

# QUALITY ASSURANCE REPORT NADP/NTN DEPOSITION MONITORING

Laboratory Operations  
Central Analytical Laboratory  
1990

## 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  
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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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**1990 QUALITY ASSURANCE REPORT  
NADP/NTN DEPOSITION MONITORING**

**Laboratory Operations  
Central Analytical Laboratory  
January 1990 through December 1990**

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## I. INTRODUCTION

Since its inception in 1978, the Central Analytical Laboratory (CAL) of NADP/NTN has operated with a strong emphasis on quality control (QC) and quality assurance (QA). The very low concentrations of dissolved chemical constituents contained in wet deposition samples demand a rigid QC program to ensure that the data are representative of the sample chemistry. The program and its evolution have been documented in previous annual reports (1-7). Detailed descriptions presented in these reports are not repeated. The Quality Assurance Reports from 1978-1989 are available from the Illinois State Water Survey or the Program Coordinator's Office at Colorado State University.

This report documents the daily, weekly, monthly, semi-annual, and annual procedures followed at CAL during 1990. The format of this report follows that of the 1989 report.

Laboratory QA begins as soon as the network samples enter the facility and the buckets are opened. The network QA plan (8) prescribes the methods used to conduct and document the chemical and physical analyses of each sample. These analyses are verified using ion balance and specific conductance calculations. External audits are performed by the U.S. Geological Survey (USGS) as a mandated portion of the program. Voluntary participation in national and international interlaboratory comparison studies serves to ensure the comparability of CAL results with those of its peers throughout the world.

A CAL systems audit was conducted on July 10-12, 1990. The audit team commissioned by the Quality Assurance Steering Committee was: Cary Eaton, Chair Network Operations Subcommittee; Jim Lynch, Chair Data Analysis Subcommittee; Linda Porter, U. S. Environmental Protection Agency (USEPA); Dave Erdman, USGS; and Dave Bigelow, NADP/NTN QA Manager. The team found that, "Overall, the laboratory is doing an excellent job and the staff appear to be competent and dedicated. The laboratory facilities are clean, organized, and pleasant. ... it was felt that the CAL is doing an excellent job of providing high quality analytical data on atmospheric deposition chemistry to the National Atmospheric Deposition Program." For additional information on the systems audit report and CAL response, contact the NADP/NTN QA Manager at the Program Coordination Office at Colorado State University.



## II. LABORATORY QUALITY ASSURANCE - A GENERAL DESCRIPTION

The 1990 CAL QA program consisted of many different procedures that had been developed as the program progressed during the last 12 years. Most of the laboratory operations described and mandated in the present QA Plan (8) were originally established by CAL as the laboratory procedures evolved. The information contained in this report is a summary of the laboratory QC data collected in 1990. There is a brief section containing a summary of the results of USGS external audits for 1990 and CAL participation in national and international interlaboratory comparisons.

Internal QA programs provide the data required to evaluate the analytical equipment, personnel performance, and analytical procedures in order that the accuracy and precision of the reported values can be assured. The internal QA components are classified in this report in accordance with the frequency of their occurrence: daily, weekly, monthly, semiannually, and annually. These activities are summarized in Table II-1 and are described in subsequent sections of this report.

In 1990, there were few modifications to the internal QA program. The flow of samples continued as it has since mid-1987 (Figure II-1). There were no laboratory personnel changes and the laboratory's procedures for evaluating blanks remained as they were at the end of 1989. Following approval at the Network Operations Subcommittee (Fall 1989), quality control solutions (QCS) were changed from several USEPA mineral and nutrient dilutions to CAL-prepared simulated rain. The concentrations of the QCS are now representative of the 25th and 75th percentile concentrations from the NADP/NTN network. These same samples were used in the internal blind audit as a substitute for the Simulated Rain prepared by the National Institute of Standards and Technology (NIST) since they were unavailable for an extended period of time. The replicate and reanalysis procedures remained as they were in 1989.

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**TABLE II-1 NADP/NTN Laboratory QC/QA Program Summary**

---

- I. Daily
    - A. Instruments calibrated, calibration curves verified using low- and high-level control standards.
      - 1. Internally formulated solutions of simulated rain representing 25th and 75th percentile concentrations of network samples used for all physical and chemical parameters.
      - 2. 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 deionized water (DI) rinse.
        - a. DI
        - b. pH 4.3 nitric acid
      - 3. Bucket leachates of 50 and 150 mL collected from upright and inverted buckets.
        - a. DI
        - b. pH 4.3 nitric acid
      - 4. Procedures expanded when contamination indicated.
    - B. Internal blind samples submitted to sample processing as sites SWS1, SHS2, and SWS3.
      - 1. SWS1 alternated 25th and 75th percentile simulated rain, unfiltered.
      - 2. SWS2 alternated deionized water and pH 4.3 nitric acid, 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 semi-annually
    - 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.
-

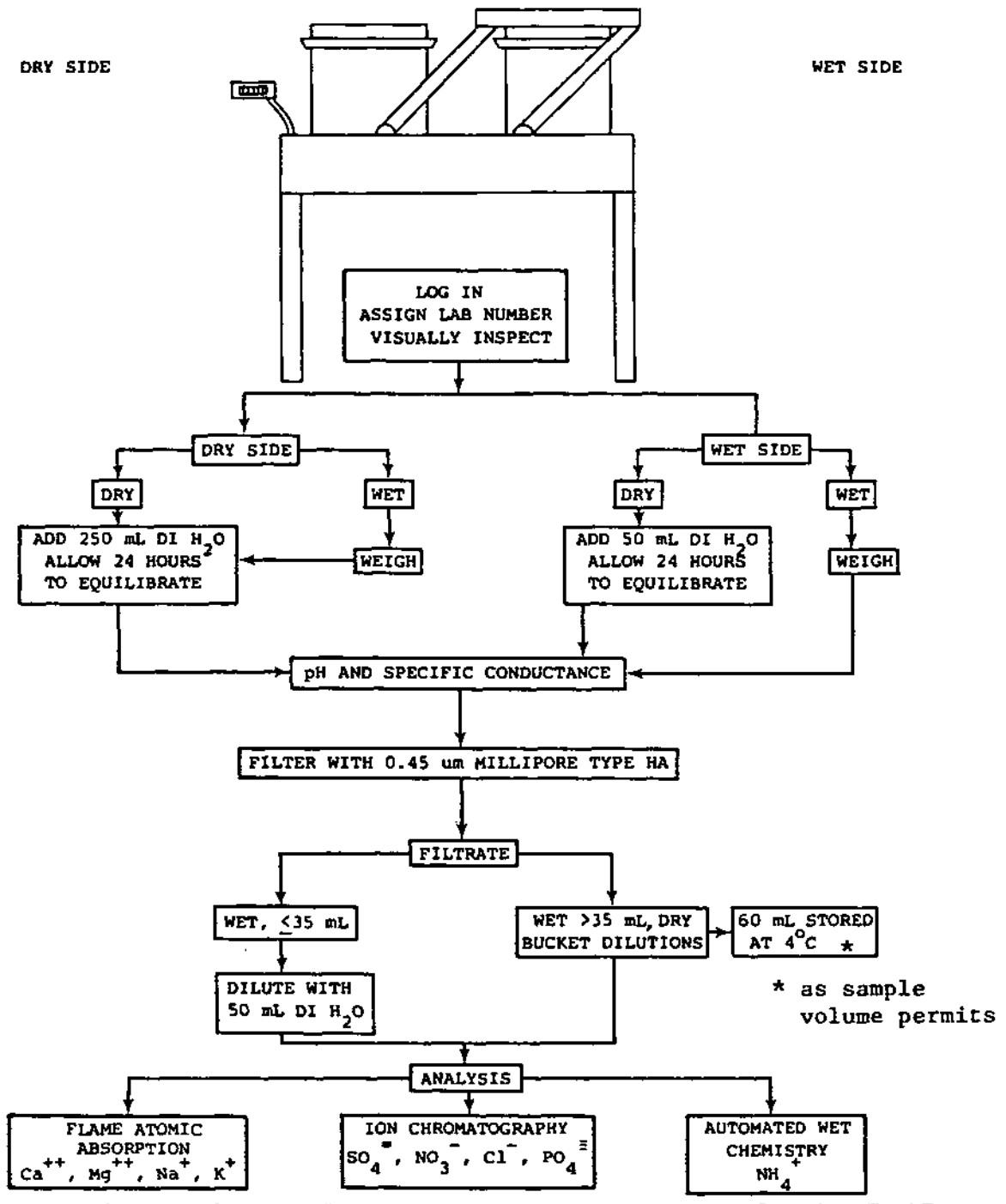


FIGURE II-1. Sample processing flowchart, January 1990-December 1990.



### III. DAILY QUALITY CONTROL PROCEDURES

NADP/NTN network samples have traditionally been collected weekly on Tuesdays as close to 0900 hours as conditions allow. Sample volume permitting, an aliquot is removed for field pH and conductivity before shipping each bucket with sealed lid back to CAL for sample processing and analysis. A portion of these 200 sample boxes arrive at the laboratory each day. The sample processing and analysis flowchart (Figure II-1) is a graphic representation of the fate of each sample. After the samples are assigned a sequential number and visually inspected, aliquots are poured into small vials for the determination of pH and conductivity. The remaining sample is then filtered, as volume permits, into two 60-milliliter (mL) bottles for holding until further analysis. The analytical staff (Table III-1) and methods (Table III-2) were the same in 1990 as at the end of 1989.

Staff Member/Job Function	Period of Employment
Sue Bachman NH <sub>4</sub> <sup>+</sup> Ca <sup>++</sup> , Mg <sup>++</sup> , Na <sup>+</sup> , K <sup>+</sup>	August 1980 - December 1990 November 1988 - December 1990
Brigita Demir SO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup>	September 1981 - December 1990
Pat Dodson Sample processing	September 1980 - December 1990
Angela Haley Sample receipt and processing	October 1989 - December 1990
Theresa Ingersoll Sample receipt and processing	March 1985 - December 1990
Kenni James Quality assurance	October 1987 - December 1990
Mark Peden Laboratory manager	July 1978 - December 1990
Jeffrey Pribble Sample receipt	July 1987 - December 1990
Jackie Damara Sample processing, pH, conductivity	September 1983 - May 1986 January 1988 - December 1990

TABLE III-2 Method Detection Limits (MDLs) for the Analysis of Precipitation Samples, 1978-1990			
Analyte	Method*	MDL (mg/L)	Dates
Calcium	Flame Atomic Absorption	0.02	7/78-10/80
		0.009	10/80-12/90
Magnesium	Flame Atomic Absorption	0.002	7/78-10/80
		0.003	10/80-12/90
Sodium	Flame Atomic Absorption	0.004	7/78-10/80
		0.003	10/80-12/90
Potassium	Flame Atomic Absorption	0.004	7/78-10/80
		0.003	10/80-12/90
Ammonium	Automated Phenate, Colorimetric	0.02	7/78-12/90**
Sulfate	Automated Methyl Thymol Blue, Colorimetric I.C. <sup>a</sup>	0.10	7/78-5/85
		0.03	5/85-12/90
Nitrate/Nitrite	Automated Cadmium Reduction, Colorimetric	0.02	7/78-5/85
Nitrate	I.C. <sup>a</sup>	0.03	5/85-12/90
Chloride	Automated Ferricyanide Colorimetric I. C. <sup>a</sup>	0.05	7/78-3/81
		0.02	3/81-5/85
		0.03	5/85-12/90
Orthophosphate	Automated Ascorbic Acid Colorimetric I. C. <sup>a</sup>	0.003	7/78-2/86
		0.01	2/86-7/87
		0.02	7/87-12/90
Notes: *For a complete description of the most recent methods , see <u>Methods for Collection and Analysis of Precipitation (10 )</u> . **Equipment upgra de in 1989 did not alter the MDL. <sup>a</sup> I.C. = ion chroma tography			



The quantification of the major inorganic species in network samples involves calibration of several instruments using standards of known concentrations. The resulting calibration curves are then verified by comparisons to analyzed reference solutions. These reference solutions are referred to as quality control solutions (QCS). In previous years, 1978-1989, two internally formulated solutions were used for pH and conductance, and dilutions of USEPA mineral and nutrient concentrates used as QCS for the cations and anions. However, the request to change to internally prepared solutions of synthetic rain was approved at the 1989 fall meeting of the Network Operations Subcommittee in Provincetown, Massachusetts.

These new solutions, made from inorganic salts and acids, contain ion concentrations approximating NADP/NTN network 25th and 75th percentile levels (Table III-3). The original stock solution was prepared at CAL as part of a separate Illinois State Water Survey U.S. Department of Energy (DOE) contract (9). The dilutions of the stock, 800:1 and 200:1, fulfilled the criteria set for a reliable QCS. The research done for the contract report shows that these solutions are NIST traceable, in-expensive, contain ionic concentrations approximating natural rainwater, and exhibit long-term stability.

The values obtained from the analyses of the QCS are recorded for each sample lot analyzed and plotted on monthly control charts. These daily values are then used to evaluate monthly bias and precision and for annual reporting summaries (Table III-4).

The percent bias for the cations is lower than in the four previous years. Chloride percent bias has been consistent for the last 5 years, nitrate exhibits a lower percent bias for both concentrations in 1990, and the two sulfate percents have decreased since 1989, after becoming less random in 1988. The pH percents exhibit little change since 1986. The specific conductance bias is the smallest in the last five years. Precision stated as percent relative standard deviation (RSD) is similar to 1989 for all parameters.

A 1990 summary of this information shows that the percent bias of each of the parameters is within the goals of the network QA Plan (8). With the exception of the pH 4.31 value (expressed as  $\mu\text{eq/L}$  for calculations), these biases are less than 5 percent. The precision, expressed as relative standard deviation (RSD), also meets or exceeds the network criteria. Note: The formulae used to calculate the values in Table III-4 are included in the glossary (Appendix A).

TABLE III-3 Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/NTN Precipitation, 1990

Percentile Concentration Value (mg/L)										
Parameter	Min.	5 <sup>th</sup>	10 <sup>th</sup>	25 <sup>th</sup>	50 <sup>th</sup>	75 <sup>th</sup>	90 <sup>th</sup>	95 <sup>th</sup>	99 <sup>th</sup>	Max.
Calcium	<0.009	0.019	0.030	0.057	0.120	0.253	0.523	0.813	2.210	14.100
Magnesium	<0.003	0.005	0.008	0.013	0.025	0.050	0.098	0.157	0.355	1.660
Potassium	<0.003	<0.003	0.005	0.010	0.019	0.039	0.079	0.120	0.358	9.600
Sodium	<0.003	0.016	0.022	0.038	0.075	0.167	0.394	0.677	2.350	32.00
Ammonium	<0.02	<0.02	0.04	0.11	0.24	0.45	0.75	1.03	1.82	18.00
Nitrate	<0.03	0.20	0.32	0.59	1.07	1.84	2.89	3.86	6.39	21.52
Chloride	<0.03	0.05	0.07	0.10	0.15	0.28	0.64	1.15	4.36	50.50
Sulfate	<0.03	0.21	0.33	0.66	1.30	2.28	3.68	4.81	8.10	22.88
Phosphate	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.04	0.13	2.3
pH (units)	3.37	4.07	4.18	4.43	4.87	5.52	6.16	6.40	6.85	8.02
Cond. ( $\mu$ S/cm)	14	3.6	4.6	7.5	13.4	23.7	37.9	49.3	80.4	259.9
Notes: Number of samples = 7,115. Mean sample volume = 1532.5 mL; median sample volume = 987.2 mL.										

Source: National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) 1990 wet-side samples.

**TABLE III-4 Analytical Bias and Precision Determined from Analysis of Simulated Rain QCS, 1990**

Parameter	Target Cone. (mg/L)	Measured Cone (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)	Critical Conc. (mg/L)	Statist. Significant Bias?
Calcium	0.077 <sup>a</sup>	0.077	537	0.000	0.0	0.003	3.9	0.002	NO
	0.307 <sup>b</sup>	0.305	510	-0.002	-0.6	0.004	1.3	0.002	NO
Magnesium	0.018	0.018	504	0.000	0.0	0.001	5.6	0.001	NO
	0.070	0.071	501	0.001	1.4	0.001	1.4	0.001	NO
Sodium	0.048	0.046	486	-0.002	-4.2	0.003	6.2	0.001	YES
	0.190	0.189	471	-0.001	-0.5	0.004	2.1	0.002	NO
Potassium	0.014	0.014	474	0.000	0.0	0.002	14.3	0.001	NO
	0.055	0.055	470	0.000	0.0	0.002	3.6	0.001	NO
Ammonium	0.09	0.09	541	0.00	0.0	0.01	11.1	0.00(5) <sup>c</sup>	NO
	0.37	0.37	404	0.00	0.0	0.02	5.4	0.00(8) <sup>c</sup>	NO
Chloride	0.14	0.14	1331	0.00	0.0	0.01	7.1	0.00(4) <sup>c</sup>	NO
	0.54	0.53	1400	-0.01	-1.8	0.01	1.8	0.00(5) <sup>c</sup>	YES
Nitrate	0.48	0.48	1228	0.00	0.0	0.01	2.1	0.00(4) <sup>c</sup>	NO
	1.94	1.96	1223	0.02	1.0	0.04	2.0	0.01(3) <sup>c</sup>	YES
Sulfate	0.64	0.64	1174	0.00	0.0	0.01	1.6	0.00(5) <sup>c</sup>	NO
	2.58	2.60	1231	0.02	0.8	0.04	1.5	0.01(4) <sup>c</sup>	YES
pH units (µeq/L)	4.90 (12.6) <sup>d</sup>	4.91 (12.3) <sup>d</sup>	1738	(-0.16) <sup>d</sup>	(-1.3) <sup>d</sup>	0.02	0.5	(0.286) <sup>c</sup>	NO
	4.31 (49.0) <sup>d</sup>	4.33 (46.8) <sup>d</sup>	1738	(-2.48) <sup>d</sup>	(-5.1) <sup>d</sup>	0.02	0.4	(0.652) <sup>c</sup>	YES
Specific Conductance (µS/cm)	7.20	7.32	1037	0.12	1.7	0.22	3.0	0.0(88) <sup>c</sup>	YES
	28.1	28.0	1037	-0.1	0.4	0.50	1.8	0.2(06) <sup>c</sup>	NO

**Notes:**

**a** The first set of values for each parameter is for the 25<sup>th</sup> percentile solution, **b** The second set of values for each parameter is for the 75<sup>th</sup> percentile solution.

**c** The values in ( ) are provided for information, **d** The pH data in ( ) have been converted to microequivalents.



#### IV. WEEKLY QUALITY ASSURANCE PROCEDURES

Several of the quality assurance (QA) procedures are conducted on a weekly basis. The weekly programs include the internal blind audit, replicate network samples, and laboratory blank solutions.

##### A. BLIND SAMPLES

The internal blind program has been in place since the summer of 1984 when it was instituted to provide another means of evaluating the quality of sample data. Since 1987, three blind samples have been submitted each week. The samples are given NADP/NTN site designations SWS1, SWS2, and SWS3. Samples from sites SWS1 and SWS2 are not filtered; the sample from SWS3 is filtered. In 1990, SWS1 samples were two concentrations of internally formulated simulated rain. This change from NIST-Simulated Rain occurred when the stocks of the solutions at NIST became depleted, and they were unable to prepare and certify another large quantity of solutions for more than a year. Other sources for certified standards would have been sought had CAL personnel been given a realistic date for the availability of NIST standards. SWS2 samples were internally formulated pH 4.3 nitric acid and deionized water. Samples from SWS3 were the four SWS1 and SWS2 solutions submitted in rotation. The SWS 3 analyses provide a method of assessing the effect of the filtering process on network samples. Tables IV-1-IV-4 summarize the results of the internal blind audit program.

Comparison of the SWS1 and the QCS analyses yields similar bias ( $\pm 0.001$  mg/L-metals,  $\pm 0.01$  mg/L-ammonium and anions) for the major ions with all percent biases within acceptable range according to the network QA Plan. The precision for the cations is not as good as the QCS, while the anion precision is comparable. Comparison of the SWS1 and SWS3 simulated rain samples shows an increase in the concentrations of calcium in the 75th percentile solution, sodium in both solutions, ammonium in the 25th percentile solution, and chloride in the 25th percentile solution of the filtered samples. Sulfate amounts decrease in the filtered sample as they have in previous years (1987-1989). The SWS2-SWS3 comparison indicates that calcium in the pH 4.3 nitric acid sample and sodium in both samples show significantly increased concentrations in the filtered solutions. These concentration increases were larger than in the simulated rain. The percent bias and relative standard deviation for the parameters measured in the blind samples are similar to those values in 1989. Tables B-1 and B-2 and the control chart figures in Appendix B (Figures B-1 - B-20) are tabular and graphic representations of the comparison of unfiltered and filtered ion concentrations.

**TABLE IV-1 Analytical Bias and Precision Determined from  
Analysis of Internal Blind Audit Samples (SWS1),  
Simulated Rain Representing the 25<sup>th</sup> and 75<sup>th</sup> Percentile  
Concentrations of NADP/NTN Network Samples, Unfiltered, 1990**

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)	Critical Conc. (mg/L)	Statist. Significant Bias?
Calcium	0.077 <sup>a</sup>	0.076	21	-0.001	-1.3	0.007	9.2	0.003	NO
	0.307 <sup>b</sup>	0.308	20	0.001	0.3	0.008	2.6	0.004	NO
Magnesium	0.018	0.017	21	-0.001	-5.6	0.002	11.8	0.001	NO
	0.070	0.071	20	0.001	1.4	0.002	2.8	0.001	NO
Sodium	0.048	0.046	21	-0.002	-4.2	0.010	21.7	0.004	NO
	0.190	0.190	19	0.000	0.0	0.005	2.6	0.003	NO
Potassium	0.014	0.014	21	0.000	0.0	0.007	50.0	0.003	NO
	0.055	0.056	19	0.001	1.8	0.005	8.9	0.003	NO
Ammonium	0.09	0.08	21	-0.01	-11.1	0.02	25.0	0.01	YES
	0.37	0.38	20	0.01	2.7	0.02	5.3	0.01	YES
Chloride	0.14	0.15	21	0.01	7.1	0.02	13.3	0.01	NO
	0.54	0.53	20	-0.01	-1.8	0.01	1.9	0.01	YES
Nitrate	0.48	0.48	21	0.00	0.0	0.01	2.1	0.01	NO
	1.94	1.95	20	0.01	0.5	0.03	1.5	0.02	YES
Sulfate	0.64	0.63	21	-0.01	-1.6	0.01	1.6	0.01	YES
	2.58	2.60	20	0.02	0.8	0.04	1.5	0.02	NO
pH units (μeq/L)	4.90 (12.6) <sup>c</sup>	4.91 (12.2) <sup>c</sup>	21	(-0.41) <sup>c</sup>	(-3.2) <sup>c</sup>	(0.77) <sup>c</sup>	(6.3) <sup>c</sup>	(0.43) <sup>c</sup>	NO
	4.31 (49.0) <sup>c</sup>	4.34 (45.3) <sup>c</sup>	20	(-3.64) <sup>c</sup>	(-7.4) <sup>c</sup>	(2.25) <sup>c</sup>	(5.0) <sup>c</sup>	(1.16) <sup>c</sup>	NO
Specific Conductance (μS/cm)	7.2	7.8	21	0.6	8.3	0.8	10.3	0.4	YES
	28.1	27.6	20	-0.5	-1.8	0.6	2.2	0.4	YES

**Notes:**

- a The first set of values for each parameter is for the 25<sup>th</sup> percentile solution.
- b The second set of values for each parameter is for the 75<sup>th</sup> percentile solution.
- c The pH data in ( ) have been converted to microequivalents.

**TABLE IV-2 Analytical Bias and Precision Determined from  
Analysis of Internal Blind Audit Samples (SWS2),  
Deionized (DI) Water and pH 4.3 QCS, Unfiltered, 1990**

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)	Critical Conc. (mg/L)	Statist. Significant Bias?
Calcium	<0.009 <sup>a</sup> <0.009 <sup>b</sup>	<0.009 <0.009	25 26						
Magnesium	<0.003 <0.003	<0.003 <0.003	25 26						
Sodium	<0.003 <0.003	<0.003 0.003	25 26						
Potassium	<0.003 <0.003	<0.003 <0.003	25 26						
Ammonium	<0.02 <0.02	<0.02 <0.02	25 26						
Chloride	<0.03 <0.03	<0.03 <0.03	25 26						
Nitrate	<0.03 3.12	<0.03 3.19	25 26	0.07	2.24	0.07	2.19	0.03	YES
Sulfate	<0.03 <0.03	<0.03 <0.03	25 26						
Phosphate	<0.02 <0.02	<0.02 <0.02	25 26						
pH units ( $\mu$ eq/L)	5.64 (2.29) <sup>c</sup> 4.30 (50.1) <sup>c</sup>	5.59 (2.59) <sup>c</sup> 4.31 (49.1) <sup>c</sup>	25 26	(0.30) <sup>c</sup> (-1.07) <sup>c</sup>	(13.06) <sup>c</sup> (-2.11) <sup>c</sup>	(0.43) <sup>c</sup> (2.01) <sup>c</sup>	(16.6) <sup>c</sup> (4.1) <sup>c</sup>	(0.18) <sup>c</sup> (2.16) <sup>c</sup>	YES NO
Specific Conductance ( $\mu$ S/cm)	0.9 21.8	13 21.4	25 26	0.4 -0.4	44.4 -1.83	0.4 0.7	30.8 3.3	0.2 2.0	YES NO

**Notes:**

- a The first set of values for each parameter is for DI water. b The second set of values for each parameter is for pH 4.3 QCS.  
c The pH data in ( ) have been converted to microequivalents.

**TABLE IV-3 Analytical Bias and Precision Determined from Analysis of Internal  
Blind Audit Samples (SWS3), Simulated Rain Representing the 25<sup>th</sup> and 75<sup>th</sup>  
Percentile Concentrations of NADP/NTN Network Samples, Filtered, 1990**

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)	Critical Conc. (mg/L)	Statist. Significant Bias?
Calcium	0.077 <sup>a</sup>	0.076	12	-0.001	-1.3	0.012	15.8	0.006	NO
	0.307 <sup>b</sup>	0.320	8	0.013	4.2	0.035	10.9	0.016	NO
Magnesium	0.018	0.018	12	0.000	0.0	0.004	22.2	0.002	NO
	0.070	0.071	8	0.001	1.4	0.003	4.2	0.002	NO
Sodium	0.048	0.064	12	0.016	33.3	0.011	17.2	0.005	YES
	0.190	0.203	7	0.013	6.8	0.010	4.9	0.005	YES
Potassium	0.014	0.016	12	0.002	14.3	0.007	43.8	0.003	NO
	0.055	0.054	7	-0.001	-1.8	0.002	3.7	0.001	YES
Ammonium	0.09	0.12	12	0.03	33.3	0.02	16.7	0.01	YES
	0.37	0.40	8	0.03	8.1	0.06	15.0	0.04	NO
Chloride	0.14	0.16	12	0.02	14.3	0.01	6.2	0.01	YES
	0.54	0.53	8	-0.01	-1.8	0.01	1.9	0.02	NO
Nitrate	0.48	0.49	12	0.01	2.1	0.01	2.0	0.01	YES
	1.94	1.91	8	-0.03	-1.6	0.04	2.1	0.03	YES
Sulfate	0.64	0.62	12	-0.02	-3.1	0.01	1.6	0.02	YES
	2.58	2.47	8	-0.11	-4.3	0.05	2.0	0.06	YES
pH units (µeq/L)	4.90 (12.6) <sup>c</sup>	4.90 (12.5) <sup>c</sup>	12	(-0.10) <sup>c</sup>	(-0.8) <sup>c</sup>	(0.84) <sup>c</sup>	(6.7) <sup>c</sup>	(1.15) <sup>c</sup>	NO
	4.31 (49.0) <sup>c</sup>	4.35 (45.1) <sup>c</sup>	8	(-3.91) <sup>c</sup>	(-8.0) <sup>c</sup>	(1.22) <sup>c</sup>	(2.7) <sup>c</sup>	(1.67) <sup>c</sup>	YES
Specific Conductance (µS/cm)	7.2	7.5	12	0.3	4.2	0.5	6.7	0.3	NO
	28.1	27.9	8	-0.2	-0.7	0.6	2.2	0.6	NO

**Notes:**

- a The first set of values for each parameter is for the 25<sup>th</sup> percentile solution.
- b The second set of values for each parameter is for the 75<sup>th</sup> percentile solution.
- c The pH data in ( ) have been converted to microequivalents.



TABLE IV-4 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS3), Deionized (DI) Water and pH 4.3 QCS, Filtered, 1990									
Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision (mg/L)	Precision RSD (%)	Critical Conc. (mg/L)	Statist. Significant Bias?
Calcium	<0.009 <sup>a</sup>	<0.009	13						
	<0.009 <sup>b</sup>	0.027	12	0.022	440.0 <sup>c</sup>	0.031	114.8	0.020	YES
Magnesium	<0.003	<0.003	13						
	<0.003	0.005	12	0.003	150.0	0.005	100.0	0.003	NO
Sodium	<0.003	0.020	13	0.018	900.0	0.010	50.0	0.006	YES
	<0.003	0.025	12	0.023	1150.0	0.014	56.0	0.009	YES
Potassium	<0.003	<0.003	13						
	<0.003	0.004	12	0.002	100.0	0.004	100.0	0.003	NO
Ammonium	<0.02	0.02	13						
	<0.02	0.03	12	0.02	100.0	0.04	100.0	0.03	NO
Chloride	<0.03	0.04	13	0.02	100.0	0.01	25.0	0.01	YES
	<0.03	0.04	12	0.02	100.0	0.02	50.0	0.01	YES
Nitrate	<0.03	0.03	13						
	3.12	3.12	12	0.00	1.1	0.09	2.88	0.06	NO
Sulfate	<0.03	<0.03	13						NO
	<0.03	<0.03	13						NO
pH units (μeq/L)	5.64 (2.29) <sup>d</sup>	5.57 (2.69) <sup>d</sup>	13	(0.40) <sup>d</sup>	(17.4) <sup>d</sup>	(0.60) <sup>d</sup>	(22.3) <sup>d</sup>	(0.36) <sup>d</sup>	YES
	4.30 (50.1) <sup>d</sup>	4.32 (48.3) <sup>d</sup>	12	(-1.84) <sup>d</sup>	(-3.7) <sup>d</sup>	(2.15) <sup>d</sup>	(4.4) <sup>d</sup>	(3.00) <sup>d</sup>	NO
Specific Conductance (μS/cm)	0.9	1.3	13	0.4	44.4	0.6	46.2	0.4	NO
	21.8	21.4	12	-0.4	-1.8	0.7	3.3	1.0	NO

Notes:  
a The first set of values for each parameter is for DI water. b The second set of values for each parameter is for pH 4.3 QCS.  
c For the purposes of calculation, 0.5 times the MDL is used. d The pH data in ( ) have been converted to microequivalents.

## B. REPLICATE SAMPLES

In an effort to further quantify precision, 2 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, the second is refrigerated for archival purposes, as are all samples of sufficient volume. The third sample is resubmitted to the laboratory for analysis with a different sequential number. After both samples have been analyzed and the data submitted, data management changes the second number back to the original "O" and codes it with a "Q" (quality assurance). The O/Q splits then appear consecutively on ion balance printouts twice a month. At this time the QA specialist inspects the split analysis in an effort to estimate the precision of network samples. The results of the replicate samples' analyses are presented as replicate sample differences and displayed as box plots in Appendix B. Box plots as used in this report have been defined in the glossary (Appendix A).

The information presented in Table IV-5 is a summary of the 173 replicates analyzed in 1990. 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 highest values (Table B-3). The mean difference of the replicate samples indicates that there is no bias when the replicate is subtracted from the original. The box plots of the differences and the standard deviation estimated from duplicate measurements, also defined in the glossary, show a range of differences for each analyte. Calcium, potassium, sodium, and chloride in the higher concentration samples have the largest standard deviations, but the calcium value is less than the standard deviation in the 75th percentile filtered blind samples. Replicate samples have been shipped to the laboratory in buckets, the sample that is analyzed for the major ions has been filtered, and the concentrations are unknown. The variation in the sodium, potassium, and chloride values compared to the blind samples and the QCS would indicate random contamination from handling or greater inherent variability between standard solutions and real samples.

TABLE IV-5 Mean Differences and Standard Deviations Estimated from Replicate Analyses of Network Precipitation Samples, 1990			
Parameter	Mean Difference <sup>a</sup>	Standard Deviation Low Conc.	Standard Deviation High Conc.
Calcium (mg/L)	0.000	0.007	0.016
Magnesium (mg/L)	0.000	0.002	0.002
Sodium (mg/L)	0.001	0.003	0.064
Potassium (mg/L)	0.000	0.003	0.017
Ammonium (mg/L)	0.00	0.02	0.05
Sulfate (mg/L)	0.00	0.01	0.07
Nitrate (mg/L)	0.00	0.02	0.02
Chloride (mg/L)	0.01	0.01	0.13
pH ( $\mu$ eq/L)	0.27	0.60	1.74
Conductivity ( $\mu$ S/cm)	0.08	0.63	0.63
Number of Pairs	173	87	86
Note: a. The difference is calculated by subtracting the reanalysis value from the original value.			

### C. BLANKS

Blank data are used to estimate the contributions of laboratory deionized water, sample filtering, and the buckets and lids used for sample collection and shipping in the measured values reported by the network. Deionized (DI) water is collected from three work areas at random times each week. Leachates from filter blanks, using both DI and pH 4.3 nitric acid, are collected at a different time each week and sent through the laboratory for analysis. Upright and inverted sample collection buckets are leached with the same two solutions overnight.

## 1. Deionized Water Blanks

Deionized water samples were collected from sources in the sample processing work area, the service work area where the buckets were washed, and the atomic absorption laboratory. The median values of the cation and anion analyses from each work area were all below the method detection limits (MDL). Table IV-6 shows the median values for pH and conductivity for the DI water in 1990.

TABLE IV-6 Median Values for pH and Conductivity for Weekly Deionized (DI) Water Blanks, 1990			
	Sample Processing Laboratory	Atomic Absorption Laboratory	Service Laboratory
pH (units)	5.64	5.66	5.64
Conductivity ( $\mu\text{S}/\text{cm}$ )	1.00	1.00	1.10

## 2. Filter Blanks

All NADP/NTN precipitation samples of sufficient volume (>35 mL) are filtered after aliquots have been removed for pH and conductivity and prior to further analysis. In order to assess the contribution of the filtering process to the chemistry of the sample, two sets of filter blanks were analyzed in 1990. The first procedure involved leaching the filter with 300 mL of DI water, then collecting two sequential 50-mL portions of DI water in two separate bottles called A and B. The second procedure was similar to the first except that two sequential 50-mL portions of pH 4.3 nitric acid followed the initial DI rinse. The results of the laboratory analysis of all four weekly filter leachates are presented in Table IV-7. Near-detection limit amounts of calcium were found in the pH 4.3 nitric acid leachates and concentrations of sodium well below the fifth percent of NADP samples (Table III-3) in the A portions of both filtrates. Bottle A most closely resembles a network sample. All other analytes were measured below the MDL. These results are consistent with previous years. The calcium concentrations in the pH 4.3 filtrates approximate the increase seen in the filtered blind samples of the same pH.

TABLE IV-7 Median Analyte Concentrations Found in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Filter Blanks, 1990

Analyte	DI Water A <sup>a</sup>	DI Water B <sup>b</sup>	pH 4.3 Nitric Acid A <sup>a</sup>	pH 4.3 Nitric Acid B <sup>b</sup>
Calcium	<0.009	<0.009	0.014	0.009
Magnesium	<0.003	<0.003	0.003	<0.003
Sodium	0.009	<0.003	0.004	<0.003
Potassium	<0.003	<0.003	<0.003	<0.003
Ammonium	<0.02	<0.02	<0.02	<0.02
Sulfate	<0.02	<0.02	<0.02	<0.02
Nitrate	<0.02	<0.02	3.16 <sup>c</sup>	3.24 <sup>c</sup>
Chloride	<0.02	<0.02	<0.02	<0.02
pH (units) [H <sup>+</sup> ] ( $\mu$ eq/L)	5.69 2.04	5.66 2.19	4.36 <sup>d</sup> 43.6	4.33 <sup>d</sup> 46.8
Conductivity ( $\mu$ S/cm)	1.3	1.1	20.5 <sup>e</sup>	21.3 <sup>e</sup>
Number of Analyses	44	44	44	44

Notes:  
a First 50-mL filtrate after 300-mL DI water filter rinse.  
b Second consecutive 50-mL filtrate after 300-mL DI water filter rinse.  
c Theoretical value equals 3.12 mg/L.  
d Theoretical value equals 4.30 pH units.  
e Theoretical value equals 21.8  $\mu$ S/cm.

### 3. Bucket Blanks

The bucket blank procedure used in 1990 was one that had evolved by the end of 1989. Deionized water in 50- and 150-mL portions and pH 4.3 nitric acid in the same amounts were poured into four separate upright sample collection buckets, swirled, and allowed to sit covered with a snap-on lid overnight. These solutions were then collected in 60-mL sample bottles and sent for analysis. The same procedure was applied to another set of four buckets using standard lids pounded onto the buckets. These buckets were inverted for 24 hours prior to collection of the solutions for analysis.

Analysis of the eight bucket-blank leachates are presented in Tables IV-8 and IV-9. The concentrations of the major ions are expressed as median-measured mass in micrograms ( $\mu\text{g}$ )/bucket. The pH and conductivity values represent the median measurements for the solutions collected from the buckets. The information gathered from these two tables serves to implicate the standard bucket lid as a source of sample contamination. The upright bucket values are at or near the MDL, while the pH and conductance are within the confidence interval for the measurement of the two solutions. The inverted bucket analyses show higher pHs, altered conductivities, and increased calcium, magnesium, sodium, potassium, sulfate, and chloride for the 50-mL leachates. The larger volume appears to have diluted the chloride contamination in the 150-mL samples, however the sulfate concentration has increased in the larger acidified samples.

Box plots of the bucket-blank leachates (Appendix B, Figures B-24-B-33) illustrate the median analyte values as well as the variance of the 1990 analyses. These plots serve to emphasize the variability of the contribution of the bucket lid to the sample chemistry. When viewing the bucket blank plots, it must be remembered that less than detection limit values are expressed as one half the MDL (in  $\mu\text{g}/\text{mL}$ ) times 50 or 150 mL and, therefore, there are no zero values. A median line at the detection limit value with no corresponding "box" indicates no variance from the tenth to ninetieth percentile.

**TABLE IV-8 Median Measured Mass as micrograms ( $\mu\text{g}$ )/Bucket<sup>a</sup> Found in Weekly Upright Bucket Blanks Using Deionized (DI) Water and pH 4.3 Nitric Acid as Leaching Agents, 1990**

Analyte	DI Water (50 mL)	DI Water (150 mL)	pH 4.3 Nitric Acid (50 mL)	pH 4.3 Nitric Acid (150 mL)
Calcium	<0.45	<0.45	0.45	<0.45
Magnesium	<0.15	<0.15	<0.15	<0.15
Sodium	0.20	<0.15	0.25	<0.15
Potassium	<0.15	<0.15	0.20	<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	153.5 (156) <sup>b</sup>	475.5 (468)
Chloride	<1.5	<1.5	<1.5	<1.5
pH (units)	5.61 (5.61)	5.61 (5.61)	4.38 (4.30)	4.35 (4.30)
[H <sup>+</sup> ] ( $\mu\text{eq/L}$ )	0.12 (0.12)	0.37 (0.37)	2.3 (2.50)	6.7 (7.52)
Conductivity ( $\mu\text{S/cm}$ )	1.4 (1.0)	1.3 (1.0)	20.2 (21.8)	21.2 (21.8)
Number of Analyses	41	41	41	41

Notes:  
a Mass/bucket = the concentration in  $\mu\text{g/mL}$  x 50 or 150 mL.  
Detection limit values are expressed as the MDL (in  $\mu\text{g/mL}$ ) x 50 mL.  
b Values in parentheses represent those of DI water or pH 4.3 nitric acid analyzed with no bucket contact.

**TABLE IV-9 Median Measured Mass as ( $\mu\text{g}$ )/Bucket<sup>a</sup> Found in Weekly Inverted Bucket Blanks Using Deionized (DI) Water and pH 4.3 Nitric Acid as Leaching Agents, 1990**

Analyte	DI Water (50 mL)	DI Water (150 mL)	pH 4.3 Nitric Acid (50 mL)	PH 4.3 Nitric Acid (150 mL)
Calcium	1.10	2.10	1.85	2.25
Magnesium	0.25	0.45	0.35	0.45
Sodium	0.80	0.90	0.90	1.20
Potassium	0.30	0.45	0.45	0.45
Ammonium	<1.0	<1.0	<1.0	<1.0
Sulfate	3.0	<1.5	4.0	6.0
Nitrate	<1.5	<1.5	150.0 (156) <sup>b</sup>	472.5 (468)
Chloride	2.0	<1.5	2.0	<1.5
pH (units)	6.24 (5.64)	6.01 (5.64)	4.56 (4.30)	4.40 (4.30)
[H <sup>+</sup> ] ( $\mu\text{eq/L}$ )	0.03 (0.11)	0.15 (0.34)	1.38 (2.50)	2.08 (7.52)
Conductivity ( $\mu\text{S/cm}$ )	2.0 (1.0)	1.3 (1.0)	15.1 (21.8)	19.0 (21.8)
Number of Analyses	41	41	41	41

**Notes:**

**a** Mass/bucket = the concentration in  $\mu\text{g/mL}$  x 50 or 150 mL.

Detection limit values are expressed as the MDL (in  $\mu\text{g/mL}$ ) x 50 mL.

**b** Values in parentheses represent those of DI water or pH 4.3 nitric acid analyzed with no bucket contact.



## V. MONTHLY QUALITY ASSURANCE PROCEDURES

Monthly laboratory QC results are evaluated as they become available. The control charts generated from the daily analysis of QCS are plotted and the monthly mean values and standard deviations are calculated for each parameter. This information is kept in notebooks in the QA specialist's office as an historical record of daily analytical results. Printouts mailed to each site from the CAL are also sent monthly to the QA specialist to allow the review of the internal blind audit samples. Twice a month the CAL data management group generates a computer printout of the most recent complete data sets of the analyses of 400 or 500 network samples. From these data, a list of samples to be reanalyzed are flagged according to reanalysis criteria discussed below. Additionally, the analyses of samples submitted to the laboratory by the USGS as part of the External Audit Interlaboratory Comparison are evaluated at the CAL prior to the data being sent to the USGS.

### A. REANALYSIS PROCEDURES

Twice a month a computer printout containing the chemical analysis of four or five hundred samples is generated by the data management staff. Samples are flagged for either an anion/cation imbalance or difference between the calculated and measured specific conductance using the same computer algorithm as in the three previous years.

#### 1. Ion Percent Difference

Ion concentrations measured in milligrams per liter (mg/L) are converted to microequivalents per liter ( $\mu\text{eq/L}$ ) using the factors listed in Table V-1 (11). The measured ion values and pH, in addition to the calculated values for bicarbonate and hydroxide, are used to calculate the ion percent difference (IPD). 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 $\mu\text{eq/L}$	and IPD > $\pm 60\%$
50 $\leq$ IS < 100 $\mu\text{eq/L}$	and IPD > $\pm 30\%$
IS $\geq$ 100 $\mu\text{eq/L}$	and IPD > $\pm 15\%$

## 2. Conductance Percent Difference

Conductance percent difference (CPD) is an operation performed to compare the calculated and measured conductivity. The ion concentrations, expressed as  $\mu\text{eq/L}$ , are multiplied by the conductance conversion factors listed in Table V-2 (12), summed, and then divided by 1000 in order to calculate the theoretical conductivity. This value is then compared to the measured conductivity and the CPD is calculated:

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

Samples are flagged for reanalysis if:  
10% < CPD < -40%

A complete reanalysis is made of all samples selected, providing sufficient volume remains and the sample is not physically or chemically contaminated. When the reanalysis of the samples chosen has been completed, the QA 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 laboratory's computerized database along with the original analyses.

## 3. IPD and CPD Histograms

Of the 11,600 sample analyses entered in 1990, 623 were flagged for reanalysis, and 242 data changes were made to 138 samples. Figures V-1 and V-2 are histograms of the IPD and CPD values for samples having a volume of more than 35 mL. The median, mean, standard deviation, and number of wet samples are presented on each figure.

The IPD histogram exhibits a positive skew as it always has and the mean (2.60%) and median (2.18%) are the lowest they have been since 1985. The CPD continues to exhibit a negative skew with a mean value (-7.94%) the least negative since the network expanded to western sites. The median value (-5.81) is similar to the 1989 value.

<b>TABLE V-1</b> <b>Factors Used to Convert Milligrams per</b> <b>Liter (mg/L) to Microequivalents per</b> <b>Liter (<math>\mu</math>eq/L) for IPD Calculations</b>	
<b>Analyte</b>	<b>Conversion</b> <b>Factor</b>
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

<b>TABLE V-2</b> <b>Factors Used to Convert Microequivalents</b> <b>per Liter (<math>\mu</math>eq/L) to Equivalent</b> <b>Conductance for CPD Calculations</b>	
<b>Analyte</b>	<b>Conversion</b> <b>Factor</b>
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

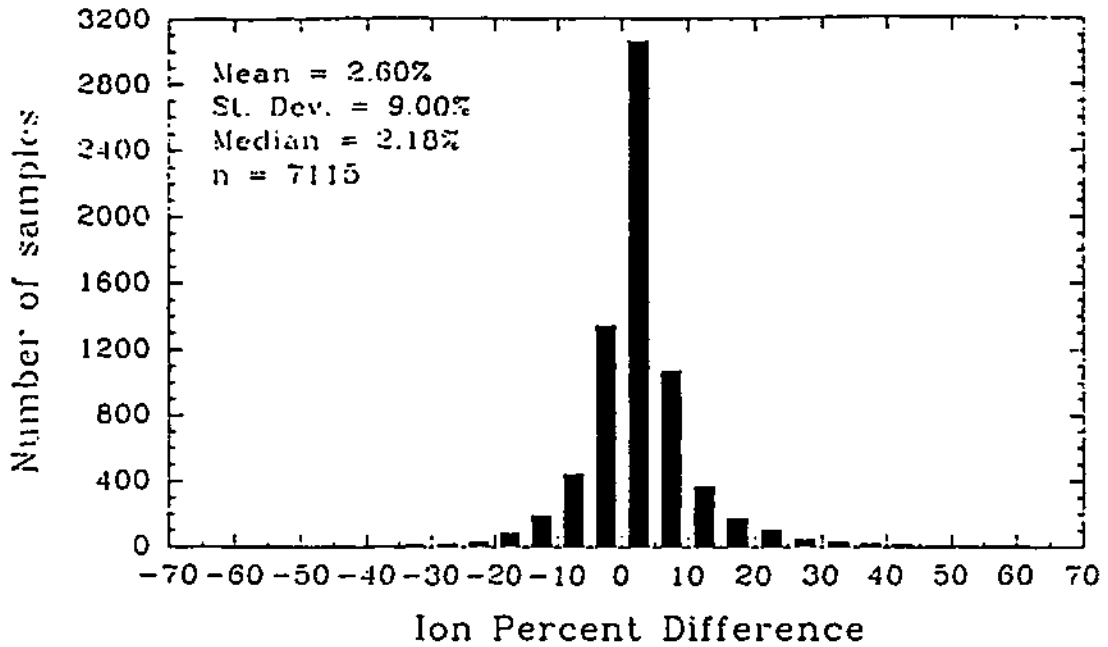


FIGURE V-1. Ion Percent Difference (IPD) histogram for NADP/NTN wet-side samples, 1990.

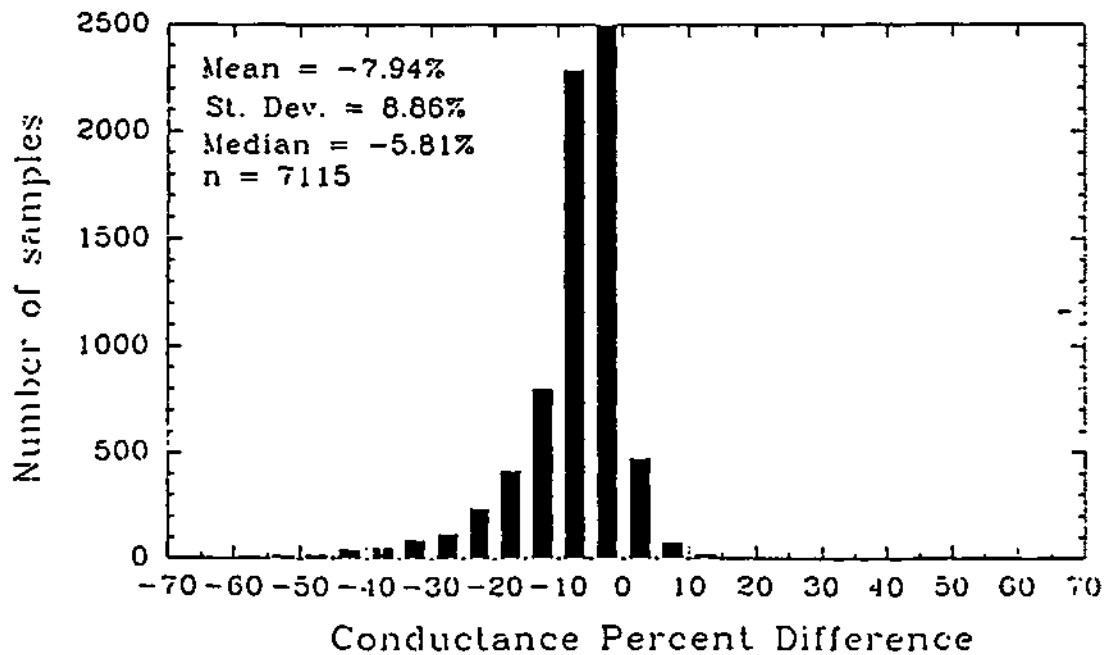


FIGURE V-2. Conductance Percent Difference (CPD) histogram for NADP/NTN wet-side samples, 1990.

## B. USGS INTERLABORATORY COMPARISON

As specified in the NADP/NTN QA program, the USGS serves as the primary external auditor of the CAL. There are several components of the external auditing process. 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 blind samples of differing matrices are mailed to the participating laboratories.

The interlaboratory-comparison program included three laboratories for either all or part of 1990: (1) CAL, (2) Inland Water Directorate, National Water Quality Laboratory (IWD), and (3) Environmental Science and Engineering, Inc. (ESE). Samples from three sources were used: (1) Synthetic wet-deposition and ultrapure deionized-water prepared by the USGS, (2) concentrates prepared by the USEPA and diluted by the USGS, (3) standard reference samples prepared and certified by the National Institute of Standards and Technology (NIST), and (4) natural wet-deposition samples prepared by CAL.(13)

Each month, as these blind samples arrive, they are analyzed by CAL chemists, and the results are recorded on interlaboratory comparison sample data sheets. The sheets are submitted to the QA specialist for inspection and then sent to data management for computer entry. The reanalysis program used for network samples is run on the intercomparison data, and the IPD and CPD are calculated. Suspect results are rechecked before the final compilation is sent to the USGS in Denver.

The analytical results from the 1990 program have been summarized in three statements. No statistically significant differences were observed between the participating laboratories. For the NIST certified samples, the CAL had the greatest number of median analyses that were significantly different from certified values. The CAL was the only laboratory that reported no false positives for the analyses of ultrapure deionized water. (13)



## **VI. SEMI-ANNUAL AND ANNUAL QUALITY ASSURANCE PROCEDURES**

Each year, when all of the data for the samples analyzed during the January 1-December 31 period have been entered into the computer files, the QA data from the several sources are retrieved and summarized for annual QA reports and scientific presentations. The results of the USGS external audit are summarized for the same period of time. This audit includes a blind audit sample procedure as well as the interlaboratory comparison. In addition, in 1990 the CAL participated, on a voluntary basis, in five interlaboratory comparison studies: two conducted by the U. S. Environmental Protection Agency (USEPA) and three conducted by the Canada National Water Research Institute.

### **A. U.S. GEOLOGICAL SURVEY EXTERNAL AUDIT PROGRAM**

The U.S. Geological Survey's NADP/NTN external audit program consists of two CAL components: a blind audit sample procedure and an interlaboratory comparison study. The data are used to evaluate the effects of sample handling and shipping on the bias and precision of analyte determinations and to determine the comparability, bias, and precision of analytical results obtained by separate laboratories routinely measuring wet deposition. The results of this program are published annually and available in report form from the USGS (13).

In 1990, thirty-two blind audit samples were sent to selected NADP/NTN site operators each quarter. In addition, 250-, 500-, and 1000-mL samples were sent to assess volume-related biases. Detailed sample processing instructions accompanied each blind-audit sample. Six solutions were used: pH 4.3 nitric acid prepared by the CAL, a solution prepared by the USGS Standard Reference Water Project, two solutions prepared by the USGS Acid Rain Project, and two concentrates prepared by the USEPA and diluted by the USGS Acid Rain Project. The samples were sent to the selected site operators and split as directed so that approximately 75 percent of the solution was shipped to the CAL in the bucket and the remaining solution was sent in the bottle. Both samples were analyzed as routine network samples in order to determine the effects of sample handling, shipping and processing. Complete bucket-bottle analyses were available for 119 of the 128 samples sent. At a significance level of  $\alpha = 0.01$ , bias existed for calcium, magnesium, sodium, potassium, chloride, nitrate, sulfate, hydrogen and specific conductance. Only ammonium was not biased. The median determinations for the bucket samples were less than the bottle samples for hydrogen and specific conductance. The other biased ions exhibited a positive bucket bias. The same positive and negative biases appeared in the 1989 bucket-bottle study.

The volume study results showed that the amount of contamination attributable to the sample collection bucket is independent of sample volume for some analytes and may be positively correlated to volume for others. Slight decreases in the median difference between the bucket and bottle analyses as volume increased were measured for calcium, magnesium, and potassium. The median absolute difference in hydrogen ion concentration and specific conductance decreased as the bucket sample volume increased. The median difference between the bucket and bottle concentrations for sodium, ammonium, chloride, nitrate, and sulfate were less in the 500 mL and 1000 mL samples compared to the 250 mL samples, although the concentration change was not consistent.(13)

The USGS interlaboratory-comparison program results are summarized in the previous section.

## **B. INTERLABORATORY COMPARISON STUDIES**

In 1990, CAL participated in interlaboratory performance studies conducted by the U.S. Environmental Protection Agency and the Canada National Water Research Institute. The analytical data for the samples analyzed are presented in the tables in Appendix C.

### **1. U.S. Environmental Protection Agency**

The USEPA in Research Triangle Park, North Carolina contracted NSI Technology Services Corporation to administer their semi-annual Acid Rain Audit in 1990. CAL participated in the studies conducted in May and November. The number of reported values within each percent difference category was corrected or normalized to 100 and presented within increments of 5 percent as in 1989. The number of participating laboratories was not included in the report.

The results of the analysis of the ten major chemical and physical parameters routinely measured by CAL are listed in Tables C-1 and C-2. The mean percent difference for the CAL analyses was 3.58 percent in June and 5.39 percent in November. These results are comparable to past CAL performances in these studies.



## 2. Canada National Water Research Institute

The Canadian program for Long-Range Transport of Atmospheric Pollutants (LRTAP) was begun in 1982. CAL has been a participant since the fourth study, which took place in the fall of 1983. In 1990, CAL participated in Studies L-23(14), L-24(15), and L-25(16). The LRTAP studies consist of selected major ions, nutrients, and physical measurements in water. Medians have been used as target values for flagging results, since true values are unknown. CAL performance in all three studies was rated "satisfactory." The CAL performance ranked first out of the 60 laboratories participating in L-23. Although no results were flagged in L-24, a slight bias high for pH was noted and the overall ranking was 17th out of 58 laboratories. Nitrate-nitrogen was flagged extremely low and chloride was low for sample #10 in L-25. The overall ranking for this study placed CAL third out of the 58 participating laboratories. The comparison of CAL-reported values to the median values for all laboratories are found on Tables C-3-C-5 in Appendix C.



## VII. SUMMARY

This QA Report summarizes the various QC procedures followed at CAL during 1990. Quality control began the moment the sample containers entered the laboratory, and it continued throughout the laboratory analyses and data reporting. The various activities of the NADP/NTN program have been described and the analytical results presented.

Calibration of the various instruments used to measure the physical and chemical characteristics of the samples occurred each time the instrument or procedure was begun. Independently produced reference solutions of simulated rain at the 25th and 75th percentile concentrations of network samples were used the entire year to monitor the accuracy of the calibration standards and instrument performance. The summary of the repeated analyses of these solutions, from which monthly control charts were produced, is presented and indicates that the bias and precision of these samples were within the goals of the network. Further bias and precision data were gathered from the analysis of samples submitted weekly in the internal blind audit program. The reference solutions used for calibration validation were also used in 1990 for the internal blind audit program. Two blank solutions were also submitted. The results from this program showed similar bias for the major ions, similar precision for the anions, and less precision for the cations compared to the results from the QCS. Comparison of the unfiltered and filtered blind solutions showed a slight increase in calcium, sodium, ammonium, and chloride in one or both concentrations. The sulfate concentrations decreased in the filtered solutions as in previous years. The variation seen in the replicate sample analyses was similar to the filtered blind samples with an implied sample-handling influence.

The DI analysis from three laboratory sources shows it to be of excellent quality. Analysis of DI and pH 4.3 nitric acid, which has passed through preleached filters, indicated near-detection limit amounts of calcium and magnesium in the pH 4.3 solution and near detection limit values of sodium in the A portions of both solutions. The results from the analysis of bucket leachates showed no influence from the upright buckets and increased concentrations of all of the metals, as well as sulfate and chloride in the inverted buckets. The pH and conductance of all four solutions were slightly altered. The effect is much more pronounced in small (50 mL) volume samples than in larger volume (150 mL) test solutions for most analytes.

The reanalysis program has not changed since 1987. Approximately 5.4 percent of the samples analyzed were flagged for reanalysis and 1.0 percent of the samples required changes to their initial chemical analysis. These changes represent 0.19 percent of all of the analytes measured. The positive skew of the IPD histogram was less than it had been since 1985. The CPD histogram exhibited a negative skew with a similar median value to 1989 and a less negative mean value than the previous year.

The USGS external audit of the CAL consisted of the blind audit sample procedure and the interlaboratory comparison study. The bucket-bottle analyses comparisons showed that only ammonium was not biased. The median bucket sample concentrations were less than the bottle values for hydrogen and conductivity. The other ions exhibited a positive bucket bias. The inter laboratory comparison showed the median values from the participating laboratories to be comparable. CAL had the most significantly different values for the NIST certified simulated rain but was the only laboratory that reported no false positives for the analysis of ultrapure deionized water.

Participation in interlaboratory comparison studies conducted by the USEPA and the Canada National Water Research Institute indicated that the CAL results compared favorably to those of its peers.

APPENDIX A

GLOSSARY OF TERMS



## GLOSSARY OF TERMS

Term	Abbreviation	Definition
<b>Accuracy</b>		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).
<b>Bias</b>		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.
<b>Box Plot</b>		A graphical summary representation of the distribution of a set of data, the top and bottom of the box representing the 25th and 75th percentile. The horizontal line represents the median concentration, and the lower and upper Ts extend to the 10th and 90th percentile concentrations.
<b>Control Chart</b>		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 (17).
<b>Critical Concentration</b>		A calculated concentration used to determine if the measured bias is or is not statistically significant (18).

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

Term	Abbreviation	Definition
		where:
		$S_{sp} = \sqrt{\frac{(n_1 - 1) s_1^2 + (n_2 - 1) s_2^2}{n_1 + n_2 - 2}}$
		S <sub>sp</sub> = pooled standard deviation
		S <sub>1</sub> = standard deviation of reference solution measurements
		s <sub>2</sub> = standard deviation of daily QCS measurements
		n = number of values
		t = t statistic at the 95% confidence level and (n <sub>1</sub> + n <sub>2</sub> ) - 2 degrees of freedom
<b>External Blind Sample</b>		A QA sample of known analyte concentrations submitted to the laboratory by an external agency. At CAL these samples arrive as normal weekly rain samples and undergo routine processing and analysis. The identity of the sample is unknown to CAL until all analyses are complete. Data are used to assess contamination potential from handling and shipping.
<b>Internal Blind Sample</b>		A QA sample of known analyte concentrations submitted to the laboratory by the QA 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.
<b>Mean</b>	$\bar{x}$	The average obtained by dividing a sum by the number of its addends. $\bar{x} = \frac{\sum_{i=1}^n x_i}{n}$



Term	Abbreviation	Definition
<b>Mean Bias</b>		The sum of the bias for each sample divided by the total number of replicates (n).
<b>Mean Percent Recovery</b>		The sum of the percent recovery for each sample divided by the number of replicates (n).
<b>Method Detection Limit</b>	<b>MDL</b>	The minimum concentration of an analyte that can be reported with 99 percent confidence that the value is greater than zero (19).
<b>Percent Bias</b>		<p>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.</p> $\%Bias = 100 * [(V_m - V)/V]$ <p>where: <math>V_m</math> = measured value <math>V_t</math> = true value</p>
<b>Precision</b>		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).
<b>Quality Assessment</b>		The system of procedures that ensures that QC practices are achieving the desired goal in terms of data quality. Included is a continuous evaluation of analytical performance data.
<b>Quality Assurance</b>	<b>QA</b>	An integrated system of activities involving planning, QC, reporting, and remedial action to ensure that a product or service meets defined standards of quality.

Term	Abbreviation	Definition
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:  $RSD = 100 * (s/\bar{x})$ 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.

$$s = \sqrt{\frac{\sum (x_1 - \bar{x})^2}{n-1}}$$

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Term	Abbreviation	Definition
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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 (17):

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

where:  $d$  = difference of duplicate measurements

$k$  = number of sets of duplicate measurements



APPENDIX B

Weekly Procedures: Tables and Figures

1990



**TABLE B-1 Comparison of Filtered and Unfiltered Internal Blind Samples  
Using Simulated Rain Representing the 25<sup>th</sup> Percentile Concentration  
of NADP/NTN Network Wet Samples, 1990**

<b>Parameter</b>	<b>Target Conc.</b>	<b>Measured Conc.</b>	<b>Number of Values (n)</b>	<b>Standard Deviation (s)</b>	<b>% RSD</b>	<b>Bias</b>	<b>%Bias</b>
<b>Calcium</b>	<b>0.077</b>	<b>0.076<sup>a</sup></b>	<b>21</b>	<b>0.007</b>	<b>9.2</b>	<b>-0.001</b>	<b>-1.3</b>
		<b>0.076<sup>b</sup></b>	<b>12</b>	<b>0.012</b>	<b>15.8</b>	<b>-0.001</b>	<b>-1.3</b>
<b>Magnesium</b>	<b>0.018</b>	<b>0.017</b>	<b>21</b>	<b>0.002</b>	<b>11.8</b>	<b>-0.001</b>	<b>-5.6</b>
		<b>0.018</b>	<b>12</b>	<b>0.004</b>	<b>22.2</b>	<b>0.000</b>	<b>0.0</b>
<b>Sodium</b>	<b>0.048</b>	<b>0.046</b>	<b>21</b>	<b>0.010</b>	<b>21.7</b>	<b>-0.002</b>	<b>-4.2</b>
		<b>0.064</b>	<b>12</b>	<b>0.011</b>	<b>17.2</b>	<b>0.016</b>	<b>33.3</b>
<b>Potassium</b>	<b>0.014</b>	<b>0.014</b>	<b>21</b>	<b>0.007</b>	<b>50.0</b>	<b>0.000</b>	<b>0.0</b>
		<b>0.016</b>	<b>12</b>	<b>0.007</b>	<b>43.8</b>	<b>0.002</b>	<b>14.3</b>
<b>Sulfate</b>	<b>0.64</b>	<b>0.63</b>	<b>21</b>	<b>0.01</b>	<b>1.6</b>	<b>-0.01</b>	<b>-1.6</b>
		<b>0.62</b>	<b>12</b>	<b>0.01</b>	<b>1.6</b>	<b>-0.02</b>	<b>-3.1</b>
<b>Nitrate</b>	<b>0.48</b>	<b>0.48</b>	<b>21</b>	<b>0.01</b>	<b>2.1</b>	<b>0.00</b>	<b>0.0</b>
		<b>0.49</b>	<b>12</b>	<b>0.01</b>	<b>2.0</b>	<b>0.01</b>	<b>2.1</b>
<b>Chloride</b>	<b>0.14</b>	<b>0.15</b>	<b>21</b>	<b>0.02</b>	<b>13.3</b>	<b>0.01</b>	<b>7.1</b>
		<b>0.16</b>	<b>12</b>	<b>0.01</b>	<b>6.2</b>	<b>0.02</b>	<b>14.3</b>
<b>Ammonium</b>	<b>0.09</b>	<b>0.08</b>	<b>21</b>	<b>0.02</b>	<b>25.0</b>	<b>-0.01</b>	<b>-11.1</b>
		<b>0.12</b>	<b>12</b>	<b>0.02</b>	<b>16.7</b>	<b>0.03</b>	<b>33.3</b>
<b>H<sup>+</sup> (<math>\mu</math>eq/L)</b>	<b>12.6</b>	<b>12.2</b>	<b>21</b>	<b>0.77</b>	<b>6.32</b>	<b>-0.41</b>	<b>-3.2</b>
		<b>12.5</b>	<b>12</b>	<b>0.84</b>	<b>6.73</b>	<b>0.10</b>	<b>-0.8</b>
<b>Conductivity (<math>\mu</math>S/cm)</b>	<b>7.2</b>	<b>7.8</b>	<b>21</b>	<b>0.8</b>	<b>10.3</b>	<b>0.6</b>	<b>8.3</b>
		<b>7.5</b>	<b>12</b>	<b>0.5</b>	<b>6.7</b>	<b>-0.3</b>	<b>-4.2</b>

**Notes:**

- a. The first set of values for each parameter is for unfiltered samples.
- b. The second set of values for each parameter is for filtered samples.

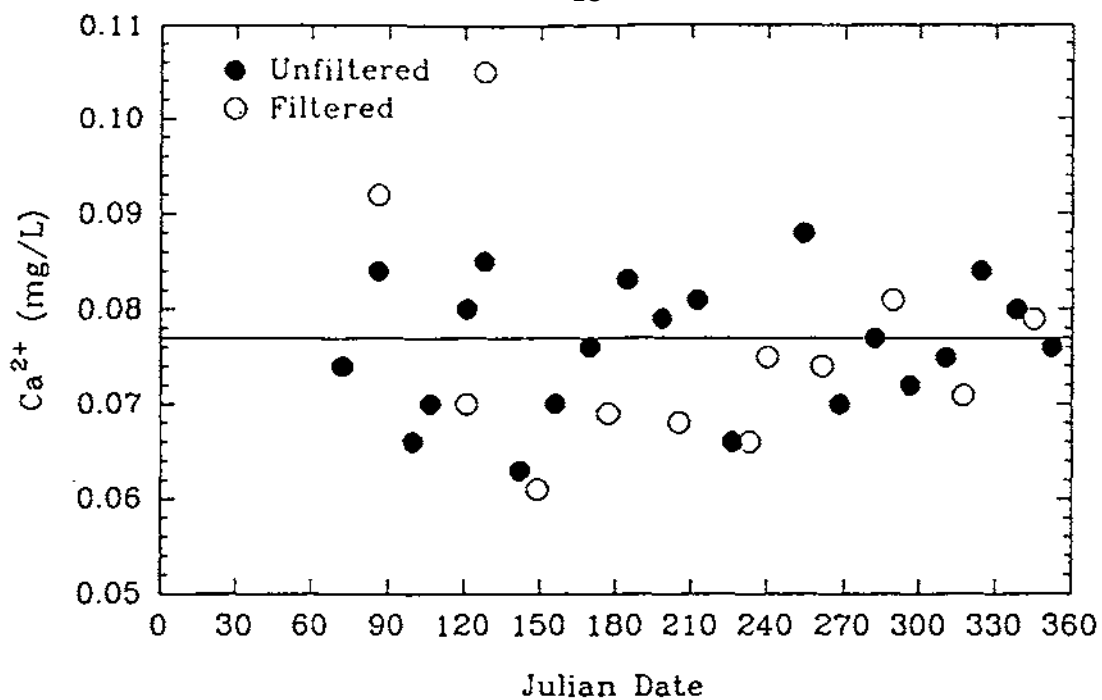


FIGURE B-1. Comparison of filtered and unfiltered internal blind samples (calcium 25th percentile), 1990.

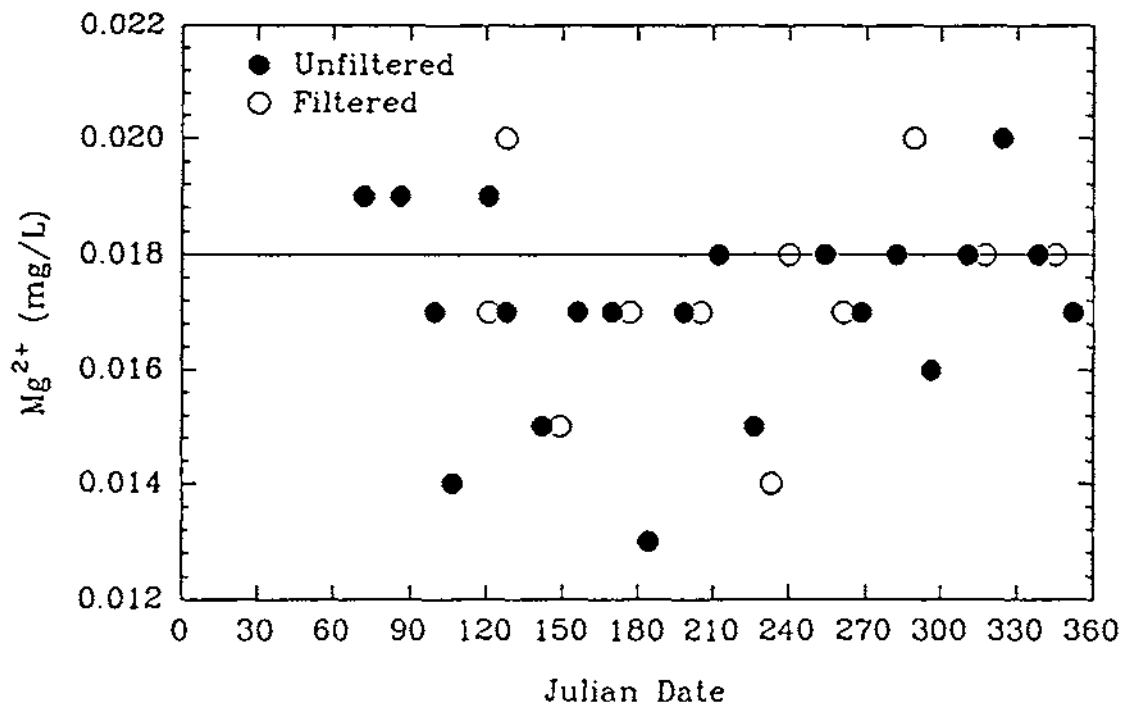


FIGURE B-2. Comparison of filtered and unfiltered internal blind samples (magnesium 25th percentile), 1990.



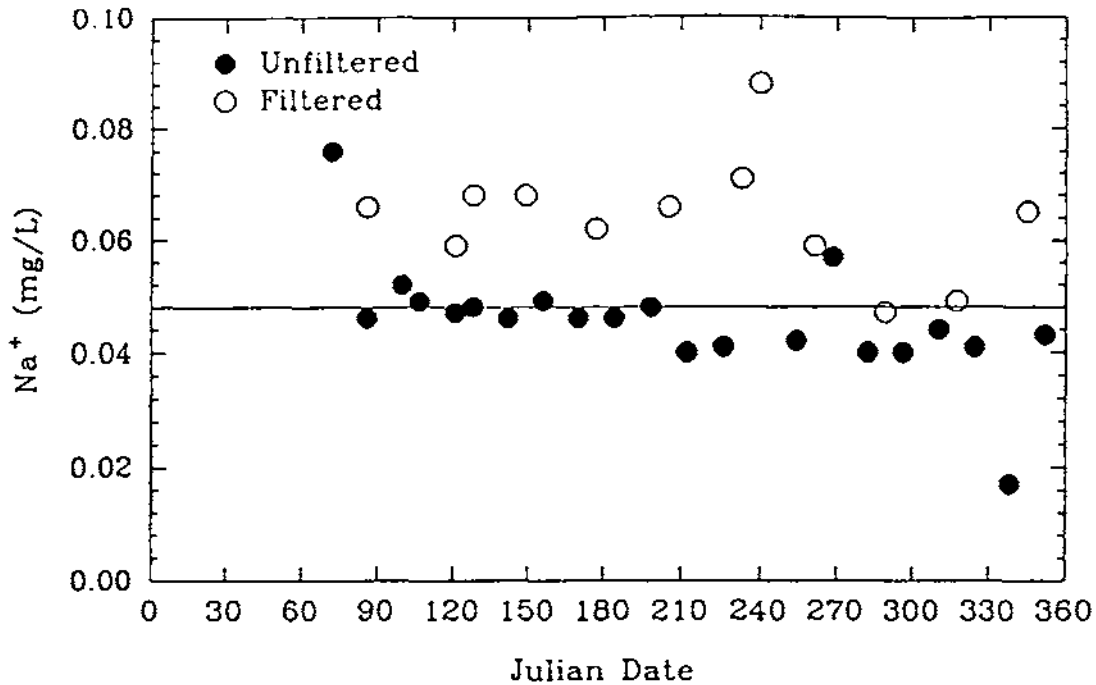


FIGURE B-3. Comparison of filtered and unfiltered internal blind samples (sodium 25th percentile), 1990.

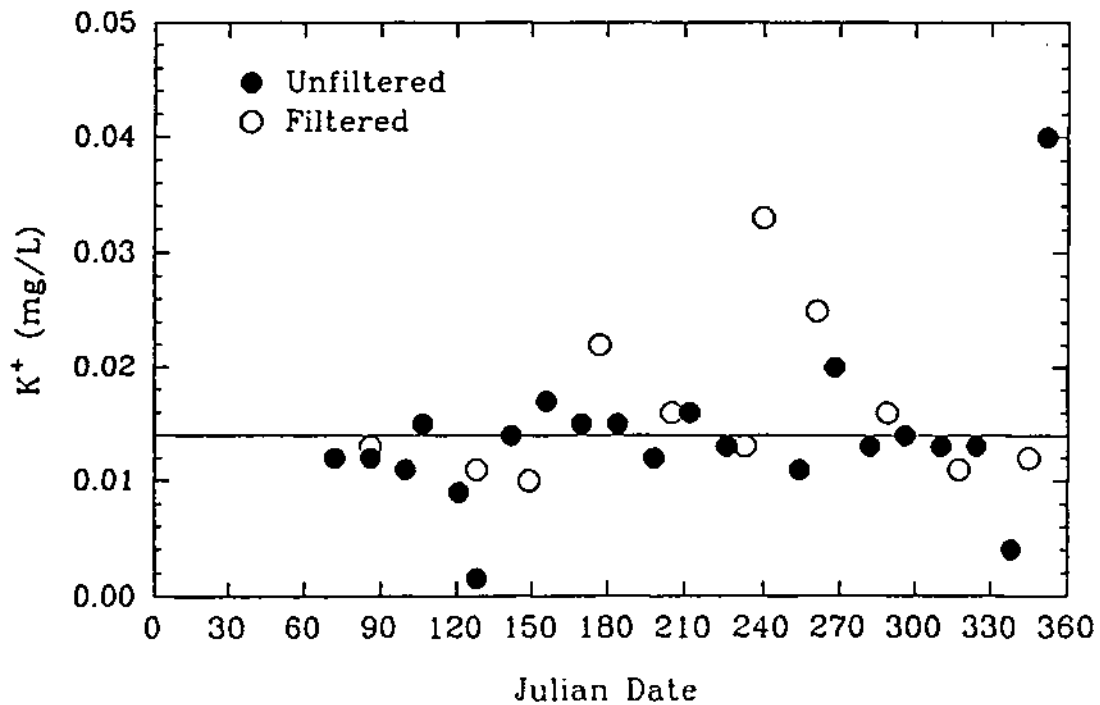


FIGURE B-4. Comparison of filtered and unfiltered internal blind samples (potassium 25th percentile), 1990.

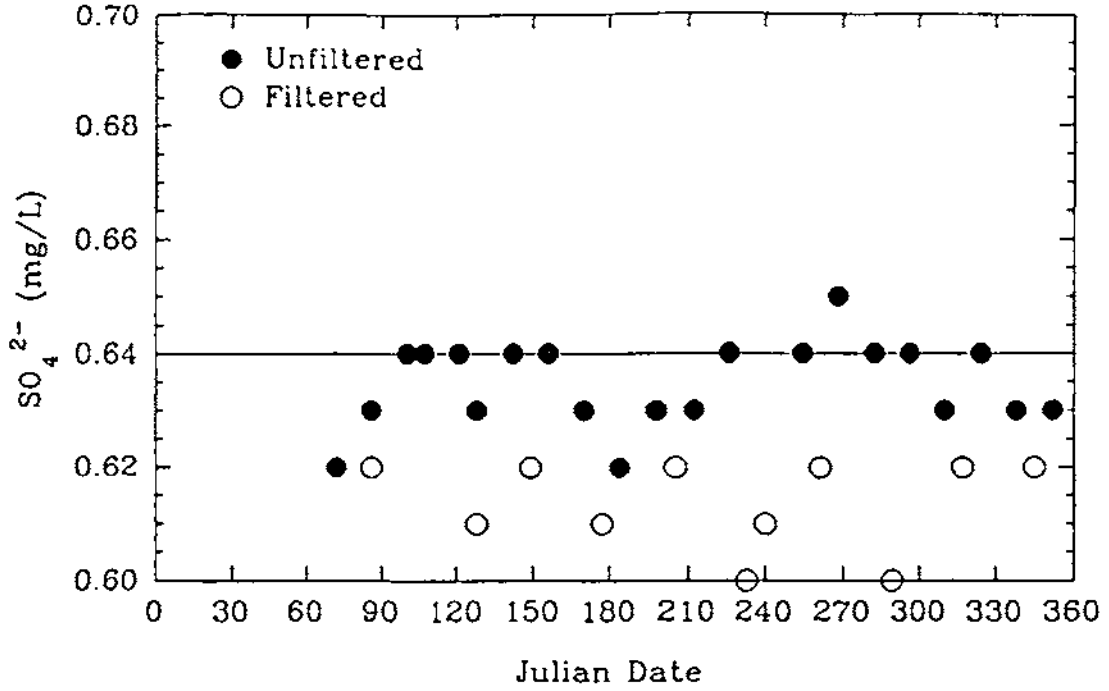


FIGURE B-5. Comparison of filtered and unfiltered internal blind samples (sulfate 25th percentile), 1990.

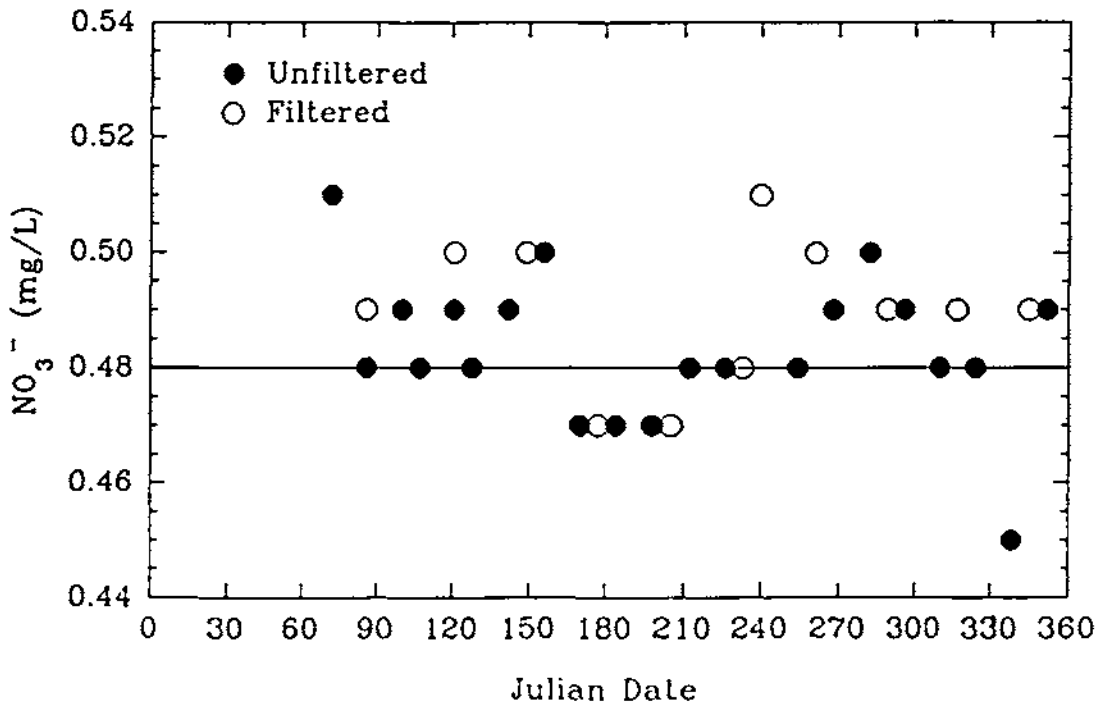


FIGURE B-6. Comparison of filtered and unfiltered internal blind samples (nitrate 25th percentile), 1990.

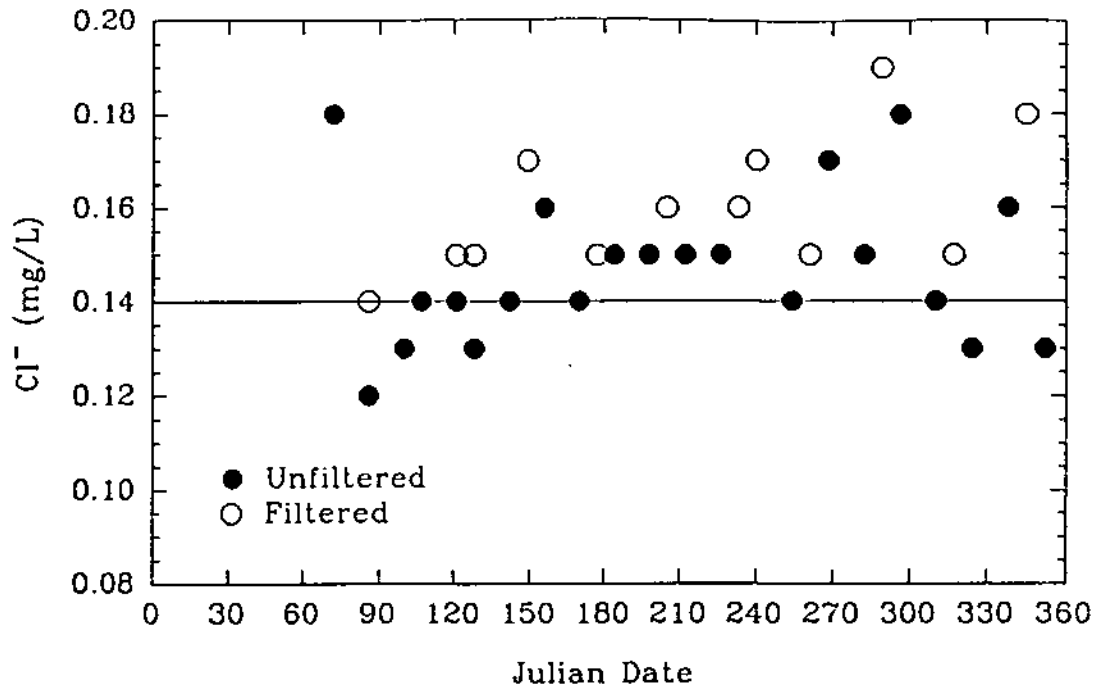


FIGURE B-7. Comparison of filtered and unfiltered internal blind samples (chloride 25th percentile), 1990.

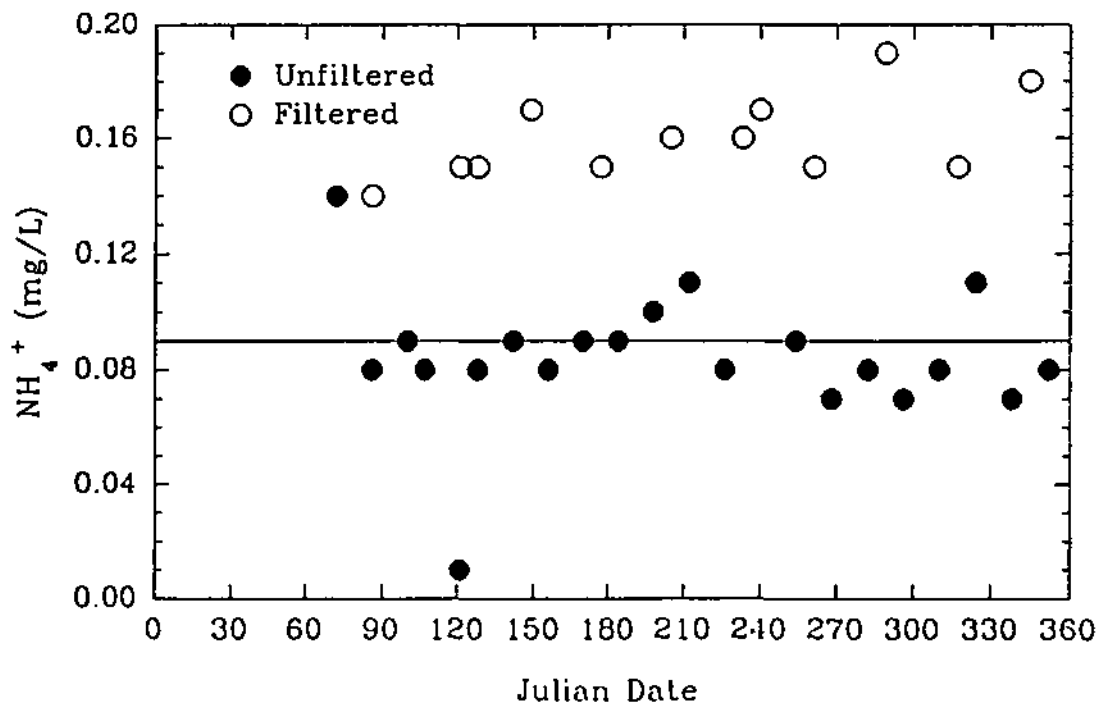


FIGURE B-8. Comparison of filtered and unfiltered internal blind samples (ammonium 25th percentile), 1990.

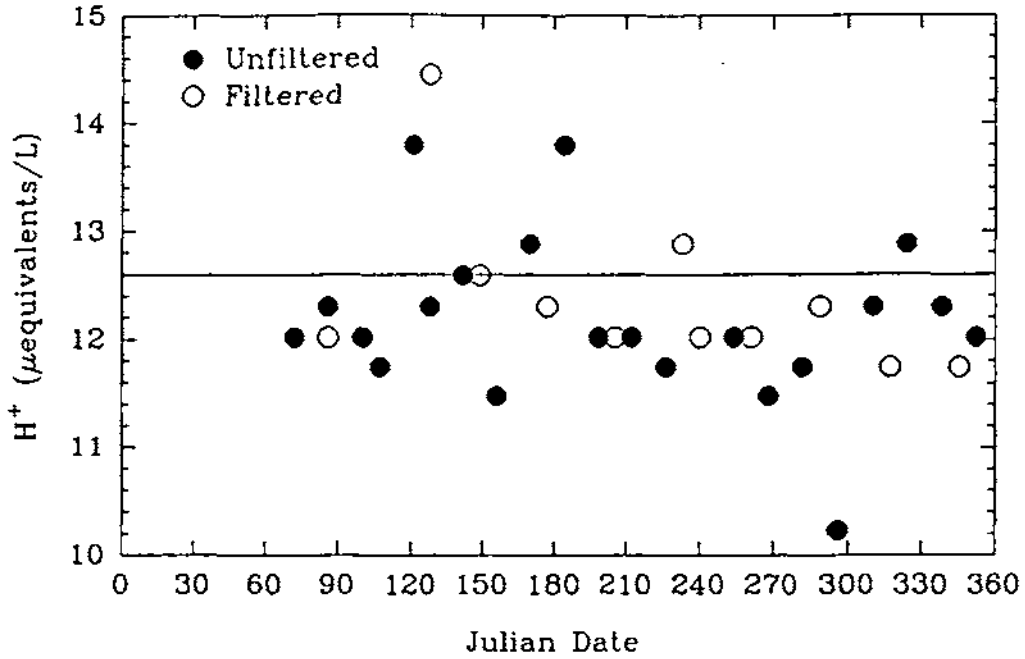


FIGURE B-9. Comparison of filtered and unfiltered internal blind samples ( $H^+$  25th percentile), 1990.

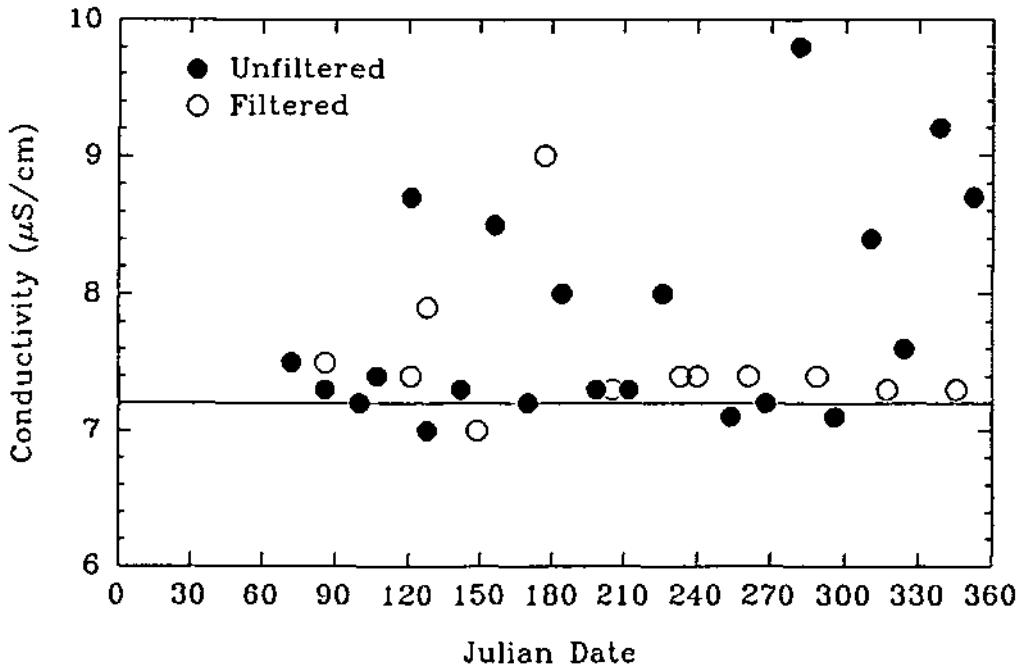


FIGURE B-10. Comparison of filtered and unfiltered internal blind samples (conductivity 25th percentile), 1990.

**TABLE B-2 Comparison of Filtered and Unfiltered Internal Blind Samples  
Using Simulated Rain Representing the 75<sup>th</sup> Percentile Concentrations  
of NADP/NTN Network Wet Samples, 1990.**

<b>Parameter</b>	<b>Target Conc.</b>	<b>Measured Conc.</b>	<b>Number of Values (n)</b>	<b>Standard Deviation (s)</b>	<b>%RSD</b>	<b>Bias</b>	<b>% Bias</b>
<b>Calcium</b>	<b>0.307</b>	<b>0.308<sup>a</sup></b>	<b>20</b>	<b>0.008</b>	<b>2.6</b>	<b>0.001</b>	<b>0.3</b>
		<b>0.320<sup>b</sup></b>	<b>8</b>	<b>0.035</b>	<b>10.9</b>	<b>0.013</b>	<b>4.2</b>
<b>Magnesium</b>	<b>0.070</b>	<b>0.071</b>	<b>20</b>	<b>0.002</b>	<b>2.8</b>	<b>0.001</b>	<b>1.4</b>
		<b>0.071</b>	<b>8</b>	<b>0.003</b>	<b>4.2</b>	<b>0.001</b>	<b>1.4</b>
<b>Sodium</b>	<b>0.190</b>	<b>0.190</b>	<b>19</b>	<b>0.005</b>	<b>2.6</b>	<b>0.000</b>	<b>0.0</b>
		<b>0.203</b>	<b>7</b>	<b>0.010</b>	<b>4.9</b>	<b>0.013</b>	<b>6.8</b>
<b>Potassium</b>	<b>0.055</b>	<b>0.056</b>	<b>19</b>	<b>0.005</b>	<b>8.9</b>	<b>0.001</b>	<b>1.8</b>
		<b>0.054</b>	<b>7</b>	<b>0.002</b>	<b>3.7</b>	<b>-0.001</b>	<b>-1.8</b>
<b>Sulfate</b>	<b>2.58</b>	<b>2.60</b>	<b>20</b>	<b>0.04</b>	<b>1.5</b>	<b>0.02</b>	<b>0.8</b>
		<b>2.47</b>	<b>8</b>	<b>0.05</b>	<b>2.0</b>	<b>-0.11</b>	<b>-4.3</b>
<b>Nitrate</b>	<b>1.94</b>	<b>1.95</b>	<b>20</b>	<b>0.03</b>	<b>1.5</b>	<b>0.01</b>	<b>0.5</b>
		<b>1.91</b>	<b>8</b>	<b>0.04</b>	<b>2.1</b>	<b>-0.03</b>	<b>-1.6</b>
<b>Chloride</b>	<b>0.54</b>	<b>0.53</b>	<b>20</b>	<b>0.01</b>	<b>1.9</b>	<b>-0.01</b>	<b>-1.8</b>
		<b>0.53</b>	<b>8</b>	<b>0.01</b>	<b>1.9</b>	<b>-0.01</b>	<b>-1.8</b>
<b>Ammonium</b>	<b>0.37</b>	<b>0.38</b>	<b>20</b>	<b>0.02</b>	<b>5.3</b>	<b>0.01</b>	<b>2.7</b>
		<b>0.40</b>	<b>8</b>	<b>0.06</b>	<b>15.0</b>	<b>0.03</b>	<b>8.1</b>
<b>H<sup>+</sup> (<math>\mu</math>eq/L)</b>	<b>49.0</b>	<b>45.3</b>	<b>20</b>	<b>2.25</b>	<b>5.0</b>	<b>-3.64</b>	<b>-7.4</b>
		<b>45.1</b>	<b>8</b>	<b>1.22</b>	<b>2.7</b>	<b>-3.91</b>	<b>-8.0</b>
<b>Conductivity (<math>\mu</math>S/cm)</b>	<b>28.1</b>	<b>27.6</b>	<b>20</b>	<b>0.6</b>	<b>2.2</b>	<b>-0.5</b>	<b>-1.8</b>
		<b>27.9</b>	<b>8</b>	<b>0.6</b>	<b>2.2</b>	<b>-0.2</b>	<b>-0.7</b>

**Notes:**

- a. The first set of values for each parameter is for unfiltered samples.
- b. The second set of values for each parameter is for filtered samples.

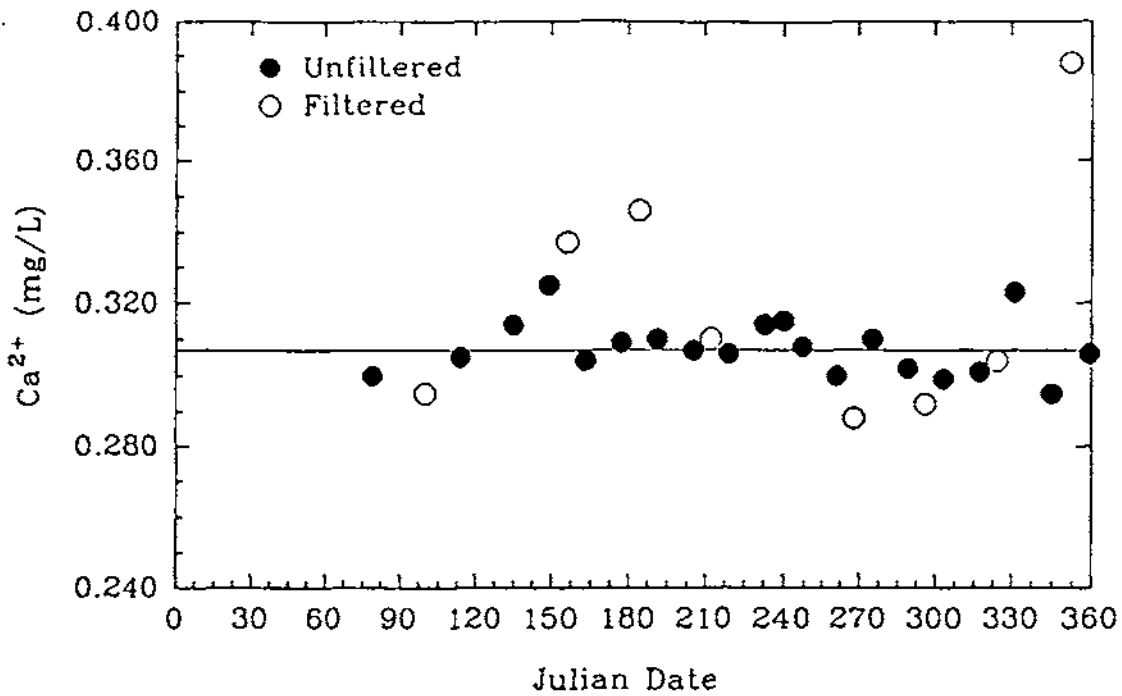


FIGURE B-11. Comparison of filtered and unfiltered internal blind samples (calcium 75th percentile), 1990.

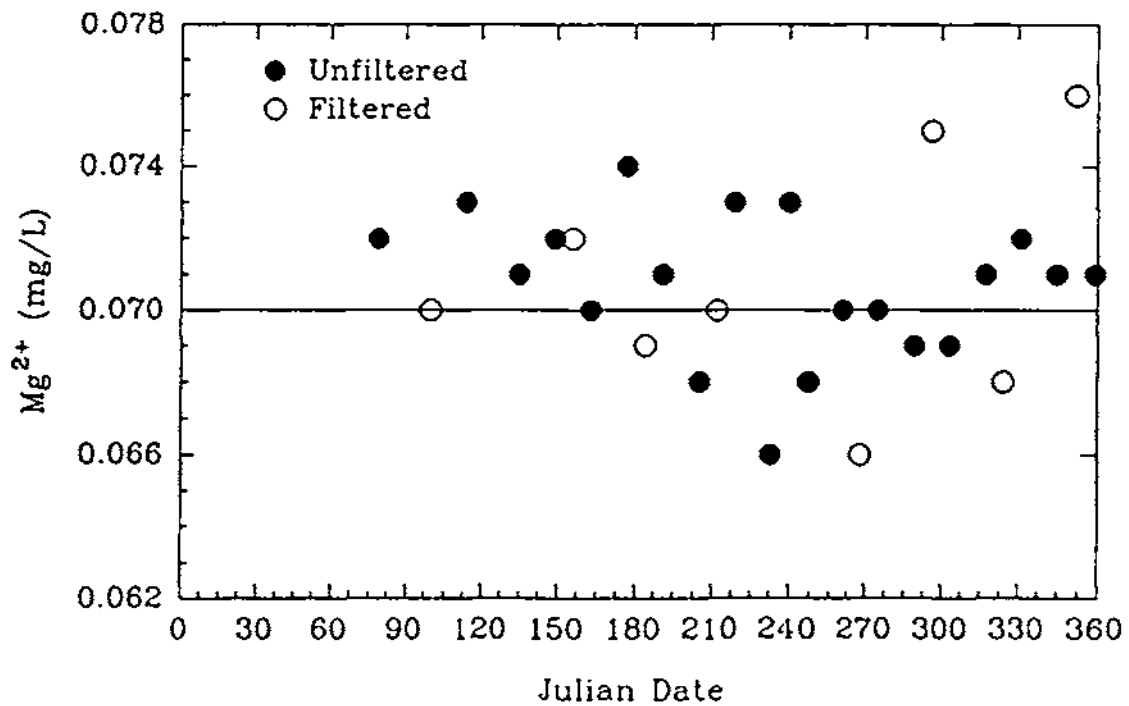


FIGURE B-12. Comparison of filtered and unfiltered internal blind samples (magnesium 75th percentile), 1990.

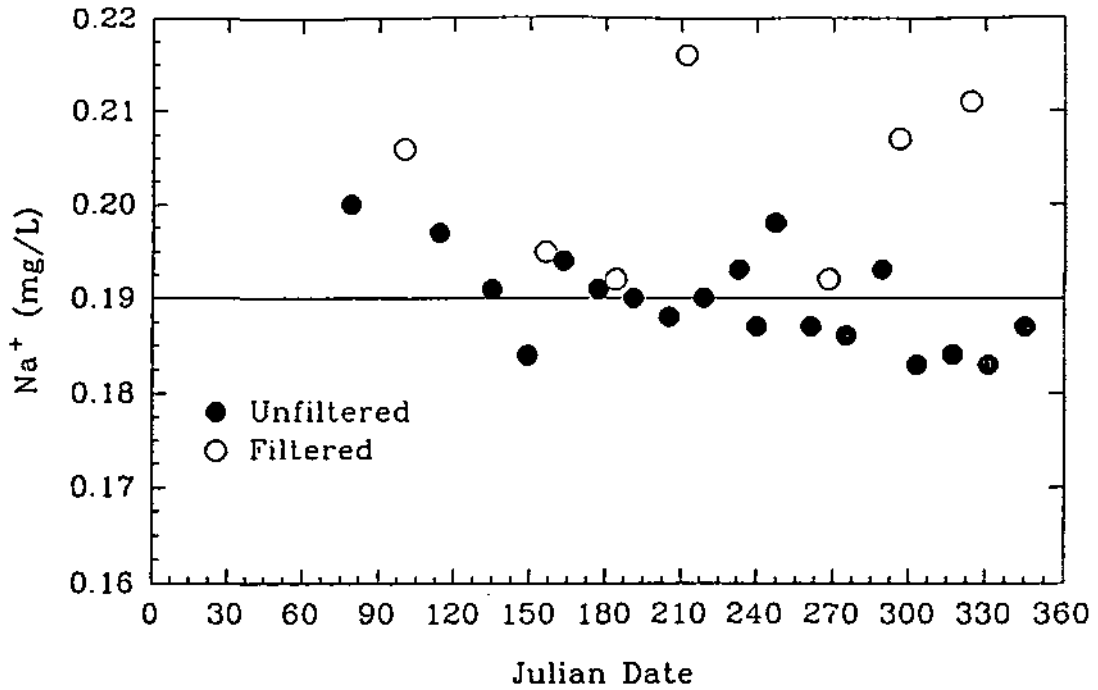


FIGURE B-13. Comparison of filtered and unfiltered internal blind samples (sodium 75th percentile), 1990.

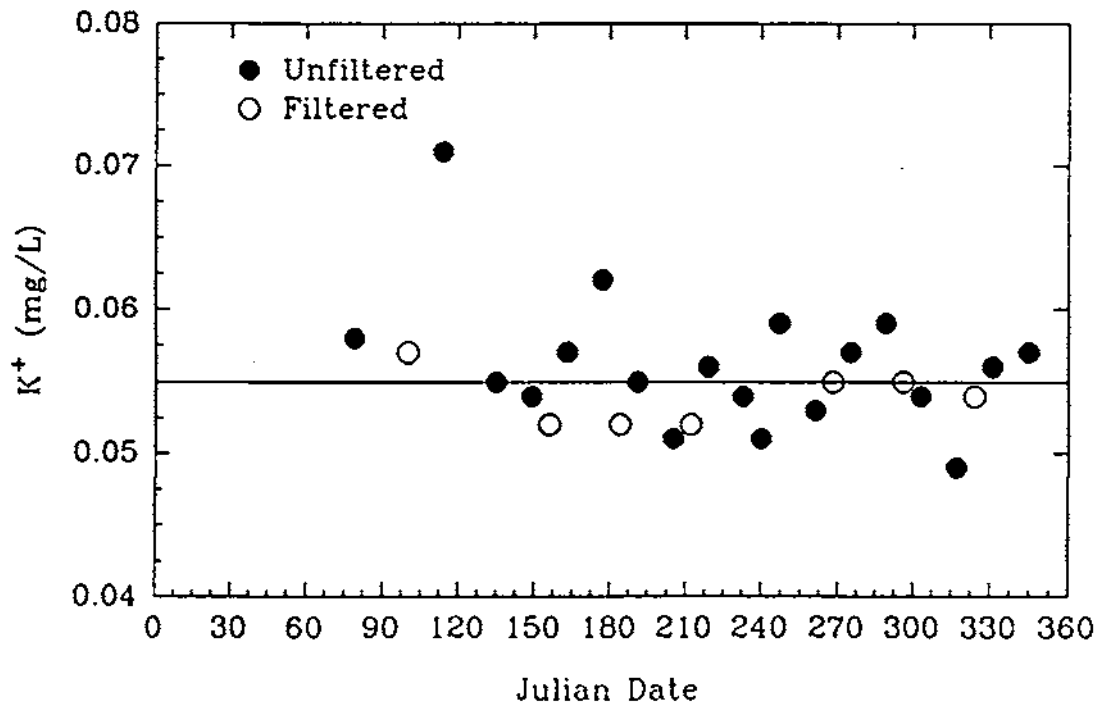


FIGURE B-14. Comparison of filtered and unfiltered internal blind samples (potassium 75th percentile), 1990.

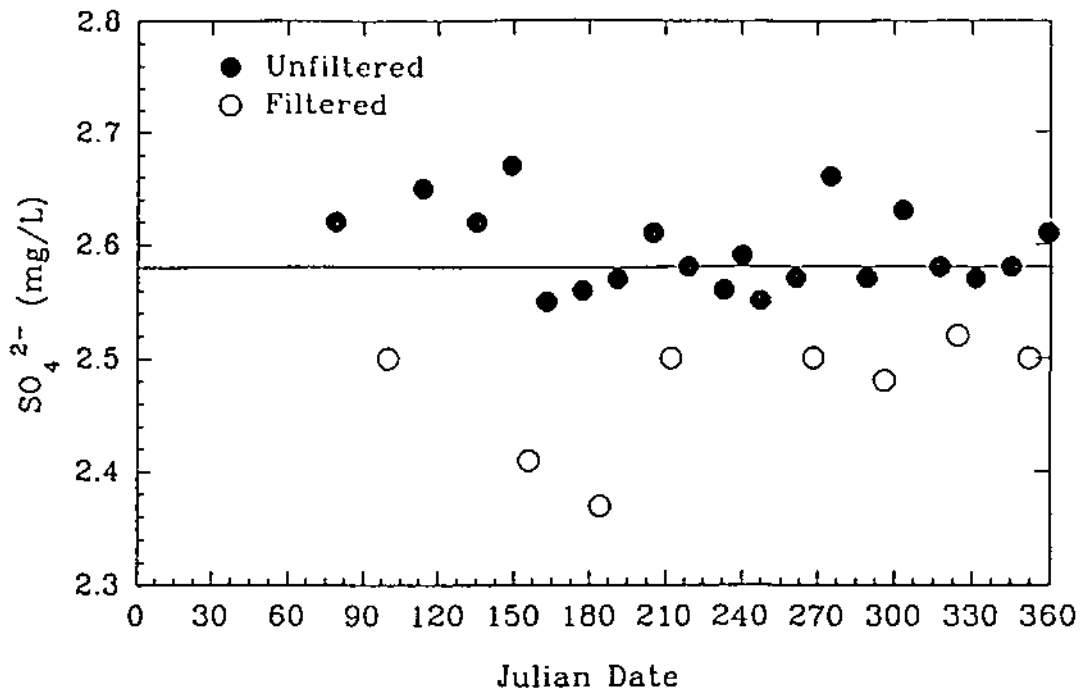


FIGURE B-15. Comparison of filtered and unfiltered internal blind samples (sulfate 75th percentile), 1990.

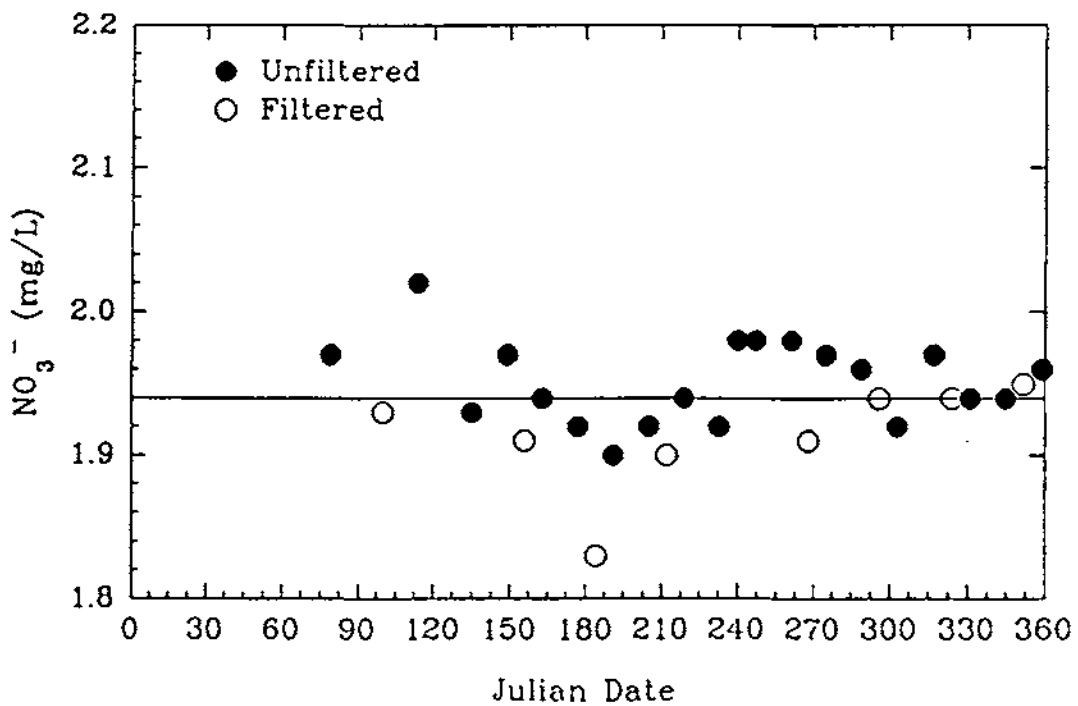


FIGURE B-16. Comparison of filtered and unfiltered internal blind samples (nitrate 75th percentile), 1990.



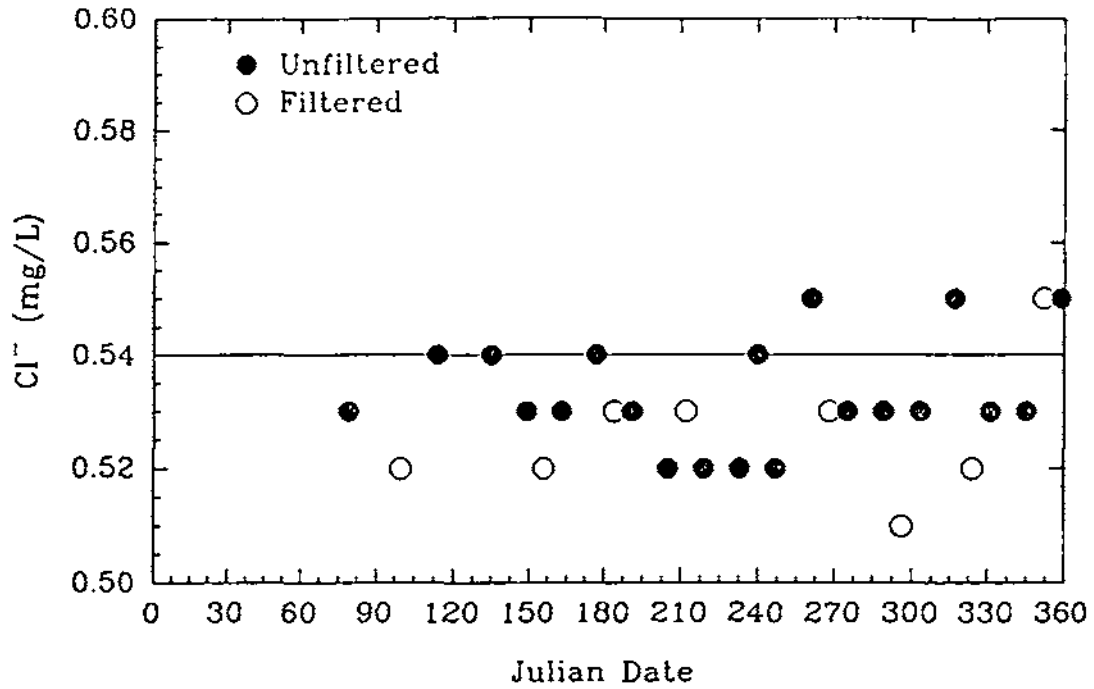


FIGURE B-17. Comparison of filtered and unfiltered internal blind samples (chloride 75th percentile), 1990.

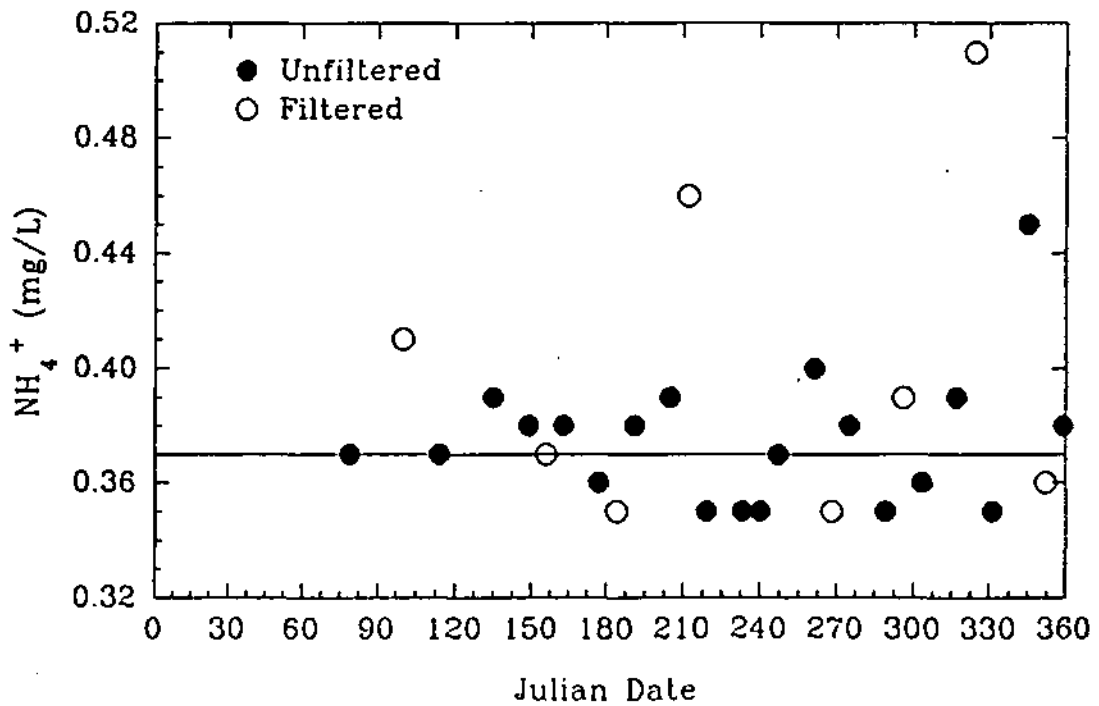


FIGURE B-18. Comparison of filtered and unfiltered internal blind samples (ammonium 75th percentile), 1990.

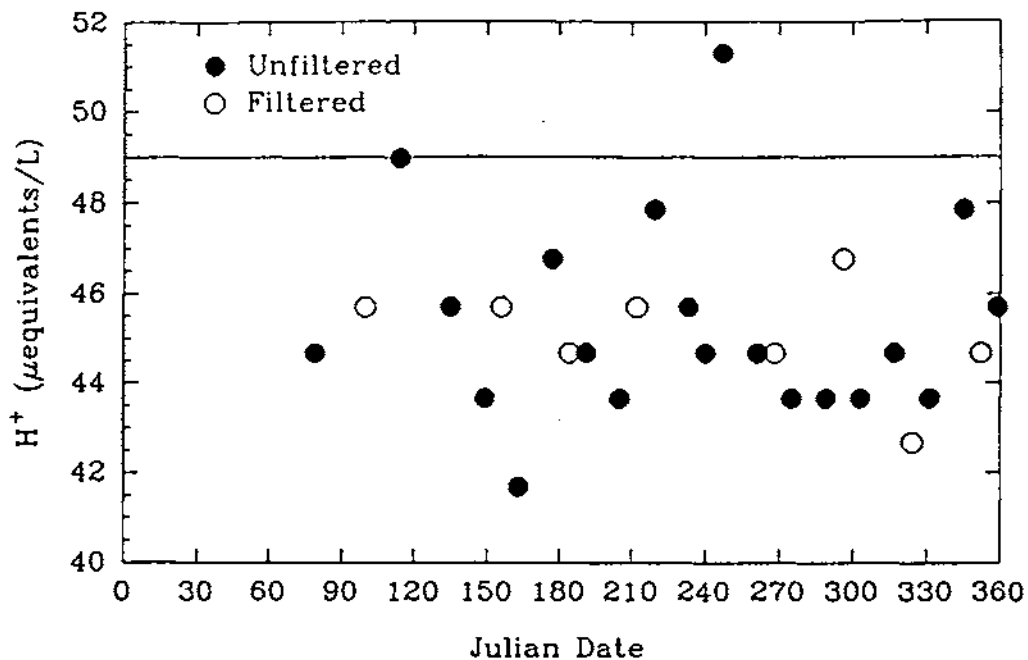


FIGURE B-19. Comparison of filtered and unfiltered internal blind samples ( $H^+$  75th percentile), 1990.

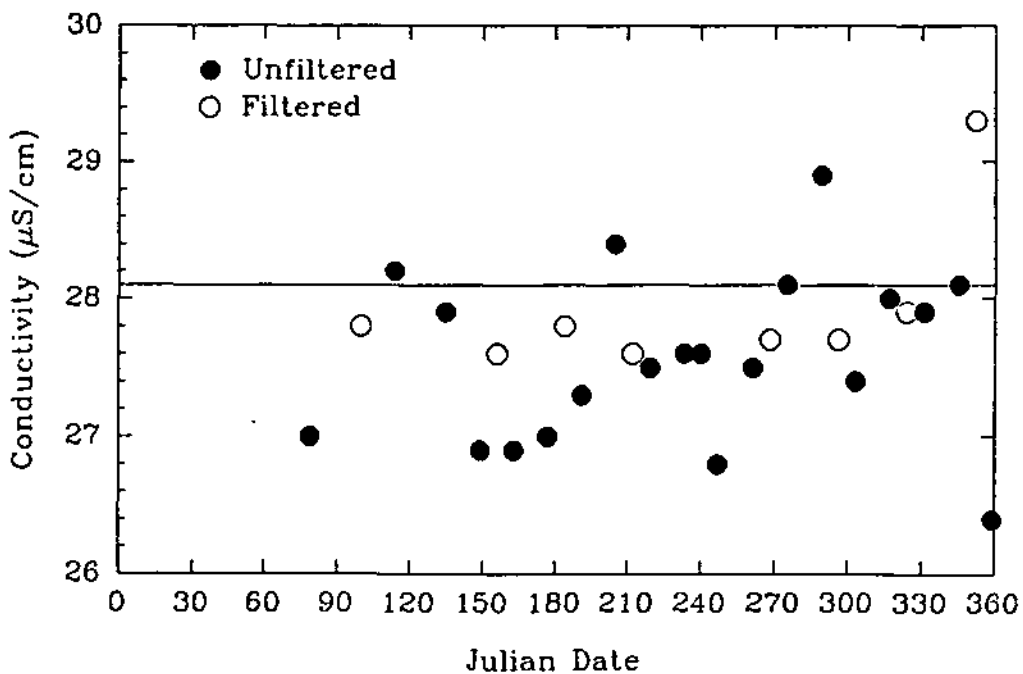
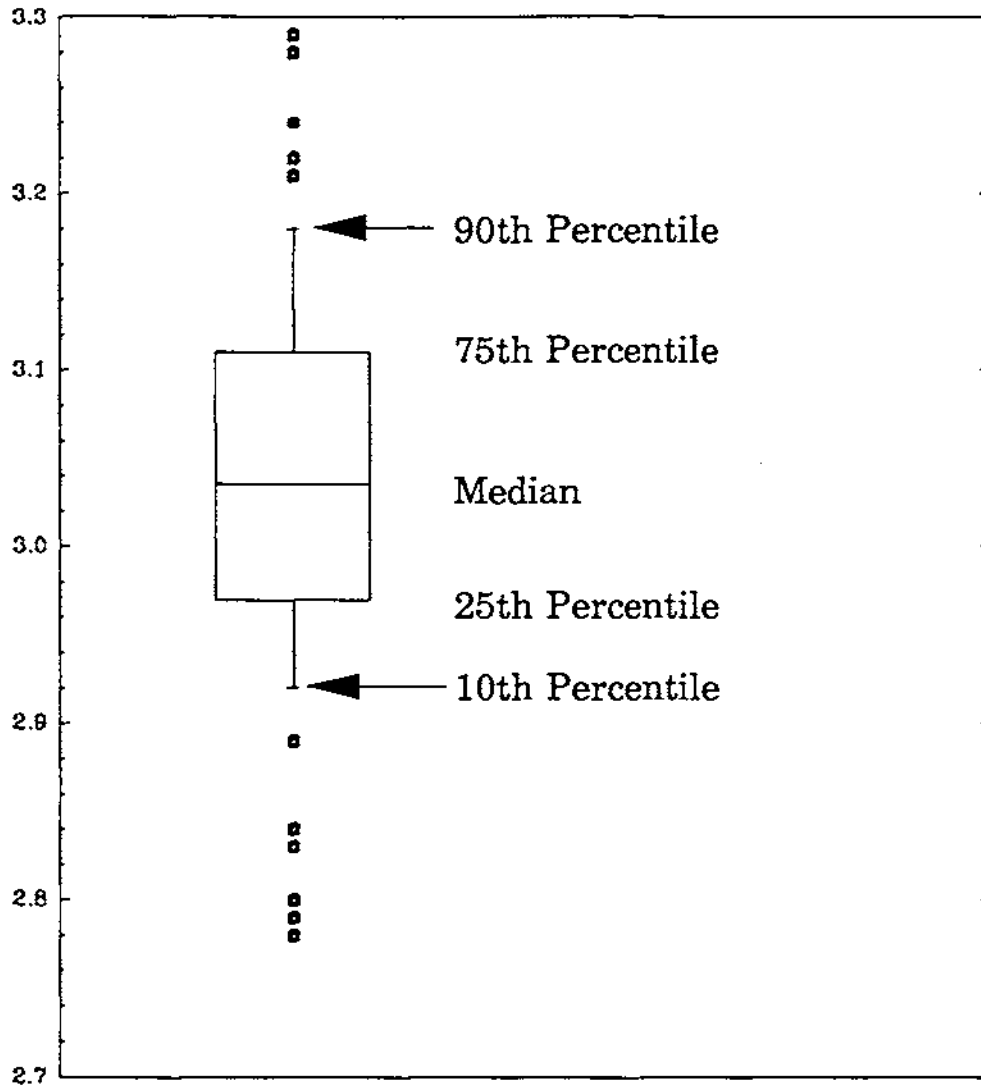


FIGURE B-20. Comparison of filtered and unfiltered internal blind samples (conductivity 75th percentile), 1990.

<b>TABLE B-3 50<sup>th</sup> and 95<sup>th</sup> Percentile Concentration Values of Chemical and Physical Parameters Measured in Replicate (O/Q) Samples, 1990</b>		
<b>Parameter</b>	<b>Percentile Concentration Values (mg/L)</b>	
	<b>50<sup>th</sup></b>	<b>95<sup>th</sup></b>
<b>Calcium</b>	<b>0.078</b>	<b>0.568</b>
<b>Magnesium</b>	<b>0.019</b>	<b>0.092</b>
<b>Sodium</b>	<b>0.061</b>	<b>0.471</b>
<b>Potassium</b>	<b>0.016</b>	<b>0.095</b>
<b>Ammonium</b>	<b>0.15</b>	<b>0.74</b>
<b>Sulfate</b>	<b>0.96</b>	<b>4.29</b>
<b>Nitrate</b>	<b>0.71</b>	<b>2.66</b>
<b>Chloride</b>	<b>0.14</b>	<b>0.86</b>
<b>Phosphate</b>	<b>&lt;0.02</b>	<b>&lt;0.02</b>
<b>pH (units)</b>	<b>4.99</b>	<b>6.02</b>
<b>H<sup>+</sup> (<math>\mu</math>eq/L)</b>	<b>10.35</b>	<b>0.95</b>
<b>Conductivity (<math>\mu</math>S/cm)</b>	<b>9.85</b>	<b>42.86</b>

## DIAGRAM OF BOXPLOTS USED ON THE FOLLOWING PAGES



All values beyond the 10th and 90th percentiles are graphed individually, as on a point graph.

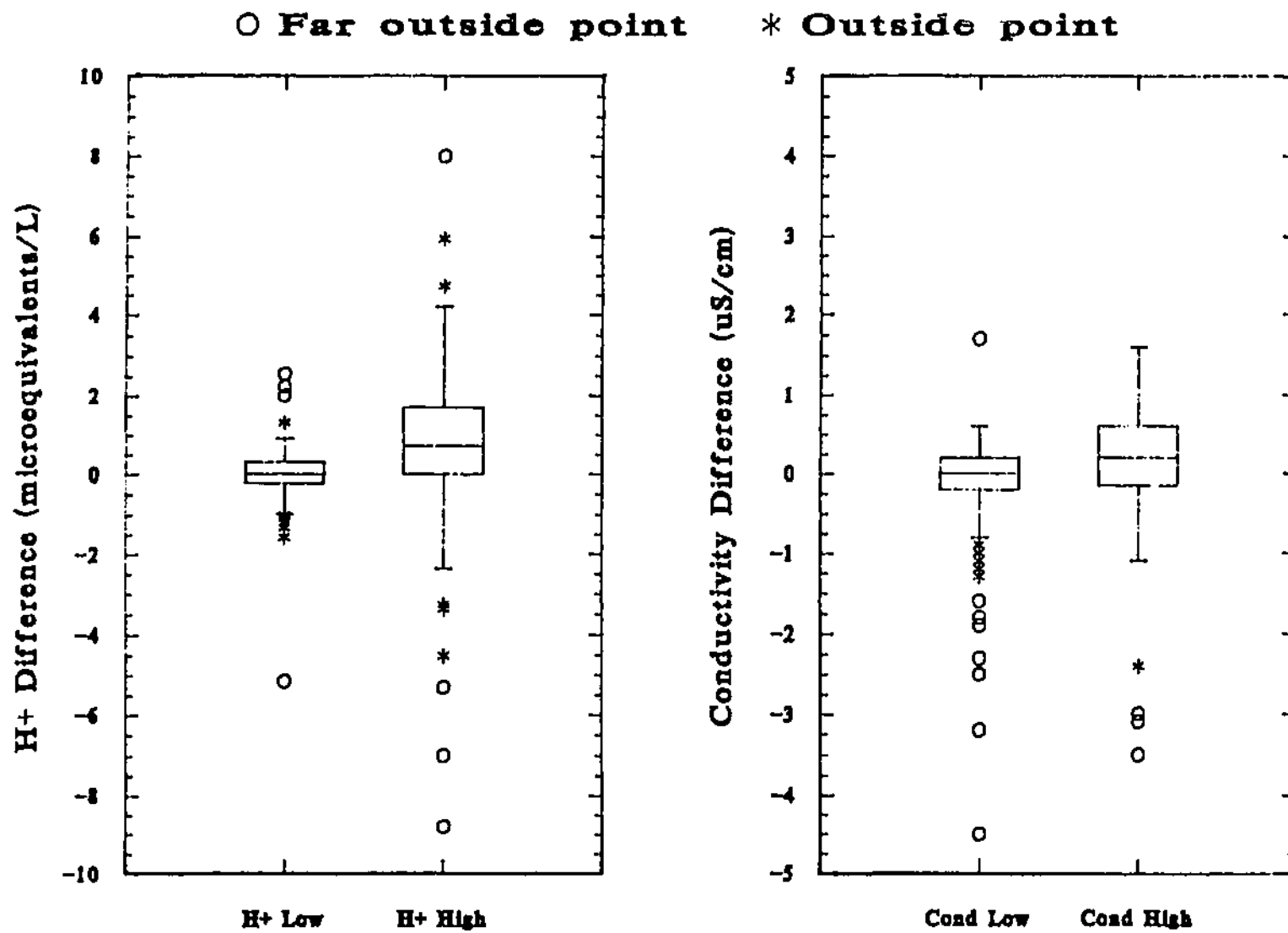


FIGURE B-21. Results of 0/Q replicate analysis, pH and conductivity, 1990.

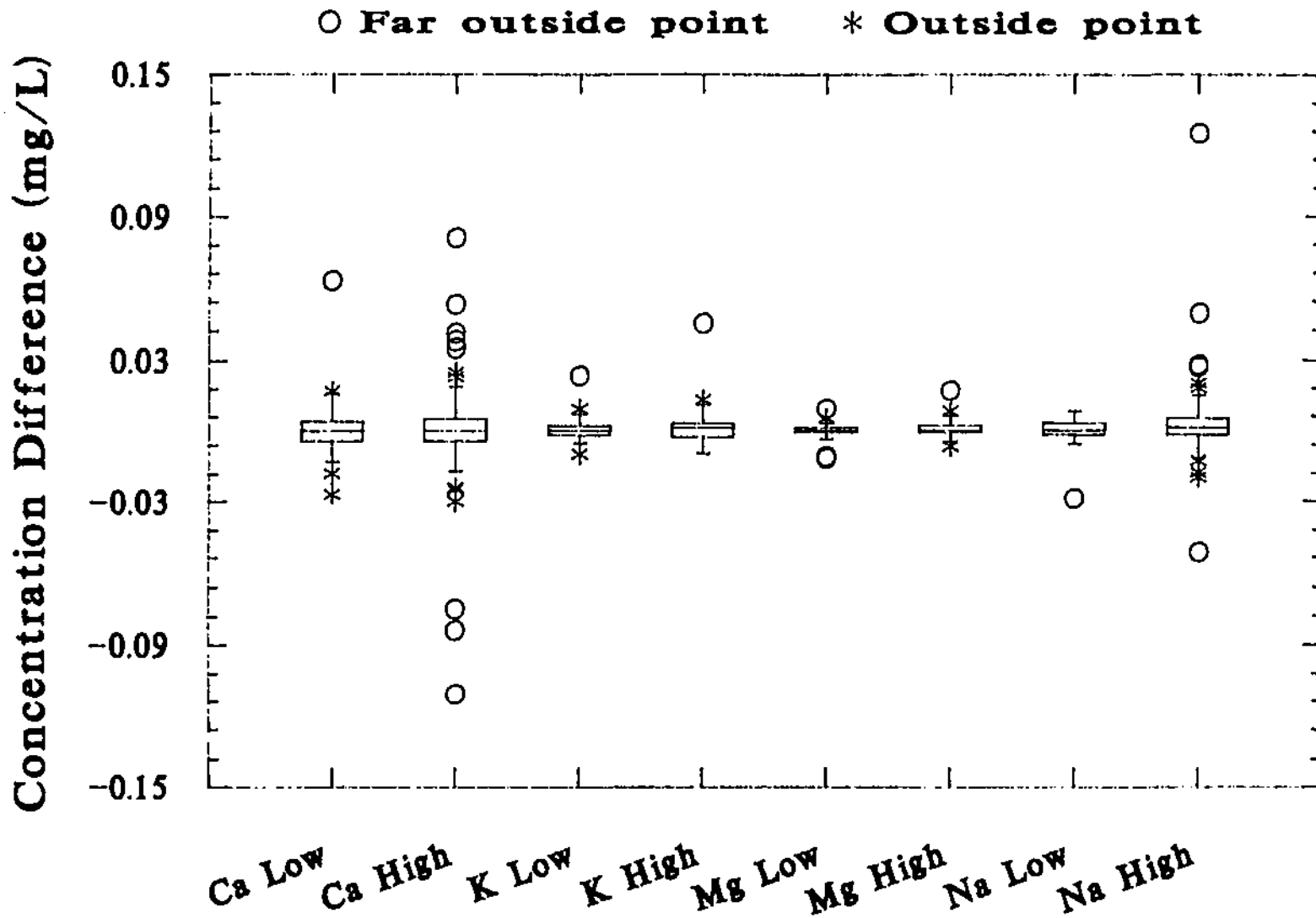


FIGURE B-22. Results of 0/Q replicate analysis for calcium (Ca), potassium (K), magnesium (Mg), and sodium (Na), 1990.



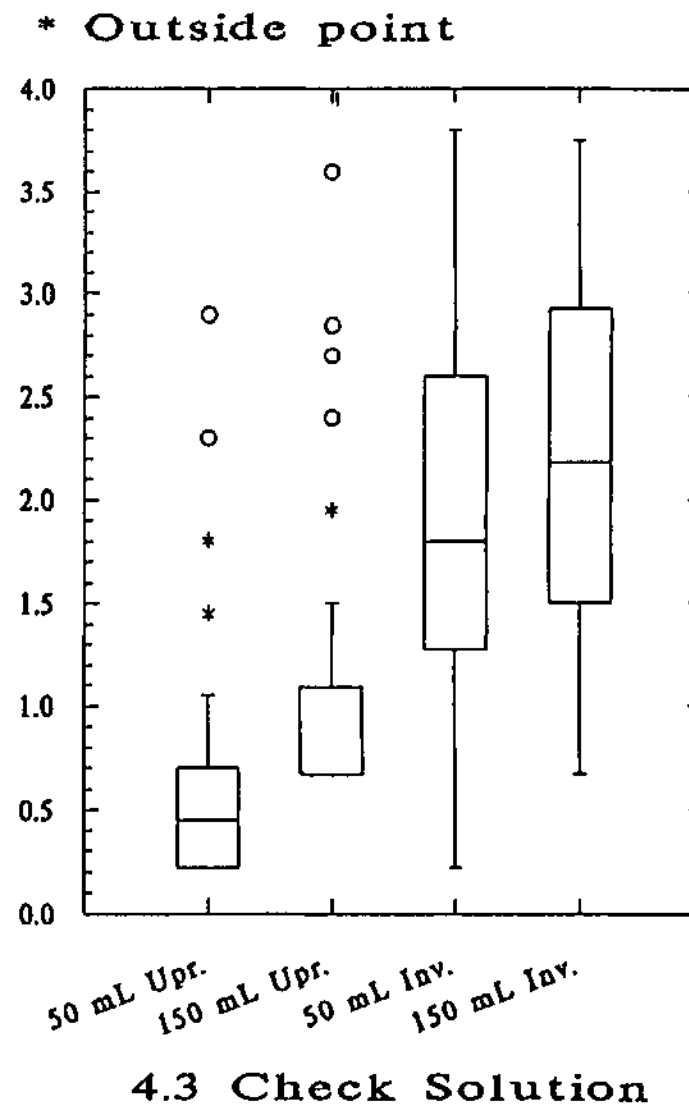
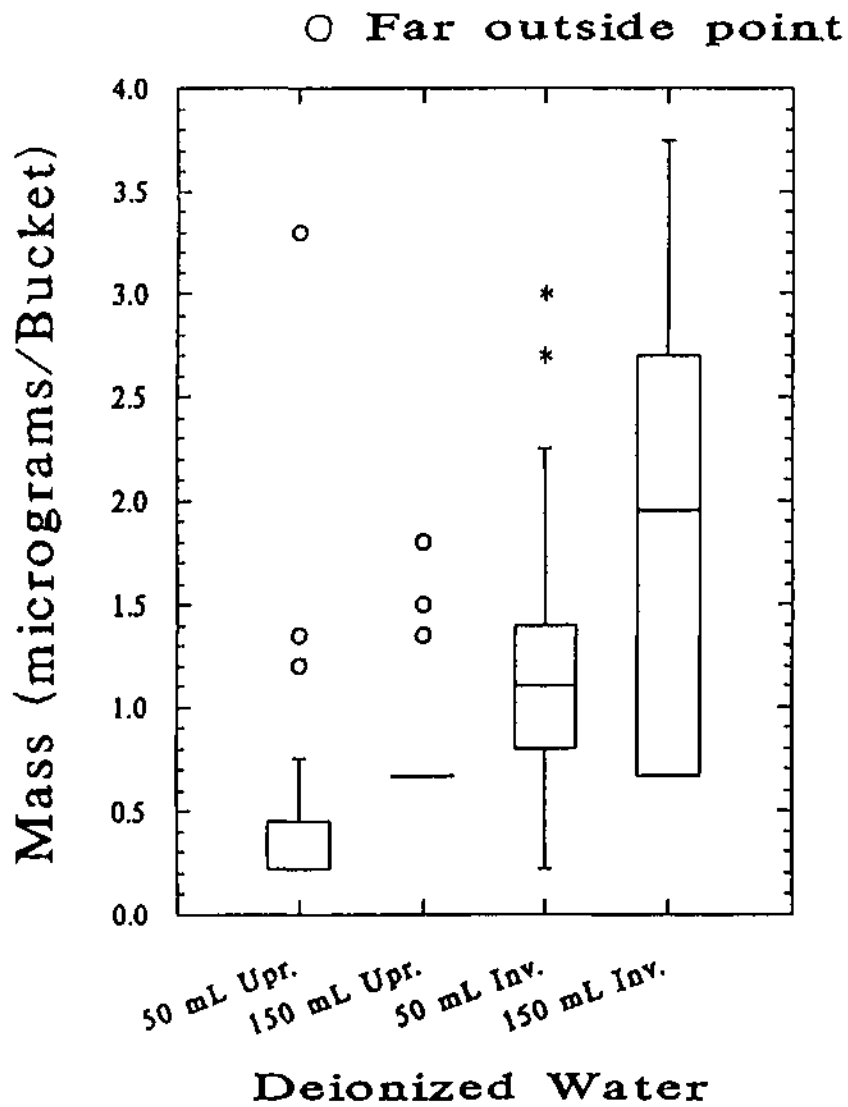


FIGURE B-24. Calcium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1990.



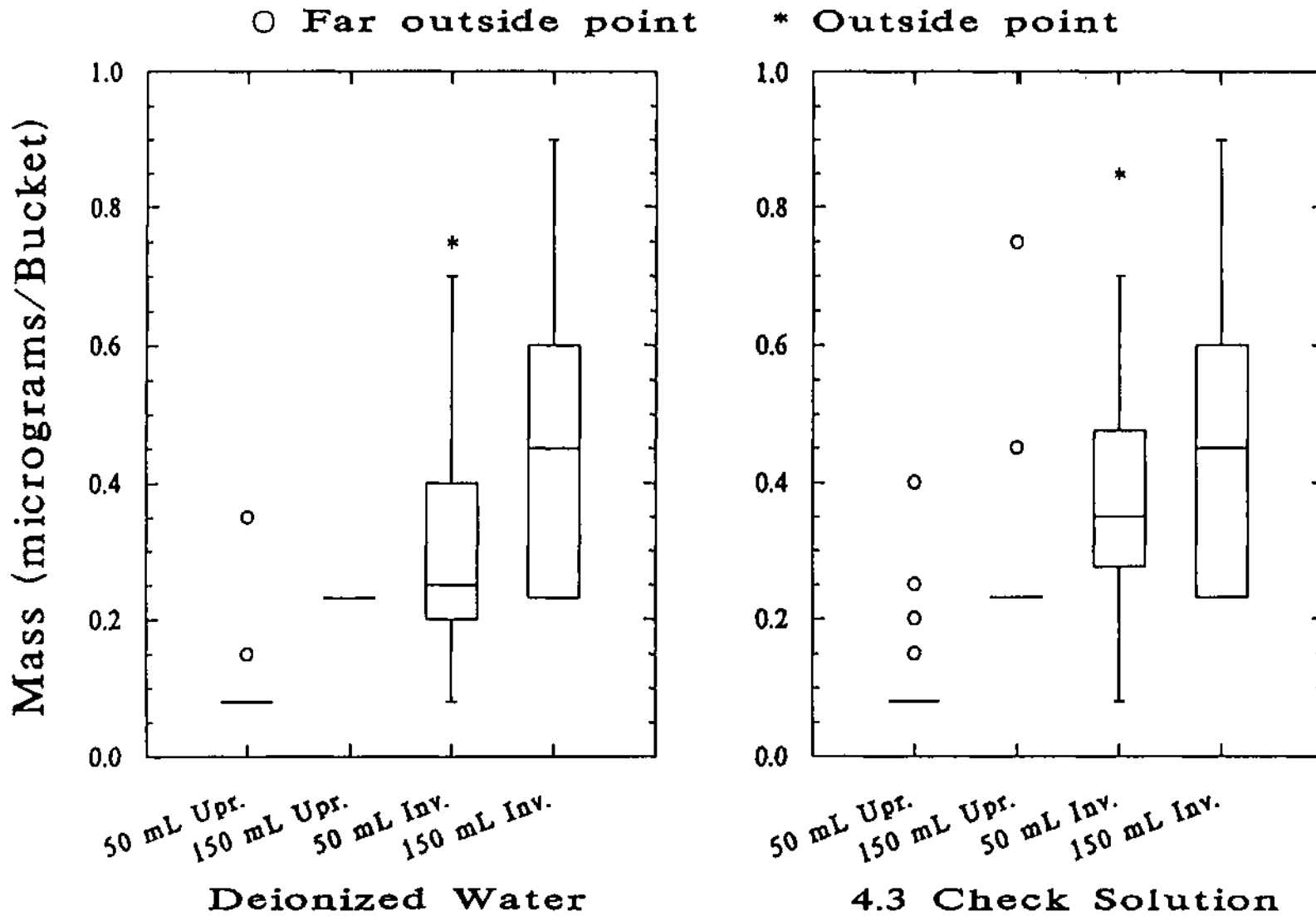


FIGURE B-25. Magnesium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1990.

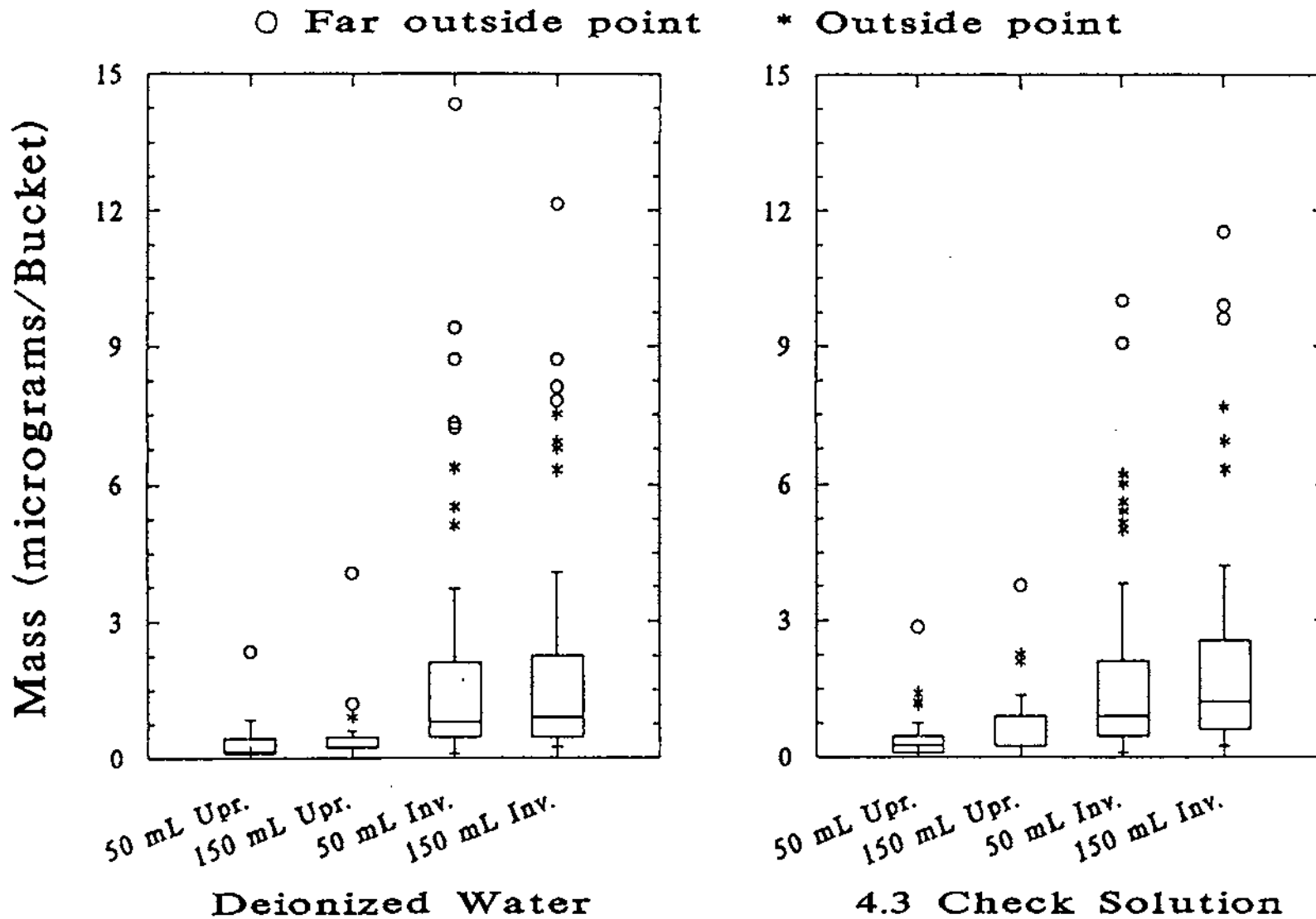


FIGURE B-26. Sodium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1990.

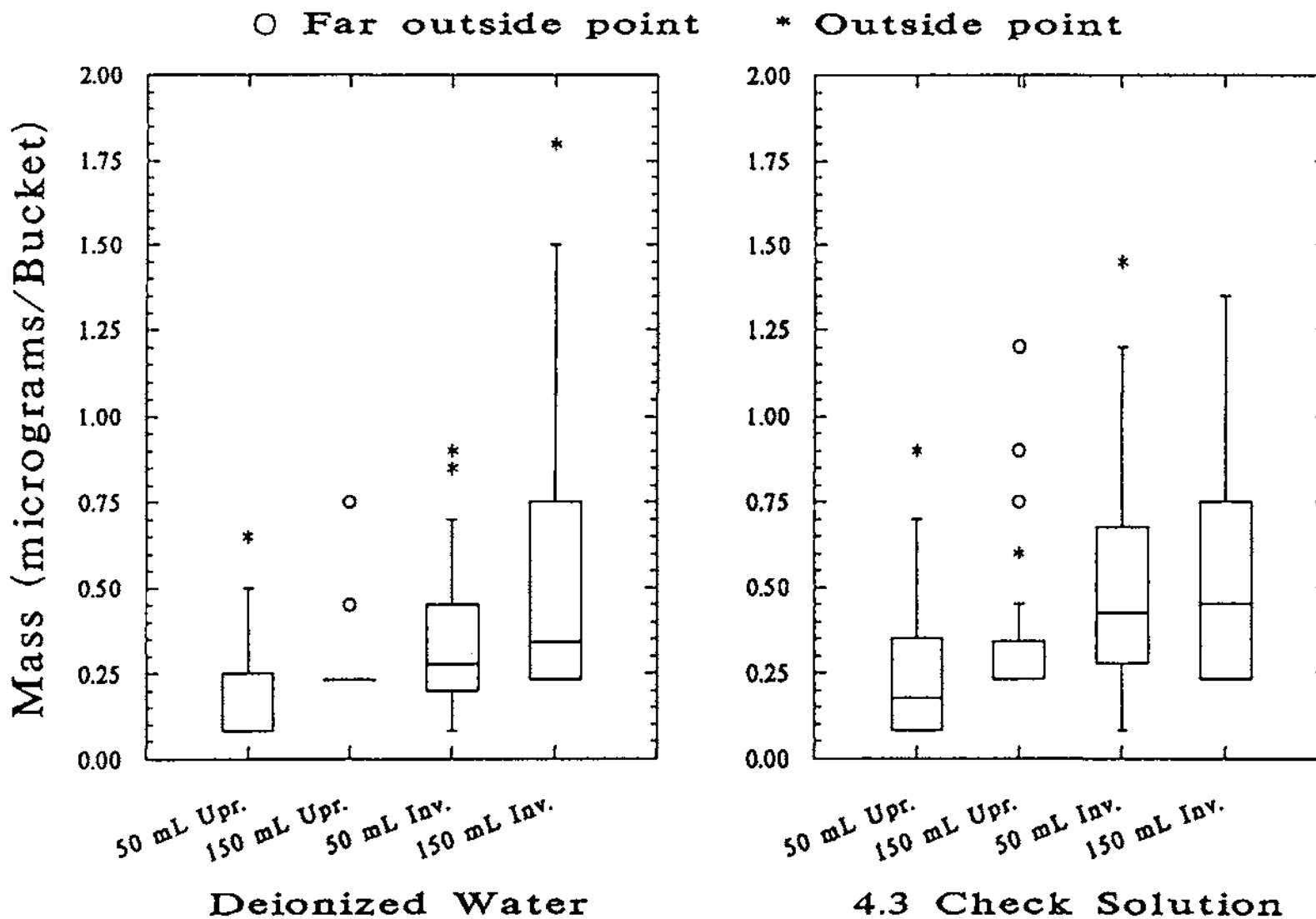


FIGURE B-27. Potassium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1990.

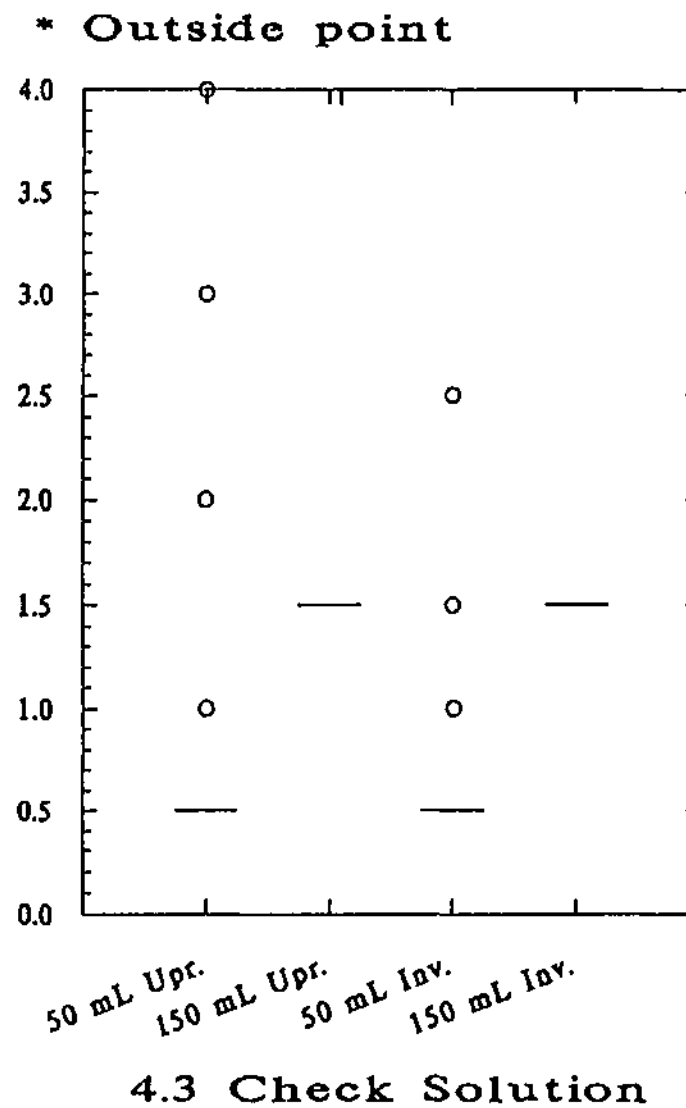
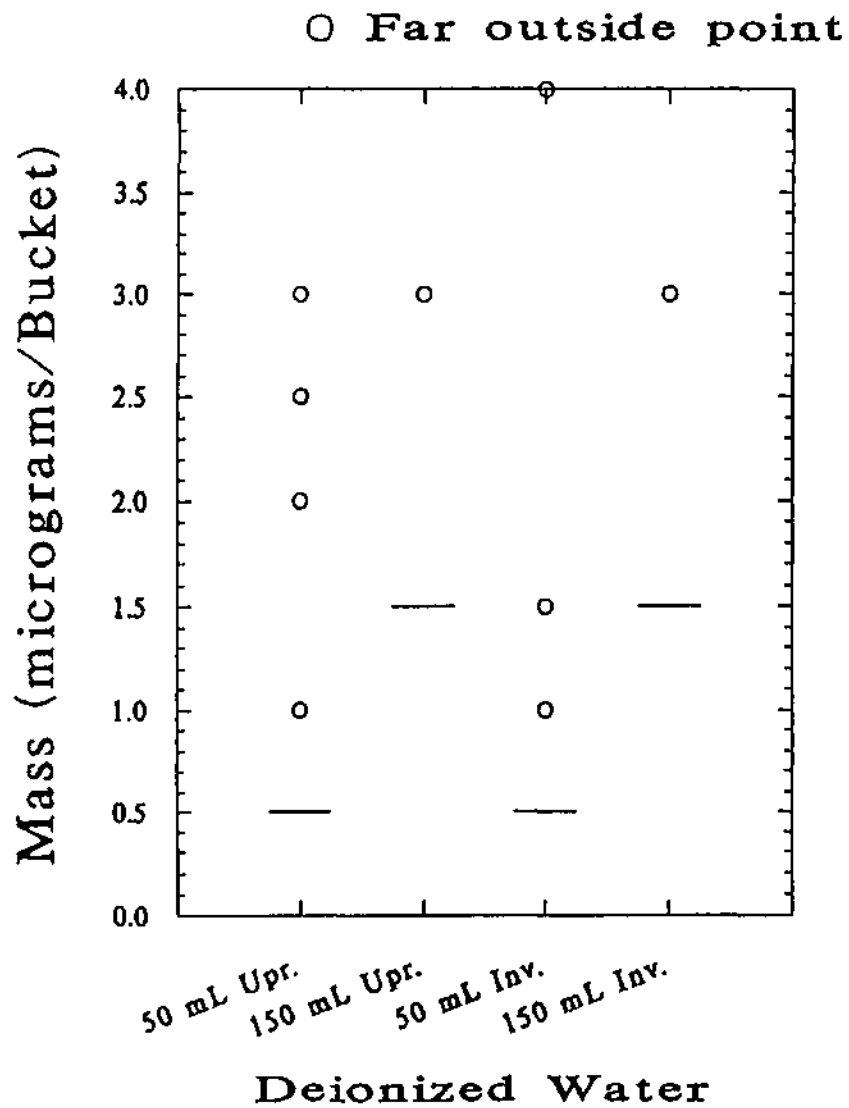


FIGURE B-28. Ammonium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1990.

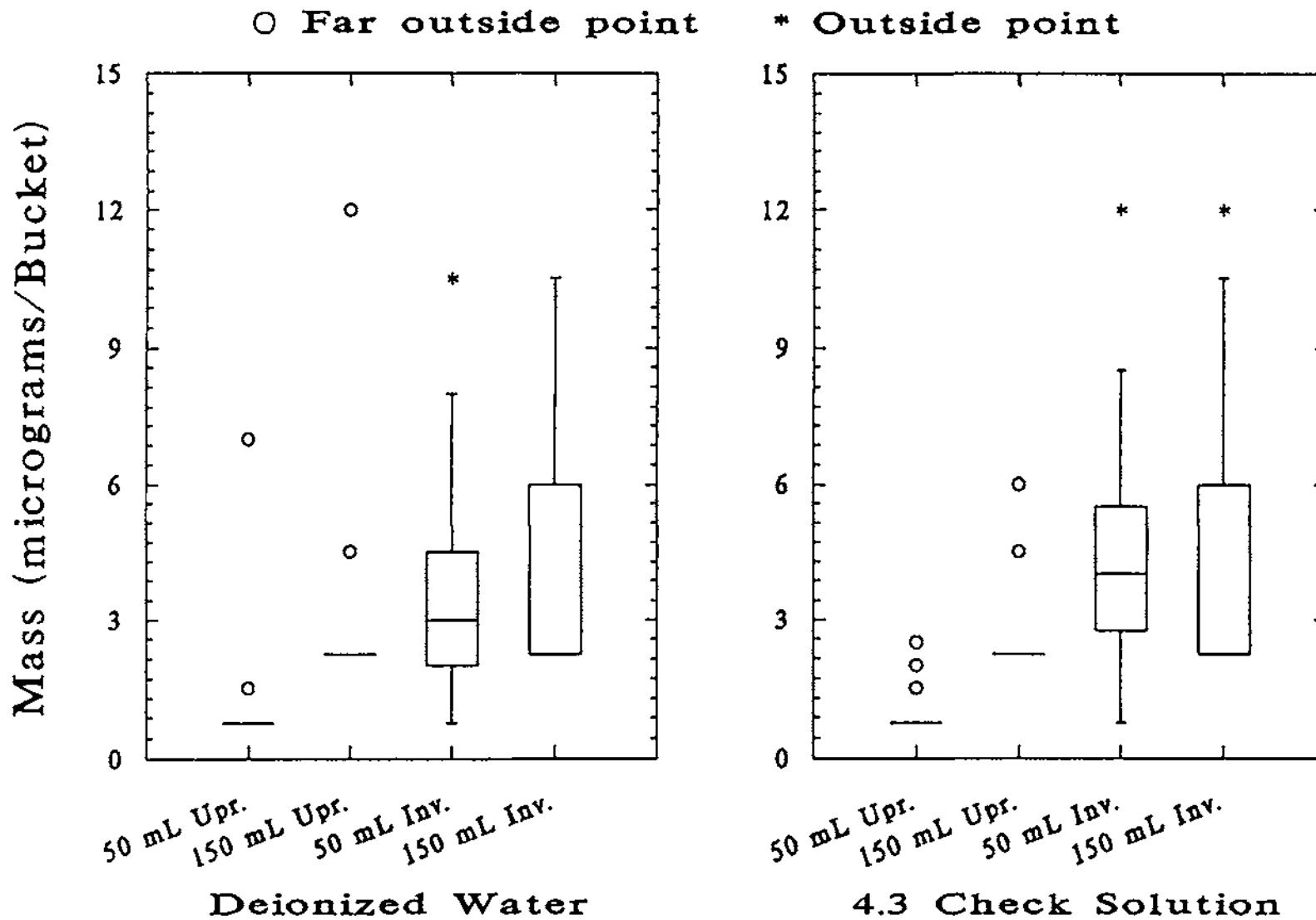


FIGURE B-29. Sulfate found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1990.

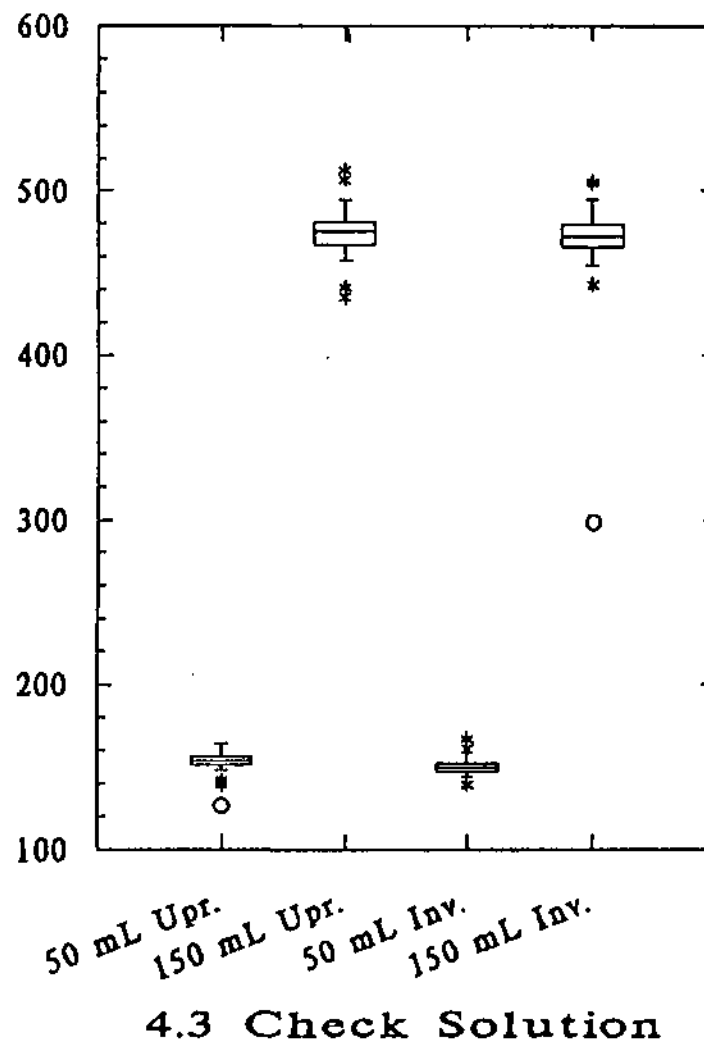
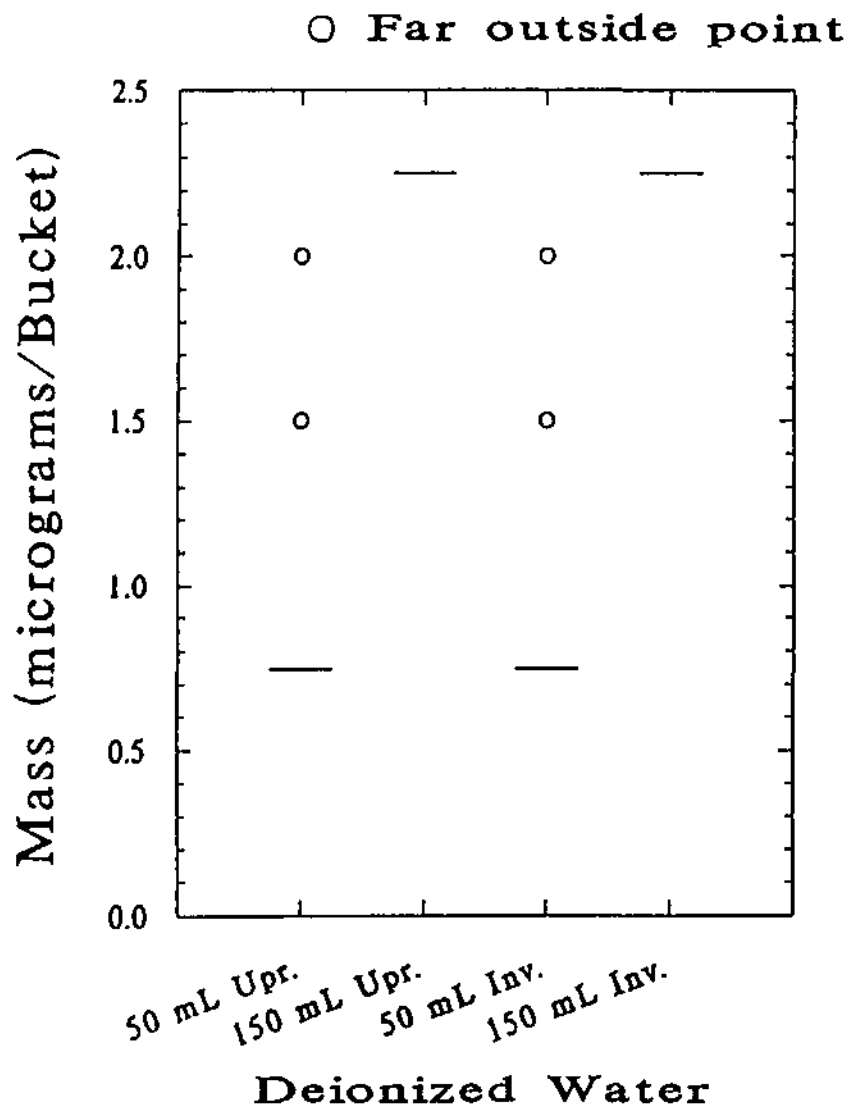
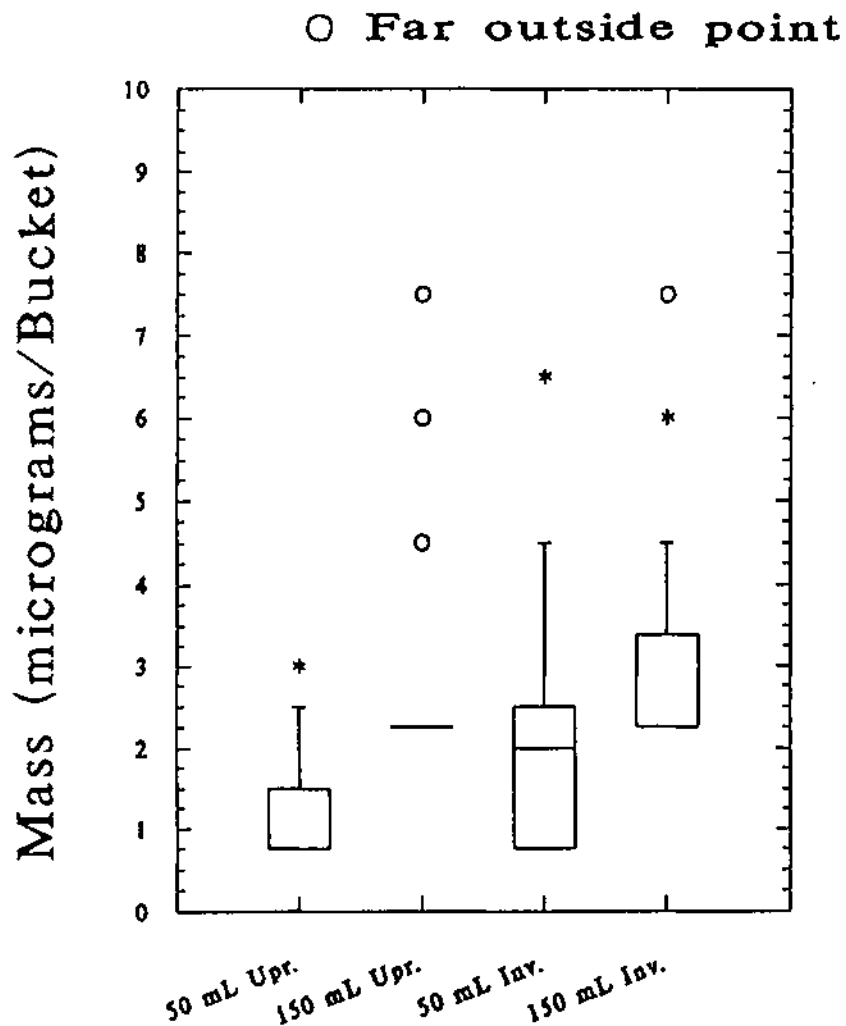
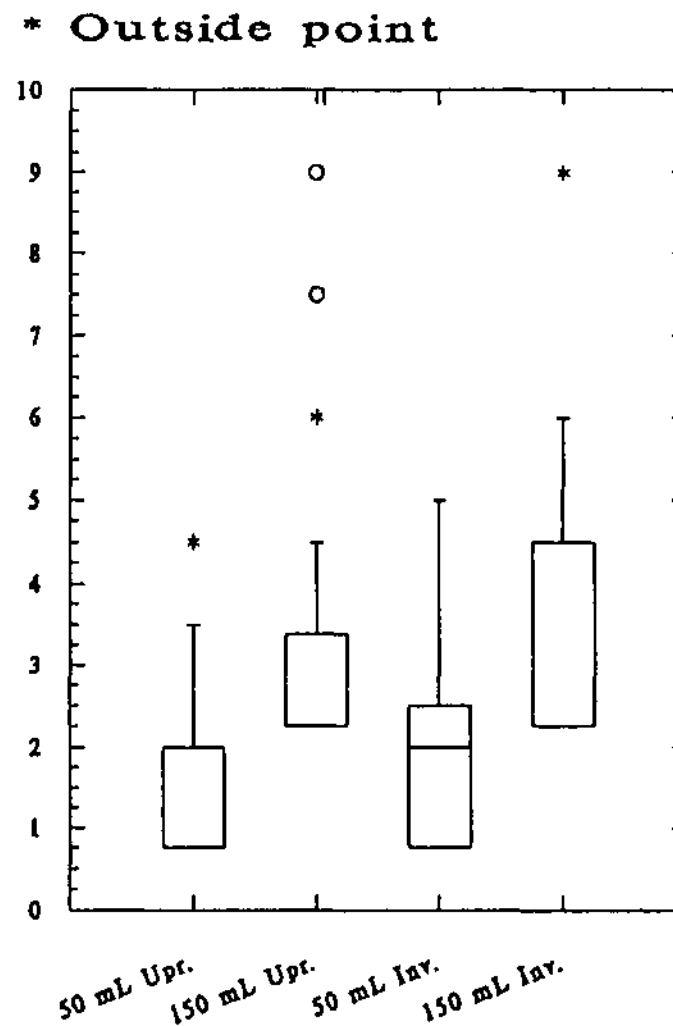


FIGURE B-30. Nitrate found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1990.



**Deionized Water**



**4.3 Check Solution**

FIGURE B-31. Chloride found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1990.

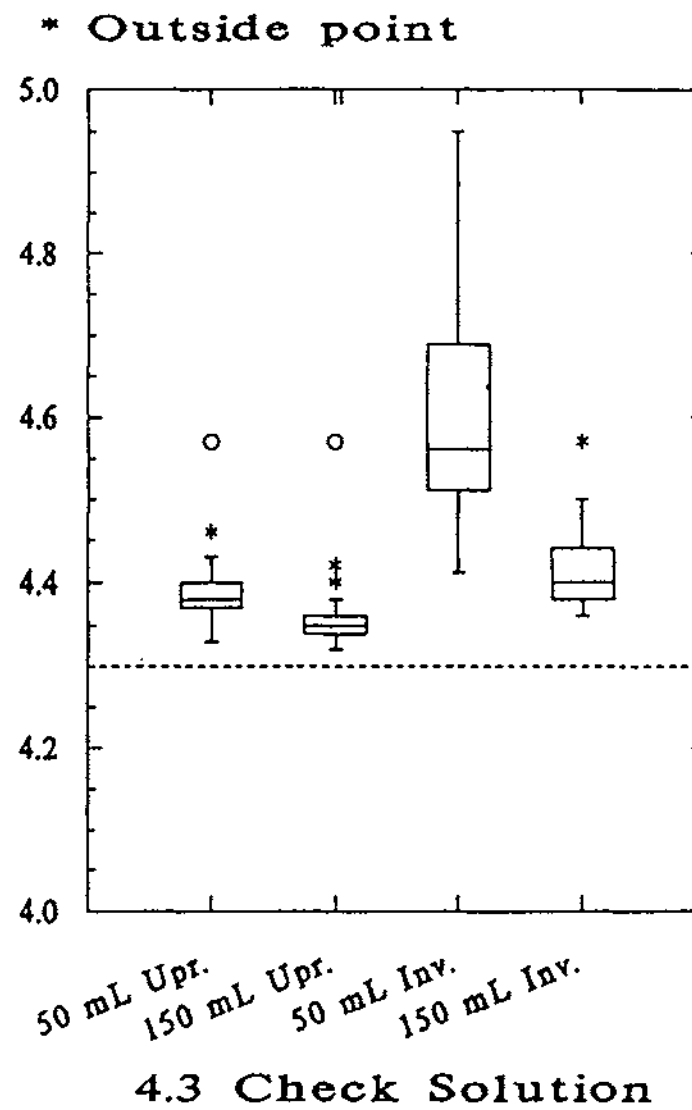
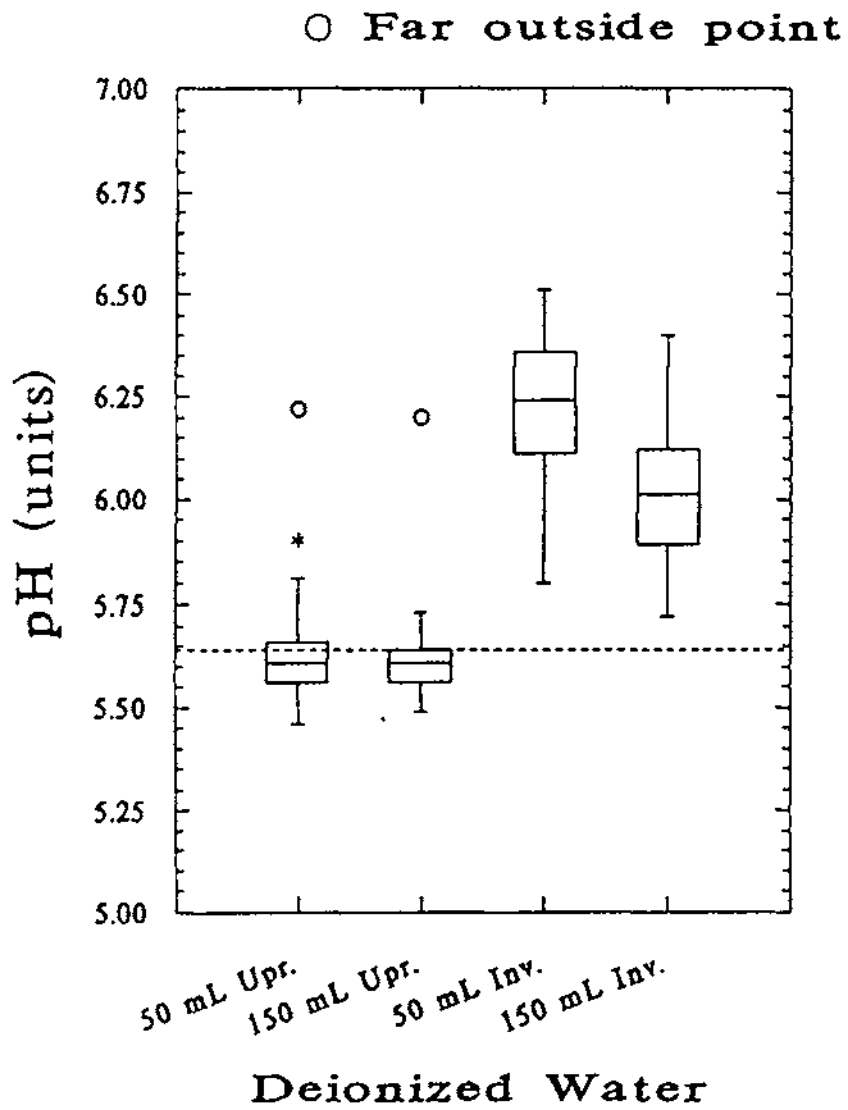


FIGURE B-32. pH of upright and inverted bucket blanks leached with DI water and pH 4.3 QCS, 1990.



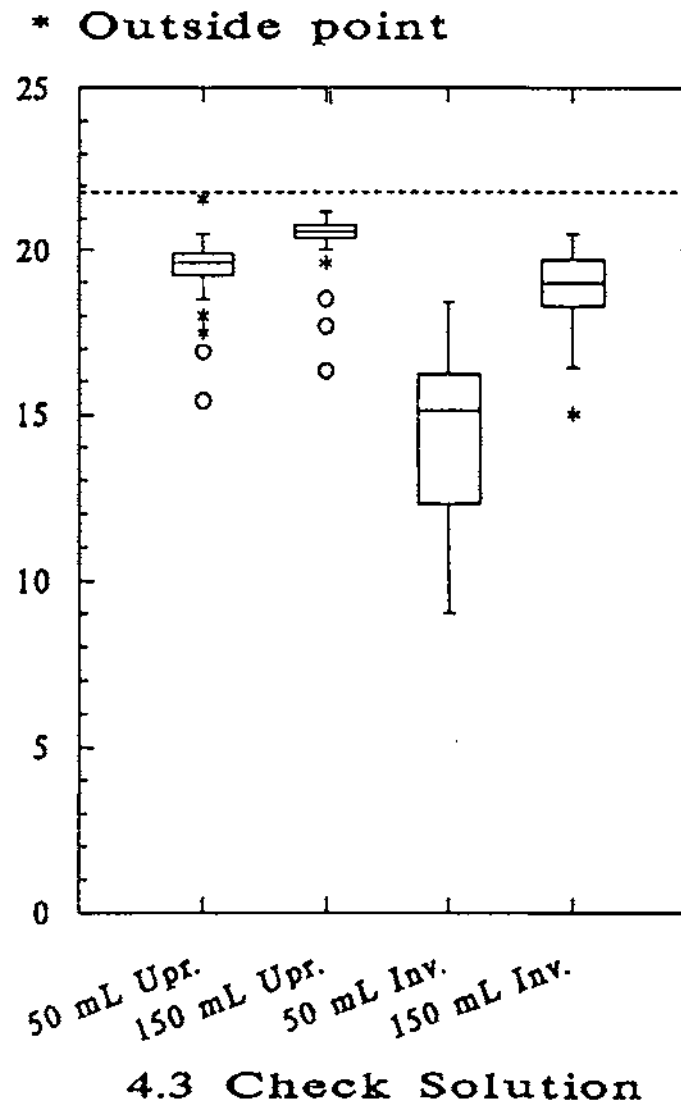
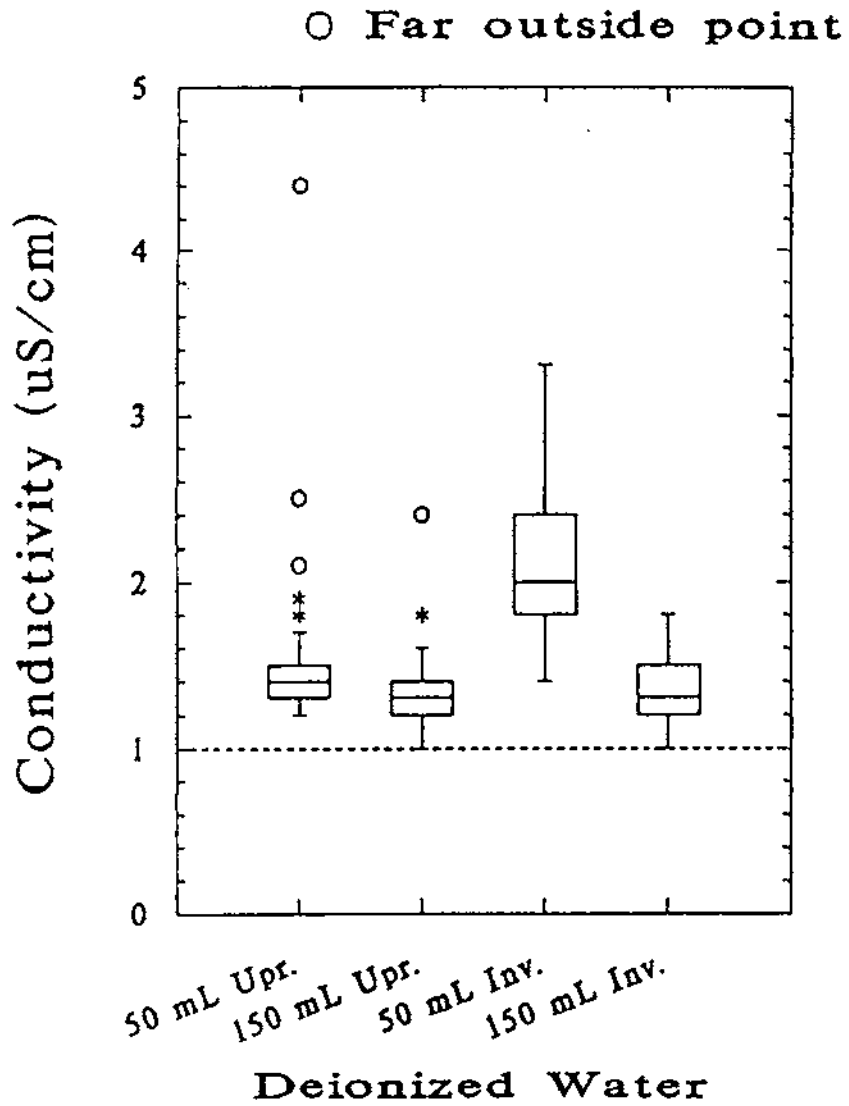


FIGURE B-33. Conductivity of upright and inverted bucket blanks leached with DI water and pH 4.3 QCS, 1990.



APPENDIX C

Interlaboratory Comparison Data:

USEPA, LRTAP

1990



<b>TABLE C-1</b>						
<b>USEPA RTP Acid Rain Performance Survey - May 1990</b>						
<b>CAL Values Compared to Expected Values</b>						
<b>Parameter (mg/L)</b>	<b>Sample Number</b>					
	<b>1737</b>		<b>2331</b>		<b>3295</b>	
	<b>CAL</b>	<b>EPA</b>	<b>CAL</b>	<b>EPA</b>	<b>CAL</b>	<b>EPA</b>
<b>Calcium</b>	<b>0.042</b>	<b>0.047</b>	<b>0.108</b>	<b>0.116</b>	<b>MDL</b>	<b>0.005</b>
<b>Magnesium</b>	<b>0.027</b>	<b>0.027</b>	<b>0.014</b>	<b>0.016</b>	<b>0.052</b>	<b>0.051</b>
<b>Sodium</b>	<b>0.218</b>	<b>0.188</b>	<b>0.252</b>	<b>0.242</b>	<b>0.497</b>	<b>0.465</b>
<b>Potassium</b>	<b>0.076</b>	<b>0.078</b>	<b>0.081</b>	<b>0.079</b>	<b>0.092</b>	<b>0.093</b>
<b>Ammonium</b>	<b>0.10</b>	<b>0.10</b>	<b>0.82</b>	<b>0.80</b>	<b>1.06</b>	<b>1.02</b>
<b>Nitrate</b>	<b>0.49</b>	<b>0.47</b>	<b>0.53</b>	<b>0.50</b>	<b>6.24</b>	<b>6.13</b>
<b>Chloride</b>	<b>0.28</b>	<b>0.27</b>	<b>0.59</b>	<b>0.58</b>	<b>6.24</b>	<b>6.13</b>
<b>Sulfate</b>	<b>2.04</b>	<b>1.98</b>	<b>8.03</b>	<b>7.93</b>	<b>11.44</b>	<b>11.30</b>
<b>pH (units)</b>	<b>4.41</b>	<b>4.41</b>	<b>3.91</b>	<b>3.89</b>	<b>3.57</b>	<b>3.53</b>
<b>Specific Conductance (<math>\mu</math>S/cm)</b>	<b>19.9</b>	<b>18.6</b>	<b>63.9</b>	<b>64.1</b>	<b>131.2</b>	<b>129.2</b>

<b>TABLE C-2</b>						
<b>USEPA RTP Acid Rain Performance Survey - November 1990</b>						
<b>CAL Values Compared to Expected Values</b>						
<b>Parameter (mg/L)</b>	<b>Sample Number</b>					
	<b>1247</b>		<b>2427</b>		<b>3754</b>	
	<b>CAL</b>	<b>EPA</b>	<b>CAL</b>	<b>EPA</b>	<b>CAL</b>	<b>EPA</b>
<b>Calcium</b>	<b>0.049</b>	<b>0.056</b>	<b>0.377</b>	<b>0.420</b>	<b>0.053</b>	<b>0.056</b>
<b>Magnesium</b>	<b>0.039</b>	<b>0.042</b>	<b>0.114</b>	<b>0.124</b>	<b>0.076</b>	<b>0.081</b>
<b>Sodium</b>	<b>0.159</b>	<b>0.156</b>	<b>1.887</b>	<b>1.835</b>	<b>0.423</b>	<b>0.403</b>
<b>Potassium</b>	<b>0.064</b>	<b>0.071</b>	<b>0.771</b>	<b>0.774</b>	<b>0.077</b>	<b>0.081</b>
<b>Ammonium</b>	<b>0.10</b>	<b>0.10</b>	<b>1.15</b>	<b>1.02</b>	<b>0.64</b>	<b>0.59</b>
<b>Nitrate</b>	<b>0.40</b>	<b>0.42</b>	<b>9.74</b>	<b>9.63</b>	<b>8.14</b>	<b>8.14</b>
<b>Chloride</b>	<b>0.30</b>	<b>0.28</b>	<b>2.84</b>	<b>2.83</b>	<b>1.29</b>	<b>1.31</b>
<b>Sulfate</b>	<b>2.79</b>	<b>2.73</b>	<b>12.22</b>	<b>11.92</b>	<b>9.08</b>	<b>8.58</b>
<b>pH (units)</b>	<b>4.29</b>	<b>4.26</b>	<b>3.53</b>	<b>3.49</b>	<b>3.56</b>	<b>3.51</b>
<b>Specific Conductance (<math>\mu</math>S/cm)</b>	<b>27.5</b>	<b>22.8</b>	<b>157.4</b>	<b>151.5</b>	<b>135.1</b>	<b>128.3</b>

**TABLE C-3**  
**LRTAP Interlaboratory Comparability Study L23-**  
**March 1990-CAL Reported Values Compared to**  
**NWRI Median Values for all Participating Laboratories**

Parameter (mg/L)	Sample Number									
	1		2		3		4		5	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	2.088	2.030	0.757	0.750	1.605	1.590	2.305	2.305	0.143	0.140
Magnesium	0.472	0.480	0.441	0.444	0.305	0.308	0.355	0.360	0.067	0.065
Sodium	0.539	0.540	3.158	3.100	1.206	1.170	0.671	0.685	0.361	0.357
Potassium	0.312	0.321	0.280	0.295	0.173	0.180	0.404	0.420	0.076	0.080
Ammonium	0.06	0.06	0.04	0.04	0.02	0.01	0.04	0.04	0.06	0.05
Nitrate	0.13	0.14	0.18	0.18	0.53	0.53	1.42	1.42	0.22	0.22
Chloride	0.35	0.36	4.11	4.25	1.20	1.13	0.49	0.50	0.60	0.60
Sulfate	5.58	5.60	1.93	1.95	1.48	1.48	6.30	6.44	0.80	0.80
pH (units)	6.03	5.92	5.30	5.28	6.58	6.58	5.56	5.52	5.20	5.23
Specific Conductance ( $\mu$ S/cm)	22.6	22.2	28.5	28.0	18.1	17.5	26.1	25.8	7.7	7.2

**TABLE C-3 (continued)**  
**LRTAP Interlaboratory Comparability Study L23-**  
**March 1990-CAL Reported Values Compared to**  
**NWRI Median Values for all Participating Laboratories**

Parameter (mg/L)	Sample Number									
	6		7		8		9		10	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	2.014	2.000	1.669	1.670	2.199	2.191	0.020	0.026	0.032	0.032
Magnesium	0.177	0.180	0.347	0.350	0.444	0.450	0.018	0.020	0.009	0.010
Sodium	0.657	0.660	0.312	0.310	0.829	0.830	0.021	0.021	0.007	0.012
Potassium	0.189	0.199	0.113	0.122	0.123	0.130	0.017	0.020	0.003	0.010
Ammonium	<0.02	0.006	0.46	0.45	0.06	0.05	<0.02	0.02	<0.02	0.005
Nitrate	0.53	0.53	1.64	1.64	<0.02	0.04	0.04	0.04	0.13	0.13
Chloride	0.189	0.199	0.113	0.122	0.123	0.130	0.017	0.020	<0.003	0.010
Sulfate	2.02	2.02	3.96	3.95	0.70	0.70	0.48	0.50	0.05	0.05
pH (units)	6.56	6.50	5.22	5.28	4.83	4.80	5.08	5.09	5.47	5.49
Specific Conductance ( $\mu$ S/cm)	19.0	18.2	23.5	23.4	22.6	22.7	4.9	4.4	2.2	1.9

*Number of participating laboratorits = 60*

**TABLE C-4**  
**LRTAP Interlaboratory Comparability Study L24-**  
**July 1990-CAL Reported Values Compared to**  
**NWRI Median Values for all Participating Laboratories**

Parameter (mg/L)	Sample Number									
	1		2		3		4		5	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	1.835	1.786	1.665	1.600	1.710	1.67	2.354	2.300	2.158	2.064
Magnesium	0.681	0.670	0.316	0.310	0.343	0.350	0.362	0.360	0.485	0.474
Sodium	4.135	4.094	1.169	1.189	0.313	0.316	0.648	0.697	0.515	0.560
Potassium	0.284	0.290	0.176	0.180	0.116	0.120	0.386	0.423	0.293	0.321
Ammonium	<0.02	.010	<0.02	0.006	0.48	0.45	0.04	0.05	0.08	0.08
Nitrate	0.22	0.21	0.53	0.53	0.164	1.64	1.46	1.43	0.13	0.13
Chloride	5.25	5.105	1.14	1.15	1.79	1.80	0.49	0.500	0.35	0.366
Sulfate	2.84	2.81	1.48	1.48	3.97	3.92	6.50	6.463	5.69	5.615
pH (units)	6.46	6.345	6.73	6.625	5.39	5.32	5.67	5.55	6.11	5.99
Specific Conductance ( $\mu$ S/cm)	36.3	36.1	17.5	17.7	22.9	23.1	25.4	25.9	22.3	22.4

**TABLE C-4 (continued)**  
**LRTAP Interlaboratory Comparability Study L24-**  
**July 1990-CAL Reported Values Compared to**  
**NWRI Median Values for all Participating Laboratories**

Parameter (mg/L)	Sample Number									
	6		7		8		9		10	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	3.190	3.070	4.227	4.101	4.246	4.100	0.599	0.580	2.271	2.200
Magnesium	0.754	0.740	0.483	0.471	0.483	0.470	0.062	0.060	0.462	0.451
Sodium	0.964	1.010	0.539	0.558	0.526	0.557	5.632	5.600	0.816	0.859
Potassium	0.500	0.531	0.193	0.216	0.199	0.212	0.194	0.210	0.114	0.130
Ammonium	<0.02	0.018	0.02	0.03	0.03	0.03	<0.02	0.007	0.06	0.05
Nitrate	0.53	0.54	3.23	3.19	3.19	3.19	1.02	1.02	<0.02	0.04
Chloride	1.22	1.250	0.17	.182	.19	.180	1.25	1.25	0.52	.564
Sulfate	7.95	7.813	5.67	5.606	5.66	5.60	2.68	2.67	0.69	0.700
pH (units)	6.66	6.54	6.83	6.60	6.84	6.62	74.14	6.965	4.90	4.805
Specific Conductance ( $\mu$ S/cm)	33.7	33.65	31.9	32.1	32.0	32.1	30.3	30.6	21.7	22.35

*Number of participating laboratories = 59*

**TABLE C-5**  
**LRTAP Interlaboratory Comparability Study L25-**  
**November 1990-CAL Reported Values Compared to**  
**NWRI Median Values for all Participating Laboratories**

Parameter (mg/L)	Sample Number									
	1		2		3		4		5	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	0.976	0.980	3.191	3.260	2.304	2.330	2.382	2.390	1.538	1.523
Magnesium	0.190	0.210	0.752	0.790	0.356	0.370	0.673	0.695	0.560	0.577
Sodium	0.092	0.100	1.063	1.080	0.689	0.700	1.199	1.180	0.537	0.543
Potassium	0.036	0.040	0.554	0.580	0.410	0.430	0.395	0.409	0.462	0.472
Ammonium	<0.02	0.01	0.13	0.11	0.09	0.09	0.05	0.05	<0.02	0.006
Nitrate	0.12	0.12	0.58	0.58	1.42	1.42	<0.02	0.04	0.93	0.93
Chloride	0.10	0.11	1.30	1.32	0.49	0.50	0.22	0.24	0.19	0.21
Sulfate	6.07	6.098	8.24	8.26	6.46	6.49	3.75	3.70	3.28	3.25
pH (units)	4.25	4.25	6.65	6.59	5.68	5.65	6.91	6.84	6.16	6.04
Specific Conductance ( $\mu$ S/cm)	35.3	33.6	36.2	36.0	25.9	26.0	26.3	26.2	18.8	19.0

**TABLE C-5 (continued)**  
**LRTAP Interlaboratory Comparability Study L25-**  
**November 1990-CAL Reported Values Compared to**  
**NWRI Median Values for all Participating Laboratories**

Parameter (mg/L)	Sample Number									
	6		7		8		9		10	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	2.430	2.437	3.861	3.900	6.444	6.530	0.224	0.237	8.466	8.650
Magnesium	0.658	0.672	0.493	0.500	0.598	0.670	0.057	0.060	2.583	2.600
Sodium	1.362	1.33	0.849	0.849	0.800	0.800	0.357	0.360	0.196	0.200
Potassium	0.212	0.220	0.127	0.131	0.273	0.280	0.035	0.040	0.311	0.320
Ammonium	<0.02	0.018	0.08	0.05	0.06	0.06	0.14	0.13	2.02	2.00
Nitrate	3.10	3.10	<0.02	0.06	0.44	0.46	1.15	1.15	12.97	14.87
Chloride	2.52	2.48	0.53	0.56	0.37	0.39	0.66	0.67	0.76	0.87
Sulfate	6.23	6.27	0.72	0.77	5.80	5.78	1.33	1.33	22.68	22.59
pH (units)	5.07	5.02	5.79	5.66	7.23	7.16	4.63	4.62	6.21	6.06
Specific Conductance ( $\mu$ S/cm)	36.0	35.2	22.9	23.0	45.3	45.0	15.8	15.0	96.6	96.4

*Number of participating laboratories = 58*



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