QUALITY ASSURANCE REPORT
NADP/NTN DEPOSITION MONITORING

Laboratory Operations
Central Analytical Laboratory
1988

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

A Cooperative Research Program of the
State Agricultural Experiment Stations
and other Federal, State and Private
Research Organizations • IR-7

A contribution to the
Task Group on Deposition Monitoring
Lead Agency: U.S. Geological Survey

The National Atmospheric Deposition Program (NADP) was organized in 1978 by the North Central Region of the State Agricultural Experiment Stations as Project NC-141 to address the problem of atmospheric deposition and its effects on agriculture, forests, rangelands, and fresh water streams and lakes. In 1982 the program was endorsed by all four regions of the State Agricultural Experiment Stations and subsequently became Interregional Project IR-7.

The assessment of the linkage between environmental effects and atmospheric deposition requires a knowledge of geographical patterns of the chemical composition and flux of deposition on a national scale. To establish long term trends in composition and flux it is necessary that these measurements be carried out for a period of ten years or longer. In response to these needs, in 1978 the National Atmospheric Deposition Program established a regional atmospheric deposition monitoring network with national coverage. In 1982, the federally-supported National Acid Precipitation Assessment Program (NAPAP) was established to provide broadened support for research into the causes and effects of acid deposition. This program included research, monitoring and assessment activities that emphasized the timely development of a firm scientific basis for decision making. As a result of its experience in designing, organizing and operating a national scale monitoring network, NADP was asked in 1982 to assume responsibility for coordinating the operation of the National Trends Network (NTN) of NAPAP. Since NADP and NTN had common siting criteria and operational procedures as well as sharing a common analytical laboratory, the networks were merged with the designation NADP/NTN. As a result of NAPAP support, approximately 50 additional sites supported by the U.S. Geological Survey (USGS) were added to the network for a total 200 sites by 1986. In addition to the State Agricultural Experiment Stations, NADP research and monitoring is supported under NAPAP by the USGS, the U.S. Department of Agriculture (USDA) Cooperative State Research Service (CSRS) and U.S. Forest Service (USFS), the National Park Service (NPS), Bureau of Land Management (BLM), National Oceanographic and Atmospheric Administration (NOAA), and the Environmental Protection Agency (EPA). Although NAPAP activities will be concluded in 1990, NADP/NTN continues to be supported by these agencies. Additional support is provided by various state agencies, public utilities and industry.

**1988 QUALITY ASSURANCE REPORT
NADP/NTN DEPOSITION MONITORING**

**Laboratory Operations
Central Analytical Laboratory
January 1988 through December 1988**

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I. INTRODUCTION

The first Quality Assurance Report for the Central Analytical Laboratory (CAL)(1) of the National Atmospheric Deposition Program (NADP) was published in 1980. It detailed the beginnings and goals of the quality assessment program being developed for the laboratory. The second report (2) incorporated the data from that original report with quality assurance data from the years 1980 through 1983, including changes that occurred as the program was refined. The report documenting the years 1984 and 1985 was published in May of 1988 (3), and the 1986 report (4) followed in October 1988. The most recent of these updates (5), which documents the Quality Assurance program at the CAL in 1987, was published in October 1989. All five of these reports serve to document the progress and results of the program during the first ten years.

In the early years, as the CAL program was evolving and the network expanded to include the National Trends Network (NTN), many noticeable changes and subtle modifications were made in the laboratory's quality assurance program. The laboratory facility moved and expanded when the Illinois State Water Survey moved to more modern accommodations. Additional staff was hired as needed. Methods changed with advances in technology. With the methods changes, detection limits also changed. As the network entered its eleventh year, 1988, a documented and viable quality assurance program was in effect. Modifications continue to be made, but most are minimal and serve as refinements to the program already in place.

This report documents the modifications made in 1988 but does not attempt to repeat the information presented in the previous editions. All of these reports are available upon request from the Illinois State Water Survey or the program Coordinator's Office at Colorado State University. Future reports will not repeat procedural information contained in earlier reports, but they will contain all of the data necessary to assess the laboratory's performance.

I. INTRODUCTION

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II. LABORATORY QUALITY ASSURANCE PROGRAM

A. GENERAL DESCRIPTION

The Quality Assurance (QA) Program at the Central Analytical Laboratory of the National Atmospheric Deposition Program/National Trends Network has been modified and improved since the beginning of the NADP network in 1978. Sample analysis methods (Table II-1) used were the same as in 1987; therefore the sample processing flow chart (Figure II-1) in effect at the end of that year was the same throughout 1988.

The internal program at this time consists of several procedures, established by the CAL, to monitor analytical equipment and personnel performance; to monitor and evaluate analytical procedures; and to assure that all reported values are precise and accurate and reflect the actual status of respective samples. The interior QA components can be subdivided into: daily procedures, weekly procedures, monthly procedures and check procedures.

Quality control samples (QCS) are analyzed daily as the sample analyses are in process. Weekly monitoring of the laboratory's deionized water, the filtering process, and the sampling containers continued. Monthly assessments of the bias and the precision of the measurements are prepared from the results of the analysis of blind quality assurance samples, actual precipitation sample replicates, and the control charts that display the results from QCS for each month. When complete, each sample analysis is subjected to a computer program that determines if the anions and cations are in balance and if the calculated and measured conductance are within established limits.

Finally there is an external quality assurance program. The United States Geological Survey (USGS), located in Denver, Colorado, serves as the external quality assurance auditor, providing a blind sample audit and an interlaboratory comparison. Participation in other national and international interlaboratory comparisons occurs on a voluntary basis by the CAL. The choice of which comparisons to participate in is based on the consensus of the CAL director, the laboratory manager and the quality assurance specialist.

B. DATA AVAILABILITY

The data presented in this report have been verified by either a double-entry procedure or a visual check. The data have been stored in the CAL database and are available from the CAL director on request.

TABLE II-1 Method Detection Limits for the Analysis of Precipitation Samples, 1978-1988

Analyte	Method[*]	MDL(mg/L)	Dates
Calcium	Flame Atomic Absorption	0.02	7/78-10/80
		0.009	10/80-12/88
Magnesium	"	0.002	7/78-10/80
	"	0.003	10/80-12/88
Sodium	"	0.004	7/78-10/80
	"	0.003	10/80-12/88
Potassium	"	0.004	7/78-10/80
	"	0.003	10/80-12/88
Ammonium	Automated Phenate, Colorimetric	0.02	7/78-12/88
Sulfate	Automated Methyl Thymol Blue, Colorimetric	0.10	7/78-5/85
	I.C.[a]	0.03	5/85-12/88
Nitrate/ Nitrite	Automated Cadmium Reduction, Colorimetric	0.02	7/78-5/85
Nitrate	I.C.[a]	0.03	5/85-12/88
Chloride	Automated Ferricyanide Colorimetric	0.05	7/78-3/81
		0.02	3/81-5/85
	I.C.[a]	0.03	5/85-12/88
Ortho- phosphate	Automated Ascorbic Acid, Colorimetric	0.003	7/78-2/86
		0.01	2/86-7/87
	I.C.[a]	0.02	7/87-12/88

[*] For a complete method description for the most recent methods, see <u>Methods for Collection and Analysis of Precipitation</u>, (6).

a. I.C. = ion chromatography

DRY SIDE

WET SIDE

LOG IN
ASSIGN LAB NUMBER
VISUALLY INSPECT

DRY SIDE

WET SIDE

DRY

WET

DRY

WET

ADD 250 mL DI H_2O
ALLOW 24 HOURS
TO EQUILIBRATE

WEIGH

ADD 50 mL DI H_2O
ALLOW 24 HOURS
TO EQUILIBRATE

WEIGH

pH AND SPECIFIC CONDUCTANCE

FILTER WITH 0.45 um MILLIPORE TYPE HA

FILTRATE

WET, ≤ 35 mL

WET >35 mL, DRY
BUCKET DILUTIONS

60 mL STORED
AT $4^{\circ}C$

DILUTE WITH
50 mL DI H_2O

ANALYSIS

FLAME ATOMIC
ABSORPTION
Ca^{++}, Mg^{++}, Na^+, K^+

ION CHROMATOGRAPHY
$SO_4^=$, NO_3^-, Cl^-, $PO_4^{\equiv}$

AUTOMATED WET
CHEMISTRY
NH_4^+

FIGURE II-1. Sample processing flowchart January 1988
through December 1988.

C.   LABORATORY PERSONNEL

In 1988 there were several changes in the analytical staff (Table II-2). Barbara Keller performed the atomic absorption analyses for metal cations from April through August. Loretta Skowron performed cation analyses until Sue Bachman was trained for the task in November. Jackie Sauer returned to the pH, conductance, and sample processing group when Sheri Uber resigned in January.

TABLE II-2   Central Analytical Laboratory (CAL)
Analytical Staff Only, 1988.

Staff Member/Job Function	Period of Employment
Beth Allhands Sample receipt and processing	February 1984 – December 1988
Sue Bachman NH_4, Ca, Mg, Na, K	August 1980 – December 1988 November 1988 – December 1988
Brigita Demir SO_4, NO_3, Cl, PO_4	September 1981 – December 1988
Pat Dodson Sample processing	September 1980 – December 1988
Theresa Ingersoll Sample receipt and processing	March 1985 – December 1988
Kenni James Quality assurance	October 1987 – December 1988
Barbara Keller Ca, Mg, Na, K	April 1988 – August 1988
Mark Peden Laboratory Manager	July 1978 – December 1988
Jeffrey Pribble Sample receipt	July 1987 – December 1988
Jackie Sauer Sample processing, pH, conductivity	January 1988 – December 1988
Loretta Skowron Ca, Mg, Na, K	July 1978 – November 1988
Sheri Uber Sample processing, pH, conductivity	April 1986 – January 1988

III. LABORATORY BLANK DATA

John Taylor says, in <u>Quality Assurance of Chemical
Measurements</u>, "The quality control program must give special
emphasis to blank control whenever a blank correction is
significant. Environmental control can range from simple good
housekeeping practices to conducting all operations in an
ultraclean room. ... Water used as a solvent, diluent, or
even for washing can be a major source of reagent blank....
Blanks can arise from the apparatus used, particularly if
chemical operations are involved. Thus beakers, bottles,
filters, mortars, sieves, stoppers, and sample lines can
contribute both positive and negative blanks."(7)

Blanks have been a mandatory portion of the weekly CAL
routine since the day the first samples were processed and
analyzed in 1978. The program for the analysis of blanks
assesses the contribution of the sample collection vessel,
the filtering process, and the laboratory's deionized water.

A. BUCKET BLANKS

The buckets used to collect samples in the field must be
as clean and contaminant-free as conditions permit. The
buckets are washed in the automatic dishwasher and sealed in
plastic bags to eliminate contamination from human handling.
Site operators have been instructed to install and remove
these buckets with minimum contact. In order to evaluate the
container contribution to sample chemistry, two buckets and
two lids are selected randomly each week and a 50- or 150-
milliliter (mL) aliquot of deionized water is added to each.
The lid is pounded on and the bucket inverted for 24 hours.
The lid is then removed and the 50-mL aliquot and 60 mL of the
150-mL portion are poured into previously rinsed 60-mL sample
bottles. These two samples, referred to as bucket blanks,
undergo the same routine sample analysis as natural
precipitation samples.

Bucket blanks are one of the most time-consuming aspects
of the quality-control activities in the laboratory. The
appearance of sodium has been random and often unexplained.
It disappeared in the same manner. Measureable calcium and
magnesium concentrations have been attributed to the o-ring.
Table III-1 is a listing of the median and mean bucket-blank
analyte masses, expressed as microequivalents (μeq) per
bucket, for 1988. Once again, sodium was the most prevalent
ion.

Box plots showing the bucket blank data for each analyte

TABLE III-1   Median/Mean Measured Mass (μg)/Bucket[a]
Found in Weekly Inverted Bucket Blanks,
1988.

Analyte	50 mL	150 mL
Calcium	1.35/1.65	2.25/2.40
Magnesium	0.30/0.55	0.15/0.25
Sodium	3.75/6.85	5.55/9.60
Potassium	0.15/0.35	<0.15/0.45
Ammonium	<1.0/<1.0	<1.0/<1.0
Sulfate	2.0/3.0	<1.5/1.5
Nitrate	<1.5/<1.5	<1.5/<1.5
Chloride	2.5/3.0	<1.5/4.5
pH (units)[b]	5.94/5.94	5.79/5.79
[H$^+$](μeq/bucket)	0.06/0.06	0.24/0.24
Conductivity (μS/cm)	1.8/2.3	1.3/1.4

Number of Analyses   44   44

a. Mass/bucket = the concentration in μg/mL x 50 or 150
mL.
Detection limit values are expressed as the MDL (in
μg/mL) x 50 mLs.
b. Median/mean pH of DI water = 5.56 and 5.46 units:
5.56 = 0.00275 μeq/mL x 50 mL = 0.14 μeq H$^+$
= 0.00275 μeq/mL x 150 mL = 0.41 μeq H$^+$
5.46 = 0.00347 μeq/mL x 50 mL = 0.17 μeq H$^+$
= 0.00347 μeq/mL x 150 mL = 0.52 μeq H$^+$

are presented in Appendix A. Box plots are a summary representation of the distribution of a set of data. The top and bottom of the box represent the 75th and 25th mass percentile, respectively. The horizontal line represents the median, the lower T extends to the 10th percentile, while the upper T extends to the 90th percentile. Extreme values are categorized as outside values and far outside values. These values are explained in relation to the Hspread, which is the difference between the 25th and 75th percentiles. Inner fences are then defined as the 25th percentile minus 1.5 times the Hspread, and the 75th percentile plus 1.5 times the Hspread. Outer fences are the 25th percentile minus 3 times the Hspread, and the 75th percentile plus 3 times the Hspread. Outside values are data points lying between the inner and outer fences. Far outside values lie beyond the outer fences.

When the buckets were washed by hand and when the dishwasher was first installed, the washing process was assumed to be the source of most contamination problems. Since the dishwasher has been using deionized water as the sole water source, it seems to contribute to bucket contamination only when cleaning or service is indicated. The major source of sampling-container contamination now appears to emanate from the o-ring used in the lid, which guarantees a complete seal and prevents samples from being lost during shipping. During 1988 several variations on the o-ring contribution hypothesis were tested at various times in the laboratory.

In April a comparison of cleaned first-time-use buckets and previously used buckets was made in the laboratory. The new buckets were found to contain a mean value of 0.119 milligrams per liter (mg/L) of sodium and trace amounts of calcium and magnesium compared to less than detection limit amounts of all ions in previously used buckets. The sample processing staff was directed to note receipt of new buckets and to run a series of blanks until no detectable ionic species were found. At that time the buckets were suitable for shipping to the field.

In July, deionized water was poured into different areas of ten lids that had been washed and bagged for shipping. These lids were resealed and left overnight on the clean air bench in the laboratory. The water was then pipetted into cleaned bottles and sent for cation analysis. The water, which never came into contact with the o-ring, had less than detection-limit cations. The water poured into the o-ring groove contained more than 0.1 mg/L calcium and small amounts (0.040 mg/L) of magnesium and sodium. The o-ring, rather than the lid surface was clearly implicated as the contamination source.

Later in the summer, it was noted that some of the o-rings and lids turned yellow when they were washed. Sodium was the detectable analyte, and the pH and conductivity were slightly elevated. These lids were not used, and the manufacturer was contacted. No reason for the discoloration was provided and replacements were made. The dishwasher steam cycle used to heat the deionized wash water was shut off, and the appearance of yellow lids abated. The dishwasher was disassembled several times and cleaned. In late August and mid-September the dishwasher was chlorinated. Four lids were washed, with the o-rings face- down in the dishwasher, to determine if this was a better way to eliminate the persisitant sodium problem. The resulting inverted bucket-blank leachates contained small amounts of calcium and magnesium and noticeable sodium concentrations (>0.100 mg/L and >0.50 mg/L in the 50- and 150-mL samples). This washing procedure was clearly not the solution, and much more time consuming. Lids continued to be leached and washed as before while more inverted bucket blank studies were conducted.

In December, 22 lids were tested, some with yellow color still remaining after a second cleaning. Three of seven lids had measurable cation concentrations after two washings. Six lids with yellow color were cleaned with hot deionized water and washed in the normal cycle. One 50- mL sample had 0.026 mg/L of sodium, the rest were below detection limit for all cations. Nine colorless lids were washed with 25°C water on two separate days in the regular cycle. One sample contained a piece of plastic and was discarded. The others contained no sodium and four had small concentrations (0.010 to 0.035 mg/L) of calcium. These studies led to a series of additional o-ring experiments which were continued into 1989.

B. FILTER BLANKS

Filter blanks were analyzed to help assess the contributions of the filtering apparatus and process to the chemistry of the sample. After the standard Millipore filter was leached with 300 mL of deionized water, two successive, filtered 50-mL aliquots of deionized water were collected. The first 50-mL aliquot was labeled A, the second B. Table III-2 lists the median and mean ion concentrations, expressed as milligrams per liter, and pH and conductivity of the filter leachates A and B in 1988. These values have remained the same as in past years with sodium being the only measurable analyte. The CAL efforts continued to reduce the sources of sodium in contact with the filtering apparatus.

**TABLE III-2 Median/Mean Analyte Concentrations Found
in Weekly Filter Blank Leachates, 1988.**

Analyte	A[a]	(mg/L)	B[b]
Calcium	<0.009/<0.009		<0.009/<0.009
Magnesium	<0.003/<0.003		<0.003/<0.003
Sodium	0.010/0.015		0.003/0.004
Potassium	<0.003/<0.003		<0.003/<0.003
Ammonium	<0.02/<0.02		<0.02/<0.02
Sulfate	<0.03/<0.03		<0.03/<0.03
Nitrate	<0.03/<0.03		<0.03/<0.03
Chloride	<0.03/<0.03		<0.03/<0.03
pH (units)	5.53/5.53		5.53/5.54
(μeq/L)	2.95/2.95		2.95/2.88
Conductivity (μS/cm)	1.2/1.2		1.0/1.0
Number of Analyses	44		44

a. First 50 mL aliquot of filtered deionized water
after 300 mL leaching.
b. Second 50 mL aliquot of filtered deionized water
after 300 mL leaching.

In June 1988 stainless steel handles were affixed to the sides of the removable portion of the filtering apparatus. This was an effort to minimize sodium contamination from human contact. Additional studies have been carried out when contamination was indicated, but they have not been as exhaustive as the bucket blank investigations.

C. DEIONIZED WATER BLANKS

The deionized (DI) water was sampled and analyzed from several laboratories at the CAL complex. Weekly samples were taken in the atomic absorption laboratory (room 304), the bucket-washing laboratory (room 323), and the sample processing laboratory (room 209). The analyses of these samples were used to monitor the central DI system, as well as to assure the analysts that the source water they used for preparing reagents and rinsing bottles was of the highest possible quality. The deionized water continued to be contaminant-free from week to week and could be eliminated as a contamination source for both the buckets and the filters.

Table III-3 lists the median and mean pH and conductivity for the deionized water collected from the three different rooms in 1988. The median values for the cations and anions were all below method detection limits.

Table III-3   Median/Mean Values for pH and Conductivity for Weekly Deionized Water Blanks, 1988.

| | Laboratory | | |
	Sample Processing	Atomic Absorption	Dishwashing
pH(units)	5.56/5.46	5.59/5.59	5.55/5.55
Conductivity (μS/cm)	0.7/0.8	0.9/0.9	0.8/0.9
Number	42	46	46

IV. LABORATORY BIAS AND PRECISION

The CAL Work Statement contains a subsection describing replicate samples as a means of producing precision statistics for all measured parameters. The final subsection states that accuracy is monitored with the use of Environmental Protection Agency (EPA) water-quality reference samples supplied to the CAL by the Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati, Ohio. In addition to these two mandated bias and precision indicators, the CAL instituted an internal blind program in 1984. This section contains brief descriptions of each procedure along with tables and plots summarizing the data.

A. QUALITY CONTROL CHECK SAMPLE DATA

The check samples used in 1988 were the same formulations or similar to those used in previous years. An internally formulated dilute nitric acid solution (5.01×10^{-5} N HNO_3) and a 5.0×10^{-4} N KCl solution are used as check samples for pH and conductance. The first solution has a theoretical pH of 4.3 $\pm$ 0.03 pH units and a conductance of 21.8 $\pm$ 2 microsiemens per centimeter ($\mu S/cm$). The second solution has a specific conductance of 74.8 $\pm$ 2 $\mu S/cm$ and a pH of 5.63 $\pm$ 0.3 pH units. Both are used in the laboratory and sent to sites for use when making field measurements. All internally formulated solutions are measured and validated by the laboratory before being put into use. The check samples used for the cations and anions are dilutions of the EPA mineral and nutrient water-quality reference concentrates. These concentrates are diluted so that the resulting ion concentrations are as close as possible to the twenty-fifth and seventy-fifth percentile concentrations of samples from the NADP/NTN network (Table IV-1).

These quality control samples are measured as soon as an instrument has been calibrated for the analysis of samples. If the QCS analysis is beyond the warning limits for the analyte being measured, the entire standardization is repeated until the process is in statistical control. QCS are measured every twelfth sample throughout the day, as long as samples are being analyzed and each time recalibration occurs. The analyses of the QCS are recorded and then entered into a computer program that generates monthly control charts, the mean percent recoveries, and standard deviations for each solution used. These charts and statistics are kept in notebooks in the quality assurance specialist's office, and copies are kept by the analysts. At the end of the year the data in the computer are compiled to present the annual summaries shown in Table IV-2.

TABLE IV-1 Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation, 1988.

Percentile Concentration Values (mg/L)

Parameter	Min.	5th	10th	25th	50th	75th	90th	95th	99th	Max.
Ca	<0.009	0.025	0.037	0.069	0.147	0.335	0.692	1.022	2.493	25.10
Mg	<0.003	0.007	0.007	0.014	0.029	0.062	0.122	0.198	0.450	1.52
K	<0.003	<0.003	<0.003	0.005	0.016	0.039	0.083	0.134	0.390	57.00
Na	<0.003	0.015	0.023	0.052	0.102	0.225	0.490	0.852	2.526	25.00
NH_4	<0.02	<0.02	<0.02	<0.02	0.10	0.31	0.59	0.85	1.72	5.71
NO_3	<0.03	<0.03	0.13	0.50	1.12	2.00	3.24	4.30	7.07	20.90
Cl	<0.03	0.04	0.05	0.09	0.16	0.32	0.76	1.37	4.26	22.72
SO_4	<0.03	0.21	0.33	0.70	1.45	2.64	4.17	5.48	9.78	40.14
PO_4	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.06	0.12	0.32	4.84
pH (units)	3.18	4.03	4.17	4.40	4.79	5.40	6.09	6.42	6.91	8.07
(μeq/L)	661.	93.	67.6	39.8	16.2	3.98	0.81	0.38	0.12	0.01
Conductivity (uS/cm)	1.1	3.5	4.7	8.2	14.6	24.6	39.0	51.7	91.2	313.6

Source: National Atmospheric Deposition Program (NADP)/National Trends Network (NTN)
1988 - wet side samples (w)   Number of samples = 6,386

TABLE IV-2 Analytical Bias and Precision Determined from Analysis of Quality Control Check Samples, 1988.

Parameter	Theoretical Concentration (mg/L)	Measured Concentration (mg/L)	Number of Replicates	Bias mg/L	Bias %	Precision s mg/L	Precision RSD %	Critical [ ]ᵃ (mg/L)	Statistically Significant Bias?[b]
Calcium	0.053	0.054	709	0.001	1.9	0.003	5.6	0.001	YES
	0.402	0.407	718	0.005	1.2	0.006	1.5	0.002	YES
Magnesium	0.018	0.018	651	0.000	0.0	0.001	5.6	0.000	NO
	0.083	0.085	724	0.002	2.4	0.001	1.2	0.001	NO
Sodium	0.041	0.042	714	0.001	2.4	0.001	2.4	0.000	YES
	0.083	0.084	42	0.001	1.2	0.001	1.2	0.002	NO
	0.230	0.237	726	0.007	3.0	0.002	0.8	0.001	YES
	0.459	0.463	42	0.004	0.9	0.002	0.4	0.007	NO
Potassium	0.011	0.011	718	0.000	0.0	0.001	9.1	0.000	NO
	0.021	0.021	718	0.000	0.0	0.001	4.8	0.000	NO
	0.050	0.050	730	0.000	0.0	0.007	14.0	0.002	NO
	0.100	0.100	42	0.000	0.0	0.002	2.0	0.000	NO
Ammonium	0.13	0.13	262	0.00	0.0	0.01	7.7	0.00	NO
	0.64	0.64	335	0.00	0.0	0.02	3.1	0.00	NO
Sulfate	0.93	0.94	585	0.01	1.1	0.02	2.1	0.01	YES
	2.81	2.89	205	0.08	2.8	0.03	1.0	0.03	YES
	3.43	3.57	375	0.14	4.1	0.03	0.8	0.06	YES
Nitrate	0.44	0.44	587	0.00	0.0	0.01	2.3	0.00	NO
	2.19	2.25	600	0.06	2.7	0.03	1.3	0.01	YES
Chloride	0.12	0.12	505	0.00	0.0	0.01	8.3	0.00	NO
	0.81	0.80	584	-0.01	-1.2	0.02	2.5	0.01	YES
pH units	4.30(50.1)	4.31	1833	-1.1	-2.2	4.33	4.7	2.60	NO
(μeq/L)	5.50(3.2)	5.47	1834	0.03	6.2	5.53	12.5	0.30	NO
Conductivity (μS/cm)	21.8	21.6	1148	-0.2	-0.9	0.6	2.8	0.4	NO

a. Critical = t x s_{pooled} $\sqrt{1/n_{EPA} + 1/n_{CAL}}$
b. At 95% confidence level

B.   REPLICATE SAMPLE DATA

The replicate sample routine has continued to be the same since early 1986. The original sample, from any random site in the network, is split by the sample processing staff and sent to the laboratory as a regular precipitation sample on different days with different numbers. The first or original (O) sample is given the next number in sequence, and the duplicate or quality control (Q) sample is held back for a few days and then given another number and sent back to the sample processing staff. When analyses are entered into the data base, the data specialist changes the number of the second sample back to the original number followed by a Q. These numbers can then be readily compared on the printouts used to identify samples for reanalysis (Section V).

The information gathered from these samples, which represent 2 percent of the sample load, are then retrieved from the database and plotted to assess precision. Figures 1 through 3 in Appendix B are box plots of the concentration differences between replicate samples O and Q expressed in the appropriate concentration units. Table IV-3 provides a quick assessment of the differences between the samples for the year. Some of these sample analyses have been excluded from the data base for not meeting the criteria of acceptable data and hence the reason for a number less than two percent of the 1988 sample load.

The information presented in Table IV-3 is different from that presented in previous reports. The mean differences for each analyte are calculated by summing the differences of each pair and dividing by the number of pairs. The estimate of the standard deviations of the differences have been calculated for two ranges for each analyte. The low range contains values from the method detection limit to the median value; the high range contains concentrations from the median to the highest (Table B-1). The equation used to estimate this standard deviation is:

$$s = \sqrt{\frac{\Sigma\, d^2}{2k}}$$

where k = number of sets of duplicate measurements
      d = difference of duplicate measurements.

In order to use this formula, the samples represented in the calculation must be similar and the precision of the measurement process essentially the same for all samples included in the calculation (7). The estimate of the standard deviations of the differences obtained from this formula should then be comparable to the standard deviations of the concentrations of the check samples and the blind samples.

**Table IV-3 Mean Differences and Standard Deviations
of the Differences of Replicate Analyses of
Network Precipitation Samples, 1988.**

Parameter	Mean Difference[a]	Standard Deviation Low []	Standard Deviation High []
Calcium (mg/L)	-0.002	0.012	0.030
Magnesium (mg/L)	-0.000	0.001	0.008
Sodium (mg/L)	-0.000	0.012	0.015
Potassium (mg/L)	0.000	0.003	0.008
Ammonium (mg/L)	0.01	0.02	0.08
Sulfate (mg/L)	0.01	0.02	0.06
Nitrate (mg/L)	0.01	0.12	0.10
Chloride (mg/L)	0.00	0.01	0.02
pH (μequiv/L)	0.306	1.00	3.25
Conductivity (μS/cm)	0.17	0.37	1.17
Number of Pairs	184	92	92

a. The difference is calculated by subtracting the reanalysis
    value from the original value.

Each of these values can be used to present a more complete evaluation of laboratory precision.

C. INTERNAL BLIND SAMPLE DATA

Three samples a week are submitted blind to the laboratory. They are given sequential numbers and analyzed as routine precipitation samples. When they are submitted to the sample processing staff, they are accompanied by an NADP/NTN Field Observer Report Form with designated sites, SWS 1, SWS 2, and SWS 3. SWS 1 samples are National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 2694I and 2694II, and they are not filtered prior to analysis. The samples from SWS 2 are deionized water from room 302 and the pH 4.3 internally prepared QCS, and are also not filtered prior to analysis. The samples from SWS 3 are all filtered, and they are SRM 2694 I and 2694 II, deionized water and the pH 4.3 QCS submitted in rotation. These samples serve to evaluate the filtering process as well as bias and precision.

D. DISCUSSION OF RESULTS

The formulas used to calculate the bias, percent bias, standard deviation, relative standard deviation, and critical concentration are explained in the Glossary. The critical concentration calculation, taken from <u>Practical Statistics for Analytical Chemists</u> by Robert Anderson (8), is made to compare the mean values of the CAL QCS to the mean value obtained by the EPA from interlaboratory performance studies. Using the formula, one is able to determine if the bias, as a function of the standard deviation, is significant.

The persistent sulfate bias for the 75th percentile solution, which was mentioned in the 1987 report (5), continued in 1988 in spite of efforts to explain consistent and repeated values greater than the EPA mean value. The percent bias was less than in 1987 and the precision has improved.

The last column of Table IV-2 indicates that 10 of the 24 solutions analyzed are significantly biased. The actual percent bias is less than 5 percent for 96 percent of the measured solutions and well within the requirements stated in the NADP/NTN QA Plan. The overall precision, expressed as relative standard deviation, has remained the same or improved with the exception of calcium and the 0.50-mg/L potassium solution.

The most obvious explanation for the poorer precision for these two ions would be the change in analytical staff during 1988. Three analysts performed the atomic absorption determinations, instead of one as in previous years.

Using the same tests as with the QCSs, the blind data were evaluated for bias and precision. The results are shown in Tables IV-4, IV-5, IV-6, and IV-7. As in the past, the results were not as good as those for the known QCS samples. The cations of the SWS 1 samples, which have been designated as biased, with the exception of the low calcium, are still within the limits provided by NIST. The sulfate and nitrate exceed NIST limits. The conductivity values are within the NIST limits, but the pH of SRM II is 0.01 unit lower than the ± 0.02 uncertainty limits provided by NIST. The same samples, submitted as SWS 3 and filtered in the laboratory, indicate a high calcium bias, low potassium bias, and sodium contamination for the SRM I. Magnesium is within the NIST limits. The sulfate values exceed the NIST limits, and the nitrate values are within acceptable limits. The pH results are the same as for the unfiltered sample and conductivity is acceptable, the SRM II being 0.5 μS/cm higher than its unfiltered counterpart. The values for all of the parameters in both samples, with the exception of the SWS3 (filtered) calcium, are within the requirements of the NADP/NTN QA Plan. In the case of all of these biased parameters, it is assumed that they may be matrix-specific. Using these data to correct network sample analyses would therefore be inappropriate. The data are used to alert the analysts to an existing condition so that steps can be taken to try to correct biases and improve precision.

The data from the SWS 2 samples show the nitrate for the pH 4.3 QCS to be biased but well within the internal specifications for this solution. The conductivity for this solution is also within specifications. The pH of the deionized water is acceptable. These same samples, as the filtered SWS 3, show calcium in the pH 4.3 QCS, sodium in both the pH 4.3 QCS and the deionized water, a less biased nitrate, and acceptable pH and conductance measurements.

The filter contribution to higher calcium and lower sulfate concentrations has been noticed in the past and is being studied using additional blanks and synthetic solutions. A possible ion exchange reaction has been suggested but not proven. Figures B-4 through B-18 are control charts comparing the nonfiltered to filtered NIST SRM I and SRM II. The filtration process introduces another sample-handling variable into the system, and therefore the precision of the blind filtered samples (SWS 3) is most comparable to the precision of the filtered replicate samples.

The precision of the known QCS, measured immediately after the instruments are calibrated is most precise. Comparing the precision of the replicates with that of the blind certified reference standards is more realistic, since the concentrations are unknown to the analysts and the samples are analyzed at random intervals after the instrument calibration. The higher concentration calcium replicate precision is considerably poorer than the comparable values from the blind samples. The standard deviations of the other replicate sample analytes appear similar to or lower than the values for the comparable filtered blind sample analytes.

TABLE IV-4 Analytical Bias and Precision Results from the Internal Blind Audit Program (SWS 1), 1988, NIST SRM 2694I and 2694II - Unfiltered.

Parameter	Theoretical Concentration (mg/L)	Measured Concentration (mg/L)	Number of Samples	Bias mg/L	Bias %	Precision s (mg/L)	Precision RSD %	Critical [ ][a] (mg/L)	Statistically Significant Bias?[b]
Calcium	0.014[c]	0.020	25	0.006	42.9	0.010	50.0	0.005	YES
	0.049[d]	0.047	27	-0.002	10.6	0.005	10.6	0.003	NO
Magnesium	0.024	0.023	25	-0.001	-4.2	0.001	4.4	0.001	YES
	0.051	0.050	27	-0.001	-2.0	0.001	2.0	0.001	NO
Sodium	0.205	0.209	25	0.004	2.0	0.003	1.4	0.002	YES
	0.419	0.419	27	0.000	0.0	0.006	1.4	0.004	NO
Potassium	0.052	0.048	25	-0.004	-7.7	0.003	6.2	0.002	YES
	0.106	0.108	27	0.002	1.9	0.002	1.8	0.002	NO
Ammonium	(1.00)[e]	1.07	27	0.07	7.0	0.04	3.7	0.02	N.A.[f]
Sulfate	2.75	2.96	25	0.21	7.6	0.08	2.7	0.05	YES
	10.90	11.54	27	0.64	5.9	0.13	1.1	0.07	YES
Nitrate	7.06	7.22	27	0.16	2.3	0.10	1.4	0.06	YES
Chloride	(0.24)	0.25	25	0.01	4.2	0.01	4.0	0.00	N.A.
	(1.00)	1.05	27	0.05	5.0	0.03	2.9	0.01	N.A.
pH units	4.27(53.7)	4.24	25	3.8	7.0	3.08	5.4	2.58	YES
(μeq/L)	3.59(257.04)	3.56	27	1.0	0.8	1.50	1.2	0.60	YES
Conductivity	26.0	26.2	25	0.2	0.8	1.1	4.2	0.5	NO
(μS/cm)	130.0	131.0	27	1.0	0.8	1.5	1.2	0.6	YES

a. Critical = $t \times s_{pooled} \sqrt{1/n_{NIST} + 1/n_{CAL}}$
b. 95 percent confidence level
c. The first set of values for each parameter is for NIST SRM 2694-I.
d. The second set of values for each parameter is for NIST SRM 2694-II.
e. Values in parentheses are not certified but are provided by NIST for information only.
f. N.A. = not applicable.

TABLE IV-5 Analytical Bias and Precision Results from the
Internal Blind Audit Program (SWS 2), 1988,
Deionized Water and pH 4.3 QCS Solution - Unfiltered.

Parameter	Theoretical Concentration (mg/L)	Measured Concentration (mg/L)	Number of Samples	Bias mg/L	Bias %	Precision s (mg/L)	Precision RSD %	Critical[a] (mg/L)	Statistically Significant Bias?[b]
Calcium	<0.009[c]	<0.009	26						
	<0.009[d]	<0.009	26						
Magnesium	<0.003	<0.003	26						
	<0.003	<0.003	26						
Sodium	<0.003	<0.003	26						
	<0.003	<0.003	26						
Potassium	<0.003	<0.003	26						
	<0.003	<0.003	26						
Ammonium	<0.02	<0.02	26						
	<0.02	<0.02	26						
Sulfate	<0.03	<0.03	26						
	<0.03	<0.03	26						
Nitrate	<0.03	<0.03	26						
	3.12	3.23	26	0.11	3.5	0.06	1.9	0.02	YES
Chloride	<0.03	<0.03	26						
	<0.03	<0.03	26						
pH units	5.65(2.24)	5.54	26	0.67	30.0	0.57	19.6	0.23	YES
(μeq/L)	4.30(50.12)	4.31	26	-1.43	-2.8	2.41	5.0	2.32	NO
Conductivity	1.0	1.0	26	0.0	0.0	0.5	50.0	0.2	NO
(μS/cm)	21.8	21.0	26	-0.8	-3.7	0.6	2.9	0.7	YES

a. Critical = $t \times s_{pooled} \sqrt{1/n_{calc.} + 1/n_{CAL}}$
b. At 95 percent confidence level
c. The first set of values for each parameter is for deionized water.
d. The second set of values for each parameter is for pH 4.3 QCS.

TABLE IV-6   Analytical Bias and Precision Results from
the Internal Blind Program (SWS 3), 1988.
NIST SRM 2694I and 2694II - Filtered.

Parameter	Theoretical Concentration (mg/L)	Measured Concentration (mg/L)	Number of Samples	Bias mg/L	%	Precision s (mg/L)	RSD %	Critical []^a (mg/L)	Statistically Significant Bias?^b
Calcium	0.014^c	0.031	14	0.017	121.4	0.010	32.3	0.005	YES
	0.049^d	0.069	12	0.020	40.8	0.015	21.7	0.008	YES
Magnesium	0.024	0.024	14	0.000	0.0	0.002	8.3	0.001	NO
	0.051	0.051	12	0.000	0.0	0.003	5.9	0.002	NO
Sodium	0.205	0.226	14	0.021	10.2	0.015	6.6	0.006	YES
	0.419	0.429	12	0.010	2.4	0.024	5.6	0.009	YES
Potassium	0.052	0.040	14	-0.012	-23.1	0.009	22.5	0.004	YES
	0.106	0.091	12	-0.015	-14.2	0.017	18.7	0.006	YES
Ammonium	(1.00)^e	0.89	12	-0.11	-11.0	0.26	29.2	0.17	N.A.^f
Sulfate	2.75	2.89	14	0.14	5.1	0.08	2.8	0.05	YES
	10.90	11.17	12	0.27	2.5	0.25	2.2	0.14	YES
Nitrate	7.06	6.98	12	-0.08	-1.1	0.16	2.3	0.09	NO
Chloride	(0.24)	0.25	14	0.01	4.2	0.02	8.0	0.01	N.A.
	(1.00)	1.03	12	0.03	3.0	0.04	3.9	0.03	N.A.
pH units	4.27(53.7)	4.24	14	3.5	6.6	2.73	4.8	2.56	YES
(µeq/L)	3.59(257.04)	3.55	12	23.6	9.2	16.42	5.8	12.79	YES
Conductivity	26.0	26.2	14	0.2	0.8	1.0	3.8	0.6	NO
(µS/cm)	130.0	131.5	12	1.5	1.2	2.2	1.7	0.9	YES

a. Critical $= t \times s_{pooled} \sqrt{1/n_{NIST} + 1/n_{CAL}}$
b. 95 percent confidence level
c. The first set of values for each parameter is for NIST SRM 2694-I.
d. The second set of values for each parameter is for NIST SRM 2694-II.
e. Values in parentheses are not certified but are provided by NIST for information only.
f. N.A. = not applicable.

TABLE IV-7 Analytical Bias and Precision Results from the
Internal Blind Audit Program (SWS 3), 1988,
Deionized Water and pH 4.3 QCS Solution - Filtered.

Parameter	Theoretical Concentration (mg/L)	Measured Concentration (mg/L)	Number of Samples	Bias mg/L	%	Precision s (mg/L)	RSD %	Critical [ ]^a (mg/L)	Statistically Significant Bias?^{b}
Calcium	<0.009^c	<0.009	13						
	<0.009^d	0.012	13	0.003		0.010	83.3	0.006	YES
Magnesium	<0.003	<0.003	13						
	<0.003	<0.003	13						
Sodium	<0.003	0.020	13	0.017		0.010	50.0	0.006	YES
	<0.003	0.015	13	0.012		0.007	46.7	0.004	YES
Potassium	values at or below MDL								
Ammonium	values at or below MDL								
Sulfate	values at or below MDL								
Nitrate	values at or below MDL								
	3.12	3.12	13	0.00	0.0	0.10	3.2	0.06	NO
Chloride	values at or below MDL								
pH units	5.65(2.24)	5.56	13	0.49	21.9	0.43	15.8	0.26	YES
(μeq/L)	4.30(50.12)	4.31	13	-0.86	-1.7	1.62	3.3	2.75	NO
Conductivity	1.0	0.9	13	-0.1	-10.0	0.1	11.1	0.1	NO
(μS/cm)	21.8	21.2	13	-0.6	-2.8	0.6	2.8	1.0	NO

a. Critical = t x s$_{pooled}$ $\sqrt{1/n_{calc.} + 1/n_{CAL}}$
b. 95 percent confidence level
c. The first set of values for each parameter is for deionized water.
d. The second set of values for each parameter is for pH 4.3 QCS.

V.   REANALYSIS   PROCEDURES

The ionic balance is calculated for each sample analyzed. The percentage difference between calculated and measured specific conductance is tabulated. Samples are then computer selected for reanalysis based on the predetermined control limits for ion balance and specific conductance differences. A complete reanalysis is carried out on all samples selected with the original versus repeat values compared to identify outliers which require further investigation. The quality assurance specialist, with input from the analysts, determines which values justify change. When no explanation can be found for a difference between original and reanalysis values, the original data are reported. For all samples reanalyzed, the original, the repeat and the corrected final data are all maintained in the computerized data base.

Previous reports contain thorough discussions of both the ion balance and calculated conductance procedures, most recently in 1987 (5).

A.   ION BALANCE CRITERIA

Ion balance calculations are part of the check procedures of the CAL quality assurance program. A large imbalance can be indicative of an analytical error or data transcription mistake. In may also be an indication that additional ionic species are present in the sample and that further analyses are necessary to characterize the sample completely.

The ion percent difference (IPD) is calculated using the formula:

$$\text{Ion \% Difference} = \frac{(\text{Anions} - \text{Cations})}{(\text{Anions} + \text{Cations})} \times 100$$

Anions = sulfate + nitrate + chloride + phosphate + hydroxide + bicarbonate

Cations = calcium + magnesium + sodium + potassium + ammonium + hydrogen ion

where all of the concentrations are expressed as microequivalents per liter. The ion concentrations are measured or calculated in milligrams per liter and converted to microequivalents using the factors listed in Table V-1.

The sum of the anions and the cations expressed in microequivalents per liter is called the ion sum (IS).

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TABLE V-1. Factors Used to Convert Milligrams per Liter to Microequivalents per Liter for Ion Percent Difference Calculations.

Analyte	Conversion Factor
Calcium	49.90
Magnesium	82.26
Sodium	43.50
Potassium	25.57
Ammonium	55.44
Sulfate	20.83
Nitrate	16.13
Chloride	28.21
Orthophosphate	31.59

Table V-2. Factors Used to Convert Microequivalents per Liter to Equivalent Conductance for Conductance Percent Diffference Calculations.

Analyte	Conversion Factor
Hydrogen	349.65
Calcium	59.47
Magnesium	53.0
Sodium	50.08
Potassium	73.48
Ammonium	73.5
Bicarbonate	44.5
Hydroxide	198
Sulfate	80.0
Nitrate	71.42
Chloride	76.31
Phosphate	69.0

Samples are flagged for reanalysis if:

    IS < 50 μeq/L   and IPD> $\pm$ 60%

    50 $\leq$ IS < 100 μeq/L   and IPD> $\pm$ 30%

    IS $\geq$ 100 μeq/L   and IPD> $\pm$ 15%

B.   SPECIFIC CONDUCTANCE CRITERIA

The ion concentrations, expressed in microequivalents per liter, are multiplied by conductance conversion factors listed in Table V-2 (9) and used to compute the calculated conductance using the ions in the following equation:

Calculated conductance = (hydrogen + bicarbonate + calcium + chloride + magnesium + potassium + sodium + nitrate + sulfate + ammonium) / 1,000

The sum of these theoretical conductance values is then compared to the measured conductance using the following equation:

Conductance percent difference (CPD) =

$$\frac{(\text{Calculated conductance} - \text{measured conductance})}{\text{Measured conductance}} \times 100$$

Using this equation, samples are reanalyzed if:

10% < CPD < -40%

C. HISTOGRAMS

Figures V-1 and V-2 are histograms of the ion percent difference values and the conductance percent difference values for samples having a volume of more than 35 mL from the NADP/NTN network for 1988. The median, mean, standard deviation, and number of wet samples are presented on each figure.

D. DISCUSSION OF RESULTS

Not all of the samples flagged for ion or conductance percent difference were reanalyzed due either to insufficient sample volume, good agreement with a laboratory replicate, or visible physical contamination. In 1988, 699 of the 6,898 wet samples with sample volumes greater than 35 mL were flagged and suitable for reanalysis. These samples were located and
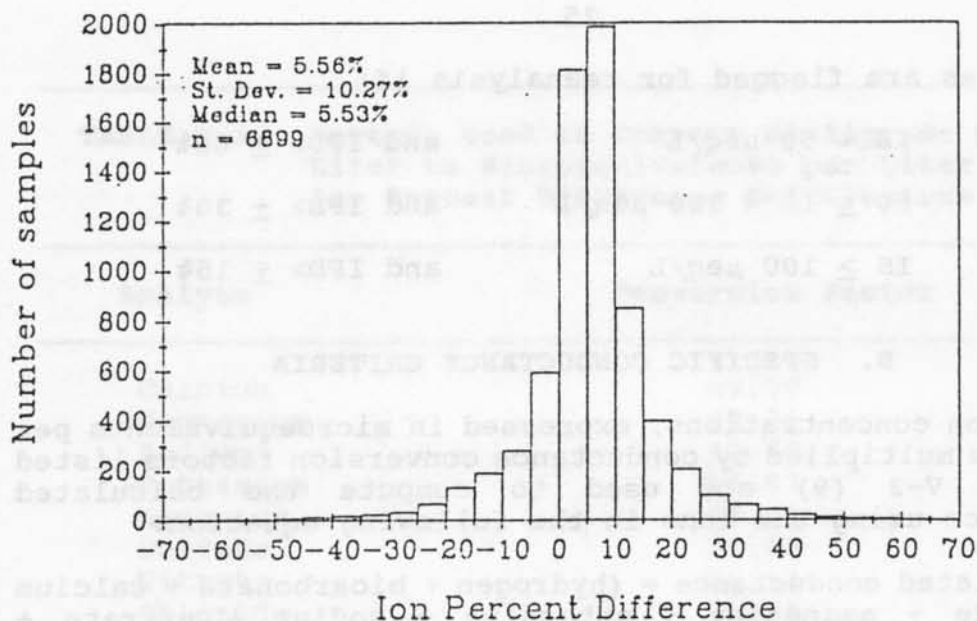
Ion Percent Difference

FIGURE V-1. Ion percent difference histogram for NADP/NTN wet-side samples, 1988.
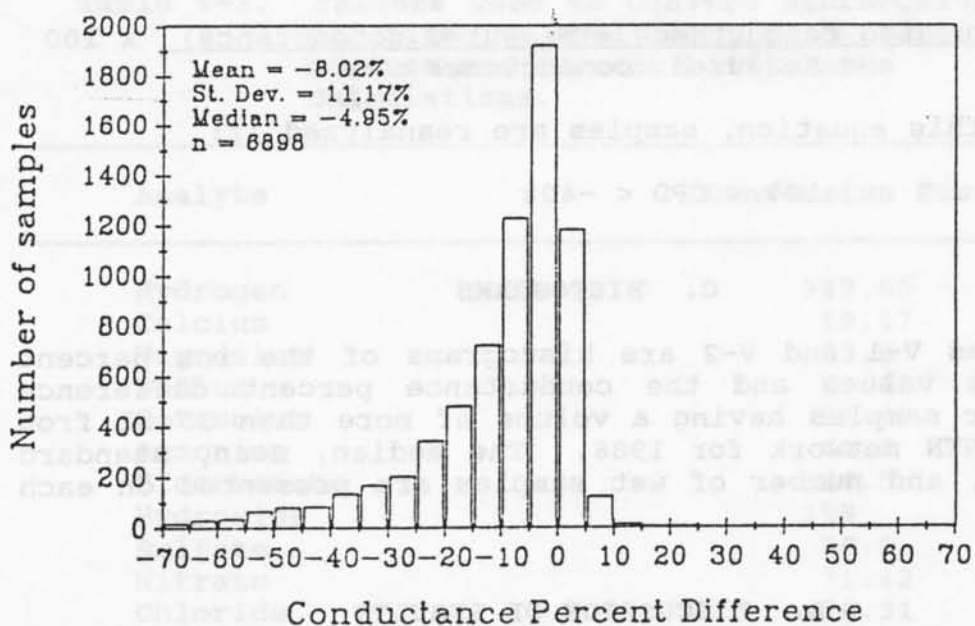

Conductance Percent Difference

FIGURE V-2. Conductance percent difference histogram for NADP/NTN wet-side samples, 1988.

the entire routine analysis performed.

The ion percent difference histogram shows a positive skew for the wet samples analyzed. The mean and median values, 5.6 percent and 5.53 percent, indicate an anion excess greater than any since the beginning of the network.

The conductance percent difference histogram, using the CRC Handbook factors in effect since 1987, is as it has been in the past. The skew is negative and indicates a smaller calculated value than measured. The large negative percentage values for small numbers of samples is a possible indication that some species are being detected in the sample conductance but are not being quantified in the routine ion analysis.

The reanalysis lists for samples collected from the beginning of April until the end of July approached 10 percent of the total sample load for that period. Many of the samples were low volume, others of larger volume were chemically unstable with unexplained changes in pH and potassium. The samples collected in the spring and selected for reanalysis were often very small and had pH values greater than 5.5, high concentrations of calcium, and a cation excess. As the summer continued, the flagged sample volumes varied. Many were insufficient for reanalysis, others with sufficient volume were often dirty and invariably unstable. It is beyond the scope of this report to characterize the chemistry site by site, and the samples in question were not confined to any specific geographical section. All of the eligible samples were reanalyzed, but few changes to the original data could be justified. Only 98 changes were made to the database during 1988.

VI. EXTERNAL QUALITY ASSURANCE

The CAL is mandated to participate in an external quality assurance program consisting of the following: a blind sample audit; an interlaboratory comparison and periodic on-site reviews. The U.S. Geological Survey (USGS) is the official external auditing agency for the CAL. In addition, the CAL participates voluntarily in other national and international interlaboratory comparison studies. An administrative audit took place in August, and "In general the NADP/NTN Coordinator's Office and Central Analytical Laboratory were found to be efficient, well-staffed and well run operations." The following section presents a brief description of the CAL's participation and performance in external audits in 1988.

A. U.S. GEOLOGICAL SURVEY EXTERNAL AUDIT PROGRAM

The U. S. Geological Survey's external audit of the CAL consists of two components: a blind audit and an interlaboratory comparison. The blind audit is used to evaluate laboratory bias and precision and to study the effects of sample handling and shipping. The interlaboratory comparison is used to evaluate the CAL and compare it to other environmental laboratories. Results of this program are published annually by the USGS (11).

The 1988 blind audit included 26 test solutions mailed during each of four quarters to specific sites according to an agreed-upon schedule. The locations were based on geographic distribution. Two-thirds of the contents of the bottle were poured into the wet-side bucket and sent to the CAL as the weekly precipitation sample. After a delay, the remaining solution in the bottle was sent directly to the CAL for analysis.

Complete bottle and bucket analyses are available for 98 of the 104 blind-audit samples sent to site operators in 1988. A paired t test was used to determine if a significant difference existed between the bucket and bottle sample. It indicated that a significant bias existed for calcium, magnesium, sodium, chloride, pH, and specific conductance. These results appear to indicate contamination due to sample handling of bucket samples throughout the network.

The interlaboratory comparisons began in the fall of 1982. The comparisons were designed to determine whether participating laboratories were producing comparable results. Samples from five sources were used for the comparison: synthetic wet-deposition and deionized water prepared by the

USGS, standard reference samples prepared and certified by the National Institute of Standards and Technology (NIST), and synthetic wet-deposition samples and natural wet-deposition samples prepared by the CAL. These samples are renumbered and distributed to the participating laboratories. In 1988 the participating laboratories, in addition to the CAL, were the Inland Water Directorate, Natural Water Quality Laboratory, Ontario, Canada; and Environmental Monitoring and Services (EMS), Combustion Engineering Inc., Camarillo, California. Examination of the data from the three laboratories indicated that no significant difference existed among laboratory determinations (10).

B. INTERLABORATORY COMPARISON STUDIES

In 1988, the CAL participated in interlaboratory performance studies conducted by the U. S. Environmental Protection Agency (USEPA), the Canada Centre for Inland Waters (CCIW) and the Norwegian Institute for Air Research. The Analytical Chemistry Unit of the Illinois State Water Survey, of which the CAL is a component, was recertified by the Illinois Environmental Protection Agency (IEPA) for the chemical analysis of public drinking water supplies. The analytical data for the samples analyzed are presented in the tables in Appendix C.

1. U.S. Environmental Protection Agency

The Environmental Monitoring Systems Laboratory of the United States Environmental Protection Agency, Research Triangle Park, North Carolina, conducts an interlaboratory comparison study for the analysis of precipitation samples. In 1988, the CAL participated in the studies in May and October.

The results of the analysis of the ten major chemical and physical parameters routinely measured by the CAL are listed in the Tables C-1 and C-2 and summarized in Table VI-1.

Table VI-1 Summary of Results from U.S. Environmental
Protection Agency Acid Rain Performance
Survey, 1988.

Date	Number of Participating Laboratories	Mean % Difference[a] from Expected Value	
		CAL	All Labs[b]
May, 1988	38	5.03	15.43
October, 1988	34	5.21	13.02

a. Mean % difference =

$$\sum \left[\frac{|\text{Expected value} - \text{reported value}|}{\text{Expected value}} \right] \times 100$$

$$n$$

where n = the number of analytes determined

b. calculated with outliers removed

2. Norwegian Institute for Air Research

The tenth intercomparison of analytical methods within the
European Monitoring and Evaluation Programme (EMEP) was
conducted by the Norwegian Institute for Air Research. The
samples of synthetic precipitation arrived and were analyzed
in early 1988. The final data analysis was completed in
November and issued in report form (11). The data are
presented in tabular form and also graphically using Youden
plots (12) to compare two solutions of similar analyte
concentrations. The CAL results for sulfate, reported as
milligrams per liter sulfur, are outside the 10 percent circle
for the theoretical value of both sample pairs. However, the
results are within 10 percent of the mean analyzed values for
both sample pairs. This information has been used in further
efforts to investigate a small but consistent sulfate bias
found in several CAL intercomparison studies. The other
parameters are well within the 10 percent boundary.

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3. Canada Centre for Inland Waters

The Canadian program for Long-Range Transport of Atmospheric Pollutants (LRTAP) was begun in December 1982. The CAL has participated since the third study. In 1988, the CAL participated in Studies L-17 and L-19. Both studies consisted of selected major ions, nutrients, and physical measurements in water. Medians were used as target values in flagging results, since true values are unknown. All of the samples, including those from surface water sources, were analyzed in these two studies. The actual CAL and median values for the parameters analyzed are presented in Tables C-4 and C-5. The CAL was ranked fourteenth of the 52 participants in L-17 (13) and ninth of the 54 participants in L-19 (14). CAL performance in these studies was rated "Satisfactory, well done" in the summary accompanying L-19.

VII. SUMMARY

This Quality Assurance Report for 1988 documents the program in place at the CAL during that year. The tables and figures represent a summary of the data collected throughout the year as the analyses of NADP/NTN network precipitation samples were taking place. The various aspects of the program are discussed briefly and presented in tabular and graphic form so that the program and report can be evaluated in an effective manner.

There were no laboratory procedural changes and only two personnel replacements during the year. The samples were processed in the same manner as was in place at the end of 1987. Detection limits were unchanged from those of the last half of 1987. Jackie Sauer returned to her previously held position responsible for sample processing and pH and conductivity. Loretta Skowron relinquished her long term as the atomic absorption analyst in November and Sue Bachman took over the analysis for all cations.

The weekly blank procedures in 1988 included two inverted bucket blanks, two filter blanks, and three deionized water blanks. The bucket blank program was modified to accommodate several studies addressing the effect of the sampling containers on the samples. It was noted that new buckets tested at random after the first washing contained measurable amounts of sodium and trace amounts of calcium and magnesium. Special attention is now given to the washing and rinsing of previously unused buckets. The contribution of the lid to inverted bucket blanks was narrowed down to the butadiene rubber o-ring used to ensure the lid seal. Modifications of the dishwashing procedure were tried, as well as chlorination and thorough cleaning of the dishwashing machine. Sodium contamination persists. The pH increases in solutions that contact the o-ring. As the sample size becomes larger, a dilution effect nullifies the o-ring impact. The filter leachates contained sodium in the same median concentrations as in previous years. The second (B) leachate continued to exhibit a lower conductivity. The deionized water was free of all of the ions evaluated at the CAL, the pHs varied only slightly from the three different sources evaluated, and the conductivity continued to be less than one $\mu S/cm$.

Bias and precision continued to be assessed using quality control check samples, blind network sample replicates, and an internal blind audit using certified reference standards, in-house deionized water, and pH 4.3 QCS. The check sample data revealed that the measured solutions were well within the requirements of the network QA plan. The precision of the replicate samples has been calculated using the formula for

estimating the standard deviation of similar replicates. Standard deviations calculated by this method are then more comparable to those calculated for the QC and blind audit samples, particularly those of the filtered portion of the CAL blind audit samples. The internal blind audit remained as it was at the end of 1987. An ion exchange phenomenon was noted in filter blanks in the past and again this year. The calcium concentration of the filtered NIST-certified samples is elevated while the sulfate concentration is lower than the comparable unfiltered sample and closer to the NIST values.

The reanalysis procedure and calculations remained the same as in 1987. The number of samples reanalyzed increased as sample volumes decreased, due presumably to the drought, which spread throughout most of the central United States. Many of the samples were just at or above the 35-mL volume that designates a wet sample, and many of these small-volume samples were physically dirty and chemically unstable.

The NADP/NTN external quality assurance program conducted by the USGS once again implicated the sample handling and containers as a significant contributor to bias for calcium, magnesium, sodium, chloride, pH and specific conductance in the blind audit. The interlaboratory comparison of the CAL with two other laboratories indicated that CAL results and those from the other participating laboratories are comparable. Participation in the USEPA Acid Rain Performance Survey, the Norwegian Institute for Air Research EMEP program, and the Canada Centre for Inland Waters LRTAP study completed the annual external effort. The CAL performance in external interlaboratory comparisons verified the results obtained from the internal laboratory QA program.

The absence of significant variation in the quality assurance program at the CAL in 1988 was due to the strength of the program in place at the end of 1987. The data presentation for the bucket blanks and replicates has been modified by using box plots. It is hoped that the information presented in this format is more informative to the reader. The results of the daily quality control efforts were reflected in the quality assurance documented at the end of the year.

The information obtained from the several sections of the internal QA program indicates that specifications for precision and bias are being met. From this information the data user can readily assess the quality of the sample data being produced at the CAL.

APPENDIX A

Bucket Blank Plots

1988
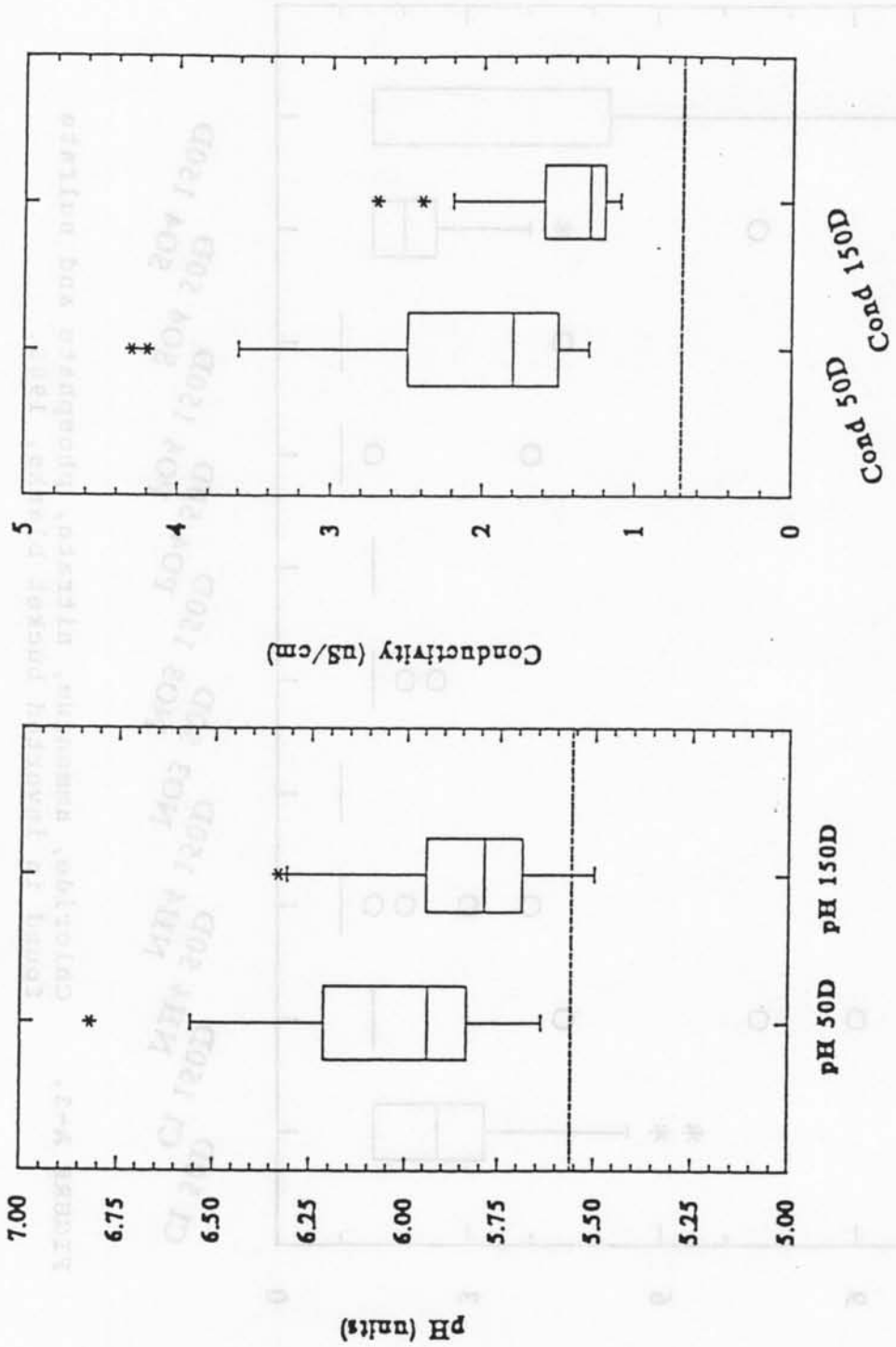
FIGURE A-1.   pH and Conductivity of inverted bucket blanks, 1988.
(Horizontal dashed lines represent values for
deionized water)

○ Far outside point * Outside point ○ Far outside point * Outside point

Mass (ug/Bucket)
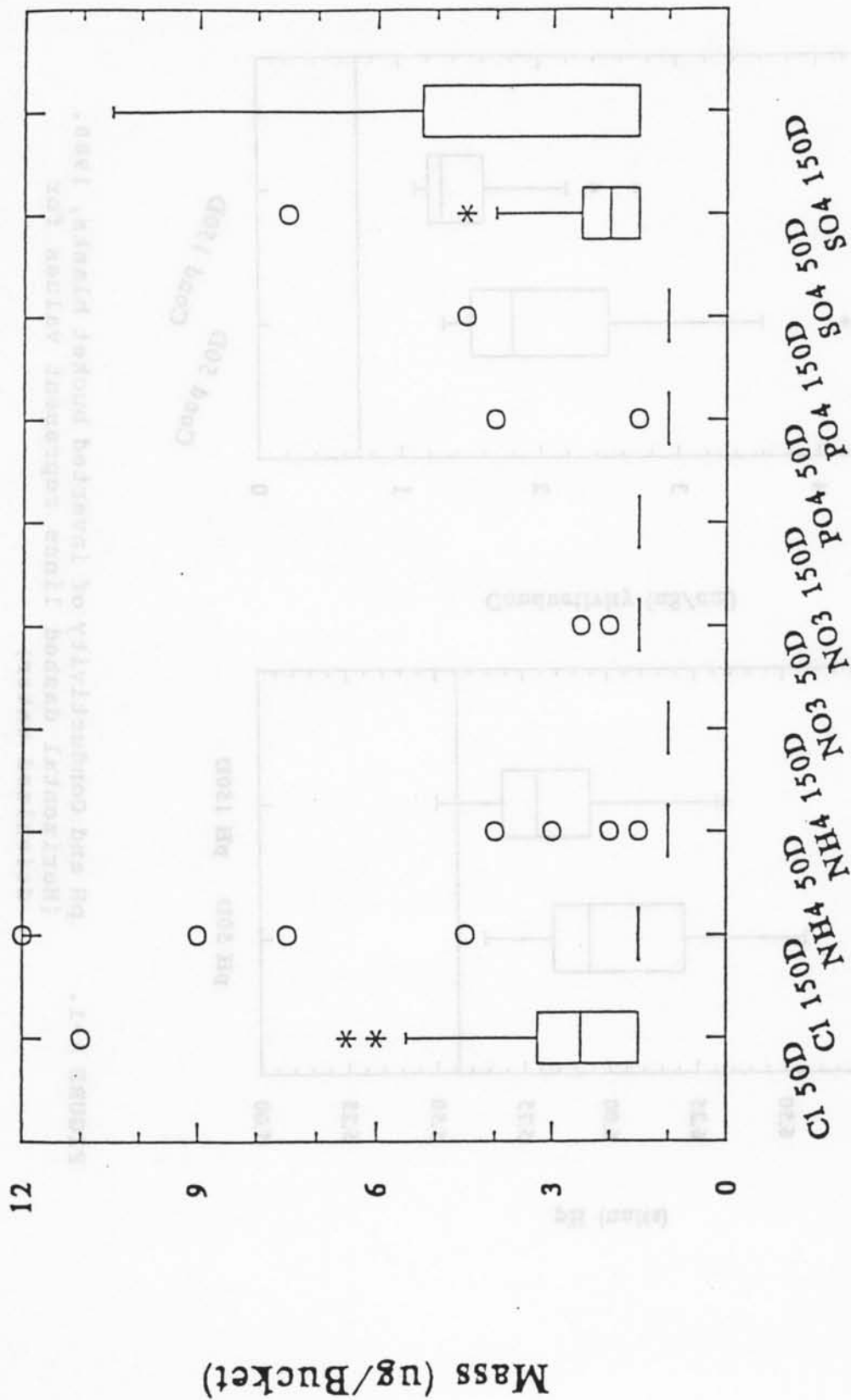
FIGURE A-3. Chloride, ammonium, nitrate, phosphate and sulfate found in inverted bucket blanks, 1988.

Cl 50D Cl 150D 50D 150D 50D 150D 50D 150D 50D 150D
NH4 NH4 NO3 NO3 PO4 PO4 SO4 SO4
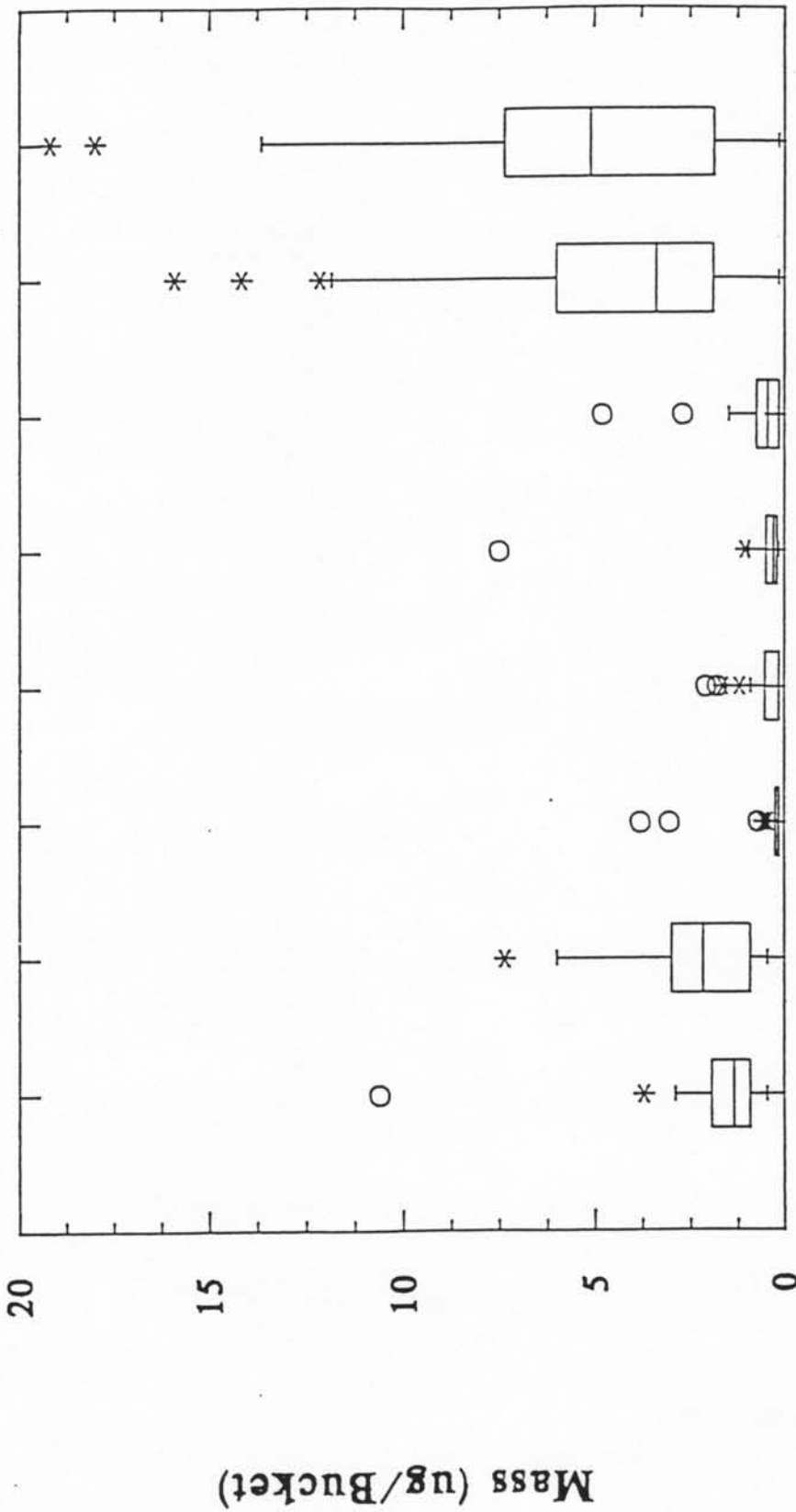
FIGURE A-2. Calcium, potassium, magnesium, and sodium found in inverted bucket blanks, 1988.

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APPENDIX B

Bias and Precision Plots and Figures

1988

APPENDIX B

Bias and Precision Plots and Figures

1980

TABLE B-1   Fiftieth and Ninety-fifth Percentile
            Concentration Values of Chemical and
            Physical Parameters Measured in
            Replicate (O/Q) Samples, 1988.

Parameter	Percentile concentration values (mg/L)	
	50th	95th
Calcium	0.133	0.859
Magnesium	0.026	0.130
Sodium	0.076	0.772
Potassium	0.015	0.119
Ammonium	0.09	0.82
Sulfate	1.42	5.17
Nitrate	0.97	3.95
Chloride	0.13	1.24
pH (μequiv/L)	17.81	90.34
(units)	4.75	6.43
Conductivity (μS/cm)	14.0	49.8

○ Far outside point   * Outside point

Cond Low   Cond High

Conductivity Difference (uS/cm)

5
4
3
2
1
0
-1
-2
-3
-4
-5

pH Low   pH High

H+ Difference (microequivalents/L)

10
8
6
4
2
0
-2
-4
-6
-8
-10

FIGURE B-1.   Results of O/Q replicate analysis, pH and conductivity, 1988.

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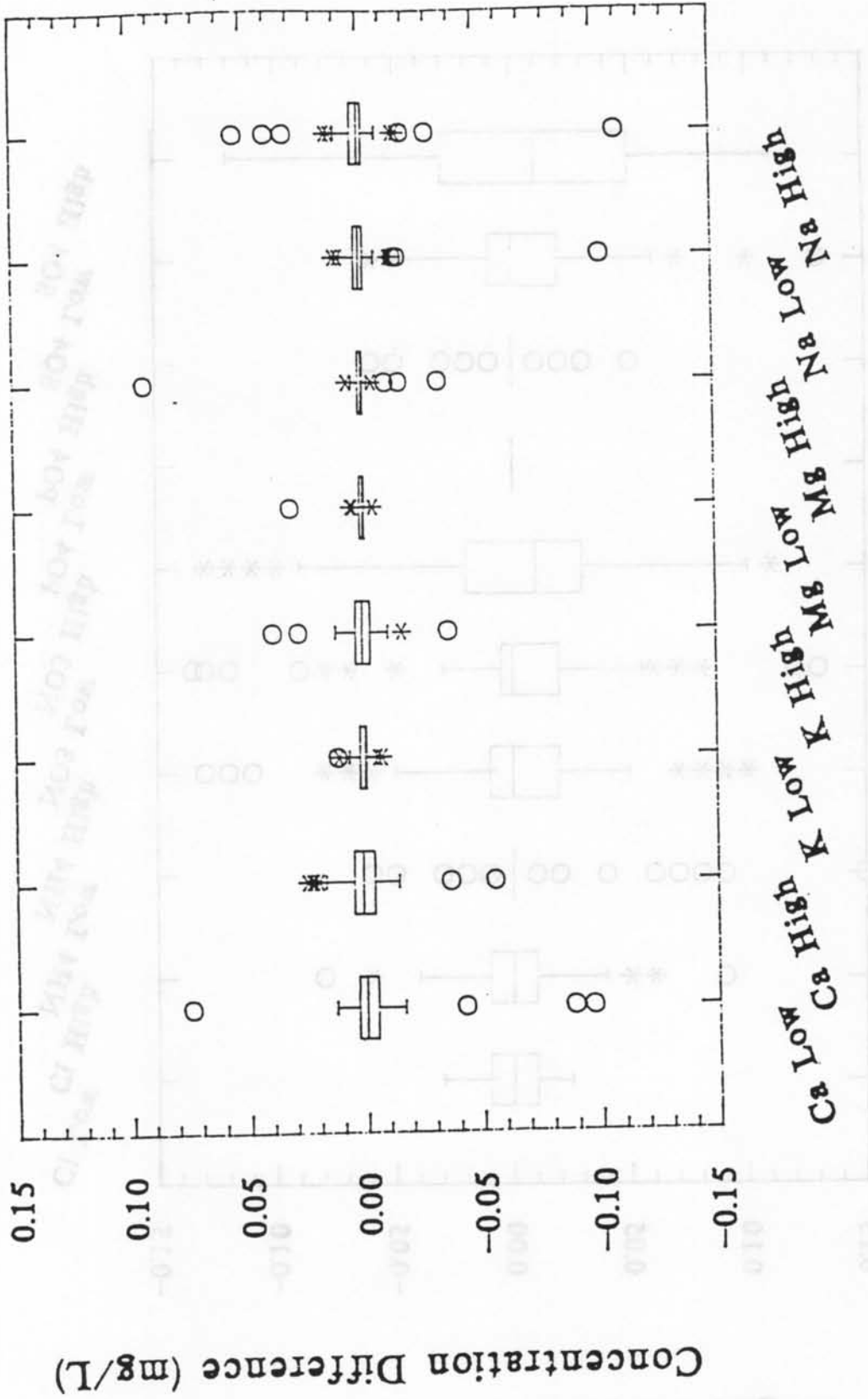
FIGURE B-2. Results of O/Q replicate analysis, calcium, magnesium, sodium, and potassium, 1988.
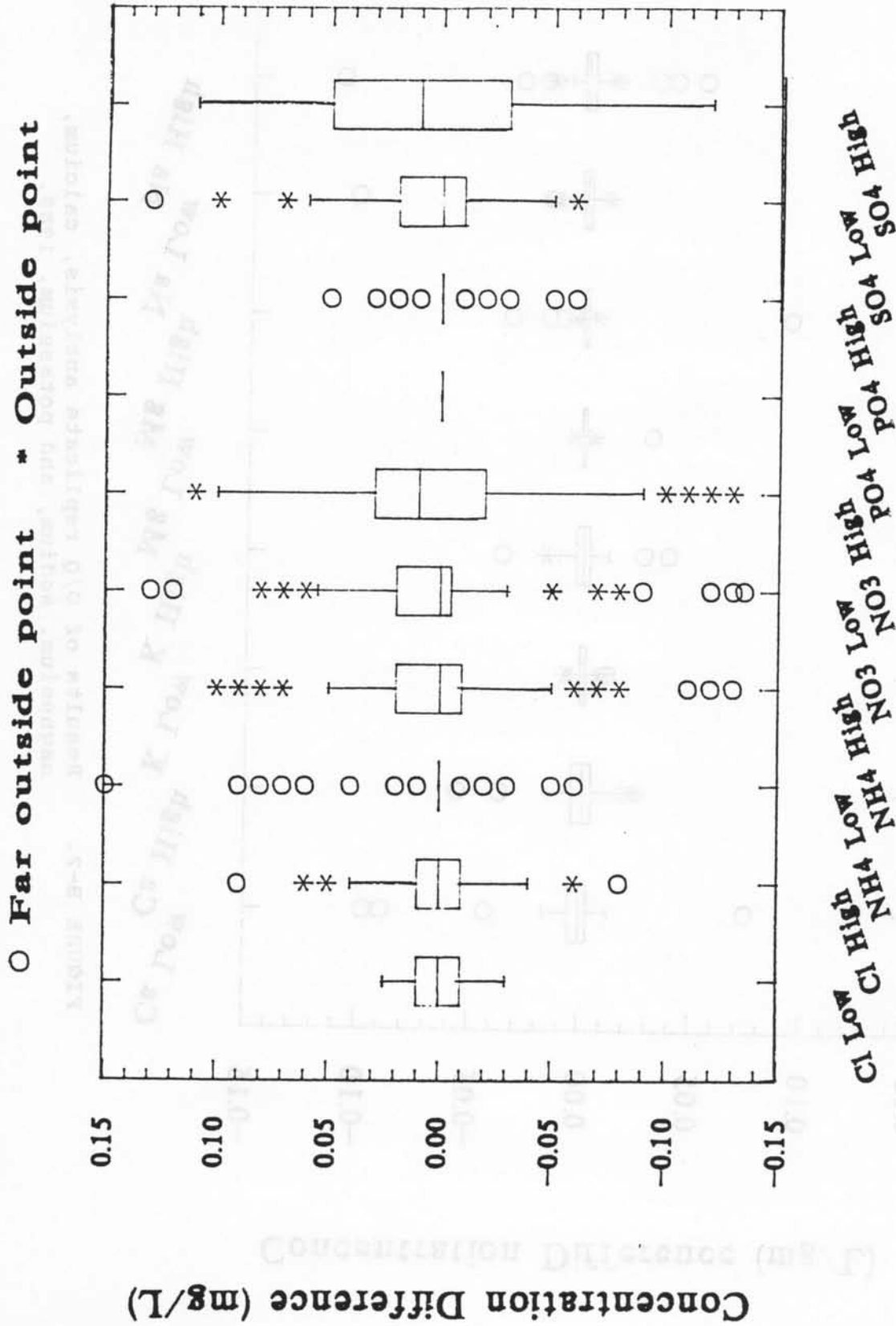
FIGURE B-3. Results of O/Q replicate analysis, chloride, ammonium, nitrate, phosphate, and sulfate, 1988.

FIGURE B-4. Comparison of filtered and unfiltered internal blind samples (calcium I), 1988.

FIGURE B-5. Comparison of filtered and unfiltered internal blind samples (magnesium I), 1988.

NBS 2694 I – Certified Sodium Value: 0.205 mg/L

FIGURE B-6.   Comparison of filtered and unfiltered internal blind
samples (sodium I), 1988.

NBS 2694 I – Certified Potassium Value: 0.052 mg/L

FIGURE B-7.   Comparison of filtered and unfiltered internal blind
samples (potassium I), 1988.

NBS 2694 I — Certified Sulfate Value: 2.75 mg/L

FIGURE B-8. Comparison of filtered and unfiltered internal blind samples (sulfate I), 1988.

FIGURE B-9. Comparison of filtered and unfiltered internal blind samples (pH I), 1988.

FIGURE B-10. Comparison of filtered and unfiltered internal blind samples (specific conductance I), 1988.

NBS 2694 II — Certified Calcium Value: 0.049 mg/L
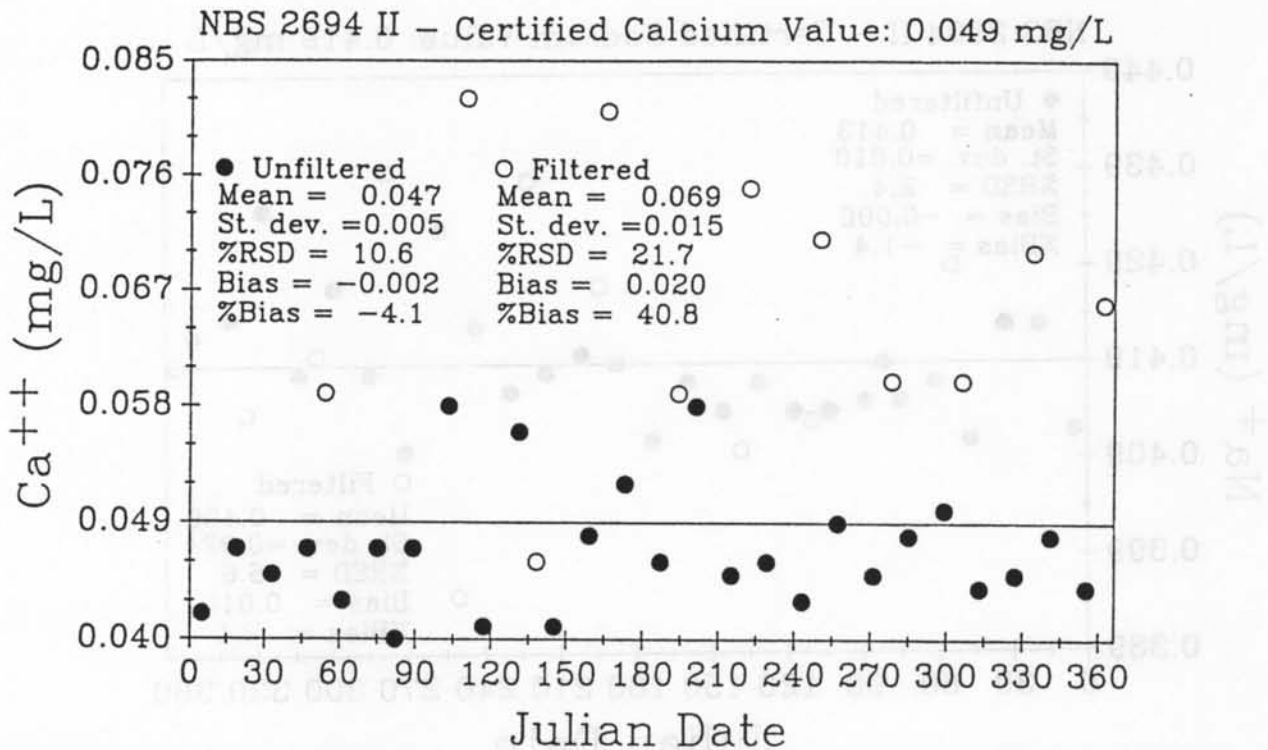
FIGURE B-11.   Comparison of filtered and unfiltered internal blind
samples (calcium II), 1988.

NBS 2694 II — Certified Magnesium Value: 0.051 mg/L
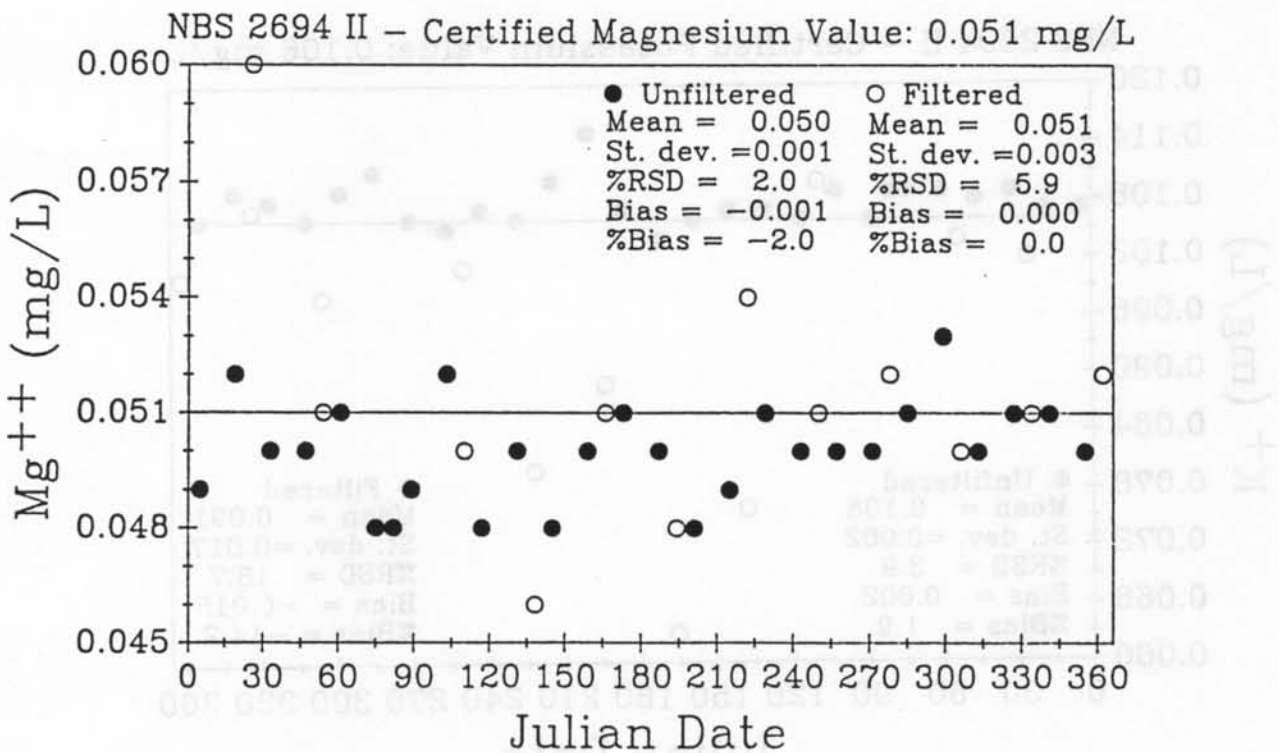
FIGURE B-12.   Comparison of filtered and unfiltered internal blind
samples (magnesium II), 1988.

NBS 2694 II – Certified Sodium Value: 0.419 mg/L

● Unfiltered
Mean = 0.413
St. dev. =0.010
%RSD = 2.4
Bias = −0.006
%Bias = −1.4

○ Filtered
Mean = 0.429
St. dev. =0.024
%RSD = 5.6
Bias = 0.010
%Bias = 2.4
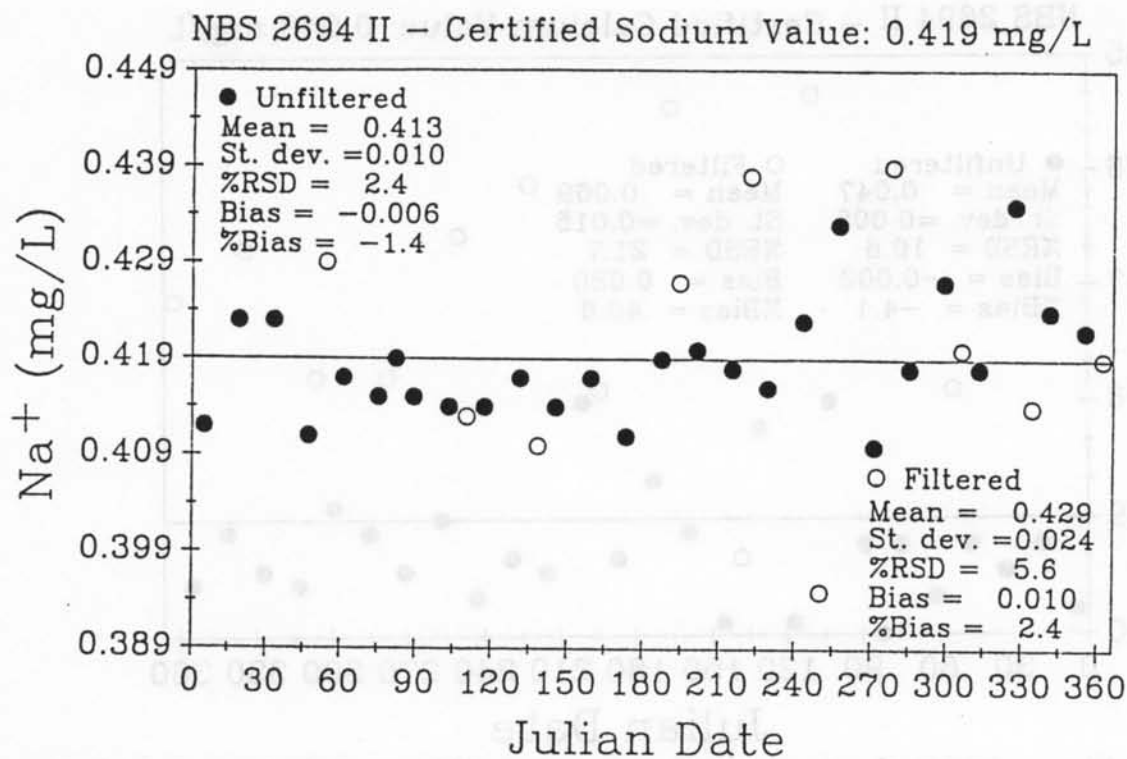
FIGURE B-13.   Comparison of filtered and unfiltered internal blind samples (sodium II), 1988.

NBS 2694 II – Certified Potassium Value: 0.106 mg/L

● Unfiltered
Mean = 0.108
St. dev. =0.002
%RSD = 3.9
Bias = 0.002
%Bias = 1.9

○ Filtered
Mean = 0.091
St. dev. =0.017
%RSD = 18.7
Bias = −0.015
%Bias = −14.2
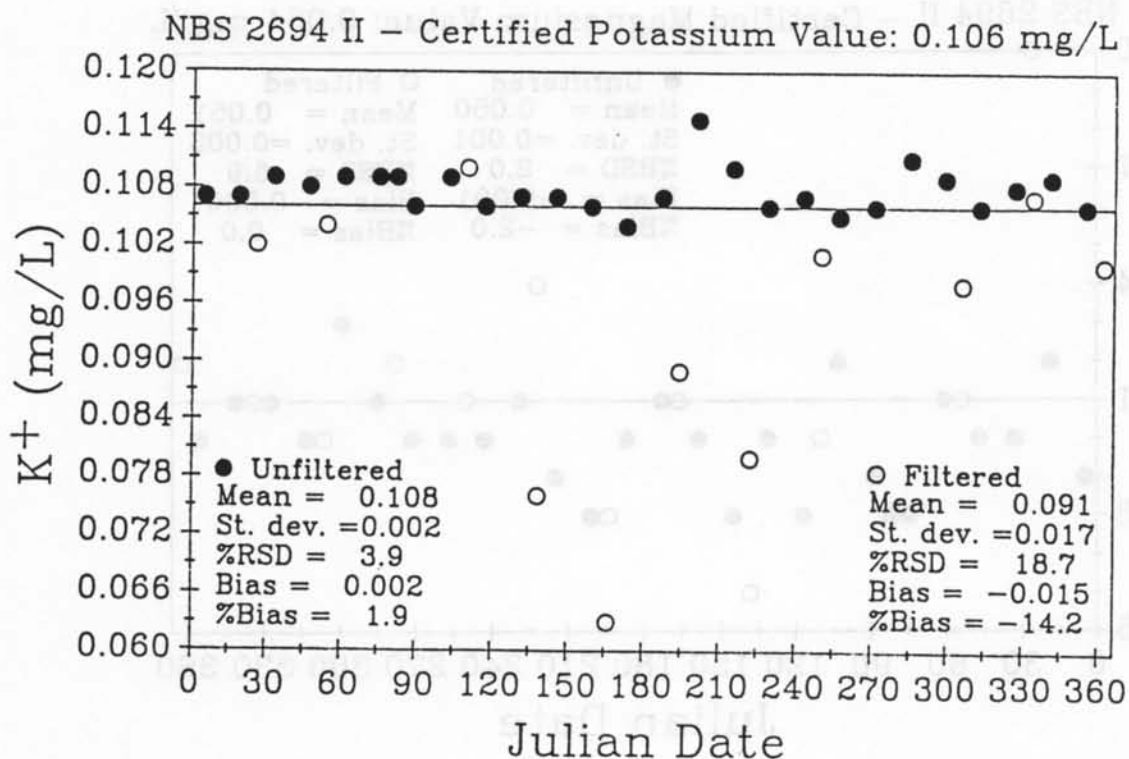
FIGURE B-14.   Comparison of filtered and unfiltered internal blind samples (potassium II), 1988.

NBS 2694 II — Certified Sulfate Value: 10.90 mg/L
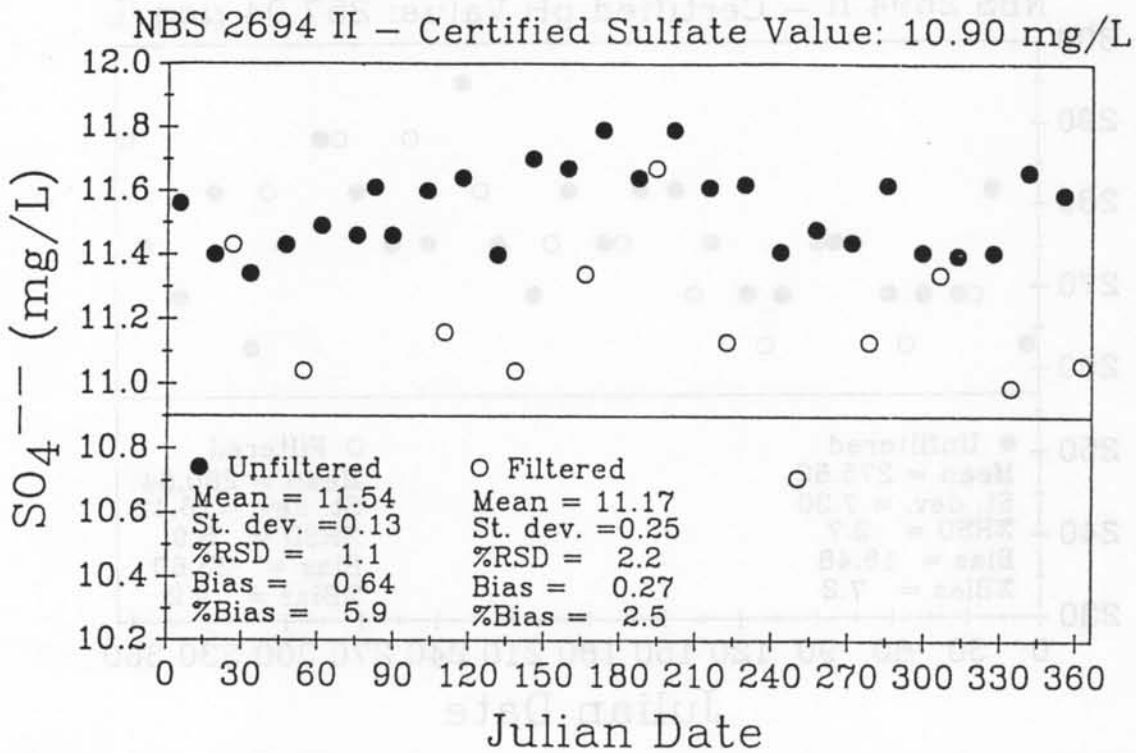
FIGURE B-15. Comparison of filtered and unfiltered internal blind samples (sulfate II), 1988.

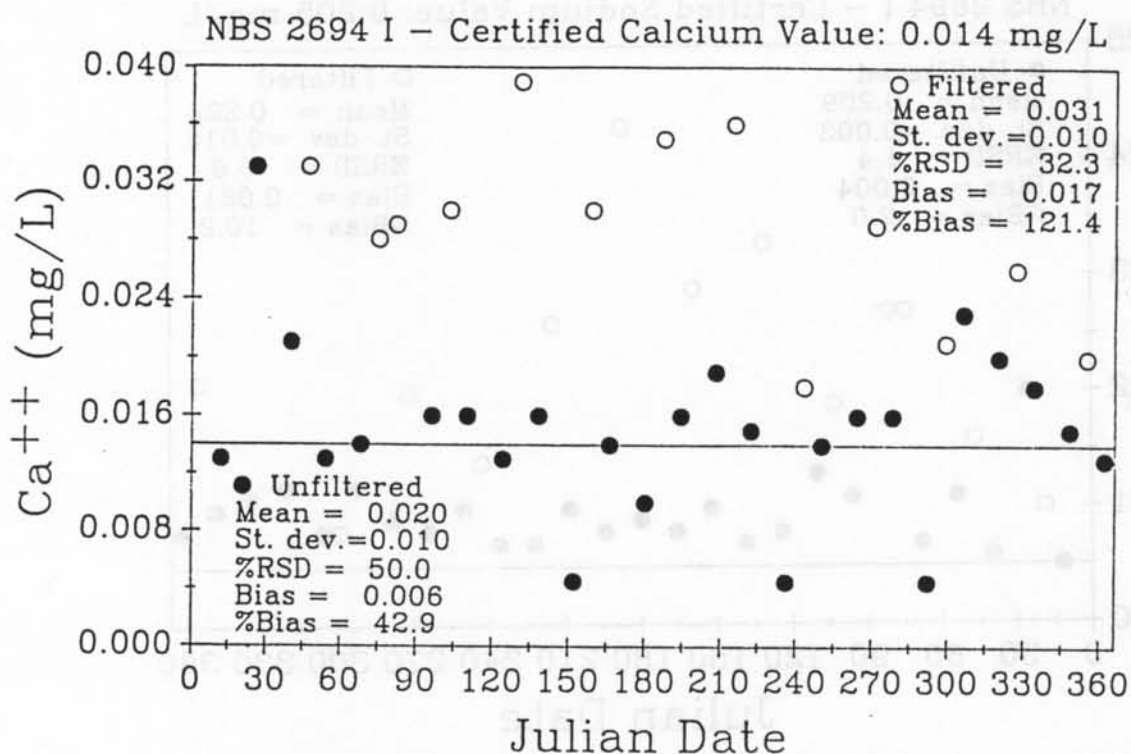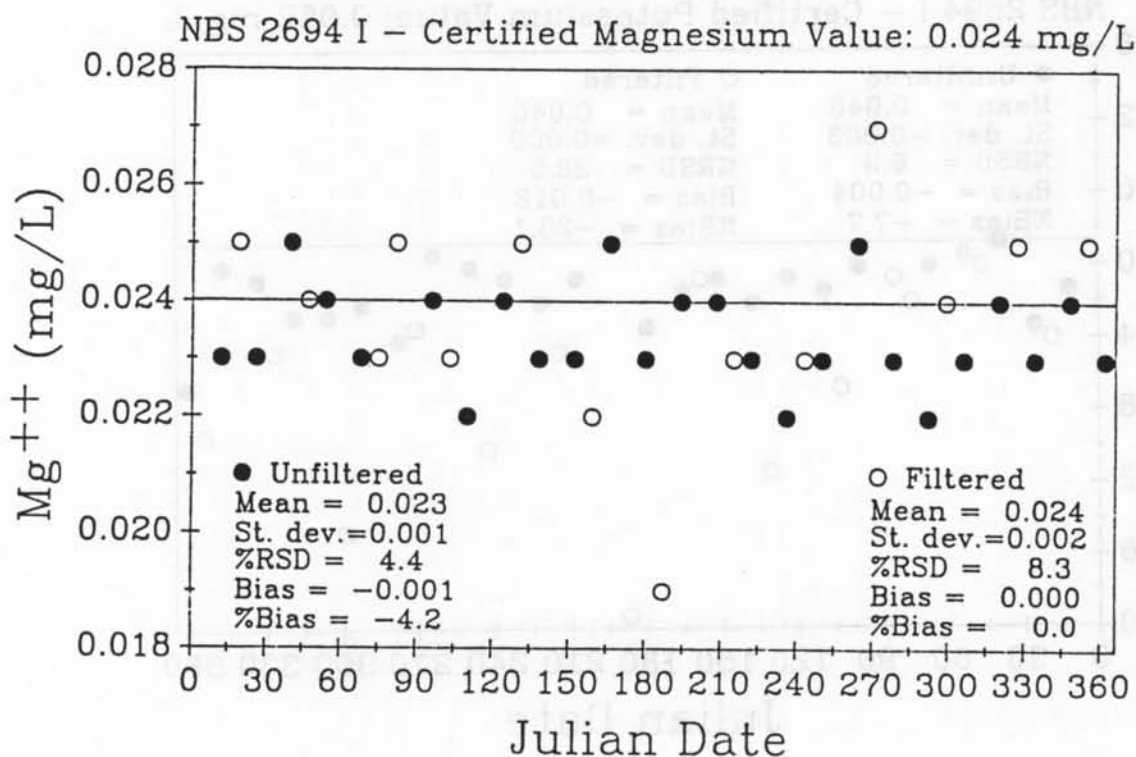NBS 2694 II — Certified Nitrate Value: 7.06 mg/L
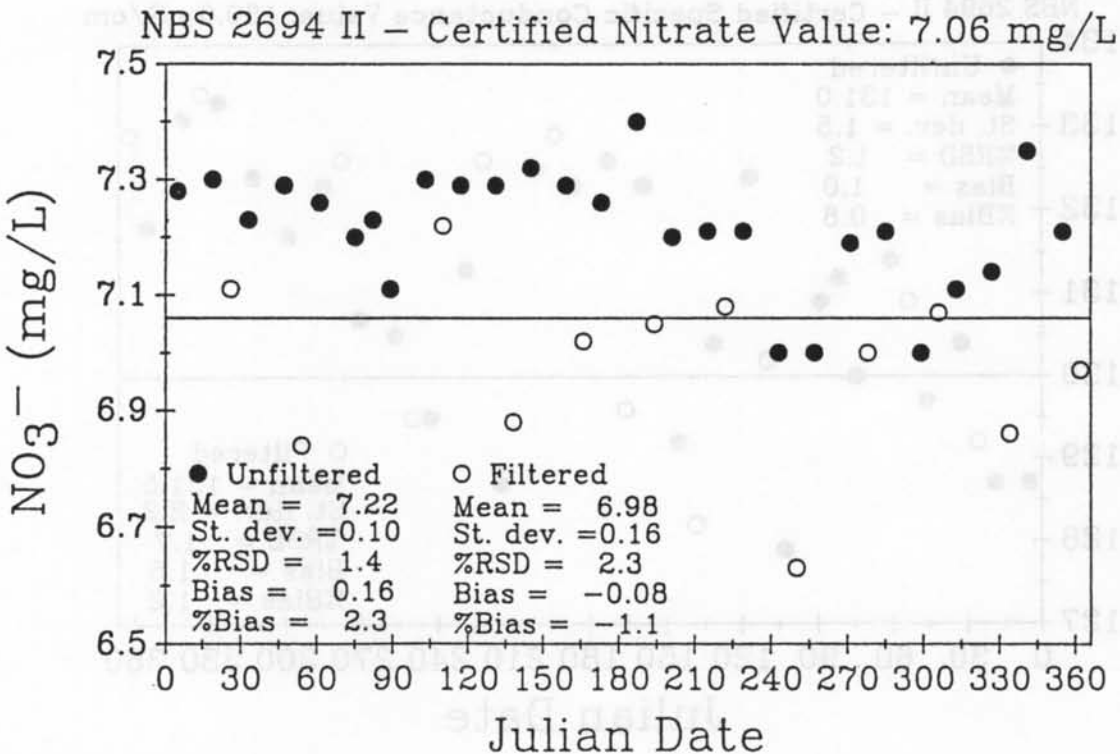
FIGURE B-16. Comparison of filtered and unfiltered internal blind samples (nitrate II), 1988.
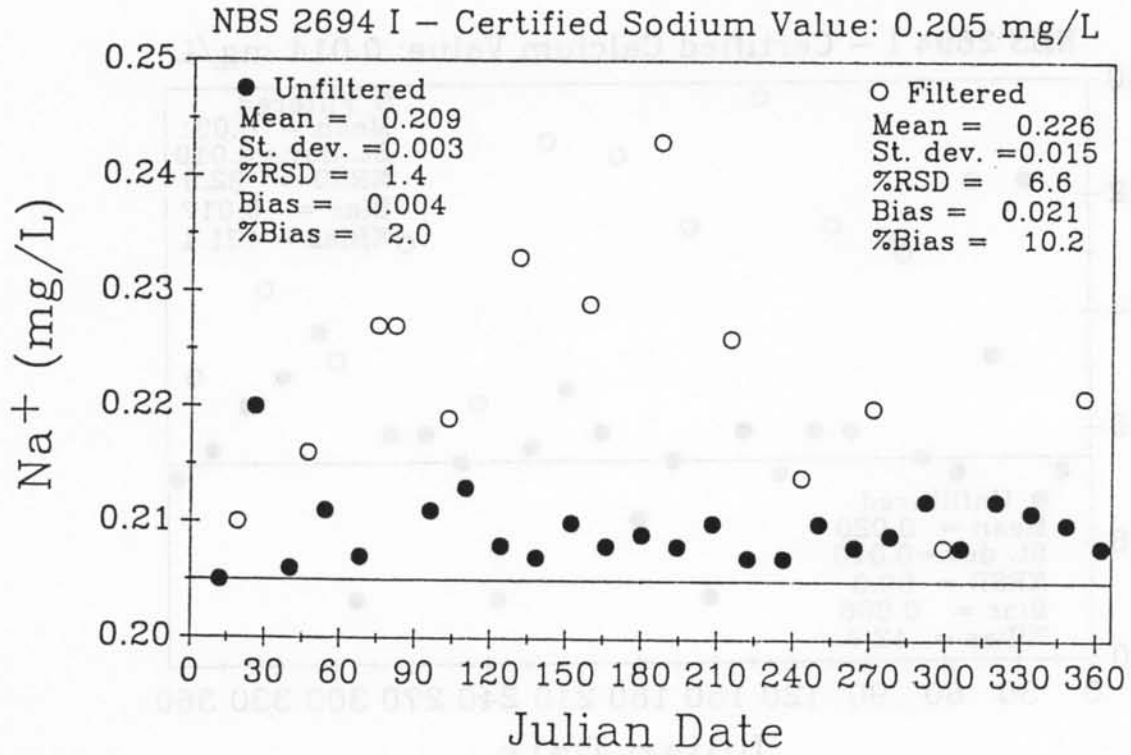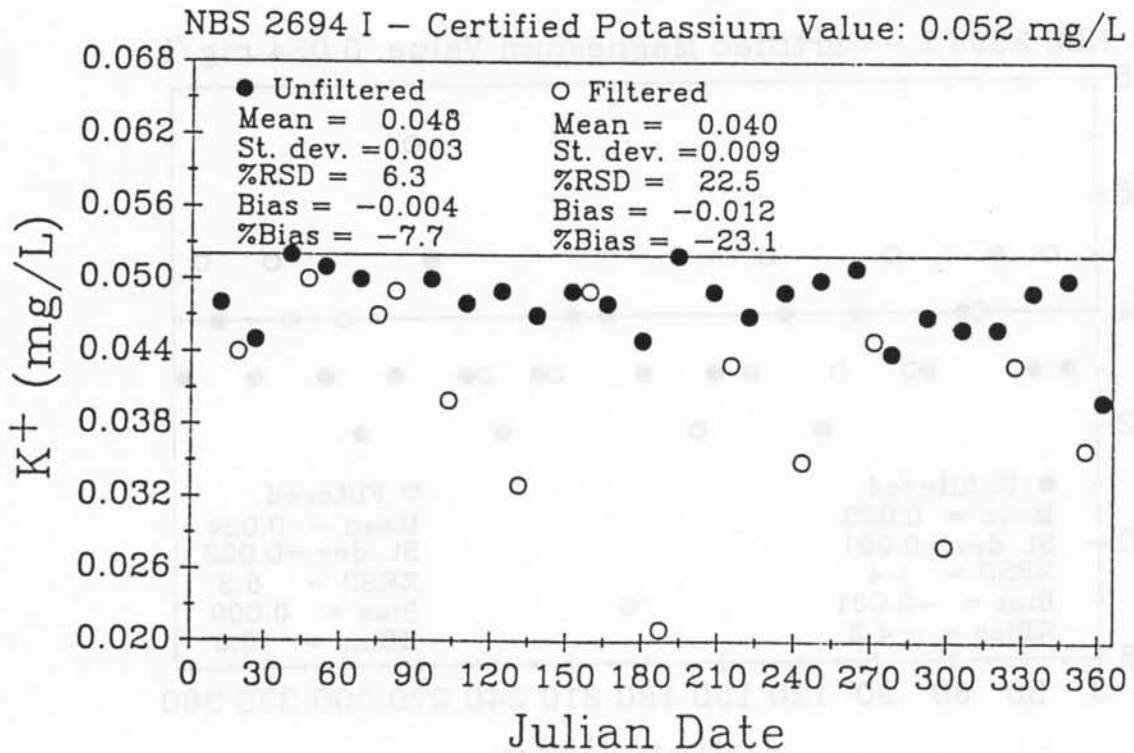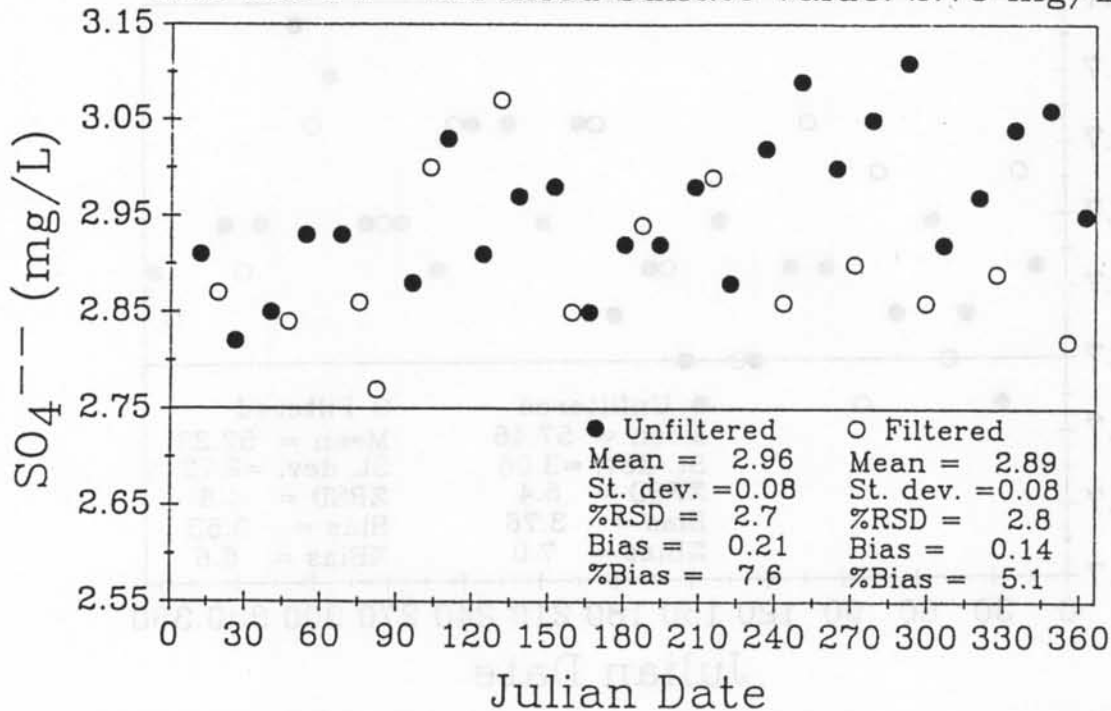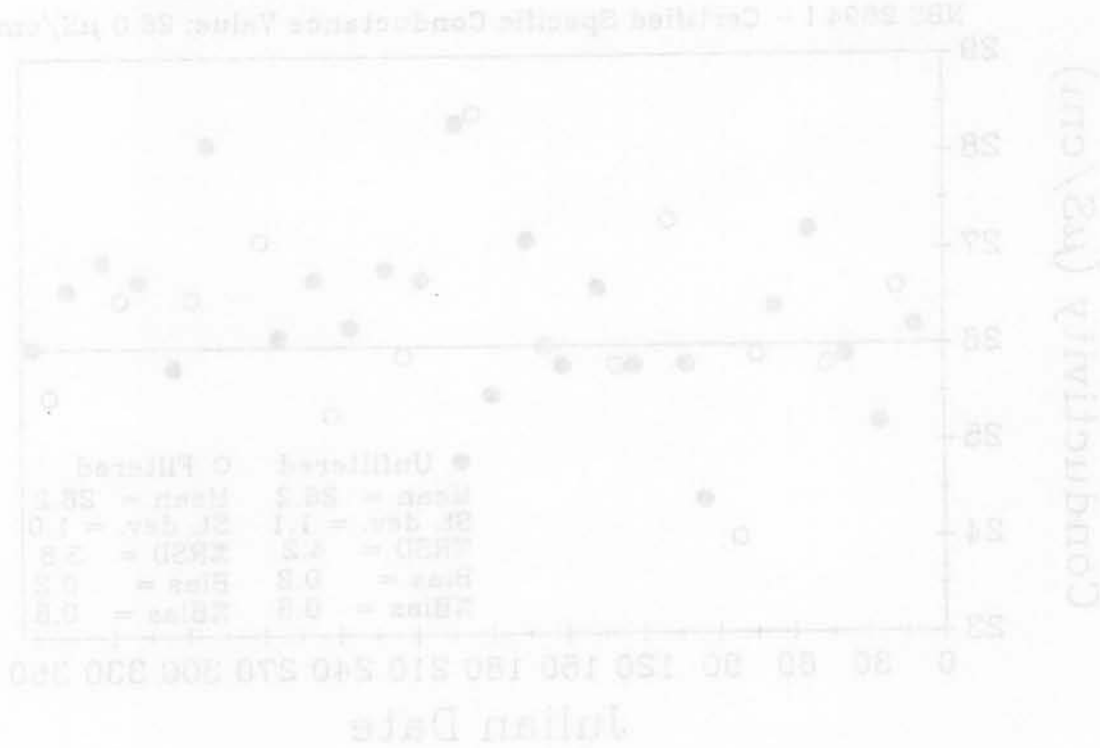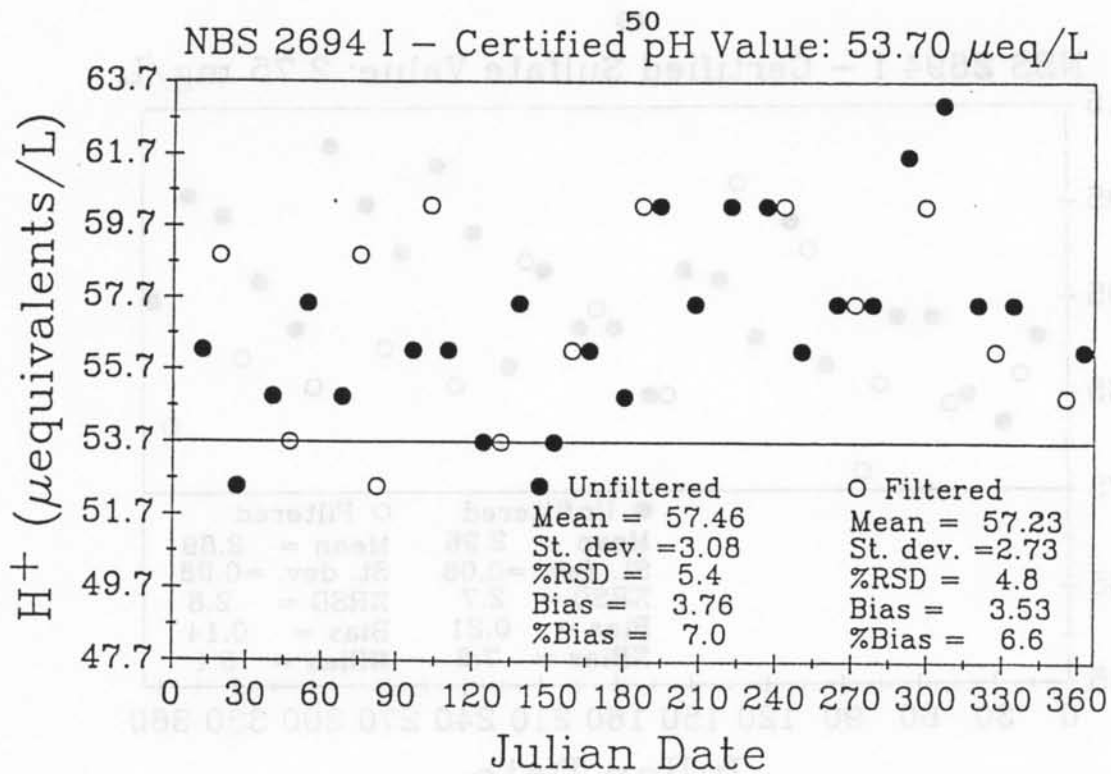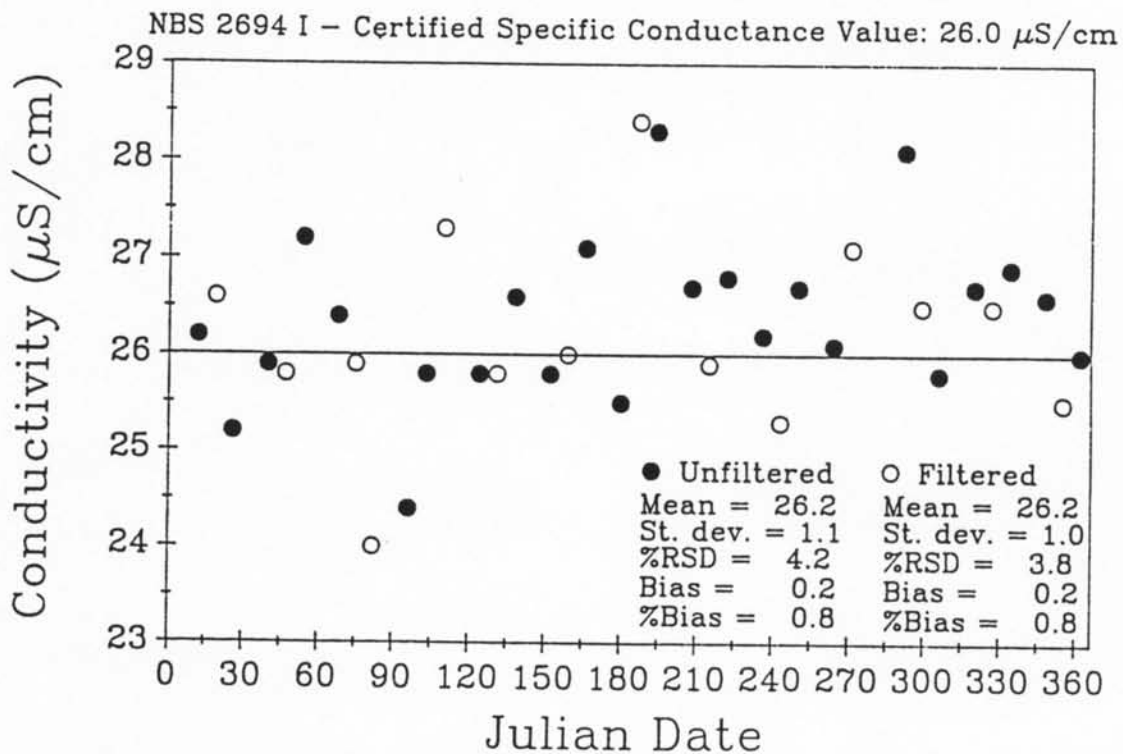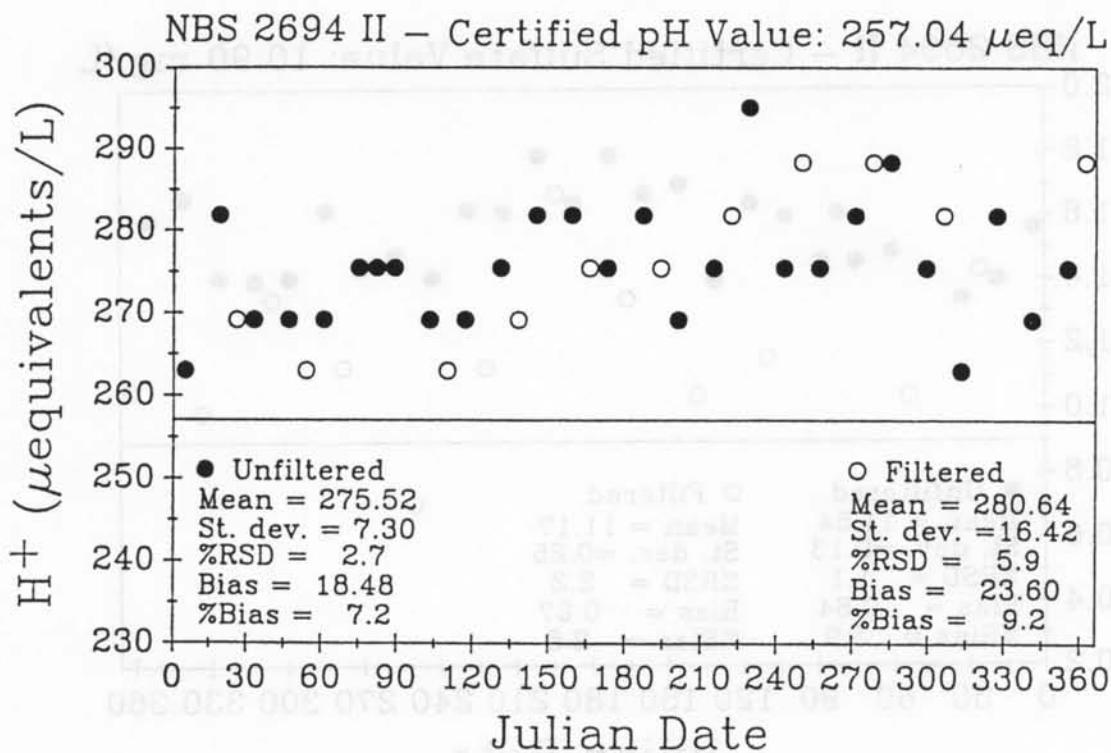
FIGURE B-17.   Comparison of filtered and unfiltered internal blind
                samples (pH II), 1988.
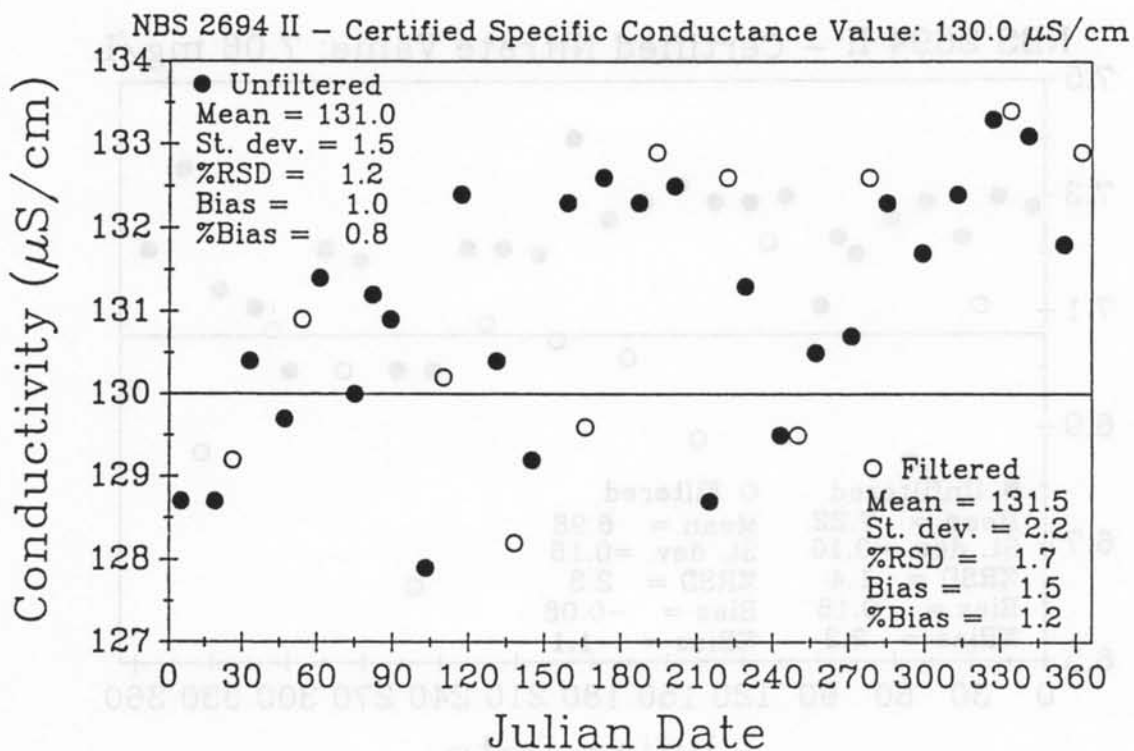
FIGURE B-18.   Comparison of filtered and unfiltered internal blind
                samples (specific conductance II), 1988.

APPENDIX   C

Interlaboratory Comparison Data

USEPA,   EMEP,   LRTAP

1988

APPENDIX C

Interlaboratory Comparison Data

USEPA, EMSP, LRTAP

1988

TABLE C-1 USEPA RTP Acid Rain Performance Survey- May 1988 - CAL Values Compared to Expected Values.

| Parameter (mg/L) | Sample Number | | | | | |
| | 1172 | | 2461 | | 3652 | |
	CAL	EPA	CAL	EPA	CAL	EPA
Calcium	0.05	0.05	0.34	0.39	0.05	0.04
Magnesium	0.02	0.02	0.06	0.06	0.04	0.04
Sodium	0.19	0.19	1.80	1.77	0.41	0.39
Potassium	0.09	0.08	0.79	0.80	0.08	0.08
Ammonium	0.12	0.10	1.13	1.07	0.64	0.60
Nitrate	0.49	0.49	9.87	9.48	8.41	8.01
Chloride	0.29	0.28	2.84	2.74	1.31	1.25
Sulfate	2.10	1.95	12.01	11.71	9.29	8.63
pH (units)	4.41	4.40	3.52	3.50	3.53	3.52
Specific Conductance (μS/cm)	20.30	16.50	157.3	156.4	135.4	130.4

Number of participating laboratories = 38

TABLE C-2   USEPA RTP Acid Rain Performance Survey -
            October 1988 - CAL Values Compared to
            Expected Values.

| Parameter | Sample Number | | | | | |
| (mg/L) | 1555 | | 2864 | | 3115 | |
	CAL	EPA	CAL	EPA	CAL	EPA
Calcium	0.123	0.115	0.045	0.047	0.046	0.046
Magnesium	0.070	0.068	0.030	0.028	0.015	0.017
Sodium	1.337	1.340	0.186	0.179	0.250	0.235
Potassium	0.541	0.524	0.078	0.073	0.083	0.077
Ammonium	0.48	0.43	0.12	0.10	0.84	0.79
Nitrate	3.94	3.84	0.49	0.57	0.53	0.50
Chloride	1.10	1.08	0.29	0.28	0.36	0.35
Sulfate	6.68	6.32	2.91	2.68	12.94	12.02
pH (units)	3.92	3.91	4.28	4.27	3.69	3.68
Specific Conductance (μS/cm)	67.1	66.1	26.0	24.1	98.4	96.4

Number of participating laboratories = 34

TABLE C-3   EMEP Study #10: Interlaboratory Comparison Study -
February 1988 - CAL Reported Values Compared to
EMEP Expected Values.

Parameter (mg/L)	Sample Number							
	G1		G2		G3		G4	
	CAL	EMEP	CAL	EMEP	CAL	EMEP	CAL	EMEP
Calcium	0.353	0.364	1.313	1.334	0.418	0.425	1.192	1.213
Magnesium	0.212	0.218	0.228	0.233	0.122	0.125	0.106	0.109
Sodium	1.52	1.537	1.52	1.544	1.44	1.469	1.47	1.484
Potassium	0.590	0.594	0.528	0.528	0.302	0.297	0.332	0.330
Ammonium	0.68	0.66	0.60	0.57	0.99	0.96	0.88	0.88
Nitrate	4.25	4.15	2.61	2.58	4.07	3.96	2.35	2.30
Chloride	2.49	2.465	2.33	2.28	2.57	2.53	2.38	2.34
Sulfate	4.97	4.72	6.38	5.96	4.64	4.38	6.50	6.14
pH (units)	4.12	4.10	4.51	4.50	4.16	4.16	4.40	4.40
Specific Conductance (μS/cm)	52.2	49.6	38.7	36.6	49.2	46.2	41.6	39.2

Number of participating laboratories = 29

Table D-4 LRTAP Interlaboratory Comparability Study L17-
Feburary 1988 - CAL Reported Values Comared to
CCIW Median Values for all Participating Laboratories.

Parameter (mg/L)	Sample Number																			
	1 CAL	1 CCIW	2 CAL	2 CCIW	3 CAL	3 CCIW	4 CAL	4 CCIW	5 CAL	5 CCIW	6 CAL	6 CCIW	7 CAL	7 CCIW	8 CAL	8 CCIW	9 CAL	9 CCIW	10 CAL	10 CCIW
Calcium	0.756	0.759	2.39	2.400	5.66	5.753	2.51	2.515	0.966	0.950	2.34	2.380	3.90	3.980	0.145	0.160	7.00	7.030	12.7	13.050
Magnesium	0.452	0.452	0.698	0.700	1.59	1.600	0.884	0.890	0.207	0.207	0.728	0.740	0.932	0.950	0.041	0.044	1.46	1.460	2.70	2.730
Sodium	3.05	3.100	0.581	0.581	6.60	6.750	0.173	0.180	0.228	0.230	0.141	0.140	0.189	0.190	0.231	0.237	3.11	3.230	1.23	1.250
Potassium	0.292	0.290	0.416	0.402	0.532	0.536	0.088	0.088	0.117	0.112	0.092	0.090	0.183	0.180	0.039	0.040	0.652	0.670	0.497	0.500
Ammonium	<0.02	0.04	<0.02	0.02	<0.02	0.01	<0.02	0.006	0.45	0.42	0.14	0.12	1.47	1.35	0.17	0.15	<0.02	0.015	<0.02	0.006
Nitrate	0.18	0.18	1.06	1.06	0.18	0.18	4.96	4.81	2.08	2.04	5.84	5.67	3.36	3.29	1.42	1.42	0.35	0.36	1.37	1.34
Chloride	4.27	4.270	0.43	0.430	12.90	12.750	0.80	0.800	0.62	0.620	0.38	0.390	4.13	4.090	0.47	0.460	5.29	5.210	1.30	1.290
Sulfate	1.96	1.925	8.63	8.300	11.20	11.050	5.98	5.820	4.43	4.253	6.68	6.415	6.94	6.825	1.25	1.200	6.69	6.590	3.23	3.145
pH (units)	5.16	5.17	5.53	5.53	7.13	7.00	5.20	5.14	4.47	4.45	4.48	4.45	6.73	6.73	4.61	4.50	7.55	7.38	7.89	7.77
Specific Conductance (µS/cm)	27.7	28.55	29.00	28.3	85.5	87.80	30.7	31.00	28.8	29.20	40.6	41.00	46.1	47.90	16.2	16.35	67.9	70.00	91.8	94.55

Number of particpating laboratories = 52

Table D-5 LRTAP Interlaboratory Comparability Study L19-
October 1988 - CAL Reported Values Comared to
CCIW Median Values for all Participating Laboratories.

Parameter (mg/L)	Sample Number 1		2		3		4		5		6		7		8		9		10	
	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium	0.760	0.768	1.807	1.753	2.428	2.380	5.76	5.750	1.900	1.882	2.642	2.610	1.128	1.120	2.092	2.035	2.986	2.988	5.65	5.855
Magnesium	0.458	0.444	0.412	0.400	0.710	0.690	1.65	1.625	0.360	0.357	0.446	0.440	0.212	0.203	0.498	0.477	0.935	0.915	1.50	1.460
Sodium	3.10	3.095	0.534	0.537	0.583	0.582	6.90	6.910	0.058	0.064	0.102	0.103	0.486	0.480	0.504	0.492	1.24	1.240	1.56	1.565
Potassium	0.292	0.297	0.146	0.150	0.418	0.420	0.525	0.550	0.145	0.150	0.168	0.170	0.026	0.030	0.224	0.212	0.551	0.544	0.736	0.736
Ammonium	0.05	0.04	<0.02	0.01	<0.02	0.026	<0.02	0.009	0.13	0.12	0.21	0.20	0.24	0.23	0.05	0.04	<0.02	0.02	<0.02	0.01
Nitrate	0.18	0.21	<0.03	0.03	1.01	1.04	0.18	0.18	1.55	1.50	0.75	0.97	0.80	0.81	0.18	0.19	0.09	0.09	0.31	0.32
Chloride	4.27	4.260	0.20	0.210	0.43	0.431	13.06	13.225	0.24	0.248	0.24	0.238	0.74	0.730	0.39	0.384	1.26	1.250	2.10	2.100
Sulfate	1.95	1.920	8.12	8.096	8.40	8.297	11.20	11.200	5.81	5.600	9.94	9.700	8.75	8.415	6.44	6.320	7.49	7.400	8.96	8.800
pH (units)	5.19	5.21	4.41	4.41	5.53	5.60	7.13	7.08	4.86	4.86	4.38	4.40	4.00	4.01	6.13	6.05	6.73	6.70	7.24	7.15
Specific Conductance (µS/cm)	28.0	28.10	36.2	35.80	28.6	28.84	86.9	87.35	24.0	24.00	41.8	41.80	56.4	55.70	22.1	22.20	34.0	34.3	54.0	54.40

Number of participating laboratories = 54

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Glossary of Terms

GLOSSARY OF TERMS

Term	Abbreviation	Definition
Accuracy		The difference between the mean value and the true value, when the latter is known or assumed. The concept of accuracy includes both bias (systematic error) and precision (random error).
Bias		A persistent positive or negative deviation of the measured value from the true value due to the experimental method. In practice, it is expressed as the difference between the mean value obtained from repetitive analysis of a homogenous sample and the accepted true value.

Bias = measured value − true value |
| Control Chart | | A graphical plot of test results with respect to time or sequence of measurement, together with limits within which they are expected to lie when the system is in a state of statistical control (6). |
| Critical Concentration | | A calculated concentration used to determine if the measured bias is or is not statistically significant (8). |

$$\text{Critical Concentration} = t \times s_{sp} \times \sqrt{1/n_1 + 1/n_2}$$

where:

$$s_{sp} = \sqrt{\frac{(n_1 - 1)s^2_1 + (n_2 - 1)s^2_2}{n_1 + n_2 - 2}}$$

s = standard deviation
n = number of values
t = t statistic at the 95% confidence level and $(n_1 + n_2) - 2$ degrees of freedom

External Blind Sample		A quality assurance sample of known analyte concentrations submitted to the laboratory by an external agency. At the CAL these samples arrive as normal weekly rain samples and undergo routine processing and analysis. The identity of the sample is unknown to the CAL until all analyses are complete. Data are used to assess contamination potential from handling and shipping.
Internal Blind Sample		A quality assurance sample of known analyte concentrations submitted to the laboratory by the quality assurance specialist. The identity of the sample is known to the processing staff only. The analyte concentrations are unknown to all. These data are valuable in assessing bias and precision for real samples.
Mean	$\overline{x}$	The average obtained by dividing a sum by the number of its addends.

$$\overline{x} = \sum_{i=1}^{n} x_i/n$$

Mean Bias		The sum of the bias for each sample divided by the total number of replicates (n).
Mean Percent Recovery		The sum of the percent recovery for each sample divided by the number of replicates (n).
Method Detection Limit	MDL	The minimum concentration of an analyte that can be reported with 99% confidence that the value is greater than zero.
Percent Bias		The difference between the mean value obtained by repeated analysis of a homogenous sample and the accepted true value expressed as a percentage of the true value.

$$\%\text{Bias} = 100 \times [(V_m - V_t)/V_t]$$

where: V_m = measured value

V_t = true value

Percent Recovery

An estimate of the bias of an analytical method determined from analyte spikes of natural samples. The percent recovery is calculated as:

$$\% \text{ Recovery} = 100 \times (a-b)/c$$

where:

a = measured concentration of a spiked sample

b = measured concentration of sample before spiking

c = calculated concentration spiked sample

Precision

The degree of agreement of repeated measurements of a homogenous sample by a specific procedure, expressed in terms of dispersion of the values obtained about the mean value. It is often reported as the sample standard deviation (s).

Quality Assessment

The system of procedures that ensures that quality control practices are achieving the desired goal in terms of data quality. Included is a continuous evaluation of analytical performance data.

Quality Assurance QA Program

A plan designed to reduce measurement error to tolerable limits and to provide the means of ensuring data validity. Included are both quality control and quality assessment activities.

Quality Control QC

The system of procedures designed to eliminate analytical error. These procedures determine potential sources of sample contamination and monitor analytical procedures to produce data within prescribed tolerance limits.

Quality Control QCS Sample

A sample containing known concentrations of analytes used by the analysts to verify calibration curves and validate sample data. The values obtained from the analysis of these samples are used for calculation of bias and precision and for the monthly control charts.

Relative Standard RSD Deviation

The standard deviation expressed as a percentage:

$$RSD = 100 \times (s/\bar{x})$$

where: s = sample standard deviation

$\bar{x}$ = mean value

Replicates (Splits)

Two aliquots of the same sample treated identically throughout the laboratory analytical procedure. Analyses of laboratory replicates are beneficial when assessing precision associated with laboratory procedures but not with collection and handling. Also referred to as splits.

Sensitivity

The method signal response per unit of analyte.

Spiked Sample

A sample of known analyte concentration to which a known volume and concentration of analyte is added. The difference in the final measured analyte concentration and the theoretical final concentration is used to calculate the percent recovery. These samples are valuable for providing an estimate of accuracy of a method of analysis.

Standard Deviation s

The number representing the dispersion of values around their mean.

$$s = \sqrt{\frac{\sum (x_i - x)^2}{n - 1}}$$

where: x_i = each individual value

$\bar{x}$ = the mean of all the values

n = number of values

Standard Deviation Estimated from Paired Measurements The standard deviation may be estimated from the differences of several sets of paired measurements using the equation (7):

$$s = \sqrt{\frac{\Sigma d^2}{2k}}$$

where: d = difference of duplicate measurements

k = number of sets of duplicate measurements

where: x = each individual value

$\bar{x}$ = the mean of all the values

n = number of values

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