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QUALITY ASSURANCE REPORT NADP/NTN DEPOSITION MONITORING

Laboratory Operations
Central Analytical Laboratory
1989

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

Illinois State Water Survey
National Atmospheric Deposition Program
2204 Griffith Dr.
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ROOM#

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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, forest, 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 of 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 States Research Service (CSRS) and U.S. Forest Service (USFS), the National Park Service (NPS), Bureau of Land Management (BLM), National Oceanic and Atmospheric Administration (NOAA), and the Environmental Protection Agency (EPA). Additional support is provided by various state agencies, public utilities, and industry.

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1989 QUALITY ASSURANCE REPORT
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Laboratory Operations
Central Analytical Laboratory
January 1989 through December 1989

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I. INTRODUCTION

Because wet deposition samples are characterized by very low concentrations of dissolved chemical constituents, quality control (QC) and quality assurance (QA) at the Central Analytical Laboratory (CAL) have been strongly emphasized. Past Quality Assurance Reports for the CAL of the National Atmospheric Deposition Program (NADP)/National Trends Network (NTN), since the inception of the NADP network in 1978, have described the evolution of the quality assurance program which is now in place (1,2,3,4,5,6).

This report documents the daily, weekly, monthly, semi-annual, and annual procedures followed at the CAL during 1989. It does not attempt to repeat information presented in previous editions. The Quality Assurance Reports from 1978 through 1988 are available from the Illinois State Water Survey or the Program Coordinator's Office at Colorado State University. The format of this report has been altered so that the reader will have an idea of the frequency of the several components of the QA program as well as the information required to assess the quality of the sample analyses performed at the CAL during 1989.

The laboratory QA program at the CAL begins as soon as the network samples enter the facility and the buckets are opened. The physical and chemical analyses of each sample are performed in accordance with standard methods documented in the network's QA plan. These analyses are then verified using ion balance and specific conductance calculations. An external audit conducted by the U. S. Geological Survey (USGS) is another mandated portion of the QA program. Voluntary participation in national and international interlaboratory comparison studies also serves to ensure the accuracy of the analyses of the network samples.

II. LABORATORY QUALITY ASSURANCE - A GENERAL DESCRIPTION

The 1989 laboratory QA program consists of several different procedures that have been developed and implemented in the past 10 years. The greater portion of this report summarizes the data obtained from the internal QA component. A brief section contains the results of the USGS external audit for 1989 and CAL participation in both national and international interlaboratory comparison studies.

The internal program consists of procedures originally established by the CAL and subsequently written into the network quality assurance plan. These procedures monitor analytical equipment and personnel performance, and they monitor and evaluate analytical procedures to ensure that the reported analytical values are accurate and precise so that the status of the actual samples is represented.

The internal QA components can be classified according to the frequency of their occurrence: daily, weekly, monthly, semiannually, and annually. These are summarized in Table II-1 and described in detail in subsequent sections of this report.

In 1989, a few modifications were made to the internal program. The ammonium analysis equipment was upgraded from segmented flow to flow injection, without a change in analytical method. One personnel change took place when Angela Haley replaced Beth Allhands in sample processing. Additional blanks were added to evaluate the effect of the pH 4.3 QC solution on the sample filters and buckets. The other procedures remained as they were in 1988.

TABLE XI-1 HAOP/NTM LABORATORY QC/QA PROGRAM SUMMARY

- I. Daily
 - A. Instruments calibrated, calibration curves verified using low- and high-level control standards.
 - 1. Internally formulated solutions used for pH and specific conductance.
 - 2. Diluted USEPA mineral and nutrient concentrates used for major ions.
 - 3. Values of control standards recorded.
 - B. Records of standard preparation and instrument maintenance updated by analysts.

 - II. Weekly
 - A. Blanks analyzed.
 - 1. Deionized water collected from sample processing, atomic absorption, and bucket washing laboratories.
 - 2. Filter leachates A and B collected after 300 mL rinse.
 - 3. Bucket leachates of 50 and 150 mL of deionized water collected from inverted buckets.
 - 4. Procedures expanded when indicated.
 - B. Internal blind samples submitted to sample processing as sites SWS1, SWS2, and SWS3.
 - 1. SWS1 alternated NIST SRM 2694 I and II, unfiltered.
 - 2. SWS2 alternated deionized water and pH 4.3 check solution, unfiltered.
 - 3. SWS3 rotated all of the above, filtered.
 - C. Newly prepared check samples validated and approved for shipment to the field.
 - D. Replicate data collected and evaluated.

 - III. Monthly
 - A. Control charts generated from daily control standards data inspected.
 - B. Chemistry of internal blind samples evaluated from field printouts.
 - C. Reanalysis list based on verification of chemical analysis using ion balance and specific conductance calculations sent to laboratory.
 - 1. Reanalyses of selected samples evaluated.
 - 2. Suggestions for data corrections made and sent to data management.
 - D. Analyses of USGS interlab comparison samples verified.

 - IV. Annually and semiannually
 - A. Summary of annual quality assurance in report form submitted for publication.
 - B. Reports for Subcommittee on Network Operations presented at spring and fall meetings.
 - C. Interlaboratory comparison samples from external agencies analyzed and data reported when requested.
-

III. DAILY QUALITY CONTROL PROCEDURES

Each day 40 or 50 of the 200 weekly NADP/NTN samples arriving at the CAL require processing and analysis. In 1989 the sample processing and analysis flow chart (Figure III-1) and analytical staff (Table III-1) were the same as in 1988 with the exception of the personnel change mentioned previously (Section II). The samples are logged in with appropriate notations, and each is given a sequential number by which it is referred to thereafter. The sample buckets then enter the laboratory where aliquots are poured into small vials for pH and conductance analysis. The remaining sample is then filtered, as volume permits, into two 60-milliliter bottles for holding until further analysis. The analytical methods used by the staff in 1989 were the same (Table III-2) as in 1988. Equipment used for the colorimetric analysis of ammonium, however, was upgraded from segmented flow analysis to flow injection analysis (Appendix A).

Prior to sample analysis, the instruments used for each determination must be calibrated using calibration standards as the method or instrument dictates. Calibration curves are then verified by the analysis of reference solutions hereafter referred to as quality control solutions (QCS). In 1989 two internally prepared solutions were used for pH and conductance (10^{-5} N HNO₃ and 5.0×10^{-4} N KCl). The remaining analytical parameters were monitored by the analysis of dilute solutions prepared from U. S. Environmental Protection Agency (USEPA) mineral and nutrient concentrates. The mineral sample was used to prepare QCS for calcium, magnesium, sodium, potassium, sulfate, and chloride. The QCS for nitrate, ammonium, and orthophosphate were prepared from the nutrient concentrates. Two solutions, approximating the 25th and 75th percentile concentrations of network samples (Table III-3), were prepared for each analyte. These solutions were analyzed repeatedly to verify instrument calibration and the correct operation of the method as sample analysis proceeded.

The values obtained from the analyses of the QCS are recorded for each sample run and entered into a computer program that plots the data as monthly control charts. These daily values are used to evaluate monthly bias and precision and for annual reporting summaries (Table III-4).

The summary of the 1989 QCS shows that the percent bias of all parameters, with the exception of the pH 4.3 solution, were 5% or less. The precision, expressed as relative standard deviation (RSD) is within the limits prescribed by the network QA plan. The formulas used to calculate the values in Table III-4 are included in the Glossary (Appendix B).

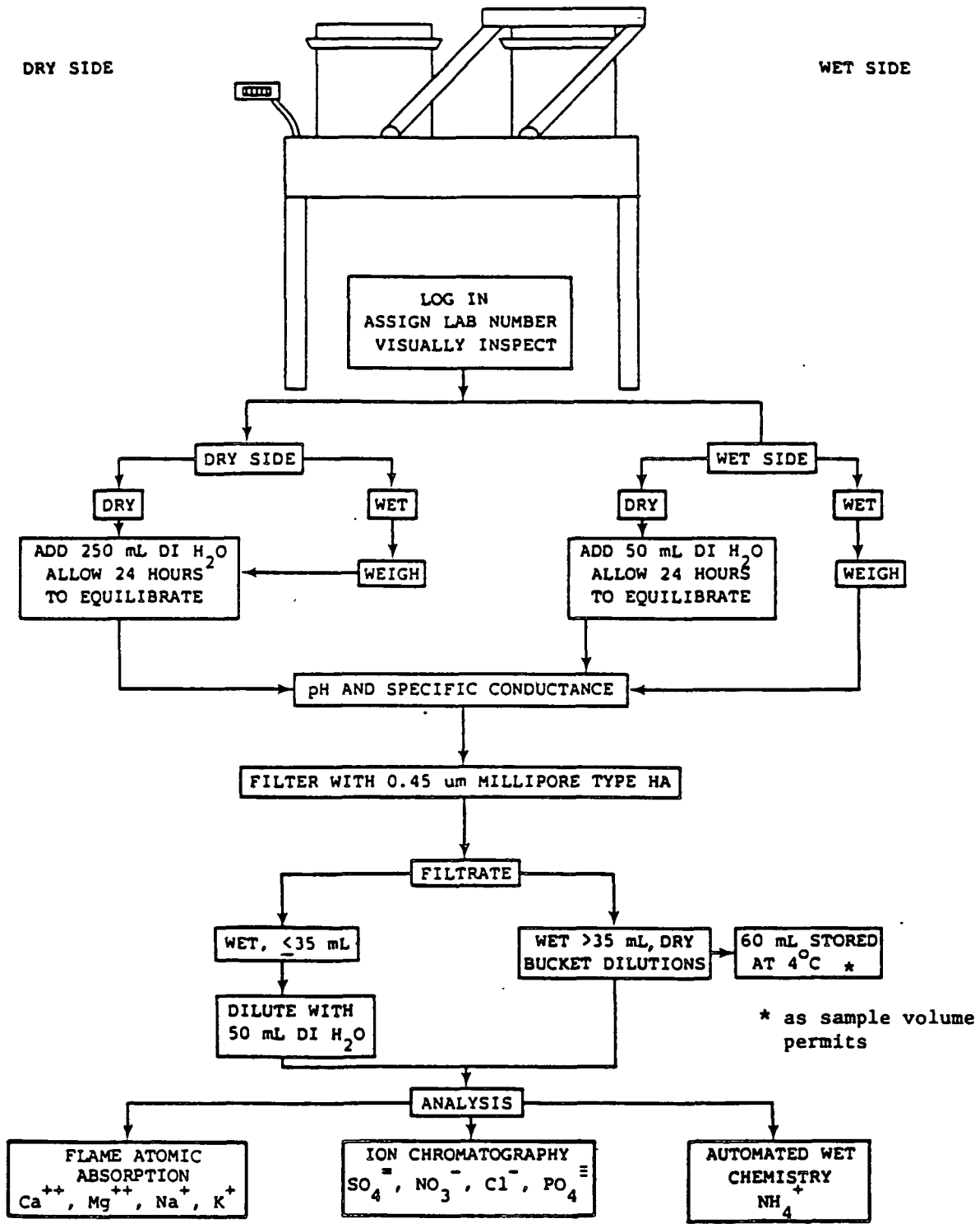


FIGURE III-1. Sample processing flowchart, January 1989 through December 1989.

**TABLE III-1 Central Analytical Laboratory
Analytical Staff, 1989.**

Staff Member/Job Function	Period of Employment
Beth Allhands Sample receipt and processing	February 1984 - October 1989
Sue Bachman NH ₄ ⁺ Ca ⁺⁺ Mg ⁺⁺ , Na ⁺ , K ⁺	August 1980 - December 1989 November 1988 - December 1989
Brigita Demir SO ₄ ⁻ NO ₃ ⁻ Cr ⁻ , PO ₃ ⁻⁴	September 1981 - December 1989
Pat Dodson Sample processing	September 1980 - December 1989
Angela Haley Sample receipt and processing	October 1989 - December 1989
Theresa Ingersoll Sample receipt and processing	March 1985 - December 1989
Kenni James Quality assurance	October 1987 - December 1989
Mark Peden Laboratory manager	July 1978 - December 1989
Jeffrey Pribble Sample receipt	July 1987 - December 1989
Jackie Sauer Sample processing, pH, conductivity	September 1983 - May 1986 January 1988 - December 1989

TABLE III-2 Method Detection Limits for the Analysis of Precipitation Samples, 1978-1989.

Analyte	Method*	MDL(mg/L)	Dates
Calcium	Flame	0.02	7/78-10/80
	Atomic	0.009	10/80-12/89
Magnesium	Absorption	0.002	7/78-10/80
	"	0.003	10/80-12/89
Sodium	"	0.004	7/78-10/80
	"	0.003	10/80-12/89
Potassium	"	0.004	7/78-10/80
	"	0.003	10/80-12/89
Ammonium	Automated Phenate, Colorimetric	0.02	7/78-12/89**
Sulfate	Automated Methyl Thymol Blue, Colorimetric	0.10	7/78-5/85
	I. C. ^a	0.03	5/85-12/89
Nitrate/ Nitrite	Automated Cadmium Reduction, Colorimetric	0.02	7/78-5/85
Nitrate	I. C. ^a	0.03	5/85-12/89
Chloride	Automated		
	Ferricyanide, Colorimetric	0.05 0.02	7/78-3/81 3/81-5/85
	I. C. ^a	0.03	5/85-12/89
Ortho- phosphate	Automated		
	Ascorbic Acid, Colorimetric	0.003 0.01	7/78-2/86 2/86-7/87
	I. C. ^a	0.02	7/87-12/89

* For a complete method description for the most recent methods, see Methods for Collection and Analysis of Precipitation (7).

** Equipment upgrade from SFA to FIA in 1989 did not alter the MDL.

a. I.C. = ion chromatography

TABLE III-3 Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation, 1989.

Parameter	Percentile Concentration Value (mg/L)									
	Min.	5th	10th	25th	50th	75th	90th	95th	99th	Max.
Ca	<0.009	0.019	0.029	0.056	0.123	0.275	0.588	0.974	2.134	18.3
Mg	<0.003	0.005	0.007	0.013	0.025	0.052	0.102	0.162	0.373	1.77
K	<0.003	<0.003	0.003	0.009	0.020	0.041	0.081	0.129	0.351	40.0
Na	<0.003	0.020	0.026	0.044	0.086	0.195	0.425	0.725	2.090	23.0
NH ₄	<0.02	<0.02	<0.02	0.09	0.22	0.44	0.76	1.04	2.00	10.75 6
NO ₃	<0.03	0.15	0.29	0.61	1.12	1.98	3.23	4.23	6.72	17.0
Cl	<0.03	0.05	0.06	0.09	0.15	0.29	0.61	1.15	3.71	25.8
SO₄	<0.03	0.21	0.31	0.68	1.26	2.44	3.90	5.12	8.33	39.0
PO ₄	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	0.04	0.13	2.3
PH	3.33	4.06	4.19	4.42	4.88	5.66	5.34	6.59	7.02	7.85
(units) COND. (MS/cm)	0.9	3.3	4.6	7.8	13.8	24.5	37.6	49.2	79.3	266.8

Source: National Atmospheric Deposition Program(NADP)/National Trends Network (NTN) 1989 wet-side samples. Number of samples = 6,970.
Mean sample volume = 1471 mL; median sample volume = 869 mL.

TABLE III-4 Analytical Bias and Precision Determined from Analysis of QCS, 1989.

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias mg/L	Bias %	Precision s mg/L	R8D %	Critical Cone. mg/L	Statist. Significant Bias?
Calcium	0.080	0.081	477	0.001	0.62	0.002	2.5	0.0008	NO
	0.398	0.400	455	0.002	0.58	0.005	1.2	0.0024	NO
Magnesium	0.020	0.020	478	0.000	1.5	0.001	5.0	0.0002	YES
	0.098	0.102	418	0.004	3.7	0.002	2.0	0.0008	YES
Sodium	0.040	0.041	474	0.001	2.0	0.002	4.9	0.0005	YES
	0.200	0.203	465	0.003	1.3	0.003	1.5	0.0012	YES
Potassium	0.010	0.010	475	0.000	0.0	0.002	20.0	0.0004	NO
	0.049	0.050	458	0.001	2.0	0.002	4.0	0.0006	YES
Ammonium	0.13	0.13	363	0.00	0.0	0.01	7.7	0.0019	YES
	0.43	0.43	158	0.00	0.0	0.02	4.6	0.0043	NO
	0.64	0.64	133	0.00	0.0	0.02	3.1	0.0058	NO
Chloride	0.10	0.11	468	0.01	5.0	0.01	9.1	0.0018	YES
	0.81	0.82	566	0.01	0.6	0.01	1.2	0.0040	YES
Nitrate	0.44	0.46	578	0.02	4.3	0.01	2.2	0.0021	YES
	2.19	2.27	597	0.08	3.8	0.02	0.9	0.0078	YES
Sulfate	0.93	0.95	584	0.02	2.5	0.01	1.1	0.0054	YES
	2.81	2.88	602	0.07	2.4	0.03	1.0	0.0203	YES
pH units (μ eq/L)	4.30(50.1)	4.32	2142	(-2.79)	5.7	(0.02)	3.5	(1.023)	YES
	5.50(3.2)	5.50	2142	(0.02)	0.8	(0.08)	16.0	(0.317)	NO
Specific Conductance μ S/cm	21.8	21.4	1336	-0.4	2.0	0.4	1.9	0.2697	YES

IV. WEEKLY QUALITY CONTROL/QUALITY ASSURANCE PROCEDURES

A weekly set of quality assurance samples is prepared and submitted to the laboratory for analysis. These samples include three samples of known concentration submitted blind to the analysts, replicate samples representing 2 percent of the total network samples, and blank samples used to evaluate - any contamination that could be traced to the laboratory's deionized water, sample filters, or the buckets used as sample collectors at the sites.

A. BLIND SAMPLES

In July 1984 an internal blind sample program was instituted to provide another means of assessing the quality of the CAL data. Since the beginning of 1987 three blind samples per week have been submitted to the laboratory for processing and analysis. These samples are given NAOP/NTN site designations of SWS1, SWS2, and SWS3. Two different samples alternate weekly for SWS1 and SWS2. These samples are not filtered. The SWS1 samples are National Institute of Standards and Technology (NIST) Simulated Rainwater, Standard Reference Material (SRM) 2694I and 2694II. The SWS2 samples are the internally formulated pH 4.3 QCS and deionized water from the ion chromatography laboratory. The SWS3 samples include all four of the SWS1 and SWS2 solutions, alternating every four weeks. Each of these SWS3 solutions is filtered. The addition of the SWS3 samples provides a method of assessing the contribution of the filtering process to network samples. Tables IV-1, IV-2, IV-3, and IV-4 summarize the results of this program in 1989.

As would be expected, the bias and precision values of the blind analytes are greater than those of the corresponding QCS. With the exception of the calcium percent bias and RSD for the near-detection-limit SRM 2694I, the SWS1 results are acceptable. The results of the SWS2 sample analyses (Table IV-2) are also acceptable; however note that one of the sodium values is at the detection level.

The SWS3 results (Tables IV-3 and IV-4) indicate that the filtration process introduces sodium contamination and increased calcium concentrations in some, but not all, of the test solutions. The calcium contamination occurs only in the NIST solutions, both of which contain calcium concentrations lower than the 25th percentile of the network. The bias is consistent for both samples. The nitrate difference between the SWS1 and SWS3 samples is not significant. Sulfate has exhibited a consistently lower bias for the filtered sample since the internal blind program began. The sulfate bias for

TABLE IV-1 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS1) MIST SRM 2694I and 2694II, Unfiltered, 1989.

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias mg/L	%	Precision s mg/L	RSD %	Critical statist. Conc. mg/L	Significant Bias?
Calcium	0.014 ^a	0.010	23	-0.004	-28.6	0.010	100.0	0.005	NO
	0.049 ^b	0.048	27	-0.001	-2.0	0.009	18.8	0.005	NO
Magnesium	0.024	0.023	23	-0.001	-4.2	0.001	4.4	0.001	YES
	0.051	0.051	27	0.000	0.0	0.005	9.8	0.002	NO
Sodium	0.205	0.209	23	0.004	2.0	0.005	2.4	0.003	YES
	0.419	0.421	27	0.002	0.5	0.009	2.1	0.004	NO
Potassium	0.052	0.047	23	-0.005	-9.6	0.003	6.4	0.002	YES
	0.106	0.105	27	-0.001	-0.9	0.005	4.8	0.002	NO
Ammonium	****								
Chloride	(1.00) ^c	1.06	27	0.06	6.0	0.07	6.6	0.03	
	(0.24)	0.25	23	0.01	4.2	0.01	4.0	0.00	
Nitrate	(1.00)	1.05	27	0.05	5.0	0.03	2.9	0.01	

Sulfate	7.06	7.13	27	0.07	1.0	0.12	1.7	0.07	YES
	2.75	2.85	23	0.10	3.6	0.06	2.1	0.04	YES
pH units	10.90	11.14	27	0.24	2.2	0.26	2.3	0.13	YES
	4.27(53,.7)	4.24(57.5)	23	(3.70)	6.9	(1.96)	3.4	(1.83)	YES
($\mu\text{eq/L}$)	3.59(257)	3.57(269)	27	(14.0)	5.4	(11.97)	4.4	(8.98)	YES
Specific									
Conductance $\mu\text{S/cm}$	26.0	27.3	23	1.3	5.0	0.7	2.6	0.5	YES
	130.0	132.8	27	2.8	2.2	1.7	1.3	0.7	YES

- a. The first set of values for each parameter is for NIST SRM 2694-I.
- b. The second set of values for each parameter is for NIST SRM 2694-II.
- c. Noncertified values in parentheses for Cl and NH₄ are provided for information only.

TABLE IV-2 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS2), Deionized Water and pH 4.3 QCS, Unfiltered, 1989.

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias mg/L	%	Precision S mg/L	RSD %	Critical. Statist. Conc. mg/L	Significant Bias?
Calcium	<0.009 ^a	<0.009	25						
	<0.009 ^b	<0.009	25						
Magnesium	<0.003	<0.003	25						
	<0.003	<0.003	25						
Sodium	<0.003	<0.003	25						
	<0.003	0.003	25						
Potassium	<0.003	<0.003	25						
	<0.003	<0.003	25						
Ammonium	<0.02	<0.02	25						
	<0.02	<0.02	25						
Chloride	<0.03	<0.03	25						
	<0.03	<0.03	25						
Nitrate	<0.03	<0.03	25						
	3.12	3.26	25	0.14	4.49	0.07	2.15i	0.03	YES
Sulfate	<0.03	<0.03	25						
	<0.03	<0.03	25						
pH units	5.64(2.29)	5.60(21.51)	25	(0.22)	9.57	(0.62)	24.7	(2.06)	NO
(μ eq/L)	4.30(50.1)	4.32(47.9)	25	(-1.76)	-3.51	(2.44)	5.0	(2.36)	NO
Specific Conductance	0.9	1.0	25	0.1	11.1	0.2	20.0	2.1	NO
μ S/cm	21.8	21.3	25	-0.5	-2.29	0.6	2.8	2.0	NO

a. The first set of values for each parameter is for deionized water.

b. The second set of values for each parameter is for pH 4.3 QCS.

TABLE IV-3 Analytical Bias and Precision Determined from
 Analysis of: Internal Blind Audit Samples (SWS3),
 NIST SRN 2694I and 2694II, Filtered, 1989.

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias		Precision		Critical. Statist. Conc. mg/L	Significant Bias?
				mg/L	%	S mg/L	RSD %		
Calcium	0.014 ^a	0.027	12	0.013	92.9	0.010	37.0	0.005	YES
	0.049 ^b	0.062	12	0.013	26.5	0.007	11.3	0.005	YES
Magnesium	0.024	0.024	12	0.000	0.0	0.003	12.5	0.002	NO
	0.051	0.055	12	0.004	7.8	0.009	16.4	0.005	NO
Sodium	0.205	0.225	12	0.020	9.8	0.009	4.0	0.004	YES
	0.419	0.430	12	0.011	2.6	0.015	3.5	0.007	YES
Potassium	0.052	0.046	12	-0.006	-11.5	0.007	15.2	0.004	YES
	0.106	0.109	12	0.003	2.8	0.006	5.5	0.003	YES
Ammonium	****								
Chloride	(1.00) ^c	1.07	12	0.07	7.0	0.06	5.6	0.04	
	(0.24)	0.27	12	0.03	12.5	0.02	7.4	0.01	
Nitrate	(1.00)	1.03	12	0.03	3.0	0.04	3.9	0.03	

Sulfate	7.06	6.99	12	-0.07	-1.0	0.11	1.6	0.07	
	2.75	2.79	12	0.04	1.4	0.09	3.2	0.06	NO
pH units	10.90	10.73	12	-0.17	-1.6	0.18	1.7	0.11	YES
	4.27(53.7)	4.25(56.7)	12	(3.0)	5.6	(1.8)	3.2	2.05	YES
(µeq/L)	3.59(257)	3.56(274)	12	(17.0)	6.6	(10.0)	3.7	8.3	YES
Specific									
Conductance µS/cm	26.0	27.4	12	1.4	5.4	0.7	2.6	0.6	YES
	130.0	133.2	12	3.2	2.5	2.0	1.5	0.9	YES

- a. The first set of values for each parameter is for NIST SRM 2694I.
 b. The second set of values for each parameter is for NIST SRM 2694II.
 c. Noncertified values in parentheses for Cl and NH₄ are provided for information only.

**TABLE IV-4 Analytical Bias and Precision Determined from
Analysis of Internal Blind Audit Samples (SWS3)
Deionized Water and pH 4.3 QCS, Filtered, 1989.**

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias		Precision		Critical. Conc. mg/L	Statist. Significant Bias?
				mg/L	%	S mg/L	RSD %		
Calcium	<0.009 ^a	<0.009	13						
	<0.009 ^b	0.010	13	0.001	22.2 ^c	0.010	100.0	0.006	NO
Magnesium	values at or below MDL								
Sodium	<0.003	0.020	13	0.017	1133.3	0.010	50.0	0.006	YES
	<0.003	0.022	13	0.019	1266.7	0.012	54.5	0.007	YES
Potassium	values below MDL								
Ammonium	<0.02	0.06	13	0.04	400.0	0.10	166.7	0.06	NO
	<0.02	0.04	13	0.02	200.0	0.04	100.0	0.02	YES
Chloride	<0.03	0.03	13			0.02	66.7	0.01	NO
	<0.03	0.03	13			0.02	66.7	0.00	YES
Nitrate	<0.03	<0.03	13						
	3.12	3.19	13	0.07	2.24	0.05	1.57	0.03	YES
Sulfate	<0.03	<0.03	13						
	<0.03	0.03	13			0.02	66.7	0.01	NO
pH units (μ eq/L)	5.64(2.29)	5.57(2.72)	13	0.43	18.7	0.64	23.5	0.39	YES
	4.30(50.1)	4.32(48.2)	13	-1.94	-3.9	2.53	5.2	3.03	NO
Specific Conductance μ S/cm	0.9	1.1	13	0.2	22.2	0.4	36.4	0.2	NO
	21.8	21.5	13	-0.3	-1.3	0.6	2.8	1.0	NO

- a. The first set of values for each parameter is for deionized water.
- b. The second set of values for each parameter is for pH 4.3 QCS.
- c. For the purposes of calculation, the value used for an MDL is 0.5 times the MDL.

both SWS1 and SWS3 decreased in 1989.

The control chart figures in Appendix C illustrate the SWS1 and SWS3 comparisons for calcium, magnesium, sodium, potassium, sulfate, pH, and conductance. These are the values that NIST has officially certified. The bias for the ions has either decreased or remained the same, while the conductance charts indicate a positive bias in 1989. The standard deviations for all the parameters plotted are approximately the same as in 1988.

Precision, expressed as standard deviation (s), is considerably better for the QCS than the internal blind samples. The apparent explanation is that the QCS are known and are usually analyzed immediately after calibration whereas the blind samples are completely unknown and can fall anywhere in the weekly sample load.

B. REPLICATE SAMPLES

A further assessment of laboratory precision can be made from the analysis of replicate network samples. Two percent of the weekly samples are selected and split into three 60-mL aliquots. Two samples are given the same number, one is analyzed routinely, and the other is refrigerated for archival purposes. The third returns to sample processing where it is given another number and resubmitted. After all chemical analyses are completed, data management changes the second number back to the original "0" and codes it with a "Q" (quality assurance). The 0/Q splits then appear consecutively on the ion balance printouts twice a month. At this time it is possible to inspect the split analyses and estimate the precision. Replicate sample differences for 1989 are displayed as box plots and are found in Appendix C. Box plots are described in the Glossary (Appendix B).

The information presented in Table IV-5 is a summary of the 173 replicates analyzed in 1989. The low range contains values from the method detection limit (MDL) to the median value; the high range contains concentrations from the median to the 95th percentile (Table C-1). The estimate of standard deviation of the differences provides precision values that most closely approximate those of the internal blind samples. The formula for calculating the estimate of standard deviation is defined in the Glossary (Appendix B).

Table IV-5 Mean Differences and Standard Deviations of the Differences Between Replicate Analyses of Network Precipitation Samples, 1989.

Parameter	Mean Difference^a	Standard Deviation Low Conc.	Standard Deviation High Conc.
Calcium (mg/L)	0.001	0.011	0.017
Magnesium (mg/L)	0.000	0.002	0.002
Sodium (mg/L)	-0.000	0.003	0.026
Potassium (mg/L)	0.001	0.003	0.022
Ammonium (mg/L)	0.01	0.04	0.12
Sulfate (mg/L)	0.00	0.03	0.07
Nitrate (mg/L)	-0.01	0.11	0.11
Chloride (mg/L)	0.01	0.01	0.12
pH (μ equiv/L)	0.75	0.88	3.13
Conductivity (μ S/cm)	0.27	0.28	0.65
Number of Pairs	173	87	86

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

C. BLANKS

The data obtained from the weekly blank procedure are used to define the potential contributions of the collection vessel and sample processing procedures to the measured concentrations in precipitation. In 1989 blanks were analyzed from three sources: the deionized water from three laboratories, leachates from the filters used to filter network samples, and the sample collection buckets. In 1989 additional blanks were begun using the pH 4.3 QCS in addition to deionized water in the filter and bucket leachate routines.

1. Deionized Water Blanks

The deionized water blanks are collected from the sample processing laboratory, the service laboratory where the buckets are washed, and the atomic absorption laboratory. The median values of the cation and anion analyses were all below the method detection limits. Table IV-6 shows the median values for pH and conductivity for the deionized water in 1989.

**TABLE IV-6 Median Values for pH and Conductivity
for Weekly Deionized Water Blanks, 1989.**

	Sample Processing	Laboratory Atomic Absorption	Service
pH (units)	5.61	5.64	5.62
Conductivity ($\mu\text{S}/\text{cm}$)	0.9	0.9	1.0

2. Filter Blanks

The deionized water from the sample processing laboratory is filtered and the filtrate analyzed in order to gain another estimate of the filter contribution to sample chemistry. All filters are rinsed with 300 mL of deionized water prior to sample filtration. In the blank procedure this initial rinse is followed by two 50-mL aliquots, which are filtered in succession and labeled "Filter Blank A" and "Filter Blank B". In March a second set of filter blanks was begun. After the deionized water rinse, pH 4.3 QCS was filtered and collected as two successive 50-mL filtrates (A and B) and sent for

laboratory analysis. The results are presented in Table IV-7. Trace amounts of calcium were noted in the pH 4.3 sample and the pH and conductance were slightly altered but still within the control limits for this solution.

TABLE IV-7 Median Analyte Concentrations Found in Weekly Deionized Water and pH 4.3 QCS Filter Blanks, 1989.

Analyte (mg/L)	Deionized Water		pH 4.3 Check Solution	
	A ^a	B ^b	A ^a	B ^b
Calcium	<0.009	<0.009	0.014	0.011
Magnesium	<0.003	<0.003	<0.003	<0.003
Sodium	0.008	<0.003	0.014	0.004
Potassium	<0.003	<0.003	<0.003	<0.003
Ammonium	<0.02	<0.02	0.03	<0.02
Sulfate	<0.02	<0.02	<0.02	<0.02
Nitrate	<0.02	<0.02	3.17	3.32
Chloride	<0.02	<0.02	<0.02	<0.02
pH (units)	5.65	5.65	4.37	4.34
[H ⁺] (µeq/L)	2.23	2.23	42.7	45.7
Conductivity (µS/cm)	1.2	1.0	20.2	21.5
Number of Analyses	48	48	32	32

- a. First 50 mL of filtrate after 300-mL deionized water filter rinse.
- b. Second consecutive 50-mL filtrate after 300-mL deionized water filter rinse.

3. Bucket Blanks

The number of bucket blanks also increased in 1989. In 1987 and 1988 there were two bucket blanks, one containing 50 mL and the other containing 150 mL of deionized water. The lids were pounded on and the buckets inverted and left for twenty-four hours. The buckets were then opened, the water poured into 60 mL sample bottles, and the solutions sent to the laboratory for analysis. In 1989 the same procedure was repeated using 50 and 150 mL portions of pH 4.3 check solution. In addition, upright buckets with snap-on lids were also evaluated in order to assess the contribution of the lid and the butadiene rubber gasket. There were two upright buckets containing deionized water and two containing pH 4.3 QCS; 50 and 150 mL portions of each. A total of 8 bucket leachate samples were analyzed weekly in 1989.

Tables IV-8 and IV-9 are summaries of the upright and inverted bucket blanks for both solutions. The upright bucket median values indicate a low sodium concentration in the 50 mL aliquots. Analytes in the upright bucket blanks are below the detection limit. Table IV-9 shows that the inverted bucket samples contain additional calcium, sodium, and sulfate. The pH of all four solutions is elevated compared to expected values. The conductivity of the pH 4.3 QCS blanks is lowered.

Box plots of the bucket blanks (Appendix C) illustrate the median analyte values as well as the variance of the 1989 analyses. These plots clearly illustrate the contribution of the o-ring in the lids of the inverted buckets. Solutions to this problem are being sought, and alternate lid sealing techniques continue to be evaluated.

TABLE IV-8 Median Measured Mass as (μg)/Bucket^a
 Found in Weekly Upright Bucket Blanks
 Using Deionized Water and pH 4.3 QCS
 as Leaching Agents, 1989.

Analyte	Deionized Water		pH 4.3 Check Solution	
	50 mL	150 mL	50 mL	150 mL
Calcium	<0.45	<0.45	<0.45	<0.45
Magnesium	<0.15	<0.15	<0.15	<0.15
Sodium	0.35	<0.15	0.25	<0.15
Potassium	0.15	<0.15	0.15	<0.15
Ammonium	<1.0	<1.0	<1.0	<1.0
Sulfate	<1.5	<1.5	<1.5	<1.5
Nitrate	<1.5	<1.5	156.0 (156) ^b	486.0 (468)
Chloride	<1.5	<1.5	<1.5	<1.5
pH (units)	5.62 (5.61)	5.62	4.38 (4.30)	4.34
[H ⁺] (μ eq/bucket)	0.12 (0.12)	0.37 (0.37)	2.1 (2.50)	6.9 (7.52)
Conductivity (μ S/cm)	1.4 (0.9)	1.3	20.2 (21.8)	21.2
Number of Analyses	22	22	22	22

- a. Mass/bucket = the concentration in $\mu g/mL$ x 50 or 150 mL.
 Detection limit values are expressed as the MDL (in $\mu g/mL$) x 50 mL.
- b. Values in parentheses represent those of deionized water or pH 4.3 check solution analyzed with no bucket contact.

TABLE IV-9 Median Measured Mass as (μg)/Bucket^a
 Found in Weekly Inverted Bucket Blanks
 Using Deionized Water and pH 4.3 QCS
 as Leaching Agents, 1989.

Analyte	Deionized Water		pH 4.3 Check Solution	
	50 mL	150 mL	50 mL	150 mL
Calcium	0.65	<0.45	1.05	1.35
Magnesium	0.15	<0.15	0.25	<0.15
Sodium	3.90	4.05	2.45	1.80
Potassium	0.20	<0.15	0.25	<0.15
Ammonium	<1.0	<1.0	<1.0	<1.0
Sulfate	2.50	<1.5	3.50	2.5
Nitrate	<1.5	<1.5	153.0 (156) ^b	474.0 (468)
Chloride	<1.5	<1.5	<1.5	<1.5
pH (units)	6.20 (5.61)	5.96	4.57 (4.30)	4.42
[H ⁺] ($\mu\text{eq}/\text{bucket}$)	0.03 (0.12)	0.12 (0.37)	1.35 (2.50)	2.08 (7.52)
Conductivity ($\mu\text{S}/\text{cm}$)	1.8 (0.9)	1.3	15.2 (21.8)	18.9
Number of Analyses	47	47	28	28

- a. Mass/bucket - the concentration in $\mu\text{g}/\text{mL}$ x 50 or 150 mL.
 Detection limit values are expressed as the MDL (in $\mu\text{g}/\text{mL}$) x 50 mL.
- b. Values in parentheses represent those of deionized water or pH 4,3 check solution analyzed with no bucket contact.

V. MONTHLY QUALITY ASSURANCE PROCEDURES

Results from several of the laboratory quality control procedures are evaluated monthly. The control charts generated from the daily analysis of QCS are plotted each month and are accompanied by the monthly mean value and standard deviation of each solution. Results from the blind program are evaluated from field site printouts routinely sent to each site (SWS1, SWS2, and SWS3). Twice monthly the data management group generates a printout of the most recent complete data sets of the analyses of four or five hundred network samples. The quality assurance specialist then compiles a list of samples to be reanalyzed from two of these printouts, based upon the criteria given below. Finally, samples are analyzed and data submitted on a monthly basis for the interlaboratory comparison, a portion of the external audit of the CAL by the United States Geological Survey (USGS).

A. REANALYSIS PROCEDURES

The computer algorithm used to select reanalysis samples was the same in 1989 as in the previous two years. Samples are flagged for either an anion/cation imbalance or a large difference between the calculated and measured conductance.

1. Ion Percent Difference

The factors used to convert ion concentrations measured in milligrams per liter to microequivalents per liter are listed in Table V-1 (8). These values are then used to calculate the Ion Percent Difference (IPD). The IPD is calculated using the measured pH, cations, and anions plus calculated values for bicarbonate and hydroxide. The ion sum (IS) is equal to the sum of the measured cations, measured anions, and calculated anions. The IPD is calculated by subtracting the sum of the cations from the sum of the anions, dividing the remainder by the IS, and multiplying the quotient by 100.

$$\text{Cation sum} = [\text{H}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+]$$

$$\text{Anion sum} = [\text{HCO}_3^-] + [\text{OH}^-] + [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{PO}_4^{3-}]$$

$$\text{IPD} = \frac{\text{Anion sum} - \text{Cation sum}}{\text{Anion sum} + \text{Cation sum}} \times 100$$

Samples are flagged for reanalysis if:

IS < 50	μequiv/L	and IPD >	± 60%
50 ≤ IS < 100	μequiv/L	and IPD >	± 30%
IS ≥ 100	μequiv/L	and IPD >	± 15%

2. Conductance Percent Difference

Conductance percent difference is the other method used by NADP/NTN to validate a sample analysis. The ion concentration values, expressed as microequivalents per liter, are multiplied by the conductance conversion factors listed in Table V-2 (9), summed, and then divided by 1000 in order to calculate the theoretical conductance. This value is then compared to the measured conductance and the Conductance Percent Difference (CPD) is calculated:

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

Samples are flagged for reanalysis if:
 $10\% < \text{CPD} < -40\%$

A complete reanalysis is carried out on all samples selected, providing sufficient sample remains and the sample has not been labeled as contaminated. The quality assurance specialist, with the suggestions of the analysts, determines which values should be corrected. When no explanation can be found for differences between the original and reanalysis values, the original data are reported. All reanalysis values are maintained in the computerized database along with the original analyses.

3. IPD and CPD Histograms

In 1989 10,000 samples were analyzed, 664 samples were flagged for reanalysis, and data changes were made to 93 samples. 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 in 1989. The median, mean, standard deviation, and number of wet samples are presented on each figure.

The Ion Percent Difference Histogram exhibits a positive skew as it always has and the mean (5.59%) and median (4.14%) values are of the same magnitude as the corresponding values in 1988. The Conductance Percent Difference continues to exhibit a negative skew with mean (-8.70%) and median (-5.86%) values slightly more negative than in 1988.

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
Hydrogen	992.2
Bicarbonate	16.39
Hydroxide	58.8

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

Analyte	Conversion Factor
Hydrogen	350
Calcium	59.5
Magnesium	53.0
Sodium	50.1
Potassium	73.5
Ammonium	73.5
Bicarbonate	44.5
Hydroxide	198
Sulfate	80.0
Nitrate	71.4
Chloride	76.3
Orthophosphate	69.0

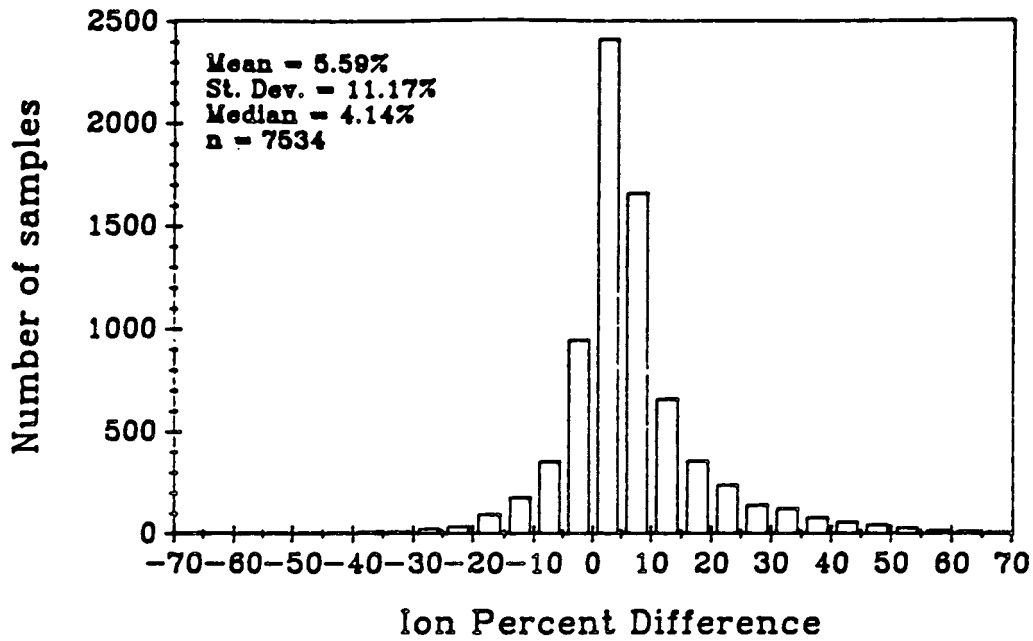


FIGURE V-1. Ion percent difference histogram for NADP/NTM wet-side samples, 1989.

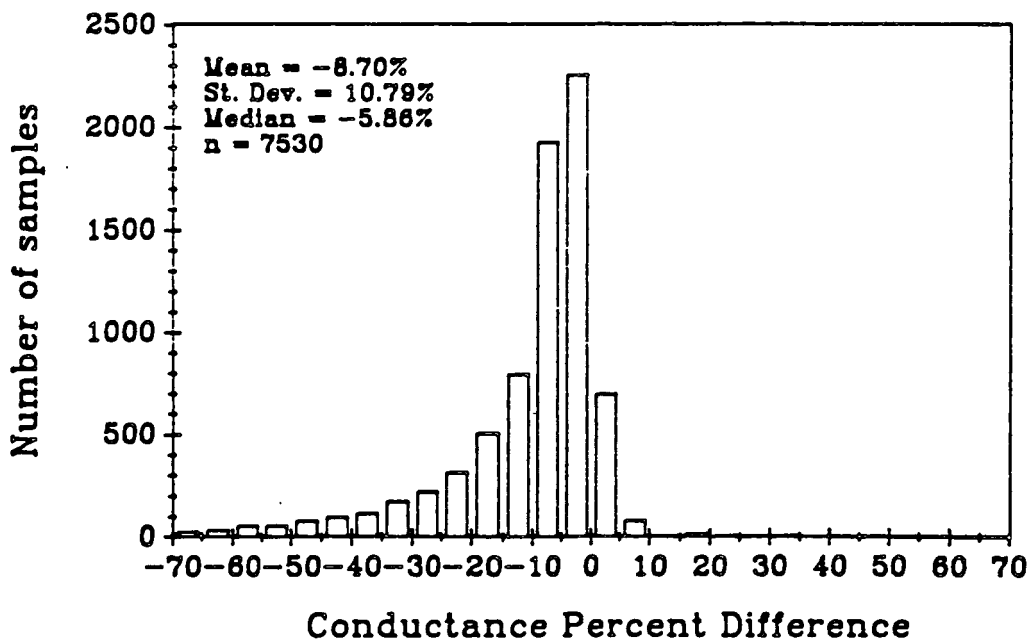


FIGURE V-2. Conductance percent difference histogram for NADP/NTM wet-side samples, 1989.

B. USGS INTERLABORATORY COMPARISON

As part of the mandated NADP/NTN quality assurance program, the USGS serves as the external auditor of the CAL. There are several components of the external audit, which is an ongoing process from year to year. The interlaboratory comparison, which began in the fall of 1982, is designed to determine whether participating laboratories are producing comparable results. Each month several sets of samples of different matrices are mailed to the participating laboratories. In all or part of 1989 the laboratories included: (1) the CAL; (2) Inland Water Directorate, National Water Quality Laboratory (IWD); and (3) Hunter, Environmental Services, Inc. (ESE). ESE joined the program in July. The samples prepared for the 1989 interlaboratory-comparison program were from three different sources: (1) Synthetic wet-deposition samples (USGS) and ultra-pure deionized water samples prepared by the USGS, (2) standard reference samples (SRM 2694-I and 2694-II) prepared and certified by NIST, and (3) synthetic wet-deposition samples and natural wet-deposition samples prepared by the CAL (10).

Each month, as these samples are submitted, they are analyzed by the CAL chemists and the results are recorded on interlaboratory comparison sample data sheets. These sheets are then submitted to the quality assurance specialist every other month. The data are visually checked and then sent to the data management group for computer entry. The same program used for the reanalysis flagging of precipitation samples is run on the intercomparison samples and the IPD and CPD are calculated. Suspect results are rechecked before the final compilation is sent to the USGS in Denver.

An examination of the data from the three participating laboratories using a Kruskal-Wallis test indicated that significant ($\alpha=0.01$) differences did not occur among laboratory determinations in 1989. Analytical results for NIST SRMs indicated that the CAL had the least number of median analyses that were significantly different from the certified values (10).

VI. SEMI-ANNUAL AND ANNUAL QUALITY ASSURANCE PROCEDURES

At the end of each year, quality assurance data from a variety of sources are gathered and summarized for this annual quality assurance report and for scientific presentations. The USGS publishes the external audit results in report form annually. Other interlaboratory performance studies in which the CAL participates occur annually, semiannually, or three or four times a year, depending on the agency conducting the program. The CAL participated on a voluntary basis in six interlaboratory comparison studies in 1989.

A. U.S. GEOLOGICAL SURVEY EXTERNAL AUDIT PROGRAM

The U.S. Geological Survey's NADP/NTN external audit program consists of two components: a blind audit sample procedure and an interlaboratory comparison study. The data are used to evaluate laboratory bias and precision and to study the effects of sample handling and shipping. The results of this program are published and available from the USGS(10).

Thirty-two blind audit samples were mailed to selected NADP/NTN sites for the first, second, and fourth quarters of 1989. Thirty-three were mailed for the third quarter. For 1989, 250-, 500-, and 1,000-mL samples were sent to the selected sites each quarter to assess volume related biases. Six solutions were used in the 1989 blind-audit program. Three of these solutions were prepared by the CAL: the pH 4.3 QCS, and two internally formulated solutions of synthetic precipitation prepared at the twenty-fifth and seventy-fifth percentile concentration levels of network samples. One solution was prepared by the USGS Standard Reference Water Sample Project and two by their Acid Rain Project. One of the latter was ultra-pure deionized water. The site operators were directed to pour a specified volume of the sample supplied into a clean bucket from inventory and remove an aliquot for field chemistry prior to shipping as a weekly sample. The portion remaining in the bottle was sent to the CAL separately and submitted blind to the analytical staff. The concentrations for the bucket and bottle samples were then compared. The results indicated that a bias existed for all analytes except ammonium. The median concentrations for bucket samples were larger than the median concentrations for bottle samples for calcium, magnesium, sodium, potassium, chloride, nitrate, and sulfate. The median determinations for bucket samples were smaller than their bottle counterpart for hydrogen and specific conductance (10).

The interlaboratory comparisons began in the fall of 1982. The results of the 1989 study are discussed in the previous chapter because the samples are received in the laboratory on a monthly basis. An examination of the data indicated that there was no significant difference among the laboratories participating in 1989. The analytical results from the NIST SRMs indicated that the CAL had the least number of analyses significantly different from the certified values (10).

B. INTERLABORATORY COMPARISON STUDIES

In 1989, the CAL participated in interlaboratory performance studies conducted by the U. S. Environmental Protection Agency (USEPA), the Norwegian Institute for Air Research, and the Canada National Water Research Institute. The analytical data for the samples analyzed are presented in the tables in Appendix D.

1. U.S. Environmental Protection Agency

The U. S. Environmental Protection Agency in Research Triangle Park, North Carolina contracted NSI Technology Services Corporation to administer their semiannual Acid Rain Audit in 1989. The CAL participated in the studies performed in June and November. The method of performance assessment was changed from previous USEPA studies. The number of reported values within each percent difference category was corrected or normalized to 100 and presented within increments of 5%, instead of listing the average percent difference and standard deviation as in past studies. The number of participating laboratories is not included in the report.

The results of the analysis of the ten major chemical and physical parameters routinely measured by the CAL are listed in Tables D-1 and D-2. The mean percent difference for the CAL analyses were 4.17% in June and 3.41% in November. These results compare favorably with past performances.

2. Norwegian Institute for Air Research

The eleventh 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 August 1989. The final data analysis was completed early in 1990 and is available in report form (11). This report has the same format as previous editions and uses Youden plots to compare two solutions of similar concentrations in graphic

form. All of the CAL values were well within the 10% of the mean circle. The sulfate bias exhibited in the 1988 intercomparison study has diminished. The numerical results comparing the CAL values to the EMEP expected values can be found on Table D-3.

3. National Water Research Institute Canada

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 1989, the CAL participated in Studies L-20 (12), L-21(13), and L-22(14). These studies traditionally have 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 three studies were rated satisfactory, there were no biases and only one flag, the pH for #5 of L-22. The summary of the CAL performance for 1989 continues to be "Satisfactory, well done". The comparison of CAL reported values to the median values for all laboratories participating are found on Tables D-4, D-5, and D-6.

An interlaboratory methods comparison study which provided QA support to the Eulerian Model Evaluation Field Study and began in June 1988 was conducted under the supervision of the Environment Canada-National Water Research Institute. The CAL was asked to participate as a referee laboratory based on past performance appraisals and participated as one of the eight laboratories involved until the spring of 1989. The studies were monthly with a 20 day data turnaround time. The CAL was involved for twelve studies, which included the LRTAP Study L-20 cited in the previous paragraph.

VII. SUMMARY

This Quality Assurance Report summarizes the various aspects of the quality control program that were in place at the CAL during 1989. In order to validate the final data it is necessary to document several aspects of the chemical analysis of precipitation samples. As the samples progress through the laboratory, every effort is made to produce valid measurements.

The accuracy of standards and instrument performance was constantly monitored with independent reference solutions. These results, used to produce monthly control charts, exhibited acceptable bias and precision. Further evaluation of bias and precision was calculated using the data from the internal blind audit program. The filtered blind samples had elevated amounts of sodium and calcium. The sulfate bias seen in past years decreased in 1989. The precision values obtained from the internal replicate sample program closely approximated those of the internal blind samples. The contributions from external contamination were evaluated with an extensive weekly blank program that was expanded during 1989. The deionized water from three different laboratory sources continued to be of excellent quality. Sodium near the MDL to five times the MDL was still present in the filter blanks, whether the leachate was deionized water or pH 4.3 QCS. Calcium at detection-limit levels was found in the pH 4.3 QCS filtrates. Inverted bucket blanks exhibited increased levels of sodium, and calcium. Sulfate was also been found when the pH 4.3 QCS was used. The pH values of the inverted solutions were elevated while the conductance of the pH 4.3 solution was correspondingly lowered.

The reanalysis program was the same in 1989 as in 1988 and 1987. Approximately seven percent of the samples analyzed were reanalyzed and less than 1 percent of the samples required changes to their initial chemical analysis. The ion percent difference and conductance percent difference histograms were similar to past years.

The USGS interlaboratory comparison audit indicated that there were no significant differences in the participating laboratories and that the CAL had the least number of analyses significantly different from the NIST certified values. The results of the bucket/bottle blind audit indicated that a bucket bias existed for all the analyte concentrations except ammonium.

Participation in interlaboratory comparison studies conducted by the USEPA, Norwegian Institute for Air Research, and the Canada National Water Research Institute produced very favorable comparisons for the CAL.

APPENDIX A

Flow Injection Analysis Method Validation

August 1, 1989

(accepted as evidence of SFA-FIA equivalency
by the NADP Network Operations Subcommittee
October 1989)

Flow Injection Analysis Method Validation Study

With advances in technology come advances in laboratory instrumentation. On August 1, 1989, beginning with sample NH6701, ammonium determinations for NADP/NTN samples were transferred from segmented flow analysis (SFA) to flow injection analysis (FIA). The reagent chemistry remained the same. In order to update the equipment, the NADP Network Operations Subcommittee required that a method validation study be performed so that it might be determined that the new equipment was comparable to the automated wet-chemical analyzer that had been in use since the start of the network.

The study investigated the analytical range, precision, bias, detection limit, and sample carryover effects. To compare FIA with SFA, two sets of natural samples were analyzed using the two methods. The first set was run on March 1, 1989, using SFA and on March 2, 1989, using FIA. The second set was analyzed by SFA on June 6, 1989, and by FIA on June 7, 1989. The same analyst performed both sets of tests.

The range of samples reflected the range of concentrations seen throughout the NADP/NTN network (6). The percentiles are listed in Table A-1. The samples chosen included the normal range, as shown in Table A-2 and Figure A-1.

Table A-3 lists the differences between the two sets of instruments. Improved efficiency of the sample analysis and data collection and reduction is the obvious advantage of the FIA.

A set of six standards is used to calibrate the FIA instrument. The calibration is accepted only if the correlation coefficient is greater than or equal to 0.999. The standards consist of a deionized water blank and solutions of ammonium concentrations of 0.07, 0.20, 0.50, 1.0, and 2.0 mg/L. On the dates that the paired samples were analyzed the FIA calibration curve had correlation coefficients of 0.9997, 0.99979, and 0.99931.

In order to compare precision, USEPA reference solutions, at two concentration levels, were analyzed as they are during a routine daily sample run. The FIA data were collected on nine dates from February 15, 1989 to June 6, 1989. The SFA precision was quantified using the QCS data used to generate control charts to that date in 1989. The results are presented in Table A-4.

A one-tailed F test was used to test the variances, the null hypothesis being that the two variances are equal (15).

TABLE A-1 Comparison of 8FA and 1988 Precipitation Percentile Ammonium Concentrations (mg/L).

Percentile	1988	SFA
Minimum	<0.02	<0.02
5th	<0.02	<0.02
10th	<0.02	<0.02
25th	<0.02	0.03
50th	0.10	0.15
75th	0.31	0.25
90th	0.59	0.54
95th	0.85	0.70
99th	1.72	1.67
Maximum	5.71	1.80
Number of Samples	6386	211

TABLE A-2 Frequency Distribution of Ammonium Concentration in SFA Samples.

Concentration Range (mg/L)	Number of Samples
<0.02	42
0.02 - 0.05	21
0.06 - 0.10	26
0.11 - 0.15	23
0.16 - 0.20	22
0.21 - 0.25	25
0.26 - 0.30	10
0.31 - 0.40	9
0.41 - 0.50	8
0.51 - 0.60	10
0.61 - 0.80	7
0.81 - 1.00	5
> 1.00	3

TABLE A-3 Comparison of 8FA and FIA Instrumentation.

Subject	SFA	FIA
Concentration Range	0.02 - 1.00 mg/L	0.02 - 2.00 mg/L
Method Detection Limit	0.02 mg/L	0.02 mg/L
Sample Cycle Time	130 seconds	54 seconds
Sample Volume	0.21 mL	3.00 mL
Start-up Time	1 hour	1 hour
Data Collection/ Reduction	Limited	Sophisticated
Total Number of Analyses/Day	~150	~400

TABLE A-4 Single Operator Bias and Precision for Ammonium Determined from EPA Reference Solutions.

Concentration (mg/L)		n	Bias		Precision	
Theoretical	Measured*		mg/L*	%	mg/L*	%
Segmented Flow Analysis (1/5/89 to 5/31/89)						
0.1275	0.1297	115	0.0022	1.7	0.0113	8.7
0.6376	0.6417	99	0.0041	0.6	0.0203	3.2
Flow Injection Analysis (2/15/89 to 6/6/89)						
0.1275	0.1263	27	-0.0012	-0.9	0.0131	10.3
0.6376	0.6438	21	0.0062	1.0	0.0186	2.9

* = Nonsignificant digits included for calculations.

Case 1 involved USEPA Standard WP4/86 with a dilution factor of 20 resulting in a theoretical mean concentration of 0.1275 mg/L NH₄. The number(n) of samples for the SFA was 115, and for the FIA it was 27. The standard deviation (s) for the SFA was 0.011274, and for the FIA it was 0.013052. Using the equation,

$$F = \frac{s_{FIA}^2}{s_{SFA}^2} = \frac{(0.013052)^2}{(0.011274)^2} = 1.340.$$

The criteria for rejection of the null hypothesis requires rejection if $F > 1.59$. It is not, so the variances are comparable at 0.1275 mg/L NH₄.

Case 2 uses the same equation to test USEPA Standard WP4/86 diluted by 4, resulting in a concentration of 0.6376 mg/L NH₄. There were 99 SFA samples and 21 FIA samples. The respective standard deviations were 0.020303 and 0.018567. Using the equation above, F equals 1.196, and the variances are judged to be comparable since F is less than 1.91, the rejection criteria.

Since the variance of FIA cannot be proven to be greater than the variance of the SFA, they must be assumed to be equal.

The bias of the method was tested using a t-test (16):

$$t = \frac{|x_1 - x_2|}{s_p \sqrt{(1/n_1) + (1/n_2)}}$$

where:

x_1 = mean value of the EPA QCS

x_2 = mean value of the FIA samples

n = the number of samples (EPA = 200)

s_p = the pooled standard deviation

For the USEPA QCS WP 4/86 diluted by 20 with a mean value of 0.1275 mg/L NH₄, the pooled standard deviation (s_p) equals 0.0075. The mean value of the QCS for the FIA for 27 samples equals 0.1263 mg/L NH₄. Using the t-test equation, t equals 0.780, which is smaller than the rejection criterion ($t > 1.971$) for 225 degrees of freedom at the 95% confidence level.

For the same solution diluted by 4, the mean value is 0.6376, and the pooled standard deviation equals 0.0312. The mean FIA value obtained from the analysis of 21 samples was 0.6438 mg/L NH₄. The calculated t at this concentration is 0.866, and the criterion for rejection is $t > 1.971$ for 219 degrees of freedom. Therefore it was concluded that FIA does not demonstrate a significant bias at the low or higher concentrations. Table A-4 lists single-operator bias and precision for both methods of analysis.

Method detection limit was established using a set of standard solutions and following the USEPA guidelines (17). The results were calculated using the low standard with a concentration of 0.07 mg/L NH₄:

Number of analyses = 48
 Mean concentration = 0.068854 mg/L NH₄
 Standard deviation = 0.009931 mg/L NH₄
 RSD = 14.42%

For 47 degrees of freedom, the t value at the 99% confidence level is 2.41.

$$\begin{aligned} \text{MDL} &= t \times s \\ &= 2.41 \times 0.009931 \\ &= 0.02398 \text{ " } 0.02 \text{ mg/L} \end{aligned}$$

The MDL for FIA is the same as the MDL calculated for SFA.

Twenty pairs of samples were run to study carryover effects. A high concentration sample (> 75th percentile) was followed by a low concentration sample (<25th percentile). Both systems produced detection limit values for all of the lower concentration samples.

A paired t test was run to study the difference between the methods (16). The difference in this case was defined as the result of the SFA minus the result of the FIA. The null hypothesis is that there is no difference between the methods. The equation used is:

$$t = \frac{|d|}{s_d / \sqrt{n}}$$

where **d** = the mean difference
n = the number of pairs
s_d = the standard deviation of the difference

Table A-5 shows the results of this calculation. The paired t-test indicates a statistically significant difference between the two methods at the 95% confidence level. The difference is, however, smaller than the uncertainty in the measurements. Figure A-2 plots the difference between SFA and FIA against SFA concentrations, and there is no significant difference.

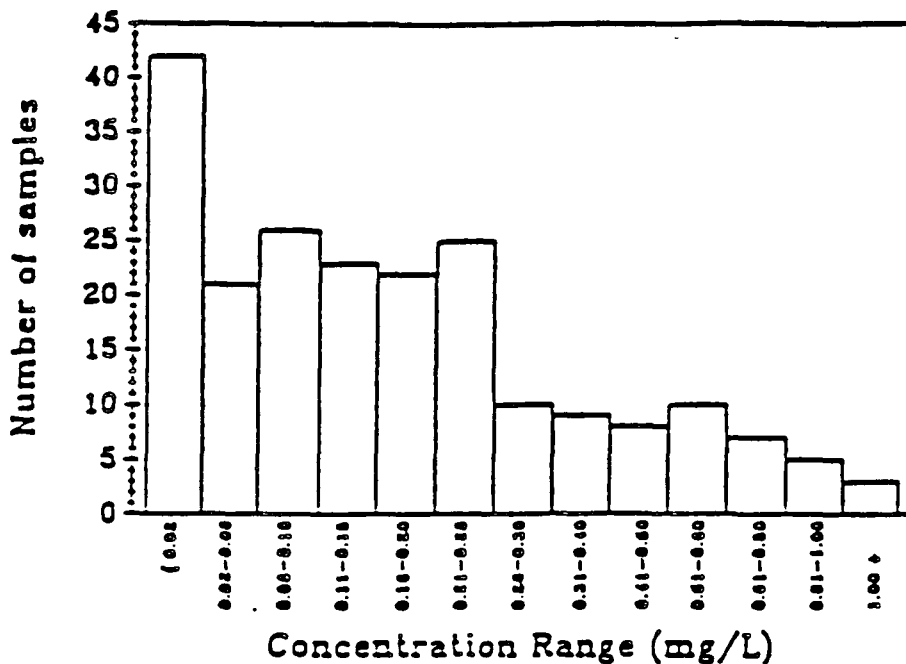


FIGURE A-1. Frequency Distribution of SFA Ammonium Concentrations

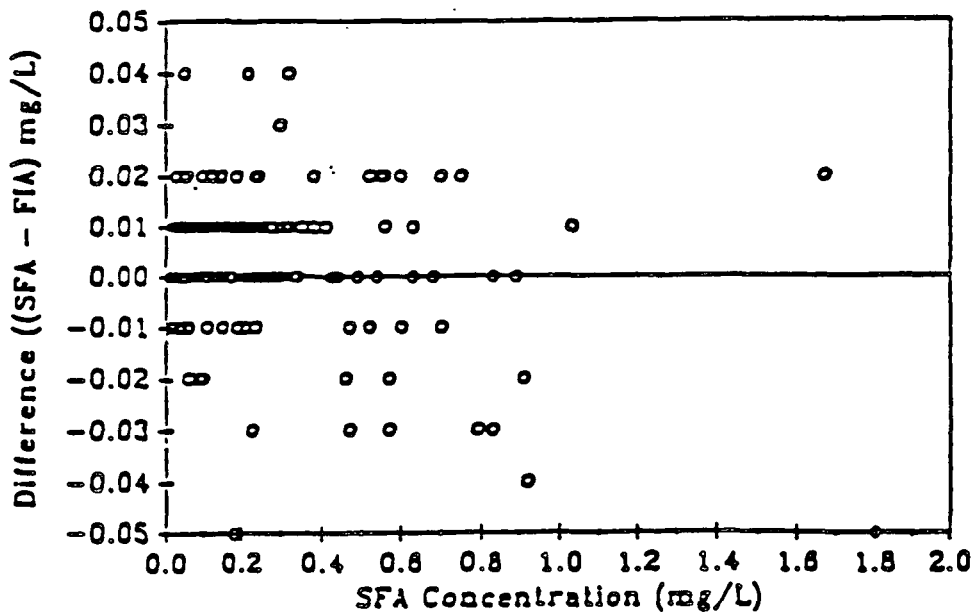


FIGURE A-2. Difference of SFA and FIA as a function of SFA Concentration - All Analyzed Samples Included.

TABLE A-5 Comparison of SPA and FIA results using a Paired t-test.

	n	Average Difference (ng/L)	t	t_{crit}	Reject?
> MDL	164	0.00317	2.928	1.975	Yes
< MDL	47	0.00055	1.891	2.010	No
All samples	211	0.00289	3.323	1.972	Yes

APPENDIX B

GLOSSARY OF TERMS

GLOSSARY OF TERMS

Term	Abbreviation	Definition
Accuracy		The degree of agreement between an observed value and an accepted reference value. 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. In practice, it is expressed as the difference between the value obtained from analysis of a homogenous sample and the accepted true value. Bias = measured value - true value.
Box Plot		A graphical summary representation of the distribution of a set of data, the top and bottom of the box representing the 75th and 25th percentile. The horizontal line represents the median concentration, and the lower and upper Ts extend to the 10th and 90th percentile concentrations.
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 (18).
Critical Concentration		A calculated concentration used to determine if the measured bias is or is not statistically significant (15).

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

where:

$$s_{sp} = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}$$

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 network samples.

Mean

 \bar{x}

The average obtained by dividing a sum by the number of its addends.

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n}$$

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
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	An integrated system of activities involving planning, quality control, reporting, and remedial action to ensure that a product or service meets defined standards of quality.
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 Solution	QCS	A solution containing known concentrations of analytes used by the analysts to verify calibration curves and validate sample data. The values obtained from the analyses of these samples are used for calculation of bias and precision and for the monthly control charts.
Relative Standard Deviation	RSD	The standard deviation expressed as a percentage: $\text{RSD} = 100 \times (s/\bar{x})$ 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.
Standard Deviation	s	The number representing the dispersion of values around their mean. $s = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{n - 1}}$ where: x^1 - each individual value \bar{x} = the mean of all the values n = number of values

**Standard Deviation Estimated
Paired Measurements**

The standard deviation may be estimated from the differences of several sets of paired measurements using the equation (18):

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

where:

d = difference of
duplicate measurements
k - number of sets of
duplicate measurements

APPENDIX C

Weekly Procedures: Figures and Table

1989

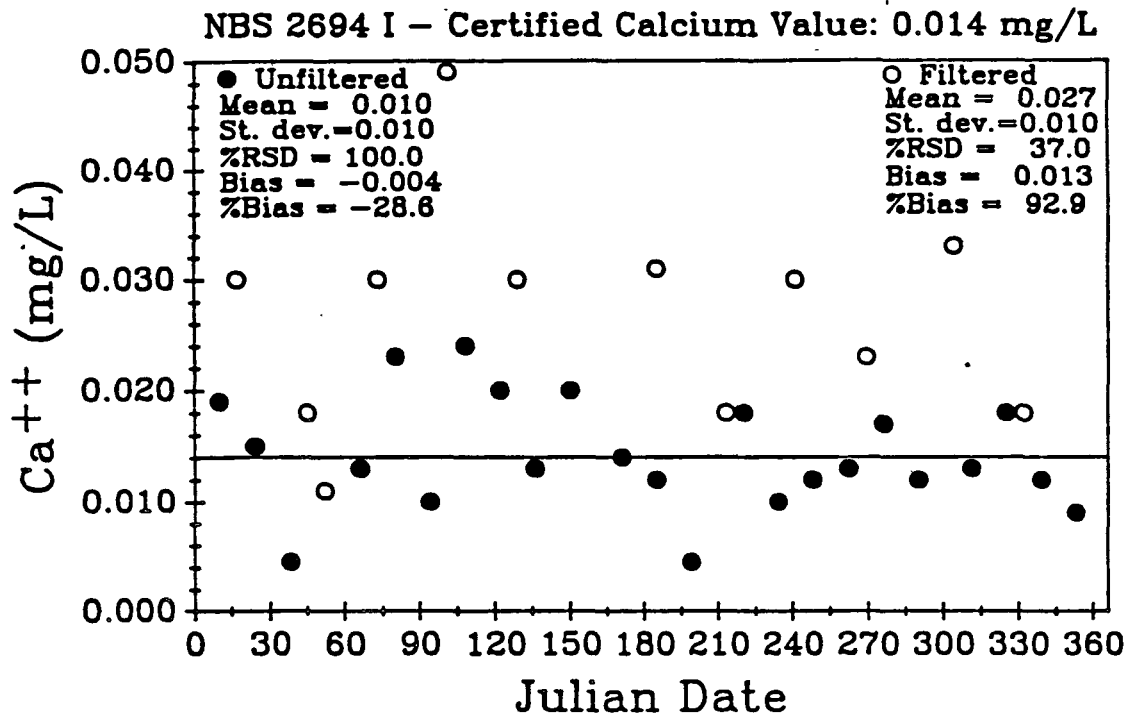


FIGURE C-1. Comparison of filtered and unfiltered internal blind samples (calcium I), 1989.

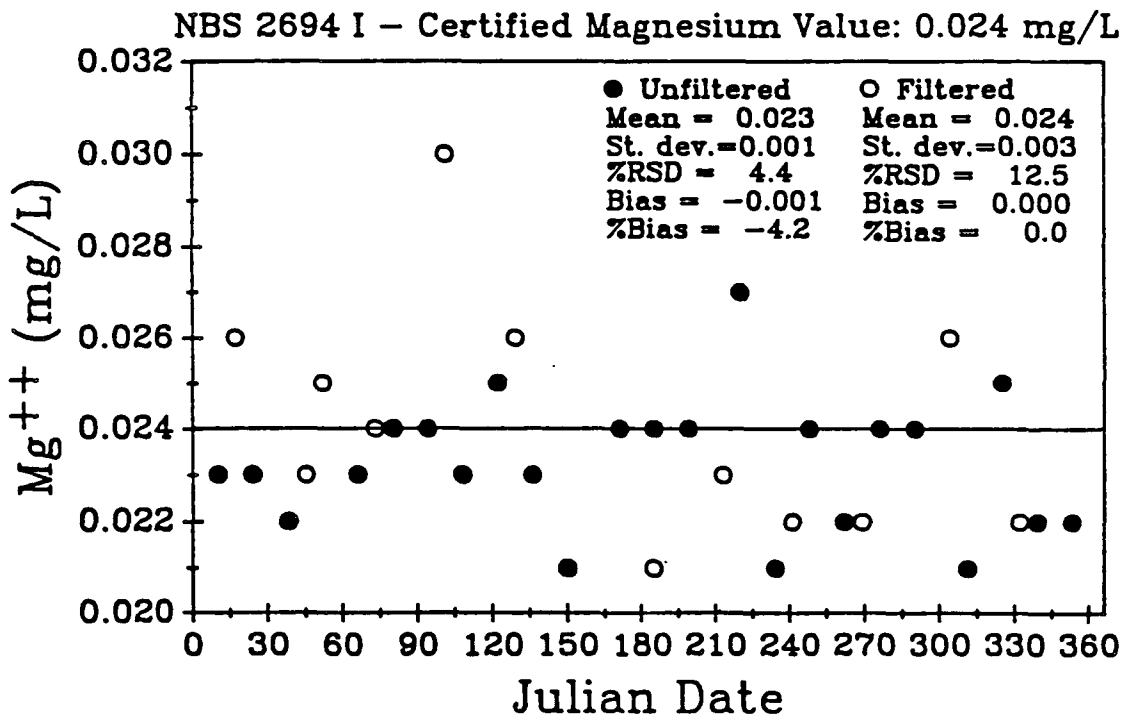


FIGURE C-2. Comparison of filtered and unfiltered internal blind samples (magnesium I), 1989.

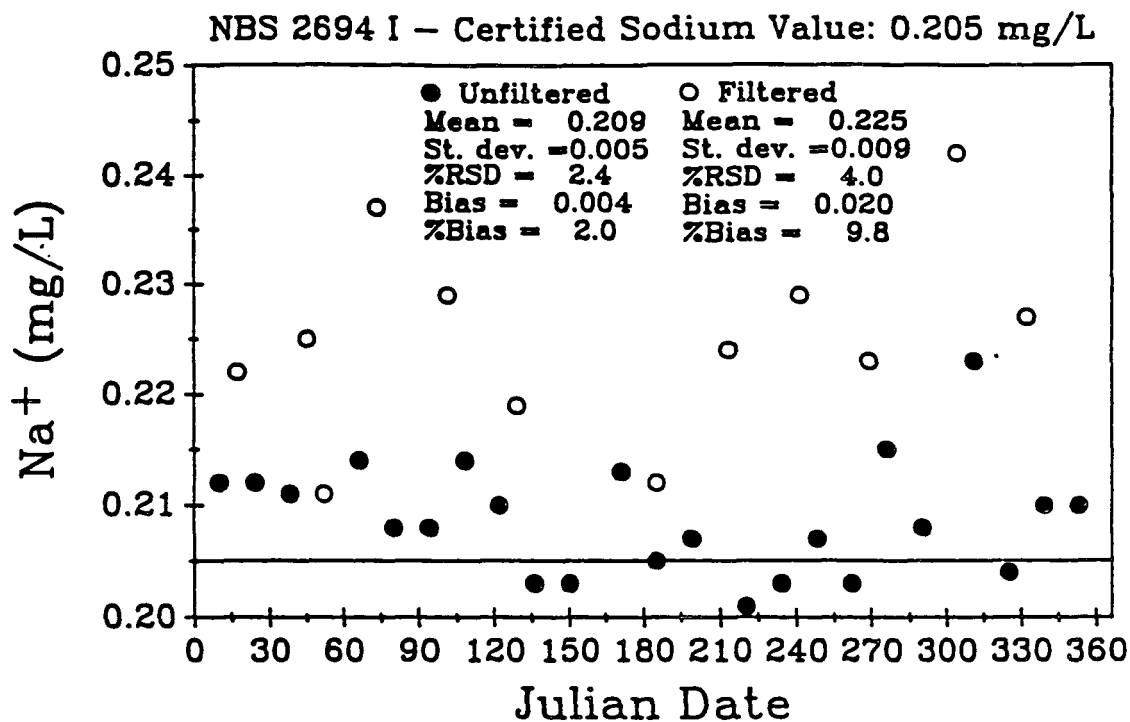


FIGURE C-3. Comparison of filtered and unfiltered internal blind samples (sodium I), 1989.

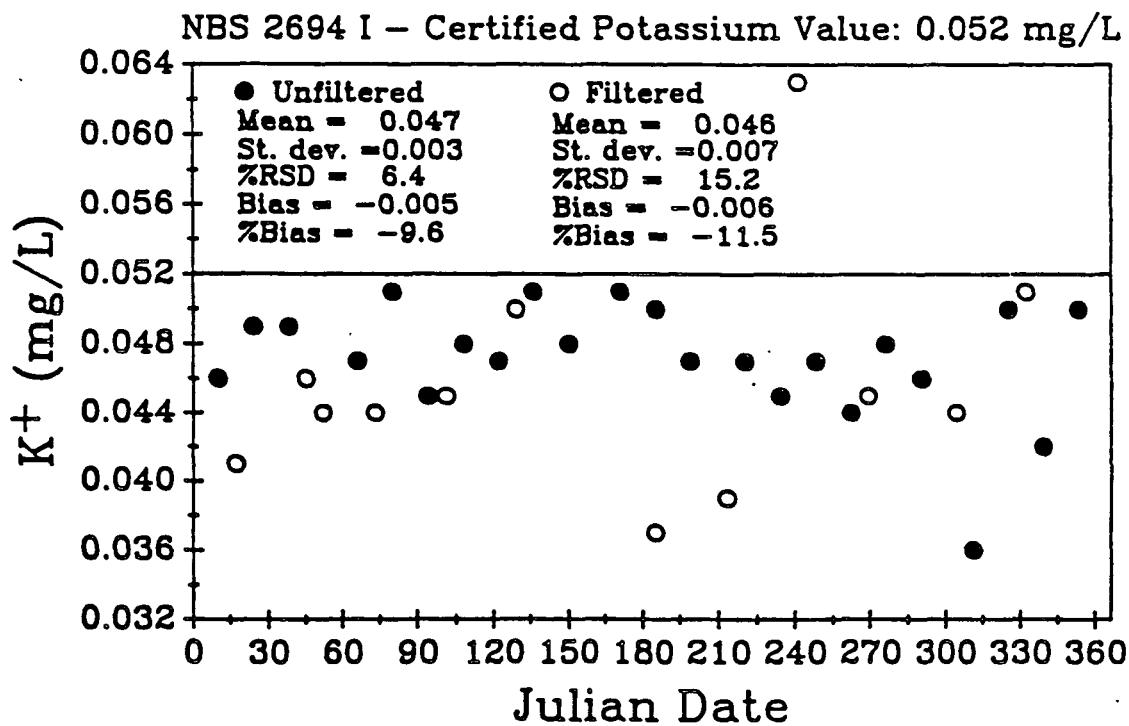


FIGURE C-4. Comparison of filtered and unfiltered internal blind samples (potassium I), 1989.

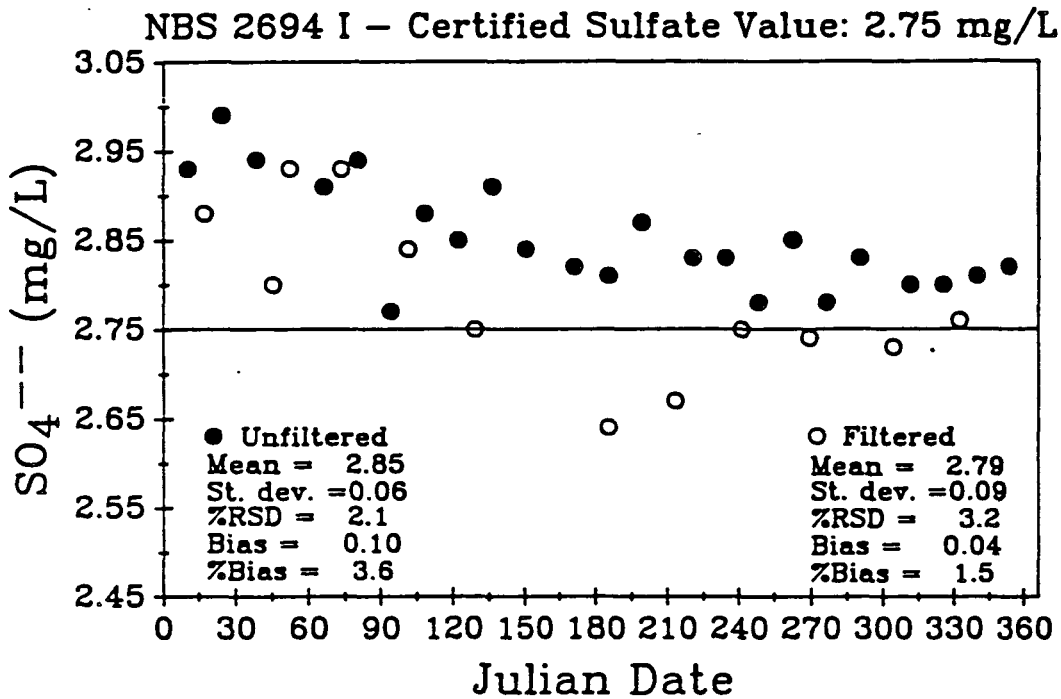


FIGURE C-5. Comparison of filtered and unfiltered internal blind samples (sulfate I), 1989.

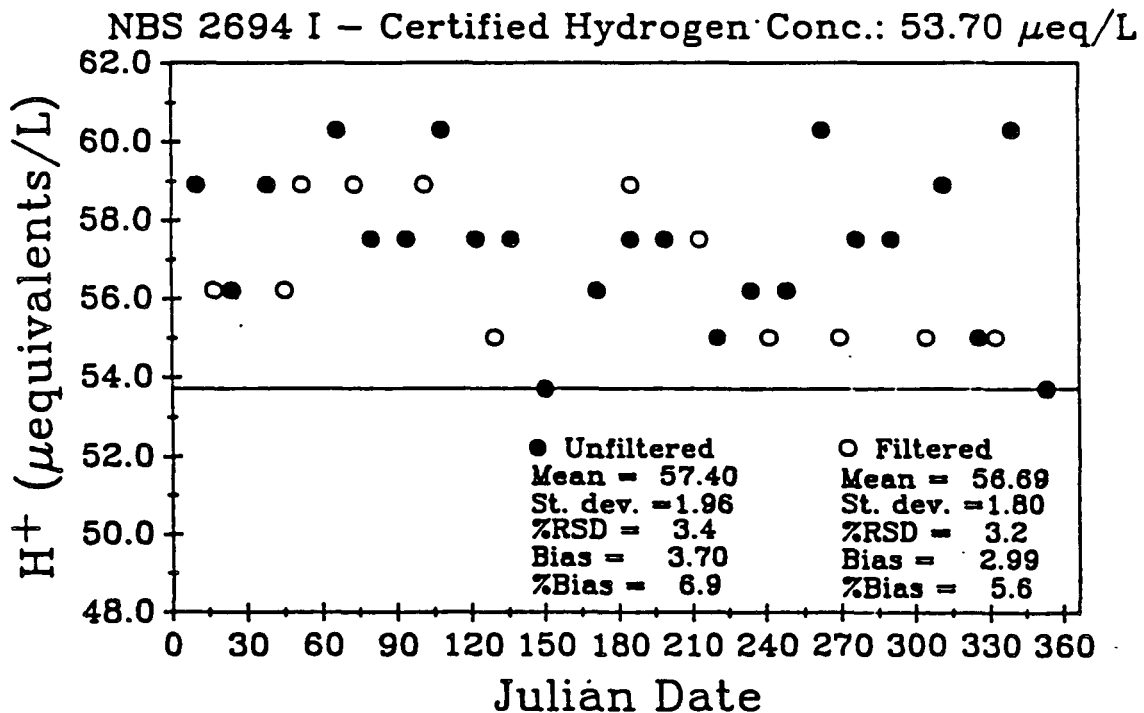


FIGURE C-6. Comparison of filtered and unfiltered internal blind samples (H^+ I), 1989.

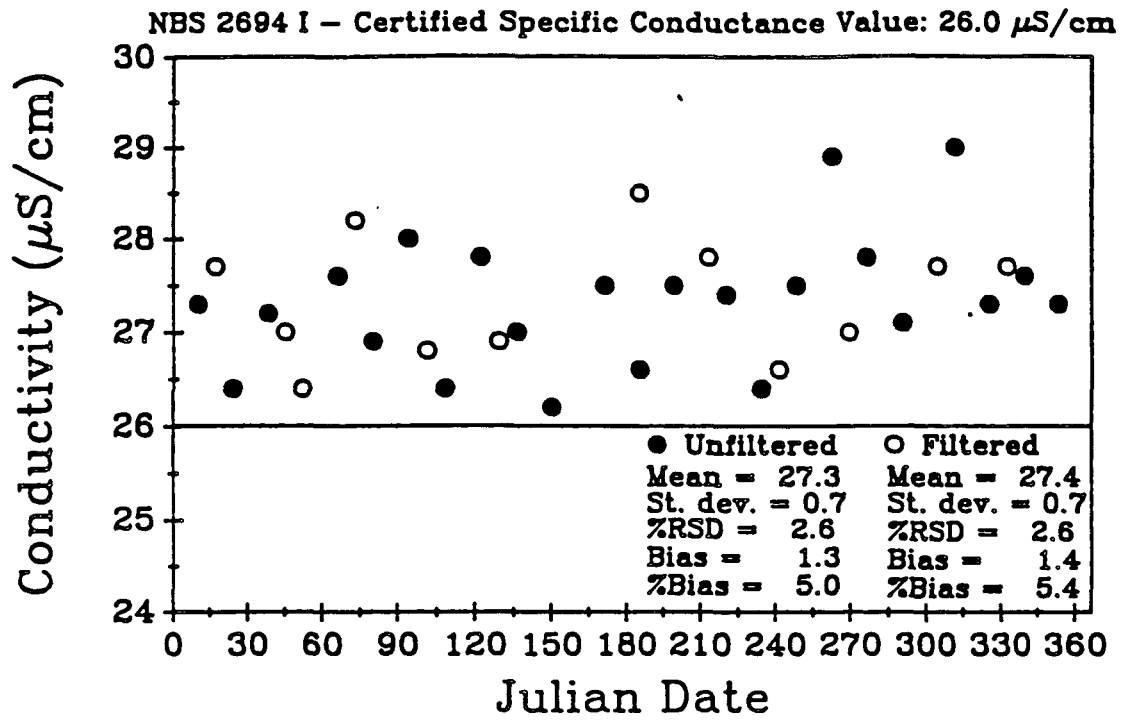


FIGURE C-7. Comparison of filtered and unfiltered internal blind samples (specific conductance I), 1989.

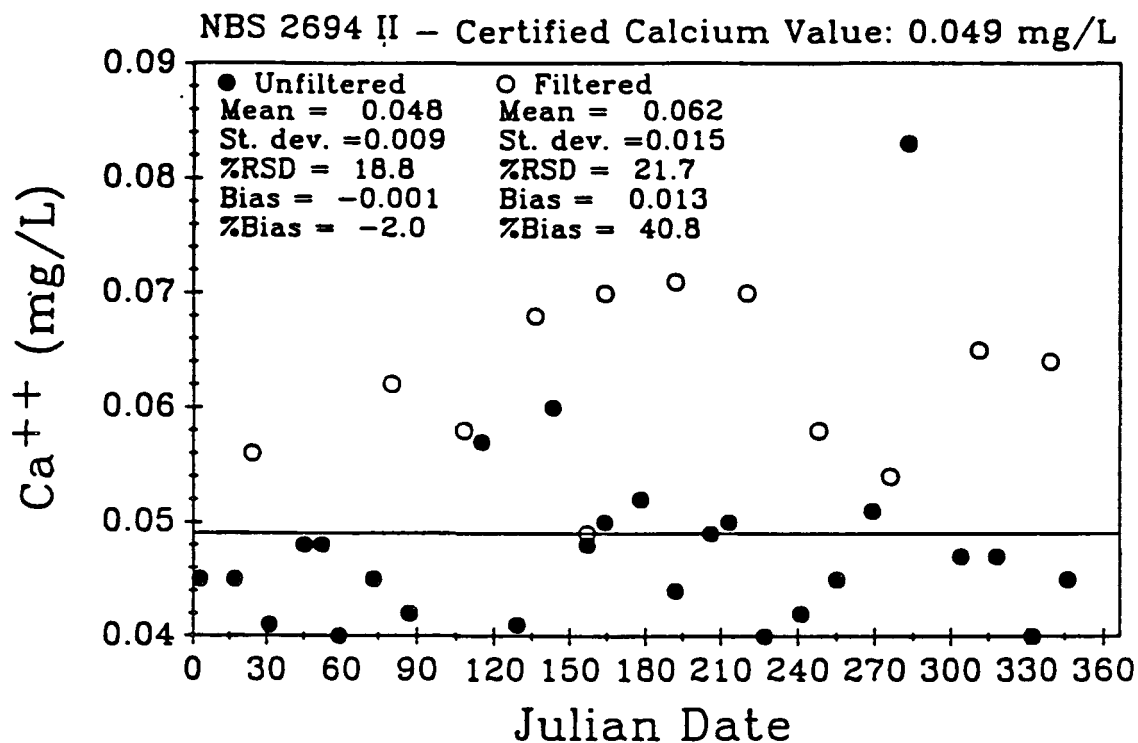


FIGURE C-8. Comparison of filtered and unfiltered internal blind samples (calcium II), 1989.

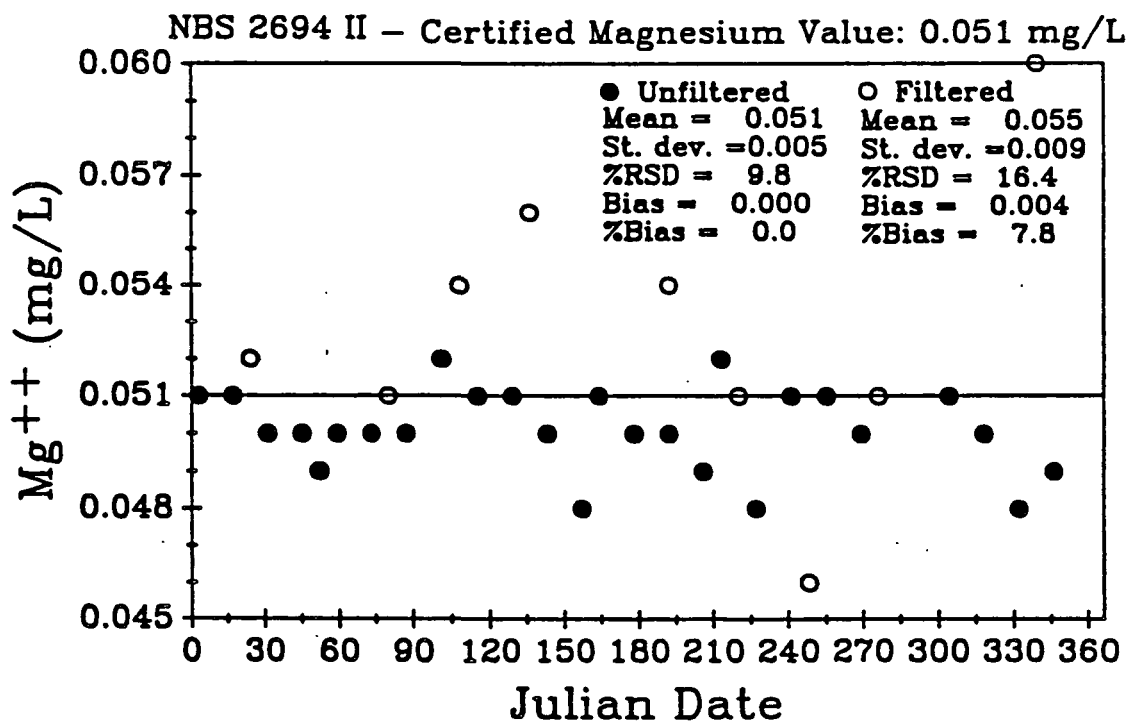


FIGURE C-9. Comparison of filtered and unfiltered internal blind samples (magnesium II), 1989.

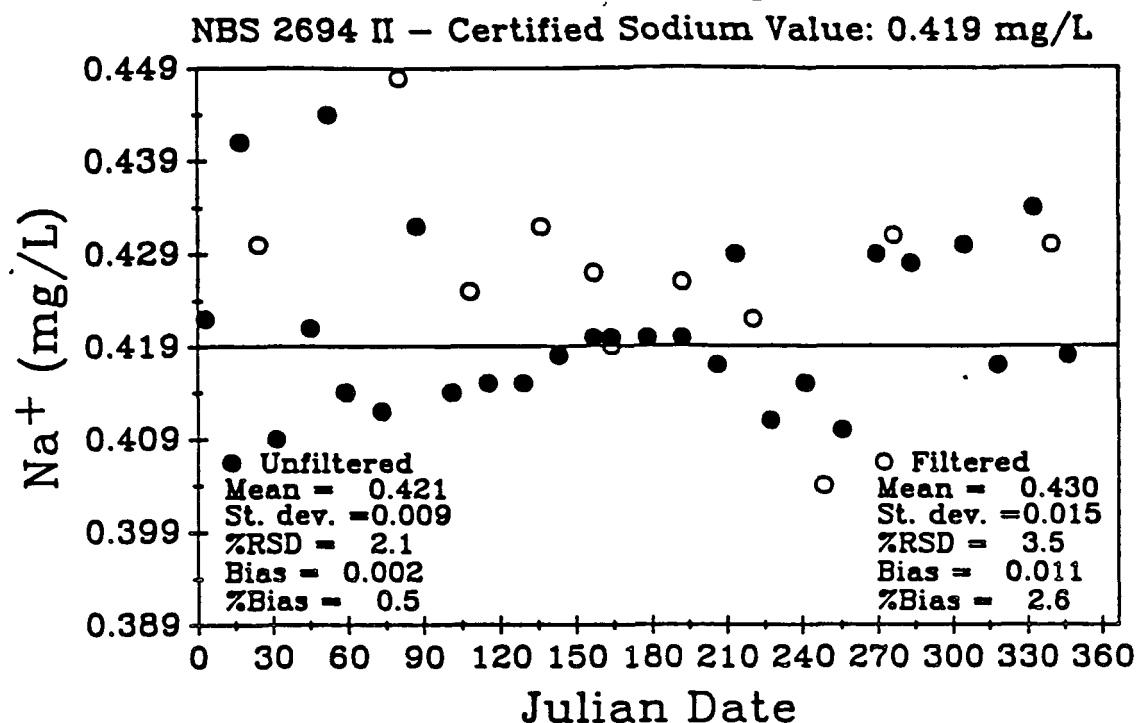


FIGURE C-10. Comparison of filtered and unfiltered internal blind samples (sodium II), 1989.

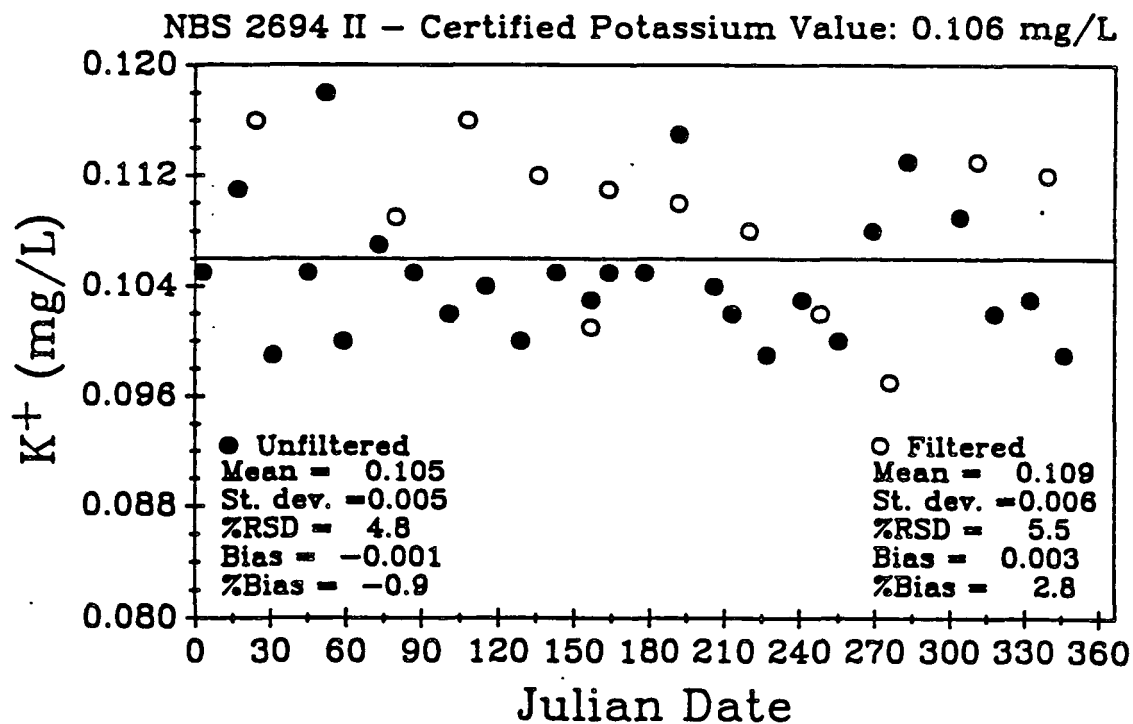


FIGURE C-11. Comparison of filtered and unfiltered internal blind samples (potassium II), 1989.

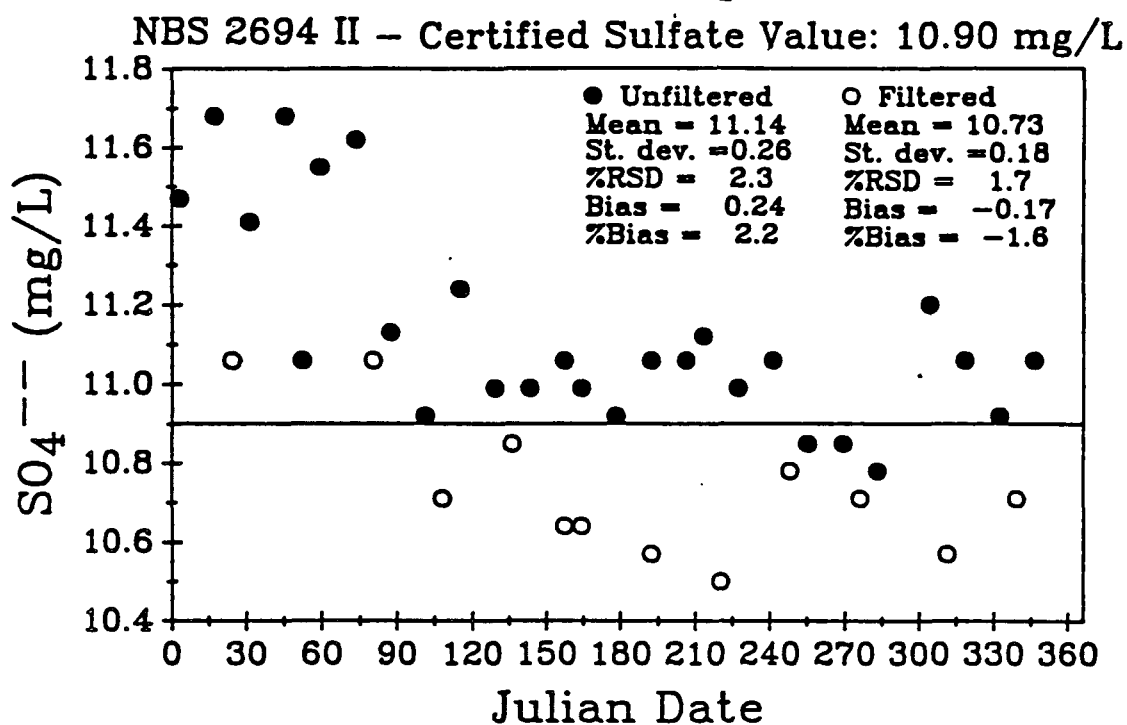


FIGURE C-12. Comparison of filtered and unfiltered internal blind samples (sulfate II), 1989.

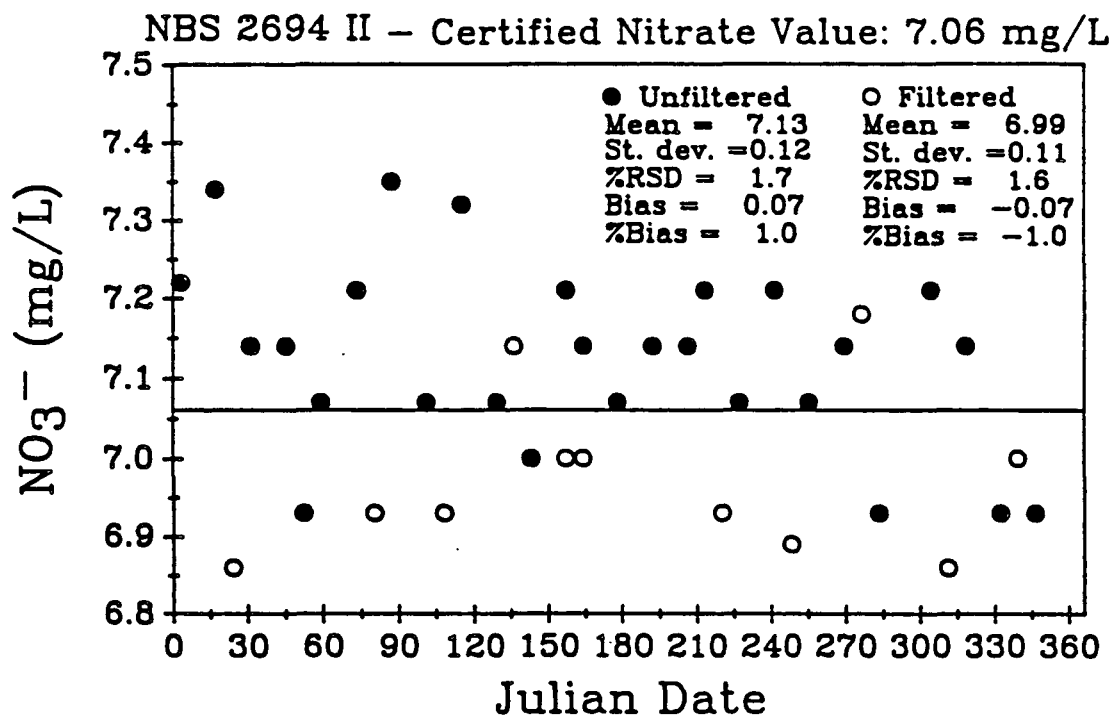


FIGURE C-13. Comparison of filtered and unfiltered internal blind samples (nitrate II), 1989.

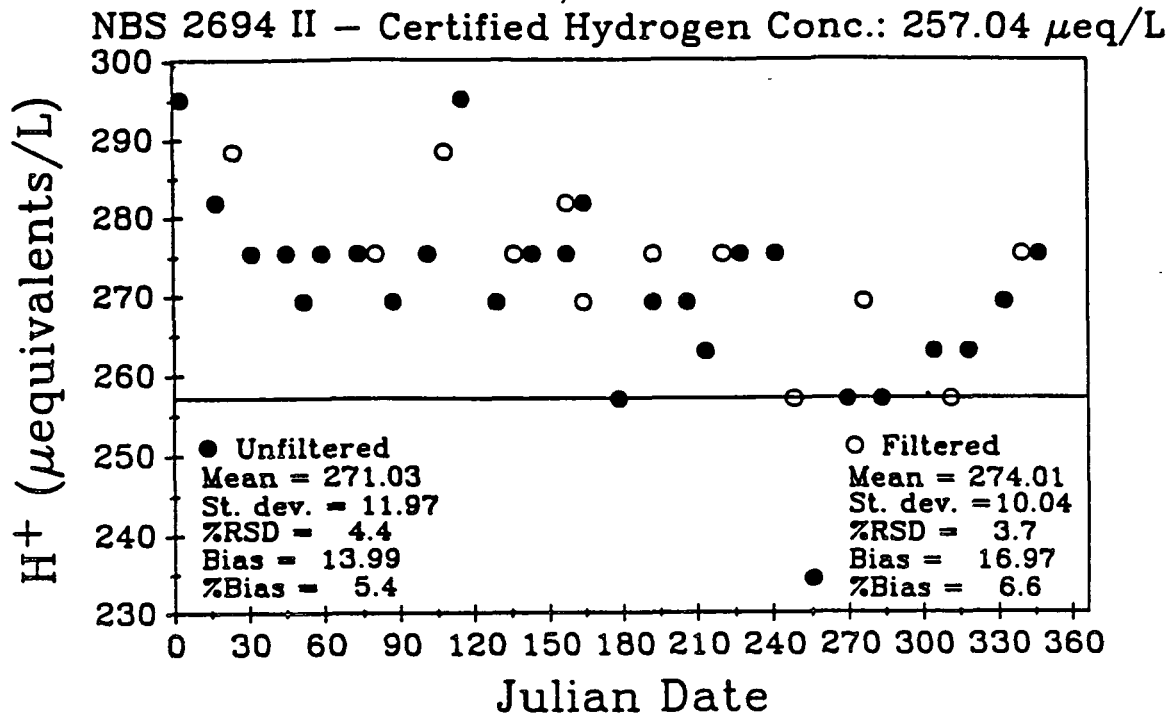


FIGURE C-14. Comparison of filtered and unfiltered internal blind samples (H^+ II), 1989.

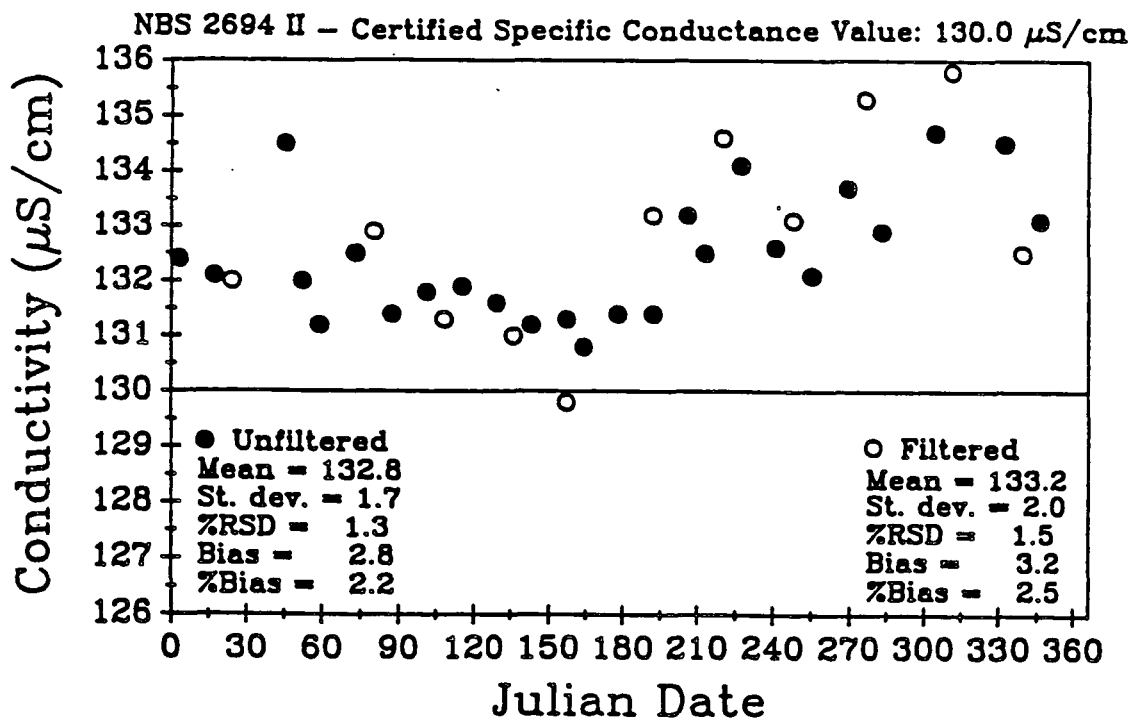


FIGURE C-15. Comparison of filtered and unfiltered internal blind samples (specific conductance II), 1989.

TABLE C-1 50th and 95th Percentile
Concentration Values of Chemical and
Physical Parameters Measured in
Replicate (O/Q) Samples, 1989.

Parameter	Percentile Concentration Values (mg/L)	
	50th	95th
Calcium	0.122	0.204
Magnesium	0.024	0.033
Sodium	0.076	0.107
Potassium	0.017	0.028
Ammonium	0.19	0.32
Sulfate	1.28	2.01
Nitrate	1.12	1.57
Chloride	0.15	0.21
pH (units) (μ equiv/L)	4.87 (3.58)	5.25 (5.62)
Conductivity (μ S/cm)	12.1	19.5

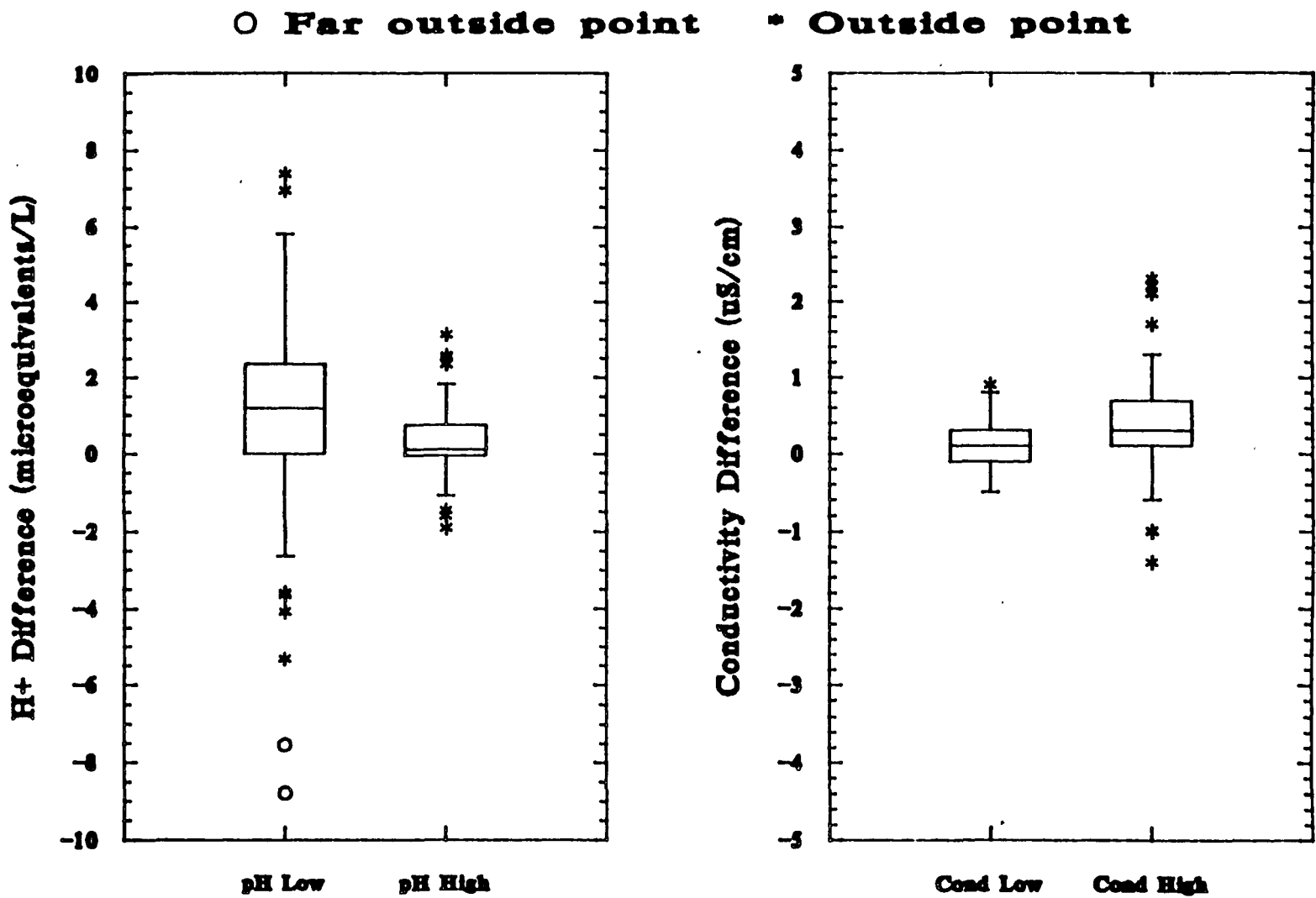


FIGURE C-16. Results of 0/Q replicate analysis, pH and conductivity, 1989.

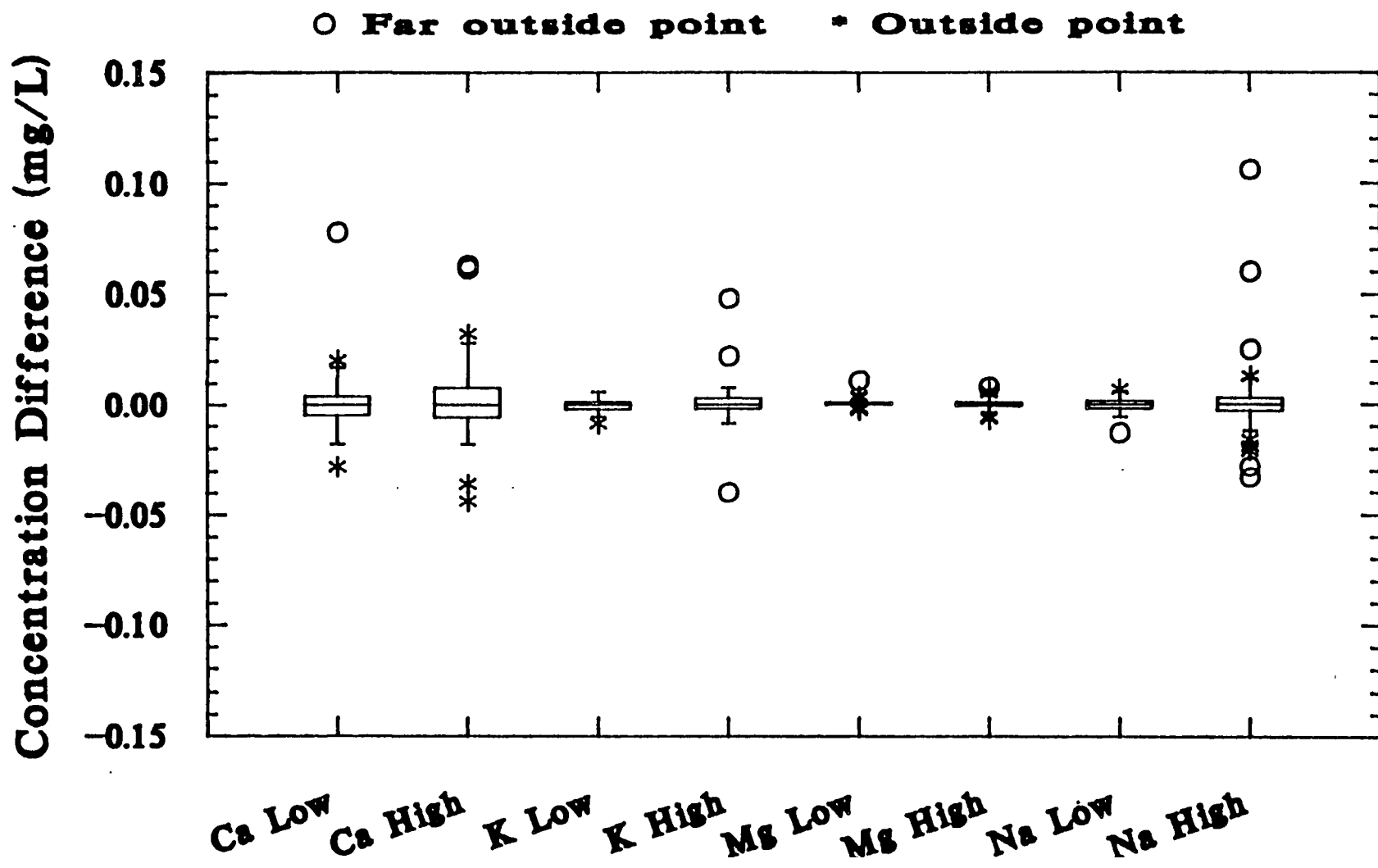


FIGURE C-17. Results of 0/Q replicate analysis, calcium, potassium, magnesium, and sodium, 1989.

Concentration Difference (mg/L)

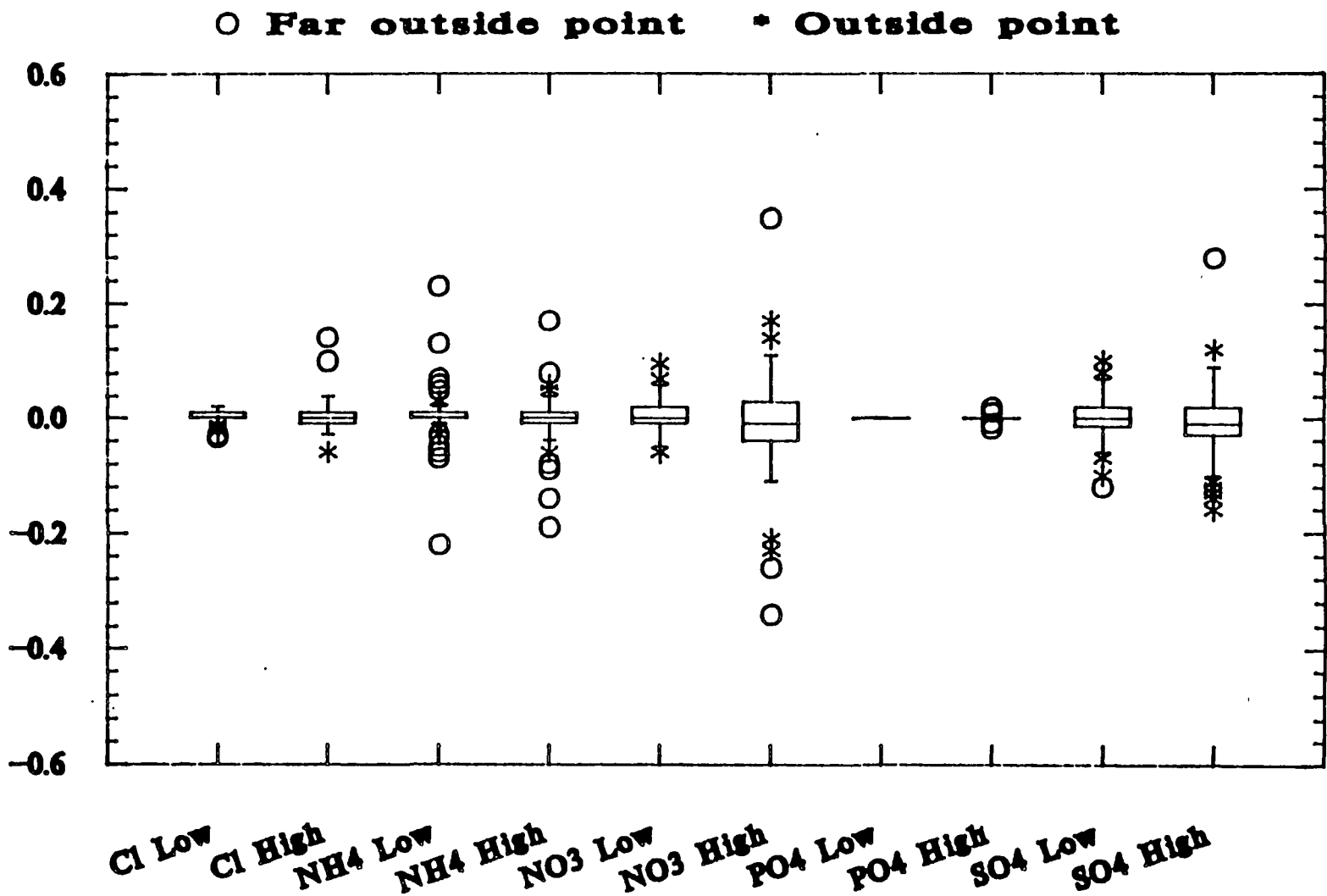


FIGURE C-18. Results of 0/Q replicate analysis, chloride, ammonium, nitrate, phosphate, and sulfate, 1989.

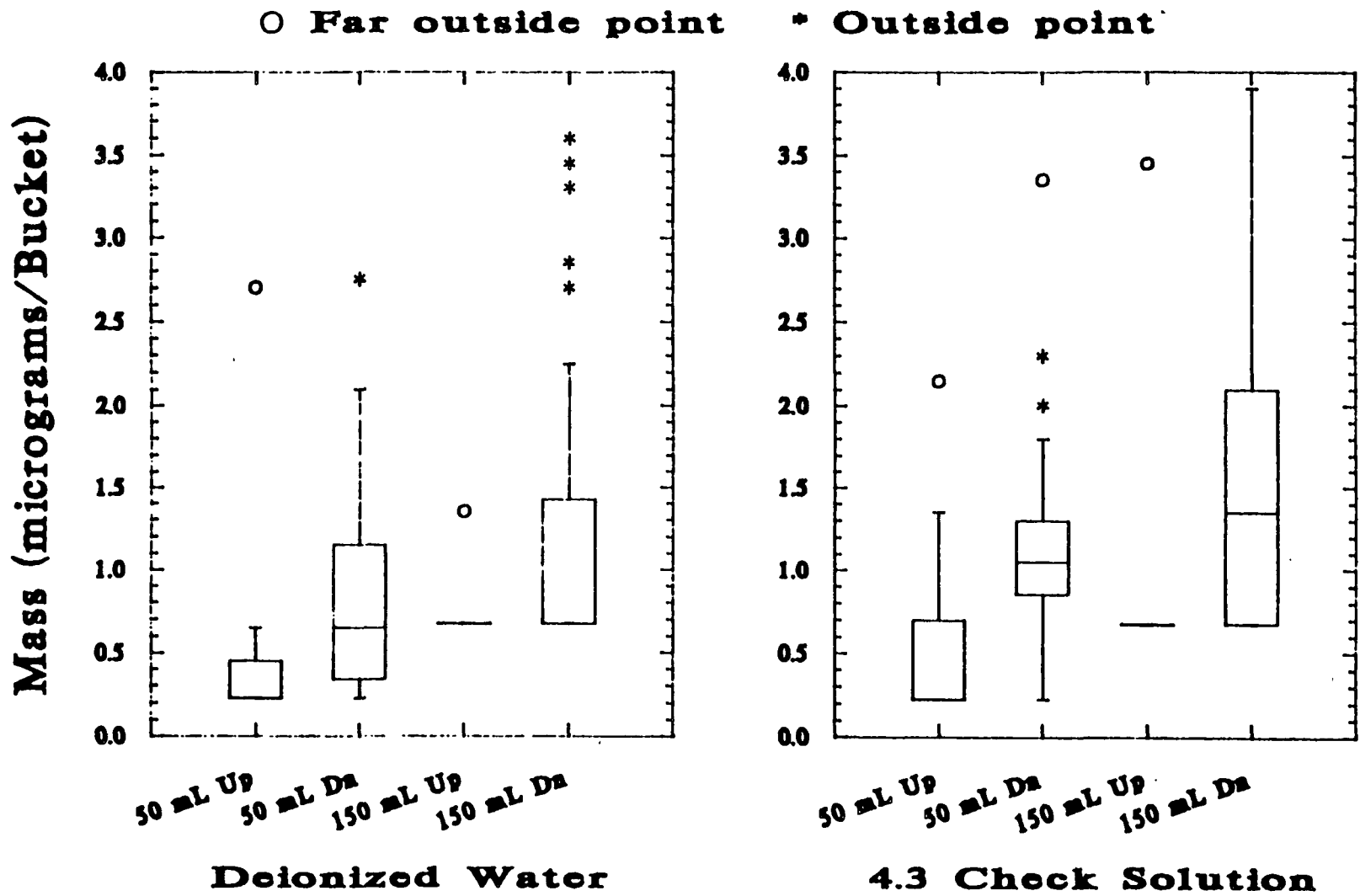


FIGURE C-19. Calcium found in upright (Up) and inverted (Dn) bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1989.

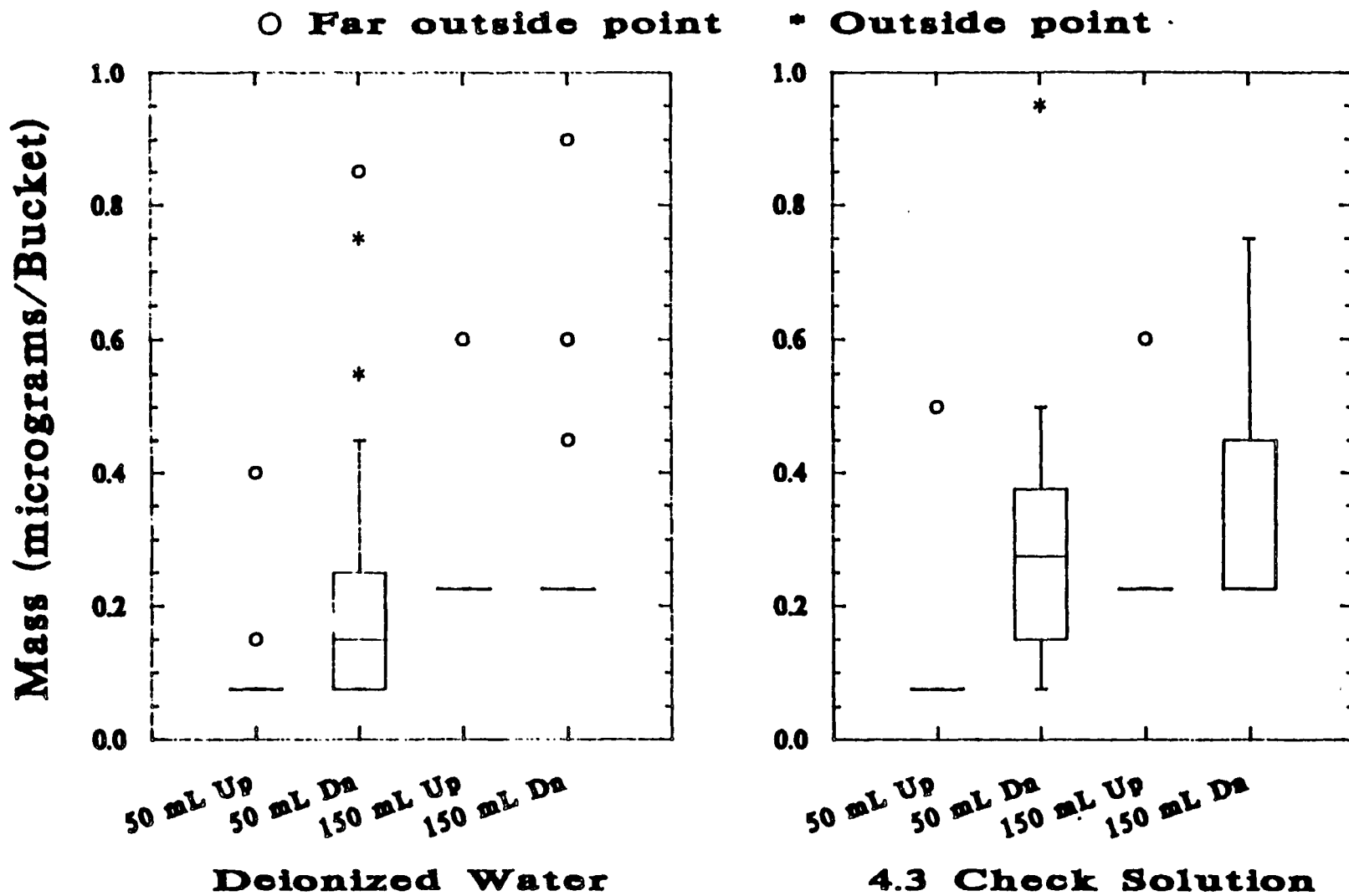


FIGURE C-20. Magnesium found in upright (Up) and inverted (Dn) bucket blanks, using DI water pH 4.3 QCB as leaching agents, 1989.

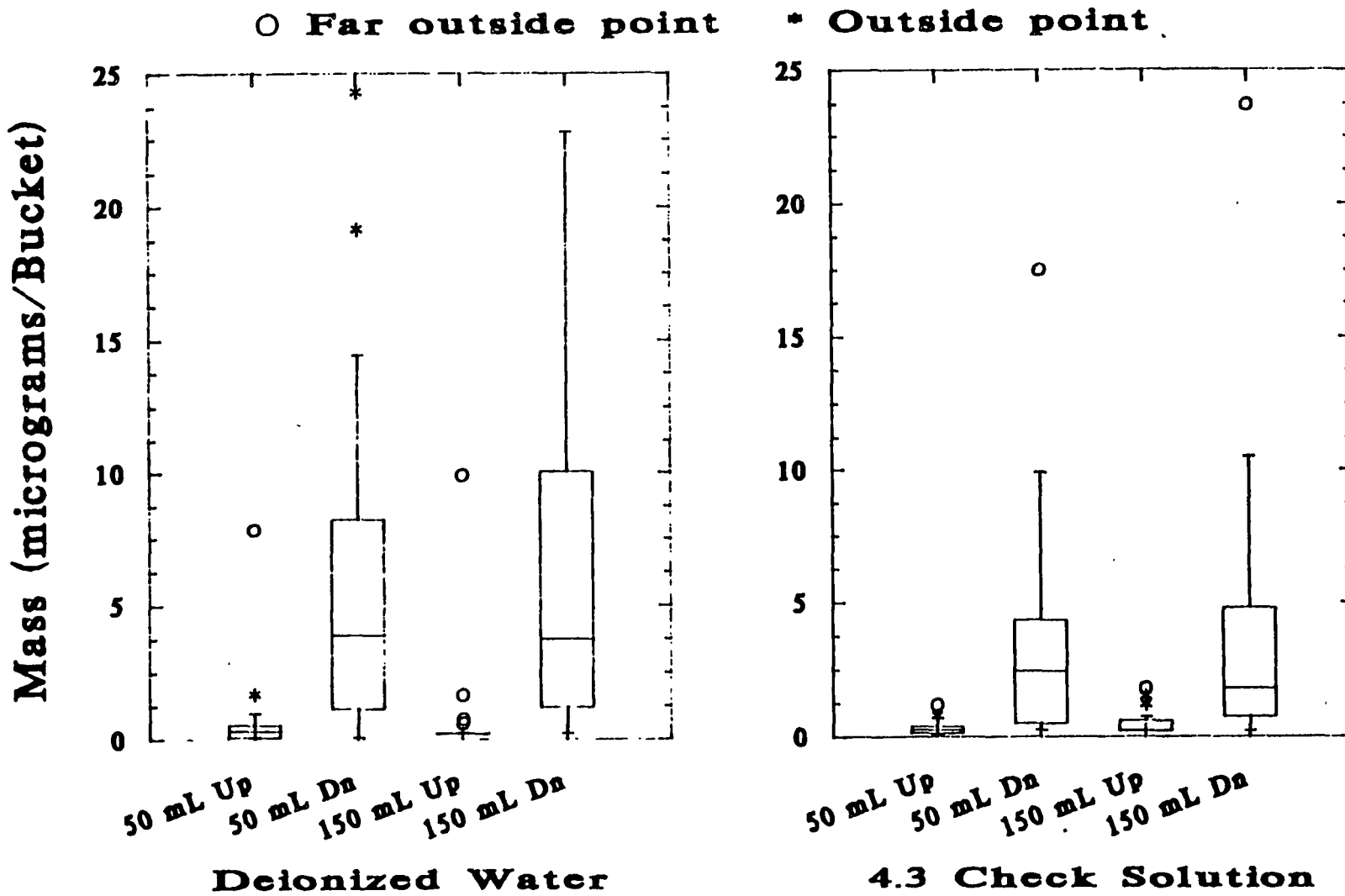
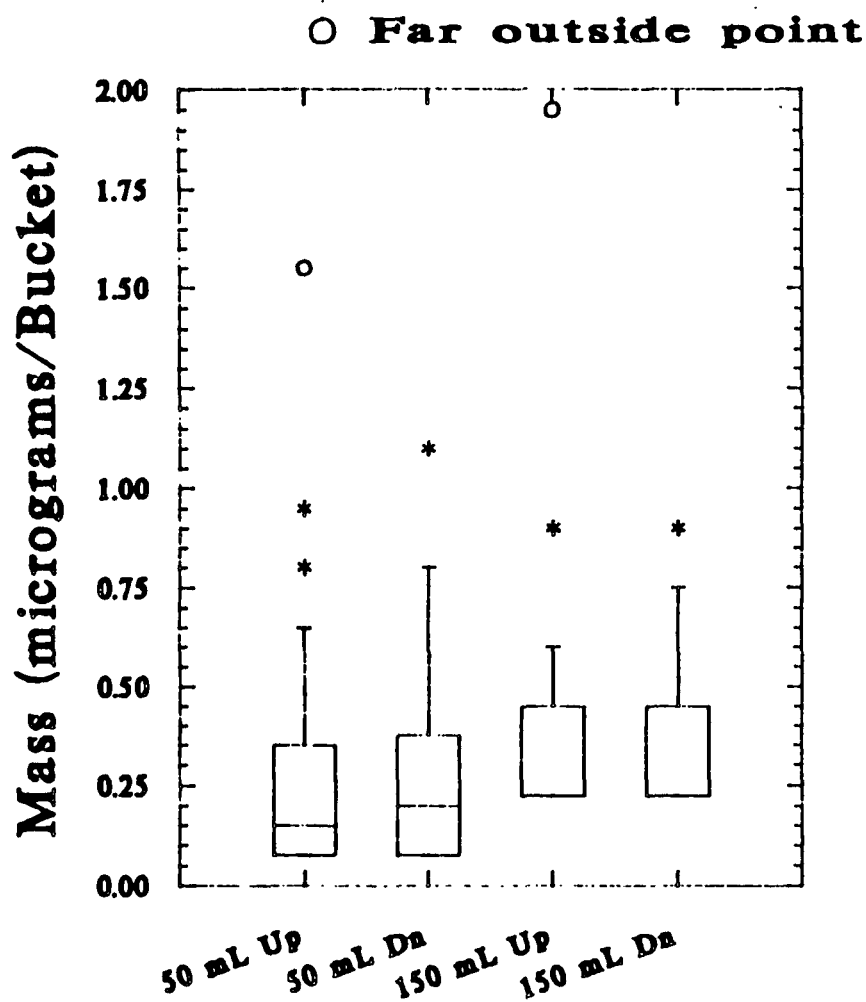
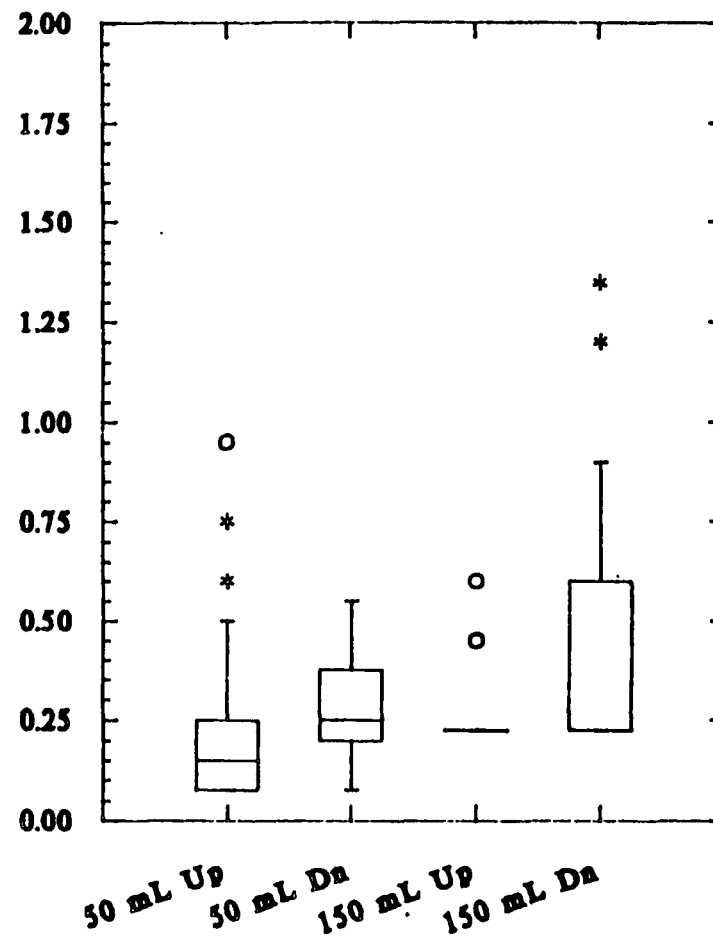


FIGURE C-21. Sodium found in upright (Up) and inverted (Dn) bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1989.



Deionized Water



4.3 Check Solution

FIGURE C-22. Potassium found in upright (Up) and inverted (Dn) bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1989.

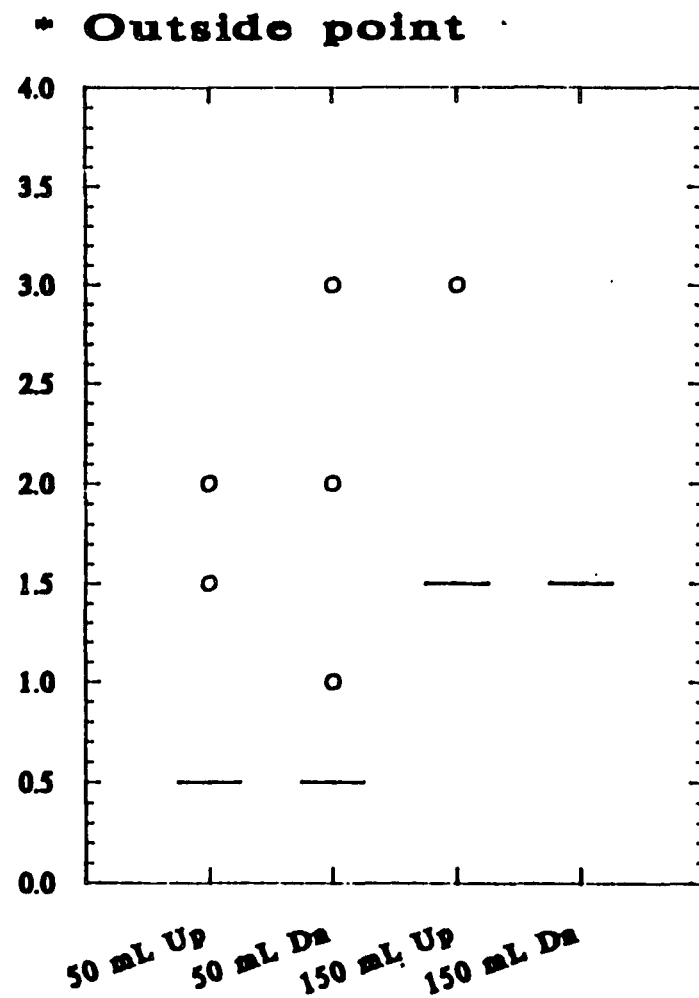
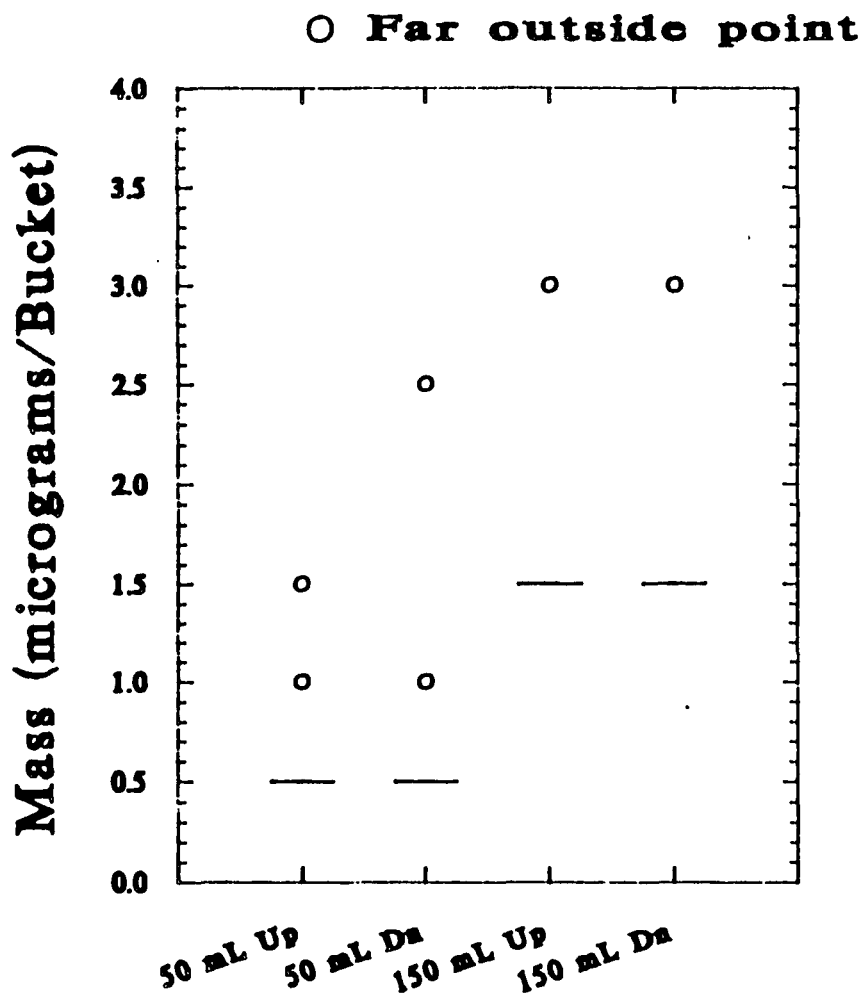


FIGURE C-23. Ammonium found in upright (Up) and inverted (Dn) bucket blanks, using DI water and pH 4.3 QC8 as leaching agents, 1989.

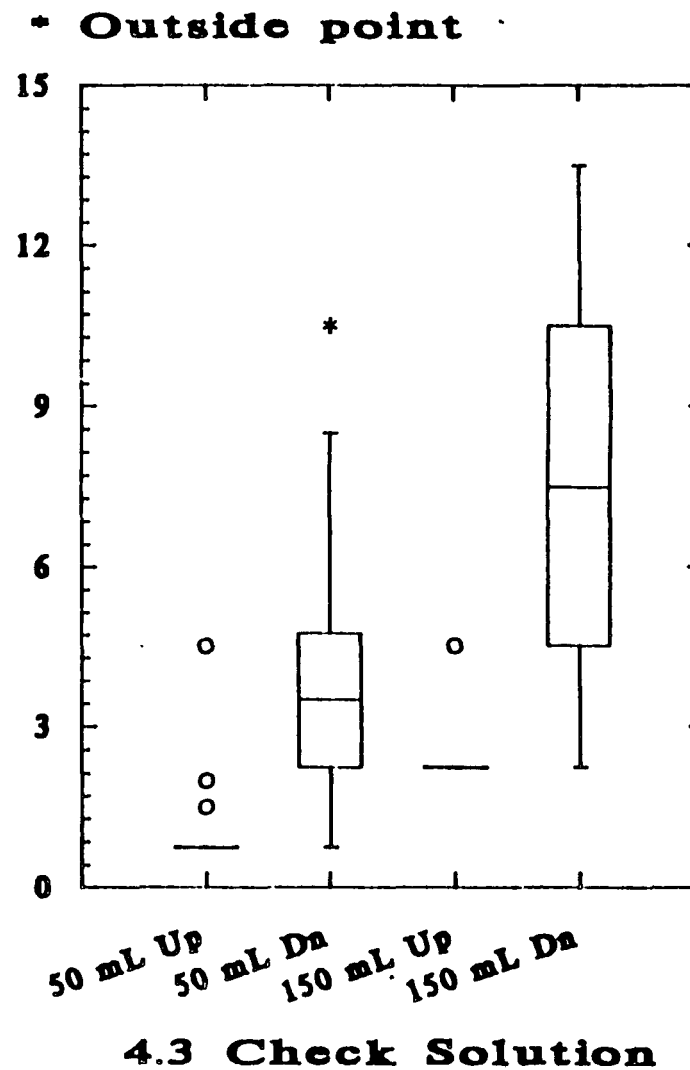
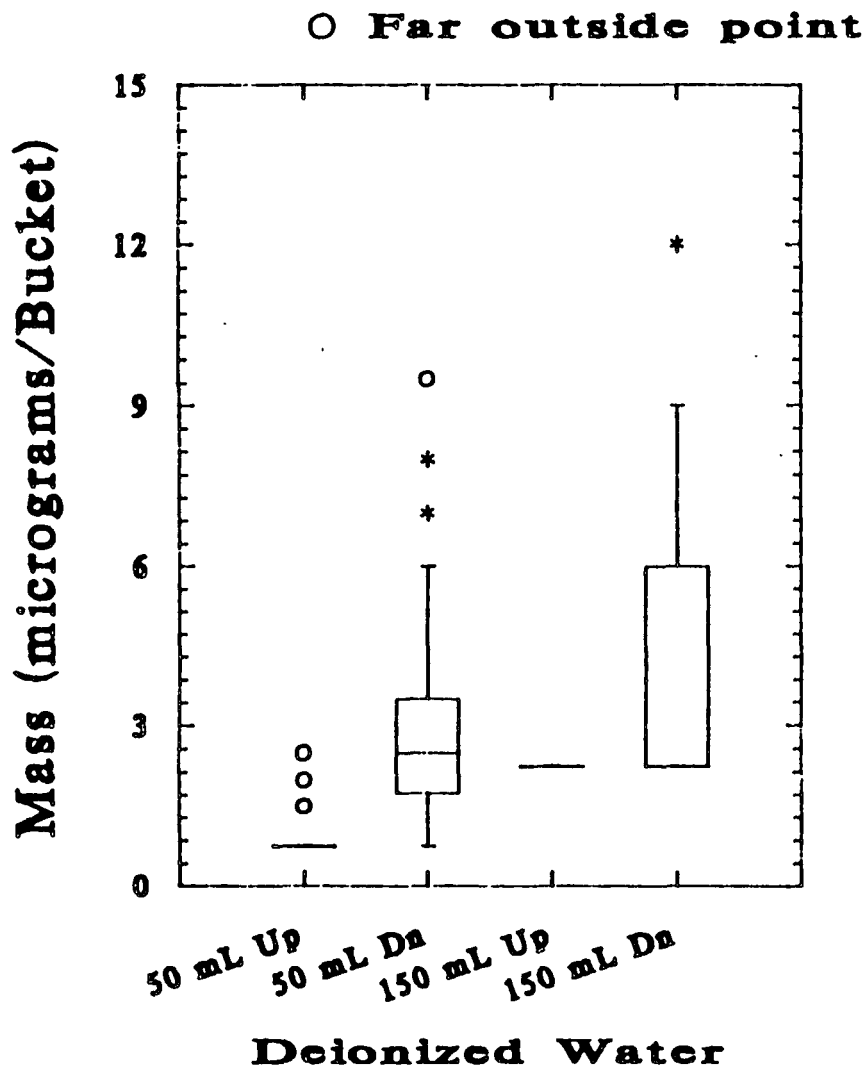


FIGURE C-24. Sulfate found in upright (Up) and inverted (Dn) bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1989.

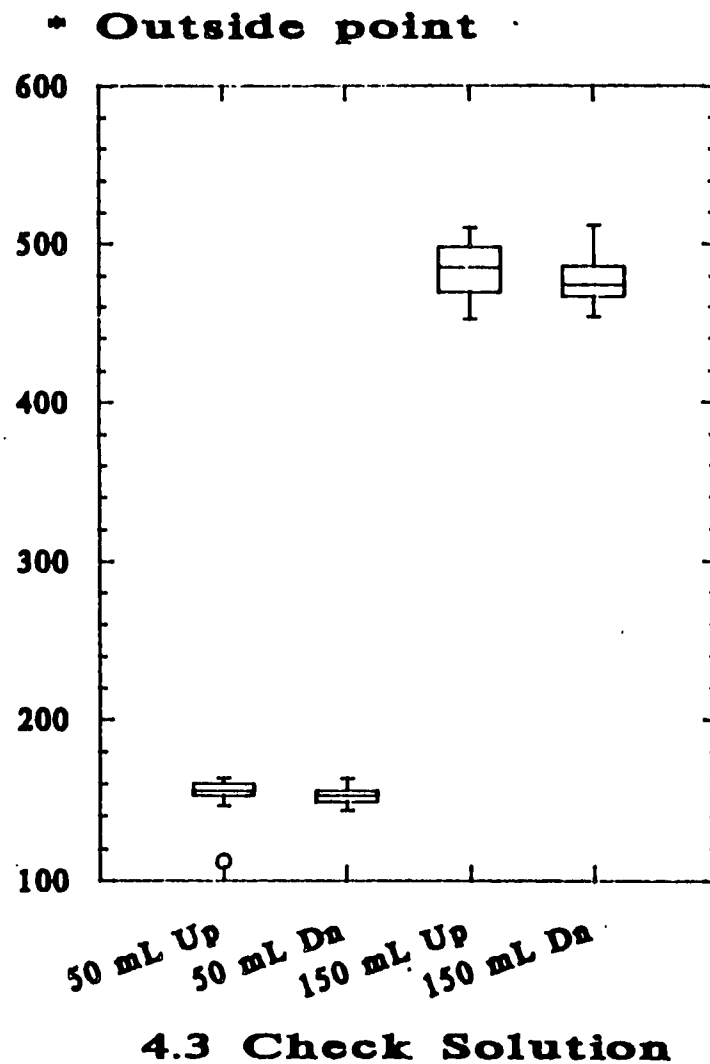
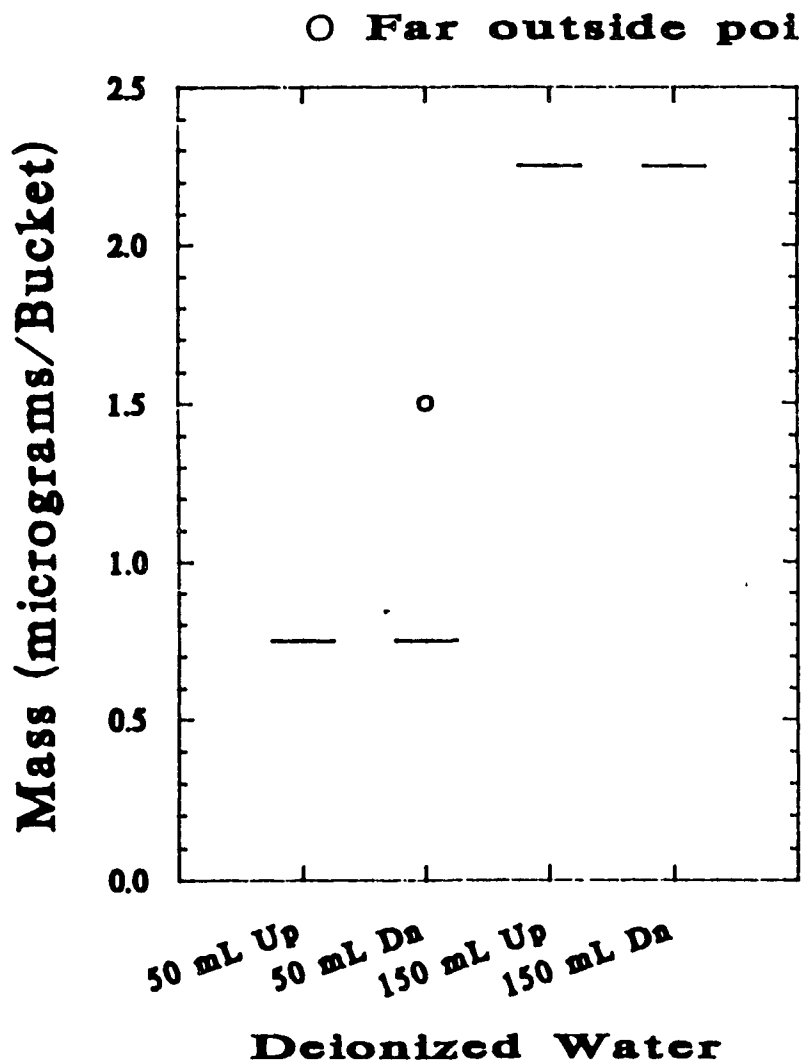


FIGURE C-25. Nitrate found in upright (Up) and inverted (Dn) bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1989.

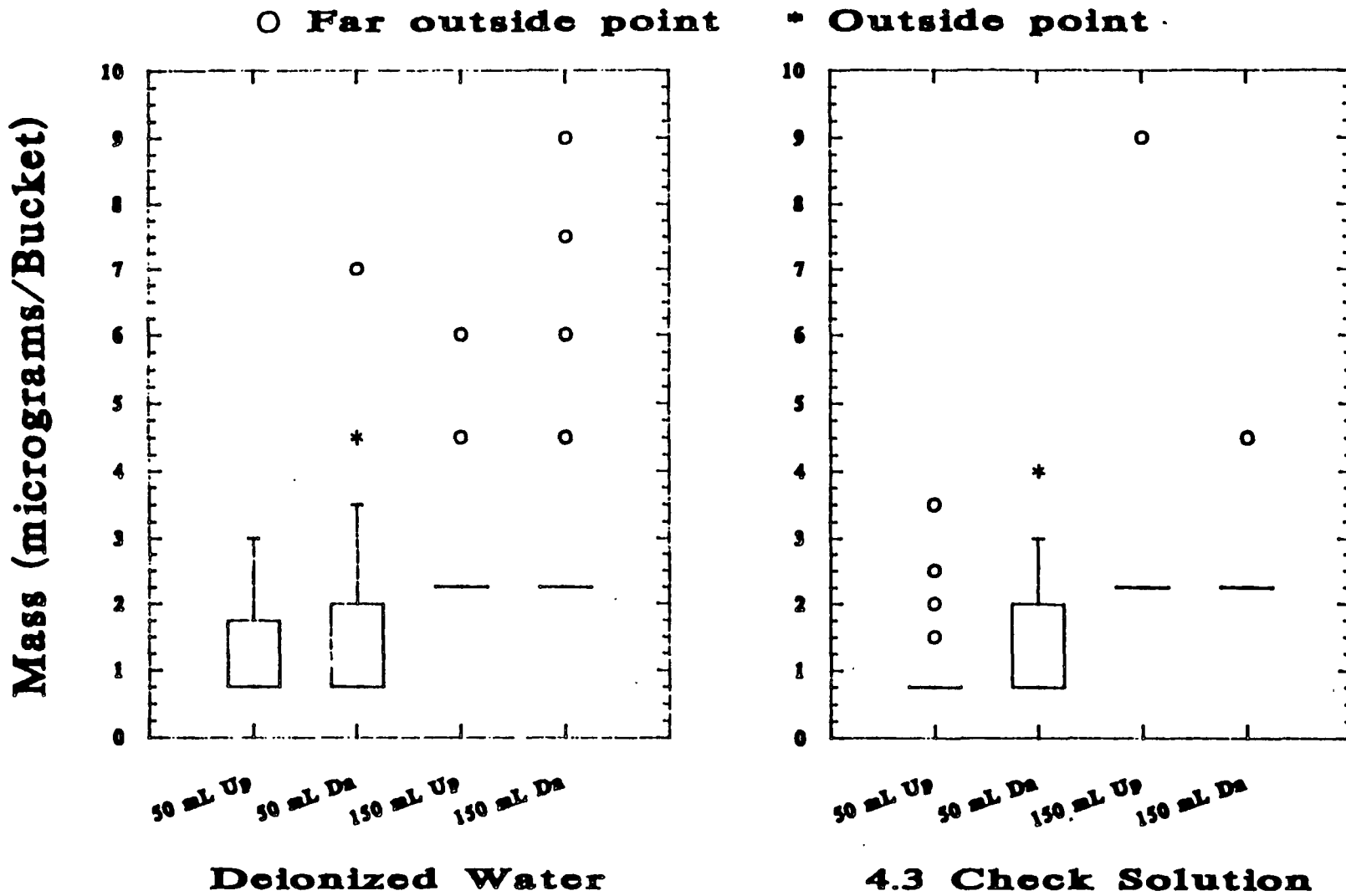


FIGURE C-26. Chloride found in upright (Up) and inverted (Dn) bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1989.

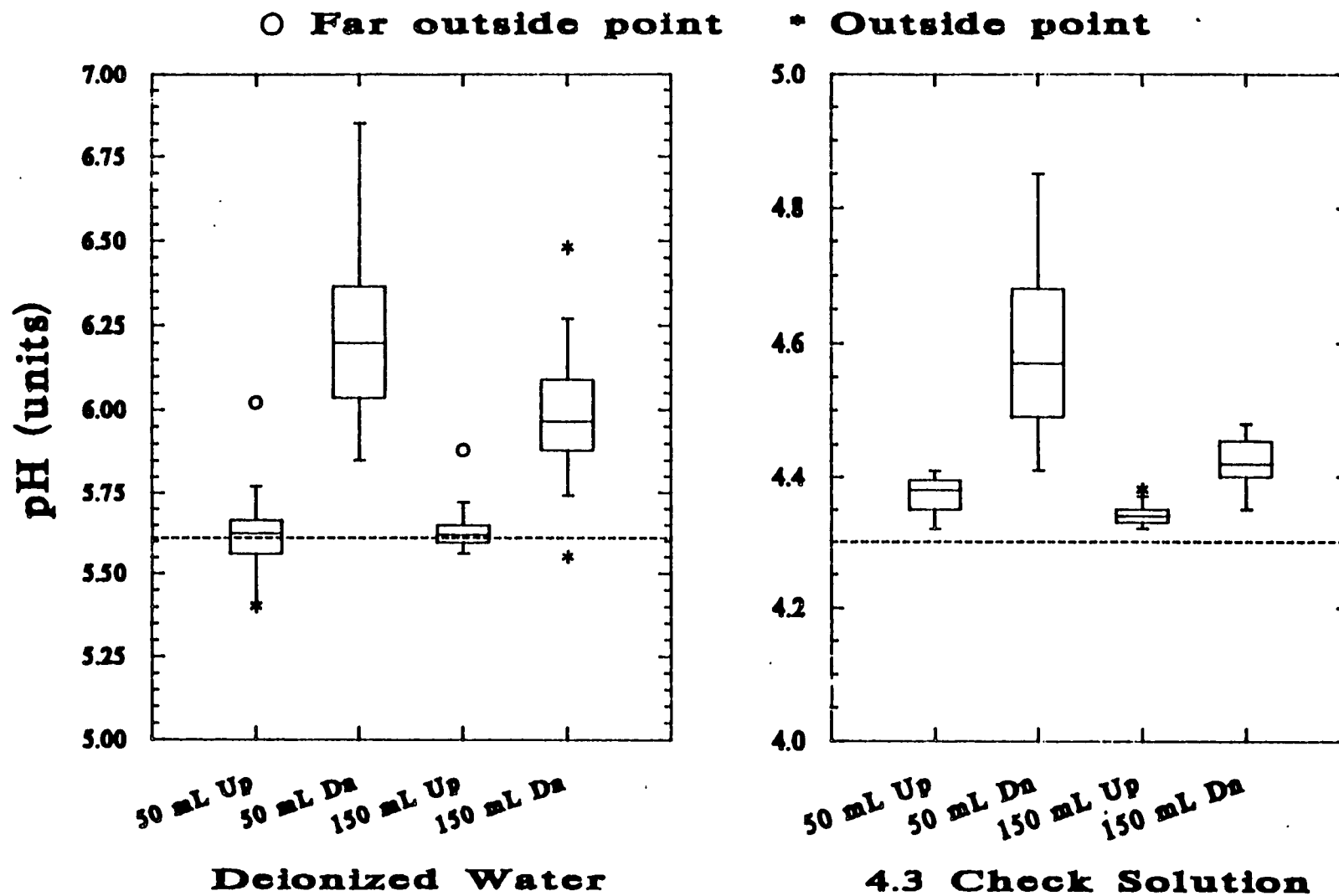


FIGURE C-27. pH of upright (Up) and inverted (Dn) bucket blanks leached with DI water and pH 4.3 QCS, 1989.

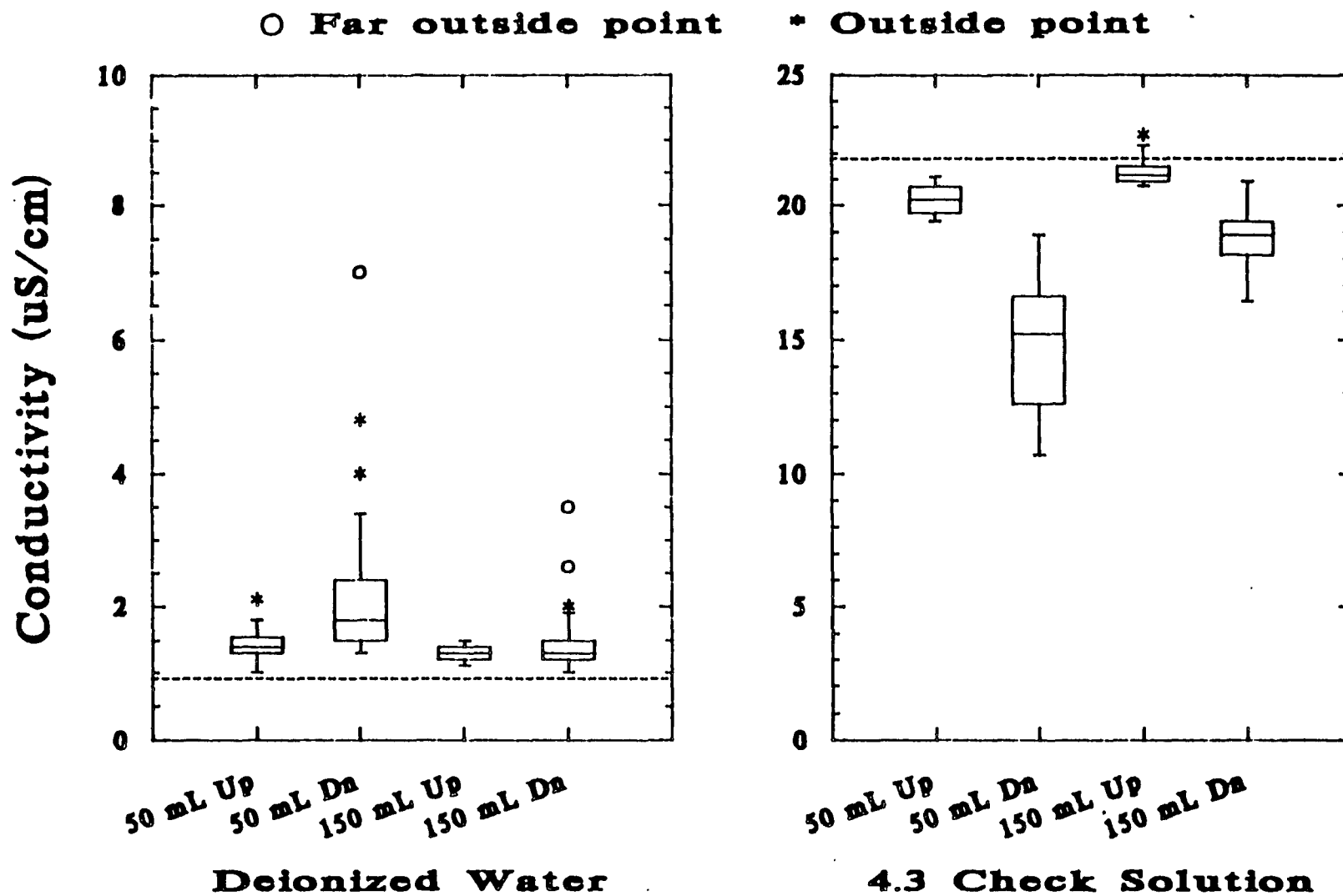


FIGURE C-28. Conductivity of upright (Up) and inverted (Dn) bucket blanks leached with DI water and pH 4.3 QCS, 1989.

APPENDIX D

Interlaboratory Comparison Data:

OSEPA, EMEP, LRTAP

1989

TABLE D-1 USEPA RTP Acid Rain Performance Survey,
June 1989, CAL Values Compared to
Expected Values.

Parameter (mg/L)	1030		Sample Number 2389		3753	
	CAL	EPA	CAL	EPA	CAL	EPA
Calcium	0.048	0.045	0.047	0.044	0.120	0.123
Magnesium	0.032	0.033	0.016	0.016	0.074	0.075
Sodium	0.179	0.266	0.243	0.228	1.290	1.219
Potassium	0.075	0.064	0.079	0.070	0.536	0.508
Ammonium	0.10	0.10	0.82	0.82	0.37	0.37
Nitrate	0.49	0.50	0.49	0.50	3.81	3.81
Chloride	0.28	0.30	0.34	0.36	0.21	0.23
Sulfate	2.64	2.68	12.19	12.16	7.34	7.33
pH (units)	4.31	4.29	3.69	3.66	3.92	3.91
Specific Conductance ($\mu\text{S}/\text{cm}$)	25.4	23.4	101.0	99.0	67.0	63.6

**TABLE D-2 USEPA RTP Acid Rain Performance Survey,
November 1989, CAL Values Compared to
Expected Values.**

Parameter (mg/L)	1527		Sample Number 2041		3520	
	CAL	EPA	CAL	EPA	CAL	EPA
Calcium	0.047	0.053	0.329	0.343	BDL	0.006
Magnesium	0.019	0.019	0.095	0.100	0.064	0.067
Sodium	0.232	0.247	1.788	1.846	0.469	0.500
Potassium	0.075	0.081	0.750	0.792	0.093	0.102
Ammonium	0.14	0.15	1.11	1.09	1.11	1.02
Nitrate	0.62	0.64	9.30	9.43	6.11	6.02
Chloride	0.37	0.38	2.65	2.72	0.93	0.93
Sulfate	1.62	1.62	11.74	11.67	11.26	11.20
pH (units)	4.52	4.50	3.54	3.51	3.58	3.55
Specific Conductance (μ S/cm)	17.1	15.8	151.3	151.2	130.7	128.2

TABLE D-3 EMEP Study #11 Interlaboratory Comparison Study,
September 1989, 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	0.402	0.396	0.207	0.198	0.273	0.264	0.540	0.528
Magnesium	0.083	0.084	0.230	0.235	0.167	0.168	0.116	0.118
Sodium	0.931	0.912	0.711	0.719	0.942	0.998	1.255	1.245
Potassium	0.212	0.204	0.116	0.102	0.139	0.127	0.272	0.255
Ammonium	0.22	0.26	0.36	0.36	0.73	0.72	0.52	0.52
Nitrate	2.66	2.66	2.17	2.13	3.54	3.55	3.90	3.92
Chloride	0.58	0.58	0.68	0.69	1.03	1.04	0.92	0.93
Sulfate	2.73	2.72	5.78	5.73	6.23	6.10	3.71	3.65
pH (units)	4.55	4.52	4.07	4.05	4.03	4.00	4.39	4.40
Specific Conductance ($\mu\text{S}/\text{cm}$)	24.0	24.1	49.0	49.4	57.2	57.9	34.8	33.8

Number of participating laboratories = 28

Table D-4 LRTAP Interlaboratory Comparability Study L20-
February 1989 • CAL Reported Values Compared to
Median Valuta for all Participating Laboratories.

Parameter (mg/L)	Sample Number																			
	1		2		3		4		5		6		7		8		9		10	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	0.194	0.196	1.615	1.600	4.040	4.000	4.445	4.447	0.426	0.430	0.725	0.717	0.543	0.540	2.094	2.085	3.168	3.155	5.766	5.770
Magnesium	0.086	0.082	0.314	0.310	0.944	0.934	0.731	0.730	0.056	0.055	0.089	0.086	0.167	0.162	0.481	0.476	0.764	0.750	1.634	1.613
Sodium	0.713	0.710	1.206	1.183	0.183	0.183	6.064	6.026	0.860	0.860	0.134	0.150	0.024	0.020	0.542	0.543	1.031	1.031	0.979	0.990
Potassium	0.118	0.110	0.181	0.173	0.180	0.178	0.766	0.791	0.009	0.012	0.028	0.030	0.021	0.022	0.321	0.320	0.545	0.550	0.722	0.730
Ammonium	0.12	0.10	0.02	0.01	0.39	0.37	<0.02	0.01	0.06	0.07	0.32	0.30	0.03	0.03	0.03	0.05	0.02	0.02	0.04	0.03
Nitrate	0.49	0.49	0.53	0.53	6.77	6.82	1.11	1.11	0.31	0.31	1.11	1.11	0.71	0.71	0.13	0.12	0.53	0.53	0.35	0.37
Chloride	1.22	1.22	1.14	1.14	4.20	4.10	11.13	11.00	1.40	1.39	0.28	0.28	0.06	0.06	0.36	0.36	1.27	1.26	0.96	0.94
Sulfate	0.94	0.93	1.53	1.51	6.93	6.91	7.47	7.42	1.67	1.63	1.95	1.92	1.80	1.74	5.66	5.60	7.99	7.98	8.44	8.42
pH (units)	5.15	5.17	6.63	6.60	4.28	4.29	6.56	6.44	4.98	4.98	5.51	5.50	5.23	5.16	5.97	5.83	6.76	6.38	7.29	7.19
Specific Conductance ($\mu S/cm$)	10.9	10.5	17.6	17.6	63.7	61.3	67.7	68.0	13.6	13.3	10.6	10.6	9.15	9.01	22.2	22.2	34.0	34.2	31.9	53.1

Number of participating laboratories – 58

Table D.5 LRTAP Intertaboratory Camparebilty Study Lit-
June 1989 - CAL Reported Values Compared to
Median Values for all Participating laboralories.

Paraaarter (mg/l)	Sample Number																			
	1		1		3		4		5		6		7		8		9		10	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium.	1.575	1.600	1.76	1.7S	11.22	11.62	1.99	2.02	0026	0.031	1.098	1.105	1.116	1.13	2.274	2.30	2.032	2.030	3.44	5.60
Magnesium	0J12	0.313	0.404	0.404	3.29	3.30	0.183	0.180	0.022	0.020	0.208	0.208	0.145	0.145	0.363	0.360	0.489	0.487	1.494	1.480
Sodiura	1.16	1.192	0.554	0.54	13.5	14.1	0.708	0.678	0.028	0.030	0.476	0.490	1.26	1.285	0.653	0.700	0.478	0.500	1.58	1.57
Potassium	0.170	0.180	0.140	0.146	1.05	1.12	0.180	0.193	0024	0.020	0.027	0.030	0.036	0.040	0.412	0.420	0.210	0.210	0.723	0.730
Ammonium	<0.02	0.01	<0.02	0.004	<0.02	0.006	<002	0.013	0.03	0.20	0.23	0.23	0.27	0.27	004	004	<0.02	0.013	<002	0.005
Nitrate	0.58	0.58	<0.03	0.04	0.40	0.42	0.53	0.54	0.22	0.24	0.80	0.80	1.20	1.21	1.42	1.42	0.18	0.19	0.04	0.07
Choi de	1.29	1.14	0.21	0.21	26.52	26.32	1.77	1.67	0.05	0.05	0.72	0.73	1.96	2.00	0.49	0.50	0.39	0J8	108	2.08
Sulfate	1.51	1.50	8.34	8.11	22.03	22.48	2.07	2.00	0.32	0.32	8.26	8.42	9.17	9.11	6.51	6.49	6.16	6J3	8.67	8.81
pH (units)	6.61	6.40	4.43	4.42	7.22	7.22	668	6.60	5.17	5 20	4.03	4.03	3.91	3.91	5.48	5.50	6.15	600	7.25	7.10
Specific Conductance (µS/cm)	17.2	17.6	35.7	35.6	170.9	173.0	18.3	18.5	4.0	3.8	55.1	55.1	72.0	71.0	25.4	26.0	21.7	22.1	53.4	54.0

Number of participating laboratories – 67 -

Table D-6 LRTAP In-laboratory Comparability Study L22.
 September 1989 – CAL Reported Values Compared Is
 Median Values for all participating Laboratories.

Parameter	Sample Number																			
	1		2		3 4		5		6		7		8		9		10			
	CAL	NWSI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	2.351	2.2	5.810	5.80	3.236	3.165	2.144	2.081	5.520	5.585	2.100	2.050	3.062	2.995	1.925	1.900	2.697	2.63	0.439	0.430
Magnesium	0.366	0.360	1.64	1.62	0.772	0.760	0.488	0.476	1.47	1.47	0.492	0.480	0.935	0.915	0.362	0.358	0.448	0.441	0.057	0.060
Sodium	0.677	0.690	0.966	0.997	1.010	1.04	0.537	0.539	1.556	1.550	0.486	0.491	1.224	1.22	0.057	0.060	0.102	0.100	0.865	0.865
Potassium	0.417	0.420	0.719	0.731	0.542	0.549	0.319	0.324	0.722	0.730	0.211	0.213	0.534	0.540	0.144	0.150	0.165	0.170	0.014	0.018
Ammonium	0.03	0.04	0.02	0.02	<0.02	0.01	0.02	0.05	<0.02	0.01	<0.02	0.005	<0.02	0.01	0.10	0.11	0.21	0.21	0.06	0.07
Nitrate	1.42	1.42	0.3	0.38	0.53	0.55	0.09	0.13	<0.03	0.04	0.18	0.18	<0.02	0.04	MI	1.51	0.80	0.97	0.31	0.31
Chloride	0.50	0.50	0.94	0.94	1.23	1.25	0.36	0.36	2.07	2.08	0.38	0.38	1.35	1.23	0.24	0.24	0.24	0.26	1.19	1.38
Sulfate	6.7	6.41	8.1	8.30	7.84	7.92	5.62	3.60	8.75	8.80	6.23	6.32	7.41	7.41	5.65	5.66	9.73	9.80	1.65	1.62
pH (units)	5.55	5.54	7.23	7.16	6.71	6.64	6.01	5.95	7.25	6.95	6.23	6.03	6.82	6.66	4.86	4.87	4.44	4.43	5.02	5.04
Specific Conductance (µS/cm)	25.4	23.8	32.0	31.6	33.7	34.1	21.8	22.1	53.9	54.0	21.9	22.1	34.7	34.3	24.6	23.9	40.9	41.0	13.4	13.1

Number of participating laboratories • 56

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