RESULTS OF EXTERNAL QUALITY-ASSURANCE PROGRAM FOR THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM AND NATIONAL TRENDS NETWORK DURING 1985

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CONVERSION FACTORS

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

Multiply Metric unit	*By*	*To obtain inch-pound unit*
liter (L)	1.0567	quart, liquid
milliliter (mL)	0.03381	ounce, fluid
micrometer (μm)	3.937×10^{-5}	inch

Other units and abbreviations used in this report are: megaohm (MΩ), microliter (μL), microgram (μg), microsiemens per centimeter at 25 degrees Celsius (μS/cm), microequivalents per liter (μeq/L), and milligram per liter (mg/L).

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ABSTRACT

External quality-assurance monitoring of the National Atmospheric Deposition Program (NADP) and National Trends Network (NTN) was performed by the U.S. Geological Survey during 1985. The monitoring consisted of three primary programs: (1) An intersite comparison program designed to assess the precision and accuracy of onsite pH and specific-conductance measurements made by NADP and NTN site operators; (2) a blind-audit sample program designed to assess the effect of routine field handling on the precision and bias of NADP and NTN wet-deposition data; and (3) an interlaboratory comparison program designed to compare analytical data from the laboratory processing NADP and NTN samples with data produced by other laboratories routinely analyzing wet-deposition samples and to provide estimates of individual laboratory precision.

An average of 94 percent of the site operators participated in the four voluntary intersite comparisons during 1985. A larger percentage of participating site operators met the accuracy goal for specific-conductance measurements (average, 87 percent) than for pH measurements (average, 67 percent). Overall precision was dependent on the actual specific conductance of the test solution and independent of the pH of the test solution. Data for the blind-audit sample program indicated slight positive biases resulting from routine field handling for all analytes except specific conductance. These biases were not large enough to be significant for most data users. Data for the blind-audit sample program also indicated that decreases in hydrogen-ion concentration were accompanied by decreases in specific conductance. Precision estimates derived from the blind-audit sample program indicate that the major source of uncertainty in wet-deposition data is the routine field handling that each wet-deposition sample receives. Results of the interlaboratory comparison program were similar to results of previous years' evaluations indicating that the participating laboratories produced comparable data when they analyzed identical wet-deposition samples and that the laboratory processing NADP and NTN samples achieved the best analyte precision of the participating laboratories.

INTRODUCTION

The National Atmospheric Deposition Program (NADP) and National Trends Network (NTN) operated about 190 wet-deposition collection sites in 47 States and two territories during 1985. Each site operator collected weekly composite wet-deposition samples using standardized procedures; the collected samples were submitted to a central analytical laboratory (Illinois State Water Survey, Champaign, Illinois) for chemical analysis. Data from the chemical analyses performed on these wet-deposition samples will be used to assess long-term trends in the chemical quality of wet deposition that occurs in the United States. In order for researchers to detect and analyze any trends within these data, the data must have associated with them some numerical estimates of their quality. The U.S. Geological Survey is providing external quality-assurance monitoring for the NADP and NTN (Schroder and Malo, 1984) to partially satisfy the requirement of the NADP and NTN for quality-assurance information. Three separate programs were managed and operated by the U.S. Geological Survey during 1985. An intersite comparison program quantified the accuracy of onsite pH and specific-conductance measurements made by NADP/NTN site operators. A blind-audit sample program was used to estimate the analyte bias introduced by routine field-handling procedures. An interlaboratory comparison program provided information on the precision of the central analytical laboratory's results, and on the comparability of those results to results produced by other laboratories measuring constituents in wet deposition. The purpose of this report is to document the quality of NADP/NTN data using information from the three different external quality-assurance programs.

INTERSITE COMPARISON PROGRAM

The intersite comparison program was designed as a periodic check on the accuracy of onsite pH and specific-conductance measurements performed by each NADP/NTN site operator and as a means of estimating the precision of onsite measurements. Participation in the program was voluntary, and every operator of an active site was given the chance to participate in each comparison. Details of the program design and assessments of the quality of onsite pH and specific-conductance data have been reported for previous years (Schroder and Brennan, 1984; Schroder and others, 1986).

Four times during 1985 (January, April, July, and October) each operator of an active site was mailed a 125-mL bottle containing a solution of dilute nitric acid. The site operator was instructed to measure the pH and specific conductance of the solution using routine procedures for onsite measurements. The site operator was asked to return the results of his or her measurements, with any unused solution remaining in the bottle, to the U.S. Geological Survey. Participating site operators received reports from the U.S. Geological Survey after each mailing detailing their measurement accuracy and suggesting corrective action when appropriate. The site operators were aware that they were participating in an external quality-assurance audit, but they did not know the pH or specific-conductance values for the solutions.

The U.S. Geological Survey reanalyzed the contents of returned sample bottles when the pH or specific-conductance values reported for the bottle were outside of preselected limits. Those limits generally were the mean reported value ±1.5 standard deviations. Reanalysis was performed to confirm that a reported value was different from the known value because of site operator error or instrument malfunction and not because of sample contamination. One or more outlying values generally had to be removed from the data set prior to the calculation of the mean and standard deviation. Suitable statistical tests for outlier rejection were not available because of the large number of observations (greater than 160) in each data set. In most cases, outlier rejection was trivial (a specific-conductance value of 550 µS/cm, when the mean was 9.8 µS/cm is an example), and outliers were rejected by inspection.

The U.S. Geological Survey compiled the individual site-operator results for each intersite comparison mailing to establish the known values for pH and specific conductance contained in each solution. Even though target values for each analyte were established prior to the preparation of each sample and even though the resulting solution pH and specific-conductance values were measured by the U.S. Geological Survey and compared to the target values, the median of the 160+ measurements provided by site operators was considered a better estimate of the true pH and specific-conductance values of the solution. The median was chosen because of its resistance to the influence of outlying or spurious data points (Hoaglin and others, 1983). Consequently, individual site-operator results were compared to the overall reported median value to establish whether or not a site operator met goals for accuracy of onsite pH and specific-conductance determinations.

Results for the four intersite comparisons conducted during 1985 are summarized in table 1; the table lists the percentage of operators of active sites that participated in each comparison, the number of values reported for each analyte, the percentage of measured values that met accuracy goals, the minimum and maximum reported values, and various percentile rankings for each analyte including the 50th percentile (median). All statistics in the table were calculated from the full data set for each mailing without any outlying values being removed; they also include a few responses from site operators that were received after the initial summary statistics had been calculated and reported back to the participating operators.

The percentage of operators of active sites that voluntarily participated in each comparison was relatively constant throughout the year. These percentages indicate that a maximum of 20 operators of active sites (October) chose not to participate during each comparison. These percentages were calculated based upon the number of site operators that responded in any way (for example, if the site operator responded by informing the U.S. Geological Survey that he or she was unable to make the requested measurements because of instrument problems, the site operator was counted as a participant in that particular comparison).

The goals for onsite-measurement accuracy were actual pH value ±0.1 pH unit and actual specific-conductance value ±4 µS/cm (National Atmospheric Deposition Program, 1984). The percentage of participating site operators that met those goals is listed in table 1 for each analyte and intersite comparison mailing. For each mailing, a larger percentage of sites met the goal for specific-conductance-measurement accuracy than met the goal for pH-measurement accuracy. Because the goals were not distribution dependent, the magnitude of the median specific-conductance value for each comparison mailing affected the percentage of site operators that met the accuracy goals. The April comparison had the largest median specific-conductance value and the smallest percentage of site operators that met the accuracy goal; the July comparison had the smallest median specific-conductance value and the largest percentage of site operators that met the accuracy goal. The magnitude of the median pH value in each comparison mailing did not result in the same type of effect.

Table 1.--*Summary statistics for intersite comparison mailings during 1985*

[N, number of results summarized]

Date	Response (percent)	Analyte	N	Accuracy goal met (percent)	Minimum	Percentile					Maximum
						10th	25th	50th (median)	75th	90th	
January	94	pH	163	65	3.97	4.37	4.46	4.55	4.60	4.71	6.60
		Specific conductance	164	90	.9	8.6	10.4	11.4	12.4	13.6	92.5
April	92	pH	161	67	3.39	3.94	4.08	4.13	4.18	4.25	6.30
		Specific conductance	161	70	2.7	24.3	27.1	30.0	31.7	33.3	45.0
July	97	pH	170	64	3.61	4.60	4.71	4.80	4.86	5.00	7.50
		Specific conductance	170	95	.6	5.0	5.8	6.6	7.1	8.2	64.0
October	90	pH	164	73	3.65	4.47	4.55	4.61	4.67	4.75	8.10
		Specific conductance	165	93	.9	7.7	8.9	9.8	10.5	11.2	550

Median values from all the site-operator measurements were considered the best estimates of the true pH or specific-conductance values for the intersite comparison solutions. Percentile rankings for each comparison mailing indicate that a majority of the participating site operators measured values that were similar to the median values. The largest difference between the 10th- and 90th-percentile pH values was 0.40 pH unit (July); the largest difference between the 10th- and 90th-percentile specific-conductance values was 9.0 µS/cm (April). The percentile rankings indicate a high degree of accuracy in onsite pH and specific-conductance determinations for at least 80 percent of the site operators that participated in the intersite comparison program during 1985.

BLIND-AUDIT SAMPLE PROGRAM

The blind-audit sample program was designed to provide estimates of analyte bias and precision that resulted from routine field operations. Known-concentration reference samples were submitted to the central analytical laboratory by network site operators. The site operators disguised the reference samples as actual wet-deposition samples; the laboratory staff analyzing the sample did not know that it was an external audit sample, and they also did not know the chemical composition of the sample. Details of program design and interpretations of program results for previous years have been published (Schroder and others, 1985; Brooks and others, 1987a).

Four types of sample matrices were used as blind-audit samples during 1985. The majority of blind-audit samples were dilutions of standard reference water samples (SRWS). SRWS were prepared from natural surface water by the U.S. Geological Survey for use in their laboratory quality-assurance program (Janzer, 1985). Because the analyte concentrations in the SRWS were substantially larger than the analyte concentrations normally encountered in wet-deposition samples, the SRWS were diluted prior to their use as blind-audit samples. Analyte concentrations in the diluted SRWS were measured by the U.S. Geological Survey to confirm that a proper dilution had been made. Measured analyte concentrations were subjected to an error analysis to determine if the diluted SRWS would be suitable for use as a known-concentration, blind-audit sample. The error-analysis calculation used the estimated error associated with the most probable value analyte concentrations (expressed as relative standard deviation) for the SRWS in question, the estimated error associated with pipetting, and the estimated analytical error of the U.S Geological Survey analysis. Diluted SRWS failing to meet the acceptability criteria set forth by the error analysis were rejected for use as blind-audit samples. Diluted SRWS that met the acceptability criteria were acidified with a small volume of perchloric acid (1-5 μL) to decrease the pH to a realistic value (pH 3.5 to 5.0). Five blind-audit samples were dilutions of National Bureau of Standards' simulated-precipitation reference material 920000 (Deardoff and others, 1980). The dilution and verification procedures followed for these blind-audit samples were identical to those followed for the SRWS blind-audit samples. Two types of blank solutions were also used during 1985; one was ultrapure (>17.6 MΩ) deionized water, and the second was dilute nitric acid. The deionized-water samples were prepared by the U.S. Geological Survey; the dilute nitric acid was prepared by the central analytical laboratory (CAL). This solution, which had a pH of 4.30 ± 0.10 pH units, normally was used as a pH-calibration-check solution by the site operators.

Blind-audit samples were submitted to the CAL by site operators when their site received no measurable wet deposition during a weekly sampling period. A part (about 2/3) of the blind-audit sample was poured into a clean sampling container (a 13-L polyethylene bucket), routine onsite measurements of the bucket contents were made and recorded, and the bucket was sealed and shipped to the CAL for analysis. Fictitious site-operation information was recorded on the field-observer report form that accompanied the simulated wet-deposition sample to the CAL, so that when the sample container arrived at the laboratory it appeared to be a normal wet-deposition sample. These blind-audit samples are referred to throughout the rest of this report as bucket samples, because they were in contact with the sampling bucket and they received the same treatment that all routine wet-deposition samples receive.

The remaining part (about 1/3) of the blind-audit sample was left in the original bottle by the participating site operator and mailed back to the U.S. Geological Survey. This aliquot then was forwarded to the CAL data section by the U.S. Geological Survey. Personnel in the CAL data section submitted the aliquot to the analytical services section for chemical analysis. The two laboratory sections operated independently; thus, this sample analysis could be considered a single blind-audit sample. These samples will be referred to throughout the remainder of this report as bottle samples, because they were the part of each blind-audit sample remaining in the original sample bottle. The bottle-sample analysis was performed to provide a check on the known concentrations in the blind-audit samples. Assuming that no sample degradation occurred between the time that the site operator poured 2/3 of the blind-audit sample contents into a clean sampling bucket and the time that the 1/3 remaining in the sample bottle was analyzed, the measured bucket-sample and bottle-sample concentrations can be compared directly to estimate analyte bias resulting from routine field-handling activities. Janzer (1985) indicates that analyte concentrations in the SRWS are stable for at least 3 years. The maximum time between bucket-sample and bottle-sample analyses of blind-audit samples during 1985 was 159 days.

The temporal distribution of blind-audit sample submissions during 1985 was more ideal than in previous years (Brooks and others, 1987a). Blind-audit samples were submitted to the CAL during 33 of the 52 possible Tuesday-to-Tuesday sampling periods that occurred during 1985. Sample submissions were reasonably well spaced throughout 1985 (a large percentage of the samples were not submitted during any short time period), and summary statistics generated from these samples should represent the analyte precision and bias associated with field-handling activities throughout 1985. Summary statistics of bucket-sample and bottle-sample analyses of blind-audit samples and of known concentrations in the blind-audit samples are listed in table 2. Only blind-audit samples that had both measured bucket and measured bottle concentrations were used to generate the summary statistics in table 2. Known values for ammonium were not available for the sample matrices used; thus, table 2 only lists the summary statistics for bucket-sample and bottle-sample analyses of this analyte. Because the majority of the blind-audit samples were diluted SRWS that had been acidified with perchloric acid, the pH and specific-conductance values were no longer known and table 2 only summarizes bucket-sample and bottle-sample results for these analytes. Only two blind-audit samples had measurable concentrations of orthophosphate, and this analyte is not included in the table. Excluding the 75th-percentile sulfate concentration, the 50th-percentile nitrate concentration, ammonium, pH, and specific conductance, the percentile rankings for all analyte concentrations were largest for the bucket samples. Differences in percentile concentrations between measured bottle-sample concentrations and known concentrations did not follow such a definite pattern, but the majority of the bottle-sample percentile concentrations were larger than the corresponding known percentile concentrations. An overall relation that can be inferred from data in the table is that measured bucket-sample concentrations were greater than measured bottle-sample concentrations and known concentrations in a majority of cases and that measured bottle-sample concentrations were commonly greater than known concentrations. For ammonium, pH, and specific conductance, the relations that can be inferred are that bucket-sample ammonium and pH values exceeded bottle-sample ammonium and pH values, while bucket-sample specific-conductance values were smaller than bottle-sample specific-conductance values.

Table 2.--*Percentile rankings for measured bucket-sample concentrations, measured bottle-sample concentrations, and known concentrations in blind-audit samples during 1985*

[--, no known concentrations; all concentrations in milligrams per liter except pH (units) and specific conductance (microsiemens per centimeter at 25 degrees Celsius]

Analyte	Number of samples	Bucket-sample concentrations			Bottle-sample concentrations			Known concentrations		
		Percentile			Percentile			Percentile		
		25th	50th	75th	25th	50th	75th	25th	50th	75th
Calcium	71	0.236	0.450	0.765	0.135	0.390	0.716	0.039	0.347	0.715
Magnesium	72	.071	.136	.282	.021	.099	.251	.010	.098	.256
Sodium	74	.121	.224	.553	.100	.178	.520	.081	.140	.531
Potassium	60	.050	.090	.146	.037	.069	.141	.038	.056	.137
Sulfate	60	.72	1.29	2.08	.67	1.28	2.01	.72	1.22	2.20
Chloride	61	.16	.38	.85	.10	.34	.75	.11	.25	.52
Nitrate	46	.19	.51	1.28	.18	.55	1.20	.16	.47	1.07
Ammonium	6	.15	.23	.34	.10	.15	.26	--	--	--
pH	73	4.06	4.32	4.61	4.04	4.22	4.38	--	--	--
Specific conductance	74	19.3	34.5	50.4	22.1	39.0	52.7	--	--	--

Ideally there should have been better agreement between the measured bottle-sample concentrations and the known concentrations than those indicated in table 2. The diluted SRWS were analyzed by the U.S. Geological Survey and the results of the analyses were subjected to an error analysis that allowed for different sources of uncertainty in the known concentrations; therefore, the measured bottle-sample concentrations did not have to match the known concentrations exactly in order to be used as blind-audit samples. However, the error-analysis procedure likely would produce an equal number of blind-audit samples with bottle-sample analyte concentrations less than the known analyte concentrations as blind-audit samples with bottle-sample analyte concentrations larger than the known analyte concentrations. Results in table 2 indicate that this did not occur and that a majority of the measured bottle-sample analyte concentrations were larger than the known-analyte concentrations. This result indicates that there was some type of systematic error associated either with preparation of the samples by the U.S. Geological Survey, measurement of the bottle-sample concentrations by the CAL, or stability of the diluted samples after preparation. No data exist to indicate which of the above possibilities or which combination of these possibilities resulted in the situation indicated by the data in table 2. Sample instability is the least likely explanation (Janzer, 1985). Because the bottle-sample-analyte concentrations did not compare well with the known concentrations, the best possible assessment of analyte bias resulting from routine field handling comes from a comparison of the measured bucket-sample and bottle-sample concentrations. This assessment effectively eliminates laboratory analyte bias and precision considerations from the data interpretation, because both sets of measurements were performed by the same laboratory (CAL) within an acceptable period of time.

The pH and specific-conductance differences shown in table 2 were examined further because the paired analyses provide information on the relative merits of using onsite versus laboratory pH and specific-conductance values. Most discussion of differences between onsite and laboratory values has centered on changes in sample composition that occur between the time that a sample is removed from the collector and the time that the laboratory makes its pH and specific-conductance measurements. Another possibility is that sample changes occur before the site operator makes onsite pH and specific-conductance measurements as a result of sample contact with the sampling container. In either case, the data summarized in table 2 provide an estimate of the magnitude of such changes. For the 73 paired bucket-sample and bottle-sample analyses of pH, 71 blind-audit samples had a decrease in hydrogen-ion concentration (increase in pH) after contact with the sampling bucket and routine field handling. The median hydrogen-ion concentration change was 10.5 μeq/L; the median pH change was 0.10 pH unit. In all cases, the quantity of hydrogen ion lost from the blind-audit sample was exceeded by the quantity of other cations gained by the blind-audit sample. Simple cation exchange occurring on the bucket surface could account for all of the hydrogen-ion loss in the blind-audit samples, but it could not account for the entire quantity of other cations being added to the blind-audit samples. Not surprisingly, because the hydrogen ion accounts for a substantial part of the specific conductance of wet-deposition samples, the specific-conductance values of the blind-audit samples decreased in 65 out of 74 instances. The median change in specific conductance was -3.6 μS/cm.

Results of a data analysis performed using the paired bucket-sample and bottle-sample analyses are listed in table 3. Analyte-concentration differences between the two analyses were converted to analyte masses by multiplying the calculated concentration differences between bucket-sample and bottle-sample analyses by the bucket-sample volume. This conversion was performed to normalize the data with respect to variations in the volume of blind-audit sample that was poured into the clean bucket by the site operator. Consequently, the values listed in table 3 are in micrograms per bucket. Positive masses indicate that analyte mass was added to the blind-audit sample by routine field handling, while negative masses indicate that analyte mass was lost from the blind-audit sample. The number of paired bucket-sample and bottle-sample analyses that are summarized; the minimum, 25th-, 50th-, and 75th-percentile, and maximum masses; and the number of positive masses are given in the table. For every analyte, the minimum calculated mass was negative; however, the majority of masses were positive for each analyte. This indicates that analyte mass was added to a majority of the blind-audit samples by routine field handling; this result also implies that similar masses were added to all NADP/NTN wet-deposition samples during 1985. Median masses were always less than 10 μg/bucket; for most weekly composite wet-deposition samples, these added masses would not markedly change the measured analyte concentrations of the wet-deposition sample. Masses of this magnitude should only be of concern for the weekly composite samples that had small volumes. As an example, consider the 25th-percentile wet-deposition sample volume for all NADP/NTN samples collected during 1985, which was 342 mL. Taking the median calcium mass of 8.2 μg/bucket from table 3 as being representative of the field-handling effect for all NADP/NTN samples during 1985, it can be determined that 25 percent of the wet-deposition samples collected during 1985 had an increase in calcium concentration of at least 0.024 mg/L. Larger volume samples, in this example 75 percent of the network's wet-deposition samples, would have had smaller calcium-concentration increases as a result of their contact with the sampling bucket and routine field handling. Similar calculations performed for all the other analytes listed in table 3 indicate that the magnitude of bias indicated by the blind-audit sample program data for wet-deposition samples collected by NADP/NTN during 1985 is small, and most likely insignificant, for most data users.

Table 3.--*Percentile rankings for calculated changes in analyte mass in blind-audit samples subjected to routine field handling during 1985*

[N,number of paired bucket and bottle samples; all masses in micrograms per bucket]

Analyte	N	Minimum	Percentile 25th	Percentile 50th	Percentile 75th	Maximum	Number of positive masses
Calcium	71	-178	4.2	8.2	15	123	60
Magnesium	72	-76	2.6	5.0	8.3	67	69
Sodium	74	-101	1.2	4.8	12	76	64
Potassium	60	-22	.1	1.9	4.6	23	45
Sulfate	60	-747	-3.1	5.9	21	132	38
Chloride	61	-21	.0	4.6	15	80	45
Nitrate	46	-233	-41	1.4	8.8	164	24
Ammonium	6	-11	-1.7	4.6	23	47	5

Blind-audit samples were prepared in batches and distributed quarterly during 1985. Batches were split into aliquots that became individual blind-audit samples. Consequently, many blind-audit samples analyzed during the year were replicates; they may be used to estimate analyte precision resulting from routine field handling. Differing quantities of perchloric acid were added to the aliquots from a single batch; thus, pH and specific-conductance results do not lend themselves to precision estimates calculated from the replicate analyses. Fifteen blind-audit sample matrices were distributed and analyzed in groups of 3, 4, or 5 to produce the data summarized in table 4. The estimates were calculated by pooling the standard deviations from individual sets of replicate analyses of bucket samples. Estimated standard deviations, the concentration ranges for each estimate, and the degrees of freedom associated with each estimate are presented in table 4 for all analytes except pH and specific conductance. Estimated standard deviations listed in table 4 are much larger than the single-operator precision values reported by the CAL for laboratory analyses (Peden, 1986) and the precision estimates obtained by the U.S. Geological Survey (Brooks and others, 1985; Brooks and others, 1987b; and elsewhere in this report). This increase suggests that the largest degree of uncertainty in NADP/NTN wet-deposition data can be traced to routine field operations and that the uncertainty introduced by laboratory analysis is smaller and less significant in comparison.

Table 4.--*Estimated analyte precision based on replicate analyses of blind-audit samples during 1985*

[mg/L, milligrams per liter]

Analyte	Range (mg/L)	Estimated standard deviation (mg/L)	Degrees of freedom
Calcium	0.011 - 6.20	0.142	40
Magnesium	.004 - 2.30	.066	40
Sodium	.007 - 3.11	.070	40
Potassium	.004 - .470	.005	40
Sulfate	.04 -18.7	.118	40
Chloride	.04 - 2.20	.073	37
Nitrate	.05 - 3.33	.135	37
Ammonium	.02 - .28	.062	11
Orthophosphate	.007 - .030	.019	7

INTERLABORATORY COMPARISON PROGRAM

The interlaboratory comparison program was designed to provide estimates of the CAL analytical precision and bias and estimates of the comparability of CAL analytical results to results produced by other laboratories measuring the chemical constituents of wet-deposition samples. Participating laboratories analyzed identical natural wet-deposition samples and their results were compared. Program results from previous years have been reported (Brooks and others, 1985; Brooks and others, 1987b).

Four laboratories participated in the program during 1985: (1) U.S. Geological Survey national water-quality laboratories in Atlanta, Georgia (ATL), and Denver, Colorado (DEN); (2) Illinois State Water Survey central analytical laboratory (CAL); and (3) Inland Waters Directorate water quality laboratory in Burlington, Ontario, Canada (IWD). The program operated throughout 1985; however, two new laboratories were added, and a new sample-distribution procedure mandated by the NADP/NTN was implemented in November. ATL was consolidated with DEN in 1985 and did not analyze any interlaboratory comparison samples after September. Consequently, the four laboratories (ATL, CAL, DEN, and IWD) are compared using the data they produced from the analysis of interlaboratory comparison samples during the first 9 months of 1985.

Participating laboratories analyzed aliquots of natural wet-deposition samples collected by the NADP/NTN. Natural wet-deposition samples received at the CAL with volumes of 750 mL or greater were eligible for use as interlaboratory comparison samples. As reported previously (Brooks and others, 1987b), this method of sample selection eliminated between 25 and 50 percent of the total wet-deposition samples collected by the NADP/NTN from use as interlaboratory comparison samples. Implications of this method of sample selection have been discussed by Brooks and others (1987b). Wet-deposition samples of sufficient volume were chosen at random by the CAL staff. The sample was split into 10 aliquots, using a decasplitter; the maximum aliquot volume obtained was 125 mL. All 10 aliquots were chilled and shipped in insulated containers to the U.S. Geological Survey in Denver, Colorado, where they were relabelled and shipped in to the participating laboratories. Each participating laboratory analyzed 2 of the 10 aliquots that were split from the original wet-deposition sample.

Summary statistics for all analyses of the interlaboratory comparison samples by the four laboratories are listed in table 5. Percentile-concentration rankings are similar for all four laboratories. The agreement between the percentile rankings in table 5 indicates that the four laboratories produce similar results when they analyze identical wet-deposition samples.

Minor differences between laboratory results were tested using analysis of variance (ANOVA). The ANOVA model was a randomized complete block design. Laboratories were the treatments and the analyte-response variable was partitioned into four concentration ranges to increase the efficiency of the model. This concentration-range variable was used as the model blocking factor. The model tested the null hypothesis that no significant differences existed between the mean analyte concentrations reported by each of the four laboratories. Significant differences between mean values ($\alpha = 0.05$) were detected for calcium, ammonium, pH, and specific conductance. These differences were examined further by calculating least-significant differences. The least-significant-difference values indicated that DEN calcium results were significantly different from the other three laboratories' calcium results and that only ATL and CAL ammonium and pH results were not significantly different from each other. Means separated using the least-significant difference differed by maximum values of 0.02 mg/L for calcium, 0.04 mg/L for ammonium, and 0.11 unit for pH. The largest difference in specific-conductance values was 2.2 μS/cm. Even though statistically significant differences were determined, the magnitude of those differences was small, and the actual relevance of the differences is probably minimal for most data users.

Interlaboratory comparison samples were sent to each laboratory in duplicate. The participating laboratory did not know which two samples were duplicate aliquots of the original wet-deposition sample; therefore, the duplicate analyses may be used to estimate analyte precision achieved by each

Table 5.--*Percentile rankings for individual labortory analyses of interlaboratory comparison samples during 1985*

[ATL, U.S. Geological Survey national water-quality laboratory, Atlanta, Georgia; CAL, Illinois State Water Survey central analytical laboratory, Champaign, Illinois; DEN, U.S. Geological Survey national water-quality laboratory, Denver, Colorado; IWD, Inland Waters Directorate national water-quality laboratory, Burlington, Ontario, Canada; N, number of samples; all values in milligrams per liter except pH (units) and specific conductance (microsiemens per centimeter at 25 degrees Celsius); --, no analysis performed]

Analyte	N	ATL			CAL			DEN			IWD		
		Percentile			Percentile			Percentile			Percentile		
		25th	50th	75th	25th	50th	75th	25th	50th	75th	25th	50th	75th
Calcium	180	0.07	0.12	0.19	0.062	0.110	0.180	0.05	0.10	0.16	0.07	0.11	0.18
Magnesium	170	.02	.03	.04	.017	.027	.040	.02	.03	.05	.02	.03	.04
Sodium	147	.03	.06	.14	.031	.065	.154	.03	.06	.19	.03	.07	.16
Potassium	154	.02	.03	.04	.015	.025	.040	.01	.02	.03	.02	.02	.04
Sulfate	173	.80	1.30	2.28	.75	1.33	2.21	.80	1.40	2.48	.77	1.42	2.31
Chloride	173	.11	.19	.35	.08	.15	.28	.09	.16	.30	.12	.17	.29
Nitrate	179	.57	.93	1.44	.62	1.00	1.53	.62	1.01	1.51	.62	1.06	1.55
Ammonium	162	.12	.22	.40	.15	.25	.41	.12	.21	.41	.092	.189	.341
Orthophosphate	28	.003	.007	.009	.007	.009	.010	.001	.002	.003	--	--	--
pH	166	4.4	4.7	5.0	4.38	4.66	5.04	4.4	4.8	5.0	4.27	4.55	4.94
Specific conductance	164	8.0	14.0	24.0	8.5	14.8	25.3	10.3	15.0	26.5	7.9	16.6	27.9

laboratory. Estimated standard deviations are presented in table 6. The estimates are similar to those reported in previous years (Brooks and others, 1985; Brooks and others, 1987b). In general, the estimated analyte standard deviations for CAL are smaller than those for IWD, which in turn are smaller than those for ATL and DEN.

Table 6.--*Estimated analyte precision for four laboratories measuring constituents in wet-deposition samples*

[ATL, U.S. Geological Survey national water quality laboratory, Atlanta, Georgia; CAL, Illinois State Water Survey central analytical laboratory, Champaign, Illinois; DEN, U.S. Geological Survey national water-quality laboratory, Denver, Colorado; IWD, Inland Waters Directorate national water-quality laboratory, Burlington, Ontario, Canada; all estimates in milligram per liter except pH (unit) and specific conductance (microsiemens per centimeter at 25 degrees Celsius]

Analyte	ATL	CAL	DEN	IWD
Calcium	0.027	0.008	0.016	0.015
Magnesium	.008	.001	.020	.002
Sodium	.013	.008	.191	.007
Potassium	.004	.006	.010	.007
Sulfate	.13	.03	.16	.03
Chloride	.07	.01	.03	.03
Nitrate	.07	.04	.01	.03
Ammonium	.031	.022	.008	.011
pH	.07	.05	.05	.08
Specific conductance	.3	.3	2.3	.4

SUMMARY

Three different external quality-assurance programs were operated by the U.S. Geological Survey in support of the NADP/NTN during 1985. The programs were designed to monitor the precision and accuracy of onsite measurements performed by site operators, to assess the effect of routine field-handling activities on the precision and bias of wet-deposition data, and to assess the comparability of analytical data produced by the CAL with analytical data produced by other laboratories measuring chemical constituents in wet deposition.

Program results indicated that an average of 67 percent of onsite pH measurements met accuracy goals, while an average of 87 percent of onsite specific-conductance measurements met accuracy goals. Precision estimates for these two analytes indicated that onsite determinations are relatively precise, but that onsite specific-conductance precision was a function of the specific-conductance value of the test solution. Routine field-handling activities introduced small, but insignificant, positive bias into wet-deposition data. Routine field handling resulted in a decrease in hydrogen-ion concentration for 71 of 73 blind-audit samples. The mechanism of this neutralization was not apparent. Field handling is a significant contributor to imprecision in wet-deposition data. The CAL achieved greater precision than three other laboratories participating in an interlaboratory comparison program. All four laboratories produced comparable results when they analyzed identical wet-deposition samples.

REFERENCES CITED

Brooks, M.H., Schroder, L.J., and Malo, B.A., 1985, Interlaboratory comparability, bias, and precision for four laboratories measuring constituents in precipitation, November 1982-August 1983: U.S. Geological Survey Water-Resources Investigations Report 85-4313, 14 p.

Brooks, M.H., Schroder, L.J., and Willoughby, T.C., 1987a, Bias and precision of selected analytes reported by the National Atmospheric Deposition Program and National Trends Network--1984: U.S. Geological Survey Water-Resources Investigations Report 87-4050, 19 p.

_____1987b, Interlaboratory comparability, bias, and precision for four laboratories measuring constituents in wet deposition, October 1983-December 1984: U.S. Geological Survey Water-Resources Investigations Report 87-4067, 15 p.

Deardoff, E.R., Rains, T.C., and Koch, W.F., 1980, Simulated precipitation reference materials, III, U.S. Department of Commerce, National Bureau of Standards NBIR 79-1953, 24 p.

Hoaglin, D.C., Mosteller, F., and Tukey, J.W., 1983, Understanding robust and exploratory data analysis: New York, Wiley-Interscience, 447 p.

Janzer, V.J., 1985, The use of natural waters as U.S. Geological Survey reference samples, *in* Taylor, J.R., and Stanley, T.W., ed., Quality assurance for environmental measurements: American Society for Testing and Materials Special Technical Publication 867, p. 319-333.

National Atmospheric Deposition Program, 1984, The NADP quality assurance plan: Ft. Collins, Colo., Colorado State University, Deposition Monitoring, Natural Resource Ecology Laboratory, 1 vol.

Peden, M.E., principal investigator, 1986, Methods for collection and analysis of precipitation: Illinois State Water Survey Contract Report 381, 18 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 1981-November 1983: U.S. Geological Survey Water Resources Investigations Report 84-4325, 11 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 National Trends Network-1983 and January 1980 through September 1984: U.S. Geological Survey Water-Resources Investigations Report 85-4275, 20 p.

Schroder, L.J., Brooks, M.H., and Willoughby, T.C., 1986, Results of intercomparisons for the measurement of pH and specific conductance at National Atmospheric Deposition Program/National Trends Network monitoring sites, October 1981-October 1985: U.S. Geological Survey Water-Resources Investigations Report 86-4363, 32 p.

Schroder, L.J. and Malo, B.A., 1984, Quality assurance program for wet deposition sampling and chemical analyses for the National Trends Network: Air Pollution Control Association International Specialty Conference, Quality Assurance in Air Pollution Measurements, Boulder, Colo., 1984, Proceedings, p. 254-260.

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