EXTERNAL QUALITY-ASSURANCE RESULTS FOR THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK DURING 1991

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CONVERSION FACTORS AND ABBREVIATIONS

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

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5\ (°C) + 32.$$

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

microsiemens per centimeter at 25 degrees Celsius (μS/cm)

megohms (MΩ)

microequivalents per liter (μeq/L)

kilograms per hectare (kg/ha)

External Quality-Assurance Results for the National Atmospheric Deposition Program/ National Trends Network During 1991

By Mark A. Nilles, John D. Gordon, LeRoy J. Schroder, *and* Charles E. Paulin

Abstract

The U.S. Geological Survey used four programs in 1991 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 four 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 93 and 86 percent of the site operators met the NADP/NTN accuracy goal for pH determinations during the two intersite-comparison studies completed during 1991. The results also indicated that 96 and 97 percent of the site operators met the NADP/NTN accuracy goal for specific-conductance determinations during the two 1991 studies. The effects of routine sample handling, processing, and shipping, determined in the blind-audit program indicated significant positive bias (α=.01) for calcium, magnesium, sodium, potassium, chloride, nitrate, and sulfate. Significant negative bias (α=.01) was determined for hydrogen ion and specific conductance. Only ammonium determinations were not biased. A Kruskal-Wallis test indicated that there were no significant (α=.01) differences in analytical results from the four laboratories participating in the interlaboratory-comparison program. Results from the collocated-sampler program indicated the median relative error for cation concentration and deposition exceeded eight percent at most sites, whereas the median relative error for sample volume, sulfate, and nitrate concentration at all sites was less than four percent. The median relative error for hydrogen ion concentration and deposition ranged from 4.6 to 18.3 percent at the four sites and as indicated in previous years of the study, was inversely proportional to the acidity of the precipitation at a given site. Overall, collocated-sampling error typically was five times that of laboratory error estimates for most analytes.

INTRODUCTION

The National Atmospheric Deposition Program (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 NADP/NTN sites in 1991 collected wet-deposition samples 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). Earlier reports have described the NADP/NTN onsite operations (Bigelow and Dossett, 1988), 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 1991. These programs are designed to: (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) estimate the comparability, bias, and precision of analytical results obtained by separate laboratories routinely measuring wet deposition when portions of common samples are sent to the participating laboratories (interlaboratory-comparison program); and (4) estimate the overall precision of the monitoring network from the point of sample collection through storage of the data in the NADP/NTN data base by the collection and analysis of paired samples from collocated samplers at selected sites in the network (collocated-sampler program). A detailed explanation of the procedures and analytical methods used in these four quality-assurance programs is given by See, Willoughby, Brooks, and Gordon (1990).

INTERSITE-COMPARISON PROGRAM

Intersite-comparison studies have been used since 1978 to assess the accuracy and precision of pH and specific conductance measurements made by NADP/NTN site operators (Gordon and others, 1991) Intersite-comparison studies 27 and 28 were done by the U.S. Geological Survey in 1991. The intersite-comparison study 27 mailing was completed in April 1991, and the intersite-comparison study 28 mailing was completed in November 1991. None of the site operators reported any equipment problems during study 27; four site operators reported equipment problems in study 28. Table 1 summarizes site operator participation in 1991. In each study, site operators were instructed to determine the pH and specific conductance of the reference solution using standard NADP/NTN procedures. Site-operator results are assessed using the NADP/NTN measurement-accuracy criteria. The NADP/NTN accuracy goal for onsite pH determinations of less than 5.0 is ±0.10 pH unit of the actual pH (Aubertin and others, 1990). This criterion increases to +0.30 pH unit when the actual pH exceeds 5.0. The NADP/NTN goal for onsite specific-conductance measurements is ±4.0 µS/cm. A flowchart depicting the intersite-comparison program is shown in figure 1.

Intersite-Comparison Study 27 Results

In study 27, all NADP/NTN site operators were mailed an aliquot of a synthetic reference solution simulating the pH and specific conductance of a natural wet-deposition sample. The reference solution used in study 27 had a target pH of 4.22 and a calculated specific conductance of 25.5 µS/cm. The median pH for the site operators responding by the closing date for study 27 was 4.24, and the median specific conductance was 26.3 µS/cm.

Of the 188 site operators submitting pH data on time in study 27, 93 percent reported pH values within ±0.10 pH unit of the overall median pH and successfully met the NADP/NTN accuracy goal. Using the median value of all responding sites as the most accurate estimate of the actual specific conductance, 96 per-

Table 1. Summary of site-operators responses for the 1991 intersite-comparison program

Site-operator responses	Intersite-comparison study	
	27	28
Number of site operator receiving samples	196	196
Number of site operators submitting pH values by closing date of study	188	181
Number of site operators submitting specific-conductance values by closing date of study	187	181
Site operators responding late	2	2
Number of nonresponding site operators	6	9
Sites that were not in operation	1	1
Sites that were not doing field chemistry	2	2
Site operators reporting equipment problems:		
pH meter/electrode completely inoperable	0	3
pH meter/electrode problems	0	0
Specific-conductance probe/meter completely inoperable	0	1
Specific-conductance probe/meter problems	0	0

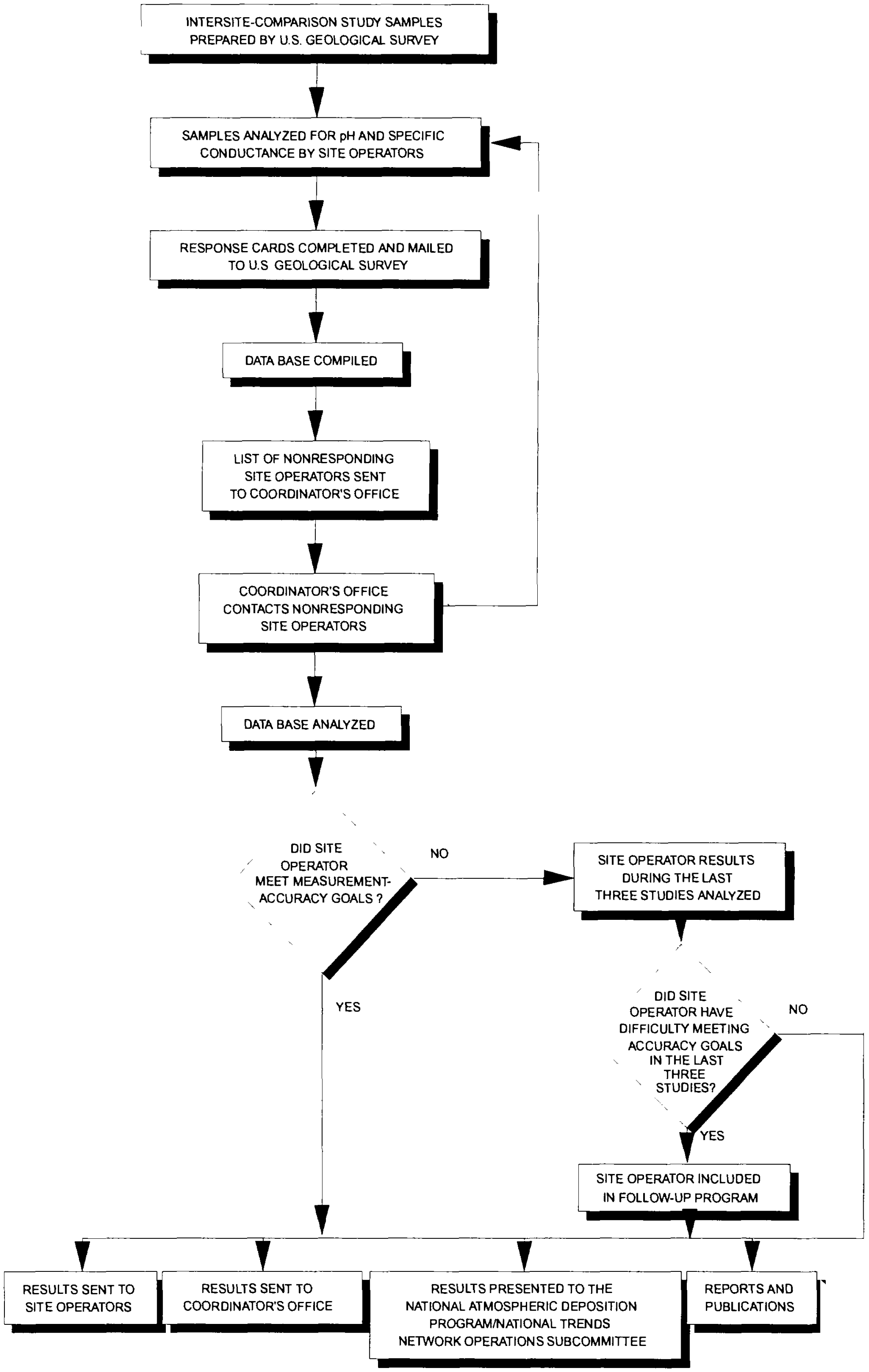


Figure 1. The intersite-comparison program of the National Atmospheric Deposition Program/National Trends Network.

cent of the site operators met the NADP/NTN specific-conductance accuracy goal (±4 µS/cm). The results of study 27 are graphically depicted in figure 2. Superimposed on the scatterplot in figure 2 are boundaries defining NADP/NTN accuracy goals for pH and specific-conductance measurements. Boundaries delineating the pH and specific conductance values for those site operators successfully meeting the goals for both measurements are also superimposed.

Intersite-Comparison Study 28 Results

In order to assess possible matrix effects on the ability of site operators to make accurate measurements, two solutions were used in intersite-comparison study 28. Solution A, a typical artificial matrix solution prepared using ultrapure-deionized water and nitric acid, was distributed to 168 site operators. Solution B, prepared by compositing 5 liters of filtered natural precipitation samples, was sent to a randomly selected subgroup of 28 site operators. The number of site operators receiving solution B was based on sample-size-determination methods by Snedecor and Cochran (1989). Solution A and Solution B each had a target pH of 4.72. The results of study 28 for solutions A and B are graphically depicted in figure 3. Superimposed on the scatterplots in figure 3 are boundaries defining NADP/NTN accuracy goals for pH and specific-conductance measurements.

To compare the results for the site operators receiving solution A and the results for site operators receiving solution B, the following tests were used: the Mann-Whitney U median test, and the Kolmogorov-Smirnov test of equal distributions. The Mann-Whitney U test was used to calculate the probability that the median pH for the site operators receiving solution A was statistically different from the median pH for site operators receiving solution B. The Kolmogorov-Smirnov test was used to compare the empirical cumulative distribution functions of the two populations.

The result of the Mann-Whitney U test was that the null hypothesis of equal medians for each group of site operators was accepted. The result of the Kolmogorov-Smirnov test was acceptance of the null hypothesis of equal distribution variability for each group of site operators.

Because no statistically significant difference were detected, the pH measurement accuracy criterion was based on the overall median pH of 4.73. Of the 181 site operators submitting pH data on time in study 28, 86 percent successfully met the accuracy goal.

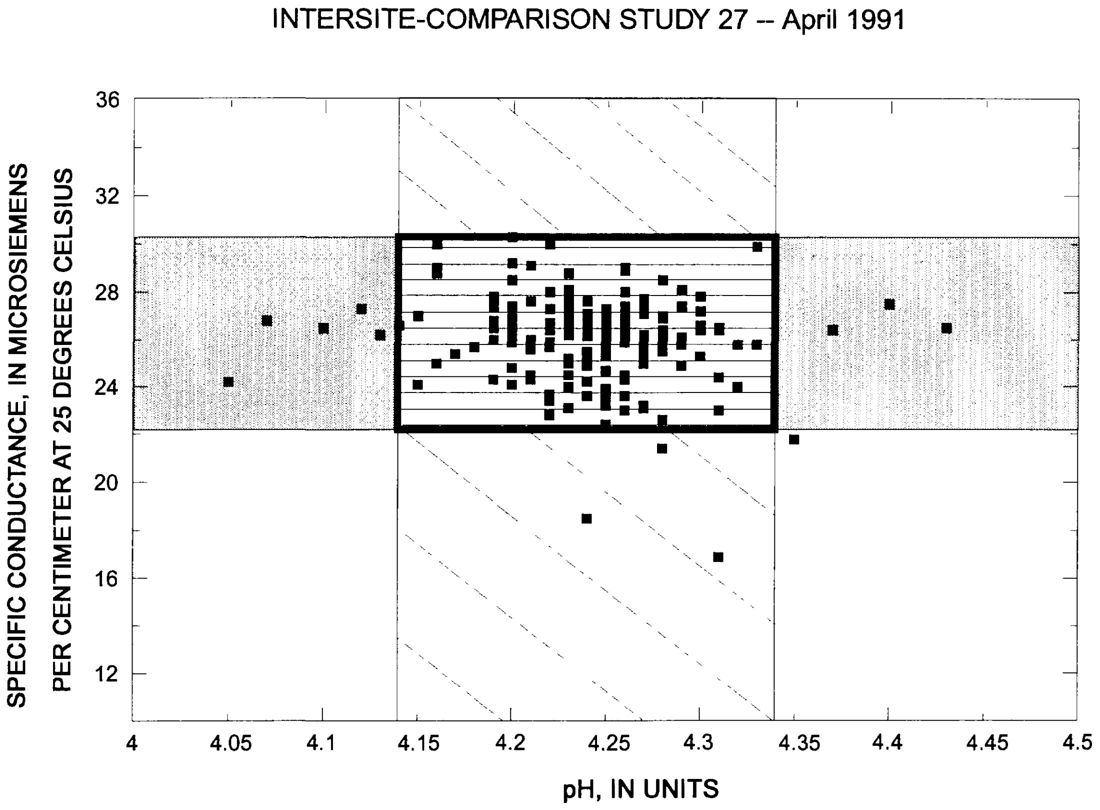
The artificial matrix solution used in study 28 had a calculated specific conductance of 8.0 µS/cm. The median of all responding site operators that received solution A was 8.6 µS/cm; the median of all responding site operators receiving solution B was 12.2. A total of 97 percent of all site operators reported specific conductance values within +4 µS/cm of the median conductance of the solution which they received. Percentiles for pH and specific conductance measurements obtained from intersite-comparison studies 27 and 28 are depicted in figure 4.

Intersite-Comparison Study Follow-Up Program

Since 1990, the intersite comparison study has included a follow-up program based on statistical quality-control procedures (See, Willoughby, Brooks, and Gordon, 1990). Based on a combination of factors, site operators failing to meet the pH accuracy goal may be asked to participate in one of four levels of follow-up. Factors include the amount by which they missed the pH measurement accuracy goal in the most recent study as well as their performance in the previous two studies. The four levels of follow-up range from a letter discussing common sources of measurement error to requests that the site operator perform one or more additional measurements (See, Willoughby, Brooks, and Gordon, 1990).

The additional aliquots distributed to site operators asked to participate follow-up levels 3 and 4 consisted of artificial matrix solutions with pH and specific conductance values different from those of the test solution distributed to all site operators in the initial portions of studies 27 and 28 but within the normal range for precipitation collected at NADP/NTN sites.

All 14 site operators that failed to meet the pH measurement accuracy goal in study 27 were included in the follow-up program. Eight of these site operators only received a letter describing common causes of measurement error, whereas five site operators were asked to perform additional pH measurements. The 26 site operators that failed to meet the pH measurement accuracy goal in study 28 were also included in the follow-up program. Ten of these site operators only received a letter describing common causes of measurement error, while 6 site operators were asked to perform additional pH measurements. A complete summary of the follow-up results for studies 27 and 28 is depicted in figure 5.



EXPLANATION

▨ MET NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK (NADP/NTN) GOALS FOR pH ONLY

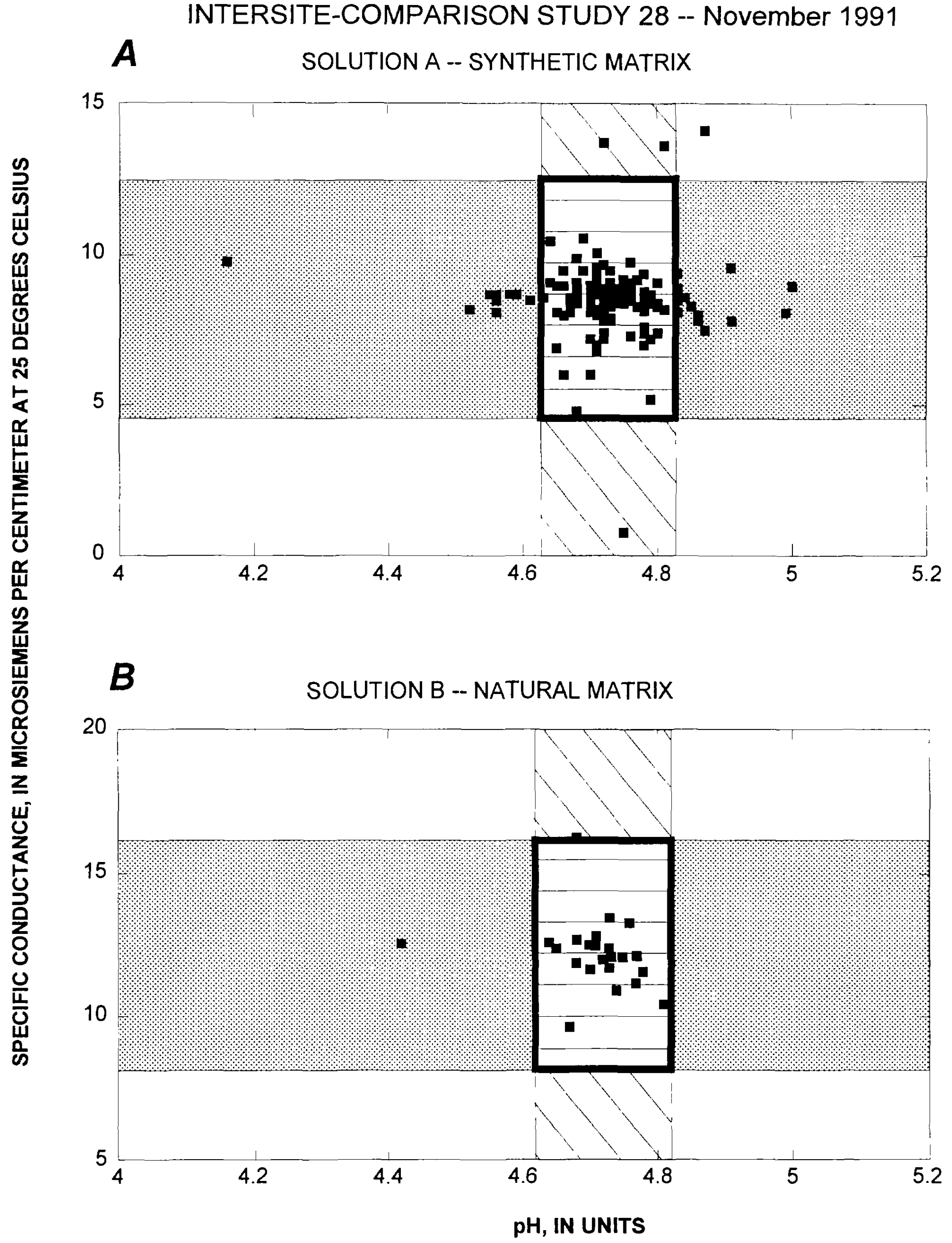
░ MET NADP/NTN GOALS FOR SPECIFIC CONDUCTANCE ONLY

☰ MET NADP/NTN GOALS FOR pH AND SPECIFIC CONDUCTANCE

Note: These data pairs were off-scale:

pH	Specific Conductance
3.64	27.4
4.57	2.70
4.73	26.7
3.80	27.5
4.20	80
4.25	3.10
4.27	3.07

Figure 2. The distribution of pH and specific conductance values for intersite-comparison study 27.



EXPLANATION

▧ MET NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK (NADP/NTN) GOALS FOR pH ONLY

▤ MET NADP/NTN GOALS FOR pH AND SPECIFIC CONDUCTANCE

▒ MET NADP/NTN GOALS FOR SPECIFIC CONDUCTANCE ONLY

NOTE: THESE DATA PAIRS WERE OFF-SCALE

pH	SPECIFIC CONDUCTANCE	SOLUTION
6.70	8.5	A
5.90	5.8	A
5.42	8.7	A
5.72	10.8	B

Figure 3. The distribution of pH and specific conductance values for intersite comparison 28.

A

PERCENTILES

FOR pH MEASUREMENTS

INTERSITE-COMPARISON STUDY NUMBER	5th	25th	50th	75th	95th
27	4.15	4.22	4.24	4.27	4.32
28 -- artificial solution	4.57	4.70	4.73	4.78	4.91
28 -- natural solution	4.50	4.68	4.72	4.75	5.40

pH, IN UNITS

B

PERCENTILES

FOR SPECIFIC CONDUCTANCE MEASUREMENTS

INTERSITE-COMPARISON STUDY NUMBER	5th	25th	50th	75th	95th
27	22.7	25.3	26.3	27.0	29.0
28 -- artificial solution	6.87	8.18	8.60	8.90	9.97
28 -- natural solution	9.98	11.7	12.2	12.7	15.3

SPECIFIC CONDUCTANCE, IN MICROSIEMENS PER CENTIMETER

<u>EXPLANATION</u>

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

ACCURACY CRITERIA FOR STUDIES 27 AND 28 WERE MEDIAN +/- .10 pH UNIT ACCURACY CRITERIA FOR A, AND MEDIAN +/- 4.0 MICROSIEMENS PER CENTIMETER FOR B

Figure 4. Percentiles for pH and specific conductance from intersite-comparisons 27 and 28.

Follow-up Level	Intersite Comparison Study Number	Number of Site Operators that Participated	Met the Goals	Failed to Meet the Goals	Mixed Results	Failed to Participate	Failed to Complete All Analysis
Level 1	27	XXXXXXXX					
	28	XXXXXXXXXX					
Level 2	27	XXX	XX	X			
	28	XXXXXX	XXXXXX				
Level 3	27	XX	X	X			
	28	XXXXX	XXX		X	X	
Level 4	27						
	28	XXXXX	XX		X	X	X

X = ONE SITE OPERATOR

LEVEL 1 FOLLOW-UP:

1) Letter discussing common sources of measurement errors

LEVEL 2 FOLLOW-UP:

1) Letter discussing common sources of measurement errors
2) Request that site operator reanalyze the remaining portion of the test solution

LEVEL 3 FOLLOW-UP:

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

LEVEL 4 FOLLOW-UP:

1) Letter discussing common sources of measurement errors
2) Request that site operator reanalyze the remaining portion of the test solution
3) Two additional aliquots of test solution

Figure 5. Summary of the follow-up results for intersite-comparison studies 27 and 28 for the National Atmospheric Deposition Program/National Trends Network.

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. In the blind-audit program, site operators submit quality-assurance samples disguised as actual precipitation samples to the Central Analytical Laboratory (CAL) for analysis. Detailed descriptions of the blind-audit program have been documented previously (See, Willoughby, Brooks, and Gordon, 1990, Bigelow and others, 1989). Figure 6 depicts all components of the blind-audit program, from sample preparation to distribution of interpretive reports.

Thirty-two blind-audit samples were sent to the operators of selected NADP/NTN sites in each quarter of 1991. The sites selected were chosen to ensure a uniform geographic distribution throughout the United States. For the third consecutive year, a range of sample volumes were distributed. Samples containing either 250-, 500-, or 1,000-mL were sent to the operators of selected sites to assess volume-related effects on biases. Site operators were provided with detailed instructions on how to process the blind-audit samples.

The solutions used in the blind-audit program are carefully selected to replicate a range of concentrations typical of what is found in actual precipitation samples collected at NADP/NTN sites. In 1991, the median analyte concentration values for bottle samples approximated the 50th percentile of actual precipitation samples collected at NADP/NTN sites for most analytes. All of the median analyte concentration values except for ammonium for the solutions used in the blind-audit program were between the 25th and 75th percentile of actual precipitation samples collected at NADP/NTN sites. A comparison of percentile concentration values of the chemical and physical parameters for samples used in the blind-audit program and precipitation samples analyzed by the CAL in 1991 is depicted in table 2. The solutions used in the 1991 blind-audit program, the names of the agencies that prepared them, and any special remarks about each solution are depicted in table 3; while the target values for solutions used in the 1991 blind-audit program are presented in table 4.

After a site has been selected for the blind-audit program and the operator of the selected site has successfully participated, the site is not selected again for the blind-audit program until the operators of all other NADP/NTN sites have participated. The operators of nearly two-thirds of all sites were requested to submit a blind-audit sample in 1991 (approximately 200 sites were in the NADP/NTN in 1991 and 32 sites were selected each quarter for the blind-audit program). Figure 7a depicts the location of all NADP/NTN sites in 1991; figure 7b depicts the location of NADP/NTN sites whose operators were requested to submit blind-audit samples in 1991.

The instructions sent to site operators prescribed that 75 percent of the blind-audit sample was to be poured into a standard, clean NADP/NTN 13-L polyethylene collection bucket and processed as if it were the wet-deposition sample from the previous week. This portion of the blind-audit sample is referred to as the bucket sample. The operator determined the weight of the bucket containing 75 percent of the blind-audit sample, then removed a 20-mL aliquot in order to measure the pH and specific conductance. 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. An 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. Figures 8a and 8b depict examples of fictitious and dummy field observer report forms, respectively.

Site operators returned the remaining 25 percent of the blind-audit sample, still 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. Because of the order in which samples and field observer report forms are processed, the CAL staff could not, at the time they received and analyzed the disguised bucket portions of the blind-audit samples, identify individual samples as being from an external quality-assurance program. Information concerning sample chemical composition was not provided to the CAL staff that did the analyses or to the site operators that did the processing. When the bottle portion of a blind-audit sample was submitted to the CAL, only the sample processing group of the laboratory staff recognized that it was not an actual NADP/NTN sample. By the time the analysis was performed, the samples appeared to be regular network precipitation samples. The analyte concentrations in bottle portions were not known by the laboratory staff.

The CAL staff that received and analyzed the actual precipitation sample could not identify from which site the sample had been sent. After all the analyses for the bucket and bottle portions of the blind-audit sample and for the actual precipitation samples were completed, the true identity of each of these samples was disclosed to the CAL Data Quality Assurance Officer. The NADP/NTN data base was then amended by matching the analytical data with the correct sample.

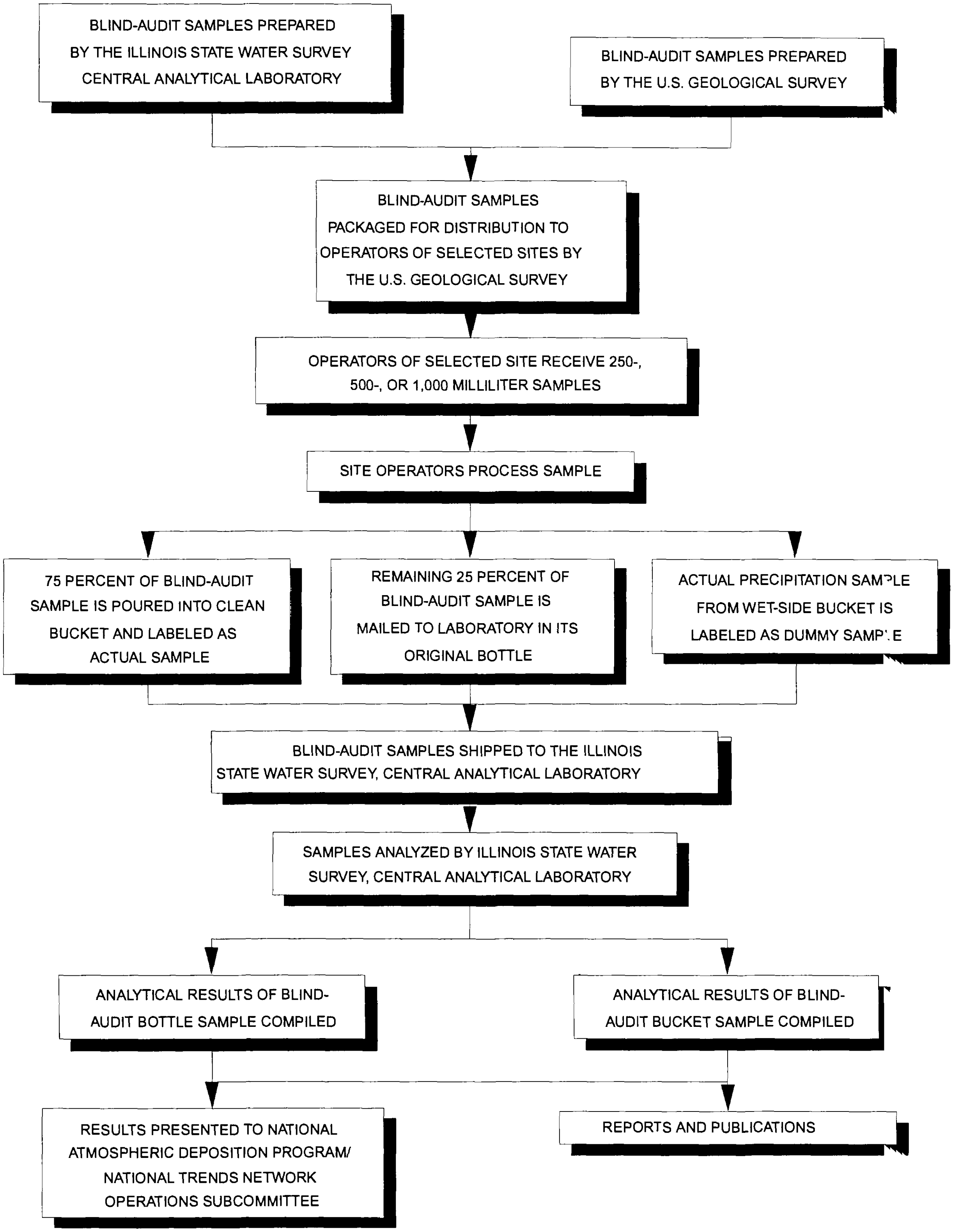


Figure 6. Blind-audit program of the National Atmospheric Deposition Program/National Trends Network.

Table 2. Comparison of the percentile concentration values of chemical and physical parameters for the solutions used in the blind-audit program and precipitation samples collected by the National Atmospheric Deposition Program/National Trends Network in 1991 (values in milligrams per liter except pH in units and specific conductance in microsiemens per centimeter); <, less than reporting limit

	Samples used in the Blind-audit program			**Precipitation samples collected by the NADP/NTN**		
Parameter	**25th**	**50th**	**75th**	**25th**	**50th**	**75th**
Calcium	0.02	0.13	0.14	0.057	0.120	0.253
Magnesium	0.01	0.03	0.03	0.013	0.025	0.050
Sodium	0.10	0.11	0.19	0.038	0.075	0.167
Potassium	0.02	0.03	0.04	0.010	0.019	0.039
Ammonium	<0.02	0.07	0.14	0.11	0.24	0.45
Chloride	0.14	0.17	0.28	0.10	0.15	0.28
Nitrate	0.50	1.01	1.07	0.59	1.07	1.84
Sulfate	0.65	0.88	1.23	0.66	1.30	2.28
Phosphate	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
pH	4.31	4.68	4.75	4.43	4.87	5.52
Specific conductance	11.12	12.20	21.87	7.5	13.4	23.7

Table 3. Solutions used in the 1991 USGS blind-audit program and interlaboratory-comparison program

Solution name	**Agency that prepared the solution**	**Remarks**
CAL 4.3	Central Analytical Laboratory	Dilution nitric acid solution
Ultrapure	U.S. Geological Survey	Deionized water
USGS	U.S. Geological Survey	Prepared from dissolved salts and deionized water
P-12	U.S. Geological Survey	Precipitation quality assurance sample prepared by the standard water reference sample project.
1088-2-1:1	U.S. Environmental Protection Agency	Supplied as a concentrated stock solution and diluted by the U.S. Geological Survey Acid Rain Project.
1088-2-2:1	U.S. Environmental Protection Agency	

Data Analysis for the Blind-Audit Program

To assess analytical bias, differences between the results from the bucket and bottle portions are evaluated. In 1991, the CAL analyzed all of the paired bucket and bottle samples within 21 days of each other; except for a small number of sample pairs, most were analyzed within 1 week of each other. 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. For the purpose of comparison, it was presumed that analyte concentrations in the bottle portion of the blind-audit sample had not changed 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. Previous sample stability studies have indicated that the analytes in quality-assurance samples used in the blind-audit program are stable for at least 45 days (Peden and Skowron, 1978; Willoughby and others, 1991). Complete bucket and bottle analyses were available for 123 of the 128 blind-audit samples sent to participating site operators in 1991. Three site operators failed to submit the blind-audit samples. One site operator poured the entire sample into the bucket; therefore, no bottle analyses were available for that

Table 4. Target values for solutions used in the 1991 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	**Concentration, in milligrams per liter**								**pH[4]**	**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	.91	.06	.71	.050	--	.66	--	.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]1088-2-1:1	.047	.028	.179	.073	.080	0.283	.57	2.68	4.27	24.1
[1,2]1088-2-2:1	.024	.014	.090	.037	.040	.142	.29	1.34	--	12.0
[2]2694-I	.014	.024	.205	.052	--	[3].24	--	2.75	4.27	26
[2]2694A-I	.013	.024	.208	.056	[3].12	[3].23	[3].53	2.69	4.30	25.4
[2]2694-II	.049	.051	.419	.106	[3]1	[3]1	7.06	10.9	3.59	130

[1] Used in the 1991 blind-audit program.

[2] Used in the 1991 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).

sample. One site operator did not secure the lid on the bucket portion of the blind-audit sample, and the sample leaked out; bucket analyses were not available for that sample.

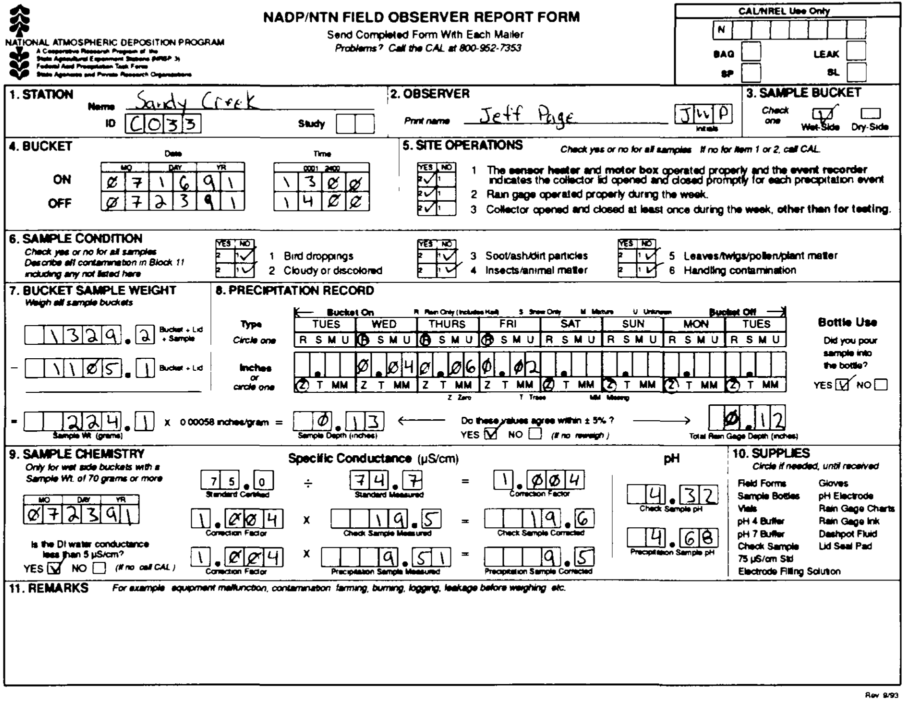
If there is physical evidence of contamination and the chemistry is abnormal, the CAL assigns actual precipitation samples a "C" code to indicate the sample is contaminated (Bowersox, 1984). All quality-assurance samples (such as the bucket and bottle portions of the blind-audit samples) that contain extrinsic material are assigned a "C" code regardless of the sample chemistry. The "C" codes are assigned after the true identities of the bucket and bottle portions of the blind-audit sample have been disclosed to the CAL Data Quality Assurance Officer. 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 1991 blind-audit statistical analyses.

The median analyte concentrations determined for the bucket and bottle results for all data pairs are presented in table 5. Bucket and bottle values reported as less than the minimum detection limit were set equal to the minimum detection limit. The median bucket-sample concentrations were larger than the median bottle-sample concentrations for calcium, magnesium, sodium, potassium, ammonium, chloride, nitrate, and sulfate. The median concentrations for bucket samples were smaller than the median concentrations for the bottle samples for hydrogen ion and specific conductance. Boxplots in figure 9 graphically depict the bucket-sample minus bottle-sample concentrations for all the major ions for all bucket and bottle data pairs.

A Wilcoxon signed-ranks test (Conover, 1980) 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 samples submitted in 1991. All blind-audit samples that had paired analyte determinations were included in the statistical analyses. Analyte concentrations reported as less than the minimum reporting limit were set equal to the minimum reporting limit (alternatively, analyte concentrations reported as less than the minimum reporting limit were set equal to zero and then to one-half the minimum reporting limit to determine if the results of Wilcoxon signed-ranks test for bias would be different; regardless of whether the less than detection values were set equal to zero, one-half the minimum reporting limit, or the minimum reporting limit, the results of the Wilcoxon signed-ranks test for bias were the same). At a significance level of $\alpha=0.01$, the Wilcoxon signed-ranks test indicated that bias existed for calcium, magnesium, sodium, potassium, chloride, nitrate, sulfate, hydrogen ion, and specific conductance. Only ammonium was not biased. The complete results of the Wilcoxon signed-ranks test for bias with values that were less than the minimum reporting limit set equal to the minimum reporting limit are shown in table 6.

Figure 7. A, Location of National Atmospheric Deposition Program/National Trends Network sites; B, location of National Atmospheric Deposition Program/National Trends Network sites whose operators participated in the 1991 blind-audit program.

A



NATIONAL ATMOSPHERIC DEPOSITION PROGRAM
A Cooperative Research Program of the
State Agricultural Experiment Stations (NRSP-3)
Federal Acid Precipitation Task Force
State Agencies and Private Research Organizations

NADP/NTN FIELD OBSERVER REPORT FORM
Send Completed Form With Each Mailer
Problems? Call the CAL at 800-952-7353

CAL/NREL Use Only
N ☐☐☐☐☐☐☐
BAG ☐ LEAK ☐
SP ☐ SL ☐

1. STATION
Name Sandy Creek
ID C033
Study ☐☐

2. OBSERVER
Print name Jeff Page
JWP Initials

3. SAMPLE BUCKET
Check one ☑ Wet-Side ☐ Dry-Side

4. BUCKET

	Date MO	DAY	YR	Time 0001–2400
ON	07	16	91	1300
OFF	07	23	91	1400

5. SITE OPERATIONS *Check yes or no for all samples. If no for item 1 or 2, call CAL.*

YES 2	NO 1	
✓		1 The sensor heater and motor box operated properly and the event recorder indicates the collector lid opened and closed promptly for each precipitation event
✓		2 Rain gage operated properly during the week.
✓		3 Collector opened and closed at least once during the week, other than for testing.

6. SAMPLE CONDITION
Check yes or no for all samples
Describe all contamination in Block 11 including any not listed here

YES 2	NO 1	
	✓	1 Bird droppings
	✓	2 Cloudy or discolored
	✓	3 Soot/ash/dirt particles
	✓	4 Insects/animal matter
	✓	5 Leaves/twigs/pollen/plant matter
	✓	6 Handling contamination

7. BUCKET SAMPLE WEIGHT
Weigh all sample buckets

1329.2 Bucket + Lid + Sample
− 1105.1 Bucket + Lid
= 224.1 Sample Wt (grams) x 0.00058 inches/gram = 0.13 Sample Depth (inches) ⟵ Do these values agree within ± 5% ? YES ☑ NO ☐ (If no reweigh) ⟶ 0.12 Total Rain Gage Depth (inches)

8. PRECIPITATION RECORD

← Bucket On — R Rain Only (Includes Hail) S Snow Only M Mixture U Unknown — Bucket Off →

	TUES	WED	THURS	FRI	SAT	SUN	MON	TUES
Type *Circle one*	R S M U	[✓ R] S M U	[✓ R] S M U	[✓ R] S M U	R S M U	R S M U	R S M U	R S M U
Inches or circle one	.	0.04	0.06	0.02	.	.	.	.
	[✓ Z] T MM	Z T MM	Z T MM	Z T MM	[✓ Z] T MM	[✓ Z] T MM	[✓ Z] T MM	[✓ Z] T MM

Z Zero T Trace MM Missing

Bottle Use
Did you pour sample into the bottle?
YES ☑ NO ☐

9. SAMPLE CHEMISTRY
Only for wet side buckets with a Sample Wt. of 70 grams or more

MO	DAY	YR
07	23	91

Is the DI water conductance less than 5 µS/cm?
YES ☑ NO ☐ (If no call CAL)

Specific Conductance (µS/cm)

75.0 Standard Certified ÷ 74.7 Standard Measured = 1.004 Correction Factor
1.004 Correction Factor x 19.5 Check Sample Measured = 19.6 Check Sample Corrected
1.004 Correction Factor x 9.51 Precipitation Sample Measured = 9.5 Precipitation Sample Corrected

pH
4.32 Check Sample pH
4.68 Precipitation Sample pH

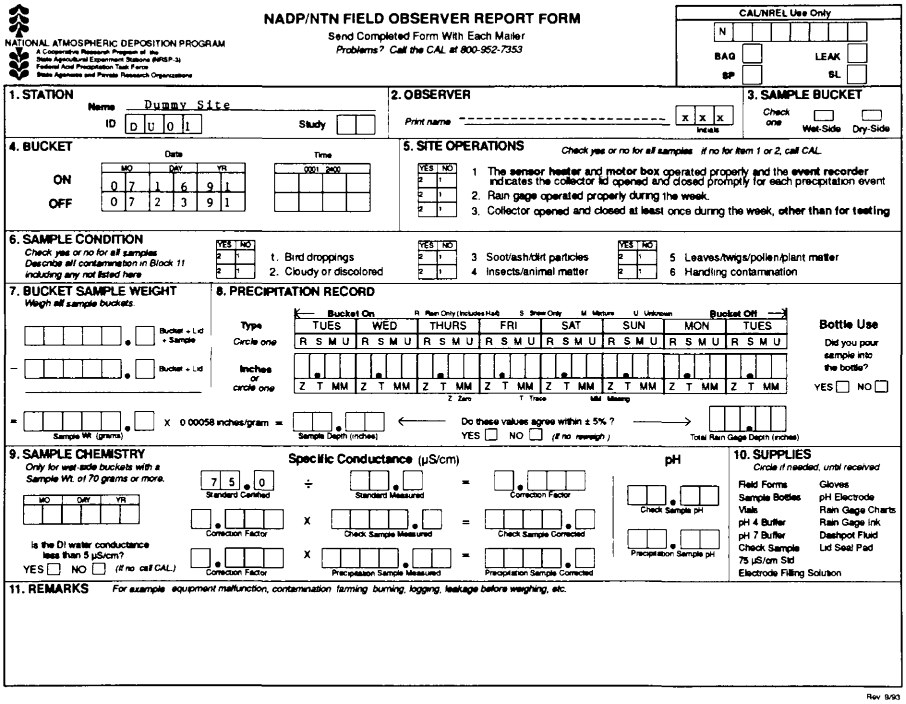
10. SUPPLIES
Circle if needed, until received

Field Forms	Gloves
Sample Bottles	pH Electrode
Vials	Rain Gage Charts
pH 4 Buffer	Rain Gage Ink
pH 7 Buffer	Dashpot Fluid
Check Sample	Lid Seal Pad
75 µS/cm Std	
Electrode Filling Solution	

11. REMARKS *For example equipment malfunction, contamination farming, burning, logging, leakage before weighing etc.*

Rev 9/93

B



NATIONAL ATMOSPHERIC DEPOSITION PROGRAM
A Cooperative Research Program of the
State Agricultural Experiment Stations (NRSP-3)
Federal Acid Precipitation Task Force
State Agencies and Private Research Organizations

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CAL/NREL Use Only
N ☐☐☐☐☐☐☐
BAG ☐ LEAK ☐
SP ☐ SL ☐

1. STATION
Name Dummy Site
ID DU01
Study ☐☐

2. OBSERVER
Print name ------------------------
x x x Initials

3. SAMPLE BUCKET
Check one ☐ Wet-Side ☐ Dry-Side

4. BUCKET

	Date MO	DAY	YR	Time 0001–2400
ON	07	16	91	
OFF	07	23	91	

5. SITE OPERATIONS *Check yes or no for all samples. If no for item 1 or 2, call CAL.*

YES 2	NO 1	
		1 The sensor heater and motor box operated properly and the event recorder indicates the collector lid opened and closed promptly for each precipitation event
		2. Rain gage operated properly during the week.
		3. Collector opened and closed at least once during the week, other than for testing

6. SAMPLE CONDITION
Check yes or no for all samples
Describe all contamination in Block 11 including any not listed here

YES 2	NO 1	
		1. Bird droppings
		2. Cloudy or discolored
		3 Soot/ash/dirt particles
		4 Insects/animal matter
		5 Leaves/twigs/pollen/plant matter
		6 Handling contamination

7. BUCKET SAMPLE WEIGHT
Weigh all sample buckets.

☐☐☐☐☐.☐ Bucket + Lid + Sample
− ☐☐☐☐☐.☐ Bucket + Lid
= ☐☐☐☐☐.☐ Sample Wt (grams) x 0.00058 inches/gram = ☐☐.☐☐ Sample Depth (inches) ⟵ Do these values agree within ± 5% ? YES ☐ NO ☐ (If no reweigh) ⟶ ☐☐.☐☐ Total Rain Gage Depth (inches)

8. PRECIPITATION RECORD

← Bucket On — R Rain Only (Includes Hail) S Snow Only M Mixture U Unknown — Bucket Off →

	TUES	WED	THURS	FRI	SAT	SUN	MON	TUES
Type *Circle one*	R S M U	R S M U	R S M U	R S M U	R S M U	R S M U	R S M U	R S M U
Inches or circle one	.	.	.	.	.	.	.	.
	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM

Z Zero T Trace MM Missing

Bottle Use
Did you pour sample into the bottle?
YES ☐ NO ☐

9. SAMPLE CHEMISTRY
Only for wet-side buckets with a Sample Wt. of 70 grams or more.

MO	DAY	YR

Is the DI water conductance less than 5 µS/cm?
YES ☐ NO ☐ (If no call CAL.)

Specific Conductance (µS/cm)

75.0 Standard Certified ÷ ☐☐.☐ Standard Measured = ☐.☐☐☐ Correction Factor
☐.☐☐☐ Correction Factor x ☐☐☐☐.☐ Check Sample Measured = ☐☐☐☐.☐ Check Sample Corrected
☐.☐☐☐ Correction Factor x ☐☐☐☐.☐☐ Precipitation Sample Measured = ☐☐☐☐.☐ Precipitation Sample Corrected

pH
☐☐.☐☐ Check Sample pH
☐☐.☐☐ Precipitation Sample pH

10. SUPPLIES
Circle if needed, until received

Field Forms	Gloves
Sample Bottles	pH Electrode
Vials	Rain Gage Charts
pH 4 Buffer	Rain Gage Ink
pH 7 Buffer	Dashpot Fluid
Check Sample	Lid Seal Pad
75 µS/cm Std	
Electrode Filling Solution	

11. REMARKS *For example equipment malfunction, contamination farming burning, logging, leakage before weighing, etc.*

Rev 9/93

Figure 8. A, Example of a fictitious National Atmospheric Deposition Program/National Trends Network field observer report form; B, Example of a dummy National Atmospheric Deposition Program/National Trends Network field observer report form.

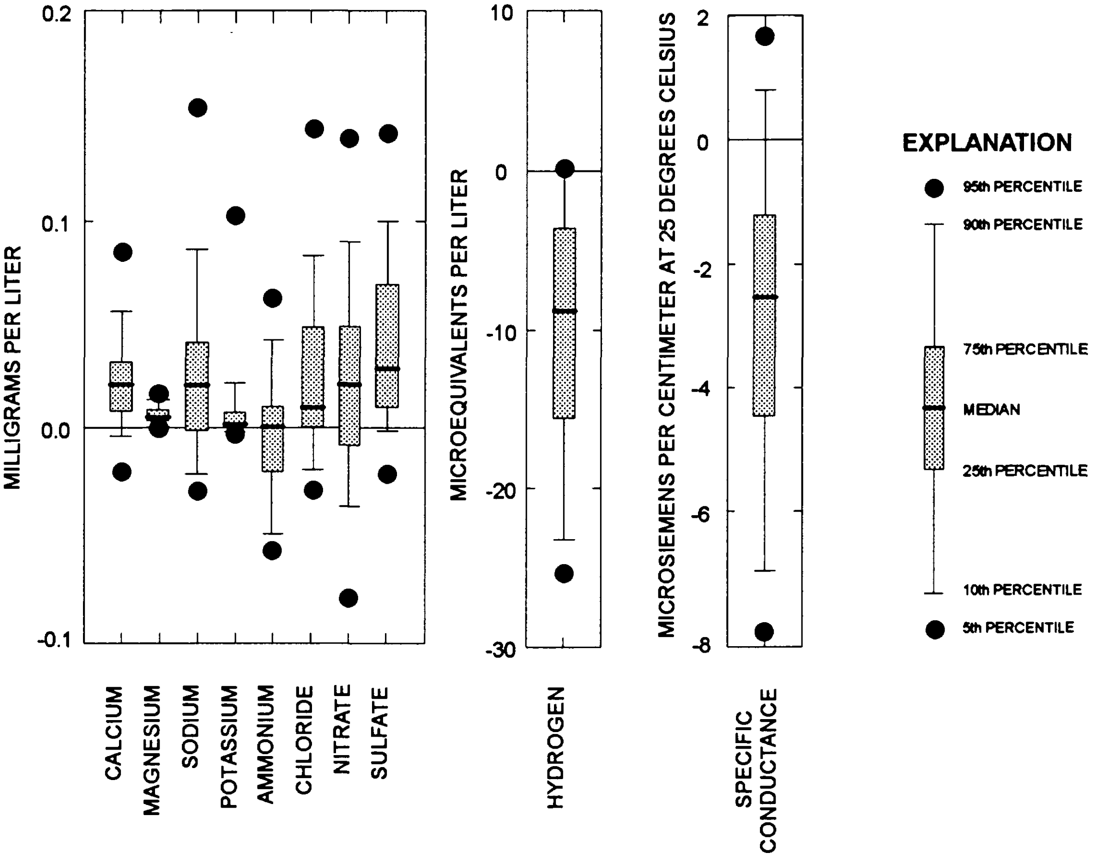


Figure 9. Bucket-sample concentrations minus bottle-sample concentrations in the blind-audit program, National Atmospheric Deposition Program/National Trends Network.

The overall precision of the 1991 blind-audit sample analyses was estimated by calculating the pooled standard deviations for all bucket portions of the blind-audit samples (Dixon and Massey, 1969, p. 113). The ultrapure samples were not included in this analyses. Analyte concentrations reported as less than the minimum reporting limit were set equal to the minimum reporting limits. The pooled standard deviations for all of the analytes measured in the bucket portions of the blind-audit samples are listed in table 7. A similar precision in the analyses of blind-audit samples (table 7) compared to interlaboratory samples analyzed at the CAL (table 11) indicates that although changes occur in samples due to sample handling and shipping procedures, the random variability is not appreciably increased as a result of sample handling and shipping procedures for most analytes in 1991.

The percent bias was calculated for all of the bucket minus bottle paired differences by calculating each paired difference as a percentage of the concentration measured in the bottle portion of the bucket-bottle data pair. The percent bias was calculated two different ways. First, all bucket-bottle data pairs were included. Bucket and bottle values reported as less than the minimum reporting limit were set equal to the minimum reporting limit. Second, bucket-bottle data pairs were excluded for a given analyte if the reported concentration for the bucket or bottle portion were less the minimum reporting limit. The percent bias was higher with all data pairs included in the analysis for calcium, sodium, and chloride compared to the censored data set. This was due to the influence of large (on a percentage basis) bucket-bottle differences when the bottle value was near the minimum reporting limit. Bucket concentrations that were only slightly larger than bottle concentrations near the minimum reporting limit resulted in excessively large percent bias results. In contrast,

Table 5. Median concentrations for the bucket and bottle portions of the samples used in the blind-audit program

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

Analyte	Median concentration in the bucket portion of the blind-audit sample	Median concentration in the bottle portion of the blind-audit sample
Calcium	0.133	0.116
Magnesium	0.030	0.027
Sodium	0.118	0.108
Potassium	0.026	0.025
Ammonium	0.06	0.05
Chloride	0.17	0.16
Nitrate	0.97	0.95
Sulfate	0.89	0.86
Hydrogen ion	11.22	19.05
Specific conductance	9.90	11.75

Table 6. Results of the tests for bias, using a Wilcoxon Signed-Rank Test

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

Analyte	The number of times the concentration in the bucket portion exceeded the concentration in the bottle portion	The number of times the concentration in the bottle portion exceeded the concentration in the bucket portion	The number of times the concentration in the bottle portion was equal to the concentration in the bucket portion	Determined to be biased?
Calcium	90	13	4	YES
Magnesium	91	9	7	YES
Sodium	77	29	1	YES
Potassium	67	26	14	YES
Ammonium	33	39	35	NO
Chloride	72	19	16	YES
Nitrate	69	31	7	YES
Sulfate	81	10	16	YES
Hydrogen ion	9	97	1	YES
Specific conductance	12	96	0	YES

bucket and bottle values for ammonium and potassium included a large number of bucket and bottle values that were both less than the minimum reporting limit. Because these values were set equal to the minimum reporting limit, the percent bias actually decreased for these analytes when all data pairs were included in the analysis. The percent bias for magnesium, chloride, nitrate, sulfate, hydrogen ion, and specific conductance were virtually identical regardless of whether all or selected data pairs were included in the analysis.

The median percent bias of -38.3 percent for hydrogen ion was the largest percent bias for all of the analytes and indicates that significant losses of hydrogen ion frequently occur from all samples collected in the 13 L polyethylene buckets used by the NADP/NTN. The percent bias for specific conductance was also very large: -21.1 percent. At the opposite extreme, the percent bias for both nitrate and sulfate was less than 5 percent. Percent bias for the remaining six analytes ranged from 7.14 to

Table 7. Pooled standard deviations of analyte data based on replicate analyses of blind-audit bucket samples

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

Analyte	Minimum value	Maximum value	Pooled standard deviation
Calcium	0.009	1.53	0.006
Magnesium	.003	.112	.001
Sodium	.006	1.085	.006
Potassium	.003	.976	.011
Ammonium	.02	.74	.007
Chloride	.03	1.36	.013
Nitrate	.03	3.39	.010
Sulfate	.03	2.77	.036
pH	4.33	6.74	.034
Specific conductance	1.3	23.8	.354

21.3 percent with all data pairs included in the analysis and from 9.1 to 15.4 percent excluding data pairs if the target concentration was less than the minimum reporting limit (table 8). 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 and sample-shipping procedures for all of the analytes except nitrate and sulfate.

To determine if a relation existed between the volume collected in the bucket and the differences between the analyte concentrations in the bucket and bottle portions of the blind-audit sample, sixteen 250-mL, fifteen 500-mL, and sixteen 1,000-mL bottles of the same solution (USGS) were sent to the operators of selected sites in 1991. 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. To analyze the differences for each analyte on a mass per bucket basis, the differences between the measured concentration in the bucket and bottle portions of the blind-audit samples were multiplied by the volume of the sample measured in the bucket. This converts the differences between the concentrations for the bucket and bottle portions of the blind-audit sample from milligrams per liter to micrograms per bucket. Boxplots in figures 10 and 11 depict the difference between the concentration measured in bucket and bottle portions of the USGS solution blind-audit samples plotted by the volume of the samples mailed to the site operators, whereas boxplots in figure 12 depict the differences for each analyte plotted by sample volume on a mass-per-bucket basis. For the 250 mL sample size, the data points representing the 95th percentile of potassium and chloride bucket minus bottle concentration differences were off scale (figs. 10 and 12), indicating probable potassium-chloride contamination from a pH electrode in one sample.

A Kruskal-Wallis test (Iman and Conover, 1983) was used to determine if there were statistically significant differences in the amount of bias determined on either a mass-per-bucket or concentration basis for the 250-, 500-, and 1,000-mL samples. Results of the Kruskal-Wallis test indicate no significant (α=0.01) difference in bucket-minus-bottle values on a mass-per-bucket basis for calcium, magnesium, potassium, ammonium, nitrate, sulfate and hydrogen ion. Statistically significant (α=0.01) differences were determined for sodium, chloride, and specific conductance. A slight decrease in the median-bucket minus-bottle difference in milligrams per bucket was measured for sodium and chloride as the sample volume increased. For all other analytes examined, the differences on a mass-per-bucket basis showed no trend as volume increased. On a concentration basis, results of the Kruskal-Wallis test indicate no significant (α=0.01) difference in bucket minus bottle concentrations for potassium, ammonium, sulfate and specific conductance, whereas statistically significant (α=0.01) differences were determined for calcium, magnesium, sodium, chloride, nitrate, and hydrogen ion (table 9).

Table 8. Median bucket minus bottle differences calculated as a percentage of the median bottle concentration for each analyte

[All units in percent]

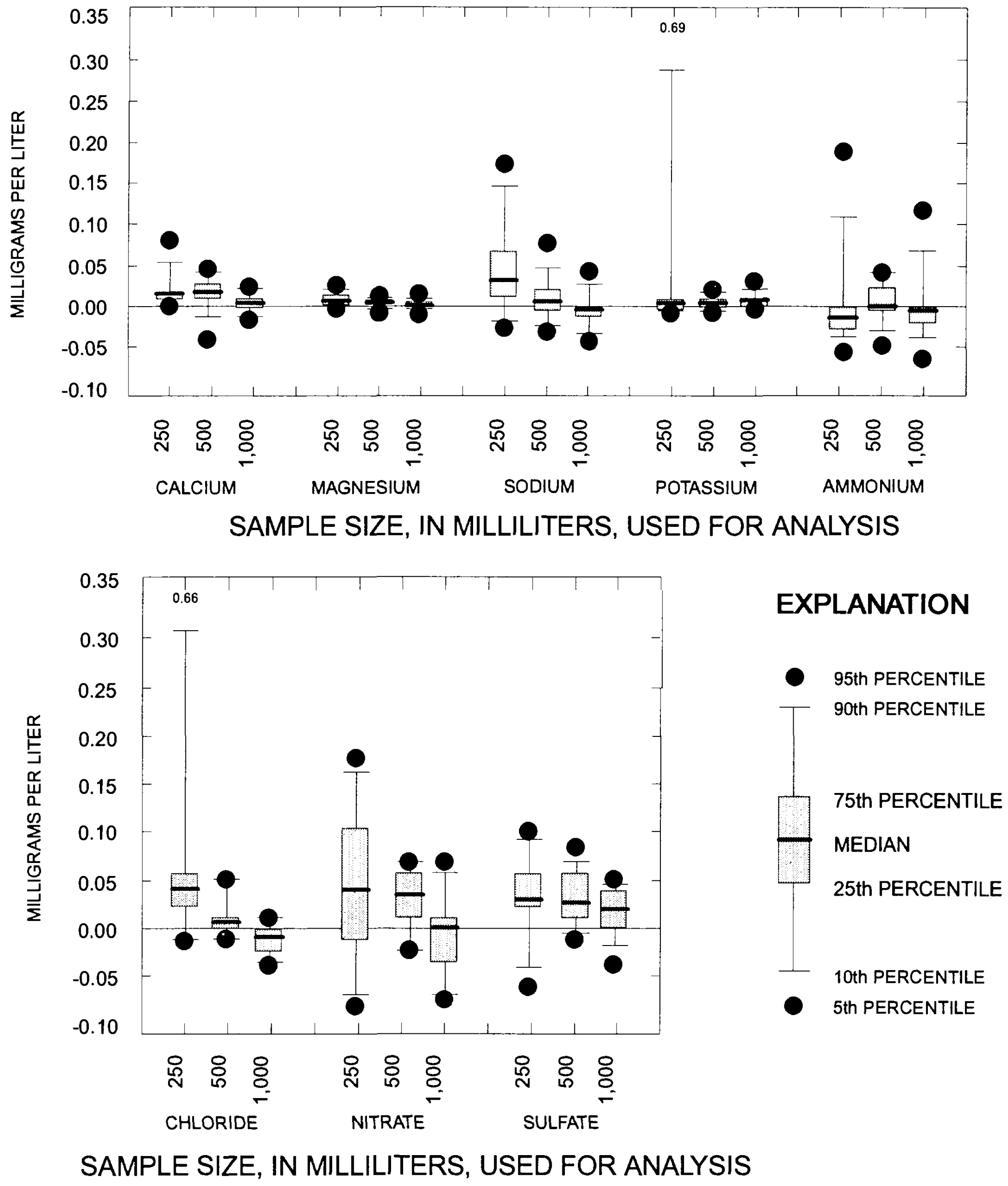
Analyte	Median bucket minus bottle differences expressed as a percentage of the corresponding bottle concentration; selected data pairs only[1]	Median bucket minus bottle differences expressed as a percentage of the corresponding bottle concentration; all data pairs[2]
Calcium	15.0	21.3
Magnesium	15.4	15.4
Sodium	12.2	19.2
Potassium	13.0	10.7
Ammonium	14.3	7.14
Chloride	9.10	11.1
Nitrate	4.35	4.85
Sulfate	3.45	3.53
Hydrogen ion	-38.3	-38.3
Specific conductance	-21.1	-21.1

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

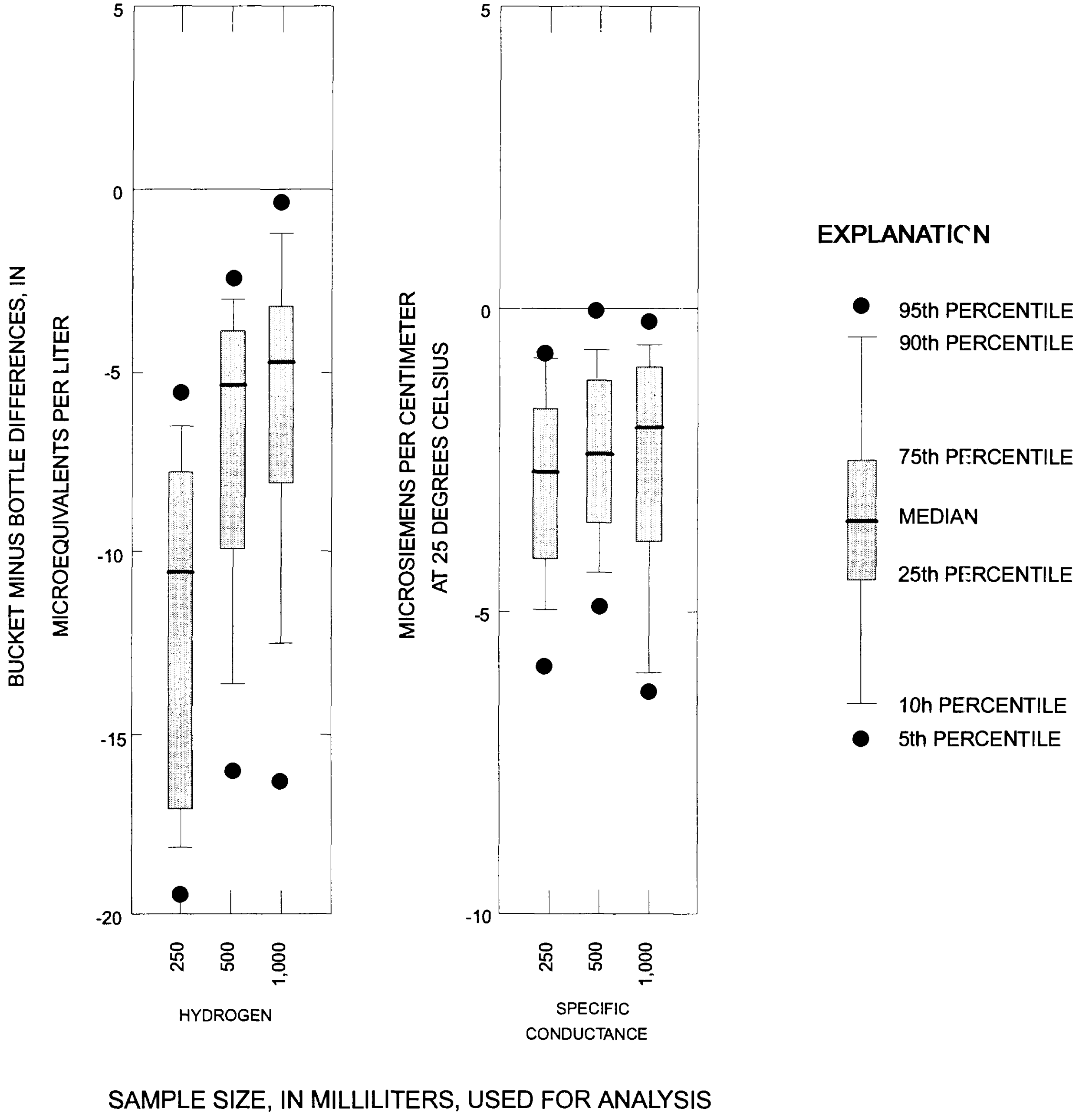
[2] All bucket minus bottle data pairs included. Bucket and bottle values reported as less than the minimum reporting limit were set equal to the minimum reporting limit.

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

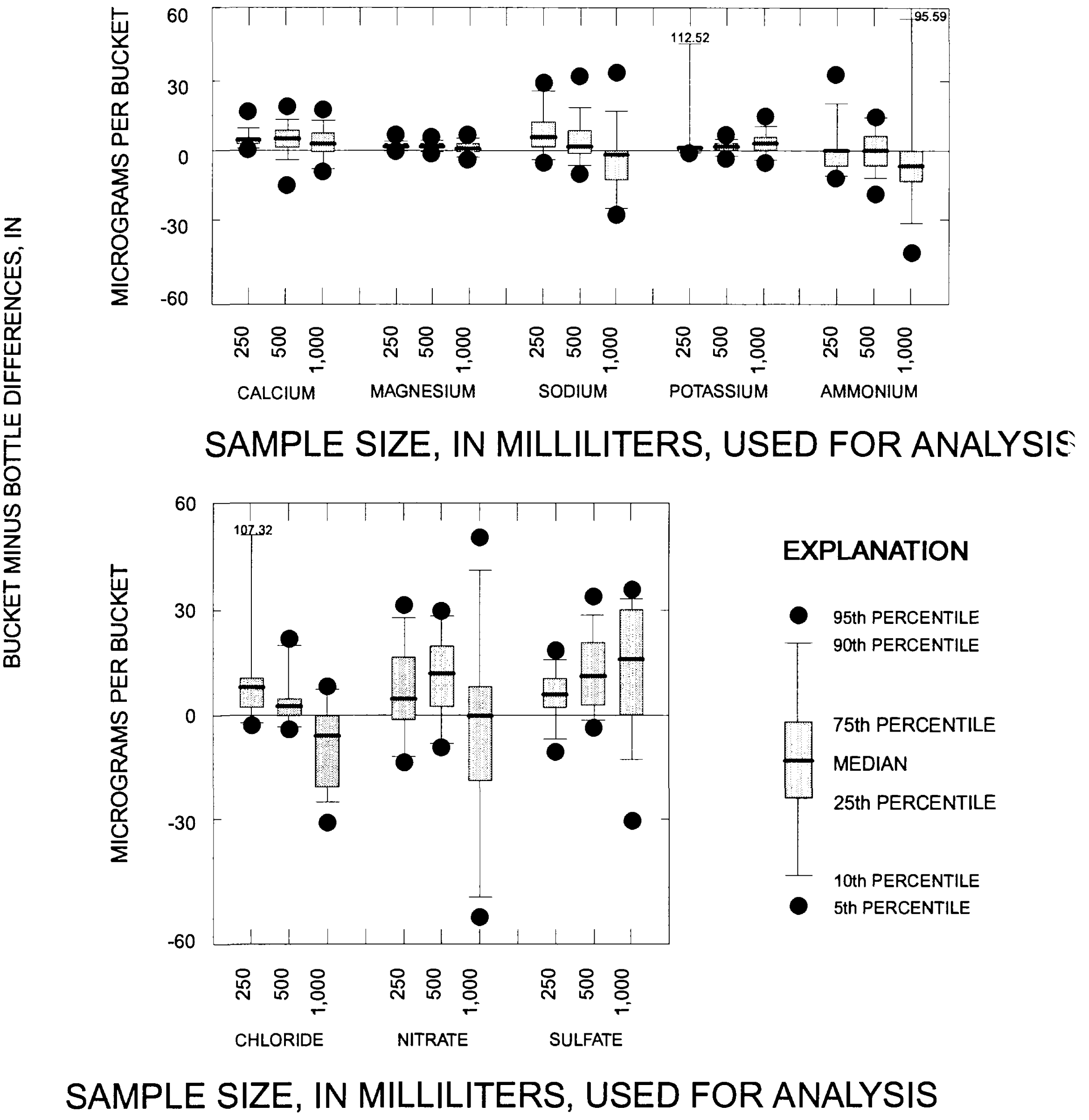
Analyte	Bucket minus bottle concentrations attained significance (P-value) levels on a mass per bucket basis	Statistically significant ($\alpha=0.01$) differences determined between 250-, 500-, and 1,000-mL USGS samples on a mass per bucket basis?	Bucket minus bottle concentrations attained significance (P-value) levels on a concentration basis	Statistically significant ($\alpha=0.01$) differences determined between 250-, 500-, and 1,000-mL USGS samples on a concentration basis?
Calcium	0.366	NO	0.000	YES
Magnesium	.569	NO	.002	YES
Sodium	.002	YES	.001	YES
Potassium	.218	NO	.937	NO
Ammonium	.448	YES	.676	NO
Chloride	.001	NO	.000	YES
Nitrate	.104	NO	.021	YES
Sulfate	.309	NO	.242	NO
Hydrogen ion	.029	NO	.001	YES
Specific conductance	.001	YES	.160	NO



Figures 10. Bucket-sample concentrations minus bottle-sample concentrations for the 250-, 500-, and 1,000-mL USGS solution samples in the blind-audit program.



Figures 11. Bucket-sample concentrations minus bottle-sample concentrations for the 250-, 500-, and 1,000-mL USGS solution samples in the blind-audit program.



Figures 12. Boxplots showing the major ions bucket-sample mass minus bottle-sample mass expressed in micrograms per bucket for the 250-, 500-, and 1,000-mL USGS solution samples in the blind-audit program.

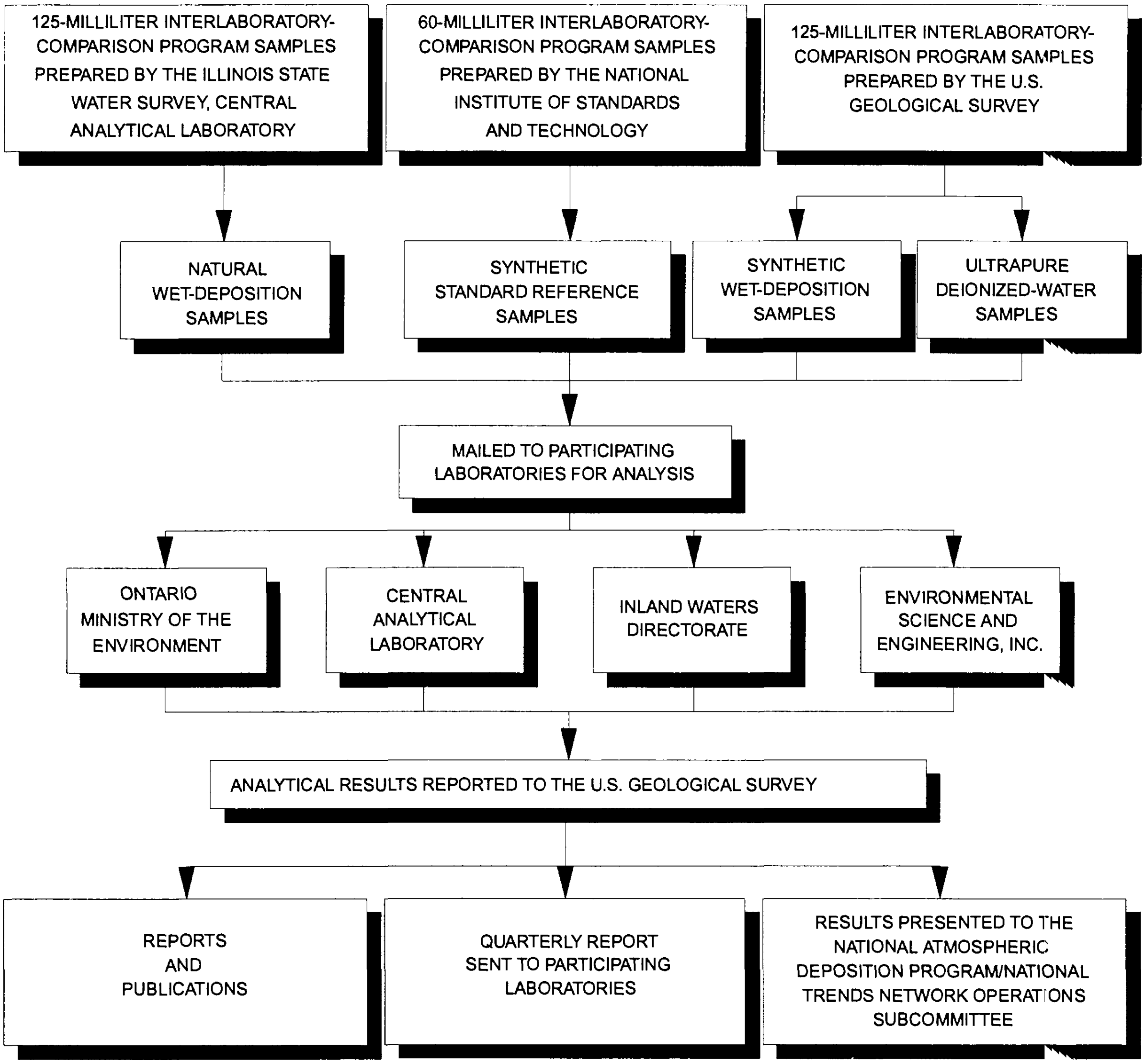


Figure 13. Interlaboratory-comparison program.

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. Four laboratories participated in the interlaboratory-comparison program for all of 1991: (1) Illinois State Water Survey, Central Analytical Laboratory (CAL); (2) Inland Waters Directorate, National Water Quality Laboratory (IWD); (3) Environmental Science and Engineering, Inc. (ESE); and (4) Ontario Ministry of the Environment, Water Quality Section (MOE).

Samples from four sources were prepared for the 1991 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 (1088-2-1:1 and 1088-1-2:1) supplied by the U.S. Environmental Protection Agency in concentrate and diluted by the U.S. Geological Survey, (3) standard reference samples (2694-I, 2564A-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 bottled 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 4.

Samples used for the 1991 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 in a 4-week period 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 synthetic wet-deposition samples. 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 13. Data listed in table 10 give the analytical methods and the minimum reporting limits for the four laboratories participating in the 1991 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

Table 10. Analytical method and minimum reporting limits for four laboratories participating in the interlaboratory-comparison program during 1991

[mg/L, milligrams per liter; 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.; MOE, Ontario Ministry of the Environment, Water Quality Section, Ontario, Canada; 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)	MOE	(Method)
Calcium	0.01	(FAA)	0.01	(FAA)	0.003	(ICP)	0.02	(FAA)
Magnesium	.003	(FAA)	.01	(FAA)	.009	(ICP)	.005	(FAA)
Sodium	.003	(FAA)	.01	(FAE)	.018	(ICP)	.005	(FAA)
Potassium	.003	(FAA)	.01	(FAE)	.005	(FAE)	.005	(FAA)
Ammonium	.02	(AP)	.001	(AP)	.013	(AP)	.003	(AP)
Chloride	.03	(IC)	.01	(IC)	.02	(IC)	.002	(IC)
Nitrate	.03	(IC)	.01	(IC)	.008	(IC)	.01	(IC)
Sulfate	.03	(IC)	.01	(IC)	.04	(IC)	.05	(IC)

(Dixon and Massey, 1969). The analyte determinations reported as less than the minimum reporting limit were set equal to the minimum reporting limit. Data from 52 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 each laboratory were used in the calculation of the pooled standard deviations for most analytes (table 11).

Precision estimates were similar to estimates made in 1990 (Nilles and others, 1992) with the following exceptions: (1) The pooled standard deviations for the results reported by the CAL for potassium, nitrate, sulfate, hydrogen, and specific conductance for the natural samples and hydrogen ion and specific conductance for synthetic samples were smaller in 1991 than in 1990; (2) The pooled standard deviations for the results reported by the IWD for calcium and sodium for the natural samples and nitrate for the synthetic samples were less in 1991 than in 1990; (3) The pooled standard deviations for the results reported by ESE for sodium and potassium for the synthetic samples were less in 1991 than in 1990; (4) The pooled standard deviations for the results reported by ESE for potassium for the natural samples and hydrogen ion for the synthetic samples were greater in 1991 than in 1990.

MOE participated in the interlaboratory-comparison program for the first time in 1991. The pooled standard deviations for the results reported by MOE were similar to the other three laboratories except for potassium. Pooled standard deviations for potassium determinations were at least 3 times greater for the MOE laboratory compared to results from the other laboratories.

To examine bias in the analytical results between 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 four laboratories. Percentile rankings for individual laboratory analyses of interlaboratory-comparison samples for 1991 are summarized in table 12. A comparison between the analyte concentrations determined by each laboratory is presented as boxplots in figure 14. Only data for the time when all four laboratories participated in the interlaboratory program are given in table 12 and figure 14.

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 materials 2694 and 2694a, 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. Each laboratory was sent 18 NIST samples in 1991. ESE, IWD, and MOE were sent 3 samples of 2694-I, 6 samples of 2694a-I, and 9 bottles of 2694-II. CAL was sent 2 samples of 2694-I, 6 samples of 2694a-I, and 10 bottles of 2694-II. Consequently the median analysis summary for each laboratory is not based on an equal number of samples at the two NIST concentration levels. In 1991, all laboratories reported all requested analysis for the NIST samples with the exception of IWD, which did not report results for specific conductance. The CAL had 12 median analyses out of 22 that were outside the NIST range of uncertainty for the certified samples. MOE and ESE had 8 and 7 median analyses, respectively, out of 22 outside the NIST range of uncertainty. IWD had 8 median analyses out of 19 outside the NIST range of uncertainty. A summary of the median-analysis estimates for each laboratory and the certified values and estimated uncertainties for the NIST standard-reference materials 2694-I 2694a-I and 2694-II is presented in table 13.

Six ultrapure deionized water samples were included among the samples submitted to the participating laboratories. Data listed in table 14 give the number of times that each laboratory reported a concentration greater than the minimum reporting limit in a solution that would not be expected to contain any detectable analyte concentrations. Measured concentrations greater than the minimum reporting limit for the ultrapure deionized water samples is an indication that there is a possible contamination problem. ESE reported eight determinations greater than the analyte minimum reporting limit. CAL, IWD, and MOE each had one determination greater than the minimum reporting limit. Six of the eight determinations reported by ESE as above detection limit were for calcium values that were below the minimum reporting limits of the other three participating laboratories. Of the 24 ultrapure samples analyzed for 8 constituents by the participating laboratories, only one individual determination was reported greater than the 5th percentile of concentration values measured in natural precipitation by the NADP/NTN in 1991 (James,1993). This was for one potassium determination reported by ESE.

Table 11. Pooled standard deviations for analytes determined by four laboratories participating in the 1991 interlaboratory-comparison program

[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., MOE, Ontario Ministry of the Environment; 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]

Analyte	CAL		IWD		ESE		MOE	
	Nat	Syn	Nat	Syn	Nat	Syn	Nat	Syn
Calcium	0.002	0.003	0.001	0.003	0.003	0.003	0.003	0.004
Magnesium	.002	.002	.001	.001	.001	.001	.001	.001
Sodium	.009	.009	.004	.005	.016	.014	.007	.006
Potassium	.018	.003	.045	.004	.047	.003	.172	.011
Ammonium	.006	.026	.003	.018	.003	.012	.002	.014
Chloride	.019	.021	.036	.013	.045	.009	.147	.018
Nitrate	.007	.042	.021	.033	.012	.018	.021	.064
Sulfate	.014	.040	.017	.061	.023	.045	.013	.114
Hydrogen ion	.62	2.92	1.05	4.17	.58	8.97	1.37	3.57
Specific conductance	.14	.56	--	--	.289	2.10	.593	1.27

Table 12. Percentile rankings for individual laboratory analyses of interlaboratory-comparison samples shipped to each of four 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; MOE, Ontario Ministry of the Environment, Ontario, Canada; 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			MOE		
	25th	50th	75th	25th	50th	75th	25th	50th	75th	25th	50th	75th
Calcium	0.020	0.050	0.123	0.018	0.046	0.130	0.022	0.048	0.118	0.020	0.044	0.117
Magnesium	.012	.024	.037	.015	.027	.039	.015	.027	.038	.013	.025	.035
Sodium	.040	.094	.199	.040	.102	.211	.044	.084	.186	.047	.095	.213
Potassium	.018	.028	.057	.020	.033	.060	.019	.035	.063	.019	.029	.068
Ammonium	0.03	0.11	0.23	0.04	0.13	0.22	0.05	0.12	0.21	0.05	0.14	0.24
Chloride	.11	.15	.31	.13	.18	.30	.11	.16	.30	.11	.15	.32
Nitrate	.28	.70	1.05	.28	.64	1.02	.26	.64	1.03	.31	.73	1.06
Sulfate	.85	1.34	2.67	.85	1.33	2.63	.90	1.33	2.69	.86	1.33	2.58
Hydrogen ion	15.9	26.0	51.0	14.8	24.0	50.1	15.1	23.4	49.0	14.1	25.1	51.3
Specific conductance	10.5	13.9	26.7	--	--	--	10.1	13.1	25.4	8.4	12.0	23.9

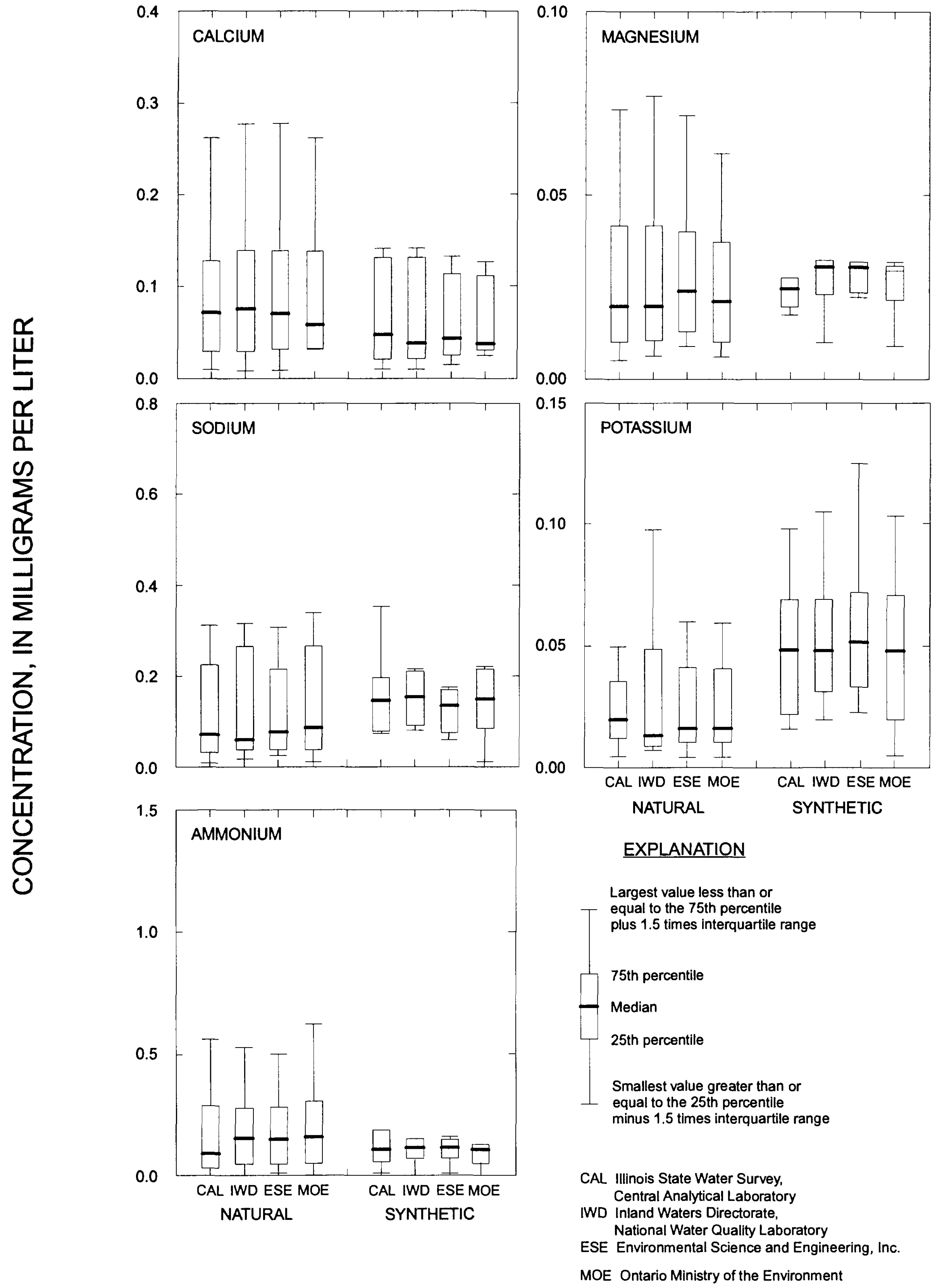


Figure 14. Analytical results for selected water-quality constituents and properties determined by four laboratories participating in the interlaboratory-comparison program.

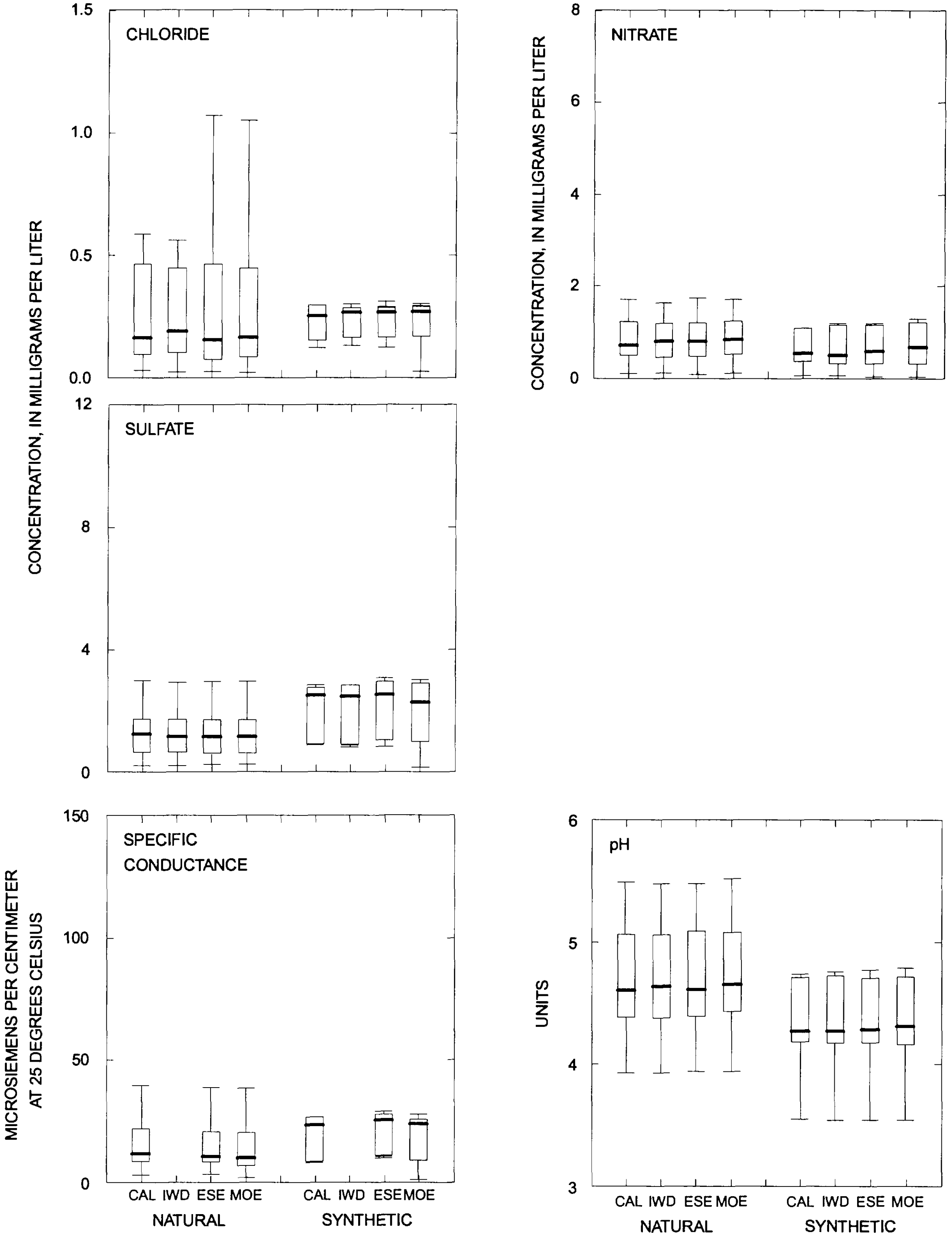


Figure 14. Analytical results for selected water-quality constituents and properties determined by four laboratories participating in the interlaboratory-comparison program--Continued.

Table 13. Median analysis estimates for standard reference materials 2694-I, 2694a-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.; MOE, Ontario Ministry of Environment, Ontario, Canada; all units in milligrams per liter except pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius; <, less than; (N), the number of reported values; *, values outside the certified value plus or minus the estimate of uncertainty]

Analyte	NIST standard	Certified NIST values	Estimate of uncertainty	Laboratory analyses							
				CAL	(N)	IWD	(N)	ESE	(N)	MOE	(N)
Calcium	2694-I	0.014	0.003	*<0.010	(2)	*0.019	(3)	0.015	(3)	<0.02	(3)
	2694A-I	.013	.0014	*.010	(6)	*.011	(6)	.014	(6)	*.023	(6)
	2694-II	.049	.011	.040	(10)	.042	(9)	.048	(9)	.044	(9)
Magnesium	2694-I	.024	.002	.024	(2)	.023	(3)	.026	(3)	.022	(3)
	2694a-I	.024	.0002	.024	(6)	*.026	(6)	*.026	(6)	.024	(6)
	2694-II	.051	.003	.048	(10)	.050	(9)	.053	(9)	.050	(9)
Sodium	2694-I	.205	.009	*.181	(2)	.212	(3)	*.189	(3)	.208	(3)
	2694a-I	.208	.002	*.199	(6)	*.211	(6)	*.176	(6)	*.213	(6)
	2694-II	.419	.015	*.384	(10)	.430	(9)	.420	(9)	.424	(9)
Potassium	2694-I	.052	.007	.045	(2)	*.043	(3)	.052	(3)	*.044	(3)
	2694a-I	.056	.002	*.053	(6)	.055	(6)	.055	(6)	*.059	(6)
	2694-II	.106	.008	*.096	(10)	.100	(9)	.114	(9)	.102	(9)
Ammonium	2694-I	--	--	<.02	(2)	<.001	(3)	<.013	(3)	<.002	(3)
	2694a-I	--	--	.115	(6)	.127	(6)	.115	(6)	.139	(6)
	2694-II	--	--	.960	(10)	.980	(9)	.992	(9)	1.015	(9)
Chloride	2694-I	--	--	.25	(2)	.27	(3)	.25	(3)	.28	(3)
	2694a-I	--	--	.22	(6)	.22	(6)	.22	(6)	.23	(6)
	2694-II	--	--	1.03	(10)	1.01	(9)	1.05	(9)	1.04	(9)
Nitrate	2694-I	--	--	<.03	(2)	<.04	(3)	<.035	(3)	<.01	(3)
	2694a-I	--	--	.54	(6)	.51	(6)	.53	(6)	.62	(6)
	2694-II	7.06	.15	7.21	(10)	6.99	(9)	7.08	(9)	7.13	(9)
Sulfate	2694-I	2.75	0.05	*2.82	(2)	*2.84	(3)	*2.84	(3)	*2.85	(3)
	2694a-I	2.69	0.03	2.69	(6)	2.68	(6)	2.70	(6)	2.68	(6)
	2694-II	10.9	.2	11.06	(10)	11.03	(9)	11.00	(9)	*10.67	(9)
pH	2694-I	4.27	.03	*4.22	(2)	*4.21	(3)	*4.21	(3)	*4.18	(3)
	2694a-I	4.30	.03	4.28	(6)	4.28	(6)	4.30	(6)	4.28	(6)
	2694-II	3.59	.02	3.57	(10)	3.57	(9)	*3.55	(9)	*3.53	(9)
Specific conductance	2694-I	26	2	*28.8	(2)	--	(0)	25.9	(3)	26.5	(3)
	2694a-I	25.4	1.2	*27.0	(6)	--	(0)	25.8	(6)	24.3	(6)
	2694-II	130	2	*135.3	(10)	--	(0)	*138	(9)	129.5	(9)

Table 14. Number of analyte determinations greater than reporting limits for the ultrapure deionized-water samples for each laboratory participating in the interlaboratory-comparison program during 1991

[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.; MOE, Ontario Ministry of Environment Ontario, Canada; N, none]

	Concentrations reported that were greater than the minimum reporting limit			
Analyte	**CAL**	**IWD**	**ESE**	**MOE**
Calcium	N	N	6	N
Magnesium	N	N	N	N
Sodium	1	N	N	N
Potassium	N	N	1	N
Ammonium	N	1	1	N
Chloride	N	N	N	1
Nitrate	N	N	N	N
Sulfate	N	N	N	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. Additional details of the collocated-sampler program along with precision estimates based upon the first 2 years of the study are provided by Nilles and others (1991). Estimates of intrasite precision are provided in this report for sites that participated in the study during water year 1991.

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 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 year 1991 are shown in figure 15.

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 each pair of collectors 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 sites were inspected in August or September 1990 after equipment installation and before collection of the first sample.

For wet-deposition samples, only data from samples with volume greater than 35 mL (lab type "W") that did not require dilution were used in the statistical summaries. Median sample concentrations in weekly samples from the four sites are presented in table 15. Annual summaries of NADP/NTN data describe precipitation chemistry in units of concentration and deposition for ionic constituents (National Atmospheric Deposition Program, 1991). 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.

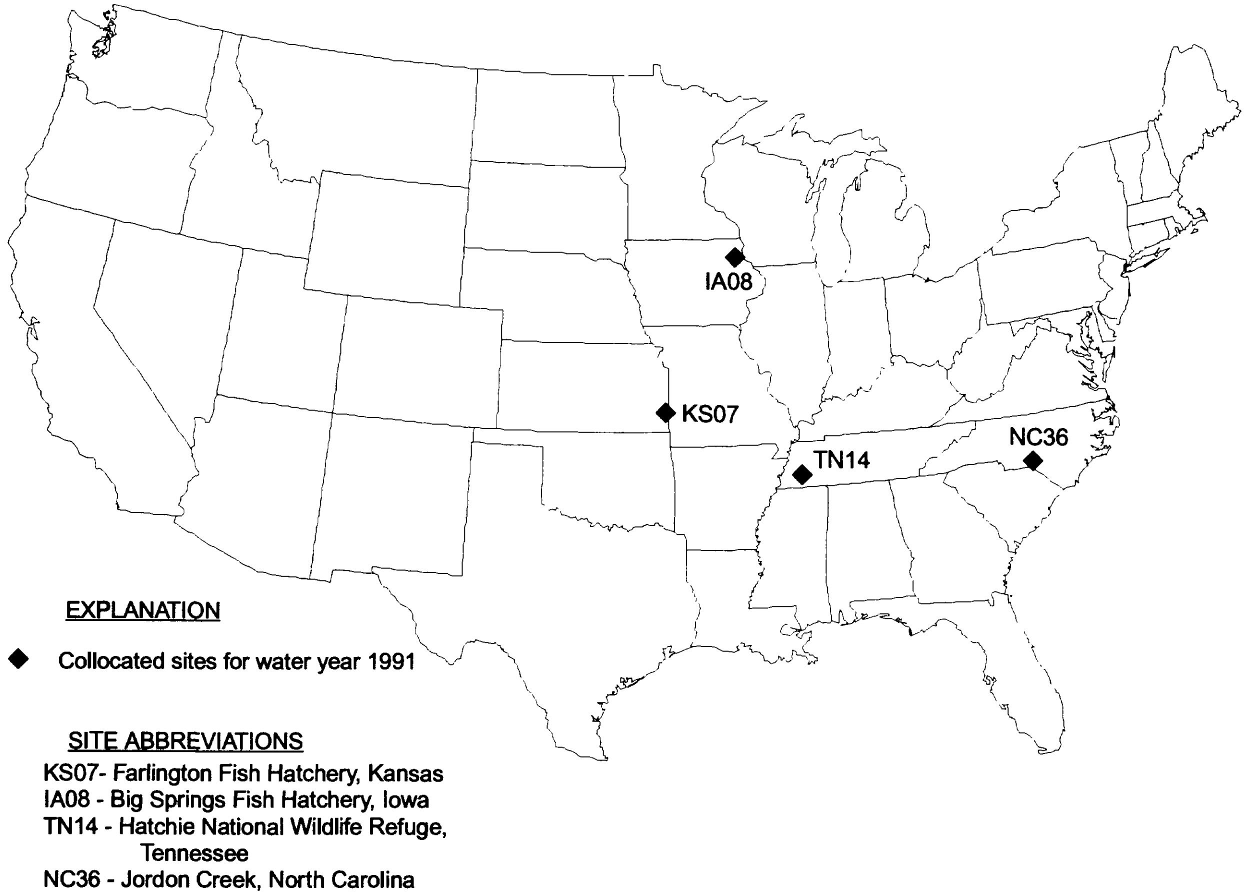


Figure 15. Location of National Atmospheric Deposition Program/National Trends Network sites with collocated samplers in water year 1991.

Table 15.--Median analyte concentrations and volume in weekly samples from collocated 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]

Analyte	Sampling sites			
	IA08	KS07	NC36	TN14
Calcium	0.434	0.243	0.059	0.087
Magnesium	0.063	0.026	0.035	0.017
Sodium	0.046	0.086	0.217	0.105
Potassium	0.052	0.041	0.026	0.021
Ammonium	0.60	0.44	0.15	0.17
Chloride	0.11	0.15	0.37	0.19
Nitrate	1.56	1.33	1.23	1.04
Sulfate	1.63	1.62	1.78	1.23
Hydrogen ion	2.46	8.13	36.74	22.39
Specific conductance	14.0	13.3	22.9	13.6
Sample volume	1178.	861.	1451.	1520.
Precipitation depth	2.21	1.63	2.12	2.24

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

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

(in percent)

and

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

(in mg/L or kg/ha)

where

M = median of all paired differences;

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

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 40 and ranged from a high of 44 at NC36 to a low of 36 at KS07. When one or both of the paired measurements for a given analyte were reported as less than method detection limits, results from those measurements were not used in the calculation of precision for that site.

Median relative differences (MRD's) were the smallest for nitrate and sulfate concentration, ranging from 2.3 percent to 3.7 percent among the sites, and was consistent with the magnitude of MRD's calculated in previous years of the study. The same characterization of precision is observed for specific conductance and collected sample volume from the AeroChem collectors. MRD's for these properties were uniformly small and consistent at all four sites despite differences in typical sample conductance and precipitation amounts between the sites. The MRD for specific conductance was 4.7 percent or less at all sites, while the MRD for sample volume collected from the AeroChem collectors was 2.8 percent or less. MRD's for the sample chemistry in terms of concentration and for sample volume is provided in table 16. MRD's for sample chemistry deposition and precipitation depth are provided in table 17.

The MRD's were larger and more variable from site to site for all cations and particularly for cations whose concentrations typically were near laboratory detection limits. Assuming that random contamination is independent of sample concentration and laboratory error increases with lower concentration samples, an increase in relative error at sites with lower concentrations would be expected. For example, the MRD for potassium concentration and deposition ranged from 12.5 percent to 31.6 percent between sites.

As in previous years, the precision for hydrogen-ion concentration and deposition varied greatly in absolute and in relative terms between the sites depending upon the acidity of the precipitation at a given collocated site. MRD's for hydrogen ion concentration ranged from 4.6 percent at NC36 to 14.9 percent at IA08. The difference in precision estimates for hydrogen ion at these sites can be accounted for by differences in median concentration. Median hydrogen-ion concentration at NC36 was 15 times greater than that of IA08.

MRD's calculated for weekly analyte deposition at the four sites incorporates variability due to differences in sample depth between the original and collocated Belfort recording rain gages as well as chemistry differences. Although not consistent among sites or analytes, median relative differences typically were 2 to 5 percentage points higher when calculated using deposition data rather than concentration data (tables 16 and 17).

An exception to this was a large increase in the MRD's for deposition compared to concentration at site KS07. A significant (α=0.01) bias of about +15 percent for the collocated rain gage compared to the original rain gage was noted by the site operator following several weeks of sampling at this site. The site supervisor made a follow-up visit to the site, checked both gages with standard calibration weights, and made minor adjustments to both gages. Following adjustment, both gages again met the NADP/NTN specifications for accuracy. Despite this effort, the bias, which may have been caused by sticking of the original rain gage during precipitation, continued for the remainder of the collocated sampling period that ended in October 1991.

In April 1992, an NADP/NTN external site auditor determined the rain gage at site KS07 to be calibrated within 0.12 cm for the 0- to 15.24-cm precipitation range and significantly out of calibration for the 15.25- to 30.48-cm range. The auditor

Table 16. 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 15 for site locations]

Analyte	Sampling sites			
	IA08	KS07	NC36	TN14
Calcium	8.6	8.3	8.0	10.4
Magnesium	10.2	11.1	5.8	11.8
Sodium	18.8	11.2	6.0	11.8
Potassium	30.5	21.6	12.5	13.2
Ammonium	8.2	7.3	14.3	11.8
Chloride	8.7	8.7	3.9	5.7
Nitrate	3.2	3.5	2.5	3.1
Sulfate	2.9	3.7	2.3	3.2
Hydrogen ion	14.9	11.5	4.6	6.9
Specific conductance	4.0	4.7	2.6	2.4
Sample volume	2.8	2.1	1.2	1.3

Table 17. Median relative error for analyte depositions in weekly samples from collocated wet-dry precipitation collectors and precipitation depth from collocated rain gages

[All data expressed in percent. See figure 15 site locations]

Analyte	Sampling sites			
	IA08	KS07	NC36	TN14
Calcium	9.2	12.6	10.9	12.5
Magnesium	12.4	16.6	7.0	14.2
Sodium	15.0	15.6	7.1	12.3
Potassium	31.6	20.4	13.3	16.2
Ammonium	7.5	12.5	15.1	13.0
Chloride	10.2	17.0	3.9	8.0
Nitrate	4.6	12.6	3.4	4.1
Sulfate	3.6	14.1	2.3	3.2
Hydrogen ion	14.5	18.3	6.4	5.8
Precipitation depth	2.9	16.1	.9	1.9

recalibrated the gage at that time. The miscalibration could have occurred during the attempt to adjust the original gage during the collocated sampling period or following the end of collocated sampling. Three conclusions result: (1) It is very unlikely that a bias in rain-gage measurements of the magnitude experienced at site KS07 would have been recognized without the presence of the collocated rain gage. (2) Field adjustments made to the gages with the aid of standard calibration weights were not successful in eliminating the bias during actual precipitation measurements even though the calibration seemed satisfactory following adjustments. (3) Bias in rain-gage measurements has a large effect on precision estimates derived from collocated measurements for deposition at an individual site.

In table 18, collocated-analyte precision estimates are compared to analytical precision estimates calculated in the same manner from 52 replicate natural precipitation samples submitted to the CAL in 1991 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

Table 18. 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. See figure 15 for site locations]

	Sampling site				
Analyte	**IA08**	**KS07**	**NC36**	**TN14**	**CAL**
Calcium	0.033	0.021	0.007	0.009	>.001
Magnesium	.007	.033	.002	.002	.001
Sodium	.009	.009	.012	.007	.002
Potassium	.011	.009	.003	.003	.001
Ammonium	.04	.03	.02	.02	>.01
Chloride	.01	.01	.01	.01	>.01
Nitrate	.05	.05	.03	.03	.01
Sulfate	.05	.07	.03	.03	>.01
Hydrogen ion	1.08	.96	1.66	1.13	.18
Specific conductance	.60	.60	.50	.40	.10

Table 19. 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 15 for site locations]

	Sampling site			
Analyte	**IA08**	**KS07**	**NC36**	**TN14**
Calcium	-4.4	6.9	-1.3	-4.5
Magnesium	-4.4	6.9	0.0	-4.7
Sodium	-6.6	-0.5	0.0	2.7
Potassium	-10.9	12.0	-3.4	-1.5
Ammonium	-2.9	3.1	0.0	-3.3
Chloride	0.0	0.0	0.0	0.0
Nitrate	-1.8	2.6	0.0	-1.8
Sulfate	-2.3	3.5	0.0	-2.2
Hydrogen ion	9.2	2.3	-3.5	0.0
Specific conductance	0.6	2.2	-1.5	-0.6
Sample volume	-1.9	1.7	0.3	-1.0
Precipitation depth	0.0	-15.4	-0.5	1.3

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. Laboratory error is calculated in this report from a random group of replicate samples selected from all 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 18 that laboratory error in the determination of magnesium accounts for 50 percent of the overall sampling error at sites NC36 and TN14. 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 those sites.

Bias was evaluated for each site and analyte by using the median signed difference between collocated sample concentrations (table 19). Bias estimates for sample volume from the precipitation collectors and precipitation depth from the recording rain gages also were calculated. Because the collocated paired samples were shipped from the sites weekly to the same laboratory at the same time, the authors attribute bias in the data-set pairs to systematic differences in: (1) sampler response, (2) sample collection, and (3) sample handling prior to shipment. With the exception of precipitation depth measurements at site KS07, and consequently all precision estimates for deposition at that site, bias for analytes accounted for less than 20 percent of the overall relative error in collocated measurements. The absence of bias as a significant contributor to overall variability in NADP/NTN wet-chemistry measurements in this study is not surprising due to the excellent precision and lack of bias in the collectors. For example, the bias at site NC36 was 0 percent for 6 of the 10 analytes examined and exceeded 3 percent only for potassium and hydrogen. The bias in sample volume collected from the samplers at NC36 was only +0.3 percent. Bias in sample volume between collectors did not exceed 2 percent, and the MRD did not exceed 3 percent at any sites operated during water year 1991.

SUMMARY

During 1991, 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 estimate the accuracy and precision of onsite pH and specific-conductance determinations. A blind-audit program was used to assess the effects of routine sample handling, processing, and shipping of wet-deposition samples on the precision and bias of NADP/NTN wet-deposition data. As part of the interlaboratory-comparison program, analytical results from four 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.

Of the 188 site operators submitting pH data on time in study 27, 93 percent reported pH values within the NADP/NTN accuracy goals of ±0.10 pH unit. For specific conductance, 96 percent of the 187 site operators that reported specific conductance values on time in study 27 met the accuracy goals of ±4.0 µS/cm. To assess possible matrix effects on the ability of site operators to make accurate measurements, two different solutions were used in study 28. Solution A was a typical intersite solution prepared from ultrapure deionized water and nitric acid. Solution B was prepared by compositing 5 liters of filtered natural precipitation samples. No statistical differences were detected between the results for the two types of solutions. Of the 181 site operators submitting pH data on time in study 28, 86 percent successfully met the accuracy goals. The artificial matrix solution used in study 28 had a calculated specific conductance of 8.0 µS/cm. The median of all responding site operators that received solution A was 8.6 µS/cm; the median of all responding site operators receiving solution B was 12.2 µS/cm. A total of 97 percent of the 181 specific-conductance values reported in study 28 were within the NADP/NTN accuracy goals.

Depending on a combination of performance factors, site operators that did not meet the pH-measurement accuracy goals in 1991 were asked to participate in the intersite-comparison study follow-up program. In study 27, a total of 14 site operators were asked to participate in the follow-up program; in study 28, there were 26 site operators that participated.

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 samples. Results for 1991 indicated significant (α=.01) positive bias for calcium, magnesium, sodium, potassium, chloride, nitrate, and sulfate. Significant (α=.01) negative bias was determined for hydrogen ion and specific conductance. The percent bias was calculated for all of the bucket-minus-bottle paired differences by calculating each paired difference as a percentage of the concentration measured in the bottle portion of the bucket-bottle data pair. The median percent bias of -38.3 percent for hydrogen ion was largest percent bias for all of the analytes, and indicates that significant losses of hydrogen ion frequently occur from all samples collected in the 13-L polyethylene buckets used by the NADP/NTN. The percent bias for specific conductance was also very large, -21.1 percent. At the opposite extreme, the percent bias for both nitrate and sulfate was less than 5 percent. Excluding bucket-bottle data pairs if the target concentration of the blind-audit sample was less than the minimum reporting limit, the percent bias for the remaining six analytes was within a range of 9.1 to 15.4 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 and sample-shipping procedures for all of the analytes except nitrate and sulfate.

To determine if a relation existed between the volume collected in the bucket and the differences between the analyte concentrations in the bucket and bottle portions of the blind-audit sample, sixteen 250-mL, fifteen 500-mL, and sixteen 1,000-mL bottles of the same solution (USGS) were sent to the operators of selected sites in 1991. Results of a Kruskal-Wallis test indicate no significant (α=0.01) difference in bucket-minus-bottle concentrations for potassium, ammonium, sulfate and specific conductance, whereas statistically significant (α=0.01) differences existed for calcium, magnesium, sodium, chloride, nitrate, and hydrogen ion.

As part of the interlaboratory-comparison program, examinations of data from four laboratories using a Kruskal-Wallis test indicated no significant difference among laboratory determinations for all analytes examined. As in 1990, 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 12 median analyses out of 22 that were significantly different from the certified values. MOE and ESE had 8 and 7 median analyses out of 22 respectively that were significantly different from the certified values. IWD had 7 median analyses out of 19 that were significantly different from the certified values. ESE reported eight determinations larger than the minimum reporting limit for the analyses of ultrapure deionized water samples, whereas CAL, IWD, and MOE reported one determination each that was greater than the minimum reporting limits. Six of the eight determinations reported by IWD as greater than reporting limits were for calcium and were values that were below the reporting limits of the other three laboratories.

An ongoing collocated-sampler program was used to estimate the overall variability of chemical measurements of wet-deposition data collected for the NADP/NTN. The estimates of precision include all variability in the data-collection system, from the point of sample collection through storage in the NADP/NTN data base. Weekly wet-deposition samples and precipitation measurements from collocated NADP/NTN sites were compared. Estimates of precision were calculated in 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, nitrate and collected sample volume was typically less than the median relative error calculated for the other analytes examined. Relative error typically was greatest for cations, with median relative error exceeding eight percent at most sites. As in previous years, the precision for hydrogen concentration and deposition varied greatly in absolute and in relative terms among the sites depending upon the acidity of the precipitation at a given collocated site. Laboratory error is estimated typically to account for one-fifth of the overall collocated-sampling error on the basis of data from replicate natural samples analyzed at the CAL. Bias in collocated measurements typically accounted for less than 25 percent of the overall error in collocated measurements although a bias in measurements between the original and collocated recording rain gage at site KS07 resulted in significantly increased differences in deposition measurements at that site.

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