

EXTERNAL QUALITY-ASSURANCE RESULTS
FOR THE NATIONAL ATMOSPHERIC DEPOSITION
PROGRAM AND THE NATIONAL TRENDS
NETWORK DURING 1987

By Randolph B. See, LeRoy J. Schroder,
and Timothy C. Willoughby

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 89-4015

Denver, Colorado
1989



DEPARTMENT OF THE INTERIOR
DONALD PAUL HODEL, Secretary
U.S. GEOLOGICAL SURVEY
Dallas L. Peck, Director

For additional information
write to:

Chief, Branch of Quality
Assurance
U.S. Geological Survey
Box 25046, Mail Stop 401
Federal Center
Denver, CO 80225-0046

Copies of this report
can be purchased from:

U.S. Geological Survey
Books and Open-File Reports
Section
Federal Center
Box 25425
Denver, CO 80225-0425
[Telephone: (303) 236-7476]

CONTENTS

	Page
Abstract-----	1
Introduction-----	1
Intersite-comparison program-----	2
Blind-audit program-----	4
Interlaboratory-comparison program-----	9
Summary and conclusions-----	14
References cited-----	15

FIGURE

	Page
Figure 1. Graph showing percentage of sites that fulfilled the goal of the National Atmospheric Deposition Program and the National Trends Network of ± 0.1 pH unit or ± 4 microsiemens per centimeter at 25 degrees Celsius in the intersite-comparison program, 1981-87-----	5

TABLES

	Page
Table 1. Summary statistics for the intersite-comparison program-----	3
2. Summary of paired t tests for the blind-audit program-----	8
3. Estimated precision of analyte data based on replicate analyses of blind-audit bucket samples-----	9
4. Pooled standard deviations for analytes determined by four laboratories that measured constituents in natural wet-deposition samples-----	10
5. Percentile ranking for individual laboratory analyses of interlaboratory-comparison samples shipped to each of four laboratories----	12
6. Mean analysis estimates for standard reference solution 2694 from the National Bureau of Standards-----	13
7. Summary of laboratory analyses of ultrapure deionized water samples-----	14

CONVERSION FACTORS

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

Multiply	By	To obtain
liter (L)	1.0567	quart, liquid
milliliter (mL)	0.03381	ounce, fluid

The following term and abbreviation also is used in this report:

microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$)

EXTERNAL QUALITY-ASSURANCE RESULTS FOR THE
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM AND
THE NATIONAL TRENDS NETWORK DURING 1987

By Randolph B. See, LeRoy J. Schroder, and Timothy C. Willoughby

ABSTRACT

The U.S. Geological Survey used three programs in 1987 to provide external quality assurance for the National Atmospheric Deposition Program and the National Trends Network. 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 National Atmospheric Deposition Program and the National Trends Network samples were evaluated in the blind-audit program. Differences between analytical results and an estimate of the analytical precision of four participating laboratories were determined by the interlaboratory-comparison program.

Results of the intersite-comparison program indicate that 72 to 77 percent of the onsite pH determinations and 90 to 95 percent of the onsite specific-conductance determinations were within program goals during 1987. The effect of routine sample handling, processing, and shipping, as determined in the blind-audit program, indicated significant increases in the concentrations of calcium, magnesium, sodium, potassium, ammonium, and chloride ions and a decrease in hydrogen ion and specific conductance for blind-audit samples handled according to program protocols. A Kruskal-Wallis test and determination of Fisher's least significant difference indicated that, except for pH determinations from DEN, significant differences did not occur between the analytical results from the four participating laboratories.

INTRODUCTION

The National Atmospheric Deposition Program (NADP) and the National Trends Network (NTN) were established to monitor spatial and temporal trends in the chemical composition of natural wet deposition. During 1987, wet-deposition samples were collected from more than 200 sites in the United States and Canada. Both networks used identical sampling and chemical-analysis protocols; the NADP and NTN were considered as one group for the analyses in this report. Earlier reports have described the NADP/NTN onsite

operations (Bigelow and Dossett, 1988) and the NTN experimental design (Robertson and Wilson, 1985).

The purpose of this report is to describe the results of the external quality-assurance programs operated by the U.S. Geological Survey during 1987 to (1) assess the precision and accuracy of onsite determinations of pH and specific conductance; (2) to evaluate the effects of onsite and laboratory protocols on the bias and precision of NADP/NTN analyte determinations; and (3) to determine the comparability, bias, and precision of analytical results obtained by separate laboratories when portions of a common sample are analyzed.

INTERSITE-COMPARISON PROGRAM

All NADP/NTN site operators were requested to participate in the intersite-comparison studies; however, their participation was voluntary. Most site operators cooperate and participate in the intersite comparisons. However, 8 percent in May and 11 percent in October 1987 did not participate in the intersite-comparison program, and their sites cannot be evaluated to ensure that onsite pH and specific-conductance data that are reported to the NADP/NTN by these sites are reliable.

A previous report has described the experimental design and protocols of the intersite-comparison program and earlier assessments of onsite pH and specific conductance measurements (Schroder and Brennan, 1984).

The U.S. Geological Survey prepared reference solutions of diluted nitric acid for use as the intersite-comparison samples. In both intersite-comparison studies that were completed in 1987, a 125-mL bottle of reference solution was mailed to each NADP/NTN site. The site operators used standard NADP/NTN protocols (Bigelow, 1982) to determine the pH and the specific conductance of the solution. The U.S. Geological Survey did not provide the site operators with any information about the pH or the specific conductance values of the solutions. Only the results from those site operators who responded within 45 days of the date the intersite-comparison samples were mailed were included in this report.

Median values of pH and specific conductance were calculated from the values reported by the site operators. The median values were used as the best estimates of the actual pH and specific conductance values for each intersite comparison solution.

To allow for rechecking any extreme pH or specific-conductance values reported by the site operators, any unused portion of the intersite-comparison solution was returned to the

U.S. Geological Survey. When a site operator reported values for pH or specific conductance that were more or less than the preselected limits of the median ± 1.5 F-pseudosigma (Hoaglin and others, 1983), the U.S. Geological Survey reanalyzed the sample. The reanalysis was made to determine if the sample had become contaminated or if the erroneous measurement was due to site-operator or instrument error. At least 15 percent of the returned intersite samples were reanalyzed by the U.S. Geological Survey. All reanalyses by the U.S. Geological Survey of pH and specific conductance were within the ± 1.5 F-pseudosigma of the median values calculated for all sites. Thus sample-bottle contamination could not explain the apparent onsite measurement errors. A statistical summary of onsite pH and specific-conductance determinations for intersite comparisons for May and October 1987 is presented in table 1.

Table 1.--Summary statistics for the intersite-comparison program
 [pH, in units; specific conductance, in microsiemens per centimeter at 25 degrees Celsius]

Statistics	May 1987		October 1987	
	pH	Specific conductance	pH	Specific conductance
Number of site operators responding	175	174	162	166
Percentage of site operators reporting values within accuracy goals	77	95	72	90
Minimum	3.71	9.8	3.65	0.7
10th percentile	4.35	12.4	4.56	6.6
25th percentile	4.45	12.9	4.67	7.1
50th percentile	4.50	13.5	4.73	7.4
75th percentile	4.54	14.0	4.79	7.9
90th percentile	4.58	14.9	4.85	8.9
Maximum	5.04	47.2	6.52	8,446

The NADP/NTN goal for onsite pH determinations of less than 5.0 is ± 0.1 pH unit. If the calculated median values for all responding sites were accepted as the most accurate estimate of pH, 77 percent (May 1987) and 72 percent (October 1987) of the site operators achieved the NADP/NTN goal for pH measurement accuracy. A bar graph of the percentage of sites that fulfilled the NADP/NTN goal for pH measurement accuracy for all of the intersite-comparison studies completed by the U.S. Geological Survey from 1981 through 1987 is shown in figure 1. The percentage of sites that fulfilled the NADP/NTN goals for pH determinations seems to have increased during 1982 through 1986. The percentage of onsite pH determinations that fulfilled NADP/NTN goals for the 1987 intersite-comparison studies was smaller than those in the three studies completed in 1986. Intersite comparisons were done quarterly during 1986 and semiannually in 1987. The change from 1986 to 1987 in the percentage of sites that fulfilled the NADP/NTN goals may indicate changes in site operators or the experience level of site operators.

The NADP/NTN goal for onsite specific-conductance measurements is ± 4 $\mu\text{S}/\text{cm}$. If the calculated median values for all responding sites were used as the most accurate estimate of actual specific conductance, 95 and 90 percent of the sites fulfilled the NADP/NTN goals in May and October 1987. The number of sites that fulfilled the NADP/NTN goals for specific-conductance determinations in 1987 was similar to earlier years. A bar graph of the percentage of sites meeting the NADP/NTN goal for specific conductance for all of the intersite-comparison studies completed by the U.S. Geological Survey from 1981 through 1987 is shown in figure 2.

BLIND-AUDIT PROGRAM

The blind-audit program was developed to provide an estimate of the analyte bias and precision that resulted from routine sample handling, processing, and shipping. In the blind-audit program, reference samples were provided to site operators who disguised them as actual wet-deposition samples and submitted the samples to the Illinois State Water Survey, Central Analytical Laboratory (CAL) for routine analysis. The CAL staff that received and analyzed the NADP/NTN samples could not identify individual samples as being from an external quality-assurance program. No information concerning the chemical composition of the samples was provided to either the site operators or the CAL staff who analyzed the samples. Details of the experimental design have been discussed in a previous report (Schroder and others, 1985).

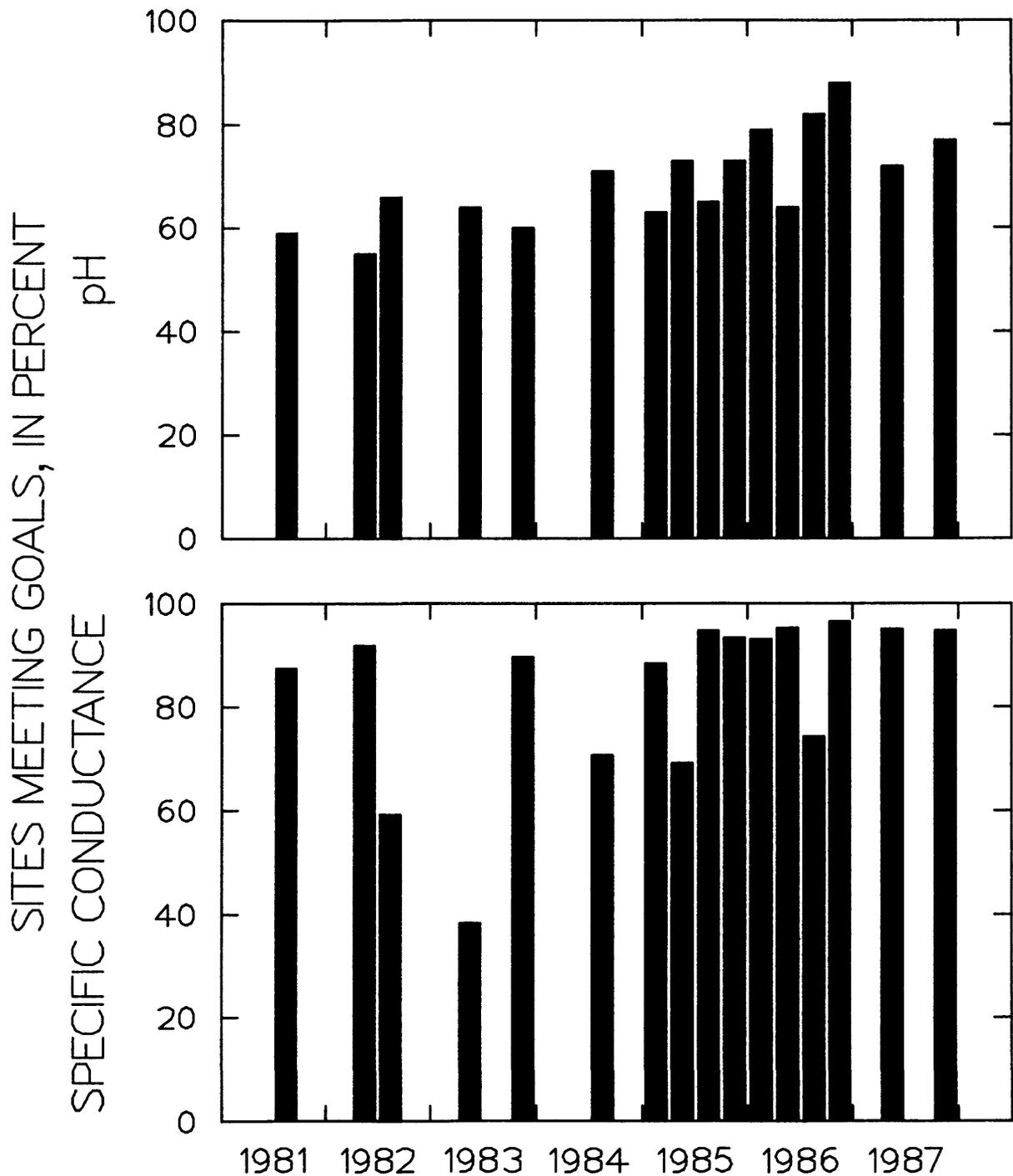


Figure 1.--Percentage of sites that fulfilled the goals of the National Atmospheric Deposition Program and the National Trends Network of ± 0.1 pH unit or ± 4 microsiemens per centimeter at 25 degrees Celsius in the intersite-comparison program 1981-87.

Blind-audit solutions were selected that had analyte concentrations that were less than the 95th percentile concentration of all natural wet-deposition samples which were collected and analyzed by the NADP/NTN during 1985. Eleven blind-audit solutions were prepared for the 1987 blind-audit program. Two of the solutions used were diluted from solution 1085, which was prepared by personnel of the U.S. Environmental Protection Agency (Parr and others, 1987). Four of the solutions used were diluted from standard reference water solutions, M-2 and M-4, which were prepared by the U.S. Geological Survey (V. J. Janzer, U.S. Geological Survey, written commun., 1985 and 1986). Three blind-audit solutions were prepared by diluting stock solutions of sodium nitrate and sulfuric acid. Two of these solutions were used as blanks in the 1987 blind-audit program. Ultrapure, deionized water also was prepared by the U.S. Geological Survey, and a diluted, pH 4.3, nitric-acid solution was prepared by CAL.

In the 1987 blind-audit program, 100 samples were mailed to selected NADP/NTN sites. Sites that received blind-audit samples were distributed evenly among four geographic areas, which included the entire United States. The site operator poured two-thirds of the blind-audit sample into a clean network sampling container (a 13-L polyethylene bucket and lid). Hereafter, this portion of the blind-audit sample is referred to as the bucket sample. Routine onsite pH, specific conductance, and weight determinations were done on the bucket samples, after which the bucket was sealed and shipped to CAL for analysis. The site operator recorded fictitious information on the field observer report form that accompanied the blind-audit sample to CAL. When the sample containers arrived at CAL, the samples appeared to be normal wet-deposition samples, and the bucket samples were treated as routine samples.

The site operators left about one-third of the blind-audit sample in the original bottle and mailed the bottle to CAL separately from the bucket samples. Hereafter, the portion of the blind-audit sample remaining in the bottle is referred to as the bottle sample.

The bottle sample was submitted to the CAL laboratory staff for routine analysis. Although the CAL laboratory staff may have been aware that bottle samples were not actual NADP/NTN samples, the analyte concentrations in bottle samples were not available to the laboratory staff. CAL analyzed the bucket and bottle samples within 1 to 2 weeks of each other.

Analytical results of the bucket and bottle portions of the blind-audit sample provided paired analyses that were compared to determine if analyte concentrations had changed in the bucket samples as a result of field and laboratory protocols. This comparison was based on the assumption that analyte concentra-

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

Of the 100 blind-audit samples sent to site operators, 7 samples were eliminated because site operators were unable to participate. An additional four blind-audit samples lacked bottle-sample analyses. Two bottle samples were eliminated from the data set because of contamination of the bottle sample. Visible contamination was identified in 19 of the remaining 87 bucket samples.

Since 1984, as much as 30 percent of the blind-audit bucket samples that were submitted each year to CAL contained extraneous debris. These contaminated samples were coded with a "C" by the CAL laboratory staff. Many of the objects that contaminated the samples were identified as fibers (possibly from packing materials). A comparison of the median differences (bucket minus bottle) between bucket samples containing visible debris and apparently uncontaminated bucket samples for 1984 through 1987 indicated that no significant differences existed in the median differences, except for magnesium, which showed a slightly higher median value in uncontaminated bucket samples. Although visible debris cannot be proven to cause a statistically significant increase in contamination levels, the presence of debris is an indication that further contamination by smaller, unobserved particles may be occurring. CAL has attempted to decrease sample contamination by sealing the fiber padding materials in polyethylene bags. The C-coded samples have been included in the 1987 summary because similar contamination may be occurring in natural wet-deposition samples collected by the NADP/NTN.

A paired t test, used to determine if a significant difference existed between the bucket- and bottle-sample analyses, indicated that a significant ($\alpha=0.01$) bias existed for all analytes except nitrate and sulfate. A summary of t-test statistics is presented in table 2. The mean concentrations for bucket samples were larger than the mean concentrations for bottle samples for all analytes, except nitrate. These results are an indication that contamination of the bucket samples and, therefore, all NADP/NTN wet-deposition samples, is occurring as a result of sample-handling procedures.

Table 2.--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]

Analyte	Sample Type	Mean	Mean difference	Number of pairs	t value	Probability of larger t
Calcium	Bucket	0.237	-0.034	75	-5.10	<0.01
	Bottle	.203				
Magnesium	Bucket	.055	-.004	76	-4.35	<.01
	Bottle	.051				
Sodium	Bucket	.234	-.105	88	-9.68	<.01
	Bottle	.139				
Potassium	Bucket	.210	-.10	51	-3.42	<.01
	Bottle	.201				
Ammonium	Bucket	.09	-.03	20	-4.73	<.01
	Bottle	.06				
Chloride	Bucket	.41	-.06	57	-4.38	<.01
	Bottle	.35				
Nitrate	Bucket	1.35	.02	57	1.08	.29
	Bottle	1.37				
Sulfate	Bucket	1.74	-.05	61	-1.82	.07
	Bottle	1.69				
pH	Bucket	4.95	-.31	88	-7.19	<.01
	Bottle	4.64				
Specific conductance	Bucket	14.5	2.6	88	7.40	<.01
	Bottle	17.1				

The precision of 1987 NADP/NTN wet-deposition analyses was estimated by pooling the variance of replicate blind-audit samples (Dixon and Massey, 1969, p. 113). The pooled standard deviations that were estimated are listed in table 3. The pooled standard deviations for 1987 are comparable to values calculated for 1985 and 1986 (Brooks and others, 1987; See and others, 1988). The precision estimates that were determined during the blind-audit program in 1987 are larger than precision estimates reported by CAL (Peden, 1986). The lower 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 may be a result of routine sample handling, rather than laboratory analyses.

Table 3.--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	Mimumum value	Maximum value	Estimated standard deviation
Calcium	0.014	0.682	0.066
Magnesium	.003	.290	.006
Sodium	.017	1.030	.111
Potassium	.003	.591	.018
Ammonium	.02	.20	.04
Chloride	.04	1.04	.10
Nitrate	.04	1.04	.10
Sulfate	.04	3.79	.17
pH	4.22	6.69	.37
Specific conductance	1.5	32.2	.01

INTERLABORATORY-COMPARISON PROGRAM

The interlaboratory-comparison program was used to determine if differences existed between the analytical results of participating laboratories and to estimate analytical precision of the participating laboratories. Four laboratories participated in the program during 1987: (1) Illinois State Water Survey, Central Analytical Laboratory (CAL); (2) Inland Waters Directorate, National Water Quality Laboratory (IWD); (3) Combustion Engineering Inc., Environmental Monitoring and Services (EMS); and (4) U.S. Geological Survey, National Water Quality Laboratory (DEN). The DEN laboratory only participated in the program during January through November 1987. All other laboratories participated for the entire year.

Samples from five sources were prepared for the 1987 interlaboratory-comparison program. Ultrapure, deionized-water and synthetic precipitation samples were prepared by the U.S. Geological Survey, and natural wet-deposition samples were prepared by CAL. Natural wet-deposition samples from the NADP/NTN that had a volume of 750 mL or greater were selected randomly by CAL for use in the interlaboratory comparison program. The natural wet-deposition samples were divided into 10 aliquots using a deca-splitter. CAL shipped the natural wet-deposition samples to the U.S. Geological Survey in chilled, insulated containers. The U.S. Geological Survey relabeled the bottles and shipped two bottles of each natural wet-deposition sample to each of the four participating laboratories. Standard-

reference samples from the U.S. Environmental Protection Agency, the National Bureau of Standards (NBS), and the U.S. Geological Survey also were used as interlaboratory comparison samples.

Laboratories were mailed duplicate natural wet-deposition samples and triplicate standard-reference water samples. Single aliquots of ultrapure, deionized water also were mailed. 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 standard-reference water samples.

Laboratory precision in determining analytes was estimated by calculating a pooled standard deviation of the duplicate natural wet-deposition samples (Taylor, 1987) and of the triplicate standard-reference water samples (Dixon and Massey, 1969) that were submitted to each laboratory. The calculated pooled standard deviations are listed in table 4. The calculated pooled standard deviations for CAL for potassium and chloride in the natural wet-deposition samples and for sulfate in the simulated wet-deposition samples were larger than those in previous years. The pooled standard deviation for IWD for

Table 4.--Pooled standard deviations for analytes determined by four laboratories that measured constituents in natural wet-deposition samples

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Waters Directorate, National Water Quality Laboratory, Ontario, Canada; EMS, Combustion Engineering, Inc., Environmental Monitoring and Services, Camarillo, Calif.; DEN, U.S. Geological Survey, National Water Quality Laboratory, Denver, Colo.; Nat, analyses of natural wet-deposition samples; Sim, analyses of simulated wet-deposition samples; all units, in milligrams per liter, except pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius]

Analyte	CAL		IWD		EMS		DEN	
	Nat	Sim	Nat	Sim	Nat	Sim	Nat	Sim
Calcium	0.004	0.008	0.003	0.008	0.007	0.011	0.006	6.491
Magnesium	.001	.006	.002	.064	.001	.004	.002	.009
Sodium	.001	.044	.027	.037	.005	.017	.256	.058
Potassium	.186	.069	.026	.140	.411	.068	.049	.081
Ammonium	<.01	.02	.01	.01	.01	.01	.03	.30
Chloride	.18	.05	.05	.11	.31	.06	.04	.20
Nitrate	.01	.08	.02	.21	.02	.06	.11	2.17
Sulfate	.02	.23	.04	.51	.01	.15	.06	2.34
pH	.01	.08	.03	.74	.04	.02	.35	.78
Specific conductance	.8	1.4	.3	1.2	1.5	1.9	17.8	25.1

sulfate in simulated wet-deposition samples was larger than those in previous years. The pooled standard deviations for EMS for potassium and chloride in natural wet-deposition samples were larger than previous years. The pooled DEN standard deviation for sodium and specific conductance in the natural wet-deposition samples and for calcium, ammonium, chloride, nitrate, sulfate, and specific conductance in the simulated wet-deposition samples were much larger than those in previous years. The larger pooled standard deviations for potassium and chloride for natural wet-deposition samples analyzed by CAL and EMS may be due to sample contamination; large concentrations of potassium were usually paired with large concentrations of chloride.

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 ($\alpha=0.01$) differences in analyte measurements, except for pH determinations. When Fisher's least significant difference procedure (Iman and Conover, 1983) is used, the mean rank for pH determinations by DEN was significantly ($\alpha=0.01$) larger than that for the other three laboratories. Percentile rankings for individual laboratory analyses of interlaboratory-comparison samples are summarized in table 5.

Analyte bias for laboratories participating in the U.S. Geological Survey interlaboratory-comparison study also were evaluated by using certified values and concentrations from standard-reference material 2694, level I and level II from the NBS. Laboratory-reported values were compared to the certified values and concentrations by using a Student t test. Bias was indicated by a significant ($\alpha=0.01$) difference between the mean analyte value from the laboratory and the certified value. A summary of the mean analytical results for each laboratory and the certified values for the NBS materials is presented in table 6. CAL had the least number of mean analyses that were significantly different from the NBS certified values.

Table 5.--Percentile ranking 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; EMS, Combustion Engineering, Inc., Environmental Monitoring and Services, Camarillo, Calif.; DEN, U.S. Geological Survey, National Water Quality Laboratory, Denver, Colo.; all units, in milligrams per liter, except pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius]

Analyte	Percentiles											
	CAL			IWD			EMS			DEN		
	25th	50th	75th	25th	50th	75th	25th	50th	75th	25th	50th	75th
Calcium	0.020	0.050	0.190	0.020	0.060	0.210	0.012	0.052	0.189	0.010	0.050	0.207
Magnesium	.010	.021	.045	<.010	.020	.040	.010	.020	.047	.010	.020	.050
Sodium	.021	.067	.203	.020	.085	.200	.026	.098	.205	.040	.115	.230
Potassium	.011	.036	.104	.020	.040	.060	.011	.044	.076	.010	.030	.057
Ammonium	<.02	.07	.21	<.02	.06	.20	<.02	.07	.19	.03	.10	.22
Chloride	.05	.13	.033	.03	.13	.31	.06	.14	.35	.12	.16	.31
Nitrate	.04	.43	.87	<.04	.42	.83	.08	.46	.90	<.04	.31	.91
Sulfate	.53	1.35	2.73	.50	1.21	2.56	.56	1.39	2.44	.48	1.15	2.77
pH	4.27	4.76	5.21	4.29	4.82	5.18	4.30	4.65	5.21	4.8	6.00	6.92
Specific conductance	5.2	13.3	26.1	5.6	11.5	19.0	5.6	15.0	26.5	5.0	9.0	16.4

Table 6.--Mean analysis estimates for standard reference material 2694 from the National Bureau of Standards

[NBS, National Bureau of Standards; CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Waters Directorate, National Water Quality Laboratory, Ontario, Canada; EMS, Combustion Engineering Inc., Environmental Monitoring and Services, Camarillo, Calif.; DEN, U.S. Geological Survey, National Water Quality Laboratory, Denver, Colo; all units in milligrams per liter except pH, in units, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius; *, indicates a significant difference from the certified values at $\alpha=0.01$ level; --, indicates data unavailable]

Analyte	NBS standard	Certified NBS values	Laboratory analyses			
			CAL	IWD	EMS	DEN
Calcium	2694-I	0.014±0.003	0.012	*0.020	*0.007	0.022
	2694-II	.049± .011	.047	.052	*.037	.033
Magnesium	2694-I	.024± .002	.024	*.020	.023	*.018
	2694-II	.051± .003	.049	*.132	*.048	.039
Sodium	2694-I	.205± .009	.152	.179	.201	.217
	2694-II	.419± .015	.412	.420	.420	.334
Potassium	2694-I	.052± .007	.102	.044	.052	.055
	2694-II	.106± .008	.105	.107	*.132	.145
Nitrate	2694-I	--	.27	.29	.18	.59
	2694-II	7.06 ± .15	*7.23	6.80	*6.95	5.78
Sulfate	2694-I	2.75 ± .005	2.84	2.58	*2.51	2.82
	2694-II	10.9 ± .2	*11.42	10.75	*10.11	7.93
pH	2694-I	4.27 ± .03	4.26	4.28	4.29	6.09
	2694-II	3.59 ± .02	3.59	3.58	3.58	*4.05
Specific conductance	2694-I	26. ±2	27	--	26	*16
	2694-II	130. ±2	129	*133	*123	*81

Ultrapure deionized water was included among the samples submitted to the laboratories to determine the percentage of times that each laboratory reported positive values in a solution that would not be expected to contain any detectable analyte levels. A summary of the laboratory analyses of ultrapure deionized water is presented in table 7. DEN had the largest number of determinations greater than the minimum detection limit for every analyte except ammonium. The positive concentrations reported by the laboratories may represent the difficulties of measuring analyte concentrations that are near the reported minimum detection limits or may represent contamination of the interlaboratory samples.

Table 7.--Summary of laboratory analyses of ultrapure, deionized water samples

[CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Ill.; IWD, Inland Waters Directorate, National Water Quality Laboratory, Ontario, Canada; EMS, Combustion Engineering, Inc., Environmental Monitoring and Services, Camarillo, Calif.; DEN, U.S. Geological Survey, National Water Quality Laboratory, Denver, Colo.; N, number of analyses that resulted in a positive concentration; median, median concentration of reported positive concentrations, in milligrams per liter]

Analyte	CAL		IWD		EMS		DEN	
	N	Median	N	Median	N	Median	N	Median
Calcium	1	0.010	2	0.010	2	0.010	4	0.004
Magnesium	0	(¹)	0	(¹)	0	(¹)	3	.002
Sodium	0	(¹)	2	.015	2	.015	4	.028
Potassium	9	.250	3	.010	3	.010	6	.005
Ammonium	0	(¹)	3	.004	3	.004	1	1.034
Chloride	2	0.16	0	(¹)	0	(¹)	6	.002
Nitrate	0	(¹)	0	(¹)	0	(¹)	11	.079
Sulfate	3	0.06	0	(¹)	0	(¹)	11	.029

¹Median concentration not applicable.

SUMMARY AND CONCLUSIONS

During 1987, the U.S. Geological Survey operated three programs to provide external quality-assurance monitoring of the National Atmospheric Deposition Program (NADP) and the National Trends Network (NTN). An intersite-comparison program was used to assess the accuracy of onsite pH and specific-conductance determinations at semiannual intervals. A blind-audit program was used to assess the effect of routine sample handling on the precision and bias of NADP/NTN wet-deposition data. Analytical results from four laboratories, which routinely analyze wet-deposition samples, were examined to determine estimates of the analytical bias and precision for each laboratory.

Two intersite-comparison studies were completed during 1987. For pH, 77 and 70 percent of the sites met the NADP/NTN accuracy goal of ± 0.1 unit for pH; 95 and 93 percent of the sites met the NADP/NTN accuracy goal of $\pm \mu\text{S}/\text{cm}$ for specific conductance.

Results from the blind-audit program indicated significant ($\alpha=0.01$) bias existed for all analytes except nitrate and sulfate. The results indicated that contamination is occurring for some analytes and that levels of hydrogen ion are reduced for blind-audit samples handled and shipped according to standard NADP/NTN protocols. An estimate of analyte precision was calculated by pooling the variance of replicate samples. A decreased precision in the analyses of blind-audit samples, when compared to interlaboratory studies indicates that most of the uncertainty in NADP/NTN deposition data results from routine field operations.

Examination of data from four laboratories indicated that no significant difference existed among laboratory analyte determinations, except for pH. The NADP/NTN's Central Analytical Laboratory had the least number of mean analyses which were significantly ($\alpha=0.01$) different from the certified values.

REFERENCES CITED

- Bigelow, D.S., 1982, NADP instruction manual, site operation: Fort Collins, Colorado State University, Natural Resources Ecology Laboratory, 30 p.
- Bigelow, D.S. and Dossett, S.R., 1988, Instruction manual, NADP/NTN site operation: Fort Collins, Colorado State University, Natural Resources Ecology Laboratory, 57 p.
- Brooks, M.H., Schroder, L.J., and Willoughby, T.C., 1987, Results of an external quality-assurance program for the National Atmospheric Deposition Program and the National Trends Network during 1985: U.S. Geological Survey Water-Resources Investigations Report 87-4219, 14 p.
- Dixon, W.J. and Massey, F.J., 1969, Introduction to statistical analysis (3d ed.): New York, McGraw-Hill, 638 p.
- Hoaglin, D.C., Moesteller, Frederick, and Tukey, J.W., 1983, Understanding robust statistics and exploratory data analysis: New York, John Wiley, 447 p.
- Iman, R.L. and Conover, W.J., 1983, A modern approach to statistics: New York, John Wiley, 496 p.
- Parr, B.F., Lampe, R.L., Pratt, G., Dowler, O.L., and Mitchell, W.J., 1987, National performance audit program--ambient air audits of analytical proficiency 1985: U.S. Environmental Protection Agency Report No. 600/4-87-002, 51 p.
- Peden, M.E., 1986, Development of standard methods for collection and analysis of precipitation, in Methods for collection and analysis of precipitation: Champaign, Illinois State Water Survey Contract Report 381, p. 19-21.
- Robertson, J.K., and Wilson, J.W., 1985, Design of the National Trends Network for monitoring the chemistry of atmospheric precipitation: U.S. Geological Survey Circular 964, 46 p.

- Schroder, L.J., and Brennan, J.O., 1984, Precision of the measurement of pH and specific conductance at National Atmospheric Deposition Program monitoring sites, October 1983-November 1983: U.S. Geological Survey Water-Resources Investigations Report 84-4325, 12 p.
- Schroder, L.J., Bricker, A.W., and Willoughby, T.C., 1985, Precision and bias of selected analytes reported by the National Atmospheric Deposition Program and the National Trends Network; 1983 and January 1980 through September 1984: U.S. Geological Survey Water-Resources Investigations Report 85-4275, 15 p.
- See, R.B., Schroder, L.J., Willoughby, T.C., 1988, External quality-assurance results for the National Atmospheric Deposition Program and the National Trends Network during 1986: U.S. Geological Survey Water-Resources Investigations Report 88-4007, 15 p.
- Taylor, J.K., 1987, Quality assurance of chemical measurements: Chelsea, Mich., Lewis Publishers, 328 p.