QUALITY ASSURANCE REPORT
NADP/NTN DEPOSITION MONITORING

Laboratory Operations
Central Analytical Laboratory
1992

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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1992 QUALITY ASSURANCE REPORT
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Laboratory Operations
Central Analytical Laboratory
January 1992 through December 1992

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ACKNOWLEDGEMENTS

This Quality Assurance Report was prepared with the help and guidance of Mark E. Peden, laboratory manager for the Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). The analytical data were produced by the dedicated laboratory personnel listed in Section III. The figures, statistical analyses, computer-generated plots, and network percentile concentrations were prepared by Leon Olszewski, whose continual assistance throughout the year is greatly appreciated. Lacie Jeffers transferred data into presentable tables. Van Bowersox, CAL director, provided continuing support and suggestions throughout the year as quality control continued. The time and effort of the following reviewers are sincerely appreciated: Mark Peden, Eva Kingston, Cary Eaton, Molly Welker, and Mark Nilles.

I. INTRODUCTION

The Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) located at the Illinois State Water Survey in Champaign, Illinois, has been analyzing weekly precipitation samples since the network began in 1978. The low ionic strength of wet deposition samples dictates that a rigid Quality Control (QC) program be enforced throughout the life of the sample so that the final data produced are representative of the chemistry of the samples that have been collected and analyzed.

Quality control begins at the sampling site and continues through the data reporting. The CAL prepares and sends quality control solutions (QCS) for pH and conductance measurements to site operators in the field. Sample receiving and processing staff adhere to strict protocols when preparing the sampling and shipping containers and logging in the samples. The lid is carefully removed from the sampling bucket and observations are written down immediately prior to decanting small aliquots of sample for pH and conductance measurements. Each sample is then filtered and forwarded to the laboratory for analysis using extreme care to avoid contamination. Cation and anion analyses include prescribed QCS. Data are reported and entered into the NADP data base. Samples not meeting an ion balance and measured versus calculated conductance criteria are reanalyzed, and data changes are made where indicated. When the laboratory data have been reported, the data management staff continues with QC edits.

The NADP/NTN Quality Assurance Plan (1) prescribes the methods used to conduct and document the chemical and physical analyses of each sample. Annual reports (2-10) describe the evolution of the laboratory quality assurance (QA) program and document the various procedures designed to enumerate bias and precision, as well as to evaluate the input from sampling containers, filters, and deionized (DI) water. This report follows the format of the 1989-1991 reports. Previous editions are available from the Illinois State Water Survey and the Program Coordinator's Office at Colorado State University. Quality assurance data summarized in these reports are also available in tabular form upon request from the CAL.

II. LABORATORY QUALITY ASSURANCE - A GENERAL DESCRIPTION

The information presented in this report summarizes the laboratory QA/QC data collected throughout 1992. The report classifies the components of the QA program according to the frequency of their occurrence: daily, weekly, monthly, semiannually, and annually. These activities are summarized in Table II-1 and are described in subsequent sections.

Internal QA/QC procedures, developed over the past 14 years provide the data required to evaluate the analytical equipment, personnel performance, and analytical procedures of the CAL. From this information the accuracy and precision of the reported values can be assured. Results from the U.S. Geological Survey (USGS) interlaboratory comparison are summarized as are data from CAL participation in national and international interlaboratory comparisons.

Few modifications to the established program occurred in 1992. The processing of samples has not changed since mid-1987 (Figure II-1). There were no personnel or analytical methods changes. Internally prepared simulated rain at concentration levels near the 25th and 75th percentile concentration values of the network continued to serve as the quality control solutions (QCS) used following instrument calibration and during sample runs. Simulated Rainwater samples obtained from High Purity Standards in Charleston, South Carolina were used in the internal blind audit program. (The standard concentration of the solutions has been certified by spectrometric analysis against an independent source which is traceable to National Institute of Standards and Technology, Standard Reference Material No. 3100 series.) The replicate and reanalysis protocols, in place since 1989, were not altered in 1992. Deionized water, filter leachates, and sample collection and shipping bucket leachates were analyzed weekly to assess their contributions to the sample chemistry.

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

I. Daily
  - A. Instruments calibrated, calibration curves verified using low- and high-level control standards.
    - 1. Internally formulated solutions of simulated rain representing 25th and 75th percentile concentrations of network samples used for all physical and chemical parameters.
    - 2. Values of control standards recorded.
  - B. Records of standard preparation and instrument maintenance updated by analysts.

II. Weekly
  - A. Blanks analyzed.
    - 1. Deionized water collected from sample processing, atomic absorption, and bucket washing laboratories.
    - 2. Filter leachates "A" and "B" collected after 300 mL deionized water (DI) rinse.
      - a. DI
      - b. pH 4.3 nitric acid
    - 3. Bucket leachates of 50 and 150 mL collected from upright and inverted buckets.
      - a. DI
      - b. pH 4.3 nitric acid
    - 4. Procedures expanded when contamination indicated.
  - B. Internal blind samples submitted to sample processing as sites SWS1, SWS2, and SWS3.
    - 1. SHS1 alternate High Purity Standards Simulated Rainwater I and II, unfiltered.
    - 2. SWS2 alternate DI and pH 4.3 nitric acid, unfiltered.
    - 3. SWS3 rotate all of the above, filtered.
  - C. Newly prepared check samples validated and approved for shipment to the field.
  - 0. Replicate data collected and evaluated.

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

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

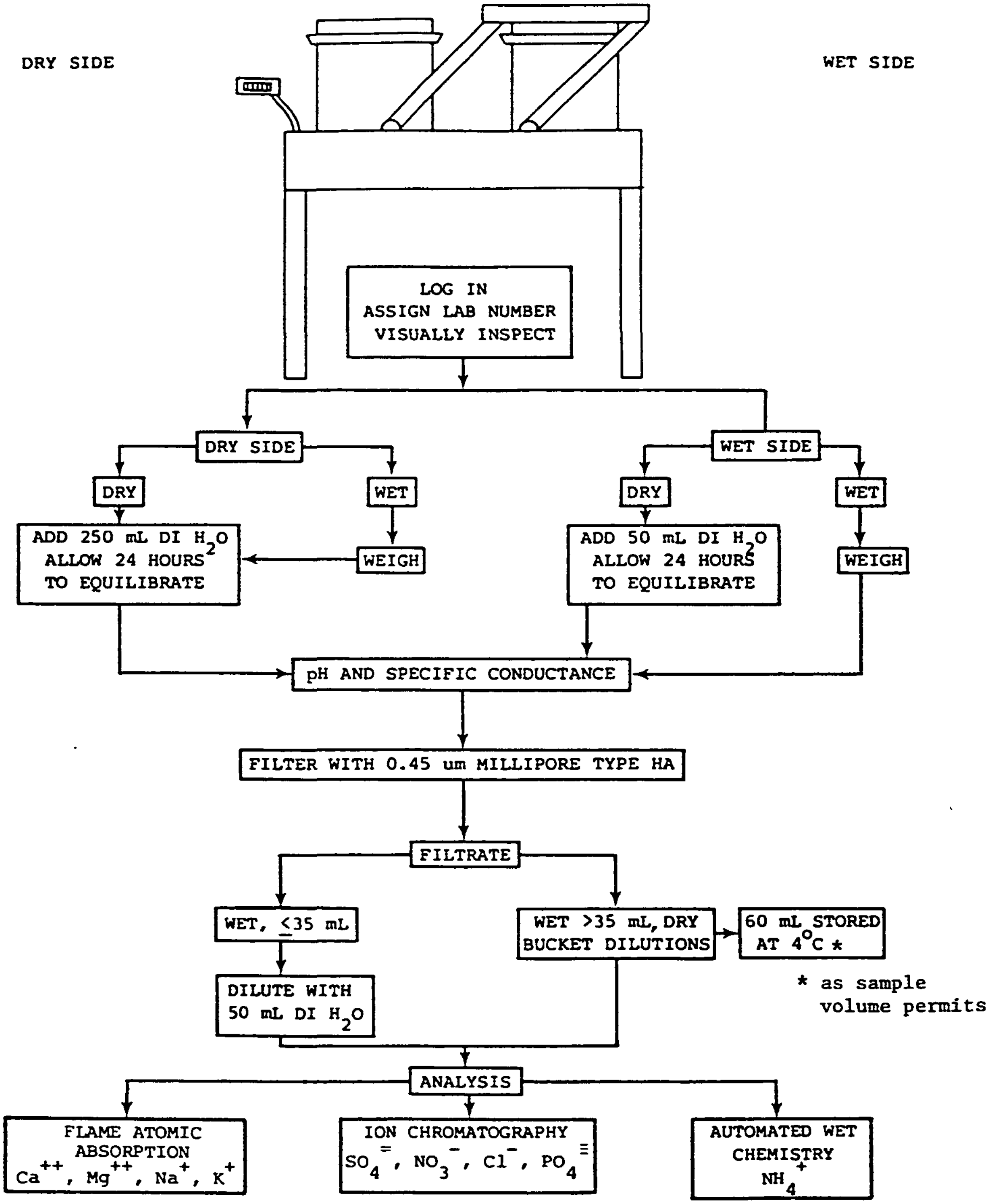


FIGURE II-1. Sample processing flowchart, January 1992-December 1992.

III. DAILY QUALITY CONTROL PROCEDURES

In 1992 201 NADP/NTN sites collected weekly precipitation samples throughout the United States. In October 1992, 11 of these sites began participation in a study to evaluate the use of bottles as shipping containers. At this time samples are collected weekly, on Tuesday mornings, field chemistry is performed, and the samples are shipped to the CAL in the collection bucket with a sealed lid.

Buckets are weighed on receipt at the CAL. If the weight of the contents indicates precipitation volumes ≥ 35 milliliters (mL), the sample is designated as "wet" and it receives the entire suite of analyses. Initially several milliliters are poured into small vials to measure laboratory pH and conductivity. A portion of the remaining sample is then filtered using Millipore™ type HAWP, 0.45µm filters into a 60 mL HDPE bottle for transport to the laboratories where the major ions are measured. If sample volume permits, an additional 60 mL of sample is filtered, labeled, and stored at 4°C for archival purposes.

The analytical staff (Table III-1) and methods of analysis (Table III-2) have remained the same since 1989.

Each of the analytical methods employed for the various parameters requires calibration of instrumentation using known standards, which are in turn verified with certified quality control solutions (QCS) or solutions traceable to certified standards. Beginning in 1990, the CAL has used two concentrations of in-house simulated rain traceable to the National Institute of Standards and Technology (NIST). These concentrations approximate the 25th and 75th percentile values for network precipitation (Table III-3). The original stock solution was prepared at the CAL as part of a separate Illinois State Water Survey U.S. Department of Energy (DOE) contract(11). Results from the U.S. Environmental Protection Agency (USEPA) diluted nutrient concentrate are used as a QCS for phosphate.

Samples are not analyzed until the instruments are calibrated to the analyst's satisfaction and the QCS results are within the control limits specified. The values of the QCS are recorded each time they are analyzed and then entered into a computer program to generate an historical record in the form of monthly control charts. The QCS data are shown in Table III-4.

TABLE III-I
Central Analytical Laboratory
Analytical Staff, 1992

Staff Member/Job Function	Period of Employment
Sue Bachman NH_4^+ Ca^{++}, Mg^{++}, Na^+, K^+	August 1980 - December 1992 November 1988 - December 1992
Jackie Damara Sample processing, pH, conductivity	September 1983 - May 1986 January 1988 - December 1992
Brigita Demir $S0_4^{=}$, $NO3^-$, Cl^-, PO_4^{3-}	September 1981 - December 1992
Pat Dodson Sample processing	September 1980 - December 1992
Angela Haley Sample receipt and processing, IonChromatography data handling	October 1989 - December 1992
Theresa Ingersoll Sample receipt and processing	March 1985 - December 1992
Kenni James Quality assurance	October 1987 - December 1992
Mark Peden Laboratory manager	July 1978 - December 1992
Jeffrey Pribble Sample receipt	July 1987 - December 1992

TABLE III-2
Method Detection Limits (MDLs) for the Analysis of Precipitation Samples, 1978-1992

Analyte	Method*	MDL (mg/L)	Dates
Calcium	Flame Atomic Absorption	0.02 0.009	7/78-10/80 10/80-12/92
Magnesium	Flame Atomic Absorption	0.002 0.003	7/78-10/80 10/80-12/92
Sodium	Flame Atomic Absorption	0.004 0.003	7/78-10/80 10/80-12/92
Potassium	Flame Atomic Absorption	0.004 0.003	7/78-10/80 10/80-12/92
Ammonium	Automated Phenate, Colorimetric	0.02	7/78-12/92**
Sulfate	Automated Methyl Thymol Blue, Colorimetric	0.10	7/78-5/85
	Ion Chromatography	0.03	5/85-12/92
Nitrate/Nitrite	Automated Cadmium Reduction, Colorimetric	0.02	7/78-5/85
Nitrate	Ion Chromatography	0.03	5/85-12/92
Chloride	Automated Ferricyanide, Colorimetric	0.05 0.02	7/78-3/81 3/81-5/85
	Ion Chromatography	0.03	5/85-12/92
Orthophosphate	Automated Ascorbic Acid, Colorimetric	0.003 0.01	7/78-2/86 2/86-7/87
	Ion Chromatography	0.02	7/87-12/92

Notes:

***For a complete description of the most recent methods, see *Methods for Collection and Analysis of Precipitation* (12).**

****Equipment upgrade in 1989 did not alter the MDL.**

TABLE III-3 Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/NTN Precipitation, 1992

	Percentile Concentration Value (mg/L)									
Parameter	Min.	5*	10*	25*	50*	75*	90*	95*	99*	Max.
Calcium	<0.009	0.016	0.024	0.048	0.107	0.234	0.525	0.850	1.893	25.10
Magnesium	<0.003	0.003	0.005	0.010	0.021	0.045	0.095	0.154	0.346	3.90
Potassium	<0.003	<0.003	0.004	0.009	0.018	0.037	0.076	0.120	0.305	3.95
Sodium	<0.003	0.017	0.023	0.038	0.073	0.165	0.407	0.740	2.050	15.60
Ammonium	<0.02	<0.02	0.03	0.09	0.21	0.43	0.76	1.05	1.92	5.41
Nitrate	<0.03	0.18	0.31	0.60	1.07	1.80	2.87	3.76	6.45	19.38
Chloride	<0.03	0.04	0.05	0.07	0.12	0.23	0.56	1.11	3.44	30.43
Sulfate	0.04	0.20	0.31	0.62	1.20	2.18	3.54	4.48	7.28	32.47
Phosphate	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	0.09	1.52
pH (units)	3.21	4.11	4.23	4.47	4.93	5.65	6.32	6.59	6.96	7.92
Cond. (µS/cm)	1.5	3.3	4.4	7.2	12.9	22.6	34.7	44.5	70.3	331

Notes:
Number of samples = 6,898
Mean sample volume = 1,443 mL; median sample volume = 914.9 mL

Source: National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) 1992 wet-side samples.

TABLE 1II-4 Analytical Bias and Precision Determined from Analysis of Simulated Rain QCS, 1992

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)	Critical Conc. (mg/L)	Statist. Significant Bias?
Calcium	0.077[a]	0.077	565	0.000	0.0	0.002	2.1	0.001	NO
	0.307[b]	0.307	530	0.000	0.0	0.002	0.7	0.001	NO
Magnesium	0.018	0.018	599	0.000	0.0	0.001	4.0	0.000	NO
	0.070	0.071	569	0.001	1.4	0.001	1.6	0.001	YES
Potassium	0.014	0.014	542	0.000	0.0	0.001	8.5	0.001	NO
	0.055	0.056	522	0.001	1.8	0.001	2.6	0.001	NO
Sodium	0.048	0.048	544	0.000	0.0	0.001	2.8	0.001	NO
	0.190	0.190	534	0.000	0.0	0.002	1.2	0.001	NO
Ammonium	0.09	0.09	543	0.00	0.0	0.01	10.0	0.00(4)[c]	NO
	0.37	0.37	426	0.00	0.0	0.01	3.8	0.00(6)	NO
Nitrate	0.48	0.49	1017	0.01	2.1	0.01	1.8	0.00(3)	YES
	1.94	1.97	1098	0.03	1.5	0.02	1.2	0.01(9)	YES
Chloride	0.14	0.13	1109	-0.01	-7.1	0.01	4.2	0.00(2)	YES
	0.54	0.52	1191	-0.02	-3.7	0.01	2.7	0.00(5)	YES
Sulfate	0.64	0.64	1026	0.00	0.0	0.01	1.4	0.00(4)	NO
	2.58	2.61	1099	0.03	1.2	0.02	0.9	0.01(0)	YES
Phosphate	0.06	0.05	321	-0.01	-16	0.01	12.9	0.00(2)	YES
	0.30	0.30	197	0.00	0.0	0.01	3.5	0.00(3)	NO
pH units (μeq/L)[d]	4.90(12.6)	4.91(12.3)	1960	(-0.26)	(-2.1)	0.02	4.6	(0.232)	YES
	4.31(49.0)	4.33(46.8)	1960	(-2..59)	(-5.3)	0.01	3.4	(0.610)	YES
Conductivity (μS/cm)	7.20	7.42	1114	0.22	3.0	0.16	2.2	0.068	YES
	28.1	28.0	1114	-0.07	-0.2	0.34	1.2	0.142	NO

Notes:
[a] The first set of values for each parameter is for the 25* percentile solution. [b] The second set of values for each parameter is for the 75th percentile solution. [c] Critical concentration values in parentheses are provided for information. [d] The pH data in parentheses are in microequivalents. See Appendix A for definitions of and formulas for Bias, Standard Deviation, Precision, and Critical Concentration.

The bias for the cations is zero with the exception of a 0.001 mg/L difference for the 75th percentile concentrations of magnesium and potassium. The precision expressed as percent relative standard deviation (RSD) is even better than the corresponding values in 1991. The anions exhibit similar biases to those of 1991. Nitrate is 0.01 and 0.02 mg/L higher for the 25th and 75th percentile concentrations, respectively. Chloride is 0.01 mg/L lower for the second QCS, and sulfate is 0.02 higher for the same solution. The bias values for phosphate are the same as values for the previous year. Nitrate, chloride, and sulfate all have the same precision or better as during 1991. The pH 4.9 solution had a mean value of 4.91 pH units compared to 4.89 pH units in 1991. The precision for that measurement improved. The pH 4.31 QCS had a mean value of 4.33 pH units, the same as the previous year, and the precision improved. The lower conductance solution bias is higher and the precision is better than during 1991, while the higher concentration solution conductance bias is smaller and the precision is slightly better.

The bias and precision data for all parameters fall well within the goals for laboratory measurements outlined in the network QA Plan (1). The percent bias exceeds 5 percent for only the low chloride and phosphate solutions and the 75th percentile pH measurements. The RSD for the 25th percentile potassium and ammonium are greater than 5 percent as is that of the lower concentration of phosphate.

IV. WEEKLY QUALITY CONTROL/QUALITY ASSURANCE PROCEDURES

Quality assurance procedures that are conducted on a weekly basis include the analysis of internal blind audit samples, replicate samples, and laboratory blank solutions.

A. INTERNAL BLIND AUDIT

The internal blind audit was instituted in the summer of 1984 to provide another means of evaluating the quality of the laboratory data. Since 1987, three blind samples have been submitted each week, each bearing special NADP/NTN site designations SWS1, SWS2, or SWS3. An estimate of the effects of filtration is gained by filtering the SWS3 sample and comparing the analyses to those from SWS1 and SWS2 samples, which are not filtered. In 1992 the samples used for SWS1 are simulated rainwater I and II, prepared by High Purity Standards (HPS) in Charleston, South Carolina. The SWS2 samples are the same as they have been, deionized (DI) water from the ion chromatography/flow injection analysis (IC/FIA) laboratory and internally formulated pH 4.3 nitric acid used as a network quality control solution (QCS). SWS3 samples are the four solutions used as SWS1 and SWS2 samples. They are submitted in rotation so that an equal number of each of the four solutions is analyzed. The data from the analyses of these samples are summarized in Tables IV-1 through IV-4.

When comparing the bias and precision results of the QCS to the SWS1, SWS2, and SWS3 samples, it is important to note the differences in the concentrations of the various solutions and also the wide difference in the number of analyses of each parameter. Whereas the QCS are formulated to emulate the 25th and 75th percentile concentrations of the network, the HPS solutions range from the 5th percentile to greater than the 99th percentile concentration values.

The bias and precision for SWS1 calcium are high, but the target concentration is near the 0.009 mg/L detection limit, and therefore the results are acceptable. A magnesium bias of 0.005 mg/L and ammonium bias of -0.01 mg/L result in a 10 percent bias. Ammonium precision for both samples is -20 percent RSD. The low nitrate, which is comparable in concentration to its QCS counterpart, has a 10 percent bias but the precision is the same as the QCS. The chloride analyses have similar bias results and are not as precise. The pH and conductance bias and precision are all well within the designated limits.

The SWS3 analyses compared to SWS1 analyses indicate an increase in calcium and sodium at their respective concentrations. Sulfate concentrations have lessened and chloride concentrations have increased to almost the target value. Precision varies by parameter but is not as good as for the nonfiltered samples.

When evaluating the results from the analyses of DI and pH 4.3 nitric acid, used for SWS2 and SWS3, note that for calculation purposes, values less than the method detection limit (MDL) are set to equal one half the MDL. This procedure produces occasional extremely large bias and precision results. Sodium contamination occurs at random. The filters appear to contribute small amounts of nitrate and chloride.

Comparing the analytical results of the blind solutions to those of the QCS samples illustrates the wider variability in random sample analysis compared to sample analysis immediately after calibration. Near detection level cation analyses results, especially, have a larger degree of uncertainty than those of higher concentrations. These results are predictable and therefore accounted for in the QA Plan by larger allowable bias and precision percentages at the lower concentrations.

Tables B-1 and B-2 and control chart figures in Appendix B 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-SR-I) and II (HPS-SR_II), Unfiltered, 1992

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)
Calcium	0.015[a] 0.052[b]	0.020 0.057	25 25	0.005 0.005	33.3 9.6	0.008 0.018	40.0 31.6
Magnesium	0.025 0.050	0.026 0.055	25 25	0.001 0.005	4.0 10.0	0.002 0.003	7.7 5.4
Potassium	0.050 0.100	0.051 0.100	25 25	0.001 0.000	2.0 0.0	0.003 0.010	5.9 10.0
Sodium	0.200 0.400	0.200 0.409	25 25	0.000 0.009	0.0 2.2	0.007 0.041	3.5 10.2
Ammonium	0.1[c] 1.0	0.09 0.98	25 25	-0.01 -0.02	-10.0 -2.0	0.02 0.21	20.0 21.0
Nitrate	0.50 7.1	0.55 7.30	25 25	0.05 0.20	10.0 2.8	0.01 0.29	1.8 2.7
Chloride	0.25 0.98	0.23 0.97	25 25	-0.02 -0.01	-8.0 -1.0	0.01 0.06	4.3 6.2
Sulfate	2.7 10.0	2.54 10.27	25 25	-0.16 0.27	-5.9 2.7	0.04 0.13	1.6 1.3
pH (units) µeq/L	(4.34)[d] 45.71 (3.57) 269.2	(4.31) 48.73 (3.60)249.9	25 25	3.02 -19.3	6.6 -7.2	2.48 15.68	5.1 6.3
Conductivity (µS/cm)	25.0 130.0	24.8 126.9	25 25	-0.2 -3.1	-0.8 -2.4	0.7 1.6	2.8 1.3

Notes:

[a] The first set of values for each parameter is for HPS-SR-I. [b] The second set of values for each parameter is for HPS-SR-2.

[c] Ammonium values are for information only, found not to be stable. [d] The pH data in parentheses are pH units. These have been converted to microequivalents per liter for calculations.

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, 1992

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)
Calcium	<0.009[a]	<0.009	25				
	<0.009[b]	<0.009	25				
Magnesium	<0.003	<0.003	25				
	<0.003	<0.003	25				
Potassium	<0.003	<0.003	25				
	<0.003	<0.003	25				
Sodium	<0.003	0.005	25	0.003c	233	0.006	120
	<0.003	0.008	25	0.006	433	0.015	188
Ammonium	<0.02	<0.02	25				
	<0.02	<0.02	25				
Nitrate	<0.03	<0.03	25				
	3.12	3.20	25	0.08	2.6	0.06	1.9
Chloride	<0.03	<0.03	25				
	<0.03	<0.03	25				
Sulfate	<0.03	<0.03	25				
	<0.03	<0.03	25				
pH (units)	(5.74)[d]1.83	(5.62) 2.41	25	0.58	31.7	0.33	13.7
μeq/L	(4.30)50.12	(4.32)48.13	25	-1.99	-4.0	2.08	4.2
Conductivity	0.9	1.3	25	0.4	44.4	0.8	61.5
(μS/cm)	21.8	21.6	25	-0.2	-0.9	0.8	3.7

Notes:

[a] The first set of values for each parameter is for DI water. [b] The second set of values for each parameter is for pH 4.3 QCS

[c] For calculation purposes MDLs are given the value of 0.5(MDL). [d] The pH data in parenthses are pH units. These have been converted to microequivalents per liter for calculations.

TABLE IV-3 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS3), High Purity Standards Simulated Rainwater I (IIPS-SR1) and II (HPS-SR-II), Filtered, 1992

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)
Calcium	0.015[a] 0.052[b]	0.023 0.060	13 13	0.008 0.008	53.3 15.4	0.005 0.007	21.7 11.7
Magnesium	0.025 0.050	0.026 0.053	13 13	0.001 0.003	4.0 6.0	0.003 0.003	11.5 5.7
Potassium	0.050 0.100	0.047 0.101	13 13	-0.003 0.001	-6.0 1.0	0.002 0.007	4.2 6.9
Sodium	0.200 0.400	0.221 0.429	13 13	0.021 0.029	10.5 7.2	0.020 0.032	9.0 7.4
Ammonium	0.1[c] 1.0	0.10 0.97	13 13	0.0 -0.03	0.0 -0.03	0.02 0.08	20.0 7.8
Nitrate	0.50 7.1	0.56 7.05	13 13	0.06 -0.05	12.0 -0.7	0.03 0.21	5.4 3.0
Chloride	0.25 0.98	0.25 0.94	13 13	0.00 -0.04	0.0 -4.1	0.02 0.06	8.0 6.4
Sulfate	2.7 10.0	2.43 9.77	13 13	-0.27 -0.23	-10.0 -2.3	0.06 0.31	2.5 3.2
pH (units) µeq/L	(4.34)[d]45.71 (3.57)269.2	(4.31) 48.87 (3.60) 251	13 13	3.16 -18.2	6.9 -6.8	2.69 11.04	5.5 4.4
Conductivity (µS/cm)	25.0 130.0	24.5 126.6	13 13	-0.5 -3.4	-2.0 -2.6	0.6 1.8	2.4 1.4

Notes:

[a] The First set of values for each parameter is for HPS-SR I. [b] The second set of values for each parameter is for HPS-SR II.

[c] Ammonium values are for information only; found not to be stable. [d] The pH data in parentheses are pH units. These have been converted to microequivalents per liter for calculations.

TABLE IV-4 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS3), Deionized (DI) Water and pH 4.3 QCS, Filtered, 1992

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)
Calcium	<0.009[a]	<0.009	12				
	<0.009[b]	<0.009	12				
Magnesium	<0.003	<0.003	12				
	<0.003	<0.003	12				
Potassium	<0.003	<0.003	12				
	<0.003	<0.003	12				
Sodium	<0.003	0.030	12	0.028[c]	1400	0.010	33.3
	<0.003	0.031	12	0.029	1450	0.019	61.3
Ammonium	<0.02	<0.02	12				
	<0.02	<0.02	12				
Nitrate	<0.03	0.05	12	0.03	150	0.02	40.0
	3.12	3.12	12	0.00	00	0.07	2.2
Chloride	<0.03	0.03	12	0.01	50	0.02	66.7
	<0.03	0.05	12	0.03	150	0.05	100.0
Sulfate	<0.03	<0.03	12				
	<0.03	<0.03	12				
pH (units)	(5.74)[d]1.83	(5.60) 2.52	12	0.69	38.0	0.42	16.7
µeq/L	(4.30)50.12	(4.31)49.11	12	-1.01	-2.0	1.90	3.9
Conductivity (µS/cm)	0.9	1.5	12	0.6	66.7	0.7	46.7
	21.8	21.7	12	-0.1	-0.5	0.7	3.2

Notes:

[a] The first set of values for each parameter is for DI water. [b] The second set of values for each parameter is for pH 4.3 QCS.

[c] For calculation purposes MDLs are given the value of 0.5 (MDL). [d] The pH data in parentheses are pH units. These have been converted to microequivalents per liter for calculations.

B. REPLICATE SAMPLES

Two percent of all weekly network samples are split into three 60-mL portions. Two samples are given the same number: one is analyzed immediately; the second is refrigerated for archival purposes. The third sample is returned to the sample processing group, given another sequential number, and then resubmitted to the laboratory. The first and third samples 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, data management staff recodes the second sample back to its original "O" designation but with an additional "Q" (quality assurance) modifier. These "O/Q" splits, as they are called, then appear consecutively twice a month on ion balance printouts. The QA specialist inspects these two analyses each time a printout is issued and estimates the precision of network samples. The results are presented as replicate sample differences and displayed as box plots in Appendix B. Box plots as used in this report are defined in the glossary (Appendix A).

The information presented in Table IV-5 is a brief summary of the replicates analyzed in 1992. The differences are calculated by subtracting the reanalysis value from the original value. The standard deviation estimated from duplicate measurements, defined in the glossary, 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 1992 O/Q dataset. This information is provided, as requested by reviewers of previous reports, for comparison.

The standard deviations estimated for each of the parameters show that the precision for these replicate network samples is better than or comparable to that of the internal blind audit samples. The mean difference for all parameters except pH and conductivity is zero. With the exception of the high sodium, sulfate and nitrate, pH and conductivity, the precision for the replicates has improved since last year.

TABLE IV-5 Variance Estimated from Analysis of Replicate Network Precipitation Samples, 1992

Parameter	Standard Deviation Estimated from Paired Measurements[a] (Low conc.)	(High conc.)	(Total)	(1.048328)x MAD (Total)
Calcium	0.007	0.010	0.008	0.005
Magnesium	0.001	0.007	0.005	0.001
Sodium	0.003	0.028	0.020	0.003
Potassium	0.003	0.006	0.004	0.002
Ammonium	0.01	0.02	0.02	0.01
Sulfate	0.01	0.06	0.04	0.01
Nitrate	0.01	0.08	0.06	0.01
Chloride	0.01	0.04	0.03	0.0
Phosphate	0.0	0.01	0.01	0.0
pH	0.57	1.92	1.41	0.66
Conductivity	0.49	0.62	0.55	0.31
Number of Pairs	90	89	179	179

Notes:
* Defined in glossary with equation

C. BLANKS

Blank data have been summarized from three sources: the laboratory deionized water, the sample filtering process, and the buckets and lids used for sample collection and shipping. These data are used to estimate the contributions from these sources to the chemistry of the sample. Deionized water is randomly collected each week from three work areas. Leachates from the filters are collected using both DI water and pH 4.3 nitric acid. Upright and inverted buckets are leached overnight with 50 and 150 mL of the same two solutions. All of these "blanks" are subjected to the entire sample analysis procedure.

1. Deionized Water Blanks

Deionized (DI) water is collected in the atomic absorption (AA) laboratory, the sample processing work area, and the bucket washing work area (service laboratory). The median values of the cation and anion analyses of the samples from each source are all below the method detection limits (MDLs). One ammonium value (0.05 mg/L) and one potassium concentration (0.003 mg/L) were above detection in the sample processing DI water. In the atomic absorption laboratory there were six values above detection: one sulfate value at 0.03 mg/L, two ammonium values (0.02 and 0.03 mg/L), and one value each for calcium (0.018 mg/L), sodium (0.005 mg/L), and potassium (0.003 mg/L). In the DI water from the service laboratory there were eight values above detection: one each for chloride (0.05 mg/L) and potassium (0.04 mg/L), two for ammonium (0.02 and 0.06 mg/L) and four for sodium (0.007, 0.003, 0.014, and 0.003 mg/L). Table IV-6 shows the median values for pH and conductivity for the DI water in 1992.

TABLE IV-6 Median Values for pH and Conductivity for Weekly Deionized (DI) Water Blanks, 1992

	Sample Processing Laboratory	Atomic Absorption Laboratory	Service Laboratory
pH (units)	5.77	5.74	5.71
Conductivity (µS/cm)	0.8	0.9	0.9
Number of weeks	48	35	35

2. Filter Blanks

In order to evaluate the contribution of the filtering procedure to the ion sample chemistry, a series of filter leachates are evaluated each week. Prior to sample filtration, 300 mL of DI water from the source in the sample processing laboratory are poured into the filtering apparatus to pre-rinse the filters. After this rinse, 50 mL of the DI water from the same source are filtered, bottled, and labeled "A"; a consecutive 50-mL DI aliquot is then filtered through the same filter, bottled, and labeled "B". The procedure is repeated with another filter and the 300 mL rinse is followed by two 50-mL portions of pH 4.3 nitric acid, which are filtered, collected, and labeled "A" and "B". The results of the laboratory analyses of these blank samples are presented in Table IV-7.

TABLE IV-7 Median Analyte Concentrations Found in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Filter Leachates, 1992

Analyte	DI Water A*	DI Water B[b]	pH 4.3 Nitric Arid A[a]	pH 4.3 Nitric Acid B[b]
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	0.022	<0.003	0.023	<0.003
Ammonium	<0.02	<0.02	<0.02	<0.02
Nitrate	0.03	<0.03	3.19[c]	3.26[c]
Chloride	<0.03	<0.03	<0.03	<0.03
Sulfate	<0.03	<0.03	<0.03	<0.03
pH (units) H^+ (µeq/L)	5.65 2.24	5.66 2.19	4.33[d] 46.8	4.32[d] 47.9
Conductivity (µS/cm)	1.2	1.0	21.2[c]	21.9[c]
Number of weeks	48	48	48	48

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.

Sodium at seven times the detection limit was found in the "A" portion of both solutions. The levels of sodium contamination correspond to approximately the 10th percentile of sodium values found in natural network samples. The median values for other ions are below detection. The pH of the DI water is not significantly different from the sample processing DI water and the pH 4.3 nitric acid pH was well within acceptable limits. The conductivities are not significantly different from the target values. (Note: The pH and conductivity are measured on unfiltered network samples.) From these summaries, with the exception of sodium, it is assumed that the filtration process has a negligible effect on the sample chemistry.

Table B-4 in Appendix B shows the percent of analytes above detection limits. From this table one observes that most of the "A" portions contain sodium, five contain sulfate, many contain nitrate, approximately one third contain chloride, and a few contain calcium and potassium. Sodium persists in one third of the "B" samples and potassium is in one or two samples. The "B" bottle of the filtered pH 4.3 nitric acid shows two or three weeks when small positive concentrations of sulfate, chloride, ammonium, calcium, and potassium remained.

3. Bucket Blanks

The bucket leachate procedure followed in 1992 has not changed since its inception at the end of 1989. Aliquots of 50 mL and 150 mL of DI water and pH 4.3 nitric acid are poured into each of four sample collection buckets, which are covered with snap-on lids and left overnight. The leachates are poured into 60-mL bottles for analysis. This procedure is repeated, and the buckets are covered and sealed with a standard water-tight lid, inverted, and left overnight. The leachates are then collected for analysis.

Analyses 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 (µg)/bucket. The pH and conductivity values are the median measurements of the solutions collected from the buckets. The upright solutions indicate slight sodium contamination in both 50-mL solutions. The anion concentrations are at the detection level with an acceptable deviation from the theoretical nitrate concentration of the nitric acid. The pH and conductivities are also within the acceptable range.

The inverted bucket leachates clearly implicate the lid or its o-ring portion. Calcium and sodium are present in all four solutions, but magnesium and potassium are not present in the 150-mL DI water leachates. Chloride and sulfate have been leached in both 50-mL solutions, and sulfate is still detectable in the 150-mL nitric acid. All four blanks are neutralized, the 50-mL portion more so than the 150-mL portion. The conductivities of the nitric acid are lower, corresponding to the higher pH, lower H^+ concentration.

Box plots of the bucket blank leachates (Appendix B, Figures B-24 - B-33) illustrate the median analyte values as well as the variance of the 1992 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 µg/mL) times 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 B-5 and B-6 show the extent of the above detection values found in the bucket blanks. These tables quantify the information shown on the box plots. Sodium is ubiquitous and calcium is contributed by the lid in every inverted sample.

TABLE IV-8 Median Measured Mass as Micrograms (µg)/Bucket[a] Found in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Upright Bucket Leachates, 1992

Analyte	DI Water (50 mL)	DI Water (150 mL)	pH 4.3 Nitric Acid (50 mL)	pH 4.3 Nitric Acid (150 mL)
Calcium	<0.225	<0.675	<0.225	<0.675
Magnesium	<0.075	<0.225	<0.075	<0.225
Potassium	<0.075	<0.225	0.300	<0.225
Sodium	0.300	<0.225	0.350	<0.225
Ammonium	<0.50	<1.50	<0.50	<1.50
Nitrate	<0.75	<2.25	150 (156)[b]	471 (468)[b]
Chloride	<0.75	<2.25	<0.75	<2.25
Sulfate	<0.75	<2.25	<0.75	<2.25
pH (units)	5.60 (5.77)[b]	5.59 (5.77)[b]	4.38 (4.30)[b]	4.34 (4.30)[b]
[H^+] (µeq/bucket)	0.126 (0.085)[b]	0.386 (0.255)[b]	2.08 (2.50)[b]	6.86 (7.52)[b]
Conductivity (µS/cm)	1.4 (0.8)[b]	1.4 (0.8)[b]	19.4 (21.8)[b]	20.8 (21.8)[b]
Number of weeks	49	49	49	49

Notes:

[a] Mass/bucket represents the concentration in µg/mL x 50 or 150 mL. Detection limit values are expressed as the MDL (in µg/mL)/2 x 50 or 150 mL.

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

TABLE IV-9 Median Measured Mass as Micrograms (µg)/Bucket[a] Found in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Inverted Bucket Leachates, 1992

Analyte	DI Water (50 mL)	DI Water (150 mL)	pH 4.3 Nitric Acid (50 mL)	pH 4.3 Nitric Arid (150 mL)
Calcium	2.40	3.30	3.35	4.65
Magnesium	0.30	<0.225	0.50	0.60
Potassium	0.30	<0.225	0.50	0.60
Sodium	2.40	2.25	2.20	2.40
Ammonium	<0.50	<1.50	<0.50	<1.50
Nitrate	<0.75	<2.25	149 (156)[b]	468 (468)[b]
Chloride	2.00	<2.25	4.50	<2.25
Sulfate	3.50	<2.25	1.50	6.00
pH (units)	6.41 (5.77)[b]	6.07 (5.77)[b]	4.82 (4.30)[b]	4.46 (4.30)[b]
$[H^+]$ (µeq/bucket)	0.019 (0.085)[b]	0.128 (0.255)[b]	0.76 (2.50)[b]	5.20 (7.52)[b]
Conductivity (µS/cm)	3.2 (0.8)[b]	1.6 (0.8)[b]	11.7 (21.8)[b]	17.5 (21.8)[b]
Number of weeks	49	49	49	49

Notes:

a. Mass/bucket represents the concentration in µg/mL x 50 or 150 mL.
Detection limit values are expressed as the MDL (in µg/mL)/2 x 50 or 150 mL

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

V. MONTHLY QUALITY ASSURANCE PROCEDURES

Quality assurance 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 inter laboratory comparison are reviewed prior to being sent to the USGS.

A. REANALYSIS PROCEDURES

Twice a month the 400-500 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 1992 has been in use since 1987.

1. Ion Percent Difference

Ion concentrations measured in milligrams per liter (mg/L) are converted to microequivalents per liter (μeq/L) using the factors listed in Table V-l (13). 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:

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

$$\text{Cation sum} = [H^+] + [Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+] + [NH_4^+]$$

$$\text{Anion sum} = [HCO_3^-] + [OH^-] + [SO_4^{2-}] + [NO_3^-] + [Cl^-] + [PO_4^{3-}]$$

Samples are flagged for reanalysis if:

$IS < 50$ μeq/L	and $IPD > \pm 60\%$
$50 \le IS < 100$ μeq/L	and $IPD > \pm 30\%$
$IS \ge 100$ μeq/L	and $IPD > \pm 15\%$

2. Conductance Percent Difference

Conductance percent difference (CPD) compares the calculated and measured conductivity. The ion concentrations, expressed as µeq/L, are multiplied by the conductance conversion factors listed in Table V-2 (14), 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:

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

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 1992, 592 of the 10,900 (-5.4 percent) samples analyzed were flagged for reanalysis. There were 357 data changes to 207 of the 592 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 always has, the mean (5.11 percent) and median (3.66 percent) are higher than in 1990 and 1991(3.70 percent and 3.39 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 (-10.82 percent) that is the most negative value since 1986 and a median value (-7.81 percent) again comparable to 1986. 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 parameters contained in precipitation.

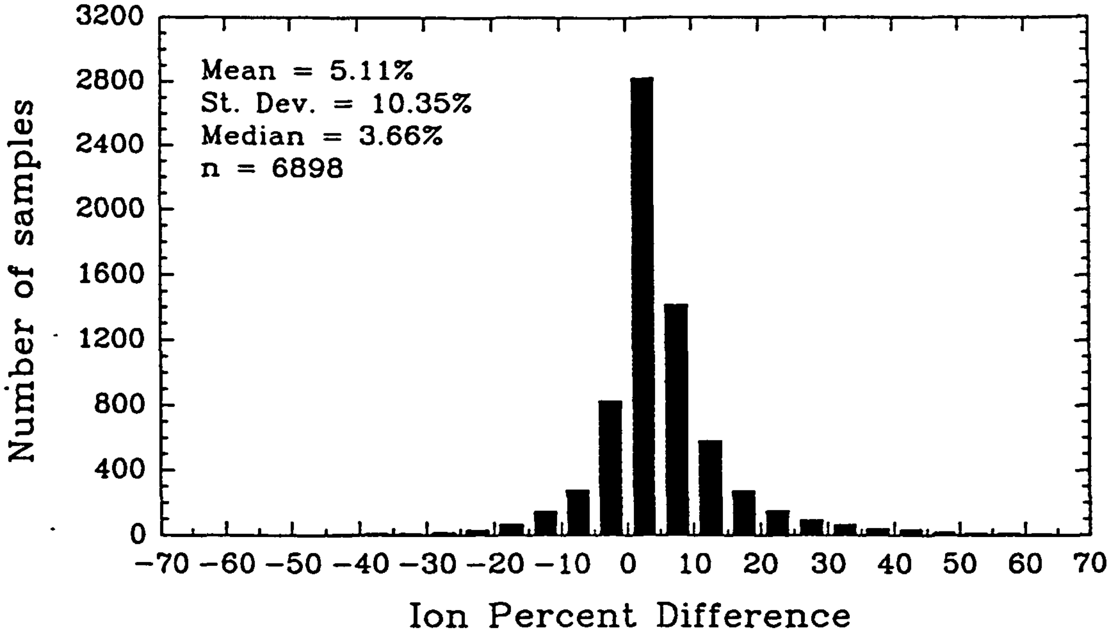


FIGURE V-1. Ion Percent Difference (IPD) histogram for NADP/NTN wet-side samples, 1992.

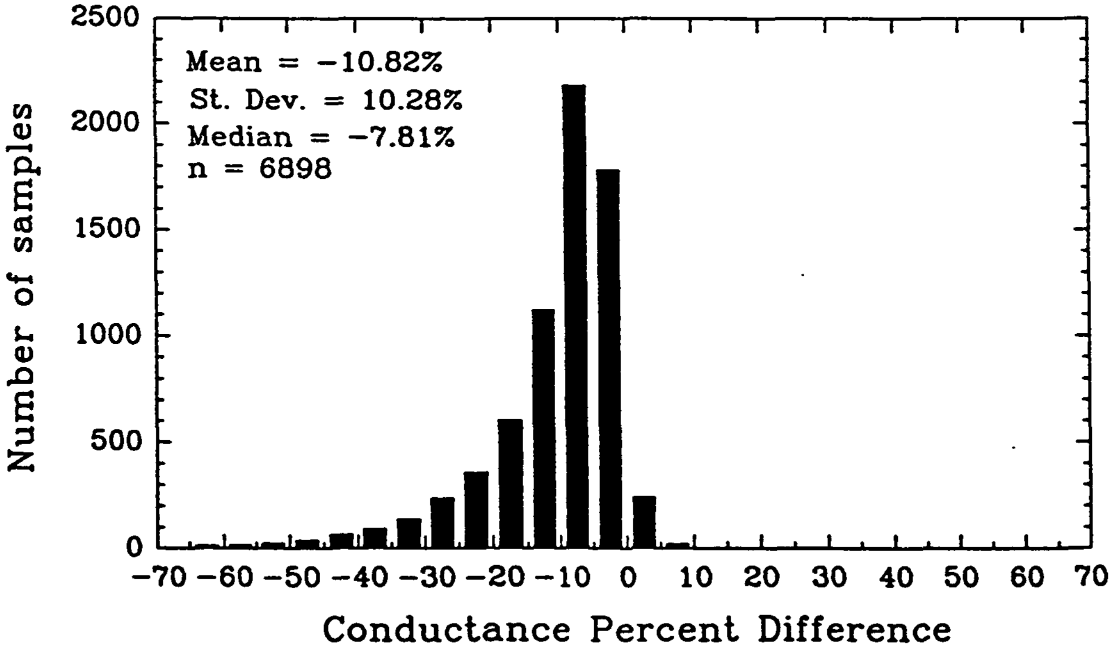


FIGURE V-2. Conductance Percent Difference (CPD) histogram for NADP/NTN wet-side samples, 1992.

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

Analyte	Conversion Factor
Calcium	49.90
Magnesium	82.26
Sodium	43.50
Potassium	25.57
Ammonium	55.44
Sulfate	20.83
Nitrate	16.13
Chloride	28.21
Orthophosphate	31.59
Hydrogen	992.2
Bicarbonate	16.39
Hydroxide	58.8

TABLE V-2
Factors Used to Convert Microequlyalents per Liter (µeq/L) to Equivalent Conductance for Conductance Percent Difference (CPD) Calculations

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

B. USGS INTERLABORATORY COMPARISON

The U.S. Geological Survey (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.

In 1992 the inter laboratory comparison program included five laboratories: (1) Illinois State Water Survey, Central Analytical Laboratory (CAL); (2) Environmental Science and Engineering, Gainsville, Florida (ESE); Inland Waters Directorate, Burlington, Ontario (IWD); (4) Ontario Ministry of the Environment, Rexdale, Ontario (MOE); and (5) Global Geochemistry Corporation, Canoga Park, California (GGC). Global Geochemistry began participating in the comparison in May of 1992.

Samples used for the 1992 program were shipped as blind samples to the participating laboratories approximately every two weeks. These samples included (1) certified samples from the National Institute of Standards and Technology; (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. Data results from the participating laboratories were submitted quarterly to the USGS.

Analyte bias for the participating laboratories was evaluated using NIST standard reference samples with certified analyte concentrations plus or minus the estimated uncertainty. Each laboratory that participated for the entire year received 18 NIST samples in 1992. The median laboratory analysis of each analyte for each certified matrix was compared to the NIST certified values. The CAL reported 7 median analyses out of 15 that were outside of the range of uncertainty for the NIST samples.

Results of the Kruskal Wallis test run by the USGS to examine bias between the laboratories indicated that the results for each analyte from the four laboratories that participated for all of 1992 are statistically comparable at alpha equal to 0.05.

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 1992 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 is available from the USGS.(15)

VI. SEMIANNUAL AND ANNUAL QUALITY ASSURANCE PROCEDURES

When all data for the samples analyzed during the January 1-December 31 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. Throughout the year the CAL participates, on a voluntary basis, in several interlaboratory comparison studies. In 1992 there were five studies in which the CAL participated: two conducted by the USEPA and three conducted by the Canada National Water Research Institute (NWRI). The analytical data for the samples analyzed are presented in the tables in Appendix C.

A. U.S. Environmental Protection Agency (Two Studies)

The USEPA in Research Triangle Park (EPA/RTP), North Carolina, contracted Management Technology for a series of acid rain audits. The CAL participated in the studies in May and November 1992. The results are compared to USEPA-determined values and the percent difference calculated. The number of participating laboratories is not provided. The CAL mean percent difference for all ten parameters is 4.65 percent in May and 8.28 percent in November. The May results are consistent with past performances in this audit. The November percent difference is higher than in the past. The large percent differences for one result each of nitrate, calcium and potassium are the cause of this higher mean percent difference. The results are listed in Tables C-l and C-2.

B. Canada National Water Research Institute (Three Studies)

The Canadian program for Long-Range Transport of Atmospheric Pollutants (LRTAP) was begun in 1982. The CAL has participated since the fourth study in fall 1983. In 1992 the CAL participated in Studies L-29 (16) , L-30 (17) , and L-31 (18) . The LRTAP studies consist of selected major ions, nutrients, and physical measurements in water. Median concentrations are used as target values for flagging results, since most of the samples are surface waters or precipitation, and calculated or certified values are unknown. The laboratory results are ranked and flagged. A score for the study is computed as the sum of the percent bias and percent flags; therefore a score of zero indicates optimum performance.

The CAL scores for 1992 are variable. In study L-29 the score is 13.16 due to a low sodium bias and three flags (one high ammonium value and two low sodium values). The overall laboratory ranking was 19th out of 67 laboratories. Study L-30 cites a low bias for magnesium and seven flags (one for a high pH, five for low magnesium values, and one extremely low chloride value). The resulting score is 17.45, placing the CAL 14th out of 60 laboratories. Study L-31 shows a big improvement. There are two flags for high pH values, leading to a final score of 2.11 and a rank of third out of 64 laboratories. LRTAP data are presented in Tables C-3-C-5 in Appendix C.

VII. SUMMARY

This QA report summarizes the results of the NADP/NTN laboratory QA program for 1992. The procedures have been described, and the analytical results presented and discussed.

The data indicate that daily QCS, two concentrations of simulated rain formulated to correspond to the 25th and 75th percentiles of network precipitation, exhibit the best accuracy and precision. The percent bias and relative standard deviation are the same or better than during the previous year. The solutions used for the internal blind audit in 1992 are simulated rainwater samples purchased from High Purity Standards in Charleston, South Carolina. The target values are provided and certified. Their concentrations are more variable than the QCS and range from the 5th to greater than the 99th percentiles of network samples. The unfiltered samples show higher percent biases due to lower concentrations, the ammonium precision is consistent, and the nitrate bias is more pronounced, but the precision of the analytical results for anions is similar to that for the QCS. The filtered internal blind samples show an increase in calcium, sodium, and chloride and a decrease in sulfate, an occurrence also observed in previous years.

Another estimate of precision is obtained from analysis of replicate samples. These samples are divided into lower and higher concentrations for comparison. The differences of the ion concentrations, pH and conductance of the original and the corresponding replicate samples are used to estimate the standard deviation. These standard deviations are better than or comparable to the precision for the internal blind audit samples. The precision for analysis of calcium, magnesium, potassium, low sodium, and chloride has improved since 1991.

The DI water from three laboratory sources continues to be of excellent quality. The median concentration of leachates from the filtering process shows sodium at seven times the detection limit in both "A" solutions, and a detection limit value for nitrate in the DI "A" sample. The percent analyte concentrations above the detection limit indicate the incidence of contaminants on the filter solutions. The median pH and conductivity values are the same as unfiltered solutions. The upright bucket blank leachates show small amounts of sodium in most of the 50-mL portions, small amounts of potassium in the pH 4.3 50-mL portion, and the other ions, in low concentrations, appear randomly. The inverted bucket blank leachates contain calcium and sodium in both volumes; magnesium and potassium in low concentrations are detectable in more than 50 percent of all the solutions.

Chloride and sulfate are detected, the pHs are raised, and the conductivities of the nitric acid rinsates are lower.

The reanalysis computer algorithm has not changed since 1987. Approximately 5.4 percent of the samples analyzed were flagged for reanalysis and 0.30 percent of the total number of analytes required changes to their initial chemical analysis. The IPD histogram has a positive skew, slightly higher than in 1990 and 1991. The CPD histogram exhibits a negative skew with a median value similar to the low minus value in 1986.

The USGS external audit of the CAL includes an interlaboratory comparison study. The interlaboratory comparison shows the median values from the participating laboratories to be comparable. The results for each analyte for the four laboratories that participated for all of 1992 are statistically comparable at alpha equal to 0.05 The CAL reported 7 median analyses out of 15 that were outside of the range of uncertainty for NIST certified samples. No false positives were reported by the CAL for ultrapure water samples.

Participation in five interlaboratory studies conducted by the USEPA and the Canadian National Water Research Institute (NWRI) indicated variable performance. The May USEPA results were consistent with past performances while the November mean percent difference from expected values was higher. The performance in the Canadian studies is also variable with less than desired performance on the first two studies and a redeeming performance on the last one.

APPENDIX A

GLOSSARY OF TERMS

GLOSSARY OF TERMS

Term	Abbreviation	Definition
Accuracy		The degree of agreement between an observed value and an accepted reference value. The concept of accuracy includes both bias (systematic error) and precision (random error).
Bias		A persistent positive or negative deviation of the measured value from the true value. In practice, it is expressed as the difference between the value obtained from analysis of a homogenous sample and the accepted. true value. Bias = measured value - true value
Box Plot		A graphical summary representation of the distribution of a set of data, the top and bottom of the box representing the 25th and 75th percentile. The horizontal line represents the median concentration, and the lower and upper Ts extend to the 10th and 90th percentile concentrations.
Control Chart		A graphical plot of test results with respect to time or sequence of measurement, together with limits within which they are expected to lie when the system is in a state of statistical control (19).
Critical Concentration		A calculated concentration used to determine whether the measured bias is statistically significant (20) . $Critical\ Concentration = t * s_{sp} * \sqrt{1/n_1 + 1/n_2}$

Term	**Abbreviation**	**Definition**
		where: $s_{sp} = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}$ s_{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.
Mean	$\bar{x}$	The average obtained by dividing a sum by the number of its addends. $\bar{x} = \sum_{i=1}^{n} x_i/n$

Term	Abbreviation	Definition
Mean Bias		The sum of the bias for each sample divided by the total number of replicates (n) .
Mean Percent Recovery		The sum of the percent recovery for each sample divided by the number of replicates (n).
Method Detection Limit	**MDL**	The minimum concentration of an analyte that can be reported with 99 percent confidence that the value is greater than zero (21) .
Percent Bias		The difference between the mean value obtained by repeated analysis of a homogenous sample and the accepted true value expressed as a percentage of the true value. $\%Bias = 100*[(V_m-V_t)/V_t]$ where: V_m = measured value V_t = true value
Precision		The degree of agreement of repeated measurements of a homogenous sample by a specific procedure, expressed in terms of dispersion of the values obtained about the mean value. It is often reported as the sample standard deviation (s).
Quality Assessment		The system of procedures that ensures that 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.

Term	Abbreviation	Definition
Quality Control	**QC**	The system of procedures designed to eliminate analytical error. These procedures determine potential sources of sample contamination and monitor analytical procedures to produce data within prescribed tolerance limits.
Quality Control Solution	**QCS**	A solution containing known concentrations of analytes used by the analysts to verify calibration curves and validate sample data. The values obtained from the analyses of these samples are used for calculation of bias and precision and for the monthly control charts.
Relative Standard Deviation	**RSD**	The standard deviation expressed as a percentage: $RSD = 100 * (s/\bar{x})$ where: s = sample standard deviation $\bar{x}$ = mean value
Replicates (Splits)		Two aliquots of the same sample treated identically throughout the laboratory analytical procedure. Analyses of laboratory replicates are beneficial when assessing precision associated with laboratory procedures but not with collection and handling. Also referred to as splits.
Sensitivity		The method signal response per unit of analyte.
Standard Deviation	**s**	The number representing the dispersion of values around their mean.

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

Term	Abbreviation	Definition
		where: x_i = each individual value $\bar{x}$ = the mean of all values n = number of values
Standard Deviation Estimated from Paired Measurements		The standard deviation may be estimated from the differences of several sets of paired measurements using the equation (19): $s = \sqrt{\frac{\sum d^2}{2k}}$ where: d = difference of duplicate measurements k = number of sets of duplicate measurements

APPENDIX B

Weekly Procedures: Tables and Figures

1992

TABLE B-1 Comparison of Filtered and Unfiltered Internal Blind Samples Using High Purity Standards Simulated Rainwater I (HPS-SRI), 1992

Parameter	Target Conc.[a]	Average Measured Conc.	Number of Values (n)	Bias	% Bias	Standard Deviation (s)	% RSD
Calcium	0.015	0.020[b] 0.023[c]	25 13	0.005 0.008	33.3 53.3	0.008 0.005	40.0 21.7
Magnesium	0.025	0.026 0.026	25 13	0.001 0.001	4.0 4.0	0.002 0.003	7.7 11.5
Potassium	0.050	0.051 0.047	25 13	0.001 -0.003	2.0 -6.0	0.003 0.002	5.9 4.2
Sodium	0.200	0.200 0.221	25 13	0.000 0.021	0.0 10.5	0.007 0.020	3.5 9.0
Ammonium	0.1	0.09 0.10	25 13	-0.01 0.00	-10.0 0.0	0.02 0.02	20.0 20.0
Nitrate	0.50	0.55 0.56	25 13	0.05 0.06	10.0 12.0	0.01 0.03	1.8 5.4
Chloride	0.25	0.23 0.25	25 13	-0.02 0.00	-8.0 0.0	0.01 0.02	4.3 8.0
Sulfate	2.7	2.54 2.43	25 13	-0.16 -0.27	-5.9 -10.0	0.04 0.06	1.6 2.5
H^+ (µeq/L)	45.71	48.73 48.87	25 13	3.02 3.16	6.6 6.9	2.48 2.69	5.1 5.5
Conductivity (µS/cm)	25.0	24.8 24.5	25 13	-0.2 -0.5	-0.8 -2.0	0.7 0.6	2.8 2.4

Notes:

Concentrations in mg/L unless otherwise noted.

[a] Target values provided by HPS for Simulated Rainwater I.

[b] The First set of values for each parameter is for unfiltered samples.

[c] The second set of values for each parameter is for Altered samples.

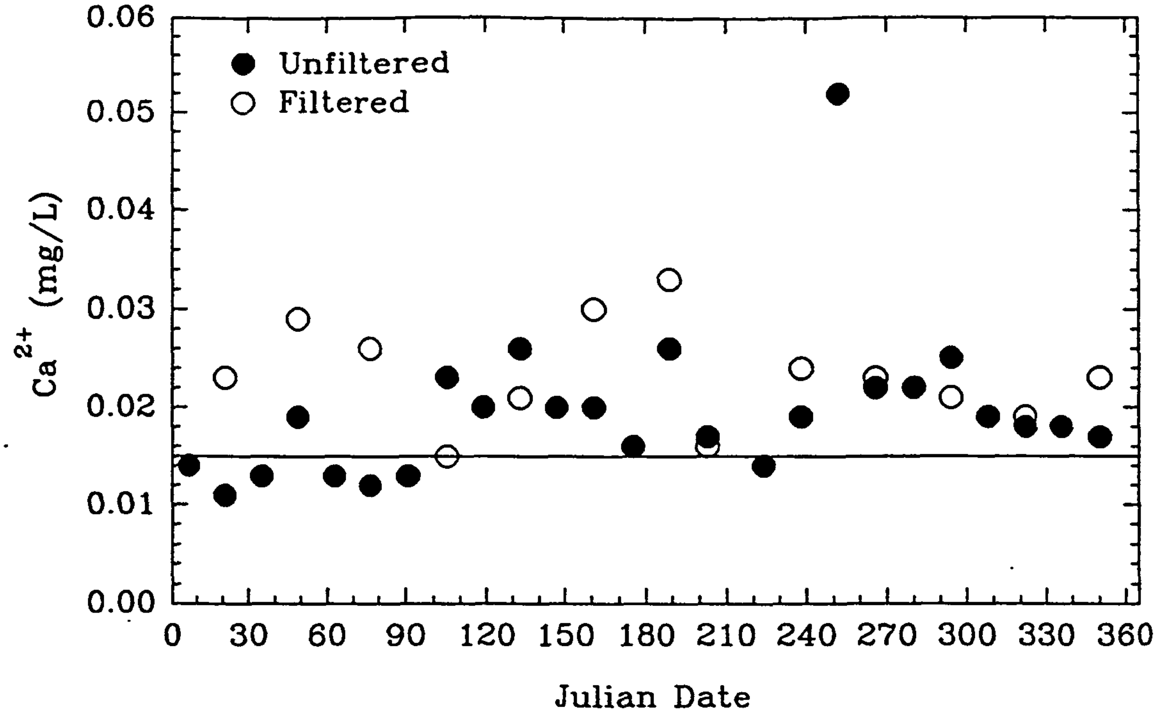


FIGURE B-1. Comparison of filtered and unfiltered internal blind samples (calcium HPS-SRI), 1992.

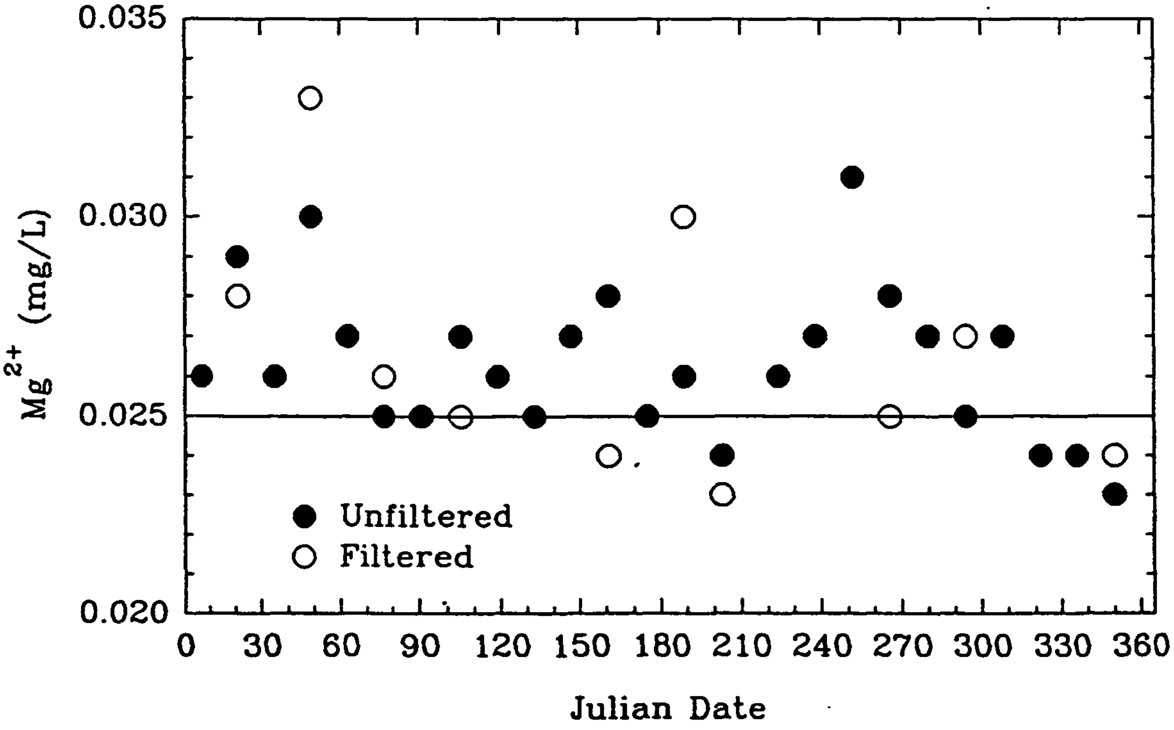


FIGURE B-2. Comparison of filtered and unfiltered internal blind samples (magnesium HPS-SRI), 1992.

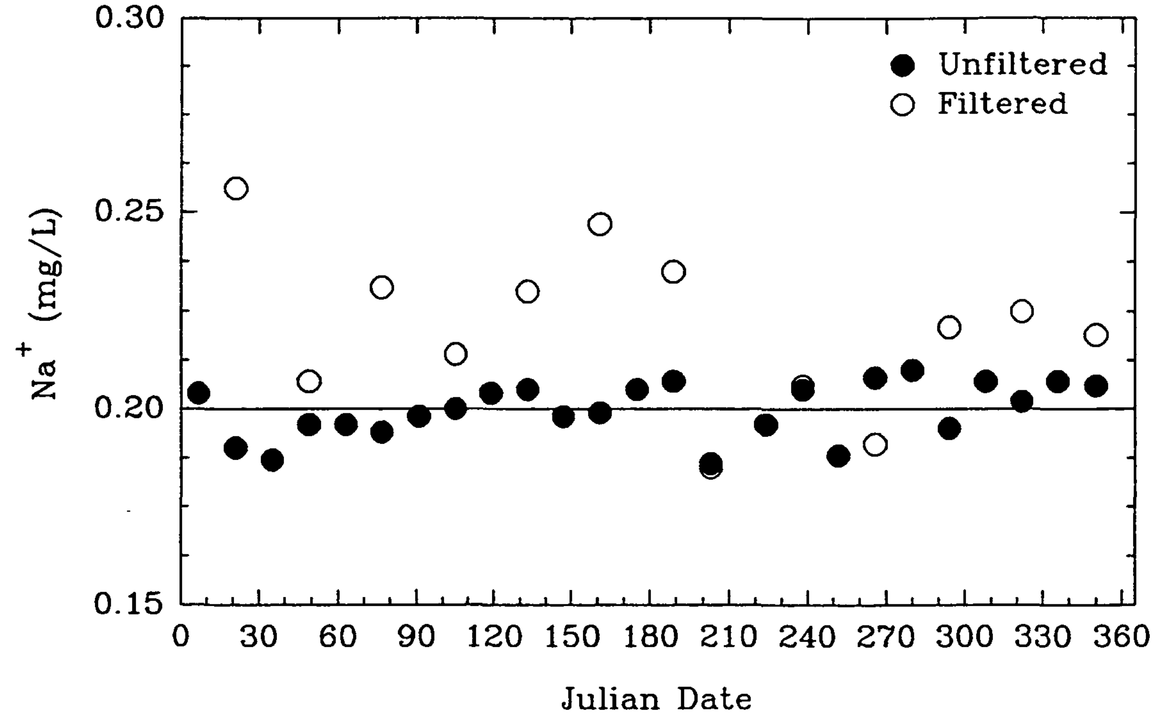


FIGURE B-3. Comparison of filtered and unfiltered internal blind samples (sodium HPS-SRI), 1992.

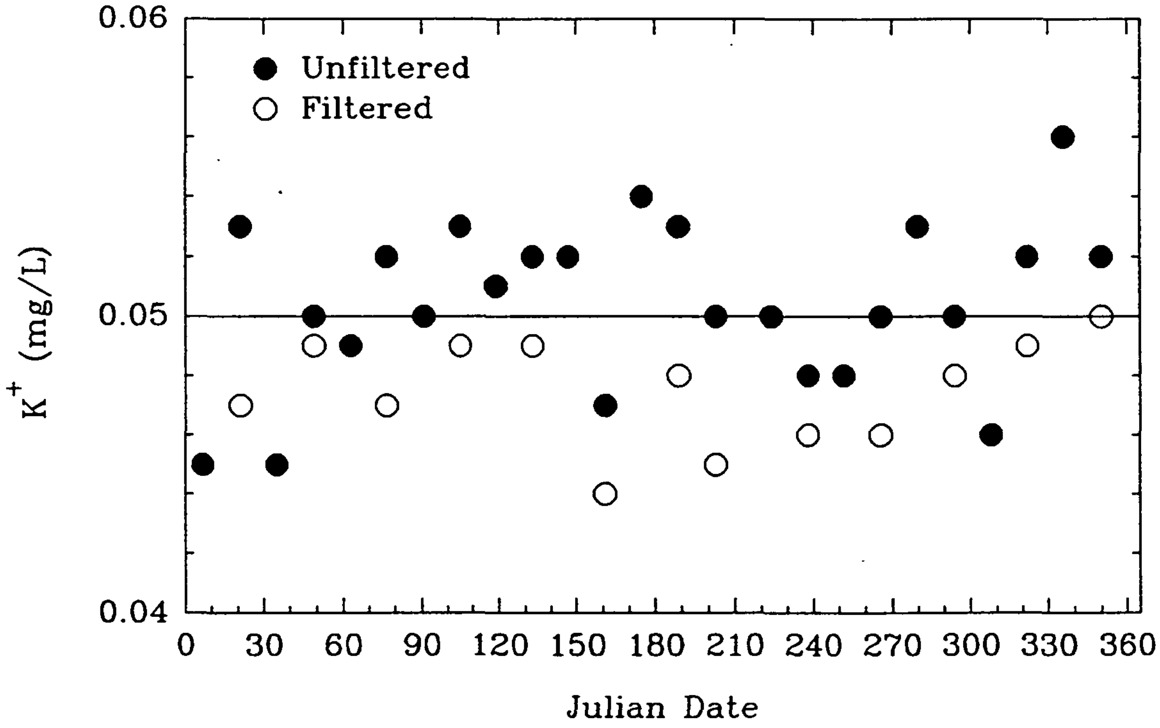


FIGURE B-4. Comparison of filtered and unfiltered internal blind samples (potassium HPS-SRI), 1992.

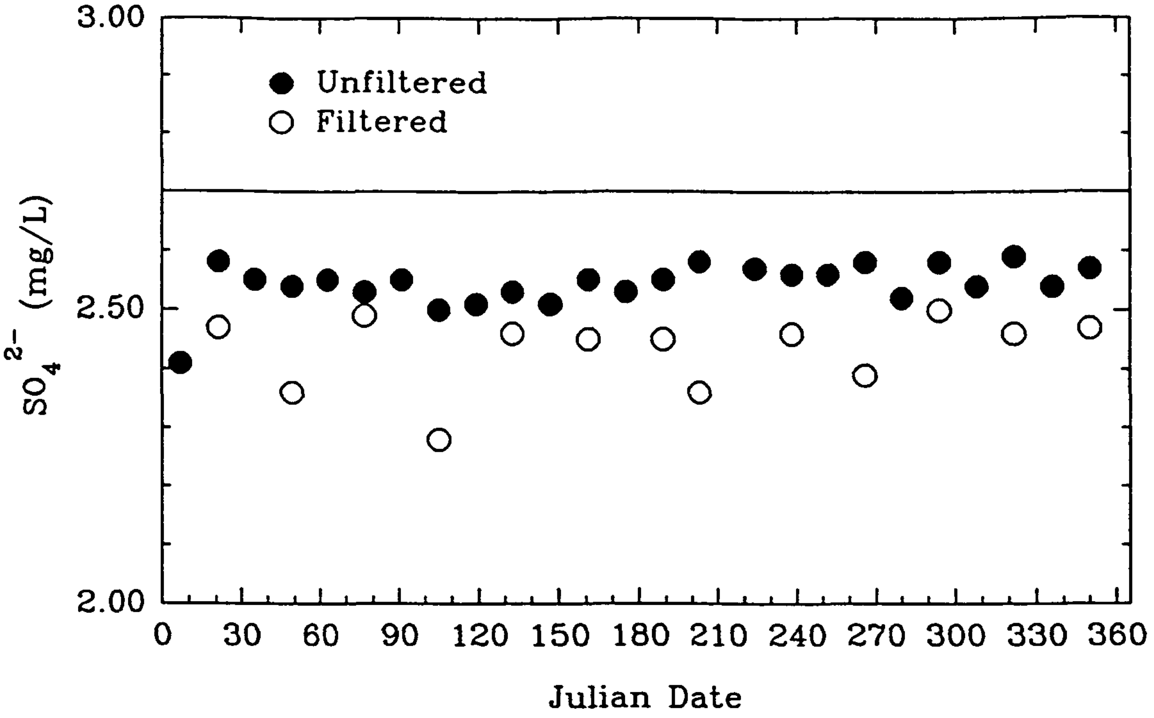


FIGURE B-5. Comparison of filtered and unfiltered internal blind samples (sulfate HPS-SRI), 1992.

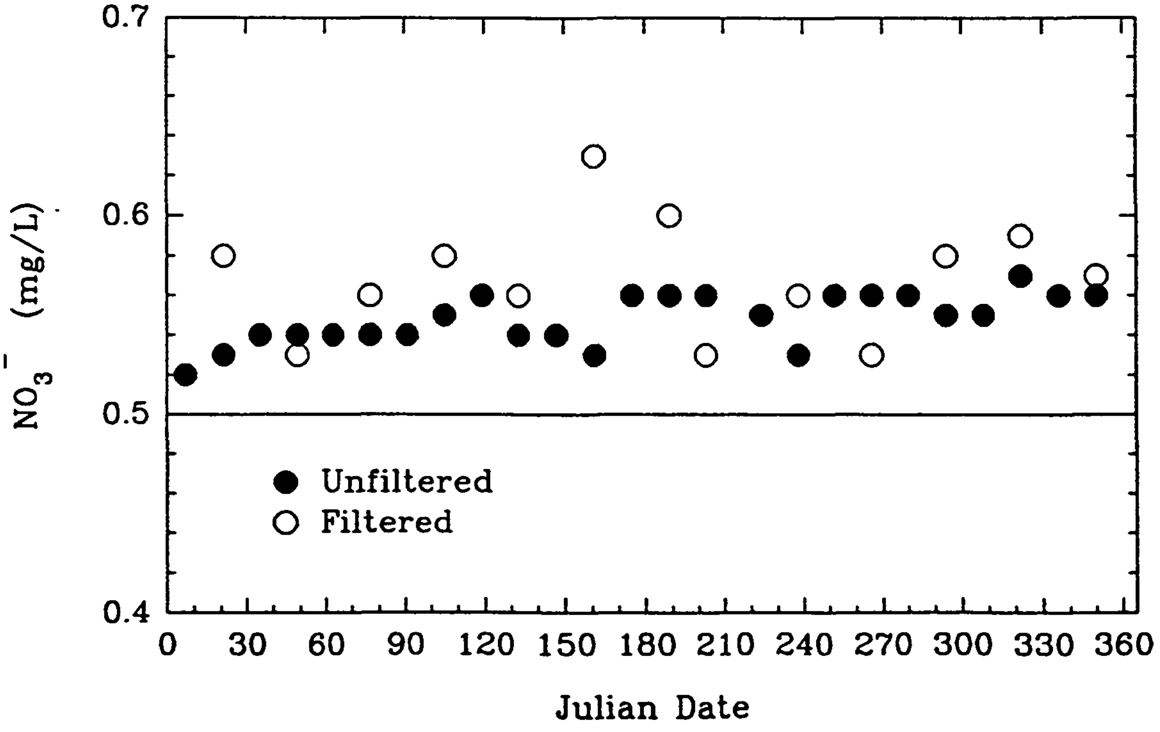


FIGURE B-6. Comparison of filtered and unfiltered internal blind samples (nitrate HPS-SRI), 1992.

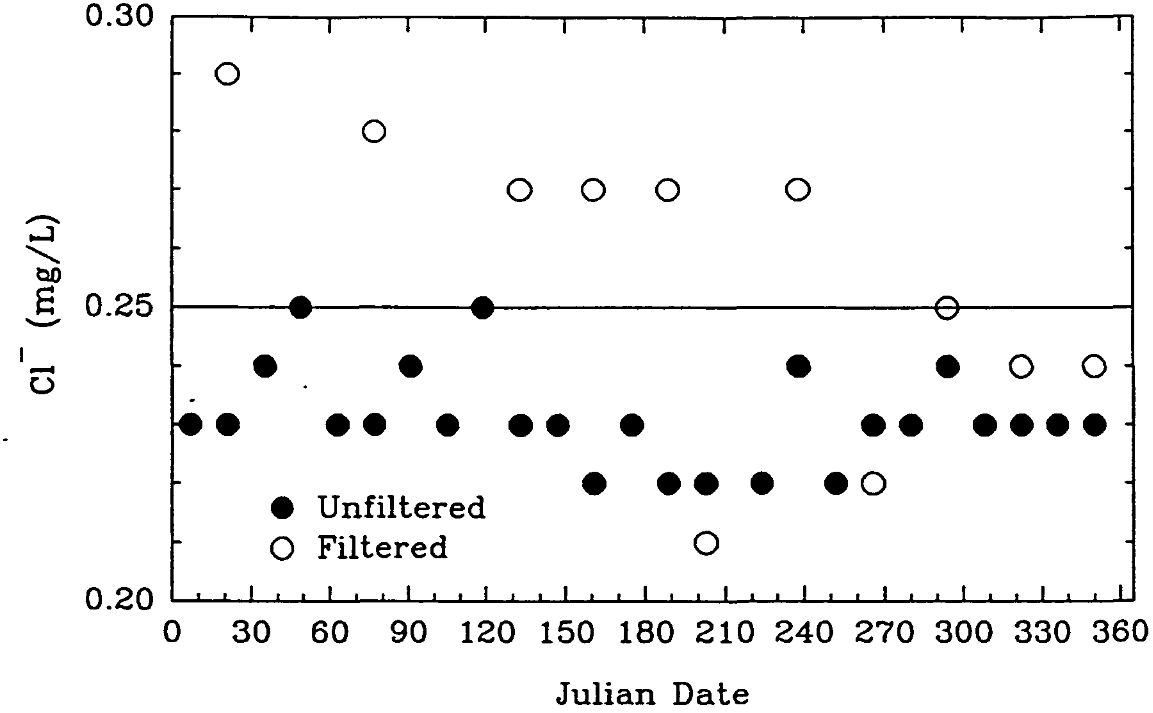


FIGURE B-7. Comparison of filtered and unfiltered internal blind samples (chloride HPS-SRI), 1992.

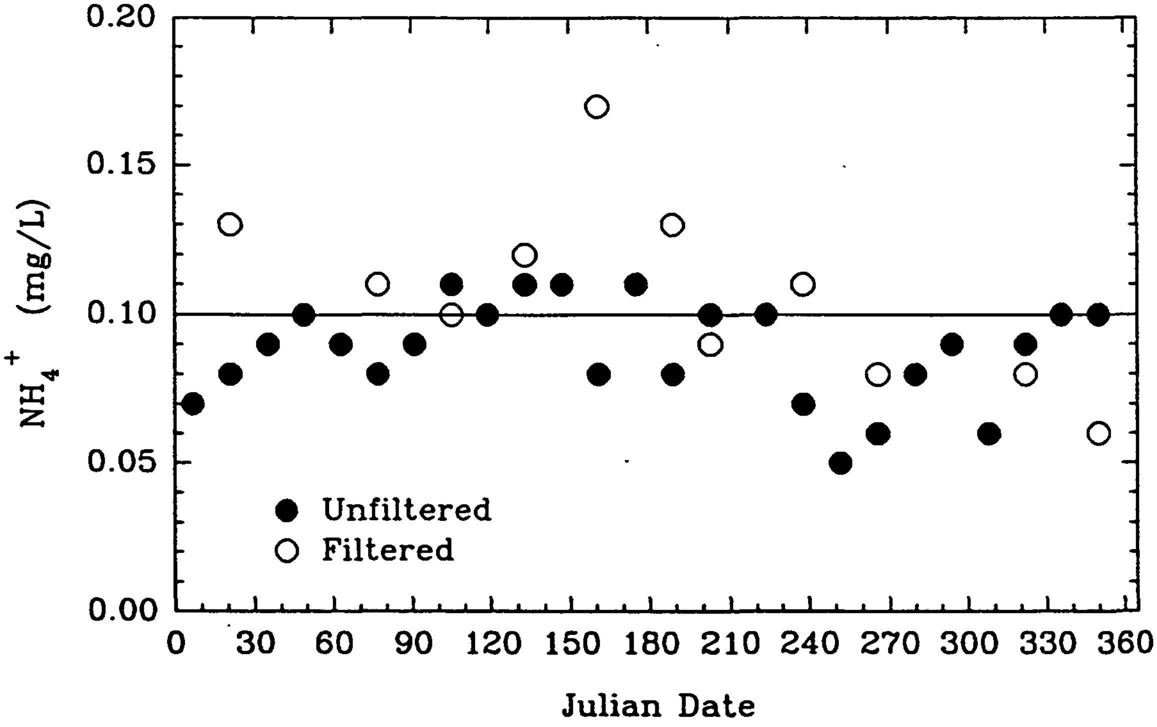


FIGURE B-8. Comparison of filtered and unfiltered internal blind samples (ammonium HPS-SRI), 1992.

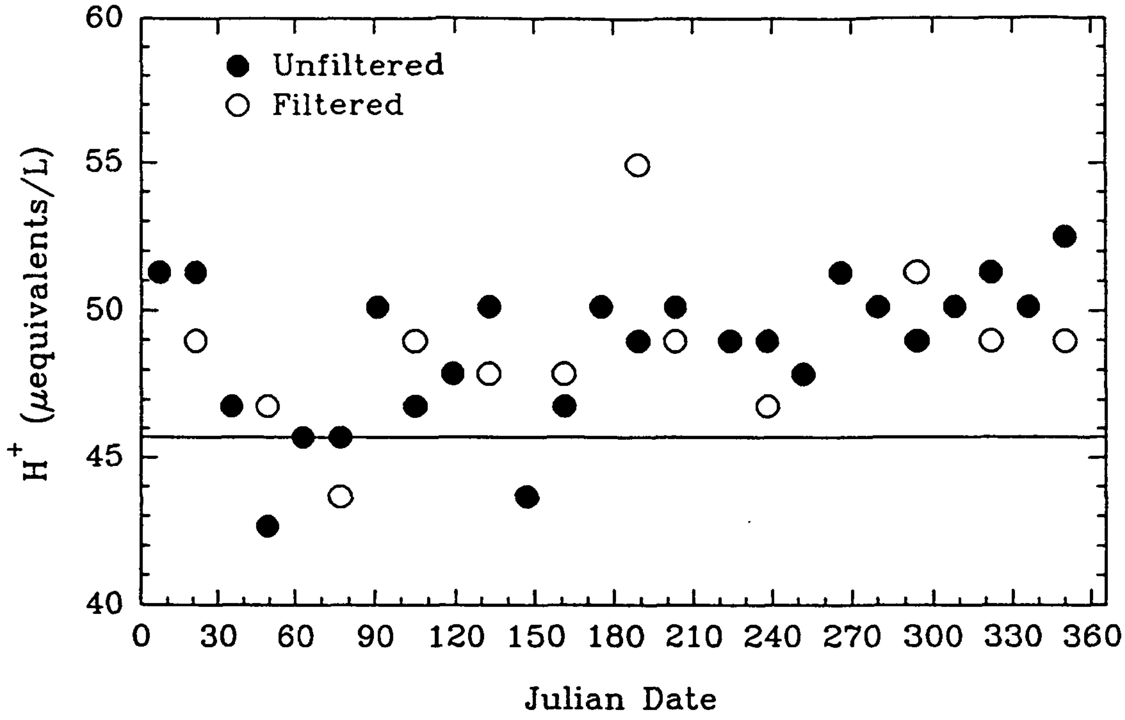


FIGURE B-9. Comparison of filtered and unfiltered internal blind samples (H$^+$ HPS-SRI), 1992.

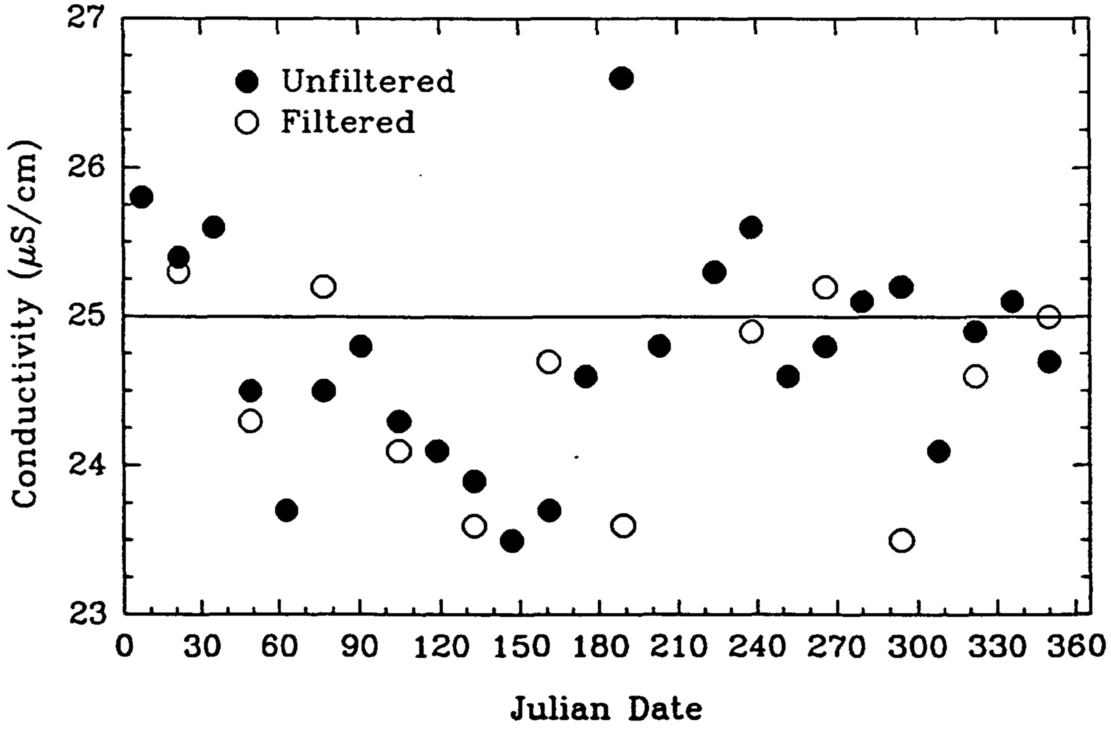


FIGURE B-10. Comparison of filtered and unfiltered internal blind samples (conductivity HPS-SRI), 1992.

TABLE B-2 Comparison of Filtered and Unfiltered Internal Blind Samples High Purity Standards Simulated Rainwater II (HPS-SRII), 1992

	Conc.[a]	Average Measured Conc.	Number of Values (n)	Bias	% Bias	Standard Deviation (s)	% RSD
Calcium	0.052	0.057[b]	25	0.005	9.6	0.018	31.6
		0.060[c]	13	0.008	15.4	0.007	11.7
Magnesium	0.050	0.055	25	0.005	10.0	0.003	5.4
		0.053	13	0.003	6..0	0.003	5.7
Potassium	0.100	0.100	25	0.000	0.0	0.010	10.0
		0.101	13	0.001	1.0	0.007	6.9
Sodium	0.400	0.409	25	0.009	2.2	0.041	10.2
		0.429	13	0.029	7.2	0.032	7.4
Ammonium	1.0	0.98	25	-0.02	-2.0	0.21	21.0
		0.97	13	-0.03	-3.0	0.08	8.0
Nitrate	7.1	7.3	25	0.20	2.8	0.29	2.7
		7.05	13	-0.05	-0.7	0.21	3.0
Chloride	0.98	0.97	25	-0.01	-1.0	0.06	6.2
		0.94	13	-0.04	-4.1	0.06	6.4
Sulfate	10.0	10.27	25	0.27	2.7	0.13	1.3
		9.77	13	-0.23	-2.3	0.31	3.2
H^+	269.2	249.9	25	-19.3	-7.2	15.68	6.3
(µeq/L)		251	13	-18.2	-6.8	11.04	4.4
Conductivity	130.0	126.9	25	-3.1	-2.4	1.6	2.8
(µS/cm)		126.6	13	-3.4	-2.6	1.8	1.4

Notes:

Concentrations are in mg/L unless otherwise noted.

[a] Target values provided by H P S for Simulated Rainwater II.

[b] The first set of values for each parameter is for unfiltered samples.

[c] The second set of values for each parameter is for filtered samples.

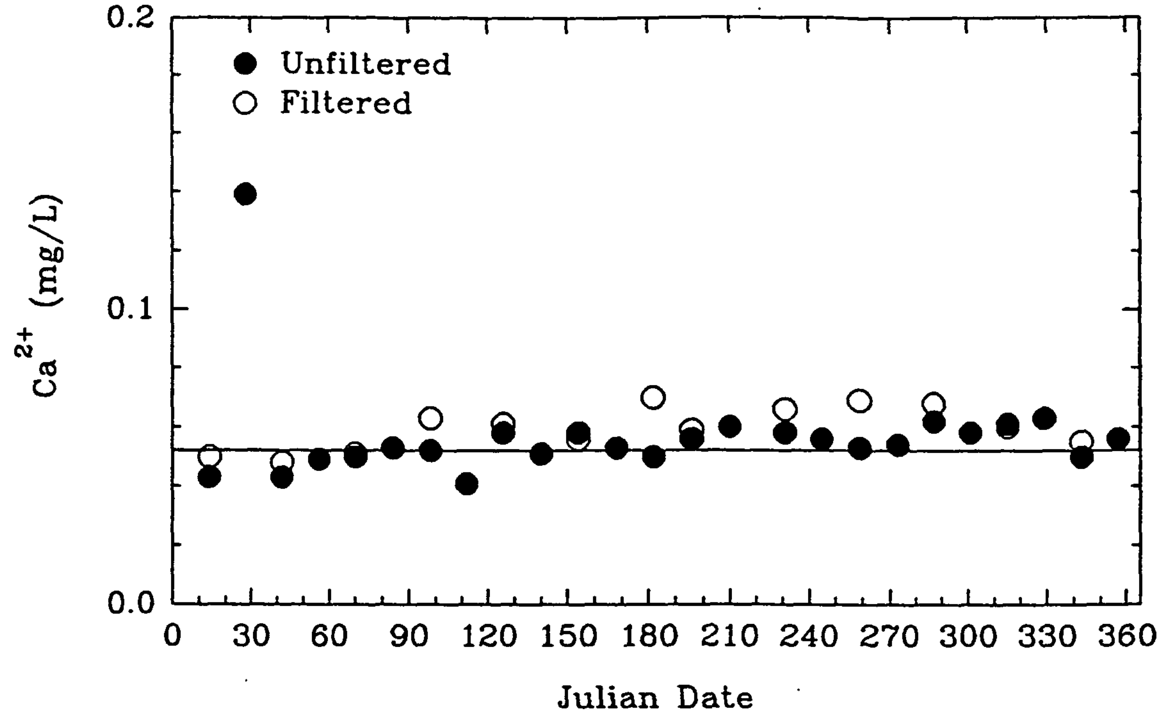


FIGURE B-11. Comparison of filtered and unfiltered internal blind samples (calcium HPS-SRII), 1992.

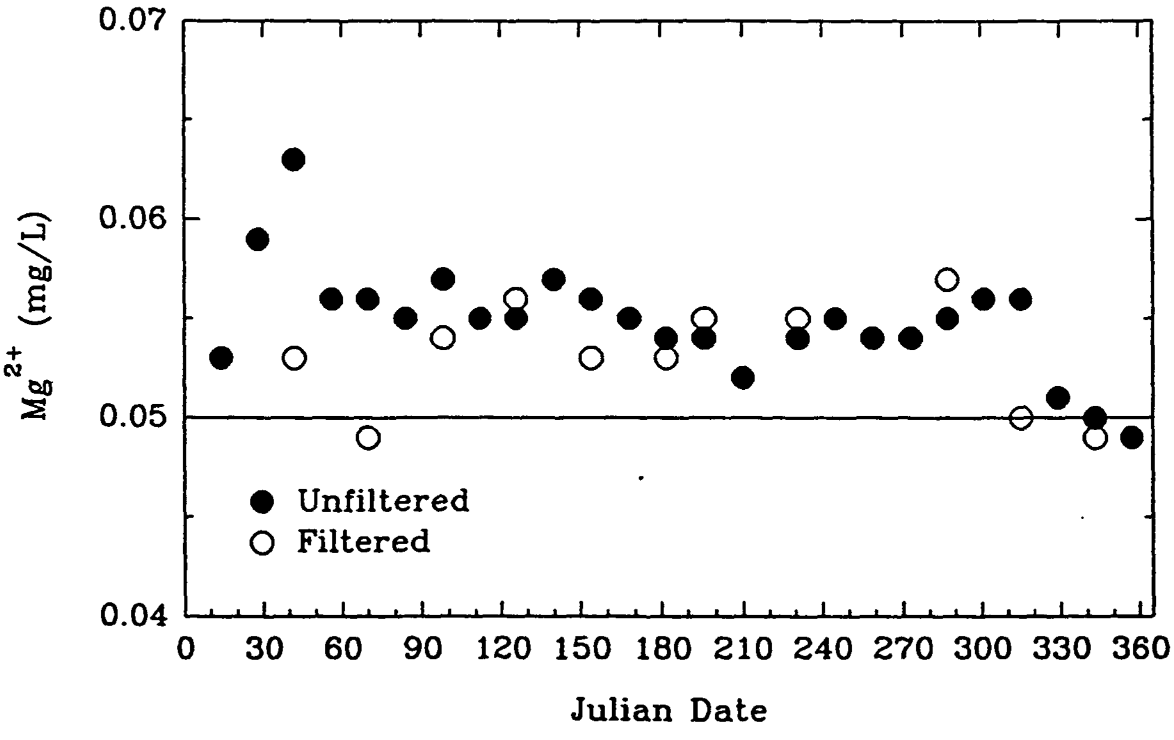


FIGURE B-12. Comparison of filtered and unfiltered internal blind samples (magnesium HPS-SRII), 1992.

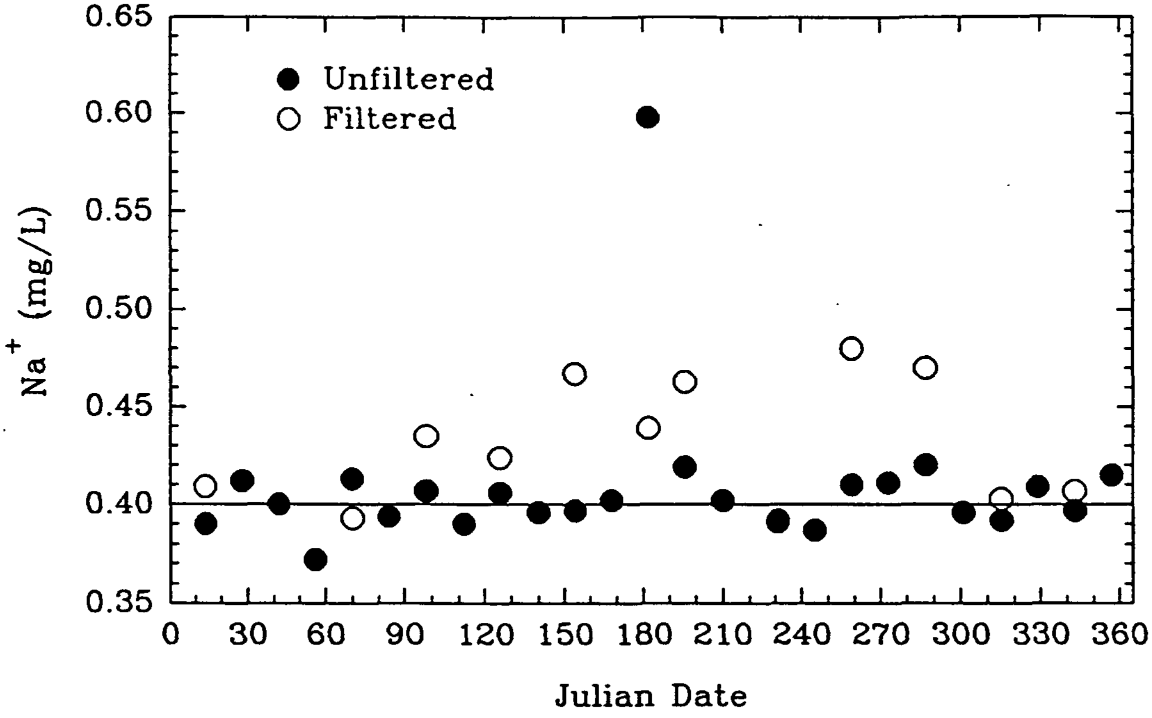


FIGURE B-13. Comparison of filtered and unfiltered internal blind samples (sodium HPS-SRII), 1992.

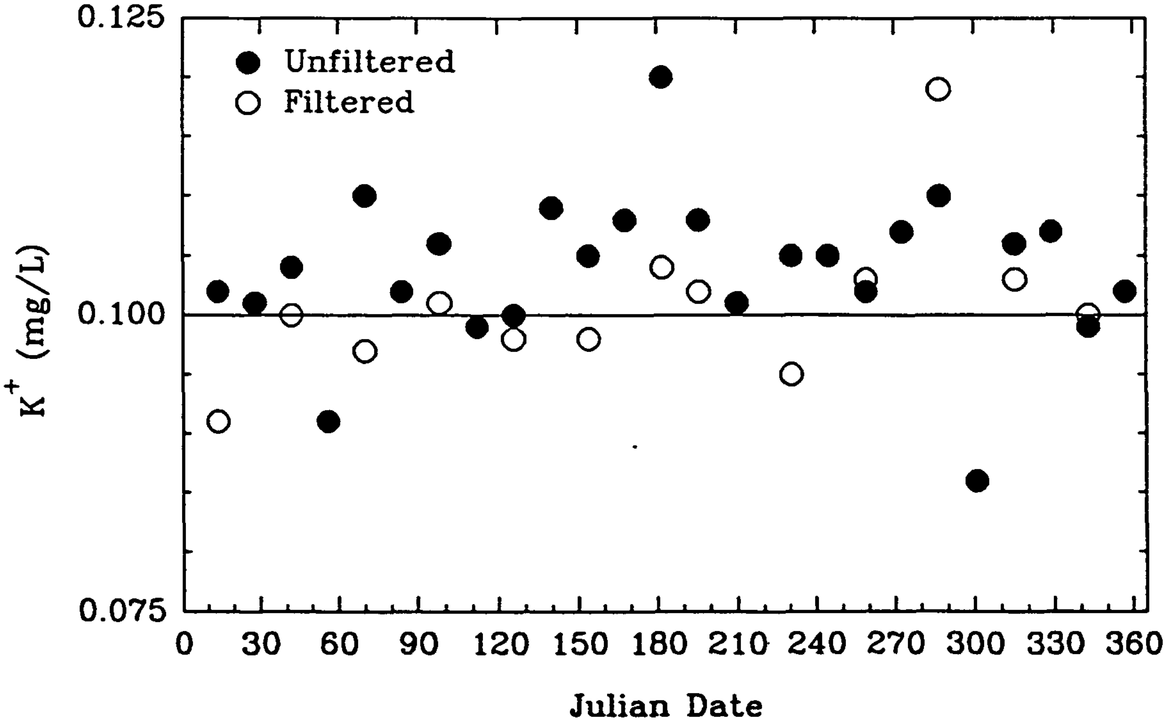


FIGURE B-14. Comparison of filtered and unfiltered internal blind samples (potassium HPS-SRII), 1992.

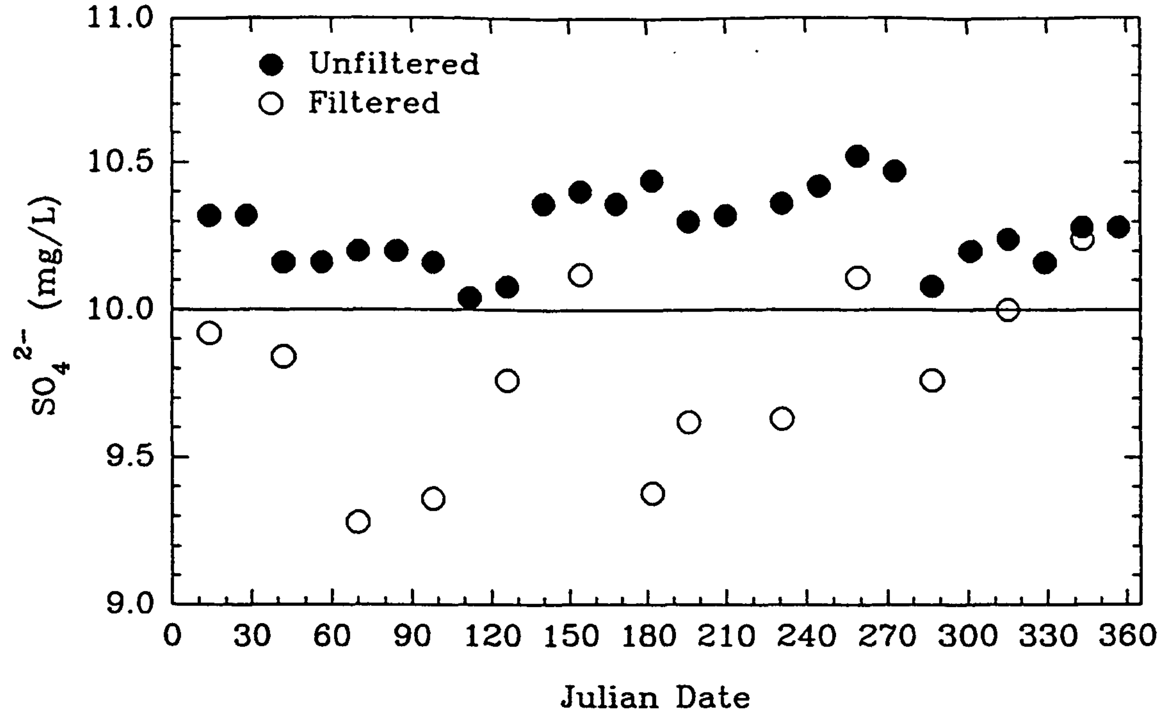


FIGURE B-15. Comparison of filtered and unfiltered internal blind samples (sulfate HPS-SRII), 1992.

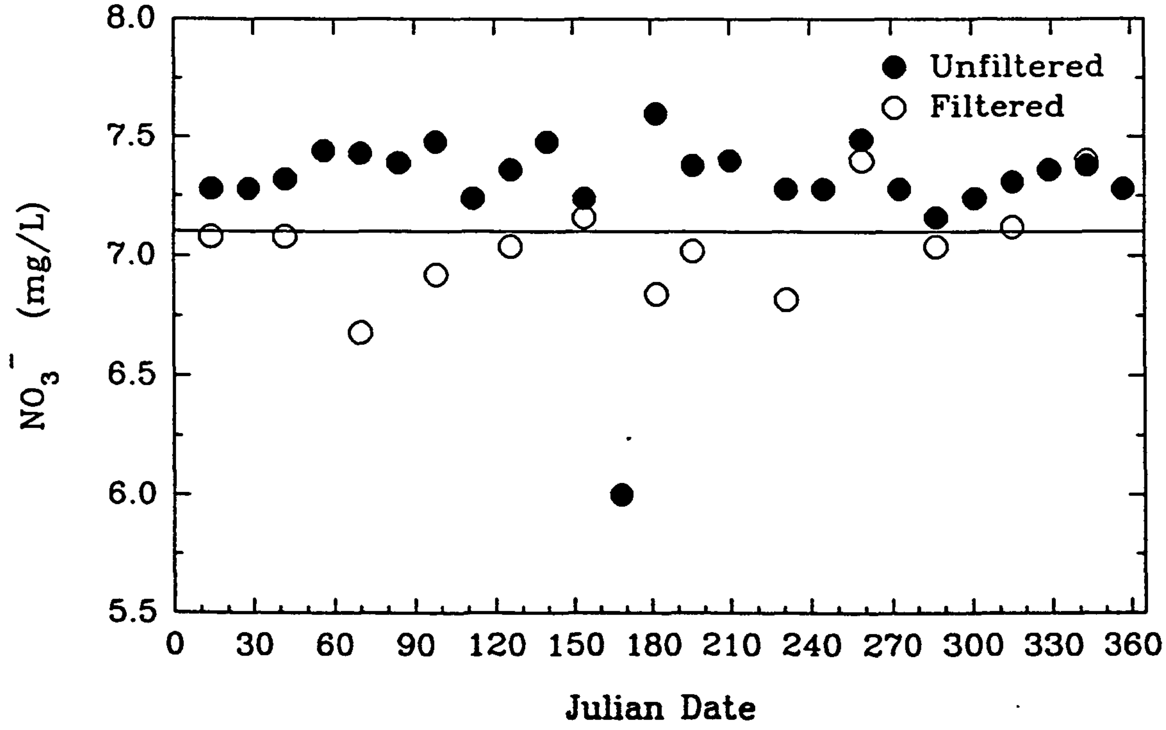


FIGURE B-16. Comparison of filtered and unfiltered internal blind samples (nitrate HPS-SRII), 1992.

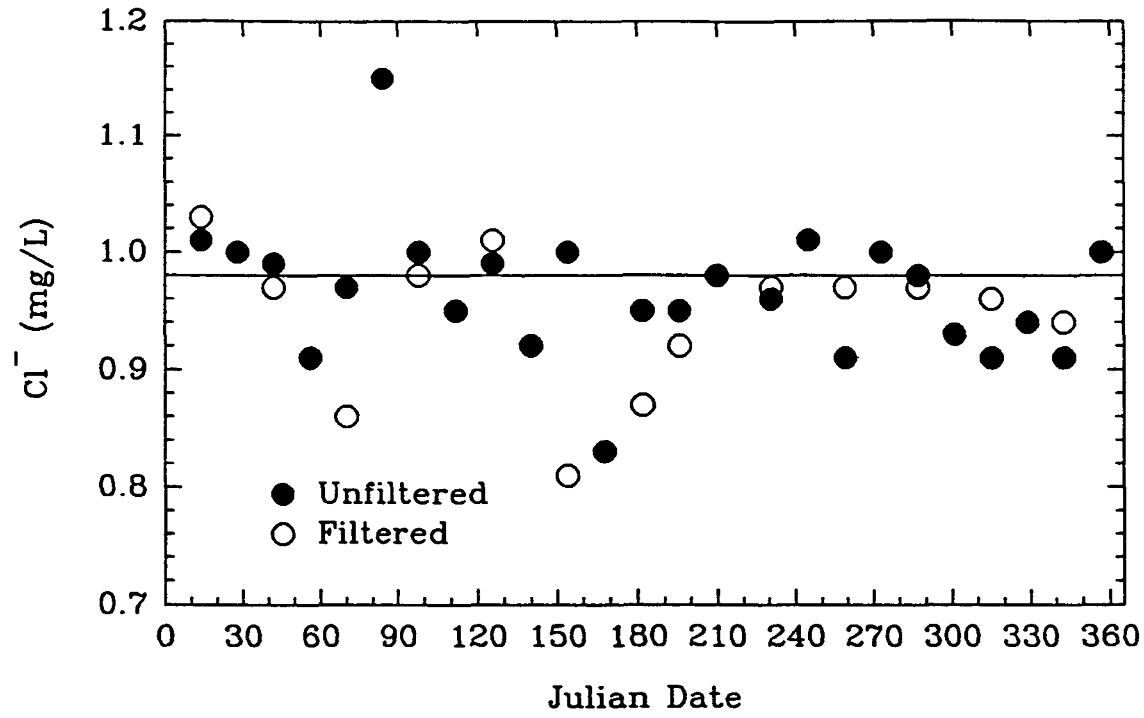


FIGURE B-17. **Comparison of filtered and unfiltered internal blind samples (chloride HPS-SRII), 1992.**

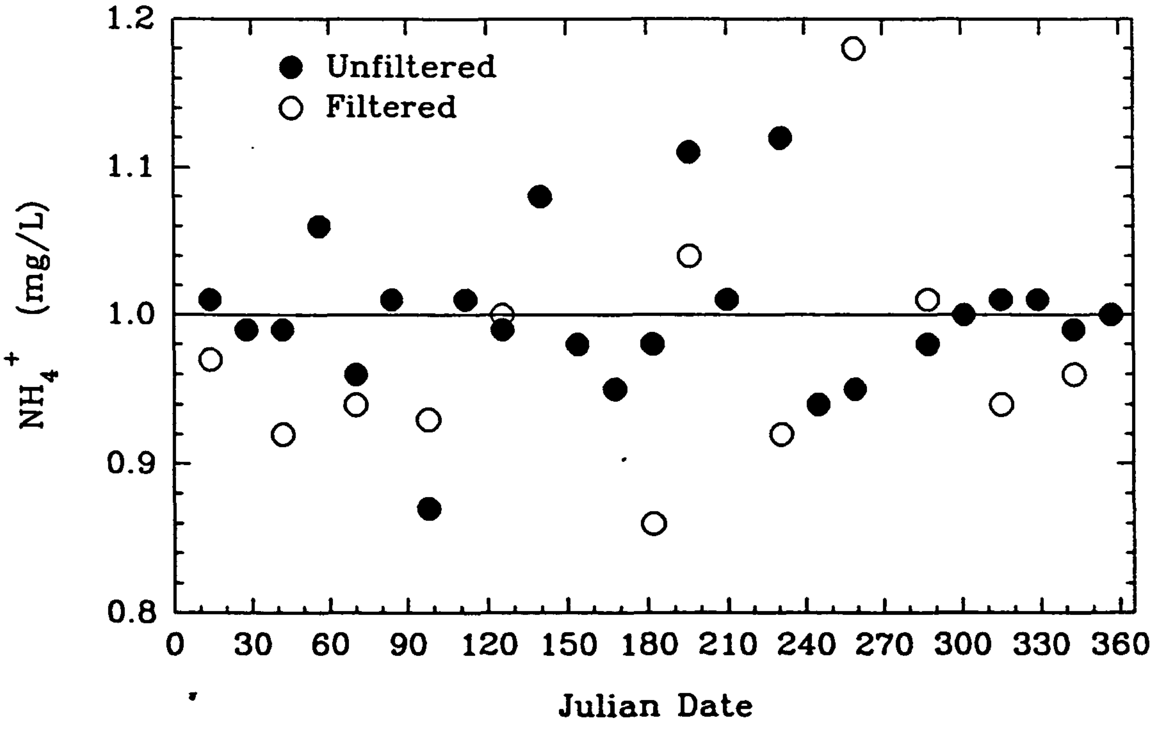


FIGURE B-18. **Comparison of filtered and unfiltered internal blind samples (ammonium HPS-SRII), 1992.**

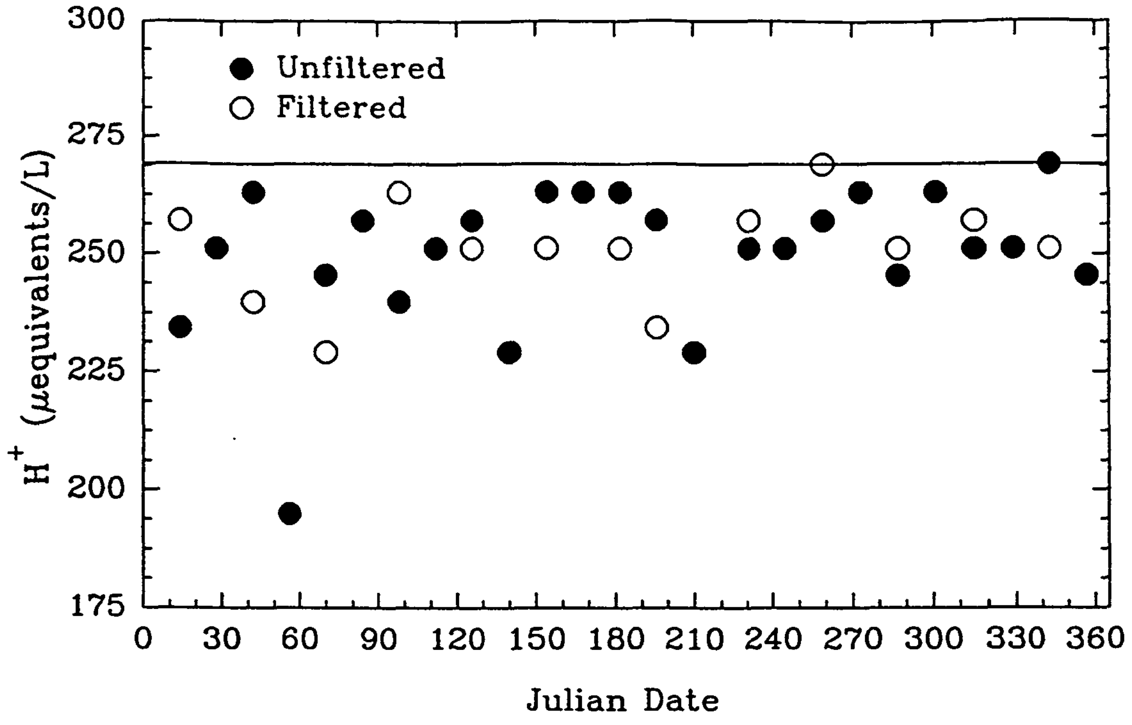


FIGURE B-19. Comparison of filtered and unfiltered internal blind samples (H^+ HPS-SRII), 1992.

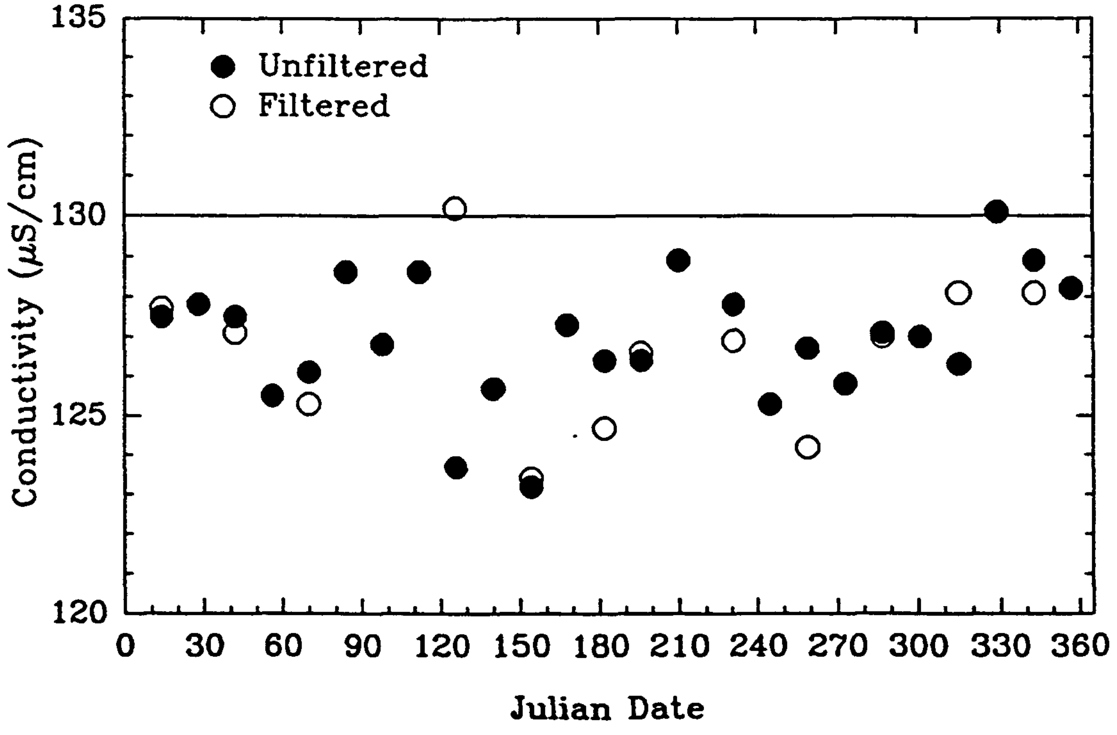
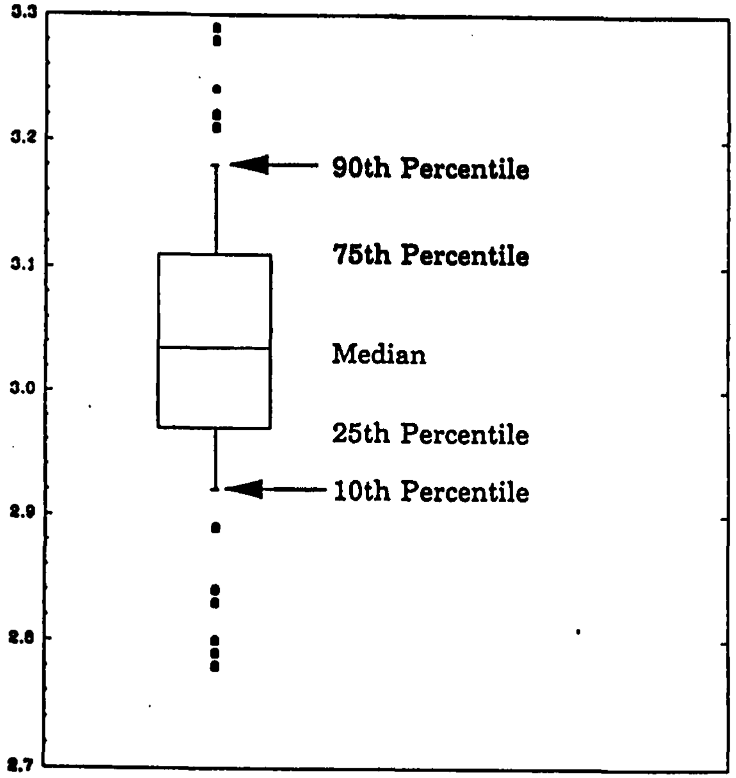


FIGURE B-20. Comparison of filtered and unfiltered internal blind samples (conductivity HPS-SRII), 1992.

TABLE B-3 50th and 95th Percentile Concentration Values of Chemical and Physical Parameters Measured in Replicate (O/Q) Samples, 1992

Parameter	Percentile Concentration Values (mg/L)	
	50th	95th
Calcium	0.076	0.452
Magnesium	0.017	0.097
Potassium	0.014	0.074
Sodium	0.046	0.582
Ammonium	0.17	0.59
Nitrate	0.93	2.42
Chloride	0.11	1.06
Sulfate	1.18	3.75
pH (units)	4.81	4.09
H^+ (μ *eq*/L)	15.15	80.36
Conductivity (μ S/cm)	12.28	41.40

DIAGRAM OF BOXPLOTS USED ON THE FOLLOWING PAGES



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

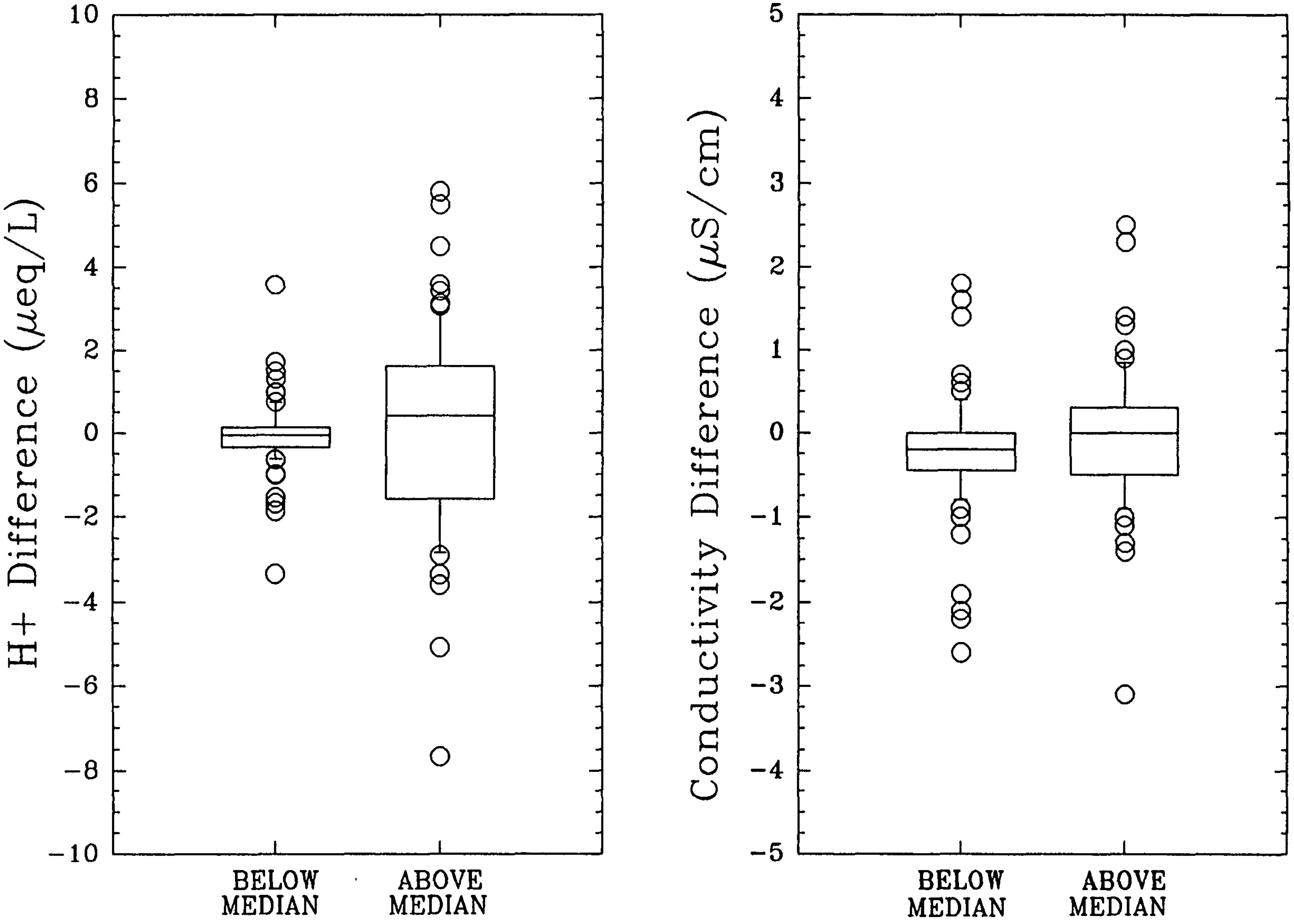


FIGURE B-21. Results of 0/Q replicate analysis, H^+ and conductivity, 1992.

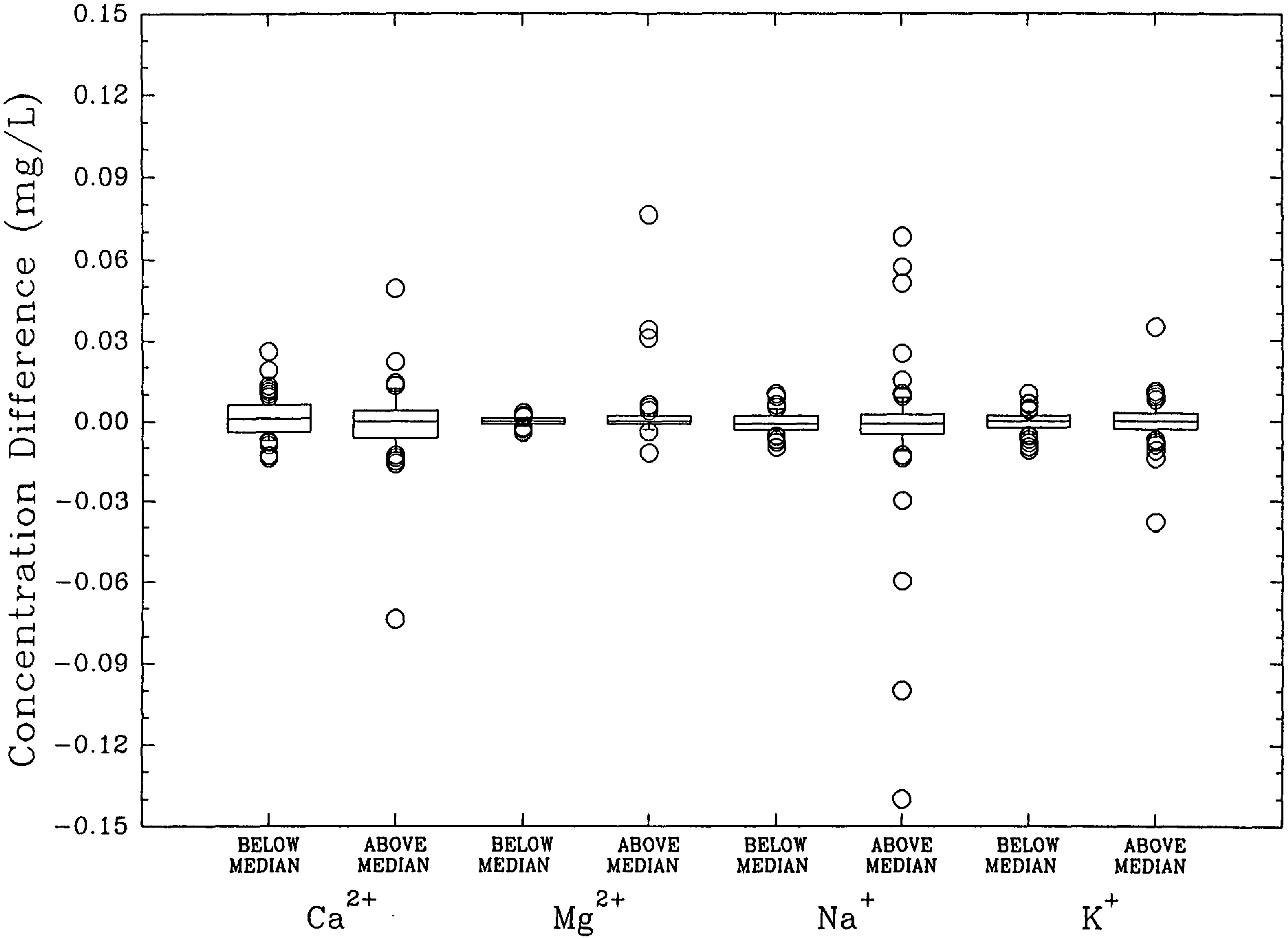


FIGURE B-22. Results of 0/Q replicate analysis for calcium (Ca^{++}), magnesium (Mg^{++}), sodium (Na^{+}), and potassium (K^{+}), 1992.

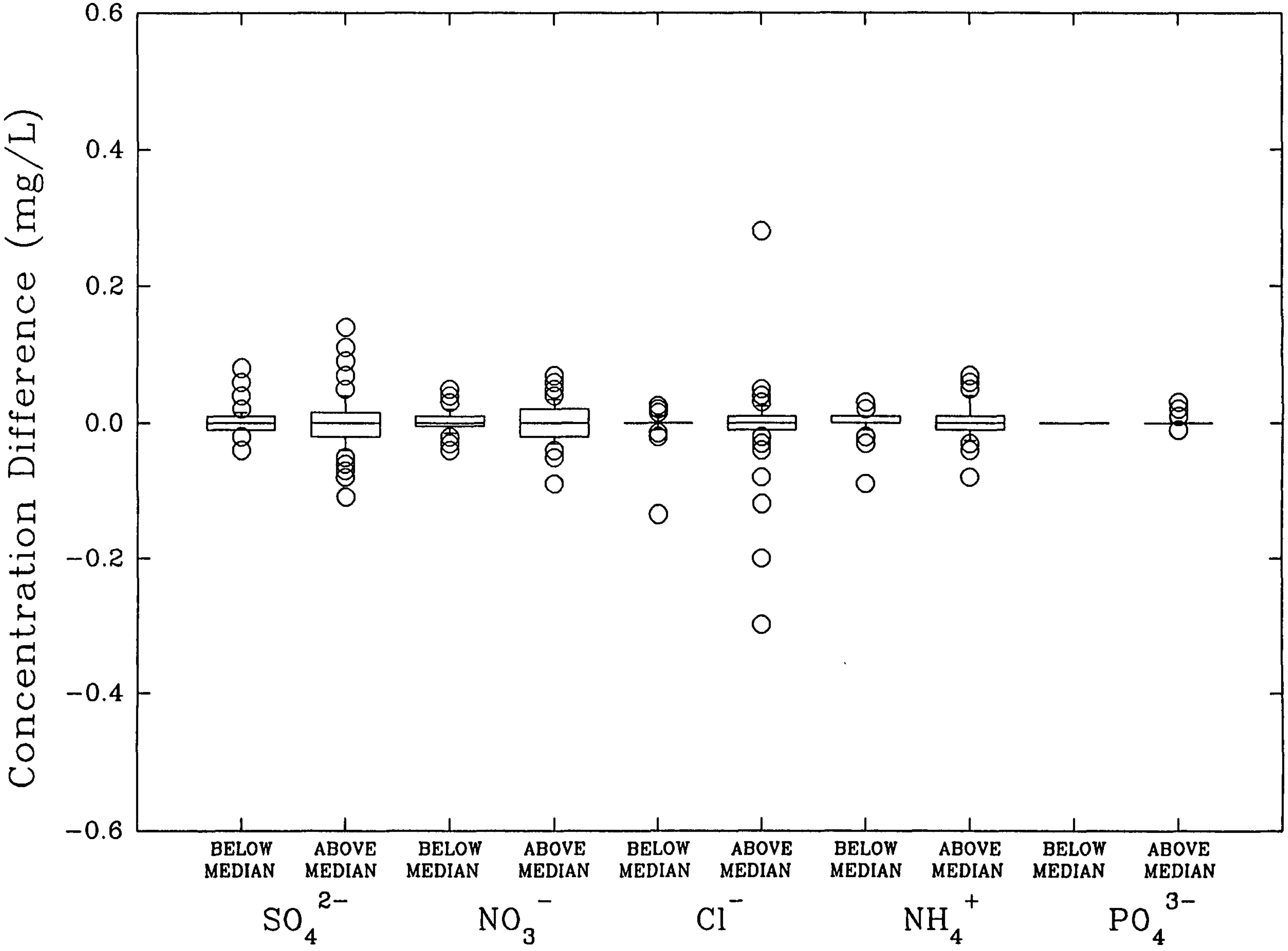


FIGURE B-23. Results of 0/Q replicate analysis for sulfate ($SO_4^=$), nitrate (NO_3-), chloride (Cl^-), ammonium (NH_4^+), and phosphate (PO_4^{3-}), 1992.

TABLE B-4 Percent of Analyte Concentrations Above MDLs Found in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Filter Leachates, 1992

Analyte	DI Water A[a]	DI Water B[b]	pH 4.3 Nitric Acid A	pH 4.3 Nitric Add B
Calcium	4.17	0.0	14.58	4.17
Magnesium	0.0	0.0	833	0.0
Potassium	10.42	4.17	833	4.17
Sodium	100.	37.5	95.83	39.58
Ammonium	6.25	0.0	6.25	2.08
Nitrate	60.42	0.0	N.A.	N.A.
Chloride	37.50	0.0	35.42	12.50
Sulfate	10.42	0.0	0.0	2.08
pH (units)[c]	5.65	5.66	4.33	432
H^+ (μeq/L) [c]	2.24	2.19	46.8	47.9
Conductivity (μS/cm)[c]	1.2	1.0	21.2	21.9
Number of weeks	48	48	48	48

Notes:

[a] Fust 50-mL filtrate after 300 mL DI water filter rinse.

[b] Second consecutive 50 mL filtrate after 300 mL DI water filter rinse.

[c] pH, H^+, and Conductivity numbers are median concentration values, not percents above detection.

TABLE B-5 Percent of Analyte Concentrations Above the MDL Found in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Upright Bucket Leachates, 1992

Analyte	DI Water (50 mL)	DI Water (150 mL)	pH 4.3 Nitric Acid (50 mL)	pH 4.3 Nitric Acid (150 mL)
Calcium	16.33	6.12	42.86	12.24
Magnesium	0.0	0.0	14.29	2.04
Potassium	40.82	18.37	57.14	18.37
Sodium	75.51	53.06	79.59	40.82
Ammonium	4.08	0.0	4.08	0.0
Nitrate	4.08	0.0	NA	NA
Chloride	28.57	2.04	38.78	8.16
Sulfate	12.24	2.04	14.29	2.04
pH (units)*	5.60	5.59	4.38	434
Conductivity (µS/cm)*	1.4	1.4	19.4	20.8
Number of weeks	49	49	49	49

Note:
•pH and conductivity values are the median concentrations, not the percent above detection.

TABLE B-6 Percent of Analyte Concentrations Above the MDL Found in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Inverted Bucket Leachates, 1992

Analyte	DI Water (50 mL)	DI Water (150 mL)	pH4.3 Nitric Acid (50 mL)	pH 4.3 Nitric Acid (150 mL)
Calcium	100.	89.80	100.	95.92
Magnesium	89.80	40.82	93.88	6939
Potassium	73.47	51.02	85.71	40.82
Sodium	100.	93.88	95.92	83.67
Ammonium	30.61	1633	32.65	20.41
Nitrate	10.20	2.04	NA	NA
Chloride	73.47	6.12	73.47	22.45
Sulfate	91.84	46.94	97.96	79.59
pH (units)*	6.41	6.07	4.82	4.46
Conductivity (µS/cm)*	3.2	1.6	11.7	17.5
Number of weeks	49	49	49	49

Note:
* pH and conductivity numbers are median concentrations, not percent above detection.

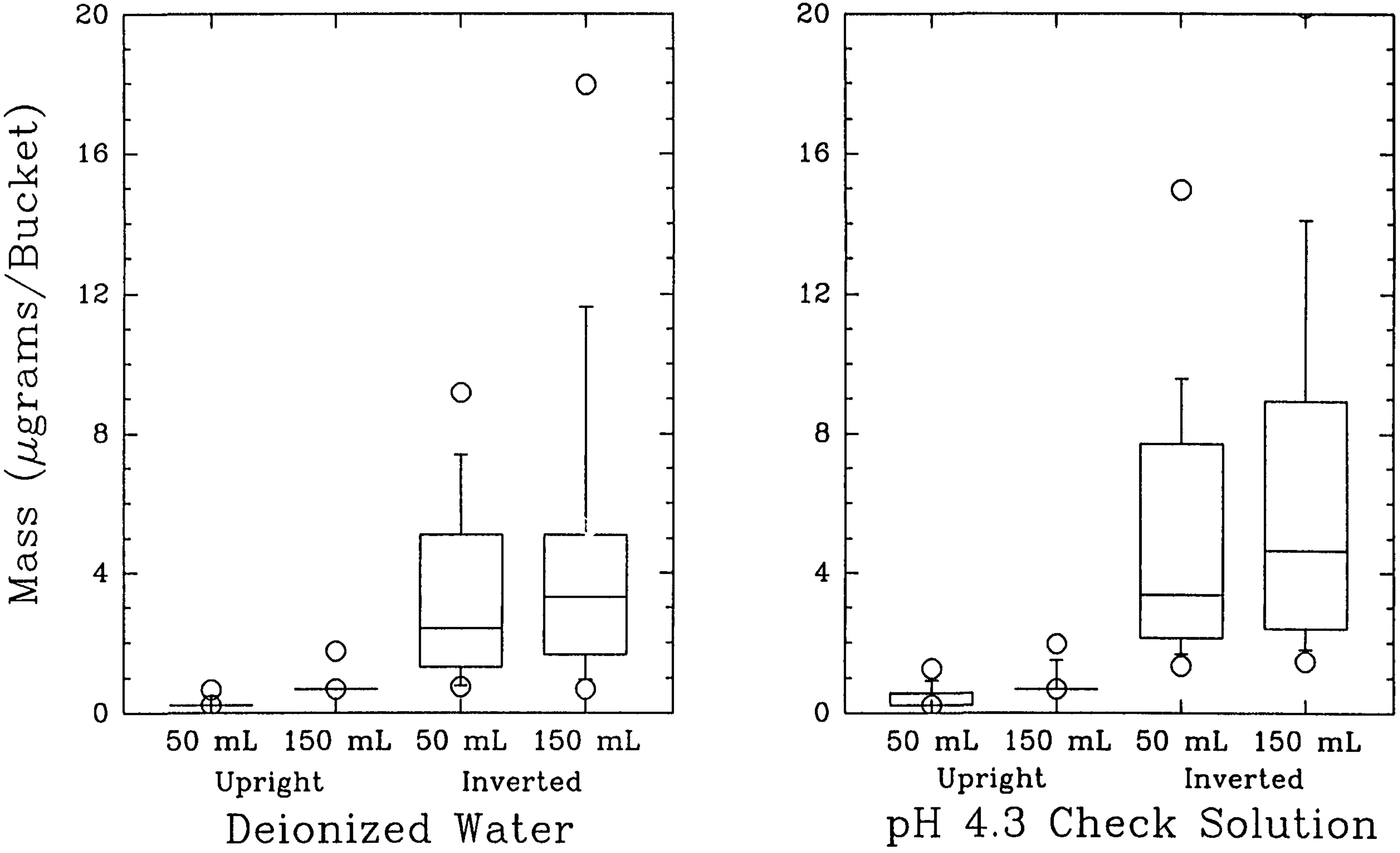


FIGURE B-24. Calcium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1992.

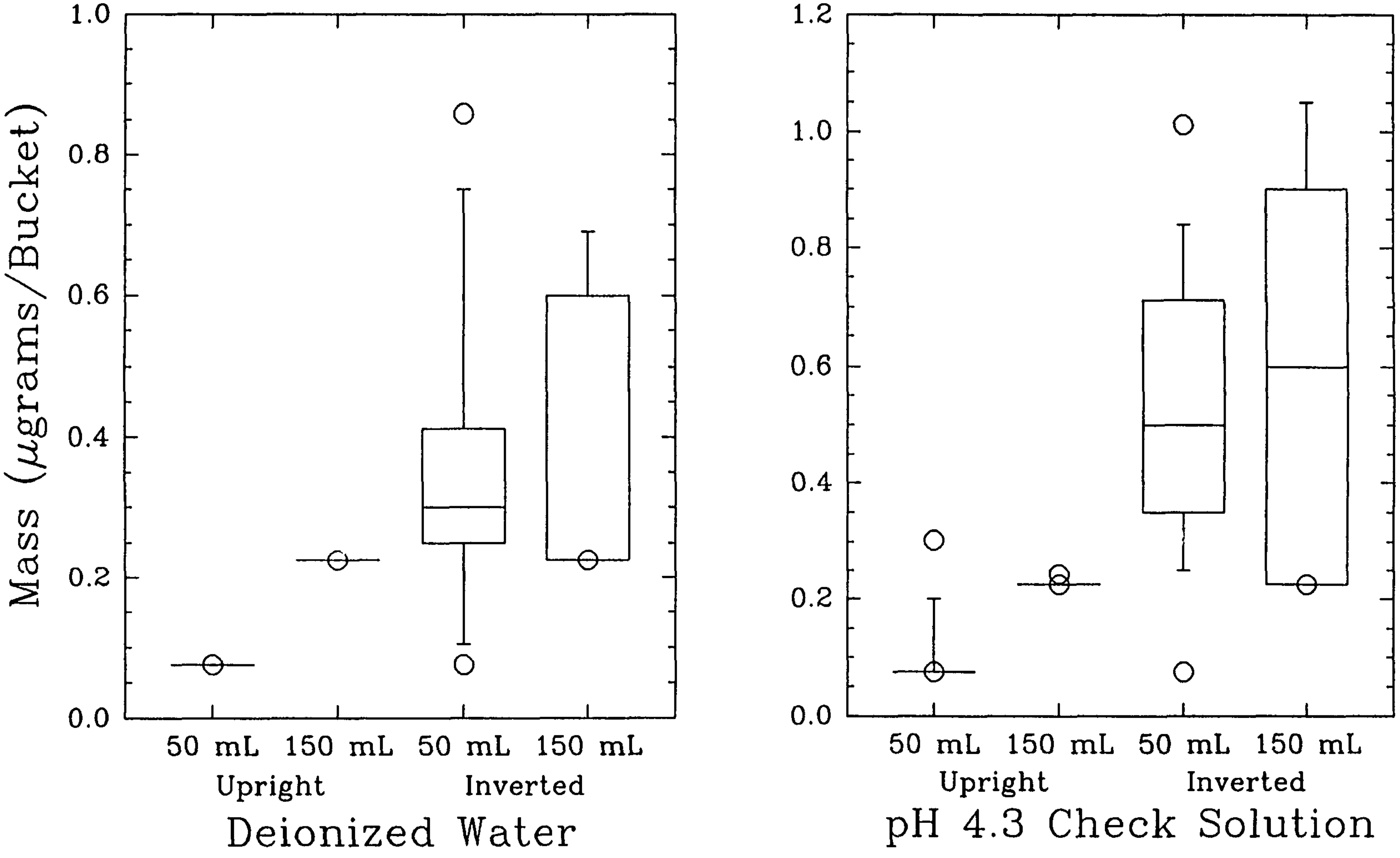


FIGURE B-25. Magnesium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1992.

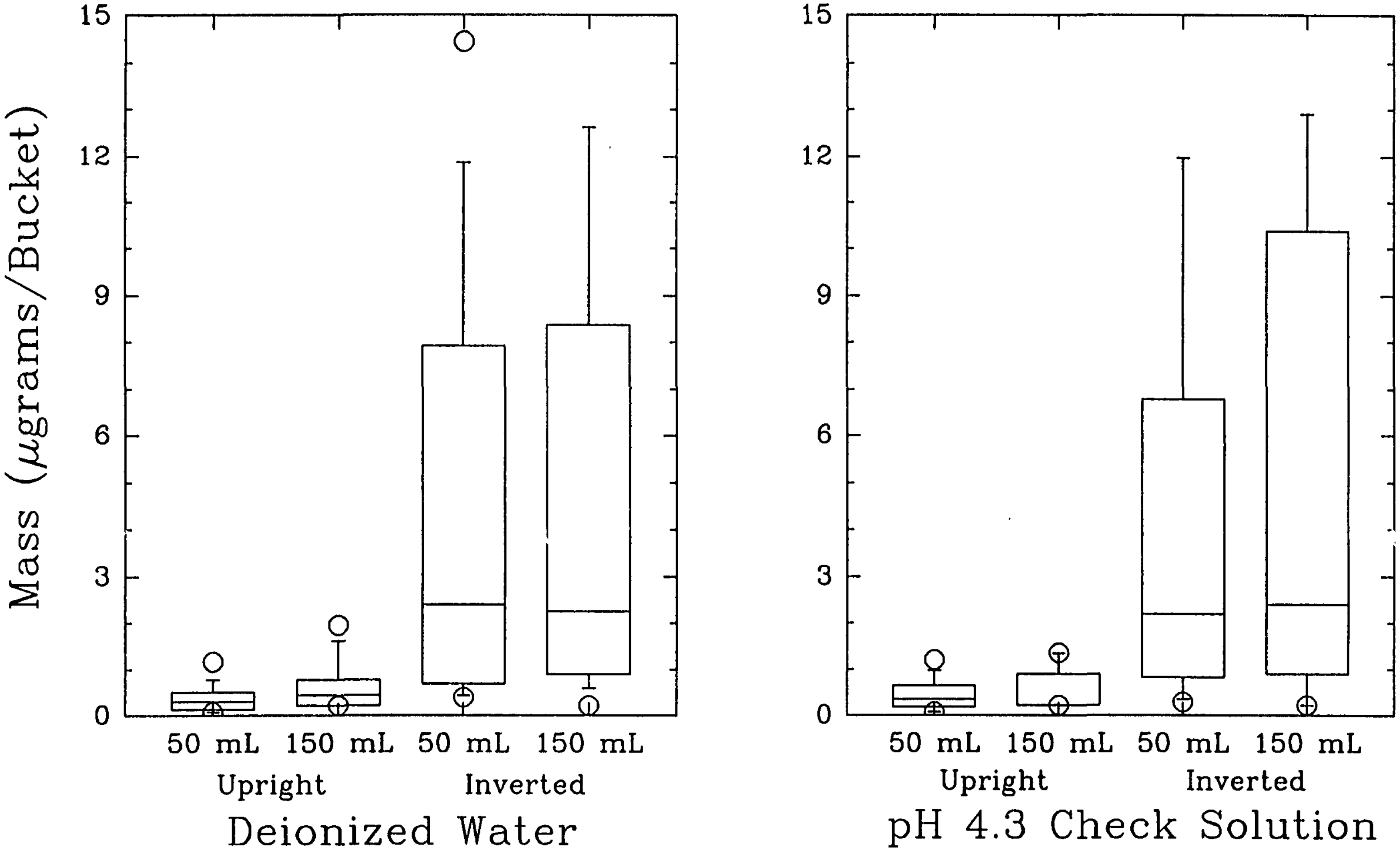


FIGURE B-26. **Sodium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1992.**

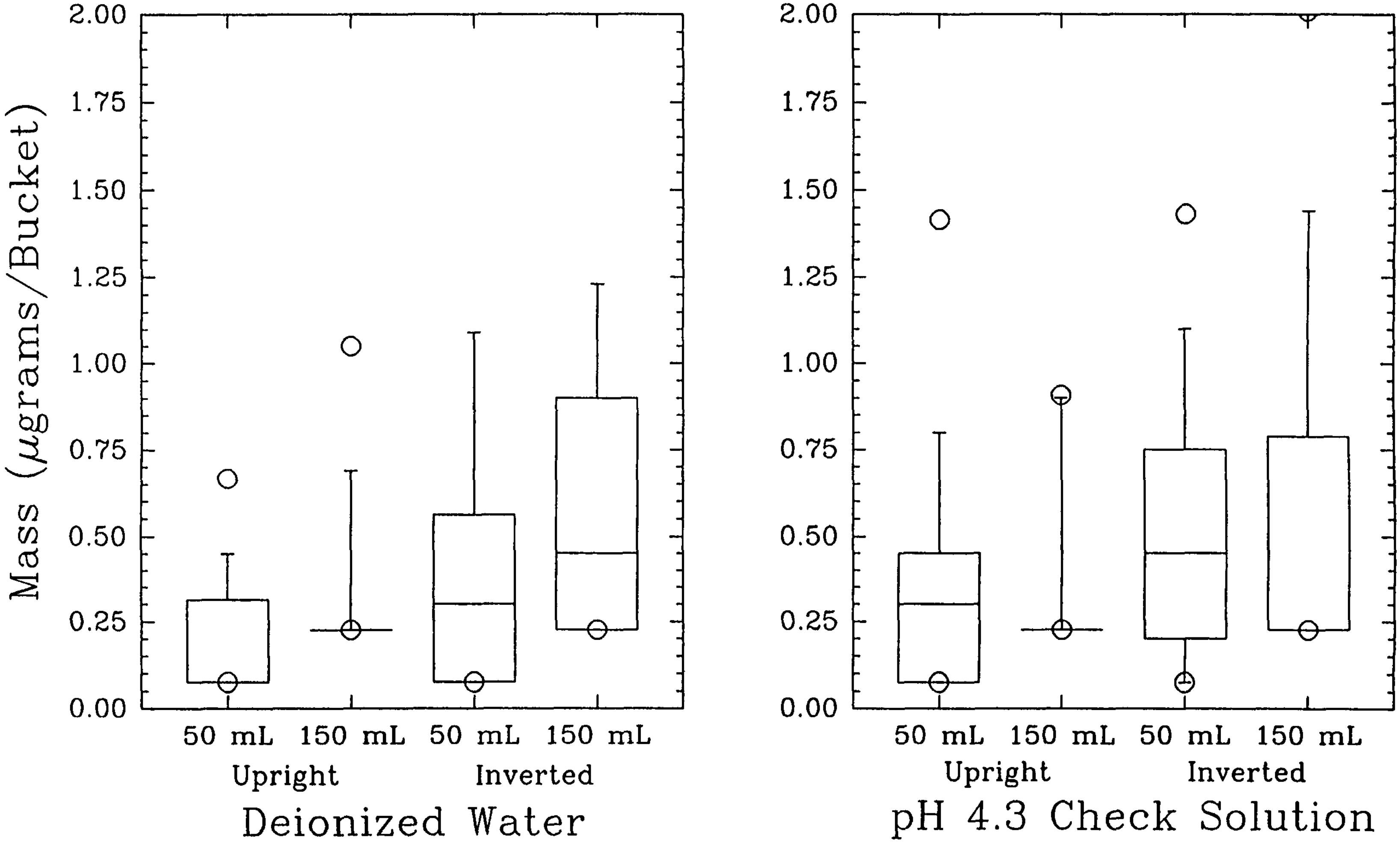


FIGURE B-27. Potassium found in upright and inverted bucket blanks, using Dl water and pH 4.3 QCS as leaching agents, 1992.

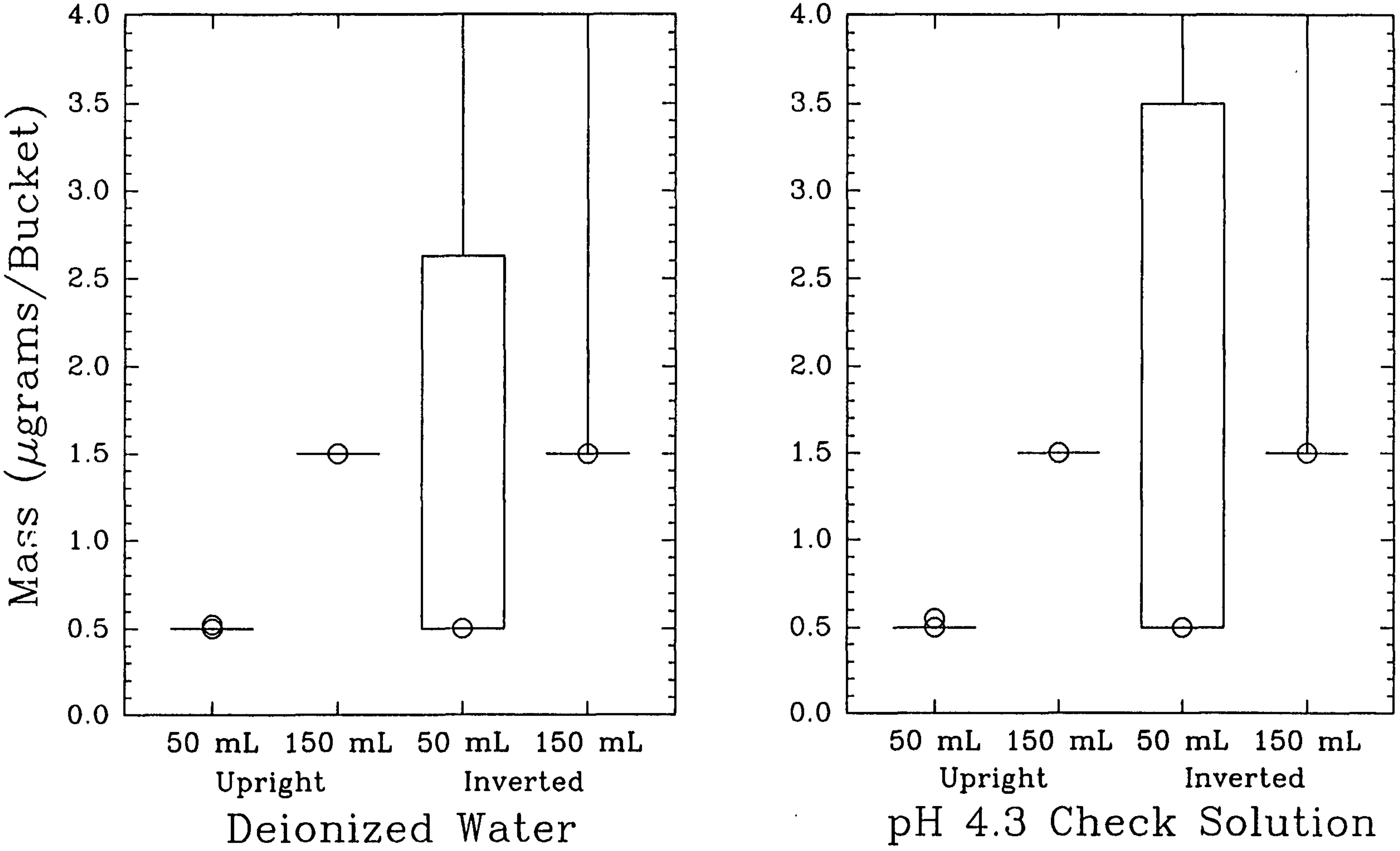


FIGURE B-28. Ammonium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1992.

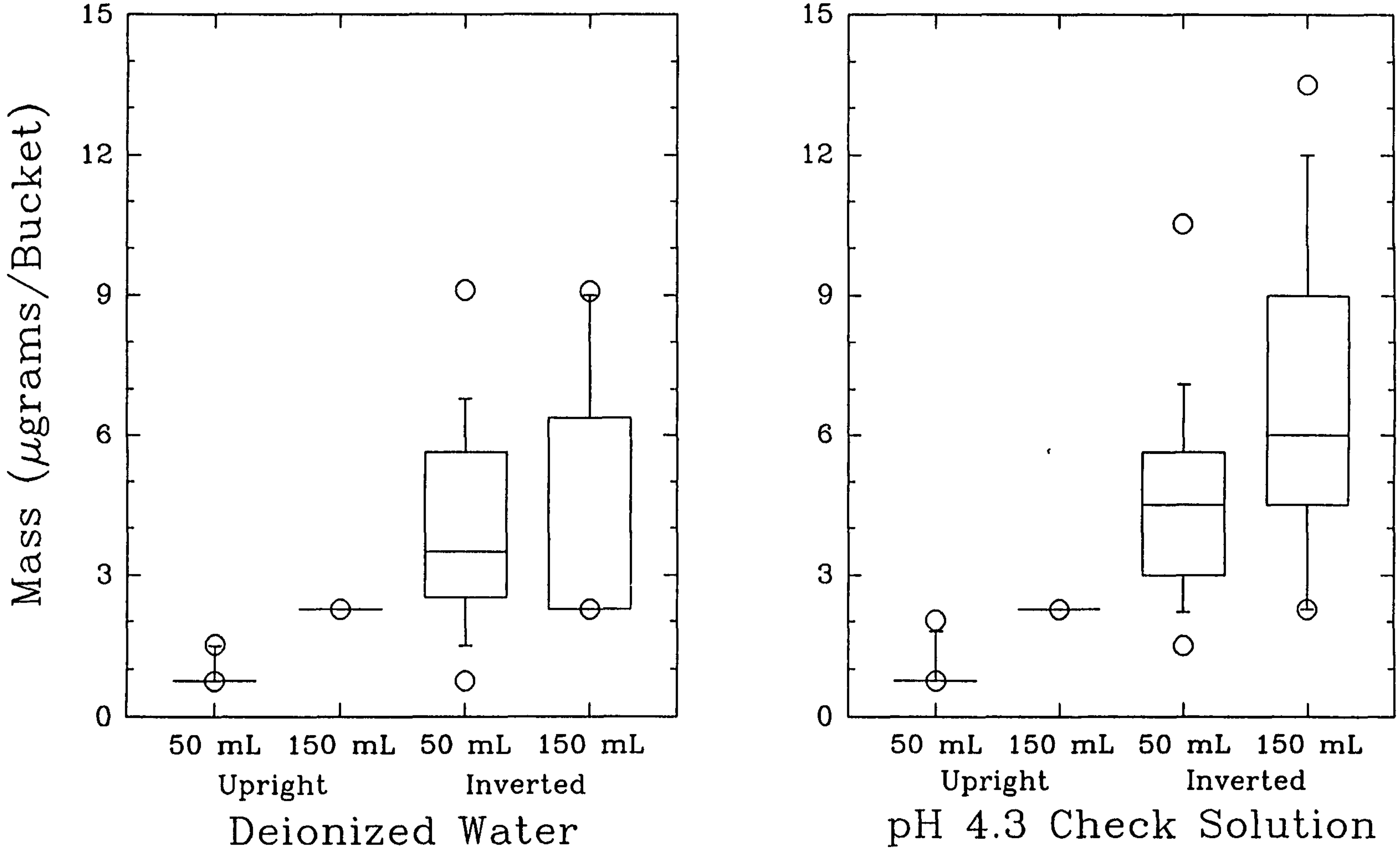


FIGURE B-29. Sulfate found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1992.

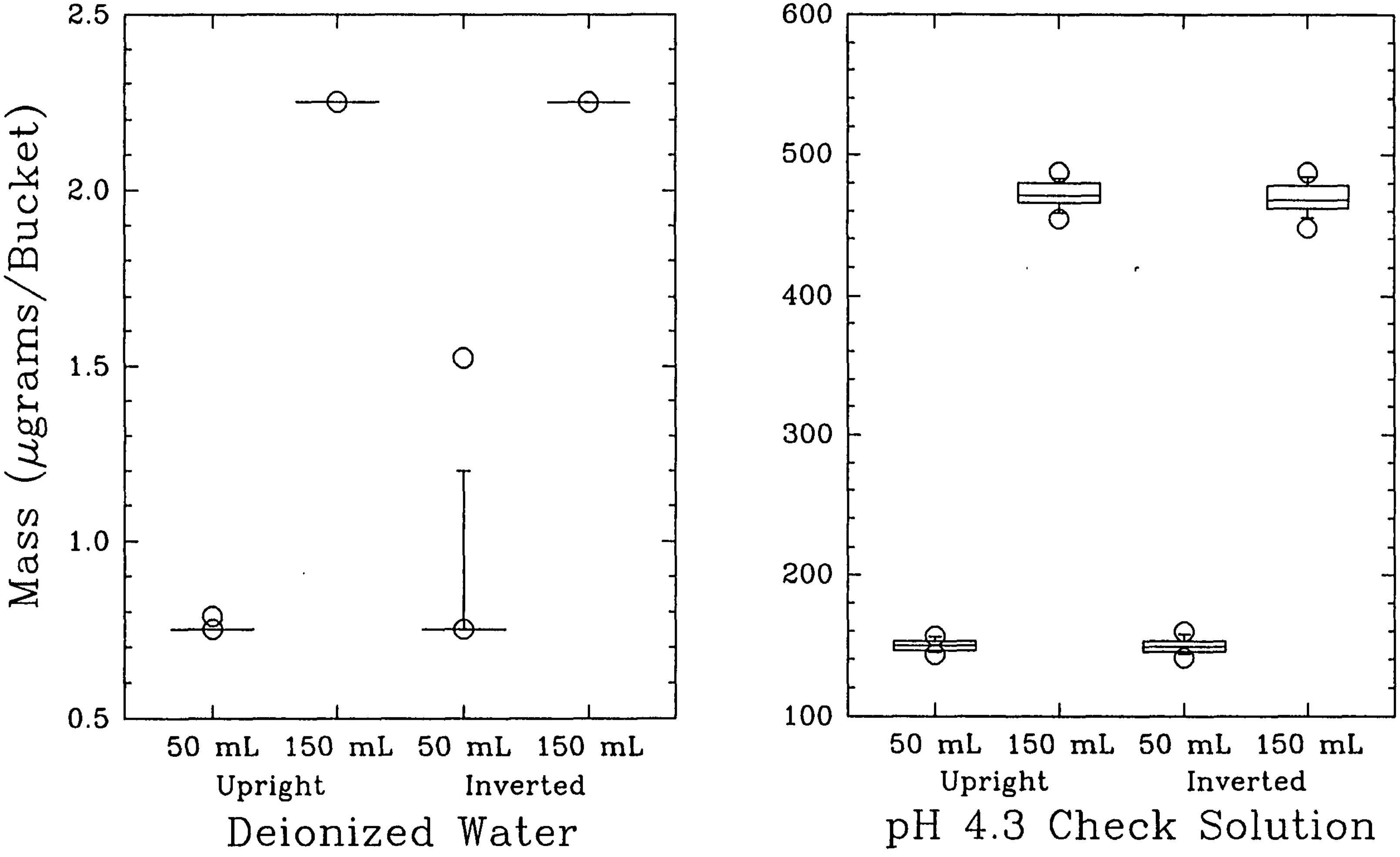


FIGURE B-30. **Nitrate found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1992.**

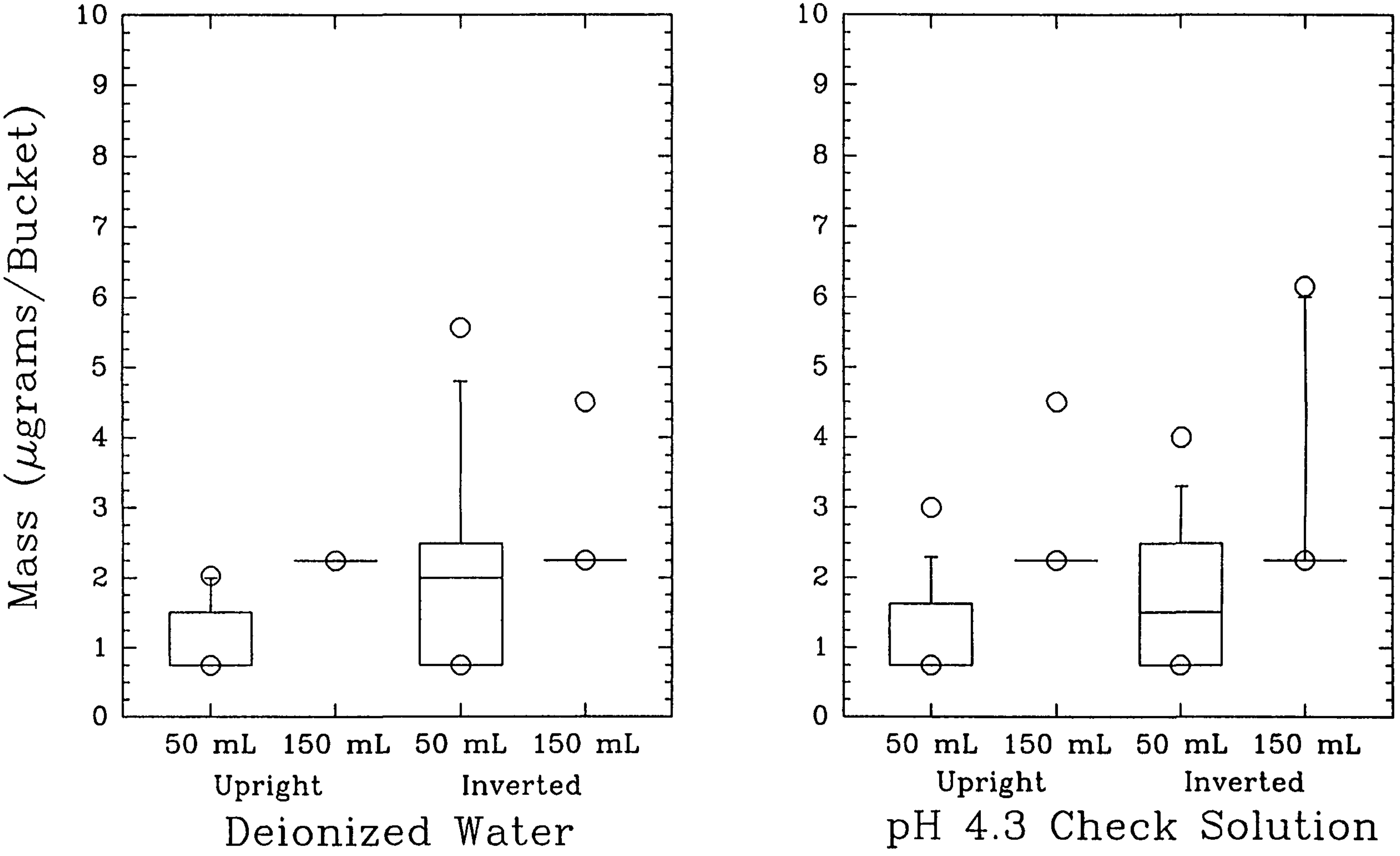


FIGURE B-31. Chloride found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1992.

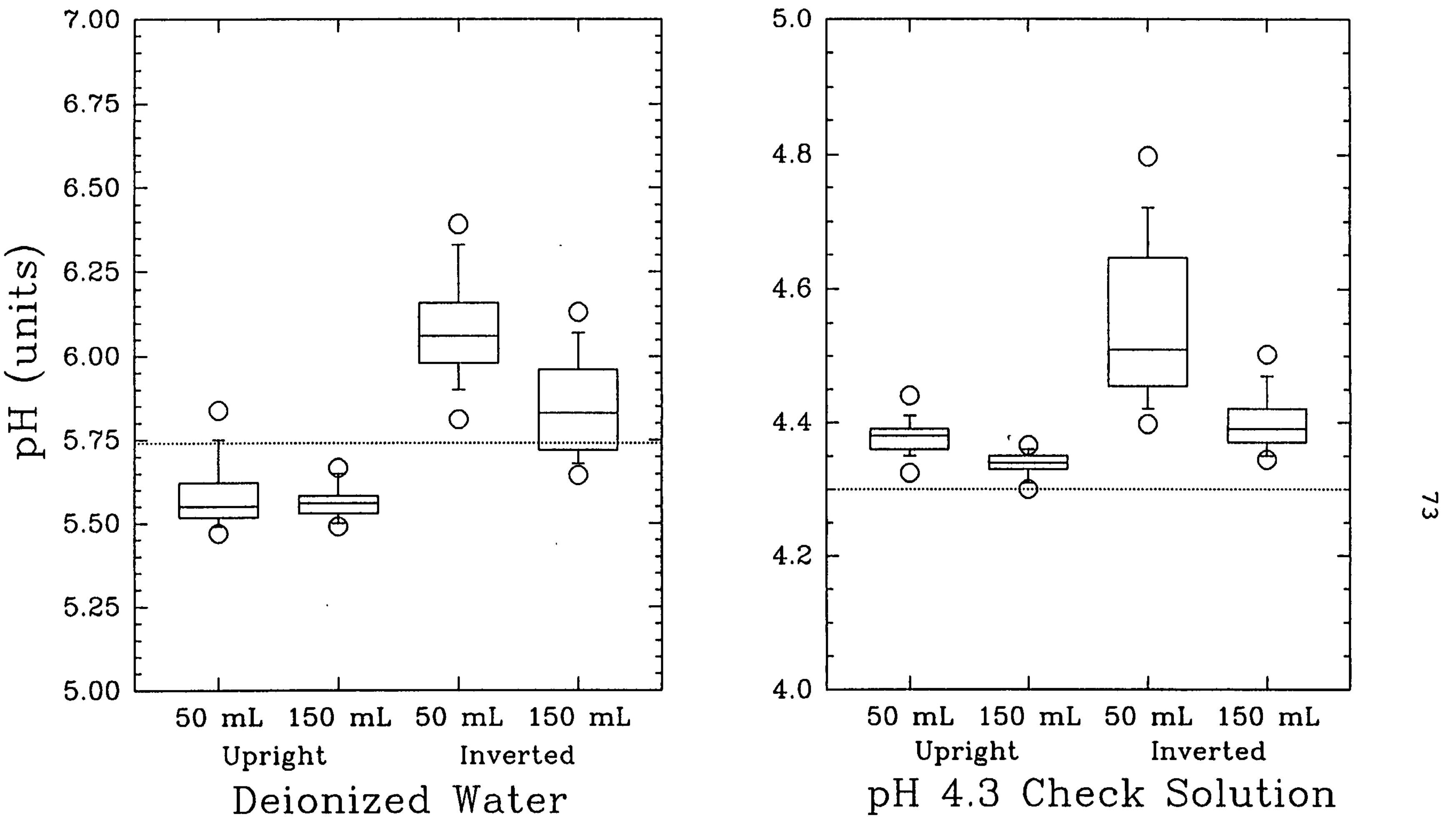


FIGURE B-32. pH of upright and inverted bucket blanks leached with DI water and pH 4.3 QCS, 1992.

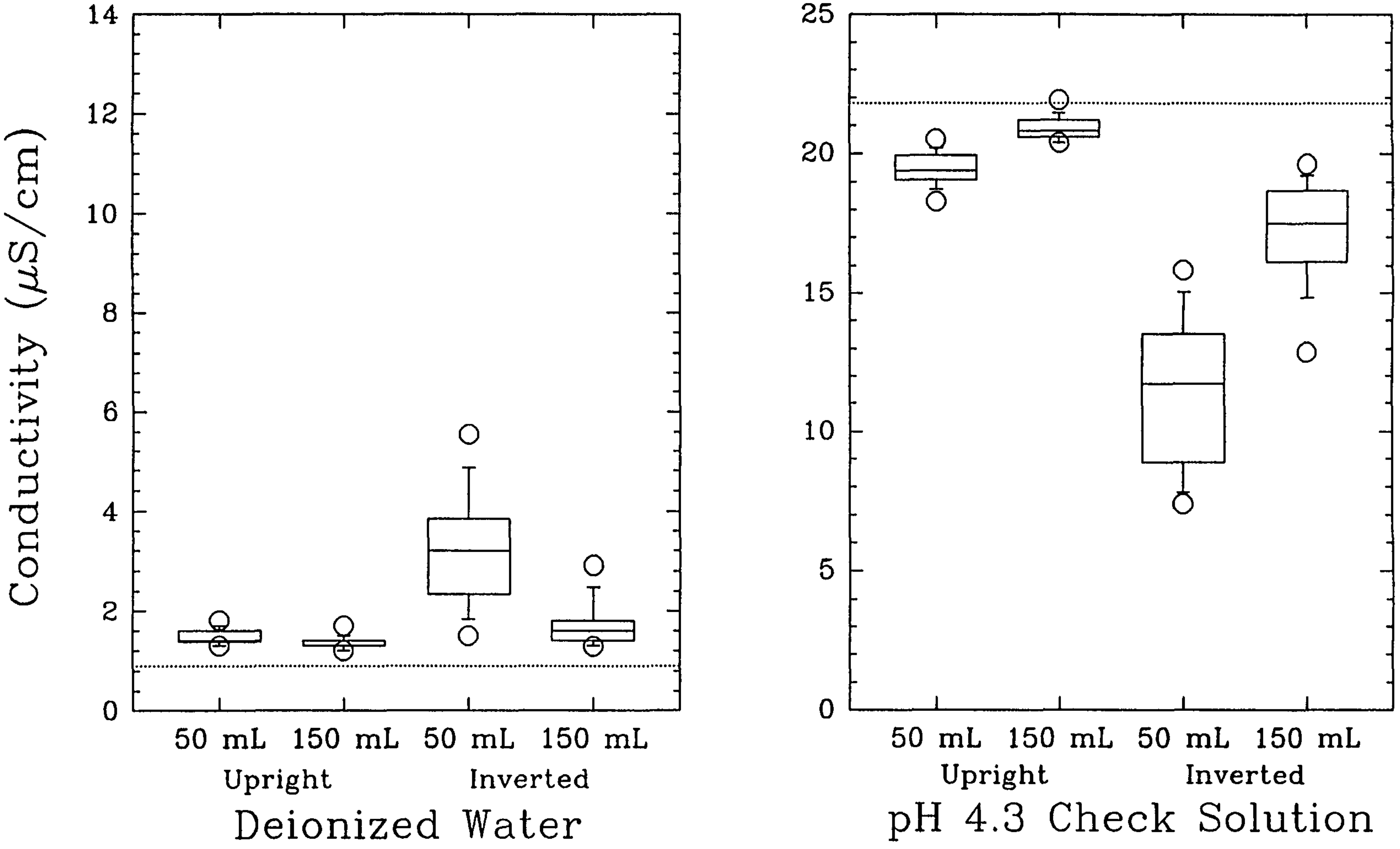


FIGURE B-33. Conductivity of upright and inverted bucket blanks leached with DI water and pH 4.3 QCS, 1992.

APPENDIX C

interlaboratory Comparison Data:

USEPA, LRTAP

1992

TABLE C-1
USEPA RTP Add Rain Performance Surrey, April 1992

Parameter (mg/L)	Sample Number					
	1832		2486		3162	
	CAL	USEPA	CAL	USEPA	CAL	USEPA
Calcium	0.056	0.053	0.143	0.133	0.155	0.146
Magnesium	0.041	0.040	0.101	0.097	0.096	0.092
Sodium	0.188	0.178	0.245	0.238	1.348	1.328
Potassium	0.080	0.069	0.087	0.083	0.533	0.537
Ammonium	0.09	0.10	0.80	0.81	0.44	0.44
Nitrate	0.49	0.50	0.53	0.52	3.85	3.85
Chloride	0.29	0.30	0.62	0.65	1.11	1.15
Sulfate	2.85	2.62	8.42	7.83	6.68	6.14
pH (units)	4.29	4.27	3.92	3.90	3.93	3.90
Conductivity (µS/cm)	26.8	24.8	66.0	62.5	68.8	66.1

TABLE C-2
USEPA RTP Add Rain Performance Surrey, November 1992

Parameter (mg/L)	Sample Number					
	1656		2867		3625	
	CAL	USEPA	CAL	USEPA	CAL	USEPA
Calcium	0.084	0.053	0.393	0.373	0.058	0.051
Magnesium	0.023	0.021	0.117	0.111	0.078	0.075
Sodium	0.257	0.237	1.825	1.776	0.396	0.393
Potassium	0.112	0.076	0.736	0.771	0.078	0.078
Ammonium	0.15	0.15	1.09	1.07	0.61	0.61
Nitrate	0.80	0.62	9.61	9.38	8.10	7.92
Chloride	0.39	0.39	2.85	2.84	1.27	1.29
Sulfate	1.65	1.55	12.6	11.05	9.17	8.13
pH (units)	4.54	4.49	3.54	3.51	3.57	3.53
Conductivity (µS/cm)	17.4	16.4	159.0	155.3	134.3	133.6

TABLE C-3
LRTAP Interlaboratory Comparability Study L-29, March 1992
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	1.350	1.330	0.761	0.750	1.807	1.780	4.209	4.110	0.985	0.981
Magnesium	0.381	0.381	0.246	0.241	0.664	0.660	0.477	0.475	0.204	0.204
Sodium	0.088	0.093	0.053	0.059	3.696	4.050	0.506	0.560	0.092	0.100
Potassium	0.077	0.076	0.044	0.050	0.282	0.289	0.210	0.214	0.037	0.040
Ammonium	<0.02	0.04	<0.02	0.01	<0.02	0.01	<0.02	0.04	<0.02	0.01
Nitrate	1.77	1.83	1.15	1.19	0.22	0.23	3.23	3.16	0.09	0.11
Chloride	0.23	0.24	0.15	0.16	5.04	5.16	0.17	0.19	0.11	0.11
Sulfate	3.63	3.62	3.69	3.66	2.84	2.80	5.64	5.60	6.03	6.08
pH (units)	5.20	5.30	4.48	4.50	6.40	6.37	6.78	6.77	4.26	4.28
Conductivity (uS/cm)	16.6	16.4	22.5	22.5	35.1	35.7	31.0	31.6	32.6	33.2

TABLE C-3 (continued)
LRTAP Interlaboratory Comparability Study L-29, March 1992,
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	3.156	3.181	8.812	8.678	2.460	2.441	3.261	3.300	4.213	4.050
Magnesium	0.757	0.757	2.689	2.640	0.691	0.698	1.050	1.080	0.517	0.510
Sodium	0.944	1.050	0.193	0.206	1.130	1.183	0.189	0.207	0.822	0.860
Potassium	0.535	0.540	0.327	0.326	0.405	0.410	0.188	0.190	0.132	0.130
Ammonium	<0.02	0.03	2.32	2.19	<0.02	0.01	0.59	0.59	<0.02	0.02
Nitrate	0.53	0.56	13.2	12.95	0.22	0.22	10.93	10.85	0.22	0.24
Chloride	1.24	1.27	0.87	0.84	0.23	0.24	0.53	0.53	0.54	0.56
Sulfate	7.92	7.94	23.1	22.7	3.76	3.70	6.76	6.81	0.79	0.80
pH (units)	6.64	6.60	6.47	6.44	6.97	6.99	4.58	4.60	5.83	5.80
Conductivity (µxS/cm)	33.2	34.0	96.4	97.6	25.4	26.0	48.6	49.2	22.7	23.0

TABLE C-4
LRTAP Interlaboratory Comparability Study L-30, Junes 1992, CAL Values Compared to NWRI Median Values for All Participating Laboratories

	Sample Number									
Parameter (mg/L)	1		2		3		4		5	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	13.2	13.1	3.12	3.28	2.96	3.07	6.78	6.73	2.89	3.00
Magnesium	2.77	2.76	0.967	1.080	0.680	0.749	0.608	0.666	0.843	0.930
Sodium	1.308	1.320	0.196	0.210	0.948	1.020	0.850	0.882	1.269	1.240
Potassium	0.467	0.500	0.188	0.190	0.508	0.540	0.290	0.294	0.536	0.543
Ammonium	<0.02	0.01	0.58	0.58	0.04	0.04	<0.02	<0.01	<0.02	<0.01
Nitrate	1.59	1.59	10.84	10.67	0.53	0.53	0.80	0.80	<0.02	0.03
Chloride	1.04	1.34	0.51	0.52	1.23	1.24	0.48	0.52	1.24	1.25
Sulfate	3.35	3.32	6.80	6.82	7.76	7.77	5.95	5.92	7.56	7.50
pH (units)	7.83	7.76	4.58	4.60	6.68	6.62	7.29	7.08	6.67	6.55
Conductivity (µS/cm)	96.0	95.1	50.1	49.0	33.7	33.6	47.3	46.8	34.9	34.7

TABLE C-4 (continued)
LRTAP Interlaboratory Comparability Study L-30-June 1992
CAL Values Compared to NWRI Median Values for All Participaing Laboratories

Parameter (mg/L)	Sample Number 6		7		8		9		10	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	7.20	7.06	5.66	5.57	1.140	1.155	1.485	1.470	1.437	1.405
Magnesium	0.706	0.770	1.447	1.460	0.481	0.514	0.264	0.280	0.267	0.272
Sodium	0.871	0.890	1.571	1.560	3.32	3.28	0.128	0.130	0.127	0.130
Potassium	0.248	0.250	0.723	0.730	0.335	0.344	0.055	0.060	0.049	0.050
Ammonium	0.06	0.06	0.04	0.04	<0.02	0.01	<0.02	<0.01	<0.02	<0.01
Nitrate	0.40	0.40	0.35	0.35	0.22	0.27	0.13	0.13	0.09	0.09
Chloride	0.32	0.34	1.97	2.08	4.50	4.47	0.14	0.14	0.13	0.13
Sulfate	6.48	6.49	8.92	8.81	1.93	1.94	5.18	5.14	3.40	3.36
pH (units)	7.48	7.29	7.33	7.22	5.49	5.45	5.01	5.02	6.34	6.22
Conductivity (µS/cm)	50.8	49.5	54.5	54.2	29.7	29.9	18.1	17.8	12.9	12.8

TABLE C-5

LRTAP Interiaboratory Comparability Study L-31, November 1992, CAL Values Compared to NWRI Median Vaalues for All Participating Laboratories

Parameter (mg/L)	Sample Number									
	1		2		3		4			
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	1.942	1.935	0.512	0.520	13.70	13.52	2.097	2.060	8.63	8.58
Magnesium	0.310	0.310	0.184	0.191	2.80	2.81	0.479	0.489	1.11	1.15
Sodium	0.565	0.600	0.160	0.180	1.355	1.367	0.480	0.499	1.465	1.462
Potassium	0.374	0.404	0.188	0.200	0.468	0.506	0.201	0.210	0.294	0.312
Ammonium	0.02	0.04	0.08	0.08	<0.02	<0.01	<0.02	<0.01	<0.02	0.03
Nitrate	1.86	1.86	0.03	0.04	1.33	1.37	<0.02	0.04	0.31	0.31
Chloride	0.42	0.42	0.11	0.12	1.32	1.42	0.37	0.38	1.44	1.53
Sulfate	5.43	5.38	0.41	0.44	3.48	3.45	6.34	6.34	7.44	7.40
pH (units)	5.38	5.38	4.60	4.62	7.83	7.77	6.33	6.07	7.46	7.40
Conductivity (µS/cm)	23.7	23.0	16.2	15.4	96.6	97.1	22.4	22.2	63.5	63.3

TABLE C-5 (continued)
LRTAP Interlaboratory Comparability Study L-31 November 1992,
CAL Valius 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	6.90	6.79	6.71	6.60	3.26	3.33	13.32	13.30	6.61	6.50
Magnesium	0.656	0.670	0.614	0.626	1.042	1.080	2.79	2.78	0.622	0.627
Sodium	0.852	0.887	0.803	0.820	0.193	0.205	1.316	1.310	0.823	0.823
Potassium	0.287	0.300	0.272	0.290	0.180	0.196	0.469	0.498	0.301	0.310
Ammonium	<0.02	<0.01	0.06	0.07	0.59	0.60	<0.02	0.02	<0.02	0.01
Nitrate	0.80	0.80	0.62	0.62	10.67	10.67	1.59	1.62	0.71	0.76
Chloride	0.48	0.52	0.35	0.38	0.50	0.52	1.25	1.34	0.39	0.43
Sulfate	5.95	5.91	5.85	5.83	6.74	6.81	3.37	3.32	5.89	5.83
pH (units)	7.45	7.26	7.44	7.32	4.60	4.60	7.90	7.77	7.35	7.12
Conductivity (µS/cm)	47.8	47.1	46.3	46.0	49.7	49.7	95.2	95.8	45.6	45.5

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