

PRECISION AND BIAS OF SELECTED ANALYTES REPORTED BY THE
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM AND
NATIONAL TRENDS NETWORK--1983 AND
JANUARY 1980 THROUGH SEPTEMBER 1984

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METRIC CONVERSION TABLE

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

<i>Multiply SI units</i>	<i>By</i>	<i>To obtain inch-pound units</i>
milliliter (mL)	.03382	ounce, fluid
micrometer (μm)	3.937×10^{-5}	inch

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ABSTRACT

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

Variances have been calculated for calcium, magnesium, sodium, potassium, chloride, and sulfate determinations. These variances should be applicable to the natural-sample analyte concentrations reported by the National Atmospheric Deposition Program and National Trends Network for 1983.

INTRODUCTION

The National Atmospheric Deposition Program (NADP) was organized in 1977 by a number of State agricultural experiment stations to provide information on the spatial and temporal trends of atmospheric deposition in the United States. Extensive participation was obtained from other organizations because of the broad interest in the subject. The National Trends Network (NTN) was established by the Deposition Monitoring Task Group of the Interagency Task Force on Acid Precipitation in 1983. Sampling sites may be part of either one or both of the monitoring networks. Therefore, this report will consider the NADP and NTN as one group known as NADP/NTN. Operators of individual sampling sites use standardized instrumentation and procedures to collect weekly wet-deposition samples. These samples are sent to the Central Analytical Laboratory (CAL) at the Illinois State Water Survey where all samples are analyzed for ammonium, calcium, magnesium, sodium, potassium, chloride,

sulfate, nitrate, and phosphate. These analyses are reported to the NADP/NTN Coordinator's Office which publishes the data and submits the data for computerized storage by Pacific Northwest Laboratory for the U.S. Environmental Protection Agency.

As part of its contribution to the NADP/NTN, a performance-audit program has operated for nearly 4 years by the U.S. Geological Survey in Denver, Colorado, in cooperation with sampling-site operators and CAL personnel. This program relies on the sampling-site operators to submit performance-audit samples to CAL after a week in which no wet deposition has occurred at their site. Site operators attempt to camouflage or disguise the performance-audit sample by submitting fictitious collection data with the sample. The goal of the performance-audit program is to have 1 sample submitted to CAL about once each week by 1 of the sampling-site operators; the actual number of samples submitted from the sites to CAL has averaged about 1 sample every 2 weeks.

This report: (1) Describes the NADP/NTN performance-audit program managed by the U.S. Geological Survey; (2) presents the absolute and relative percent differences between the NADP/NTN reported analyte concentrations and the performance-sample concentrations; and (3) presents the precision of the NADP/NTN reported concentrations, using the estimated variance. The report documents the results of the program for 1983 and for January 1980 through September 1984.

PREPARATION AND ANALYSIS OF PERFORMANCE-AUDIT SAMPLES

Performance-audit samples are prepared by the U.S. Geological Survey in Denver, Colorado. The samples are prepared by diluting standard reference water samples (Schroder and others, 1980; Skougstad and Fishman, 1974) with deionized water. A sample volume of 2,000 milliliters is prepared for each mixture and divided into 500 milliliter aliquots; then the pH of each solution is lowered to less than 5.0, using perchloric acid. The performance-audit samples are sent directly to NADP/NTN site operators on a quarterly basis. After a week in which no wet deposition has occurred, site operators take a 20 milliliter aliquot from the sample and determine the pH and specific conductivity of the sample. A portion (about 80 percent) of the remaining sample is poured into a pre-cleaned polyethylene sample container; then the container is sealed and shipped to CAL without prior notification. CAL filters all precipitation samples, using 0.45-micrometer pore-size filters, before analysis. All CAL analytical data are transmitted to the U.S. Geological Survey at Denver, Colorado; this laboratory identifies the performance-audit-sample data and notifies CAL that the data are to be removed from their data files. The diluted standard reference water samples do not contain ammonia at a detectable concentration; nitrate and phosphate are lost from the samples after dilution by the U.S. Geological Survey and before analysis by CAL.

CAL reanalyzes all performance-audit samples after the samples are identified by the U.S. Geological Survey. These samples normally are stored for 3 to 4 months at room temperature before the second analysis occurs. These data are transmitted to the U.S. Geological Survey after analysis. CAL may analyze each performance-audit sample a total of 8 times: 4 analyses of the individual 500-milliliter aliquots sent to CAL from sampling-site operators, and 4 reanalyses of aliquots. CAL has analyzed individual performance-audit samples an average of 5 times from January 1980 through September 1984.

PRECISION AND BIAS OF SELECTED ANALYTES

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

Results for 1983

The 1983 natural precipitation samples collected by the NADP/NTN have relatively low analyte concentrations. A summary of these analyte-percentile concentrations is presented in table 1. The concentration range of analytes in the 1983 performance-audit samples is summarized in table 2. Comparison of the data from tables 1 and 2 indicates that the performance-audit-sample analyte concentrations for several analytes are usually greater than the 50th percentile natural-sample analyte concentrations. This was necessary to produce stable analyte concentrations in the performance-audit samples.

Table 1.--Concentrations of analytes (5th, 50th, and 95th percentiles) in precipitation samples collected for the National Atmospheric Deposition Program and National Trends Network during 1983.

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

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

Table 2.--Performance-audit-sample concentration range for the National Atmospheric Deposition Program and National Trends Network during 1983.

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

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

$$\frac{\text{CAL reported concentration} - \text{known concentration}}{\text{Known concentration}} \times 100. \quad (1)$$

The relative-percent differences for the 1983 performance-audit samples are summarized in table 3. The median and mean relative-percent differences are positive for each analyte except sulfate. The median relative-percent difference probably is a better description of the bias than the mean for this data set because of the range of data. For example, relative-percent differences for calcium ranged from -2.07 to 69.4 percent.

Table 3.--*Relative-percent difference between the National Atmospheric Deposition Program and National Trends Network reported analyte concentrations and the known performance-audit-sample concentrations for 1983.*

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

Bias for the analyte concentrations is determined by comparing the CAL-reported analyte concentrations to the known audit-sample concentrations. These comparisons are shown in figures 1 through 6. Peart and Thomas (1983) and Grant and Leavenworth (1974) present a binomial-probability-distribution equation in which the probability of having X or more points on the same side of zero can be calculated. If X or more points occur on the same side of zero, bias is assumed. Bias was tested at 1-percent probability and summarized on table 4. Reported concentrations of calcium, magnesium, sodium, and chloride were determined to be biased for 1983.

A paired t-test (Dixon and Massey, 1969) was used to test the hypothesis that the initial NADP reported results were equal to reanalysis results for 1983. This hypothesis is accepted for the analytes calcium, magnesium, sodium, potassium, sulfate, and chloride.

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

Pooled standard deviations for 1983 performance-audit samples are presented in table 5. If these pooled standard deviations are applied to analyte concentrations beyond the concentration limits tested, caution is suggested.

Results for January 1980 through September 1984

Performance-audit-sample data for January 1980 through September 1984 are summarized in tables 6 and 7. Median relative percent differences are given because the median appears to give a better description of the bias than the mean. For example, relative-percent differences for calcium ranged from -6.5 percent to 263 percent. Reported concentrations for calcium, magnesium, sodium, sulfate, and chloride were determined to be biased, as summarized in table 7.

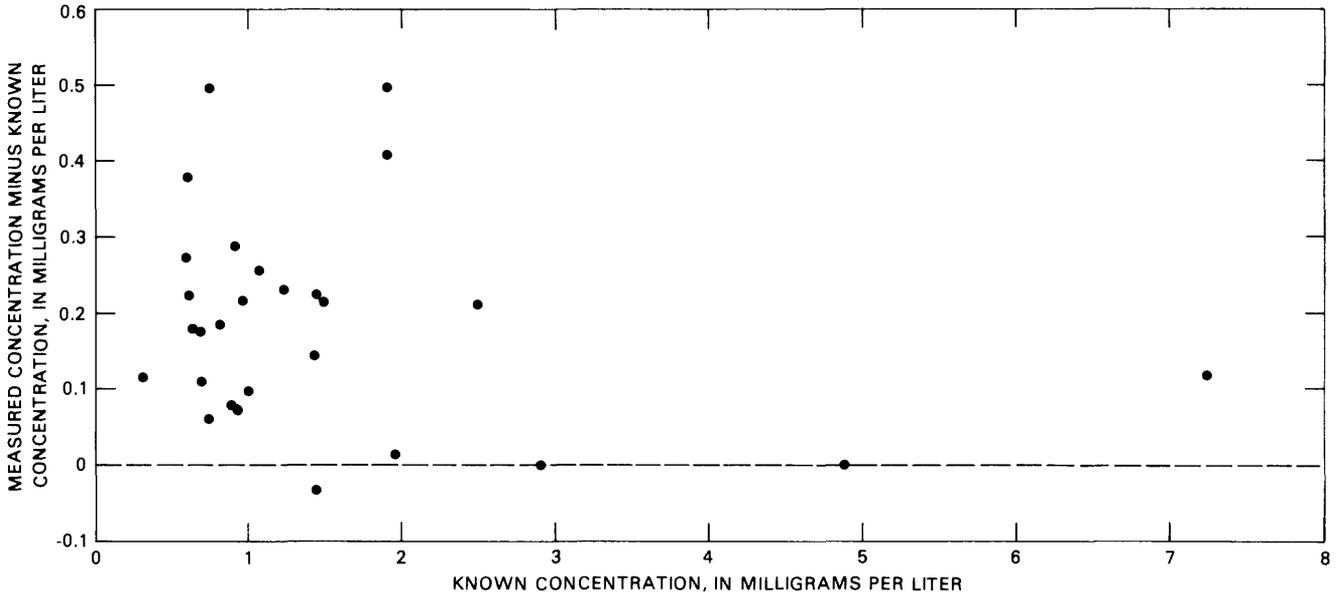


Figure 1.--Degree of bias based on known calcium concentration in performance-audit samples for 1983.

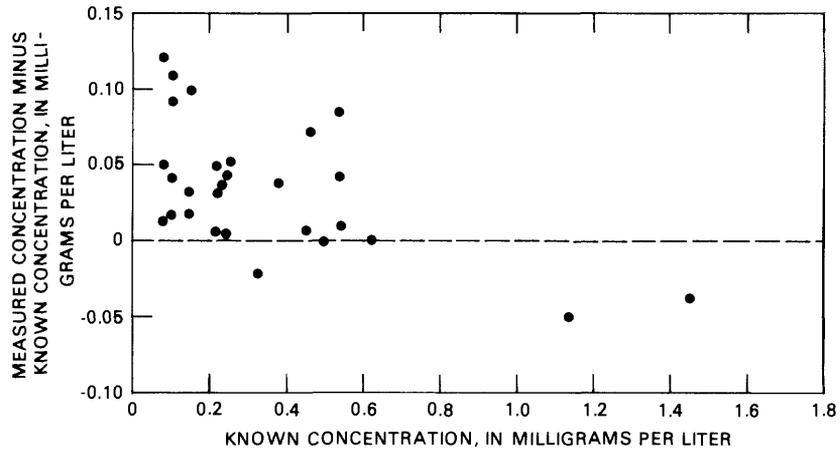


Figure 2.--Degree of bias based on known magnesium concentration in performance-audit samples for 1983.

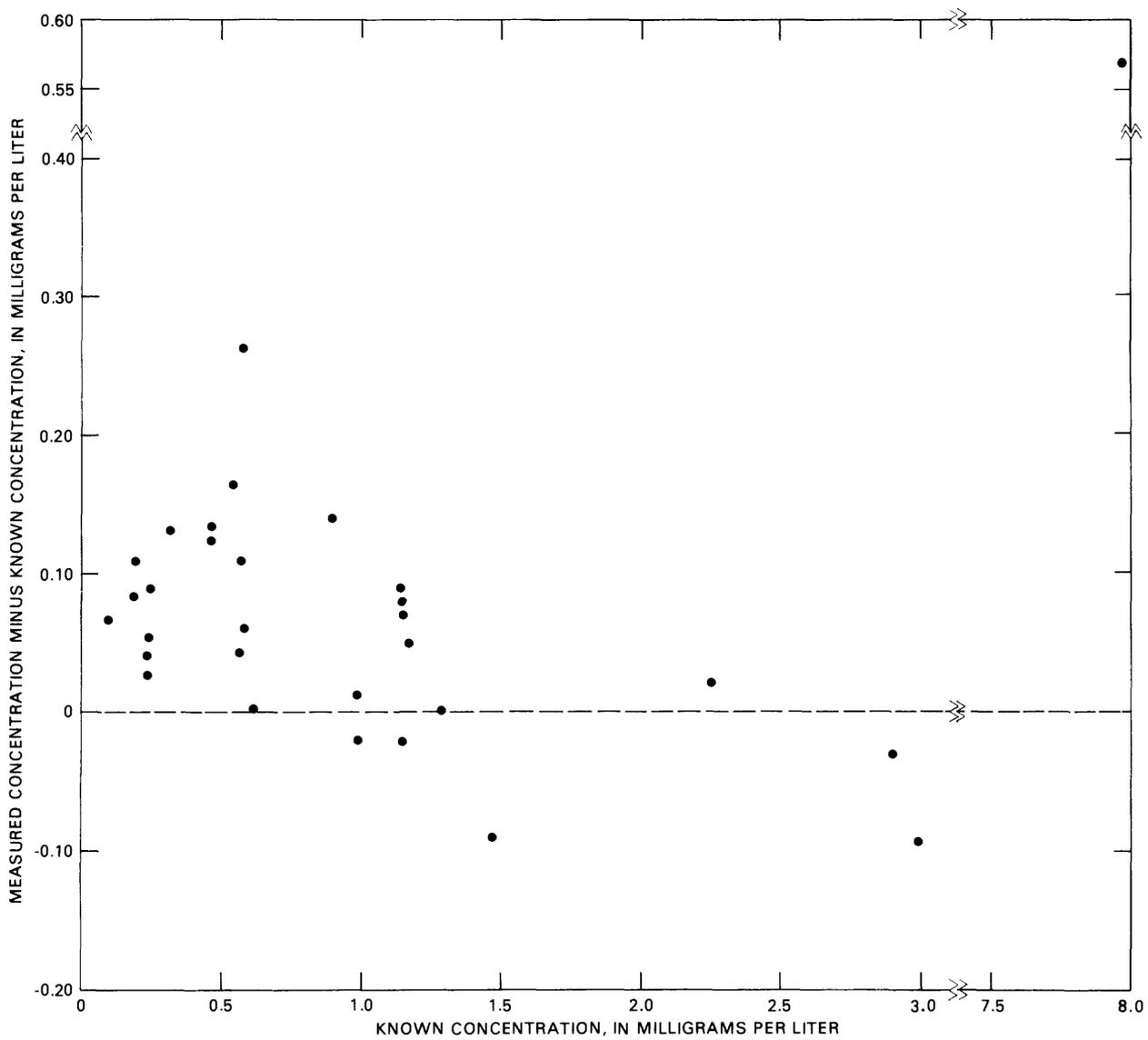


Figure 3.--Degree of bias based on known sodium concentration in performance-audit samples for 1983.

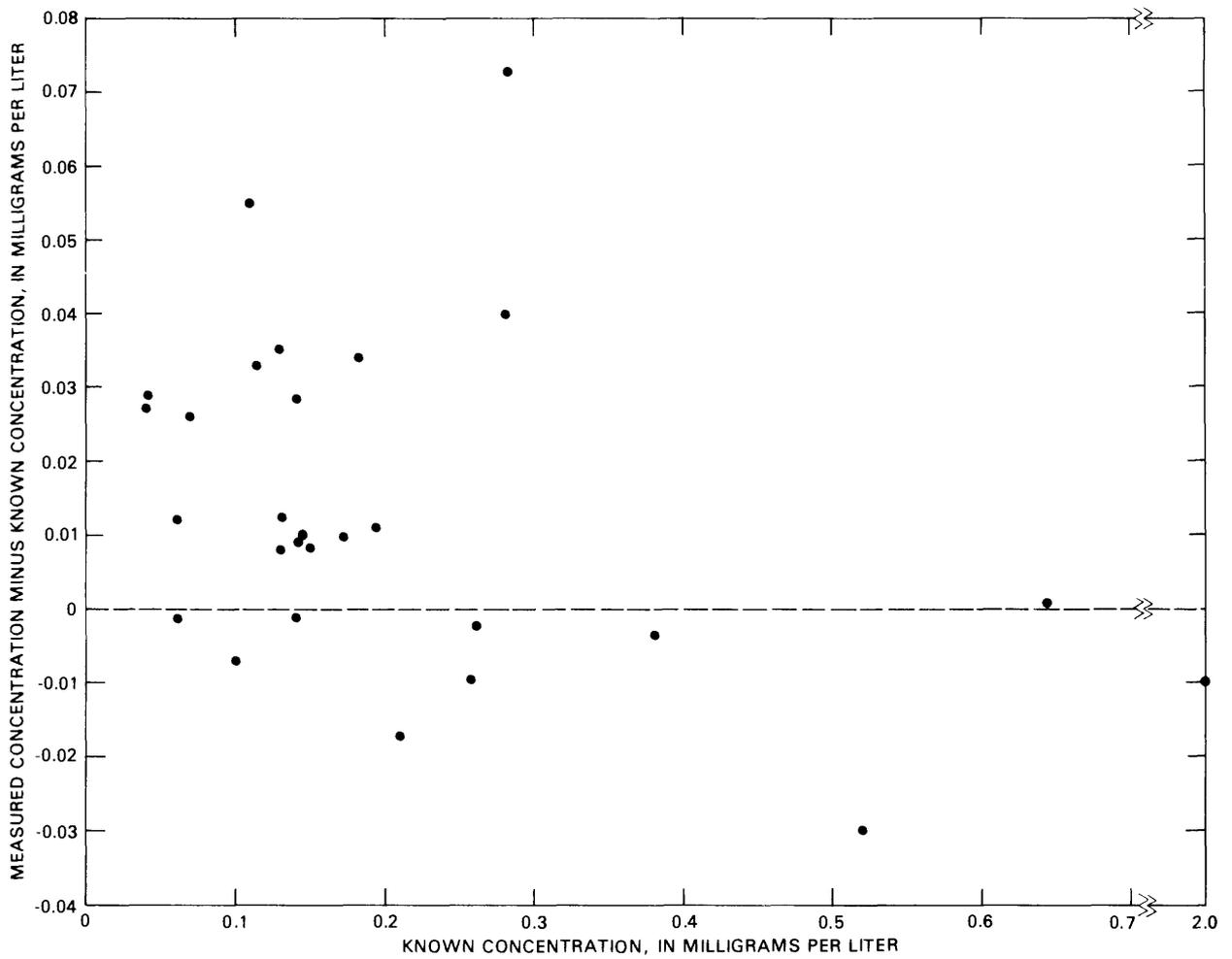


Figure 4.--Degree of bias based on known potassium concentration in performance-audit samples for 1983.

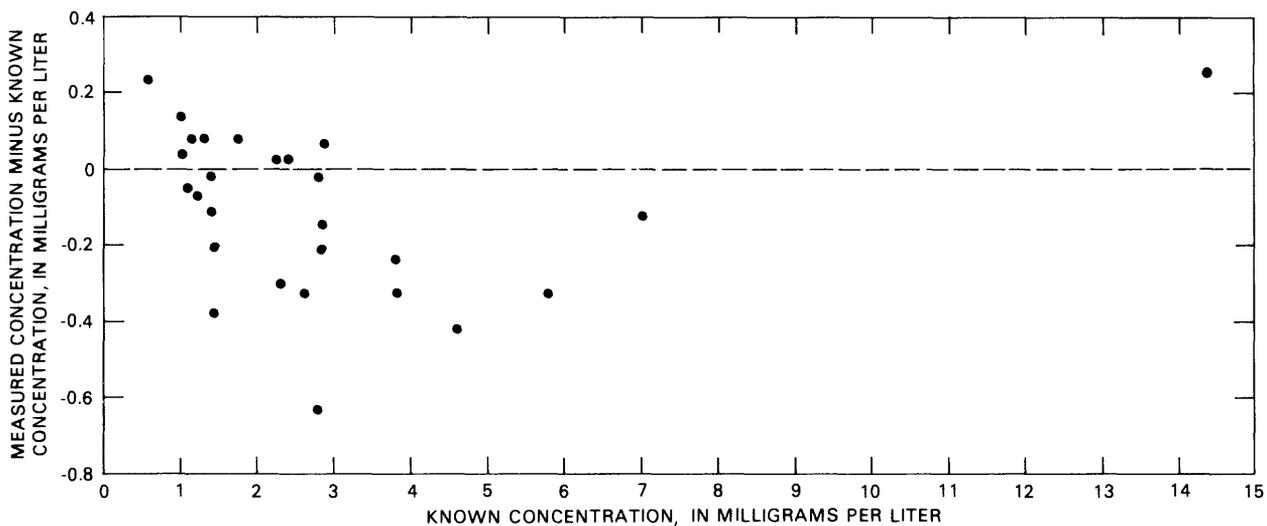


Figure 5.--Degree of bias based on known sulfate concentration in performance-audit samples for 1983.

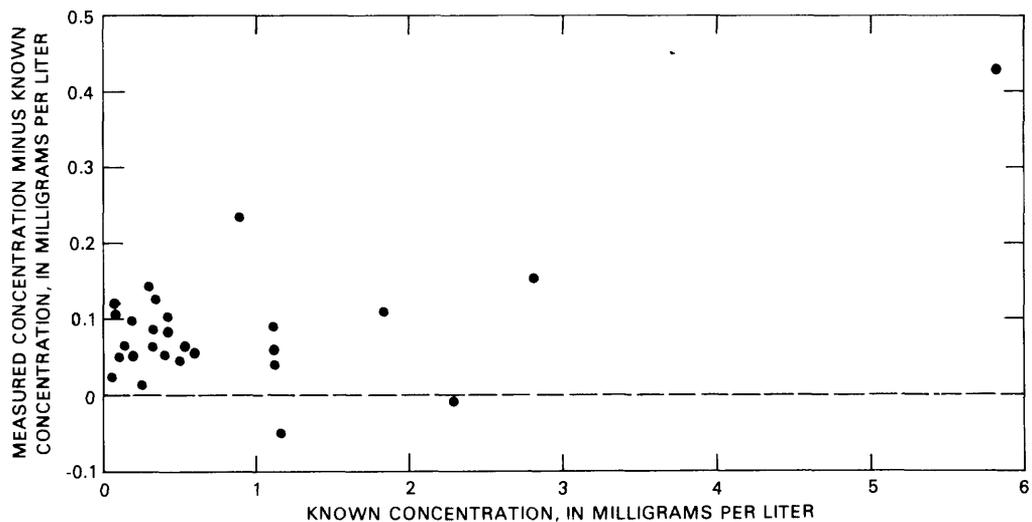


Figure 6.--Degree of bias based on known chloride concentration in performance-audit samples for 1983.

Table 4.--Bias determination from comparing the National Atmospheric Deposition Program and National Trends Network reported analyte concentrations and the known performance-audit-sample concentrations for 1983.

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

Table 5.--Estimated pooled standard deviation and 95 percent confidence limits of the National Atmospheric Deposition Program and National Trends Network reported analytes for 1983.
[mg/L, milligrams per liter]

Analyte	Concentration range (mg/L)	Pooled standard deviation (mg/L)	95-percent confidence limits of pooled standard deviation (mg/L)
Calcium	0.30 - 7.24	0.08	0.07 - 0.10
Magnesium	.080 - 1.54	.03	.03 - .04
Sodium	.24 - 7.43	.05	.04 - .06
Potassium	.060 - 1.87	.01	.01 - .01
Sulfate	.58 - 14.40	.13	.11 - .16
Chloride	.056 - 3.87	.04	.03 - .05

Table 6.--Median relative-percent difference between the National Atmospheric Deposition Program and National Trends Network reported analyte concentrations and the known performance-audit-sample concentrations for January 1980 through September 1984.

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

Table 7.--Bias determination from comparing the National Atmospheric Deposition Program and National Trends Network reported analyte concentrations and the known performance-audit-sample concentrations for January 1980 through September 1984.

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

Comparison of Results for the Two Periods

Analyses of performance-audit samples have been used to estimate the variances of the NADP/NTN-reported analyte concentrations. Variances for calcium, magnesium, sodium, potassium, sulfate, and chloride are given in tables 8 and 9. The variances for each analyte are estimated using a pooling or averaging technique from Dixon and Massey (1969) and Walpole and Myers (1972). The formula used for this estimate is:

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

- where s_p^2 = the unbiased estimate of the variance σ^2 for each analyte;
 n = the number of times each performance-audit sample was analyzed;
 s^2 = the variance for each particular performance-audit sample;
 and
 k = the number of different performance-audit samples used in the population.

Only performance-audit samples that were analyzed three or more times were used to calculate the variance for each analyte. These estimated variances should be valid for natural samples with analytes in the concentration ranges shown in tables 8 and 9. Caution needs to be used if the variances are applied to analyte concentrations beyond the limits of the concentrations tested, because the variances may not be applicable.

Table 8.--*Estimated variance of the National Atmospheric Deposition Program and National Trends Network reported analyte concentrations for 1983.*

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

Table 9.--*Estimated variance of the National Atmospheric Deposition Program and National Trends Network reported analyte concentrations for January 1980 through September 1984.*

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

SUMMARY

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

Median relative-percent differences were determined for each analyte. Median values are reported because the median gives a better description of the bias than the mean. From January 1980 through September 1984 median relative-percent differences were positive for all six analytes. Median relative-percent differences were positive for all analytes except sulfate in the 1983 performance-audit samples; the median relative-percent difference was negative.

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

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

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