked with KCl (table 2). The median pH of the intersite-comparison 37 reference solution was the same as the target pH—4.47. A total of 167 site operators that responded by the closing date of the study met the pH accuracy goals of 4.35 to 4.57 pH. The median specific-conductance value was 26.3; 93.9 percent of site operators achieved the $\pm 4 \mu\text{S}/\text{cm}$ of the median value accuracy goal.

The reference solution used in intersite-comparison study 38 had both a target and median pH of 4.22 and a target specific conductance of 26.8 $\mu\text{S}/\text{cm}$. One hundred fifty-four site operators, submitting pH values on time, met the pH accuracy goals of 4.12 to 4.29. This means that 87.5 percent of the operators reporting by the closing date met the goals for pH. The median specific conductance was 26.8, with 94.9 percent of site operators achieving the $\pm 4 \mu\text{S}/\text{cm}$ of the median value accuracy goal.

Scatterplots of the results of pH and specific-conductance values for all participating site operators in intersite-comparison study numbers 35 and 36 are shown in figure 2; the results for study numbers 37 and 38 are given in figure 3. The boundaries depicted on the scatterplots in figures 2 and 3 are defined as the NADP/NTN accuracy goals set for each study. The boundaries delineate the pH and specific-conductance values for those site operators that meet the accuracy goals for pH or specific conductance, or both measurements as well as those not meeting the accuracy goals. The percentile distributions for the reported pH and specific-conductance values for study numbers 35-38 are listed in figure 4.



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

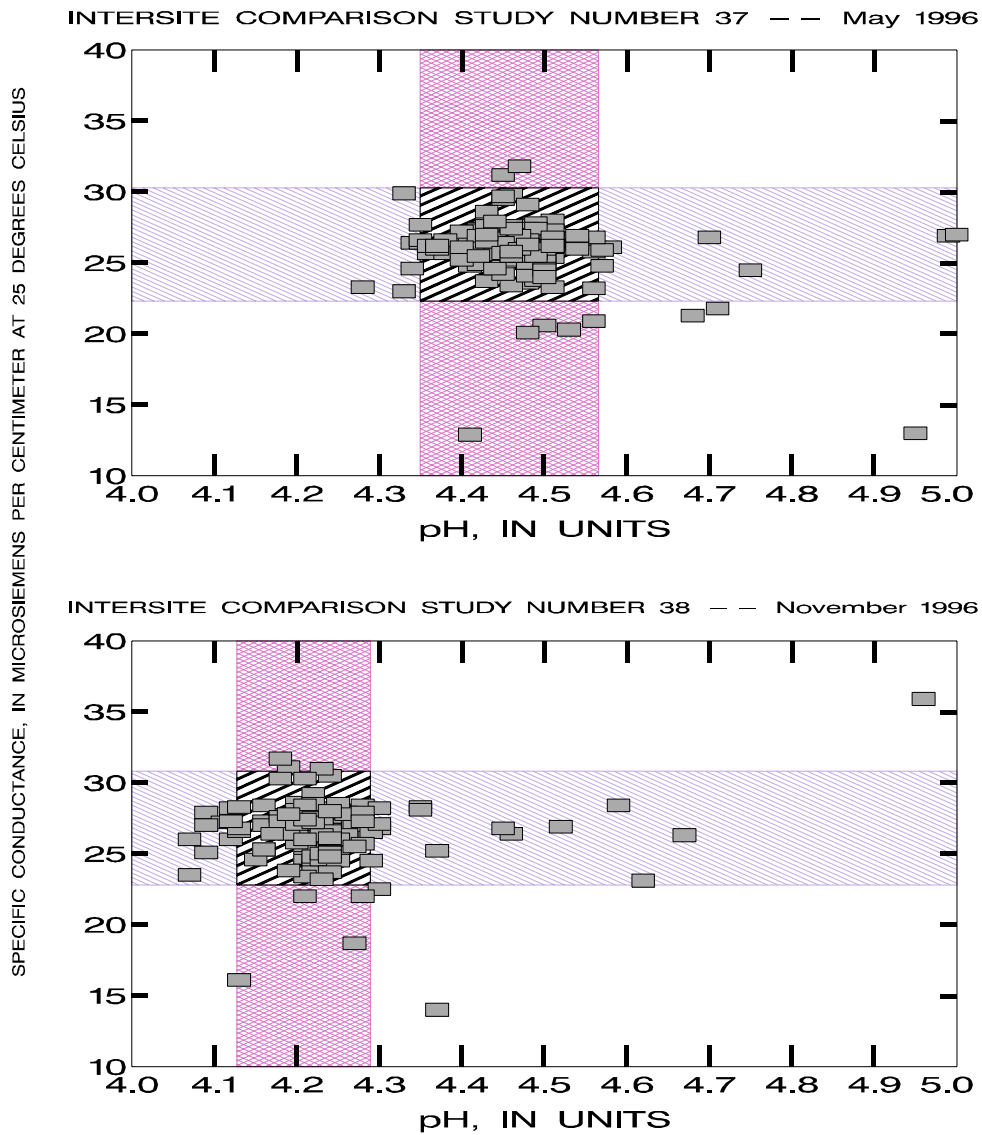
These data pairs were off scale in study number 35:

pH, Specific Conductance	pH, Specific Conductance
4.89, 0.7	5.45, 16.5
5.50, 14.0	4.92, 73.5
4.94, 1.5	4.18, 15.7
5.94, 16.1	

These data pairs were off scale in study number 36:

pH, Specific Conductance	pH, Specific Conductance
5.00, 10.5	4.92, 53.9
4.80, 13.3	0.80, 5.3
5.51, 5.6	4.91, 69.9
4.98, 66.7	

Figure 2. Distribution of pH and specific-conductance values for intersite-comparison study numbers 35 and 36, completed in 1995.



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

These data pairs were off scale in study number 37:

pH, Specific Conductance	pH, Specific Conductance
4.46, 2.8	4.51, 2.7
4.47, 2.7	

These data pairs were off scale in study number 38:

pH, Specific Conductance	pH, Specific Conductance
4.30, 2.7	4.15, 2.9
4.30, 7.9	4.23, 127

Figure 3. Distribution of pH and specific-conductance values for intersite-comparison study numbers 37 and 38, completed in 1996.

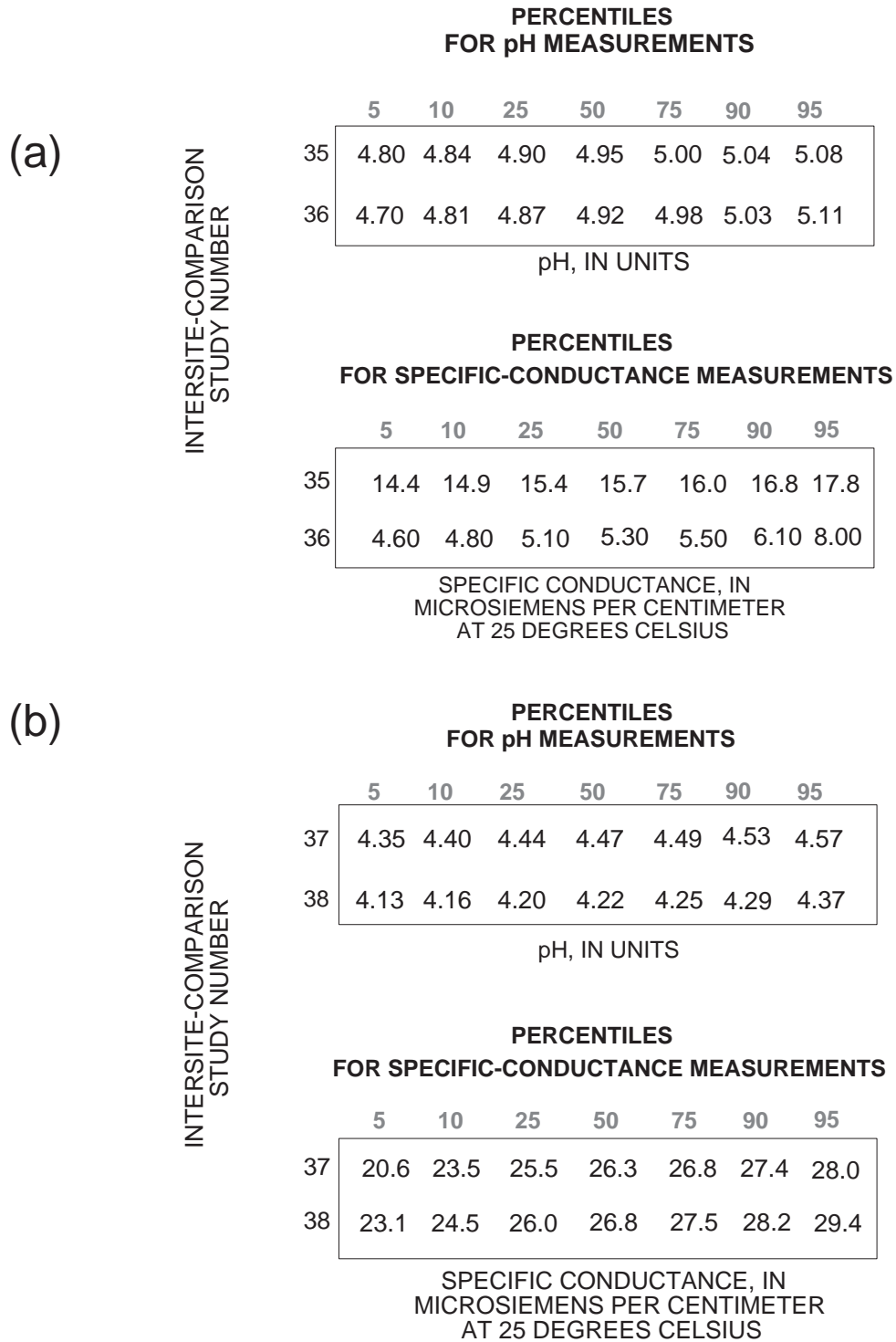


Figure 4. Percentiles for pH and specific conductance from intersite-comparison study numbers (a) 35 and 36 and (b) 37 and 38.

Intersite-Comparison Study Follow-up Program

Results from the intersite-comparison studies are compiled and the operator's performance is evaluated against the NADP/NTN accuracy goals applicable for each intersite study (tables 1 and 2). Accuracy is evaluated by converting reported values into standardized z -values. A z -value is analogous to a z -score, which is described by Iman and Conover (1983). To produce a z -value, nonparametric estimators replace the traditional parametric estimators used by Iman and Conover. The formulas for z -scores and z -values are as follows:

$$z \text{ score} = \frac{x - \bar{x}}{S} \text{ and}$$

$$z \text{ value} = \frac{x - \tilde{x}}{fps},$$

where x = an individual observation;

\bar{x} = the mean of all observations;

\tilde{x} = the median of all observations;

S = standard deviation of all observations;
and

fps = f -pseudostigma of all observations:

$$\frac{(75^{th} - 25^{th} \text{ percentile})}{1.349}$$

By using standardized z -values, each site operator's performance relative to 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 difficulty of measuring the pH of the solution on the basis of its hydrogen-ion concentration. By using a cumulative z -value total for the three most recent studies, each site operator that fails to meet the accuracy goals is placed into one of the following four categories:

Level 1. Operators receive a letter stating the problem with the recent results and suggestions for troubleshooting and improving field techniques.

Level 2. Operators are asked to remeasure and resubmit results for the current intersite study.

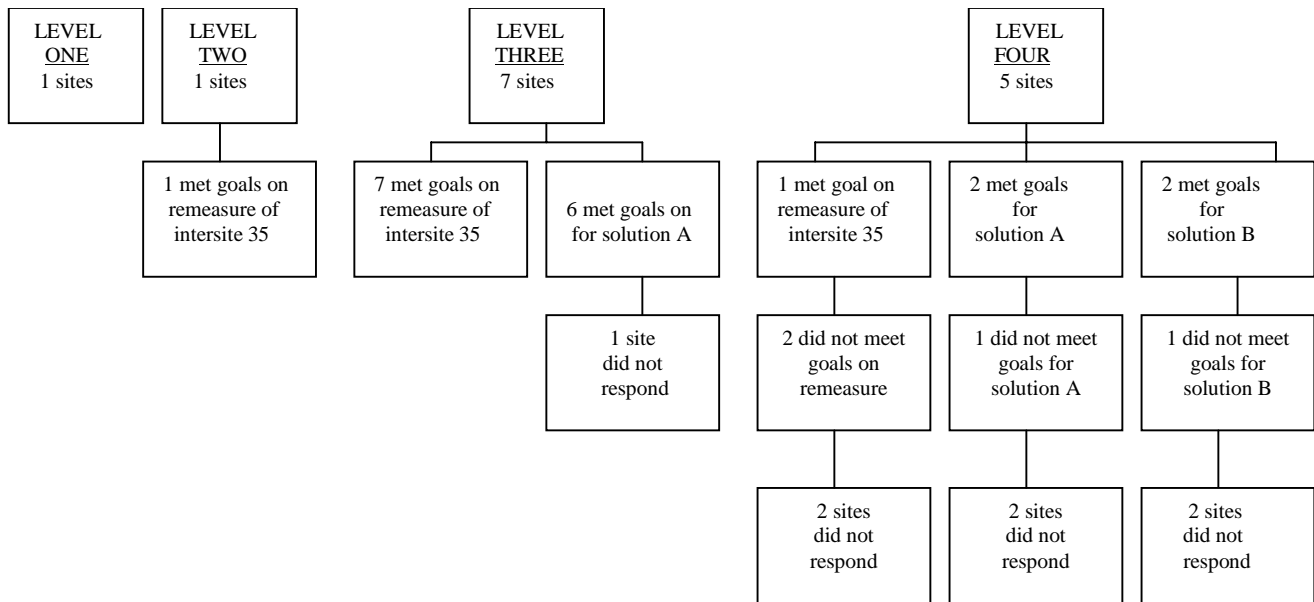
Level 3. Operators are given one additional check sample to measure.

Level 4. Operators are given two additional check samples to measure.

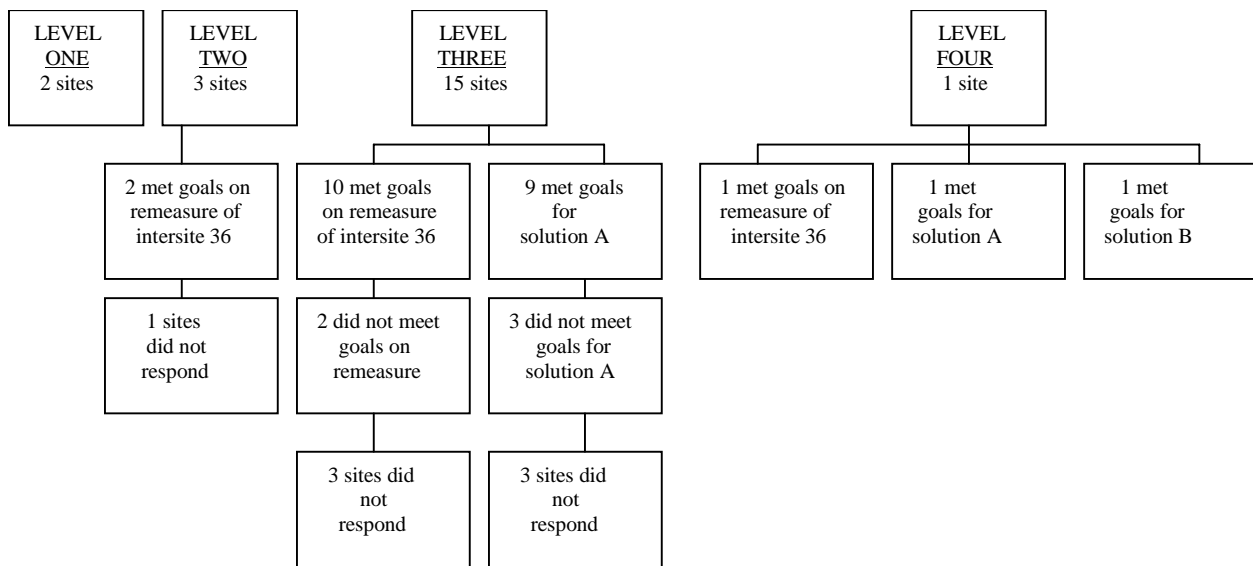
The categories are additive in that Level 3 site operators remeasure the original study solution and an additional check sample (solution A). Level 4 site operators remeasure the original study solution and two additional check samples (solutions A and B). The additional check samples used for follow up in Levels 3 and 4 are unopened aliquots of past intersite-comparison study samples that have been continuously chilled at 4°C since they were made. The pH and specific-conductance values of these additional check samples are within the ranges of natural precipitation. The stability of the hydrogen-ion concentration in synthetic precipitation samples stored as described is sufficient to allow use of the previous intersite samples in the follow-up analysis (Gordon and others, 1995).

For intersite-comparison study number 35, 14 sites were included in the follow-up study. Thirteen of these site operators were asked to perform additional pH measurements. Nine of these site operators met the accuracy goals for the pH measurements, and three did not respond. Intersite-comparison study number 36 included 21 follow-up study sites, with 16 included in Levels 3 and 4. Twelve out of the 18 site operators that responded met all the NADP/NTN goals for pH measurements; this indicates that the original measurement difficulties had been resolved. The follow-up results for study numbers 35 and 36 are summarized in figure 5, and the follow-up results for study numbers 37 and 38 are summarized in figure 6.

FOLLOW-UP RESULTS FOR INTERSITE-COMPARISON STUDY NUMBER 35



FOLLOW-UP RESULTS FOR INTERSITE-COMPARISON STUDY NUMBER 36



Explanation

Level 1 follow-up:

- (1) Letter discussing common sources of measurement errors

Level 2 follow-up:

- (1) Letter discussing common sources of measurement errors
- (2) Request that site operator remeasure the remaining portion of the intersite solution

Level 3 follow-up:

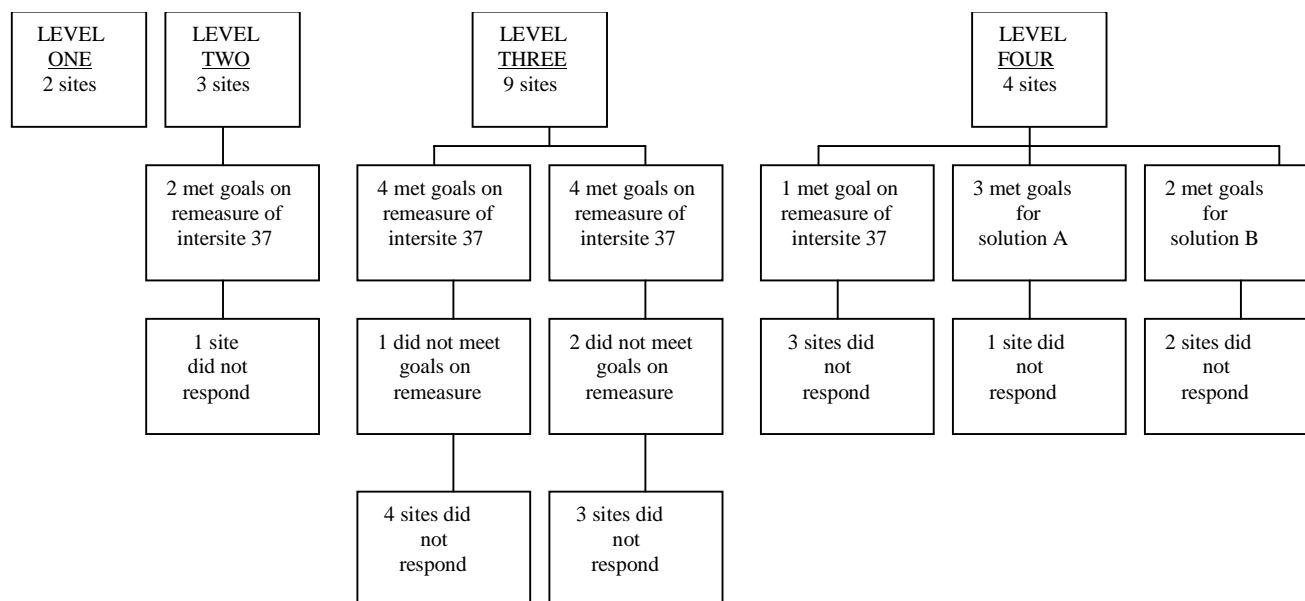
- (1) Letter discussing common sources of measurement errors
- (2) Request that site operator remeasure the remaining portion of the intersite solution
- (3) Measure one additional aliquots – solutions A

Level 4 follow-up:

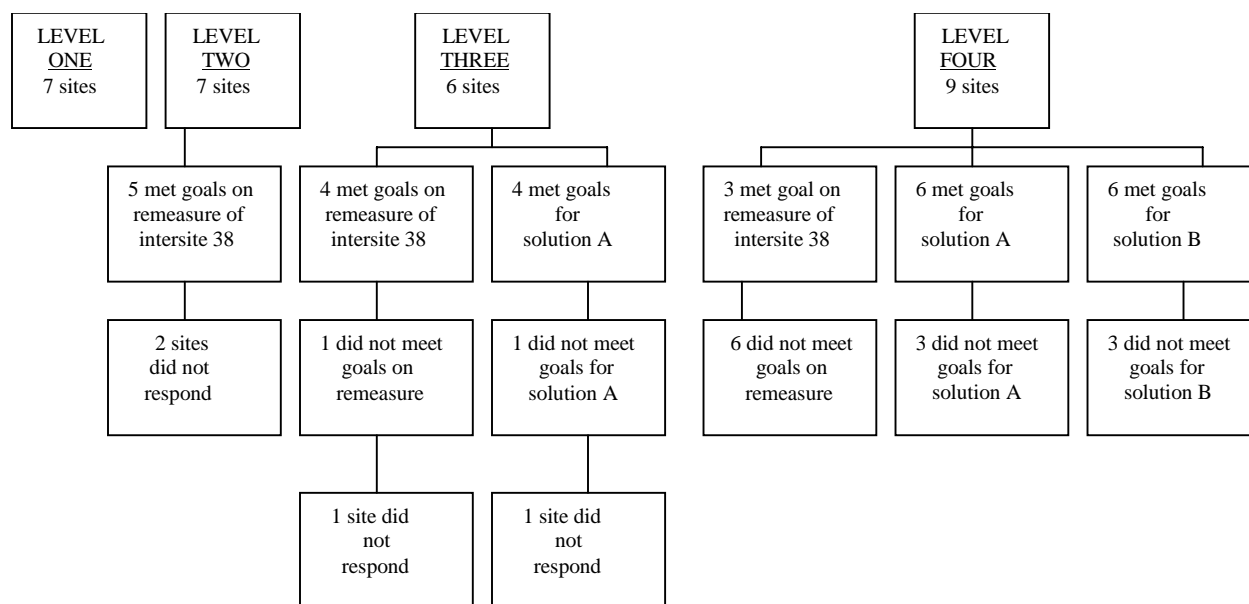
- (1) Letter discussing common sources of measurement errors
- (2) Request that site operator remeasure the remaining portion of the intersite solution
- (3) Measure two additional aliquots – solutions A and B

Figure 5. Follow-up study results for intersite-comparison study numbers 35 and 36.

FOLLOW-UP RESULTS FOR INTERSITE-COMPARISON STUDY NUMBER 37



FOLLOW-UP RESULTS FOR INTERSITE-COMPARISON STUDY NUMBER 38



Explanation

Level 1 follow-up:

- (1) Letter discussing common sources of measurement errors

Level 2 follow-up:

- (1) Letter discussing common sources of measurement errors
- (2) Request that site operator remeasure the remaining portion of the intersite solution

Level 3 follow-up:

- (1) Letter discussing common sources of measurement errors
- (2) Request that site operator remeasure the remaining portion of the intersite solution
- (3) Measure one additional aliquot – solution A

Level 4 follow-up:

- (1) Letter discussing common sources of measurement errors
- (2) Request that site operator remeasure the remaining portion of the intersite solution
- (3) Measure two additional aliquots – solutions A and B

Figure 6. Follow-up study results for intersite-comparison study numbers 37 and 38.

Blind-Audit Program

The purpose of the blind-audit program is to assess the effects of routine sample handling, processing, and shipping of wet-deposition samples on analyte precision and bias. In this program, the site operator submits a portion of a synthetic precipitation sample disguised as a natural precipitation sample to the Central Analytical Laboratory (CAL) for analysis. The portion of the blind-audit sample disguised as a natural precipitation sample is subject to all of the normal processing and handling steps of a regular weekly sample. The remaining minimally handled portion of the blind-audit sample also is sent to the CAL for analysis, but under separate cover, and is analyzed independently of the portion subject to the same processing and handling as an actual weekly precipitation sample. 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).

Throughout 1995 and 1996, on a quarterly basis, 32 blind-audit samples were sent to the operators of selected NADP/NTN sites. The sites selected on a quarterly basis were chosen to ensure a uniform geographic distribution throughout the United States. After a site has been selected for the blind-audit program (assuming successful participation), the site is not selected again for the blind-audit program until the operators of all other NADP/NTN sites have participated. All of the NADP/NTN sites participated at least once in the blind-audit program between 1995 and 1996. Three different sample volumes were distributed for one of the sample matrices. Samples containing 250, 500, or 1,000 mL of the USGS solution were sent to the operators of selected sites to assess volume-related effects on biases. The volume of USGS solution that a site received was determined on a random basis. Additional information regarding the blind-audit program is available in previous reports (Gordon and others, 1997; See and others, 1990). All components of the blind-audit program, from sample preparation to distribution of interpretive reports, are shown in figure 7.

The solutions used in the blind-audit program are intended to replicate the range of concentrations typical of what is found in natural precipitation samples collected at NADP/NTN sites. With the exception of the Ultrapure deionized-water samples, all of the median analyte-concentration values for the solutions used in the blind-audit program were between the 25th and 75th percentile of natural precipitation samples collected at NADP/NTN sites. The solutions used in the 1995-96 blind-audit program, the names of the agencies that prepared them, and any special remarks about each solution are listed in table 3. The target values for these solutions are presented in table 4.

Table 3. Solutions used in the 1995-96 blind-audit and interlaboratory-comparison programs

[M Ω , megohms]

Solution	Preparing agency	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 M Ω .
USGS SP-1 SP-2	U.S. Geological Survey	Prepared from dissolved salts and deionized water.
P-17	U.S. Geological Survey	A low ionic strength reference sample prepared by the Standard Reference Sample Project. Dilution not required.
P-96	U.S. Geological Survey	Prepared from a low ionic strength reference sample collected by the Standard Reference Sample Project. Diluted with deionized water to achieve concentration levels similar to those found in precipitation.
2694A-I 2694A-II	National Institute of Standards and Technology	Supplied as certified reference solutions.

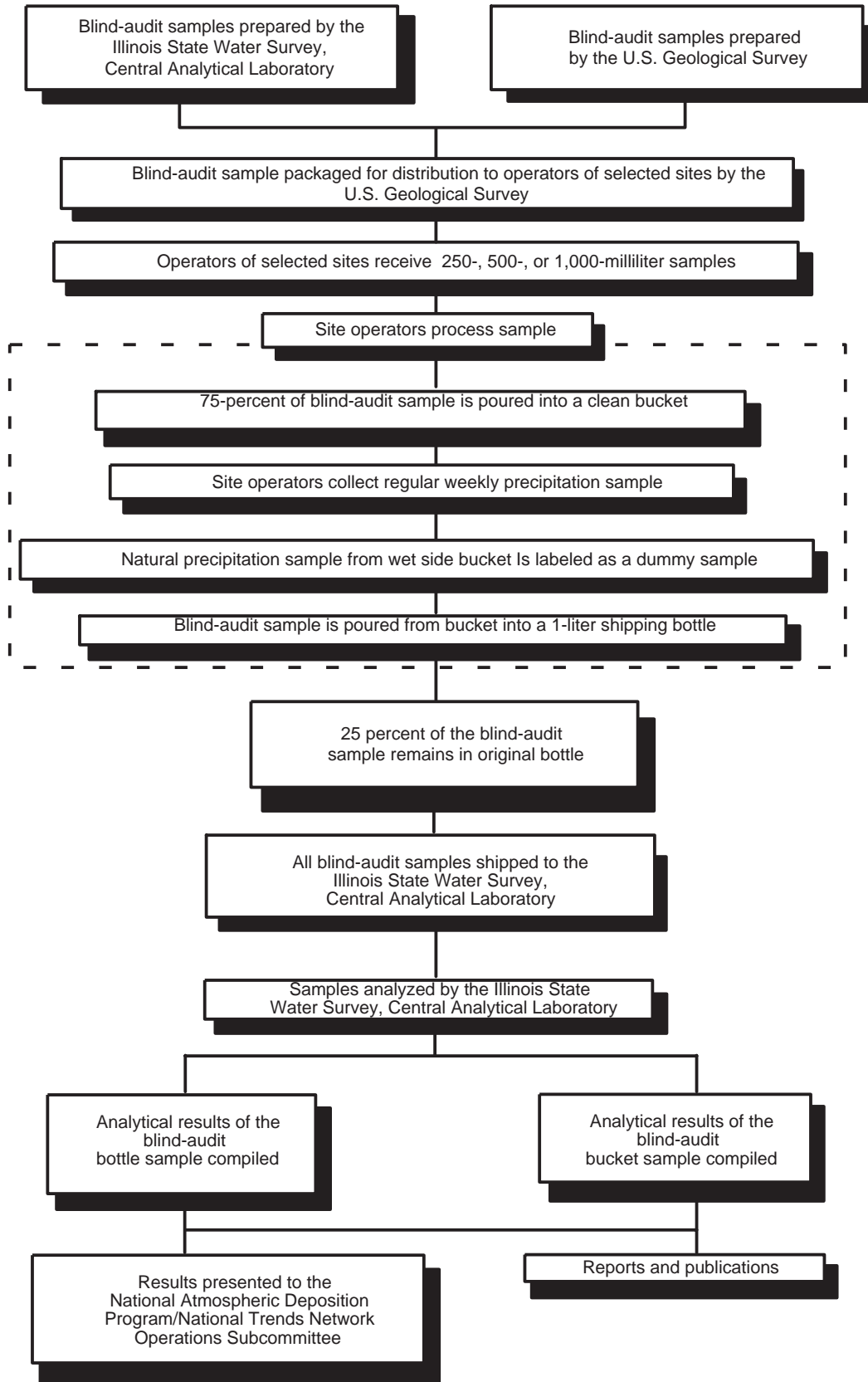


Figure 7. Blind-audit program of the U.S. Geological Survey.

Table 4. Target values for solutions used in the 1995-96 U.S. Geological Survey blind-audit program and interlaboratory-comparison program

[pH, in units; specific conductance, in microsiemens per centimeter at 25 degrees Celsius; <dl, indicates value less than method detection limit; --, indicates no value available; significant figures vary because of differences in laboratory precision; Ca²⁺, calcium; Mg²⁺, magnesium; Na⁺, sodium; K⁺, potassium; Cl⁻, chloride; SO₄²⁻, sulfate; NH₄⁺, ammonium; NO₃²⁻, nitrate]

Solution	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	Cl ⁻	NO ₃ ²⁻	SO ₄ ²⁻	pH	Specific conductance
^a CAL 4.3	<dl	<dl	<dl	<dl	<dl	<dl	3.14	<dl	4.30	^e 21.8
^a P-17	0.30	0.045	0.283	0.057	0.10	0.416	1.12	0.50	5.55	^e 7.0
^{a,b} USGS	0.14	0.029	0.113	0.024	0.16	0.16	1.05	0.88	4.8	^e 8.0
^{a,b} Ultrapure	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl	5.65	^e 0.064
^{a,b} SP-1	0.46	0.092	0.420	0.076	0.680	0.590	2.100	3.850	4.36	^e 30.27
^{a,b} SP-2	0.46	0.070	0.360	0.060	0.560	0.450	3.000	2.334	4.51	^e 23.47
^b 2694A-I	^c 0.0126	^c 0.0242	^c 0.208	^c 0.056	^d 0.120	^d 0.230	^d 0.530	^c 2.69	^e 4.3	^e 25.4
^b 2694A-II	^c 0.0364	^c 0.0484	^c 0.423	^c 0.108	^d 1.06	^d 0.940	^c 7.19	^c 10.6	^e 3.6	^e 129.3
^f P-96	0.28	0.06	0.21	0.09	--	0.22	--	0.39	5.72	^e 4.80

^a Used in the 1995-96 blind-audit program.

^b Used in the 1995-96 interlaboratory-comparison program.

^c Concentration certified by the National Institute of Standards and Technology.

^d Concentration not certified by the National Institute of Standards and Technology.

^e At 25 degrees Celsius and 1 atmosphere pressure (Hem, 1985; Dean, 1979).

^f Used in the 1996 blind-audit program.

Site operators were provided detailed instructions on how to process the blind-audit samples. The instructions sent to site operators prescribed that 75 percent of the blind-audit sample was to be poured into a standard, clean, NADP/NTN 13-L polyethylene collection bucket and processed as if it were the wet-deposition sample from the previous week. The blind-audit samples sent to the site operators are marked with a line circumscribing the bottle, which indicates how much sample the operator is to pour into the clean bucket. This poured-out portion of the blind-audit sample is referred to as the bucket sample. The operator determines the weight of the bucket containing 75 percent of the blind-audit sample, then removes a 20-mL aliquot in order to measure the pH and specific conductance. The instructions to the site operator specify that, after a minimum residence time of 24 hours, the sample is to be transferred from the bucket into a clean 1-L shipping bottle. During this entire process, all of the handling and processing steps to which a regular weekly precipitation sample is subject are duplicated as closely as possible. By using a fictitious NADP/NTN field-observer report form, the shipping bottle is disguised as a routine wet-deposition sample and submitted to the CAL for analysis. The site operator also collects a natural precipitation sample during the

assigned week for submitting the blind-audit sample. The actual precipitation sample is submitted to the CAL using a "dummy" field-observer report form. Site operators then return the remaining 25 percent of the blind-audit sample, still in the original sample bottle, to the CAL for analysis. This portion of the blind-audit sample is referred to as the bottle sample. In order to keep their identities concealed, the actual precipitation sample and the two portions of the blind-audit sample are all shipped separately to the CAL. A report by Gordon and others (1997) contains additional details on the submission of blind-audit samples.

Because of the order in which samples and field-observer report forms are processed, it is unlikely that the CAL staff could identify individual samples as being from an external QA program. Information concerning sample chemical composition was not provided to the CAL staff that did the analyses or to the site operators that did the processing. When the bottle portion of a blind-audit sample is submitted to the CAL, only the sample-processing group of the laboratory staff recognizes that it is not an actual NADP/NTN sample. By the time the analysis is performed, the samples appear to be regular network precipitation samples. The laboratory staff does not know the analyte concentrations in the bottle portions.

The CAL staff that receives and analyzes the actual precipitation sample cannot identify from which site the sample has been sent. After all the analyses for the bucket and bottle portions of the blind-audit sample and for the actual precipitation samples are completed, the identity of each of these samples is disclosed to the CAL Data Quality-Assurance Officer. The NADP/NTN data base then is corrected by matching the proper analytical data with each sample.

Assessing Analytical Bias

To assess analytical bias, differences between the results from the bucket and bottle portions are evaluated. The CAL analyzes all of the paired bucket and bottle samples within 21 days of each other. Analytical results of the bucket and bottle portions of the blind-audit sample provide paired analyses to determine if analyte concentrations have changed in the bucket samples as a result of sample handling, shipping, and processing protocols. Previous 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 (Peden and Skowron, 1978; Willoughby and others, 1991). In 1995 and 1996, complete bucket and bottle analyses were available for 124 of the 128 blind-audit samples sent to participating site operators. The incidence of four operators failing to submit the blind-audit sample in each of these years was similar to the participation rate in previous years (Gordon and others, 1997).

If there is physical evidence of contamination and the chemistry is abnormal, the CAL assigns natural precipitation samples a C code to indicate the sample is contaminated (James, 1996). All quality-assurance samples, such as the bucket and bottle portions of the blind-audit samples that contain extrinsic material are assigned a C code, regardless of the sample chemistry. The C codes are assigned after the true identities of the bucket and bottle portions of the blind-audit samples have been disclosed to the CAL Data Quality-Assurance Officer. The Wilcoxon signed-rank test was used to compare the differences for the two groups of blind-audit samples (C coded samples and samples without C codes) for all major ions, and no statistically significant differences were found at the $\alpha = 0.05$ level in either 1995 or 1996. These results are consistent with those from past years for C coded (contaminated) and uncontaminated blind-audit analyses. In 1995 and 1996, there

were no significant differences in analytical results when differences between uncontaminated bottle samples and contaminated bucket samples were compared to the differences between uncontaminated bottle samples and uncontaminated bucket samples based on Wilcoxon signed-rank test results. Data from the five samples assigned a C code in 1995 and the 14 samples assigned a C code in 1996 were, therefore, included in the overall statistical analysis of blind-audit samples for each of these years.

Paired Blind-Audit Sample Differences

Paired bucket minus bottle differences were calculated for the purpose of determining analytical bias. Before determining paired bucket minus bottle differences (listed in tables 5 and 6), bucket and bottle values reported as less than the minimum detection limit were set equal to the minimum detection limit. The median paired bucket minus bottle differences for all analytes in 1995 and 1996 are presented in tables 5 and 6, respectively, along with the minimum and maximum values, the upper and lower quartiles, and the interquartile range. In 1995, the median bucket-sample concentrations were larger than the median bottle-sample concentrations for calcium, magnesium, and specific conductance. In 1996, the median bucket-sample concentrations were larger than the median bottle-sample concentrations for calcium, magnesium, and potassium.

Between 1995 and 1996, the median bucket minus bottle differences for major ions ranged from -0.020 mg/L for ammonium and nitrate to 0.006 mg/L for calcium. Median paired differences for hydrogen ion and specific conductance were 0.000 $\mu\text{eq/L}$ and 0.200 $\mu\text{S/cm}$, respectively, in 1995. In 1996, the median paired differences for hydrogen ion and specific conductance were -0.357 $\mu\text{eq/L}$ and 0.000 $\mu\text{S/cm}$, respectively. Boxplots in figures 8 and 9 graphically depict the paired bucket-sample minus bottle-sample concentration differences for all the major ions, as well as pH and specific conductance. The upper and lower lines defining the "box" portions, in yellow, of the graphs depict the interquartile range of the differences for each analyte. The "whisker" portions of the boxplots are defined by the largest value within ± 1.5 times the interquartile range extending from either the top or bottom of the box portion. A detailed explanation of the style of boxplot used throughout this report is shown in lower right portion of figures 8 and 9.

The interquartile ranges for all of the major ions in 1995 and 1996 were very similar to those in 1994 and ranged from 0.003 mg/L for magnesium to 0.075 mg/L for ammonium. The length and position of the boxplot whiskers were very similar in 1996 to the results for 1995, narrowing slightly in 1996 compared to 1995 for nitrate and ammonium. For hydrogen ion and specific conductance, both the box and whisker portions of the graphs were slightly wider in 1995 compared to 1996, reflecting slightly greater variance for these parameters in 1995. In terms of chemical significance, the change in the NADP/NTN shipping protocol

in 1994 continues to have a major effect. Since the 1994 protocol change, there is no longer a significant loss of hydrogen ion, an observation first noted in the report on 1994 external quality-assurance results (Gordon and others, 1997) and again demonstrated by the 1995 and 1996 results. The quartiles of the hydrogen-ion differences indicated that 50 percent of the samples experienced a change in hydrogen-ion concentration of between -1.90 and +1.78 µeq/L, which is a very small percentage of the hydrogen-ion concentration present in the reference samples used in the program.

Table 5. Selected statistics for the paired bucket-sample concentration minus bottle-sample concentration differences in the blind-audit program during 1995

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

Analyte	N	Minimum	Median	Quartiles		Maximum	Interquartile range
				Q1	Q3		
Calcium	124	-0.365	0.002	-0.001	0.011	0.089	0.012
Magnesium	124	-0.091	0.001	-0.001	0.002	0.011	0.003
Sodium	124	-0.362	-0.017	-0.040	-0.003	0.063	0.037
Potassium	124	-0.045	0.000	-0.002	0.004	0.222	0.006
Ammonium	124	-0.390	-0.020	-0.060	0.000	0.140	0.060
Chloride	124	-0.410	-0.010	-0.030	0.010	0.330	0.040
Nitrate	124	-0.370	-0.020	-0.045	0.020	0.720	0.065
Sulfate	124	-0.850	0.000	0.000	0.020	0.080	0.020
Hydrogen ion	124	-10.310	0.000	-1.900	1.780	43.440	3.680
Specific conductance	124	-3.600	0.200	-0.400	0.800	10.900	1.200

Table 6. Selected statistics for the paired bucket-sample concentration minus bottle-sample concentration differences in the blind-audit program during 1996

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

Analyte	N	Minimum	Median	Quartiles		Maximum	Interquartile range
				Q1	Q3		
Calcium	124	-0.210	0.006	0.000	0.016	0.167	0.016
Magnesium	124	-0.007	0.001	0.000	0.003	0.055	0.003
Sodium	124	-0.087	-0.015	-0.033	0.002	0.052	0.035
Potassium	124	-0.026	0.001	-0.001	0.004	0.113	0.005
Ammonium	124	-0.290	-0.020	-0.070	0.005	0.100	0.075
Chloride	124	-4.900	-0.020	-0.040	0.000	0.090	0.040
Nitrate	124	-0.390	-0.010	-0.030	0.020	0.170	0.050
Sulfate	124	-0.090	0.000	0.000	0.020	0.230	0.020
Hydrogen ion	124	-12.100	-0.357	-1.890	0.755	9.180	2.650
Specific conductance	124	-6.600	0.000	-0.650	0.400	3.100	1.050

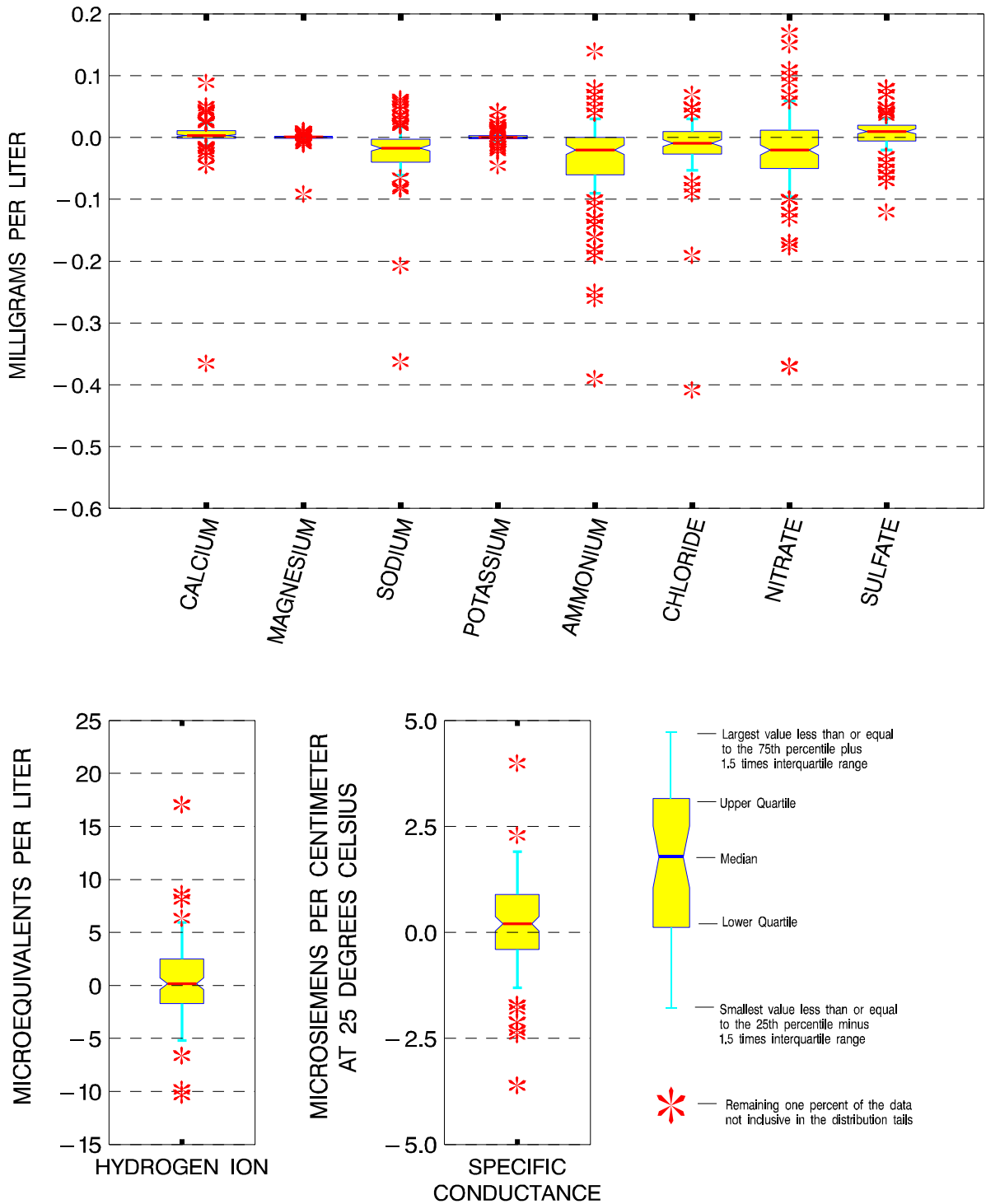


Figure 8. Paired bucket-sample concentrations minus bottle-sample concentrations in the blind-audit program for 1995.

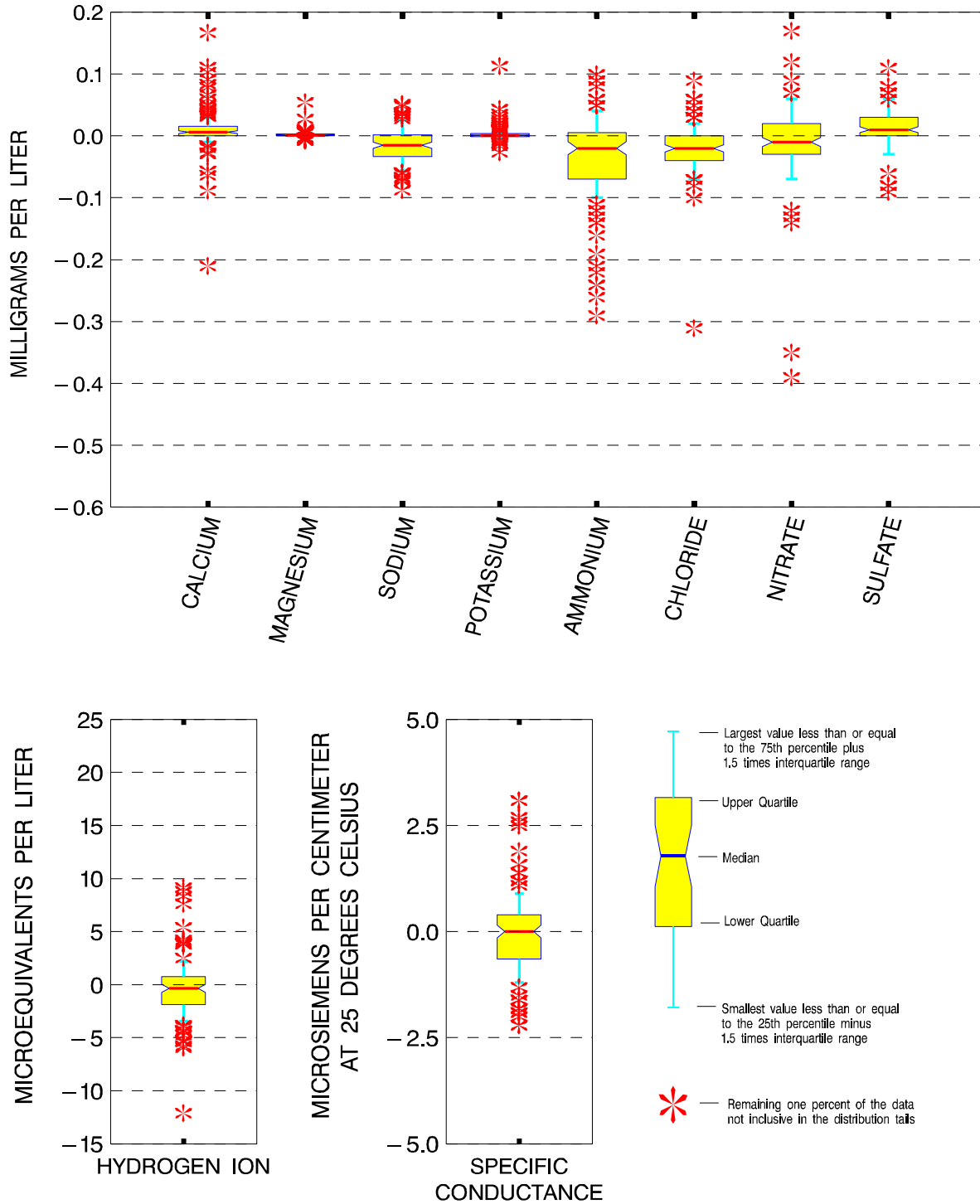


Figure 9. Paired bucket-sample concentrations minus bottle-sample concentrations in the blind-audit program for 1996.

Statistical Significance

A Wilcoxon signed-ranks test (Conover, 1980) and paired t-test (Kanji, 1993) were 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 1995 and 1996. Analytical results were evaluated for evidence of systematic bias by using both the paired t-test and the Wilcoxon signed-rank test because of the different advantages of each test. The paired t-test is a much more powerful test than the Wilcoxon signed-ranks test for paired observations (Kanji, 1993), and the blind-audit program uses a paired sample design. However, the paired t-test loses some of its power if the populations are not normal (Kanji, 1993). The Wilcoxon signed-ranks test is a distribution-free test with the assumption of random samples from independent populations (Conover, 1980). For the Wilcoxon signed-rank test, the differences between pairs of observations are calculated and then ranked. Where ties occur, the average of the corresponding ranks is used (Conover, 1980; Kanji, 1993). All blind-audit samples that had paired analyte determinations were included in both statistical analyses. Analyte concentrations reported as less than the minimum reporting limit were set equal to one-half the minimum reporting limit. (Alternatively, analyte concentrations reported as less than the minimum reporting limit were set equal to the minimum reporting limit and then to zero in order to determine if the results of the Wilcoxon signed-ranks test for bias would be different. Regardless of whether the values less than detection were set equal to zero, one-half the minimum reporting limit, or the minimum reporting limit, the results of the Wilcoxon signed-ranks test for bias were the same.)

At a probability level of $\alpha=0.05$, the Wilcoxon signed-ranks test indicated that a negative bias existed for ammonium in 1995, whereas the paired t-test indicated statistically significant negative bias for sodium and ammonium and positive bias for hydrogen ion and specific conductance (table 7). The negative bias for ammonium and sodium reflects the tendency for the portion of the blind-audit samples that was exposed to all of the handling and processing steps to actually have a lower concentration of these analytes than the minimally handled control portion of the blind-audit samples. This tendency has occurred since the NADP/NTN changed its sample shipping protocol in 1994.

The results for 1996 (table 8 and fig. 9) were generally similar to those for 1995. The probability level for ammonium differences in the Wilcoxon signed-rank test were fractionally higher than the $\alpha=0.05$ level, and the paired t-test indicated statistically significant negative bias for sodium and ammonium and statistically significant positive bias for calcium, magnesium, potassium, and sulfate. The complete results of the paired t-test and Wilcoxon signed-ranks test for bias with values that were less than the minimum reporting limit set equal to one-half the minimum reporting limit are shown in tables 7 and 8 for 1995 and 1996, respectively.

Analyte Concentration Effects

Boxplots in figures 10 and 11 depict paired blind-audit differences by sample concentration. The paired blind-audit differences for hydrogen ion and specific conductance, arranged by sample concentration, are shown in figures 12 and 13. A relation between sample concentration and paired blind-audit differences is not readily apparent for most analytes upon visual inspection of these graphs. Figures 10 through 13 do illustrate two important points: the data

Table 7. Results of the tests for bias in the blind-audit program during 1995, using the paired t-test and a Wilcoxon signed-rank test

[Bucket and bottle values less than the minimum reporting limit set equal to one-half the minimum reporting limit; Probability (Prob.), number of outcomes in the event divided by the total number of outcomes in the sample space; α , the maximum probability of making a Type I error; t, test statistic for the paired t-test; z, test statistic for the Wilcoxon signed-rank test; C coded, samples coded with a C to indicate possible contamination]

Analyte	Probability > t C coded samples included (test 1)		Probability > z C coded samples included (test 2)		Probability > z C coded samples removed (test 3)		Determined to be biased ($\alpha=0.05$)?		
	t	Prob.> t	z	Prob.> z	z	Prob.> z	test 1	test 2	test 3
	Calcium	0.815	0.4166	0.587	0.5571	0.571	0.5675	NO	NO
Magnesium	0.233	.8161	0.611	.5410	0.641	0.5216	NO	NO	NO
Sodium	-4.954	.0001	-1.822	.0685	-1.850	0.0643	YES	NO	NO
Potassium	1.466	.1452	0.179	.8582	0.096	0.9231	NO	NO	NO
Ammonium	-6.220	.0001	-2.622	.0087	-2.698	0.0070	YES	YES	YES
Chloride	-1.877	.0629	-0.921	.3571	-0.976	0.3292	NO	NO	NO
Nitrate	-1.581	.1165	-0.843	.3991	-0.864	0.3877	NO	NO	NO
Sulfate	-0.232	.8172	0.726	.4678	0.724	0.4692	NO	NO	NO
Hydrogen ion	3.370	.0010	0.785	.4322	0.881	0.3785	YES	NO	NO
Specific conductance	2.168	.0321	0.796	.4261	0.804	0.4213	YES	NO	NO

in these figures cluster around zero and display heteroscedasticity (Helsel and Hirsch, 1992). The Kruskal-Wallis test (Iman and Conover, 1983) was used to determine the relation between paired blind-audit sample differences and the target concentrations used in the blind-audit program in 1995 and 1996. Table 9 contains the p-values associated with the Kruskal-Wallis test statistic for each analyte, representing the level of significance of the data with respect to the test in question. The level of significance was evaluated to determine whether to accept or reject the null hypothesis. The value for α , the maximum probability of making a Type I error (Iman and Conover, 1983), was set to 0.05. Although results of a Kruskal-Wallis test indicate statistically significant relationships between the magnitude of paired blind-audit differences and sample concentration for potassium, ammonium, sulfate, hydrogen ion, and specific conductance in 1995 and 1996 (table 9), the heteroscedasticity of the data must be considered. Heteroscedasticity tempers the weight one can place on the results of the Kruskal-Wallis test somewhat. The departure from equal variances was not large enough to nullify the results (Dr. Luther Smith, ManTech Environmental Technology, written commun., 1998). The implication from this analysis is that the larger the concentration in a blind-audit sample, the greater the magnitude of the paired blind-audit sample differences for these analytes.

Ultrapure Sample Analyses

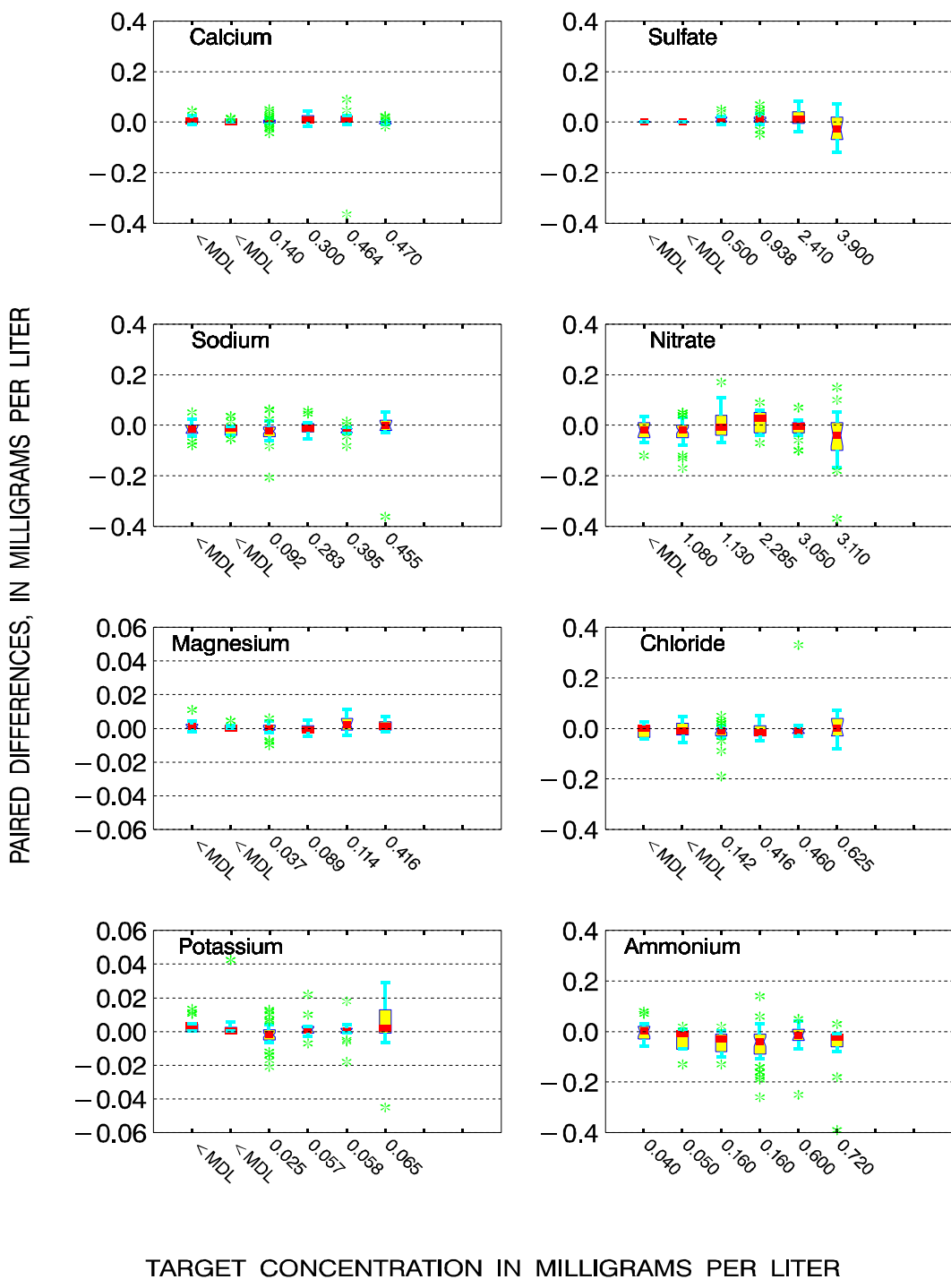
Sixteen Ultrapure deionized-water samples were included in the blind-audit program in 1995 and again in 1996. Fifteen of the 16 Ultrapure samples were submitted correctly each year, resulting in complete data pairs. As with all blind-audit samples, deionized samples were processed in two parts; the first part was

exposed to all normal sample-handling steps, which represented a field-exposed portion, and the second part was subject to minimal handling, which represented a control portion. In all of the deionized-water samples submitted in 1995 and 1996, sodium was detected in the field-exposed and the control portions. Ammonium, nitrate, and chloride also were commonly detected in both sample portions (table 10). As with the statistical evaluation of the entire blind-audit data sets discussed previously, the paired t-test and Wilcoxon signed-rank test were used in the statistical assessment of Ultrapure sample results. Statistical significance at a probability level of $\alpha = 0.05$ was reported if the probability of exceeding the test statistic for both the paired t- and Wilcoxon signed-rank tests were less than or equal to 0.05. The analysis of Ultrapure samples indicated positive bias for calcium, magnesium, and hydrogen ion in 1995. In 1995, the Ultrapure samples also indicated negative bias for ammonium. In 1996, potassium and specific conductance were the only two ions that indicated any bias (positive for both of these ions) in the Ultrapure samples. Below-detection-limit cases for the Ultrapure samples were handled in the same manner described for the analysis of all blind-audit samples. Unlike the analysis for the full data set where the treatment of values below detection limit had no effect on the results of the Wilcoxon signed-rank test, the treatment of values below detection limit in the Ultrapure samples did affect the results somewhat. The most conservative results of the below-detection-limit treatments were used, decreasing the number of ions with significant differences between paired bucket and bottle analytes in 1995. The treatment of values below detection limit did not affect the Wilcoxon signed-rank results for Ultrapure samples in 1996.

Table 8. Results of the tests for bias in the blind-audit program during 1996, using the paired t-test and a Wilcoxon signed-rank test

[Bucket and bottle values less than the minimum reporting limit set equal to one-half the minimum reporting limit; Probability (Prob.), number of outcomes in the event divided by the total number of outcomes in the sample space; α , the maximum probability of making a Type I error; t, test statistic for the paired t-test; z, test statistic for the Wilcoxon signed-rank test; C coded, samples coded with a C to indicate possible contamination]

Analyte	Probability > t C coded samples included (test 1)		Probability > z C-coded samples included (test 2)		Probability > z C-coded samples removed (test 3)		Determined to be biased ($\alpha=0.05$)?		
	t	Prob.> t	z	Prob.> z	z	Prob.> z	test 1	test 2	test 3
	Calcium	3.118	0.0023	1.466	0.1426	1.373	0.1699	YES	NO
Magnesium	3.336	.0011	1.269	.2045	1.325	0.1852	YES	NO	NO
Sodium	-6.255	.0001	-1.423	.1549	-1.339	0.1806	YES	NO	NO
Potassium	2.784	.0062	0.930	.3526	0.894	0.3716	YES	NO	NO
Ammonium	-5.488	.0001	-1.876	.0607	-1.922	0.0546	YES	NO	NO
Chloride	-1.447	.1503	-1.227	.2200	-1.171	0.2416	NO	NO	NO
Nitrate	-1.756	.0815	-0.478	.6330	-0.558	0.5771	NO	NO	NO
Sulfate	3.682	.0003	1.017	.3091	0.955	0.3397	YES	NO	NO
Hydrogen ion	0.308	.7585	-0.577	.5643	-0.484	0.6282	NO	NO	NO
Specific conductance	-0.930	.3540	-0.385	.7001	-0.342	0.7322	NO	NO	NO

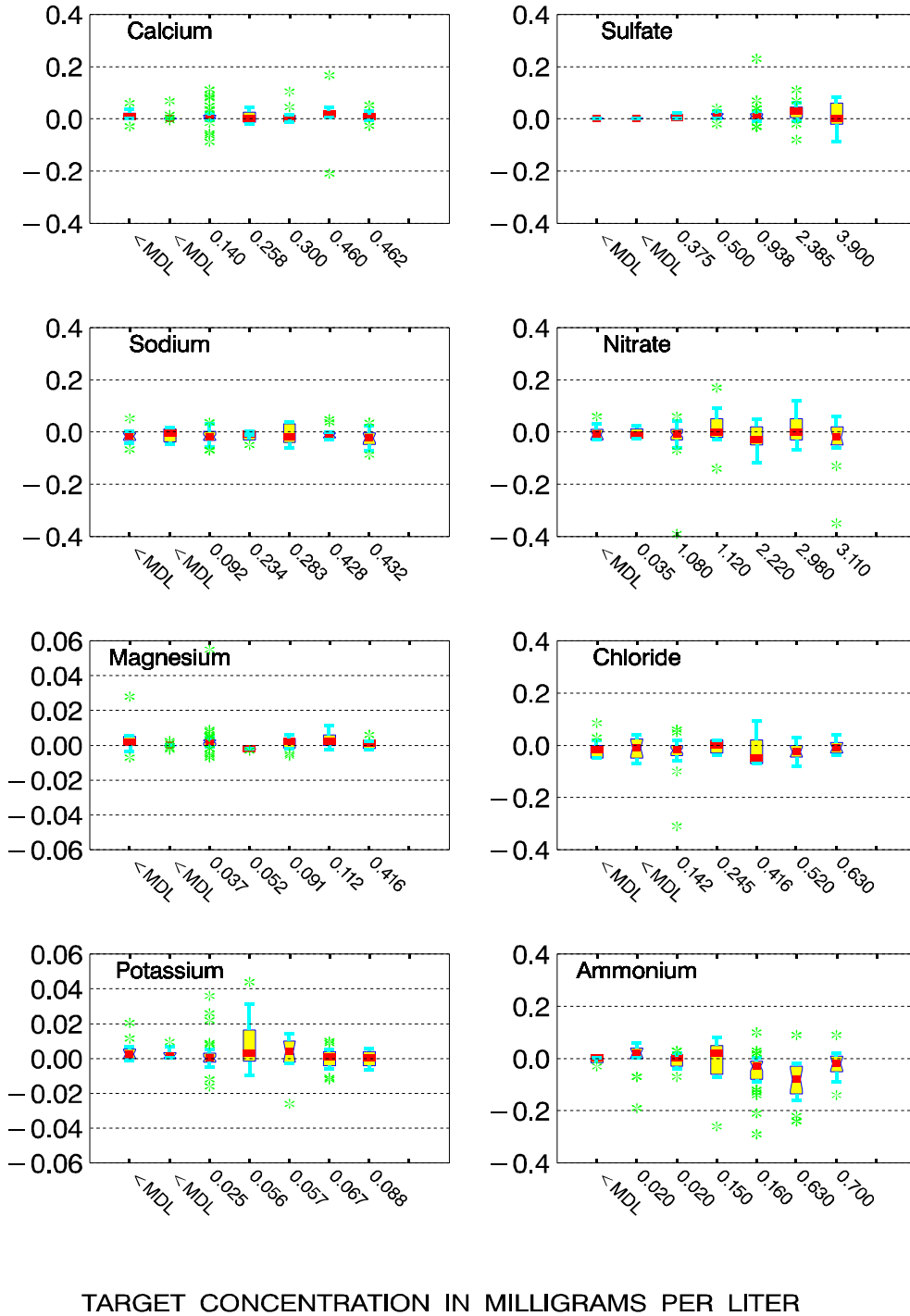


EXPLANATION

- < MDL Target less than method detection limit
- *, Remaining 1 percent of data not inclusive in the distribution tails

Figure 10. Relation between paired blind-audit differences for major ions and the analyte concentrations of solutions used in the blind-audit program in 1995.

PAIRED DIFFERENCES, IN MILLIGRAMS PER LITER

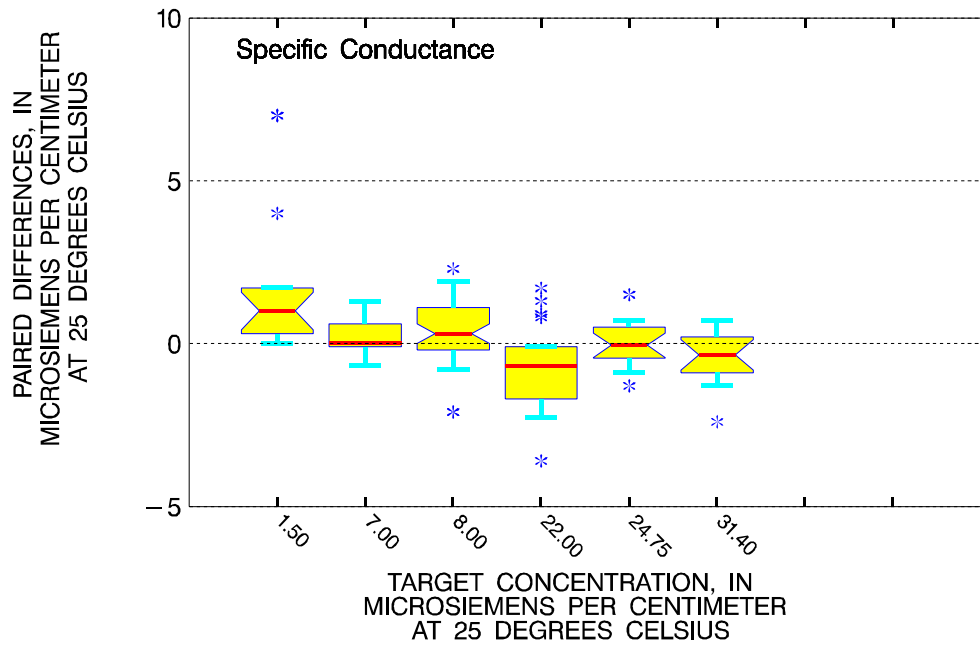
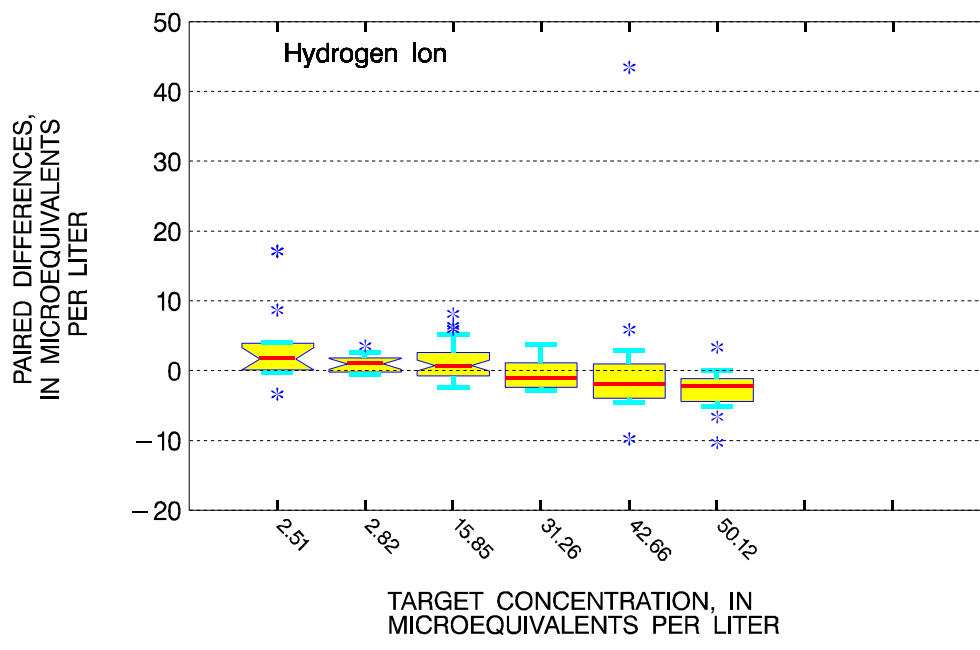


TARGET CONCENTRATION IN MILLIGRAMS PER LITER

EXPLANATION

- < MDL Target less than method detection limit
- *, Remaining 1 percent of data not inclusive in the distribution tails

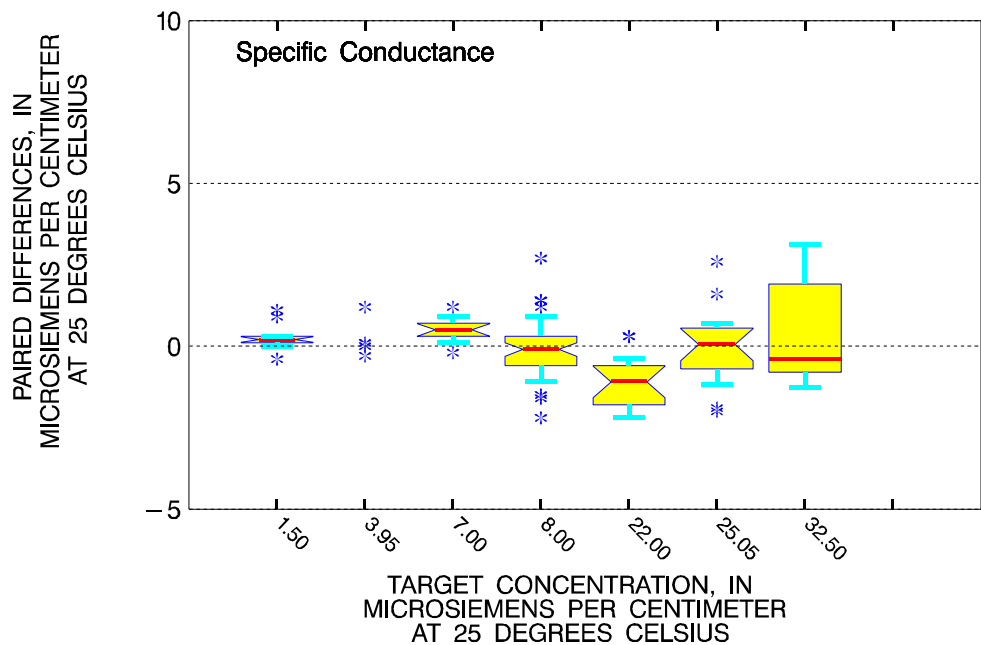
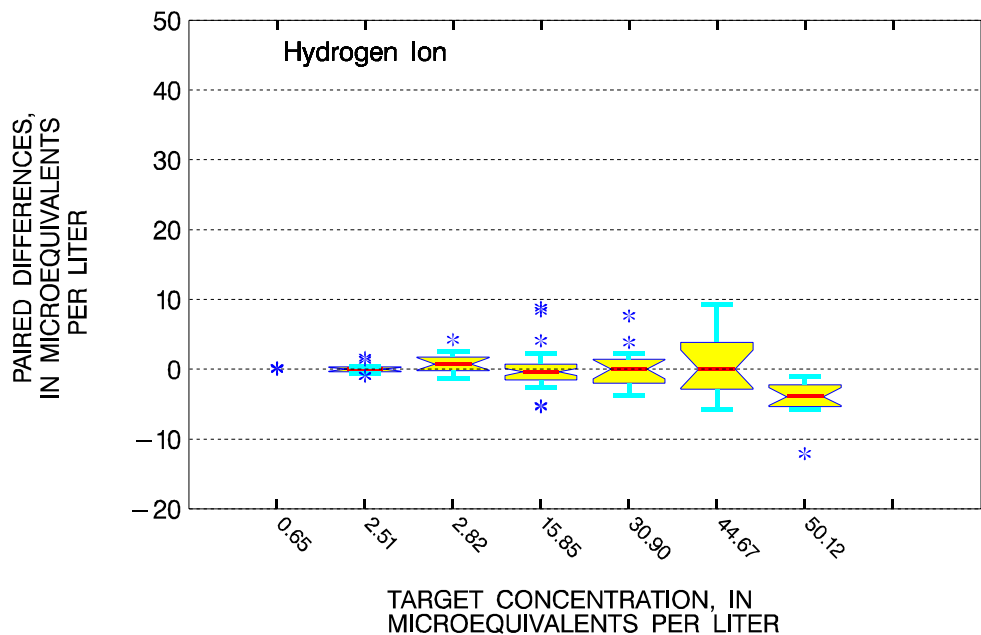
Figure 11. Relation between paired blind-audit differences for major ions and the analyte concentrations of solutions used in the blind-audit program in 1996.



EXPLANATION

*, Remaining 1 percent of data not inclusive in the distribution tails

Figure 12. Relation between paired blind-audit differences for hydrogen-ion and specific conductance and the analyte concentrations of solutions used in the blind-audit program in 1995.



EXPLANATION

*, Remaining 1 percent of data not inclusive in the distribution tails

Figure 13. Relation between paired blind-audit differences for hydrogen ion and specific conductance and the analyte concentrations of solutions used in the blind-audit program in 1996.

Table 9. 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 in 1995 and 1996

[All paired blind-audit differences expressed in milligrams per liter except specific conductance, in microsiemens per centimeter at 25 degrees celsius, and hydrogen ion, in microequivalents per liter]

Analyte	Bucket minus bottle differences in significance levels (p-values) by target concentration		Statistically significant ($\alpha=0.05$)?	
	1995	1996	1995	1996
Calcium	0.081	0.094	NO	NO
Magnesium	.085	.014	NO	YES
Sodium	.137	.787	NO	NO
Potassium	.002	.116	YES	NO
Ammonium	.048	.000	YES	YES
Chloride	.912	.628	NO	NO
Nitrate	.189	.625	NO	NO
Sulfate	.002	.017	YES	YES
Hydrogen ion	.0001	.003	YES	YES
Specific conductance	.0001	.0001	YES	YES

Table 10. Number of determinations exceeding the method detection limit for the Ultrapure deionized water samples submitted annually as part of the blind-audit program, 1995-1996

Analyte	Field-exposed bucket portion		Minimally handled bottle portion	
	1995	1996	1995	1996
Calcium	5	0	3	1
Magnesium	6	1	3	3
Sodium	15	15	15	15
Potassium	5	0	11	3
Ammonium	12	12	9	8
Chloride	11	13	14	12
Nitrate	15	14	13	14
Sulfate	0	0	0	0

Percent Differences

The relative and absolute percent differences were calculated for all of the paired blind-audit samples. As long as the distribution of relative and absolute percent differences is considered, relative percent differences are useful for understanding bias in the data set, whereas absolute percent differences help to show the variability. The upper and lower quartiles as well as the median relative and absolute percent differences are listed in tables 11 and 12. The relative and absolute percent differences were determined by calculating each paired blind-audit difference as a percentage of the known sample concentration:

$$\text{Relative percent difference} = (C_1 - C_2) / C_3 \times 100 ,$$

and

$$\text{Absolute percent difference} = |(C_1 - C_2) / C_3| \times 100 ,$$

where

C_1 = Sample concentration, in milligrams per liter, from the portion of the blind-audit sample that is exposed to all of the handling and processing steps of a normal weekly precipitation sample (bucket portion);

C_2 = Sample concentration, in milligrams per liter, from the control portion of the blind-audit sample subject to minimal handling and processing (bottle portion); and

C_3 = Known concentration of the blind-audit sample, in milligrams per liter.

Bucket-bottle data pairs were excluded for a given analyte if the known concentration was less than or equal to the minimum reporting limit. The percent differences are inflated by the influence of large (on a percentage basis) bucket minus bottle differences when the known concentration was less than or equal to the minimum reporting limit (Nilles and others, 1995).

The median (50th percentile) relative percent bias for most analytes was within a narrow range of -5 to +5 percent, indicating a low occurrence of either positive or negative bias. Exceptions were ammonium, which had a median relative bias of -9.72 percent in 1995 and -12.50 percent in 1996. The median relative percent bias of -12.50 percent for ammonium in 1996 was the largest for all of the analytes. The median relative percent bias also was fairly large for sodium at -7.99 percent in 1995 and -7.00 percent in 1996. Chloride also had a median relative percent bias of -7.04 percent in 1996.

One way to evaluate bias is to determine if the paired differences for a given analyte are evenly distributed about the zero difference line. If the paired differences for a given analyte were completely free of bias, the median difference would be zero and the upper quartile would be the same distance from the median difference of zero as the lower quartile. Sodium, potassium, chloride, and ammonium failed to display this type of pattern in 1995 or 1996.

Table 11. Relative and absolute bucket minus bottle differences calculated as a percentage of the target bottle concentration for each analyte in 1995

Analyte	Relative bucket minus bottle differences, expressed as a percentage of corresponding target bottle concentration (selected data pairs only)			Absolute bucket minus bottle differences, expressed as a percentage of corresponding target bottle concentration (selected data pairs only)		
	Percentiles			Percentiles		
	25 th	50 th	75 th	25 th	50 th	75 th
Calcium	-1.35	1.43	4.62	1.43	2.86	6.02
Magnesium	-2.25	0.36	2.70	0.96	2.70	5.41
Sodium	-34.24	-7.99	-0.66	4.88	11.13	39.13
Potassium	-9.48	0.00	5.26	3.45	8.00	24.00
Ammonium	-37.50	-9.72	-1.67	6.25	12.50	37.50
Chloride	-8.41	-2.29	0.80	2.17	7.04	14.08
Nitrate	-3.22	-0.93	0.88	0.93	2.19	3.70
Sulfate	-0.41	0.46	2.13	0.41	1.07	2.13
Hydrogen ion	-6.64	2.19	14.48	4.61	8.95	16.71
Specific conductance	-2.46	1.25	7.50	1.76	4.57	10.00

None of the analytes display a strong tendency for a positive bias in 1995. This is made clear by the fact that the interquartile range for relative percent difference spans zero for 8 of the 10 analytes. In contrast, virtually all of the paired differences for ammonium and sodium were negative values, reflecting the negative bias for these two analytes. In addition to depicting a negative bias, ammonium and sodium paired-sample differences also had the most variability of all of the analytes. This is illustrated by the fact that these two analytes have the highest median absolute percent differences of all 10 analytes.

The size of the interquartile range was a useful indicator of the amount of variability associated with a given analyte. Sodium and ammonium had interquartile ranges exceeding 15 percent on both a relative and an absolute basis in 1995 (table 11). This indicates that these analytes had the most variability associated with their paired blind-audit differences. In 1996, the interquartile range of relative and absolute percent differences exceeded 15 percent only for sodium, ammonium, and chloride (table 12). It is worth noting that ammonium and sodium paired sample differences in 1995 indicate that a quarter of the paired observations had over a third less ammonium and sodium in the bottle portion than in the bucket portion. This is evident in table 11, which depicts the lower quartile (25th percentile) of paired observations for sodium and ammo-

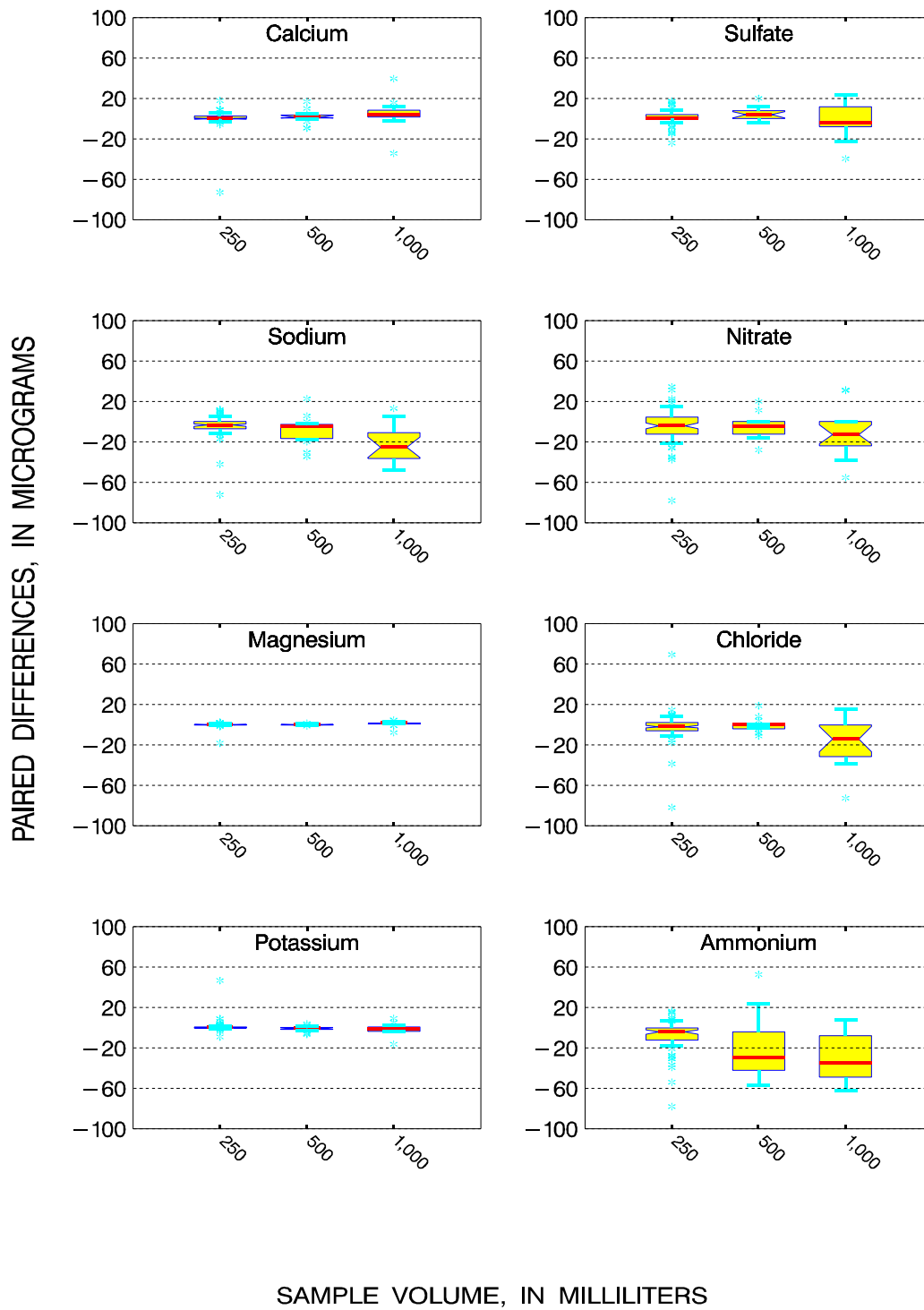
nium as -34.24 and -37.50 percent, respectively. Table 12 depicts that, in 1996, only the lower quartile of paired bucket minus bottle relative percent differences for ammonium indicated over a third less ammonium (-34.92 percent) in the bottle portion in a quarter of all data pairs. The fact that the interquartile range of their paired differences for most analytes did not exceed 15 percent in 1995 or 1996 is an important indicator that users of NADP/NTN weekly precipitation data during this time period can be assured that the variability of the data for most analytes was not large.

Sample Volume Effects

A variety of sample volumes were used in the blind-audit program in order to investigate if a relationship existed between the volume collected in weekly NADP/NTN samples and the amount of contamination introduced through shipping and handling procedures. Differences between the bucket and bottle pairs were analyzed in their original concentration units and in units of mass. To convert differences from concentration units to mass units (micrograms), the concentration differences were multiplied by the volume, in liters, of sample poured into the bucket. Boxplots in figures 14 through 17 depict the differences for each analyte plotted by sample concentrations after converting the differences to units of mass.

Table 12. Relative and absolute bucket minus bottle differences calculated as a percentage of the target bottle concentration for each analyte in 1996

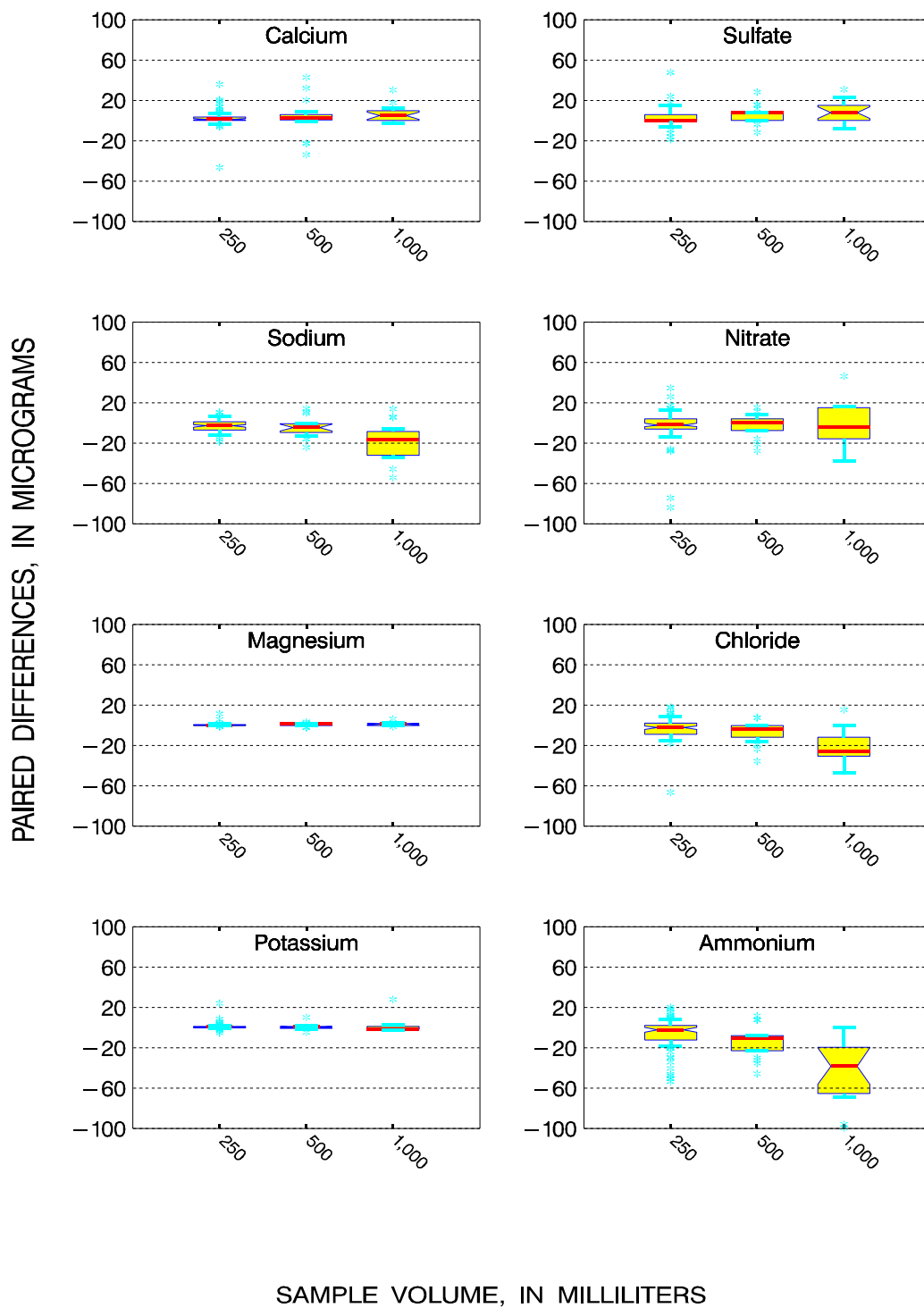
Analyte	Relative bucket minus bottle differences, expressed as a percentage of corresponding target bottle concentration (selected data pairs only)			Absolute bucket minus bottle differences, expressed as a percentage of corresponding target bottle concentration (selected data pairs only)		
	Percentiles			Percentiles		
	25 th	50 th	75 th	25 th	50 th	75 th
Calcium	0.00	3.57	6.96	2.14	4.29	9.13
Magnesium	0.00	2.20	5.41	1.10	3.59	6.25
Sodium	-21.74	-7.00	-0.46	5.37	12.88	22.83
Potassium	-5.36	1.49	12.00	4.00	8.00	15.79
Ammonium	-34.92	-12.50	-0.00	6.25	14.29	38.10
Chloride	-21.13	-7.04	0.00	3.85	7.45	21.13
Nitrate	-1.85	-0.34	1.29	0.93	1.85	2.78
Sulfate	0.00	1.07	2.13	0.42	1.27	2.67
Hydrogen ion	-7.15	0.00	8.60	4.50	8.42	13.58
Specific conductance	-3.75	0.00	5.00	2.15	4.54	8.75



EXPLANATION

* Remaining 1 percent of data not inclusive in the distribution tails

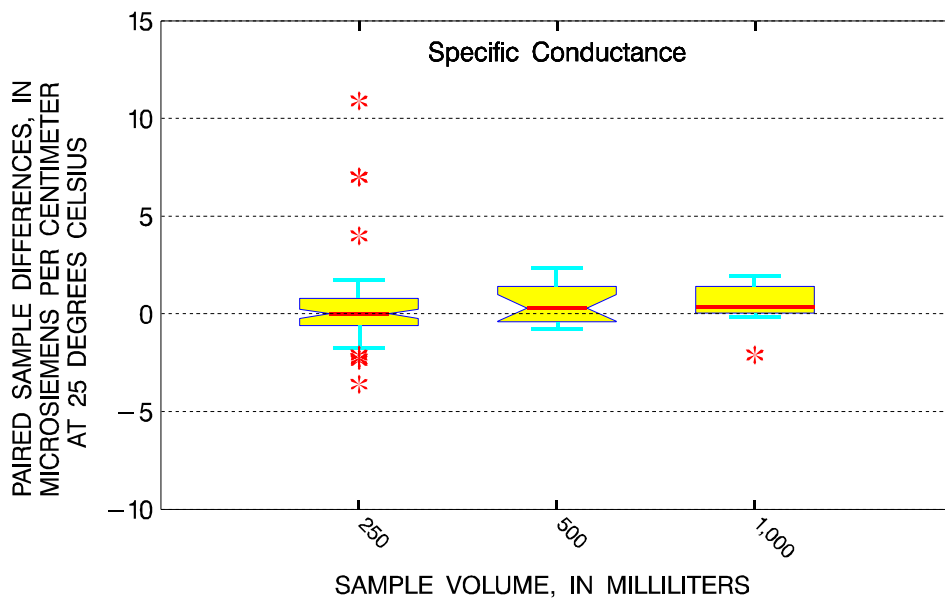
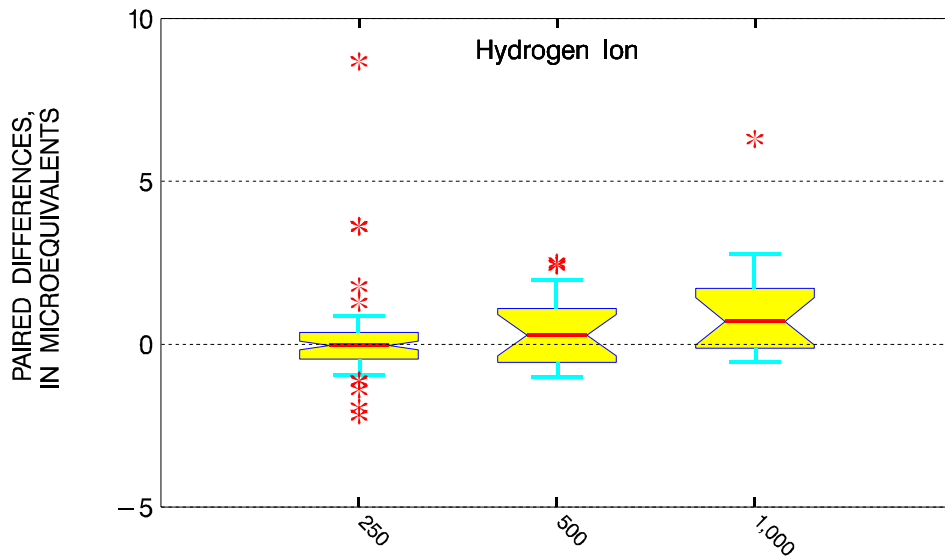
Figure 14. Relation between paired blind-audit differences for the major ions and sample volume for the 250-, 500-, and 1,000-milliliter U.S. Geological Survey solution samples in 1995.



EXPLANATION

* Remaining 1 percent of data not inclusive in the distribution tails

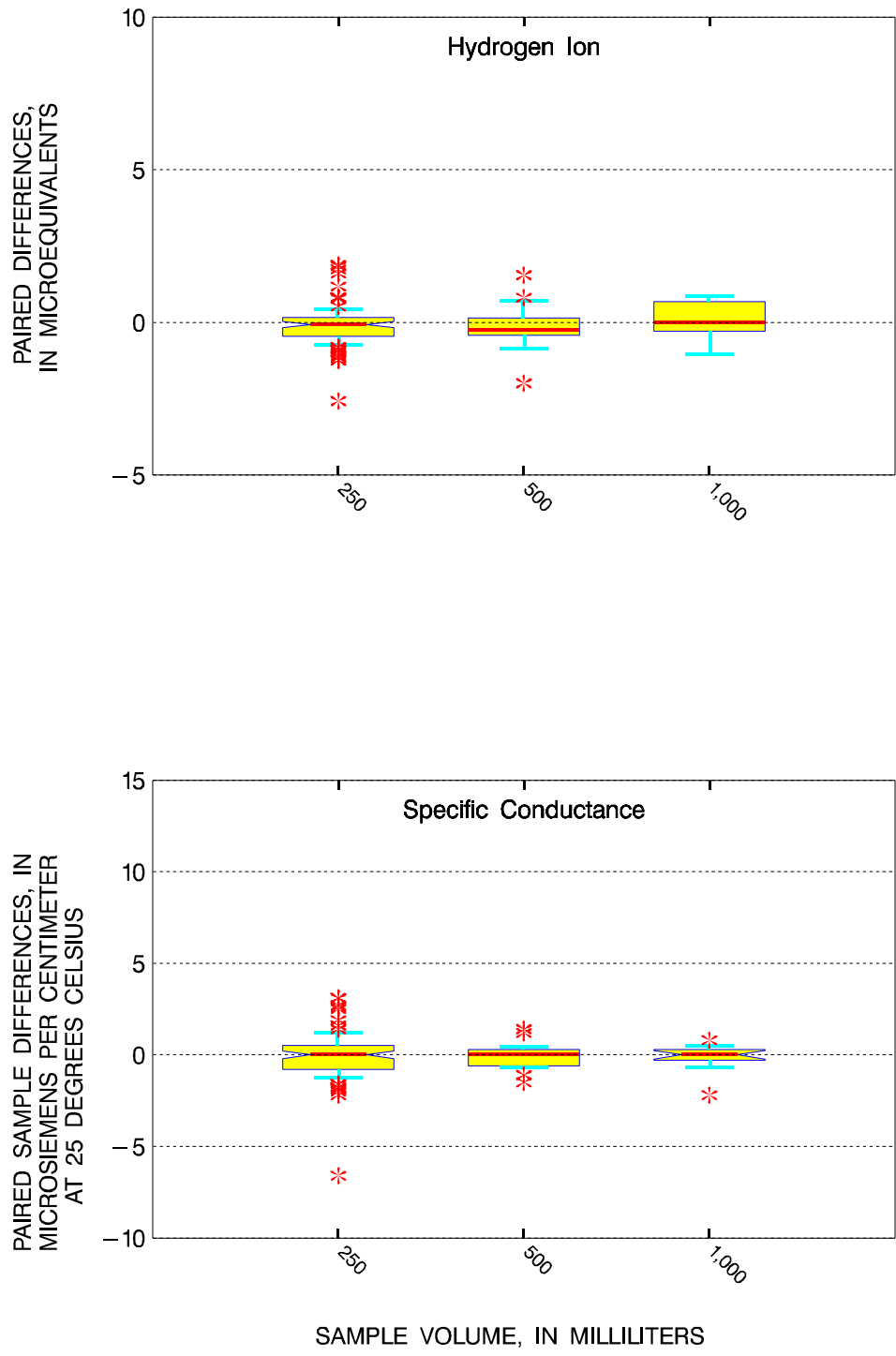
Figure 15. Relation between paired blind-audit differences for the major ions and sample volume for the 250-, 500-, and 1,000-milliliter USGS solution samples in 1996.



EXPLANATION

* Remaining 1 percent of data not inclusive in the distribution tails

Figure 16. Relation between paired blind-audit differences and sample volume for pH and specific conductance for the 250-, 500-, and 1,000-milliliter USGS solution samples in 1995.



EXPLANATION

* Remaining 1 percent of data not inclusive in the distribution tails

Figure 17. Relation between paired blind-audit differences for pH and specific conductance and sample volume for the 250-, 500-, and 1,000-milliliter USGS solution samples in 1996.

To determine if there was a statistically significant relation between paired blind-audit differences and the volume of the sample, a Kruskal-Wallis test was performed. As in past years, an equal number of samples containing 250, 500, or 1,000 mL of USGS solution were included in the 1995 and 1996 blind audits. Results of the Kruskal-Wallis test indicate no significant ($\alpha=0.05$) relation between paired blind-audit sample differences in units of concentration and sample volume for any of the analytes in 1995, except for potassium (table 13). This is in marked contrast with the results from previous years when at least 5 of the 10 measured analytes displayed a statistically significant relation between paired blind-audit differences in units of concentration and sample volume. When paired differences were converted to units of mass, however, the outcome of the Kruskal-Wallis test was markedly different; all of the analytes, except sulfate and nitrate, had statistically significant ($\alpha=0.05$) differences between the

bucket and bottle pairs in 1995. Furthermore, the boxplots in figures 14 and 15 show that the bucket minus bottle differences in units of mass were usually negative.

Paired differences in units of mass tended to become more negative with increasing sample volume. This tendency has been observed since the protocol change in 1994 and is in sharp contrast to the results observed before 1994. Before 1994, paired differences in units of mass increased with increasing sample volume (Nilles and others, 1993). Because contamination from major sources, such as the o-ring bucket and bucket walls, have been removed from the system, contamination from other sources, such as the contaminated filters discussed previously, are exerting a more noticeable influence on the paired blind-audit results than previously observed from these sources. Upon arrival at the CAL, both the bucket and the bottle portions are subjected to a filtering process.

Table 13. Results of the 1995 Kruskal-Wallis analysis of variance tests to determine if bucket minus bottle differences for the 250-, 500-, and 1,000-mL samples of the USGS solution used in the blind-audit program have equivalent distributions [mL, milliliter]

Analyte	Bucket minus bottle concentrations attained significance (p-value) levels on a concentration basis	Statistically significant ($\alpha=0.05$) differences determined between 250-, 500-, and 1,000-mL USGS samples on a concentration basis	Bucket minus bottle concentrations attained significance (p-value) levels on a mass per bucket basis	Statistically significant ($\alpha=0.05$) differences determined between 250-, 500-, and 1,000-mL USGS samples on a mass per bucket basis
Calcium	0.503	NO	0.012	YES
Magnesium	0.088	NO	0.001	YES
Sodium	0.125	NO	0.000	YES
Potassium	0.014	YES	0.013	YES
Ammonium	0.082	NO	0.000	YES
Chloride	0.231	NO	0.025	YES
Nitrate	0.998	NO	0.204	NO
Sulfate	0.184	NO	0.141	NO
Hydrogen ion	0.067	NO	0.023	YES
Specific conductance	0.118	NO	0.006	YES

Before collecting the final aliquot for analysis from the bucket and bottle portions, the technician pours the excess sample volume through the filtering apparatus. If the filter is a source of contamination, then the amount of an analyte contributed to the aliquot collected for analyses will be inversely proportional to the amount of sample poured through the filter before collecting the aliquot. Bucket-sample portions have more water available to rinse the filter before collecting the final aliquot for analysis and would, therefore, be subject to less contamination than bottle samples, which have less volume available for rinsing. The maximum excess bucket-sample volume available for rinsing was 200 mL, the limit of volume the filtering apparatus can hold. The results for 1996 were similar to those observed in 1995, except that only 5 of the 10 analytes had statistically significant ($\alpha=0.05$) differences between the bucket and bottle portions when the differences were converted to units of mass (table 14).

For 1995, sodium and ammonium differences become less negative with increasing volume while increasing in terms of magnitude, as indicated by the increasing spread in the interquartile range with increasing volume (fig. 15). The finding that the sodium bias becomes less negative with increasing volume supports the theory that the amount of sodium leached from the filters decreases with increasing rinse volume. In October 1998, the author discussed the results of the blind-audit program with Jane Rothert of the Illinois State Water Survey. Together, the author and Ms. Rothert traced the probable source of sodium contamination to the brand of filters used to process samples at the CAL prior to analysis. For 1996, the volume-based results of the blind-audit program indicate a situation similar to the situation indicated by the results in 1995, but sulfate differences became more positive as volume increased.

Table 14. Results of the 1996 Kruskal-Wallis analysis of variance tests to determine if bucket minus bottle differences for the 250-, 500-, and 1,000-mL samples of the USGS solution used in the blind-audit program have equivalent distributions

[mL, milliliter]

Analyte	Bucket minus bottle concentrations attained significance (p-value) levels on a concentration basis	Statistically significant ($\alpha=0.05$) differences determined between 250-, 500-, and 1,000-mL USGS samples on a concentration basis	Bucket minus bottle concentrations attained significance (p-value) levels on a mass per bucket basis	Statistically significant ($\alpha=0.05$) differences determined between 250-, 500-, and 1,000-mL USGS samples on a mass per bucket basis
Calcium	0.992	NO	0.116	NO
Magnesium	0.944	NO	0.020	YES
Sodium	0.393	NO	0.001	YES
Potassium	0.066	NO	0.076	NO
Ammonium	0.030	YES	0.000	YES
Chloride	0.205	NO	0.000	YES
Nitrate	0.914	NO	0.994	NO
Sulfate	0.326	NO	0.008	YES
Hydrogen ion	0.341	NO	0.410	NO
Specific conductance	0.972	NO	0.972	NO

Interlaboratory-Comparison Program

The two objectives of the interlaboratory-comparison program are: (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. The following laboratories participated in the interlaboratory-comparison program in 1995 and 1996: (1) Illinois State Water Survey, Central Analytical Laboratory (CAL) in Champaign, Illinois; (2) Atmospheric Environment Service, Environment Canada (AES) in Ontario, Canada; (3) QST Environmental (QST), formerly known as Environmental Science and Engineering, Inc., in Gainesville, Florida; (4) Ontario Ministry of the Environment, Water Quality Section (MOE), in Ontario, Canada; (5) Global Geochemistry Corporation (GGC) in Canoga Park, California; and (6) Shepard Analytical Services (SA) in Simi Valley, California. GGC dropped out of the program and was replaced by Shepard Analytical Services in the third quarter of 1996. The same analyst that analyzed the samples at GGC analyzed the samples at SA using the same analytical methods. Therefore, GGC/SA is used in some of the figures to signify data reported collectively by the two laboratories in 1996, with annotation to indicate when the change in laboratories occurred.

Samples from three sources were used in the interlaboratory-comparison program in 1995 and 1996: (1) synthetic wet-deposition samples and Ultrapure deionized-water samples prepared by the USGS, (2) standard reference samples (2694A-I, and 2694A-II) prepared and certified by the National Institute of Standards and Technology (NIST) (National Institute of Standards and Technology, 1991), and (3) natural wet-deposition samples collected at NADP/NTN sites and bottled by the CAL. Table 3 contains information on the preparation of the synthetic solutions made by the USGS or the 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 4. Each of the five participating laboratories received 104 samples in 1995 and 1996. In each year, 52 were aliquots of natural precipitation bottled by the CAL, 12 were

synthetic samples made by the USGS and referred to as USGS solution, 18 were NIST-certified samples, 8 were synthetic samples made by the USGS and referred to as SP-1 solution, 8 were synthetic samples made by the USGS and referred to as SP-2 solution, and 6 were Ultrapure deionized-water samples bottled by the USGS.

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 (a device used to split samples into ten parts). 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. For the analysis of all samples, except the natural samples, the concentration of each analyte was known either because the sample was a certified reference sample or because it was prepared by the USGS and tested to verify the target values. The analysis of the natural samples was limited to comparing differences between laboratories on identical sets of replicate samples (26 replicate pairs per laboratory) in a given year.

Samples used in the 1995-96 interlaboratory-comparison program were relabeled and shipped by the USGS to the five participating laboratories approximately every 2 weeks. All samples were relabeled with only 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. 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. A flowchart of the interlaboratory-comparison program is shown in figure 18.

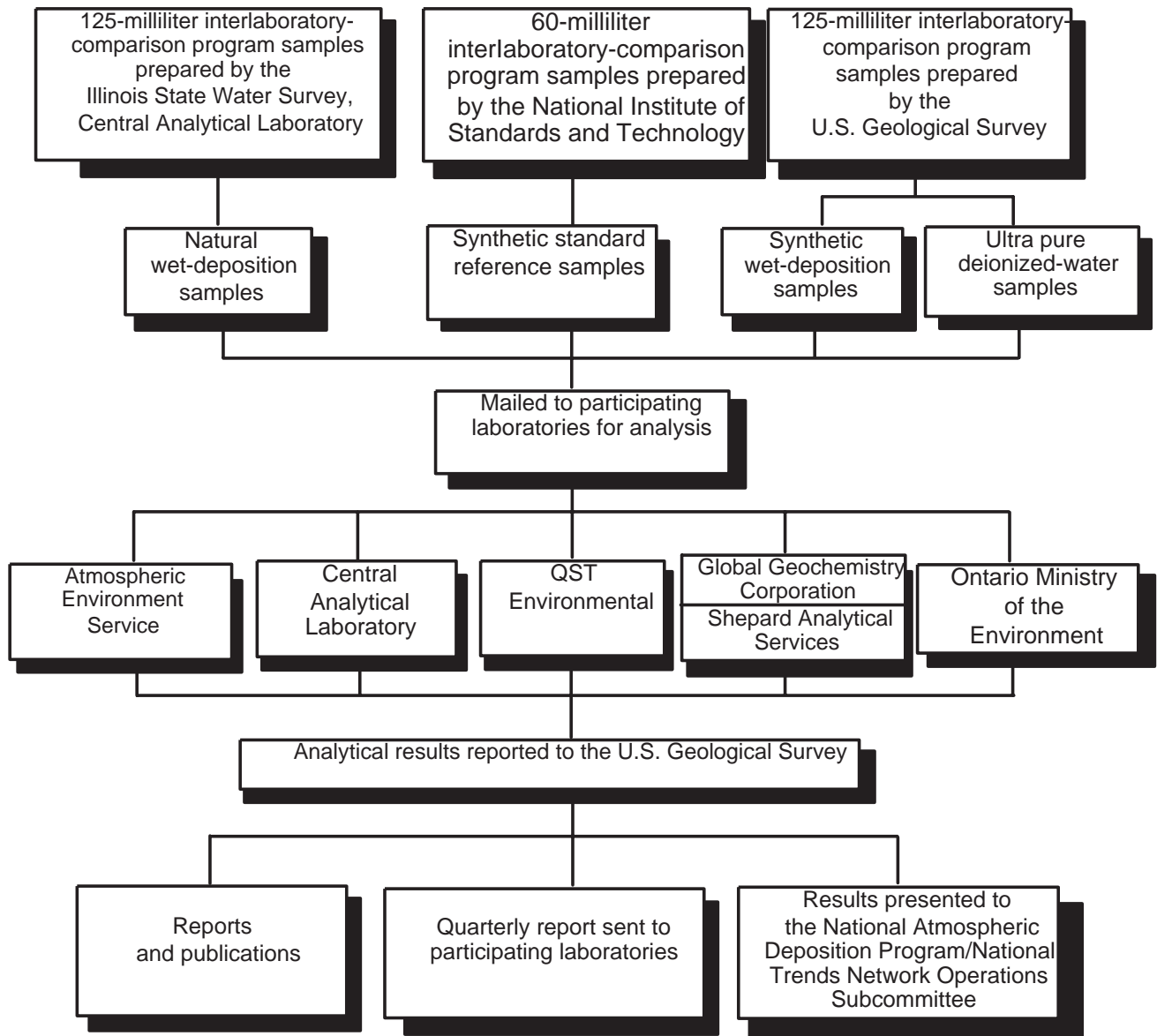


Figure 18. Interlaboratory-comparison program of the U.S. Geological Survey.

Laboratory Precision

Precision is defined by the extent to which a given set of measurements of the same sample agrees with its mean. For this analysis, 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 (tables 15 and 16). Differences were calculated from 26 sample pairs of replicate natural samples for each laboratory in 1995 and in 1996. Analyte concentrations reported as less than the minimum reporting limit were set equal to the minimum reporting limit.

In 1995 and 1996, 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. Larger differences between laboratories were apparent for precision estimates at the 90th percentile for cations. In 1995, cation precision estimates at the 90th percentile ranged from 0.001 to 0.038 mg/L. In 1996, the 50th percentile for cation precision estimates were less than or equal to 0.004 mg/L, whereas the 90th percentile for cation precision estimates ranged from 0.000 to 0.019 mg/L in 1996.

Anion precision estimates at the 50th percentile exhibited greater variability among laboratories than was observed for the cations. Median absolute differ-

ences ranged from 0.000 to 0.015 mg/L in 1995-96. Differences among laboratories in 1995 for precision estimates at the 90th percentile for anions ranged from 0.010 to 0.050 mg/L. Differences among laboratories were more apparent in 1996 for precision estimates at the 90th percentile for the anions, ranging from 0.01 to 0.085 mg/L.

The pH (expressed as hydrogen ion) precision estimates at both the 50th and 90th percentile exhibited scant variability among laboratories in 1995-96. The 50th percentile precision estimates for hydrogen ion ranged from 0.075 to 0.687 µeq/L in 1995; in 1996 the range was 0.000 to 0.448 µeq/L. Precision estimates at the 90th percentile ranged from 0.746 to 1.649 µeq/L in 1995 and from 1.040 to 1.838 µeq/L in 1996.

Four laboratories routinely reported specific-conductance results. The AES does not routinely report specific-conductance measurements. There was very little variability among laboratories in their reported specific-conductance measurements in 1995: The 50th percentile precision estimate ranged from 0 to 0.200 µS/cm in 1995 for all four participating laboratories, whereas the 90th percentile ranged from .80 to 1.65 µS/cm. In 1996, the 50th percentile precision estimate for specific conductance ranged from 0.050 to 0.100 µS/cm and the 90th percentile ranged from 0.200 to 1.500 µS/cm.

Table 15. Fiftieth and ninetieth percentile absolute differences for analyses of replicate samples determined by five laboratories participating in the 1995 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; QST: QST Environmental; MOE: Ontario Ministry of the Environment, Water Quality Section; GGC: Global Geochemistry Corporation; --: not calculated]

Analyte	CAL		AES		QST		GGC		MOE	
	50 th	90 th	50 th	90 th	50 th	90 th	50 th	90 th	50 th	90 th
Calcium	0.000	0.010	0.003	0.010	0.001	0.003	0.001	0.004	0.002	0.009
Magnesium	.000	.001	.000	.001	.000	.001	.000	.002	.001	.002
Sodium	.002	.006	.001	.005	.001	.003	.001	.005	.003	.023
Potassium	.001	.019	.002	.016	.000	.001	.001	.005	.001	.038
Ammonium	.000	.010	.001	.005	.003	.010	.002	.005	.001	.006
Chloride	.000	.020	.002	.017	.001	.010	.002	.005	.000	.000
Nitrate	.000	.010	.010	.024	.002	.009	.006	.026	.000	.018
Sulfate	.000	.010	.005	.026	.004	.020	.005	.010	.005	.050
Hydrogen ion	.094	.800	.163	.746	.687	1.649	.320	1.391	.075	1.040
Specific conductance	.000	.300	--	--	.200	.400	.050	.200	.100	1.000

Table 16. Fiftieth and ninetieth percentile absolute differences for analyses of replicate samples determined by five laboratories participating in the 1996 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; QST: QST Environmental; MOE: Ontario Ministry of the Environment, Water Quality Section; GGC: Global Geochemistry Corporation; --: not calculated]

Analyte	CAL		AES		QST		GGC		MOE	
	50 th	90 th	50 th	90 th	50 th	90 th	50 th	90 th	50 th	90 th
Calcium	0.000	0.000	.002	.006	0.001	.008	.001	.009	0.001	.007
Magnesium	.000	.001	.000	.004	.000	.003	.001	.002	.000	.002
Sodium	.001	.004	.001	.007	.001	.011	.002	.009	.002	.007
Potassium	.001	.002	.000	.008	.000	.019	.001	.002	.001	.006
Ammonium	.000	.010	.001	.005	.004	.018	.002	.014	.001	.006
Chloride	.000	.010	.006	.023	.002	.085	.003	.012	.000	.010
Nitrate	.000	.020	.011	.034	.004	.013	.012	.029	.000	.027
Sulfate	.010	.020	.005	.025	.002	.010	.015	.055	.010	.050
Hydrogen ion	.000	1.040	.448	1.756	.000	1.838	.265	1.456	.180	1.372
Specific conductance	.050	.200	--	--	.100	1.500	.030	.200	.000	.500

Interlaboratory Bias

Interlaboratory bias (bias among 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 examine potential bias in the analytical results among the laboratories, a Friedman test was performed. A Friedman test is used to investigate the significance of the differences in response to multiple treatments for more than two subjects without assuming the data are from normal distributions (Kanji, 1993). In this application, the multiple treatments are the different sample matrices, and the subjects are the various laboratories. This allows the comparison of paired data from each of the participating laboratories, while controlling for the different sample matrices sent in different mailings. In 1995, results of the Friedman test indicated significant ($\alpha=0.05$) differences in analyte measurements for calcium, potassium, sulfate, nitrate, and hydrogen ion among the five laboratories. In 1996, the Friedman test indicated significant ($\alpha=0.05$) differences in analyte measurements for potassium, ammonium, chloride, sulfate, nitrate, and hydrogen ion.

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 the control charts shown in figures 19 through 28. The warning limits are positioned at ± 2 F-pseudosigmas from the zero difference line, whereas the

control limits were placed at ± 3 F-pseudosigmas from the zero difference line. Control limits (3-sigma) define the bounds of virtually all values produced by a system in statistical control. Modern control charts commonly have additional limits called warning limits (2-sigma) within which most (95 percent) of the values should lie (Taylor, 1987).

There are some important features in figures 19-28 of which the reader should be aware. First, the graph for each analyte is scaled to reflect the maximum scatter for a given analyte in the data for one of the five participating laboratories. That means that the graph for each analyte is scaled to reflect the maximum range of difference between a participating laboratory's measured values and the median value of all participating laboratories. When viewing figures 19-28, the reader should first note the different scale for each analyte depicted in figure 19. Scaling differences are visual clues of differences in performance in the analysis of a given analyte for the laboratories as a group. For example, the graphs for sulfate and nitrate are scaled the widest of any of the graphs for the major ions, indicating that, as a group, the laboratories had the most variability in measured minus median values for these two analytes. It also is important to note that the scales for a given analyte are consistent in figures 19-28. This facilitates comparison of performance in the analysis of a given analyte among laboratories. This approach has its drawbacks in that comparison of a given laboratory's performance on the measurement of various analytes puts an extra burden on the reader to adjust

to changing analyte scales. However, if the graphs for all of the analytes had been scaled to facilitate comparison of analytes, then comparison of laboratory performance would be very difficult because the scaling of the graphs would obscure these differences. Differences between laboratories would be difficult to detect, and the main purpose is to compare laboratory performance.

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 to 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 to those expected for Ultrapure deionized-water samples (table 4).

National Institute of Standards and Technology Standard Reference Samples

Potential bias was examined by comparing the median laboratory values to the certified values reported by the NIST. The NIST certifies values for seven measurements from standard reference sample 2694A-I samples and eight measurements from standard reference sample 2694A-II samples. Bias could be indicated if laboratory median values were outside the NIST-certified values by a chemically significant amount, plus or minus the estimated uncertainty reported by NIST (table 17). In 1995, interlaboratory-comparison study results indicated that 5 of 7 median values at CAL and at QST for

Table 17. Summary of laboratory median values per analyte in 1995 and the 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: hydrogen ion, in microequivalents per liter, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius. AES, Atmospheric Environment Service; CAL, Illinois State Water Survey, Central Analytical Laboratory; QST, QST Environmental; GGC, Global Geochemistry Corporation; MOE, Ontario Ministry of the Environment, Water Quality Section; shading indicates that the median value reported by a given laboratory for a given analyte is outside NIST range; NIST ranges are from NIST Certificate for Standard Reference Material 2694A, dated June 10, 1991; boxed areas indicate a median value was calculated from less than nine (maximum possible) reported values]

	ANALYTE									
	Hydrogen ion	Specific conductance	Calcium	Magnesium	Sodium	Potassium	Ammonium	Chloride	Nitrate	Sulfate
NIST RANGE, 2694A-I										
Lower	46.77	24.2	0.011	0.024	0.206	0.054	¹ 0.12	¹ 0.23	¹ 0.53	2.66
Upper	53.70	26.6	0.014	0.024	0.210	0.058	¹ 0.12	¹ 0.23	¹ 0.53	2.72
LABORATORY MEDIAN, 2694A-I										
AES	53.70	(2)	(2)	0.023	0.205	0.054	0.12	0.23	0.52	2.64
CAL	57.54	28.1	0.010	0.025	0.207	0.056	0.12	0.24	0.54	2.75
QST	57.54	27.5	0.013	0.024	0.193	0.053	0.11	0.22	0.53	2.63
GGC	56.23	26.5	0.013	0.025	0.204	0.053	0.12	0.22	0.55	2.68
MOE	53.70	25.7	0.020	0.024	0.208	0.054	0.12	0.22	0.54	2.70
NIST RANGE, 2694A-II										
Lower	234.4	128.0	0.036	0.047	0.411	0.105	¹ 1.06	¹ 0.94	7.03	10.5
Upper	269.2	130.6	0.037	0.049	0.435	0.111	¹ 1.06	¹ 0.94	7.35	10.7
LABORATORY MEDIAN, 2694A-II										
AES	257.0	(2)	0.038	0.049	0.419	0.103	1.06	0.94	7.13	10.8
CAL	257.0	132.7	0.040	0.049	0.429	0.105	1.10	1.00	7.16	10.8
QST	281.8	133.0	0.038	0.050	0.398	0.108	1.09	0.96	7.13	10.7
GGC	269.2	130.6	0.036	0.050	0.412	0.102	1.07	0.96	7.15	10.4
MOE	263.0	129.0	0.036	0.052	0.412	0.107	1.06	0.99	7.08	9.8

¹Value not certified by NIST.

²Data not available.

sample 2694A-I were outside the NIST-certified ranges for a given analyte. The GGC had four median values that were outside the NIST-certified range for a given analyte, whereas AES had three and the MOE had one median value that was outside the NIST-certified range for a given analyte.

In 1996, MOE had 6 of 7 median values outside the NIST-certified range for a given analyte for certified sample 2694A-I (table 18). The GGC had five median values that were outside the NIST-certified range for a given analyte. CAL and QST each had four median values outside the NIST-certified range in sample 2694A-I, while AES had three median values outside the NIST-certified range. The similarity, in general, among laboratories in terms of their ability to achieve the NIST-certified range was noteworthy. The concentrations measured in sample

2694A-II are commonly much higher than the values measured in precipitation and usually require dilution before analysis. It is, therefore, important not to read too much into an assessment of laboratory results analyzing sample 2694A-II.

Furthermore, the certified ranges supplied by NIST for both sample types are generally extremely narrow or a single point value; it is not of great concern that many of the laboratories were only able to achieve these narrow ranges for a few analytes. Median values outside the range usually were different from the NIST range by only 0.01 to 0.05 mg/L for the major ions. A summary of the estimated uncertainty ranges for the NIST standard-reference materials 2694A-I and 2694A-II and of the median values for each laboratory is presented in tables 17 and 18.

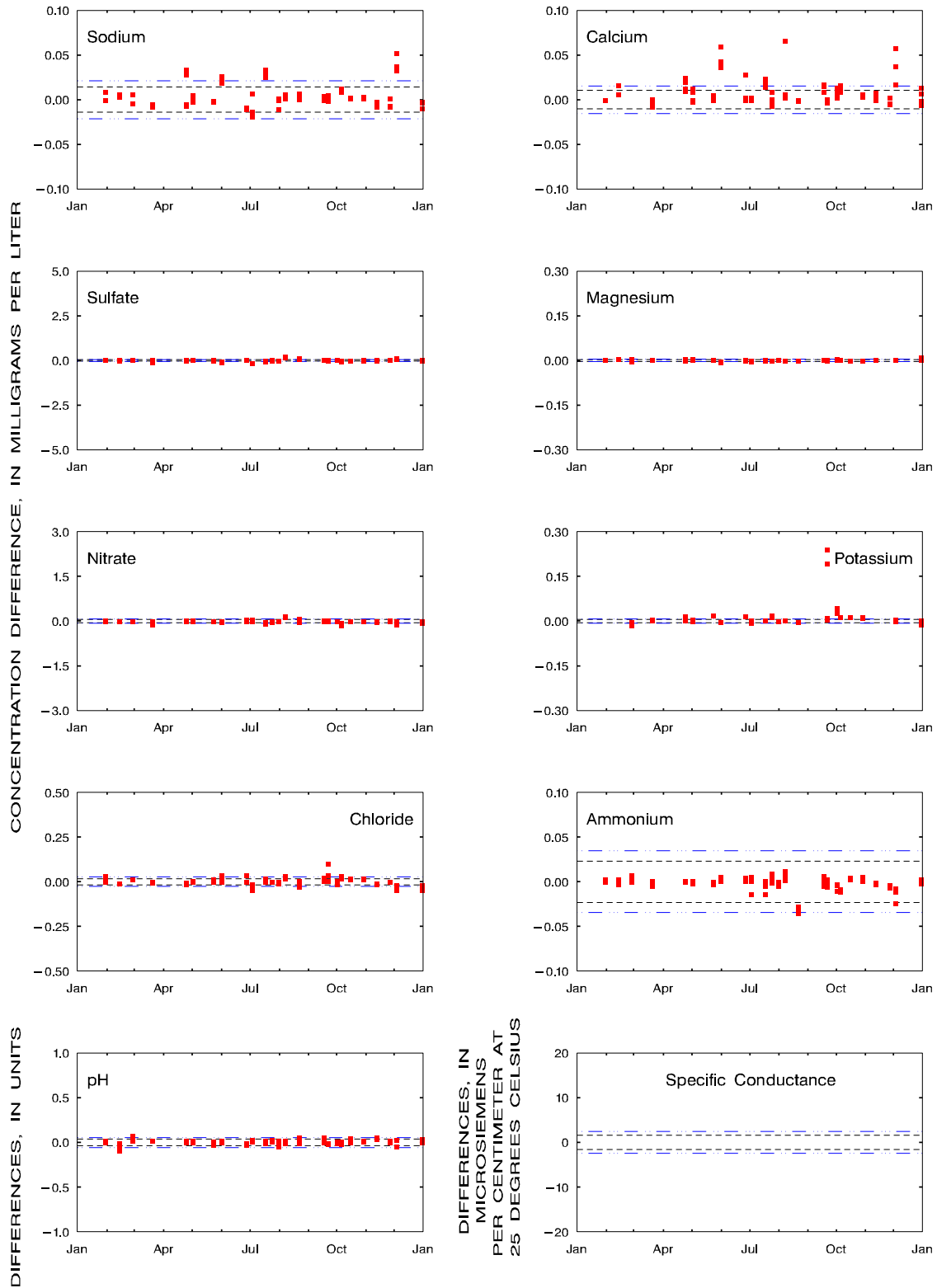
Table 18. Summary of laboratory median values per analyte in 1996 and the analyte range reported by the National Institute of Standards and Technology (NIST) for standard reference materials 2694A-I and 2694A-II

[All units in milligrams per liter except: hydrogen ion, in microequivalents per liter, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius. AES, Atmospheric Environment Service; CAL, Illinois State Water Survey, Central Analytical Laboratory; QST, QST Environmental; GGC, Global Geochemistry Corporation; MOE, Ontario Ministry of the Environment, Water Quality Section; shading indicates that the median value reported by a given laboratory for a given analyte is outside NIST range; NIST ranges are from NIST Certificate for Standard Reference Material 2694A, dated June 10, 1991; boxed areas indicate a median value was calculated from less than nine (maximum possible) reported values]

	ANALYTE									
	Hydrogen ion	Specific Conductance	Calcium	Magnesium	Sodium	Potassium	Ammonium	Chloride	Nitrate	Sulfate
NIST RANGE, 2694A-I										
Lower	46.77	24.2	0.011	0.024	0.206	0.054	¹ 0.12	¹ 0.23	¹ 0.53	2.66
Upper	53.70	26.6	0.014	0.024	0.210	0.058	¹ 0.12	¹ 0.23	¹ 0.53	2.72
LABORATORY MEDIAN, 2694A-I										
AES	53.70	(2)	(2)	0.025	0.201	0.052	0.11	0.22	0.53	2.68
CAL	54.95	28.7	0.010	0.024	0.207	0.055	0.11	0.22	0.53	2.78
QST	60.25	26.7	0.013	0.024	0.195	0.055	0.11	0.23	0.53	2.78
GGC	57.54	27.6	0.014	0.027	0.203	0.051	0.12	0.22	0.56	2.68
MOE	56.23	27.1	0.019	0.025	0.210	0.050	0.12	0.24	0.53	2.49
NIST RANGE, 2694A-II										
Lower	234.4	128.0	0.036	0.047	0.411	0.105	¹ 1.06	¹ 0.94	7.03	10.5
Upper	269.2	130.6	0.037	0.049	0.435	0.111	¹ 1.06	¹ 0.94	7.35	10.7
LABORATORY MEDIAN, 2694A-II										
AES	265.5	(2)	0.033	0.052	0.416	0.105	1.05	0.89	7.03	10.5
CAL	263.0	133.8	0.040	0.048	0.416	0.106	1.04	0.99	7.15	10.7
QST	275.4	121.5	0.038	0.051	0.408	0.107	1.06	0.98	7.15	10.8
GGC	281.8	130.7	0.037	0.051	0.409	0.101	1.06	0.96	7.24	10.4
MOE	263.0	130.0	0.044	0.050	0.417	0.102	1.08	1.00	7.22	10.2

¹Value not certified by NIST.

²Data not available.



EXPLANATION

- Warning limits (+2 and -2 F-pseudosigmas from zero difference line)
- Control limits (+3 and -3 F-pseudosigmas from zero difference line)

Figure 19. 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 1995. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.

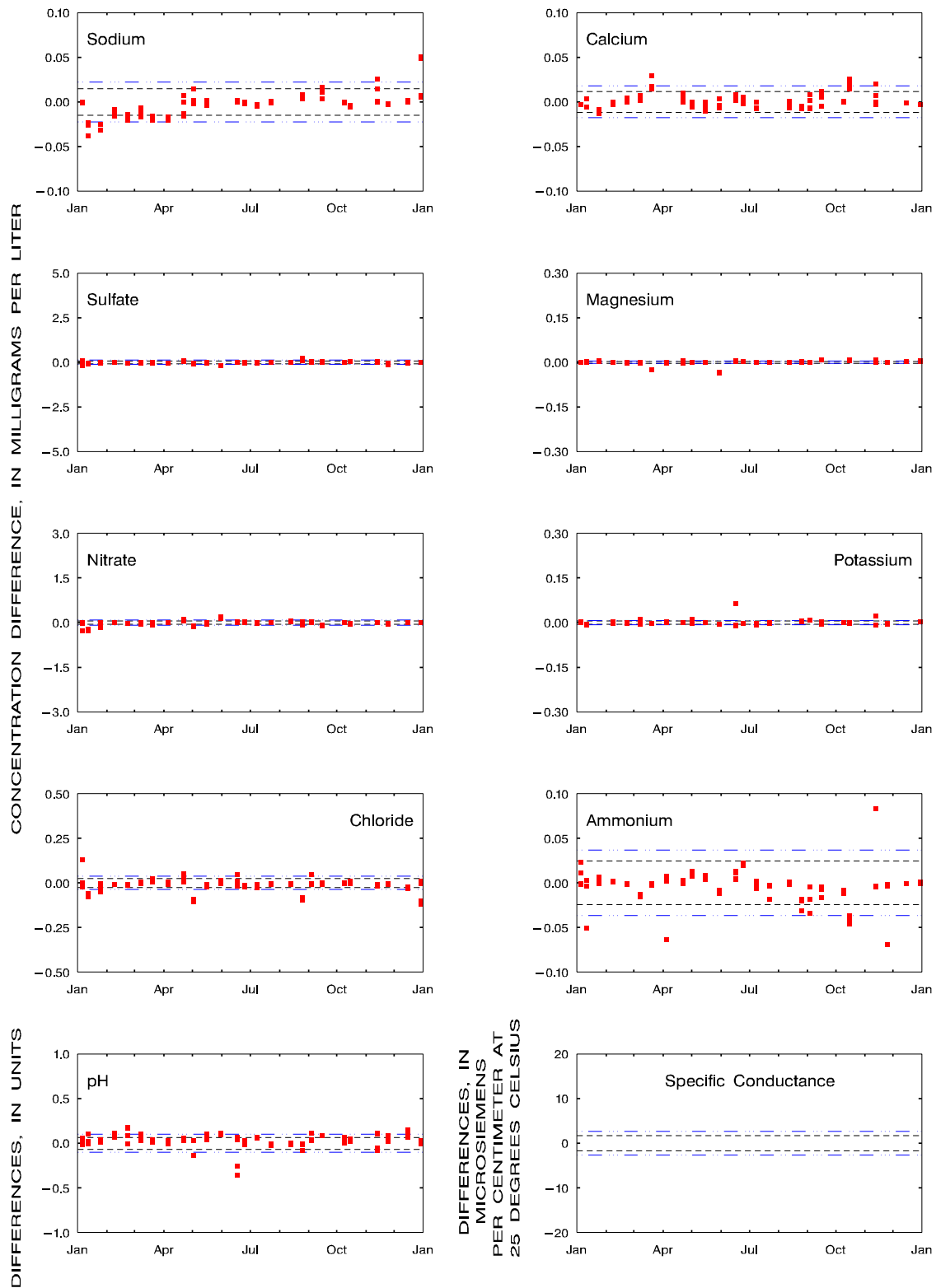
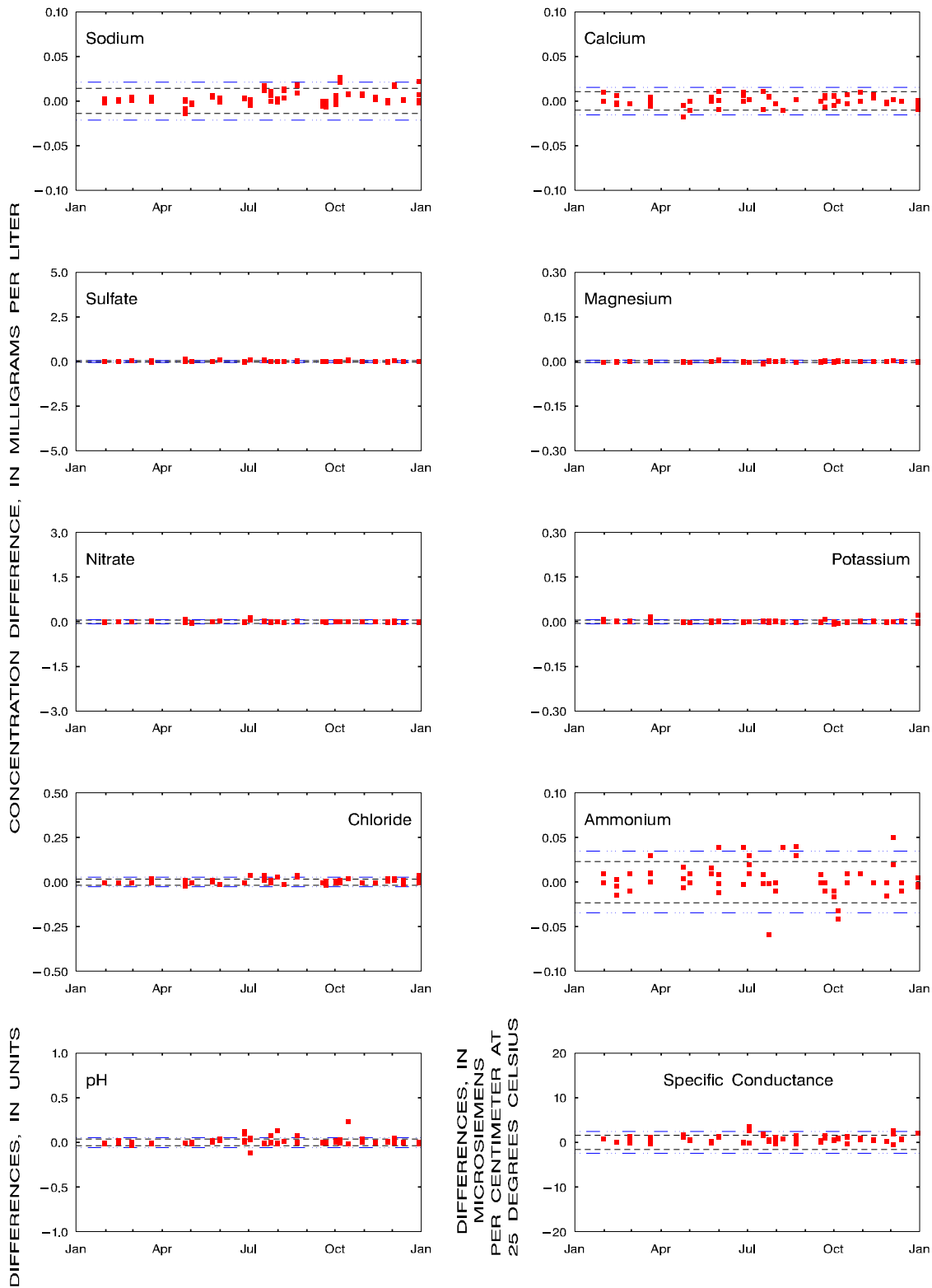


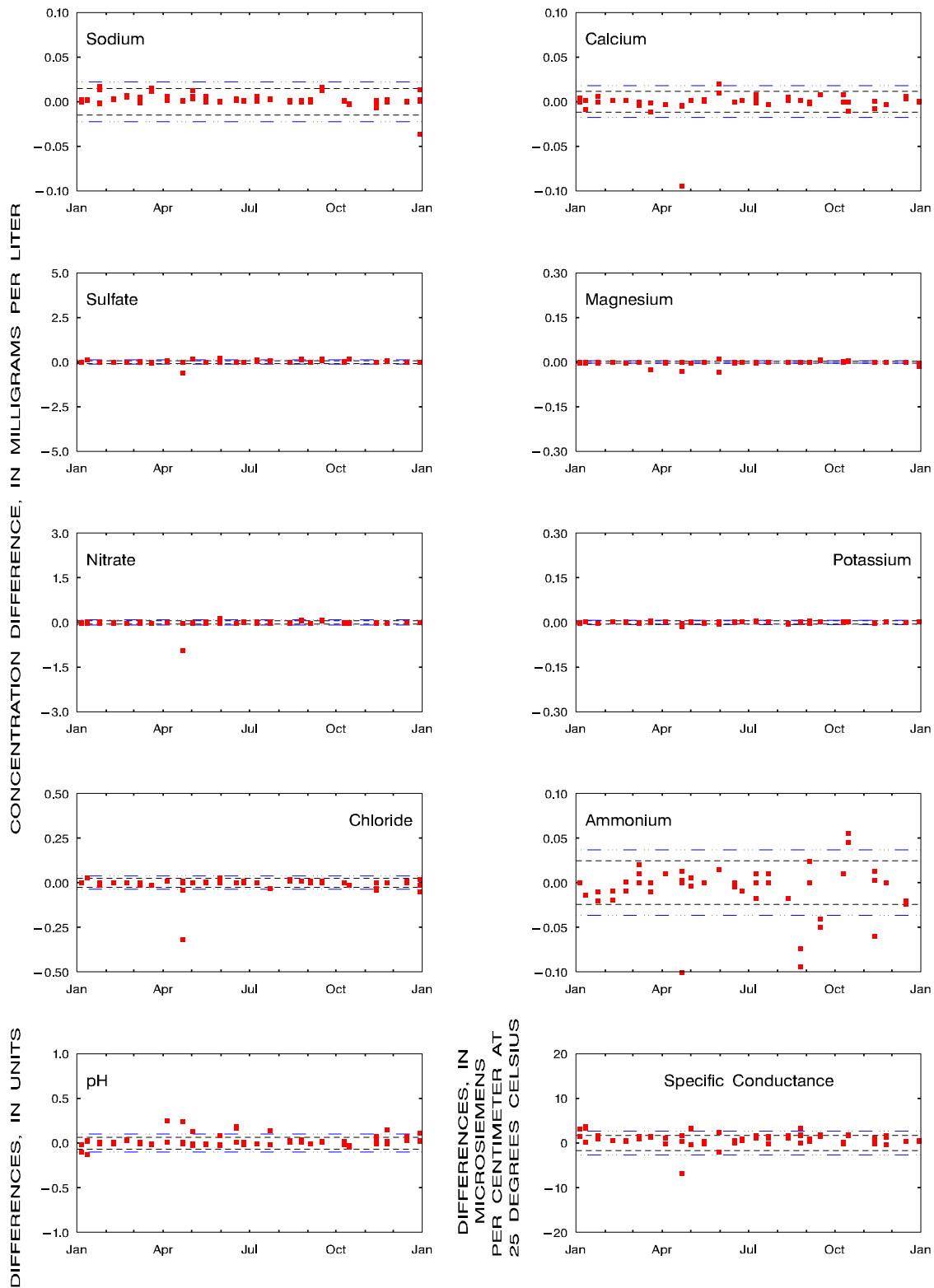
Figure 20. Difference between the measured value reported by the Atmospheric Environment Service and the median value calculated for all participating laboratories in the interlaboratory-comparison program during 1996. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.



EXPLANATION

- Warning limits (+2 and -2 F-pseudosigmas from zero difference line)
- Control limits (+3 and -3 F-pseudosigmas from zero difference line)

Figure 21. 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 1995. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.



EXPLANATION

- Warning limits (+2 and -2 F-pseudosigmas from zero difference line)
- · - · - Control limits (+3 and -3 F-pseudosigmas from zero difference line)

Figure 22. 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 1996. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.

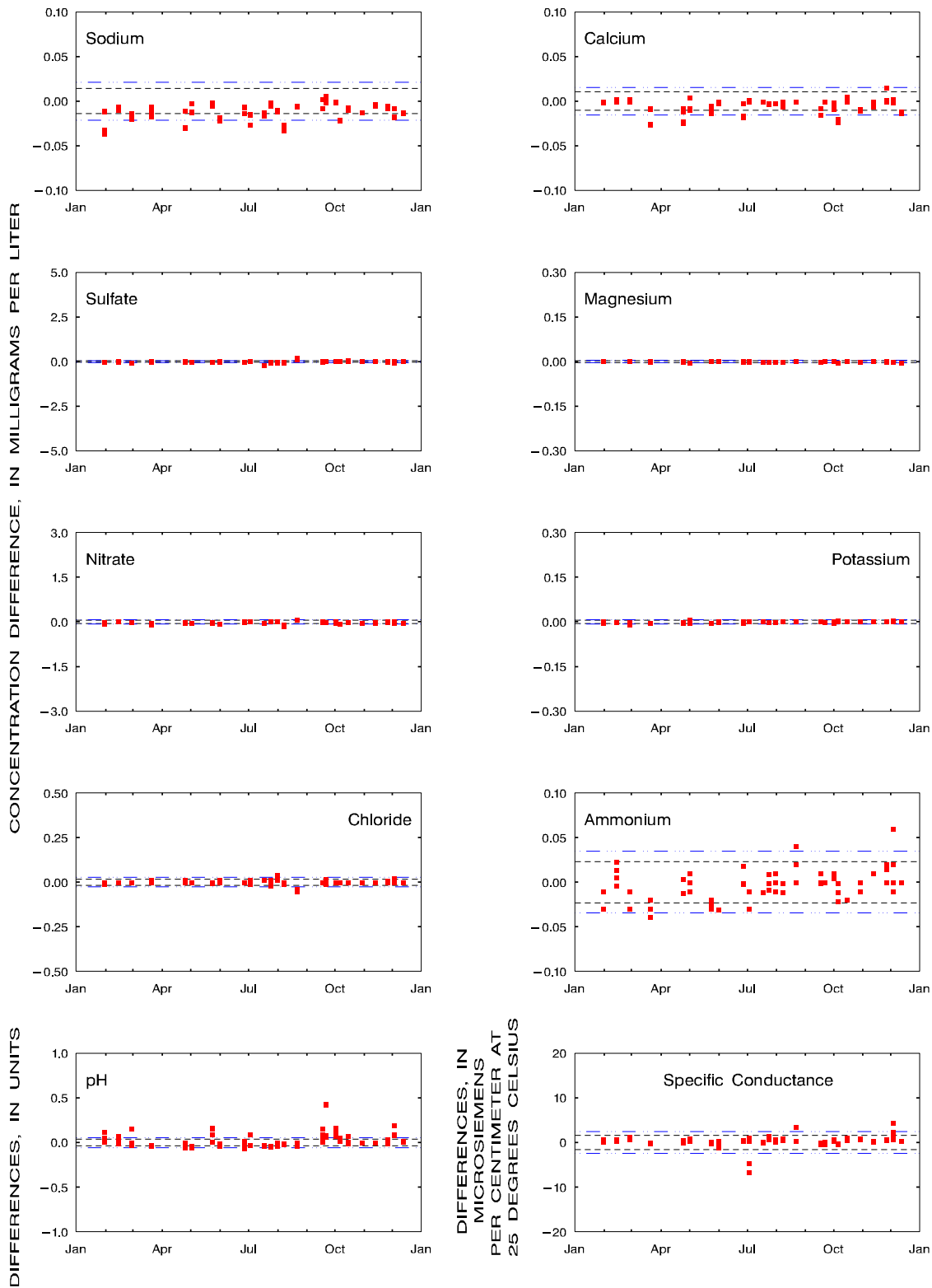
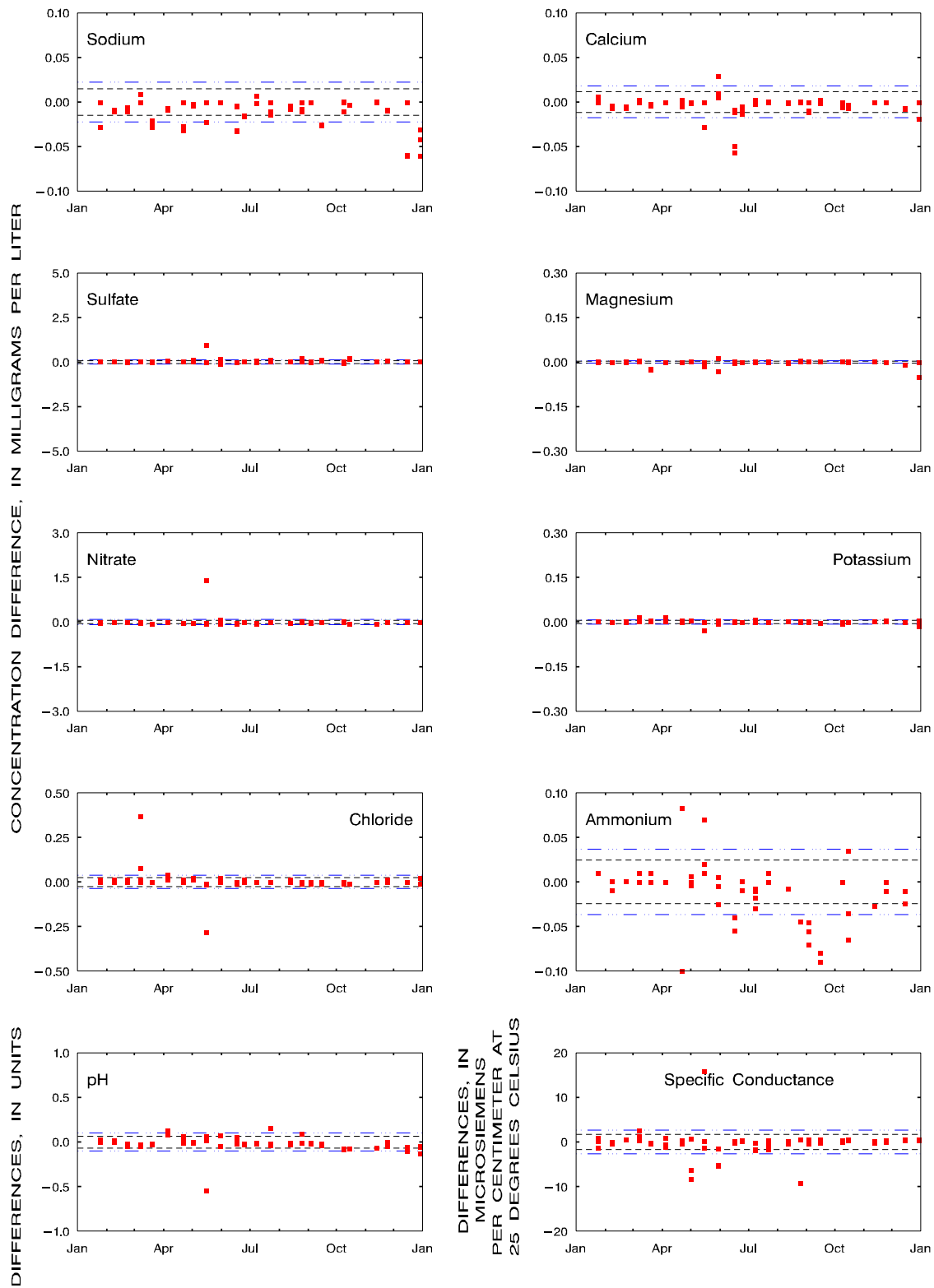


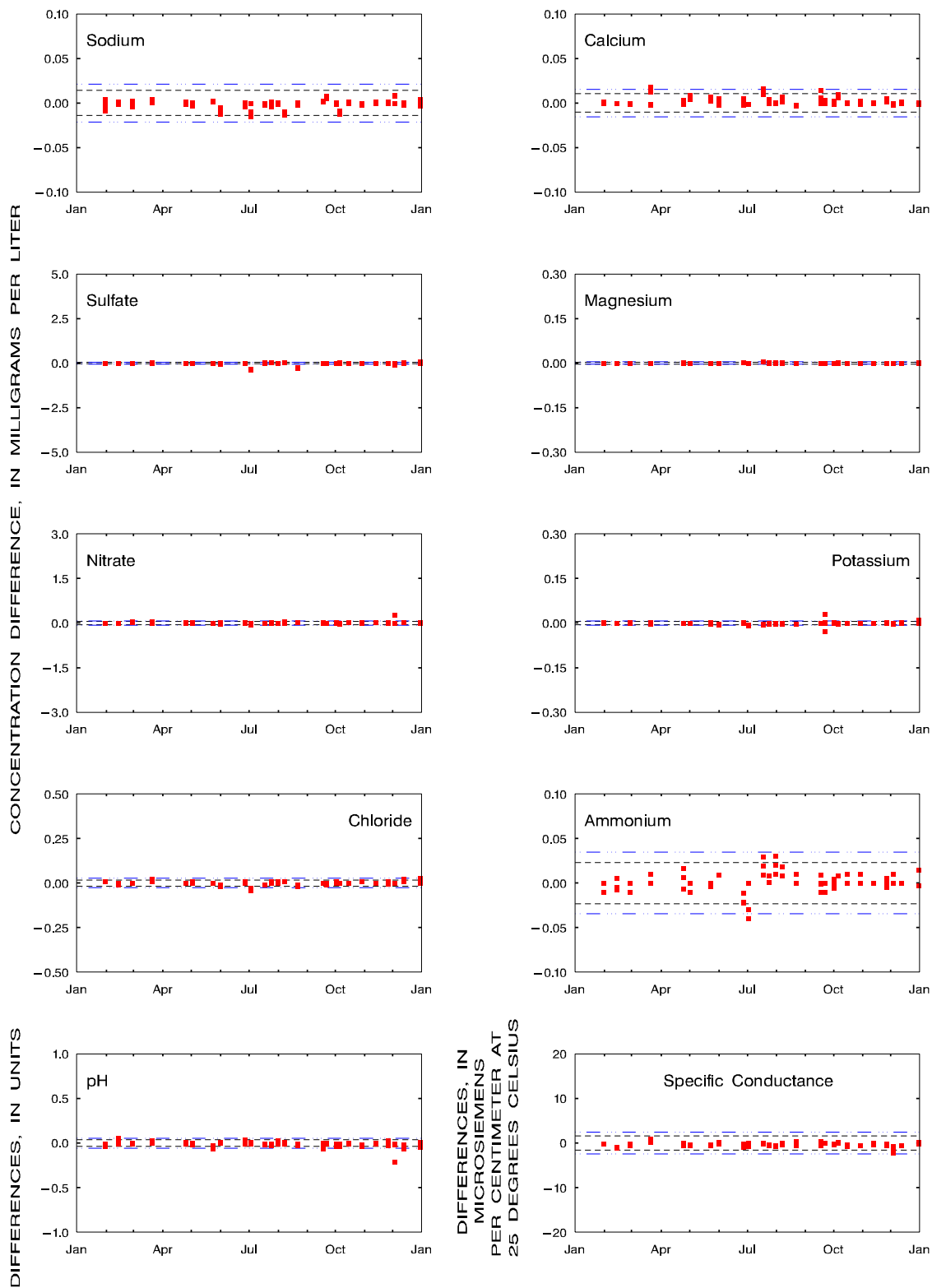
Figure 23. Difference between the measured value reported by QST Environmental and the median value calculated for all participating laboratories in the interlaboratory-comparison program during 1995. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.



EXPLANATION

- Warning limits (+2 and -2 F-pseudosigmas from zero difference line)
- · - · - Control limits (+3 and -3 F-pseudosigmas from zero difference line)

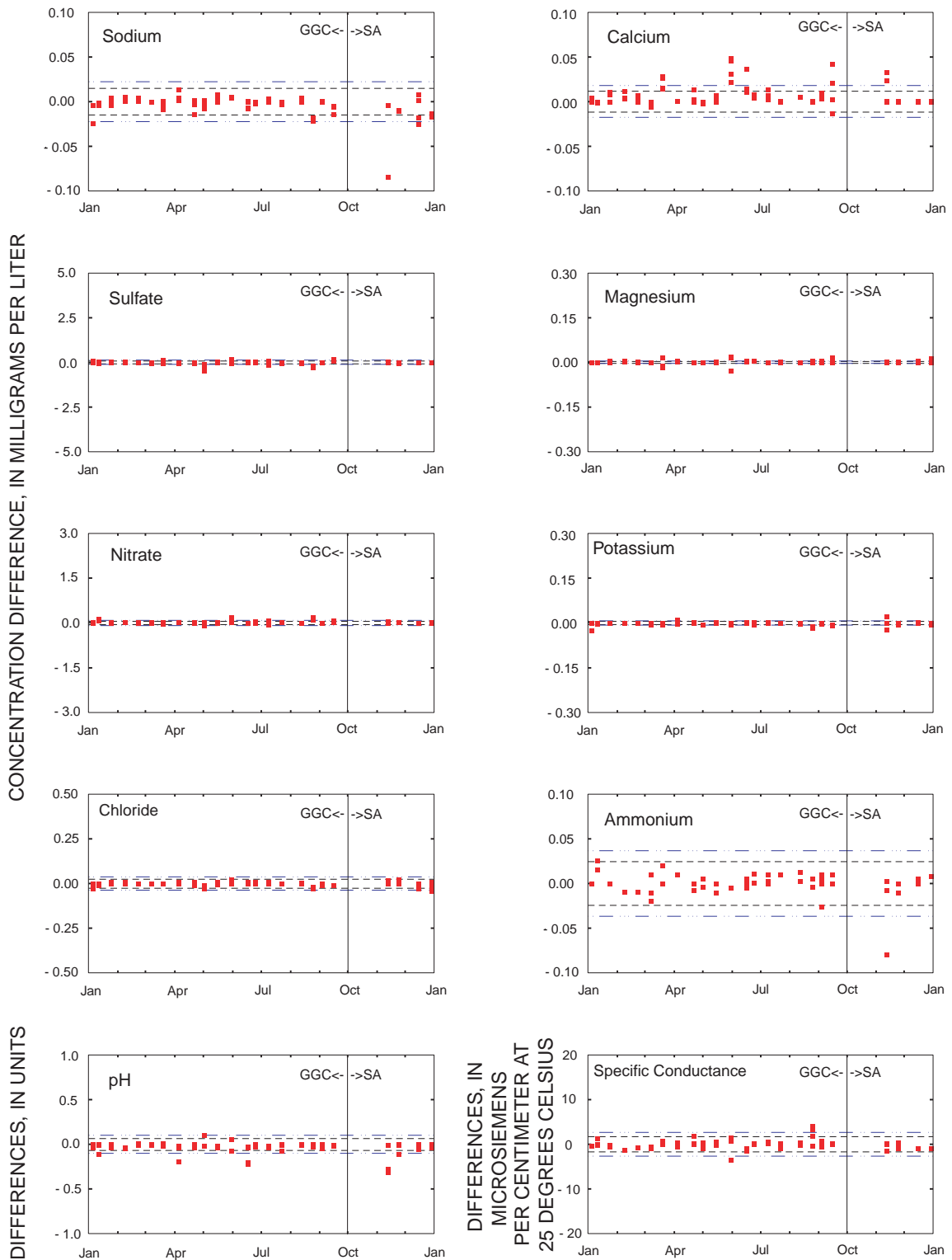
Figure 24. Difference between the measured value reported by QST Environmental and the median value calculated for all participating laboratories in the interlaboratory-comparison program during 1996. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.



EXPLANATION

- - - - - Warning limits (+2 and -2 F-pseudosigmas from zero difference line)
- · - · - Control limits (+3 and -3 F-pseudosigmas from zero difference line)

Figure 25. 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 1995. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.



EXPLANATION

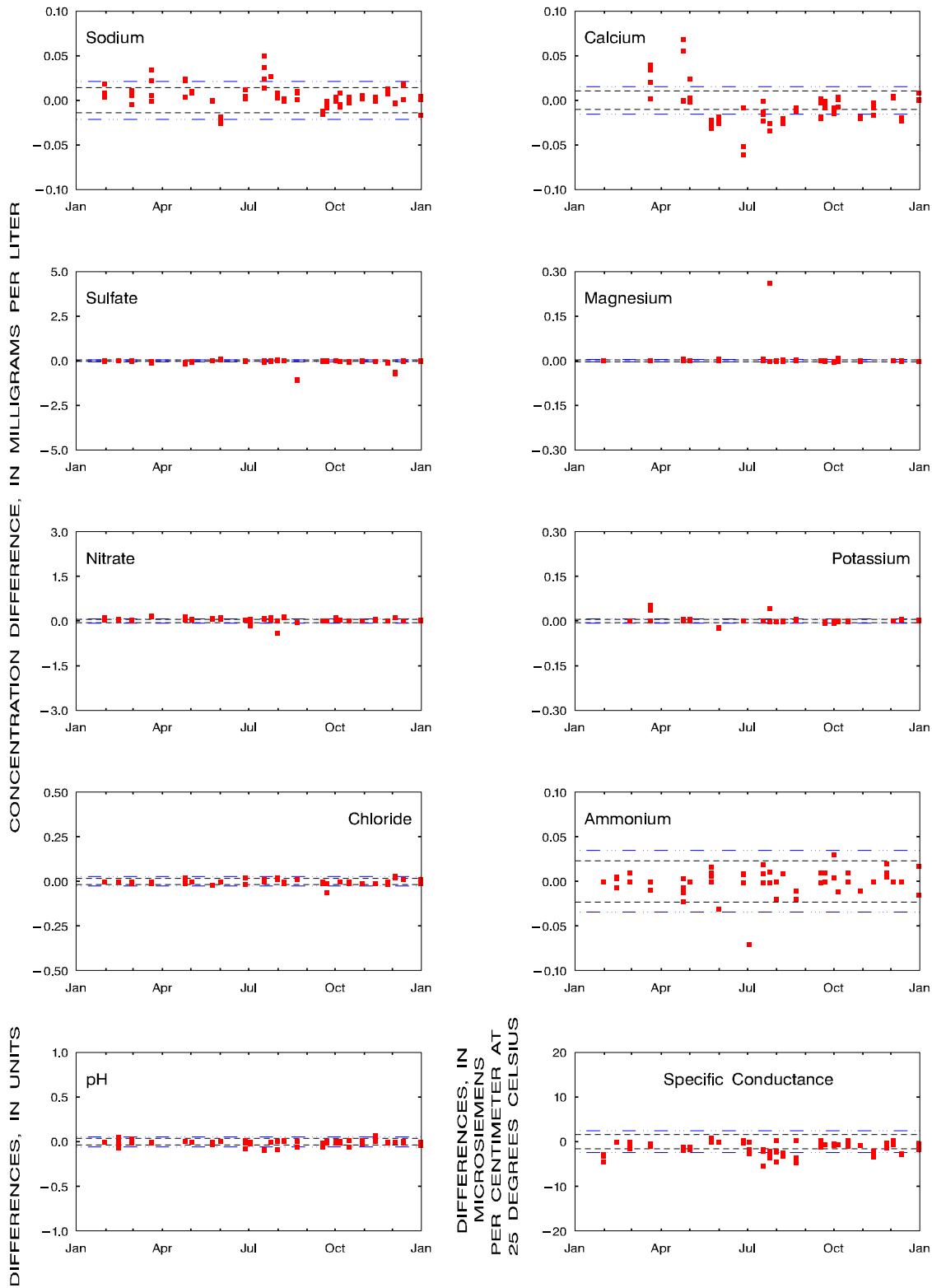
----- Warning limits (+ 2 and -2 F - pseudosigmas from zero difference line)

----- Control limits (+ 3 and - 3 F - pseudosigmas from zero difference line)

GGC Global Geochemistry Corporation, January 1, 1996 through September 30, 1996

SA Shepard Analytical Services, November 18, 1996 through December 31, 1996

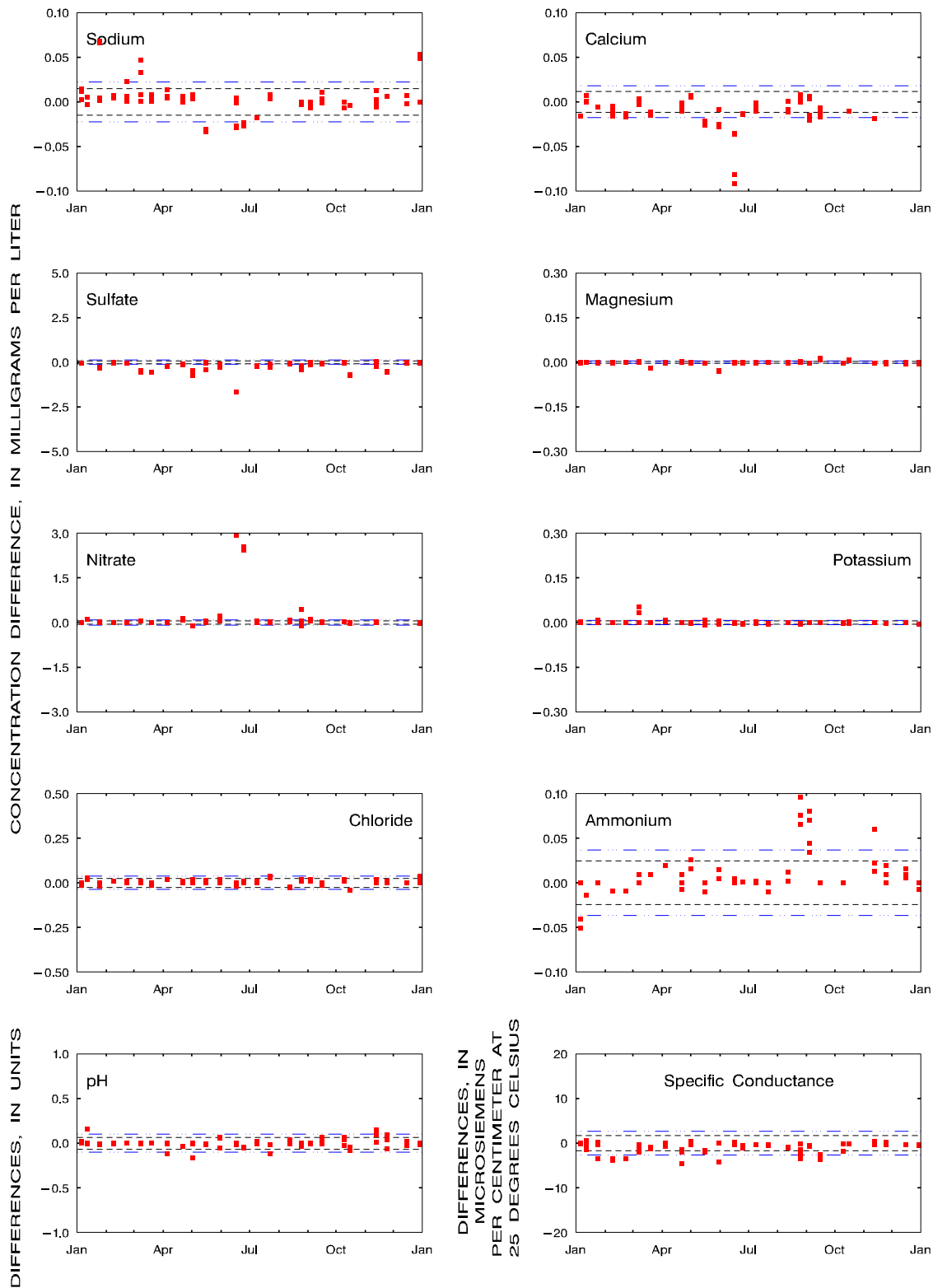
Figure 26. Difference between the measured value reported by the Global Geochemistry Corporation/Shepard Analytical Services and the median value calculated for all participating laboratories in the interlaboratory-comparison program during 1996. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.



EXPLANATION

- Warning limits (+2 and -2 F-pseudosigmas from zero difference line)
- · - · - Control limits (+3 and -3 F-pseudosigmas from zero difference line)

Figure 27. Difference between the measured value reported by the Ontario Ministry of the Environment, Water Quality Section, and the median value calculated for all participating laboratories in the interlaboratory-comparison program during 1995. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.



EXPLANATION

- Warning limits (+2 and -2 F-pseudosigmas from zero difference line)
- Control limits (+3 and -3 F-pseudosigmas from zero difference line)

Figure 28. Difference between the measured value reported by the Ontario Ministry of the Environment, Water Quality Section, and the median value calculated for all participating laboratories in the interlaboratory-comparison program during 1996. Samples reported as less than the detection limit (about 3 percent of the samples) were removed.

Ultrapure Deionized-Water Samples

In order to detect possible low-level sample contamination resulting from laboratory analyses, six Ultrapure deionized-water samples were included among the samples submitted to the participating laboratories throughout 1995. Table 19 shows the number of times each laboratory reported a concentration greater than the “standardized” minimum reporting limit in a solution not expected to contain detectable analyte concentrations. In order to facilitate the inter-comparison among laboratories using different reporting limits, all data for a given ion less than the largest minimum reporting limit used by any of the five participating laboratories were set equal to the largest minimum reporting limit. If the reporting limits were not standardized in this manner, a comparison among laboratories would be heavily influenced by differences in reporting limits. Laboratories with lower reporting limits would have a much higher incidence of “hits” for the deionized-water samples than laboratories with higher reporting limits. In 1995 and again in 1996, QST reported two values greater than the “standardized” reporting limit for ammonium. None of the other laboratories reported any ion values greater than the “standardized” reporting limit in either year (tables 19 and 20). Measured concentrations greater than the minimum reporting limit for the Ultrapure deionized-water samples is an indication of possible contamination.

Table 19. Number of analyte determinations greater than the largest minimum reporting limit used by any participating laboratory for each ion for the Ultrapure deionized-water samples during 1995

[CAL, Illinois State Water Survey, Central Analytical Laboratory; AES, Atmospheric Environment Service; QST, QST Environmental; MOE, Ontario Ministry of the Environment, Water Quality Section; GGC/SA, Global Geochemistry Corporation/Shepard Analytical]

Analyte	CAL	AES	QST	MOE	GGC
Calcium	0	0	0	0	0
Magnesium	0	0	0	0	0
Sodium	0	0	0	0	0
Potassium	0	0	0	0	0
Ammonium	0	0	2	0	0
Chloride	0	0	0	0	0
Nitrate	0	0	0	0	0
Sulfate	0	0	0	0	0

Table 20. Number of analyte determinations greater than the largest minimum reporting limit used by any participating laboratory for each ion for the Ultrapure deionized-water samples during 1996

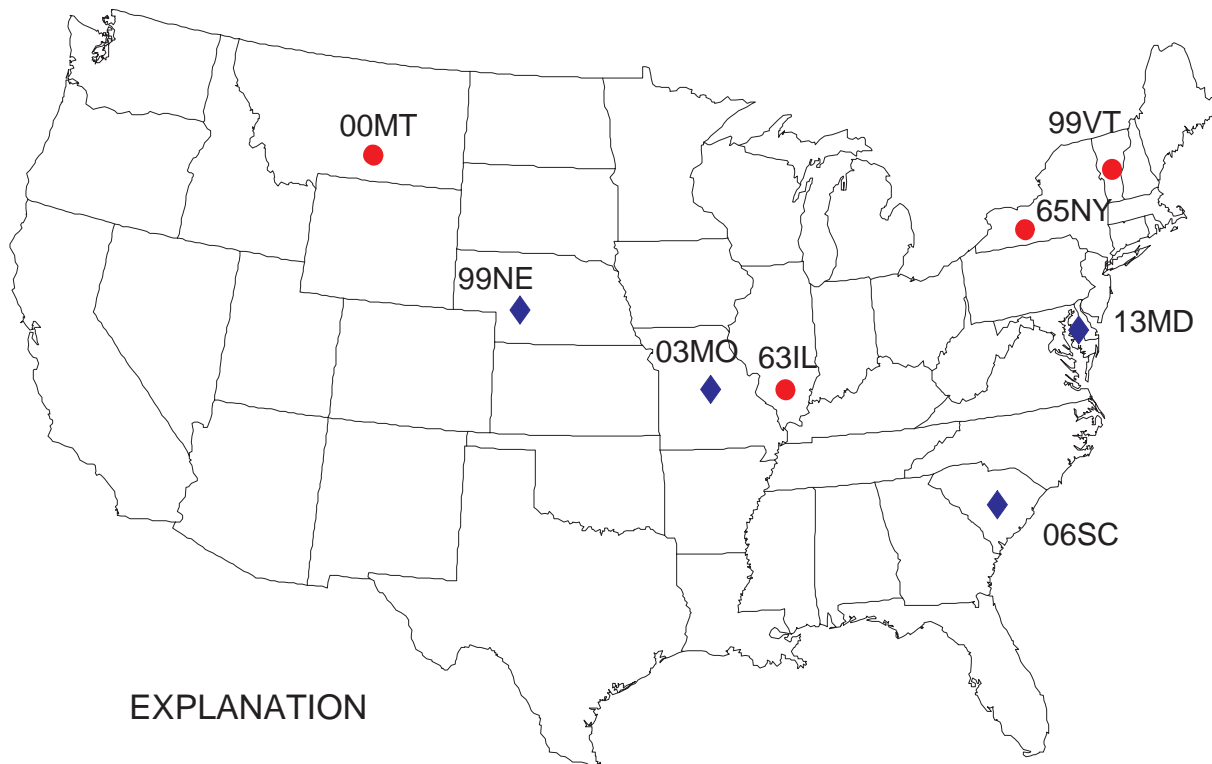
[CAL, Illinois State Water Survey, Central Analytical Laboratory; AES, Atmospheric Environment Service; QST, QST Environmental; MOE, Ontario Ministry of the Environment, Water Quality Section; GGC/SA, Global Geochemistry Corporation/Shepard Analytical]

Analyte	CAL	AES	QST	MOE	GGC/SA
Calcium	0	0	0	0	0
Magnesium	0	0	0	0	0
Sodium	0	0	0	0	0
Potassium	0	0	0	0	0
Ammonium	0	0	2	0	0
Chloride	0	0	0	0	0
Nitrate	0	0	0	0	0
Sulfate	0	0	0	0	0

Collocated-Sampler Program

The collocated-sampler program has been operational since October 1988 and provides a method of estimating the overall precision of the precipitation-monitoring system used by the NADP/NTN. Variability from the point of sample collection through storage of the data in the data base is included in this estimate of NADP/NTN precision (Gordon and others, 1997). Nilles and others (1991) provide a detailed description of the collocated-sampler program. Unlike 1994, when the collocated-sampler program was operated on a calendar-year basis because of special circumstances (Gordon and others, 1997), the collocated sites were operated on a water-year basis (October through September) in 1995 and 1996. Since the study began in 1988, collocated sites have been operated on a water-year basis every year except 1994.

New sites are selected for each year of the study and provide estimates of precision on a networkwide basis. Four sites participated in the collocated study between October 1, 1994, and September 30, 1995–water year 1995. In water year 1996, four new sites were selected for participation in the collocated study. The locations of sites participating in the collocated-sampler study in water years 1995 and 1996 are shown in figure 29.



EXPLANATION

◆ Collocated-sampler sites for water year 1995

Collocated Site Code	Original Site Code	Site Name
13MD	MD13	WYE, MARYLAND
03MO	MO03	ASHLAND WILDLIFE AREA, MISSOURI
99NE	NE99	NORTH PLATTE AGRICULTURAL EXPERIMENT STATION, NEBRASKA
06SC	SC06	SANTEE NATIONAL WILDLIFE REFUGE, SOUTH CAROLINA

● Collocated-sampler sites for water year 1996

Collocated Site Code	Original Site Code	Site Name
63IL	IL63	DIXON SPRINGS AGRICULTURAL CENTER, ILLINOIS
00MT	MT00	LITTLE BIGHORN BATTLEFIELD NATIONAL MONUMENT, MONTANA
65NY	NY65	JASPER, NEW YORK
99VT	VT99	UNDERHILL, VERMONT

Figure 29. Location of National Atmospheric Deposition Program/National Trends Network sites with collocated samplers in water years 1995-96.

Sites must meet preestablished criteria to be considered for the collocated study. NADP/NTN guidelines for site selection and installation (Bigelow, 1984) are used in the establishment of each collocated site. Site selection is made with the goal of distributing sites among diverse regional locations and precipitation regimes. To minimize data loss due to changes in personnel, only those sites with stable operational histories are considered. The lack of room at the site for collocated equipment is, unfortunately, another reason sites are sometimes dropped from consideration.

After the sites for the collocated-sampler program were selected, equipment was shipped by the USGS to each site, installed by USGS personnel with assistance from site personnel, and field tested by USGS personnel to ensure that the equipment was in good working order. The principal investigator for the collocated-sampler study inspects new collocated sites in either August or September before sampling begins at the site in October. Site inspection takes place immediately after equipment installation and before collection of the first sample. The site operator processes samples from each pair of collectors, according to 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 processing to both samples from the collocated-sampler site. All samples were analyzed as routine weekly NADP/NTN samples by the CAL.

Data from the original and collocated equipment were analyzed in two ways. For the purpose of site characterization (that is, determining the median sample chemistry or median precipitation), the data from the original and collocated sites were pooled. For the purpose of comparing an original site and a collocated site, the data from the original and collocated sites were analyzed for differences in 1995 and 1996. Data from an original site and a collocated site are formally referred to by the four character site code of the original site, followed by the four character site code of the collocated site. For instance, the Wye, Maryland, site is formally referred to as MD13/13MD. For this analysis, the data used were from wet-deposition samples with volume greater than 35 mL (laboratory type "W") that did not require dilution. Samples requiring dilution are inherently prone to a greater error component. Median concentrations for selected analytes in

weekly samples that were collected at the 1995 and 1996 collocated sites are depicted in figure 30 and figure 31, respectively. Figures 32 and 33 depict the median hydrogen-ion concentration, median specific conductance, median sample volume, and median precipitation depth for the collocated sites in 1995 and 1996.

Median sample chemistry varied considerably among sites, reflecting their diverse climate, human influence, and wet-deposition regimes. For example, the median annual chloride concentration is about 4 times higher at the two marine-affected sampling locations, Santee National Wildlife Refuge, South Carolina (SC06/06SC), and Wye, Maryland (MD13/13MD), than at the two inland sampling locations, Ashland Wildlife Refuge, Missouri (MO03/03MO), and North Platte Agricultural Experiment Station (NE99/99NE). The median annual ammonium concentration at NE99/99NE is more than double the median ammonium concentration at any of the other sites, reflecting the intensive livestock activity in the area of Nebraska where NE99/99NE is located; such activity is not found in the vicinity of MD13/13MD, MO03/03MO, or SC06/06SC. Sulfate, nitrate, and hydrogen-ion concentrations are generally highest in the northeastern United States (National Atmospheric Deposition Program, 1996). Reflecting this, the collocated site nearest the northeastern United States in 1995 (MD13/13MD) had the highest median sulfate and nitrate concentrations and the most acidic precipitation (highest median hydrogen-ion concentration) of any of the four 1995 collocated sites. The median hydrogen-ion concentration for MD13/13MD was nearly 10 times higher than the median hydrogen-ion concentration from NE99/99NE.

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 provided by the NADP Program Office (<http://nadp.sws.uiuc.edu/>). The weekly precipitation depth associated with each Belfort recording rain gage was used to calculate deposition values at the collocated sites. Concentration, in milligrams per liter, is multiplied by 10^{-1} times the rainfall depth in centimeters to yield deposition in kilograms per hectare. The variability in deposition amounts due to differences in rain-gage collection efficiency at collocated sites provides an estimate of the variability in deposition amounts at other NADP/NTN sites.

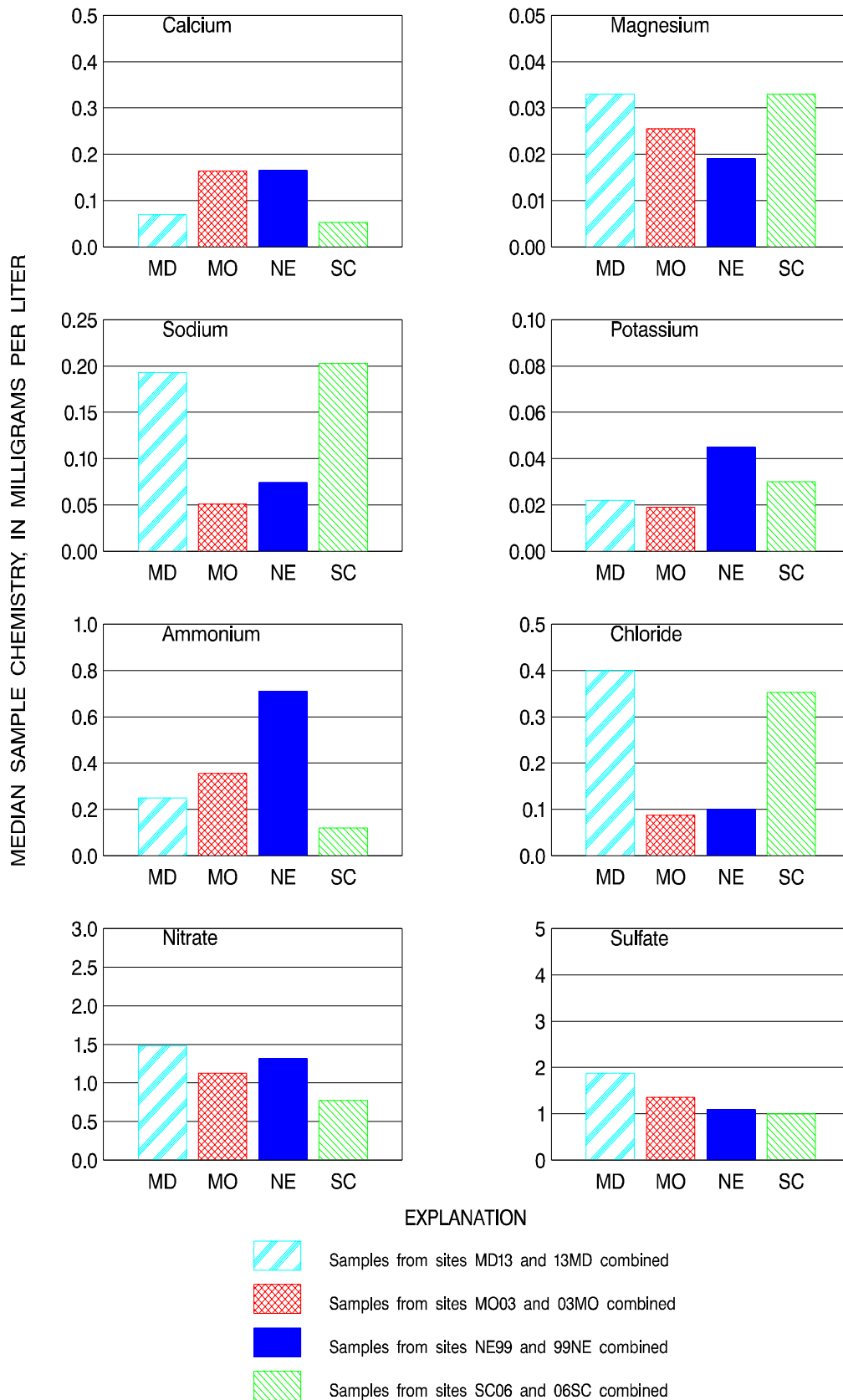


Figure 30. Median sample chemistry for selected analytes at four National Atmospheric Deposition Program/National Trends Network sites with collocated samplers in 1995.

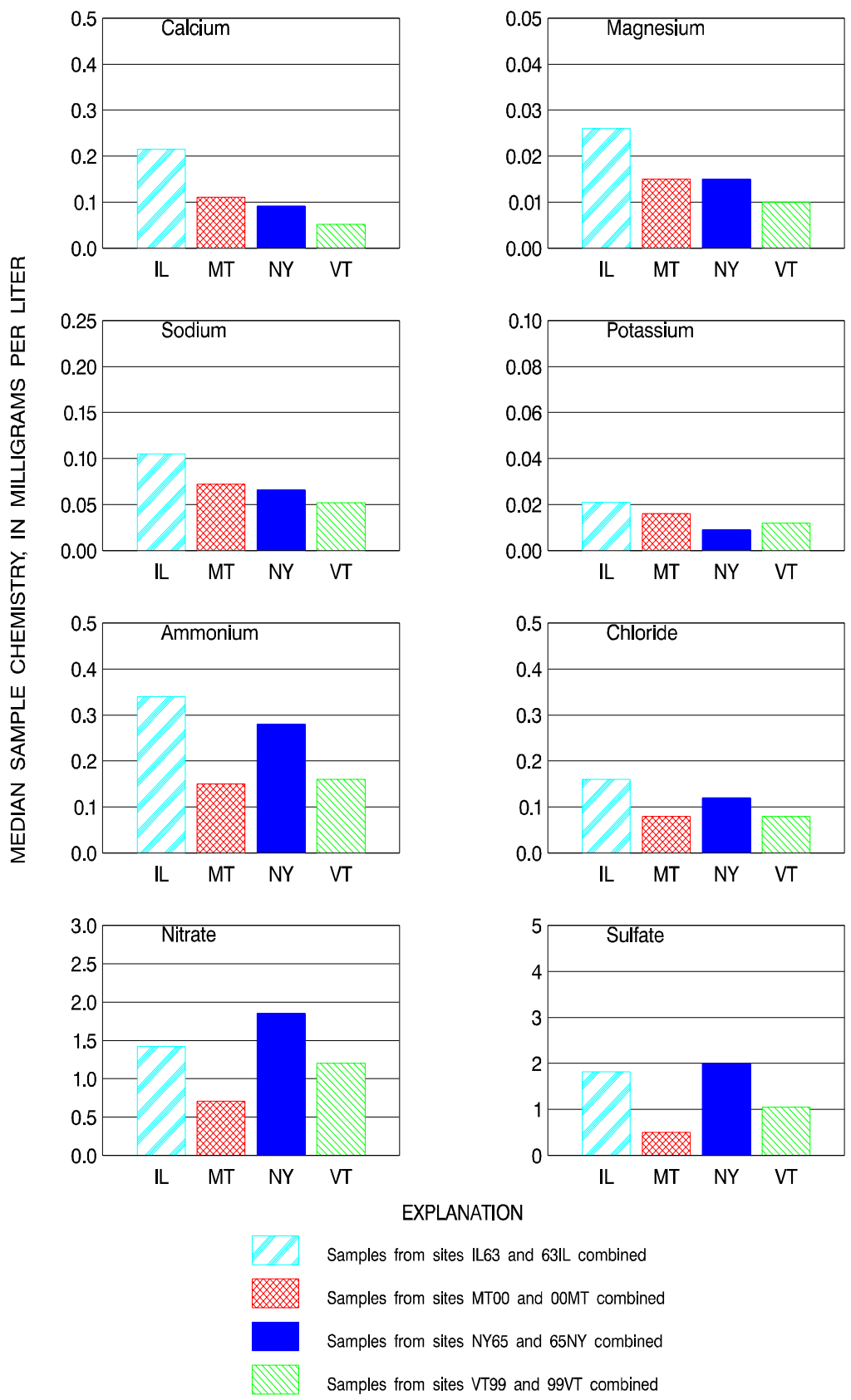


Figure 31. Median sample chemistry for selected analytes at four National Atmospheric Deposition Program/National Trends Network sites with collocated samplers in 1996.

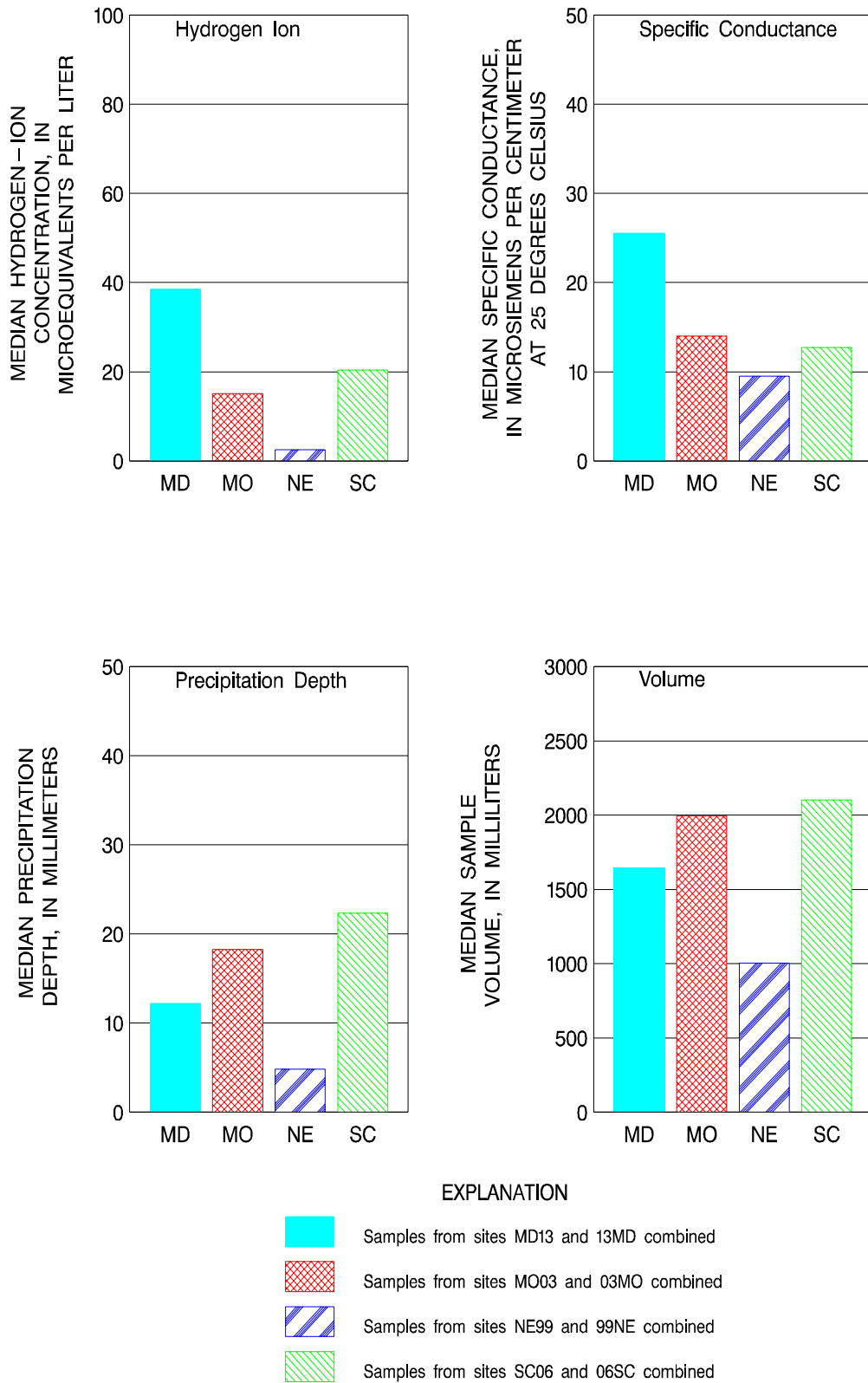


Figure 32. Median hydrogen-ion concentration, specific conductance, sample volume, and precipitation depth for four National Atmospheric Deposition Program/National Trends Network sites with collocated samplers in 1995.

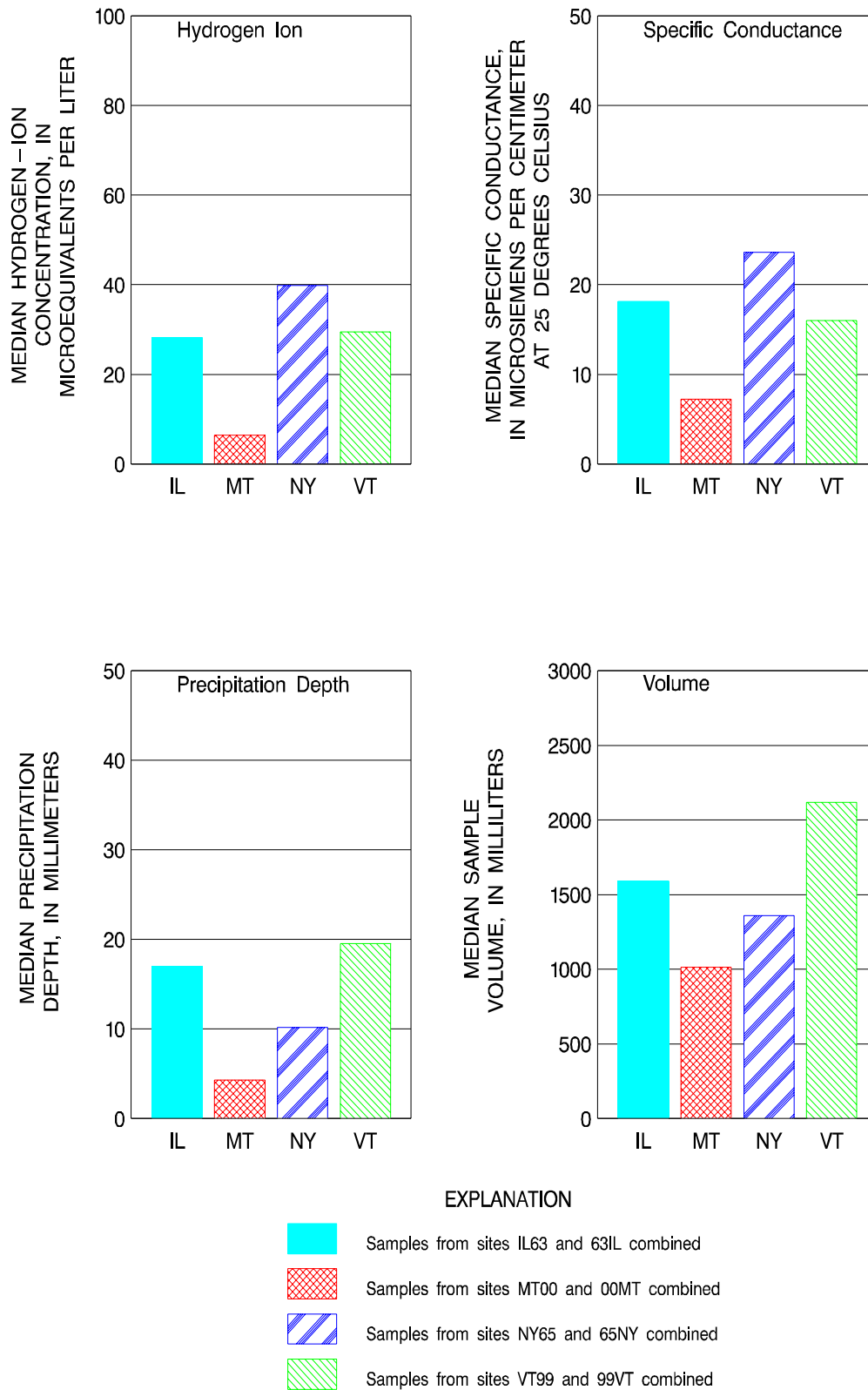


Figure 33. Median hydrogen-ion concentration, specific conductance, sample volume, and precipitation depth for four National Atmospheric Deposition Program/National Trends Network sites with collocated samplers in 1996.

In the analysis of collocated data, care was taken to select statistics that were meaningful in describing overall sampling precision and that were not overly sensitive to a few extreme values. Precision estimates for each site are calculated from the relative and absolute differences between the pairs of collocated samplers 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:

$$\text{Median relative error} = M | C_1 - C_2 / (C_1 + C_2) / 2 | \times 100,$$

and

$$\text{Median absolute error} = M | C_1 - C_2 |,$$

where

M = Median of all paired differences;

C₁ = Sample concentration, in milligrams per liter, from the original precipitation sampler, or deposition, in kilograms per hectare, from the original precipitation sampler and rain gage; and

C₂ = Sample concentration, in milligrams per liter, from the collocated precipitation sampler, or deposition, in kilograms per hectare, 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 1995, sites MD13/13MD, MO03/03MO, and SC06/06SC each had 44 valid sample pairs that were used to calculate precision estimates. (A sample pair refers to the collection of a valid sample from both the original and collocated sampler.) NE99/99NE had 42 valid sample pairs. In 1996, there were generally fewer sample pairs: only 37, 38, and 39 valid sample pairs were available from NY65/65NY, MT00/00MT and IL63/63IL, respectively. The other site that operated in 1996, VT99/99VT, had the highest number of valid samples pairs (47) of any collocated site operated in 1995-96. Typically, sites located in more arid climates have fewer valid sample pairs than sites located in humid climates (Gordon and others, 1997). Surprisingly, the number of valid sample pairs was not strongly correlated with the annual amount of precipitation at 1995-96 collocated sites. For example, the sampling locations with the least amount of precipitation, MT00/00MT and NE99/99NE, had a number of

valid samples comparable to SC06/06SC, a sampling location with much greater precipitation.

In 1995, the median relative error (MRE) for chemical determinations was the smallest for nitrate concentration and was less than 5 percent at each of the four sites. The MRE's for sulfate in 1995, at 6 percent or less, were almost as small as those measured for nitrate. Upon converting concentration amounts to deposition totals, the MRE's for most constituents increase (figs. 34 and 35). For clarity of information shown in the graphs, only the four digit codes of the original sites are displayed in figures 34 and 35 in lieu of the formal convention of referring to data from an original site and a collocated site by the four character site code of the original site followed by the four character site code of the collocated site. For some analytes, the magnitude of the MRE for deposition totals is more than twice the magnitude of the MRE for concentration (for example, sulfate at NE99/99NE).

General agreement of precision was observed for specific conductance, sample volume (measured from the Aerochem Metrics wet-deposition collectors), and precipitation depth (measured from the Belfort rain gages). The MRE's for these properties were uniformly small (less than 10 percent) and fairly consistent at all four 1995 sites despite differences in typical sample chemistry and precipitation amounts among the sites. More variability in the MRE's for specific conductance, sample volume, and precipitation depth was measured at the collocated sites in 1996 than in 1995. For example, the precipitation depth MRE ranged from 5 to 15 percent at the four collocated sites in 1996. Graphical depictions of all MRE's for collocated sites are shown for concentration, for deposition, and for the physical measurements of sample volume and precipitation depth in figures 34 and 35.

As in past years, the MRE's were larger and more variable from site to site for cations and particularly for cations whose concentrations typically were near laboratory detection limits. Estimates of network precision covering several previous years of collocated sampling are given in Nilles and others (1993). The MRE's for cations exceeded 7 percent at most sites in 1995 and 1996 and frequently exceeded 20 percent. Assuming that random contamination is independent of sample concentration and that laboratory error increases as analyte concentration decreases, an increase in relative error at sites with lower concentrations would be expected. For example, the MRE for potassium concentration, an analyte detected at very low levels in precipitation, ranged from 18.0 percent to 40.1 percent at the 1995-96 collocated sites.

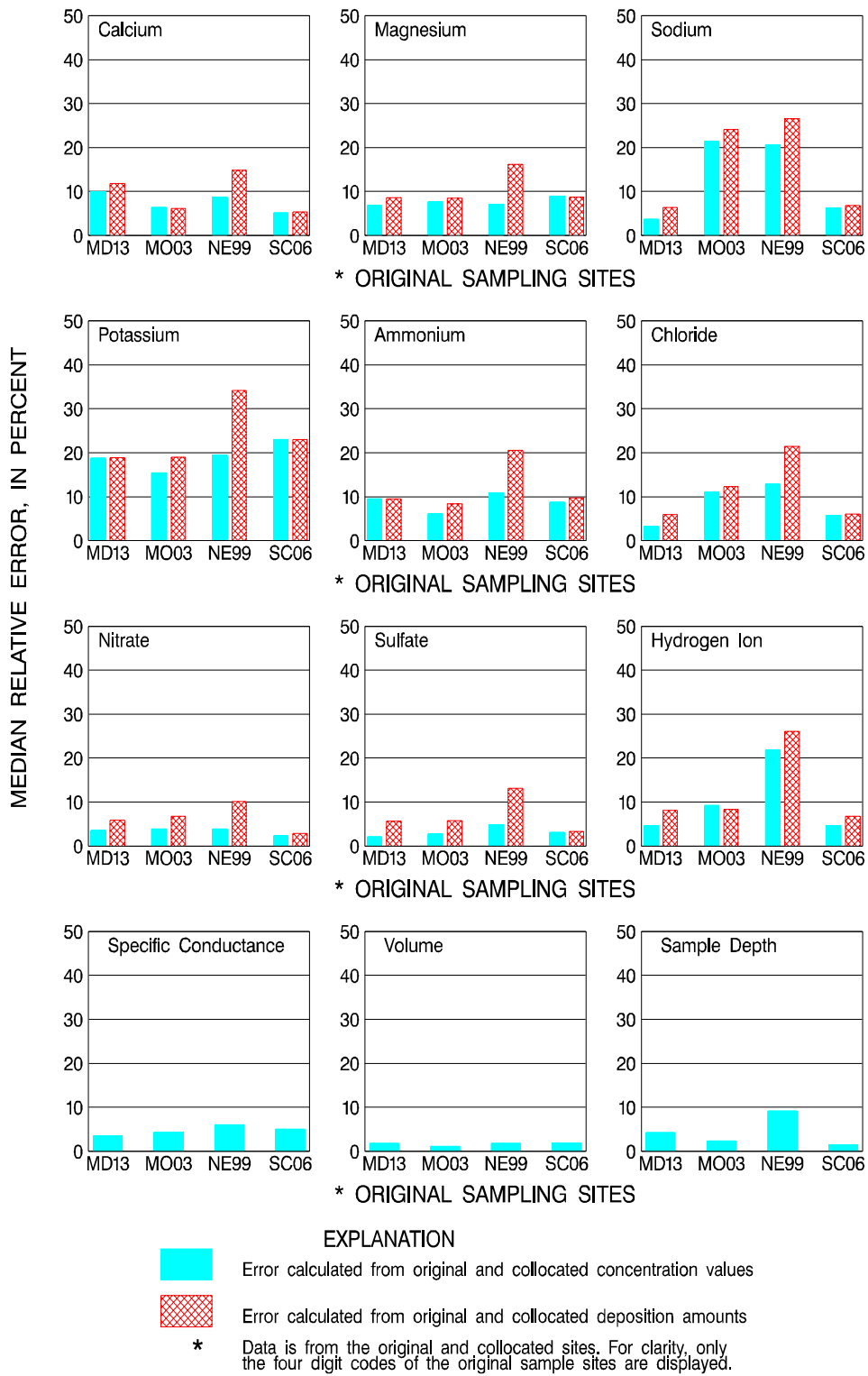


Figure 34. Median relative error for analyte concentration, deposition, and other physical parameters for weekly samples from collocated wet-dry precipitation collectors and precipitation depth from collocated rain gauges in 1995. All data are in percent.

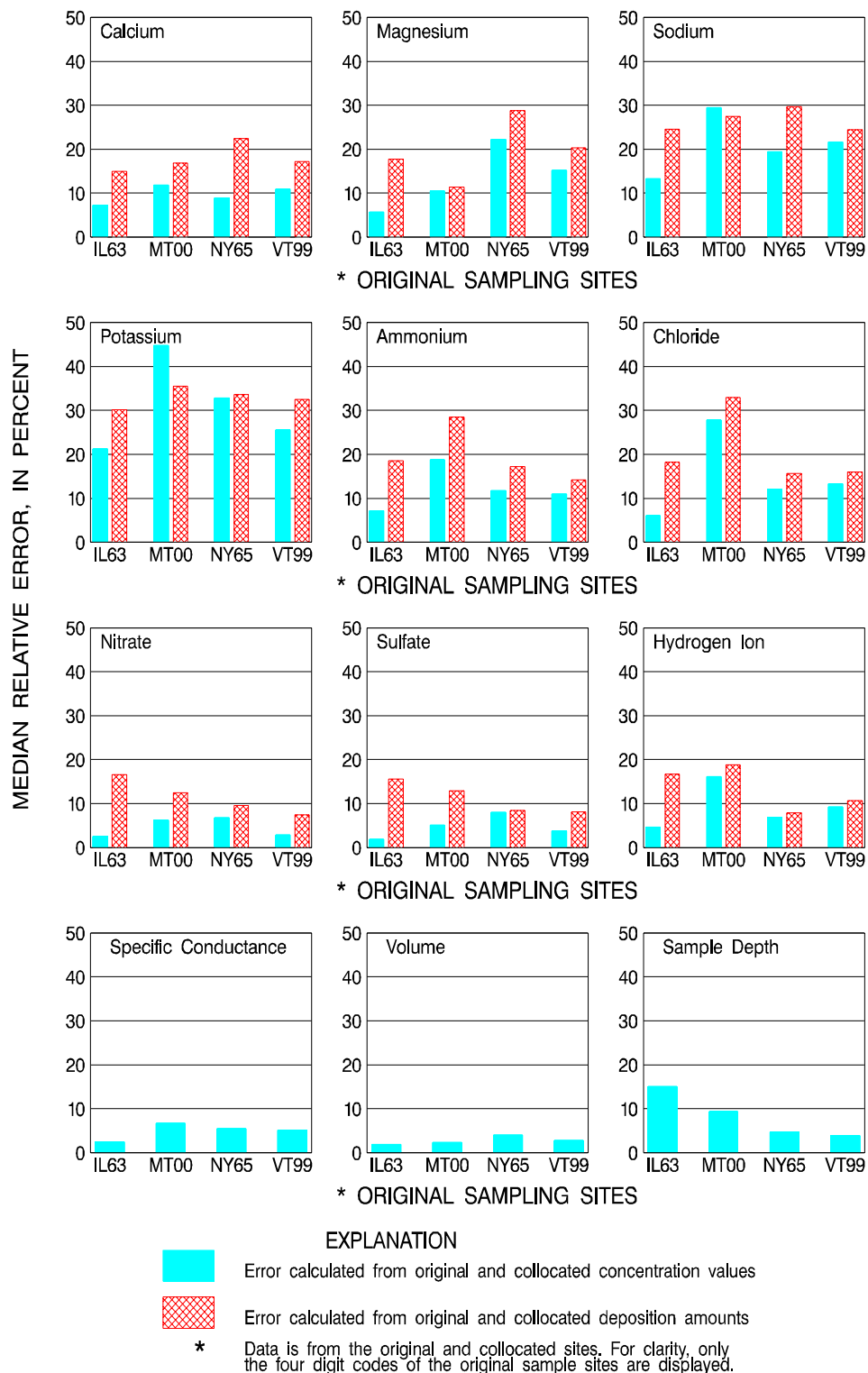


Figure 35. Median relative error for analyte concentration, deposition, and other physical parameters for weekly samples from collocated wet-dry precipitation collectors and precipitation depth from collocated rain gages in 1996. All data are in percent.

Consistent with the results from previous years of this study, 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 sites with the lowest median hydrogen-ion concentrations had the highest median relative errors associated with their paired-sample analyses. The MRE's for hydrogen-ion concentration were less than 10 percent at sites with median hydrogen-ion concentrations of 20 µeq/L or greater. For sites with median hydrogen-ion concentrations less than 20 µeq/L, the MRE's exceeded 15 percent (figs. 32 through 35).

Collocated-analyte precision estimates in tables 21 and 22 can be compared to analytical precision estimates calculated in the same manner from 90 sample pairs submitted in 1995 and 1996 to the CAL as part of the interlaboratory-comparison program. The interlaboratory-comparison program is 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.

Table 21. Median absolute error for analyte concentration and deposition values determined from weekly collocated precipitation samples and replicate samples measured by the Illinois State Water Survey, Central Analytical Laboratory in 1995

[All units in milligrams per liter except: hydrogen ion, in microequivalents per liter; specific conductance, in microsiemens per centimeter at 25 degrees Celsius; and precipitation depth, in millimeters; CAL, Illinois State Water Survey, Central Analytical Laboratory; --, no data]

Analyte	Sampling site								
	Wye, Maryland		Ashland Wildlife Area, Missouri		North Platte Agricultural Experiment Station, Nebraska		Santee National Wildlife Refuge, South Carolina		CAL
	Concentration	Deposition	Concentration	Deposition	Concentration	Deposition	Concentration	Deposition	Concentration
Calcium	0.009	0.003	0.011	0.009	0.022	0.009	0.004	0.004	0.000
Magnesium	0.002	0.001	0.002	0.002	0.003	0.002	0.002	0.002	0.000
Sodium	0.009	0.009	0.009	0.007	0.014	0.005	0.012	0.017	0.002
Potassium	0.004	0.002	0.003	0.002	0.009	0.004	0.006	0.005	0.001
Ammonium	0.020	0.010	0.020	0.017	0.090	0.038	0.020	0.019	0.000
Chloride	0.010	0.015	0.010	0.007	0.010	0.005	0.020	0.016	0.000
Nitrate	0.046	0.043	0.055	0.065	0.055	0.042	0.020	0.025	0.010
Sulfate	0.050	0.045	0.045	0.058	0.055	0.046	0.030	0.032	0.000
Hydrogen ion	1.638	1.504	1.302	1.145	0.335	0.120	1.272	1.394	0.361
Specific conductance	1.000	--	0.800	--	0.800	--	0.600	--	0.100
Precipitation depth	0.020	--	0.020	--	0.030	--	0.020	--	--

Table 22. Median absolute error for analyte concentration and deposition values determined from weekly collocated precipitation samples and replicate samples measured by the Illinois State Water Survey, Central Analytical Laboratory in 1996

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

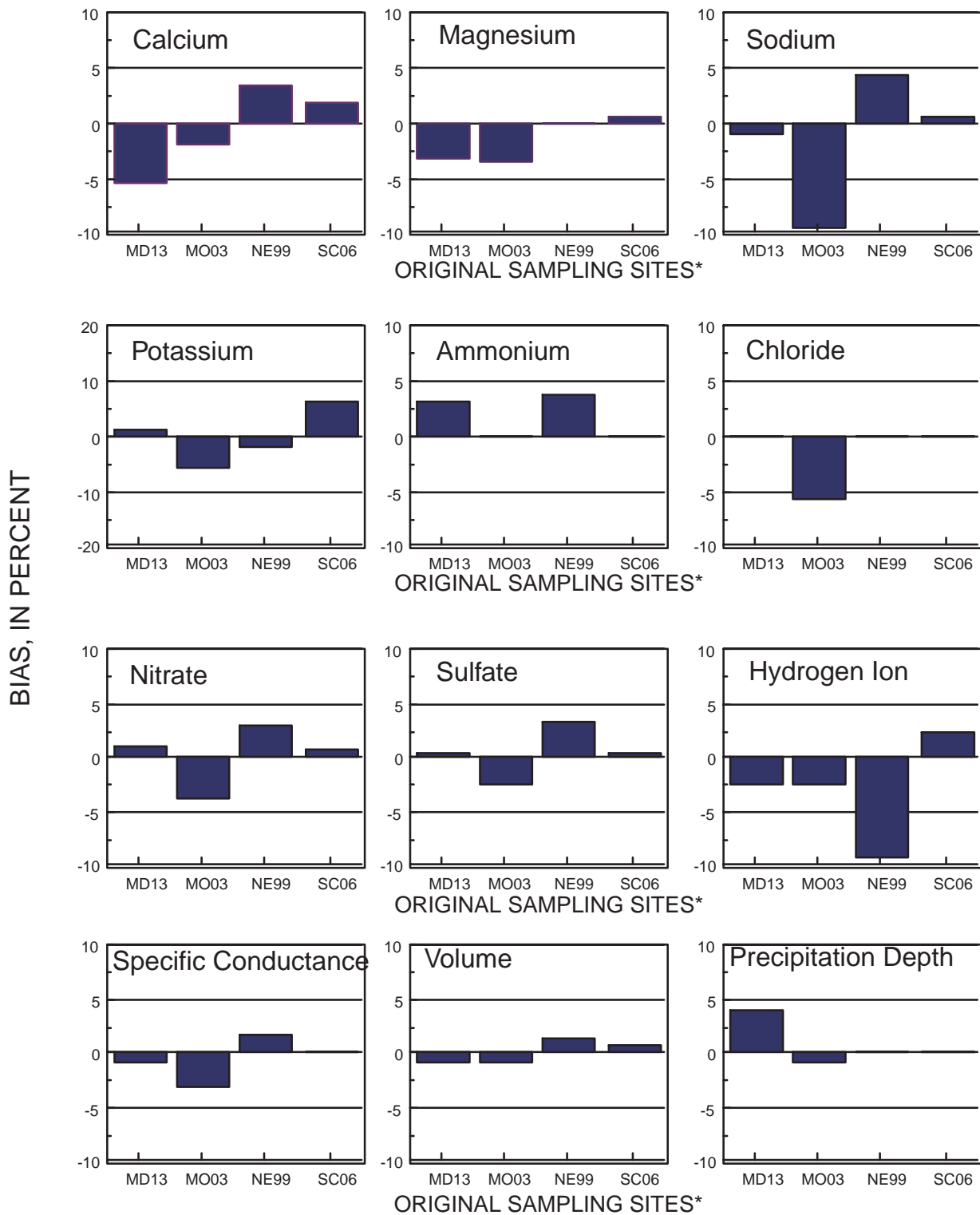
Analyte	Sampling site								
	Dixon Springs Agricultural Center, Illinois		Little Bighorn Battlefield National Monument, Montana		Jasper, New York		Underhill, Vermont		CAL
	Concentration	Deposition	Concentration	Deposition	Concentration	Deposition	Concentration	Deposition	Concentration
Calcium	0.017	0.023	0.013	0.005	0.016	0.011	0.007	0.007	0.000
Magnesium	0.002	0.003	0.002	0.001	0.003	0.001	0.002	0.002	0.000
Sodium	0.012	0.018	0.020	0.003	0.013	0.006	0.012	0.009	0.001
Potassium	0.004	0.003	0.006	0.001	0.003	0.002	0.003	0.002	0.001
Ammonium	0.025	0.047	0.055	0.012	0.040	0.023	0.020	0.012	0.000
Chloride	0.010	0.021	0.020	0.004	0.020	0.011	0.010	0.009	0.000
Nitrate	0.035	0.174	0.060	0.021	0.140	0.104	0.045	0.057	0.005
Sulfate	0.040	0.231	0.035	0.010	0.100	0.132	0.050	0.052	0.010
Hydrogen ion	1.340	3.244	0.840	0.152	2.688	2.634	2.373	2.695	0.289
Specific conductance	0.500	--	0.500	--	1.450	--	0.900	--	0.100
Precipitation depth	0.140	--	0.010	--	0.020	--	0.030	--	--

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 in the interlaboratory comparison program, typically accounted for between one-sixth to one-fourth 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 meaningful if the laboratory error term was calculated from a number of replicate samples collected at sites with similar hydrogen-ion concentration values.

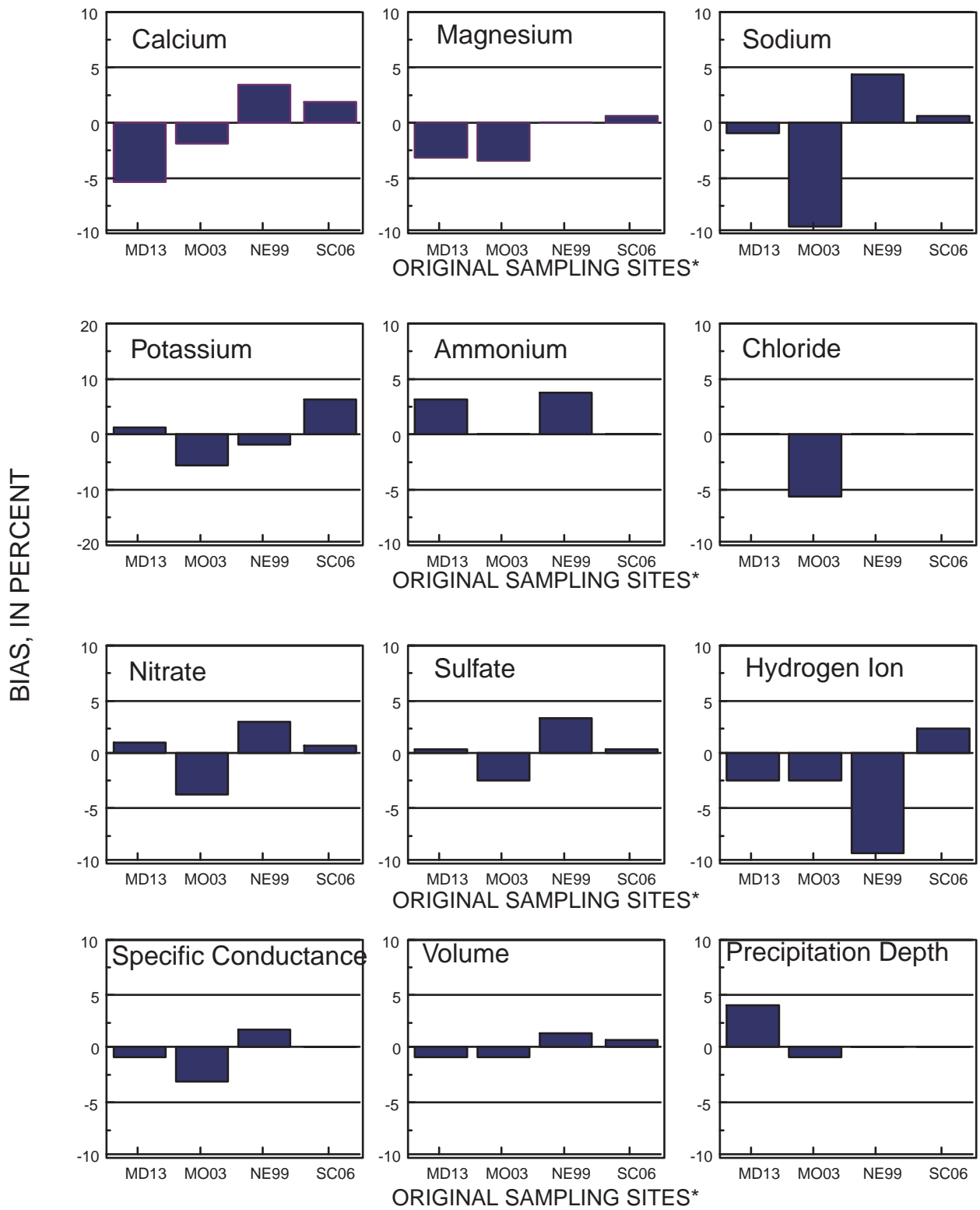
Bias was evaluated for each site and analyte by using the median signed difference between collocated-sample concentrations (figs. 36 and 37). Bias estimates for sample volume from the precipitation

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 author attributes bias in the data-set pairs to systematic differences in: (1) sampler response, (2) sample collection, and (3) sample handling before 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 collocated sites was attributed to good precision and low bias associated with the collectors used in 1995 and 1996. The small amount of bias that was associated with one of the collectors was usually due to small differences in lid opening and closing rates caused by sensor differences. Bias in sample volume between collectors varied from -1.5 to +3.5 percent at collocated sites operated during 1995 or 1996. These results are not as good as the results from the 1994 collocated program but are more in agreement with the results from previous years in the collocated program when bias in sample volume was as large as -7.0 percent and frequently exceeded ± 1.5 percent.



* Data is from the original (C_1) and collocated (C_2) sites. For clarity, only the four digit code of the original sampling sites is displayed. Bias in Percent = $(C_1 - C_2) / (C_1 + C_2 / 2) \times 100$.

Figure 36. Bias for analyte concentration, deposition, and other physical parameters for weekly samples from collocated wet-dry precipitation collectors and precipitation depth from collocated rain gages in 1995. All data are in percent.



* Data is from the original (C_1) and collocated (C_2) sites. For clarity, only the four digit code of the original sampling sites is displayed. Bias in Percent = $(C_1 - C_2) / (C_1 + C_2 / 2) \times 100$.

Figure 37. Bias for analyte concentration, deposition, and other physical parameters for weekly samples from collocated wet-dry precipitation collectors and precipitation depth from collocated rain gages in 1996. All data are in percent.

SUMMARY

During 1995 and 1996, the U.S. Geological Survey used four programs 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 study numbers 35 through 38 were conducted between May of 1995 and November of 1996. As in previous years, these studies were made on a semiannual basis. In the four studies, the percentage of site operators that responded on time and that met the accuracy goals ranged from 87.5 to 94.6 percent; about 94 to 98 percent of the site operators met the accuracy goals for specific conductance in these same studies. The solutions used in the intersite comparison program are designed to simulate natural rainwater and are prepared to replicate the wide range of hydrogen-ion concentration found in natural precipitation samples throughout the United States. In 1995-96, intersite samples were prepared with median pH values that ranged from 4.95 in study number 35 to 4.22 in study number 38.

For the blind-audit program, the Wilcoxon signed-rank test and the paired t-test were used to determine if significant statistical differences existed between the analyte concentrations measured in paired blind-audit samples. The paired t-test is based on blind-audit samples that are paired analyses, whereas the Wilcoxon signed-rank test is based on ranks instead of the actual data, but assumes the data consist of random, independent samples. One part of the blind-audit sample was subject to all of the normal onsite handling and processing steps to which a regular weekly precipitation sample is subject, whereas the other part received only minimal handling. The change in network sample-shipment protocol from 13-L buckets to 1-L bottles in 1994

(and the corresponding change in the blind-audit procedures) continued to affect the results of the blind-audit program in 1995 and 1996. Before the protocol change, statistically significant positive bias between the intensively handled bucket portion and the minimally handled bottle portion of the blind-audit sample was routinely observed. During 1995-96, the paired t-test indicated significant ($\alpha=0.05$) positive bias for four or fewer analytes each year: hydrogen ion and specific conductance in 1995 and calcium, magnesium, potassium, and sulfate in 1996. Significant ($\alpha=0.05$) negative bias was determined using the paired t-test for ammonium and sodium in 1995 and 1996.

The Wilcoxon signed-rank test for bias indicated positive bias for ammonium in 1995 ($\alpha=0.05$), but this same test indicated that none of the analytes were biased significantly ($\alpha=0.05$) in 1996. During 1995-96, the median paired differences between the bucket and bottle portions ranged from -0.020 mg/L for ammonium to +0.006 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 minus bottle data pair. The median relative percent bias for hydrogen ion ranged from 0.00 percent in 1995 to 2.19 percent in 1996, indicating virtually no change 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 was miniscule, ranging from 1.25 percent in 1995 to 0.00 percent in 1996. In 1995 and 1996, the median relative percent difference was within a range of -5 to +5 percent for all major ions, except ammonium and sodium. The magnitude of the median relative percent bias for sodium continued to decrease slightly in 1995 and 1996 (-7.99 percent in 1995, and -7.00 percent in 1996), compared to -10.96 percent in 1994.

During 1995 and 1996, the median relative percent bias values for ammonium were -9.72 and -12.50 percent, respectively. The absolute percent bias values were similar in magnitude to the relative percent bias values for calcium, magnesium, nitrate, sulfate, hydrogen ion, and specific conductance. The absolute percent bias was much larger than the relative percent bias for ammonium, chloride, potassium, and sodium.

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 1995 and again

in 1996 to test volume effects on paired sample results. The use of different sample volumes allowed the determination of whether a relation existed between the volume collected in the bucket and the differences between the analyte amounts in the bucket and bottle portions of the blind-audit sample. Results of a Kruskal-Wallis test indicated no significant ($\alpha=0.05$) difference in bucket minus bottle differences on a mass per bucket basis for nitrate in 1995 and 1996, whereas statistically significant ($\alpha=0.05$) differences were determined in 1995 and 1996 for magnesium, sodium, ammonium, and chloride. The magnitude of the negative bias of sodium, ammonium, and chloride in units of mass increased with increasing sample volume.

In 1995 and 1996, sodium, ammonium, nitrate, and chloride were reported at concentration levels that exceeded the method detection limit in more than one-half of the Ultrapure deionized-water samples submitted each year as part of the blind-audit program. Sodium was detected at levels greater than the method detection limit in all 15 of the Ultrapure samples used in 1995 and 1996.

In 1995, results of the Friedman test indicated significant ($\alpha=0.05$) differences in analyte measurements for calcium, potassium, sulfate, nitrate, and hydrogen ion among the five laboratories that participated in the interlaboratory comparison program. In 1996, the Friedman test indicated significant ($\alpha=0.05$) differences in analyte measurements for potassium, ammonium, chloride, sulfate, nitrate, and hydrogen ion. Cation precision estimates at the 50th percentile exhibited less variability than anions, 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. All participating laboratories had median absolute differences that were less than or equal to 0.004 mg/L for cations during 1995-96. Anion precision estimates at the 50th percentile exhibited greater variability among laboratories than observed for the cations. For the anions, all of the participating laboratories in 1995-96 had median absolute differences that were less than or equal to 0.015 mg/L.

In order to detect possible low-level sample contamination resulting from laboratory analyses, six Ultrapure deionized-water samples were included among the samples submitted to the participating laboratories in 1995 and 1996. For the purpose of comparing deionized analyses uniformly, reporting

limits for all five laboratories were standardized: if a minimum reporting limit was lower than the reporting limit used by the CAL for a certain analysis, the higher reporting limit used by the CAL was substituted. The CAL, AES, GGC, and MOE did not detect concentrations greater than the "standardized" reporting limits for the six Ultrapure samples for any analytes. The QST reported two concentrations greater than the "standardized" reporting limit for ammonium in 1995 and again in 1996.

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 concentration and deposition of the ionic constituents. 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 was greater for cations, with median relative error exceeding 7 percent at most sites. As in previous years, the precision for hydrogen-ion 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. Bias was not a major component of collocated results; bias in collocated measurements accounted for less than 20 percent of the overall error in collocated measurements. By comparing results from the interlaboratory program (replicate natural samples analyzed at the CAL) with results from the blind-audit and collocated programs, laboratory error was estimated in 1995-96 to account typically for one-sixth to one-fourth of the overall sampling error.

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