

# QUALITY ASSURANCE REPORT NADP/NTN DEPOSITION MONITORING

Laboratory Operations  
Central Analytical Laboratory  
1993



## NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

A Cooperative Research Program of the  
State Agricultural Experiment Stations (NRSP-3)  
Federal Acid Precipitation Task Force  
State Agencies and Private Research Organizations

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



The National Atmospheric Deposition Program (NADP) was initiated in 1977 under the leadership of the State Agricultural Experiment Stations (SAES) to address the problem of atmospheric deposition and its effects on agricultural crops, forests, rangelands, surface waters and other natural and cultural resources. In 1978, the first sites of the NADP's precipitation chemistry network were established to provide information about geographical patterns and temporal trends in the deposition of acidic chemicals and nutrients. Initially organized as Regional Project NC-141 by the North Central Region of the SAES, the NADP was endorsed by all four regions in 1982, at which time it became Interregional Project IR-7. A decade later, the SAES reclassified IR-7 as a National Research Support Project, NRSP-3.

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 includes research, monitoring and assessment activities that emphasize the timely development of a firm scientific basis for decision making. Because of its experience in designing, organizing and operating a national-scale monitoring network, the NADP was asked to assume responsibility for coordinating the operation of the National Trends Network (NTN) of NAPAP. As the NADP and NTN had common siting criteria and operational procedures, and shared a common analytical laboratory, the networks were merged with the designation NADP/NTN. Many of the NTN sites are supported by the U.S. Geological Survey (USGS), which serves as the lead federal agency for deposition monitoring under NAPAP.

Seven federal agencies support NADP/NTN research and monitoring under NAPAP: the USGS, U.S. Department of Agriculture (USDA) Cooperative State Research Service (CSRS) and U.S. Forest Service (USFS), 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 other federal agencies, state agencies, universities, public utilities and industry, as well as the SAES. The current network consists of approximately 200 sites.

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**1993 QUALITY ASSURANCE REPORT  
NADP/NTN DEPOSITION MONITORING**

**Laboratory Operations  
Central Analytical Laboratory  
January 1993 through December 1993**

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ANNUAL DEPOSITION MONITORING  
AIR QUALITY ASSESSMENT REPORT

January 1993 through December 1993  
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## I. INTRODUCTION

The National Atmospheric Deposition Program/National Trends Network (NADP/NTN), a cooperative effort between state agricultural experiment stations, federal and state agencies, public and private universities, and industry, began in 1978. The Illinois State Water Survey in Champaign, Illinois was chosen as the site of the Central Analytical Laboratory (CAL) for the network. The 120,000th wet deposition sample arrived and was processed there in May of 1993..

Precipitation samples, collected weekly at approximately 200 sites, are sent to the CAL after site operators visually inspect the sample and decant approximately 20 milliliters (mL) for field pH and conductivity measurements. These samples arrive at the CAL throughout the following week, and their journey through the laboratory begins. The low ionic strength of precipitation samples dictates a strict quality control (QC) protocol for the life of the analytical process. Quality control solutions (QCS) for site pH and conductance measurements are prepared at the CAL and sent out to site operators. Operators are instructed and trained to be particularly careful when handling the sample buckets and making their measurements in order to minimize human contamination. Laboratory personnel follow strict standard operating procedures (SOPs) designed to preserve the integrity of the precipitation throughout the filtration, measurements, and storage.

All analyses are made after the instrumentation has been calibrated and two QCS (emulating the 25th and 75th percentile concentrations of all network samples) are analyzed and their values verified as being within the control limits for their concentrations. Data for all sample measurements are stored in the NADP/NTN data base. The analyses are then submitted to an ion balance algorithm and a calculated compared to measured conductance calculation. Those samples whose analytical results fall outside of the established limits are submitted to the chemists for reanalysis. Data changes are made when indicated.

An audit of the analytical, data management, and quality assurance procedures of the NADP/NTN CAL occurred on July 27-29, 1994. The audit team included the team leader F. Paul Kapinos, U. S. Geological Survey (USGS); H. Keith Long, USGS; Curtis M. Morris, U. S. Environmental Protection Agency (USEPA); John K. Robertson, U. S. Military Academy (USMA); David S. Bigelow, Colorado State University (CSU); and William J. Parkhurst, Tennessee Valley Authority (TVA). The Final Report concluded with "Overall, it was felt that CAL is doing an excellent job of providing high quality data to the National

## Atmospheric Deposition Program/National Trends Network."(1)

The NADP/NTN Quality Assurance Plan (2) summarizes the methods used to analyze and document each sample. The annual quality assurance (QA) reports (3-12) describe the evolution of the laboratory program and the measures used to evaluate sample bias and precision as well as to evaluate background contributions from the sampling containers, filters, and deionized reagent water. This report is in the format of the 1989-1992 reports. Previous reports are available from the Illinois State Water Survey and the Program Coordinator's Office at CSU. QA data summarized in these reports are also available in tabular form from the CAL upon request.

## II. LABORATORY QUALITY ASSURANCE - A GENERAL DESCRIPTION

This report summarizes the internal and external QA/QC data from the laboratory throughout 1993. The data are summarized and presented in order of the frequency with which activities occur: daily, weekly, monthly, semiannually, and annually. Table II-1 summarizes the program which is described in the following sections.

The internal QA/QC program has evolved along with the network over the past 15 years. The data produced help quantify and subsequently evaluate the analytical equipment, personnel performance, and analytical procedures employed by the CAL. From the internal program, the laboratory bias and precision of the reported values can be ascertained. The USGS conducts the official external interlaboratory comparison. The CAL voluntarily participates in national and international interlaboratory comparisons. These data are summarized.

Processing for traditional NADP/NTN samples has not changed since 1987 (Figure II-1). Analysis of samples collected and processed for the Atmospheric Integrated Research Monitoring Network (AIRMoN) began in April 1993. Because AIRMoN samples are subject to the same analytical procedures as those used for NADP samples, laboratory QC is standard for both groups. Two employees, Jane Rothert and Lori Henry, were reassigned to the AIRMoN project.

Internally prepared NIST traceable simulated rainwater at concentration levels near the 25th and 75th percentile concentration values of the network, verified by the Canadian Centre for Inland Waters laboratory, are used as quality control standards (QCS) to validate instrument calibration and verify the same during sample runs. Simulated rainwater purchased from High Purity Standards (HPS) in Charleston, South Carolina is used as blind samples in the internal program. (HPS solutions are certified as traceable to NIST-certified standards.) Replicate samples and reanalysis sample selection follow the same protocol in 1993 as they have since 1989. In anticipation of the change in shipping protocol for 1994, the procedure to evaluate blanks solutions expanded to include analysis of the leachate from 1 liter high density polyethylene (HDPE) bottles. Additionally, a change of method for the analysis of orthophosphate from ion chromatography to flow injection automated wet chemistry to begin in January 1994, was approved at the November 1993 NADP/NTN Technical Committee Meeting in Nashville, Tennessee. The validation study for this change is presented in Appendix A.



**TABLE II-1 NADP/NTN Laboratory QC/QA Program Summary,  
1993**

- I. Daily**
  - A. Instruments calibrated, calibration curves verified using control standards.**
    - 1. Control standards are CAL formulated solutions of simulated rain representing the 25th and 75th percentile concentrations of network samples used for all parameters.
    - 2. Control standards values recorded.
  - B. Records of standards preparation and instrument maintenance updated.**
- II. Weekly**
  - A. Blanks analyzed.**
    - 1. Deionized (DI) water.
    - 2. Filter leachates using DI water and pH 4.3 nitric acid.
    - 3. Upright and inverted bucket leachates using DI water and pH 4.3 nitric acid.
    - 4. Liter bottle leachates using pH 4.3 nitric acid.
  - B. Internal blind audit samples from sites SWS1, SWS2, SWS3.**
    - 1. SWS1: High Purity Standards (HPS) simulated rainwater I and II, unfiltered.
    - 2. SWS2: DI and pH 4.3 nitric acid, unfiltered.
    - 3. SWS3: all four of the above solutions in rotation, filtered.
  - C. Quality control solutions validated prior to shipment to sites.**
- III. Monthly**
  - A. Inspection of control charts generated from control standards.**
  - B. Internal blind and replicate data evaluated from printout.**
  - C. Reanalysis of samples selected by computer based on ion balance and conductance calculations.**
    - 1. Reanalysis data evaluated.
    - 2. Suggestions for data changes made to data management.
  - D. USGS interlaboratory comparison analyses evaluated prior to transmission.**
- IV. Annually and semiannually**
  - A. Quality assurance report submitted for publication.**
  - B. Subcommittee reports prepared for spring and fall NADP/NTN meetings.**
  - C. Participation in external interlaboratory comparisons.**

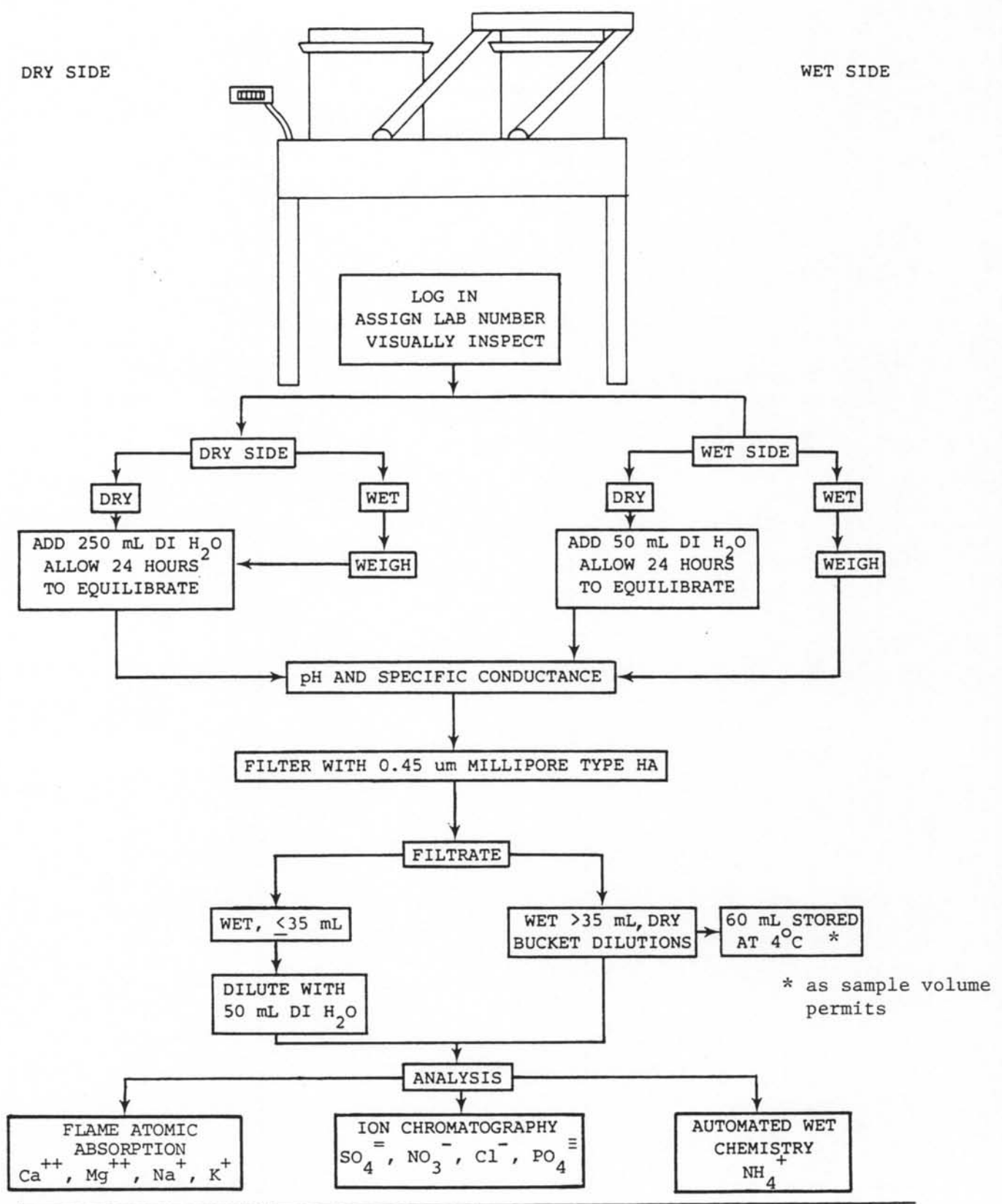


FIGURE II-1 Sample processing flowchart, January 1993-December 1993

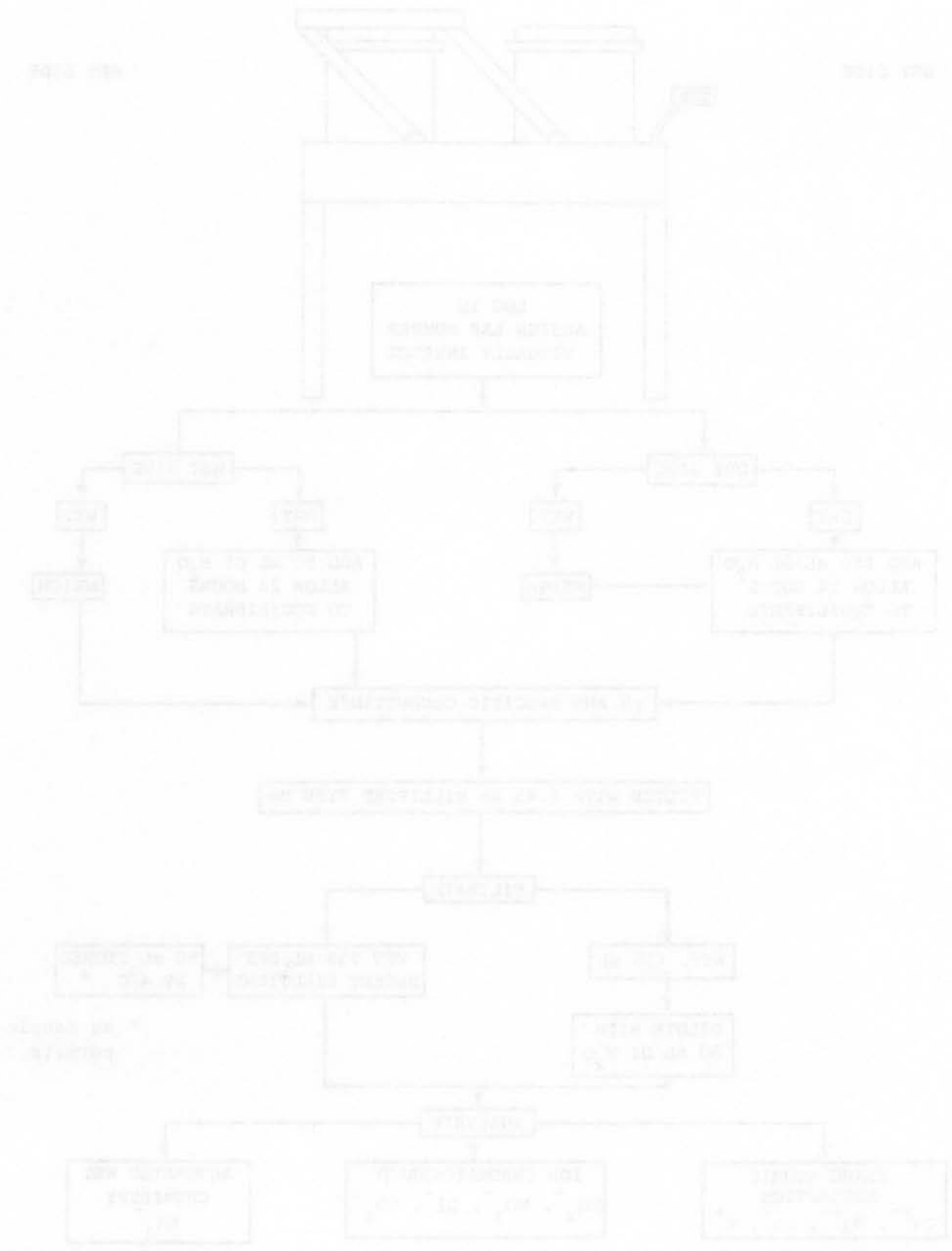


FIGURE 1-1. Sample processing flow chart, December 1972

### III. DAILY QUALITY CONTROL PROCEDURES

In 1993 there were 199 sites at 195 monitoring locations collecting weekly precipitation samples throughout the United States. Two special studies—one to evaluate the use of bottles as shipping containers and the other to compare a two-week sampling interval to the current one-week period,—were conducted at 11 and 7 sites, respectively, during part of the year, appreciably increasing the sample load at the CAL. Samples collected on Tuesday morning begin arriving at the CAL that afternoon and continue to arrive throughout the following week. Each day they are unpacked, their field forms are read, and they progress through sample processing and into the laboratory for pH and conductance measurements prior to filtration through Millipore™ type HAWP, 0.45-micrometer ( $\mu\text{m}$ ) filters into 60-mL HDPE bottles. If sample volume is sufficient, an additional 60-mL sample is filtered, labeled, and stored at 4<sup>o</sup> C for archival purposes.

Filtered bottled samples are placed on a tray in numerical order. Full trays are transported to the holding area in the laboratory building so that the samples are available for anion and cation analysis. The CAL analytical staff (Table III-1) expanded by two with the increased tasks for the AIRMoN project. Methods of analysis and method detection limits (MDLs) (Table III-2) have remained the same since 1987. Standard operating procedures (SOPs) for all laboratory tasks were revised and compiled in notebook form in time for the CAL audit in July.

Calibration of analytical instruments is verified using QCS. Internally formulated simulated rain, traceable to NIST-certified standards, has been used since 1990 as the QCS. Two concentrations, that approximate the 25th and 75th percentile values for network precipitation (Table III-3), are analyzed immediately after calibration and continually throughout the sample run to verify that the calibration remains stable. (This year there are two batches of 75th percentile solution due to a spigot leak in the carboy.) USEPA diluted nutrient concentrate is used for the phosphate QCS. The analytical values for the QCS are recorded and entered into a computer program that generates monthly control charts from the data. The QCS data are summarized in tabular form for this report in order to provide estimates of bias and precision (Table III-4).

The mean bias for the cations is zero with five exceptions: 0.001 mg/L of calcium for the second 75th percentile solution, potassium for both 25th percentile solutions and the first 75th percentile solution, and sodium for the 25th percentile solution. The precision expressed as percent relative standard deviation (RSD) is

consistent with the values found in 1992. The mean anion biases are smaller than the corresponding values from the previous year and the percent RSD is similar for each. The hydrogen ion bias is smaller and the precision better than the values reported in 1992. Conductivity precision is the same and the bias smaller for the 25th percentile and second 75th percentile solutions than last year. All bias and precision measurements fall within the goals for laboratory measurements outlined in the network QA plan (2).

**TABLE III-1 Central Analytical Laboratory Analytical Staff, 1993**

<b>Staff Member</b>	<b>Job Function</b>	<b>Period of Employment</b>
<b>Sue Bachman</b>	<b>Ammonium Calcium, Magnesium, Sodium, and Potassium</b>	<b>8/80 - 12/93</b>
		<b>11/88 - 12/93</b>
<b>Jackie Damara</b>	<b>Sample processing supervision</b>	<b>9/83 - 5/86 1/88 - 12/93</b>
<b>Brigita Demir</b>	<b>Anions analysis</b>	<b>9/81 - 12/93</b>
<b>Patricia Dodson</b>	<b>Sample processing</b>	<b>9/80 - 12/93</b>
<b>Lori Henry</b>	<b>AIRMoN sample processing and metals analysis</b>	<b>8/92 - 12/93</b>
<b>Theresa Ingersoll</b>	<b>Sample receipt and processing</b>	<b>3/85 - 12/93</b>
<b>Kenni James</b>	<b>Quality assurance</b>	<b>10/87 - 12/93</b>
<b>Mark Peden</b>	<b>Laboratory Manager</b>	<b>7/78 - 12/93</b>
<b>Jeffrey Pribble</b>	<b>Sample receipt and supply procurement</b>	<b>7/87 - 12/93</b>
<b>Jane Rothert</b>	<b>AIRMoN coordinator</b>	<b>5/92 - 12/93</b>
<b>Angela Weddle</b>	<b>pH, conductivity IC data reduction</b>	<b>10/89 - 12/93</b>
		<b>8/92 - 12/93</b>

**TABLE III-2 Method Detection Limits (MDLs)  
for Precipitation Analysis, 1993**

<b>Analyte</b>	<b>MDL (mg/L)</b>	<b>Dates</b>	<b>Method</b>
<b>Calcium</b>	<b>0.02</b>	<b>7/78 - 10/80</b>	<b>Flame Atomic Absorption</b>
	<b>0.009</b>	<b>10/80 - 12/93</b>	
<b>Magnesium</b>	<b>0.002</b>	<b>7/78 - 10/80</b>	<b>Flame Atomic Absorption</b>
	<b>0.003</b>	<b>10/80 - 12/93</b>	
<b>Sodium</b>	<b>0.004</b>	<b>7/78 - 10/80</b>	<b>Flame Atomic Absorption</b>
	<b>0.003</b>	<b>10/80 - 12/93</b>	
<b>Potassium</b>	<b>0.004</b>	<b>7/78 - 10/80</b>	<b>Flame Atomic Absorption</b>
	<b>0.003</b>	<b>10/80 - 12/93</b>	
<b>Ammonium</b>	<b>0.02</b>	<b>7/78 - 12/93</b>	<b>Automated Phenate, Colorimetric</b>
<b>Sulfate</b>	<b>0.10</b>	<b>7/78 - 5/85</b>	<b>Automated Methyl Thymol Blue, Colorimetric Ion Chromatography</b>
	<b>0.03</b>	<b>5/85 - 12/93</b>	
<b>Nitrate/Nitrite</b>	<b>0.02</b>	<b>7/78 - 5/85</b>	<b>Automated Cadmium Reduction, Colorimetric</b>
<b>Nitrate</b>	<b>0.03</b>	<b>5/85 - 12/93</b>	<b>Ion Chromatography</b>
<b>Chloride</b>	<b>0.05</b>	<b>7/78 - 3/81</b>	<b>Automated Ferricyanide, Colorimetric Ion Chromatography</b>
	<b>0.02</b>	<b>3/81 - 5/85</b>	
	<b>0.03</b>	<b>5/85 - 12/93</b>	
<b>O-phosphate</b>	<b>0.003</b>	<b>7/78 - 2/86</b>	<b>Automated Ascorbic Acid, Colorimetric Ion Chromatography</b>
	<b>0.01</b>	<b>2/86 - 7/87</b>	
	<b>0.02</b>	<b>7/87 - 12/93</b>	

**Notes: *Methods for Collection and Analysis of Precipitation* (13) describes methods as they were in 1986. Instrument and software upgrades and method modifications are contained in the laboratory procedures manual, which is continually being updated.**



**TABLE III-3 Percentile Concentration Values of Chemical and Physical Parameters Measured  
in NADP/NTN Precipitation, 1993**

Parameter	Min.	Percentile Concentration Value (mg/L)										Max.
		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>			
Calcium	<0.009	0.016	0.024	0.046	0.102	0.221	0.453	0.686	1.558	35.60		
Magnesium	<0.003	0.004	0.006	0.011	0.022	0.042	0.082	0.128	0.288	2.49		
Potassium	<0.003	<0.003	0.004	0.009	0.017	0.035	0.068	0.107	0.317	3.30		
Sodium	0.004	0.019	0.025	0.040	0.075	0.159	0.369	0.639	1.841	36.00		
Ammonium	<0.02	<0.02	0.03	0.09	0.20	0.38	0.64	0.87	1.57	12.95		
Nitrate	<0.03	0.21	0.32	0.61	1.10	1.83	2.85	3.73	6.24	14.91		
Chloride	<0.03	0.04	0.05	0.07	0.12	0.24	0.53	0.98	3.08	18.25		
Sulfate	0.04	0.20	0.31	0.61	1.17	2.17	3.48	4.52	7.39	37.13		
Phosphate	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.10	3.20		
pH (units)	3.51	4.08	4.21	4.44	4.88	5.52	6.16	6.46	6.86	8.04		
Cond. ( $\mu$ S/cm)	1.4	3.2	4.3	7.0	12.6	22.7	34.7	45.5	74.3	280.4		

**Notes:**

Number of samples = 6,993

Mean sample volume = 1,416 mL; median sample volume = 936.6 mL

Source: National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) 1993 wet-side samples.

TABLE III-4 Analytical Bias and Precision Determined from Analysis of Simulated Rain QCS, 1993

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision $\bar{y}$ (mg/L)	Precision RSD (%)	Critical Conc. (mg/L)	Statist. Significant Bias?
Calcium	0.062 <sup>a</sup>	0.062	734	0.000	0.0	0.001	2.3	0.001	NO
	0.300 <sup>b</sup>	0.300	414	0.000	0.0	0.002	0.7	0.001	NO
	0.292 <sup>c</sup>	0.293	441	0.001	0.3	0.003	0.9	0.001	NO
Magnesium	0.014	0.014	818	0.000	0.0	0.001	7.1	0.000	NO
	0.070	0.070	494	0.000	0.0	0.001	1.7	0.001	NO
	0.069	0.069	270	0.000	0.0	0.001	1.5	0.001	NO
Potassium	0.010	0.011	766	0.001	10.0	0.001	10.3	0.001	YES
	0.054	0.055	439	0.001	1.8	0.001	2.0	0.001	YES
	0.056	0.056	254	0.000	0.0	0.001	2.1	0.001	NO
Sodium	0.037	0.038	944	0.001	2.7	0.001	2.4	0.000	YES
	0.191	0.191	543	0.000	0.0	0.002	0.8	0.001	NO
	0.191	0.191	310	0.000	0.0	0.002	0.8	0.001	NO
Ammonium	0.07	0.07	699	0.00	0.0	0.01	12.9	0.00(4) <sup>d</sup>	NO
	0.36	0.36	329	0.00	0.0	0.01	3.4	0.00(6)	NO
	0.36	0.36	210	0.00	0.0	0.01	3.3	0.00(6)	NO
Nitrate	0.42	0.42	1110	0.00	0.0	0.01	1.9	0.00(3)	NO
	1.96	1.96	765	0.00	0.0	0.02	1.0	0.01(7)	NO
	1.95	1.94	370	-0.01	-0.5	0.03	1.5	0.01(0)	NO
Chloride	0.11	0.11	1159	0.00	0.0	0.01	5.9	0.00(2)	NO
	0.52	0.52	765	0.00	0.0	0.01	2.4	0.00(5)	NO
	0.51	0.51	426	0.00	0.0	0.01	2.4	0.00(5)	NO
Sulfate	0.53	0.54	1094	0.01	1.9	0.01	1.7	0.00(3)	YES
	2.59	2.60	772	0.01	0.4	0.02	0.8	0.00(9)	NO
	2.47	2.47	374	0.00	0.0	0.03	1.2	0.01(1)	NO
Phosphate	0.06	0.05	495	-0.01	-16.7	0.01	12.9	0.00(2)	YES
	0.30	0.30	407	0.00	0.0	0.01	3.0	0.00(3)	NO

TABLE III-4 Analytical Bias and Precision Determined from Analysis of Simulated Rain QCS, 1993, continued

Parameter	Target Conc.	Measured Conc.	Number of Replicates	Bias (mg/L)	Bias (%)	Precision $\bar{s}$ (mg/L)	Precision RSD (%)	Critical Conc. (mg/L)	Statist. Significant Bias?
pH units ( $\mu\text{eq/L}$ ) <sup>a</sup>	4.97(10.7)	4.96(11.0)	2173	(0.27)	(2.5)	0.02	0.4	(0.207)	YES
	4.32(47.9)	4.33(46.9)	1426	(-0.95)	(-2.0)	0.01	0.3	(0.559)	YES
	4.34(45.7)	4.35(44.7)	740	(-0.99)	(-2.2)	0.01	0.2	(0.408)	YES
Conductivity ( $\mu\text{S/cm}$ )	6.51	6.38	1228	-0.13	-2.0	0.16	2.5	0.066	YES
	28.2	27.8	774	-0.42	-1.5	0.33	1.2	0.141	YES
	27.0	26.9	506	-0.08	-0.3	0.24	0.9	0.103	NO

Notes:

<sup>a</sup> The first set of values for each parameter is for the 25<sup>th</sup> percentile solution. <sup>b</sup> The second set of values for each parameter is for the 75<sup>th</sup> percentile solution. <sup>c</sup> The third set of values for each parameter is for a second preparation of 75th percentile solution. <sup>d</sup> Critical concentration values in parentheses are provided for information. <sup>e</sup> The pH data in parentheses are in microequivalents.

See Appendix B for definitions of and formulas for Bias, Standard Deviation, Precision, and Critical Concentration.

#### **IV. WEEKLY QUALITY CONTROL/QUALITY ASSURANCE PROCEDURES**

QA procedures that occur on a weekly basis include the submission and analysis of internal blind audit samples, the selection and analysis of replicate network samples, and the collection and analysis of a suite of laboratory blank solutions.

##### **A. Internal Blind Audit**

The internal blind audit, begun in 1984, provides another vehicle for the evaluation of bias and precision. Since 1987, three blind samples have been submitted on a weekly basis. These samples are given the site designations of SWS1, SWS2, and SWS3. Simulated rainwater, purchased from High Purity Standards (HPS), Charleston, South Carolina, formulated in two concentrations, alternate as the SWS1 samples. Deionized (DI) water from the IC/FIA laboratory and pH 4.3 nitric acid check solution are the alternating SWS2 solutions. In order to estimate the effects of filtration, all four of the aforementioned solutions are submitted in rotation as SWS3 samples and filtered after pH and conductivity are measured and prior to ion analysis. SWS1 and SWS2 samples are decanted into another 60-mL bottle after the measurement of pH and conductivity and placed in the queue on the trays with the network samples awaiting ion analysis. The analytical data from these samples are summarized in Tables IV-1 through IV-4.

Comparison of the SWS1 samples' bias and precision results to those of the QCS show increased bias and worse precision numbers. It is important to note the differences in the concentrations of the various solutions and the wide difference in the number of analyses of each parameter. The QCS are formulated to emulate the 25th and 75th percentile concentrations of the network, while the concentrations of the HPS solutions range from the 5th to greater than the 99th percentile concentration values. There are considerably more QCS than blind results. The percent bias and RSD values for all of the SWS parameters fall within the goals of the QA plan.

SWS2 samples provide an opportunity to look at blank solutions as blind samples. These could indicate carry-over problems for each of the measurements or aberrant calibration numbers near the blank standard. The mean data values indicate that unfiltered blanks show detection or near detection limit values when analyzed at random. It is also important to note that, for calculation purposes,

values less than the method detection limit (MDL) are set to equal one half of the MDL. This procedure produces extremely large bias and precision results for values near the MDL.

The results for the filtered SWS3 samples show that the filtering process has introduced sodium in all instances and calcium for the simulated rain samples. As in previous years, the filtered sulfate concentration bias is more negative. The precision of the filtered simulated rain is worse for all ions but potassium. pH and conductivity are always measured on nonfiltered samples. Again, the number of SWS3 solutions analyzed is half of either the SWS1 or SWS2 sample numbers.

Comparing the analytical results of the blind solutions to those of the QCS serves to illustrate the wider variability in random sample analysis compared to analysis of known solutions immediately after calibration. The variation in the analytical results at differing concentrations is predictable and accounted for in the QA Plan by allowing larger bias and precision percentages at lower concentrations.

Tables C-1 and C-2 and control chart figures in Appendix C (Figures C-1 through C-20) are tabular and graphic representations of the filtered and unfiltered ion concentrations in the High Purity Standards simulated rainwater I and II.



TABLE IV-1 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS1). High Purity Standards Simulated Rainwater I (HPS-SRI) and II (HPS-SRII). Unfiltered. 1993									
Parameter	Target Concentration (mg/L)	Measured Concentration (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision <sub>s</sub> (mg/L)	Precision RSD (%)		
Calcium	0.015 <sup>a</sup>	0.016	26	0.001	6.7	0.005	31.2		
	0.052 <sup>b</sup>	0.055	25	0.003	5.8	0.009	16.4		
Magnesium	0.025	0.024	26	-0.001	-4.0	0.002	8.3		
	0.047	0.050	25	0.003	6.4	0.001	2.0		
Sodium	0.200	0.204	26	0.004	2.0	0.014	6.9		
	0.400	0.407	25	0.007	1.8	0.011	2.7		
Potassium	0.048	0.050	26	0.002	4.2	0.003	6.0		
	0.100	0.104	25	0.004	4.0	0.002	1.9		
Ammonium	0.10 <sup>c</sup>	0.09	26	-0.01	-10.0	0.03	33.3		
	1.00	0.95	25	-0.05	- 5.0	0.03	3.0		
Sulfate	2.70	2.57	26	-0.13	-4.8	0.05	1.9		
	10.00	10.24	25	0.24	2.4	0.19	1.8		
Nitrate	0.50	0.55	26	0.05	10.0	0.02	3.6		
	7.10	7.34	25	0.24	3.4	0.13	1.8		
Chloride	0.25	0.24	26	-0.01	-4.0	0.03	12.5		
	0.98	0.98	25	0.00	0.0	0.04	4.1		
pH (units)	(4.27) <sup>d</sup>	53.7	26	(0.01) -1.2	(0.2) -2.3	(0.03) 3.01	(0.7) 5.7		
	(3.57)	269	25	(0.02) -11	(0.6) -4.1	(0.02) 8.31	(5.6) 3.2		
Conductivity (µS/cm)	25.1	25.4	26	0.3	1.2	1.0	3.9		
	126.6	126.8	25	0.2	0.2	1.7	1.3		

Notes: <sup>a</sup> The first set of values for each parameter is for HPS-SRI. <sup>b</sup> The second set of values for each parameter is for HPS-SRII.

<sup>c</sup> Ammonium values are for information only, found not to be stable. <sup>d</sup> pH values in parentheses are in pH units.



**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, 1993**

Parameter	Target Concentration (mg/L)	Measured Concentration (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision <sup>s</sup> (mg/L)	Precision RSD (%)
Calcium	<0.009	<0.009	25	0.000	0.0	0.002	40.0 <sup>c</sup>
	<0.009	<0.009	25	0.000	0.0	0.001	20.0
Magnesium	<0.003	<0.003	25	0.000	0.0	0.000	0.0
	<0.003	<0.003	25	0.000	0.0	0.000	0.0
Sodium	<0.003	0.003	25	0.001	50.0	0.003	166.7
	<0.003	0.003	25	0.001	50.0	0.002	66.7
Potassium	<0.003	<0.003	25	0.000	0.0	0.000	0.0
	<0.003	<0.003	25	0.000	0.0	0.000	0.0
Ammonium	<0.02	0.02	25	0.01	100	0.01	50.0
	<0.02	0.02	25	0.01	100	0.04	200.0
Sulfate	<0.03	<0.03	25	0.00	0.0	0.01	50.0
	<0.03	<0.03	25	0.00	0.0	0.00	0.0
Nitrates	<0.03	<0.03	25	0.00	0.0	0.01	50.0
	3.12	3.24	25	0.12	3.8	0.05	1.5
Chloride	<0.03	<0.03	25	0.00	0.0	0.01	50.0
	<0.03	<0.03	25	0.00	0.0	0.01	50.0
pH (units) <sup>d</sup> H <sup>+</sup> µeq/L	(5.76) 1.74	(5.61) 2.44	25	(-0.15) 0.70	(-2.6) 40.4	(0.07) 0.35	(1.2) 14.3
	(4.30) 50.1	(4.31) 49.3	25	(0.01) -0.8	(0.2) -1.6	(0.02) 1.39	(0.5) 2.82
Conductivity µS/cm	0.8	1.1	25	0.3	37.5	0.4	36.4
	21.8	21.5	25	-0.3	-1.4	0.6	2.8

Notes: <sup>a</sup> The first set of values for each parameter is for DI water. <sup>b</sup> The second set of values for each parameter is for pH 4.3 QCS.

<sup>c</sup> For calculation purposes MDLs are assigned the value of 0.5(MDL). <sup>d</sup> pH values in parenthesis are pH units.

**TABLE IV-3 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS3), High Purity Standards Simulated Rainwater I (HPS-SRI) and II (HPS-SRII), Filtered, 1993**

Parameter	Target Concentration (mg/L)	Measured Concentration (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision <sub>s</sub> (mg/L)	Precision RSD (%)
Calcium	0.015 <sup>a</sup>	0.026	13	0.011	73.3	0.015	57.7
	0.052 <sup>b</sup>	0.067	13	0.015	28.8	0.010	14.9
Magnesium	0.025	0.026	13	0.001	4.0	0.003	11.5
	0.047	0.051	13	0.004	8.5	0.002	3.9
Sodium	0.200	0.252	13	0.052	26.0	0.044	17.5
	0.400	0.441	13	0.041	10.2	0.026	5.9
Potassium	0.048	0.049	13	0.001	2.1	0.002	4.1
	0.100	0.101	13	0.001	1.0	0.003	3.0
Ammonium	0.10 <sup>c</sup>	0.13	13	0.03	30.0	0.10	76.9
	1.00	0.93	13	-0.07	-7.0	0.07	7.5
Sulfate	2.70	2.47	13	-0.23	-8.5	0.08	3.2
	10.00	9.84	13	-0.16	-1.6	0.28	2.8
Nitrate	0.50	0.59	13	0.09	18.0	0.04	6.8
	7.10	7.12	13	0.02	0.3	0.20	2.8
Chloride	0.25	0.28	13	0.03	12.0	0.05	17.9
	0.98	0.99	13	0.01	1.0	0.06	6.1
pH (units)	(4.27) <sup>d</sup> 53.7	(4.27) 53.09	13	(0.0) -0.61	(0.0) -1.14	(0.03) 2.43	(0.7) 4.5
	(3.57) 269	(3.58) 260	13	(0.01) -8.6	(0.3) -3.21	(0.03) 12.6	(0.8) 4.8
Conductivity (µS/cm)	25.1	25.6	13	0.5	2.0	0.8	3.1
	126.6	127.5	13	0.9	0.7	2.3	1.8

Notes: <sup>a</sup> The first set of values for each parameter is for HPS-SRI. <sup>b</sup> The second set of values for each parameter is for HPS-SRII. <sup>c</sup> Ammonium values are for information only, found not to be stable. <sup>d</sup> pH values in parentheses are in pH units.

TABLE IV-4 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SW53), Deionized (DI) Water and pH 4.3 QCS, Filtered, 1993

Parameter	Target Concentration (mg/L)	Measured Concentration (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision <sup>s</sup> (mg/L)	Precision RSD (%)
Calcium	<0.009 <sup>a</sup>	<0.009	13	0.000	0.0	0.002	40.0 <sup>c</sup>
	<0.009 <sup>b</sup>	<0.009	12	0.000	0.0	0.005	83.3
Magnesium	<0.003	<0.003	13	0.000	0.0	0.000	0.0
	<0.003	<0.003	12	0.000	0.0	0.001	50.0
Sodium	<0.003	0.040	13	0.038	1900	0.030	75.0
	<0.003	0.057	12	0.055	2750	0.047	82.5
Potassium	<0.003	<0.003	13	0.000	0.0	0.001	50.0
	<0.003	<0.003	12	0.000	0.0	0.001	50.0
Ammonium	<0.02	0.02	13	0.01	100.0	0.01	50.0
	<0.02	0.04	12	0.03	300.0	0.05	125
Sulfate	<0.03	<0.03	13	0.00	0.0	0.00	0.0
	<0.03	<0.03	12	0.00	0.0	0.00	0.0
Nitrate	<0.03	0.05	13	0.03	150	0.03	60.0
	3.12	3.20	12	0.08	2.6	0.13	4.1
Chloride	<0.03	0.04	13	0.02	100	0.03	75.0
	<0.03	0.05	12	0.03	150	0.03	60.0
pH (units) <sup>d</sup> H <sup>+</sup> µeq/L	(5.74) 1.83	(5.58) 2.66	13	(-0.16) 0.83	(2.8) 45.6	(0.05) 0.31	(0.9) 45.6
	(4.30) 50.1	(4.31) 48.71	12	(0.01) -1.41	(0.2) -2.81	(0.01) 1.28	(0.2) 2.6
Conductivity (µS/cm)	0.9	1.1	13	0.2	25.8	0.2	18.2
	21.8	21.7	12	-0.1	-0.46	0.6	2.76

Notes: <sup>a</sup> The first set of values for each parameter is for DI water. <sup>b</sup> The second set of values for each parameter is for pH 4.3 QCS. <sup>c</sup> For calculation purposes MDLs are given the value of 0.5(MDL). <sup>d</sup> pH data in parentheses are pH units.

## B. REPLICATE SAMPLES

Two percent of all weekly network samples are split into three 60-mL portions. Two portions are the traditional analytical and archival samples, while the third is returned to sample processing to be assigned a later sequential number and resubmitted. The first and third portions may be analyzed on the same day or on different days, but usually within one week. When both samples have been analyzed and the data submitted, the data management staff recodes the second sample with the original (O) number followed by a "Q" modifier. These O (original)/Q(quality control) designations appear on the "ionbal" printout of all sample analyses twice a month. At these times the QA specialist inspects the data and notes the differences in the analytical values for the O/Q sample parameters. Reanalysis is then requested for questionable replicate samples in addition to any sample which the reanalysis algorithm identifies (see section V). The results for O/Q samples cannot be changed in the data base unless they are selected for the official reanalysis list.

The information presented in Table IV-5 is a summary of the replicate analyses performed in 1993. The differences are obtained by subtracting the reanalysis value from the original. The standard deviation estimated from duplicate measurements, defined in the glossary (Appendix B), has been used to calculate the standard deviations for three categories: concentrations below the ion median concentration, concentrations above the ion median concentration, and the entire population. A fourth column presents a nonparametric estimator of variance from duplicate determinations, where 1.048328 times the Median Absolute Difference (MAD) is the estimator of the standard deviation for the 1993 O/Q data set. The high and low concentration estimated standard deviations for the O/Q set are comparable to or better than the standard deviations for the unfiltered SWS1 internal blind samples.

Box plots are used to graphically represent the replicate sample differences in Appendix C. Box plots as used in this report are defined in the glossary (Appendix B) and explained in a diagram just prior to Figure C-21 in Appendix C.



**TABLE IV-5 Variance Estimated  
from Analysis of Replicate Network Precipitation Samples, 1993**

Parameter	Standard Deviation Estimated from Paired Measurements <sup>a</sup>			(1.048328)x MAD <sup>b</sup>
	(Low conc.)	(High conc.)	(Total)	(Total)
Calcium	0.003	0.007	0.006	0.003
Magnesium	0.001	0.002	0.002	0.001
Sodium	0.002	0.011	0.008	0.002
Potassium	0.002	0.008	0.006	0.002
Ammonium	0.02	0.07	0.05	0.01
Sulfate	0.01	0.04	0.03	0.02
Nitrate	0.04	0.03	0.03	0.02
Chloride	0.01	0.03	0.02	0.01
Phosphate	0.0	0.03	0.02	0.0
H <sup>+</sup> (µeq/L)	1.07	1.66	1.40	0.53
Conductivity (µS/cm)	0.62	0.76	0.70	0.31
Number of Pairs	100	99	199	199

Notes:  
<sup>a</sup> Defined in glossary with equation  
<sup>b</sup> MAD = Median Absolute Difference

### C. BLANKS

Each week DI water is collected from the atomic absorption laboratory, the bucket washing laboratory and the sample processing laboratory. Following an initial filter rinse of 300 mL, DI water from the latter source is filtered in two 50-mL portions through a filter identical to the type used for sample filtration. The first 50 mL portion is labeled "A", the second "B". The same procedure is then repeated with a new DI water-rinsed filter using pH 4.3 nitric acid QCS to generate the "A" and "B" filtrates. Upright sample collection buckets are leached overnight with 50- and 150-mL portions of DI water and pH 4.3 nitric acid. Sample collection buckets, chosen at random, containing the same four solutions have their lids pounded on and are

inverted. Finally 50 mL of pH 4.3 nitric acid is placed in each of two 1-liter HDPE bottles chosen at random. All of these rinsates are collected in DI water rinsed 60-mL sample bottles at random times during the week. pH and conductivity measurements are made, and the bottled blanks are then forwarded, without further filtration, for ionic analyses as a group of 17 samples. Tables C-4 through C-8 in Appendix C list the percent of analyte concentrations above the MDLs found in each of the blank solutions.

## 1. Deionized Water Blanks

The DI water blanks collected from the three laboratories each week have consistently, from year to year, exhibited median ion concentrations below the MDL. The median values for pH and conductivity, which have been observed to change, are presented in tabular form. Table IV-6 contains this information for 1993.

Analyte	Sample Processing Laboratory	Atomic Absorption Laboratory	Service Laboratory
pH (units)	5.73	5.76	5.74
Conductivity ( $\mu\text{S}/\text{cm}$ )	0.8	0.8	0.8
Number of weeks	45	36	36

## 2. Filter Blanks

The contamination from the filters used to filter each sample following pH and conductivity measurements and prior to ion analysis is estimated from the analytical results of a series of four filter blanks described in the introduction. The median values obtained from the analysis of these filter blanks are summarized in Table IV-7.



**TABLE IV-7 Median Analyte Concentrations Found  
in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Filter Leachates, 1993**

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	<0.009	<0.009
Magnesium	<0.003	<0.003	<0.003	<0.003
Potassium	<0.003	<0.003	<0.003	<0.003
Sodium	0.032	0.006	0.036	0.007
Ammonium	<0.02	<0.02	<0.02	<0.02
Nitrate	0.04	<0.03	3.18 <sup>c</sup>	3.23 <sup>c</sup>
Chloride	0.04	<0.03	0.03	<0.03
Sulfate	<0.03	<0.03	<0.03	<0.03
pH (units)	5.64	5.64	4.34 <sup>d</sup>	4.31 <sup>d</sup>
H <sup>+</sup> (µeq/L)	2.29	2.29	45.7	49.0
Conductivity (µS/cm)	1.4	1.0	21.0 <sup>e</sup>	21.7 <sup>e</sup>
Number of weeks	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 µS/cm.

These median values indicate that the filter contributes near detection values of nitrate and chloride and, in the "A" portions, sodium at 10 times the MDL. Sodium persists in both "A" solutions and is minimal in the "B" filtrate. These results are consistent with the comparison of the filtered and unfiltered sodium results from the internal blind samples' analytical summaries. For the four blind solutions the sodium differences range from 0.034-0.051 mg/L, further implicating the filtering process. The bias values in 1992 were smaller (~0.021-0.030 mg/L) but persistent. These values correspond to approximately the 25th percentile sodium

values for the network, and traces of sodium are found in nearly all blank filtrates.

Table C-4 in Appendix C summarizes the percent of analytes above the MDL. From this information, it is apparent that the sodium is consistent, nitrate and chloride are often present in the "A" DI water filtrate, and calcium at three times the MDL appears in the "A" portion of the acidic solution. Past efforts to ameliorate this situation have proven unsuccessful, including the testing of alternate filters.

### **3. Bucket Blanks**

The bucket blank procedure briefly described in the introduction to this section is conducted each week using 50- and 150- mL portions of DI water and pH 4.3 nitric acid as leaching agents. After the solutions have been in contact with either the bucket or the lid for at least 24 hours, they are poured into the standard 60-mL HDPE sample bottle and grouped with the other blanks for the analytical tour. The analysis summaries 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 ( $\mu\text{g}$ ) per bucket. The pH and conductivity values are the median measurements of the collected solutions. Hydrogen ion concentrations are, as indicated, in microequivalents ( $\mu\text{eq}$ ) per bucket.

The median concentrations of ions found in the upright bucket leachates are minimal. Sodium is present only in small amounts. The anions are all below detection or near levels expected for the pH 4.3 nitric acid solution. From these results, it appears that the upright polyethylene bucket is not a source of sample contamination. The inverted samples are not as clean. As in the previous years, the bucket lid and its accompanying butadiene gasket contribute to the chemistry of the sample contained in the bucket by unavoidable contact during shipping. All cations are present in both solutions' 50-mL aliquots. Sodium and the other cations are present in both pH 4.3 nitric acid volumes. Nitrate remains below detection, there is slight chloride contamination in the smaller volume, and sulfate is present in all four solutions. The pH is raised for all four solutions, with larger differences in the smaller volumes. The lowered conductivity of the pH 4.3 nitric acid has been accounted for by the higher pH. It is due to this inverted bucket contamination phenomenon that the shipping protocol will be changed beginning January 4, 1994.

Box plots of the bucket blank leachates (Appendix C, Figures C-24-C-33) illustrate the median analyte values as well as the variance of the 1993 analyses. These plots emphasize the variability of the contribution of the bucket lid to the

sample chemistry. For calculation purposes, detection limit values are expressed as one-half the MDL (in  $\mu\text{g}/\text{mL}$ ) times either 50 or 150 mL; thus there are no zero values. A median line at the detection limit value with no corresponding "box" indicates no variance from the 10th to the 90th percentile. Tables C-5 and C-6 show the percent of the above detection values found in the bucket blanks. The tables quantify the information shown on the box plots.

<b>TABLE IV-8 Median Measured Mass as Micrograms (<math>\mu\text{g}</math>)/Bucket<sup>a</sup> Found in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Upright Bucket Leachates, 1993</b>				
<b>Analyte</b>	<b>DI Water (50 mL)</b>	<b>DI Water (150 mL)</b>	<b>pH 4.3 Nitric Acid (50 mL)</b>	<b>pH 4.3 Nitric Acid (150 mL)</b>
<b>Calcium</b>	<0.225	<0.675	<0.225	<0.675
<b>Magnesium</b>	<0.075	<0.225	<0.075	<0.225
<b>Potassium</b>	0.150	<0.225	0.300	<0.225
<b>Sodium</b>	0.400	0.450	0.600	.600
<b>Ammonium</b>	<0.50	<1.50	<0.50	<1.50
<b>Nitrate</b>	<0.75	<2.25	151 (156) <sup>b</sup>	474 (468) <sup>b</sup>
<b>Chloride</b>	<0.75	<2.25	<0.75	<2.25
<b>Sulfate</b>	<0.75	<2.25	<0.75	<2.25
<b>pH (units)</b>	5.61 (5.73) <sup>b</sup>	5.59 (5.73) <sup>b</sup>	4.37 (4.30) <sup>b</sup>	4.34 (4.30) <sup>b</sup>
<b>[H<sup>+</sup>] (<math>\mu\text{eq}/\text{bucket}</math>)</b>	0.126 (0.093) <sup>b</sup>	0.386 (0.255) <sup>b</sup>	2.13 (2.50) <sup>b</sup>	6.86 (7.52) <sup>b</sup>
<b>Conductivity (<math>\mu\text{S}/\text{cm}</math>)</b>	1.5 (0.8) <sup>b</sup>	1.4 (0.8) <sup>b</sup>	19.4 (21.8) <sup>b</sup>	20.8 (21.8) <sup>b</sup>
<b>Number of weeks</b>	45	45	45	45
<b>Notes:</b>				
<sup>a</sup> Mass/bucket represents the concentration in $\mu\text{g}/\text{mL} \times 50$ or $150$ mL. Detection limit values are expressed as the MDL (in $\mu\text{g}/\text{mL}$ )/2 $\times$ 50 or 150 mL.				
<sup>b</sup> 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 Micrograms ( $\mu\text{g}$ )/Bucket<sup>a</sup> Found  
in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid  
Inverted Bucket Leachates, 1993**

Analyte	DI Water (50 mL)	DI Water (150 mL)	pH 4.3 Nitric Acid (50 mL)	pH 4.3 Nitric Acid (150 mL)
Calcium	1.200	<0.675	1.550	1.650
Magnesium	0.400	<0.225	0.450	0.600
Potassium	0.700	0.450	0.700	0.600
Sodium	2.150	2.700	2.300	2.850
Ammonium	<0.50	<1.50	<0.50	<1.50
Nitrate	<0.75	<2.25	149 (156) <sup>b</sup>	470 (468) <sup>b</sup>
Chloride	2.00	<2.25	2.50	<2.25
Sulfate	4.50	6.00	5.50	10.5
pH (units)	6.25 (5.73) <sup>b</sup>	5.96 (5.73) <sup>b</sup>	4.61 (4.30) <sup>b</sup>	4.43 (4.30) <sup>b</sup>
[H <sup>+</sup> ] ( $\mu\text{eq}/\text{bucket}$ )	0.028 (0.093) <sup>b</sup>	0.055 (0.255) <sup>b</sup>	1.23 (2.50) <sup>b</sup>	5.57 (7.52) <sup>b</sup>
Conductivity ( $\mu\text{S}/\text{cm}$ )	2.8 (0.8) <sup>b</sup>	1.5 (0.8) <sup>b</sup>	14.1 (21.8) <sup>b</sup>	18.2 (21.8) <sup>b</sup>
Number of weeks	45	45	45	45

**Notes:**

- a. Mass/bucket represents the concentration in  $\mu\text{g}/\text{mL} \times 50$  or  $150$  mL.  
Detection limit values are expressed as the MDL (in  $\mu\text{g}/\text{mL}$ )/2  $\times$  50 or 150 mL.
- b. Values in parentheses represent those of DI water or pH 4.3 nitric acid analyzed with no bucket contact.

#### 4. Bottle Blanks

Beginning in 1993, two 1-liter HDPE bottles (to be used for shipping the precipitation samples from the sites instead of the buckets with the incriminated lids) are leached each week with 50 mL each of pH 4.3 nitric acid. These leachates are then poured into the 60-mL bottles for inclusion in the blank analyses. Table IV-10 shows the median value for 90 50-mL leachates and shows the bottles to be cleaner than the upright bucket. Table C-8 in Appendix C shows that very few analyte concentrations are above the MDL; sodium is the highest at 37.8 percent.

<b>Analyte</b>	<b>50 mL pH 4.3 Nitric Acid</b>
<b>Calcium</b>	<b>&lt;0.009</b>
<b>Magnesium</b>	<b>&lt;0.003</b>
<b>Sodium</b>	<b>&lt;0.003</b>
<b>Potassium</b>	<b>&lt;0.003</b>
<b>Ammonium</b>	<b>&lt;0.02</b>
<b>Sulfate</b>	<b>&lt;0.03</b>
<b>Nitrate</b>	<b>3.14</b>
<b>Chloride</b>	<b>&lt;0.03</b>
<b>pH (units)</b>	<b>4.32</b>
<b>H<sup>+</sup> (μeq/L)</b>	<b>47.9</b>
<b>Conductivity (μS/cm)</b>	<b>21.3</b>
<b>Number of bottles</b>	<b>90</b>



## V. MONTHLY QUALITY ASSURANCE PROCEDURES

QA procedures that occur on a monthly basis include the evaluation of the control charts generated from the daily analysis of QCS, the review of site printouts of the internal blind samples, and the reanalysis of samples that did not meet the ion balance and conductance criteria. Additionally, the analyses of samples submitted to the laboratory as part of the USGS interlaboratory comparison are reviewed prior to being sent to the USGS.

### A. REANALYSIS PROCEDURES

Twice a month the 500 samples analyzed during the previous two weeks are subjected to a reanalysis selection test. Samples are flagged for either an anion/cation imbalance or difference between the calculated and measured specific conductance. The algorithm used in 1993 has been in use since 1987.

#### 1. Ion Percent Difference (IPD)

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 (14). 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 as follows:

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

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

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

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 (CPD)

Conductance percent difference (CPD) compares 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 (15), summed, and then divided by 1000 in order to calculate the theoretical conductivity. This value is then compared to the measured conductivity. The CPD is calculated as follows:

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

Samples are flagged for reanalysis if:

$$10\% < \text{CPD} < -40\%$$

All samples selected are reanalyzed, providing sufficient volume remains and the sample has not been flagged as being contaminated. When the reanalysis is completed, the QA specialist, with documentation from the analysts, determines which values, if any, 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.

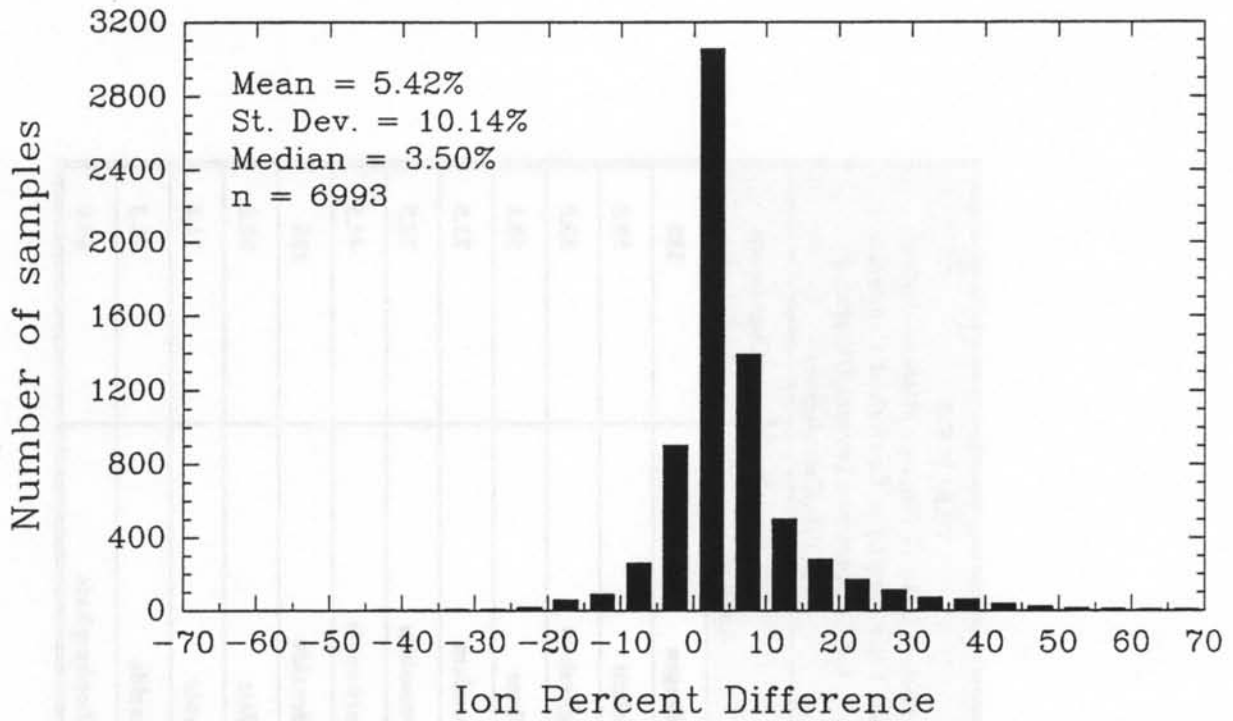
## 3. IPD and CPD Histograms

In 1993, 549 of the 12,500 (~4.4 percent) NADP/NTN samples analyzed were flagged for reanalysis. There were 97 data changes to 73 of the 549 samples selected. Figures V-1 and V-2 are histograms of the IPD and CPD values, respectively, for samples whose volume exceeded 35 mL. The mean, standard deviation, median, and number of wet samples are presented on each figure.

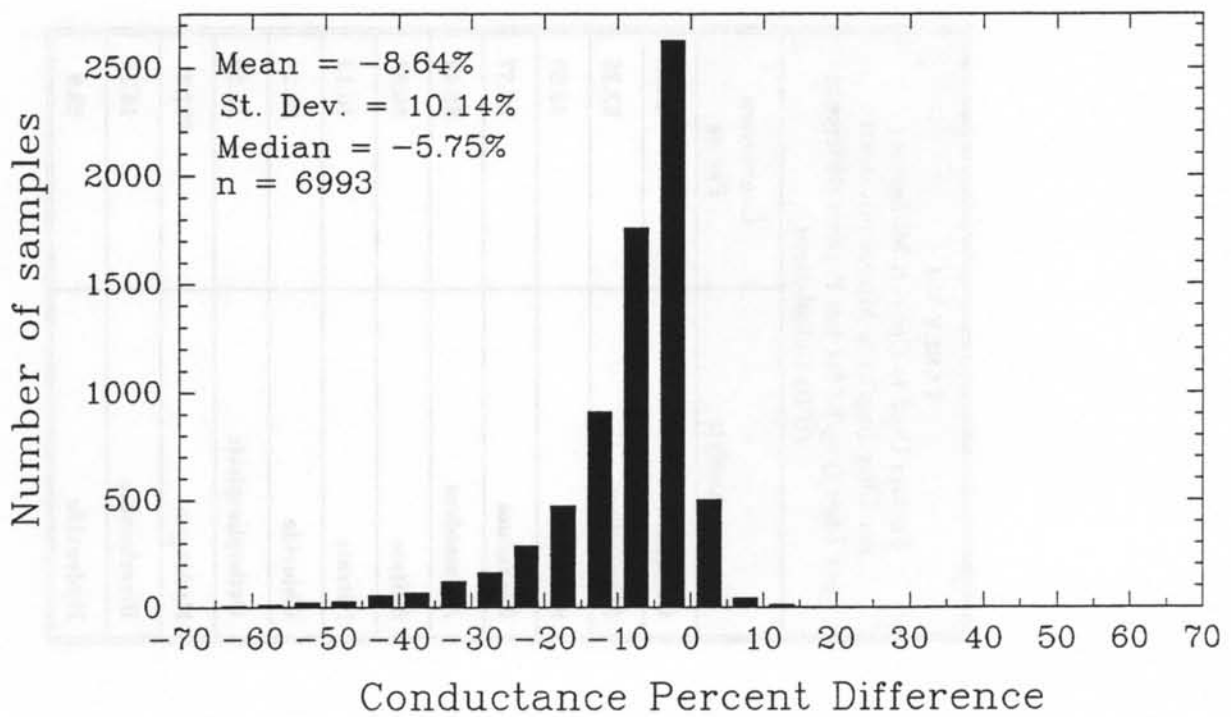
The IPD histogram exhibits a positive skew as it has for 14 of the network's 16 years. The mean (5.42 percent) and median (3.50 percent) are similar to the 1992 values (5.11 percent and 3.66 percent, respectively) but lower than in 1988 and 1989. These positive skews indicate a slight anion excess. The CPD continues to exhibit a negative skew with a mean value of -8.64 percent, the same as 1991, and a median value of -5.75 percent, the highest value since 1988. A negative skew is indicative of a measured conductance higher than the calculated conductance, as expected since the basic analysis may not account for all analytes contained in precipitation.

<b>TABLE V-1</b> <b>Factors Used to Convert Milligrams per Liter (mg/L) to Microequivalents per Liter (µeq/L) for Ion Percent Difference (IPD) Calculations</b>	
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

<b>TABLE V-2</b> <b>Factors Used to Convert Microequivalents per Liter (µeq/L) to Equivalent Conductance for Conductance Percent Difference (CPD) Calculations</b>	
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 (IPD) histogram for NADP/NTN wet-side samples, 1993.**



**FIGURE V-2. Conductance Percent Difference (CPD) histogram for NADP/NTN wet-side samples, 1993.**

## B. USGS INTERLABORATORY COMPARISON

The USGS serves as the primary external auditor of the CAL. The interlaboratory comparison, which began in fall 1982, is one of several components of the external audit. The audit 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 for analysis.

Samples used for the program were shipped to the participating laboratories approximately every two weeks. The samples used in 1993 included (1) certified samples (samples prepared and certified by NIST); (2) uncertified synthetic reference samples prepared and bottled by the USEPA and USGS; (3) natural-deposition samples collected at NADP/NTN sites and bottled by the CAL; and (4) ultrapure deionized water samples prepared by the USGS. The data reports from the participating laboratories were submitted quarterly to the USGS. The 1993 interlaboratory comparison program included five laboratories: (1) Illinois State Water Survey (CAL); (2) Environmental Science and Engineering, Gainesville, FL (ESE); (3) Atmospheric Environment Service, Downsview, Ontario (AES); (4) Ontario Ministry of the Environment, Rexdale, Ontario (MOE); and (5) Global Geochemistry Corporation, Canoga Park, CA (GGC).

Analyte bias for the participating laboratories was evaluated using NIST standard reference samples with certified analyte concentrations +/- the estimated uncertainty. Each laboratory that participated for the entire year received 18 NIST samples in 1993. The median laboratory analysis of each analyte for each certified matrix was compared to the NIST certified values. The CAL reported the fewest median analyses that were outside the range of uncertainty for the NIST samples (5 out of 15). The other participating laboratories' results ranged from 9 to 11 median analyses out of 15 that were outside the range of uncertainty for the NIST samples.

Results for a Friedman test for interlaboratory bias indicate statistically significant ( $\alpha = 0.01$ ) differences in analyte measurements for magnesium, sodium, potassium, ammonium, nitrate, sulfate, and hydrogen ion between the five laboratories.

Six ultrapure DI water samples were submitted to the laboratories. Values in excess of the minimum reporting limits indicate possible contamination. The CAL reported no analytes above reporting limits for all the DI samples analyzed. The CAL was the only participating laboratory in 1993 that did not report at least one analyte determination above reporting limits for the DI samples.

The final report containing the entire external NADP/NTN audit results is available from the U.S. Geological Survey.(16)



## **VI. SEMIANNUAL AND ANNUAL QUALITY ASSURANCE PROCEDURES**

When the data for the samples analyzed during the January-December period have been verified and entered in the computer database, the daily, weekly, and monthly QA data are summarized for the annual report and scientific presentations. In addition to the USGS laboratory intercomparison study, the CAL participates in international intercomparison studies throughout the year. In 1993 there were six such studies: one from the USEPA at Research Triangle Park (USEPA/RTP), North Carolina, three from the National Water Research Institute, Burlington, Ontario, Canada, one from the Norwegian Institute for Air Research in Lillestrom, Norway and one from the World Meteorological Organization (WMO) conducted by the USEPA/RTP. The data from these studies are presented in Appendix D.

### **A. US ENVIRONMENTAL PROTECTION AGENCY (One Study)**

The USEPA/RTP contracted Management Technology Environmental for a spring acid rain audit that had a closing date of May 14, 1993. The analytical results for this study are compared to USEPA-determined target values, and the percent differences are calculated. The CAL mean percent difference for all ten parameters for three samples is 3.40 percent. These results are better than either study in 1992 and 1991. The analysis results are presented in Table D-1 of Appendix D.

### **B. CANADA NATIONAL WATER RESEARCH INSTITUTE (Three Studies)**

The Canadian program for Long-Range Transport of Atmospheric Pollutants (LRTAP) began in 1982 and the CAL has been a participant since the fourth study in fall 1983. In 1993 the CAL participated in the March (L-32), June (L-33), and October (L-34) studies (17, 18, and 19). LRTAP studies are for selected major ions, nutrients, and physical parameters in water. Median concentrations are used as target values for flagging results. Most of the samples are surface waters or precipitation, and calculated or certified values are not known. Biased analytical results are flagged and the laboratories are ranked. The final score is computed as the sum of the percent bias and the percent of flags; therefore zero indicates optimum performance.

The CAL scores for 1993 show a large improvement over the variable results from the previous year. The score is 1.04 for Study L-32 (a flag was given for a low chloride on sample 5) and for Study L-35 (flagged for a high pH on

sample 6). Study L-34 had a slightly higher score, 2.06, due to a number transposition for the ammonium on sample 8 and a low chloride on sample 4. These scores result in the CAL ranking second out of all 61 laboratories and first of 41 for more than 10 parameters for L-32, fifth out of 57 and first for more than 8 parameters for L-33, and third out of 53 or first of 36 for 10 or more parameters for L-34. These LRTAP analytical data are presented in Tables D-2 through D-4.

### **C. NORWEGIAN INSTITUTE FOR AIR RESEARCH (One Study)**

The thirteenth intercomparison of analytical methods within the European Monitoring and Evaluation Programme (EMEP) was conducted by the Norwegian Institute for Air Research in May 1993. The samples are prepared using distilled water and inorganic salts in concentrations similar to precipitation. The CAL results are within plus or minus 4 percent of the expected values, with the exception of one potassium that was reported incorrectly and one low chloride that was 0.01 mg/L lower than expected. These data are presented in Table D-5.

### **D. WORLD METEOROLOGICAL ORGANIZATION (One Study)**

The sixteenth analysis on Reference Precipitation Samples was conducted by the WMO in collaboration with the Precipitation Reference Laboratory (PRL, co-located with the USEPA). The procedure is similar to that followed for the USEPA study, the samples are treated in the same manner. The true values followed by the results from the participating laboratories are returned some time later from Geneva. The CAL mean percent difference this year is 3.76%. The standard deviation of the percent differences is 3.56%, indicating the variation in the analytical results in this study. There are ten values greater than 4 percent; two calcium, two potassium, three sulfate, two nitrate, and one conductivity. One ammonium shows a minus ten percent difference due to the difference of 0.01 mg/L. The data for this study are presented in Table D-6.

## VII. SUMMARY

This report summarizes the results of the NADP/NTN laboratory QA program for 1993. The components are addressed in the order of their occurrence, and the data for each are summarized in tabular form with short explanations. This information is supplemented where necessary by figures and additional explanations in the appendices.

Two new employees were added to the laboratory staff to accommodate the additional sample load from the AIRMoN sites. The analytical methods and MDLs remain as they have been since 1987. The SOPs for all phases of sample shipping and receipt, sample processing and analysis were revised in a standardized format and compiled in one volume.

Internally formulated simulated rain emulating the 25th and 75th percentile concentration levels of the network wet samples continued to be used as QCS. The data from these samples, measured immediately after instrument calibration, provide optimum bias and precision quantification. These data are summarized monthly for control charts and annually for inclusion in this report. The 1993 values are comparable to or better than those for 1992 and well within the goals of the network QA Plan.

Simulated rainwater, in two concentrations from High Purity Standards in Charleston, South Carolina, serves as two of the internal blind audit samples. DI water and pH 4.3 nitric acid are the other two solutions for the audit. This program provides another estimate of bias and precision and assesses the effect of filtration using differing matrices. The bias and precision of these samples are not as good as the QCS but well within the limits of the NADP/NTN QA Plan. The effect of filtration is seen in the increased sodium concentrations of all four solutions and increased calcium and reduced sulfate concentrations in the simulated rain.

Replicate or split samples are introduced into the sampling scheme in order to provide another estimate of precision. The standard deviations estimated from duplicate measurements show the precision of these samples to be better than or comparable to the unfiltered simulated rain analyses from the internal blind audit.

In order to provide an estimate of external sources of sample contamination, a set of weekly blanks is analyzed for all parameters. The DI water continues to be of excellent quality. The filter leachates contain varying amounts of sodium. Nitrate and chloride appear in the first DI water filtrate, and calcium is sometimes present in the first acid filtrate. As in the past, the sample collection buckets DI water and pH 4.3 nitric acid leachates have ion concentrations at or near detection limits. The pound-on lids are the source, contributing cations, chloride, and sulfate as well as raising the pH and lowering the conductance. The lid effect is more pronounced in smaller volume samples. After January 1994, samples will be shipped from the site to the CAL in wide-mouth HDPE bottles. Ninety of these bottles were leached with 50 mL each of pH 4.3 nitric acid, and the analysis of the leachates showed below detection limit ion concentrations and nitrate, pH, and conductance values within the limits for the solution.

The sample reanalysis procedure has remained the same since 1987. Approximately 4.4 percent of the samples analyzed were flagged and 0.58 percent of samples analyzed required data changes to one or more parameters. The IPD continues to exhibit a positive skew similar to 1992 and the negative skew of the CPD is the same as 1991.

The USGS Interlaboratory Comparison showed that the CAL reported the fewest (5 out of 15) median analyses that were outside the range of the NIST samples submitted blind to the laboratory in an effort to evaluate analyte bias. Results of a Friedman test for interlaboratory bias indicate statistically significant differences in analyte measurements for magnesium, sodium, potassium, ammonium, nitrate, sulfate, and hydrogen ion among the five laboratories participating in 1993. The CAL was the only laboratory reporting no measurable analyte concentrations for the Ultrapure DI water samples.

Six interlaboratory studies conducted by national and international agencies show the CAL results to be comparable to or better than those of its peers.

**APPENDIX A**

**METHOD VALIDATION STUDY FOR THE DETERMINATION OF**

**ORTHOPHOSPHATE BY FLOW INJECTION ANALYSIS**



APPENDIX A

METHOD OF DETERMINATION FOR THE DETERMINATION OF

DETERMINATION OF FLOW INJECTION ANALYSIS

## METHOD VALIDATION STUDY FOR THE DETERMINATION OF ORTHOPHOSPHATE BY FLOW INJECTION ANALYSIS

by Leon M. Olszewski, Susan R. Bachman, and Kenni O.W. James

Flow Injection Analysis (FIA) for the determination of orthophosphate ( $\text{o-PO}_4$ ) is an automated colorimetric method using ascorbic acid reduction. Ammonium molybdate and antimony potassium tartrate react with orthophosphate to form an antimony-phosphate-molybdate complex. The complex is reduced with ascorbic acid to form a colored, blue molybdenum complex. The color intensity is proportional to the phosphorus concentration. The method was developed by the instrument manufacturer, Lachat Instruments, for the analytical range of 0.003 to 0.613 milligrams  $\text{o-PO}_4$  per liter for photometric measurements made at 880 nm in a 10-15 mm flow cell.

The key factors to be considered in this validation were: analytical range, method detection limit (MDL), precision, analyte recovery (bias), carry-over, and potential interferences. The proposed method should produce comparable or better results than the method that it is replacing. The FIA is being proposed to replace analysis by ion chromatography (IC).

The FIA instrument is calibrated with a set of six standards, a regression is calculated and the calibration is accepted if the correlation coefficient is greater than or equal to 0.999. The six standards used for this study were a deionized (DI) water blank, and solutions of 0.010, 0.025, 0.050, 0.100, and 0.500 mg/L  $\text{o-PO}_4$ . The lower MDL will allow detection of values in the 0.003-0.02 mg/L range which were not detected by IC. This is a benefit as the network phosphate concentrations have been historically low, with only five percent of the samples exhibiting detection level or above values.

The **method detection limit** was calculated using the formula  $\text{MDL} = t \cdot s$ . The 0.01 mg/L standard was run 24 times with an average concentration of 0.00967 mg/L and a standard deviation of 0.000963 mg/L. The  $t$  value at the 99% confidence level, 1 tail, is 2.50. The MDL is then  $2.5 \cdot 0.000963 = 0.00241$  or 0.003.

There are very **few potential interferences** for this method, especially with precipitation samples. Glassware, that has never been washed with detergents or used for other analyses will eliminate most contamination problems.

Carry-over effects were studied by placing DI water blanks next to samples and standards with higher concentrations. **No false positives or carry-over effects** were observed.

## Precision

There are several ways of comparing the precision of the two methods. First, for the standards and EPA Nutrient WP1188 #1 (dilution factor = 20) the precision of each solution for each method can be calculated. The precision, represented by the variance, can then be compared using the F test. Second, the variances for the four solutions can be combined and tested, again using the F test. Finally, the precision of the methods can be estimated using the replicate samples analyzed a week apart. The precision can be estimated using the differences between the IC and FIA values (20).

Table 1. Methods Comparison Statistics

	Calibration Standards					Reference Material - EPA Nutrient WP1188 #1	
	#1	#2	#3	#4	#5	1x20	1x50
Target	0.500	0.100	0.050	0.025	0.010	0.0598	0.0239
<b>Ion Chromatography</b>							
Number	17	16	18	-	-	20	-
Mean	0.4836	0.0870	0.0428	-	-	0.0510	-
Std. dev.	0.0084	0.0046	0.0037	-	-	0.0041	-
Bias	-	-	-	-	-	-15.1%	-
<b>Flow Injection Analysis</b>							
Number	10	11	12	16	24	17	18
Mean	0.4989	0.0979	0.0543	0.0236	0.0097	0.0611	0.0229
Std. dev.	0.0040	0.0008	0.0008	0.0015	0.0010	0.0018	0.0015
Bias	-	-	-	-	-	1.86%	-4.63%
Biased?	-	-	-	-	-	No	No
<b>Validation</b>							
F	4.46	31.2	23.5	-	-	5.29	-
F <sub>crit</sub>	2.99	2.85	2.70	-	-	2.29	-

All units are in mg/L.

To compare the precision of the two methods, 3 standards and an EPA nutrient standard (dilution factor = 20) were run using both methods. (Summary in Table 1) The estimate of the precision, the standard deviation, is calculated. The variance, defined as the square of the standard deviation, is also calculated.

To test the precision of the two methods, the F test is used. The null hypothesis is that there is no difference between the two variances at the 95% confidence level. The F statistic, a ratio of the two variances, is compared with a  $F_{crit}$  which is obtained from a table. If F is less than or equal to  $F_{crit}$  then the null hypothesis is accepted as correct. If F is greater than  $F_{crit}$  then the null hypothesis is rejected. The  $F_{crit}$  values were interpolated from Appendix D, Table 2A, pp 290-1, Anderson (20).

$$F = \frac{\sigma_1^2}{\sigma_2^2} = \frac{Var_1}{Var_2}$$

$\sigma_1$  = larger standard deviation

$\sigma_2$  = smaller standard deviation

In addition, the variances of the 4 solutions were combined for each method, and compared using the F test.

$$F = \frac{\sum Var_{IC}}{\sum Var_{FIA}} = \frac{\sum \sigma_{IC}^2}{\sum \sigma_{FIA}^2} = \frac{3.00 \times 10^{-5}}{4.52 \times 10^{-6}} = 6.633$$

$\sigma_{IC}$  = standard deviation of IC

$\sigma_{FIA}$  = standard deviation of FIA

$$df_{IC} = \text{degrees of freedom} = n_{IC} - 4 = 71 - 4 = 67$$

$$df_{FIA} = \text{degrees of freedom} = n_{FIA} - 4 = 50 - 4 = 46$$

$$F_{crit} = 1.595$$

A third way to compare the precision of the two methods is to look at the precision estimated from the differences for the samples which were analyzed a week apart. The standard deviation of the differences is calculated for each method.

Table 2. Comparison of Precision - Replicates Analyzed One Week Apart

	Ion Chromatography	Flow Injection Analysis
	Week 1 - Week 2	Week 1 - Week 2
Number	30	30
Mean	0.0096	-0.0002
Standard deviation	0.0153	0.0047

$$F = \frac{\sigma_{IC}^2}{\sigma_{PIA}^2} = \frac{(1.532 \times 10^{-2})^2}{(4.724 \times 10^{-3})^2} = 10.53$$

$$df_{IC} = \text{degrees of freedom} = n_{IC} - 1 = 29$$

$$df_{PIA} = \text{degrees of freedom} = n_{PIA} - 1 = 29$$

$$F_{crit} = 1.85$$

In all the cases, as F is greater than  $F_{crit}$  we reject the null hypothesis. There is a difference between the two variances. However, the FIA variance was expected to be smaller than the IC variance. For each case, the variance of the IC was greater than that for FIA, so the FIA variance is shown to be significantly smaller than the IC variance.

#### Analyte Recovery (Bias)

The EPA nutrient standards were used for the determination of bias. The concentrations were 0.0239 and 0.0598 mg/L. For the one solution analyzed by both methods, the bias for the FIA method is less than the bias for the IC method. Even close to the detection limit, FIA has better precision and accuracy than IC. The t test was used to determine if the biases were statistically significant.

The Reference Material results were tested using the following t test (20). The number of observations for EPA Nutrient WP1188 #1 is 200. The standard deviation for Nut 1x20 is 0.006132, for Nut 1x50 is 0.002452 mg/L.

$$t = \frac{|\bar{X}_1 - \bar{X}_2|}{s_p \sqrt{1/n_1 + 1/n_2}} = \frac{|\bar{X}_1 - \bar{X}_2|}{s_p} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$



where

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

$\bar{X}_1$  = average of samples in sample set 1

$\bar{X}_2$  = average of samples in sample set 2

$n_1$  = number of observations in sample set 1

$n_2$  = number of observations in sample set 2

$s_p$  = pooled standard deviation of the standard deviations  $s_1$  and  $s_2$  for the first and second sets of data

df = degrees of freedom =  $n_1 + n_2 - 2$

For both of the Reference Material solutions there was no significant difference between the results of the FIA analysis and the true value ( $t$  is less than  $t_{crit}$ ). The biases are also within the goals established in the NADP Quality Assurance Plan, 20% at 10 times the detection limit and 10% at 100 times the detection limit (2).

#### Comparison with approved method

A set of ten natural samples, with detectable amounts of orthophosphate was analyzed by both methods. A set of twenty natural samples, selected randomly, was also analyzed using both methods. As all twenty of the random samples were below detection for both methods, ten were spiked with approximately 0.05 mg/L o-PO<sub>4</sub><sup>-3</sup> and the other ten were spiked with approximately 0.10 mg/L o-PO<sub>4</sub><sup>-3</sup>. The spiked samples were analyzed by both methods. After a week, the spiked samples were analyzed again by both methods.

Three data sets were tested for differences between IC and FIA. The first set, Week 1, was composed of the 10 natural samples with detectable concentrations of orthophosphate and the 30 spiked samples. The second data set, Week 2, was composed of the 30 spiked samples after one week. The third data set is the union of the first and second data sets. Each difference was obtained by subtracting the FIA value from the IC value. (Tables 3 and 4)

One of the assumptions of the  $t$  test is that the sample being tested is drawn from a normal population. To test whether the differences are from a normal population, a Kolmogorov Smirnov test was used. A Kolmogorov Smirnov test measures the maximum difference between the expected frequency of the distribution and the actual distribution.

Table 3. Statistics Used to Determine Normalcy

	Week 1	Week 2	Combined
Maximum difference	0.0783	0.1002	0.0835
Approx. Significance Level	0.967	0.924	0.714
Assume Normal?	Yes	Yes	Yes

As the data are assumed to be normal, then the t test is appropriate for testing the differences. The null hypothesis is that there is no difference between the two methods at the 95% confidence level. The test for paired differences is (20):

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

*df* = degrees of freedom = *n*-1

*difference* = IC - FIA

$\bar{d}$  = average difference

*s<sub>d</sub>* = standard deviation of differences

Table 4. t-Test for Paired Differences

	Week 1	Week 2	Combined
Average difference (mg/L)	0.0038	-0.00546	-0.00017
Standard deviation (mg/L)	0.013546	0.016272	0.015373
degrees of freedom	39	29	69
t	1.774	1.840	0.093
t <sub>crit</sub>	2.02	2.05	2.00

As all the t's are less than the corresponding t<sub>crit</sub>, the null hypothesis is correct for each data set, and there is no difference between the results of the two methods.

Table 5. Instrument Comparison Summary

	Ion Chromatography	Flow Injection Analyses
Manufacturer	Dionex Corp.	Lachat Instruments
Concentration range	0.02 - 0.50 mg/L	0.003 - 0.500 mg/L
Sample cycle time	11 minutes	54 seconds
Sample volume	3 mL	3 mL
Start-up time	~1 hours	~1 hour
Total number of analyses per day	~70	~300



**APPENDIX B**  
**GLOSSARY OF TERMS**



APPENDIX B  
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>		<p>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.</p> <p>Bias = measured value - true value</p>
<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 <u>T</u> s 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 (21).
<b>Critical Concentration</b>		A calculated concentration used to determine whether the measured bias is statistically significant (20).

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

Term	Abbreviation	Definition
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where:

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

- $s_{sp}$  = pooled standard deviation
- $s_1$  = standard deviation of reference solution measurements
- $s_2$  = standard deviation of daily QCS measurements
- $n$  = number of values
- $t$  = t statistic at the 95% confidence level and  $(n_1 + n_2) - 2$  degrees of freedom

**External Blind Sample**

A QA sample of known analyte concentrations submitted to the laboratory by an external agency. These samples arrive at the CAL 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 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.

Term	Abbreviation	Definition
<b>Mean</b>	$\bar{x}$	The average obtained by dividing a number of its addends. $x = \sum_{i=1}^n x_i/n$
<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 (22).
<b>Percent Bias</b>		The difference between the mean value obtained by repeated analysis of a homogeneous sample and the accepted true value expressed as a percentage of the true value. $\%Bias = 100 * [(V_m - V_t)/V_t]$ <i>where: <math>V_m</math> = measured value</i> <i><math>V_t</math> = true value</i>
<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).

Term	Abbreviation	Definition
Quality Assessment		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.
Quality Assurance	QA	An integrated system of activities involving planning, QC, 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	RSD	The standard deviation expressed as <b>Deviation</b> a percentage:  $RSD = 100 * (s/\bar{x})$ <p>where: <math>s</math> = sample standard deviation  <math>\bar{x}</math> = mean value</p>

Term	Abbreviation	Definition
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<b>Replicates (Splits)</b>		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.
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<b>Sensitivity</b>		The method signal response per unit of analyte.
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<b>Standard Deviation</b>	s	The number representing the dispersion of values around their mean.
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$$s = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n-1}}$$

where:  $x_i$  = each individual value  
 $\bar{x}$  = the mean of all values  
n = number of values

<b>Standard Deviation Estimated from Paired Measurements</b>		The standard deviation may be estimated from the differences of several sets of paired measurements using the equation (21):
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$$s = \sqrt{\frac{\sum d^2}{2k}}$$

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



Term	Abbreviation	Definition
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**Regression (R)**  
 The algebra of the least squares method is usually developed in the laboratory setting. Atoms of laboratory experiments are handled when working practice is associated with primary procedures but not with objectives and handling. Also related to it will be

The method of least squares for the fit of curves

The method of determining the dispersion of data around the mean

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

where  $s$  = standard deviation  
 $\bar{x}$  = the mean of all values  
 $n$  = number of values

The standard deviation may be estimated from the difference of several sets of data measurements using the equation (11)

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

where  $s$  = standard deviation  
 $\bar{x}$  = mean of all values  
 $n$  = number of measurements

**APPENDIX C**

**WEEKLY QC/QA PROCEDURES: TABLES AND FIGURES**

**1993**

APPENDIX C

WEEKLY QOQA PROCEDURES, TABLES AND FIGURES

1993

TABLE C-1 Comparison of Filtered and Unfiltered Internal Blind Samples  
High Purity Standards Simulated Rainwater I (HPS-SRI), 1993

Parameter	Target Conc. <sup>a</sup>	Average Measured Conc.	Number of Values (n)	Bias	% Bias	Standard Deviation (s)	% RSD
Calcium	0.015	0.016 <sup>b</sup>	26	0.001	6.7	0.005	31.2
		0.026 <sup>c</sup>	13	0.011	73.3	0.015	57.7
Magnesium	0.025	0.024	26	-0.001	-4.0	0.002	8.3
		0.026	13	0.001	4.0	0.003	11.5
Sodium	0.200	0.204	26	0.004	2.0	0.014	6.9
		0.252	13	0.052	26.0	0.044	17.5
Potassium	0.048	0.050	26	0.002	4.2	0.003	6.0
		0.049	13	0.001	2.1	0.002	4.1
Ammonium	0.10	0.09	26	-0.01	-10.0	0.03	33.3
		0.13	13	0.03	30.0	0.10	76.9
Sulfate	2.70	2.57	26	-0.13	-4.8	0.05	1.9
		2.47	13	-0.23	-8.5	0.08	3.2
Nitrate	0.50	0.55	26	0.05	10.0	0.02	3.6
		0.59	13	0.09	18.0	0.04	6.8
Chloride	0.25	0.24	26	-0.01	-4.0	0.03	12.5
		0.28	13	0.03	12.0	0.05	17.9
H <sup>+</sup> (µeq/L)	53.7	52.5	26	-1.2	-2.3	3.01	5.7
		53.1	13	-0.61	-1.1	2.43	4.5
Conductivity (µS/cm)	25.1	25.4	26	0.3	1.2	1.0	3.9
		25.6	13	0.5	2.0	0.8	3.1

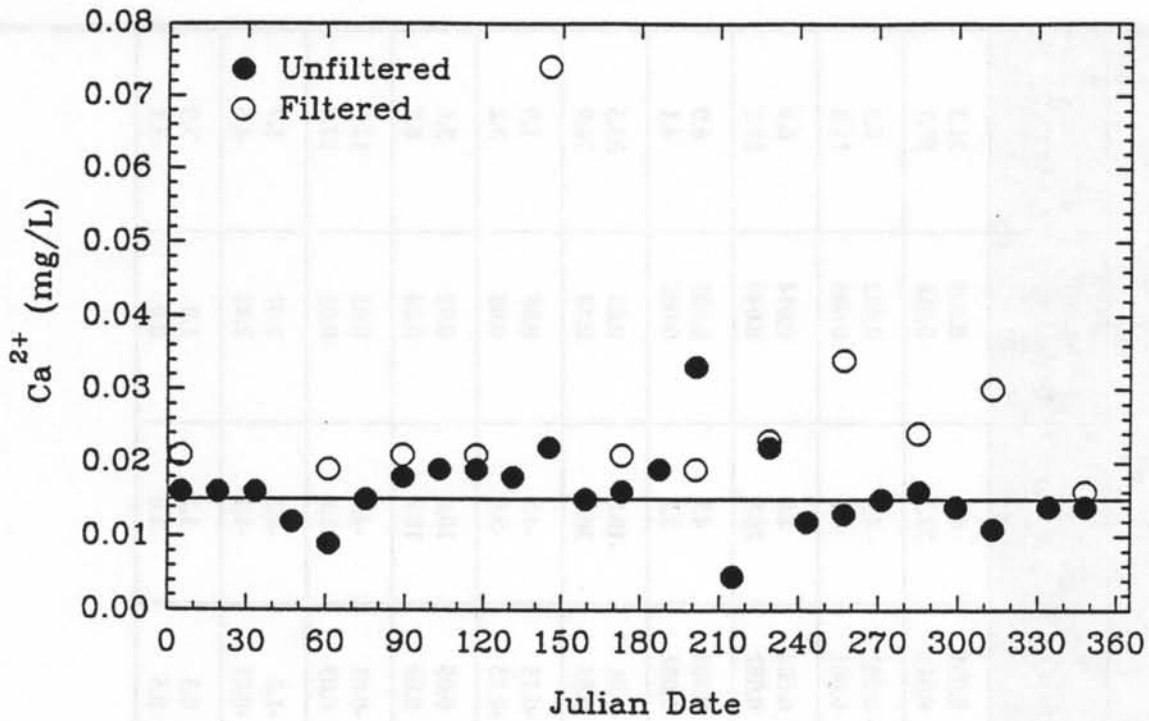
Notes:

Concentrations in mg/L unless otherwise noted.

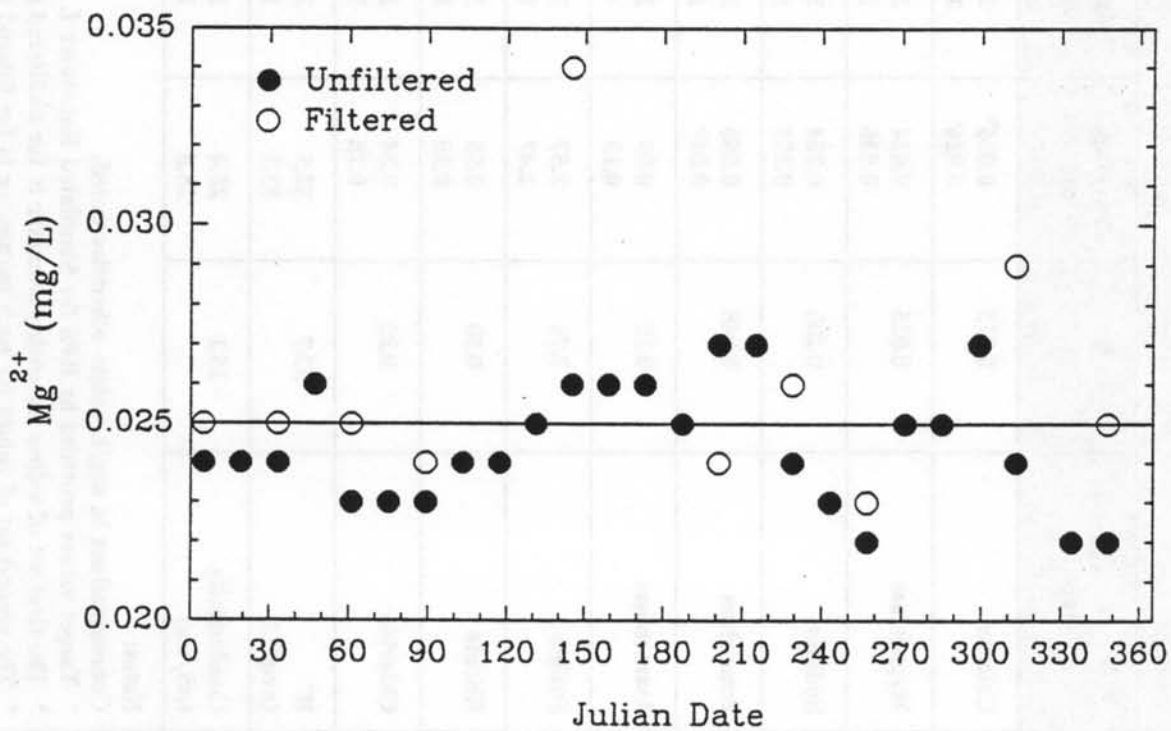
<sup>a</sup> Target values provided by HPS for Simulated Rainwater I.

<sup>b</sup> The first set of values for each parameter is for unfiltered samples.

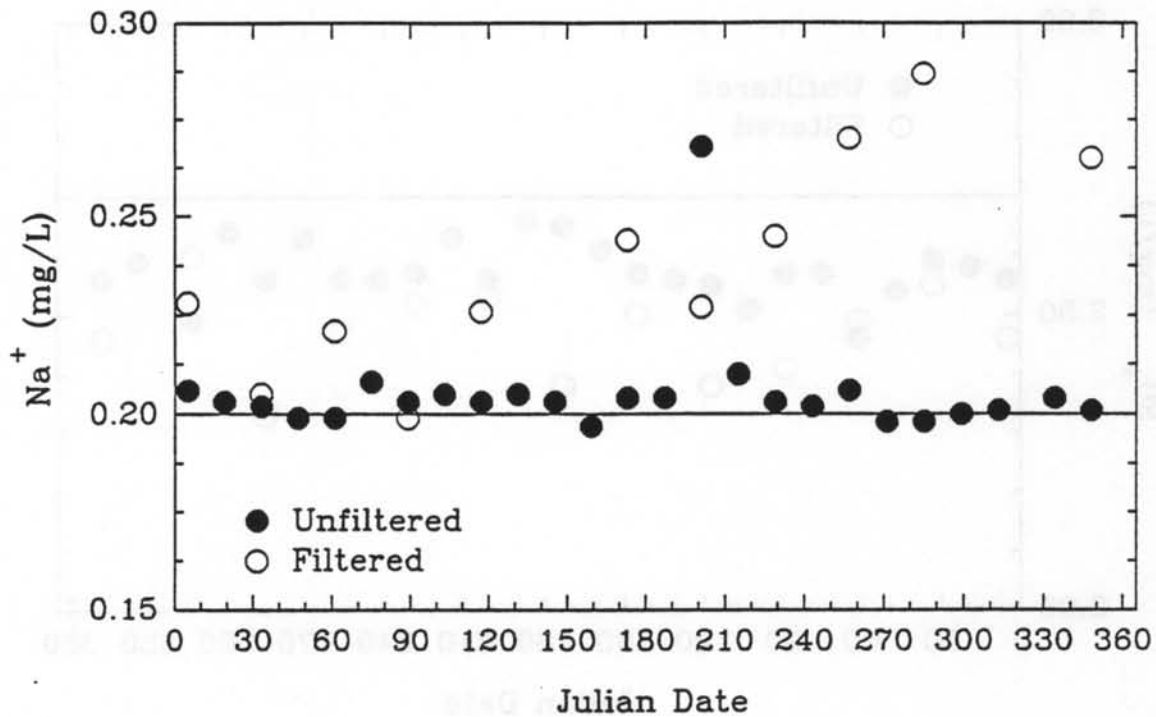
<sup>c</sup> The second set of values for each parameter is for filtered samples.



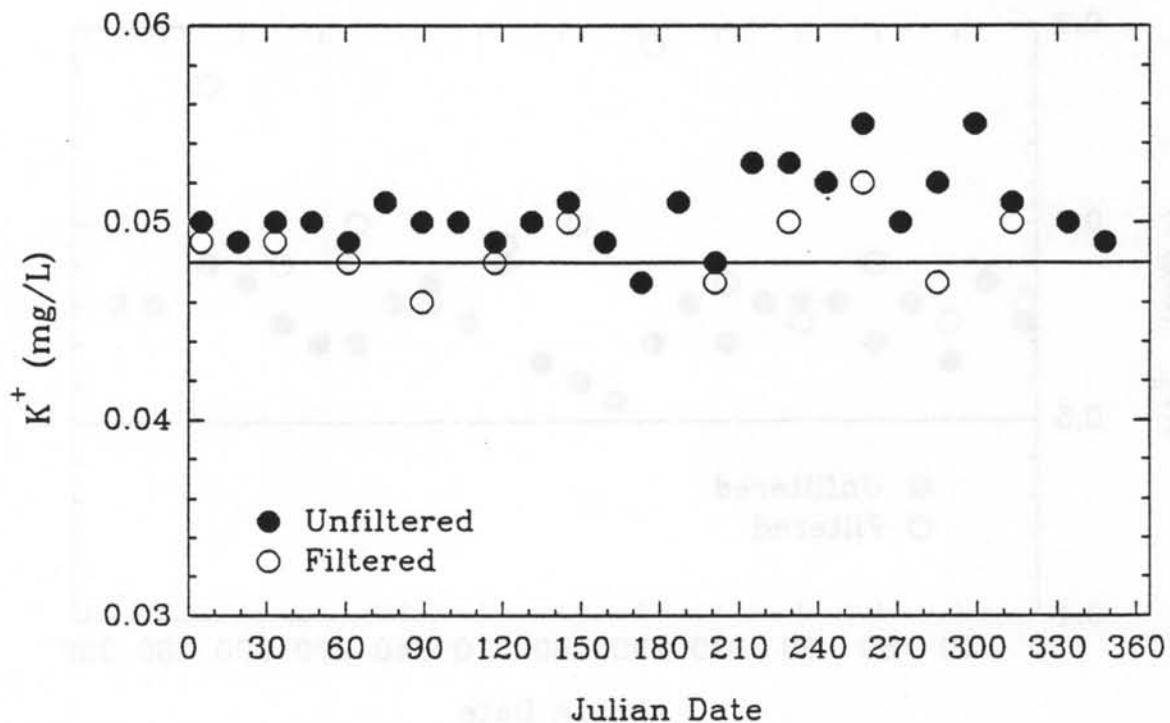
**FIGURE C-1. Comparison of filtered and unfiltered internal blind samples (calcium HPS-SRI), 1993.**



**FIGURE C-2. Comparison of filtered and unfiltered internal blind samples (magnesium HPS-SRI), 1993.**

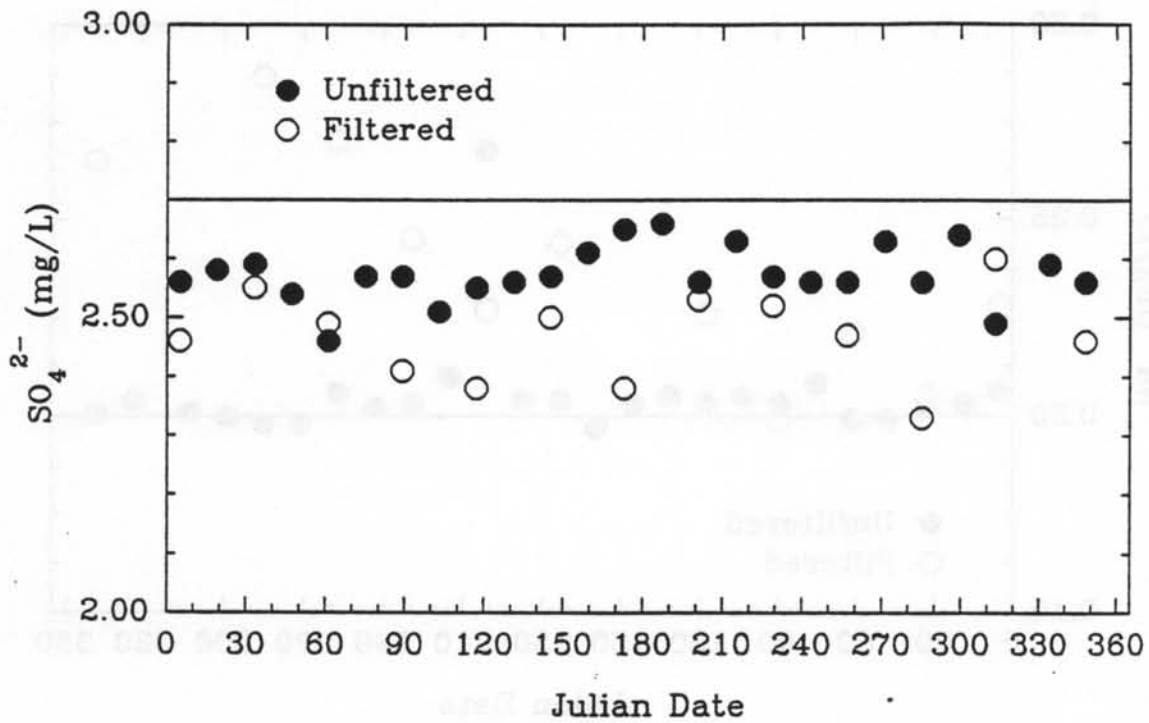


**FIGURE C-3. Comparison of filtered and unfiltered internal blind samples (sodium HPS-SRI), 1993.**

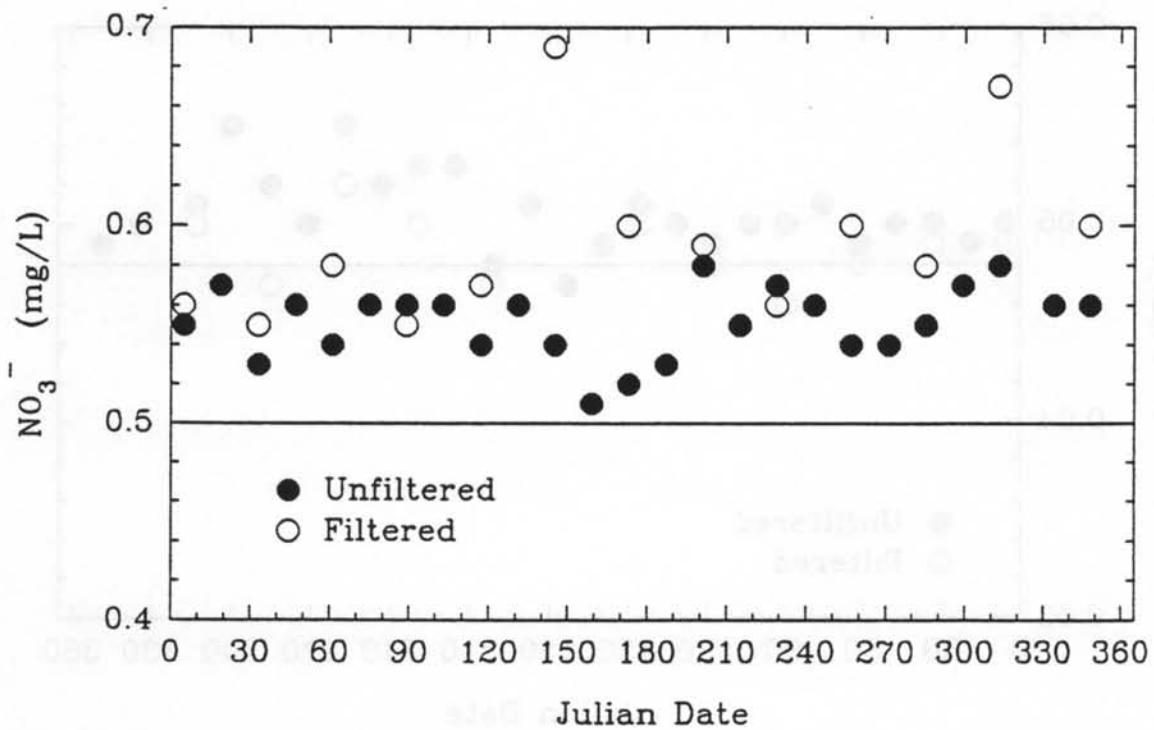


**FIGURE C-4. Comparison of filtered and unfiltered internal blind samples (potassium HPS-SRI), 1993.**

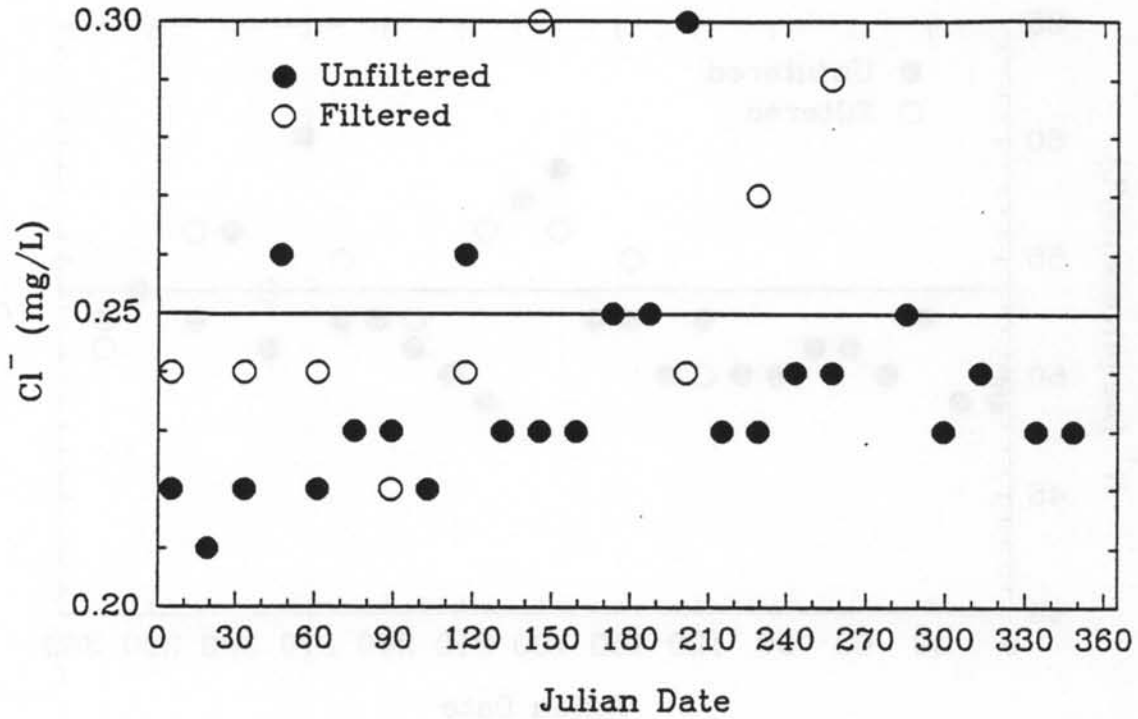




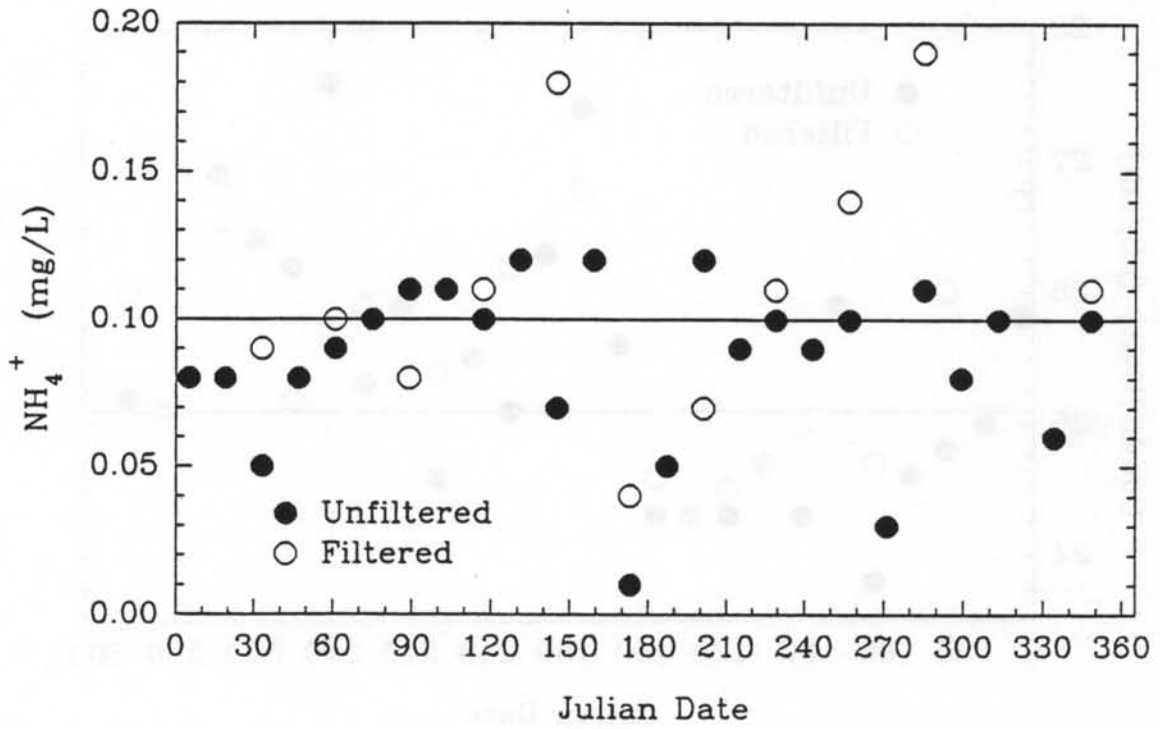
**FIGURE C-5. Comparison of filtered and unfiltered internal blind samples (sulfate HPS-SRI), 1993.**



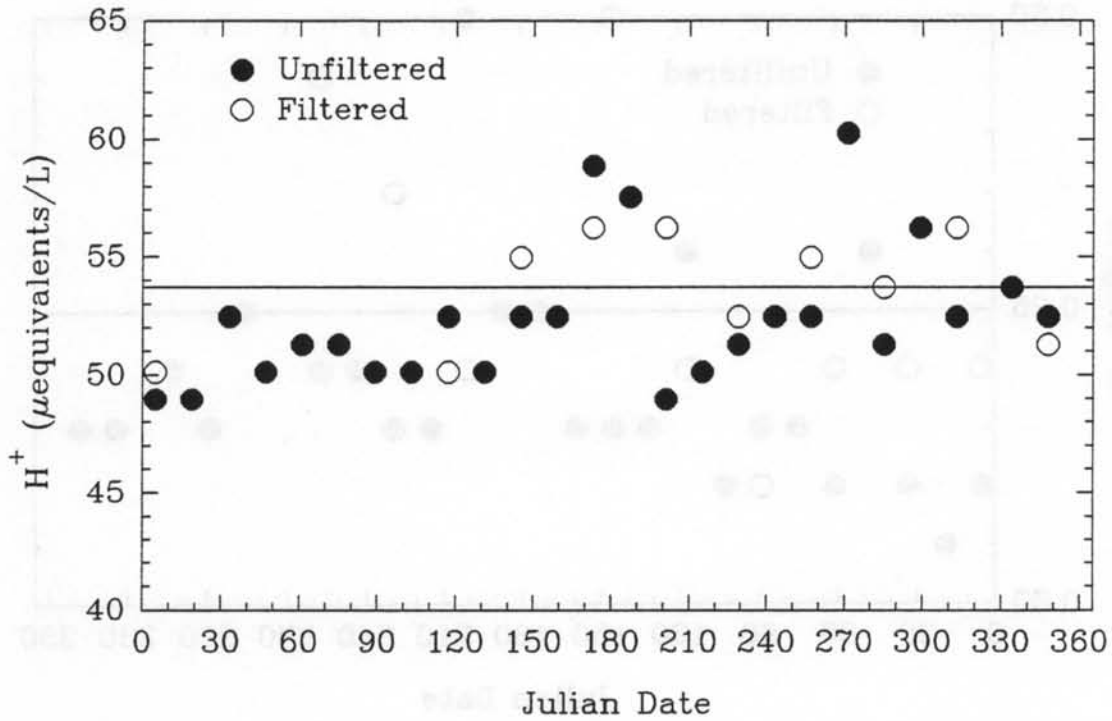
**FIGURE C-6. Comparison of filtered and unfiltered internal blind samples (nitrate HPS-SRI), 1993.**



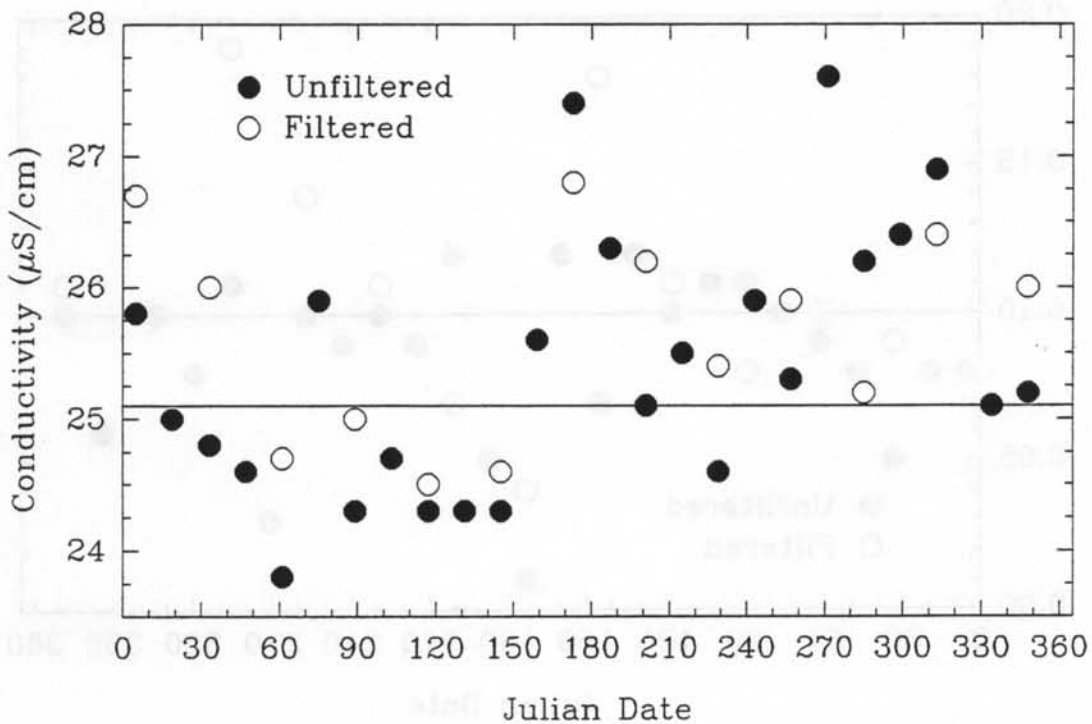
**FIGURE C -7. Comparison of filtered and unfiltered internal blind samples (chloride HPS-SRI), 1993.**



**FIGURE C-8. Comparison of filtered and unfiltered internal blind samples (ammonium HPS-SRI), 1993.**



**FIGURE C - 9. Comparison of filtered and unfiltered internal blind samples ( $H^+$  HPS-SRI), 1993.**



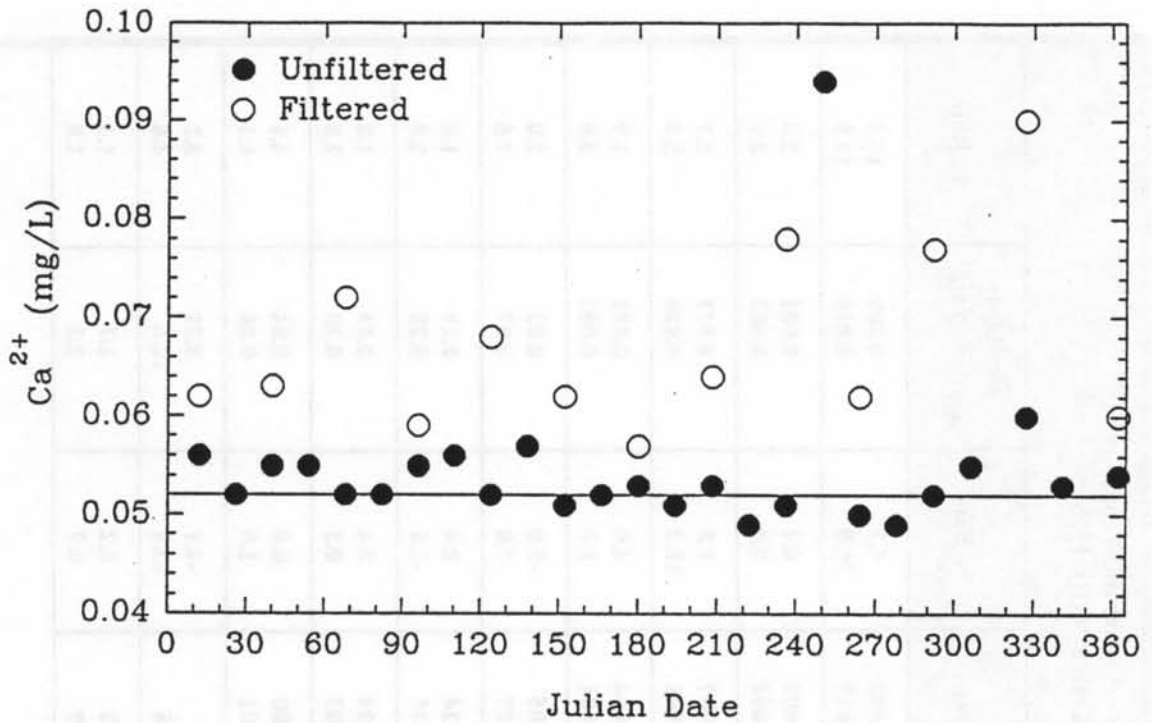
**FIGURE C - 10. Comparison of filtered and unfiltered internal blind samples (conductivity HPS-SRI), 1993.**

**TABLE C-2 Comparison of Filtered and Unfiltered Internal Blind Samples  
High Purity Standards Simulated Rainwater II (HPS-SRID), 1993**

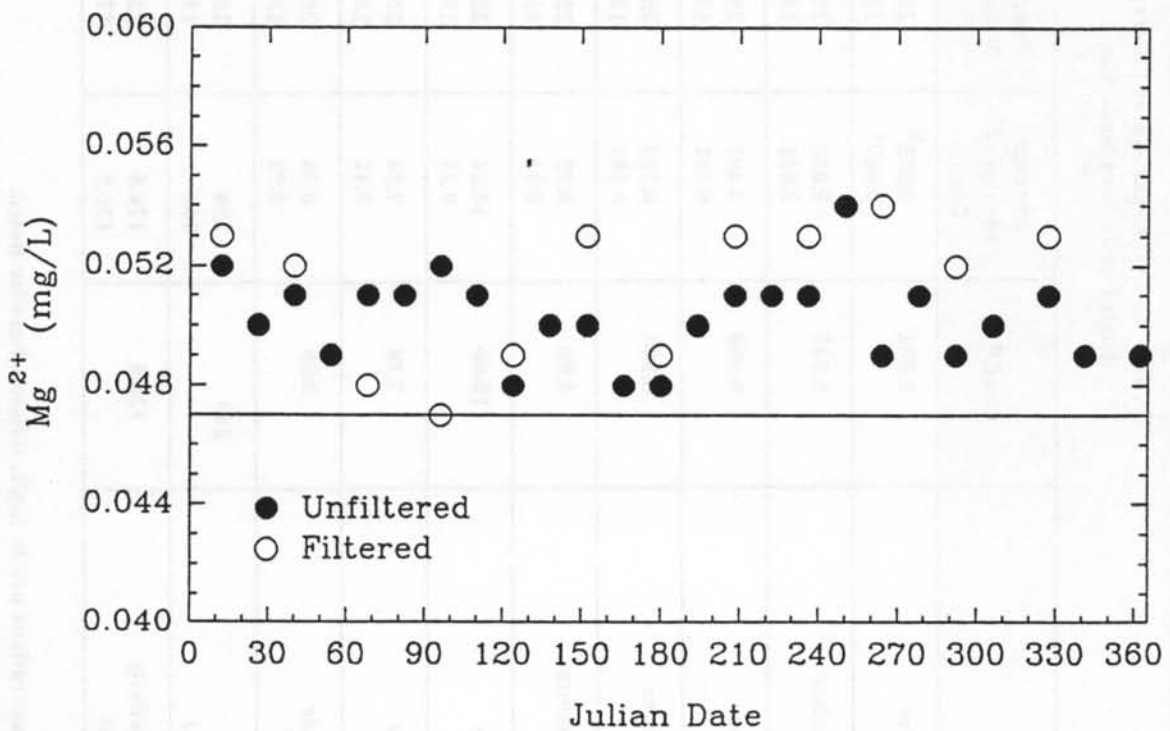
	Conc. <sup>a</sup>	Average Measured Conc.	Number of Values (n)	Bias	% Bias	Standard Deviation (s)	% RSD
Calcium	0.052	0.055 <sup>b</sup> 0.067 <sup>c</sup>	25 13	0.003 0.015	6.7 28.8	0.009 0.010	16.4 14.9
Magnesium	0.047	0.050 0.051	25 13	0.003 0.004	6.4 8.5	0.001 0.002	2.0 3.9
Sodium	0.400	0.407 0.441	25 13	0.007 0.041	1.8 10.2	0.011 0.026	2.7 5.9
Potassium	0.100	0.104 0.101	25 13	0.004 0.001	4.0 1.0	0.002 0.003	1.9 3.0
Ammonium	1.00	0.95 0.93	25 13	-0.05 -0.07	-5.0 -7.0	0.03 0.07	3.0 7.5
Sulfate	10.00	10.24 9.84	25 13	0.24 -0.16	2.4 -1.6	0.19 0.28	1.8 2.8
Nitrate	7.10	7.34 7.12	25 13	0.24 0.02	3.4 0.3	0.13 0.20	1.8 2.8
Chloride	0.98	0.98 0.99	25 13	0.00 0.01	0.0 1.0	0.04 0.06	4.1 6.1
H <sup>+</sup> (µeq/L)	269	258 260	25 13	-11 -8.6	-4.1 -3.2	8.31 12.6	3.2 4.8
Conductivity (µS/cm)	126.6	126.8 126.5	25 13	0.2 0.9	0.2 0.7	1.7 2.3	1.3 1.8

**Notes:**

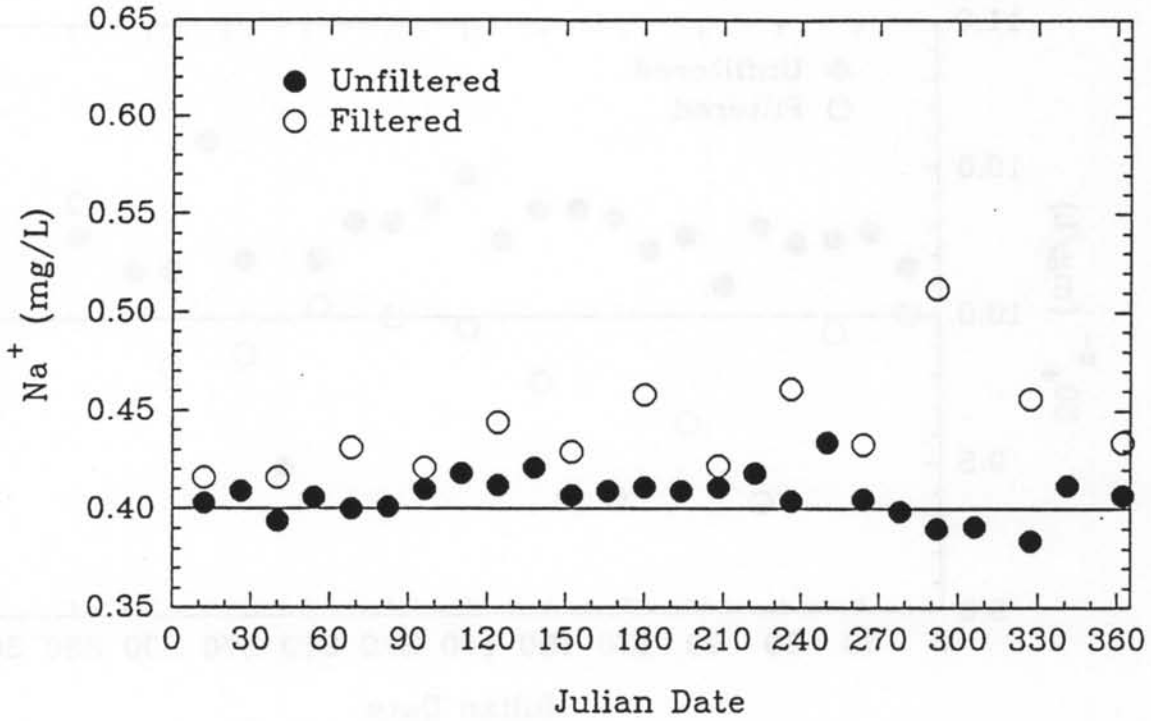
- Concentrations are in mg/L unless otherwise noted.
- <sup>a</sup> Target values provided by HPS for Simulated Rainwater II.
- <sup>b</sup> The first set of values for each parameter is for unfiltered samples.
- <sup>c</sup> The second set of values for each parameter is for filtered samples.



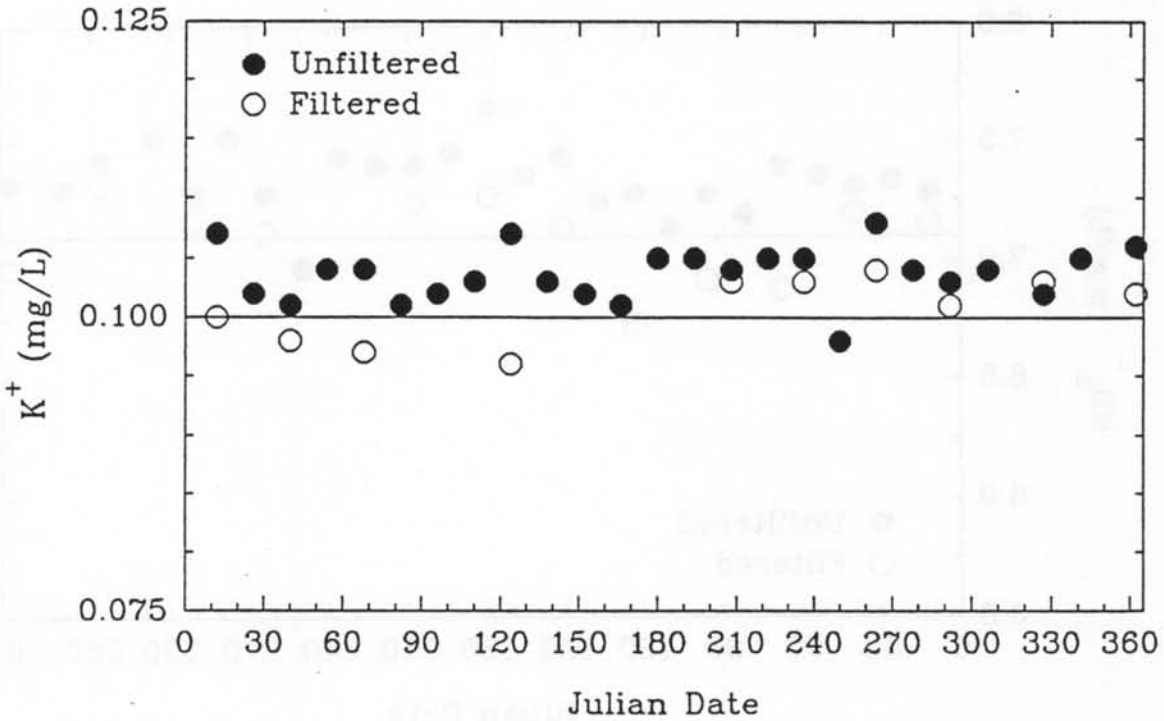
**FIGURE C-11. Comparison of filtered and unfiltered internal blind samples (calcium HPS-SRII), 1993.**



**FIGURE C-12. Comparison of filtered and unfiltered internal blind samples (magnesium HPS-SRII), 1993.**

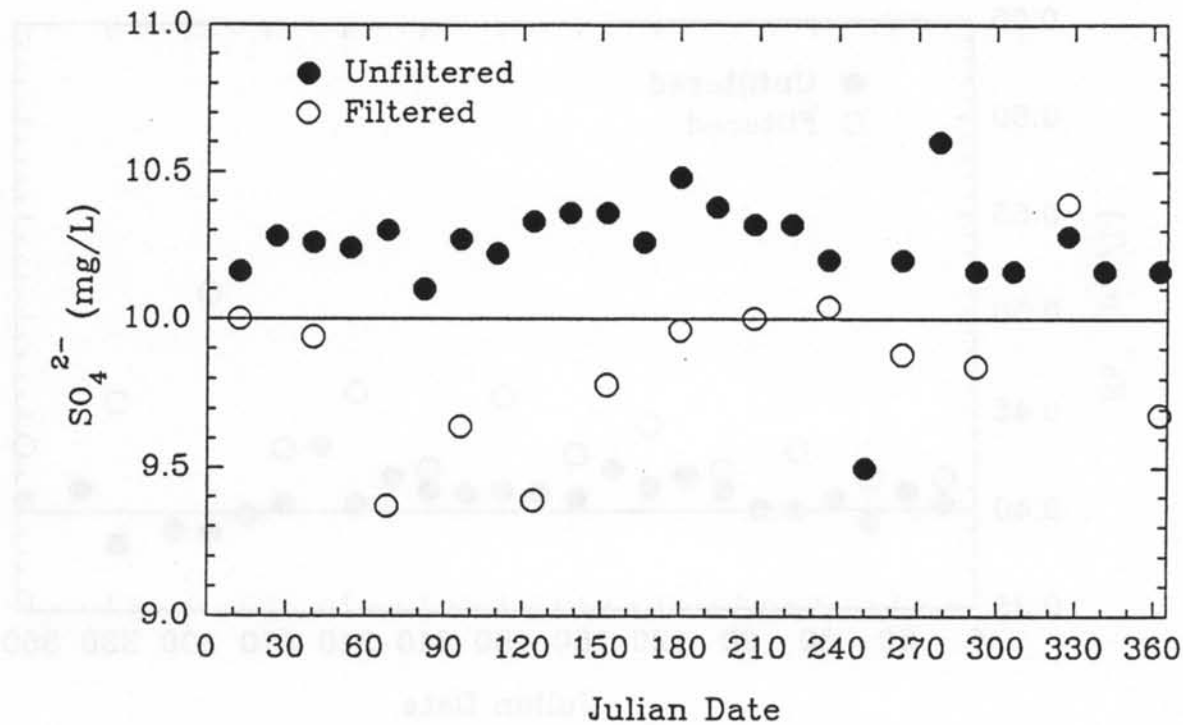


**FIGURE C-13.** Comparison of filtered and unfiltered internal blind samples (sodium HPS-SRII), 1993.

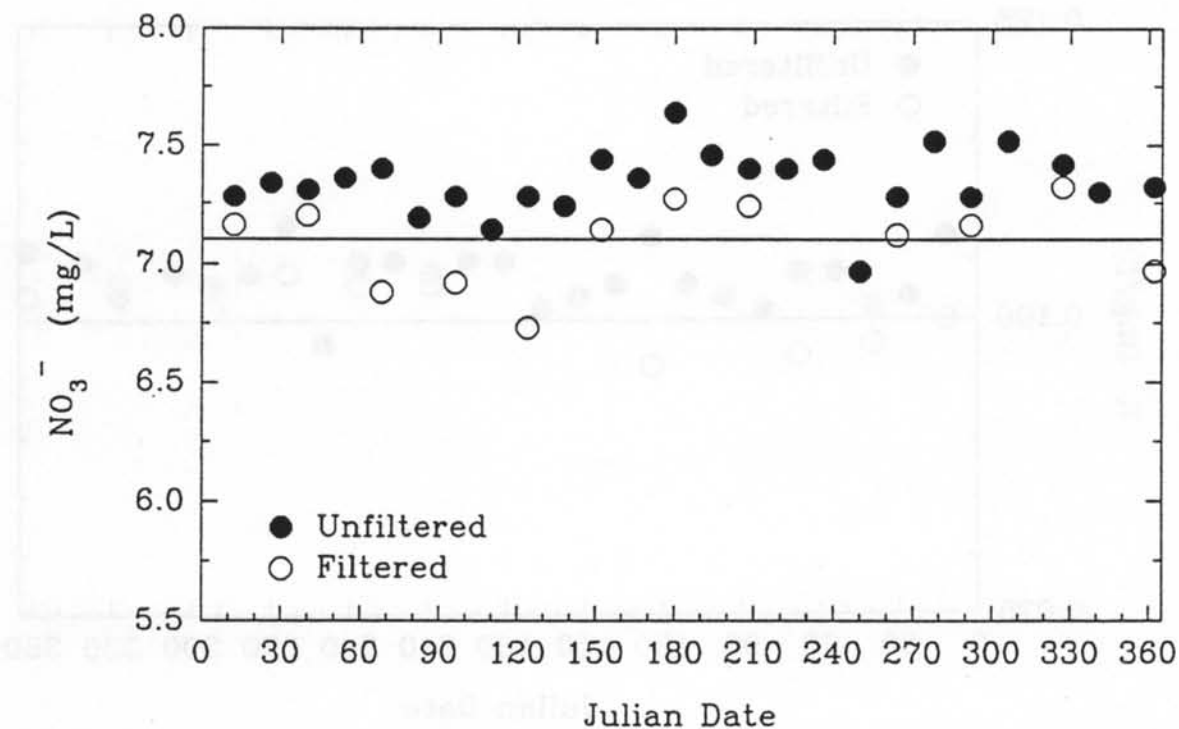


**FIGURE C-14.** Comparison of filtered and unfiltered internal blind samples (potassium HPS-SRII), 1993.

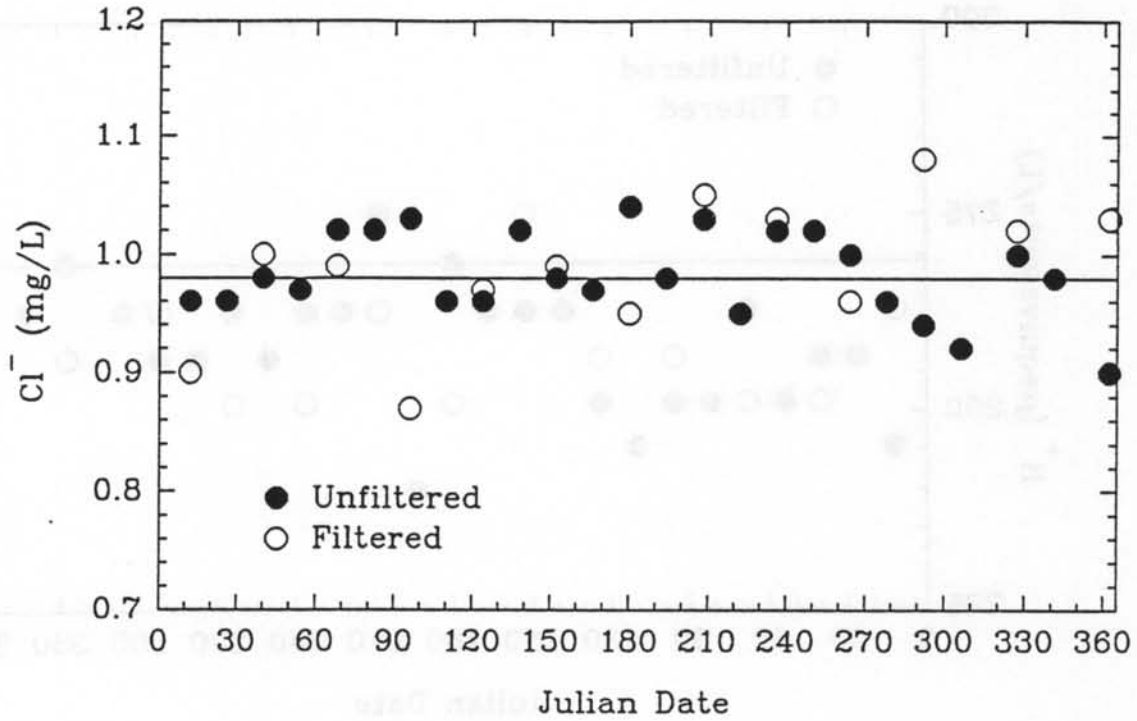




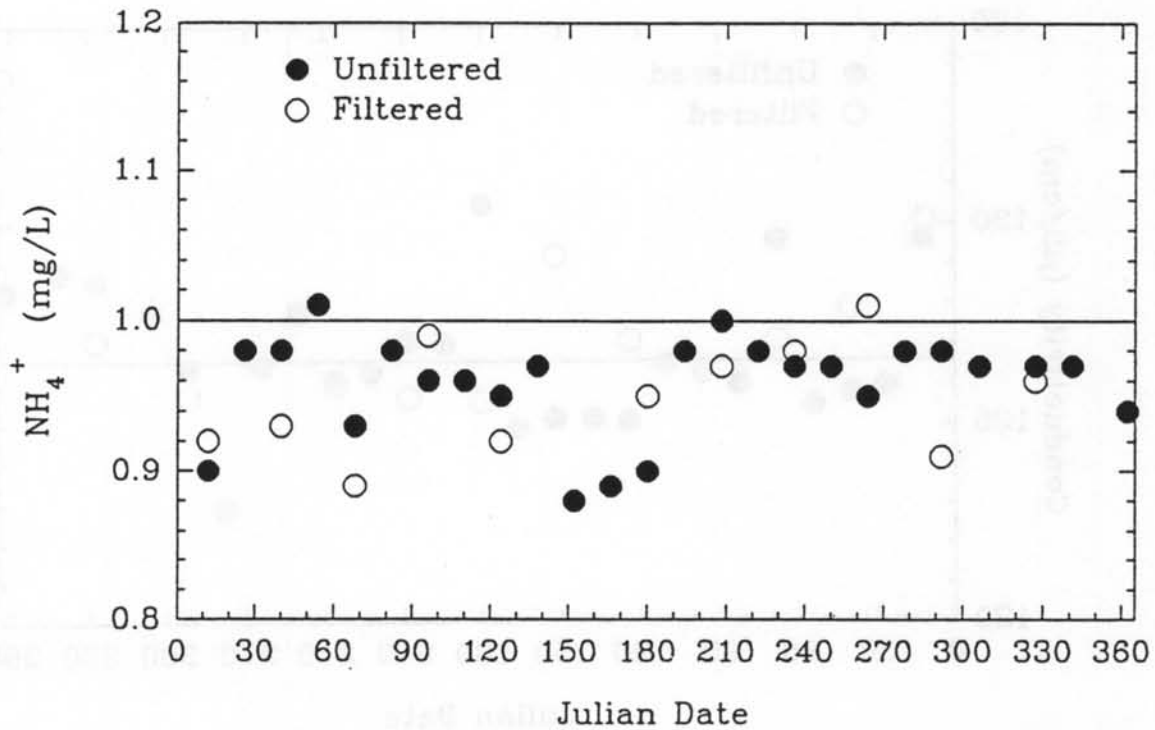
**FIGURE C-15. Comparison of filtered and unfiltered internal blind samples (sulfate HPS-SRII), 1993.**



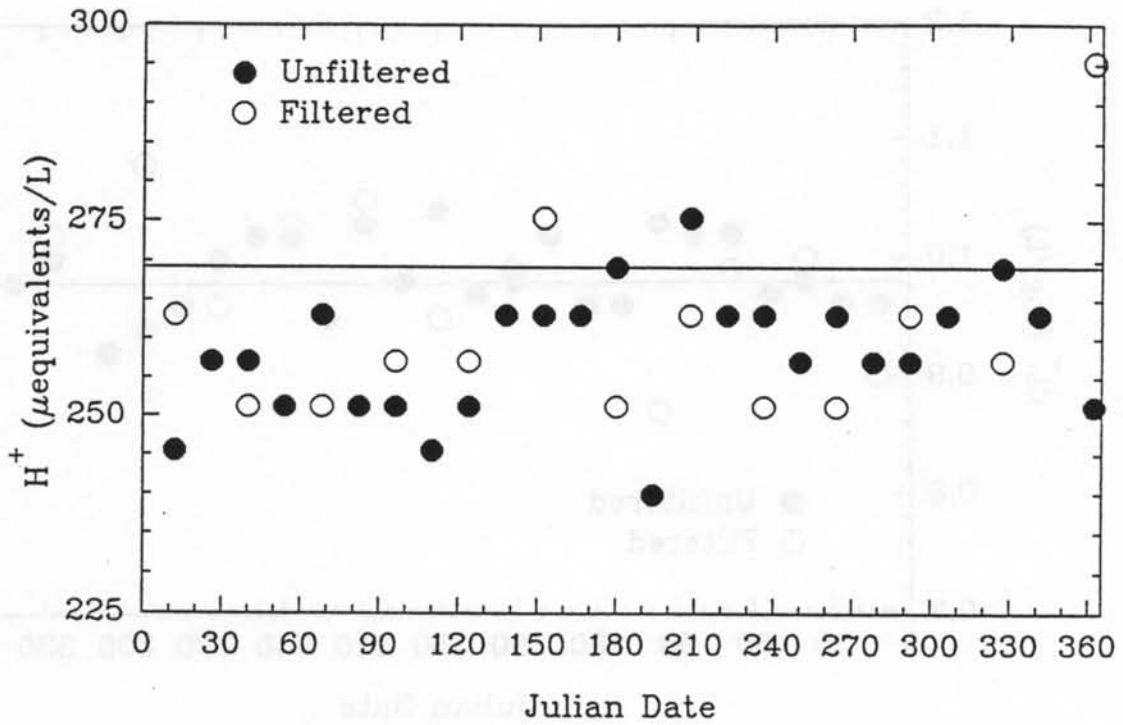
**FIGURE C-16. Comparison of filtered and unfiltered internal blind samples (nitrate HPS-SRII), 1993.**



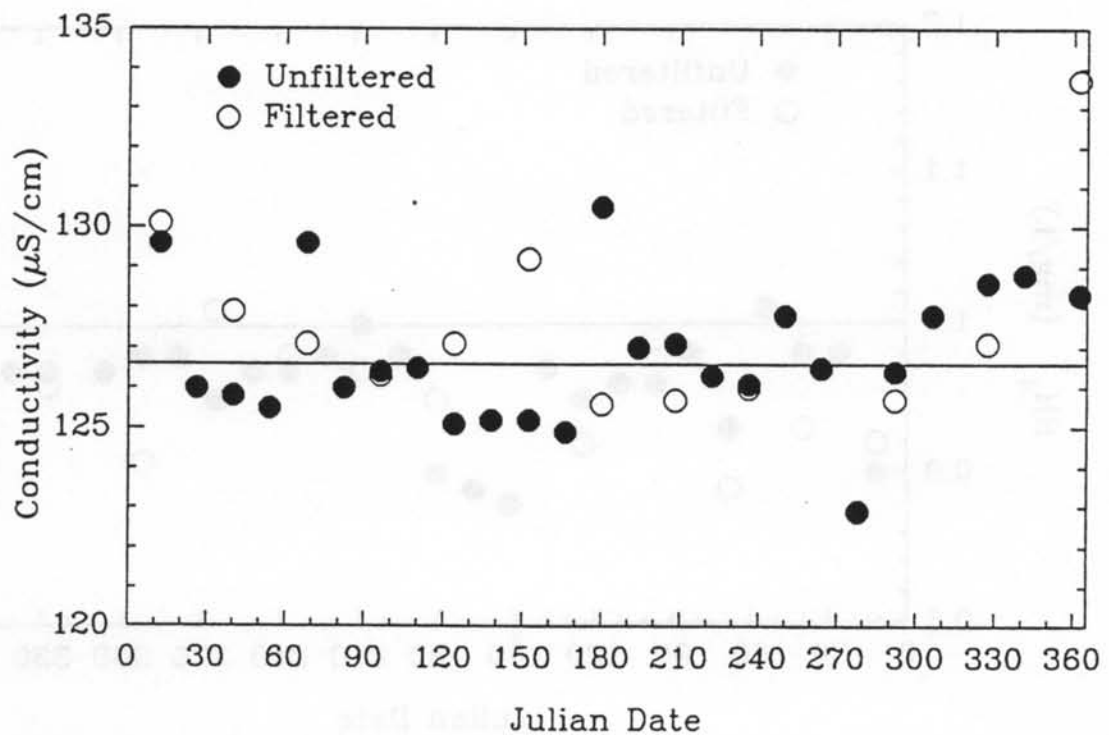
**FIGURE C-17. Comparison of filtered and unfiltered internal blind samples (chloride HPS-SRII), 1993.**



**FIGURE C-18. Comparison of filtered and unfiltered internal blind samples (ammonium HPS-SRII), 1993.**

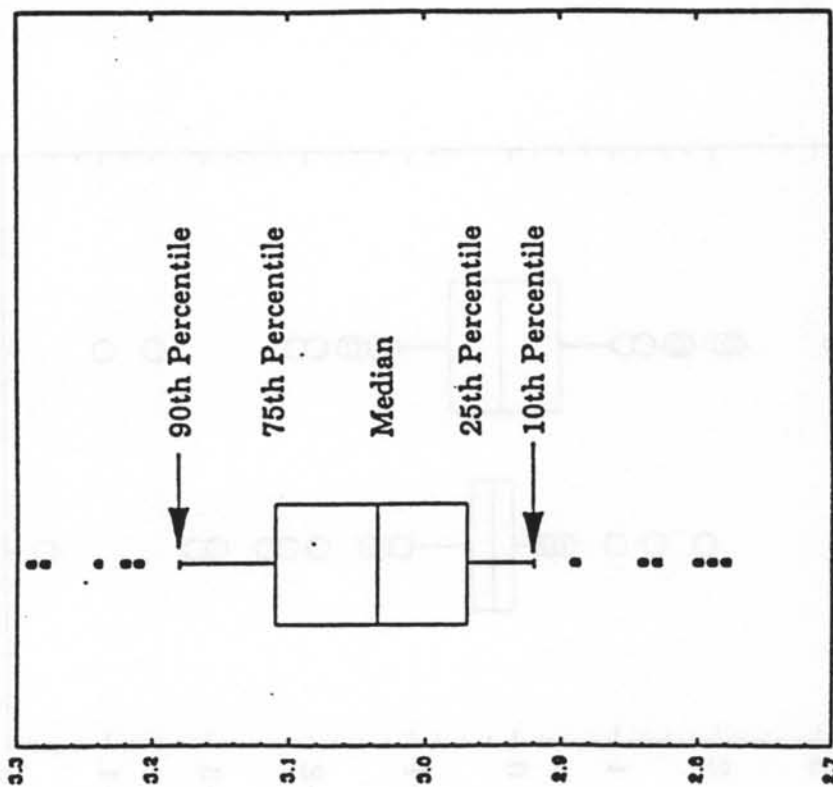


**FIGURE C-19.** Comparison of filtered and unfiltered internal blind samples (H<sup>+</sup> HPS-SRII), 1993.



**FIGURE C-20.** Comparison of filtered and unfiltered internal blind samples (conductivity HPS-SRII), 1993.

DIAGRAM OF BOXPLOTS USED ON THE  
FOLLOWING PAGES



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

TABLE C-3 50<sup>th</sup> and 95<sup>th</sup> Percentile Concentration Values of  
Chemical and Physical Parameters Measured  
In Replicate (O/Q) Samples, 1993

Parameter	Percentile Concentration Values (mg/L)	
	50 <sup>th</sup>	95 <sup>th</sup>
Calcium	0.084	0.569
Magnesium	0.018	0.092
Sodium	0.052	0.547
Potassium	0.015	0.155
Ammonium	0.18	0.80
Sulfate	1.13	4.47
Nitrate	0.95	3.14
Chloride	0.10	0.84
pH (units)	4.81	4.12
H <sup>+</sup> (µeq/L)	15.32	75.86
Conductivity (µS/cm)	11.75	41.53

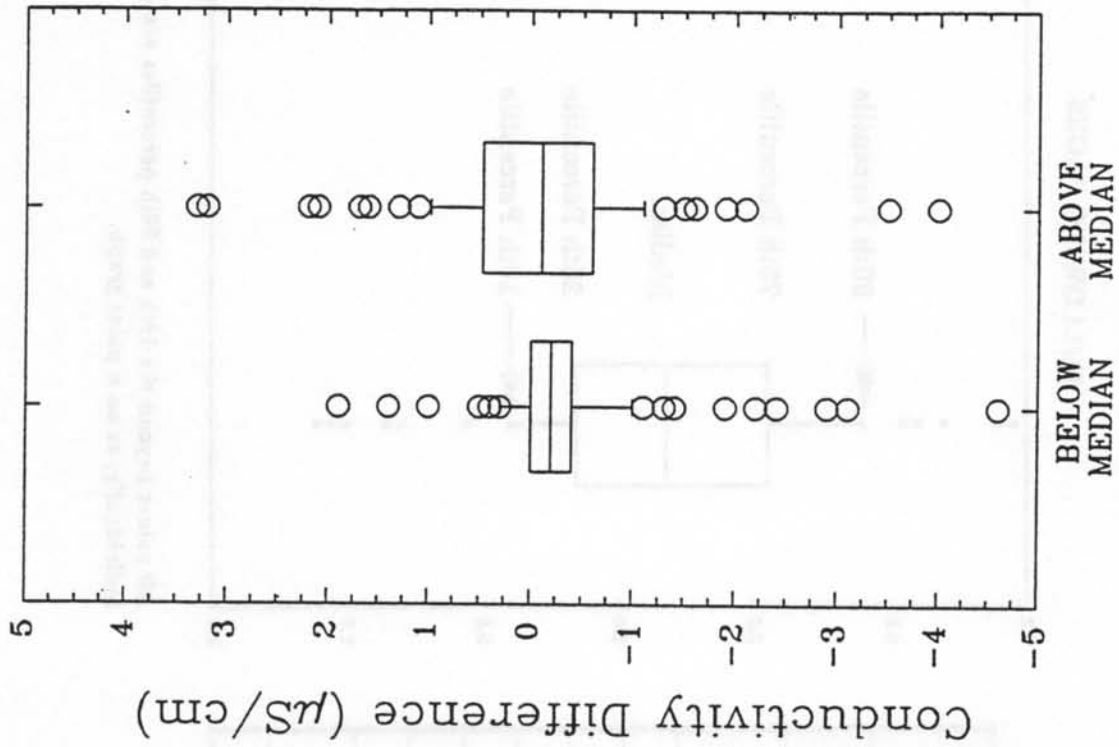
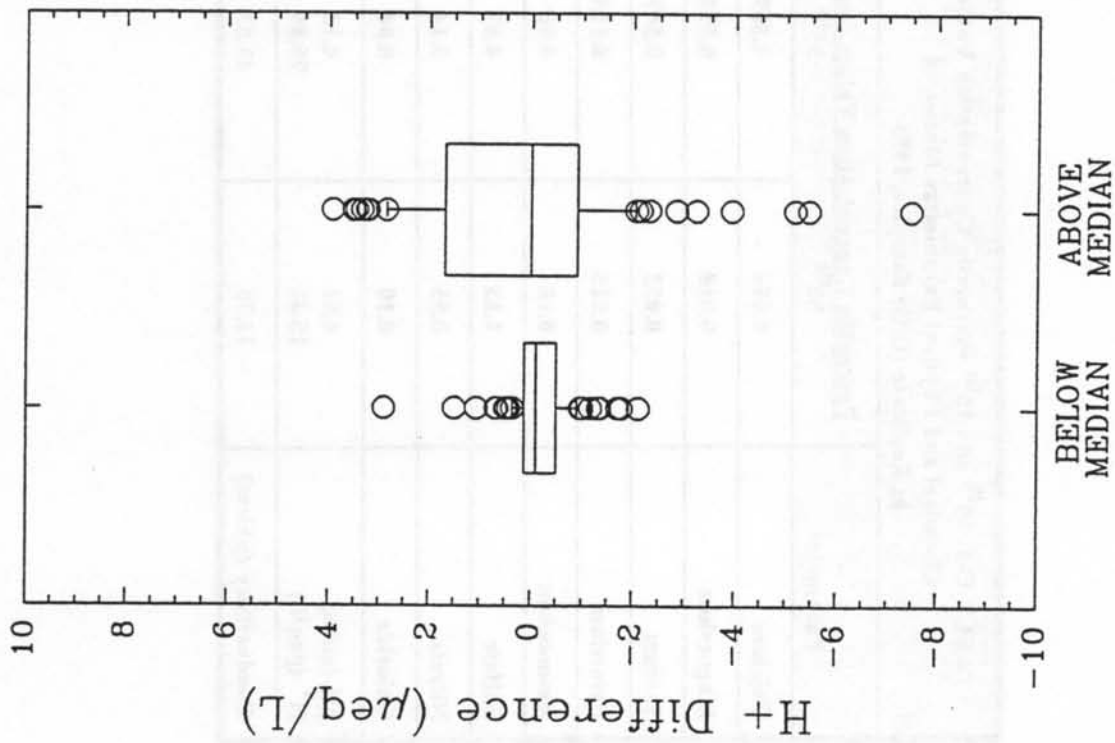


FIGURE C-21. Results of O/Q replicate analysis, H<sup>+</sup> and conductivity, 1993.

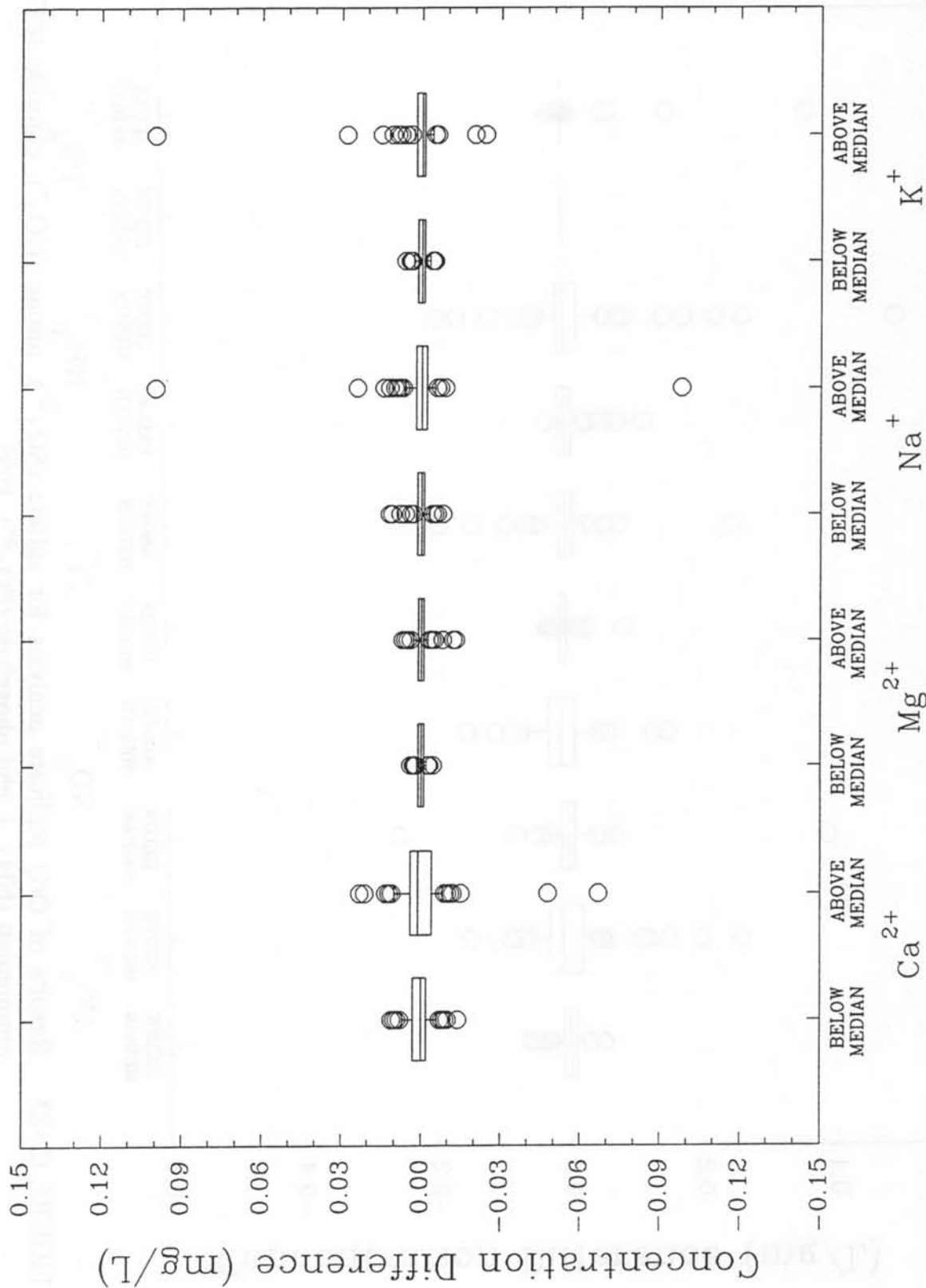


FIGURE C-22. Results of O/Q replicate analysis for calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), sodium (Na<sup>+</sup>), and potassium (K<sup>+</sup>), 1993.



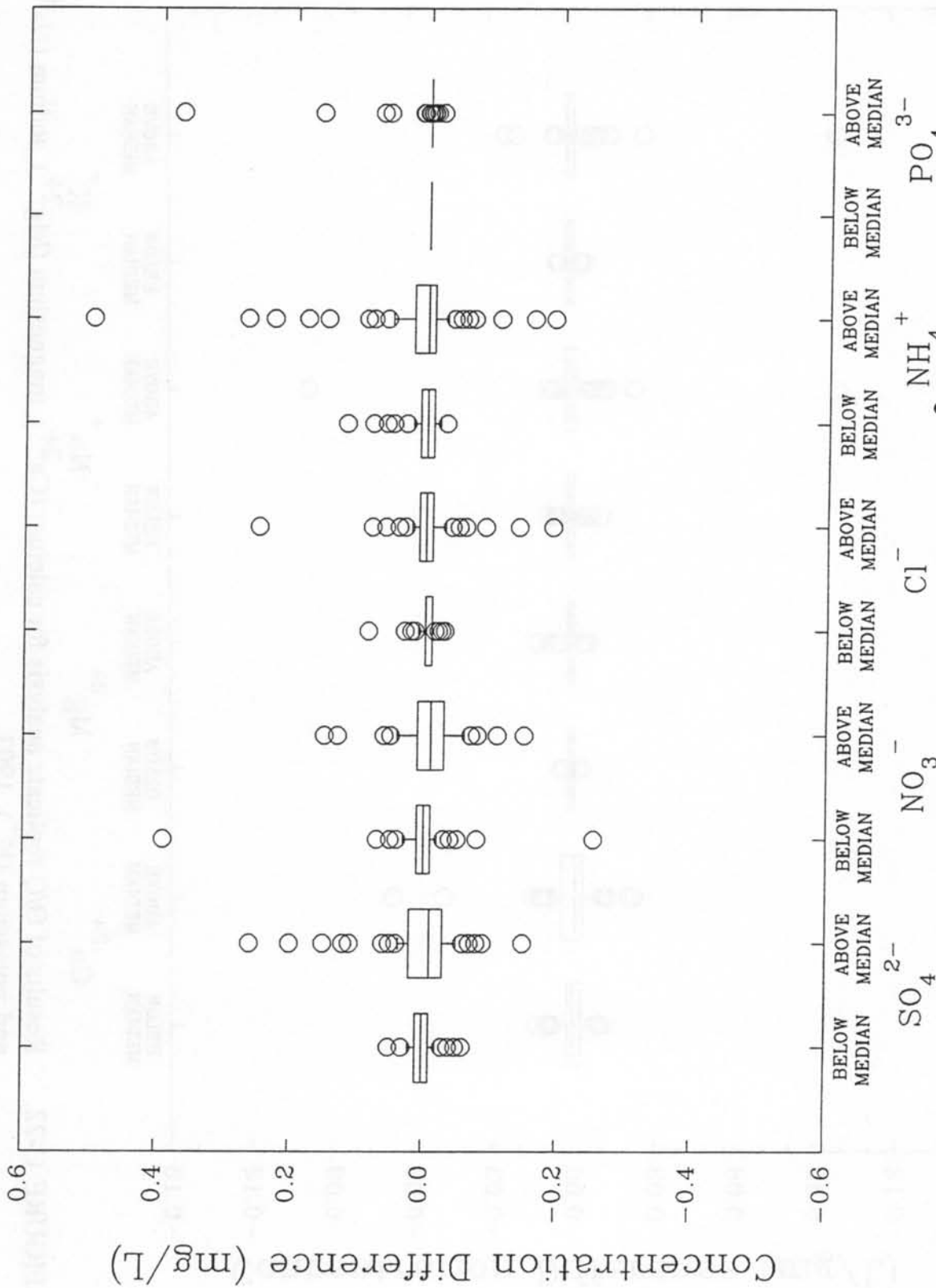


FIGURE C -23 Results of O/Q replicate analysis for sulfate ( $SO_4^{2-}$ ), nitrate ( $NO_3^-$ ), chloride ( $Cl^-$ ), ammonium ( $NH_4^+$ ), and phosphate ( $PO_4^{3-}$ ), 1993.

**TABLE C-4 Percent of Analyte Concentrations Above MDLs Found  
in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Filter Leachates, 1993**

Analyte	DI Water A <sup>a</sup>	DI Water B <sup>b</sup>	pH 4.3 Nitric Acid A	pH 4.3 Nitric Acid B
Calcium	9.09	2.27	27.27	4.54
Magnesium	6.82	0.0	25.00	11.36
Potassium	13.64	2.27	6.82	2.28
Sodium	97.73	77.27	93.18	81.82
Ammonium	2.27	2.27	18.18	0.00
Nitrate	68.18	0.0	N.A.	N.A.
Chloride	65.91	6.82	54.55	4.55
Sulfate	6.82	2.27	0.0	0.00
pH (units) <sup>c</sup>	5.64	5.64	4.34	4.31
H <sup>+</sup> (µeq/L) <sup>c</sup>	2.29	2.29	45.7	49.0
Conductivity (µS/cm) <sup>c</sup>	1.4	1.0	21.0	21.7
Number of weeks	44	44	44	44

**Notes:**

<sup>a</sup> First 50-mL filtrate after 300 mL DI water filter rinse.

<sup>b</sup> Second consecutive 50-mL filtrate after 300 mL DI water filter rinse.

<sup>c</sup> pH, H<sup>+</sup>, and conductivity values are median concentration values, not percents above detection.

TABLE C-5 Percent of Analyte Concentrations Above the MDL Found in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Upright Bucket Leachates, 1993				
Analyte	DI Water (50 mL)	DI Water (150 mL)	pH 4.3 Nitric Acid (50 mL)	pH 4.3 Nitric Acid (150 mL)
Calcium	42.22	26.67	64.44	40.00
Magnesium	11.11	6.67	26.67	15.56
Potassium	55.56	20.00	80.00	31.11
Sodium	86.67	55.57	97.78	64.44
Ammonium	13.33	2.22	15.56	4.44
Nitrate	20.00	6.67	NA	NA
Chloride	35.56	8.89	48.89	11.11
Sulfate	11.11	0.00	13.33	4.44
pH (units)*	5.61	5.59	4.37	4.34
Conductivity ( $\mu\text{S/cm}$ )*	1.5	1.4	19.4	20.8
Number of weeks	45	45	45	45
Note: *pH and conductivity values are the median concentrations, not percent above detection.				

TABLE C-6 Percent of Analyte Concentrations Above the MDL Found in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Inverted Bucket Leachates, 1993				
Analyte	DI Water (50 mL)	DI Water (150 mL)	pH 4.3 Nitric Acid (50 mL)	pH 4.3 Nitric Acid (150 mL)
Calcium	91.11	48.89	97.78	57.78
Magnesium	84.44	33.33	95.56	57.78
Potassium	88.89	53.33	91.11	57.78
Sodium	100.	93.33	100.00	95.56
Ammonium	26.67	8.89	15.56	2.22
Nitrate	20.00	8.89	NA	NA
Chloride	80.00	26.67	86.67	22.22
Sulfate	97.78	75.56	100.	57.78
pH (units)*	6.25	6.07	4.61	4.43
Conductivity ( $\mu\text{S/cm}$ )*	2.8	1.5	14.1	18.2
Number of weeks	45	45	45	45
Note: * pH and conductivity values are median concentrations, not percent above detection.				

<b>C-7 Percent of Analyte Concentrations Above the MDL Found in DI Water, 1993</b>			
<b>Analyte</b>	<b>Sample Processing Laboratory</b>	<b>Atomic Absorption Laboratory</b>	<b>Service Laboratory</b>
Calcium	0.00	2.78	2.78
Magnesium	0.00	2.78	8.33
Sodium	13.33	5.56	5.56
Potassium	2.22	0.00	0.00
Ammonium	4.44	5.56	4.44
Sulfate	0.00	0.00	2.78
Nitrate	0.00	0.00	0.00
Chloride	2.22	2.78	2.78
Number of weeks	45	36	36

<b>TABLE C-8 Percent of Analyte Concentrations Above the MDL Found in Weekly HDPE Liter Bottle Nitric Acid Leachates, 1993.</b>	
<b>Analyte</b>	<b>pH 4.3 Nitric Acid</b>
Calcium	7.78
Magnesium	4.44
Sodium	37.8
Potassium	22.2
Ammonium	3.33
Sulfate	14.4
Nitrate	NA
Chloride	7.78
pH (units)	4.32
H <sup>+</sup> $\mu$ eq/L (median value)	47.9
Conductivity ( $\mu$ S/cm) (median value)	21.3
Number of bottles	90

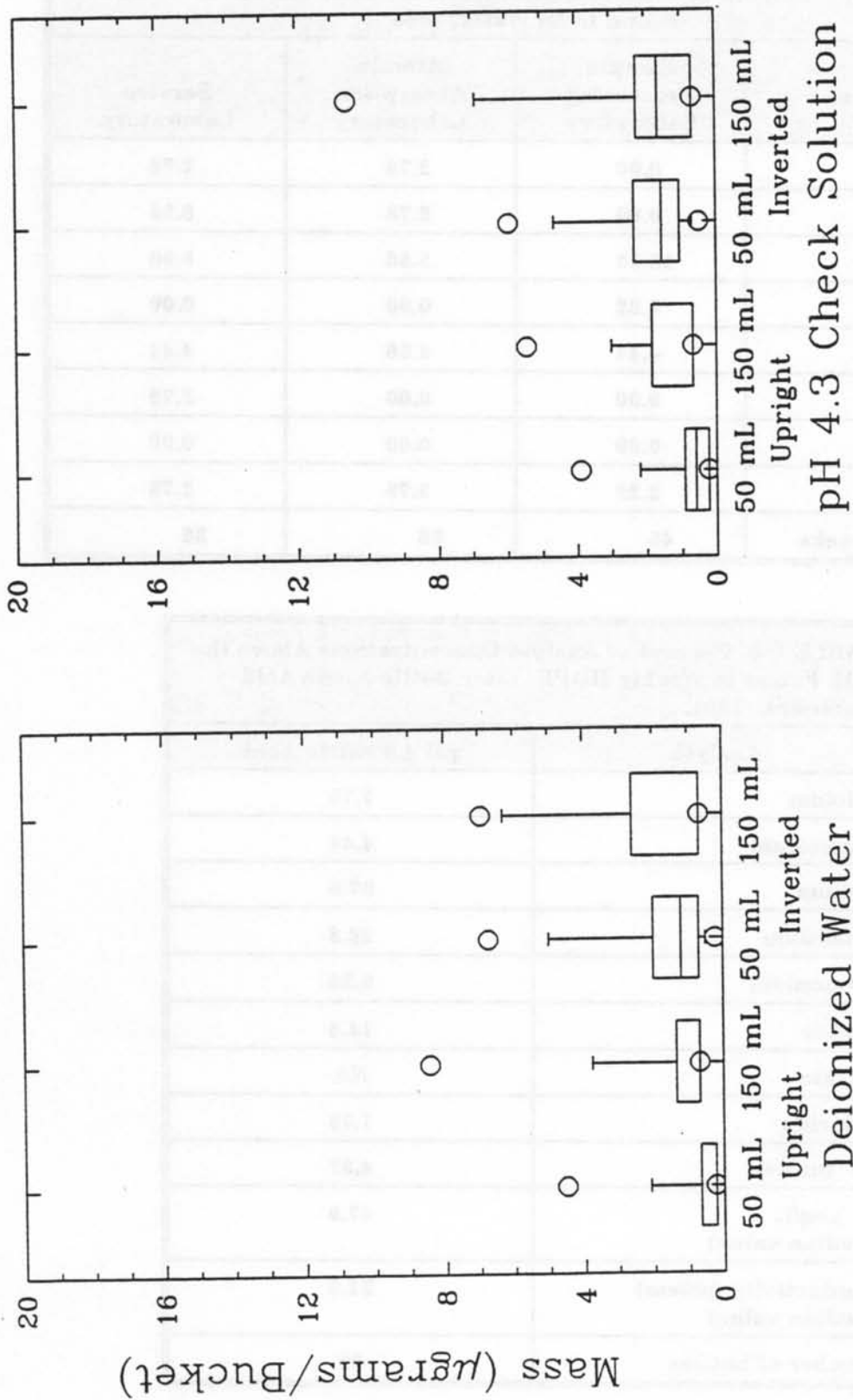


FIGURE C-24. Calcium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1993.

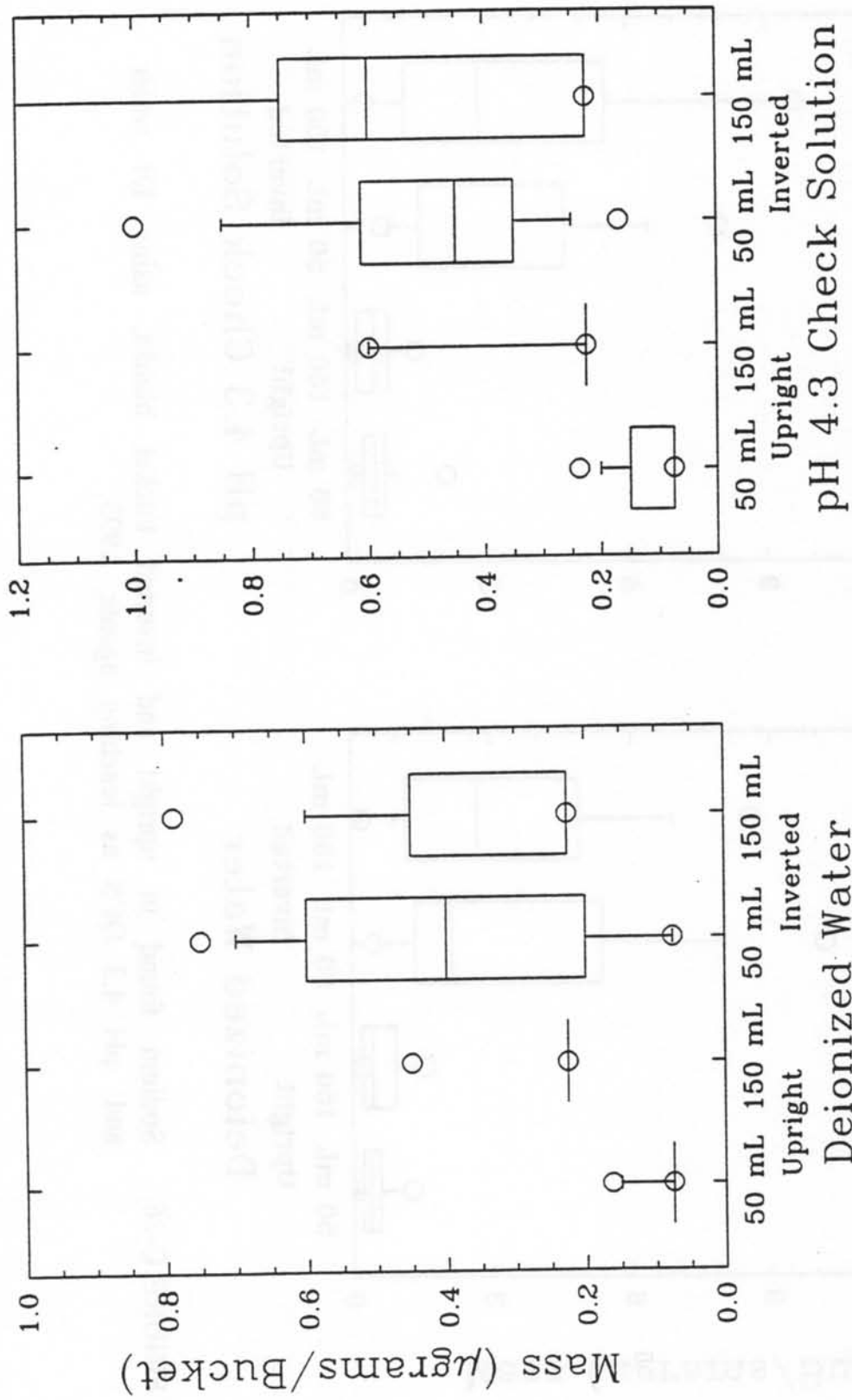


FIGURE C-25. Magnesium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1993.



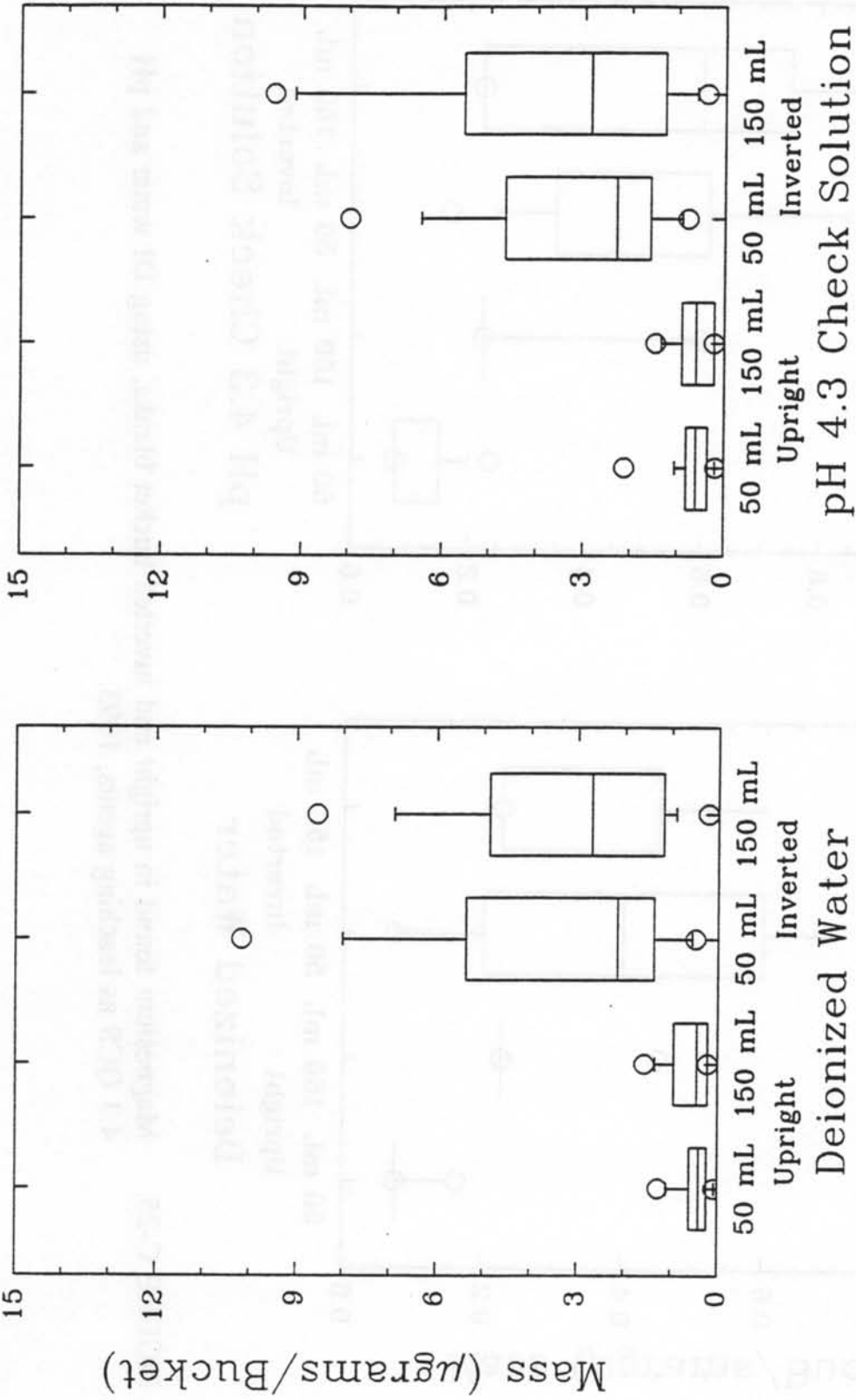


FIGURE C-26. Sodium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1993.

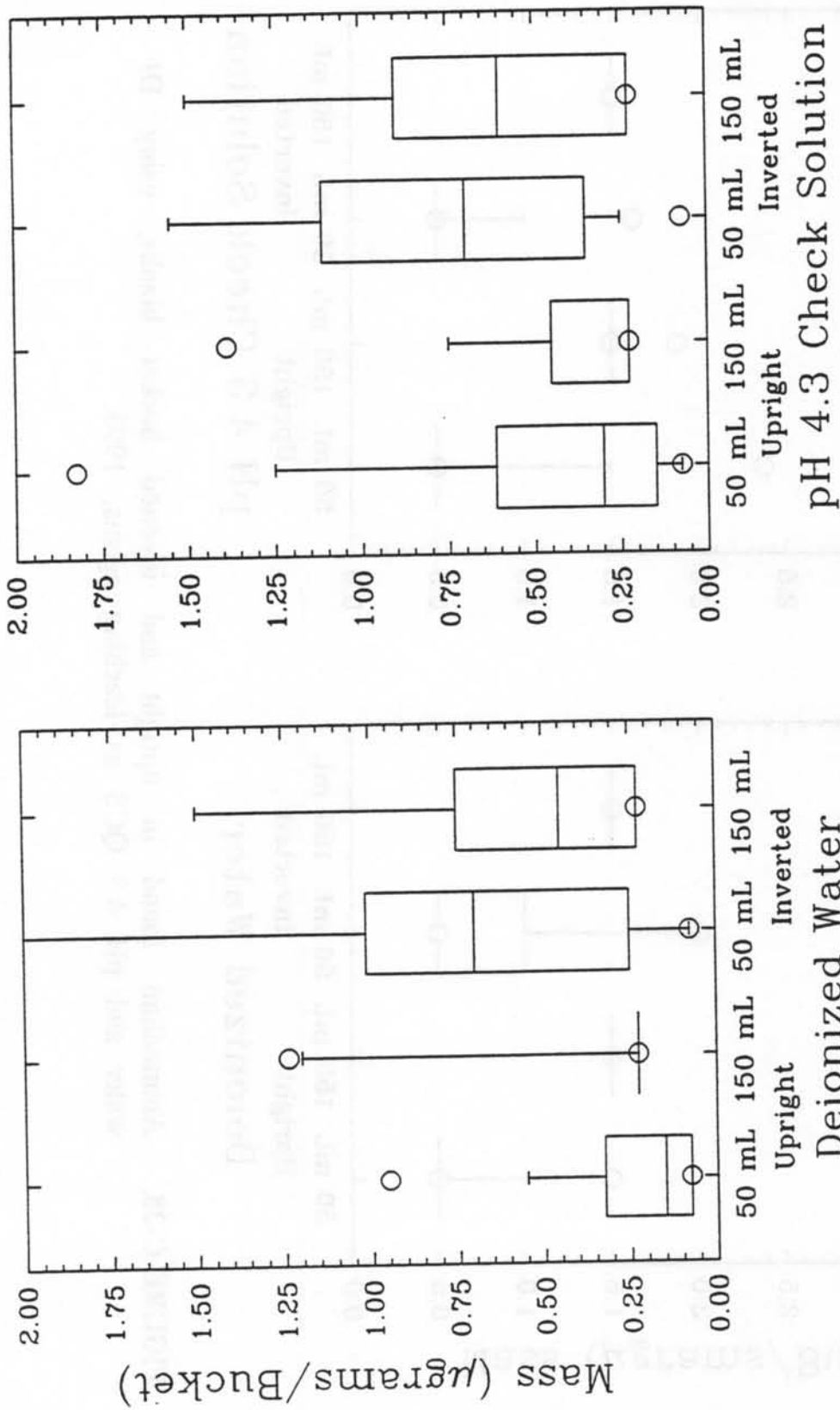


FIGURE C-27. Potassium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1993.

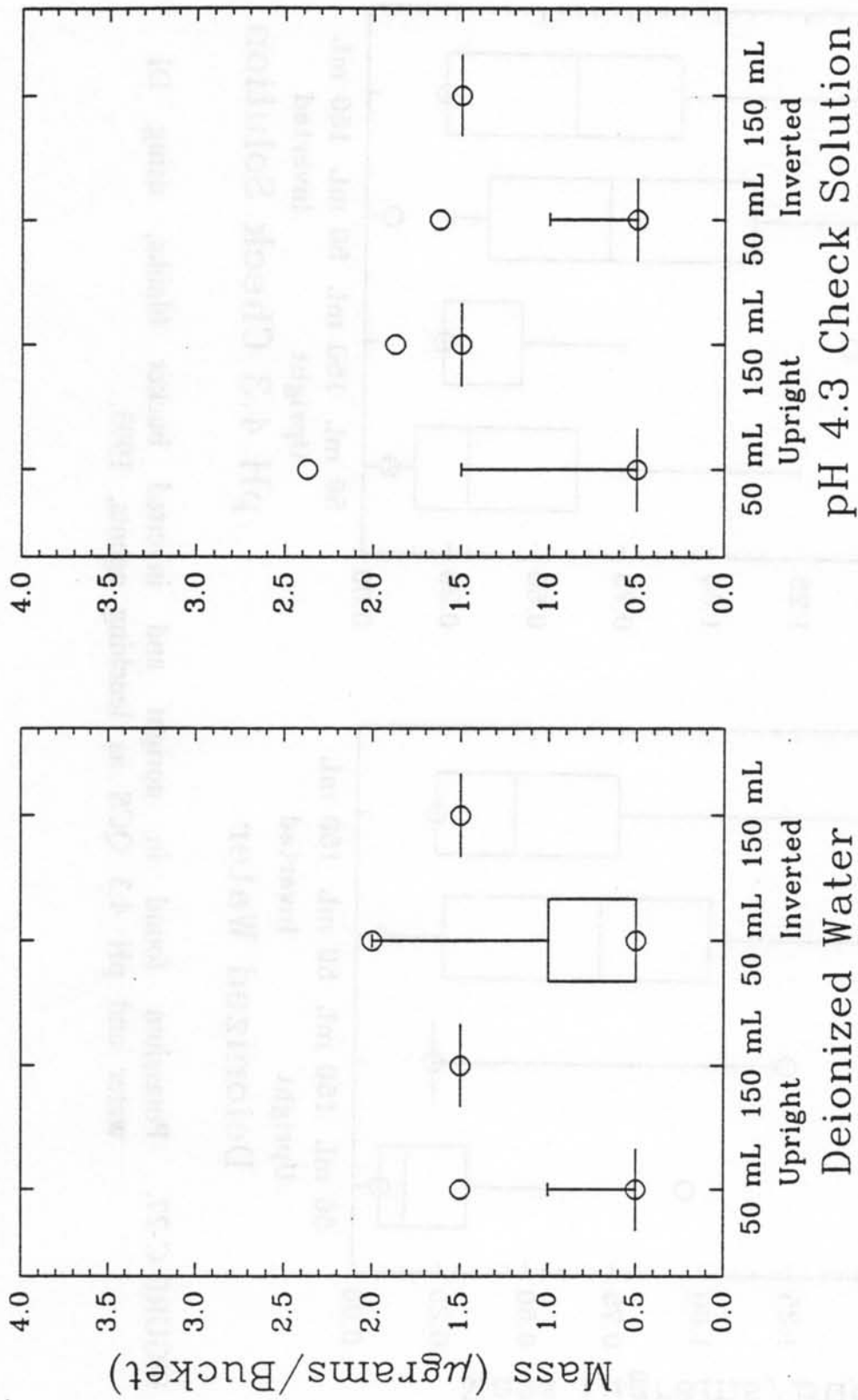


FIGURE C-28. Ammonium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1993.

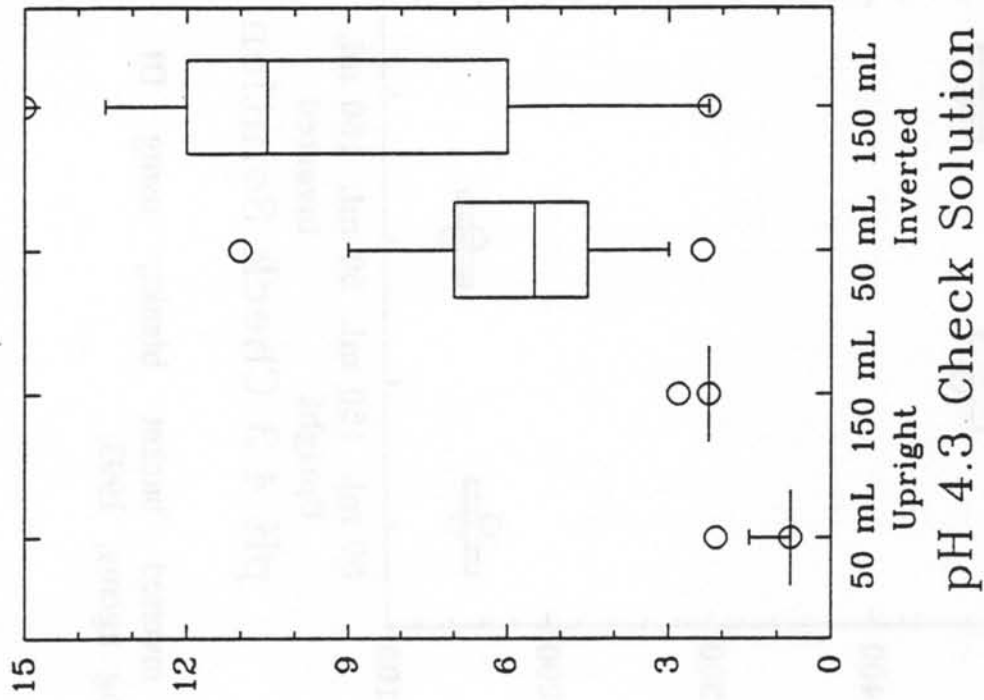
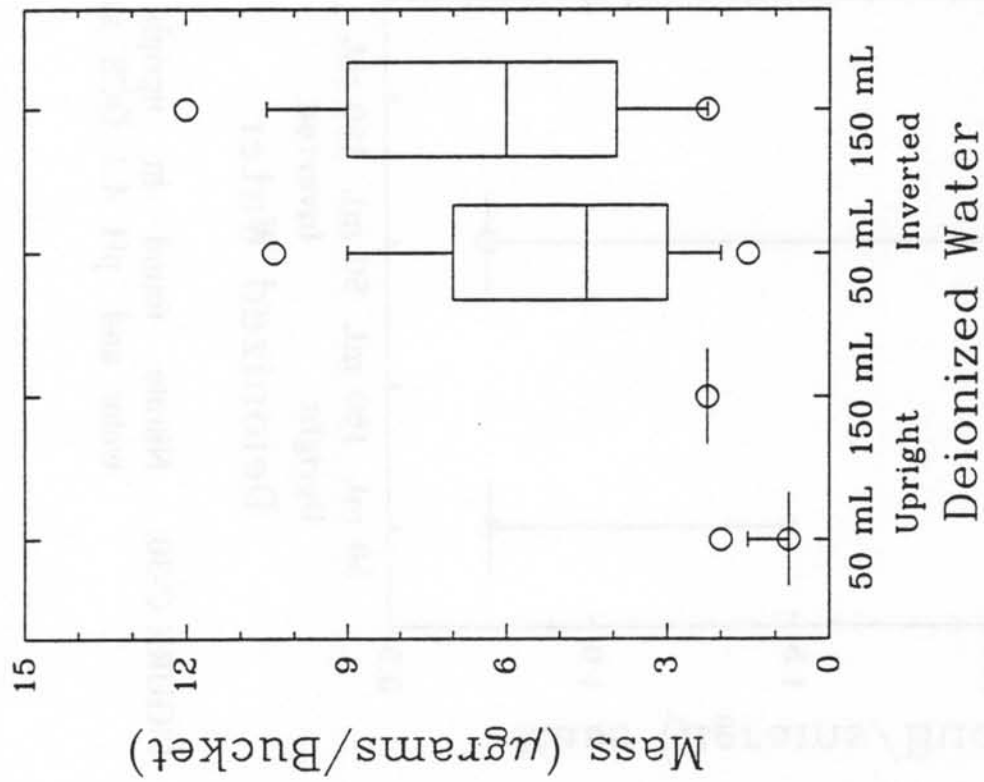


FIGURE C-29. Sulfate found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1993.

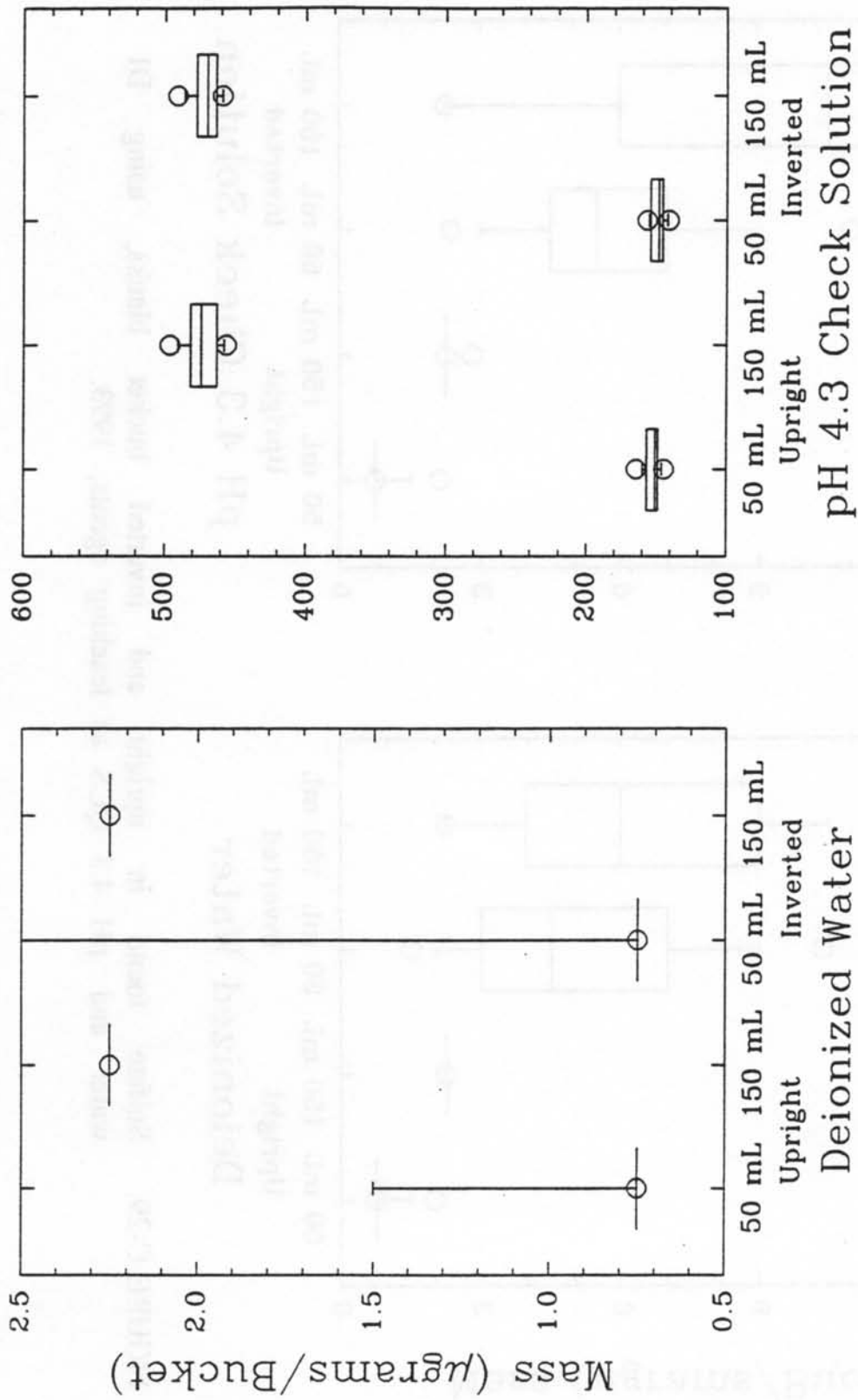


FIGURE C-30. Nitrate found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1993.

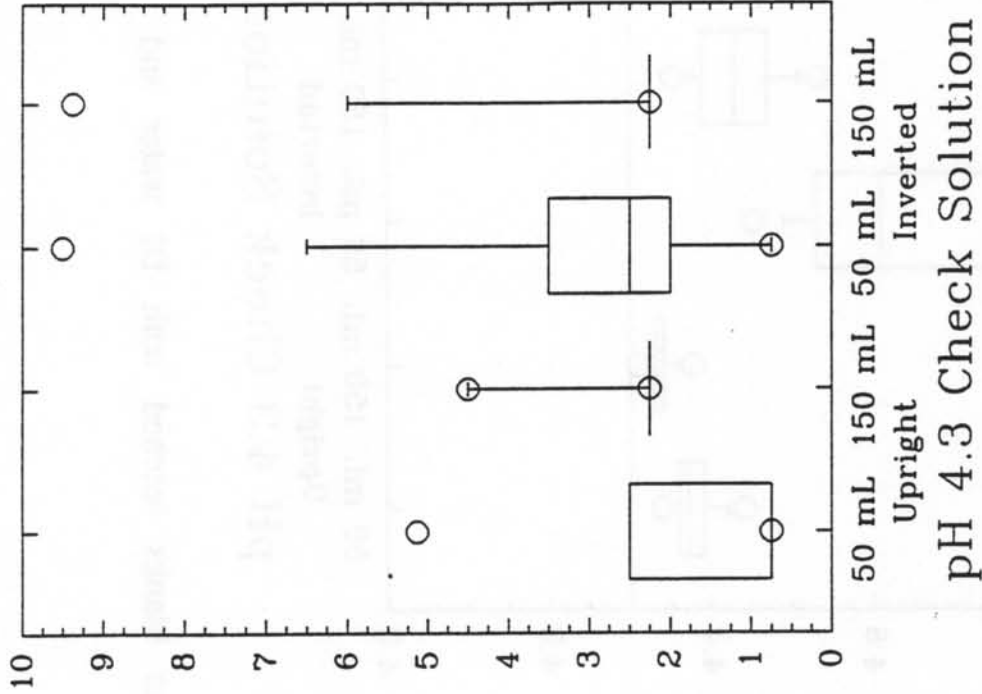
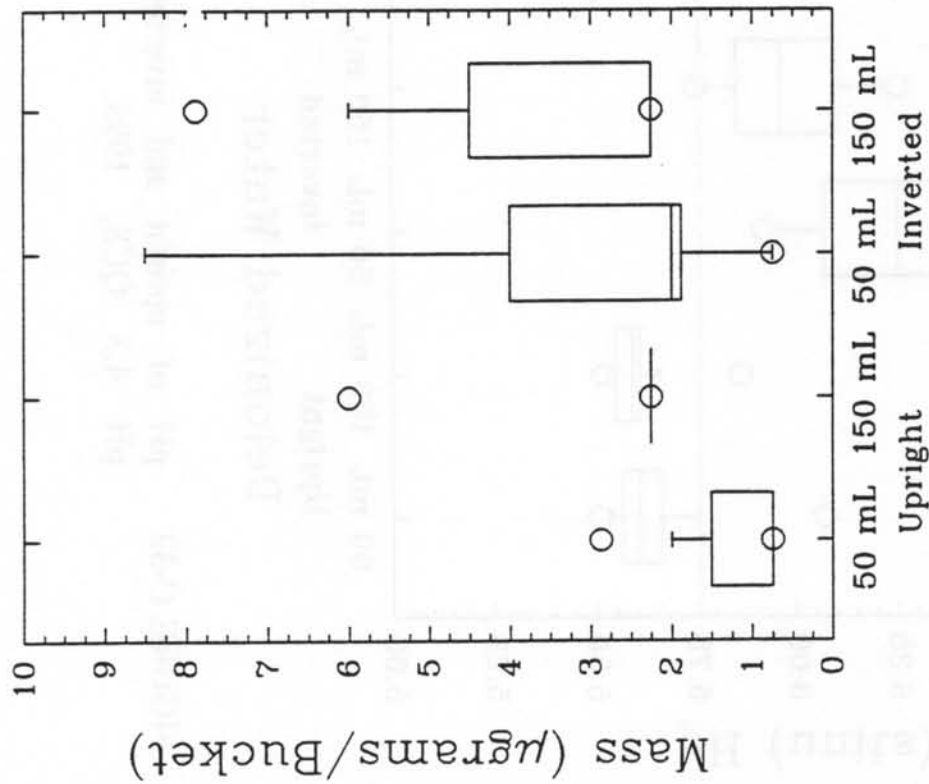


FIGURE C-31. Chloride found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1993.



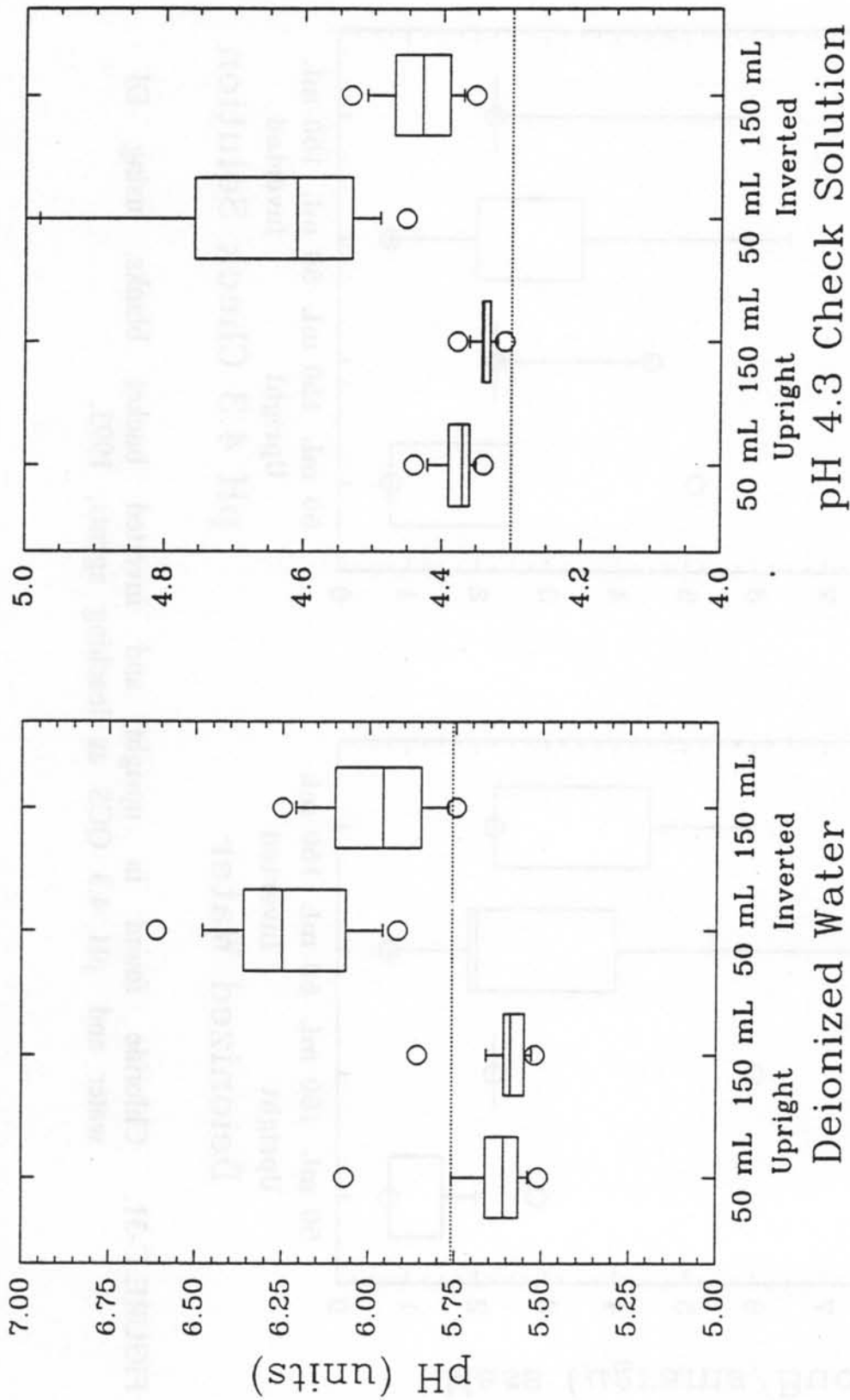


FIGURE C-32. pH of upright and inverted bucket blanks leached with DI water and pH 4.3 QCS, 1993.

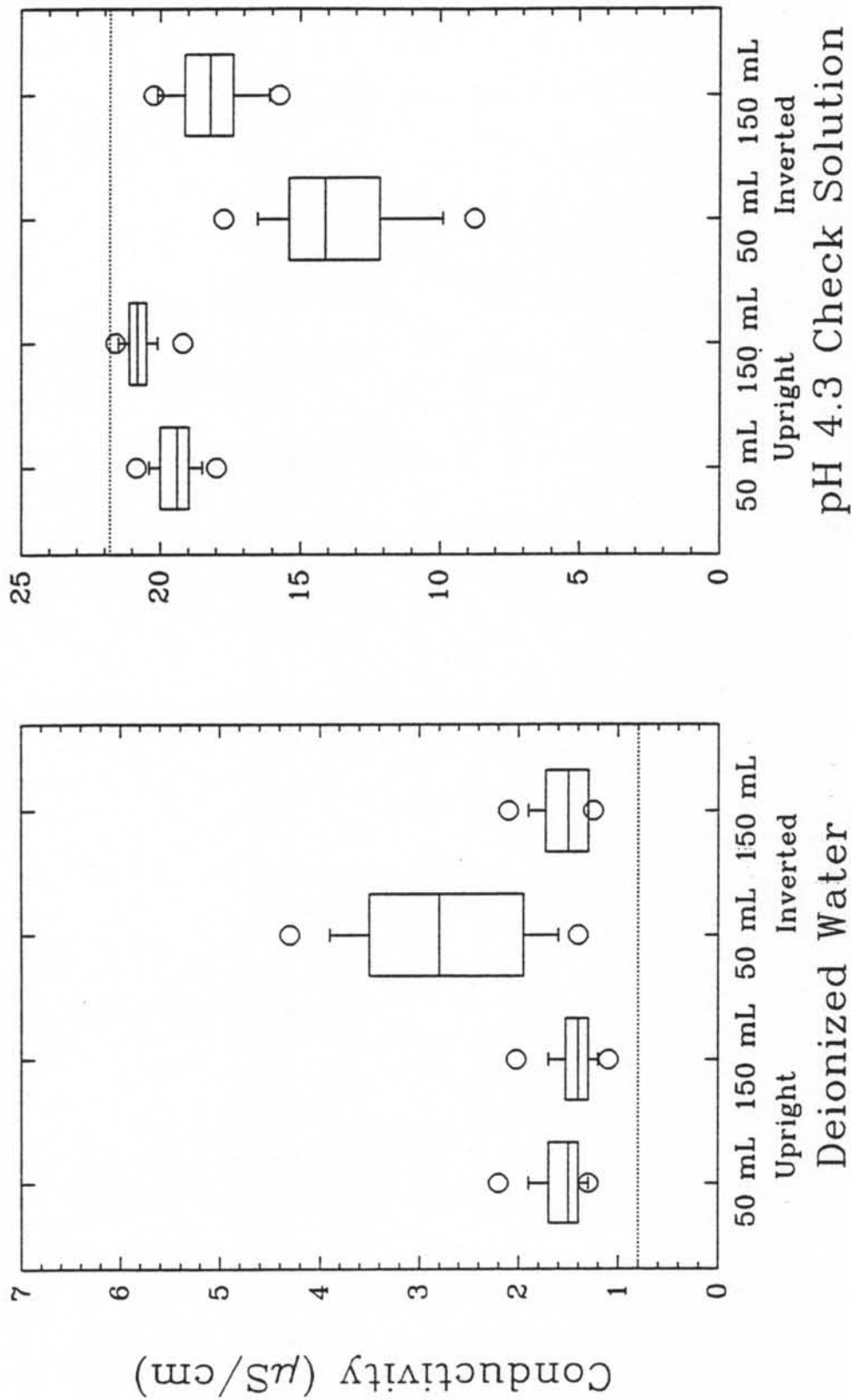


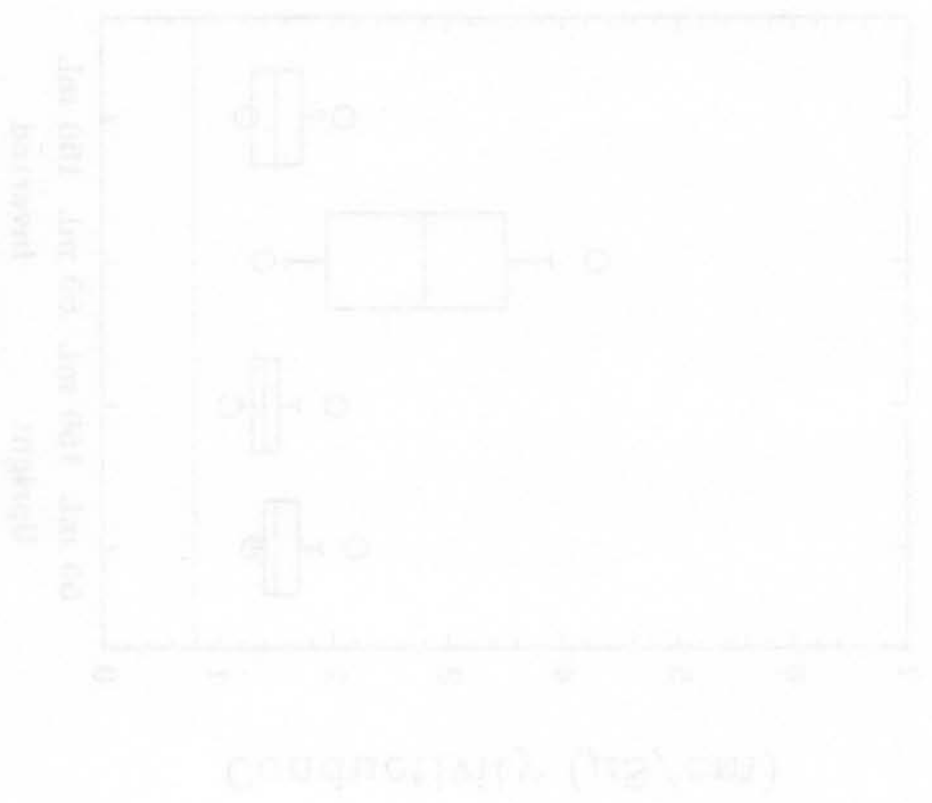
FIGURE C-33. Conductivity of upright and inverted bucket blanks leached with DI water and pH 4.3 QCS, 1993.

Figure 1: Comparison of the distribution of the number of visits to the site between the two groups. The y-axis represents the number of visits (0 to 20) and the x-axis represents the group (Control and Intervention). The distribution for the Control group is centered around 10 visits, while the Intervention group is centered around 15 visits. Both distributions are roughly symmetric and bell-shaped.

Figure 2: Comparison of the distribution of the number of visits to the site between the two groups. The y-axis represents the number of visits (0 to 20) and the x-axis represents the group (Control and Intervention). The distribution for the Control group is centered around 10 visits, while the Intervention group is centered around 15 visits. Both distributions are roughly symmetric and bell-shaped.



Figure 3: Comparison of the distribution of the number of visits to the site between the two groups. The y-axis represents the number of visits (0 to 20) and the x-axis represents the group (Control and Intervention). The distribution for the Control group is centered around 10 visits, while the Intervention group is centered around 15 visits. Both distributions are roughly symmetric and bell-shaped.



**APPENDIX D**

**INTERLABORATORY COMPARISON DATA:**

**USEPA, LRTAP, EMEP, WMO**

**1993**

APPENDIX D

INTERLABORATORY COMPARISON DATA

USRYA, LRTAP, LMRP, WMO

1993

**TABLE D-1  
USEPA/RTP Acid Rain Performance Audit, May 1993**

Parameter (mg/L)	Sample Number			
	1249		3453	
	CAL	USEPA	CAL	USEPA
Calcium	0.056	0.053	0.401	0.391
Magnesium	0.041	0.039	0.120	0.117
Sodium	0.190	0.186	1.848	1.866
Potassium	0.072	0.069	0.777	0.777
Ammonium	0.11	0.14	1.06	1.08
Nitrate	0.49	0.49	10.89	10.07
Chloride	0.29	0.30	2.88	2.82
Sulfate	2.73	2.64	12.55	11.50
pH (units)	4.30	4.29	3.51	3.49
Conductivity ( $\mu$ S/cm)	25.4	24.1	164.7	164.4
			133.2	133.4



TABLE D-2  
 LRTAP Interlaboratory Comparability Study L-32, March 1993  
 CAL Values Compared to NWRI Median Values for All Participating Laboratories

Parameter	Sample Number									
	1		2		3		4		5	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	1.784	1.787	8.655	8.685	6.992	6.941	7.132	7.141	13.995	13.675
Magnesium	0.662	0.670	2.588	2.670	0.740	0.750	0.760	0.771	2.761	2.820
Sodium	4.013	4.070	0.200	0.204	0.853	0.866	0.899	0.900	1.376	1.372
Potassium	0.290	0.290	0.325	0.326	0.244	0.236	0.258	0.250	0.500	0.490
Ammonium	<0.02	0.01	2.15	2.21	<0.02	0.01	0.09	0.09	<0.02	<0.01
Nitrate	0.31	0.27	13.06	15.10	0.40	0.40	0.40	0.40	1.33	1.33
Chloride	5.16	5.08	0.78	0.84	0.26	0.29	0.31	0.35	1.28	1.43
Sulfate	2.85	2.83	23.1	22.9	6.28	6.28	6.53	6.54	3.50	3.47
pH (units)	6.49	6.42	6.50	6.48	7.35	7.30	7.44	7.31	7.87	7.76
Conductivity (uS/cm)	35.7	36.2	98.9	98.5	48.1	48.2	50.4	50.4	97.8	97.6

TABLE D-2 (continued)  
 LRTAP Interlaboratory Comparability Study L-32, March 1993,  
 CAL 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	3.413	3.400	2.087	2.075	5.899	5.899	7.617	7.620	3.177	3.105
Magnesium	0.774	0.790	0.564	0.563	1.777	1.780	1.629	1.620	0.742	0.750
Sodium	3.363	3.380	1.135	1.130	0.282	0.280	0.453	0.450	1.028	1.020
Potassium	0.487	0.479	0.258	0.250	0.135	0.130	0.240	0.221	0.544	0.530
Ammonium	0.03	0.03	<0.02	0.01	<0.02	0.01	<0.02	0.01	0.05	0.05
Nitrate	0.66	0.66	0.18	0.16	8.63	8.63	8.76	8.76	0.58	0.54
Chloride	2.96	3.00	1.72	1.72	0.47	0.50	0.85	0.92	1.23	1.23
Sulfate	5.13	5.12	2.59	2.56	5.04	5.00	8.09	8.08	7.78	7.78
pH (units)	7.26	7.07	6.95	6.84	7.22	7.13	7.19	7.12	6.84	6.72
Conductivity ( $\mu$ S/cm)	43.6	43.6	23.6	23.8	51.5	51.7	61.6	61.9	33.7	34.0

TABLE D-3  
 LRTAP Interlaboratory Comparability Study L-33, June 1993,  
 CAL 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	1.825	1.800	1.964	1.925	3.338	3.295	3.223	3.145	6.155	6.000
Magnesium	0.676	0.660	0.316	0.310	1.087	1.080	0.968	0.969	1.536	1.505
Sodium	4.084	4.060	0.609	0.590	0.208	0.200	0.345	0.330	1.178	1.150
Potassium	0.295	0.291	0.409	0.408	0.198	0.198	0.098	0.098	0.280	0.270
Ammonium	<0.02	0.01	0.02	0.03	0.66	0.66	0.89	0.90	0.93	0.93
Nitrate	0.31	0.29	1.86	1.82	10.85	10.71	6.29	6.24	5.40	5.30
Chloride	5.15	5.11	0.41	0.43	0.51	0.54	0.73	0.76	2.11	2.14
Sulfate	2.87	2.82	5.44	5.40	6.86	6.90	6.90	6.89	8.95	8.81
pH (units)	6.52	6.46	5.37	5.37	4.64	4.64	6.39	6.29	7.06	6.96
Conductivity ( $\mu$ S/cm)	36.2	36.4	23.1	23.2	50.1	49.2	39.0	39.2	62.5	62.9

TABLE D-3 (continued)  
 LRTAP Interlaboratory Comparability Study L-33-June 1993  
 CAL Values Compared to NWRI Median Values for All Participating Laboratories

Parameter (mg/L)	Sample Number											
	6	7	8	9	10	6	7	8	9	10		
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	1.511	1.480	13.36	13.20	2.102	2.060	0.990	2.060	0.990	0.953	6.795	6.680
Magnesium	0.499	0.490	2.838	2.780	0.582	0.560	0.210	0.560	0.210	0.200	0.685	0.660
Sodium	0.234	0.220	1.392	1.350	1.173	1.120	0.097	1.120	0.097	0.090	0.912	0.870
Potassium	.055	0.050	0.517	0.502	0.263	0.257	0.039	0.257	0.039	0.039	0.311	0.295
Ammonium	0.60	0.08	<0.02	<0.01	<0.02	<0.01	<0.02	<0.01	<0.02	<0.01	<0.02	<0.01
Nitrate	2.74	2.74	1.46	1.42	0.09	0.11	0.09	0.11	0.09	0.09	0.80	0.80
Chloride	0.52	0.53	1.31	1.43	1.71	1.74	0.09	1.74	0.09	0.10	0.48	0.54
Sulfate	4.15	4.14	3.53	3.48	2.59	2.56	0.23	2.56	0.23	0.25	5.98	5.94
pH (units)	6.18	6.00	7.82	7.80	6.98	6.90	6.86	6.90	6.86	6.79	7.38	7.32
Conductivity ( $\mu$ S/cm)	21.6	21.8	96.3	96.9	23.6	24.0	7.6	24.0	7.6	7.7	47.0	47.4



TABLE D-4  
 ERTAP Interlaboratory Comparability Study L-34, October 1993,  
 CAL 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	2.097	2.06	8.66	8.70	3.392	3.345	13.37	13.40	6.64	6.62
Magnesium	0.575	0.560	2.695	2.680	1.097	1.100	2.836	2.880	0.634	0.630
Sodium	1.155	1.130	0.202	0.202	0.206	0.200	1.326	1.320	0.828	0.820
Potassium	0.264	0.260	0.333	0.330	0.200	0.200	0.519	0.500	0.299	0.295
Ammonium	<0.02	<0.01	1.28	1.28	0.77	0.76	<0.02	<0.01	0.11	0.11
Nitrate	0.04	0.05	18.9	18.6	11.0	10.8	1.82	1.81	0.62	0.62
Chloride	1.68	1.74	0.87	0.86	0.56	0.55	1.16	1.35	0.40	0.40
Sulfate	2.59	2.57	23.4	23.3	6.84	6.93	3.40	3.33	5.92	5.83
pH (units)	6.84	6.83	4.37	4.37	4.75	4.74	7.92	7.77	7.54	7.35
Conductivity ( $\mu$ S/cm)	23.9	23.6	113.6	111.1	49.4	48.4	96.2	96.2	46.9	46.9

TABLE D-4 (continued)  
 LRTAP Interlaboratory Comparability Study L-34 October 1993,  
 CAL 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	8.505	8.517	6.831	6.790	3.214	3.200	1.516	1.490	1.371	1.365
Magnesium	1.149	1.140	0.745	0.745	0.975	0.980	0.500	0.490	0.283	0.280
Sodium	1.484	1.460	0.855	0.856	0.341	0.334	0.233	0.228	0.141	0.140
Potassium	0.319	0.310	0.247	0.240	0.099	0.101	0.055	0.060	0.053	0.050
Ammonium	0.02	0.03	<0.02	0.01	0.09*	0.90	0.63	0.63	<0.02	<0.01
Nitrate	0.31	0.31	0.31	0.30	6.29	6.29	2.79	2.79	0.13	0.13
Chloride	1.53	1.54	0.29	0.29	0.76	0.76	0.55	0.54	0.16	0.16
Sulfate	7.39	7.39	6.21	6.27	6.86	6.86	4.20	4.13	7.06	7.13
pH (units)	7.60	7.42	7.42	7.36	6.54	6.41	6.18	6.02	4.29	4.28
Conductivity ( $\mu$ S/cm)	64.3	63.2	47.8	48.0	39.6	39.7	22.0	22.0	35.6	35.2

\*NH<sub>4</sub> value reversed on data sheet

**TABLE D-5 EMEP Thirteenth intercomparison of methods, April 1993**

Parameter (mg/L)	Sample Number											
	G 1			G 2			G 3			G 4		
	CAL	EMEP	EMEP	CAL	EMEP	EMEP	CAL	EMEP	EMEP	CAL	EMEP	EMEP
Calcium	0.293	0.287	0.622	0.613	0.675	0.671	0.312	0.307				
Magnesium	0.142	0.139	0.174	0.170	0.272	0.263	0.241	0.232				
Sodium	0.360	0.349	0.372	0.365	0.815	0.810	0.832	0.827				
Potassium	0.280	0.204	0.258	0.255	0.411	0.407	0.509	0.509				
Ammonium	0.41	0.41	0.46	0.46	0.60	0.62	0.66	0.67				
Nitrate	2.21	2.18	2.66	2.58	3.76	3.64	4.25	4.13				
Chloride	0.28	0.29	0.22	0.23	0.75	0.75	0.70	0.69				
Sulfate	5.45	5.37	6.56	6.56	4.46	4.37	3.86	3.77				
pH (units)	4.09	4.06	4.06	4.04	4.45	4.44	4.37	4.36				
Conductivity (µS/cm)	45.5	46.38	51.4	52.24	33.8	33.85	35.3	35.29				



**TABLE D-6 WMO Acid Rain Performance Survey, September 1993**

Parameter (mg/L)	Sample Number					
	1219		2717		3431	
	CAL	WMO	CAL	WMO	CAL	WMO
Calcium	0.058	0.053	0.405	0.391	0.059	0.053
Magnesium	0.040	0.039	0.119	0.117	0.078	0.078
Sodium	0.188	0.186	1.845	1.866	0.412	0.412
Potassium	0.074	0.069	0.797	0.777	0.082	0.077
Ammonium	0.09	0.10	1.04	1.08	0.59	0.60
Nitrate	0.53	0.49	10.76	10.07	8.10	7.99
Chloride	0.29	0.30	2.81	2.82	1.30	1.29
Sulfate	2.76	2.64	12.58	11.50	9.20	8.48
pH (units)	4.30	4.29	3.50	3.49	3.54	3.53
Conductivity ( $\mu$ S/cm)	25.2	24.1	162.1	164.4	131.5	133.4

Category	2013	2014	2015	2016	2017	2018	2019
Oil (barrel)	5.28	4.20	3.88	3.58	3.28	3.24	3.24
Zinc (lb)	3.24	3.14	3.28	3.28	3.28	3.28	3.28
Aluminum	4.28	4.28	4.28	4.28	4.28	4.28	4.28
Steel	4.28	4.28	4.28	4.28	4.28	4.28	4.28
Iron	4.28	4.28	4.28	4.28	4.28	4.28	4.28
Coal	4.28	4.28	4.28	4.28	4.28	4.28	4.28
Gas	4.28	4.28	4.28	4.28	4.28	4.28	4.28
Electricity	4.28	4.28	4.28	4.28	4.28	4.28	4.28
Water	4.28	4.28	4.28	4.28	4.28	4.28	4.28
Other	4.28	4.28	4.28	4.28	4.28	4.28	4.28
Total	4.28	4.28	4.28	4.28	4.28	4.28	4.28

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