QUALITY-ASSURANCE RESULTS FOR FIELD pH AND SPECIFIC-CONDUCTANCE MEASUREMENTS, AND FOR LABORATORY ANALYSIS, NATIONAL ATMOSPHERIC DEPOSITION PROGRAM AND NATIONAL TRENDS NETWORK--JANUARY 1980-SEPTEMBER 1984

By LeRoy J. Schroder, Myron H. Brooks, and Bernard A. Malo,
U.S. Geological Survey,
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METRIC CONVERSION TABLE

For the reader who may prefer to use inch-pound units, conversion factors for terms used in this report are:

Multiply SI units	*By*	*To obtain inch-pound units*
liter (L)	1.057	quart
milliliter (mL)	0.03382	ounce, fluid
micrometer (μm)	3.937×10^{-5}	inch
meter (m)	39.37	inch

Water-quality term and abbreviation used in this report:

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

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ABSTRACT

Five intersite comparison studies for the field determination of pH and specific conductance, using simulated-precipitation samples, were conducted by the U.S. Geological Survey for the National Atmospheric Deposition Program and National Trends Network. These five intersite comparisons were performed to estimate the precision of pH and specific-conductance determinations made by sampling-site operators. Simulated-precipitation samples were prepared from nitric acid and deionized water. The estimated standard deviation for site-operator determination of pH was 0.25 for pH values ranging from 3.79 to 4.64; the estimated standard deviation for specific conductance was 4.6 microsiemens per centimeter at 25 °Celsius for specific-conductance values ranging from 10.4 to 59.0 microsiemens per centimeter at 25 °Celsius. These estimated variances were for determinations made from October 1981 to November 1983.

Performance-audit samples with known analyte concentrations were prepared by the U.S. Geological Survey and distributed to the National Atmospheric Deposition Program's Central Analytical Laboratory. The differences between the National Atmospheric Deposition Program and National Trends Network-reported analyte concentrations and known analyte concentrations were calculated, and the bias and precision were determined. For 1983, concentrations of calcium, magnesium, sodium, and chloride were biased at the 99-percent confidence limit; concentrations of potassium and sulfate were unbiased at the 99-percent confidence limit. Relative-percent differences between the measured and known analyte concentration for calcium, magnesium, sodium, potassium, chloride, and sulfate were calculated for 1983. The median relative-percent differences were: calcium, 17.0; magnesium, 6.4; sodium, 10.8; potassium, 6.4; chloride, 17.2; and sulfate, -5.3. These relative-percent differences need to be considered before user analysis of the 1983 data.

Four analytical laboratories routinely analyzing precipitation were evaluated in their analysis of identical natural- and simulated-precipitation samples. One participating laboratory was the National Atmospheric Deposition Program's Central Analytical Laboratory. Interlaboratory comparability was evaluated, using analysis of variance coupled with Duncan's multiple-range test, and linear-regression models describing the relation between individual laboratory analytical results for natural-precipitation samples. Analyte bias for each laboratory was examined using analysis of variance coupled with Duncan's multiple-range test on data produced by these laboratories, from the analysis of identical simulated-precipitation samples. Bias for a given

analyte produced by a single laboratory is indicated when the laboratory mean for that analyte is shown to be significantly different from the mean of the most-probable analyte concentrations in the simulated-precipitation samples. Analyte precision for each laboratory has been estimated by calculating a pooled variance for each analyte. Analyte-estimated precisions have been compared using F-tests and differences in analyte precisions for laboratory pairs have been reported. Interlaboratory comparability results may be used to normalize natural-precipitation chemistry data obtained from two or more of these laboratories.

INTRODUCTION

The National Atmospheric Deposition Program (NADP) was organized in 1977 by a number of State agricultural experiment stations to provide information on the spatial and temporal trends of atmospheric deposition in the United States. Extensive participation was obtained from other organizations, because of the broad interest in the subject. The National Trends Network (NTN) was established by the Deposition Monitoring Task Group of the Interagency Task Force on Acid Precipitation in 1983 as a minimum network for determining spatial and temporal trends in precipitation in the United States. Sampling sites may be included in either one or both of the monitoring networks. Therefore, this report will consider the NADP and NTN as one group known as NADP/NTN. Operators at all sampling sites use standardized instrumentation and procedures to collect weekly wet-deposition samples. These samples are sent to the Central Analytical Laboratory (CAL) at the Illinois State Water Survey, where all samples are analyzed for dissolved ammonium, calcium, magnesium, potassium, sodium, chloride, sulfate, nitrate, and orthophosphate. These analyses are reported to the NADP/NTN Coordinator's Office; this office publishes the data and submits the data for computerized storage in the Atmospheric Deposition System, operated by Pacific Northwest Laboratory for the U.S. Environmental Protection Agency.

The goal of the quality assurance program of the NADP/NTN is to produce a sufficient data base, containing documented and quality information, to reduce or eliminate the uncertainties of long-term wet-deposition monitoring. The quality assurance program has divided wet-deposition monitoring into five components: (1) Sampling-site selection, (2) sampling device, (3) determination of pH and specific conductance at sampling sites, (4) sample handling, and (5) laboratory analysis.

Sampling-site selection was based on the initial siting criteria developed by the NADP and supplemented by the Federal Interagency Task Group on Deposition Monitoring. The principal siting criteria are:

1. Sampling sites are to be located in areas where the prevailing land use is unlikely to change for decades.
2. Land at the sampling site is to be grass covered or equivalent.
3. Sampling sites are to be located in rural areas.
4. Sampling sites are to be a few kilometers from areas where controlled-burning techniques are used for land management.
5. Sampling sites are to be located to minimize influence of emissions from highways, airports, and railroads.
6. Sampling sites are to be located to minimize influence from topographic features, such as rain shadows.

7. Locations at which research in wet deposition is ongoing will be given priority, if other aspects of the siting criteria are met.

8. Logistics will have priority when choosing sampling-site locations that meet the siting criteria.

All NADP/NTN sites were visited and evaluated by an auditing team from the U.S. Military Academy during 1982. A detailed description of the siting and audit criteria was reported by Wilson and Robertson (1983) and Schroder and Malo (1984).

Wet-dry atmospheric-deposition collectors based on the Health and Safety Laboratory design (Volchock and Graveson, 1976) and manufactured by Aerochem Metrics[1] were chosen by the NADP/NTN. Ten collectors were installed at Raleigh, N.C., and were operated for nearly 18 months. Four samplers were operated for daily sampling; six samplers were operated for weekly sampling. This design was used to determine if: (1) Collection efficiencies for precipitation are affected by small distances between a rain gage and collector, (2) collection efficiencies are affected by evaporation loss, and (3) chemical changes or alterations in samples are possible when sampling is conducted for collection periods longer than daily sampling. Schroder and others (1984) indicated that a collector 76 m from the rain gage has the same collection efficiency as collectors only a few meters from the gage; evaporation losses in collectors, based on the Health and Safety Laboratory design, were not a problem in a subtropical climate; and correlation of pH and specific-conductance data from collector to collector was excellent.

This paper describes in detail three of the five components of the quality-assurance program: (1) Determination of pH and specific conductance at the sampling sites, (2) sample handling, and (3) laboratory analysis.

DETERMINATION OF pH AND SPECIFIC CONDUCTANCE AT MONITORING SITES

Sample Preparation

Dilute nitric-acid solutions (simulated-precipitation samples) were prepared by adding reagent-grade nitric acid to 20.0 L of 1.5-Ω ohm (megohm) deionized water. The required volume of nitric acid to prepare the simulated-precipitation sample was calculated as follows (Dean, 1978):

1. Target pH of the simulated-precipitation sample was chosen.
2. Hydrogen-ion concentration was calculated from the equation

$$pH=-\log[H^+].$$

3. Molarity of the solution was calculated from the hydrogen-ion concentration.
4. Volume of nitric acid required was calculated.

The equation for required acid volume is:

$$V= \frac{100wM}{pd} \times 20 \qquad (1)$$

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

where V is the volume of nitric acid, in milliliters;
w is the molecular weight of nitric acid, in grams per mole;
M is the desired molarity;
p is the assayed weight percent of nitric acid; and
d is the density of nitric acid, in grams per milliliter.

After addition of the required volume of nitric acid to 20.0 L of deionized water, the solution was mechanically stirred for at least 24 hours in a sealed container. About 150 subsamples were transferred into 125-mL, high-density polyethylene bottles. Measurements of pH were made on four of the subsamples. Hydrogen-ion concentration was calculated using the average pH from the four subsample measurements. Nitrate concentration (equivalents per liter) of the solution was assumed to be the same as the hydrogen-ion concentration. Conductivity of the solution was calculated using the equation (Castellan, 1971):

$$K=k(1/1000)\ \Sigma_i C_i Z_i \tag{2}$$

where K is the conductivity in millisiemens;
k is the constant of proportionality (reciprocal ohms, centimeter, and equivalents per liter);
C is the concentration of ions in the solution (equivalents per liter); and
Z is the equivalent conductivity of the ion ($H^+=349.8$, $NO_3^-=71.44$).

The conductivity measured for the same four subsamples used to measure the pH was compared to the calculated conductivity using the equation:

$$E=\frac{\text{measured conductivity}-\text{calculated conductivity}}{\text{calculated conductivity}} \times 100 \tag{3}$$

where E is the percent error.

The percent error for conductivity was less than 5 percent for all five audit samples.

Sample Stability

Dilute nitric-acid solutions have stable pH and specific conductance for at least 10 weeks, when they are stored at ambient temperature in sealed, high-density polyethylene bottles. Ten subsamples of the nitric acid solutions, prepared for the April 1982 and November 1982 intersite comparisons, were analyzed for pH and specific conductance at a rate of one per week for the 10 weeks after solution preparation. The stability experiments were concurrent with the two intersite comparisons. Both pH and specific conductance were measured by one individual using the same instruments on each sample. Three additional samples from the April 1982 solution were analyzed for pH and specific conductance 22 weeks after preparation.

The solution prepared for the April 1982 intersite comparison had a calculated pH of 4.52. The mean of pH determinations made on 10 subsamples by the U.S. Geological Survey was 4.53±0.02. The mean of 10 pH determinations made during 10 weeks, using a different subsample each week, was 4.55±0.03. The solution prepared for the November 1982 intersite comparison had a calculated pH of 3.95. Ten replicate determinations by the U.S. Geological Survey had a mean pH of 3.90±0.03. Ten different subsamples were analyzed at a rate of one per week for 10 weeks. The mean of the 10 determinations for pH was 3.92±0.05.

Specific conductance was measured by the U.S. Geological Survey for both the April and November 1982 solutions. The April 1982 solution had a calculated specific conductance of 12.7 µS/cm. The mean of 10 replicate determinations for specific conductance by the U.S. Geological Survey was 11.5±0.4 µS/cm. Mean specific conductance was 11.4±0.9 µS/cm for 10 subsamples analyzed at a rate of one per week for 10 weeks. The nitric-acid solution prepared for the November 1982 intercomparison had a calculated specific conductance of 47.2 µS/cm. Ten replicate analyses of the solution for specific conductance gave a mean of 37.2±0.7 µS/cm. Mean specific conductance of 10 subsamples analyzed during the 10 weeks was 37.0±0.8 µS/cm.

Subsamples of the April 1982 nitric-acid solution were analyzed 22 weeks after preparation and storage. Results from two of the three samples were nearly identical to the mean obtained from the 10-week study for both pH and specific conductance. However, results from one sample were different. The measured pH of this sample was 4.26, and the specific conductance was 13.5 µS/cm; the reason for the different pH and specific conductance is unknown.

A visual inspection of the pH and specific-conductance results from the two 10-week studies did not indicate any time dependency. Results obtained from the three samples analyzed 22 weeks after preparation indicated that the pH and specific conductance had changed for one subsample. Therefore, the dilute nitric-acid solutions were stable for at least 10 weeks; and they may have been stable for longer periods.

Sample-Analysis Protocol

NADP/NTN sampling-site operators received the simulated-precipitation samples through the mail. Operators were instructed to determine the pH and specific conductance of each sample, using the NADP/NTN guidelines (Bigelow, 1982). The pH-determination protocol required that the sampling-site operators use the following procedure: (1) Standardize their pH meter using a 7.00 pH standard supplied by CAL, (2) rinse the pH electrode with deionized water, (3) determine the pH of a 4.01 pH standard supplied by CAL, (4) adjust the pH-meter slope control to obtain a pH reading of 4.01, (5) rinse the pH electrode with deionized water, (6) determine the pH of the simulated-precipitation sample, and (7) report the value obtained from the simulated-precipitation sample to the nearest 0.01 pH unit.

The specific-conductance-measurement protocol required that sampling-site operators use the following procedure: (1) Standardize their conductance meter, using a potassium chloride solution (specific conductance 75 µS/cm) supplied by CAL; (2) remeasure the specific conductance of the potassium chloride solution; (3) rinse the conductivity cell three times with deionized water; (4) measure the conductivity of the simulated-precipitation sample; and (5) report the specific conductance of the simulated-precipitation sample in microsiemens per centimeter using the formula:

$$\text{Specific conductance}=(75\div\text{measured standard conductivity}) \times \text{measured simulated-precipitation sample conductivity} \qquad (4)$$

Sample Handling and Data Analysis

Sampling-site operators measured the pH and specific conductance using the protocols listed in the previous section. Measurements by these operators usually required less than 40 mL of the 125-mL sample. The remainder of the sample and the operator's analytical results were returned to the U.S. Geological Survey. The U.S. Geological Survey analyzed all returned samples for pH or specific conductance, or both, when: (1) Reported pH was more than ±0.4 unit from the calculated pH; or (2) reported specific conductance was more than ±20 percent from the calculated specific conductance. These limits were chosen arbitrarily for the October 1981 study; they were used for all subsequent studies.

The U.S. Geological Survey analysis of the returned audit samples was used to determine if either the pH or specific conductance of the samples had changed. If the pH measured by the U.S. Geological Survey was sithin ±0.15 pH unit, or if the specific conductance was within ±10 percent of the calculated value, the sample was considered unchanged. If U.S. Geological Survey analytical results were outside these limits, the sample was declared "different," and the site-operator results were flagged in the data sets.

Means and standard deviations for pH and specific conductance were calculated for each intersite comparison, using all unflagged results obtained from the site operators. Reported pH values were converted to hydrogen-ion concentrations prior to the calculations. All site-operator results that were greater than 1.5 standard deviations from the intersite comparison means were noted. Each sample for which the pH or specific-conductance results were greated than 1.5 standard deviations from the mean also were analyzed by the U.S. Geological Survey. The manager and operator of each NADP/NTN sampling site were sent the results for each intersite comparison. The information sent included: (1) Frequency distribution of pH and specific-conductance results; (2) mean and standard deviation for both properties; (3) U.S. Geological Survey analytical results, if applicable; and (4) notice that the sampling-site operator's results were greater than 1.5 standard deviations from the mean, if applicable.

Results of Intersite Comparison Studies

Summaries of data for the five separate NADP intersite comparisons for pH and specific conductance are given in table 1. Standard deviations for pH determinations from these studies ranged from 0.19 to 0.30 unit; and the relative standard deviations ranged from 4.7 to 6.9 percent. The pooled

Table 1.--*Results of pH and specific-conductance determinations from five intersite comparison studies*

[μS/cm=microsiemens per centimeter at 25 °Celsius]

Study date	pH		Specific conductance (μS/cm)		Range		Number of site-operators reporting
	Mean	Standard deviation	Mean	Standard deviation	pH	Specific conductance (μS/cm)	
October 1981-----------	4.27	0.26	20.6	3.1	3.3-5.4	14 -26	73
April 1982-------------	4.54	.24	12.2	2.2	3.7-5.9	6.0-56	98
November 1982----------	4.02	.19	37.9	5.3	3.3-4.5	3.2-52	93
May 1983---------------	3.79	.26	59.0	7.4	3.3-4.4	6.0-90	100
November 1983----------	4.62	.30	10.4	2.2	3.5-5.9	2.4-21	108

standard deviation (Dixon and Massey, 1969) for pH from the five studies was 0.25 unit. Standard deviations for specific-conductance determinations ranged from 2.2 to 7.4 µS/cm. The relative standard deviation ranged from 12.2 to 21.2 percent. The pooled standard deviation for specific conductance was 4.6 µS/cm.

The American Society for Testing and Materials (1984) recommends a test for bias. Percent bias between the calculated pH and specific-conductance values and intersite-comparison means for each study are given in table 2. The mean pH value for four of the five intersites comparisons is higher than the calculated pH value, indicating a positive bias for site-operator determinations of pH. However, the magnitude of the pH bias is small. A consistent pattern for bias occurs when comparing the specific-conductance means and calculated values.

Each NADP/NTN sampling-site operator was mailed a sample for each intersite comparison study. However, the U.S. Geological Survey did not receive results or the remainder of the sample from all sampling-site operators. About 3 percent of the sampling-site operators reported that they had instrument problems at the time of sample receipt. These operators normally were told to retain the intersite-comparison sample, and to determine the pH and specific conductance when their instruments were repaired. They also were requested to compare their results with the reported study results mailed to them by the U.S. Geological Survey. Several operators from each study reported results weeks or even months after the scheduled final date to return samples and results to the U.S. Geological Survey. Site operators not returning results and not explaining the reason usually constituted less than 4 percent of the sampling-site operators. However, for the November 1983 intersite comparison, 20 sampling-site operators--nearly 15 percent of the operators--did not report results. The reason for this large number of unreported results is unknown.

SAMPLE-HANDLING AND LABORATORY-ANALYSIS MONITORING

Preparation and Analysis of Performance-audit Samples

Performance-audit samples are prepared by the U.S. Geological Survey in Denver, Colo. The samples are prepared by diluting Standard Reference Water Samples (SRWS) (Schroder and others, 1980; Skougstad and Fishman, 1974) with deionized water. A sample volume of 2,000 mL is prepared for each mixture and divided into 500-mL aliquots; then the pH of each solution is lowered to less than 5.0, using perchloric acid. Performance-audit samples are sent directly to NADP/NTN site operators on a quarterly basis. After a week in which no wet deposition has occurred, site operators take a 20-mL aliquot from the sample and determine the pH and specific conductance of the sample. A portion (about 80 percent) of the remaining sample is poured into a precleaned polyethylene sample container; then the container is sealed and shipped to CAL without prior notification. CAL filters all precipitation samples, using 0.45-µm pore-size filters, before analysis. All CAL analytical data are transmitted to the U.S. Geological Survey at Denver, Colo.; this laboratory identifies the performance-audit-sample data and notifies CAL that the data are to be removed

Table 2.--*Comparison of calculated and determined pH and specific conductance from five intersite comparison studies*

[µS/cm=microsiemens per centimeter at 25 °Celsius]

	pH				Specific conductance (µS/cm)			
Study date	Calculated	Intersite mean	±Percent bias	Statistically significant (95-percent confidence level)	Calculated	Intersite mean	±Percent bias	Statistically significant (95-percent confidence level)
October 1981---------	4.10	4.27	+4.1	Yes	33.5	20.6	-38.5	Yes
April 1982-----------	4.52	4.54	+0.4	No	12.7	12.2	-3.9	Yes
November 1982--------	3.95	3.94	-0.2	No	[1]37.2	37.9	+1.9	No
May 1983-------------	3.79	3.79	0.0	No	68.3	59.0	-13.6	Yes
November 1983--------	4.51	4.62	+2.4	Yes	13.0	10.4	-20.0	Yes

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[1] U.S. Geological Survey measured value used because of sample-preparation problems.

from their data files. The diluted SRWS do not contain ammonium at a detectable concentration; nitrate and orthophosphate are lost from the samples after dilution by the U.S. Geological Survey and before analysis by CAL.

CAL reanalyzes all performance-audit samples after the samples are identified by the U.S. Geological Survey. These samples normally are stored for 3 to 4 months at room temperature before the second analysis is made. These data are transmitted to the U.S. Geological Survey after analysis. CAL may analyze each performance-audit solution a maximum of eight times: four analyses of the individual 500-mL aliquots sent to CAL from sampling-site operators, and four reanalyses of aliquots. CAL analyzed individual performance-audit samples an average of five times from January 1980 through 1984.

Precision and Bias of Selected Analytes

Performance-audit samples are stored in a polyethylene bottles, handled by the site operator, transported to the laboratory in a polyethylene sampling bucket, and filtered at the laboratory. This series of steps is nearly identical to the handling of a natural-precipitation sample. Analyte concentrations for calcium, magnesium, sodium, potassium, chloride, and sulfate reported to the U.S. Geological Survey probably are affected by the sample-handling process prior to the laboratory determination. Therefore, the data obtained from the performance-audit sample are considered to be a monitor for the entire NADP/NTN sample handling, transportation, and analysis routine.

Results for 1983

The 1983 natural-precipitation samples collected by the NADP/NTN had relatively low analyte concentrations. A summary of these analyte-percentile concentrations is presented in table 3. The concentration range of analytes in the 1983 performance-audit samples is summarized in table 4. Comparison of the data from tables 3 and 4 indicates that the performance-audit-sample analyte concentrations for all analytes except sulfate were greater than the 50th percentile natural-sample analyte concentrations. The higher concentratations were necessary to produce stable analyte concentrations in the performance-audit samples.

Analyte concentrations obtained from the CAL analyses of the performance-audit samples were compared to the most-probable values or known analyte concentrations by the U.S. Geological Survey at Denver, Colo. The relative-percent difference between CAL-reported analyte concentrations and the known performance-audit-sample concentrations were calculated by:

$$\frac{\text{CAL reported concentration-known concentration}}{\text{Known concentration}} \times 100 \qquad (5)$$

The relative-percent differences for the 1983 performance-audit samples are summarized in table 5. The median and mean relative-percent differences are positive for each analyte except sulfate. The median relative-percent difference probably is a better description of the bias than the mean for this data set because of the range of data. For example, relative-percent differences for calcium ranged from -2.07 to 69.4 percent.

Table 3.--*Concentrations of analytes (5th, 50th, and 95th percentiles) in precipitation samples collected for the National Atmospheric Deposition Program and National Trends Network during 1983*

[Mark Peden, Illinois State Water Survey, written commun., 1985; mg/L, milligrams per liter]

Analyte	Concentration (mg/L) for indicated percentile		
	5th (mg/L)	50th (mg/L)	95th (mg/L)
Calcium	0.027	0.160	1.51
Magnesium	.010	.040	.259
Sodium	.022	.102	1.089
Potassium	.007	.031	.192
Chloride	.05	.17	1.73
Sulfate	.32	1.38	5.92

Table 4.--*Performance-audit-sample concentration range for the National Atmospheric Deposition Program and National Trends Network during 1983*

Analyte	Concentration range (milligrams per liter)	Number of samples
Calcium	0.30 - 7.24	28
Magnesium	.08 - 1.54	28
Sodium	.24 - 7.43	28
Potassium	.06 - 1.87	28
Chloride	.056- 3.87	28
Sulfate	.58 -14.40	28

Table 5.--*Relative-percent difference between the National Atmospheric Deposition Program and National Trends Network-reported analyte concentrations and the known performance-audit-sample concentrations for 1983*

Analyte	Relative percent difference			Number of samples
	Median	Mean	Standard deviation	
Calcium	17.0	20.4	18.2	28
Magnesium	6.4	14.3	21.2	28
Sodium	10.8	17.3	19.3	28
Potassium	6.4	14.3	21.2	28
Chloride	17.2	27.2	28.4	28
Sulfate	-5.3	-2.8	11.9	28

Bias for the analyte concentrations is determined by comparing the CAL-reported analyte concentrations to the known audit-sample concentrations. These comparisons are shown in figures 1 through 6. Peart and Thomas (1983) and Grant and Leavenworth (1974) present a binomial-probability-distribution equation in which the probability of having a specific number of points (X) on the same side of zero can be calculated. If X or more points occur on the same side of zero, bias is assumed. Bias was tested at 1-percent probability and summarized in table 6. Reported concentrations of calcium, magnesium, sodium, and chloride were determined to have positive biases for 1983.

A paired t-test (Dixon and Massey, 1969) was used to test the hypothesis that the initial NADP/NTN-reported results were equal to reanalysis results for 1983. This hypothesis is accepted for the analytes calcium, magnesium, sodium, potassium, chloride, and sulfate, indicating the samples were stable when stored at room temperature.

Least-squares equations were calculated to determine if a significant relation existed between the standard deviation of the performance-audit samples and the analyte concentrations in these same samples. It was determined that the standard deviation is not significantly dependent on the analyte concentration (Dixon and Massey, 1969).

Pooled standard deviations for 1983 performance-audit samples are presented in table 7. These pooled standard deviations may not be applicable to analyte concentrations beyond the concentration limits tested.

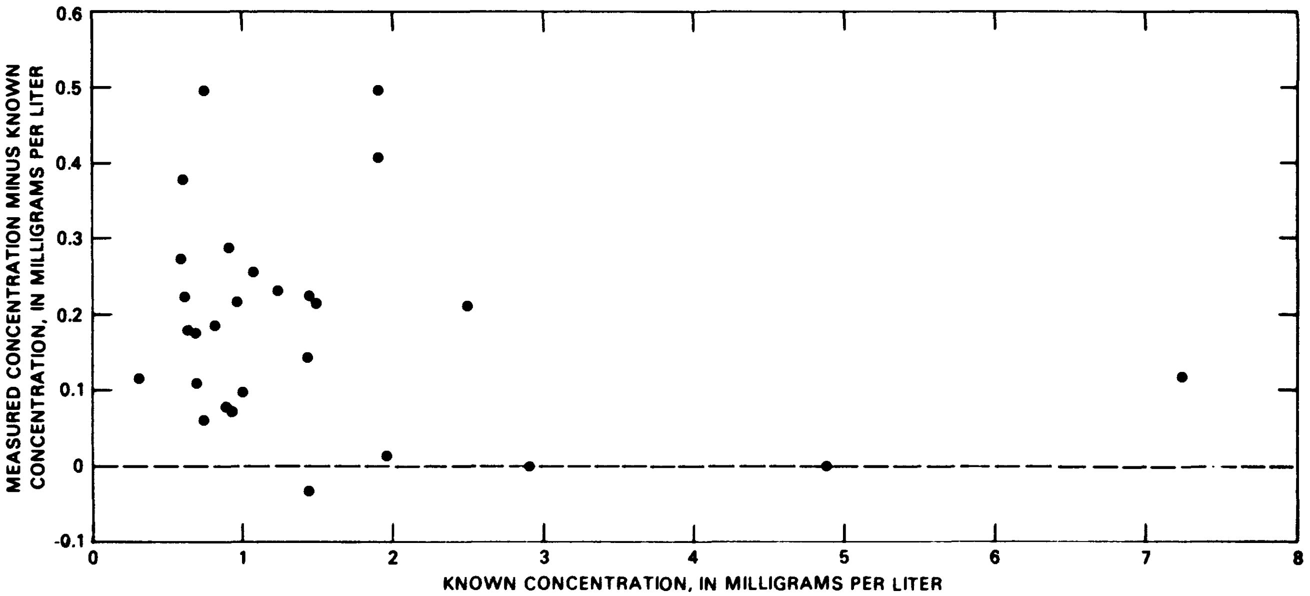

Figure 1.--Degree of bias based on known calcium concentration in performance-audit samples for 1983.

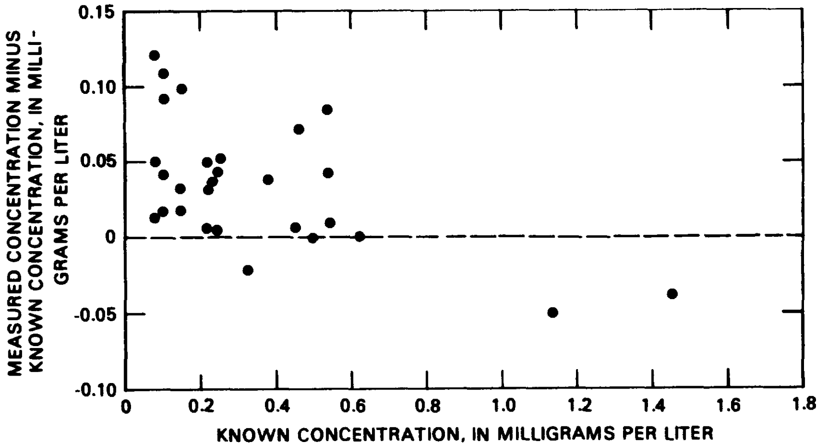

Figure 2.--Degree of bias based on known magnesium concentration in performance-audit samples for 1983.

Table 6.--*Bias determination from comparing the National Atmospheric Deposition Program and National Trends Network-reported analyte concentrations and the known performance-audit-sample concentrations for 1983*

Analyte	Number of values on the same side of zero	Number of samples	Bias
Calcium-------------	25	28	Positive
Magnesium-----------	23	28	Positive
Sodium--------------	22	28	Positive
Potassium-----------	19	28	None
Chloride------------	26	28	Positive
Sulfate-------------	17	28	None

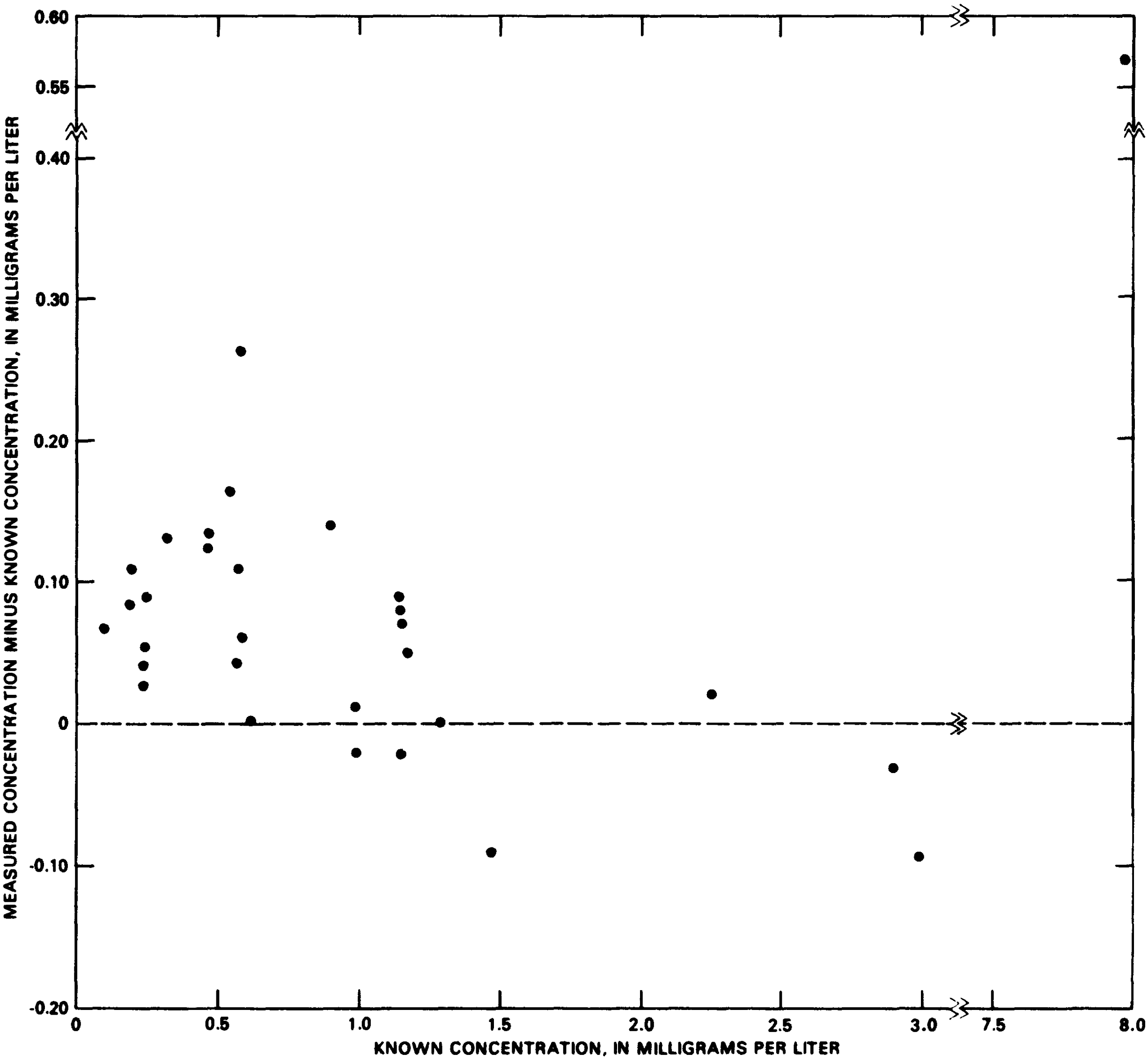

Figure 3.--Degree of bias based on known sodium concentration in performance-audit samples for 1983.

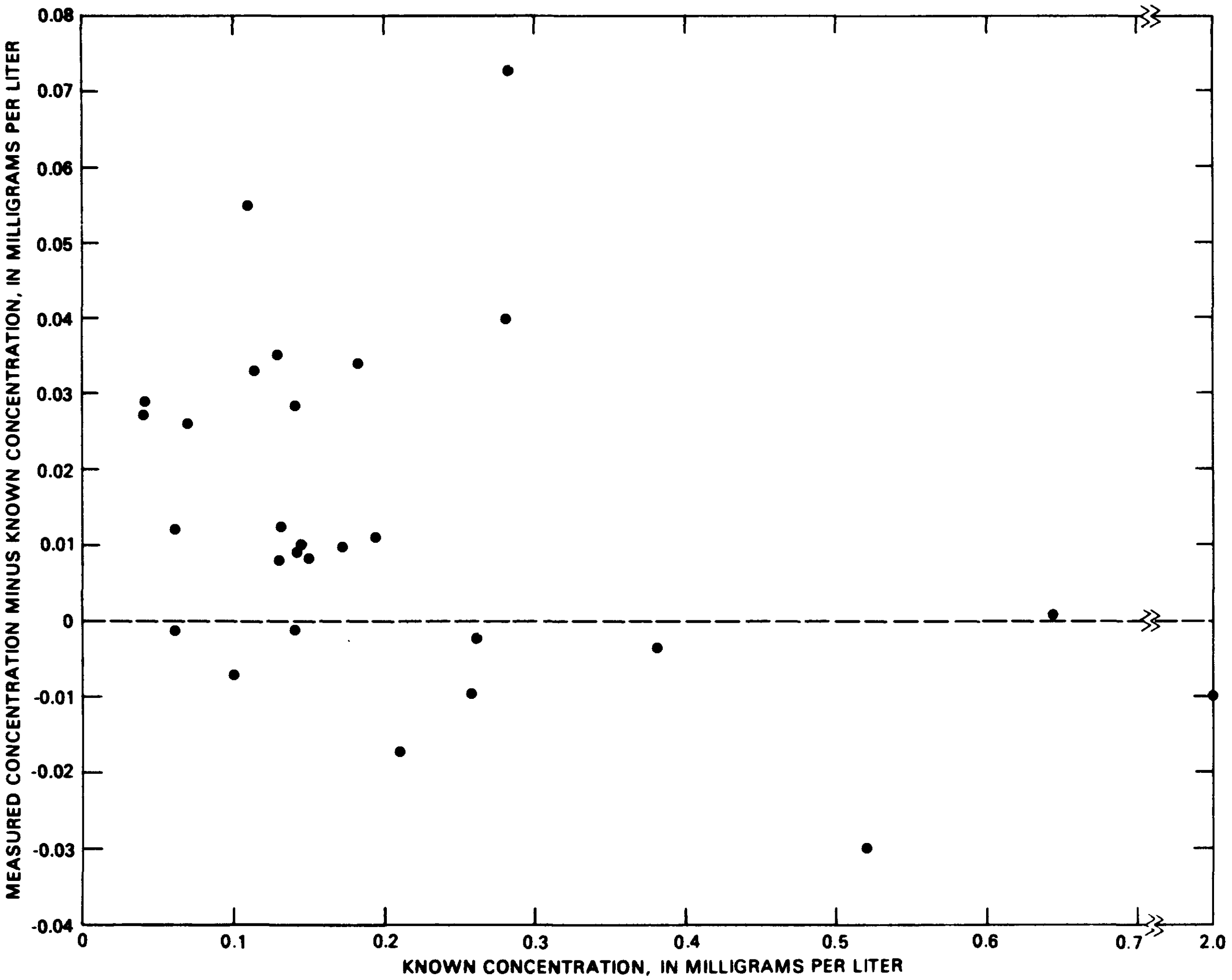

Figure 4.--Degree of bias based on known potassium concentration in performance-audit samples for 1983.

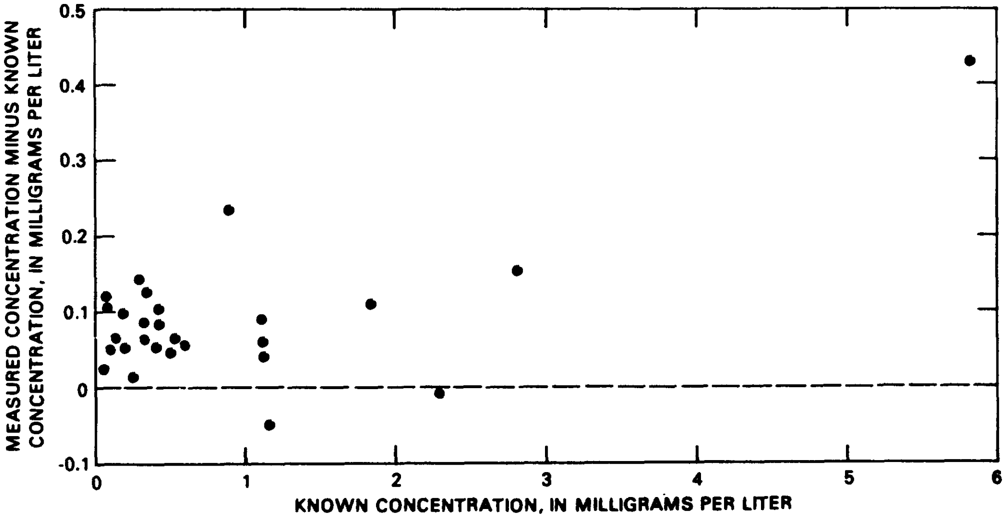

Figure 5.--Degree of bias based on known chloride concentration in performance-audit samples for 1983.

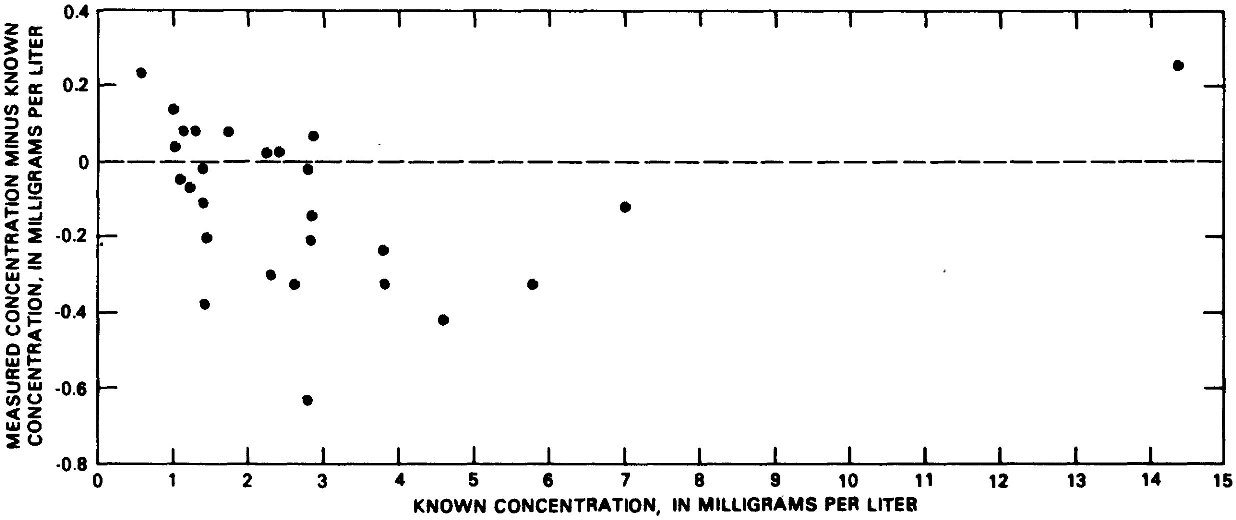

Figure 6.--Degree of bias based on known sulfate concentration in performance-audit samples for 1983.

Table 7.--*Estimated pooled standard deviation and 95-percent confidence limits of the National Atmospheric Deposition Program and National Trends Network-reported analytes for 1983*

[mg/L, milligrams per liter]

Analyte	Concentration range (mg/L)	Pooled standard deviation (mg/L)	95-percent confidence limits of pooled standard deviation (mg/L)
Calcium------------------	0.03 - 7.24	0.08	0.07 - 0.10
Magnesium----------------	.080- 1.54	.03	.03 - .04
Sodium-------------------	.24 - 7.43	.05	.04 - .06
Potassium----------------	.060- 1.87	.01	.01 - .01
Chloride-----------------	.056- 3.87	.04	.03 - .05
Sulfate------------------	.58 -14.40	.13	.11 - .16

Results for January 1980 through September 1984

Performance-audit-sample data for January 1980 through September 1984 are summarized in tables 8 and 9. Median relative percent differences are given because the median appears to give a better description of the bias than the mean. For example, relative-percent differences for calcium ranged from -6.5 percent to 263 percent. Reported concentrations for calcium, magnesium, sodium, chloride, and sulfate were determined to have positive bias.

Comparison of Results for the Two Periods

Analyses of performance-audit samples have been used to estimate the variances of the NADP/NTN-reported analyte concentrations. Variances for calcium, magnesium, sodium, potassium, chloride, and sulfate are given in tables 10 and 11. The variances for each analyte are estimated using a pooling or averaging technique from Dixon and Massey (1969) and Walpole and Myers (1972). The formula used for this estimate is:

$$s_p^2 = \frac{(n_1-1)s_1^2+(n_2-1)s_2^2+\ldots+(n_k-1)s_k^2}{n_1+n_2+\ldots+n_k-k} \qquad (6)$$

where

s_p^2 is the unbiased estimate of the variance for each analyte;

n is the number of times each performance-audit sample was analyzed;

s^2 is the variance for each particular performance-audit sample; and

k is the number of difference performance-audit samples used in the population.

Table 8.--*Median relative-percent difference between the National Atmospheric Deposition Program and National Trends Network-reported analyte concentrations and the known performance-audit-sample concentrations for January 1980 through September 1984*

Analyte	Median relative percent difference	Number of samples
Calcium------------	6.08	135
Magnesium----------	6.42	135
Sodium-------------	5.21	133
Potassium----------	1.00	135
Chloride-----------	10.9	133
Sulfate------------	3.05	133

Table 9.--*Bias determination from comparing the National Atmospheric Deposition Program and National Trends Network-reported analyte concentrations and the known performance-audit-sample concentrations for January 1980 through September 1984*

Analyte	Maximum number of values on the same side of zero	Number of samples	Bias
Calcium--------------	107	135	Positive
Magnesium------------	100	135	Positive
Sodium---------------	94	133	Positive
Potassium------------	73	135	None
Chloride-------------	105	133	Positive
Sulfate--------------	90	133	Positive

Only performance-audit samples that were analyzed three or more times were used to calculate the variance for each analyte. These estimated variances should be valid for natural samples with analytes in the concentration ranges shown in tables 10 and 11. Caution needs to be used if the variances are applied to analyte concentrations beyond the limits of the concentrations tested, because the variances may not be applicable.

Table 10.--*Estimated variance of the National Atmospheric Deposition Program and National Trends Network-reported analyte concentrations for 1983*

Analyte	Concentration range (milligrams per liter)	Estimated variance
Calcium----------------	0.30 - 7.24	0.006
Magnesium--------------	.080- 1.54	.001
Sodium-----------------	.24 - 7.43	.003
Potassium--------------	.060- 1.87	.0002
Chloride---------------	.056- 3.87	.002
Sulfate----------------	.58 -14.40	.018

Table 11.--*Estimated variance of the National Atmospheric Deposition Program and National Trends Network-reported analyte concentrations for January 1980 through September 1984*

Analyte	Concentration range (milligrams per liter)	Estimated variance
Calcium----------------	0.30 - 7.48	0.023
Magnesium--------------	.04 - 2.58	.006
Sodium-----------------	.11 - 7.43	.015
Potassium--------------	.04 - 1.87	.001
Chloride---------------	.06 - 5.80	.012
Sulfate----------------	.58 -15.52	.058

INTERLABORATORY COMPARISON

Four laboratories participated in a continuous interlaboratory comparison study examining laboratory analysis of major chemical constituents detected in precipitation. Laboratories participating in the study were: (1) Inland Waters Directorate, Ontario, Canada (IWD); (2) Illinois State Water Survey, Champaign, Ill. (CAL); U.S. Geological Survey, Atlanta, Ga. (ATL); and (4) U.S. Geological Survey, Denver, Colo. (DEN). The interlaboratory comparison began in November 1982 with ATL, CAL, and DEN participating. IWD joined the study in February 1983. Each laboratory received both natural- and simulated-precipitation samples to be analyzed for dissolved calcium, magnesium, potassium, sodium, ammonium, chloride, nitrate, sulfate, orthophosphate, pH, and specific conductance. Analytical results for calcium, magnesium, potassium, sodium, chloride, nitrate, sulfate, pH, and specific conductance were compared in the study. The stability of ammonium was unknown, and orthophosphate concentration was below the detection limit in most samples.

Experimental Design

Sample Selection and Distribution

Analytical results for both natural- and simulated-precipitation samples were compared. Natural-precipitation samples were selected from those received each week at CAL from the NADP/NTN sampling sites. CAL personnel selected samples using a random-number table (Dixon and Massey, 1969). Selected samples with volumes less than 750 mL were rejected for use as interlaboratory-study samples, and the next suitable sample in sequence was evaluated. This selection process continued until three or four samples with volumes greater than 750 mL were obtained. The chosen samples then were filtered, using a 0.45 μm pore-size organic-membrane filter, and a subsample was retained by CAL and analyzed as required by the NADP/NTN. The remaining sample was split into 10 aliquots using a sample splitter developed by the U.S. Geological Survey. Each aliquot was stored in a deionized-water-rinsed, 125-mL, high-density polyethylene bottle. All aliquots were stored at 4 °C until they were shipped in insulated containers to U.S. Geological Survey personnel responsible for quality assurance in Denver, Colo. The U.S. Geological Survey personnel relabeled the samples, then distributed them in duplicate among the participating laboratories.

Simulated-precipitation samples were prepared by the U.S. Geological Survey personnel. These samples primarily were dilutions of SRWS for which MPV (most-probable value) had been established previously (Malo and others, 1978; and Schroder and others, 1980). Dilutions were made with 2.5-Ω ohm deionized water, and the hydrogen-ion concentration was increased with perchloric acid to a pH between 4.0 and 6.5. Dilution factors were chosen to approximate the concentrations of various analytes normally found in precipitation. Concentrations of analytes in the dilutions were checked by atomic-absorption spectrophotometry and compared with the concentrations calculated for each dilution factor. Prepared dilutions having analyte relative errors greater than ±10 percent were rejected for use as simulated-precipitation samples. Each simulated-precipitation sample was split into 12 identical aliquots and distributed in triplicate to the participating laboratories.

A deionized-water blank was prepared periodically at CAL by passing deionized water through the U.S. Geological Survey sample splitter. The purposes of the blank were to: (1) Determine if the samples were being contaminated by handling and bottling at CAL, and (2) monitor the laboratories for reporting of false positive values. One aliquot of each blank sample was analyzed at a U.S. Geological Survey research laboratory using atomic-absorption spectrophotometry and ion-chromatography. The remaining aliquots were distributed in duplicate to the participating laboratories for analysis.

Laboratory Analysis and Reporting

Because the natural precipitation samples were filtered prior to splitting at CAL, and the simulated-precipitation and deionized water samples required no filtration, the participating laboratories were asked not to filter the samples after receipt. With this exception, all laboratories were requested to receive, process, and analyze the intercomparison samples using their routine precipitation-analysis procedures. The laboratories were requested to receive, process, and analyze the intercomparison samples using their routine precipitation-analysis procedures. The laboratories were aware that the samples received were not normal-precipitation samples, but did not know which type of intercomparison sample they were receiving. The laboratories determined calcium, magnesium, sodium, and potassium by atomic-absorption spectrophotometry, except IWD, which determined sodium and potassium using flame-photometric procedures. All laboratories used colorimetric methods to determine chloride, ammonium, nitrate, sulfate, and orthophosphate. ATL and DEN switched to a turbidimetric method for determining sulfate during the study period. All laboratories determined pH and specific conductance electrometrically. Documentation of the analytical methods and quality assurance practices used by the laboratories are described in the following references: (1) ATL and DEN (Skougstad and others, 1979); (2) CAL (Peden and others, 1979); and (3) IWD (Environment Canada, 1979).

During the study, ion-chromatographic methods for the determination of chloride, sulfate, and nitrate were being developed at ATL, DEN, and IWD. Data generated by these methods were reported, in addition to those data generated by the colorimetric methods in use during this time.

All analyte concentrations were reported in accordance with the individual laboratory's procedures. Individual analyte-detection limits and number of significant figures reported varied from laboratory to laboratory. Concentrations reported as below the limit of detection were considered as missing data and not used in the determination of comparability, bias, and estimated precision.

Interlaboratory-Comparison Results

Results from the analyses of deionized water blanks prepared at CAL are listed in table 12. ATL, DEN, and CAL analyzed duplicates of four blank samples, whereas IWD analyzed duplicates of two of the four blanks. IWD reported the least number of false positive concentrations, reporting concentrations for chloride twice and sulfate once. CAL reported concentrations for sodium, potassium, sulfate, and nitrate. ATL reported concentrations for calcium, magnesium, sodium, potassium, chloride, sulfate, and nitrate. ATL reported a false positive concentration for calcium each of the eight times a blank sample was analyzed. DEN reported a concentration at least once for every analyte checked, and reported a false positive concentration for chloride each of the eight times a blank sample was analyzed. With few exceptions, all reported concentrations were at or near the limit of detection for the laboratory generating the false positive concentrations. For example, the detection limit for calcium at ATL was

Table 12.--*Percentage of false positive concentrations reported by laboratories for the analysis of deionized water blanks*

[ATL, U.S. Geological Survey, Atlanta, Georgia; DEN, U.S. Geological Survey, Denver, Colorado; CAL, Illinois State Water Survey, Champaign, Illinois; IWD, Inland Waters Directorate, Ontario, Canada; n, number of analyses performed]

Analyte	Percentage of analyses of deionized water resulting in a report of a false positive concentration			
	ATL n=8	DEN n=8	CAL n=8	IWD n=4
Calcium----------------	100	62.5	0	0
Magnesium--------------	75	37.5	0	0
Sodium-----------------	62.5	25	75	0
Potassium--------------	75	50	87.5	0
Chloride---------------	75	100	0	50
Sulfate----------------	25	12.5	25	25
Nitrate----------------	0	50	12.5	0

0.01 mg/L. Of the eight values that ATL reported for the eight blank samples, six values were 0.01 mg/L, and two values were 0.20 mg/L. As another example, ATL reported five values of 0.01 mg/L for sodium. The ATL detection limit for sodium also was 0.01 mg/L.

Comparability of results from each of the four laboratories was examined using data from natural-precipitation samples. To facilitate the statistical analysis of these data, only samples for which all four laboratories reported a value for a given analyte were used for comparison of laboratory measurements of that analyte. Laboratories were compared by a two-way analysis of variance. Relations between laboratory results were described by formulating linear-regression models for all possible laboratory pairs for each analyte. The analysis of variance results and linear-regression model parameters were generated using SAS (SAS Institute Inc., 1982), a statistical analysis package available on the U.S. Geological Survey's Amdahl computer. Analysis-of-variance results indicated that laboratory treatment resulted in significantly different means for every analyte examined. To further investigate these differences, Duncan's multiple-range test for means was used. Results from this test are presented in table 13. Laboratories whose analyte means are significantly different at alpha=0.05 have different letters in the column labeled "Group." According to the test results, all six possible laboratory pairs produced significantly different results for calcium, sodium, chloride, sulfate, and nitrate. Test results for magnesium indicated the following pairs of laboratories produced significantly different results for this analyte: ATL and DEN, DEN and IWD, and CAL and IWD. Test results for potassium indicated that DEN and IWD and ATL and IWD produced significantly different results for this analyte. Test results for pH indicated that only DEN and CAL results were not significantly different for this analyte. Test results for specific conductance indicated that ATL and IWD

Table 13.--*Duncan's multiple-range-test results for laboratory means from the analysis of natural-precipitation samples*

[ATL, U.S. Geological Survey, Atlanta, Georgia; DEN, U.S. Geological Survey, Denver, Colorado; CAL, Illinois State Water Survey, Champaign, Illinois; IWD, Inland Waters Directorate, Ontario, Canada; group, Duncan's multiple-range-test grouping of laboratories having different group values, such as A and B, have significantly different means at alpha=0.05; mean, mean of all analyses; n, number of analyses performed; lab, laboratory performing the analyses; µS/cm, microsiemens per centimeter at 25 °Celsius; mg/L, milligrams per liter]

Calcium				Magnesium				Sodium			
Group	Mean (mg/L)	n	Lab	Group	Mean (mg/L)	n	Lab	Group	Mean (mg/L)	n	Lab
A	0.328	28	CAL	A	0.054	47	DEN	A	0.264	49	ATL
B	.302	28	ATL	BA	.051	47	CAL	B	.254	49	CAL
C	.291	28	IWD	BC	.050	47	ATL	C	.241	49	IWD
D	.279	28	DEN	C	.047	47	IWD	D	.187	49	DEN

Potassium				Chloride				Sulfate			
Group	Mean (mg/L)	n	Lab	Group	Mean (mg/L)	n	Lab	Group	Mean (mg/L)	n	Lab
A	0.059	34	DEN	A	0.470	49	DEN	A	1.64	54	IWD
A	.057	34	ATL	B	.435	49	ATL	B	1.60	54	ATL
BA	.054	34	CAL	C	.410	49	CAL	C	1.53	54	DEN
B	.051	34	IWD	D	.390	49	IWD	D	1.46	54	CAL

Nitrate				pH				Specific conductance			
Group	Mean (mg/L)	n	Lab	Group	Mean (mg/L)	n	Lab	Group	Mean (mg/L)	n	Lab
A	0.254	54	CAL	A	5.38	55	ATL	A	14.3	54	ATL
B	.197	54	DEN	B	5.06	55	CAL	BA	13.9	54	DEN
C	.195	54	ATL	B	5.05	55	DEN	BA	13.7	54	CAL
D	.175	54	IWD	C	4.98	55	IWD	B	13.2	54	IWD

Table 14.--*Linear-regression model coefficients for analytes and laboratory pairs analyzing natural-precipitation samples*

[ATL, U.S. Geological Survey, Atlanta, Georgia; DEN, U.S. Geological Survey, Denver, Colorado; CAL, Illinois State Water Survey, Champaign, Illinois; IWD, Inland Waters Directorate, Ontario, Canada; a, slope of regression; b, intercept of regression line; laboratory listed first has results modeled as dependent variable]

	Linear-regression model parameters for laboratory pairs											
	DEN-ATL		DEN-CAL		DEN-IWD		ATL-CAL		ATL-IWD		IWD-CAL	
Analyte	a	b	a	b	a	b	a	b	a	b	a	b
Calcium------------	0.799	0.038	0.894	-0.013	0.918	0.012	1.029	-0.035	1.049	-0.003	0.968	-0.027
Magnesium----------	.789	.014	.850	.010	.869	.013	1.006	-.002	1.030	.002	.959	-.003
Sodium-------------	.834	-.034	.858	-.031	.851	.019	1.026	.004	1.021	.018	.997	-.012
Potassium----------	1.026	.001	1.096	.000	1.171	-.001	1.070	.000	1.121	.000	.914	.002
Chloride-----------	.993	.039	1.004	.059	.979	.088	1.001	.024	.980	.052	.995	-.017
Sulfate------------	.941	.020	1.000	.069	.945	-.024	1.060	.055	.993	-.028	1.007	.173
Nitrate------------	.888	.024	.749	.007	1.032	.016	.820	-.013	1.141	-.004	.712	-.006
pH-----------------	.453	2.612	1.026	-.146	1.016	-.017	.652	2.080	.805	1.367	.961	.120
Specific conductance---------	.864	1.571	1.047	-.429	1.026	.336	.773	3.692	.729	4.627	1.023	-.769

produced significantly different results for this analyte. Linear-regression model parameters for all possible analyte and laboratory pair combinations are presented in table 14. The laboratory listed first in table 14 is modeled as the dependent variable in the regression equation. For example, under the heading DEN-ATL, and in the row labeled calcium, the following relation is described:

$$Y=X\times 0.799+0.038; \tag{7}$$

where Y=DEN calcium results, and
X=ATL calcium results.

Data users interested in data from two or more precipitation sampling networks, generated by different laboratories that are compared in this report, need to decide whether or not to employ the linear-regression model parameters as correction factors between the two different data sets.

Analyte bias for each laboratory was evaluated using data from laboratory analysis of simulated-precipitation samples only. Laboratory-reported analyte concentrations were compared against MPV for analyte concentrations in the simulated-precipitation samples. The pH and specific conductance of the simulated-precipitation samples were measured only once after the addition of perchloric acid; thus, a most-probable analyte concentration for pH and specific conductance was not available. Nitrate was not stable in the simulated-precipitation samples. Only samples for which all four laboratories reported concentrations for a given analyte were used for comparison of laboratory measurements of that analyte. Comparison was by two-way analysis of variance. Analysis of variance results indicated that the laboratory means for all analytes considered were significantly different. Duncan's multiple-range test was used to investigate these differences further. Results of these tests are presented in table 15. A fifth sample-treatment designation (laboratory), MPV, is included in the table. Laboratory analyte means that are significantly different from the MPV mean are judged biased. Using this criterion, DEN analyses of simulated precipitation had bias for calcium, magnesium, sodium, chloride, and sulfate. ATL analyses of simulated precipitation had bias for calcium, magnesium, and potassium. CAL analyses of simulated precipitation had bias for sodium. IWD analyses of simulated precipitation had bias for calcium, magnesium, and sodium. These bias estimates need to be interpreted with caution because analyte concentrations were considerably higher in the simulated-precipitation samples than the concentrations normally encountered in natural precipitation (table 3). The bias estimates presented in table 16 are only valid for samples with analyte concentrations that are similar to the concentrations of the simulated-precipitation samples. The bias estimates may or may not reflect laboratory analyte bias at the lower concentrations often encountered in natural-precipitation samples. This weakness in study design subsequently was corrected.

Ion-chromatographic methods were in development at ATL, DEN, and IWD during the study period. Consequently, data for chloride and sulfate from these three laboratories were produced by two different methods, colorimetry and ion-chromatography. Comparison of the two methods for each of the three laboratories used data from both natural- and simulated-precipitation samples.

Table 15.--*Duncan's multiple-range-test results for laboratory means from the analysis of simulated precipitation samples*

[ATL, U.S. Geological Survey, Atlanta, Georgia; DEN, U.S. Geological Survey, Denver, Colorado; CAL, Illinois State Water Survey, Champaign, Illinois; IWD, Inland Waters Directorate, Ontario, Canada; group, Duncan's multiple-range-test grouping of laboratories having different group values, such as A and B, have significantly different means at alpha=0.05; MPV, most-probable analyte concentrations in the simulated-precipitation samples; mean, mean of all analyses; n, number of analyses performed; lab, laboratory performing the analyses; mg/L, milligrams per liter]

Calcium				Magnesium				Sodium			
Group	Mean (mg/L)	n	Lab	Group	Mean (mg/L)	n	Lab	Group	Mean (mg/L)	n	Lab
A	1.82	37	CAL	A	0.707	37	MPV	A	1.48	44	MPV
A	1.81	37	MPV	A	.705	37	CAL	A	1.48	44	ATL
B	1.78	37	IWD	B	.694	37	ATL	B	1.45	44	IWD
B	1.76	37	ATL	B	.686	37	DEN	C	1.43	44	CAL
C	1.58	37	DEN	C	.594	37	IWD	D	1.23	44	DEN

Potassium				Chloride				Sulfate			
Group	Mean (mg/L)	n	Lab	Group	Mean (mg/L)	n	Lab	Group	Mean (mg/L)	n	Lab
A	0.224	45	ATL	A	0.918	48	DEN	A	4.76	50	DEN
B	.213	45	MPV	BA	.841	48	ATL	B	4.49	50	IWD
B	.207	45	CAL	B	.828	48	MPV	B	4.48	50	CAL
B	.207	45	IWD	B	.824	48	CAL	B	4.44	50	ATL
B	.203	45	DEN	B	.781	48	IWD	B	4.40	50	MPV

Two-way analysis of variance was coupled with Duncan's multiple-range test to produce the desired comparisons. Duncan's multiple-range-test results are presented in table 16. Laboratory means resulting from ion-chromatographic analyses have their associated laboratory name suffixed with the letters "IC." The test results indicate significant differences between colorimetric and ion-chromatographic results for ATL analyses of chloride, DEN analyses of sulfate, and IWD analyses of chloride.

Table 16.--*Duncan's multiple-range-test results for laboratory means from the analysis of anions in natural- and simulated-precipitation samples by colorimetry and ion-chromatography*

[ATL, U.S. Geological Survey, Atlanta, Georgia, analyses performed by colorimetry; DEN, U.S. Geological Survey, Denver, Colorado, analyses performed by colorimetry; IWD, Inland Waters Directorate, Ontario, Canada, analyses performed by colorimetry; ATLIC, analyses performed by ion-chromatography; DENIC, analyses performed by ion-chromatography; IWDIC, analyses performed by ion-chromatography; group, Duncan's multiple-range-test grouping of laboratories having different group values, such as A and B, have significantly different means at alpha=0.05; MPV, most-probable analyte concentrations in the simulated precipitation samples; mean, mean of all analyses; n, number of analyses performed; lab, laboratory performing the analyses; mg/L, milligrams per liter]

Chloride				Sulfate			
Group	Mean (mg/L)	n	Lab and analytical method	Group	Mean (mg/L)	n	Lab and analytical method
A	0.793	82	DEN	A	2.47	116	DEN
A	.791	82	ATL	BA	2.44	116	IWD
A	.778	82	DENIC	BA	2.41	116	ATL
B	.747	82	ATLIC	BAC	2.37	116	IWDIC
B	.746	82	IWDIC	BC	2.35	116	ATLIC
C	.705	82	IWD	C	2.30	116	DENIC

Analyte precisions for each laboratory and analyte were estimated by calculating a pooled variance for each laboratory and analyte. Pooled variances were calculated according to the equation (6). Data used for the calculations were tested for relations between concentration level and standard deviation prior to use. Linear-regression models for the mean concentrations of replicate measurements versus the standard deviations of those measurements were formulated. Regression-model parameters indicated that no significant relations between concentration level and standard deviation existed for any analyte reported by any of the four participating laboratories; thus, pooling was justified. Pooled variances are listed in table 17. As indicated in table 17, CAL results were the least disperse of the four laboratories. In general, IWD results were more disperse than CAL results, and ATL and DEN dispersions were approximately equal and greater than IWD dispersion. Pooled variances for each analyte were compared for all possible laboratory pairs using F-tests at the 5-percent confidence level.

Table 17.--*Laboratory-pooled variances for analytes in precipitation*

[ATL, U.S. Geological Survey, Atlanta, Georgia; DEN, U.S. Geological Survey, Denver, Colorado; CAL, Illinois State Water Survey, Champaign, Illinois; IWD, Inland Waters Directorate, Ontario, Canada; mg^2/L^2, milligrams squared per liter squared]

Analyte	Number of determinations	Laboratory-pooled variance (mg^2/L^2) ATL	CAL	DEN	IWD	Concentration range
Calcium-------	60	0.087	0.016	0.075	0.032	0.31 - 5.4
Magnesium-----	60	.027	.008	.054	.019	.096- 2.93
Potassium-----	60	.051	.003	.054	.007	.048- .92
Sodium--------	60	.045	.021	.098	.045	.14 - 5.80
Chloride------	60	.049	.025	.089	.049	.09 - 8.80
Sulfate-------	60	.132	.062	.58	.34	.67 - 23
pH------------	60	.084	.007	.011	.044	4.7 - 7.7
Specific conductance-	60	2.15	.28	1.03	.89	5.4 - 98

F-tests evaluate a null hypothesis that no significant difference exists between the variances of two sets of laboratory measurements of identical samples. Results of F-test analyses are summarized in table 18. No significant difference at the 5-percent confidence level was demonstrated for ATL and DEN variances for calcium and potassium, for DEN and CAL variances for pH, for DEN and IWD variances for specific conductance, and for ATL and IWD variances for sodium and chloride. At the 5-percent confidence level, the remaining differences in analyte variances were determined to be significant.

SUMMARY AND CONCLUSIONS

The goal of the quality-assurance program of the NADP/NTN is to produce sufficient information and data to reduce or eliminate the uncertainties in a long-term wet-deposition monitoring data base. The quality-assurance program for the NADP/NTN is expected to operate concurrently with precipitation sampling and analysis. The quality-assurance program has divided the wet-deposition monitoring into five components: (1) Sampling-site selection, (2) sampling device, (3) determination of pH and specific conductance at sampling sites, (4) sample handling, and (5) laboratory analysis. This report summarizes results from all five components of the quality-assurance program.

Sampling-site selection criteria were developed by the NADP and Federal Interagency Task Group on monitoring. All NADP/NTN sites were audited by an auditing team from the U.S. Military Academy. Results from a comparison

Table 18.--*F-test analyses of pooled variances for laboratory pairs*

[ATL, U.S. Geological Survey, Atlanta, Georgia; DEN, U.S. Geological Survey, Denver, Colorado; CAL, Illinois State Water Survey, Champaign, Illinois; IWD, Inland Waters Directorate, Ontario, Canada; F, test value; null, accept or reject null hypothesis]

	F-test results for pairs of laboratory variances											
	DEN-ATL		DEN-CAL		DEN-IWD		ATL-CAL		ATL-IWD		IWD-CAL	
Analyte	F	Null	F	Null	F	Null	F	Null	F	Null	F	Null
Calcium----------------	1.16	Accept	4.69	Reject	2.34	Reject	5.44	Reject	2.72	Reject	2.00	Reject
Magnesium-------------	2.00	Reject	6.75	Reject	2.84	Reject	3.38	Reject	1.42	Accept	2.38	Reject
Potassium-------------	1.06	Accept	18.0	Reject	7.71	Reject	17.0	Reject	7.29	Reject	2.33	Reject
Sodium-----------------	2.18	Reject	4.67	Reject	2.18	Reject	2.14	Reject	1.00	Accept	2.14	Reject
Chloride---------------	1.82	Reject	3.56	Reject	1.82	Reject	1.96	Reject	1.00	Accept	1.96	Reject
Nitrate----------------	1.18	Accept	5.50	Reject	5.50	Reject	4.67	Reject	4.67	Reject	1.00	Accept
Sulfate----------------	4.39	Reject	9.36	Reject	1.71	Reject	2.13	Reject	2.58	Reject	5.48	Reject
pH--------------------	7.63	Reject	1.58	Accept	4.00	Reject	12.0	Reject	1.91	Reject	6.29	Reject
Specific con- ductance------------	2.09	Reject	3.68	Reject	1.16	Accept	7.68	Reject	2.42	Reject	3.18	Reject

study of 10 Aerochem Metrics deposition collectors indicated that collection efficiency is not a function of the distance between sampler and rain gage; evaporation losses from the collector were not significant; and pH and specific conductance data virtually were uniform among the collectors.

Results from the five intersite comparison studies for site-operator determination of pH and specific conductance were used to estimate the precision of the NADP/NTN monitoring-network site-operator analysis. The estimated standard deviation for site-operator determination of pH is 0.25 for samples with a pH range from 3.7 to 4.6. Estimated standard deviation for site-operator determination of specific conductance is 4.6 µS/cm for samples having a specific-conductance range from 10 to 59 µS/cm. The precision estimates are for sampling-site analytical results from October 1981 through November 1983. These precision estimates may be valid for NADP/NTN sampling-site analytical results obtained during 1984.

Each intersite-comparison mean for pH and specific conductance was tested for bias at the 95-percent confidence level. The bias was significant for the October 1981 and May and November 1983 studies. The magnitude of the pH bias was small but always positive; specific-conductance bias was not consistent.

Performance-audit samples were used to assess the bias of the concentrations of calcium, magnesium, sodium, potassium, chloride, and sulfate reported by NADP/NTN for 1983 and for January 1980 through September 1984. Bias was tested at 1-percent probability. Calcium, magnesium, sodium, and chloride results were biased for both time periods. Sulfate results were determined to be unbiased for 1983 but biased for January 1980 through September 1984. Potassium results were determined to be unbiased for both time periods.

Median relative-percent differences were determined for calcium, magnesium, sodium, potassium, chloride, and sulfate. Median values are reported because the median gives a better description of the bias than does the mean. The median relative-percent differences were calcium, 17.0; magnesium, 6.4; sodium, 10.8; potassium, 6.4; chloride, 17.2; and sulfate, -5.3. These relative-percent differences need to be considered before user-analysis of the 1983 data.

Estimated variances were determined for the six analytes reported by the NADP/NTN for January 1980 through September 1984; they can be used to estimate the precision of these data. Estimated pooled standard deviations and 95-percent confidence limits for calcium, magnesium, sodium, potassium, chloride, and sulfate are reported for calendar year 1983.

All estimates of the variances and relative-percent differences for the six analytes (calcium, magnesium, sodium, potassium, chloride, and sulfate) reported by the NADP/NTN are based on performance-audit sample results. All performance-audit samples were submitted to CAL through NADP/NTN field-sampling sites. These data are valid for the concentration ranges monitored by the performance-audit samples; however, these data may not be valid if applied to natural-precipitation-sample concentrations beyond the concentration limits tested.

Four laboratories analyzed identical natural- and simulated-precipitation samples from November 1982 through August 1983. Analyte results compared were those for calcium, magnesium, sodium, potassium, chloride, sulfate, nitrate, pH, and specific conductance. Analytical results were interpreted to provide measures of interlaboratory comparability, possible analyte bias, and estimated precision for each laboratory. Interlaboratory comparibility was evaluated using results of laboratory analyses of natural-precipitation samples. Analysis of variance, Duncan's multiple-range test for means, and linear-regression model parameters were used to test for significant differences between laboratory means, and to describe those differences mathematically. Thirty-one of the 54 possible analyte and laboratory-pair combinations were significantly different at alpha=0.05. Analyte bias for each laboratory was evaluated using the most probable value of simulated-precipitation samples. Analysis of variance and Duncan's multiple-range test were used to compare laboratory analyte means versus most-probable analyte-concentration means. Test results for the simulated-precipitation analyses indicated bias for CAL analyses of sodium; IWD analyses of calcium, magnesium, and sodium; ATL analyses of calcium, magnesium, and potassium; and DEN analyses of calcium, magnesium, sodium, chloride, and sulfate. Bias estimates are valid only within the analyte-concentration ranges of the simulated-precipitation samples, which are greater than the concentrations determined in natural precipitation. Ion-chromatographic methods being developed at ATL, DEN, and IWD for the measurement of chloride, nitrate, and sulfate were compared with colorimetric methods in use at these laboratories during the same time. Four of the nine possible sets of colorimetric versus ion-chromatographic data pairings were significantly different at alpha=0.05. Analyte precision was estimated using pooled variances. In general, CAL achieved greater precision than IWD, and IWD achieved greater precision than ATL and DEN.

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