EXTERNAL QUALITY-ASSURANCE RESULTS FOR THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK DURING 1990

by Mark A. Nilles, John D. Gordon, Timothy C. Willoughby, and
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CONVERSION FACTORS AND RELATED INFORMATION

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:

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

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

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

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ABSTRACT

The U.S. Geological Survey used four programs in 1990 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, processing, and shipping 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. Overall precision estimates for the precipitation-monitoring system were determined for selected sites by a collocated-sampler program.

Results of the intersite-comparison program indicated that 80 and 74 percent of the site operators met the NADP/NTN accuracy goal for pH determinations during the two intersite-comparison studies done during 1990. The results also indicated that 98 and 95 percent of the site operators met the NADP/NTN accuracy goal for specific-conductance determinations during the two 1990 studies. The effects of routine sample handling, processing, and shipping determined in the blind-audit program indicated significant positive bias ($\alpha=0.01$) for calcium, magnesium, sodium, potassium, chloride, nitrate, and sulfate. Significant negative bias ($\alpha=0.01$) was determined for hydrogen ion and specific conductance. Only the bias for hydrogen ion and specific conductance exceeded the bias goals for laboratory measurements. Ammonium was not biased. 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. Results from the collocated-sampler program indicated the median relative error for potassium and ammonium concentration and deposition exceeded 15 percent at most sites. The median relative error for sulfate and nitrate at all sites was less than 6 percent for concentration and was less than 15 percent for deposition. The median relative error for hydrogen ion deposition ranged from 4.6 to 37.6 percent at the eight sites. Overall, collocated-sampling error typically was five times that of laboratory error estimates for most analytes.

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 wet deposition and to provide accurate data to individual scientists or agencies involved in research on the effects of acidic deposition. Operators of about 200 sites in 1990 collected wet-deposition samples within the two combined programs in the United States and Canada. All site operators of NADP/NTN sites used the same type of wet-deposition collectors, which are described by

Bigelow and Dossett (1988). All site operators also used the same sample-handling protocols (Bigelow and Dossett, 1988) and sent their samples for chemical analysis to the Illinois State Water Survey, Central Analytical Laboratory (CAL). 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 (USGS) in support of the NADP/NTN during 1990. 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); (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); and (4) determine 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 collection and analysis of paired samples from collocated samplers at selected sites in the network (collocated-sampler program).

QUALITY-ASSURANCE PROGRAMS

Intersite-Comparison Program

The USGS completed intersite-comparison studies 25 and 26 in May and November 1990, respectively. In each intersite-comparison study, all NADP/NTN site operators were mailed an aliquot of a reference solution simulating the pH and specific conductance of a natural wet-deposition sample. Site operators were instructed to determine the pH and specific conductance of the reference solution using standard NADP/NTN procedures.

For each of the 1990 intersite-comparison studies, a reference solution consisting of ultrapure deionized water and dilute nitric acid was prepared by the USGS. The reference solution used in study 25 had a target pH of 4.55 and a target specific conductance of 11.9 μS/cm. The median pH of all site operators responding by the closing date for study 25 was 4.57, whereas the median specific conductance was 12.3 μS/cm. In study 26 the reference solution had a target pH of 4.83 and a target specific conductance of 5.95 μS/cm; the median pH of all site operators responding by the closing date for study 26 was 4.85 and the median specific conductance was 6.5 μS/cm. The equations for determining target values in the intersite-comparison program were published in a previous report (See and others, 1990).

The NADP/NTN accuracy goal for onsite pH determinations of less than 5.0 is ±0.10 pH unit of the actual pH; the accuracy goal increases to ±0.30 pH unit when the actual pH exceeds 5.0. Using the median values of all responding site operators as the most accurate estimate of pH, 80 percent (intersite comparison 25) and 74 percent (intersite comparison 26) of the participating site operators achieved the NADP/NTN pH measurement accuracy goals in 1990. The rationale for using the median values rather than target values as the best estimates of the actual values is discussed in a previous report (Gordon and others, 1991).

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, 98 and 95 percent of the site operators met the NADP/NTN specific-conductance goal for accuracy in studies 25 and 26.

The results of the 1990 intersite-comparison studies are graphically depicted in figures 1-3. Superimposed on the scatterplots in figure 1 are boundaries defining NADP/NTN accuracy goals for pH and specific-conductance measurements. Boundaries extending from the median values also are superimposed, delineating pH and specific-conductance values for site operators successfully meeting the accuracy goals for both measurements. Histograms depicting the distribution of pH and specific-conductance values for studies 25 and 26 are shown in figures 2 and 3. Site-operator responses in the 1990 intersite-comparison studies are summarized in table 1.

In 1990, the intersite-comparison program was expanded to include a followup program. The purpose of the followup program is to improve site-operator performance, thereby facilitating achievement of the NADP/NTN objective that 100 percent of all site operators meet the measurement accuracy goals (NADP, 1990). Depending on a combination of factors, site operators failing to meet the pH accuracy goals were selectively asked to participate in the followup program. Factors were the magnitude by which they missed the pH measurement accuracy goals in the most recent study as well as their performance in the previous two studies. Depending on their results, site operators selected for the followup program received a combination of the following: additional aliquots of solution to measure; a letter requesting that the remaining portion of the solution from the current study be remeasured; a list of suggestions for making more accurate pH measurements. A flowchart depicting the expanded intersite-comparison program is depicted in figure 4.

Table 1.--Summary of site-operator responses for the 1990 intersite-comparison program

Site-operator responses	Intersite-comparison study	
	25	26
Number of site operators receiving samples	196	196
Number of site operators submitting pH values by closing date of study	183	181
Number of site operators submitting specific-conductance values by closing date of study	183	185
Number of site operators responding late	2	1
Number of site operators not responding	6	4
Number of sites that were not operating	2	3
Number of site operators reporting equipment problems:		
pH meter/electrode inoperable	3	7
pH meter/electrode problems	5	3
Specific-conductance probe/meter inoperable	3	3
Specific-conductance probe/meter problems	0	0

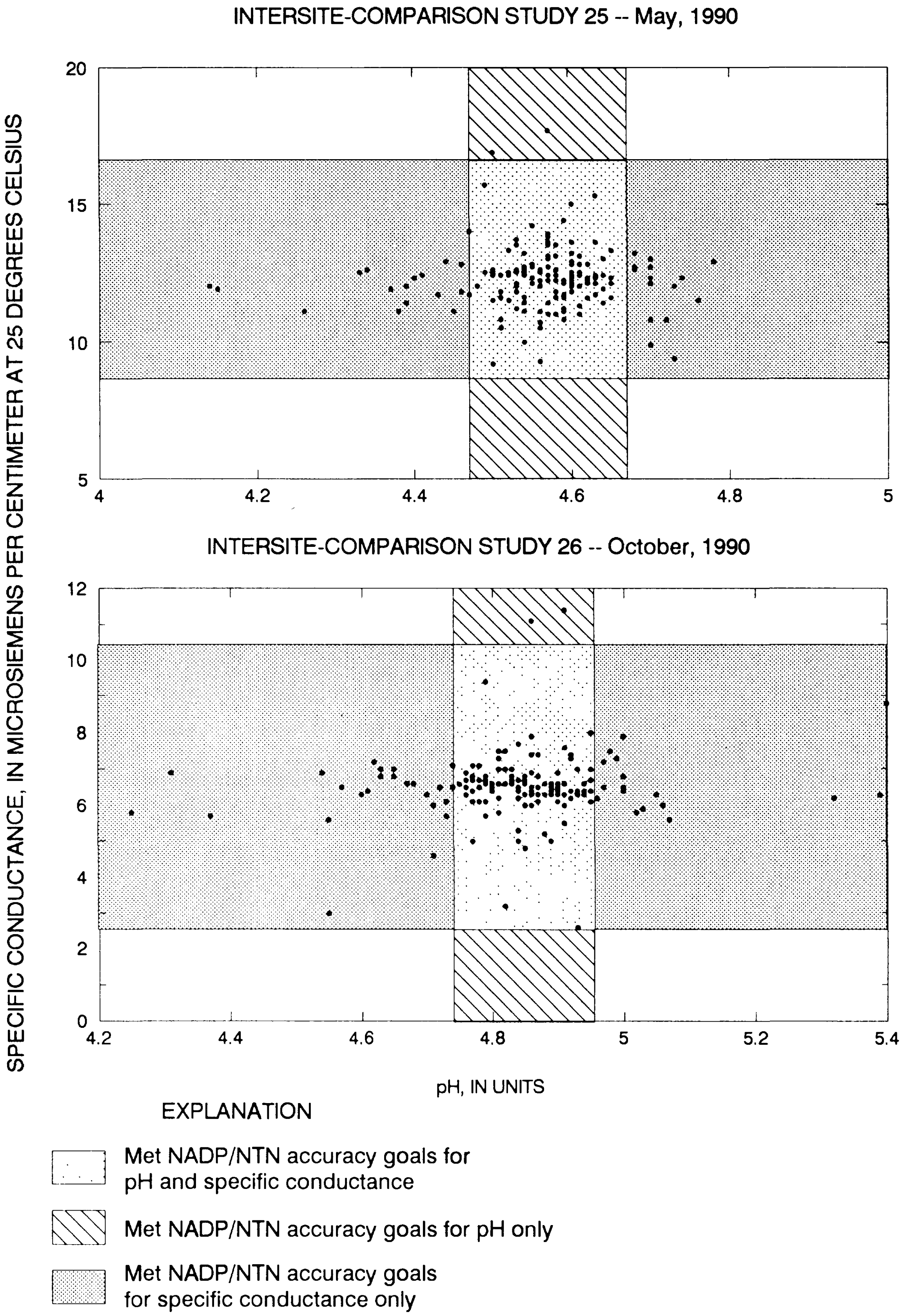
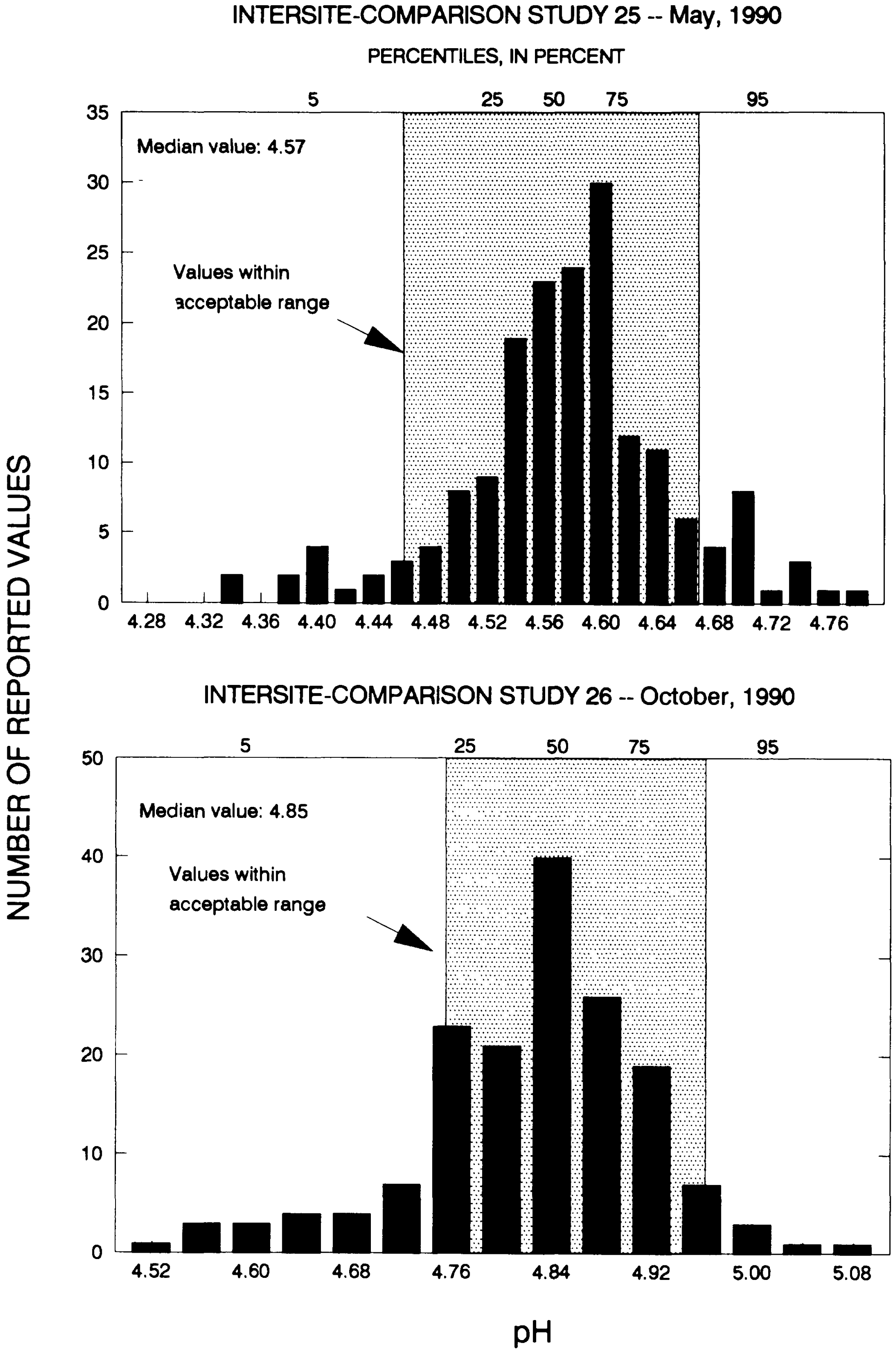


Figure 1.--Analytical results from intersite-comparison studies 25 and 26.



INTERSITE-COMPARISON STUDY 25 -- May, 1990

INTERSITE-COMPARISON STUDY 26 -- October, 1990

Figure 2.--Distribution of pH values for intersite-comparison studies 25 and 26.

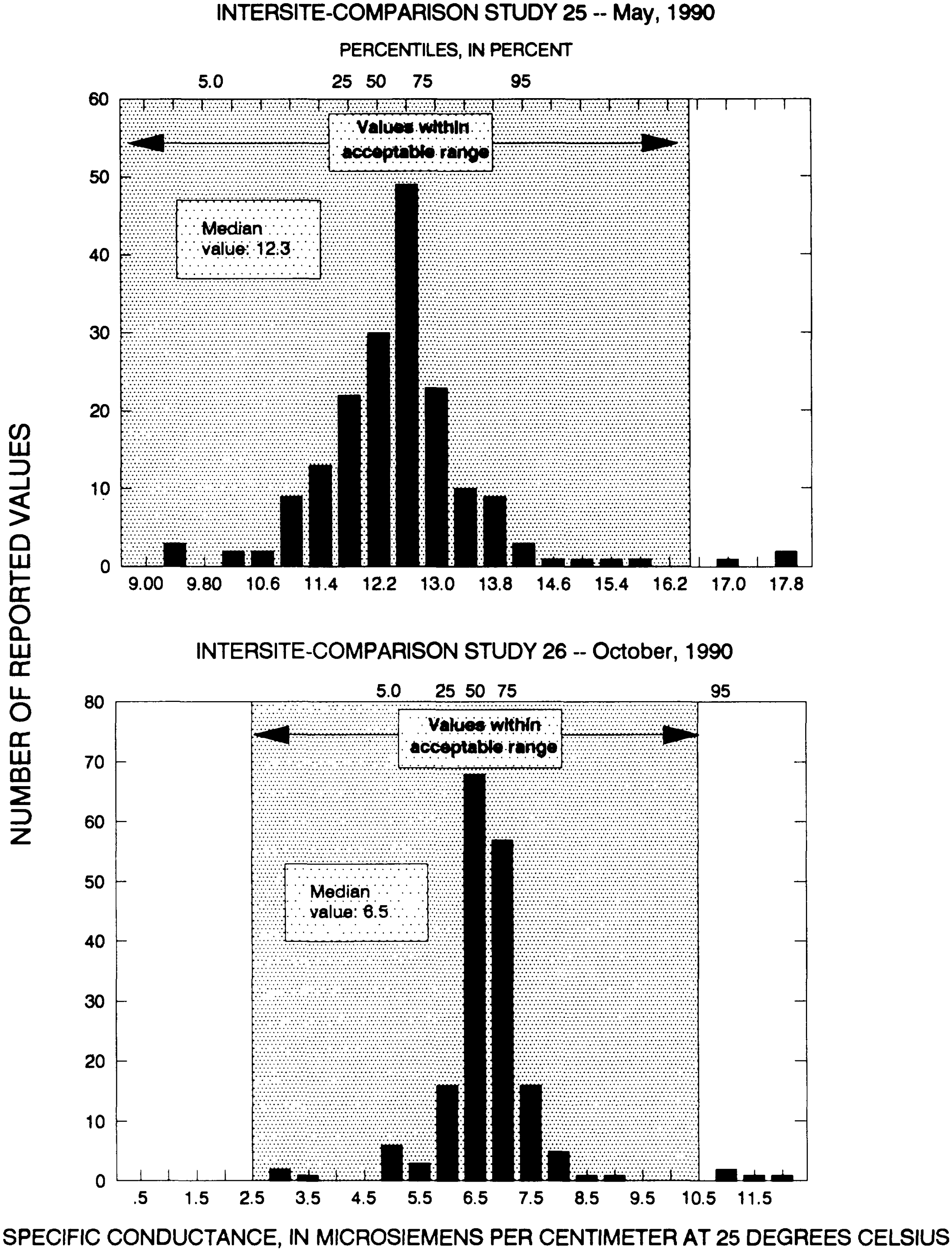


Figure 3.--Distribution of specific-conductance values for intersite-comparison studies 25 and 26.

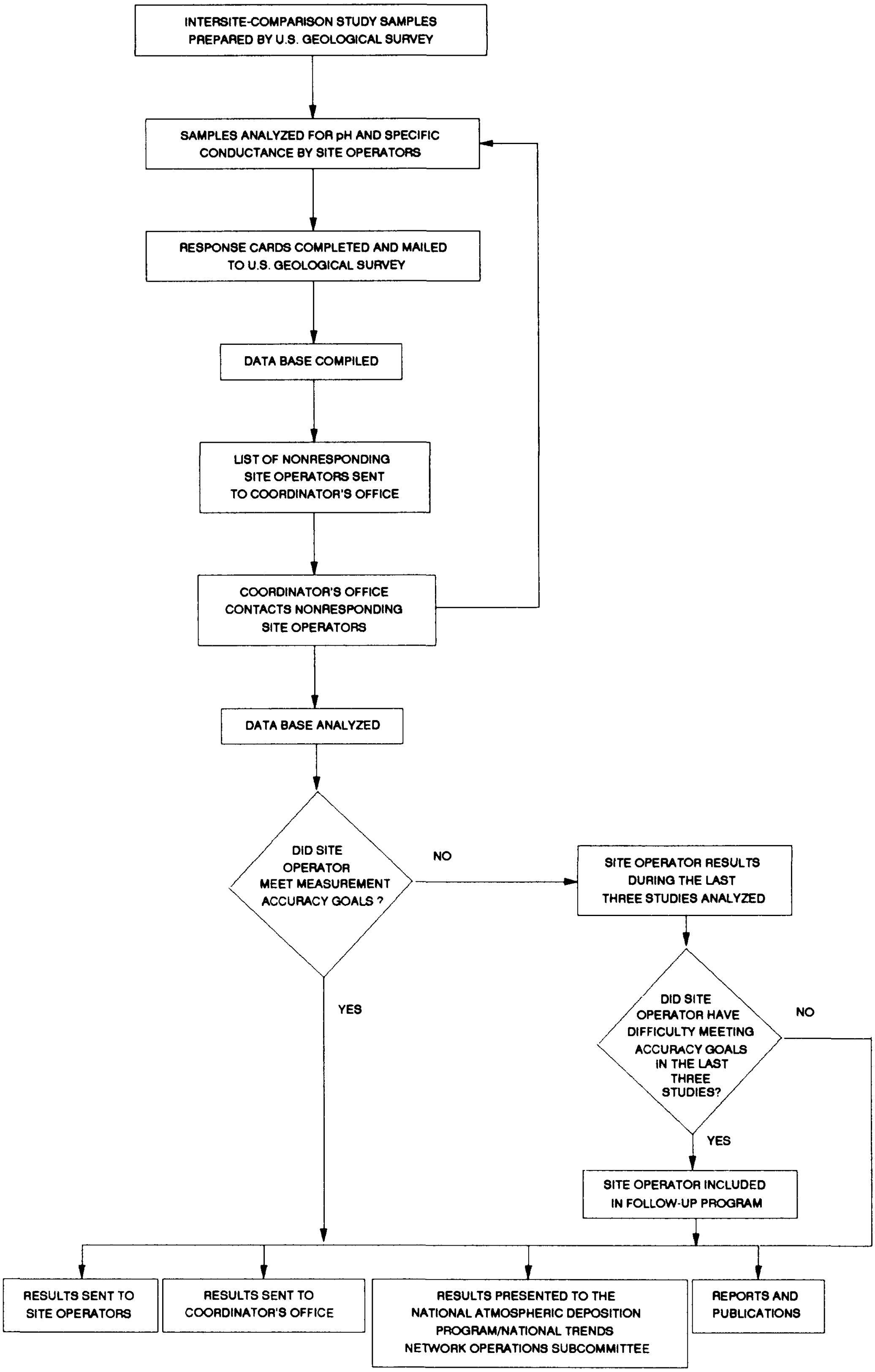


Figure 4.--Intersite-comparison program.

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 is provided by Schroder and others (1985). A flowchart showing the operation of the blind-audit program is presented in figure 5. Thirty-two blind-audit samples were sent to selected NADP/NTN site operators in each quarter of 1990. The site operators receiving blind-audit samples in each quarter were selected to ensure a uniform geographic distribution. For 1990, 250-, 500-, and 1,000-mL samples were sent to selected site operators each quarter to assess volume-related effects on biases. Site operators also were provided with detailed instructions on how to process the blind-audit samples.

Six solutions were used in the 1990 blind-audit program. One of the solutions was prepared by the CAL staff--a dilute nitric-acid solution, referred to as CAL 4.3. One solution was prepared by the U.S. Geological Survey Standard Reference Water Project; this solution was referred to as P-12. Two solutions were prepared by the U.S. Geological Survey Acid Rain Project; these solutions were referred to as USGS and ultrapure. The ultrapure solution is ultrapure deionized water with a measured resistivity greater than 16.7 MΩ. Two solutions were supplied by the U.S. Environmental Protection Agency as stock solutions and were diluted and prepared by the U.S. Geological Survey Acid Rain Project. These two solutions were referred to as 1085-1-1:1 and 1085-1-2:1. The target values for solutions used in the 1990 blind-audit program are presented in table 2.

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. Over one-half of all site operators were requested to submit a blind-audit sample in 1990. The location of sites whose operators participated in the 1990 blind-audit program is presented in figure 6.

Site operators were instructed to pour about 80 percent of the blind-audit sample into a clean NADP/NTN standard 13-L polyethylene collection 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. The operator then removed a 20-mL aliquot for onsite measurements of pH and specific conductance, and the weight was determined for the bucket sample. The bucket then was sealed, disguised as a routine wet-deposition sample with a fictitious NADP/NTN field-observer report form, and submitted to the CAL for analysis. 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 the bucket and bottle portions form the basis for determining bias. The CAL staff that received and analyzed the disguised 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 either to the site operators or the CAL staff that analyzed the samples.

The actual precipitation sample was also collected by the site operator who was submitting a blind audit sample. The actual sample was submitted to the CAL using a dummy field-observer report form. The CAL staff that received and analyzed the actual precipitation sample could not identify which site the sample had been sent from. After the blind-audit sample and the actual precipitation sample were analyzed by the CAL, the CAL was notified by the USGS that the analytical data for 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 qual-

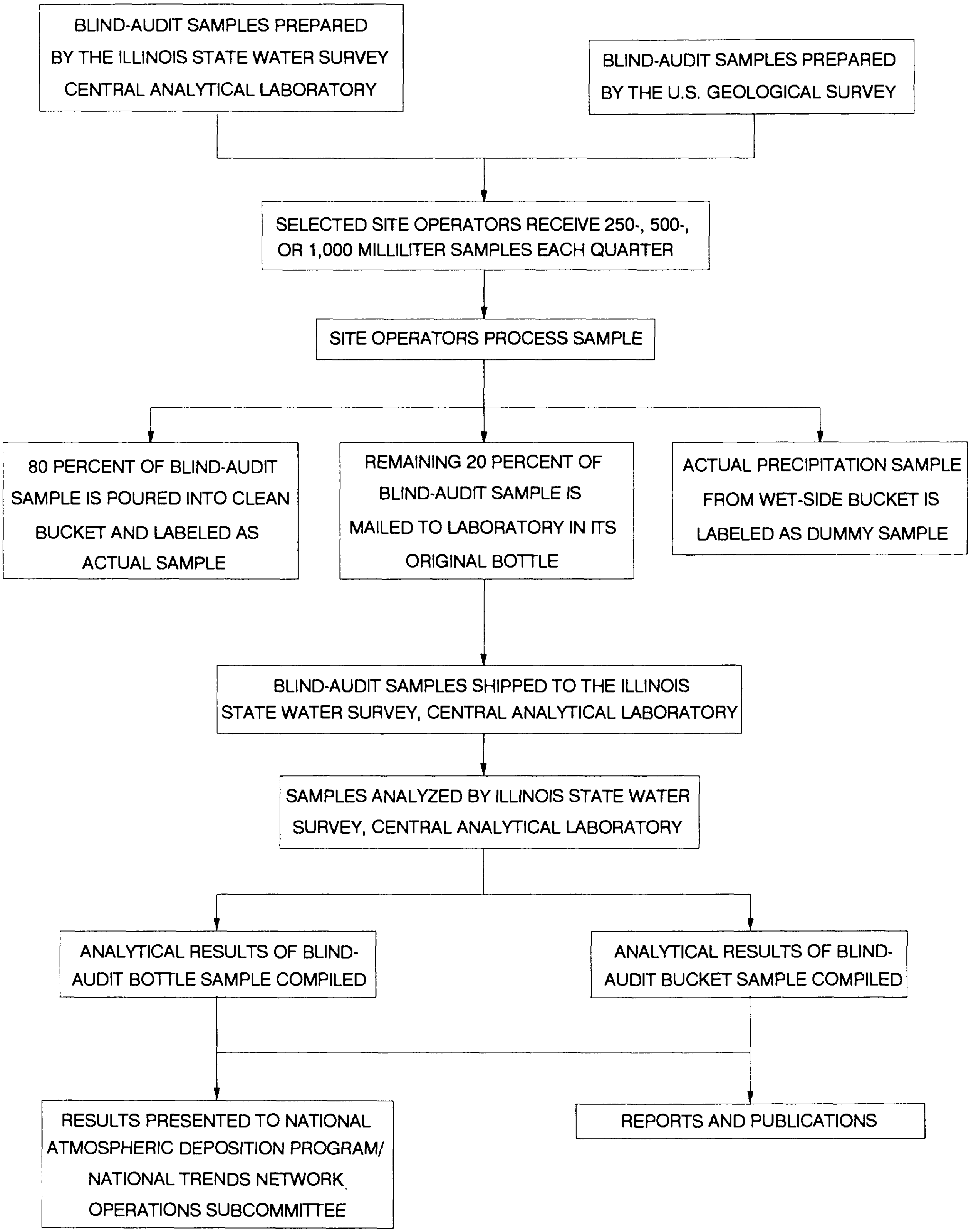


Figure 5.--Blind-audit program.

Table 2.--Target values for solutions used in the 1990 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]

Solution name	Milligrams per liter								pH	Specific conductance
	Ca	Mg	Na	K	NH_4	Cl	NO_3	SO_4		
[1]CAL 4.3	<dl	<dl	<dl	<dl	<dl	<dl	3.11	<dl	4.3	22
[1]P-12	0.91	0.06	0.71	0.05	--	0.66	--	0.65	6.58	10.0
[1,2]USGS	.14	.037	.092	.025	0.160	.142	1.08	.938	4.80	8.0
[1,2]Ultrapure	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl	[4]5.65	[4].064
[1,2]1085-1-1:1	.065	.021	.182	.079	--	.289	.61	2.75	4.29	24.7
[1,2]1085-1-2:1	.033	.011	.091	.040	--	.145	.31	1.38	--	12.4
[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] Used in the 1990 blind-audit program.

[2] Used in the 1990 interlaboratory-comparison program.

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

[4] At 25 degrees Celsius and 1 atmosphere pressure (Hem, 1985; Dean, 1979).

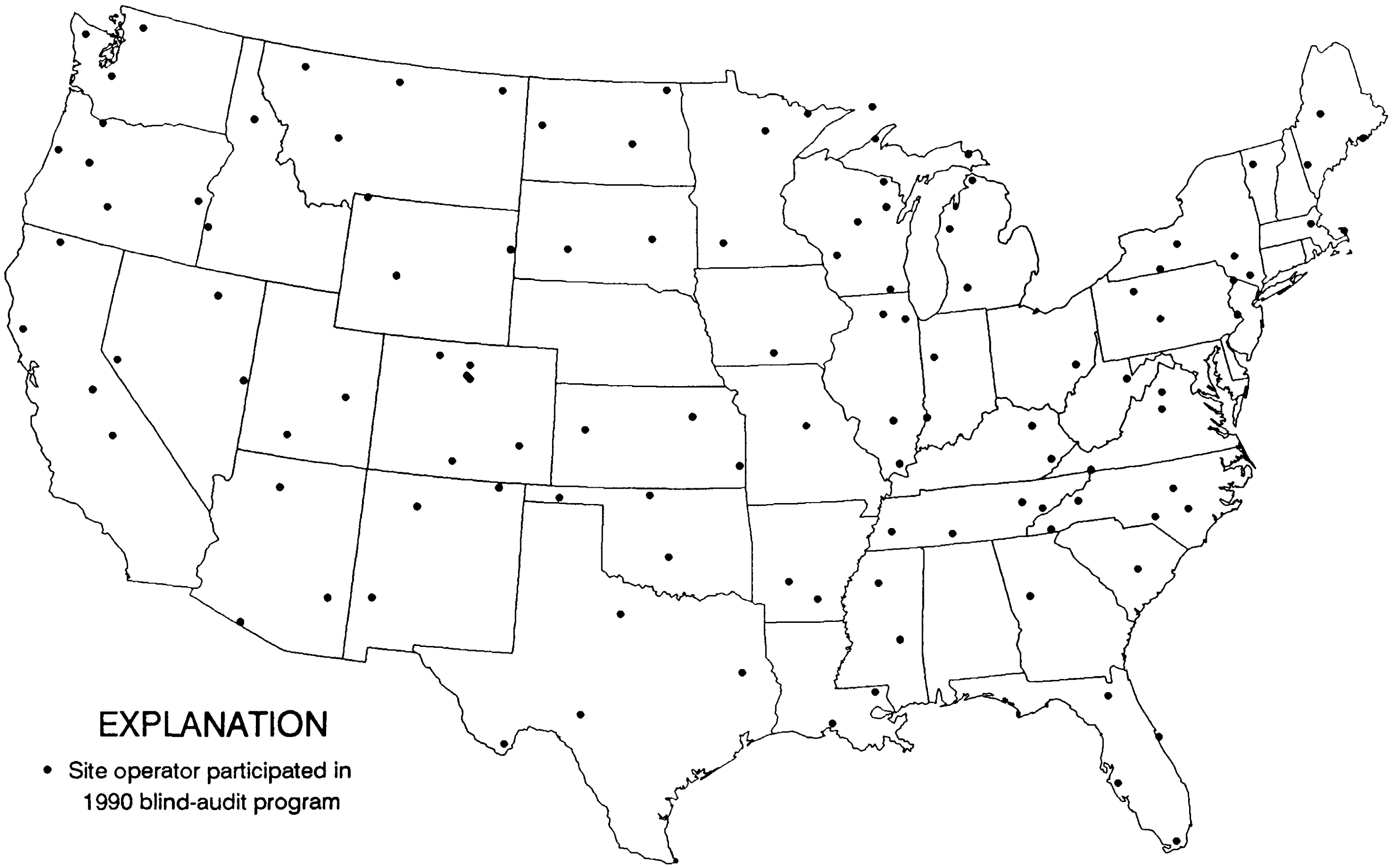


Figure 6.--Location of National Atmospheric Deposition Program/National Trends Network sites whose operators participated in the 1990 blind-audit program.

ity-assurance officer to the CAL laboratory staff for routine analysis. Although the CAL staff knew that bottle samples were not actual NADP/NTN samples, the analyte concentrations in bottle samples were not known by the laboratory staff. During 1990, the CAL analyzed the paired bucket and bottle samples within 20 days of each other, while most sample pairs were analyzed within one week 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 sample handling, shipping and processing 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 the site operator poured an aliquot of the bottle sample into the bucket and the time the CAL analyzed the bottle portion of the blind-audit sample.

Complete bucket and bottle analyses were available for 119 of the 128 blind-audit samples sent to participating site operators in 1990. Six site operators failed to submit the blind-audit samples. One site operator had discontinued operation. Two site operators poured their entire sample into the bucket; therefore, no bottle analysis was available for those samples.

For actual precipitation samples, the CAL assigns, based on physical evidence plus anomalous chemistry, a "C" code to indicate the sample is contaminated (Bowersox, 1984). For quality-assurance samples, the CAL takes a more conservative approach; all quality-assurance samples containing extrinsic material are assigned a "C" code. Because prior investigations have indicated no significant differences in analytical results among uncontaminated bottle samples and contaminated bucket samples (See and others, 1989), data from all bucket samples assigned a contamination code were included in the 1990 blind-audit statistical analyses.

In 1990, analyte concentrations reported as less than the minimum reporting limit were set equal to the minimum reporting limit. The median analyte concentration values for bottle samples in 1990 were between the 25th and 75th percentile of all natural wet-deposition samples collected at NADP/NTN sites in 1990. A Wilcoxon signed-ranks test was used to determine if any significant differences existed between the analyte concentrations measured for the paired 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 difference from all paired analyte determinations. All blind-audit samples that had paired analyte determinations except the ultrapure samples were included in the statistical analyses. Median concentrations determined from 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 ion, 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, ammonium, 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.

When median bucket minus bottle differences are calculated as a percentage of the median bottle concentration, three logical groupings become apparent for categorizing the magnitude of analyte bias. Percent bias for pH and specific conductance exceed negative 20 percent, whereas the bias for nitrate and sulfate is less than 4 percent. Percent bias for the remaining six analytes falls within a narrow range of 7.5 to 11 percent. 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. To evaluate

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

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

Analyte	Sample type	Median	Median difference	Number of pairs
Calcium	Bucket	0.138	0.013	105
	Bottle	.130		
Magnesium	Bucket	.030	.003	105
	Bottle	.028		
Sodium	Bucket	.132	.009	105
	Bottle	.120		
Potassium	Bucket	.035	.003	105
	Bottle	.030		
Ammonium	Bucket	.14	-.01	105
	Bottle	.12		
Chloride	Bucket	.20	.02	105
	Bottle	.18		
Nitrate	Bucket	1.03	.02	105
	Bottle	1.02		
Sulfate	Bucket	.91	.03	105
	Bottle	.88		
Hydrogen ion	Bucket	11.75	-8.92	105
	Bottle	18.2		
Specific conductance	Bucket	10.3	-2.7	105
	Bottle	11.6		

the magnitude of the bias as estimated by the blind-audit program, the percent bias for each analyte was compared to the bias goals for laboratory measurements defined in the quality-assurance plan for NADP/NTN deposition monitoring (NADP, 1990a). The bias estimates from the blind-audit program exceeded the bias goals in laboratory measurements only for hydrogen ion and specific conductance. Differences between the bucket-sample and bottle-sample concentrations are depicted using box plots (figure 7). The box plots in figure 7 are patterned after the style described by Chambers and others (1983). Using their definition of a box plot, the upper and lower quartiles are portrayed by the top and bottom of the rectangle. Lines called whiskers extend from the ends of the box to two "adjacent values." The "upper adjacent value" is defined as the largest data point less than or equal to the upper quartile plus 1.5 times the interquartile range (IQR). The "lower adjacent value" is defined as smallest data point greater than or equal to the lower quartile minus 1.5 times the IQR. The IQR equals the upper quartile minus the lower quartile. To set the length of the top whisker, a computerized search routine determines the largest value within the upper whisker limit (defined as 1.5 times the IQR) and sets the end of the whiskers equal to this value. The whisker will extend to 1.5 times the IQR if no data values are found or a value is found at 1.5 times the IQR. The search routine for setting the lower whisker limit works similarly.

To compare the differences measured in the analyte concentrations for the bucket and bottle portion of the blind-audit samples for 1990 with the differences for 1989, the same statistical methods were used on the bucket and bottle portions of the blind-audit samples for

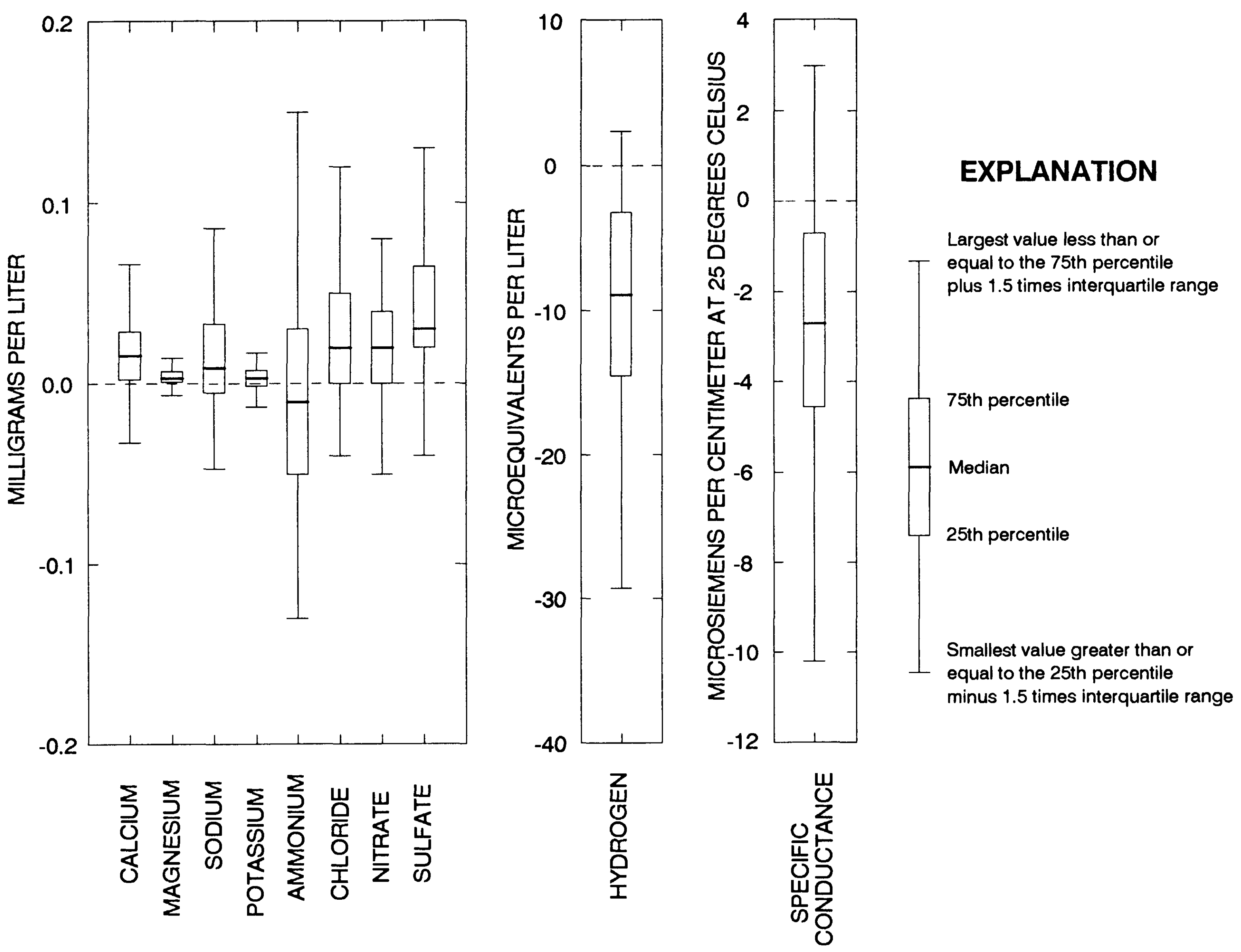


Figure 7.--Bucket-sample concentrations minus bottle-sample concentrations in the blind-audit program.

1989. Two solutions used in 1989 were not used in 1990; however, the median bottle concentrations for 1990 were nearly identical to the median bottle concentrations for 1989. As in 1990, for 1989 the bucket results for all analytes examined were statistically different (α=0.01) from the bottle results except for ammonium. The median differences between the bucket and bottle results in 1990 were greater than in 1989 for calcium, potassium, ammonium, and chloride. The median differences between the bucket and bottle results in 1990 were less than in 1989 for sodium, sulfate, and hydrogen ion. However, the measured changes between the 1989 and 1990 median differences for the bucket and bottle samples were less than 10 micrograms for all analytes except sodium. The median difference for sodium between bucket and bottle samples decreased from 0.025 mg/L in 1989 to 0.009 mg/L in 1990.

The precision of the 1990 NADP/NTN wet-deposition analyses was estimated by pooling the standard deviations of replicate blind-audit bucket samples (Dixon and Massey, 1969, p. 113). The ultrapure samples were not included in this analysis. Two determinations for the pooled standard deviations were made as follows: (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 occurred for the estimated pooled standard deviations when using these two methods. The estimated standard deviations are listed in table 4.

To compare the precision determined for the 1990 blind-audit program, the same statistical procedures also were done on the 1989 blind-audit results. No significant differences were determined between the 1989 and 1990 estimated pooled standard deviations. The analyte precision reported by the CAL for the 1990 blind-audit program was consistent with the analyte precision reported for the 1989 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, sixteen 250-mL, fifteen 500-mL, and sixteen

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; <, less than]

Analyte	Minimum value	Maximum value	Pooled standard deviation
Calcium	0.014	0.920	0.003
Magnesium	.006	.085	.001
Sodium	.015	.861	.004
Potassium	<.003	.258	.003
Ammonium	<.02	.44	.01
Chloride	.04	.83	.01
Nitrate	<.03	3.32	.01
Sulfate	<.03	2.73	.04
pH	4.28	6.94	.04
Specific conductance	3.0	26.4	.4

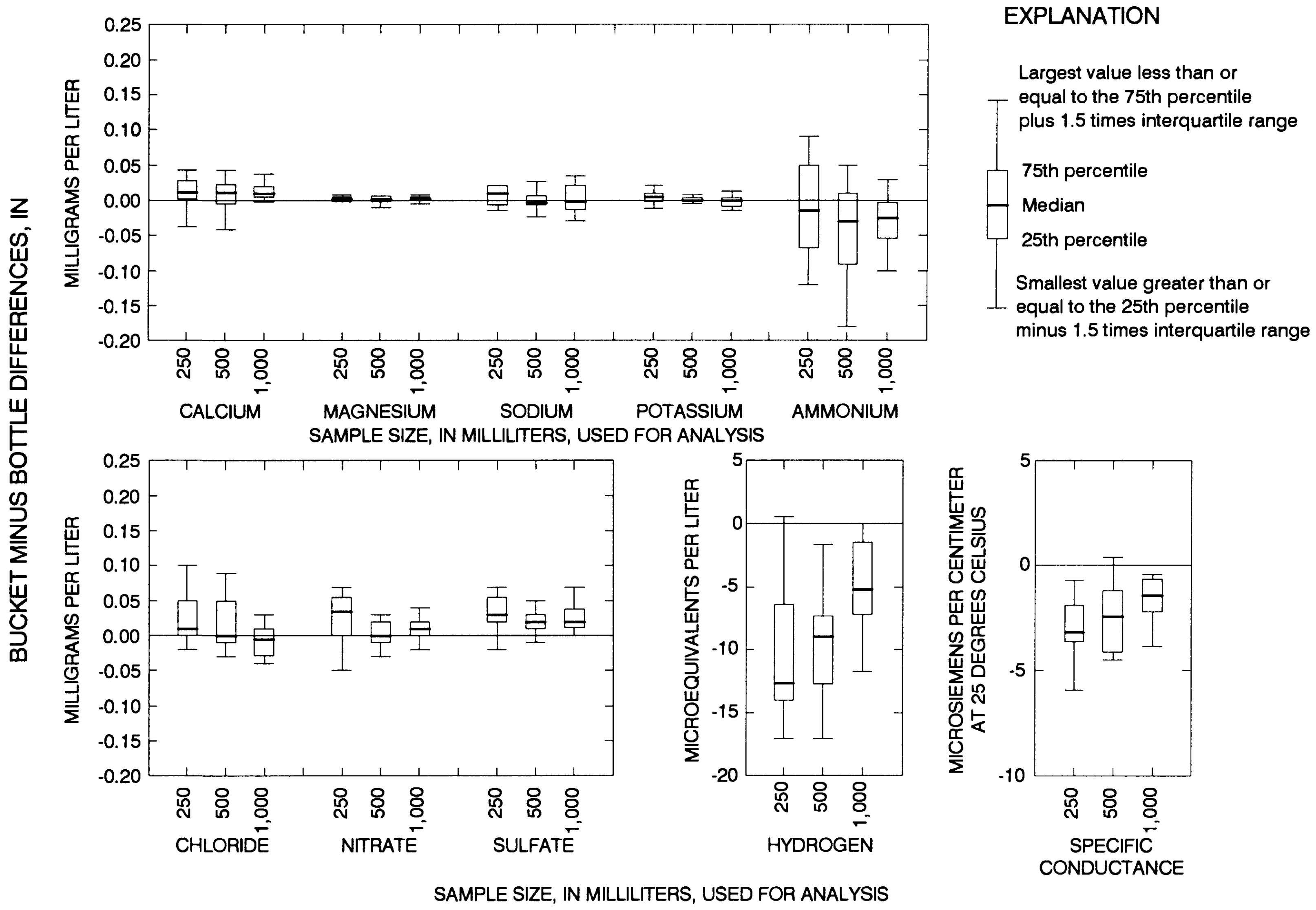


Figure 8.--Bucket-sample concentrations minus bottle-sample concentrations for the 250-, 500-, and 1,000-mL USGS solution samples in the blind-audit program.

1,000-mL bottles of the same solution (USGS) were sent to site operators in 1990. The site operators poured about 75 percent of each bottle into a 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 1990 was 987 mL and is best represented by the 1,000-mL blind-audit sample.

Box plots in figure 8 indicate the difference between the measured bucket and bottle concentrations of the USGS solution blind-audit samples for the different volumes of sample mailed to the site operators. The analyte concentrations that measured less than the minimum reporting limit were set equal to the minimum reporting limit, having the effect of minimizing the difference between the bucket and bottle analyses when the bucket concentration measured greater than the minimum reporting limit and the bottle concentration measured less than the minimum reporting limit. If the bucket and bottle analyses measured less than the minimum reporting limit, the resulting differences are zero. As volume increased, slight decreases in the median difference between the bucket and bottle analyses were measured for calcium, magnesium, potassium, hydrogen ion and specific conductance. In 1990, the magnitude of the decrease in hydrogen-ion concentration and specific conductance as volume increased was consistent with the changes observed in samples submitted in 1989.

Although sodium, chloride, nitrate, and sulfate did not have a consistent change in concentration as volume increased, the median difference between the bucket and bottle concentrations were less in the 500-mL and 1,000-mL samples compared to the 250-mL samples for these analytes. The absolute median difference between the bucket and bottle samples for ammonium did not decrease as volume increased. Since more than 85 percent of blind-audit samples are 250 mL and the median NADP/NTN sample was 987 mL for 1990, the median bucket minus bottle differences in concentration reported in table 3 likely overestimate the typical changes occurring in actual NADP/NTN wet-deposition samples for all analytes except ammonium.

To further evaluate the effect of sample volume on changes in sample chemistry, the differences between the measured concentration in the bucket and bottle portions of the blind-audit samples were then multiplied 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. A slight decrease in median bucket versus bottle mass difference, in milligrams per bucket, was measured for potassium. In 1989, bucket versus bottle mass differences in sodium and chloride decreased as volume increased; whereas in 1990, sodium and chloride differences were unrelated to volume. For all other analytes examined, the differences on a mass basis increased or showed no trend as volume increased. No analytes examined showed a decrease in bucket versus bottle differences as volume increased in both 1989 and 1990. This indicates that the amount of contamination attributable to the sample-collection bucket is independent of sample volume for some analytes and may be positively correlated to volume for others. The bucket may be contributing a consistent mass of sodium, potassium, chloride, and nitrate. The bucket may be contributing an increasing mass of calcium, magnesium, and sulfate and may be removing an increasing mass of hydrogen ion as volume increases.

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 all or part of 1990: (1) Illinois State Water Survey, Central Analytical Laboratory (CAL); (2) Inland Water Directorate, National Water Quality Laboratory (IWD); and (3) Environmental Science and Engineering, Inc. (ESE).

Samples from four sources were prepared for the 1990 interlaboratory-comparison program: (1) Synthetic wet-deposition samples (USGS) and ultrapure deionized water samples (ultrapure) prepared by the U.S. Geological Survey, (2) synthetic wet-deposition stock solutions (1085-1-1:1 and 1085-1-1:2) supplied by the U.S. Environmental Protection Agency and diluted by the U.S. Geological Survey, (3) standard reference samples (2694-I and 2694 II) prepared and certified by the National Institute of Standards and Technology (NIST), and (4) natural wet-deposition samples collected at NADP/NTN sites and 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. These natural wet-deposition samples were divided into 10 aliquots by using a deca-splitter. The aliquots were bottled in 125-mL polyethylene bottles and shipped to the USGS, Denver, Colorado, in chilled, insulated containers. Natural samples were kept refrigerated and were reshipped to participating laboratories within 10 days of receipt by the USGS. Target values for synthetic wet-deposition solutions used in the interlaboratory-comparison program are listed in table 2.

Samples used for the 1990 interlaboratory-comparison program were relabeled and shipped by the USGS 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 NIST and a single aliquot of ultrapure deionized water or four aliquots of the synthetic wet-deposition samples prepared by the USGS. All samples were relabeled with a sample number only; therefore, 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 9. Data listed in table 5 give the analytical methods and the minimum reporting limits for the three laboratories participating in the 1990 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. Data from 44 natural samples analyzed at each laboratory were used in the calculation of the standard deviations for natural samples. Data from 46 synthetic samples analyzed by the CAL and IWD and 39 synthetic samples analyzed by ESE were used in the calculation of the pooled standard deviations for most analytes. The IWD reported data from only 41 synthetic samples for calcium, magnesium, and ammonium. Using these two methods, no significant differences existed for the estimated pooled standard deviations. The pooled standard deviations for the results reported by the CAL for potassium, nitrate, and sulfate for the natural samples were larger in 1990 than in 1989. The pooled standard deviations for the results reported by the IWD for potassium for the natural samples were greater in 1990 than in 1989. The pooled standard deviations for the results reported by ESE for sodium and potassium for the natural samples and sodium and sulfate for the synthetic samples were greater in 1990 than in 1989. A similar precision in the analyses of interlaboratory samples compared to blind-audit samples analyzed at the CAL indicates that although changes occur

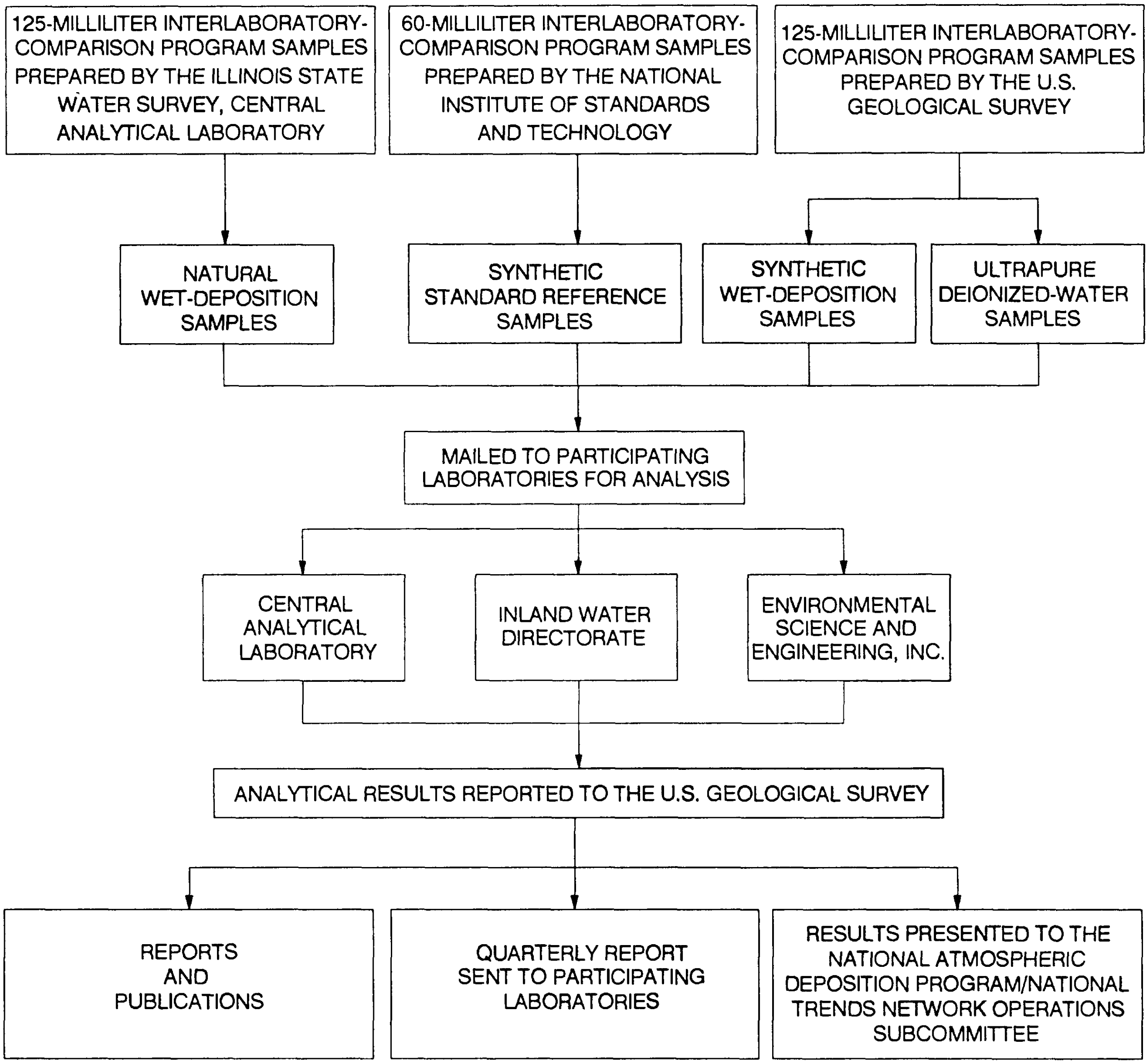


Figure 9.--Interlaboratory-comparison program.

Table 5.--Analytical method and minimum reporting limits for three laboratories participating in the 1990 interlaboratory-comparison program

[mg/L, milligram per liter; CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Water Directorate, National Water Quality Laboratory, Ontario, Canada; ESE, Environmental Science and Engineering, 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 (mg/L)					
	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	.02	(AP)	.001	(AP)	.013	(AP)
Chloride	.03	(IC)	.01	(IC)	.02	(IC)
Nitrate	.03	(IC)	.01	(IC)	.008	(IC)
Sulfate	.03	(IC)	.01	(IC)	.04	(IC)

in samples due to sample handling and shipping procedures, the variability is not increased appreciably for most analytes. The calculated pooled standard deviations are listed in table 6.

To examine bias in the analytical results from the laboratories, a Kruskal-Wallis test (Iman and Conover, 1983) was done. Results of the Kruskal-Wallis test indicate no significant ($\alpha=0.01$) 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 1990 are summarized in table 7. A comparison of the analyte concentrations determined by each laboratory is presented as box plots in figure 10. Only data for the time when all three laboratories participated in the interlaboratory program are given in table 7 and figure 10.

Analyte bias for laboratories participating in the interlaboratory-comparison program also was evaluated by using the certified values and the estimated uncertainties reported by the 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 the NIST-certified values plus or minus the estimated uncertainty reported by the NIST. Although each laboratory was sent 18 NIST samples in 1990, the number of NIST samples analyzed by the participating laboratories was not equal. Consequently the median analysis summary for each laboratory is not based on an equal number of samples for many analytes at the two NIST concentration levels. Only the CAL analyzed all 18 samples for all of the determinations requested. The CAL had eight median analyses that were outside the range of uncertainty for the NIST samples. ESE and IWD had four and two median analyses respectively outside the NIST range of uncertainty. A summary of the median-analysis estimates for each laboratory and the certified values and estimated uncer-

Table 6.--Pooled standard deviations for analytes determined by three laboratories participating in the 1990 interlaboratory-comparison program

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign Ill.; IWD, Inland Water Directorate, National Water Quality Laboratory, Ontario, Canada; ESE, Environmental Science and Engineering, 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; --, no data; <, less than]

Analyte	CAL		IWD		ESE	
	Nat	Syn	Nat	Syn	Nat	Syn
Calcium	0.002	0.004	0.004	0.005	0.002	0.003
Magnesium	.001	.001	.002	.002	.001	.002
Sodium	.003	.011	.010	.007	.011	.036
Potassium	.051	.004	.035	.005	.023	.010
Ammonium	.02	.03	<.01	.01	.003	.013
Chloride	.05	.02	0.03	.02	.03	.04
Nitrate	.06	.02	.02	.07	.01	.02
Sulfate	.05	.04	.03	.09	.01	.09
Hydrogen ion	1.28	4.37	.99	3.29	.71	2.77
Specific conductance	.68	1.04	--	--	.3	2.30

tainties for the NIST standard-reference materials 2694-I and 2694-II is presented in table 8.

Twelve ultrapure deionized water samples were included among the samples submitted to the CAL and the IWD. Ten ultrapure deionized water samples were submitted to ESE. Data listed in table 9 indicate the number of times that each laboratory reported a concentration greater than the laboratories' minimum reporting limit in a solution that would not be expected to contain any detectable analyte concentrations. Measured concentrations greater than the minimum reporting limit for the ultrapure deionized water samples is an indication that there is a possible contamination problem. The IWD reported eight determinations greater than the analyte minimum reporting limit. ESE had one determination greater than the minimum reporting limit while the CAL reported none. Four of the determinations reported by IWD as above reporting limit were values that were below the minimum reporting limits of the other two participating laboratories. Of the 34 ultrapure samples analyzed for eight constituents by the participating laboratories, only four individual determinations were reported greater than the 5th percentile of concentration values measured in precipitation by the NADP/NTN in 1990 (James, 1992). These were one sodium and two potassium determinations reported by IWD and one ammonium determination reported by ESE.

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, Environmental Science and Engineering, Inc., Gainesville, Fla; all units are in milligrams per liter, except hydrogen ion, in microequivalents per liter, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius; --, no data]

Analyte	Percentiles								
	CAL			IWD			ESE		
	25th	50th	75th	25th	50th	75th	25th	50th	75th
Calcium	0.030	0.050	0.130	0.030	0.080	0.140	0.031	0.052	0.122
Magnesium	.015	.023	.032	.019	.026	.040	.019	.026	.033
Sodium	.045	.099	.205	.050	.110	.210	.048	.090	.187
Potassium	.018	.028	.063	.020	.033	.070	.019	.026	.070
Ammonium	.07	.12	.32	.08	.17	.31	.084	.157	.337
Chloride	.13	.19	.29	.13	.18	.30	.14	.17	.31
Nitrate	.49	.89	1.20	.35	.84	1.22	.47	.89	1.19
Sulfate	.90	1.32	2.78	.91	1.28	2.69	.91	1.30	2.73
Hydrogen	15.1	25.1	52.5	15.5	22.4	51.3	13.8	21.9	46.8
Specific conductance	10.6	13.7	27.8	--	--	--	10.4	13.7	25.5

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, Environmental Science and Engineering 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), the number of reported values; *, values outside the NIST-certified value plus or minus the estimate of uncertainty; --, data not available; <, less than]

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	(9)	0.015	(6)	0.015	(6)
	2694-II	.049	.011	.040	(9)	.042	(7)	.043	(9)
Magnesium	2694-I	.024	.002	.023	(9)	.026	(6)	.026	(6)
	2694-II	.051	.003	*.045	(9)	.050	(7)	*.047	(9)
Sodium	2694-I	.205	.009	.202	(9)	.208	(9)	*.176	(6)
	2694-II	.419	.015	*.396	(9)	.420	(9)	*.391	(9)
Potassium	2694-I	.052	.007	*.044	(9)	.050	(9)	.048	(6)
	2694-II	.106	.008	*.094	(9)	.110	(9)	.112	(9)
Ammonium	2694-I	--	--	<.02	(9)	<.001	(9)	<.013	(6)
	2694-II	--	--	1.03	(9)	1.02	(7)	0.98	(9)
Chloride	2694-I	--	--	.26	(9)	.25	(9)	.26	(6)
	2694-II	--	--	1.00	(9)	1.02	(8)	1.05	(9)
Nitrate	2694-I	--	--	<.03	(9)	<.04	(9)	<.035	(6)
	2694-II	7.06	.15	7.10	(9)	*6.82	(9)	7.04	(9)
Sulfate	2694-I	2.75	0.05	2.80	(9)	2.73	(9)	2.75	(6)
	2694-II	10.9	.2	11.04	(9)	10.88	(8)	11.00	(9)
pH	2694-I	4.27	.03	*4.23	(9)	*4.23	(9)	4.25	(6)
	2694-II	3.59	.02	3.57	(9)	3.58	(9)	3.57	(9)
Specific conductance	2694-I	26	2	*29	(9)	--	(0)	27	(6)
	2694-II	130	2	*136	(9)	--	(0)	*135	(9)

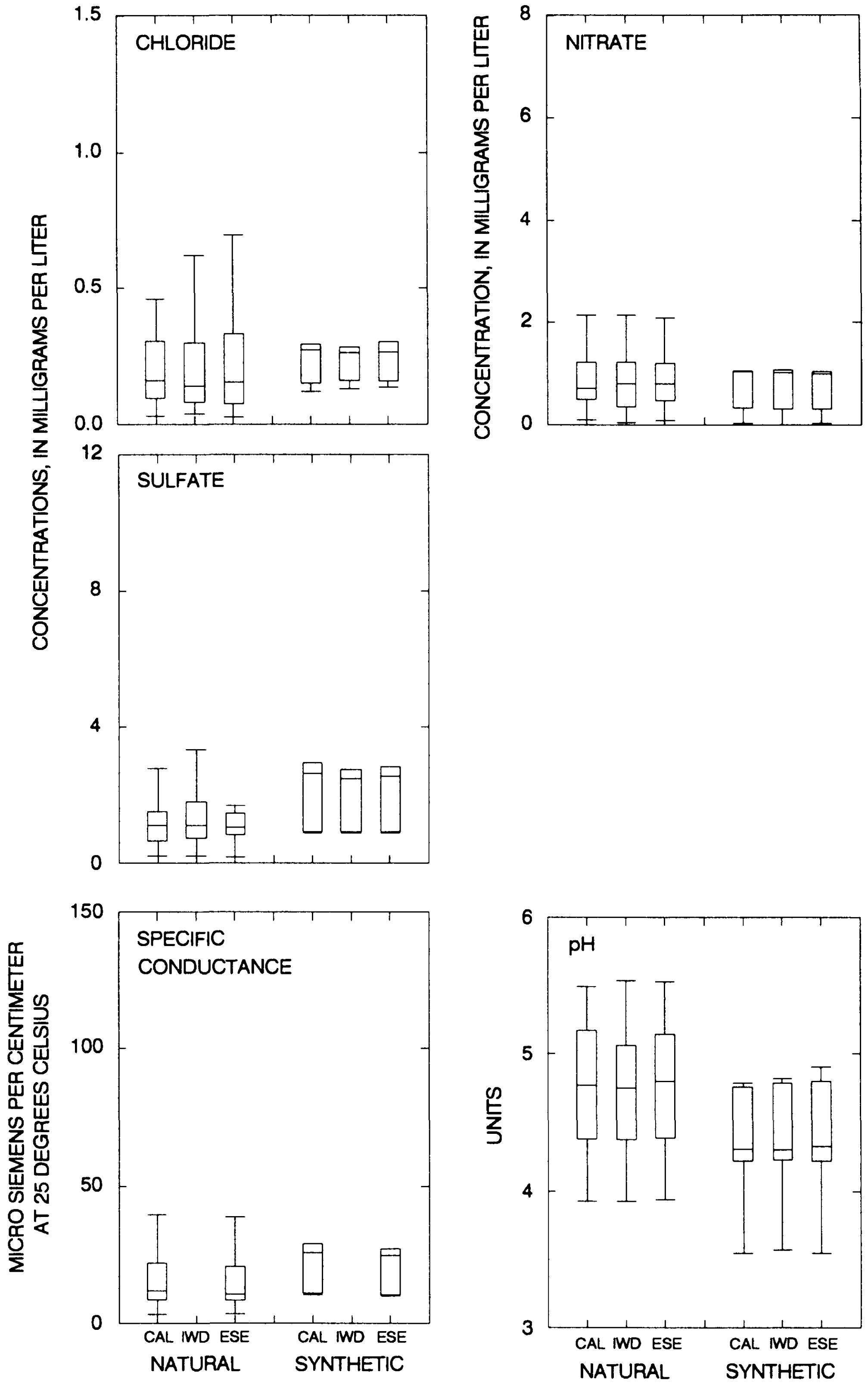


Figure 10.--Analytical results for selected water-quality constituents and properties determined by three laboratories participating in the interlaboratory-comparison program.

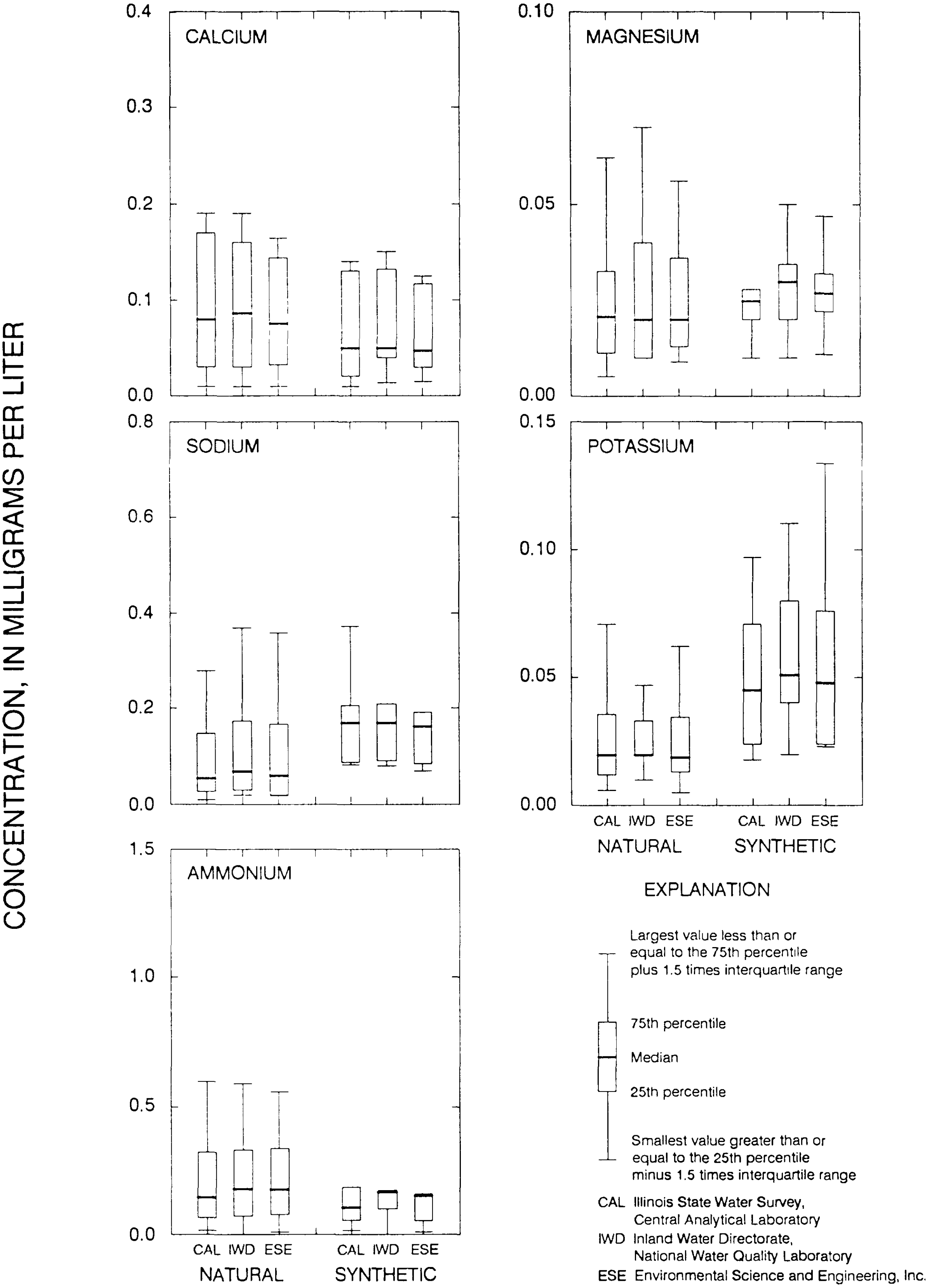


Figure 10.--Analytical results for selected water-quality constituents and properties determined by three laboratories participating in the interlaboratory-comparison program.--Continued

Table 9.--Reported analyte concentrations that were greater than the minimum reporting limit for the ultrapure deionized-water samples for each laboratory participating in the interlaboratory-comparison program during 1990

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Waters Directorate, National Water Quality Laboratory, Ontario, Canada; ESE, Environmental Science and Engineering, Inc., Gainesville, Fla.; all concentrations are in milligrams per liter; N, none]

Analyte	Laboratory		
	CAL	IWD	ESE
Calcium	N	N	N
Magnesium	N	N	N
Sodium	N	0.06	N
Potassium	N	0.02, 0.04	N
Ammonium	N	0.001, 0.005	0.014
Chloride	N	0.02	N
Nitrate	N	N	N
Sulfate	N	0.08, 0.03	N

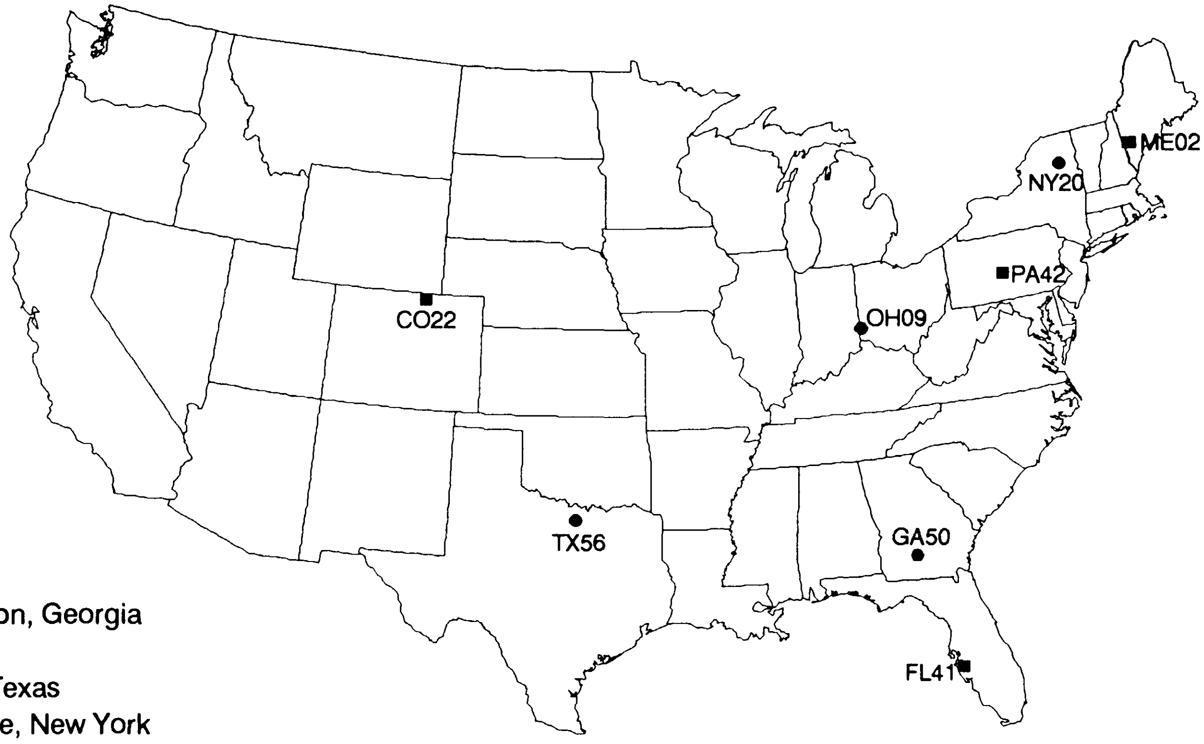
Collocated-Sampler Program

The collocated-sampler program was established in October 1988 to estimate the overall precision of the precipitation-monitoring system. This estimate of precision includes variability in the data-collection system from the point of sample collection through storage of the data in the NADP/NTN data base. This program is described in detail by Nilles and others (1991). Estimates of intrasite precision are provided for sites that participated in the first 2 years of the study.

Four sites that met several criteria were selected for each year of the collocated-sampler study. NADP/NTN guidelines for site selection and installation (Bigelow, 1984) were used in the establishment of each collocated-sampler site. A distribution of sites among diverse regional locations and among a range of precipitation regimes was needed. Only those sites with stable operational histories were considered to minimize data loss due to changes in personnel. Lack of room for collocated equipment was a common reason for eliminating from consideration several otherwise suitable fenced sites. The locations of sites participating in the collocated-sampler study in water years (October-September) 1989 and 1990 are shown in figure 11. Because results from the first 2 years of the collocated-sampler study have not been included in previous annual external quality-assurance reports, results from the first 2 years of the study are included here.

After the sites for the collocated-sampler program were selected, equipment was shipped by the USGS to each site and site supervisors or operators completed the installation of the equipment. Samples from the original and collocated samplers were processed by the site operator by using standard NADP/NTN procedures (Bigelow and Dossett, 1988). Onsite pH and specific-conductance measurements on the samples from the newly installed collocated-samplers were not required; however, a 20-mL aliquot was removed from samples of 70 mL or larger to provide equivalent treatments to both samples from the collocated-sampler site. All samples were analyzed by the CAL and all sites selected for the collocated-sampler study were inspected by USGS personnel. The four water year 1989 sites were inspected in the spring of 1989 after several months of sampling. The water year 1990 sites were inspected in August or September after equipment installation and before collection of the first sample.

Only data from normal wet-deposition samples with volume greater than 35 mL (lab type "W") that did not require dilution were used in the statistical summaries. Median sample concentrations in weekly samples from the eight sites are presented in table 10. Annual summaries of NADP/NTN data describe precipitation chemistry in units of concentration and deposition for ionic constituents (National Atmospheric Deposition Pro-



Site Abbreviations

GA50 - Tifton Ag. Research Station, Georgia
OH09 - Oxford, Ohio
TX56 - LBJ National Grassland, Texas
NY20 - Huntington Wildlife Refuge, New York
ME02 - Bridgeton, Maine
FL41 - Verna Well Field, Florida
PA42 - Leading Ridge, Pennsylvania
CO22 - Pawnee, Colorado

EXPLANATION

● Collocated sampler sites for water year 1989

■ Collocated sampler sites for water year 1990

Figure 11.--Location of National Atmospheric Deposition Program/National Trends Network sites with collocated samplers.

Table 10.--Median analyte concentrations and volume in weekly samples from collocated wet-dry precipitation collectors and precipitation depth from collocated rain gages

[All units in milligrams per liter except: hydrogen ion in microequivalents per liter; specific conductance in microsiemens per centimeter at 25 degrees Celsius; sample volume in milliliters; and precipitation depth in centimeters. See figure 11 for an explanation of site abbreviations]

Analyte	Sampling sites							
	GA50	OH09	TX56	NY20	ME02	FL41	PA42	CO22
Calcium	0.099	0.154	0.351	0.093	0.045	0.139	0.135	0.189
Magnesium	0.045	0.026	0.043	0.017	0.015	0.058	0.025	0.028
Sodium	0.225	0.064	0.176	0.052	0.078	0.405	0.059	0.084
Potassium	0.038	0.018	0.050	0.014	0.018	0.027	0.022	0.036
Ammonium	0.18	0.39	0.31	0.23	0.23	0.18	0.38	0.54
Chloride	0.45	0.16	0.26	0.12	0.17	0.72	0.21	0.15
Nitrate	0.83	1.63	1.37	1.95	1.38	0.69	2.58	1.73
Sulfate	1.16	2.53	1.35	1.89	1.82	0.93	3.07	0.99
Hydrogen ion	14.6	44.2	3.0	36.8	42.7	8.8	66.1	0.9
Specific conductance	12.7	25.0	12.2	2.2	22.1	11.4	37.2	9.9
Sample volume	1,157	1,299	1,365	998	1,147	1,791	883	495
Precipitation depth	1.94	2.06	2.08	1.68	1.77	2.27	1.73	0.80

gram, 1990). Precision estimates for both concentration and deposition of ionic constituents are included in this report. The weekly precipitation depth associated with each Belfort recording rain gage was used in this report to calculate deposition values. This approach accounts for the variability due to differences in rain-gage collection efficiency to be included in the precision estimates for deposition. Care was taken to select statistics that were meaningful in describing overall sampling precision and that were not overly sensitive to a few extreme outliers.

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

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

and

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

where

M = median of all paired differences;

C_1 = Sample concentration (mg/L) from the original precipitation sampler, or deposition(kg/ha) from the original precipitation sampler and rain gage;

C_2 = Sample concentration (mg/L) from the collocated precipitation sampler, or deposition (kg/ha) from the collocated precipitation sampler and rain gage.

Precision estimates defined by the median of the unsigned absolute or relative percent difference are fairly insensitive to a few extreme values. For sample pairs with low concentrations of ionic constituents, the relative percent error can be very large, although the absolute difference between the samples is small. The median number of valid sample pairs per site was 45 and ranged from a high of 51 at NY20 to a low of 32 at TX56. When one or both of the paired measurements for a given analyte were reported as less than method detection limits, results from that date were not used in the calculation of precision for that site.

Precision estimates of precipitation chemical concentration and deposition for the eight sites are presented in tables 11 and 12. Nitrate and sulfate concentration had the smallest relative error, ranging from 1.8 percent to 5.9 percent among the sites (table 11). Typical nitrate and sulfate concentrations were much greater than method detection limits reported by the CAL. Relative error for potassium and ammonium concentration and deposition exceeded 15 percent at most sites (tables 11 and 12). The larger relative error for potassium and ammonium compared to other analytes might be attributable to concentrations that were near method detection limits for many samples. The greatest variation in precision between any two of the eight sites occurred for hydrogen-ion deposition, with median relative error ranging from 4.6 percent at PA42 to 37.6 percent at CO22 (table 12). The large difference in precision estimates for hydrogen ion at those two sites can be accounted for by the difference in median concentration. Median hydrogen-ion concentration at PA42 was more than 70 times greater than that of CO22 (table 10). The smallest variation in median relative error was noted for sulfate concentration, which ranged from 1.9 percent to 4.8 percent among the eight sites.

Median relative error calculated for weekly analyte deposition at the eight sites incorporates variability due to differences in sample depth between the original and collocated Belfort recording rain gages. Although not consistent among sites or analytes, median relative

Table 11.--Median relative error for analyte concentrations and sample volume in weekly samples from collocated wet-dry precipitation collectors

[All data expressed in percent. See figure 11 for an explanation of site abbreviations]

Analyte	Sampling sites							
	GA50	OH09	TX56	NY20	ME02	FL41	PA42	CO22
Calcium	13.1	10.8	7.6	20.4	25.9	10.5	12.4	9.1
Magnesium	9.1	9.5	12.5	22.2	18.2	6.3	13.3	15.4
Sodium	4.7	11.5	6.6	20.2	13.7	4.5	14.4	22.3
Potassium	19.3	19.2	26.1	43.5	28.5	21.0	46.9	29.6
Ammonium	16.1	9.5	21.1	21.3	17.1	22.2	9.8	19.0
Chloride	2.4	6.5	6.9	13.3	11.7	6.1	9.2	12.2
Nitrate	3.2	3.3	3.5	5.9	2.8	2.8	1.8	4.5
Sulfate	2.3	3.5	3.6	3.5	3.1	3.4	1.9	4.8
Hydrogen ion	16.1	4.6	28.6	13.8	4.6	11.5	3.5	34.2
Specific conductance	3.1	5.8	7.0	6.3	3.2	4.9	2.2	5.2
Sample volume	1.2	2.0	1.5	3.4	1.1	1.5	1.5	4.2

Table 12.--Median relative error for analyte deposition in weekly samples from collocated wet-dry precipitation collectors and precipitation depth from collocated rain gages

[All data expressed in percent. See figure 11 for an explanation of site abbreviations]

Analyte	Sampling sites							
	GA50	OH09	TX56	NY20	ME02	FL41	PA42	CO22
Calcium	20.8	14.0	8.0	21.6	28.7	10.6	14.8	15.8
Magnesium	12.8	8.7	8.5	19.0	17.1	6.6	12.8	19.2
Sodium	7.2	13.5	6.7	25.8	16.6	5.1	14.6	24.0
Potassium	23.1	23.3	26.1	38.2	29.4	24.6	48.3	21.4
Ammonium	20.3	10.1	22.2	20.5	19.5	21.2	9.9	33.9
Chloride	7.5	7.4	11.4	20.7	14.9	4.0	9.9	12.5
Nitrate	5.8	4.9	4.9	10.7	8.7	3.8	3.9	12.2
Sulfate	6.3	4.2	4.2	11.0	8.2	4.5	2.9	14.6
Hydrogen ion	13.6	7.4	27.2	13.2	9.2	13.7	4.6	37.6
Precipitation depth	4.8	2.2	1.1	8.0	2.8	3.3	1.2	5.9

errors typically were 2-5 percentage points greater when calculated using deposition data rather than concentration data.

In table 13 collocated-analyte precision estimates are compared to analytical precision estimates calculated in the same manner from 104 replicate natural precipitation samples submitted to the CAL in 1989 and 1990 as part of an interlaboratory-comparison program. Aliquots of natural, weekly, wet-deposition samples with volumes greater than 750 mL are used in the USGS interlaboratory-comparison programs. The natural interlaboratory samples had slightly lower specific conductance and median concentrations of analytes when compared to all NADP/NTN network samples analyzed at the CAL. This program is described in detail in the Interlaboratory Comparison Program section of this report.

Laboratory random error, as calculated from replicate samples submitted to the CAL for analysis, is estimated typically to account for one-fifth of the overall collocated-sampling error, although the fraction of sampling error attributable to laboratory random error varies with site and with analyte. Estimated laboratory error typically exceeded 25 percent of the median collocated-sampling error for chloride ion. Laboratory error is calculated in this report from a random group of replicate samples selected from the universe of NADP/NTN wet-deposition samples submitted to the CAL for analysis. Comparisons of laboratory random error calculated this way to sampling error has limitations, because sampling error is very site specific for some analytes. For example, one might infer from table 13 that laboratory error in the determination of hydrogen ion accounts for 100 percent of the overall sampling error at site CO22. This type of specific partitioning of error would only be valid if the laboratory error term was calculated from a number of replicate samples collected at site CO22.

Bias was evaluated for each site and analyte by using the median signed difference between collocated-sample concentrations and is presented in table 14. Bias estimates for sample volume from the precipitation collectors and precipitation depth from the recording rain gages are also provided. Because the collocated paired samples were shipped from the sites weekly to the same laboratory at the same time, bias in the data-set pairs is attributed to systematic differences in sampler response, sample collection, and sample handling prior to shipment. Bias for most analytes accounted for less than 25 percent of the overall relative error in collocated-sampler measurements.

SUMMARY

During 1990, the U.S. Geological Survey used four programs designed to provide external quality-assurance monitoring for the National Atmospheric Deposition Program and the National Trends Network (NADP/NTN). An intersite-comparison program was used to assess 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 three 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.

Two intersite-comparison studies were completed during 1990. For pH, 80 percent of site operators met the NADP/NTN goals for intersite-comparison study 25, and 74 percent met the goals for intersite-comparison study 26. For specific conductance, 98 percent of site operators met the NADP/NTN goals for intersite-comparison study 25, and 95 percent met the goals for intersite-comparison study 26.

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

[All units in milligrams per liter except: hydrogen ion in microequivalents per liter, and specific conductance in microsiemens per centimeter at 25 degrees Celsius. CAL, Central Analytical Laboratory, Illinois State Water Survey; >, greater than. See figure 11 for an explanation of site abbreviations]

Analyte	Sampling site								
	GA50	OH09	TX56	NY20	ME02	FL41	PA42	CO22	CAL
Calcium	0.009	0.018	0.024	0.018	0.012	0.010	0.019	0.016	>0.001
Magnesium	0.004	0.003	0.003	0.003	0.003	0.004	0.003	0.004	0.001
Sodium	0.012	0.007	0.008	0.012	0.012	0.016	0.010	0.015	0.001
Potassium	0.005	0.004	0.014	0.005	0.004	0.005	0.010	0.009	0.002
Ammonium	0.03	0.03	0.07	0.04	0.03	0.04	0.03	0.08	>0.01
Chloride	0.01	0.01	0.02	0.01	0.02	0.02	0.02	0.02	>0.01
Nitrate	0.02	0.06	0.04	0.13	0.05	0.02	0.04	0.06	0.01
Sulfate	0.03	0.11	0.04	0.08	0.05	0.02	0.06	0.03	0.01
Hydrogen ion	1.85	3.05	0.49	2.86	2.45	1.03	2.01	0.29	0.31
Specific conductance	0.50	1.50	0.65	1.40	0.70	0.60	0.70	0.50	0.20

Table 14.--Bias for analyte concentrations and sample volume in weekly samples from collocated wet-dry precipitation collectors and precipitation depth from collocated rain gages

[All data expressed in percent. See figure 11 for an explanation of site abbreviations]

Analyte	Sampling site							
	GA50	OH09	TX56	NY20	ME02	FL41	PA42	CO22
Calcium	2.1	-10.3	5.4	-6.2	0.0	5.6	0.7	-3.3
Magnesium	0.0	-4.7	4.7	-6.9	0.0	-4.2	0.0	0.0
Sodium	0.0	0.0	3.3	-4.7	6.3	-4.4	8.3	0.0
Potassium	0.0	-10.5	0.0	-34.8	0.0	-6.9	23.9	1.8
Ammonium	0.0	-2.8	-6.3	-5.4	6.4	-8.7	0.0	-2.1
Chloride	0.0	0.0	2.2	0.0	5.2	-5.5	7.4	0.0
Nitrate	0.0	-2.9	3.5	-2.9	0.0	-2.7	0.9	-2.4
Sulfate	-0.3	-2.3	-2.0	-1.2	0.0	-2.6	0.5	-1.2
Hydrogen ion	0.0	2.3	0.0	0.0	-2.3	0.0	2.3	-27.5
Specific conductance	1.0	-3.5	5.9	-1.6	-0.6	-2.6	1.0	2.0
Sample volume	0.2	-1.9	0.8	-1.3	-0.1	-1.2	0.6	-3.3
Precipitation depth	-3.9	0.0	0.0	2.4	0.6	1.8	0.0	-2.0

In an effort to improve site operator performance, the intersite comparison study was expanded in 1990 to include a followup program. Depending on a combination of factors, site operators failing to meet the pH-measurement-accuracy goals were asked to participate in the followup program. Factors were the magnitude by which they missed the pH measurement accuracy goals in the most recent study as well as their performance in the previous two studies.

Results for the blind-audit program indicated significant ($\alpha=0.01$) positive bias for calcium, magnesium, sodium, potassium, chloride, nitrate, and sulfate. Significant ($\alpha=0.01$) negative bias was determined for hydrogen ion and specific conductance. Only the bias for hydrogen ion and specific conductance exceeded the bias goals for laboratory measurements. An estimate of analytical precision was calculated using a pooled standard deviation.

As part of the interlaboratory-comparison program, Kruskal-Wallis tests on data from three laboratories indicated no significant difference among laboratory determinations for all analytes examined. A similar degree of precision in the analyses of interlaboratory samples compared to blind-audit samples analyzed at the CAL indicates that although significant changes occur in samples due to sample handling and shipping procedures, the variability is not increased appreciably for most analytes. Analytical results from National Institute of Standards and Technology reference solutions indicated that the CAL had eight median analyses that were significantly different from the certified values. ESE and IWD had four and two median analyses respectively that were significantly different from the certified values. The IWD reported eight determinations larger than the minimum reporting limit for the analyses of ultrapure deionized-water samples, whereas ESE and the CAL reported one and zero determinations respectively that were greater than the minimum reporting limits. Four of the eight determinations reported by IWD as greater than reporting limits were for values that were below the reporting limits of the other two laboratories.

An ongoing collocated-sampler program was established 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 units of median relative difference and in terms of median absolute difference for both concentration and deposition of ionic constituents of wet deposition.

The median relative error for sulfate and nitrate was typically less than the median relative error calculated for all other analytes examined. Relative error typically was greatest for potassium and ammonium ion, with median relative error exceeding 15 percent at most sites. Laboratory error is estimated to account for typically one-fifth of the overall collocated-sampling error on the basis of data from replicate natural samples analyzed at the CAL. Bias in collocated measurements typically accounted for less than 25 percent of the overall error in collocated measurements.

REFERENCES CITED

Bigelow, D.S., 1984, Instruction manual: NADP/NTN site selection and installation: National Atmospheric Deposition Program, Natural Resources Ecology Laboratory, Fort Collins, Colorado State University, 23 p.

Bigelow, D.S., and Dossett, S.R., 1982, Instruction manual, NADP/NTN site operation: Fort Collins, Colorado State University, Natural Resources Ecology Laboratory, 30 p.

Bigelow, D.S., and Dossett, S.R., 1988, Instruction manual—NADP/NTN site operation: National Atmospheric Deposition Program/National Trends

Network, Fort Collins, Colorado State University, Natural Resources Ecology Laboratory, 114 p.

Bowersox, V.C., 1984, Data validation procedures for wet deposition samples at the Central Analytical Laboratory of the National Atmospheric Deposition Program, *in* Quality Assurance in Air Pollution Measurements, Johnson and Penkala (eds.): Pittsburgh, Penn., Air Pollution Control Association, p. 500-524.

Chambers, J.M., Cleveland, W.S., Kleiner, Beat, and Tukey, P.A., 1983, Graphical methods for data analysis: Boston, Duxbury Press, 395 p.

Dean, J.A., ed., 1979, Lange's handbook of chemistry (12th ed.): New York, McGraw-Hill, 644 p.

Dixon, W.J., and Massey, F.J., 1969, Introduction to statistical analysis (3d ed.): New York, McGraw-Hill, 638 p.

Gordon, J.D., Willoughby, T.C., and Schroder, L.J., 1991, Summary of the National Atmospheric Deposition Program/National Trends Network intersite-comparison program, November 1978-November 1989: U.S. Geological Survey Water-Resources Investigations Report 91-4061, 26 p.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water-Supply Paper 2252, p. 62-63.

Iman, R.L. and Conover, W.J., 1983, A modern approach to statistics: New York, John Wiley, 496 p.

James, K.O., 1992, 1990 Quality Assurance Report, NADP/NTN Deposition monitoring, laboratory operations, Central Analytical Laboratory, January 1991 through December 1991: National Atmospheric Deposition Program/National Trends Network Coordinator's Office, Natural Resources Ecology Laboratory, Fort Collins, Colorado State University, p. 9.

National Atmospheric Deposition Program, 1990a, Quality assurance plan, NADP/NTN deposition monitoring: Natural Resources Ecology Laboratory, Fort Collins, Colorado State University, p. 2-5.

________, 1990b, NADP/NTN Annual data summary--Precipitation chemistry in the United States, 1989: Natural Resources Ecology Laboratory, Fort Collins, Colorado State University, p. 17-20.

Nilles, M.A., See, R.B., Willoughby, T.C., and Gordon, J.D., 1991, Variability in wet atmospheric deposition data determined with collocated samplers: U.S. Geological Survey Water-Resources Investigations Report 91-4143, 30 p.

Peden, M.E., 1986, Development of standard methods for collection and analysis of precipitation, *in* Methods for collection and analysis of precipitation: Champaign, Illinois State Water Survey Contract Report 381, p. 19-21.

Robertson, J.K., and Wilson, J.W., 1985, Design of the National Trends Network for monitoring the chemistry of atmospheric precipitation: U.S. Geological Survey Circular 964, 46 p.

Schroder, L.J., Bricker, A.W., and Willoughby, T.C., 1985, Precision and bias of selected analytes reported by the National Atmospheric Deposition Program and the National Trends Network--1983 and January 1980 through September 1984: U.S. Geological Survey Water-Resources Investigations Report 85-4275, 15 p.

See, R.B., Willoughby, T.C., and Schroder, L.J.,1989, External quality-assurance results for the National Atmospheric Deposition Program/National Trends Network during 1987: U.S. Geological Survey Water-Resources Investigations Report 89-4015, 16 p.

See, R.B., Willoughby, T.C., and Gordon, J.D., 1990, External quality-assurance results for the National Atmospheric Deposition Program/National Trends Network during 1988: U.S. Geological Survey Water-Resources Investigations Report 90-4030, 27 p.

Taylor, J.K., 1987, Quality assurance of chemical measurements: Chelsea, Mich., Lewis Publishers, 328 p.

Willoughby, T.C., Gordon, J.D., Schroder, L.J., and Nilles, M.A., 1991, External quality-assurance results for the National Atmospheric Deposition Program/National Trends Network during 1989: U.S. Geological Survey Water-Resources Investigations Report 91-4039, 26 p.

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