INTERLABORATORY COMPARABILITY, BIAS, AND PRECISION FOR FOUR LABORATORIES MEASURING ANALYTES IN WET DEPOSITION, OCTOBER 1983—DECEMBER 1984

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CONTENTS

TABLES

CONVERSION FACTORS

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

Multiply units	*By*	*To obtain inch-pound units*
micrometer (µm)	3.397×10^{-5}	inch
microliter (µL)	3.381×10^{-5}	ounce, fluid
milliliter (mL)	0.03381	ounce, fluid
liter (L)	1.0567	quart, liquid

Additional abbreviations used in this report: megaohm (MΩ), milligram per liter (mg/L), and microsiemens per centimeter at 25 degrees Celsius (µS/cm).

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ABSTRACT

Four laboratories involved in the routine analysis of wet-deposition samples participated in an interlaboratory comparison program managed by the U.S. Geological Survey. The four participants were: Illinois State Water Survey central analytical laboratory in Champaign, Illinois; U.S. Geological Survey national water-quality laboratories in Atlanta, Georgia, and Denver, Colorado; and Inland Waters Directorate national water-quality laboratory in Burlington, Ontario, Canada. Analyses of interlaboratory samples performed by the four laboratories from October 1983 through December 1984 were compared.

Participating laboratories analyzed three types of interlaboratory samples--natural wet deposition, simulated wet deposition, and deionized water--for pH and specific conductance, and for dissolved calcium, magnesium, sodium, sodium, potassium, chloride, sulfate, nitrate, ammonium, and orthophosphate. Natural wet-deposition samples were aliquots of actual wet-deposition samples. Analyses of these samples by the four laboratories were compared using analysis of variance. Test results indicated that pH, calcium, nitrate, and ammonium results were not directly comparable among the four laboratories. Statistically significant differences between laboratory results probably only were meaningful for analyses of dissolved calcium. Simulated wet-deposition samples with known analyte concentrations were used to test each laboratory for analyte bias. Laboratory analyses of calcium, magnesium, sodium, potassium, chloride, sulfate, and nitrate were not significantly different from the known concentrations of these analytes when tested using analysis of variance. Deionized-water samples were used to test each laboratory for reporting of false positive values. The Illinois State Water Survey Laboratory reported the smallest percentage of false positive values for most analytes. Analyte precision was estimated for each laboratory from results of replicate measurements. In general, the Illinois State Water Survey laboratory achieved the greatest precision, whereas the U.S. Geological Survey laboratories achieved the least precision.

INTRODUCTION

The U.S. Geological Survey is providing external quality-assurance support to the National Atmospheric Deposition Program (NADP) and National Trends Network (NTN) (Schroder and Malo, 1984). These two networks use identical onsite sampling and analytical methods for the collection and analysis of weekly composite wet-deposition samples. The networks use a common laboratory, the Illinois State Water Survey central analytical laboratory. These networks are considered in this report as one network, the NADP/NTN, and will be referred to throughout the remainder of the report as the network. A part of the overall external quality-assurance effort for the network is an ongoing interlaboratory comparison program. The objectives of the interlaboratory comparison program are to provide information on the comparability of analytical results of the Illinois State Water Survey laboratory with the analytical results of other laboratories analyzing wet-deposition samples, to quantify the precision achieved by each laboratory, and to quantify any biases associated with the analytical results of each laboratory. Information of this type is needed if data users wish to merge data from two or more laboratories.

The design of the interlaboratory comparison program required that all participating laboratories analyze identical samples. The interlaboratory samples included natural wet-deposition samples with analyte concentrations that were unknown, simulated wet-deposition samples with analyte concentrations that were known, and ultrapure deionized-water samples with no measurable dissolved analyte concentrations. None of the participating laboratories were aware of the composition of any of the interlaboratory samples that they analyzed. During October 1983-December 1984, four laboratories reported enough results to be included in the comparison. The four laboratories were: Illinois State Water Survey central analytical laboratory, Champaign, Illinois (CAL); U.S. Geological Survey national water-quality laboratory, Atlanta, Georgia (ATL); U.S. Geological Survey national water-quality laboratory, Denver, Colorado (DEN); and Inland Waters Directorate national water-quality laboratory, Burlington, Ontario, Canada (IWD). This report presents summaries of data obtained from each participating laboratory that were used to document the comparability of wet-deposition analytical results reported by each laboratory, quantify any biases associated with individual laboratory results, and estimate the analyte precision associated with individual labortory results. Earlier interlaboratory comparison results have been reported previously (Brooks and others, 1985).

PROGRAM DESIGN

Participating laboratories received from six to nine interlaboratory samples weekly. Samples were chilled and shipped in insulated containers to minimize degradation of unstable analytes. Samples were of three types: natural wet deposition, simulated wet deposition, and ultrapure deionized water.

Preparation of Interlaboratory Comparison Samples

The natural wet-deposition samples were aliquots of weekly composite samples that were selected randomly from network samples by the laboratory staff at CAL. Only samples with volumes equal to or greater than 750 m were eligible for splitting into the 10 aliquots that constituted an interlaboratory sample. Sufficient volume had to remain after splitting to allow analysis by CAL and subsequent inclusion of the analytical results into the network data base. Upon receipt at CAL, each weekly composite sample of sufficient volume for analysis was filtered through a cellulose-acetate filter with a pore size of 0.45 μm. The aliquots that served as interlaboratory samples were obtained by passing a suitable volume of a filtered sample through a decasplitter. Interlaboratory sample bottles were 125-mL, high-density polyethylene; thus, the maximum aliquot volume obtained was 125 mL. The 10 aliquots of each wet-deposition sample then were mailed to the U.S. Geological Survey project office in Arvada, Colorado, where they were relabeled and distributed as interlaboratory samples. In general, the analyte concentrations in composite wet-deposition samples decrease with increasing volume; therefore, the method used for selection of interlaboratory samples probably excluded some network samples with greater analyte concentrations from being used as interlaboratory samples. Analyses of these interlaboratory samples were used to assess the direct comparability of the four laboratories' measurements of constituents in natural wet-deposition samples.

Simulated wet-deposition interlaboratory samples were diluted standard-reference water samples (SRWS). SRWS were prepared by the U.S. Geological Survey from surface-water sources for use in the U.S. Geological Survey's internal quality-assurance program (Malo and others, 1978; Schroder and others, 1980; Janzer, 1985). Because these samples were prepared from surface water, the concentrations of major cations and anions in the SRWS were substantially greater than the concentrations normally present in wet-deposition samples. Consequently, the SRWS were diluted by an appropriate factor to decrease the major cation and anion concentrations to concentrations characteristic of wet deposition. The diluted SRWS were acidified with a small quantity (1 to 10 μL) of perchloric acid in order to adjust the solution pH values to values characteristic of wet depostion (4.5 to 5.5 pH). Perchloric acid was chosen because other mineral acids would have added to the known analyte concentrations of chloride, sulfate, or nitrate. Diluted SRWS were analyzed by the U.S. Geological Survey for at least three analytes to confirm the accuracy of the dilution. Diluted SRWS having analyte relative errors of greater than ±10 percent, or all positive or all negative analyte relative errors, regardless of their magnitude, were rejected for use as interlaboratory samples. Analytical results from the simulated wet-deposition interlaboratory samples were used to quantify any analyte biases associated with individual laboratory results.

Ultrapure deionized-water samples had resistivities of 2.5 MΩ or greater. Analytical results from the ultrapure deionized-water samples were used to assess the number of false or positive values that were reported by each laboratory. Simulated wet-deposition and ultrapure deionized-water samples were distributed along with the natural wet-deposition samples to the participating laboratories. Participating laboratories knew that the interlaboratory samples were not routine wet-deposition samples, but did not know the composition of any of the samples included in each shipment.

Laboratory Analysis and Reporting

The participating laboratories were asked to analyze the interlaboratory samples for pH and specific conductance, and for dissolved calcium, magnesium, potassium, sodium, chloride, sulfate, nitrate, ammonium, and orthophosphate. IWD did not perform dissolved-orthophosphate analyses. Because the natural wet-deposition interlaboratory samples had been filtered and the simulated wet-deposition and deionized-water samples required no filtration, the laboratories were instructed to analyze the samples as received, even if their analytical protocol required filtration prior to analysis. The laboratories reported the results of their analyses periodically to the U.S. Geological Survey project office. The U.S. Geological Survey project office did not review these data after receipt, nor did it request any reanalyses to check the validity of questionable values. Consequently, the data from each laboratory could reflect errors introduced during both analysis and transcription. Record-keeping discrepancies by U.S. Geological Survey project personnel resulted in the deletion of data for 12 interlaboratory samples from the final data set. This loss represented a small fraction of the total number of samples analyzed by the laboratories during October 1983-December 1984, and, therefore, likely did not affect the statistical analysis. Few data were edited from the final data set. Only gross outliers were removed, amounting to less than 0.1 percent of the total data set. All data were analyzed using P-STAT[1] (P-Stat, Inc., 1986), an interactive statistical software package.

INTERLABORATORY COMPARABILITY

The analytical methods utilized by each laboratory and the limits of detection for each method are listed in tables 1 through 3. CAL had the lowest limits of detection for calcium, magnesium, sodium, and potassium. ATL and DEN had the lowest limits of detection for orthophosphate. IWD had the lowest limits of detection for sulfate and ammonium. ATL, DEN, and IWD had the lowest limits of detection for chloride and nitrate. Limits of detection are established by each laboratory, and they may differ among laboratories even though identical methods of analysis are being used. Limits of detection are defined in various ways; the American Society for Testing and Materials (1986) defines the limit of detection as the concentration at which there is equal probability of reporting a quantity of analyte when it is actually not present, and of not reporting a quantity of analyte when it actually is present. The differing limits of detection among the four laboratories affected the number of comparisons that could be made among the four laboratories. The percentage of analyses of natural and simulated wet-deposition interlaboratory samples that were reported as less than the limit of detection by each laboratory is listed in table 4.

Comparison of data in tables 1 through 4 indicates some predictable relations between analytical limits of detection and data reported as less than the limit of detection; this comparison also provides some clues about

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

Table 1.--*Analytical methods and limits of detection for analyses of wet deposition performed by the Illinois State Water Survey central analytical laboratory*

[mg/L = milligrams per liter; N/A = limit of detection not applicable for this analyte]

Analyte	Method	Limit of detection (mg/L)
pH	Electrometry	N/A
Specific conductance	Electrometry	N/A
Calcium	Atomic-absorption spectrometry	0.009
Magnesium	Atomic-absorption spectrometry	.003
Sodium	Atomic-absorption spectrometry	.003
Potassium	Atomic-absorption spectrometry	.003
Chloride	Colorimetry, automated ferricyanide	.02
Sulfate	Colorimetry, automated methyl thymol blue	.10
Nitrate	Colorimetry, automated cadmium reduction	.02
Ammonium	Colorimetry, automated phenate	.02
Orthophosphate	Colorimetry, automated ascorbic acid	.003

Table 2.--*Analytical methods and limits of detection for analyses of wet deposition performed by U.S. Geological Survey national water-quality laboratories*

[mg/L = milligrams per liter; N/A = limit of detection not applicable for this analyte]

Analyte	Method	Limit of detection (mg/L)
pH	Electrometry	N/A
Specific conductance	Electrometry	N/A
Calcium	Atomic-absorption spectrometry	0.01
Magnesium	Atomic-absorption spectrometry	.01
Sodium	Atomic-absorption spectrometry	.01
Potassium	Atomic-absorption spectrometry	.01
Chloride	Colorimetry, ferric thiocyanate	.01
Sulfate	Turbidimetry, barium sulfate	.20
Nitrate	Colorimetry, automated cadmium reduction	.01
Ammonium	Colorimetry, automated salicylate hypochlorite	.002
Orthophosphate	Colorimetry, phosphomolybdate	.001

Table 3.--*Analytical methods and limits of detection for analyses of wet deposition performed by the Inland Waters Directorate national water-quality laboratory*

[mg/L = milligrams per liter; N/A = limit of detection not applicable for this analyte; -- = analysis not performed]

Analyte	Method	Limit of detection (mg/L)
pH	Electrometry	N/A
Specific conductance	Electrometry	N/A
Calcium	Atomic-absorption spectrometry	0.05
Magnesium	Atomic-absorption spectrometry	.01
Sodium	Automated flame photometry	.02
Potassium	Automated flame photometry	.02
Chloride	Ion chromatography	.01
Sulfate	Ion chromatography	.01
Nitrate	Ion chromatography	.01
Ammonium	Colorimetry, automated phenate	.001
Orthophosphate	--	--

Table 4.--*Percentage of analyses that were reported as less than the limit of detection for four laboratories analyzing natural and simulated wet-deposition samples*

[CAL = Illinois State Water Survey central analytical laboratory, Champaign, Illinois; ATL = U.S. Geological Survey national water-quality laboratory, Atlanta, Georgia; DEN = U.S. Geological Survey national water-quality laboratory, Denver, Colorado; IWD = Inland Waters Directorate national water-quality laboratory, Burlington, Ontario, Canada; Nat = analyses of natural wet-deposition samples; Sim = analyses of simulated wet-deposition samples; -- = analysis not performed]

Analyte	CAL		ATL		DEN		IWD	
	Nat	Sim	Nat	Sim	Nat	Sim	Nat	Sim
Calcium	1	0	0	2	8	0	19	0
Magnesium	0	0	3	2	3	0	7	0
Sodium	0	0	2	6	0	0	13	4
Potassium	0	0	4	6	10	0	26	4
Chloride	4	0	3	1	7	0	1	4
Sulfate	3	0	5	1	8	0	2	0
Nitrate	3	18	8	36	11	28	6	40
Ammonium	10	59	10	49	6	14	7	45
Orthophosphate	86	14	59	27	65	19	--	--

the general nature of the natural and simulated wet-deposition samples that were analyzed by each laboratory. For example, IWD had a limit of detection for calcium (0.05 mg/L, table 3) that was more than five times larger than the CAL limit of detection for calcium (0.009 mg/L, table 2). Not surprisingly, the percentage of calcium concentrations reported as less than the limit of detection for IWD analyses of natural wet-deposition samples (19 percent) is greater than those reported by CAL (2 percent). Several other similar examples of relations among limits of detection and percentages of analyses reported as less than the limit of detection are listed in tables 1 through 4. The data in table 4 indicate that, in general, a greater percentage of analyses of natural wet-deposition samples were reported as less than the limit of detection compared to analyses of simulated wet-deposition samples. This indicates that the simulated wet-deposition samples had fewer analyte concentrations at or near the limits of detection than did the natural wet-deposition samples. Further, as will be discussed later, the simulated wet-deposition samples had greater overall analyte concentrations than did the natural wet-deposition samples. Two exceptions to this generalization are the reported concentrations of nitrate and ammonium. As reported previously (Schroder and others 1985; Brooks and others, 1985), these two analytes are not stable in the diluted SRWS that are used as simulated wet-deposition samples, and they decrease in concentration (presumably through microbial degradation) in the samples with time.

Percentile rankings for the measured values and concentrations in natural wet-deposition samples, the known concentrations in the simulated wet-deposition samples, and the measured values and concentrations in all network wet-deposition samples analyzed during 1984 are listed in table 5. Percentile rankings for measured values and concentrations in natural wet-deposition samples were based on the results reported by all four laboratories, and summarize 270 analyses of aliquots of network wet-deposition samples that were collectively performed by those laboratories. Percentile rankings for known concentrations in simulated wet-deposition samples were based on the known analyte concentrations in the 26 dilutions of various SRWS that were used as interlaboratory samples. Percentile rankings for measured values and concentrations in all network wet-deposition samples summarize the 5,450 analyses that were performed by CAL for the network during 1984. The percentile rankings in table 5 indicate that the analyte concentrations in the simulated wet-deposition interlaboratory samples were greater than those in the natural wet-deposition interlaboratory samples. For some analytes, namely the major cations, those differences are as much as 1 order of magnitude. The natural wet-deposition interlaboratory samples and the network wet-deposition samples analyzed during 1984 had much more comparable analyte concentrations. In most cases, for the slight difference in concentrations that did exist, concentrations in the natural wet-deposition interlaboratory samples were smaller than those for all of the wet-deposition network samples. This type of relation was expected, because, as was mentioned earlier, the natural wet-deposition interlaboratory samples were aliquots of actual network wet-deposition samples that had volumes of 750 mL or more. The 25th-percentile volume for all network wet-deposition samples analyzed during 1984 was 365 mL; the 50th-percentile volume was 989 mL. Therefore, somewhere between 25 and 50 percent of the smaller volume network wet-deposition samples (which presumably had greater analyte concentrations) were excluded from use as interlaboratory samples.

Table 5.--*Percentile rankings for measured values in natural wet-deposition interlaboratory samples, known concentrations in simulated wet-deposition interlaboratory samples, and measured values in all network wet-deposition samples analyzed during 1984*

Analyte and reporting units[1]	Measured values and concentrations in natural wet-deposition samples for indicated percentile			Known concentrations in simulated wet-deposition samples for indicated percentile			Measured values and concentrations in all network wet-deposition samples for indicated percentile[4]		
	25th	50th	75th	25th	50th	75th	25th	50th	75th
pH[2]	4.40	4.70	5.20	(5)	(5)	(5)	4.38	4.80	5.46
Specific conductance[3]	8.0	13.2	23.0	(5)	(5)	(5)	8.5	15.2	26.9
Calcium	.05	.08	.15	0.54	1.20	1.95	.08	.17	.38
Magnesium	.01	.02	.04	.20	.37	.58	.03	.05	.09
Sodium	.03	.06	.17	.32	.78	1.55	.06	.12	.27
Potassium	.01	.02	.04	.05	.12	.29	.02	.03	.06
Chloride	.10	.18	.34	.25	.39	1.13	.11	.19	.39
Sulfate	.77	1.30	2.34	1.40	2.84	4.74	.83	1.49	2.65
Nitrate	.10	.19	.30	.04	.13	.44	.58	1.13	1.99
Ammonium	.06	.12	.22	(5)	(5)	(5)	.08	.19	.40
Orthophosphate	.00	.01	.01	.04	.10	.19	(6)	(6)	(6)

[1] Milligrams per liter, except for pH and specific conductance.
[2] Standard units.
[3] Microsiemens per centimeter at 25 degrees Celsius.
[4] Peden, 1986.
[5] Known values or concentrations not available.
[6] All concentrations less than limit of detection.

Summaries of each laboratory's analyses of deionized-water samples are presented in table 6. The percentage of times that each laboratory reported a false positive value and the median concentration of those false positive values are listed for each laboratory. CAL analyzed 18 deionized-water samples, ATL analyzed 17 samples, and DEN and IWD analyzed 20 samples. In general, CAL reported the smallest percentage of false positive values for analyses of almost every analyte, and in three instances (calcium, magnesium, and nitrate), CAL reported no false positive values. ATL reported the largest percentage of false positive values for analyses of calcium, magnesium, sodium, potassium, and chloride. DEN reported the largest percentage of false positive values for analyses of ammonium and orthophosphate; IWD reported the largest percentage of false positive values for sulfate. Comparison of the data in table 6 and tables 1 through 3 indicates that the median concentrations of the false positive values are similar to the limits of detection for each laboratory in most instances. Therefore, the false positive values reported by the laboratories probably are not indicative of problems related to contamination within each laboratory, but rather indicative of an inability of the laboratory to measure analyte concentrations that are similar to the stated limit of detection.

Table 6.--*Summary of laboratory analyses of deionized-water samples*

[CAL = Illinois State Water Survey central analytical laboratory, Champaign, Illinois; ATL = U.S. Geological Survey national water-quality laboratory, Atlanta, Georgia; DEN = U.S. Geological Survey national water-quality laboratory, Denver, Colorado; IWD = Inland Waters Directorate national water-quality laboratory, Burlington, Ontario, Canada; percent = percentage of analyses resulting in a false positive report; median = median concentration of reported false positive values; mg/L = milligrams per liter; -- = analysis not performed]

Analyte	CAL		ATL		DEN		IWD	
	Percent	Median (mg/L)	Percent	Median (mg/L)	Percent	Median (mg/L)	Percent	Median (mg/L)
Calcium	0	(1)	94	0.04	60	0.01	10	0.02
Magnesium	0	(1)	65	.01	25	.01	5	.01
Sodium	39	0.01	65	.01	20	.03	25	.02
Potassium	33	.01	53	.02	50	.02	35	.02
Chloride	11	.05	94	.13	20	.06	25	.04
Sulfate	28	.25	29	.20	15	.50	45	.04
Nitrate	0	(1)	0	(1)	15	.14	15	.01
Ammonium	11	.05	53	.04	55	.03	25	.00
Orthophosphate	6	.01	35	.00	40	.01	--	--

[1] Median value not applicable.

Results from all four laboratories' analyses of natural wet-deposition interlaboratory samples are summarized in table 7. Only samples for which all four laboratories reported results are included in these summary statistics. Therefore, even though there were 270 total samples in the data set, the maximum number of samples summarized in table 7 is 152. Missing values in the original data set of 270 samples resulted from concentrations less than the limit of detection, lost samples, and mistakes resulting in uneven distribution of samples by the U.S. Geological Survey project. Only samples for which all four laboratories reported results were included to facilitate direct comparison of laboratory results, and to simplify statistical hypothesis testing. There were no samples for which all four laboratories reported measurable concentrations of orthophosphate, thus this analyte is not included in the table. The number of samples, the mean and median analyte values or concentrations, the actual significance of the calculated F ratio, and where applicable, the least significance difference between mean values or concentrations are listed for each laboratory and analyte. The largest difference in median pH values is 0.06 unit, and the largest difference in median specific-conductance values is 1.5 µS/cm. Differences in mean and median values or concentrations generally are quite small, and they indicate a significant degree of comparability between the wet-deposition analytical results produced by the four laboratories. The majority of the differences in median concentration among laboratories is in the range of 0.01 to 0.02 mg/L. A few exceptions to this generalization exist, but the largest difference in median concentrations in table 7 is 0.10 mg/L (CAL and ATL analyses of chloride).

Table 7.--*Summary statistics and tests for significant differences among individual laboratory analyses of natural wet-deposition interlaboratory samples*

[CAL = Illinois State Water Survey central analytical laboratory, Champaign, Illinois; ATL = U.S. Geological Survey national water-quality laboratory, Atlanta, Georgia; DEN = U.S. Geological Survey national water-quality laboratory, Denver, Colorado; IWD = Inland Waters Directorate national water-quality laboratory, Burlington, Ontario, Canada; Least significant difference = least significant difference between mean values or concentrations; N/A = not applicable]

Analyte and reporting unit[1]	Number of samples	CAL		ATL		DEN		IWD		F ratio significance	Least significant difference
		Mean	Median	Mean	Median	Mean	Median	Mean	Median		
pH[2]	141	4.86	4.72	4.81	4.70	4.88	4.70	4.80	4.66	0.0178	0.01
Specific conductance[3]	152	16.1	13.3	15.8	13.0	16.5	14.0	17.0	14.5	.4899	N/A
Calcium	111	.189	.090	.18	.10	.15	.08	.19	.10	.0344	.003
Magnesium	135	.043	.025	.04	.02	.04	.02	.04	.02	.9997	N/A
Sodium	127	.214	.075	.20	.07	.19	.06	.23	.06	.9203	N/A
Potassium	99	.116	.025	.12	.03	.12	.02	.17	.04	.6886	N/A
Chloride	131	.39	.15	.46	.25	.44	.19	.41	.21	.8990	N/A
Sulfate	134	1.61	1.35	1.69	1.35	1.81	1.40	1.70	1.35	.3463	N/A
Nitrate	130	1.08	.860	1.08	.91	1.12	.87	1.04	.84	.0001	.03
Ammonium	123	.25	.17	.263	.213	.260	.172	.221	.155	.0458	.004

[1] Milligrams per liter, except for pH and specific conductance.

[2] Standard units.

[3] Microsiemens per centimeter at 25 degrees Celsius.

Tests for statistically significant differences among individual laboratory results for the analyses of natural wet-deposition samples were performed by using analysis of variance (ANOVA). The model formulated 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 with respect to detection of possible treatment differences. These four concentration ranges were based on the 25th, 50th-, and 75th-percentile rankings for all network wet-deposition samples analyzed during 1984 (table 5). Values or concentrations equal to or less than the 25th-percentile value or concentration were assigned a value or concentration level of 1, those between the 25th and 50th percentile were assigned a value or concentration level of 2, and so on. The concentration-level variable was used as the model blocking factor.

Model results are shown in the last two columns of table 7. The actual significance of the calculated F ratio, and, where applicable, the least significance difference between mean values or concentrations are listed. Values of the actual F ratio significance of 0.05 or less indicate that at least one of the four mean values or concentrations is significantly different from the other three at the 5-percent confidence level. Significant differences of this type were determined for pH, calcium, nitrate, and ammonium. Least-significant-difference values associated with these analytes indicate which of the four mean values or concentrations are significantly different from each other. To properly apply the least-significance-difference values, the mean values or concentrations are ranked from smallest to largest, and only adjacent mean values or concentrations are compared. Adjacent mean values or concentrations with a difference larger than the least significance difference, are significantly different from each other at the 5-percent confidence level, and by implication the laboratory results for that analyte from those two laboratories are not directly comparable. The data in table 7 indicate that only ATL and IWD analyses of pH are directly comparable; that only CAL and IWD analyses of calcium are directly comparable; and that only CAL and ATL analyses of nitrate and ammonium are directly comparable. All four laboratories produce directly comparable results for specific conductance, magnesium, sodium, potassium, chloride, and sulfate, when judged using a randomized block-design ANOVA.

Significant differences in pH values indicated in table 7 are of questionable importance based on the degree of agreement indicated by the similarity of both the mean and median values. Significant differences in laboratory analyses of nitrogen species most probably reflect the instability of these species in unpreserved samples, and are also of questionable importance. Significant differences associated with laboratory analyses of calcium are of importance, and need to be considered by data users comparing results from any of the laboratories.

LABORATORY BIAS

Results from the four laboratories' analyses of simulated wet-deposition interlaboratory samples are summarized in table 8. The column labeled SRWS summarizes the known concentrations in the diluted SRWS. Only samples for which all four laboratories reported a result are included in the data set

Table 8.--*Summary statistics and tests for significant differences among individual laboratory analyses and known concentrations of simulated wet-deposition interlaboratory samples*

[CAL = Illinois State Water Survey central analytical laboratory, Champaign, Illinois; ATL = U.S. Geological Survey national water-quality laboratory, Atlanta, Georgia; DEN = U.S. Geological Survey national water-quality laboratory, Denver, Colorado; IWD = Inland Waters Directorate national water-quality laboratory, Burlington, Ontario, Canada; standard reference water samples = known concentration in standard-reference water samples; all values in milligrams per liter]

Analyte	Number of samples	CAL		ATL		DEN		IWD		Standard-reference water samples		F ratio significance
		Mean	Median	Mean	Median	Mean	Median	Mean	Median	Mean	Median	
Calcium	75	1.561	1.013	1.47	0.86	1.38	0.910	1.53	0.94	1.52	0.867	0.5418
Magnesium	75	.504	.374	.50	.36	.49	.370	.49	.380	.506	.390	.9964
Sodium	69	1.372	.788	1.36	.73	1.30	.630	1.35	.72	1.36	.797	.9850
Potassium	69	.269	.125	.27	.18	.26	.11	.27	.11	.271	.128	.9997
Chloride	73	1.01	.48	1.02	.47	.98	.42	.95	.47	.990	.500	.9758
Sulfate	76	4.21	2.71	4.12	2.80	4.19	3.00	4.13	2.88	4.07	2.86	.9951
Nitrate	30	.95	.70	.91	.67	.99	.73	.87	.46	.901	.700	.9249

summarized in the table; this allowed direct comparison of laboratory-determined and known concentrations, and simplified the statistical comparisons. The pH and specific-conductance values of the diluted SRWS were no longer known because the samples had been acidified with $HClO_4$; these analytes are not included in the table. Ammonium and orthophosphate were present in small concentrations in the diluted SRWS, but not enough reported concentrations were in the data set to provide any meaningful comparisons; hence, these two analytes also are not included in the table. The table lists the number of samples, mean and median concentrations, and values of actual F ratio significance, for each laboratory and analyte. The relative percentage differences among individual laboratory-determined and known concentrations for simulated wet-deposition samples were comparable to the relative percentage differences determined among laboratories for natural wet-deposition samples.

Tests for statistically significant differences between individual laboratory results and known concentrations in the simulated wet-deposition samples were performed by using the same randomized block-design ANOVA used for the natural wet-deposition interlaboratory samples. Because the analyte concentrations in the simulated wet-deposition samples were much greater than those in the network wet-deposition samples analyzed during 1984, percentile rankings for the known concentrations (table 5) were used to generate the blocking-factor variable. The model results indicated no statistically significant differences among individual laboratory results and known concentrations in the simulated wet-deposition samples. Consequently least-significant-difference values were not needed. The model results indicate that at the concentrations in the diluted SRWS, no significant analyte bias was associated with any of the four laboratories' results for the seven analytes listed in the table.

LABORATORY PRECISION

Analyte precision was estimated for each laboratory from the results of replicate analyses of interlaboratory samples performed by each laboratory. Natural wet-deposition samples were unknowingly analyzed in duplicate by each laboratory as each laboratory received two aliquots of each wet-deposition sample. Duplicate analyses of natural wet-deposition samples were used to estimate the analyte standard deviations for these samples presented in table 9. Simulated wet-deposition samples were analyzed in triplicate. An estimated standard deviation was calculated for each triplicate analysis, and these estimates were pooled to obtain the analyte standard deviations for these samples listed in table 9. In general, CAL achieved the greatest analyte precision (smallest standard deviation), IWD achieved the second greatest, DEN achieved the third greatest, and ATL achieved the fourth greatest. Exceptions to this generalization are indicated by the data in the table. For example, pH precision by ATL was greater than that achieved by DEN, and sulfate precision by CAL was second to the precision achieved by IWD. Results summarized in table 9 agree with previous analyte-precision estimates obtained for these four laboratories (Brooks and others, 1985) in that they indicate the least uncertainty is associated with wet-deposition data reported by CAL and the greatest uncertainty is associated with the wet-deposition data reported by ATL.

Table 9.--*Estimates of analyte standard deviation based on replicate analyses of natural and simulated wet-deposition interlaboratory samples*

[CAL = Illinois State Water Survey central analytical laboratory, Champaign, Illinois; ATL = U.S. Geological Survey national water-quality laboratory, Atlanta, Georgia; DEN = U.S. Geological Survey national water-quality laboratory, Denver, Colorado; IWD = Inland Waters Directorate national water-quality laboratory, Burlington, Ontario, Canada; Nat = analyses of natural wet-deposition samples; Sim = analyses of simulated wet-deposition samples; -- = analysis not performed]

Analyte and reporting unit[1]	CAL		ATL		DEN		IWD	
	Nat	Sim	Nat	Sim	Nat	Sim	Nat	Sim
pH[2]	0.03	0.02	0.09	0.08	0.20	0.06	0.05	0.02
Specific conductance[3]	.4	.3	.8	.7	1.3	.9	.7	.2
Calcium	.004	.008	.06	.09	.01	.03	.01	.02
Magnesium	.001	.005	.04	.06	.02	.01	.01	.01
Sodium	.003	.007	.07	.09	.01	.07	.15	.01
Potassium	.049	.002	.17	.03	.05	.02	.11	.01
Chloride	.04	.02	.09	.07	.32	.10	.07	.06
Sulfate	.10	.20	.23	.26	.15	.23	.06	.22
Nitrate	.01	.02	.07	.18	.07	.33	.06	.14
Ammonium	.01	.01	.043	.042	.014	.005	.030	.004
Orthophosphate	.004	(4)	(4)	(4)	.032	(4)	--	--

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[1] Milligrams per liter, except for pH and specific conductance.

[2] Standard units.

[3] Microsiemens per centimeter at 25 degrees Celsius.

[4] Insufficient data for estimate.

SUMMARY AND CONCLUSIONS

Four laboratories analyzed identical natural wet-deposition, simulated wet-deposition, and ultrapure deionized-water samples from October 1983 through December 1984. Each laboratory performed analyses for pH and specific conductance, and for dissolved calcium, magnesium, sodium, potassium, chloride, sulfate, nitrate, and ammonium. Three of the four laboratories analyzed each sample for dissolved orthophosphate. Analytical results reported by each laboratory were interpreted to provide estimates of the direct comparability between laboratories, possible laboratory bias, and laboratory precision. Analyses of ultrapure deionized water by each of the four laboratories indicated that false positive values were more likely to be reported by some laboratories than by others. All reported false positive values were similar to the stated analytical limit of detection for the laboratory in question. Interlaboratory comparability was estimated by using analytical results from the analyses of natural wet-deposition samples. Statistically significant differences between one or more laboratories were determined for analyses of pH, calcium, nitrate, and ammonium. The only significant difference of interest to users of data from two or more laboratories was probably that for calcium analyses. Not enough data were reported for an evaluation of the comparability orthophosphate analyses. Possible laboratory bias was estimated by using analytical results for simulated wet-deposition samples. Statistically significant differences indicating that at least one laboratory's results were biased were not determined for calcium, magnesium, sodium, potassium, chloride, sulfate, or nitrate. At the concentrations in the simulated wet-deposition samples, laboratory bias was not evident. Precision estimates indicated that, in general, precision achieved by the different laboratories was not similar, and that the laboratory achieving the greatest precision had also achieved the greatest precision during previous study periods.

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Brooks and others—INTERLABORATORY COMPARABILITY, BIAS, AND PRECISION FOR FOUR LABS MEASURING ANALYTES IN WET DEPOSITION, OCT 1983—DEC 1984 USGS/WRIR 87-4067