EXTERNAL QUALITY-ASSURANCE RESULTS FOR THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/ NATIONAL TRENDS NETWORK DURING 1989

By Timothy C. Willoughby, John D. Gordon, Leroy J. Schroder,
and Mark A. Nilles

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CONVERSION FACTORS

Multiply	*By*	*To obtain*
milliliter (mL)	0.03381	ounce, fluid

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

$$°F = 9/5\ (°C) + 32$$

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

megohm (MΩ)
microequivalents per liter (μequiv./L)
microsiemens per centimeter at 25 degrees Celsius (μS/cm)

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ABSTRACT

The U.S. Geological Survey used three programs in 1989 to provide external quality assurance for the National Atmospheric Deposition Program/ National Trends Network (NADP/NTN). An intersite-comparison program was used to evaluate onsite pH and specific-conductance determinations. The effects of routine sample handling, shipping, and processing of wet-deposition samples on analyte determinations and an estimated precision of analyte values and concentrations were evaluated in the blind-audit program. Differences between analytical results and an estimate of the analytical precision of three laboratories routinely measuring wet deposition were determined by an interlaboratory-comparison program.

Results of the intersite-comparison program indicate that 75 and 91 percent of the site operators met the NADP/NTN goals for pH determination during the two intersite-comparison studies done during 1989. The results also indicate that 97 and 82 percent of the site operators met the NADP/NTN goals for specific-conductance determination during the two studies in 1989. The effects of routine sample handling, shipping, and processing, determined in the blind-audit program, indicated significant positive bias for calcium, magnesium, sodium, potassium, chloride, nitrate, and sulfate. Significant negative bias was determined for hydrogen ion and specific conductance. A Kruskal-Wallis test indicated that there were no significant ($\alpha=0.01$) differences in analytical results from the three laboratories participating in the interlaboratory-comparison program.

INTRODUCTION

The National Atmospheric Deposition Program (NADP) was established in 1978 to investigate the occurrence and effects of acid deposition. The National Trends Network (NTN) was established in 1982 to expand the NADP monitoring effort into areas not previously sampled. Data collected as part of the NADP/NTN programs are used to monitor spatial and temporal trends in the chemical composition of natural wet deposition and to provide accurate data to individual scientists or agencies involved in research on the effects of acid deposition. Operators of approximately 200 sites currently are collecting wet-deposition samples within the two combined programs in the United States and Canada. All site operators of NADP/NTN sites use the same type of wet-deposition collectors, which are described by Volchok and Graveson (1976). All site operators also used the same sample-handling protocols (Bigelow and Dossett, 1988) and sent their samples to the Illinois State Water

Survey, Central Analytical Laboratory (CAL) for chemical analyses. Because both networks used identical sampling and chemical-analysis protocols, the NADP/NTN monitoring effort is presented as one network for the analyses in this report. Earlier reports have described the NADP/NTN onsite operations (Bigelow and Dossett, 1982), the NTN design (Robertson and Wilson, 1985), and laboratory methods (Peden, 1986).

This report describes the results of the external quality-assurance programs operated by the U.S. Geological Survey in support of the NADP/NTN during 1989. These programs: (1) Assess the precision and accuracy of onsite determinations of pH and specific conductance (intersite-comparison program); (2) evaluate the effects of sample handling, processing, and shipping of samples collected within the NADP/NTN on the bias and precision of analyte determinations (blind-audit program); and (3) determine the comparability, bias, and precision of analytical results obtained by separate laboratories routinely measuring wet deposition when portions of common samples are sent to the participating laboratories (interlaboratory-comparison program).

INTERSITE-COMPARISON PROGRAM

During 1989, the U.S. Geological Survey completed intersite-comparison studies 23 and 24. Study 23 was completed in May, and study 24 was completed in November. In each intersite-comparison study, active NADP/NTN site operators are mailed an aliquot of a reference solution simulating the pH and specific conductance of natural wet deposition. Included with this aliquot are instructions for the site operator to determine the pH and specific conductance using standard NADP/NTN procedures. A flowchart depicting the intersite-comparison program is presented in figure 1. Participation in the intersite-comparison program is voluntary; most site operators are cooperative and do the requested analyses within the specified 45-day response period. Data in table 1 summarize site-operator participation and responses made by site operators for the two intersite-comparison studies done during 1989.

For each of the 1989 intersite-comparison studies, a reference solution was prepared by the U.S. Geological Survey using ultrapure deionized water (>16.7 MΩ) and dilute nitric acid. The target pH value for the reference solution used in study 23 was 4.70, and the calculated specific-conductance value was 8.4 µS/cm. The target pH for the reference solution used in study 24 was 4.00, and the calculated specific conductance was 42.1 µS/cm.

The NADP/NTN goal for onsite pH determinations of less than 5.0 is +0.10 pH unit of the actual pH. These criteria increase to +0.30 pH unit when the actual pH exceeds 5.0. By using the median value of all responding site operators as the most accurate estimate of pH, 75 percent (intersite-comparison study 23) and 91 percent (intersite-comparison study 24) of the participating site operators met the NADP/NTN pH measurement-accuracy goals in 1989.

The NADP/NTN goal for onsite specific-conductance measurements is +4.0 µS/cm. By using the median value of all responding site operators as the most accurate estimate of the actual specific conductance, 97 percent (intersite-comparison study 23) and 82 percent (intersite-comparison study 24) of the participating site operators achieved the NADP/NTN specific-conductance measurement-accuracy goals in 1989.

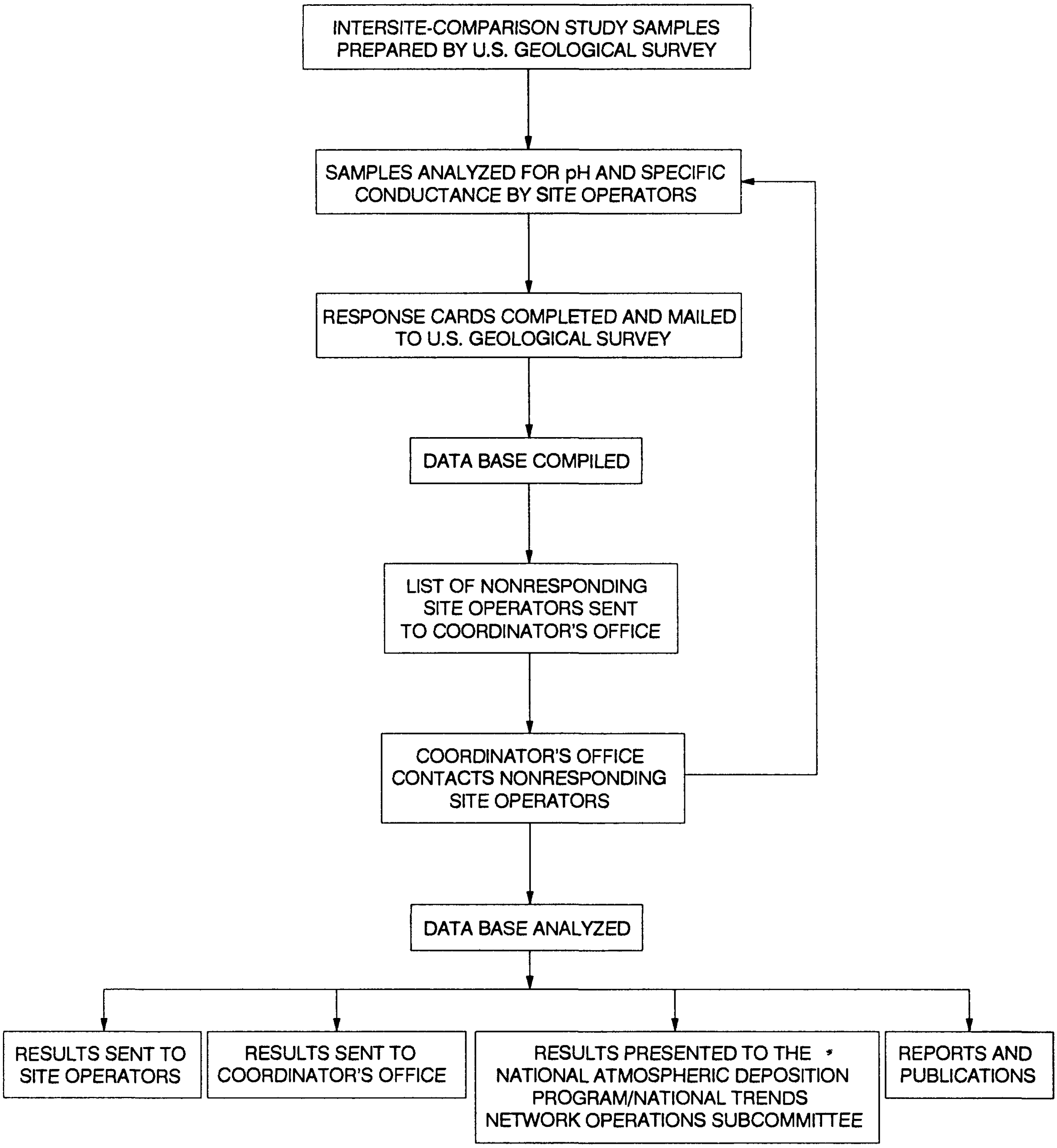

Figure 1.--Intersite-comparison program.

Table 1.--*Summary of site-operator responses for the 1989 intersite-comparison program*

Site-operator responses	Intersite-comparison study	
	23	24
Number of site operators receiving samples	201	197
Number of nonresponding site operators	9	8
Site operators reporting equipment problems	5	9
pH meter/electrode malfunctions	5	6
Specific-conductance equipment malfunctions	1	3

The results of the 1989 intersite-comparison studies are shown in figures 2 and 3. Boxplots depicting the distribution of pH and specific-conductance values for studies 23 and 24 are shown in figure 2. Superimposed on the scatterplots in figure 3 are boundaries defining NADP/NTN accuracy goals for pH and specific-conductance measurements. Boundaries also are superimposed that delineate pH and specific-conductance values for those site operators successfully meeting the goals for both measurements.

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 bias and precision. A detailed description of the blind-audit program was discussed by Schroder and others (1985). A flowchart showing the operation of the blind-audit program is presented in figure 4. Thirty-two blind-audit samples were sent to selected NADP/NTN site operators for the first, second, and fourth quarters of 1989. Thirty-three blind-audit samples were sent to selected NADP/NTN site operators for the third quarter of 1989. The site operators receiving blind-audit samples during each mailing were selected to ensure an even geographic distribution. For 1989, 250-, 500-, and 1,000-mL samples were sent to the selected site operators each quarter to assess volume-related biases. Site operators also were provided with detailed instructions on how to process the blind-audit sample.

Six solutions were used in the 1989 blind-audit program. All of the solutions used in 1989 also were used in 1988 (See and others, 1990). Three of the solutions were prepared by the CAL staff: A dilute nitric-acid solution, referred to as CAL 4.3, and two synthetic wet-deposition solutions, referred to as CAL A and CAL B. One solution was prepared by the U.S. Geological Survey Standard Reference Water Project, referred to as P-12, and two solutions were prepared by the U.S. Geological Survey Acid Rain Project, referred to as USGS and ultrapure. The ultrapure solution is ultrapure deionized water. The target values for solutions used for the 1989 blind-audit program are presented in table 2.

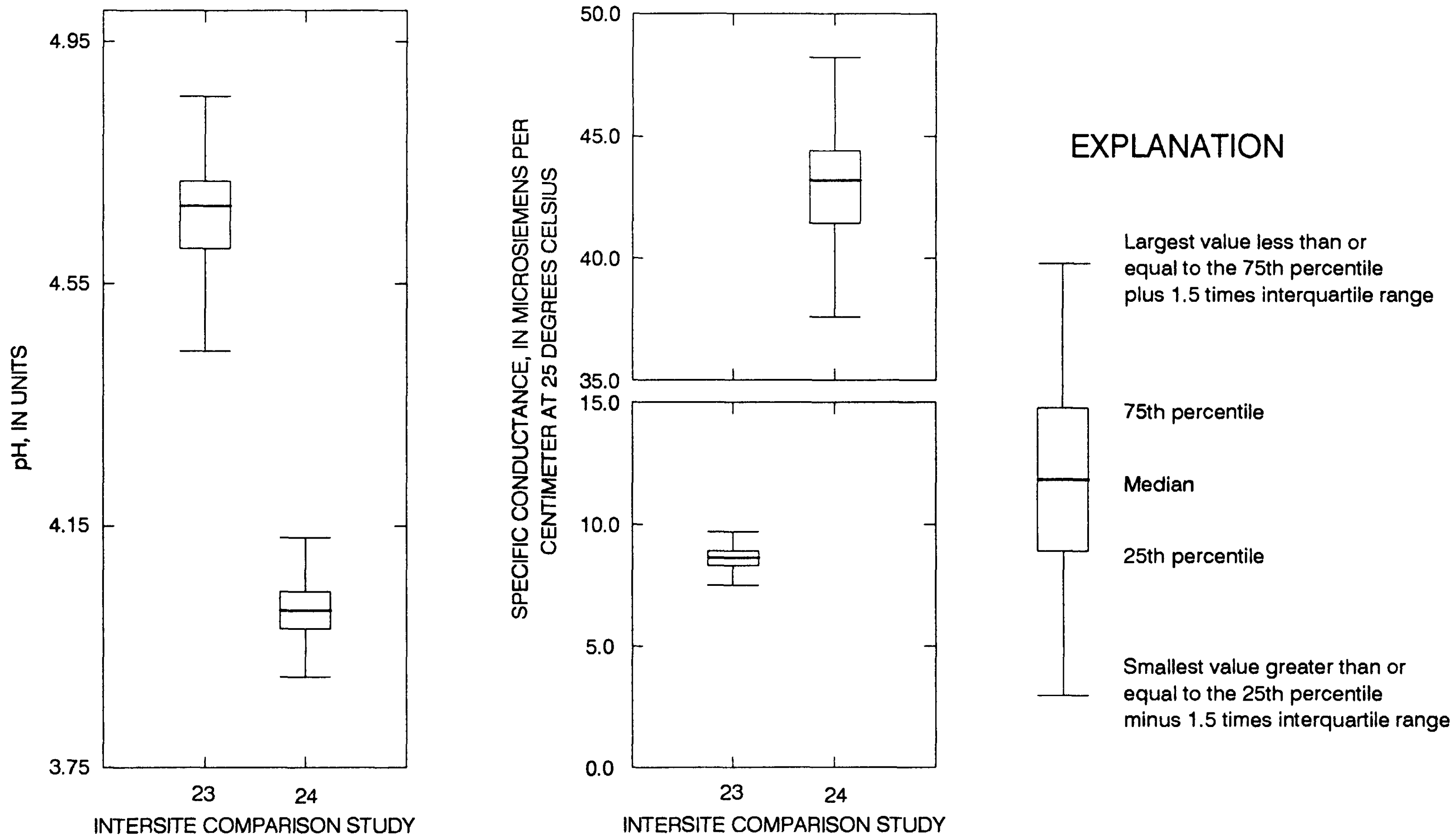

Figure 2.--Results of pH and specific-conductance analyses for intersite-comparison studies 23 and 24.

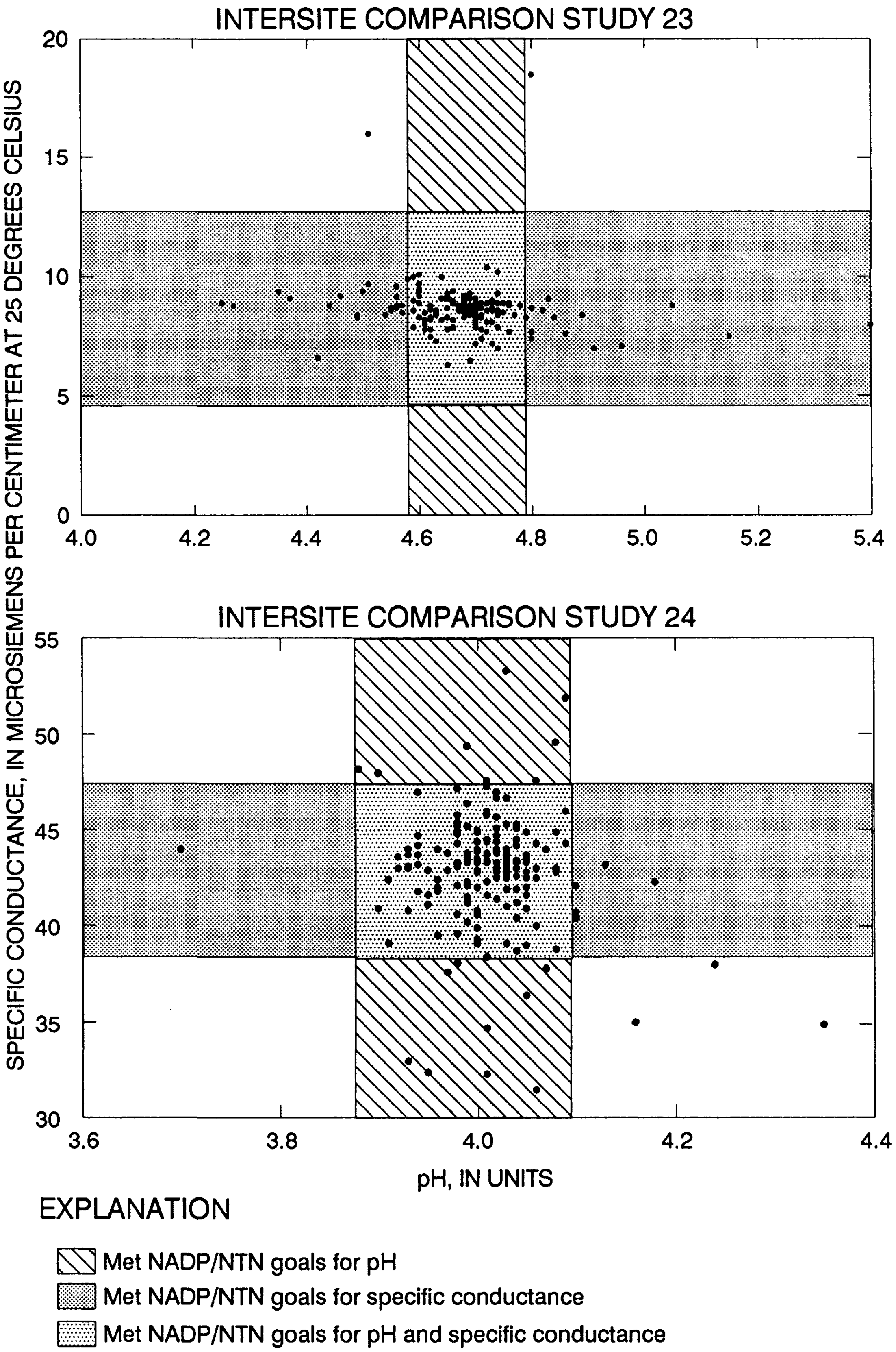

Figure 3.--Results of pH and specific-conductance analyses for intersite-comparison studies 23 and 24.

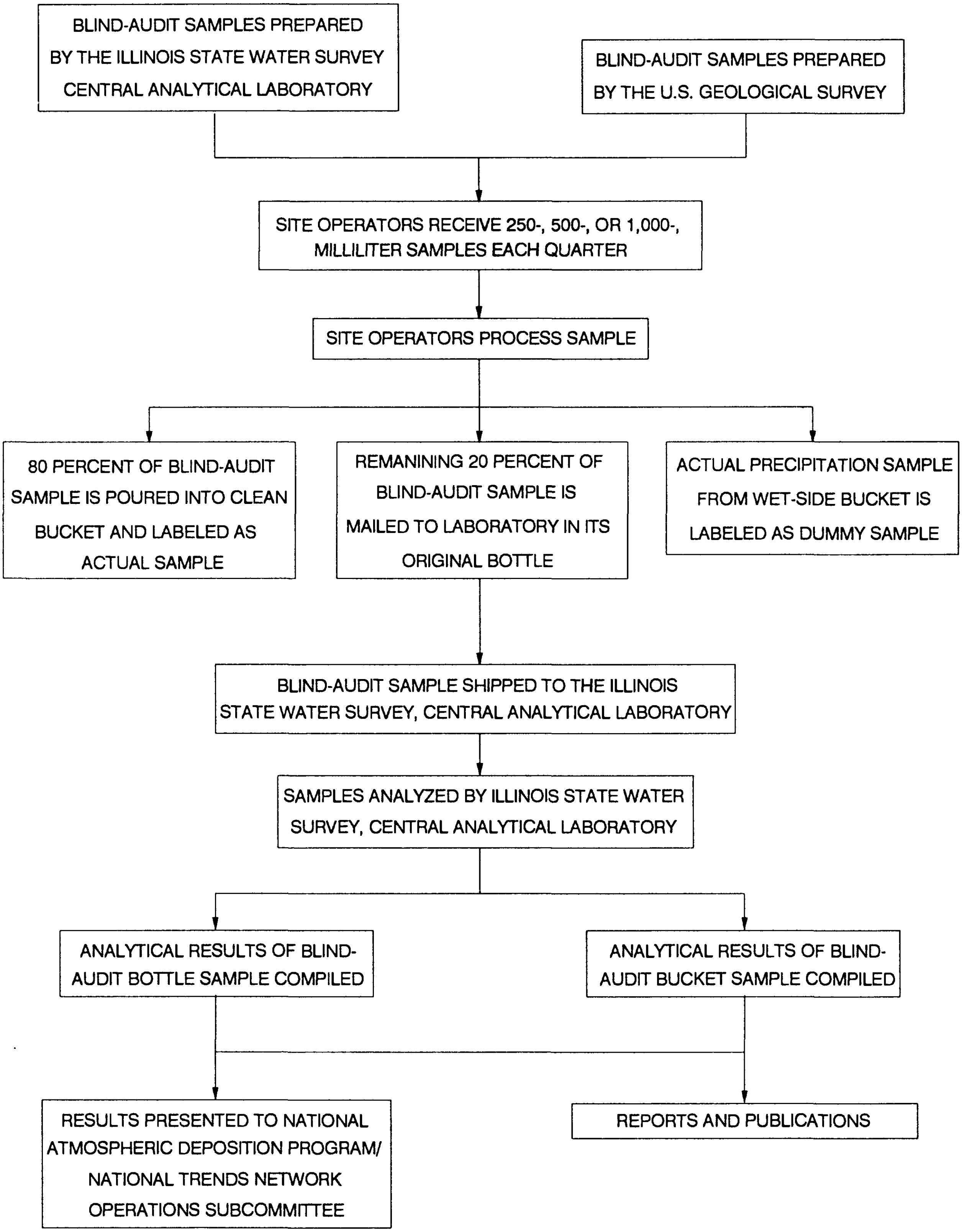

Figure 4.--Blind-audit program.

Table 2.--*Target values for solutions used in the 1989 U.S. Geological Survey blind-audit program and interlaboratory-comparison program*

[All units in milligrams per liter, except pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius; --, indicates no value available; significant figures vary because of differences in laboratory precision; <dl, indicates value less than method detection limit]

Solution Name	Ca	Mg	Na	K	NH4	Cl	NO3	SO4	pH	Specific conductance
[1]CAL 4.3	<dl	<dl	<dl	<dl	<dl	<dl	3.11	<dl	4.3	22
[1,2]CAL A	0.069	0.017	0.050	0.016	--	0.12	.50	0.67	4.84	7.5
[1,2]CAL B	.282	.070	.187	.051	--	.51	1.98	2.66	4.31	27.6
[1]P-12	.91	.06	.71	.05	--	.66	--	.65	6.58	10.0
[1,2]USGS	.14	.037	.092	.025	0.160	.142	1.08	.938	4.80	8.0
[2]2694-I	.014	.024	.205	.052	--	[3].24	--	2.75	4.27	26
[2]2694-II	.049	.051	.419	.106	[3]1	[3]1	7.06	10.9	3.59	130
[1,2]Ultrapure	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl	[4]5.65	[4].064

[1] Used in the 1989 blind-audit program.

[2] Used in the 1989 interlaboratory-comparison program.

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

[4] At 25 degrees Celsius and one atmosphere pressure (Hem, 1985 and Dean, 1979).

After a site operator participates in the blind-audit program, participation is not requested again until all the site operators in the NADP/NTN have participated. The locations of sites whose operators participated in the 1989 blind-audit program are presented in figure 5.

Site operators were instructed to pour approximately 75 percent of the blind-audit sample into a clean 13-L polyethylene bucket and process it as if it were the wet-deposition sample from the previous week. This portion of the blind-audit sample is referred to as the bucket sample. Onsite measurements of pH and specific conductance were made, and the weight was determined for the bucket sample. The bucket then was sealed and submitted to the CAL for analyses disguised as a routine wet-deposition sample with a fictitious NADP/NTN field-observer report form. Site operators returned that portion of the blind-audit sample remaining in the original sample bottle to the CAL in a separate mailing container. This portion of the blind-audit sample is referred to as the bottle sample. The comparison of the analytical results from these two portions is the basis for determining bias. The CAL staff that received and analyzed the blind-audit samples could not identify individual samples as being from an external quality-assurance program. Information concerning the chemical composition of the samples was not provided to either the site operators or the CAL staff that analyzed the samples.

If a natural wet-deposition sample was collected for the previous week by a site operator also submitting a blind-audit sample, the natural sample was submitted to the CAL using a "dummy" field observer report form. The CAL staff that received and analyzed the natural wet-deposition sample could not identify which site had collected the natural wet-deposition sample. After the blind-audit sample and the natural wet-deposition sample were analyzed by the CAL, the CAL was notified that these two samples should be exchanged in the NADP/NTN data base.

The bottle portion of the blind-audit sample was submitted separately by the CAL Quality Assurance officer to the CAL laboratory staff for routine analysis. Although the CAL staff knows that bottle samples are not actual NADP/NTN samples, the analyte concentrations in bottle samples are not known by the laboratory staff. During 1989, the CAL analyzed the bucket portion and bottle portion of the blind-audit sample within 2 weeks of each other.

Analytical results of the bucket and bottle portions of the blind-audit sample provided paired analyses to determine if analyte concentrations had changed in the bucket samples as a result of onsite and laboratory protocols. This comparison was based on the assumption that analyte concentrations in the bottle portion of the blind-audit sample did not change from the time that the site operator poured an aliquot of the original sample into the bucket and the time that the CAL analyzed the bottle portion of the blind-audit sample.

Complete bucket and bottle analyses were available for 123 of the 129 blind-audit samples sent to participating site operators in 1989. Five site operators failed to submit the blind-audit samples; one site operator had discontinued operation.

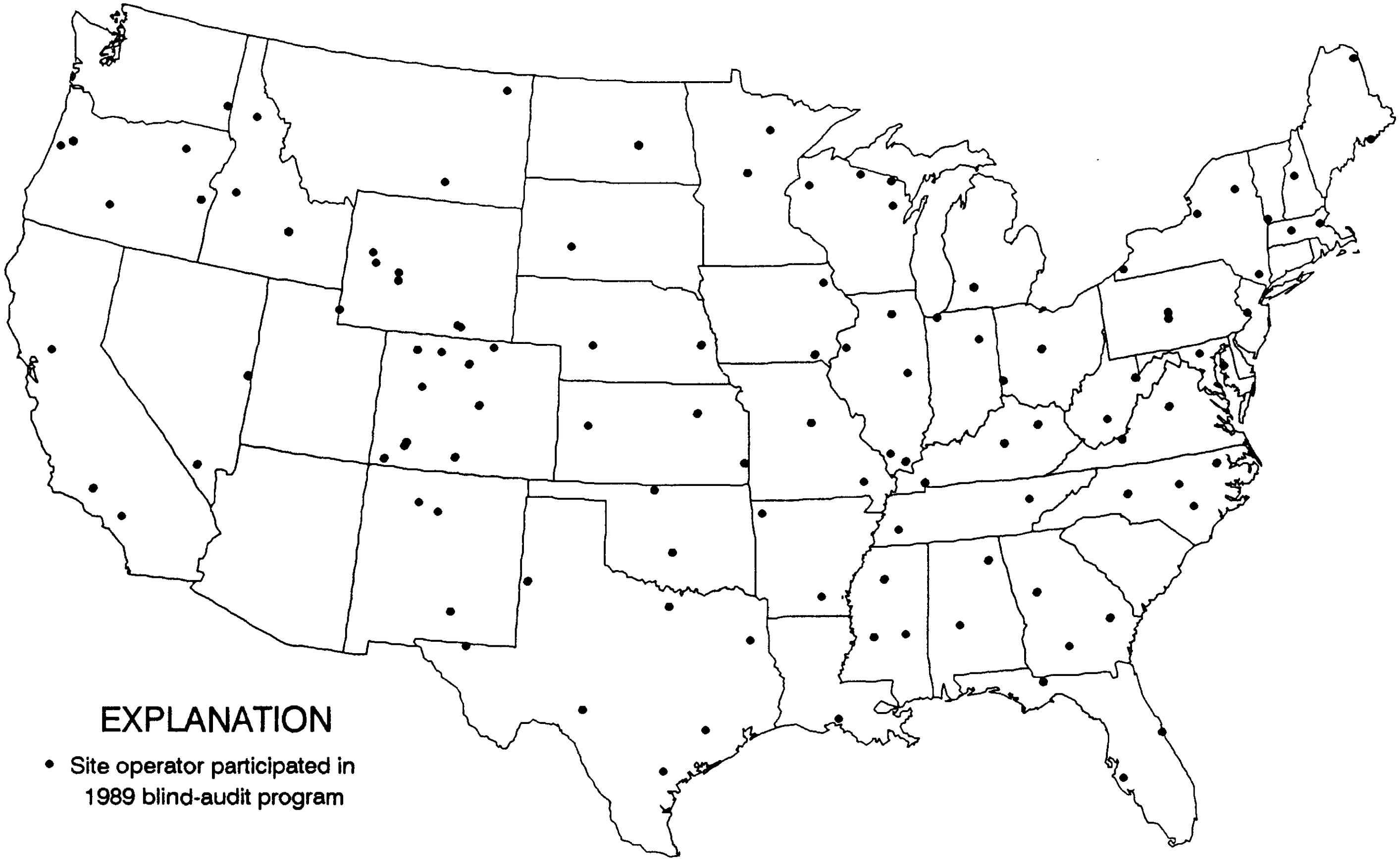

Figure 5.--Location of National Atmospheric Deposition Program/National Trends Network sites whose operators participated in the 1989 blind-audit program.

The CAL identifies samples that contain extraneous debris with a contamination code (C). Because prior investigations have indicated no significant differences in analytical results among uncontaminated bottle samples and contaminated bucket samples (See and others, 1990), and because similar contamination problems occur in natural wet-deposition samples collected by the site operators, data from contaminated bucket samples were included in the 1989 blind-audit statistical analyses. One bucket sample was removed from the 1989 blind-audit statistical analyses because it had received a contamination code (F), which indicates there was a gross sample-handling protocol violation in the field.

In 1988, a paired t-test was used to determine if any significant differences existed between the bucket- and bottle-sample analyses. The paired t-test was done after the analyte concentrations reported as less than the minimum reporting limit were removed.

In 1989, analyte concentrations reported as less than the minimum reporting limit were set equal to the minimum reporting limit. A Wilcoxon signed ranks test was used to determine if any significant differences existed between the analyte concentrations measured for the bucket and bottle portions of the blind-audit sample. The magnitude of the difference between the bucket and bottle portions of the blind-audit sample was determined to be the median differences from all paired analyte determinations. All blind-audit samples that had paired analyte determinations were included in the statistical analyses except the ultrapure samples. Median concentrations determined for the bucket and bottle results and the median difference between the bucket and bottle concentrations are presented in table 3.

At a significance level of $\alpha=0.01$, bias existed for calcium, magnesium, sodium, potassium, chloride, nitrate, sulfate, hydrogen, and specific conductance. Only ammonium was not biased. The median concentrations for the bucket samples were larger than the median concentrations for bottle samples for calcium, magnesium, sodium, potassium, chloride, nitrate, and sulfate. The median determinations for bucket samples were smaller than the median determinations for the bottle samples for hydrogen ion and specific conductance. There was no difference between the median concentration determined for the bucket sample and the median concentration determined for the bottle sample for ammonium. These results are an indication that contamination of the bucket samples, and probably all NADP/NTN wet-deposition samples, was occurring as a result of sample-handling procedures. The bucket-sample minus bottle-sample concentration differences are presented in figure 6.

To compare the differences measured in the analyte concentrations for the bucket and bottle portion of the blind-audit samples for 1989, the same statistical methods were utilized on the bucket and bottle portions of the blind-audit samples for 1988. In 1988, the bucket results for nitrate were not statistically different from the bottle results; however, nitrate was determined to be statistically different in 1989. The median differences between the bucket and bottle results in 1989 were less than in 1988 for calcium, magnesium, sodium, and potassium. The median differences between the bucket and bottle results in 1989 were greater than in 1988 for chloride, nitrate, sulfate, hydrogen ion, and specific conductance. However, the measured changes between the 1988 and 1989 median differences for the bucket and bottle samples were small.

Table 3.--*Median bucket and bottle concentrations and median concentration difference between the bucket and bottle for the blind-audit program*

[All units in milligrams per liter except hydrogen, in microequivalents per liter, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius]

Analyte	Sample type	Median	Median Difference	Number of pairs
Calcium	Bucket	0.143	0.008	107
	Bottle	.135		
Magnesium	Bucket	.031	.003	107
	Bottle	.029		
Sodium	Bucket	.140	.025	107
	Bottle	.108		
Potassium	Bucket	.024	.001	107
	Bottle	.021		
Ammonium	Bucket	.13	.00	107
	Bottle	.13		
Chloride	Bucket	.18	.01	107
	Bottle	.17		
Nitrate	Bucket	1.06	.02	107
	Bottle	1.04		
Sulfate	Bucket	.91	.04	107
	Bottle	.88		
Hydrogen ion	Bucket	5.62	-9.61	107
	Bottle	16.6		
Specific conductance	Bucket	9.0	-2.7	107
	Bottle	10.7		

The precision of the 1989 NADP/NTN wet-deposition analyses was estimated by pooling the standard deviations of replicate blind-audit samples (Dixon and Massey, 1969, p. 113). Two determinations for the pooled standard deviations were determined: (1) The analyte determinations reported as less than the minimum reporting limit were set equal to the minimum reporting limit, and (2) the analyte determinations reported as less than the minimum reporting limit were set equal to zero. No significant differences existed for the estimated pooled standard deviations using these two methods. The estimated standard deviations are listed in table 4.

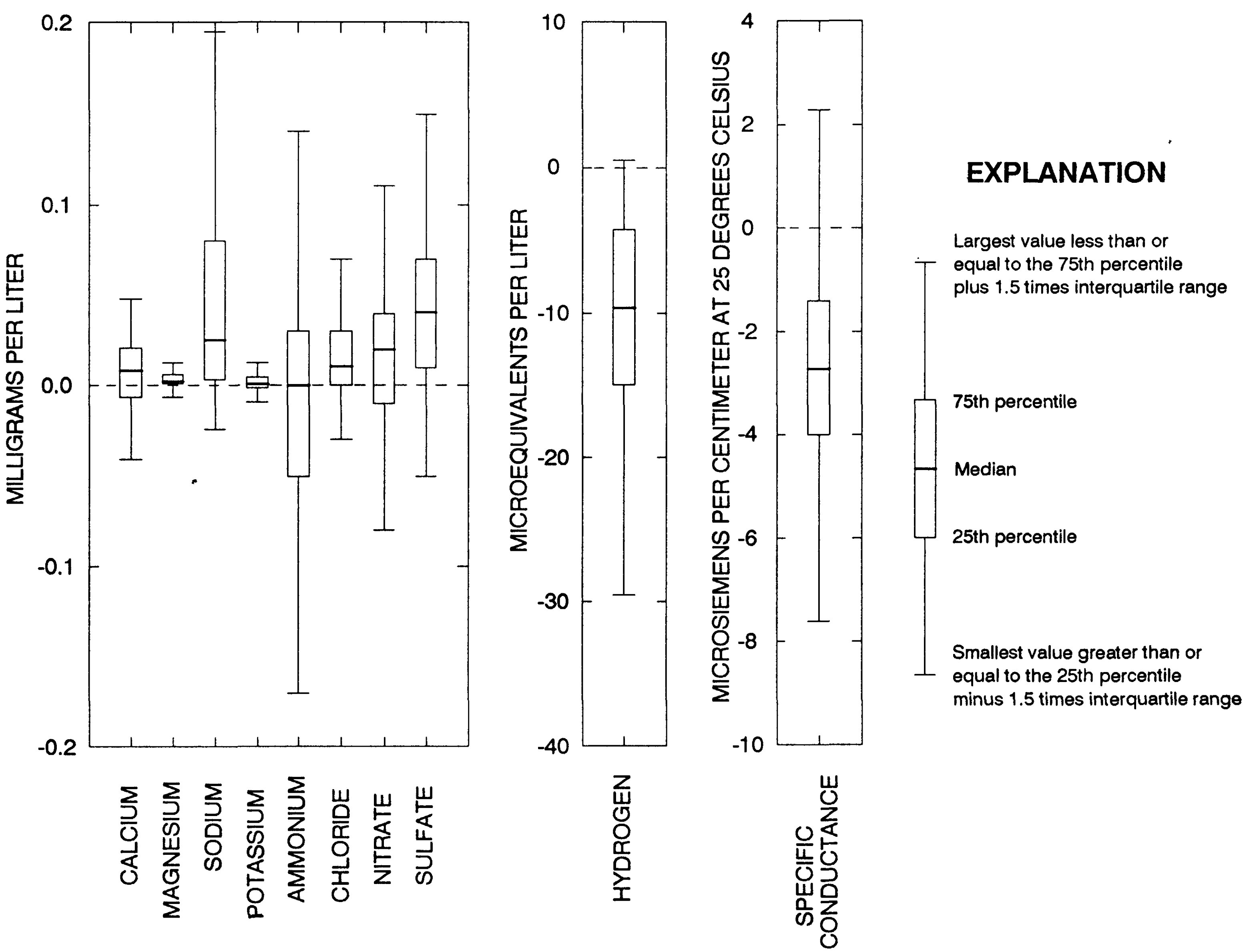

Figure 6.--Bucket-sample concentrations minus bottle-sample concentrations in the blind-audit program.

Table 4.--*Pooled standard deviations of analyte data based on replicate analyses of blind-audit bucket samples*

[All units in milligrams per liter except pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius]

Analyte	Minimum value	Maximum value	Pooled standard deviation
Calcium	0.014	1.066	0.004
Magnesium	<.003	.297	.003
Sodium	.013	.945	.006
Potassium	<.003	.067	.001
Ammonium	<.02	.69	.01
Chloride	<.03	.88	.01
Nitrate	<.03	3.40	.02
Sulfate	<.03	2.78	.01
pH	4.37	7.07	.04
Specific conductance	4.3	26.3	.2

To compare the precision determined for the 1989 blind-audit program, the same statistical procedures also were done on the 1988 blind-audit results. No significant differences were determined between the 1988 and 1989 estimated pooled standard deviations. The analyte precision reported by the CAL for the 1989 blind-audit program was consistent with the analyte precision reported for the 1988 blind-audit program.

To determine if there existed a relation between the volume collected in the bucket and the analyte difference between the bucket and bottle portions of the blind-audit sample, seventeen 250-mL, fifteen 500-mL, and fourteen 1,000-mL bottles of the same solution (USGS) were sent to site operators in 1989. The site operators poured approximately 75 percent of each bottle into the clean 13-L polyethylene bucket and processed it as if it were the wet-deposition sample from the previous week.

The median volume of precipitation collected at all NADP/NTN sites for 1989 was 869 mL. The volume is best simulated by the 1,000-mL blind-audit sample.

Boxplots in figure 7 display the difference between the measured bucket and bottle portions of the USGS solution blind-audit samples plotted by the volume of the samples mailed to the site operators. The analyte concentrations that were measured less than the minimum reporting limit were set equal to the minimum reporting limit, minimizing the difference between the bucket and bottle analyses when the bucket analysis was measured greater than the minimum reporting limit, and the bottle analysis was measured less than the minimum reporting limit. If the bucket and bottle analyses were measured less than the minimum reporting limit, the resulting differences are zero.

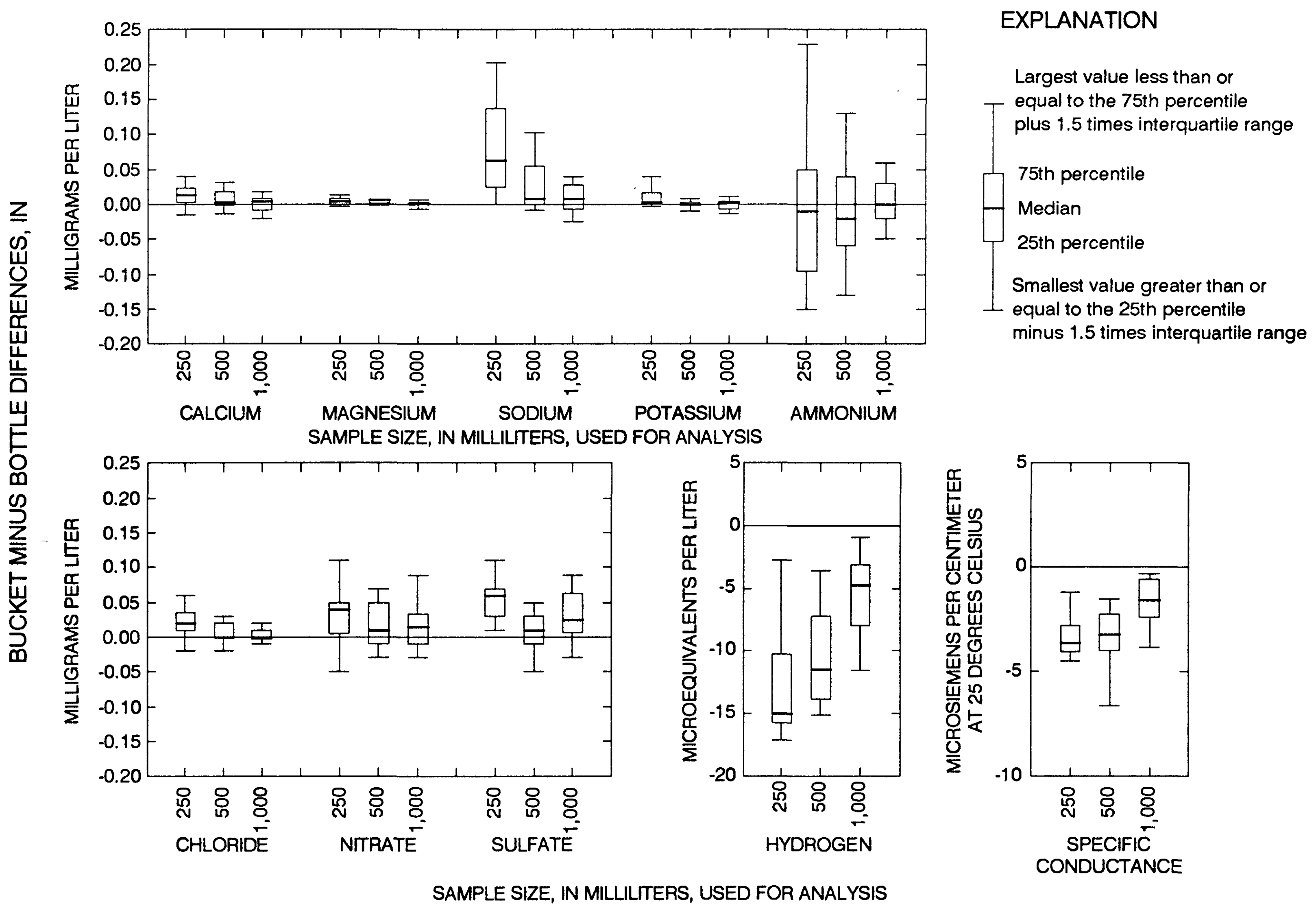

Figure 7.--Bucket-sample concentrations minus bottle-sample concentrations for the 250-, 500-, and 1,000-mL USGS solution samples in the blind-audit program.

Decreases in the median difference between the bucket and bottle analyses as volume increased were measured for calcium, sodium, and chloride. As volume increased, the median absolute difference between the measured hydrogen ion concentration in the bucket decreased when compared to the measured concentrations in the bottle. Magnesium, potassium, ammonium, nitrate, and sulfate did not have a consistent change in concentration as volume increased.

The differences between the measured concentration in the bucket and bottle portions of the blind-audit sample were then divided by the volume of the sample measured in the bucket. This converts the measured concentrations for the bucket and bottle portions of the blind-audit sample from milligrams per liter to milligrams per bucket. Decreases in bucket and bottle differences, in milligrams per bucket, still were measured for sodium and chloride as the volume increased, which indicates that the mass determined in the bucket is volume dependent for only sodium and chloride.

The contamination appears to be independent of volume for calcium, magnesium, potassium, ammonium, nitrate, and sulfate. The decrease in hydrogen ion concentration does not appear to be related to volume. These data indicate that the bucket may be contributing a consistent mass of calcium, magnesium, potassium, ammonium, nitrate, or sulfate contamination and/or removing a consistent mass of hydrogen ion from each sample collected at NADP/NTN sites. The changes observed in the specific conductance are related to the observed loss of hydrogen ion. As the volume increased, the spread between the 25th and the 75th percentile of the bucket and bottle differences decreased for calcium and ammonium. Decreases in the spread between the 25th and 75th percentile of the bucket and bottle differences are an indication that the contamination observed in the bucket samples for small volume samples was more noticeable than in large volume samples.

INTERLABORATORY-COMPARISON PROGRAM

The interlaboratory-comparison program was used to determine if differences existed among the analytical results of participating laboratories routinely measuring wet deposition and to estimate analytical precision of the participating laboratories. Three laboratories participated in the interlaboratory-comparison program for either all or part of 1989: (1) Illinois State Water Survey, Central Analytical Laboratory (CAL); (2) Inland Water Directorate, National Water Quality Laboratory (IWD); and (3) Hunter, Environmental Services, Inc.[1] (ESE). ESE joined the interlaboratory-comparison program in July 1989.

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

Samples from three sources were prepared for the 1989 interlaboratory-comparison program: (1) Synthetic wet-deposition samples (USGS) and ultrapure deionized-water samples (ultrapure) prepared by the U.S. Geological Survey, (2) standard references samples (2694-I and 2694-II) prepared and certified by the National Institute of Standards and Technology (NIST), and (3) synthetic wet-deposition samples (CAL A and CAL B) and natural wet-deposition samples prepared by the CAL. 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. The natural wet-deposition samples were divided into 10 aliquots using a deca-splitter. The aliquots were bottled in 125-mL polyethylene bottles and shipped to the U.S. Geological Survey in chilled, insulated containers. Target values for synthetic wet-deposition solutions used in the interlaboratory-comparison program are listed in table 2.

Samples used for the 1989 interlaboratory-comparison program were relabeled and shipped by the U.S. Geological Survey to the participating laboratories approximately every 2 weeks. Each laboratory received four samples per shipment. The first shipment consisted of two natural wet-deposition samples, in duplicate. The second shipment consisted of triplicate synthetic wet-deposition samples prepared by the CAL or NIST and a single aliquot of ultrapure deionized water or four aliquots of the synthetic wet-deposition samples prepared by the U.S. Geological Survey. The laboratory staffs were unaware of the actual analyte concentrations in the samples and did not know if the samples were ultrapure deionized water, natural wet-deposition samples, or synthetic wet-deposition samples. A flowchart of the interlaboratory-comparison program is shown in figure 8. Data in table 5 list the analytical method and the minimum reporting limits for the three laboratories participating in the 1989 interlaboratory-comparison program.

Laboratory precision was estimated for each analyte by calculating a pooled standard deviation for the results reported for the duplicate natural wet-deposition samples (Taylor, 1987) and the results reported for the synthetic wet-deposition samples (Dixon and Massey, 1969). Two determinations for the pooled standard deviations were made: (1) The analyte determinations reported as less than the minimum reporting limit were set equal to the minimum reporting limit, and (2) the analyte determinations reported as less than the minimum reporting limit were set equal to zero. No significant differences existed for the estimated pooled standard deviations using these two methods. The pooled standard deviations for the results reported by the CAL for sodium and ammonium for the natural samples, and sodium for the synthetic samples, were larger in 1989 than in 1988. The pooled standard deviations for the results reported by the IWD for potassium, ammonium, chloride, nitrate, and sulfate for the natural samples, and sodium, chloride, nitrate, and sulfate for the synthetic samples, were smaller in 1989 than in 1988. An increased precision in the analyses of interlaboratory-comparison samples, when compared to blind-audit samples, indicates that a large degree of uncertainty in NADP/NTN deposition data results from routine onsite operations. The calculated pooled standard deviations are listed in table 6.

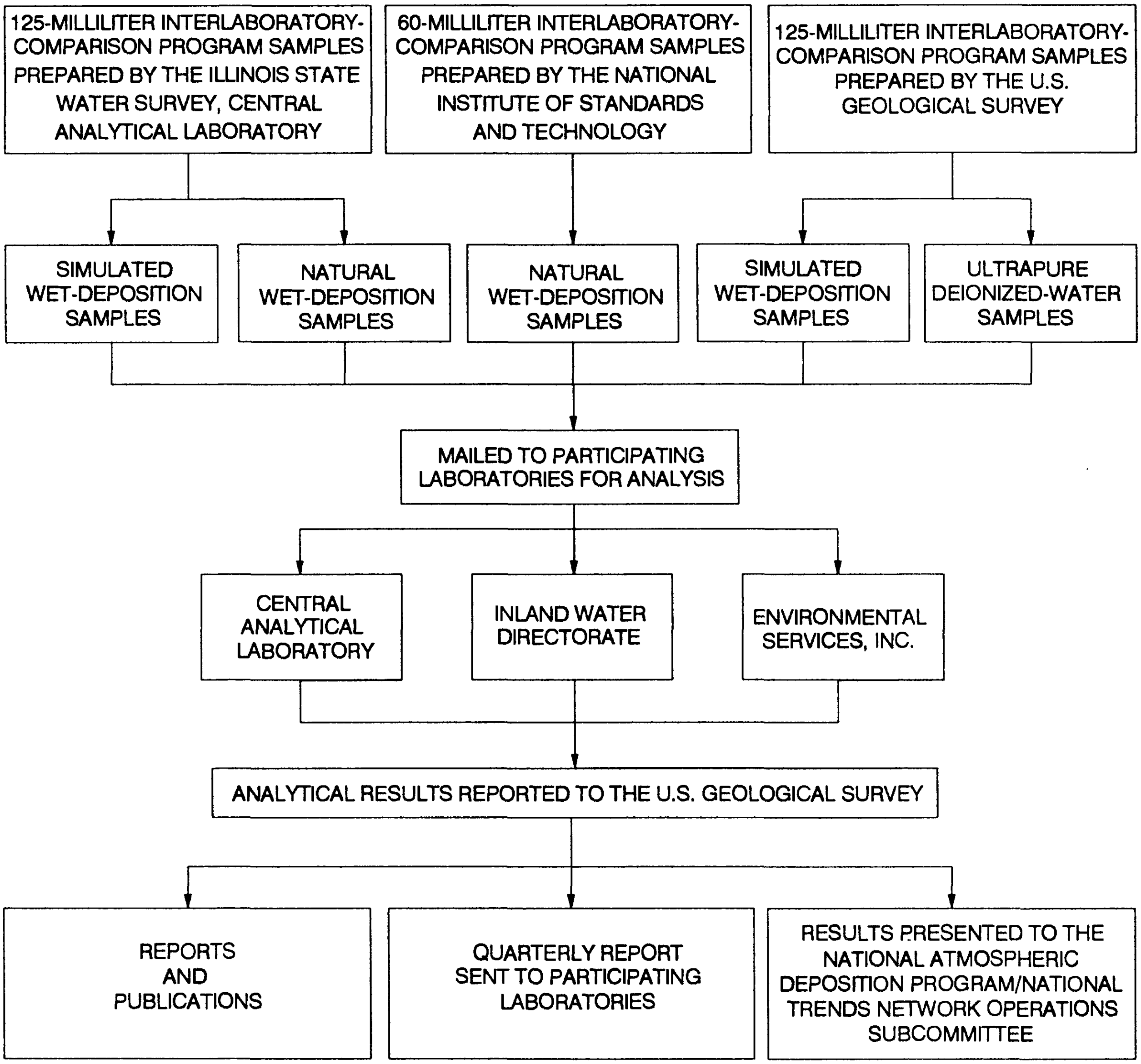

Figure 8.--Interlaboratory-comparison program.

Table 5.--*Analytical method and minimum reporting limits for three laboratories participating in the interlaboratory-comparison program during 1989*

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Water Directorate, National Water Quality Laboratory, Ontario, Canada; ESE, Hunter, Environmental Services, Inc., Gainesville, Fla.; FAA, flame atomic absorption spectrometry; FAE, flame atomic emission spectrometry; ICP, inductively coupled plasma, atomic emission spectrometry; AP, automated phenate, colorimetric; IC, ion chromatography]

Analyte	Minimum reporting limit		
	CAL (Method)	IWD (Method)	ESE (Method)
Calcium	0.01 (FAA)	0.01 (FAA)	0.003 (ICP)
Magnesium	.003 (FAA)	.01 (FAA)	.009 (ICP)
Sodium	.003 (FAA)	.01 (FAE)	.018 (ICP)
Potassium	.003 (FAA)	.01 (FAE)	.005 (FAE)
Ammonium	.03 (AP)	.001 (AP)	.013 (AP)
Chloride	.03 (IC)	.01 (IC)	.02 (IC)
Nitrate	.03 (IC)	.04 (IC)	.035 (IC)
Sulfate	.03 (IC)	.01 (IC)	.04 (IC)

Table 6.--*Pooled standard deviations for analytes determined by three laboratories participating in the 1989 interlaboratory-comparison program*

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Water Directorate, National Water Quality Laboratory, Ontario, Canada; ESE, Hunter, Environmental Services, Inc., Gainesville, Fla.; Nat, analyses of natural wet-deposition samples; Syn, analyses of synthetic wet-deposition samples and standard reference samples; all units in milligrams per liter except hydrogen ion, in microequivalents per liter, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius]

Analyte	CAL		IWD		ESE	
	Nat	Syn	Nat	Syn	Nat	Syn
Calcium	0.003	0.005	0.004	0.010	0.002	0.004
Magnesium	.001	.001	.001	<.001	.001	.001
Sodium	.015	.146	.005	.006	.003	.007
Potassium	.011	.002	.004	.007	.005	.007
Ammonium	.01	.07	<.01	.04	.003	.006
Chloride	.03	.03	.05	.02	.01	.02
Nitrate	.01	.04	.04	.11	.01	.06
Sulfate	.01	.05	.01	.09	.01	.02
Hydrogen ion	.88	9.05	.30	2.42	.82	7.97
Specific conductance	.19	.67	.1	.5	.2	2.2

To examine bias among the analytical results of the laboratories, a Kruskal-Wallis test (Iman and Conover, 1983) was done. Results of the Kruskal-Wallis test indicate no significant (a=0.01) difference in analyte measurements for calcium, magnesium, sodium, potassium, ammonium, chloride, nitrate, sulfate, hydrogen ion, or specific conductance from any of the three laboratories.

Percentile rankings for individual laboratory analyses of interlaboratory-comparison samples for 1989 are summarized in table 7. A comparison between the analyte concentrations determined by each laboratory for the time that all three laboratories participated in the interlaboratory-comparison program (July 1-December 31, 1989) is presented as boxplots in figure 9.

Analyte bias for laboratories participating in the interlaboratory-comparison program also was evaluated by using the certified values and the estimated uncertainties reported by NIST for standard reference material 2694, level I and level II. Bias was examined by comparing the median laboratory-reported values and the certified values reported by NIST. Bias was indicated when the laboratory-reported values were outside of the NIST certified values plus or minus the estimated uncertainty reported by NIST. A summary of the median-analysis estimates for each laboratory and the certified values and estimated uncertainties for the NIST standard-reference materials 2694-I and 2694-II is presented in table 8. The CAL had the least number of median analyses that were significantly different from the NIST certified values.

Table 7.--Percentile ranking for individual laboratory analyses of interlaboratory-comparison samples shipped to each of three laboratories

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill., IWD, Inland Waters Directorate, National Water Quality Laboratory, Ontario, Canada; ESE, Hunter, Environmental Services, Inc., Gainesville, Fla; all units are in milligrams per liter, except hydrogen, in microequivalents per liter, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius]

	Percentiles								
	CAL			IWD			ESE		
	25th	50th	75th	25th	50th	75th	25th	50th	75th
Calcium	0.022	0.080	0.130	0.020	0.080	0.130	0.016	0.043	0.117
Magnesium	.015	.026	.047	.015	.020	.045	*.003	.027	.046
Sodium	.043	.093	.193	.040	.100	.210	.035	.083	.188
Potassium	.013	.024	.045	.020	.030	.040	.013	.023	.042
Ammonium	.05	.19	.34	.03	.15	.24	.037	.128	.317
Chloride	.13	.17	.28	.09	.16	.26	.12	.17	.46
Nitrate	.38	1.00	1.64	.49	.97	1.90	.33	1.01	1.78
Sulfate	.86	1.09	2.77	.85	1.14	2.60	.76	1.08	2.78
Hydrogen	12.0	19.1	57.2	11.1	18.6	57.5	9.8	18.6	56.6
Specific conductance	7.9	12.6	28.2	11.2	11.3	23.1	10.1	11.7	28.0

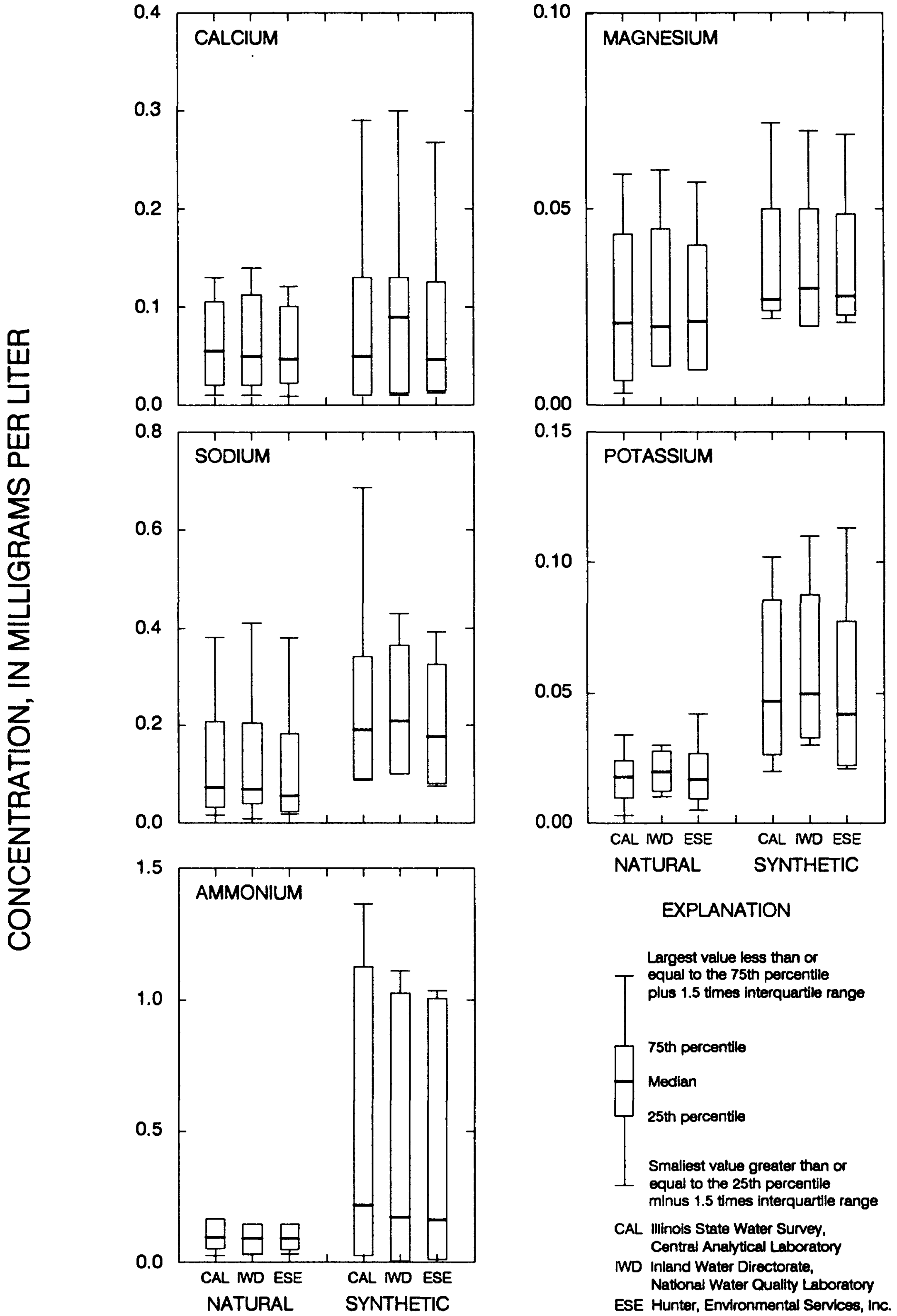

Figure 9.--Analytical results for selected water-quality constituents and properties determined by three laboratories participating in the inter-laboratory-comparison program.

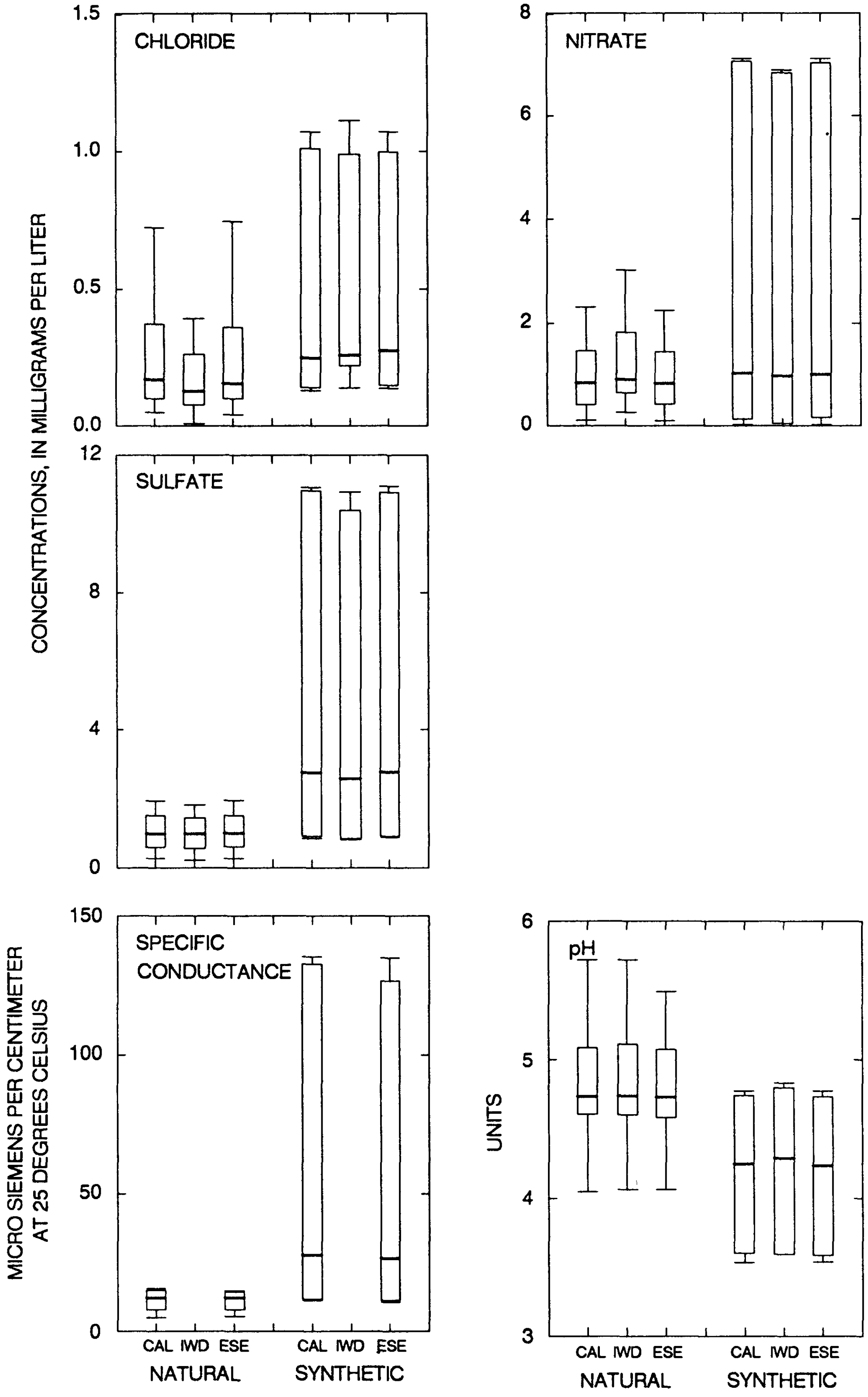

Figure 9.--Analytical results for selected water-quality constituents and properties determined by three laboratories participating in the interlaboratory-comparison program--Continued.

Table 8.--*Median analysis estimates for standard reference materials 2694-I and 2694-II from the National Institute of Standards and Technology*

[NIST, National Institute of Standards and Technology; CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Waters Directorate, National Water Quality Laboratory, Ontario, Canada; ESE, Hunter, Environmental Services Inc., Gainesville, Fla.; all units in milligrams per liter except pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius; N, indicates the number of reported values; *, indicates values outside the certified value plus or minus the estimate of uncertainty; --, indicates data not avaliable]

Analyte	NIST standard	Certified NIST values	Estimate of uncertainty	Laboratory analyses					
				CAL	(N)	IWD	(N)	ESE	(N)
Calcium	2694-I	0.014	0.003	*0.010	(12)	*0.010	(12)	0.013	(6)
	2694-II	.049	.011	.040	(9)	.040	(6)	.044	(6)
Magnesium	2694-I	.024	.002	.024	(12)	*.020	(12)	.022	(6)
	2694-II	.051	.003	.049	(9)	.050	(6)	.048	(6)
Sodium	2694-I	.205	.009	*.193	(12)	.210	(12)	*.176	(6)
	2694-II	.419	.015	.415	(9)	.420	(8)	*.389	(6)
Potassium	2694-I	.052	.007	.046	(12)	.050	(12)	*.044	(6)
	2694-II	.106	.008	.101	(9)	.110	(8)	.111	(6)
Ammonium	2694-I	--	--	<.02	(9)	<.001	(12)	<.013	(6)
	2694-II	--	--	1.31	(9)	1.07	(9)	1.02	(6)
Chloride	2694-I	--	--	.25	(12)	.24	(12)	.25	(6)
	2694-II	--	--	1.02	(9)	1.04	(9)	1.04	(6)
Nitrate	2694-I	--	--	<.03	(6)	<.04	(12)	<.035	(6)
	2694-II	7.06	.15	7.07	(9)	*6.86	(9)	7.08	(6)
Sulfate	2694-I	2.75	.05	*2.81	(12)	*2.64	(12)	*2.92	(6)
	2694-II	10.9	.2	10.99	(9)	*10.52	(9)	10.95	(6)
pH	2694-I	4.27	.03	4.24	(12)	4.24	(12)	*4.23	(6)
	2694-II	3.59	.02	3.59	(9)	3.59	(9)	*3.56	(6)
Specific conductance	2694-I	26	2	27	(12)	--	(0)	26	(6)
	2694-II	130	2	*134	(9)	--	(0)	130	(6)

Eight ultrapure deionized-water samples were included among the samples submitted to the CAL and the IWD. Five ultrapure deionized-water samples were submitted to ESE. Data in table 9 list the number of times that each laboratory reported a concentration greater than the minimum reporting limit in a solution that would not be expected to contain any detectable analyte concentrations. The IWD had the largest number of determinations greater than the analyte minimum reporting limit. Measured concentrations greater than the minimum reporting limit for the ultrapure deionized-water samples is an indication that there is a possible contamination problem. However, the magnitude of the concentrations reported as greater than the minimum reporting limit for the ultrapure deionized-water samples for each of the participating laboratories was small.

Table 9.--*Reported analyte concentrations for the ultrapure deionized-water samples for each laboratory participating in the interlaboratory-comparison program during 1989*

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Waters Directorate, National Water Quality Laboratory, Ontario, Canada; ESE, Hunter, Environmental Services, Inc., Gainesville, Fla.; all concentrations are in milligrams per liter]

Analyte	Concentrations reported that were greater than the minimum reporting limit		
	CAL	IWD	ESE
Calcium	(1)	(1)	(1)
Magnesium	(1)	(1)	(1)
Sodium	0.006, 0.042	(1)	(1)
Potassium	(1)	0.010	0.021
Ammonium	(1)	0.003, 0.003, 0.006	(1)
Chloride	(1)	(1)	(1)
Nitrate	(1)	(1)	(1)
Sulfate	.03	(1)	(1)

(1) No concentrations reported that were greater than the minimum reporting limit.

SUMMARY

During 1989, the U.S. Geological Survey operated three programs designed to provide external quality-assurance monitoring for the National Atmospheric Deposition Program (NADP) and the National Trends Network (NTN). An intersite-comparison program was used to assess the accuracy of onsite pH and specific-conductance determinations at semiannual intervals. 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 three laboratories, which routinely analyze wet-deposition samples, were examined to determine estimates of analytical bias and precision for major constituents found in wet deposition from each laboratory.

Two intersite-comparison studies were completed during 1989. For pH, 75 percent of site operators met the NADP/NTN goals for intersite-comparison study 23, and 91 percent met the goals for intersite-comparison study 24. For specific conductance, 97 percent of site operators met the NADP/NTN goals for intersite-comparison study 23, and 82 percent met the goals for intersite-comparison study 24.

Results for the blind-audit program indicated significant positive bias for calcium, magnesium, sodium, potassium, chloride, nitrate, and sulfate. Significant negative bias was determined for hydrogen ion and specific conductance. An estimate of analytical precision was calculated using a pooled standard deviation. A decreased precision in the analyses of blind-audit samples, when compared to interlaboratory-comparison studies, indicates that a large degree of uncertainty in NADP/NTN deposition data results from routine onsite operations and sample shipping.

As part of the interlaboratory-comparison program, examinations of data from three laboratories using a Kruskal-Wallis test indicated no significant difference among laboratory determinations for calcium, magnesium, sodium, potassium, ammonium, chloride, nitrate, sulfate, hydrogen ion, and specific conductance. Analytical results from National Institute of Standards and Technology reference solutions indicated that the CAL had the least number of median analyses that were significantly different from the certified values. The IWD had the largest number of determinations larger than the minimum reporting limit for analyses of ultrapure deionized water.

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