EXTERNAL QUALITY-ASSURANCE RESULTS FOR THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK DURING 1988

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and Timothy C. Willoughby

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CONTENTS

FIGURES

TABLES

CONVERSION FACTORS

Metric units (International System) in this report may be converted to inch-pound units by using the following conversion factors:

Multiply metric unit	*By*	*To obtain inch-pound unit*
liter (L)	1.0567	quart, liquid
milliliter (mL)	0.03381	ounce, fluid

The following terms and abbreviations also are used in this report:
microsiemens per centimeter at 25 degrees Celsius (μS/cm)
megohm (MΩ)

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ABSTRACT

The U.S. Geological Survey used four programs in 1988 to provide external quality assurance for the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Onsite pH and specific-conductance determinations were evaluated in the intersite-comparison program. The effects of routine sample handling on analyte determinations and an estimated precision of analyte values and concentrations determined in the NADP/NTN samples were evaluated in the blind-audit program. Differences between analytical results and an estimate of the analytical precision of three participating laboratories were determined by the interlaboratory-comparison program. An estimate of overall sampling precision was determined by the collocated-sampler program.

Results of the intersite-comparison program indicate that 88 to 94 percent of the onsite pH determinations and 95 to 96 percent of the onsite specific-conductance determinations were within program goals during 1988. The effect of routine sample handling, processing, and shipping, as determined in the blind-audit program, indicated significant positive bias of calcium, magnesium, sodium, and chloride and a negative bias for hydrogen ion and specific conductance for blind-audit samples handled according to program protocols. A Kruskal-Wallis test indicated that significant ($\alpha=0.01$) differences did not occur among the analytical results from the three laboratories participating in the interlaboratory-comparison program. Insufficient data were obtained during 1988 to estimate the precision of data collected using collocated samplers.

INTRODUCTION

The National Atmospheric Deposition Program (NADP) was established in 1978 as a national monitoring network to investigate acid deposition. The National Trends Network (NTN) was established in 1982 to expand the NADP effort into areas not previously sampled. Most sites in the NADP were incorporated into the NTN operation. 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. In 1988, wet-deposition samples were collected from more than 200 sites across the United States and Canada. All site operators used the same type of sample-collection device, the same sample-handling protocols (Bigelow and Dossett, 1988), and they all 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 experimental 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 during 1988. These programs: (1) Assess the precision and accuracy of onsite determinations of pH and specific conductance; (2) evaluate the effects of onsite and laboratory protocols on the bias and precision of NADP/NTN analyte determinations; (3) determine the comparability, bias, and precision of analytical results obtained by separate laboratories when portions of a common sample were analyzed; and (4) estimate the precision of the entire sampling system.

INTERSITE-COMPARISON PROGRAM

The U.S. Geological Survey conducted intersite-comparison studies during May and October 1988 (studies 21 and 22). All NADP/NTN site operators were mailed an intersite-comparison sample and asked to determine pH and specific conductance during each intersite-comparison study. Participation in the intersite-comparison program was voluntary; most site operators were cooperative and performed the requested analyses in a timely manner. Equipment malfunctions prevented some site operators from participating, whereas others simply did not respond (table 1). The accuracy and precision of onsite pH and specific-conductance determinations from sites whose operators infrequently participate in the intersite-comparison program cannot be evaluated adequately.

Table 1.--*Summary of site-operator responses for 1988 intersite-comparison studies*

Site-operator responses	Intersite-comparison study	
	21	22
Number of site operators receiving samples	203	201
Number of nonresponding site operators	14	14
Site operators reporting equipment problems	5	3
pH meter/electrode malfunctioned	3	2
Specific-conductance equipment malfunctioned	2	1

Intersite-comparison solutions were prepared by the U.S. Geological Survey for each of the 1988 intersite-comparison studies. Target pH and specific-conductance values for the intersite-comparison solutions simulated the pH and specific conductance of natural wet-deposition. Intersite-comparison solution 21 was prepared from dilute nitric acid. The target pH for intersite-comparison solution 21 was 4.40, and the target specific conductance was 15 to 20 µS/cm. Nitric acid and potassium chloride were used to prepare intersite-comparison solution 22. The target pH for intersite-comparison solution 22 was 5.20, and the target specific conductance was 20 to 25 µS/cm. High density polyethylene bottles that contained 125 mL of the intersite-comparison solution were sent to all site operators for analysis. No information was provided to the site operator regarding the pH or specific conductance of the samples. The experimental design and protocols of the intersite-comparison program previously have been described in detail (Schroder and Brennan, 1984). A flowchart depicting the intersite-comparison program is presented in figure 1.

Median values of pH and specific conductance were calculated from values reported by the site operators. Median values were used as the best estimates of actual pH and specific-conductance values for each intersite-comparison solution for several reasons. Since the inception of the intersite-comparison program, the distributions of pH and specific-conductance values frequently have been nonnormal, and a median value represents a nonnormal data set more accurately than does a mean value. Mean values can be markedly affected by outlying values. The effect of even slightly outlying values on a mean pH value is magnified by the logarithmic nature of pH. Experience has shown that the median value of about 200 analyses by the site operators is a better estimate of the actual values of these properties than a few in-house laboratory analyses.

Site operators were instructed to return all unused portions of the intersite-comparison study 21 sample to the U.S. Geological Survey for possible re-analysis. These samples, however, were re-analyzed by the U.S. Geological Survey only when a site operator reported values for pH or specific conductance that exceeded the preselected limits of the median ±1.5 F-pseudosigma (Hoaglin and others, 1983). The F-pseudosigma is a robust statistic analogous to the standard deviation of the mean and provides an alternative measure of site-operator performance. Re-analysis determined if the sample had become contaminated or if the erroneous measurement was because of site-operator or instrument error. Twenty-one percent of the pH determinations and 24 percent of the specific-conductance determinations for intersite-comparison study 21 were re-analyzed. As in previous intersite-comparison studies, re-analyses of pH and specific conductance by the U.S. Geological Survey were within the limit of the median ±1.5 F-pseudosigma values calculated for all sites. For this reason, the practice of returning intersite-comparison solutions to the U.S. Geological Survey and re-analyzing all samples outside the ±1.5 F-pseudosigma limit was discontinued beginning with the October 1988 intersite-comparison study 22. If site operators report a value or values outside the NADP/NTN goals or ±1.5 F-pseudosigma limit, and believe that their measurement(s) are accurate, they are encouraged to review their results. Site operators can return individual intersite-comparison samples for re-analysis by the U.S. Geological Survey.

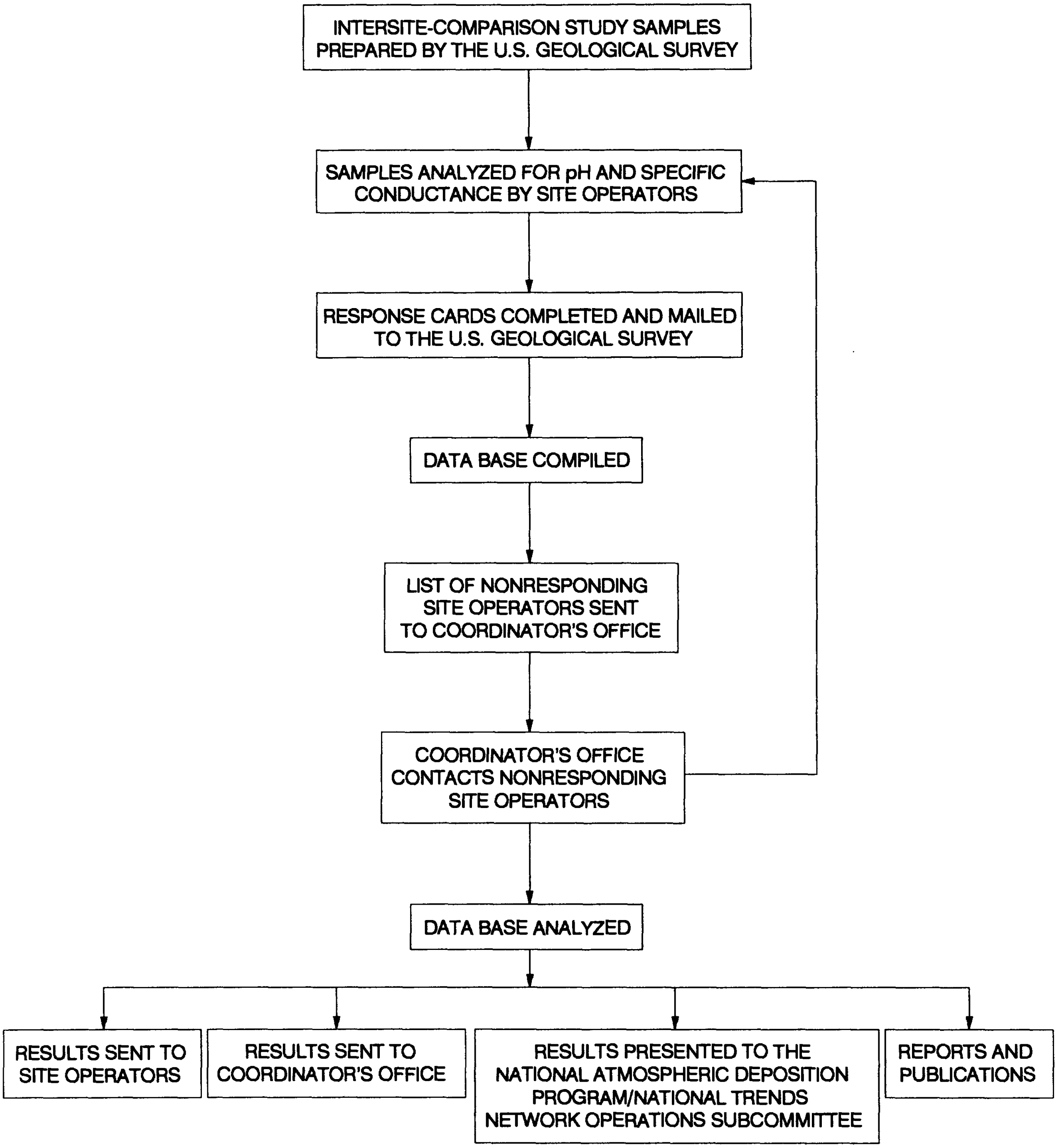

Figure 1.--Intersite-comparison program.

The results of the 1988 intersite-comparison studies are shown in figure 2. Superimposed on these scatterplots comparing pH to specific conductance are rectangles defining NADP/NTN measurement accuracy goals and the ±1.5 F-pseudosigma limits. Boxplots that show the distribution of pH and specific-conductance values determined by site operators are presented in figure 3.

The NADP/NTN goal for onsite pH determinations of less than 5.0 is ±0.10 pH unit of the actual pH. This criteria increases to ±0.3 0 pH unit when the actual pH exceeds 5.0. By using the median value of all responding sites as the most accurate estimate of pH, 88 percent (intersite comparison 21) and 94 percent (intersite comparison 22) of the participating site operators achieved the NADP/NTN goal for pH-measurement accuracy. Because of differences in hydrogen-ion concentrations in the samples, the acceptance criteria for intersite-comparison study 21 was ±0.10 pH unit and for intersite-comparison study 22 was ±0.30 pH unit.

The NADP/NTN goal for onsite specific-conductance measurements is ±4.0 µS/cm. By using the median value of all responding sites as the most accurate estimate of the actual specific conductance, 95 and 96 percent of the site operators fulfilled NADP/NTN specific-conductance goals for accuracy in intersite comparison 21 and intersite comparison 22. Results in 1988 are similar to those of previous intersite-comparison studies with comparable median specific-conductance values.

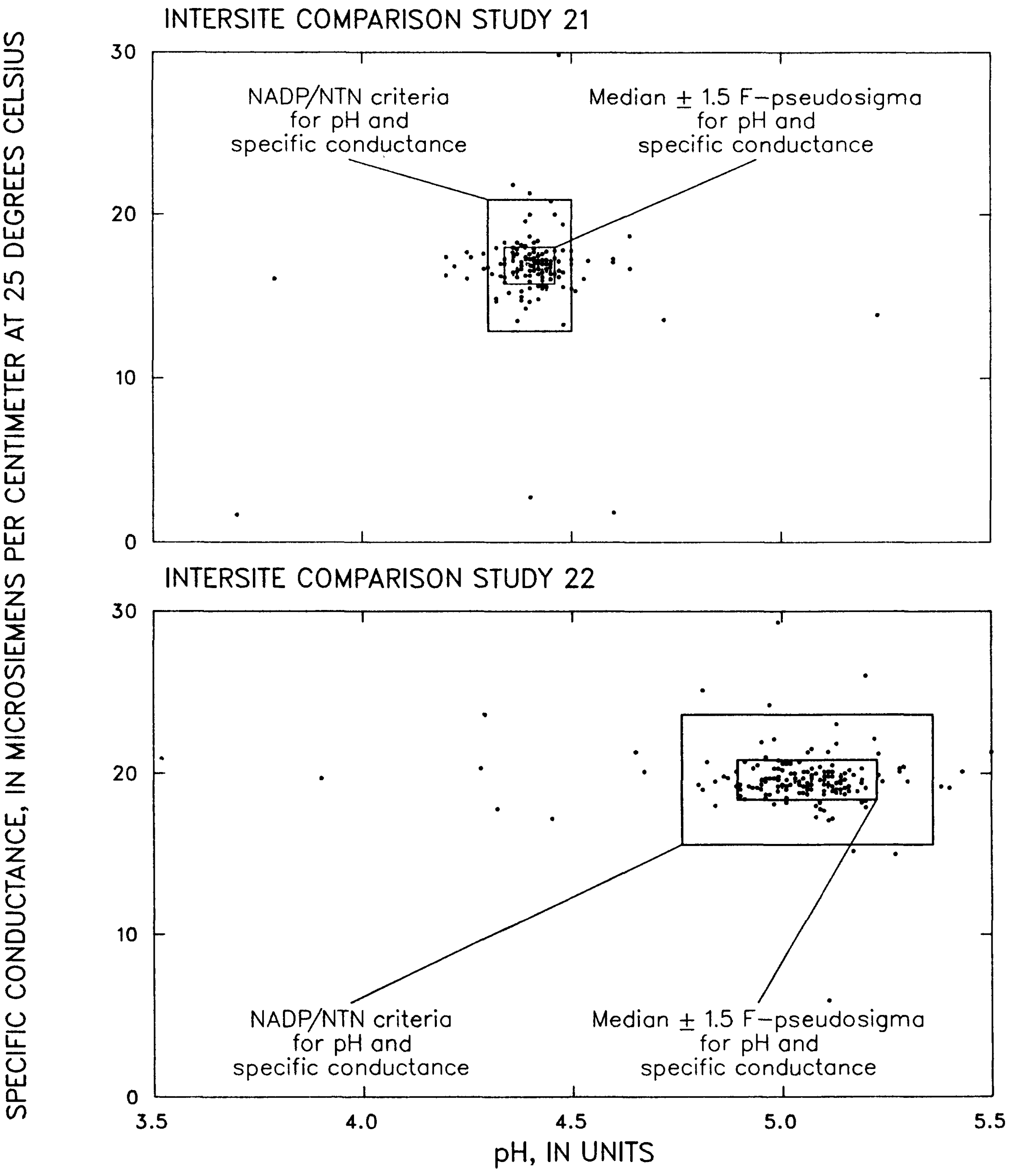

Figure 2.--Analytical results from intersite-comparison studies 21 and 22.

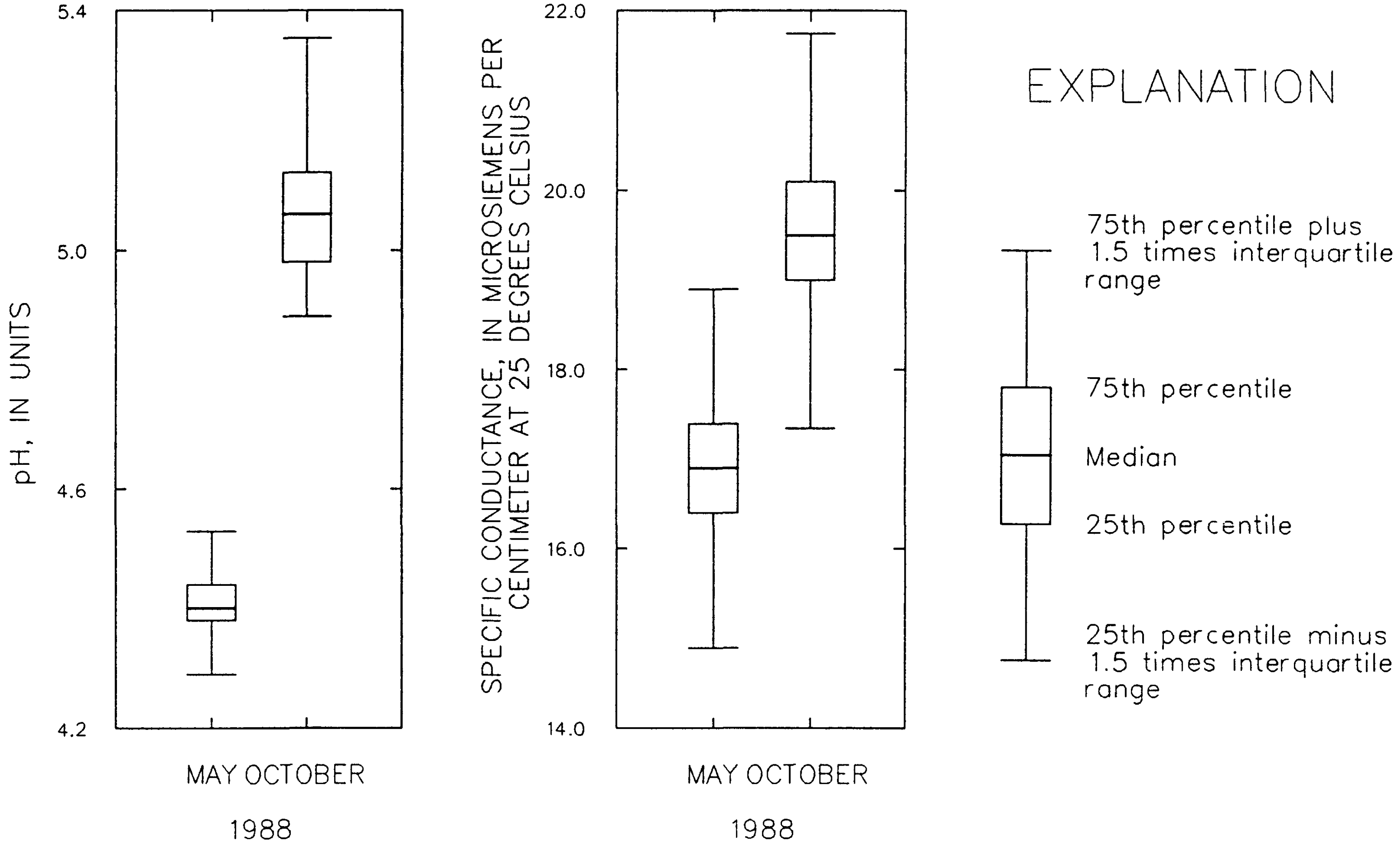

Figure 3.--Results of pH and specific-conductance analyses in the intersite-comparison program.

BLIND-AUDIT PROGRAM

The purpose of the blind-audit program was to quantify the effects of routine sample handling, processing, and shipping on analyte bias and precision. Details of the experimental design have been discussed in a previous report (Schroder and others, 1985). In the blind-audit program, site operators are mailed blind-audit samples and detailed processing instructions. A portion of each blind-audit sample was submitted to the CAL disguised as an actual wet-deposition sample. Site operators were provided a preaddressed mailing envelope to return the remaining portion of the blind-audit sample to the CAL for separate analysis. The comparison of 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.

Eleven solutions were used in the 1988 blind-audit program. Solutions are replaced in the blind-audit program when the supply is exhausted, and seven of the solutions used in 1988 had not been used previously. The four solutions used during 1988 that were used in previous years included two prepared by diluting U.S. Environmental Protection Agency solution 1085, referred to as 1085-I and 1085-III; ultrapure (greater than 16.7 MΩ) deionized water prepared by the U.S. Geological Survey (referred to as nanopure in previous years); and a dilute nitric-acid solution prepared by the CAL with a pH of 4.3, referred to as CAL 4.3. The remaining solutions that were included in the 1988 blind-audit program, but not used in the blind-audit program in 1987, were: Two synthetic wet-deposition samples prepared by the CAL and referred to as CAL A and CAL B; a synthetic wet-deposition sample prepared by the U.S. Environmental Protection Agency, referred to as 485-I; two natural wet-deposition samples prepared by the U.S. Geological Survey referred to as P-8 and P-12; and two synthetic wet-deposition samples, prepared by the U.S. Geological Survey and referred to as USGS1 and USGS2. Target values for solutions used in the blind-audit program during 1988 are given in table 2.

Twenty-six samples were sent to selected NADP/NTN sites during each of four quarterly mailings in 1988. Submissions of blind-audit samples were distributed among four geographic regions of the United States during each mailing to ensure an even geographic distribution. After a site operator participates in the blind-audit program, participation is not requested again until all other sites in the network have participated. The location of sites whose operators participated in the 1988 blind-audit program is shown in figure 4.

Site operators were instructed to pour 80 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 CAL for analysis

Table 2.--*Target values for solutions used in the 1988 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]

Name	Dilution	Ca	Mg	Na	K	NH4	SO4	Cl	NO3	pH	Specific conductance
[1]1085-I	2:1	0.033	0.011	0.091	0.040	--	1.38	0.14	0.305	--	12.4
[1]1085-III	10:1	.370	.039	.051	.514	--	3.38	.825	.871	--	31.8
Ultrapure	--	--	--	--	--	--	--	--	--	--	--
[1]CAL 4.3	--	--	--	--	--	--	--	--	3.11	4.3	22
[2]CAL A1	--	.069	.017	.050	.016	--	.67	.12	.50	4.84	7.5
[2]CAL B1	--	.282	.070	.187	.051	--	2.66	.51	1.98	4.31	27.6
0485-11	2:1	.031	.009	.096	.041	--	1.16	.179	.273	--	9.9
[1]P-8	--	.230	.030	.070	.050	--	.45	.170	--	5.97	3.77
[1]P-12	--	.910	.060	.710	.050	--	.65	.660	--	6.58	10.0
[1,2]USGS1	--	.140	.037	.092	.025	0.160	.938	.142	1.08	4.80	8.0
[1]USGS2	--	.140	.037	.092	.025	.160	.938	.142	1.08	4.80	8.0
[2]2694-I	--	.014	.024	.205	.052	--	2.75	.24[3]	--	4.27	26
[2]2694-II	--	.049	.051	.419	.106	--	10.9	1[3]	7.06	13.59	130

[1] Used in the blind-audit program.
[2] Used in the interlaboratory-comparison program.
[3] Not certified by NIST.

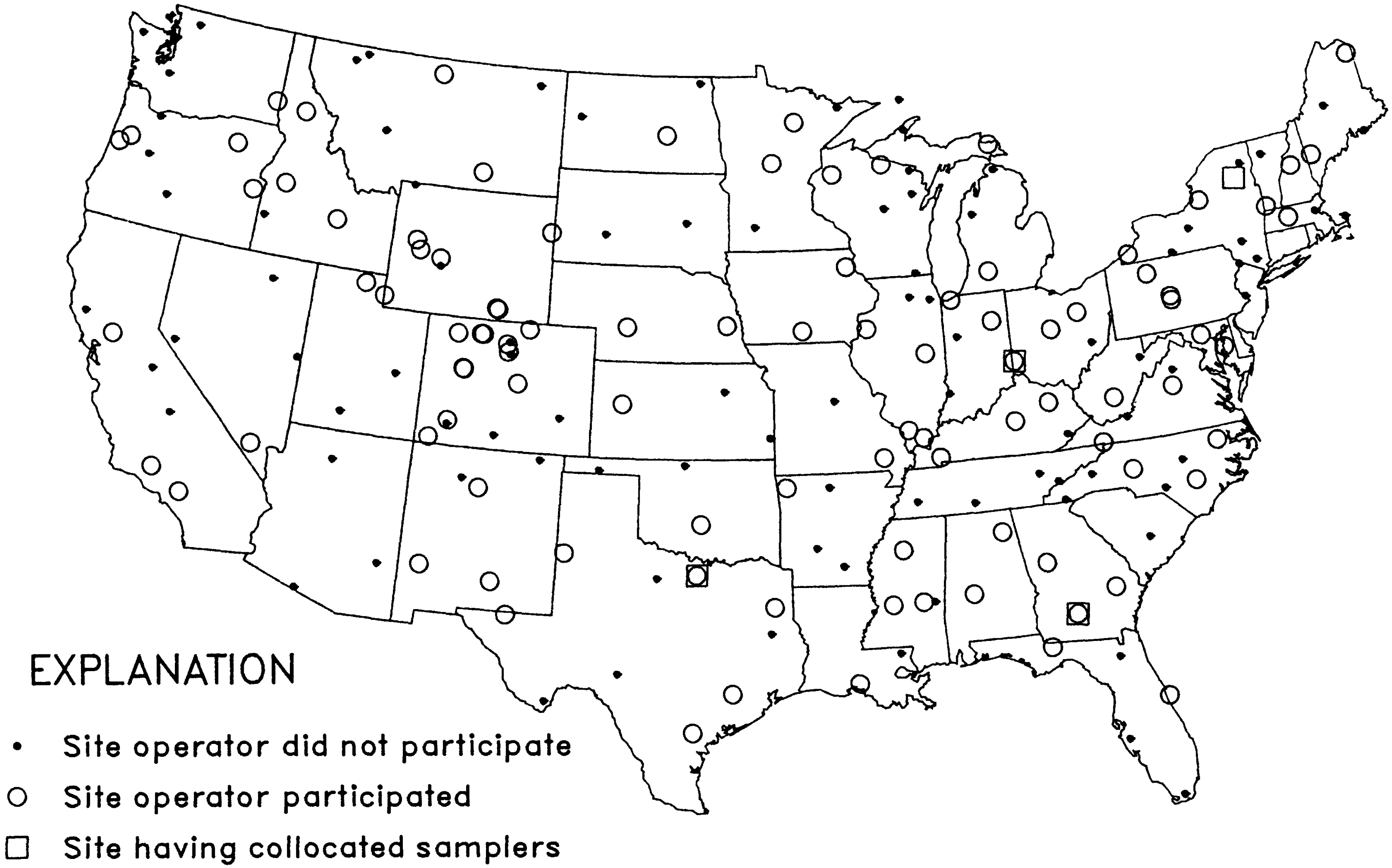

Figure 4.--Location of National Atmospheric Deposition Program/National Trends Network sites whose operators did or did not participate in the 1988 blind-audit program, and sites with collocated samplers.

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 CAL, using separate mailing containers. This portion of the blind-audit sample is referred to as the bottle sample.

The bottle sample was submitted separately by the CAL Quality Assurance officer to the CAL laboratory staff for routine analysis. Although the CAL staff may have discovered that bottle samples were not actual NADP/NTN samples, the analyte concentrations in bottle samples were not available to the laboratory staff. During 1988, CAL analyzed the bucket and bottle samples within 1 to 2 weeks of each other. A flowchart showing the operation of the blind-audit program is presented in figure 5.

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 did not change from the time that the site operator poured an aliquot of the original blind-audit sample into the bucket and the time that CAL analyzed the bottle sample.

Complete bucket and bottle analyses were available for 98 of the 104 blind-audit samples sent to site operators in 1988. Three samples missing bottle analyses were the result of failure on the part of site operators to submit the bottle sample to CAL for analysis. Of the remaining three sites with lost data, one site operator reported that they lost their blind-audit sample, one site operator declined to participate in the program, and one site discontinued operation.

Samples that contain extraneous debris are identified by the CAL with a contamination code. Because prior investigations have indicated no significant differences in analytical results among uncontaminated bucket samples and contaminated bucket samples (See and others, 1989), 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 1988 blind-audit statistical analyses. Data from bottle samples that were contaminated were removed from the statistical analyses.

A paired-t test that was used to determine if a significant difference existed between the bucket- and bottle-sample analyses indicated that a significant (probability of a larger t <0.01) bias existed for calcium, magnesium, sodium, chloride, pH, and specific conductance. A summary of the t-test statistics is presented in table 3. The mean concentrations or values for bucket samples were larger than the mean concentrations or values for bottle samples for all analytes, except for nitrate and specific conductance. These results are an indication that contamination of the bucket samples, and therefore, all NADP/NTN wet-deposition samples, was occurring as a result of sample-handling procedures. The bucket- minus bottle-sample differences are presented in figure 6.

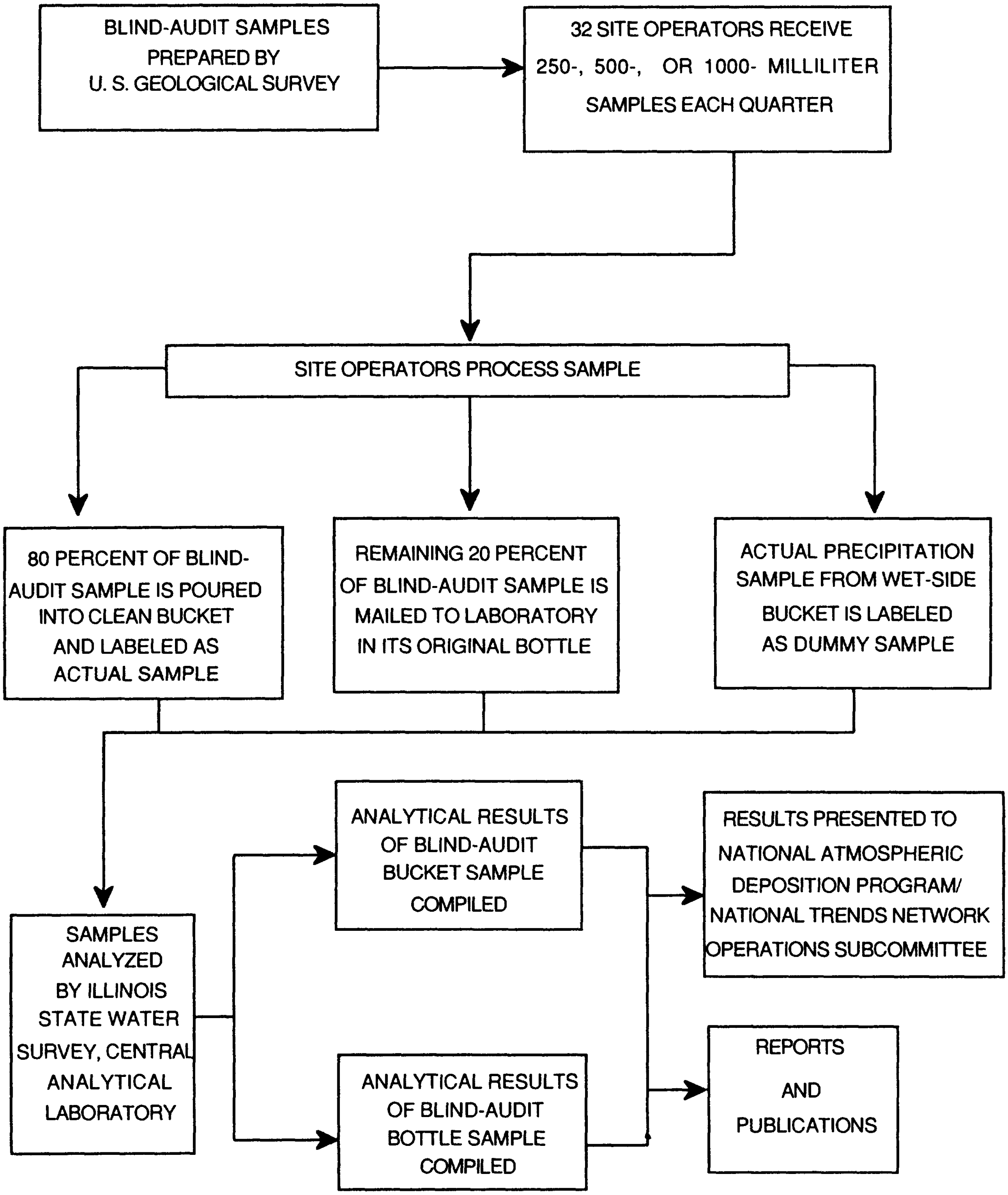

Figure 5.--Blind-audit program.

Table 3.--*Summary of paired t-tests for the blind-audit program*

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

Analyte	Sample type	Mean	Mean difference	Number of pairs	t value	Probability of larger t
Calcium	Bucket	0.208	-0.038	83	-5.54	<0.01
	Bottle	.170				
Magnesium	Bucket	.035	-.009	73	-8.88	<.01
	Bottle	.027				
Sodium	Bucket	.228	-.089	98	-4.43	<.01
	Bottle	.139				
Potassium	Bucket	.076	-.01	69	-0.97	.34
	Bottle	.068				
Ammonium	Bucket	.15	-.04	18	-1.20	.25
	Bottle	.11				
Sulfate	Bucket	1.43	-.01	84	-1.04	.30
	Bottle	1.42				
Chloride	Bucket	.36	-.06	73	-4.59	<.01
	Bottle	.30				
Nitrate	Bucket	1.21	.00	71	-0.30	.77
	Bottle	1.21				
pH	Bucket	5.11	-.26	98	-7.65	<.01
	Bottle	4.85				
Specific conductance	Bucket	13.5	1.6	98	4.77	<.01
	Bottle	15.1				

The precision of 1988 NADP/NTN wet-deposition analyses was estimated by pooling the variance of replicate blind-audit samples (Dixon and Massey, 1969, p. 113). The estimated standard deviations are listed in table 4. The pooled standard deviations for 1988 are comparable to values calculated in previous years. The lesser precision in the analyses of blind-audit samples, when compared to the interlaboratory studies and single-operator studies at CAL, indicates that a large proportion of the uncertainty in wet-deposition data might be a result of routine sample handling, rather than laboratory analyses.

INTERLABORATORY-COMPARISON PROGRAM

The interlaboratory-comparison program was used to determine if differences existed among the analytical results of participating laboratories and to estimate analytical precision of the participating laboratories. Three laboratories participated in the interlaboratory-comparison program during 1988: (1) Illinois State Water Survey, Central Analytical Laboratory (CAL); (2) Inland Water Directorate, National Water Quality Laboratory (IWD); and (3) Environmental Monitoring & Services, Inc. (EMSI).

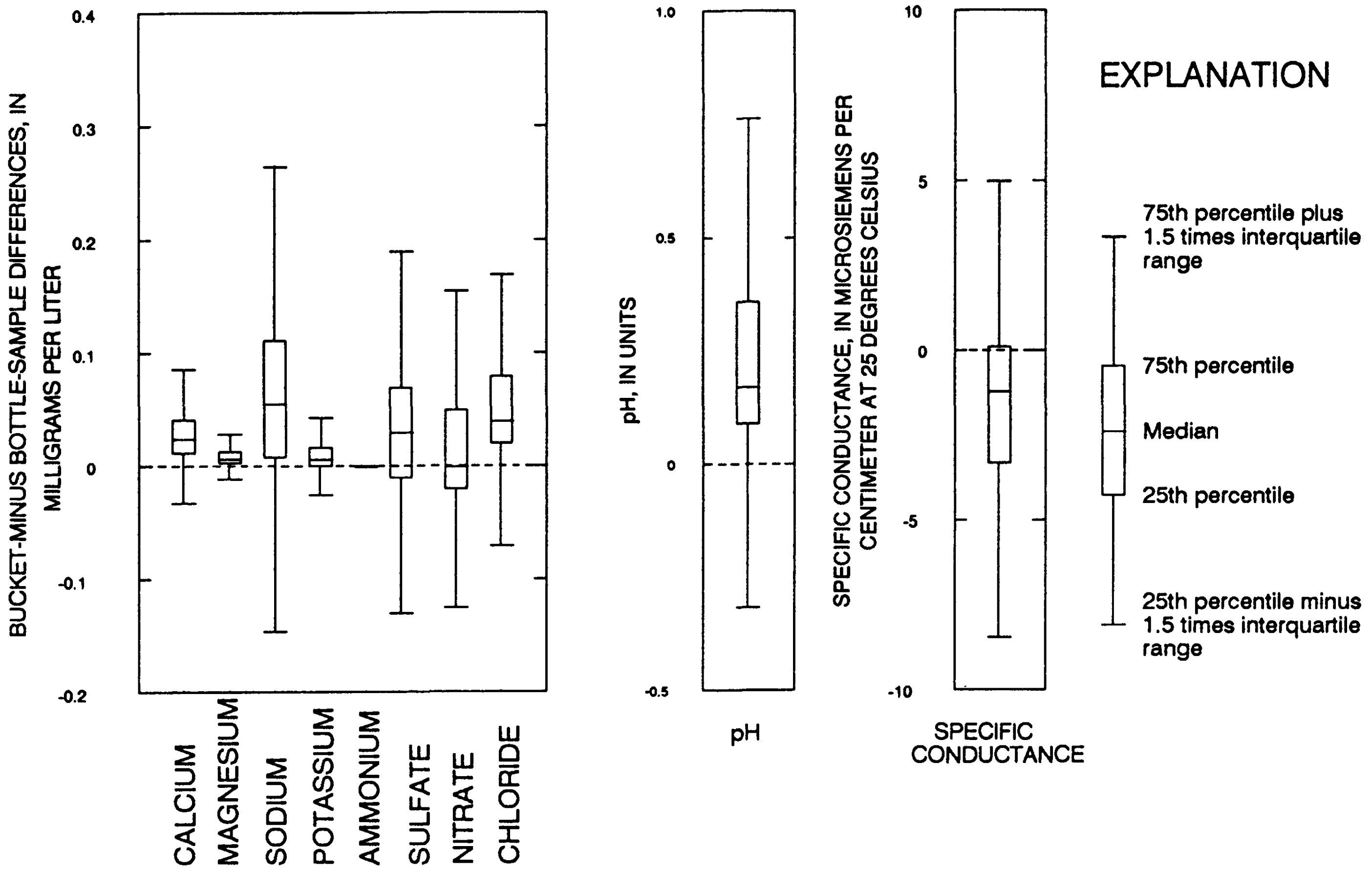

Figure 6.--Bucket- minus bottle-sample differences in the blind-audit program.

Table 4.--*Estimated precision 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	Estimated standard deviation
Calcium	0.009	1.108	0.061
Magnesium	.003	0.086	.008
Sodium	.010	2.280	.178
Potassium	.003	.544	.054
Ammonium	.02	.66	.14
Sulfate	.03	3.72	.07
Chloride	.03	1.18	.10
Nitrate	.03	3.33	.18
pH	4.22	7.01	.25
Specific conductance	1.3	34.1	2.2

Samples from five sources were prepared for the 1988 interlaboratory-comparison program. Synthetic wet-deposition samples and ultrapure deionized-water samples were prepared by the U.S. Geological Survey. Standard reference samples prepared and certified by the National Institute of Standards and Technology (NIST) also were used in the interlaboratory-comparison program. Synthetic wet-deposition samples and natural wet-deposition samples were prepared by the CAL. Natural wet-deposition samples collected at NADP/NTN sites that had a volume 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 interlaboratory-comparison program were re-labeled and shipped by the U.S. Geological Survey to the participating laboratories twice a month. 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 CAL or NIST and a single aliquot of ultrapure deionized water or four aliquots of the synthetic wet-deposition sample 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 samples, natural wet-deposition samples, or simulated wet-deposition samples. A flow chart of the interlaboratory-comparison program is shown in figure 7.

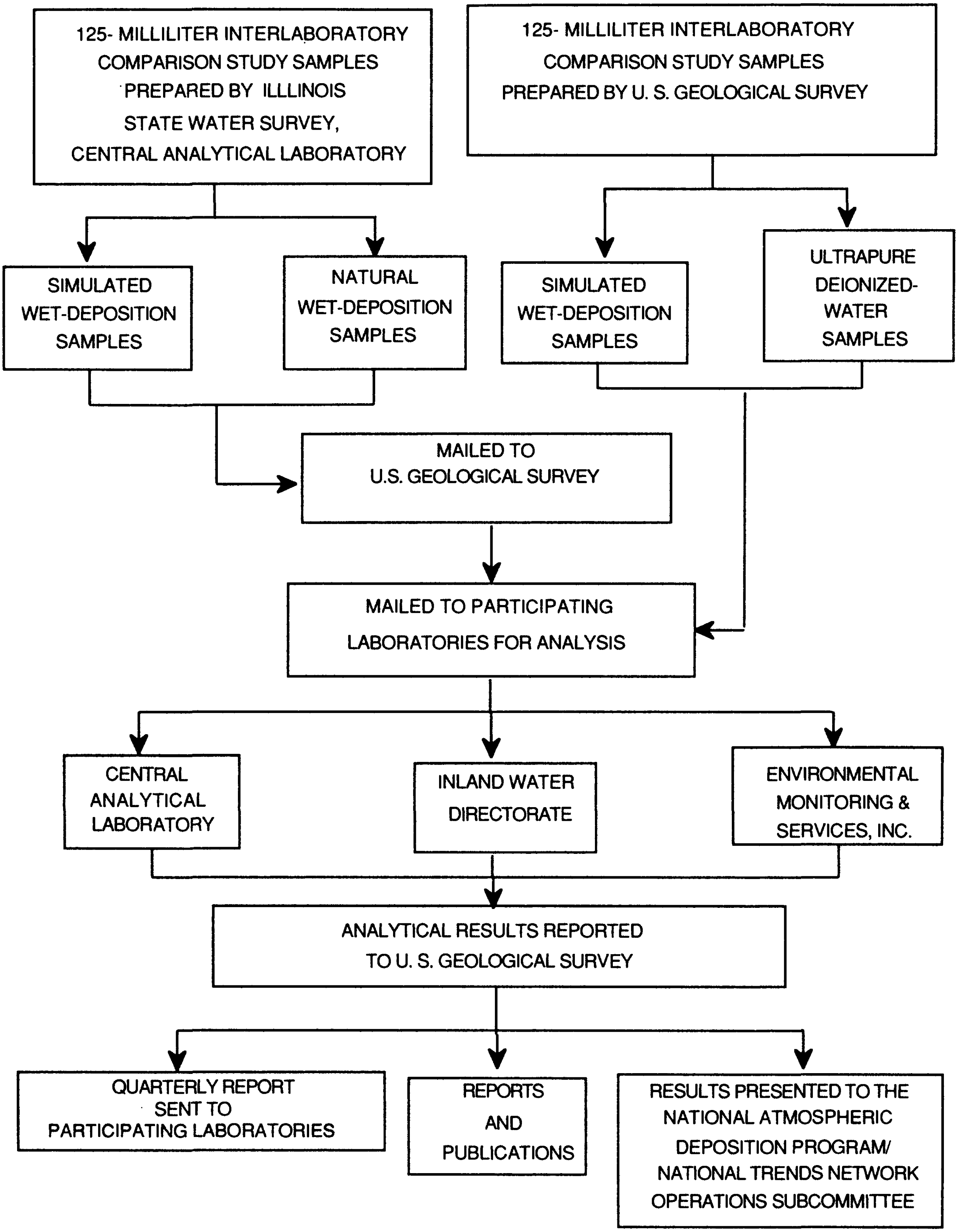

Figure 7.--Interlaboratory-comparison program.

The CAL and IWD did not report analyte concentrations that were measured at less than the reported method detection limits. EMSI did not report method detection limits for 1988; however, the U.S. Geological Survey was able to obtain the minimum reported concentrations for each analyte analyzed by EMSI (A. Bergeron, Environmental Monitoring & Services, Inc., oral commun., 1989). The analytical methods and the method detection limits or minimum reporting limits for each of the participating laboratories are listed in table 5.

Table 5.--*Analytical method and method detection limits and minimum reporting limits for the interlaboratory-comparison program during 1988*

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Water Directorate, National Water Quality Laboratory, Ontario, Canada; EMSI, Environmental Monitoring & Services, Inc., Camarillo, Calif.; FAA, flame atomic absorption spectrometry; ICP, induced coupled plasma; FAE, flame atomic emission spectrometry; AP, automated phenate, colorimetric; IC, ion chromatography]

Analyte	Method detection limit				Minimum reporting limit	
	CAL	(Method)	IWD	(Method)	EMSI	(Method)
Calcium	0.009	(FAA)	0.01	(FAA)	0.005	(ICP)
Magnesium	.003	(FAA)	.01	(FAA)	.005	(ICP)
Sodium	.003	(FAA)	.01	(FAE)	.025	(FAA)
Potassium	.003	(FAA)	.01	(FAE)	.025	(FAA)
Ammonium	.02	(AP)	.001	(AP)	.01	(AP)
Sulfate	.03	(IC)	.01	(IC)	.01	(IC)
Chloride	.03	(IC)	.01	(IC)	.04	(IC)
Nitrate	.03	(IC)	.04	(IC)	.04	(IC)

Laboratory precision of analyte concentrations was estimated 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). Values reported as less than the method detection limit or less than the minimum reporting limit were removed prior to calculating the pooled standard deviations. The calculated pooled standard deviations for each of the analytes were consistent with previous years. See and others (1989) reported that the calculated pooled standard deviations for the potassium and chloride determinations by CAL and EMSI in the natural wet-deposition samples, and that the calculated pooled standard deviations for sulfate determinations by IWD were larger in the synthetic wet-deposition samples in 1987 than in previous years. The calculated pooled standard deviations for these analytes were smaller in 1988. The calculated pooled standard deviations are listed in table 6.

Table 6.--*Pooled standard deviations for analytes determined by three laboratories that measured constituents and properties in natural wet-deposition samples*

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Water Directorate, National Water Quality Laboratory, Ontario, Canada; EMSI, Environmental Monitoring & Services, Inc., Camarillo, Calif.; 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 pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius; <, less than]

Analyte	CAL		IWD		EMSI	
	Nat	Syn	Nat	Syn	Nat	Syn
Calcium	0.004	0.005	0.006	0.011	0.008	0.010
Magnesium	<.001	.001	<.001	.003	.001	.004
Sodium	.004	.022	<.006	.022	.007	.013
Potassium	.017	.002	.085	.011	.022	.002
Ammonium	.01	.03	.04	.02	<.01	<.01
Sulfate	.01	.04	.05	.24	.05	.12
Chloride	.02	.01	.08	.08	.02	.03
Nitrate	.02	.05	.08	.26	.03	.17
pH	.02	.02	.02	.03	.05	.48
Specific conductance	.1	1.5	.4	3.5	.2	3.3

To examine bias among the analytical results of the laboratories, a Kruskal-Wallis test (Iman and Conover, 1983) was done. The Kruskal-Wallis test is a one-way analysis of variance on the ranked, transformed data. Results of the Kruskal-Wallis test indicated no significant (α=0.01) difference in analyte measurements for any of the laboratories. Percentile rankings for individual laboratory analyses of interlaboratory-comparison samples are summarized in table 7. The analyte concentrations determined by each laboratory are presented as boxplots in figures 8 and 9.

Analyte bias for laboratories participating in the U.S. Geological Survey interlaboratory-comparison study also was evaluated by using the certified concentrations or values and the estimated uncertainties reported by NIST for standard-reference material 2694, level I and level II. Bias was examined by comparing the mean laboratory-reported concentrations or values and the certified concentrations or values reported by NIST. Bias was indicated when the laboratory-reported concentrations or values were outside of the NIST certified concentrations or values plus or minus the estimated uncertainty reported by NIST. A summary of the median analysis estimates for each laboratory and the certified concentrations or values and estimated uncertainties for the NIST standard-reference material 2694 is presented in table 8. EMSI had the least number of median analyses that were significantly different from the NIST certified concentrations or 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; EMSI, Environmental Monitoring & Services, Inc., Camarillo, Calif.; all units in milligrams per liter except pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius; <, less than]

Analyte	Percentiles								
	CAL			IWD			EMSI		
	25th	50th	75th	25th	50th	75th	25th	50th	75th
Calcium	0.023	0.050	0.140	0.020	0.060	0.150	0.025	0.050	0.141
Magnesium	.011	.027	.049	<.010	.020	.040	.015	.027	.050
Sodium	.037	.096	.219	.040	.100	.210	.042	.100	.228
Potassium	.016	.042	.051	.010	.030	.050	<.010	.043	.050
Ammonium	<.02	.14	.35	<.02	.16	.31	.02	.15	.31
Sulfate	.68	1.04	2.77	.71	1.06	2.54	.68	1.05	2.61
Chloride	.09	.17	.51	.06	.16	.50	.07	.17	.51
Nitrate	.33	.81	1.71	.31	.80	1.42	.39	.97	1.70
pH	4.31	4.73	4.98	4.33	4.74	5.00	4.34	4.75	4.94
Specific conductance	5.4	9.4	26.9	7.7	11.2	19.5	10.1	11.7	28.0

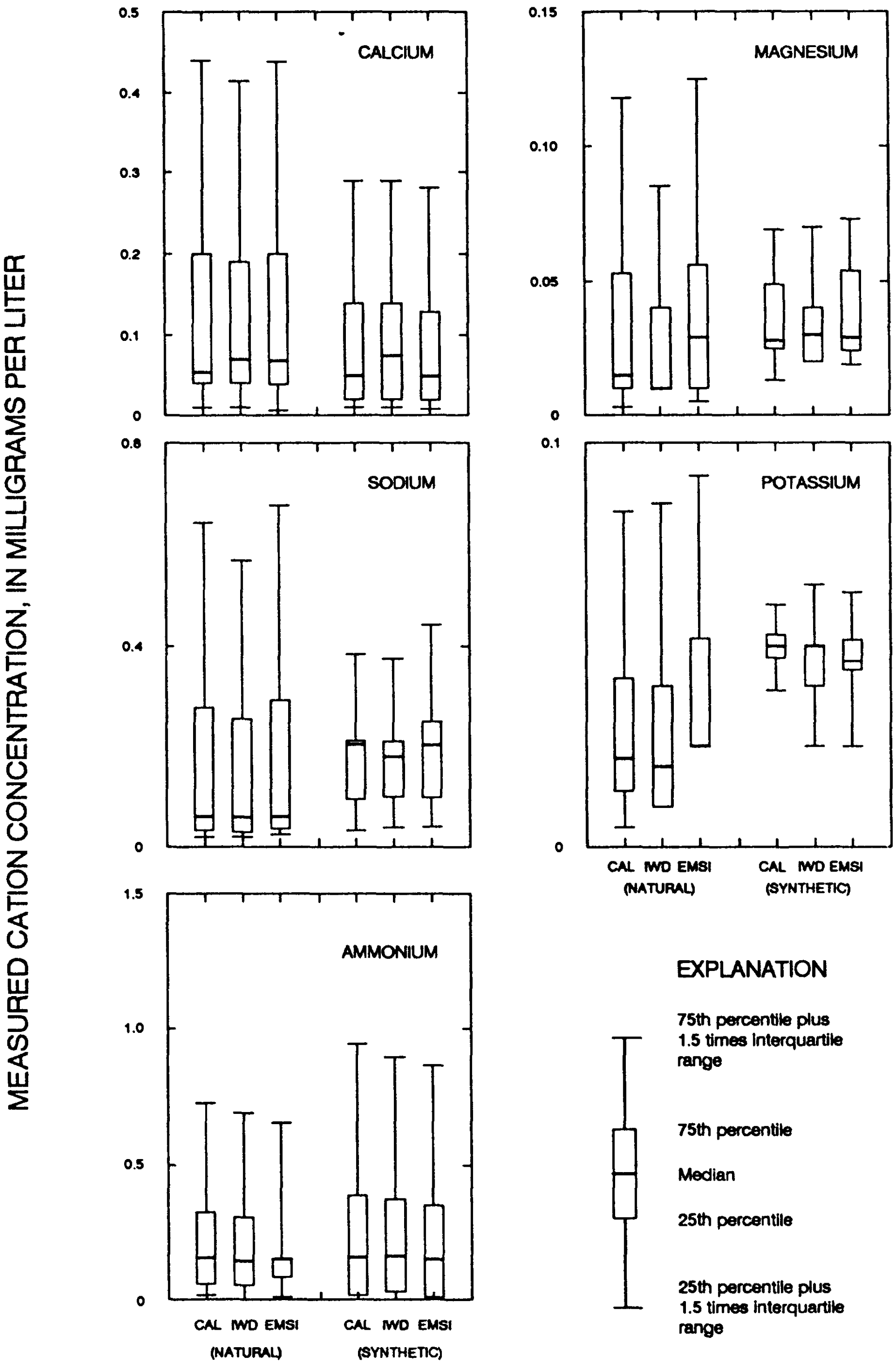

Figure 8.--Cation concentrations determined by three laboratories participating in the interlaboratory-comparison program.

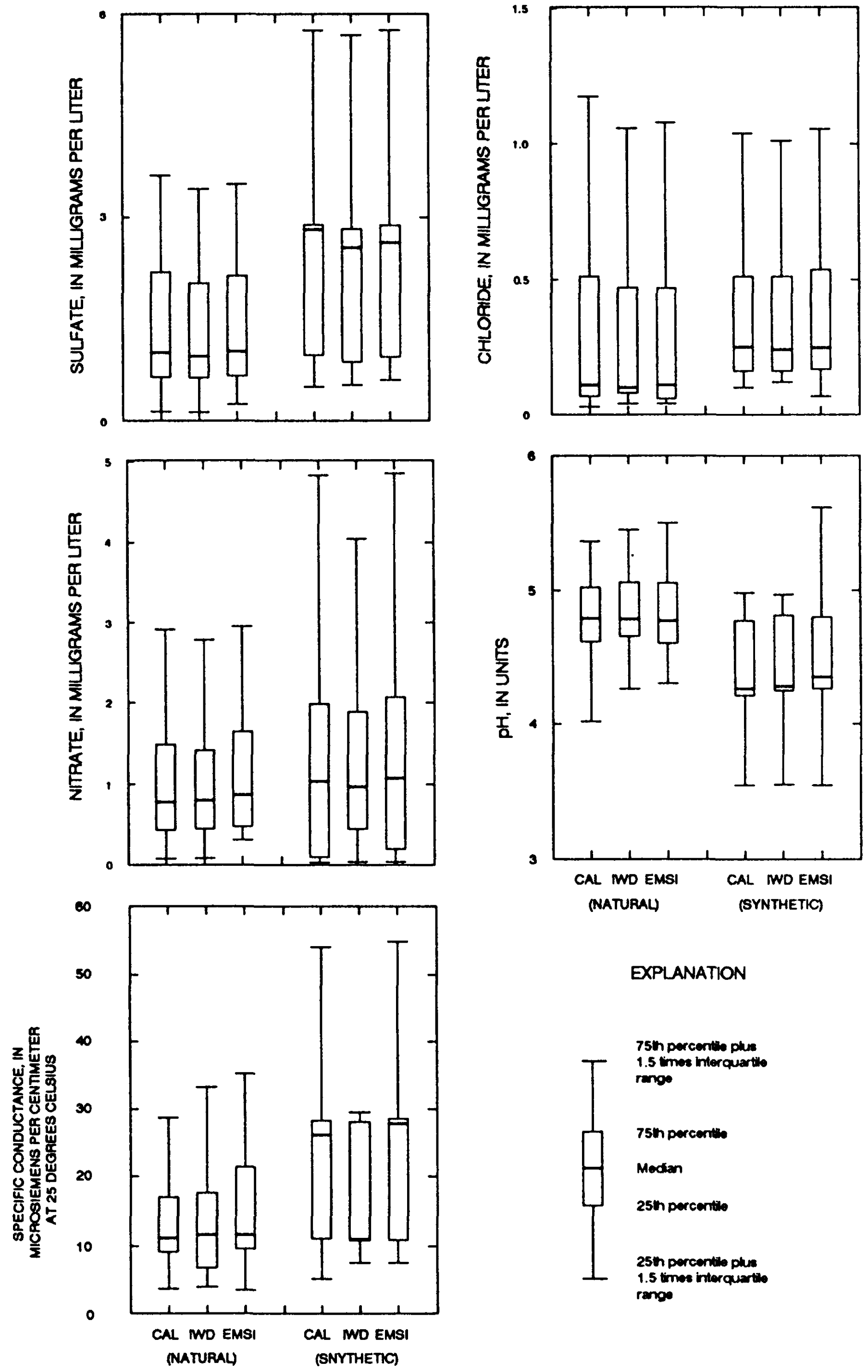

Figure 9.--Anion concentrations and properties determined by three laboratories participating in the interlaboratory-comparison program.

Table 8.--*Median analysis estimates for standard reference material 2694 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; EMSI, Environmental Monitoring & Services, Inc., Camarillo, Calif.; 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 concentrations or values; *, indicates concentrations or values outside the certified concentration or value plus or minus the estimate of uncertainty; <, less than; --, indicates data unavailable]

Analyte	NIST standard	Certified NIST concentrations or values	Estimate of uncertainty	Median laboratory analyses					
				CAL	(N)	IWD	(N)	EMSI	(N)
Calcium	2694-I	0.014	0.003	*0.010	(12)	*<0.010	(11)	0.013	(12)
	2694-II	.049	.011	.050	(9)	.045	(6)	.046	(9)
Magnesium	2694-I	.024	.002	.025	(12)	*.020	(11)	.024	(12)
	2694-II	.051	.003	.049	(9)	*.045	(6)	*.056	(9)
Sodium	2694-I	.205	.009	.207	(12)	.210	(11)	.208	(12)
	2694-II	.419	.015	.416	(9)	.420	(5)	.422	(9)
Potassium	2694-I	.052	.007	.051	(12)	.050	(11)	.046	(12)
	2694-II	.106	.008	.106	(9)	.110	(5)	.100	(9)
Sulfate	2694-I	2.75	.05	*2.85	(12)	*2.60	(12)	*2.82	(12)
	2694-II	10.9	.2	*11.43	(9)	*10.34	(9)	10.78	(9)
Chloride	2694-I	--	--	.250	(12)	.240	(12)	.250	(12)
	2694-II	--	--	1.04	(9)	.990	(9)	1.04	(9)
Nitrate	2694-I	--	--	<.03	(12)	<.04	(12)	.04	(12)
	2694-II	7.06	.15	7.19	(9)	*6.68	(9)	7.18	(9)
pH	2694-I	4.27	.03	*4.23	(12)	4.26	(12)	4.28	(12)
	2694-II	3.59	.02	3.56	(9)	3.57	(9)	*3.60	(9)
Specific conductance	2694-I	26	2	27	(12)	28	(4)	28	(12)
	2694-II	130	2	129	(9)	*21	(4)	*133	(9)

Seven ultrapure deionized-water samples were included among the samples submitted to the laboratories to determine the number of times that each laboratory reported positive values in a solution that would not be expected to contain any detectable analytes. A summary of the laboratory analyses of ultrapure deionized-water samples is presented in table 9. EMSI had the largest number of determinations greater than the minimum reporting limit for calcium, magnesium, potassium, and nitrate. The CAL had the largest number of determinations greater than the minimum detection limit for sulfate.

Table 9.--*Summary of laboratory analyses of seven ultrapure deionized-water samples*

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Waters Directorate, National Water Quality Laboratory, Ontario, Canada; EMSI, Environmental Monitoring & Services, Inc., Camarillo, Calif.; all concentrations, in milligrams per liter]

Analyte	Concentrations reported that were greater than the detection limit		
	CAL	IWD	EMSI
Calcium	([1])	0.010	0.007, .006
Magnesium	([1])	([1])	.022
Sodium	0.016	([1])	.042
Potassium	([1])	([1])	.058
Ammonium	([1])	([1])	([1])
Sulfate	.04, .04, .03, .03	([1])	.042
Chloride	([1])	([1])	([1])
Nitrate	([1])	([1])	.048

[1] No concentrations reported that were greater than the detection limit.

COLLOCATED-SAMPLER PROGRAM

The U.S. Geological Survey has begun a collocated-sampler program in association with the NADP/NTN monitoring program. The purpose of the program is to estimate the overall precision for chemical measurements of wet-deposition samples. The precision estimate includes variability because of the data-collection system, from the point of sample collection through storage of the data in the NADP/NTN data base. Data collected during the program also might be used to evaluate the effect of selected siting-criteria violations on NADP/NTN sample data. This program further expands the geographic and climatological coverage of the data for sampling precision for NADP/NTN.

The details of the collocated-sampler program that follow describe the installation of equipment, location of sites, and site visits for each site included in the study. Data-analysis techniques and future plans for the collocated-sampler program also are discussed.

Every collocated sampler was installed and equipped according to the NADP/NTN protocols. An Aerochem Metrics[1] wet/dry deposition sampler and a Belfort rain gage with an event recorder were installed with the sampler and rain gages currently in operation at each of four NADP/NTN sites. Alterations to the wet/dry samplers, such as peaked roofs, were duplicated at individual sites. The sites were selected for the first year of the program using the following criteria:

1. Sites were distributed among diverse regional locations.
2. Sites were distributed among regions that receive large, moderate, and small quantities of precipitation.
3. Stable site-operational histories were required to ensure that minimal data were lost because of changes in operators.

The sites selected for the first year of the program were Tifton, Ga. (GA50); Huntington Forest, N.Y. (NY20); Oxford, Ohio (OH09); and LBJ Grasslands, Tex. (TX56). Site codes for the associated collocated sites are 50GA, 20NY, 09OH, and 56TX. The location of the four sites is shown in figure 4. The four pairs of collocated wet/dry deposition samplers are to be operated for 1 year.

Equipment was activated at all four collocated sites on October 25, 1988. The first samples were removed from the samplers on November 1, 1988. Samples from each pair of sites were processed by the site operator using standard NADP/NTN procedures. Onsite pH and specific-conductance measurements were not made for the samples from the newly installed collocated samplers. An aliquot was withdrawn and discarded, however, to emulate the subsampling routine. All samples were analyzed by the CAL.

A review of the data from the collocated sites identified a few operational problems. One sample from site 50GA contained a combination of contaminants that affected several of the analyte concentrations and values.

The wet/dry deposition samplers at sites NY20 and 20NY were stuck open during Nov. 1-8, 1988, because of heavy snow on the lid; both samples were exposed to about the same quantity of dry deposition. The sampler at site 20NY also malfunctioned from Dec. 27 through Jan. 17, 1989, and did not collect wet-deposition samples.

The wet/dry deposition samplers at sites OH09 and 09OH were stuck open from Dec. 27 through Jan. 3, 1989, because the lids were frozen open; samples from both sites were exposed to excess dry deposition. Two samples also contained a combination of contaminants.

Some differences in sample volumes exist for the data set from site 56TX, particularly for samples collected during the latter one-half of the time period. These differences might be an effect of the faulty sensor on one of the wet/dry deposition samplers.

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[1] The use of trade or product names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

An insufficient quantity of data was obtained during 1988 to determine an estimate of the precision of the data collected by the entire NADP/NTN Network using standard NADP/NTN procedures. Samples will be collected at additional collocated sampler sites through at least September 1991.

SUMMARY AND CONCLUSIONS

During 1988, the U.S. Geological Survey operated four programs designed to provide external quality-assurance monitoring of the National Atmospheric Deposition Program (NADP) and 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 effect of routine sample handling 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 each laboratory. A collocated-sampler program was begun to provide an overall estimate of precision for NADP/NTN data-collection procedures.

Two intersite-comparison studies were completed during 1988. For pH, 88 to 94 percent of the site operators met the NADP/NTN accuracy goal; 95 to 96 percent of the site operators met the NADP/NTN accuracy goal for specific conductance.

Results from the blind-audit program indicated significant positive bias for calcium, magnesium, sodium, and chloride, and a significant negative bias for hydrogen ions and specific conductance. The results indicate that contamination is occurring for some analytes, and that concentrations of hydrogen ions are decreased in blind-audit samples handled and shipped according to NADP/NTN protocols. An estimate of analytical precision was calculated using a pooled variance. 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.

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. Analytical results from National Institute of Standards and Technology reference solutions indicated that EMSI had the least number of median analyses that were significantly different from the certified concentrations or values. EMSI had the largest number of determinations larger than the minimum reporting limit for calcium, magnesium, potassium, and nitrate analyses of ultrapure deionized water.

A collocated-sampler program was begun with four NADP/NTN sites to estimate the overall precision of NADP/NTN data. The sites were distributed among diverse regional locations that had a range of precipitation quantities. The initial four sites were operated for 1 year. Because of the November 1988 start of the program, insufficient data were obtained during 1988 to estimate precision for the data collection procedures.

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