BIAS AND PRECISION OF SELECTED ANALYTES REPORTED BY THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM AND NATIONAL TRENDS NETWORK, 1984

By Myron H. Brooks and LeRoy J. Schroder, U.S. Geological Survey, and
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METRIC CONVERSION FACTORS

For the reader who prefers to use inch-pound units, conversion factors for terms used in this report are listed below.

Multiply SI Units	*By*	*To obtain inch-pound units*
liter (L)	1.0567	quart, liquid
milliliter (mL)	0.03381	ounce, fluid
microliter (mL)	3.381×10^{-5}	ounce, fluid
milligram (mg)	3.527×10^{-5}	ounce, avoirdupois
microgram (mg)	3.527×10^{-8}	ounce, avoirdupois
micron	3.397×10^{-5}	inch

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ABSTRACT

The U.S. Geological Survey operated a blind-audit sample program during 1984 to test the effects of the sample-handling and -shipping procedures used by the National Atmospheric Deposition Program and National Trends Network on the quality of wet-deposition data produced by the combined networks. Blind-audit samples, which were dilutions of standard-reference water samples, were submitted by network-site operators to the central analytical laboratory disguised as actual wet-deposition samples. Results from the analyses of blind-audit samples were used to calculate estimates of analyte bias associated with all network wet-deposition samples analyzed in 1984 and to estimate analyte precision.

Concentration differences between double-blind samples that were submitted to the central analytical laboratory and separate analyses of aliqouts of those blind-audit samples that had not undergone network sample handling and shipping were used to calculate analyte masses that apparently were added to each blind-audit sample by routine network-handling and -shipping procedures. These calculated masses indicated statistically significant biases for magnesium, sodium, potassium, chloride, and sulfate. Median calculated masses were 41.4 micrograms for calcium, 14.9 micrograms for magnesium, 23.3 micrograms for sodium, 0.7 microgram for potassium, 16.5 micrograms for chloride, and 55.3 micrograms for sulfate. Analyte precision was estimated using two different sets of replicate measures performed by the central analytical laboratory. Estimated standard deviations were similar to those previously reported.

INTRODUCTION

The National Atmospheric Deposition Program (NADP) was established in 1977 to provide information about the chemical content of wet deposition throughout United States. This information was needed for assessment of the impact of precipitation-borne pollutants on crops, soils, forests, surface waters, and materials. The National Trends Network (NTN) was established in 1983 to provide long-term monitoring of the major inorganic constituents in wet deposition. Both networks use identical standardized procedures for the collection and analysis of wet-deposition samples and the same laboratory (the Illinois State Water Survey central analytical laboratory). Therefore, this report will consider them as one network. The network operated over 170 wet-deposition sample-collection sites during 1984. Each site was equipped with a wet-dry deposition collector and a recording rain gage; weekly composite wet-deposition samples were collected at each site.

The U. S. Geological Survey (USGS) is providing external quality-assurance support to the network (Schroder and Malo, 1984). A double-blind audit-sample program is part of this overall effort. The program was designed to identify and quantify any biases in network data resulting from routine field operations (including sample contact with the sample container, sample handling, and sample shipping). In addition to bias estimates, replicate analyses generated from the program may be used to provide estimates of analyte precision. Results from this quality-assurance program for previous years have been reported (Schroder and others, 1985); this report summarizes analytical results for quality-assurance samples that were submitted to the laboratory during 1984.

PROGRAM DESIGN

The double-blind audit-sample program was designed to meet two distinct goals. A primary goal of the sample program was to have the composition of each quality-assurance sample mimic, as nearly as possible, that of a typical network wet-deposition sample. Another principal goal was to have each quality-assurance sample that was submitted to the laboratory for analysis be handled and analyzed by the laboratory personnel unaware that it was an external quality-assurance sample. Ideally, the data generated for each quality-assurance sample would be entered into the network wet-deposition data base without there being any indication that the sample was an external quality-assurance sample. Only when this occurred was the program functioning as intended.

Preparation of Blind-Audit Samples

The quality-assurance samples, hereafter referred to as blind-audit samples, were solutions whose analyte concentrations simulated the concentrations normally encountered in wet deposition; they were prepared by diluting standard reference water samples. The reference samples were prepared by the U.S. Geological Survey for use in its internal quality-assurance program (Malo and others, 1978; Schroder and others, 1980, and Janzer, 1985) by homogenizing large quantities of surface water. An extensive study was used to establish the most probable analyte concentrations in each of the reference samples. The analyte concentrations in the reference samples were larger than analyte concentrations normally present in wet deposition; thus, the reference samples were diluted prior to being used as blind-audit samples. Major cation concentrations in the diluted reference samples were analyzed by atomic-absorption spectroscopy, and the measured values were compared with the calculated analyte concentrations for the dilution factor in question. Diluted reference samples that had analyte-relative percent errors greater than ±10 percent or that had all measured major cation concentrations either larger or smaller than the calculated concentrations were rejected for use as blind-audit samples. Many of the diluted reference samples had pH values of 7 or above; following verification, a small quantity of $HClO_4$ was added to these blind-audit samples to adjust the pH to a more realistic value (4.5-5.5 pH units). Blind-audit samples and specific instructions for their submission to the laboratory were distributed quarterly to selected network sites in 500 mL (milliliter) polyethylene bottles.

Submission of Blind-Audit Samples

Each network site collected weekly composite wet-deposition samples following established network procedures (Bigelow, 1982). Network site operators changed the wet-side sample-collection container (a 13 L (liter) polyethylene bucket) at approximately 9:00 a.m. local time every Tuesday. The site operator weighed the sample and container to provide an independent measure of wet-deposition volume, removed a 40-mL aliquot from the weekly composite wet-deposition sample for onsite pH and specific-conductance determinations, sealed the sample bucket with a polyethylene lid, and shipped the entire bucket, containing the wet-deposition sample, to the laboratory for analysis. Upon receipt, the laboratory filtered each wet-deposition sample through a 0.45-micron pore-size organic membrane and analyzed for pH, specific conductance, and dissolved concentrations of calcium, magnesium, sodium, potassium, ammonium, chloride, sulfate, nitrate, and ortho-phosphate.

Network sites that received blind-audit samples were asked to submit them to the laboratory for analysis when the site received no wet deposition during a sampling period. The site operator's instructions were to pour approximately two-thirds of the 500 mL blind-audit sample into a clean 13-L bucket and to treat this as if it were a wet-deposition sample that had been collected at the site during the previous week. Onsite measurements were performed and recorded, and the blind-audit sample was submitted to the laboratory for analysis. The site operator prepared a false weekly record of rainfall and site-operating conditions that corresponded to the volume of the blind-audit sample being submitted and provided this false information on the site-observer report form that accompanied the blind-audit sample to the laboratory. The remaining one-third of the blind-audit sample was sent back to the U.S. Geological Survey; the U.S. Geological Survey then mailed this aliquot of the original 500-mL blind-audit sample to the laboratory, where it was analyzed to provide an independent check of the known analyte concentrations in each blind-audit sample.

The laboratory analyzed and reported analyte concentrations for the blind-audit samples that were submitted by site operators unaware that these samples were not actual network wet-deposition samples. These samples will be referred to hereafter as bucket samples, so as to differentiate them from the aliquots that were left in the original sample bottles, which will be referred to as bottle samples. The laboratory periodically sent preliminary analytical results for the entire network to the U.S. Geological Survey, so that analytical results for the bucket samples could be identified and thus prevented from being reported as actual wet-deposition data. When the U.S. Geological Survey notified the laboratory of the identity of a bucket sample, the laboratory reanalyzed an archived aliqout of the sample; consequently, two analyses of each bucket sample were performed. Bottle samples were analyzed at the laboratory as many times as the bottle-sample volume would allow.

BIAS AND PRECISION OF SELECTED ANALYTES

Thirty-eight bucket samples were submitted to the laboratory by network site operators during 1984. The temporal distribution of those sample submissions is shown in figure 1. Sample submissions were reasonably constant during the year, with the exception of the large number of samples submitted during November and the lack of samples during October and December. Since lack of wet deposition at a site controlled when the blind-audit sample was submitted to the laboratory, the blind-audit sample program would not be representative of the entire year if a majority of the blind-audit samples were submitted to the laboratory in a relatively small part of the year. Beginning in 1986, a new procedure that allowed for constant submission of blind-audit samples throughout the year was implemented by the U.S. Geological Survey at the request of the network.

Of the 38 blind-audit samples submitted during 1984, data from 25 were usable. Two bucket samples leaked in transit to the laboratory; no part of those remained for analysis upon arrival. Two bucket samples arrived at the laboratory with visible contamination in the bucket; although they were analyzed, the data were not used in the statistical analysis. Nine blind-audit samples were contaminated at the U.S Geological Survey laboratory, as indicated by anomalously large chloride concentrations (it was assumed that the analyst acidified the diluted and verified reference samples with hydrochloric acid); the data from these bucket and bottle samples were eliminated from the statistical analysis. All nine of these samples were submitted by site operators during November; hence, the usable data are for the first 9 months of 1984. Because some bottles never were returned to the U.S. Geological Survey, and because some leaked in transit, only 20 of the 25 bucket analyses could be paired with corresponding bottle analyses.

Concentrations of dissolved ammonium, nitrate, and orthophosphate were not stable in the blind-audit samples; consequently, the majority of analyses for these three analytes were reported as less than the limit of detection. This problem has been reported previously (Schroder and others, 1985; Brooks and others, 1985) when diluted reference samples have been used as known-value samples for bias estimation; consequently, analytical results for these three analytes were eliminated from the statistical estimation of bias and precision. Analytical results for concentrations of dissolved calcium, magnesium, sodium, potassium, chloride, and sulfate from both bucket and bottle samples were used in estimating bias and precision.

Although one program goal was to provide blind-audit samples that had realistic analyte concentrations, many of the diluted reference samples used as blind-audit samples had analyte concentrations that exceeded those normally encountered by the laboratory in network wet-deposition samples. The known analyte concentrations of dissolved calcium, magnesium, sodium, potassium, chloride, and sulfate in the 25 uncontaminated bucket samples are shown in figure 2 as a function of the percentile rankings for all network wet-deposition samples analyzed by the laboratory during 1984. Known concentrations of major cations in the blind-audit samples were almost exclusively at or above the 75th percentile concentrations for all network wet-deposition samples; whereas, chloride and sulfate known concentrations in the blind-audit samples were more evenly distributed among the percentile rankings for all network 1984 wet-deposition samples.

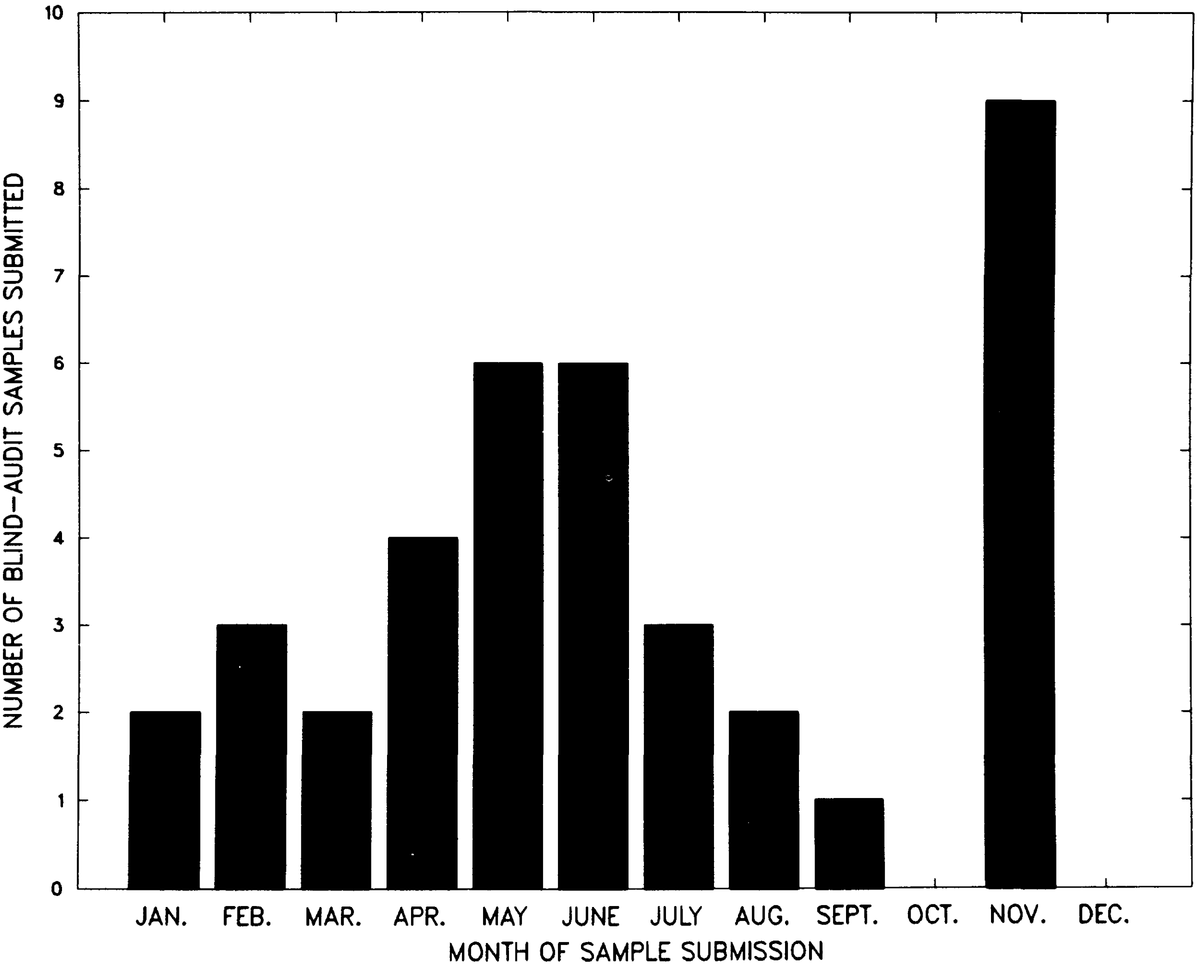

Figure 1.--Temporal distribution of blind-audit samples during 1984.

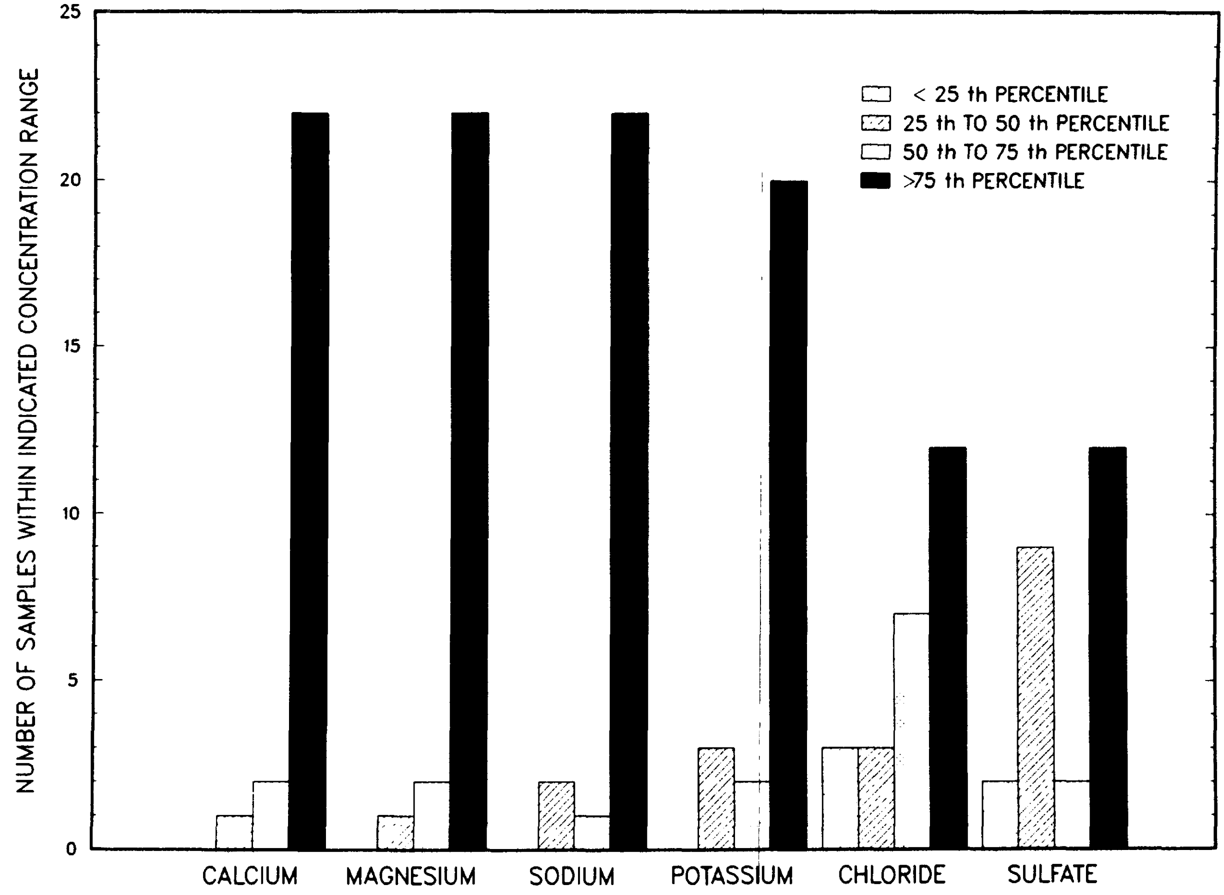

Figure 2.--Known analyte concentrations in 1984 blind-audit samples as a function of percentile rankings for all 1984 network wet-deposition samples.

Summary statistics for measured bucket concentrations, measured bottle concentrations, and known concentrations are presented in table 1. Only results for blind-audit samples that had both bucket and bottle analyses performed are included in the table, which allows direct comparison of the three concentrations types for each analyte. A general pattern of mean and median bucket concentrations being greater than mean and median bottle concentrations, which in turn are greater than mean and median known concentrations, is apparent. The standard-deviation values are not appropriate for comparing overlap between the three concentration types because they are significantly influenced by the range of analyte concentrations in the 20 blind-audit samples. In fact, classical statistical measures, such as means and standard deviations, and hypothesis testing, such as analysis of variance, will not discern statistically significant differences among the three concentration types. This is because the actual concentration differences are typically 0.1 mg/L (milligram per liter) or less, whereas the known-concentration ranges are typically 4 to 8 mg/L and can be as much as 30 mg/L (sulfate).

A more useful statistical approach involves pair-wise comparison of the three different concentration types. The three possible pairings for the results summarized in table 1 are: bucket versus bottle, bucket versus known, and bottle versus known. Calculated concentration differences for these three different pairings are summarized in table 2. Median concentration differences and the number of positive differences are listed for each analyte. A bias test employing a binomial-distribution probability function (Friedman and others, 1983) indicates that for 20 samples, 17 or more positive calculated differences indicate positive bias at an approximate confidence level of 99 percent. Application of this test to the results of table 2 indicate that: (1) Calculated concentration differences between bucket and bottle samples indicate positive bias for all analytes except calcium; (2) calculated concentration differences between bucket and known concentrations indicate positive bias for all analytes except potassium, and (3) calculated concentration differences between bottle and known concentrations indicate positive bias for chloride only. In addition, the two analytes for which bucket minus bottle (calcium) and bucket minus known (postassium) concentrations are not significant have 16 positive differences each; they are very close to statistical significance. The data summarized in table 2 indicate that analyte concentrations in blind-audit samples that had undergone routine network field handling (bucket samples) during 1984 were elevated compared to both known and measured bottle concentrations. This fact implies that all wet-deposition samples that were collected and analyzed by the network during the same time period experienced similar increases in analyte concentration. Calculated differences between bottle samples and known values were smaller than those differences calculated between bucket samples and known values, but the median concentration differences were 0.00 mg/L for only two analytes. Earlier examinations of the blind-audit sample-program data (Schroder and others, 1985) only compared bucket concentrations to known concentrations. This approach underestimates the analyte-concentration increase for a blind-audit sample when the measured bottle concentration is less than the reported known concentration and overestimates the analyte-concentration increase when the measured bottle concentration is greater than the reported known concentration. Based on the summary values listed in table 2, this approach would have overestimated the sulfate-concentration increase for 1984 blind-audit samples and underestimated the magnesium-concentration increase for the same samples.

Table 1.--*Summary statistics for measured bucket concentrations, measured bottle concentrations, and known concentrations in blind-audit samples during 1984*

[mg/L, milligrams per liter; s, standard deviation]

Analyte	Measured bucket concentration (mg/L)			Measured bottle concentration (mg/L)			Known concentration (mg/L)		
	Mean	Median	s	Mean	Median	s	Mean	Median	s
Calcium-----	2.46	2.16	1.91	2.27	1.81	1.93	2.14	1.48	2.00
Magnesium---	.83	.42	1.08	.73	.35	1.10	.74	.37	1.11
Sodium------	1.76	1.05	2.01	1.65	1.06	1.97	1.62	.87	2.00
Potassium---	.30	.22	.40	.29	.23	.38	.28	.40	.21
Chloride----	1.02	.51	1.32	.97	.50	1.31	.91	.45	1.29
Sulfate-----	6.14	2.94	8.87	5.91	2.67	8.81	5.92	2.84	8.70

Table 2.--*Summary of calculated concentration differences between bucket samples, bottle samples, and known values for blind-audit samples during 1984*

[mg/L, milligrams per liter; N.P.D.; number of positive differences]

Analyte	Bucket minus bottle concentration		Bucket minus known concentration		Bottle minus known concentration	
	Median difference (mg/L)	N.P.D.	Median difference (mg/L)	N.P.D.	Median difference (mg/L)	N.P.D.
Calcium-----	0.17	16	0.17	19	0.00	10
Magnesium---	.08	19	.06	19	-.01	3
Sodium------	.10	18	.12	19	.00	12
Potassium---	.01	17	.01	16	-.01	8
Chloride----	.07	17	.11	18	.03	17
Sulfate-----	.39	17	.40	17	.11	9

One possible explanation for the consistent positive concentration differences in table 2 is that some small mass of each analyte is present in the network sample containers. These masses are then added into solution when a blind-audit (or wet-deposition) sample is brought into contact with the container. The magnitude of analyte mass being added to network wet-deposition samples by this mechanism, or any other factor in the routine network sample-handling procedures, can be estimated by calculating the change in analyte mass in blind-audit samples from the existing data. Because, as indicated by table 2, the bottle concentrations and known concentrations do not necessarily agree, the calculated analyte-concentration difference between a bucket sample and its paired bottle sample multiplied by the volume of the bucket sample will provide the best estimate of the change in analyte mass in a given blind-audit sample. Calculated analyte masses that were added to the 20 bucket samples having paired bottle analyses are presented for 6 analytes in figures 3 through 8. Summary statistics of the calculated analyte masses are presented in table 3. The bias-test results for bucket minus bottle concentrations presented in table 2 are applicable to masses enumerated in table 3.

Table 3.--*Summary statistics for calculated changes in analyte mass in blind-audit samples during 1984*

[μg; micrograms]

Analite	Mean (μg)	Median (μg)	Standard deviation (μg)
Calcium----------	52.1	41.4	87.1
Magnesium--------	27.0	14.9	35.1
Sodium-----------	29.6	23.3	36.0
Potassium--------	2.3	.7	11.7
Chloride---------	13.5	16.5	28.3
Sulfate----------	56.7	55.3	95.8

For all six analytes, the majority of calculated values are positive. A few negative values exist for each analyte. These could result from dilution during handling or analyte adsorption onto the sample container. The positive values far outweigh the few negative values. No relation between the measured bottle concentration and magnitude of analyte change is apparent for any of the six analytes (figs. 3-8); the calculated changes appear to be independent of the initial analyte concentrations present in the blind-audit samples. Mean changes and standard deviations (table 3) are highly influenced by a few large values for most analytes (figs. 3-8); hence the mean and median changes in analyte mass are very different for most analytes. Because of its resistance to outlying observations, the median is recommended as the best estimate of analyte mass added to network samples during 1984.

The information on analyte mass correlates with information provided by laboratory personnel. Sample containers (buckets) are cleaned at the laboratory and reused. During 1984, the cleaning process consisted of a tap-water rinse followed by a deionized-water rinse in a dishwashing machine. Cleaned sample containers periodically were tested at the laboratory by adding 500 mL of deionized water, sealing the container, and allowing it to sit, either upright or inverted, for 1 week. A sample of the deionized water then was analyzed for the constituents normally measured by the laboratory in wet deposition. Unusually large concentrations of dissolved calcium and magnesium were found in these test samples during August 1984 through January 1985 (J.M. Lockard, Illinois State Water Survey, written commun., 1986). This problem was traced to a poorly functioning dishwashing machine and was corrected in January 1985 by machine repair and the use of deionized water only. The positive bias indicated by the 1984 blind-audit sample calculated masses may be partially explained by the sample-container cleaning problem; however, the period reported by the laboratory for this problem does not coincide with the majority of 1984 blind-audit sample submissions by network-site operators.

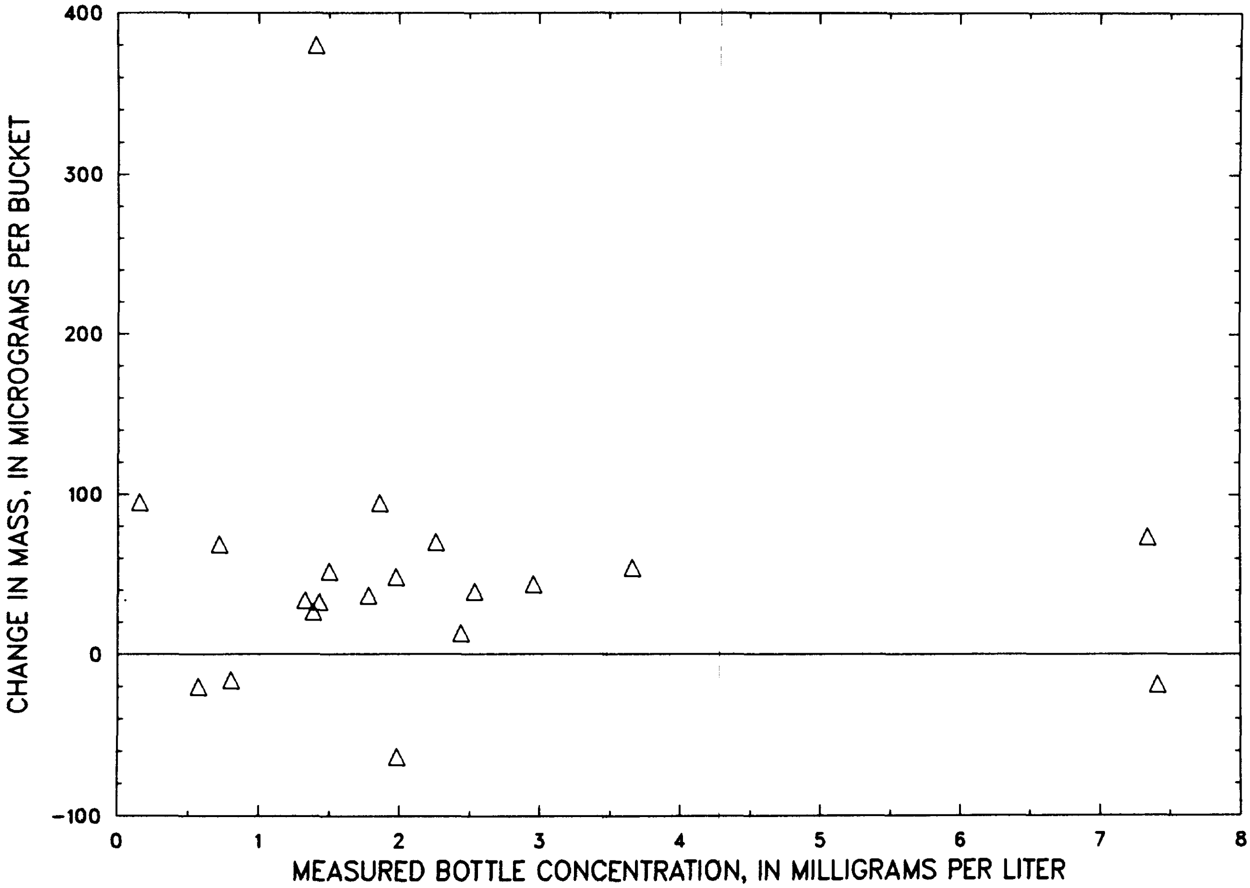

Figure 3.--Calculated change in analyte mass versus measured bottle concentration for analyses of calcium in 1984 blind-audit samples.

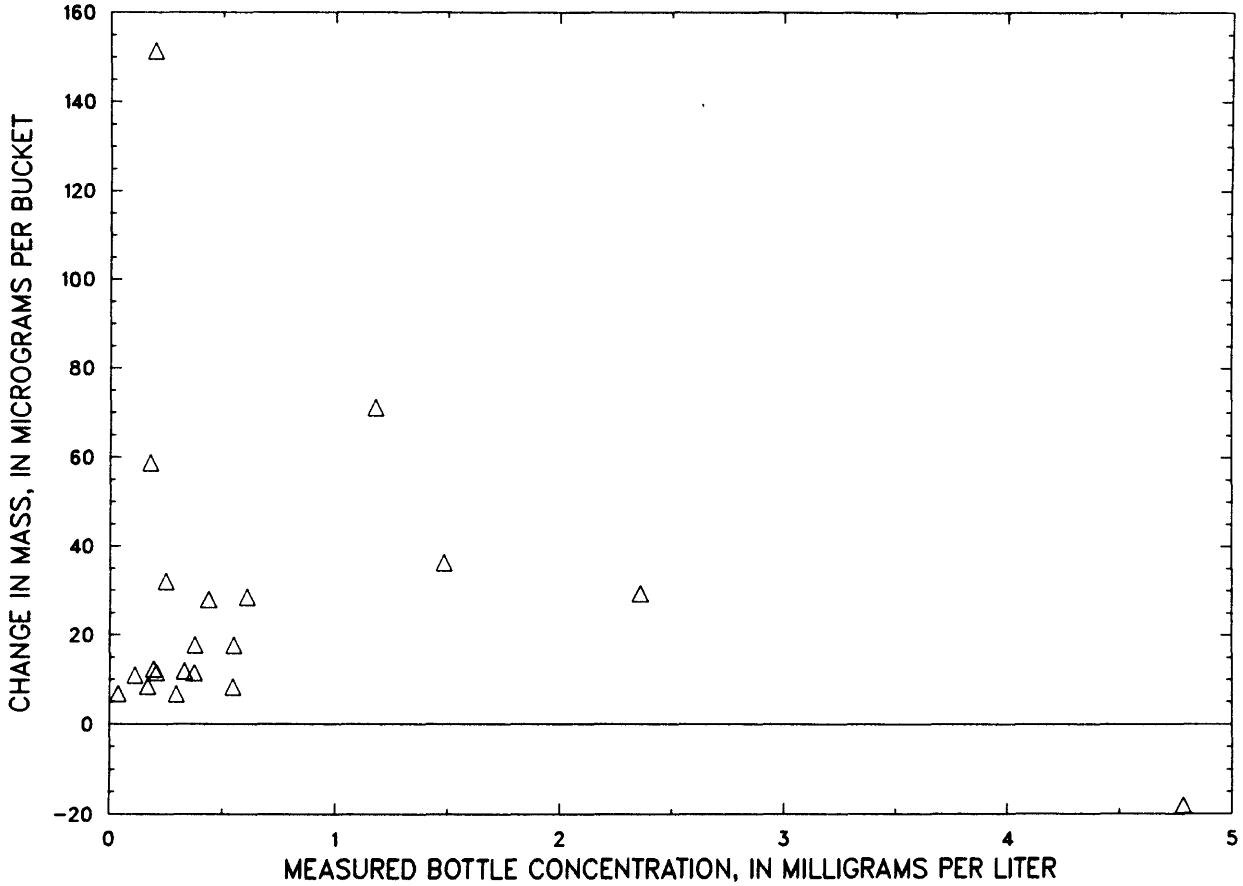

Figure 4.--Calculated change in analyte mass versus measured bottle concentration for analyses of magnesium in 1984 blind-audit samples.

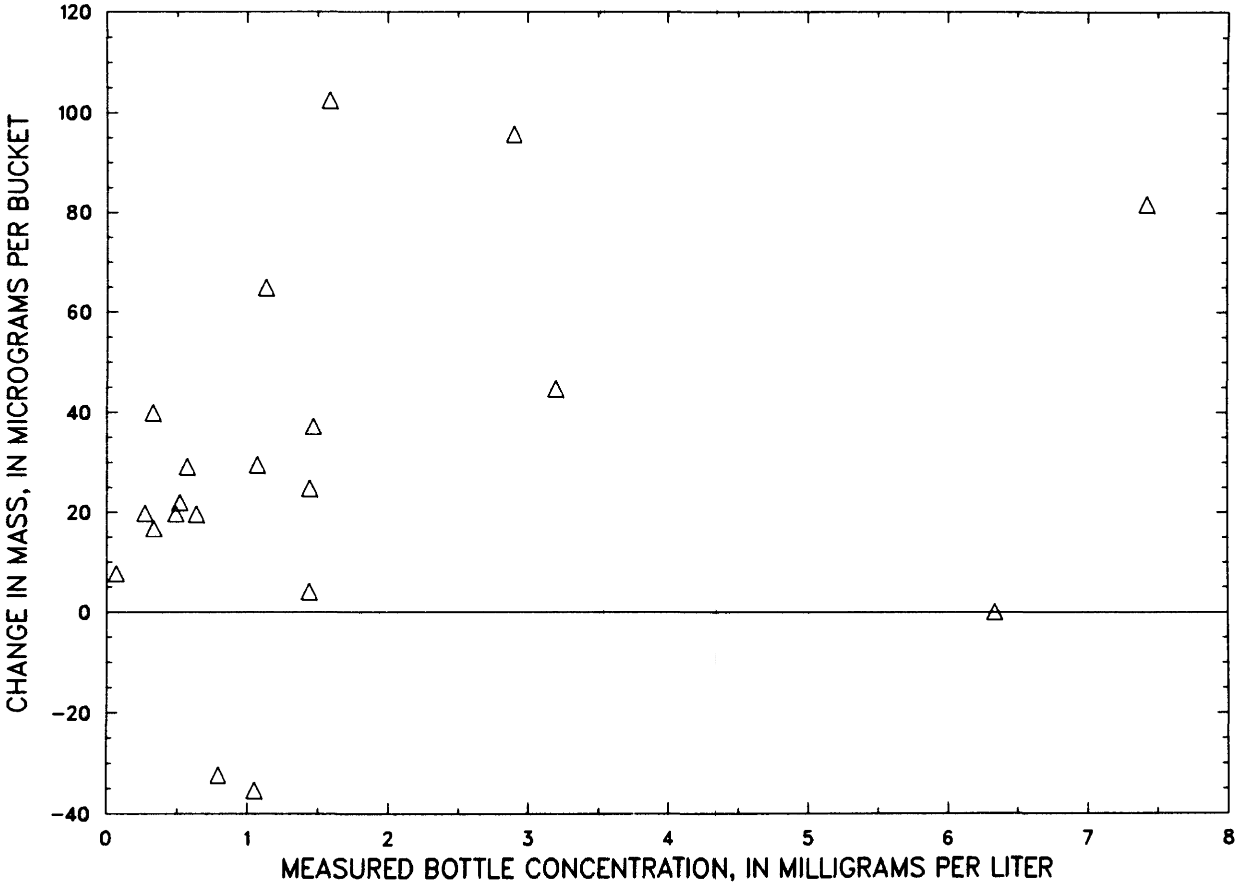

Figure 5.--Calculated change in analyte mass versus measured bottle concentration for analyses of sodium in 1984 blind-audit samples.

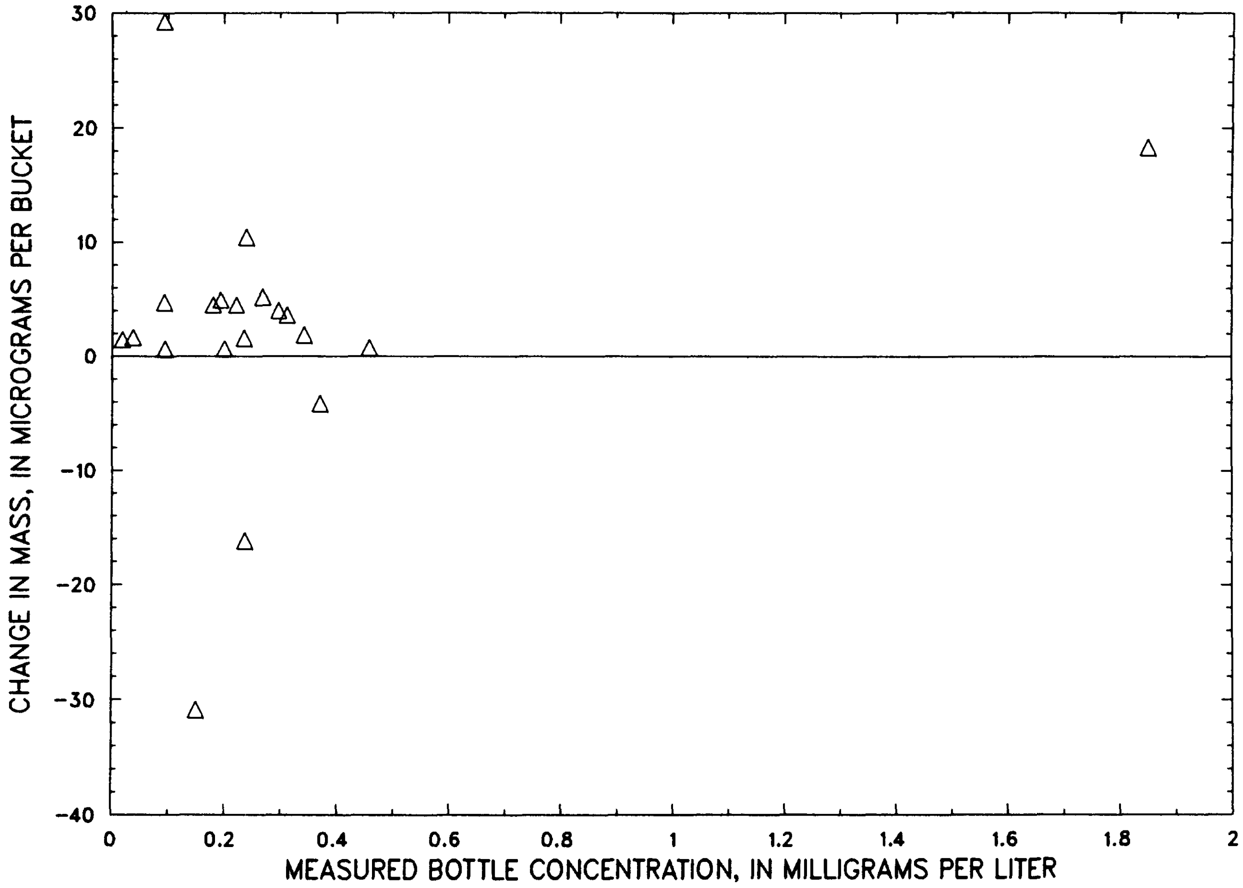

Figure 6.--Calculated change in analyte mass versus measured bottle concentration for analyses of potassium in 1984 blind-audit samples.

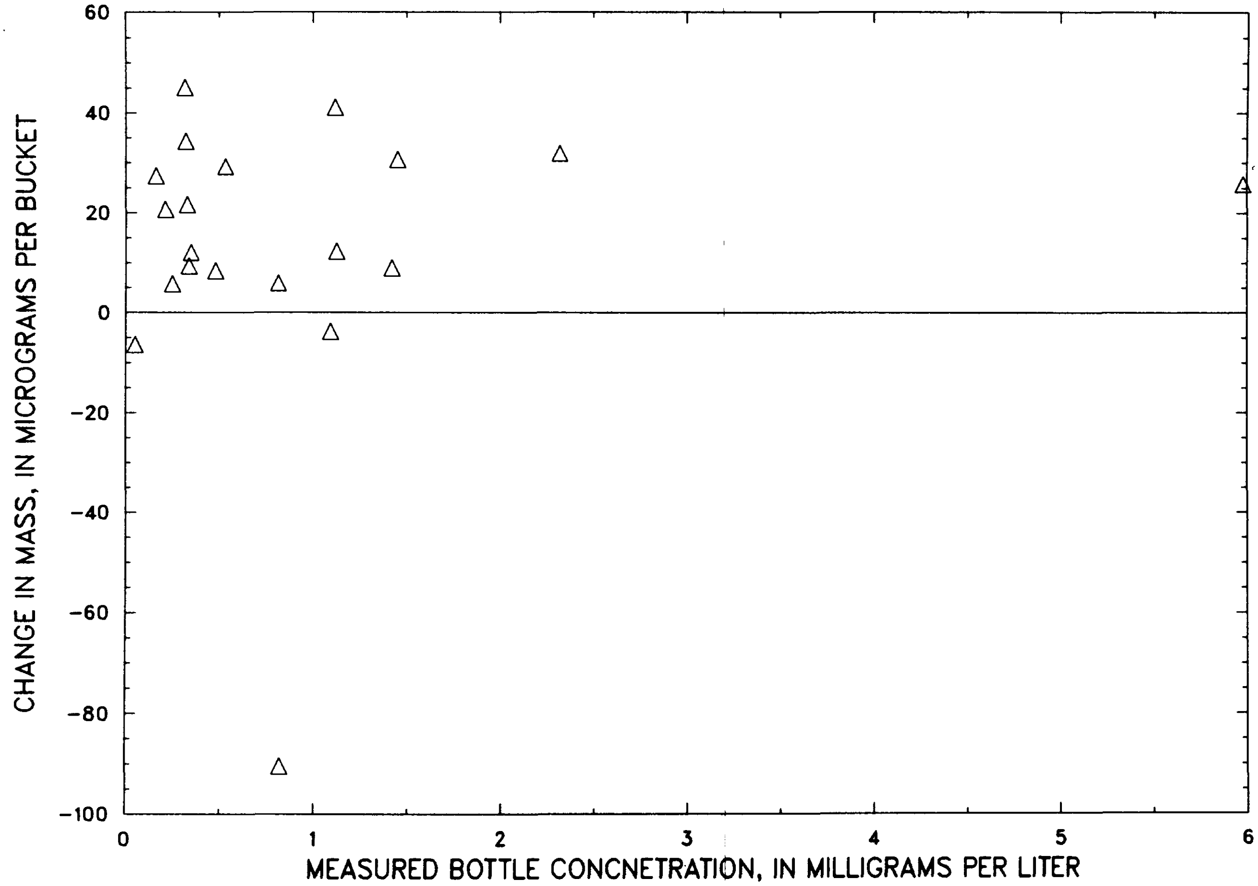

Figure 7.--Calculated change in analyte mass versus measured bottle concentration for analyses of chloride in 1984 blind-audit samples.

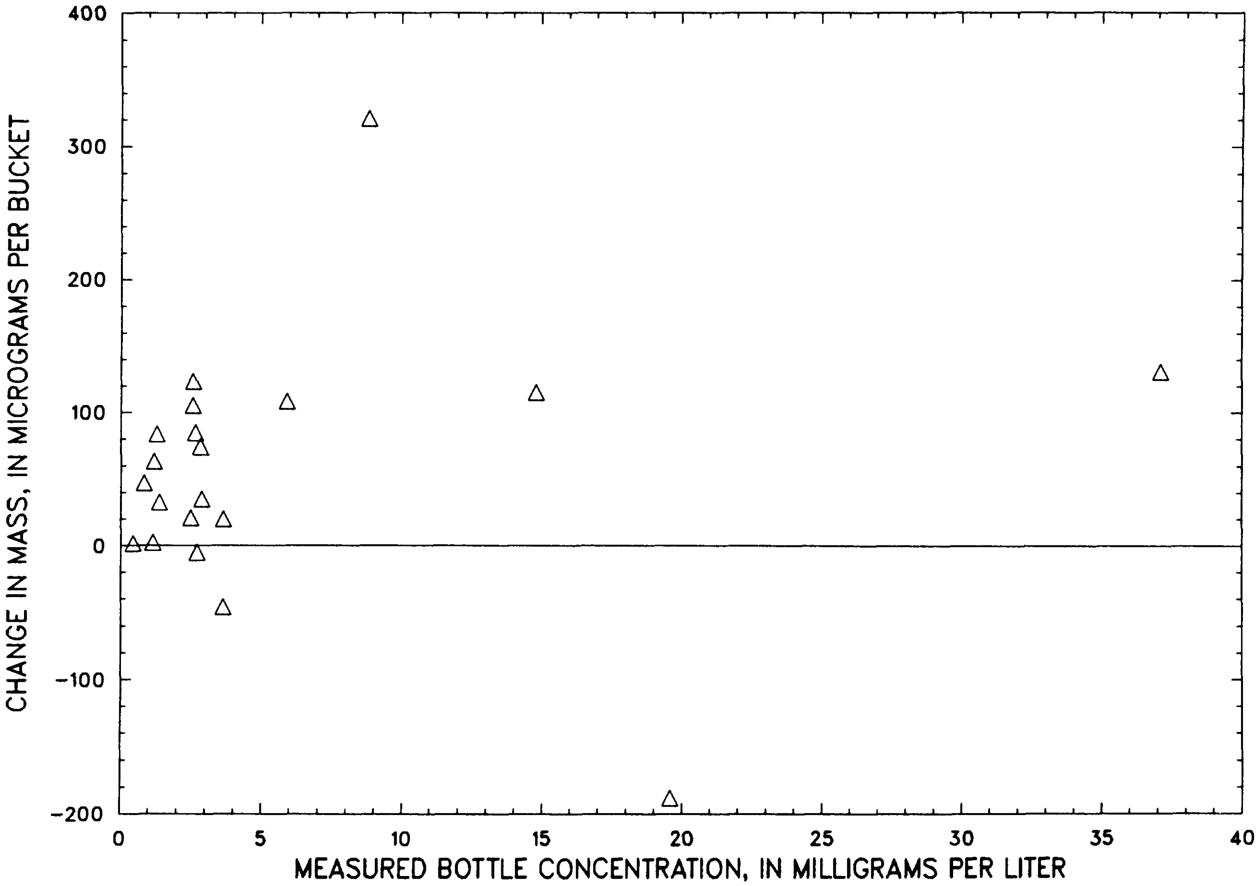

Figure 8.--Calculated change in analyte mass versus measured bottle concentration for analyses of sulfate in 1984 blind-audit samples.

All median calculated changes in analyte mass are less than 60 μg (micrograms); although these are very small masses, they can significantly affect the measured analyte concentrations in wet-deposition samples collected by the network. The network locates its sampling sites in rural areas to avoid influences from local point sources of atmospheric pollutants. Consequently, most network sites receive relatively pristine wet deposition during most of the year. Therefore, the addition of microgram quantities of analyte mass can result in rather significant changes in analyte concentration. Measured analyte concentrations are coupled with measured wet-deposition amounts to calculate representative wet-deposition values for the geographic area in which a site is located. Using calcium as an example, the median analyte mass that was added to the blind-audit samples during 1984 was 41.4 μg. The median calcium concentration measured for all network samples during 1984 was 0.170 mg/L. The median volume for all 1984 network wet-deposition samples was 988.7 mL. The median added mass of calcium (41.4 μg) increased the calcium concentration in 50 percent of all the 1984 network samples by at least 0.042 mg/L. This value is 25 percent of the median reported calcium concentration for all network samples. The example only uses overall network statistics; sites that receive more wet deposition, or less dilute wet deposition, would be affected less than the example indicates. Conversely, sites that receive scant amounts of dilute wet deposition (as do many western sites) would be impacted to a greater extent than indicated by the example. Clearly, the effect of the addition of analyte masses that were calculated from the 1984 blind-audit data will be determined by individual site conditions; however, the relatively small analyte masses that apparently were added to all network wet-deposition samples collected during the first 9 months of 1984 did significantly bias the wet-deposition values that were reported for many network sites.

Repetitive measurements of bucket and bottle samples allowed for the calculation of analyte precision values. As was previously mentioned, archived aliquots of each bucket sample were reanalyzed by the laboratory upon notification of the identity of each blind-audit sample. Estimated standard deviations and 95-percent confidence limits for the estimates were calculated for the original and reanalyzed bucket concentrations by treating the paired results as duplicate analyses. These estimates are presented in table 4. Repetitive measurements were performed on 16 of the bottle samples that were analyzed during 1984. Of those 16, 14 were analyzed twice, 1 three times, and 1 four times. Results from these repetitive analyses were pooled to provide estimates of analyte standard deviations. These estimates and 95-percent confidence limits are presented in table 5. The estimates presented in tables 4 and 5 agree reasonably well with the estimates reported by Schroder, Bricker, and Willoughby (1985).

Table 4.--*Estimated standard deviations from duplicate measurements of bucket samples and 95-percent confidence limits for six analytes measured in blind-audit samples during 1984*

Analyte	Estimated standard deviation (milligrams per liter)	Degrees of freedom	95-percent confidence limits for estimated standard deviation (milligrams per liter)
Calcium--------	0.024	24	0.019 to 0.033
Magnesium------	.030	24	.023 to .041
Sodium---------	.047	25	.036 to .064
Potassium------	.013	25	.010 to .018
Chloride-------	.019	24	.015 to .026
Sulfate--------	.099	25	.011 to .135

Table 5.--*Pooled estimates of standard deviations from repetitive measurements of bottle samples and 95-percent confidence limits for six analytes measured in blind-audit samples during 1984*

Analyte	Estimated standard deviation (milligrams per liter)	Degrees of freedom	95-percent confidence limits for estimated standard deviation (milligrams per liter)
Calcium--------	0.073	19	0.055 to 0.105
Magnesium------	.025	19	.019 to .036
Sodium---------	.090	18	.067 to .130
Potassium------	.042	18	.031 to .061
Chloride-------	.129	19	.097 to .185
Sulfate--------	.256	19	.192 to .367

SUMMARY

Blind-audit samples were submitted during 1984 to the network central analytical laboratory by network site operators in clean network-sample containers disguised as actual wet-deposition samples. Two different analyses were performed by the network laboratory on blind-audit samples. Parts of each sample that arrived at the laboratory disguised as an actual wet-deposition sample were analyzed by the laboratory and constituted the double-blind part of the program (bucket samples). Aliquots of each blind-audit sample that remained in the original sample container, as prepared by the U.S. Geological Survey, also were analyzed (bottle samples). Analytical results from both bottle and bucket samples were used to estimate analyte bias and precision for network wet-deposition samples that were collected and analyzed during the first 9 months of 1984.

Analyte bias was estimated for network measurements of dissolved calcium, magnesium, sodium, potassium, chloride, and sulfate in wet deposition. Bias estimates were based upon calculated analyte masses that apparently were added to or removed from the blind-audit samples during 1984. Changes in mass were calculated by multiplying the concentration difference between bucket- and bottle-measured concentrations by the bucket-sample volume. Positive calculated masses indicated positive bias; negative calculated masses indicated negative bias. The majority of calculated masses for all six analytes were positive. Except for calcium, the number of positive calculated masses indicated statistically significant positive bias for all analytes. Median calculated analyte masses that were added to blind-audit samples during 1984 were: calcium, 41.4 μg; magnesium, 14.9 μg; sodium, 23.3 μg; potassium, 0.7 μg; chloride, 16.5 μg; and sulfate, 53.3 μg.

Repetitive measurements of both bucket and bottle samples were used to estimate analyte precision. Analysis and reanalysis results for bucket samples were treated as duplicate analyses, and analyte standard deviations were calculated. Repetitive measurements of bottle samples were used to calculate pooled analyte standard deviations. Analyte precision thus calculated was similar to that reported for previous years.

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