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QUALITY ASSURANCE REPORT
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM, 1996 and 1997

Laboratory Operations
Central Analytical Laboratory

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

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

QUALITY ASSURANCE REPORT
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM,
1996 and 1997

Laboratory Operations
Central Analytical Laboratory

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ACKNOWLEDGMENTS

This Laboratory Operations Quality Assurance Report, a summary of the quality control/quality assurance measures in place at the Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) and NADP/Atmospheric Integrated Research Monitoring Network (NADP/AIRMoN), is the product of many individuals. The U.S. Geological Survey Branch of Quality Systems coordinates the external interlaboratory comparison program. Karen Harlin, Mark Peden, and Van Bowersox of the NADP Program Office provide ongoing input and support throughout the year. A dedicated staff of analysts analyzes thousands of samples with the support of conscientious sample receiving and processing personnel. Andrea Morden-Moore contributed computer products for the 1996 data. Pam Bedient helped format the text, tables, and figures. The following reviewers and editors contributed their time and input to the final report and without whom this report could not be completed: John Gordon, Karen Harlin, Linda Hascall, Laura Hult, Eva Kingston, Mark Peden, John Sherwell, and Luther Smith.

I. INTRODUCTION

The 1996 and 1997 Quality Assurance Report for the National Atmospheric Deposition Program (NADP) describes and summarizes the results of the Central Analytical Laboratory's (CAL) quality assurance program for 1996 and 1997. The procedures for supporting reliable data are demonstrated through a quality assurance program. This report, through text, figures, and tables, defines the quality assurance program in place at the CAL and assesses the precision and accuracy of the data generated and reported through the NADP.

The Atmospheric Chemistry Laboratory at the Illinois State Water Survey (ISWS) was selected in the summer of 1978 to be the CAL for the NADP. CAL operations began on October 1, 1978, with 14 NADP sites. Thirty-five sites were in operation by December 1979. In 1996, the NADP CAL was still at the ISWS and there were approximately 200 NADP/National Trends Network (NTN) sites collecting precipitation throughout the United States. The samples are collected in buckets using a specified wet/dry sampler. The buckets are removed each Tuesday morning. Beginning in January 1994, each sample was decanted from the collection bucket into a 1-liter, wide-mouth, high-density polyethylene (HDPE) bottle and shipped with the sampling bucket to the CAL each week. Figure I-1 illustrates the sample's journey after its arrival at the CAL.

The Atmospheric Integrated Research Monitoring Network (AIRMoN) protocol was defined in1994, and its Quality Assurance (QA) program was put into place. Since that time NADP/AIRMoN and NADP/NTN have shared the same analytical staff and methodology. AIRMoN sample protocol differs in that samples are collected daily if a precipitation event occurs and then chilled and shipped in an insulated container. The sample's pH and conductivity are measured upon receipt at the CAL. The sample remains in its original 250 milliliter (mL) HDPE bottle and is refrigerated at all times except when portions are decanted for ion analysis. The parameters are analyzed in a specified order; pH and conductivity are measured first followed in order by ammonium and phosphate, the anions (SO_4^{-2}, NO_3^-, Cl^-), and finally the remaining cations (Ca^{+2}, Mg^{+2}, Na^+, K^+).

Table I-1 (1996) and Table I-2 (1997) list the staff who are responsible for samples from the time they reach the ISWS until the analytical data have been verified and transmitted to the Coordination Office at Colorado State University (prior to October 1997) or the Program Office at the ISWS (after October 1997). The majority of the staff have been employed at the ISWS for more than ten years, and all are committed to the project. In both 1996 and 1997 there were several changes in personnel at the CAL. Patricia Dotson retired from the CAL in 1996 after working for 16 years in sample processing. Kaye Surratt was hired part time to replace Patricia Dotson and to assist with the sample processing until a new person, Pamela Scales, was hired. Kaye continued to work part time in sample processing as needed for the rest of the year and on into 1997. In July 1997, Kenni James, Quality Assurance Specialist for almost ten years, retired and left the ISWS. In the fall of 1997, Pam Scales returned to school, and Laura Zangori was hired as her replacement as the sample processing coordinator. Phyllis Ballard was also hired in the fall of 1997 to help with bucket and bottle cleaning.

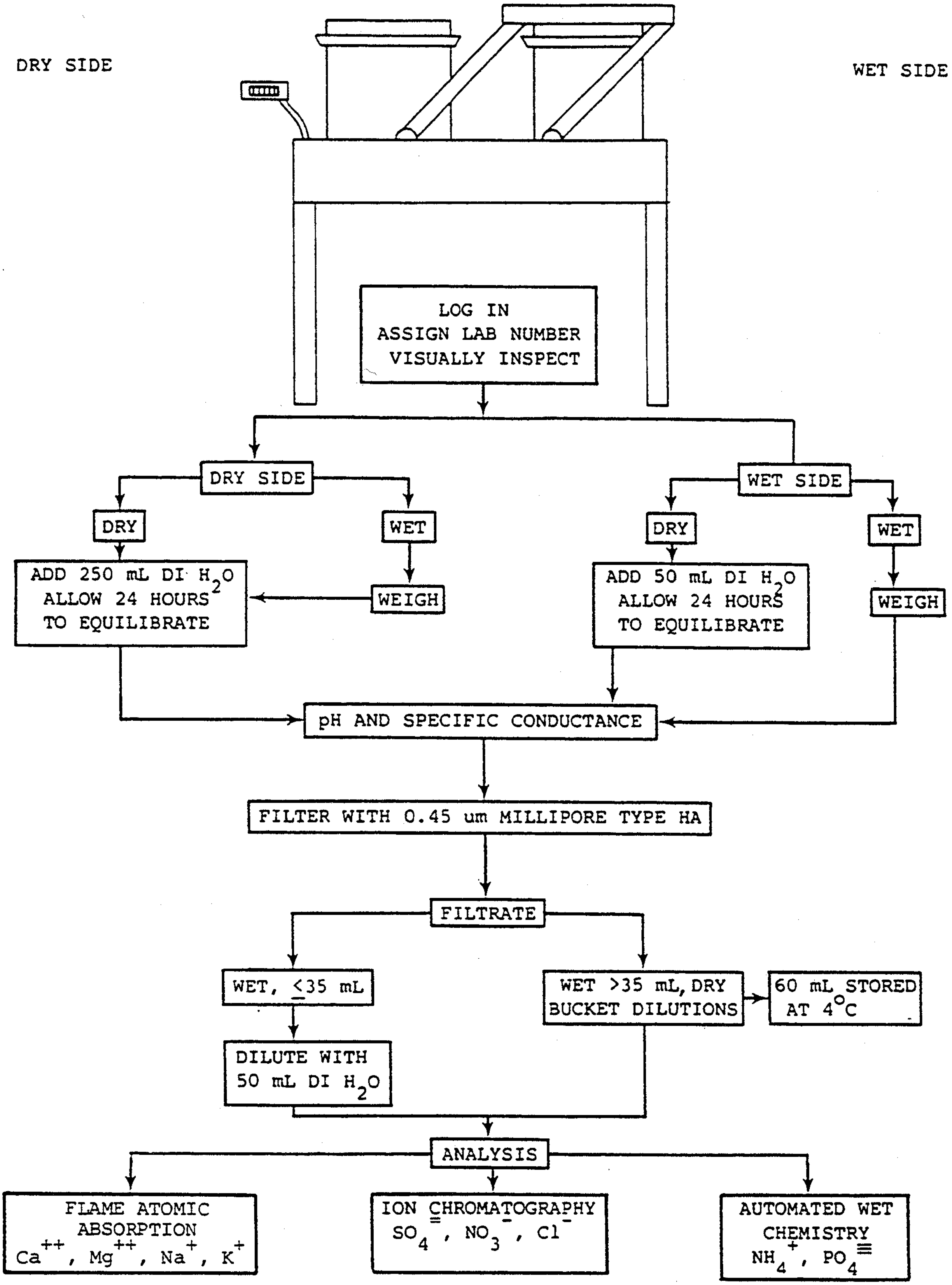


FIGURE I-1. Sample processing flowchart, January 1996 - December 1997.

TABLE I-1. Central Analytical Laboratory Analytical Staff, 1996

Staff Member	*Job Function*	*Period of Employment*
Sue Bachman	Ammonium (NH_4) analysis	08/80 - 12/96
	Ca, Mg, Na, K analysis	11/88 - 12/96
	ortho-Phosphate (PO_4) analysis	01/94 - 12/96
Brigita Demir	Anion analysis	09/81 - 12/96
Patricia Dodson	Sample processing	09/80 - 08/96
Lori Henry	AIRMoN sample processing and Ca, Mg, Na, K analysis	08/92 - 12/96
Theresa Ingersoll	Sample receipt and processing	03/85 - 12/96
Kenni James	Lab Quality Assurance Specialist	10/87 - 12/96
Mark Peden	Laboratory Manager	07/78 - 12/96
Jeffrey Pribble	Sample receipt, supply procurement and shipping, and Lab Site Liaison	07/87 - 12/96
Jane Rothert	AIRMoN Coordinator	05/92 - 12/96
Pamela Scales	Sample processing, pH and conductivity analysis	10/96 - 12/96
Kaye Surratt	Sample processing	08/96 - 12/96
Angela Weddle	pH and conductivity analysis	10/89 - 12/96
	Sample Processing Coordinator	06/95 - 12/96

TABLE I-2. Central Analytical Laboratory Analytical Staff, 1997

Staff Member	*Job Function*	*Period of Employment*
Sue Bachman	Ammonium (NH_4) analysis	08/80 - 12/97
	Ca, Mg, Na, K analysis	11/88 - 12/97
	ortho-Phosphate (PO_4) analysis	01/94 - 12/97
Phyllis Ballard	Bucket and bottle cleaning	09/97 - 12/97
Brigita Demir	Anions analysis	09/81 - 12/97
Lori Henry	AIRMoN sample processing and Ca, Mg, Na, K analysis	08/92 - 12/97
Theresa Ingersoll	Sample receipt and processing	03/85 - 12/97
Kenni James	Lab Quality Assurance Specialist	10/87 - 06/97
Mark Peden	Laboratory Manager	07/78 - 12/97
Jeffrey Pribble	Sample receipt, supply procurement and shipping, and Lab Site Liaison	07/87 - 12/97
Jane Rothert	AIRMoN Coordinator	05/92 - 12/97
	Lab Quality Assurance Specialist	07/97 - 12/97
Pamela Scales	pH and conductivity analysis	10/96 - 08/97
	Sample Processing Coordinator	01/97 - 08/97
Kaye Surratt	Sample processing	08/96 - 04/97
Angela Weddle	Sample Processing Coordinator	06/95 - 12/96
	pH and conductivity analysis	10/89 - 12/97
Laura Zangori	pH and conductivity analysis and Sample Processing Coordinator	08/97 - 12/97

The employees performing the sample analyses are responsible for implementing quality control (QC) procedures within their analytical scheme. Analytical methods are revised as technology improves and as new instruments are purchased. Each time an instrument update occurs, a comprehensive study is performed to assure comparability of the data and detection limits are verified and reported. Table I-3 lists the CAL method detection limits (MDLs) for the ions of interest as well as the method. Neither the MDLs nor the analytical methods changed in 1996 or 1997.

From the beginning of the network, the analytical data have been entered into a large central database. These data were hand-entered using a double-entry system as a means of verification in the early years. Currently, the data from the atomic absorption, ion chromatography, and flow injection instruments are electronically transferred to the database. The pH and conductivity measurements are still double-entered manually. Once the data are verified and checked by the Coordination Office (1996) or the Program Office (1997), they are loaded onto a World Wide Web server and are available for general usage. Table I-4 lists the percentile concentration values for all samples of volume greater than 35 mL analyzed by the CAL in 1996. Table I-5 lists the percentile concentration values for 1997. Both tables also include the number of “wet” (W) samples and the mean and median sample volumes for each year. The concentration values show a slight decrease in all parameters except for ammonium when compared with the median percentile concentration values found in 1983, the year corresponding to the expansion of the network to include the entire United States. Table I-6 (1996) and Table I-7 (1997) list the percentile concentration values for the AIRMoN samples for 1996 and 1997 where sample volume (wet samples only) was large enough for a complete chemical analysis.

The ion concentrations displayed on Tables I-4 and I-5 indicate the dilute nature of the precipitation samples analyzed in the laboratory. In order for the data to be meaningful, it is necessary to incorporate an extensive quality assurance (QA) program in the laboratory. Several components of the QA program have evolved from the time the very first sample was analyzed. The Network Quality Assurance Plan (1) summarizes the methods used to document the analysis of each sample. The various facets of the program have been modified and refined over the years. The quality control (QC) samples are known to the analysts, who use them as guides to ensure the accuracy of their work. Other samples are unknown or blind to the analyst and are valuable ways of assessing the actual bias and/or precision of samples in the NADP/NTN/AIRMoN daily queue. Extensive analysis of blank solutions are performed every week in order to identify and/or eliminate sources of contamination. Participation in several international laboratory intercomparison studies in addition to the mandated study performed by the U. S. Geological Survey (USGS) enables the CAL to evaluate the quality of its work compared to peer laboratories throughout the United States, Canada, and Europe. The history of the CAL program can be found in the Laboratory QA reports published annually since 1986 and available from the CAL or the Program Office (2-14). This report presents and discusses summaries of the results of QA programs in place in 1996 and 1997.

TABLE I-3. Method Detection Limits (MDLs) for Precipitation Analysis

Ion	*MDL (mg/L)*	*Dates*	*Method*
Calcium	0.02	07/78 - 10/80	Flame atomic absorption
	0.009	10/80 - 12/97	
Magnesium	0.002	07/78 - 10/80	Flame atomic absorption
	0.003	10/80 - 12/97	
Sodium	0.004	07/78 - 10/80	Flame atomic absorption
	0.003	10/80 - 12/97	
Potassium	0.004	07/78 - 10/80	Flame atomic absorption
	0.003	10/80 - 12/97	
Ammonium	0.02	07/78 - 12/97	Automated phenate, colorimetric
Sulfate	0.10	07/78 - 05/85	Automated methyl thymol blue
	0.03	05/85 - 12/97	Ion chromatography
Nitrate/Nitrite	0.02	07/78 - 05/85	Automated cadmium reduction
Nitrate	0.03	05/85 - 12/97	Ion chromatography
Chloride	0.05	07/78 - 03/81	Automated ferricyanide,
	0.02	03/81 - 05/85	Colorimetric
	0.03	05/85 - 12/97	Ion chromatography
ortho-Phosphate	0.003	07/78 - 02/86	Automated ascorbic acid,
	0.01	02/86 - 07/87	Colorimetric
	0.02	07/87 - 12/93	Ion chromatography
	0.003	01/94 - 12/97	Automated ascorbic acid, colorimetric

TABLE I-4. Percentile Concentration Values of Chemical and Physical Parameters Measured by the CAL in NADP/NTN Precipitation Samples with Volumes Greater than 35 mL, 1996

	Percentile Concentration Value (mg/L)									
Parameter	*Min.*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*99th*	*Max.*
Calcium	-0.009	0.013	0.021	0.044	0.105	0.239	0.498	0.782	2.015	19.07
Magnesium	-0.003	0.003	0.005	0.010	0.021	0.043	0.082	0.121	0.315	2.090
Sodium	0.006	0.026	0.032	0.050	0.089	0.180	0.379	0.623	2.152	15.850
Potassium	-0.003	-0.003	0.004	0.009	0.018	0.035	0.067	0.105	0.312	4.200
Ammonium	-0.02	-0.02	0.03	0.09	0.20	0.41	0.69	0.91	1.63	5.86
Sulfate	-0.03	0.11	0.20	0.49	1.04	1.84	2.90	3.77	6.13	19.76
Nitrate	-0.03	0.14	0.25	0.55	1.05	1.81	2.76	3.67	6.02	15.98
Chloride	-0.03	0.04	0.08	0.08	0.15	0.28	0.62	1.05	3.37	22.42
ortho-Phosphate	-0.003	-0.003	-0.003	-0.003	-0.003	-0.003	-0.003	-0.003	0.01	1.580
pH (units)	3.51	4.14	4.26	4.49	4.81	5.28	5.82	6.23	6.82	7.67
Conductivity (µS/cm)	1.3	3.0	4.2	7.4	12.6	21.2	32.6	42.3	68.0	169.2

Notes: Number of samples = 6982; mean sample volume = 1618 mL; median sample volume = 1023 mL. The negative values in the table are the negative of the method detection limit (MDL) for that ion.

TABLE I-5. Percentile Concentration Values of Chemical and Physical Parameters Measured by the CAL in NADP/NTN Precipitation Samples with Volumes Greater than 35 mL, 1997

	Percentile Concentration Value (mg/L)									
Parameter	*Min.*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*99th*	*Max.*
Calcium	-0.009	0.014	0.021	0.042	0.095	0.215	0.444	0.687	1.521	19.6
Magnesium	-0.003	0.003	0.005	0.009	0.018	0.037	0.073	0.111	0.257	1.43
Sodium	0.003	0.016	0.021	0.031	0.056	0.120	0.281	0.490	1.620	16.4
Potassium	-0.003	-0.003	0.004	0.009	0.017	0.034	0.063	0.094	0.241	4.85
Ammonium	-0.02	-0.02	0.03	0.08	0.19	0.40	0.68	0.93	1.56	6.93
Sulfate	-0.03	0.14	0.22	0.49	1.05	1.85	2.89	3.67	5.79	15.0
Nitrate	-0.03	0.19	0.31	0.58	1.09	1.85	2.84	3.65	5.98	21.7
Chloride	-0.03	0.03	0.04	0.06	0.11	0.22	0.49	0.86	2.65	14.4
ortho-Phosphate	-0.003	-0.003	-0.003	-0.003	-0.003	-0.003	-0.003	-0.003	0.020	0.903
pH (units)	3.51	4.14	4.25	4.46	4.79	5.19	5.70	6.18	6.71	7.83
Conductivity (µS/cm)	1.5	3.4	4.5	7.4	12.5	21.3	32.9	40.8	65.0	191.6

Notes: Number of samples = 7118; mean sample volume = 1467.43 mL; median sample volume = 908.5 mL. The negative values in the table are the negative of the method detection limit (MDL) for that ion.

TABLE I-6. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/AIRMoN Precipitation, 1996

Percentile Concentration Values (mg/L)

Parameter	*Min.*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*Max.*
Calcium	-0.001	0.009	0.018	0.044	0.099	0.225	0.478	0.805	3.25
Magnesium	-0.001	0.001	0.003	0.008	0.023	0.063	0.154	0.248	1.55
Sodium	0.000	0.005	0.008	0.018	0.055	0.262	0.858	1.71	13.3
Potassium	-0.003	0.003	0.004	0.010	0.021	0.044	0.086	0.129	7.36
Ammonium	0.00	0.04	0.06	0.14	0.28	0.54	1.05	1.42	5.72
Sulfate	0.03	0.34	0.62	1.03	1.87	3.14	5.35	7.12	23.45
Nitrate	0.02	0.31	0.46	0.83	1.56	3.05	4.90	6.28	21.88
Chloride	0.00	0.03	0.05	0.08	0.19	0.57	1.52	3.37	22.71
ortho-Phosphate	0.000	0.000	0.000	0.000	0.004	0.007	0.015	0.030	8.6
pH (units)	3.28	3.78	3.92	4.15	4.37	4.61	4.95	5.21	7.06
Conductivity (µS/cm)	1.6	8.2	10.8	17.0	26.7	42.5	68.3	90.1	278.2

Notes: Number of wet samples = 998; mean sample volume = 714.5 mL; median sample volume = 369.4 mL. Negative values indicate actual measured concentrations, not method detection limits (MDLs).

TABLE I-7. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/AIRMoN Precipitation, 1997

Percentile Concentration Values (mg/L)

Parameter	*Min.*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*Max.*
Calcium	-0.006	0.013	0.021	0.043	0.090	0.240	0.525	0.802	4.22
Magnesium	-0.001	0.002	0.003	0.008	0.023	0.071	0.149	0.225	2.87
Sodium	0.001	0.006	0.009	0.018	0.047	0.270	0.885	1.58	24.5
Potassium	-0.001	0.004	0.006	0.011	0.023	0.047	0.090	0.144	2.18
Ammonium	-0.01	0.05	0.08	0.14	0.30	0.58	1.05	1.40	15.7
Sulfate	0.06	0.49	0.70	1.19	1.92	3.44	5.38	6.91	20.6
Nitrate	0.08	0.35	0.48	0.90	1.64	3.04	5.00	6.39	20.6
Chloride	0.00	0.03	0.05	0.09	0.20	0.63	1.84	296.	44.0
ortho-Phosphate	0.00	0.00	0.00	0.00	0.004	0.012	0.030	0.056	1.33
pH (units)	3.36	3.81	3.92	4.11	4.33	4.57	4.85	5.13	6.65
Conductivity (µS/cm)	2.7	8.75	11.4	17.6	27.4	44.1	69.6	87.5	226.

Notes: Number of samples = 1063; mean sample volume = 594.3 mL; median sample volume = 306.1mL. Negative numbers in this table are actual values measured, not method detection limits (MDLs).

II. LABORATORY QUALITY ASSURANCE - A GENERAL DESCRIPTION

This report summarizes the results of the quality assurance (QA) program in effect at the CAL for 1996 and 1997. Table II-1 summarizes the various QA/Quality Control (QC) components and their frequency of occurrence. The QA of chemical and physical measurements begins in the field where pH and specific conductance are measured soon after sample collection and prior to shipping. Quality Control Standard (QCS) solutions are formulated and prepared at the CAL and shipped to the sites. The two QCS solutions in 1996 and 1997 were a potassium chloride solution with a specific conductance of 75 microsiemens per centimeter (µS/cm) and a dilute nitric acid/sodium chloride solution with a pH of 4.9 and a specific conductance of 14 µS/cm. The first solution is used to calibrate the conductivity cell and to correct the conductivity readings to ambient temperature; the second solution is used as the QCS for the pH measurement. Since calibration buffer solutions are of high ionic strength, it is necessary to verify that the probe will measure solutions that are similar in ionic strength to precipitation samples. The second solution is also used as a conductivity QCS.

When the field samples reach the CAL, they are unpacked carefully. The information and requests written on the field forms are noted. The samples are then transported to sample processing where they are visually inspected and assigned a sequential number. After the identifying laboratory number is assigned to the samples, the 1-liter shipping bottles are taken to the laboratory where pH and conductivity are measured after which each sample is filtered into a 60-mL round bottle using a 0.45 micrometer (µm) filter. When there is sufficient volume, the samples are filtered into two smaller bottles: one in a round bottle for immediate chemical analysis, the other into a square bottle for archival purposes. Samples from the Atmospheric Integrated Research Monitoring Network (AIRMoN) are never filtered, but are kept at 4 degrees Celsius in the 250-mL bottles into which they were decanted at the site during shipping and storage.

The pH meter is calibrated with commercially prepared buffer solutions of pH 7 and 4. The ability of the electrode to measure low ionic strength precipitation solutions is verified by measuring two solutions of simulated rainwater at ionic strengths emulating the 25th and 75th percentile concentrations of the network. These solutions are made in-house and are tested extensively prior to being made available for use as QCS solutions. These solutions, referred to as Faux Rain 25 (FR25) and Faux Rain 75 (FR75), are used as QCS solutions for the entire suite of measurements except for phosphate, which is too unstable, especially at the low concentrations found in NADP samples (15). U.S. Environmental Protection Agency (USEPA) nutrient concentrates are diluted and used for phosphate QCS.

After filtration, the samples in the round 60-mL bottles are placed on a tray that contains nine rows of 12 bottles each. The tray is taken to the main laboratory building and placed with other sample trays containing samples awaiting analysis for the major ions. AIRMoN samples are stored on trays in the walk-in cooler in the sample processing area and are analyzed in a specified order: pH and conductivity; ammonium and phosphate; chloride, nitrate, and sulfate; and finally calcium, magnesium, sodium, and potassium. Analysts select the trays containing the samples with numbers in the next sequence and analyze them either by atomic absorption, ion chromatography, or flow injection automated colorimetric analyses. These instruments are standardized using solutions that bracket the expected concentration range of the samples. Samples with concentrations outside the

TABLE II-1. NADP/NTN Laboratory QC/QA Program Summary, 1996 and 1997

I. Daily
  A. Standardize instruments and verify standardization curves using QCS.
    1. CAL-formulated solutions of simulated rainwater, QCS, represent the 25th and 75th percentile concentrations of network samples.
    2. Measure QCS every 12-15 samples depending on the instrumentation.
    3. Repeat standardization as indicated by the QCS measurements.
    4. Record and plot QCS values on daily control charts.
  B. Prepare records of standards preparation and update instrument maintenance.

II. Weekly
  A. Analyze blanks.
    1. Deionized (DI) water.
    2. Filter leachates using DI water and simulated rainwater.
    3. Upright bucket leachates using DI water and simulated rainwater.
    4. Liter bottle leachates using DI water and simulated rainwater.
    5. Snap-on lid leachates using DI water and simulated rainwater.
  B. Analyze internal blind audit samples from sites SWS1, SWS2, and SWS3.
    1. SWS1: High Purity Standards (HPS) simulated rainwater I and II, unfiltered.
    2. SWS2: DI water and pH 4.3 nitric acid, unfiltered.
    3. SWS3: all four of the above solutions in rotation, filtered.
  C. Split 2 percent of NTN samples for duplicate analysis.
  D. Split 2 percent of AIRMoN samples for duplicate analysis.
  E. Analyze internal blind audit sample for AIRMoN from site IL11.
  F. Validate QCS prior to shipment to sites.

III. Monthly
  A. Leach AIRMoN 250-mL HDPE bottles with simulated rainwater; analyze leachates with weekly blanks.
  B. Collect AIRMoN field blanks and analyze with weekly blanks.
  C. Inspect control charts (generated from QCS responses).
  D. Evaluate internal blind audit and replicate data from printouts.
  E. Select samples for reanalysis by computer based on ion balance and conductance calculations.
    1. Evaluate reanalysis data.
    2. Suggest data changes to data management.
  F. Measure USGS interlaboratory comparison samples measured every 2 weeks and send to the USGS in Denver once every 3 months.

TABLE II-1. (concluded)

- IV. Semiannually
  - A. Prepare subcommittee reports for spring and fall NADP/NTN meetings.
  - B. Participate in external interlaboratory comparisons.

- V. Annually
  - A. Submit QA report for publication.
  - B. Participate in external interlaboratory comparisons (some intercomparison studies are annual, others are semiannual).

expected range of standardization are diluted and reanalyzed using the diluted value to calculate the concentration of that parameter. The standardization curve is then verified with the two QCS solutions, FR25 and FR75. The values of these two solutions are recorded daily and summarized monthly for control charts, and monthly means and standard deviations are calculated. These statistics represent optimum analytical conditions. These standards are analyzed immediately after standardization solutions and blanks have been analyzed and then regularly throughout the run. The analyst is fully aware of their concentration values and uses them to ascertain whether or not the instrument initially is standardized properly and then is maintaining its standardized analytical curve throughout the day.

Each week blank solutions are collected from various sources and submitted as a batch to the laboratory for analysis as blank samples. These samples are used to indicate possible sources of contamination both from the samples collection and shipping activity and the materials used in the laboratory. The deionized (DI) water used for standards preparation, bucket and bottle washing, rinse water, and filter leaching is monitored regularly. Samples are collected each week from the DI water faucets in the atomic absorption laboratory, the sample preparation laboratory, and the bucket washing laboratory. The DI water and FR25 blank solutions are allowed to remain in sample collection buckets and lids, shipping bottles, and AIRMoN bottles for 24 hours before being decanted into 60-mL bottles for analysis. These leachates, along with filtrates from two filters, complete the weekly blank solutions.

Other weekly components of the program are three samples submitted as internal blinds and four or five samples that are split so that the originals and duplicates are separated for analysis. The duplicates are submitted with new sample identification numbers unknown to the analysts and are analyzed in the order of their new number, approximately 50 samples away from the original sample. The duplicates, therefore, are analyzed at a different time than the original samples, possibly on a separate day, with new calibration standards and check samples. AIRMoN uses split samples that are identical to the NADP duplicate program. In addition, a sample of known concentration is submitted by the IL11 Site Operator as a real precipitation sample on a weekly basis. This internal blind goes through the entire AIRMoN system of sample log-in through final analysis to monitor all laboratory systems.

Events that occur on a monthly rotation are the submission of reanalysis lists to the laboratory so that randomly selected samples and samples with an ion or conductance imbalance can be reanalyzed. Archival samples, if available, are used to support either the original values or the reanalysis values if there is a large discrepancy in the analytical results. Every two weeks, the USGS ships the CAL intercomparison samples, which are analyzed as a group upon their arrival. The analysts know that the samples are intercomparison samples; however, they do not know the concentrations of the parameters in the samples. Every three months, the results from these analyses are submitted, reviewed, and sent to the USGS in Denver.

Other external agencies that conduct interlaboratory comparisons operate on an annual or semiannual schedule. These samples are analyzed with network samples but are identified as interlaboratory comparison samples. The results of these studies are used to evaluate the performance of the CAL in relation to peer laboratories in North America, Europe, and the rest of the world.

III. DAILY QUALITY CONTROL PROCEDURES

Each morning prior to analysis, the analysts prepare reagents and standards and evaluate the performance of the analytical instrumentation. Standards preparation and instrument maintenance information are recorded in notebooks that are kept in the individual laboratories. Calibration standards are analyzed according to the standard operating procedure of the method and are followed by the measurement of the quality control solutions (QCS) in order to confirm the validity of the calibration curve. Both FR25 and FR75 solutions are used to test the standards at two levels that are relevant to the precipitation samples being measured. Each time QCS are measured throughout the sample run, the values are recorded and graphed on a daily control chart located near the instrument. These daily data are combined monthly for the monthly control charts kept on file in the Quality Assurance (QA) Coordinator's office. The same data are compiled and summarized at the end of each calendar year: Table III-1 (1996) and Table III-2 (1997).

The data presented in these tables represent bias and precision estimates under optimum conditions. Since the precision and bias in these tables were generated using QCS rather than precipitation samples, they represent the optimum precision and bias to be expected from the analysis of the samples. They are comparable to previous years and fall within the specifications the laboratory is expected to meet. When the absolute bias exceeds the critical concentration, the bias is considered to be statistically significant (see Appendix A, Glossary of Terms). Refer to the laboratory portion of the Network QA Plan (1) for more information.

TABLE III-1. Analytical Bias and Precision Determined from Analysis of Simulated Rain QCS, 1996

Parameter	*Target Concentration (mg/L)*	*Measured Concentration (mg/L)*	*Number of Replicates*	*Bias (mg/L)*	*Bias %*	*Precision (mg/L)*	*Precision %*	*Critical Concentration (mg/L)*	*Statistically Significant Bias?*
Calcium	0.072[a]	0.073	1497	0.001	1.8	0.002	2.8	0.001	YES
	0.290[b]	0.291	509	0.001	0.3	0.005	1.8	0.003	NO
Magnesium	0.017	0.017	1382	-0.0	-1.0	0.001	4.5	0.000	NO
	0.069	0.067	518	-0.002	-2.3	0.002	2.7	0.001	YES
Sodium	0.047	0.046	1466	-0.001	-1.1	0.001	2.4	0.001	NO
	0.193	0.192	529	-0.001	-0.3	0.003	1.6	0.002	NO
Potassium	0.014	0.014	1378	0.0	1.5	0.001	7.2	0.001	NO
	0.056	0.055	515	-0.001	-1.7	0.002	3.1	0.001	NO
Ammonium	0.09	0.09	497	-0.0	-3.5	0.01	10.7	0.01	NO
	0.37	0.37	352	0.0	0.6	0.01	3.1	0.01	NO
Sulfate	0.62	0.61	1050	-0.01	-1.1	0.01	1.3	0.00	YES
	2.54	2.54	1173	-0.0	-0.0	0.01	0.4	0.01	NO
Nitrate	0.47	0.46	1046	-0.01	-1.2	0.01	1.3	0.00	YES
	1.93	1.93	1171	-0.0	-0.0	0.02	0.8	0.01	NO
Chloride	0.13	0.13	1047	-0.0	-2.1	0.01	6.2	0.00	NO
	0.54	0.53	1171	-0.01	-2.7	0.01	2.4	0.01	YES
ortho-Phosphate	0.024	0.021	333	-0.003	-12.1	0.003	12.7	0.002	YES
	0.060	0.055	304	-0.005	-9.1	0.005	9.0	0.001	YES
pH units (µeq/L)	4.93(11.7)[c]	4.92(11.9)	1360	-0.01(0.2)	-0.11(1.3)	0.02(0.56)	0.4(4.7)	0.01(0.35)	NO
	4.35(44.7)	4.35(44.3)	1360	0.0(-0.3)	0.08(-0.8)	0.01(1.40)	0.3(3.2)	0.01(0.87)	NO
Conductivity (µS/cm)	7.2	7.2	761	-0.10	-0.01	0.13	1.8	0.08	NO
	27.6	27.7	761	0.09	0.3	0.12	0.4	0.07	YES

Notes: [a] The first set of values for each parameter is for the 25th percentile solution. [b] The second set of values for each parameter is for the 75th percentile solution. [c] The pH data in parentheses are hydrogen ion concentrations expressed in microequivalents per liter. See Appendix A for definitions and formulas for Bias, Standard Deviation, Precision, and Critical Concentrations.

TABLE III-2. Analytical Bias and Precision Determined from Analysis of Simulated Rain QCS, 1997

Parameter	*Target Concentrations (mg/L)*	*Measured Concentrations (mg/L)*	*Number of Replicates*	*Bias (mg/L)*	*Bias (%)*	*Precision (mg/L)*	*Precision (%)*	*Critical Concentration (mg/L)*	*Statistically Significant Bias?*
Calcium	0.074[a]	0.073	1372	-0.001	-1.4	0.002	2.7	0.001	NO
	0.285[b]	0.287	502	0.002	0.7	0.008	2.8	0.006	NO
Magnesium	0.016	0.016	1350	0.0	0.0	0.0007	4.7	0.0005	NO
	0.065	0.065	486	0.0	0.0	0.002	3.1	0.006	NO
Sodium	0.048	0.046	1440	-0.002	-4.2	0.001	2.2	0.0007	YES
	0.185	0.184	518	-0.001	-0.5	0.003	1.6	0.008	NO
Potassium	0.014	0.013	1373	-0.001	-7.1	0.001	7.7	0.0007	YES
	0.052	0.053	503	0.001	1.9	0.002	3.8	0.004	NO
Ammonium	0.088	0.085	1016	-0.003	-3.4	0.008	8.9	0.005	NO
	0.38	0.35	485	-0.03	-7.9	0.01	2.9	0.003	YES
Sulfate	0.61	0.62	1293	0.01	1.6	0.009	1.5	0.003	YES
	2.49	2.50	1213	0.01	0.4	0.01	0.4	0.003	YES
Nitrate	0.46	0.47	1289	0.01	2.2	0.007	1.5	0.004	YES
	1.88	1.89	1192	0.01	0.5	0.01	0.5	0.003	YES
Chloride	0.13	0.13	1293	0.0	0.0	0.008	6.2	0.006	NO
	0.50	0.52	1238	0.02	4.0	0.01	1.9	0.08	NO
ortho-Phosphate	0.024	0.021	401	-0.003	-12.5	0.003	14.3	0.002	YES
	0.060	0.056	246	-0.003	-5.1	0.004	7.1	0.003	YES
pH units	4.92(12.0)[c]	4.91(12.2)	1455	-0.01(0.2)	-0.2(1.7)	0.03(0.77)	0.6(6.3)	0.02(0.5)	NO(NO)
(µeq/L)	4.36(43.6)	4.36(44.0)	1451	0(0.4)	0(0.9)	0.02(1.7)	0.5(3.9)	0.01(1.11)	NO(NO)
Conductivity	7.20	7.29	937	0.09	1.2	0.19	2.6	0.12	NO
(µS/cm)	27.1	27.2	937	0.1	0.4	0.29	1.1	0.19	NO

Notes: [a] The first set of values for each parameter is for the 25th percentile solution. [b] The second set of values for each parameter is for the 75th percentile solution. [c]The pH data in parentheses are hydrogen ion concentrations expressed in microequivalents per liter. See Appendix A for definitions and formulas for Bias, Standard Deviation, Precision, and Critical Concentration.

IV. WEEKLY QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES

Three Quality Assurance (QA) activities occur on a weekly basis: three solutions are submitted as internal blind samples for which only the QA Specialist knows the concentrations; 2 percent of the network samples are split and analyzed in duplicate; and 17-19 blanks and container leachates are bottled and analyzed. AIRMoN internal blinds are also submitted on a weekly schedule.

A. Internal Blind Audit

1. NADP/NTN

Each week the QA Coordinator submits three solutions of known concentrations and accompanying field forms to the sample processing area where laboratory identification numbers are assigned. These samples are taken into the laboratory with the network samples and treated as such except that two of the three samples bypass the filtering process. The sites for these samples are coded as SWS1, SWS2, and SWS3. In 1996 and 1997, SWS1 samples were High Purity Standards Simulated Rainwater I (HPS-SRI) and II (HPS-SRII), which were alternated weekly. SWS2 samples were DI water from the ion chromatography laboratory and pH 4.3 nitric acid QCS solution, which were also alternated weekly. SWS1 and SWS2 samples are not filtered. SWS3 samples were HPS-SRI, HPS-SRII, DI water, and pH 4.3 nitric acid QCS samples submitted in rotation. SWS3 samples are filtered.

Tables IV-1 – IV-4 summarize the 1996 data from the weekly internal blind audit samples. Tables IV-5 – IV-8 summarize the 1997 data. It is important to remember that the blind sample population is considerably smaller than that of the QCS. Blind samples may fall anywhere in the sample queue, for example, right after calibration or prior to the next QCS. The bias and precision estimates derived are, therefore, more like those of the real samples sent from the sites. Samples from SWS1 and SWS2 show fewer contaminants and less variability than the filtered counterparts from SWS3 (which has an even smaller sample population for each solution). The bias percentages for most of the parameters are higher for the blind samples than for the QCS, the exceptions being, for 1996, the higher calcium concentration, the lower sodium concentration, the lower magnesium concentration, the lower ammonium concentration, and the lower chloride concentration. Percent relative standard deviation (RSD) is more variable than percent bias when the two groups of solutions are compared. The percent RSD is higher for the blind samples than for the QCS for the cations analyzed by atomic absorption except for magnesium, higher for ammonium, and similar for the lower concentrations of the anions analyzed by ion chromatography. The certified pH value for HPS-SRI, 4.40, is considerably higher than the value measured at the CAL. When an ion balance is calculated using the certified concentrations, the pH value 4.31 is obtained. This value is much more in agreement with the value, 4.29, that is obtained at the CAL. Using the calculated pH for the High Purity Standards Standard Reference Material results in a bias for the CAL measurements of -0.02 pH units and -1.8 µeq/L H or a percent bias of -0.46 percent and -3.7 percent, respectively.

For 1997, shown in Tables IV-5 – IV-8, two different concentrations of both HPS-SRI and HPS-SRII were used. For Lot # 690826 (HPS-SRI) and #691025 (HPS-SRII), the percent bias for the lower concentration of magnesium was the same for the internal blind audit sample as for the

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, 1996

Parameter	*Target Concentration (mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias %*	*Precision (mg/L)*	*Precision (%)*
Calcium	0.015[a]	0.014	25	-0.001	-6.7	0.006	42.9
	0.049[b]	0.055	24	0.006	12.2	0.004	7.3
Magnesium	0.026	0.026	25	0.0	0.0	0.001	3.8
	0.050	0.048	24	-0.002	-4.0	0.001	2.1
Sodium	0.20	0.20	25	0.0	0.0	0.010	5.0
	0.39	0.41	24	0.02	5.1	0.022	5.4
Potassium	0.050	0.054	25	0.004	8.0	0.006	11.1
	0.100	0.107	24	0.007	7.0	0.011	10.3
Ammonium	0.100[c]	0.10	25	0.0	0.0	0.013	13.0
	1.0	1.01	24	0.01	1.0	0.051	5.0
Sulfate	2.5	2.6	25	0.1	4.0	0.027	1.0
	10.1	10.3	24	0.2	2.0	0.24	2.3
Nitrate	0.50	0.51	25	0.01	2.0	0.009	1.8
	7.1	7.18	24	0.08	1.1	0.16	2.2
Chloride	0.25	0.25	25	0.0	0.0	0.01	4.0
	0.97	1.03	24	0.06	6.2	0.02	1.9
pH units (µeq/L)	4.40(39.8)[d]	4.29(50.8)	25	-0.11(11)	-2.5(27.6)	0.018(2.07)	0.42(4.1)
	3.42(380)	3.61(248)	24	0.19(-132)	5.6(-34.7)	0.024(13.7)	0.66(5.5)
Conductivity (µS/cm)	23.2	25.8	25	2.6	11.2	0.56	2.2
	128.0	128.7	24	0.7	0.5	3.13	2.4

Notes: [a] The first set of values for each parameter is for HPS-SRI. [b] The second set of values for each parameter is for HPS-SRII. [c] Ammonium values are for information only since ammonium in these standards has been found to be unstable. [d] Values in parentheses represent hydrogen ion concentrations expressed as microequivalents per liter.

TABLE IV-2. Analytical Bias and Precision from Analysis of Internal Blind Audit Samples (SWS2), Deionized (DI) Water and pH 4.3 QCS, Unfiltered, 1996

Parameter	*Target Concentration[a] (mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias %*	*Precision (mg/L)*	*Precision (%)*
Calcium	<0.009[a]	<0.009	23			0.000	
	<0.009[b]	<0.009	25			0.001	
Magnesium	<0.003	<0.003	23			0.000	
	<0.003	<0.003	25			0.000	
Sodium	<0.003	<0.003	23			0.000	
	<0.003	0.004	25			0.006	138.0
Potassium	<0.003	<0.003	23			0.000	
	<0.003	0.004	25			0.006	149.1
Ammonium	<0.02	<0.02	23			0.00	
	<0.02	<0.02	25			0.01	
Sulfate	<0.03	<0.03	23			0.00	
	<0.03	<0.03	25			0.00	
Nitrate	<0.03	<0.03	23			0.00	
	3.11	3.23	25	0.12	3.9	0.06	2.0
Chloride	<0.03	<0.03	23			0.02	
	<0.03	<0.03	25			0.01	
pH (units)	5.65(2.24)[c]	5.60(2.55)	23	-0.05(0.31)	-0.8(13.9)	0.11(0.57)	1.9(22.5)
µeq/L	4.30(50.1)	4.32(47.89)	25	0.02(-2.2)	0.50(-4.4)	0.02(1.66)	0.3(3.5)
Conductivity	0.8	1.0	23	0.2	23.4	0.2	19.3
(µS/cm)	21.8	21.7	25	-0.1	-0.4	0.6	2.6

Notes: For calculations, method detection limits (MDL) are given the value of 0.5 x (MDL). [a] The first set of values for each parameter is for DI water. [b] The second set of values for each parameter is for pH 4.3 QCS. [c] The pH data in parentheses are hydrogen ion concentrations in microequivalents per liter.

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, 1996

Parameter	*Mean Target Concentrations (mg/L)*	*Mean Measured Concentrations (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias (%)*	*Precision (mg/L)*	*Precision (%)*
Calcium	0.015[a]	0.021	13	0.006	40	0.008	38.1
	0.049[b]	0.085	12	0.036	73.5	0.034	40
Magnesium	0.026	0.026	13	0.0	0.0	0.002	7.7
	0.050	0.059	12	0.009	18	0.020	33.9
Sodium	0.20	0.288	13	0.088	44	0.033	11.5
	0.39	0.524	12	0.134	34.4	0.060	11.5
Potassium	0.050	0.051	13	0.001	2.0	0.006	11.8
	0.100	0.102	12	0.002	2.0	0.004	3.9
Ammonium	0.100[c]	0.175	13	0.075	75	0.06	34.3
	1.0	1.04	12	0.04	4.0	0.05	4.8
Sulfate	2.5	2.52	13	0.02	0.8	0.06	2.4
	10.1	9.90	12	-0.2	-2.0	0.17	1.7
Nitrate	0.50	0.55	13	0.05	10	0.02	3.6
	7.1	7.01	12	-0.09	-1.3	0.14	2.0
Chloride	0.25	0.33	13	0.08	32	0.05	15.2
	0.97	1.09	12	0.12	12.4	0.05	4.6
pH units	4.40(39.8)[d]	4.30(50.4)	13	-0.1(10.6)	-2.3(26.6)	0.02(2.42)	0.5(4.8)
(µeq/L)	3.42(380)	3.60(251.5)	12	0.18(-128.5)	5.3(-33.8)	0.02(12.7)	0.6(5.0)
Conductivity	23.2	25.7	13	2.5	10.8	0.67	2.6
(µS/cm)	128.0	129.2	12	1.2	0.9	2.34	1.8

Notes: [a] The first set of values for each parameter is for HPS-SRI. [b] The second set of values for each parameter is for HPS-SRII. [c] Ammonium values are for information only since the ammonium in these standards has been found to be unstable by High Purity Standards. [d] Values in parentheses represent hydrogen ion concentrations expressed in microequivalents per liter.

TABLE IV-4. Analytical Bias and Precision from Analysis of Internal Blind Audit Samples (SWS3), Deionized (DI) Water and pH 4.3 QCS, Filtered, 1996

Parameter	*Target Concentration[a] (mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias %*	*Precision (mg/L)*	*Precision (%)*
Calcium	<0.009[a]	<0.009	12			0.002	
	<0.009[b]	<0.009	12			0.005	
Magnesium	<0.003	<0.003	12			0.000	
	<0.003	<0.003	12			0.001	
Sodium	<0.003	0.071	12	0.069	3433.3	0.041	57.6
	<0.003	0.061	12	0.059	2966.7	0.036	58.0
Potassium	<0.003	<0.003	12			0.002	
	<0.003	<0.003	12			0.001	
Ammonium	<0.02	0.05	12	0.04	425.0	0.06	100.0
	<0.02	0.06	12	0.05	508.3	0.05	88.3
Sulfate	<0.03	<0.03	12			0.00	
	<0.03	<0.03	12			0.00	
Nitrate	<0.03	0.06	12	0.04	220.8	0.03	46.8
	3.11	3.18	12	0.07	2.3	0.07	2.2
Chloride	<0.03	0.09	12	0.07	345.8	0.05	57.9
	<0.03	0.07	12	0.05	250.0	0.04	61.4
pH units	5.65(2.24)[c]	5.59(2.60)	12	-0.06(0.36)	-1.1(16.3)	0.08(0.45)	1.4(17.4)
(μeq/L)	4.30(50.1)	4.32(47.34)	12	0.02(-2.76)	0.6(-5.5)	0.01(1.55)	0.2(3.3)
Conductivity	0.8	1.0	12	0.2	30.2	0.2	22.4
(μS/cm)	21.8	21.6	12	-0.2	-0.9	0.7	3.2

Notes: For calculations, method detection limits (MDL) are given the value of 0.5 x (MDL). [a] The first set of values for each parameter is for DI water. [b] The second set of values for each parameter is for pH 4.3 QCS. [c] The pH data in parentheses are hydrogen ion concentrations in microequivalents per liter.

TABLE IV-5a. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS1), High Purity Standards Simulated Rainwater I (HPS-SRI, lot #690826) and II (HPS-SRII, lot #691025), Unfiltered, 1997

Parameter	*Target Concentration (mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias %*	*Precision (mg/L)*	*Precision (%)*
Calcium	0.015[a]	0.016	25	0.001	6.7	0.003	18.8
	0.051[b]	0.050	17	-0.001	-2.0	0.002	4.0
Magnesium	0.025	0.025	25	0.0	0.0	0.001	4.0
	0.051	0.046	17	-0.005	-9.8	0.0008	1.7
Sodium	0.21	0.227	25	0.017	8.1	0.013	5.7
	0.37	0.39	17	0.02	5.4	0.011	2.8
Potassium	0.050	0.046	25	-0.004	-8.0	0.002	4.3
	0.099	0.100	17	0.001	10.1	0.003	3.0
Ammonium	0.100[c]	0.09	25	-0.01	-10.	0.0095	10.6
	1.0	0.98	17	-0.02	-2.0	0.044	4.5
Sulfate	2.5	2.71	25	0.21	8.4	0.027	1.0
	10.1	10.1	17	0.0	0.0	0.12	1.2
Nitrate	0.50	0.54	25	0.04	8.0	0.017	3.1
	7.0	7.05	17	0.05	0.7	0.065	0.92
Chloride	0.25	0.25	25	0.0	0.0	0.014	5.6
	0.98	1.0	17	0.02	2.0	0.022	2.2
pH units	4.30(50.1)[d]	4.29(51.6)	25	-0.01(1.5)	-0.2(3.0)	0.022(2.64)	0.51(5.1)
(µeq/L)	3.33(467.7)	3.62(242.7)	17	0.29(-225)	8.7(-48.1)	0.017(9.11)	0.47(3.8)
Conductivity	25.9	26.2	25	0.3	1.2	0.62	2.4
(µS/cm)	130.6	125.8	17	-4.8	-3.7	1.29	1.0

Notes: [a] The first set of values for each parameter is for HPS-SRI. [b] The second set of values for each parameter is for HPS-SRII. [c] Ammonium values are for information only since ammonium in these standards has been found to be unstable. [d] Values in parentheses represent hydrogen ion concentrations expressed as microequivalents per liter.

TABLE IV-5b. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS1), High Purity Standards Simulated Rainwater I (HPS-SRI, lot #691219) and II (HPS-SRII, lot #691218), Unfiltered, 1997

Parameter	*Target Concentration (mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias %*	*Precision (mg/L)*	*Precision (%)*
Calcium	0.015[a]	0.015	1	0.0	0.0		
	0.053[b]	0.052	9	-0.001	-1.9	0.007	13.5
Magnesium	0.022	0.023	1	0.001	4.5		
	0.050	0.048	9	-0.002	-4.0	0.002	4.2
Sodium	0.18	0.20	1	0.02	11.1		
	0.37	0.40	9	0.03	8.1	0.078	19.5
Potassium	0.052	0.049	1	-0.003	-5.8		
	0.099	0.100	9	0.001	1.0	0.002	2.0
Ammonium	0.100[c]	0.08	1	-0.02	-20		
	1.0	0.96	9	-0.04	-4.0	0.022	2.3
Sulfate	2.5	2.51	1	0.01	0.4		
	10.1	10.0	9	-0.1	-0.99	0.12	1.2
Nitrate	0.50	0.52	1	0.02	4.0		
	7.0	7.09	9	0.09	1.3	0.086	1.2
Chloride	0.25	0.22	1	-0.03	12.		
	0.98	1.02	9	0.04	4.1	0.064	6.3
pH units	4.11(77.6)[d]	4.30(50.1)	1	0.19(-27.5)	4.6(-35.4)		
(µeq/L)	3.43(371.5)	3.62(238.9)	9	0.19(-132.6)	5.5(-35.7)	0.019(10.6)	0.5(4.4)
Conductivity	21.2	24.9	1	3.7	17.5		
(µS/cm)	116.5	125.6	9	9.1	7.8	1.44	1.

Notes: [a] The first set of values for each parameter is for HPS-SRI. [b] The second set of values for each parameter is for HPS-SRII. [c] Ammonium values are for information only since ammonium in these standards has been found to be unstable. [d] Values in parentheses represent hydrogen ion concentrations expressed as microequivalents per liter.

TABLE IV-6. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS2), Deionized (DI) Water and pH 4.3 QCS, unfiltered, 1997

Parameter	*Target Concentration (mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias (%)*	*Precision (mg/L)*	*Precision (%)*
Calcium	<0.009[a]	<0.009	26				
	<0.009[b]	<0.009	26				
Magnesium	<0.003	<0.003	26				
	<0.003	<0.003	26				
Sodium	<0.003	<0.003	26			0.009	
	<0.003	0.004	26			0.011	275
Potassium	<0.003	<0.003	26				
	<0.003	<0.003	26				
Ammonium	<0.02	<0.02	26				
	<0.02	<0.02	26				
Sulfate	<0.03	<0.03	26				
	<0.03	<0.03	26				
Nitrate	<0.03	<0.03	26				
	3.11	3.25	26	0.14	4.5	0.045	1.4
Chloride	<0.03	<0.03	26				
	<0.03	<0.03	26				
pH units	5.65(2.24)[c]	5.59(2.61)	26	-0.06(0.37)	-1.06(16.5)	0.06(0.34)	1.1(13.0)
(µeq/L)	4.30(50.1)	4.32(48.1)	26	0.02(-2.0)	0.47(-4.0)	0.02(1.93)	0.46(4.0)
Conductivity	0.8	1.02	26	0.22	27.5	0.18	17.6
(µS/cm)	21.8	21.8	26	0.0	0.0	0.38	1.7

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] The pH data in parentheses are hydrogen ion concentrations in microequivalents per liter.

TABLE IV-7a. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS3), High Purity Standards Simulated Rainwater I (HPS-SRI, lot #690826) and II (HPS-SRII, lot #691025), Filtered, 1997

Parameter	*Target Concentration (mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias %*	*Precision (mg/L)*	*Precision (%)*
Calcium	0.015[a]	0.025	13	0.010	66.7	0.008	32.0
	0.051[b]	0.067	10	0.016	31.4	0.014	20.9
Magnesium	0.025	0.026	13	0.001	4.0	0.001	3.8
	0.051	0.048	10	-0.003	-5.9	0.004	8.3
Sodium	0.21	0.264	13	0.054	25.7	0.017	6.4
	0.37	0.43	10	0.06	16.2	0.020	4.7
Potassium	0.050	0.044	13	-0.006	-12.0	0.001	2.3
	0.099	0.097	10	-0.002	-2.0	0.003	3.1
Ammonium	0.100[c]	0.10	13	0.0	0.0	0.013	13.0
	1.0	0.99	10	-0.01	-1.0	0.042	4.2
Sulfate	2.5	2.62	13	0.12	4.8	0.029	1.1
	10.1	9.74	10	-0.36	-3.6	0.10	1.0
Nitrate	0.50	0.58	13	0.08	16.0	0.025	4.3
	7.0	6.94	10	-0.06	-0.09	0.048	0.69
Chloride	0.25	0.27	13	0.02	8.0	0.023	8.5
	0.98	1.01	10	0.03	3.1	0.024	2.4
pH units	4.30(50.1)[d]	4.28(52.4)	13	-0.02(2.3)	-0.5(4.6)	0.02 (2.95)	0.47(5.6)
(µeq/L)	3.33(467.7)	3.62(237.4)	10	0.29(-230)	8.7(-49.2)	0.02(10.8)	0.55(4.5)
Conductivity	25.9	26.1	13	0.2	0.8	0.77	3.0
(µS/cm)	130.6	125.3	10	-5.3	-4.1	1.88	1.5

Notes: [a] The first set of values for each parameter is for HPS-SRI. [b] The second set of values for each parameter is for HPS-SRII. [c] Ammonium values are for information only since ammonium in these standards has been found to be unstable. [d] Values in parentheses represent hydrogen ion concentrations expressed as microequivalents per liter.

TABLE IV-7b. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS3), High Purity Standards Simulated Rainwater II (HPS-SRII, lot #691218), Filtered, 1997

Parameter	*Target Concentration (mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias %*	*Precision (mg/L)*	*Precision (%)*
Calcium	0.053	0.072	3	0.019	35.8	0.015	20.8
Magnesium	0.050	0.052	3	0.002	4.0	0.004	7.7
Sodium	0.37	0.43	3	0.06	16.2	0.012	2.8
Potassium	0.099	0.096	3	-0.003	-3.0	0.001	1.0
Ammonium	1.0[a]	0.94	3	-0.06	-6.0	0.02	2.1
Sulfate	10.1	9.67	3	-0.43	-4.3	0.07	0.7
Nitrate	7.0	6.96	3	-0.04	-0.6	0.08	1.1
Chloride	0.98	1.02	3	0.04	4.1	0.02	2.0
pH units (µeq/L)	3.43(371.5)[b]	3.61(241.7)	3	0.18(-129.8)	5.2(-34.9)	0.005(2.63)	0.1(1.1)
Conductivity (µS/cm)	116.5	126.5	3	10.0	8.6	1.60	1.3

Notes: [a] Ammonium values are for information only since ammonium in these standards has been found to be unstable. [b] Values in parentheses represent hydrogen ion concentrations expressed as microequivalents per liter.

TABLE IV-8. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS3), Deionized (DI) Water, and pH 4.3 QCS, Filtered, 1997

Parameter	*Target Concentration (mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias (%)*	*Precision (mg/L)*	*Precision (%)*
Calcium	<0.009[a]	<0.009	13			0.0	
	<0.009[b]	0.010	13	0.006[c]	133	0.008	80
Magnesium	<0.003	<0.003	13			0.0	
	<0.003	<0.003	13			0.002	
Sodium	<0.003	0.040	13	0.038	2533	0.017	42.5
	<0.003	0.039	13	0.038	2533	0.019	48.7
Potassium	<0.003	<0.003	13			0.0	
	<0.003	<0.003	13			0.001	
Ammonium	<0.02	<0.02	13			0.013	
	<0.02	<0.02	13			0.008	
Sulfate	<0.03	<0.03	13			0.0	
	<0.03	<0.03	13			0.01	
Nitrate	<0.03	0.07	13	0.06	400	0.03	42.9
	3.11	3.22	13	0.11	3.5	0.05	1.6
Chloride	<0.03	0.03	13	0.015	100	0.02	66.7
	<0.03	0.05	13	0.035	233	0.06	120.
pH units	5.65(2.24)[d]	5.58(2.64)	13	-0.07(0.4)	-1.2(17.9)	0.05(0.30)	0.9(11.4)
(µeq/L)	4.30(50.1)	4.31(48.7)	13	0.01(-1.4)	0.23(-2.8)	0.01(1.33)	0.23(2.7)
Conductivity	0.8	1.1	13	0.3	37.5	0.34	30.9
(µS/cm)	21.8	21.8	13	0.0	0.0	0.33	1.5

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 calculations, MDLs are given the value of 0.5x (MDL). [d] The pH data in parentheses are hydrogen ion concentrations in microequivalents per liter.

QCS, lower for the higher ammonium concentration, lower for the higher sulfate concentration, and lower for the higher conductivity measurement. It was the same for the lower chloride concentration and the higher pH value (the lower hydrogen ion concentration). The RSD was lower for the cations by atomic absorption, except for calcium, higher for the ammonium, and about the same for the anions by ion chromatography except for the lower nitrate value where the RSD was higher. In this case the certified pH value for HPS-SRII is 3.33, considerably less than the 3.62 measured at the CAL on the average. When an ion balance of HPS-SRII, Lot #691025, is calculated, the expected pH should be 3.57. Using this number for the target concentration of the pH, the bias for the CAL is 0.05 or 1.4 percent. For hydrogen ion, the use of the calculated H^+ concentration for the expected value would result in a bias of -26.4 μeq/L H or -9.8 percent.

For HPS-SRII, Lot #691218, there is a lower sample population, but the results are similar. There are not enough replicates of HPS-SRI for statistical evaluation. For HPS-SRII, the percent bias is lower for calcium, potassium, and ammonium. Due to the small sample population, there is a larger RSD for all parameters except potassium, ammonium, and specific conductance, which are lower. Again, the pH value reported as the certified value for both standards is inconsistent with the ion balance for the other certified values. For HPS-SRI the calculated pH value is 4.30 pH units, not 4.11 pH units as quoted. Using this number instead of 4.11, the CAL shows no bias in their pH measurement. For HPS-SRII, the calculated pH value is again 3.57 rather than 3.43 pH units. Using this value the bias for the CAL measurements is 0.05 (-30.25 μeq/L H) or 1.4 percent (-11.2 percent).

The SWS2 solutions are, for the most part, blanks. One is DI water and the other is acidified DI water. These solutions are placed randomly among the network samples so that their analytical results can indicate if there is a problem with sample carryover or false positives. Tables IV-2 (1996) and IV-6 (1997) show that the measured concentrations for DI water were all less than the method detection limit (MDL). Only small amounts of sodium and nitrate in the nitric acid solution are present in both 1996 and 1997 and a small amount of potassium in 1996 in the QCS, although the amount of potassium is very close to the MDL. No DI water samples appear to have any contamination or instrument carryover in them for 1996 and 1997.

The SWS3 values using HPS solutions (Tables IV-3, IV-7a, and IV-7b) are highly variable showing high percent bias for calcium and sodium at both concentrations for both years, although sodium improved in 1997. Ammonium for 1996 at the lower concentration is highly biased although there is no bias for ammonium in 1997. Chloride for 1996 is also considerably biased, implying a possible NaCl (sodium chloride) contamination during filtration. The chloride bias seems to have disappeared in 1997. Again, the high bias in pH is due to an apparently incorrectly certified pH value rather than to the actual laboratory measurements. The RSD for both years is also high for calcium at both concentration levels, and high for the lower concentration level for ammonium. The other parameters for 1997, although higher than the unfiltered samples, are not extreme. The RSD for 1996 is high for the higher magnesium concentration, for both sodium concentrations, and for the higher concentrations for chloride and potassium. Filtered blank solutions (Tables IV-4 and IV-8) contain large amounts of sodium as well. The large RSD indicates that the amount varies considerably between samples. There was also a large ammonium bias and a consistent nitrate and chloride bias in 1996 and 1997. The source of the calcium and sodium bias is the filter itself. (An experiment comparing a Gelman filter to the Millipore filter used by NADP/NTN to filter samples was conducted at the end of 1997. Preliminary results show no sodium or calcium bias in the Gelman filters. The new filters will be beginning in 1998 and further results will be given in the 1998 Quality Assurance report) The source of the sodium, chloride, and ammonium biases is undetermined. Tables B-1 – B-4 in Appendix B are tabular comparisons of the filtered and unfiltered solutions from HPS submitted as internal blind samples. They are followed by figures displaying the data for each parameter.

High Purity Standards was contacted regarding the large differences between the CAL pH values for both SRI and SRII and the certified values. No satisfactory explanation was found to explain what was happening to the solutions. There is an ongoing study looking into the pH of the certified samples.

2. AIRMoN

Four times per month, the IL11 (Bondville, Illinois) Site Operator submits a laboratory QA sample for inclusion in the AIRMoN analysis queue. These samples were either FR75 or FR25 solutions in 1996 and either FR25 or pH 4.3 nitric acid solutions in 1997. The Site Operator receives these samples from the AIRMoN Laboratory Coordinator. Each sample is sealed in a bottle and enclosed in a plastic bag. The weight of the bottle and the type of solution are written on the bag. Quality assurance samples are submitted only on days when no wet deposition was collected. In fact, the sample bucket on the collector is not affected in any way. An AIRMoN Field Observer Form (FOF) accompanies each sample. The sealed QA sample is weighed, and the sample volume and a corresponding precipitation amount are recorded on the form. In addition, target pH and conductivity values are reported on the field chemistry section of the FOF. Throughout these steps, the Site Operator never opens the bottle but delivers it to the sample receiving person at the CAL. “On” and “off” dates and times are recorded on the FOF and bottle as if the sample were a real wet deposition sample. Every effort is made to ensure that the sample is “blind” to the analytical and receiving staff. When the sample is submitted, a copy of the FOF is sent to the AIRMoN Laboratory Coordinator so that the database can be edited to show the true identity of the sample, and the correct date and time “on” can be corrected for the real sample submitted immediately after the QA sample. These samples travel through the laboratory as AIRMoN network precipitation samples.

Tables IV-9 (1996) and IV-10 (1997) summarize the results of the AIRMoN internal blind samples. Although AIRMoN does have an MDL, all values are reported as measured, even negative values. As a consequence, the pH 4.3 nitric acid solutions used in 1997 have parameters that would have a large negative percent bias and a large relative standard deviation (RSD) for those values at or below the MDL and have not been included in the table.

The RSD reported in these tables for FR25 (1996 and 1997) and FR75 (1996) solutions are within the data quality objectives of the AIRMoN Quality Assurance Plan. Only ammonium is outside these objectives. Ammonium is not stable and the lower amounts found in the internal blind samples indicates that some loss of ammonium is occurring in the lower concentration FR25 solutions.

A comparison of the values obtained for the pH 4.3 nitric acid solution in the AIRMoN internal blind program with those of the unfiltered NADP/NTN internal blind samples (Tables IV-2

TABLE IV-9. AIRMoN Internal Blind Samples, 1996

Internally Formulated Simulated Rain, 75th Percentile Solution (FR75)

Parameter	*Target (mg/L)*	*Measured (mg/L)*	*Bias (mg/L)*	*Bias %*	*Std. Dev. (mg/L)*	*Std. Dev. %*
Calcium	0.389	0.3463	-0.0427	-11.0	0.047	13.6
Magnesium	0.069	0.0687	-0.0003	0.4	0.0006	0. 87
Sodium	0.187	0.1910	0.0040	2.1	0.002	1.0
Potassium	0.053	0.0537	0.0007	1.3	0.0035	6.5
Ammonium	0.38	0.380	0.0	0.0	0.01	2.6
Sulfate	2.43	2.473	0.043	1.8	0.049	2.0
Nitrate	1.96	1.947	-0.013	-0.7	0.015	0.8
Chloride	0.69	0.627	-0.063	9.1	0.085	13.6
pH (units)	4.36	4.313	-0.047	-1.1	0.098	2.3
H^+ (µeq/L)	43.7	49.47	5.77	13.2	11.8	23.9
Conductivity (µS/cm)	27.5	28.73	1.23	3.8	1.882	6.6

Note: Total number of samples was 3.

Internally Formulated Simulated Rain, 25th Percentile Solution (FR25)

Parameter	*Target (mg/L)*	*Measured (mg/L)*	*Bias (mg/L)*	*Bias %*	*Std. Dev. (mg/L)*	*Std. Dev. %*
Calcium	0.093	0.0961	0.0031	3.3	0.0029	3.0
Magnesium	0.016	0.0166	0.0006	3.8	0.0009	5.4
Sodium	0.047	0.0476	0.0006	1.3	0.0014	2.9
Potassium	0.014	0.0132	-0.0008	-5.7	0.0012	9.1
Ammonium	0.09	0.084	-0.006	-6.7	0.020	23.8
Sulfate	0.59	0.597	0.007	1.2	0.009	1.5
Nitrate	0.48	0.473	-0.007	-1.5	0.006	1.3
Chloride	0.16	0.167	0.007	6.2	0.010	6.0
pH (units)	4.92	4.911	-0.009	-0.2	0.027	0.2
H^+ (µeq/L)	12.0	12.29	0.29	2.4	0.759	6.2
Conductivity (µS/cm)	7.16	7.653	0.493	6.9	0.32	4.2

Note: Total number of samples was 45.

TABLE IV-10 AIRMoN Internal Blind Samples, 1997

pH 4.3 Nitric Acid QCS

Parameter	*Target (mg/L)*	*Measured (mg/L)*	*Bias (mg/L)*	*Bias %*	*Std. Dev. (mg/L)*	*Std. Dev. %*
Calcium	0.0	0.002	0.002		0.006	
Magnesium	0.0	-0.0004	-0.0004		0.0005	
Sodium	0.0	0.0	0.0		0.002	
Potassium	0.0	-0.001	-0.001		0.0007	
Ammonium	0.0	-0.004	-0.004		0.007	
Sulfate	0.0	0.019	0.019		0.01	
Nitrate	3.11	3.21	0.10	3.22	0.03	0.93
Chloride	0.0	0.0	0.0		0.0	
pH (units)	4.30	4.30	0.0	0.0	0.01	0.23
H^+(µeq/L)	50.1	50.3	0.2	0.4	1.4	2.8
Conductivity (µS/cm)	21.8	22.5	0.7	3.2	0.52	2.3

Note: The number of samples was 8.

Internally Formulated Simulated Rain, 25th Percentile Solution (FR25)

Parameter	*Target (mg/L)*	*Measured (mg/L)*	*Bias (mg/L)*	*Bias %*	*Std. Dev. (mg/L)*	*Std. Dev. %*
Calcium	0.093	0.094	0.001	1.08	0.007	7.45
Magnesium	0.016	0.016	0.0	0.0	0.0006	3.75
Sodium	0.047	0.047	0.0	0.0	0.001	2.13
Potassium	0.014	0.013	-0.001	-7.14	0.001	7.69
Ammonium	0.09	0.05	-0.04	-44.4	0.02	40.0
Sulfate	0.59	0.60	0.01	1.69	0.009	1.50
Nitrate	0.48	0.48	0.0	0.0	0.008	1.67
Chloride	0.16	0.17	0.01	6.25	0.017	10.0
pH (units)	4.92	4.82	-0.1	-2.03	0.04	0.83
H^+(µeq/L)	12.0	15.0	3.0	25.0	1.22	8.1
Conductivity (µS/cm)	7.16	8.19	1.03	14.4	0.44	5.4

Note: The number of samples was 40.

and IV-6) shows the RSDs to be very similar. This is a good indication that the values for NADP/AIRMoN samples are comparable to the NADP/NTN analytical results.

B. Replicate Samples

Two percent of the weekly samples are split for duplicate analysis and separated in both time and space. They are divided at the time of filtration into three 60-mL portions: one is put on the tray for transfer to the laboratory for initial analysis at its regular place in the queue, one is filtered into a square bottle for archival purposes, and one is sent back to sample processing to be assigned a higher laboratory identification number and submitted for analysis at a later time in keeping with its new identification number. The original and the duplicate sample may be analyzed on the same day or several days apart depending on their location on the tray, but never one immediately after the other. After analysis, the data management staff recodes the duplicate with the original sample number followed by a "Q" (quality control sample) to distinguish it from the original that has the letter "S" (sample). With the same numeric part to the identification number, the original and the duplicate analytical results will appear consecutively on the data printouts. AIRMoN samples are split in a similar manner to the NADP samples although they are not filtered. The laboratory ID for original AIRMoN samples, however, is "L" rather than "S". Duplicates are still coded with a "Q" to indicate that they are real samples but are still quality control samples.

Replicate samples serve as another estimator of sample precision. Since these are blind samples, their concentration values should produce representative precision data. The analyses of replicate samples performed in 1996 and 1997 for both NADP and AIRMoN are summarized in Tables IV-11 – IV-14. Differences are calculated by subtracting the reanalysis value from the original value. The annual summaries of each ion have been split into two sections. The median concentration for the year is determined for each analyte (Appendix B, Table B-5 – B-8). The box plots (Figure B-41 – B-74) are constructed to show differences for the low concentrations (from zero to the median) and the high concentrations (from the median to the highest concentrations). The standard deviation estimated from duplicate measurements, defined in the glossary (Appendix A), has been used to calculate the standard deviations for three categories: concentrations below the median concentration, concentrations above the median concentration, and the entire population. The fourth column of Tables IV-11 – IV-14 shows a nonparametric estimator of variability from duplicate determinations, where 1.48 times the Median Absolute Difference (MAD) is the estimator of dispersion of the 1996 and 1997 data sets (16). This value is given in column four. A comparison of the standard deviation values for the QCS, SWS1, and SWS3 samples to the f-pseudosigma for the replicate samples shows the cation and anion precisions to be comparable. The precision of the duplicate pH and conductance for the samples is better than that of the QCS and the internal blinds.

TABLE IV-11. Variance Estimated from Analysis of Replicate NADP/NTN Precipitation Samples, 1996

Parameter	*Standard Deviation Estimated from Paired Measurements*[a] *(mg/L)* *Low*	*High*	*Total*	*(1.48) x MAD*[b]
Calcium	0.007	0.008	0.007	0.004
Magnesium	0.001	0.001	0.001	0.001
Sodium	0.005	0.019	0.014	0.003
Potassium	0.002	0.002	0.002	0.001
Ammonium	0.01	0.02	0.02	0.01
Sulfate	0.01	0.01	0.01	0.01
Nitrate	0.01	0.01	0.01	0.01
Chloride	0.01	0.02	0.02	0.01
ortho-Phosphate	0.000	0.001	0.001	0.000
H^+ (µeq/L)	0.50	1.32	0.99	0.64
Conductivity (µS/cm)	0.25	0.44	0.36	0.44
Number of Pairs	89	90	179	179

Notes: [a] Defined in glossary with equation. [b] MAD = Median Absolute Difference.

TABLE IV-12. Variance Estimated from Analysis of Replicate NADP/NTN Precipitation Samples, 1997

	Standard Deviation Estimated from Paired Measurements [a] *(mg/L)*			
Parameter	*Low*	*High*	*Total*	*(1.48) x MAD*[b]
Calcium	0.005	0.007	0.006	0.004
Magnesium	0.001	0.003	0.002	0.001
Sodium	0.002	0.019	0.014	0.001
Potassium	0.002	0.007	0.005	0.001
Ammonium	0.02	0.01	0.016	0.01
Sulfate	0.04	0.02	0.029	0.01
Nitrate	0.05	0.02	0.038	0.01
Chloride	0.02	0.03	0.023	0.01
ortho-Phosphate	0.000	0.005	0.003	0.000
H^+ (μeq/L)	1.26	2.10	1.73	1.41
Conductivity (μS/cm)	0.45	0.66	0.56	0.44
Number of Pairs	101	102	203	203

Notes: [a] Defined in glossary with equation. [b] MAD = Median Absolute Difference.

TABLE IV-13. Variance Estimated from Analysis of Replicate AIRMoN Precipitation Samples, 1996

Parameter	*Standard Deviation Estimated from Paired Measurements[a] (mg/L)* *Low*	 *High*	 *Total*	*(1.48) x MAD[b]*
Calcium	0.003	0.006	0.004	0.004
Magnesium	0.0008	0.013	0.009	0.001
Sodium	0.0009	0.026	0.018	0.001
Potassium	0.001	0.009	0.006	0.003
Ammonium	0.01	0.28	0.20	0.01
Sulfate	0.009	0.02	0.02	0.01
Nitrate	0.01	0.008	0.009	0.01
Chloride	0.009	0.08	0.06	0.01
Phosphate	0.0008	0.02	0.01	0.004
H^+ (µeq/L)	1.04	3.78	2.77	2.16
Conductivity (µS/cm)	0.79	2.31	1.53	1.2
Number of Pairs	14	14	28	28

Notes: [a] Defined in glossary with equation. [b] MAD = Median Absolute Difference.

TABLE IV-14. Variance Estimated from Analysis of Replicate AIRMoN Precipitation Samples, 1997

	Standard Deviation Estimated from Paired Measurements[a] *(mg/L)*			
Parameter	*Low*	*High*	*Total*	*(1.48) x MAD*[b]
Calcium	0.005	0.004	0.005	0.006
Magnesium	0.0006	0.006	0.002	0.001
Sodium	0.001	0.018	0.012	0.003
Potassium	0.001	0.004	0.003	0.001
Ammonium	0.01	0.24	0.02	0.01
Sulfate	0.01	0.03	0.02	0.01
Nitrate	0.009	0.02	0.02	0.01
Chloride	0.01	0.05	0.04	0.01
Phosphate	0.000	0.01	0.02	0.000
H^+ (µeq/L)	2.12	3.91	2.97	2.80
Conductivity (µS/cm)	0.85	1.55	1.17	1.0
Number of Pairs	16	16	32	32

Notes: [a] Defined in glossary with equation. [b] MAD = Median Absolute Difference.

C. Blanks

Solutions referred to as “blanks” are known to the analysts and identified by numbers that correspond to their various sources. The solutions are collected and grouped by the sample processing staff. Both pH and conductivity are measured prior to transport of the samples to the ion chromatography and atomic absorption laboratories, as a set of blanks, for inclusion in the weekly analytical scheme. In 1996 and 1997, two solutions were used to leach filters, bottles, buckets, and lids. The solutions used were DI water from the sample processing laboratory and the low concentration QCS (FR25).

1. Deionized Water Blanks

The conductivity or resistance of deionized (DI) water used for rinsing, leaching, and making reagents and standards is monitored constantly at several places. There is an in-line resistivity meter at the source of all DI water in the laboratory building and in all of the laboratories on the wall-mounted polishing units. Once a week, 60-mL samples are collected from three sources: the atomic absorption laboratory, the bucket-washing service laboratory, and the sample processing laboratory. These samples undergo a complete analysis in addition to specific conductance. The DI water showed no median ion values above the MDLs. Table IV-15 (1996) and Table IV-16 (1997) show the median pH and conductivity for the DI from the three laboratories for the two years. These values are similar to those of past years.

2. Filter Leachates

Prior to filtering a weekly sample, the Millipore^{TM} type HAWP, 0.45 micrometer (μm) filter is rinsed with 250-300 mL of DI water. Following the DI rinse, all samples with a volume greater than 35 mL are poured from the 1-liter shipping bottle through the filter into a 60-mL wide-mouth HDPE bottle. In order to estimate any contribution from the filter to the sample chemistry, two sets of filter leachates are collected and analyzed each week. The filter is rinsed, 50 mL of DI water is filtered into a sample bottle and labeled “A”. Another 50 mL of DI water is filtered through the same filter and labeled “B”. This procedure is repeated with another DI water-rinsed filter using FR25 for the “A” and “B” filtrates.

Tables IV-17 (1996) and IV-18 (1997) show median analyte concentrations for these filtrates. The DI water samples show a sodium contribution to the “A” portion and a resulting higher conductivity. The FR25 filtrates show a high sodium bias in the “A” filtrate that is considerably less in the “B” portion. All other analytes are close to the expected values.

3. Bucket Blanks

Sample collection buckets are made of high density polyethylene (HDPE) and have a 13-liter capacity. These buckets are washed at the CAL, bagged upon removal from the washing machine, and shipped to sites for weekly (NADP) or daily (AIRMoN) placement on the samplers. Buckets on the “wet” side remain on the collector for one week for NADP and collect whatever precipitation falls from Tuesday to Tuesday. AIRMoN buckets are changed only if there is a precipitation event

TABLE IV-15. Median pH and Conductivity Values for Weekly Deionized (DI) Water Blanks, 1996

Parameter	*Sample Processing Laboratory*	*Atomic Absorption Laboratory*	*Service Laboratory*
pH (units)	5.69	5.68	5.69
Conductivity (µS/cm)	0.7	0.7	0.7
Number of weeks	47	47	47

TABLE IV-16. Median pH and Conductivity Values for Weekly Deionized (DI) Water Blanks, 1997

Parameter	*Sample Processing Laboratory*	*Atomic Absorption Laboratory*	*Service Laboratory*
pH (units)	5.63	5.63	5.64
Conductivity (µS/cm)	0.8	0.8	0.8
Number of weeks	52	52	52

TABLE IV-17. Median Analyte Concentrations Found in Filter Leachates, 1996

Analyte	*DI Water A[a] (mg/L)*	*DI Water B[b] (mg/L)*	*FR25[c] A[a] (mg/L)*	*FR25 B[b] (mg/L)*
Calcium	<0.009	<0.009	0.093	0.098
Magnesium	<0.003	<0.003	0.018	0.019
Sodium	0.049	0.011	0.130	0.082
Potassium	<0.003	<0.003	0.014	0.014
Ammonium	<0.02	<0.02	0.10	0.08
Sulfate	<0.03	<0.03	0.58	0.60
Nitrate	0.05	<0.03	0.50	0.48
Chloride	0.06	<0.03	0.24	0.18
pH	5.65	5.63	5.02	4.98
Conductivity (µS/cm)	1.4	1.0	7.1	7.1
Number of weeks	47	47	47	47

Notes: [a] First 50-mL filtrate after 300-mL DI water rinse. [b] Second consecutive 50-mL filtrate after 300-mL DI water filter rinse. FR25 concentrations (mg/L) Ca = 0.095, Mg = 0.017, Na = 0.048, K = 0.015, NH_4 = 0.09, SO_4 = 0.61, NO_3 = 0.49, Cl = 0.17, pH = 4.92, and Conductivity = 7.3 µS/cm.

TABLE IV-18. Median Analyte Concentrations Found in Filter Leachates, 1997

Analyte	*DI Water A[a] (mg/L)*	*DI Water B[b] (mg/L)*	*FR25 A[a] (mg/L)*	*FR25 B[b] (mg/L)*	*FR25 target conc. (mg/L)*
Calcium	<0.009	<0.009	0.091	0.094	0.094
Magnesium	<0.003	<0.003	0.016	0.017	0.016
Sodium	0.039	0.007	0.088	0.055	0.048
Potassium	<0.003	<0.003	0.013	0.013	0.014
Ammonium	<0.02	<0.02	0.09	0.09	0.09
Sulfate	<0.03	<0.03	0.58	0.60	0.59
Nitrate	0.07	<0.03	0.51	0.48	0.47
Chloride	0.03	<0.03	0.19	0.17	0.17
pH	5.59	5.61	4.95	4.93	4.93
Conductivity	1.3	1.1	7.3	7.3	7.2
Number of weeks	52	52	52	52	

Notes: [a] First 50-mL filtrate after 300-mL DI water rinse. [b] Second consecutive 50-mL filtrate after 300-mL DI water filter rinse.

within the last 24 hours or once a week if there is no precipitation. The sample is transported from the collector to the site laboratory in this bucket. The effect of buckets on sample chemistry has been a subject of interest for many years. The USGS performs an ongoing blind audit study where a portion of a sample of known concentration is poured from a bottle into the bucket at the site and submitted as a network sample while the bottle portion is returned to the CAL and analyzed for comparison. The CAL has performed bucket studies since the beginning of the network.

The weekly procedure for "bucket blanks" includes leaching four buckets for five days with two solutions of two different volumes: DI water and FR25 in 50- and 150-mL portions. The solutions are measured into the buckets and left covered with snap-on lids in the sample processing laboratory. At the end of five days, the four solutions are poured into appropriately labeled 60-mL bottles for inclusion in the blanks set.

Tables IV-19 and IV-20 show median mass per bucket found in these weekly leachates for 1996 and 1997, respectively. Note that these values are the leachate concentrations in μg/mL times the number of milliliters of leachate for the DI water and the concentrations minus the FR25 target value times the number of milliliters for the FR25. Calcium, sodium, potassium, and chloride lead the list of possible bucket contaminants. There are higher concentrations in the 50 mL portions. This contamination would contribute significantly to the chemistry of small volume deposition samples if small deposition samples were clean; however, that is not usually the case. Small volume precipitation samples generally contain high concentrations of the ions generally measured in acidic deposition and these concentrations overwhelm the bucket input. The small volume samples are slightly neutralized by the contact with the bucket and the corresponding conductance is lower.

4. Bottle Blanks

One-liter HDPE wide-mouth bottles have been used as shipping containers for the NADP/NTN samples since January 1994. The sample collected in the bucket is transported back to the field laboratory and then poured into the shipping bottle. (If the sample is frozen, it is necessary to wait until the entire sample volume thaws and can be poured.) Portions of sample from the bottle are then poured into small vials for determinations of pH and specific conductance. The remaining bottled sample, the Field Observer Report Form (FORF), and the empty bucket and lid are returned to the CAL in the black mailer as soon as possible. Portions of the samples are removed for pH and conductivity measurements and additional portions are filtered and collected in one or two 60 milliliter bottles, depending on sample size. The remaining sample is discarded. The shipping bottles are washed and reused.

Tables IV-21 and IV-22 show the median measured mass found in bottle leachates and show them to be clean. Only a small percentage of these blanks contain any analytes above the method detection level (MDL) or beyond the limits for the FR25.

5. Snap-on Lid Blanks

Snap-on lids are used to contain the sample in the bucket between the collector and the site laboratory. At the CAL two lids are inverted on the laboratory bench and 50 mL of DI water is

TABLE IV-19. Median Measured Mass as Micrograms (µg)/Bucket[a] Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) Upright Bucket Leachates, 1996

Analyte	*DI Water (50 mL)*	*DI Water (150 mL)*	*FR25 (50 mL)*[b]	*FR25 (150 mL)*[b]
Calcium	0.550	<0.675	0.200	0.900
Magnesium	<0.075	<0.225	<0.075	<0.225
Sodium	0.550	0.750	0.400	0.750
Potassium	0.650	0.600	0.650	0.900
Ammonium	<0.50	<1.5	<0.50	<1.5
Sulfate	<0.75	<2.25	<0.75	<2.25
Nitrate	<0.75	<2.25	<0.75	<2.25
Chloride	1.50	<2.25	0.50	1.50
pH (units)	5.68	5.63	5.13 (4.94)[c]	5.02 (4.94)[c]
[H+] (µeq/bucket)	0.104	0.352	0.371 (0.574)[c]	1.432 (1.722)[c]
Conductivity	1.5	1.3	6.2 (7.31)[c]	6.8 (7.31)[c]
Number of weeks	47	47	47	47

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] FR25 measured mass = (median concentration measured un upright bucket leachates - target FR25 concentration) x 50 or 150 mL. Detection values are assigned to negative differences. [c] Values in parentheses represent target values for FR25 with no bucket contact.

TABLE IV-20. Median Measured Mass as Micrograms (µg)/Bucket[a] Found in Weekly Deionized (DI) Water and Simulated Rain 25 (FR25) Upright Bucket Leachate, 1997

Analyte	*DI Water (50 mL)*	*DI Water (150 mL)*	*FR25 (50 mL)*[b]	*FR25 (150 mL)*[b]
Calcium	0.45	<0.675	0.15	0.45
Magnesium	<0.075	<0.225	0.050	0.150
Sodium	0.55	0.60	0.30	0.30
Potassium	0.35	<0.225	0.30	0.15
Ammonium	<0.50	<1.5	<0.50	<1.5
Sulfate	<0.75	<2.25	<0.75	<2.25
Nitrate	<0.75	<2.25	<0.75	<2.25
Chloride	2.0	<2.25	1.0	1.5
pH (units)	5.64	5.60	5.07(4.93)[c]	4.99(4.93)[c]
[H+](µeq/bucket)	0.115	0.377	0.426(0.587)[c]	1.535(1.762)[c]
Conductivity (µS/cm)	1.5	1.4	6.49(7.2)[c]	7.00(7.2)[c]
Number of weeks	52	52	52	52

Notes: [a] Mass/bucket represents the concentration in mg/L x 50 or 150 mL. Detection limit values are expressed as the (MDL in mg/L)/2 x 50 or 150 mL. [b]FR25 measured mass = (median concentration measured in upright bucket leachates - target FR25 concentration) x 50 or 150 mL. [c] Values in parentheses represent target values for FR25 with no bucket contact.

TABLE IV-21. Median Measured Mass as Micrograms (µg)/Bottle[a] Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) HDPE 1-Liter Bottle Leachates, 1996

Analyte	*DI Water (50 mL)*	*DI Water (150 mL)*	*FR25 (50 mL)[b]*	*FR25 (50 mL)[b]*
Calcium	<0.225	<0.675	<0.225	<0.675
Magnesium	<0.075	<0.225	<0.075	<0.225
Sodium	<0.075	<0.225	<0.075	<0.225
Potassium	0.350	<0.225	0.400	0.300
Ammonium	<0.50	<1.5	<0.50	<1.5
Sulfate	<0.75	<2.25	<0.75	<2.25
Nitrate	<0.75	<2.25	<0.75	<2.25
Chloride	<0.75	<2.25	<0.75	<2.25
pH (units)	5.59	5.58	4.95 (4.94)[c]	4.94 (4.94)[c]
[H+] (µeq/bucket)	0.13	0.39	0.561 (0.574)[c]	1.762 (1.722)[c]
Conductivity	1.4	1.3	7.3 (7.31)[c]	7.4 (7.31)[c]
Number of weeks	47	47	47	47

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] FR25 measured mass = (median concentration measured un upright bucket leachates - target FR25 concentration) x 50 or 150 mL. Detection values are assigned to negative differences. [c] Values in parentheses represent target values for FR25 with no bottle contact.

TABLE IV-22. Median Measured Mass as Micrograms (µg)/Bottle[a] Found in Weekly Deionized (DI) Water and Simulated Rain 25 (FR25) HDPE 1-Liter Bottle Leachates, 1997

Analyte	*DI Water (50 mL)*	*DI Water (150 mL)*	*FR25 (50 mL)*[b]	*FR25 (150 mL)*[b]
Calcium	<0.225	<0.675	<0.225	<0.675
Magnesium	<0.075	<0.225	<0.075	<0.075
Sodium	<0.075	<0.225	<0.075	<0.225
Potassium	0.15	<0.225	0.15	<0.225
Ammonium	<0.50	<1.5	<0.50	<1.5
Sulfate	<0.75	<2.25	<0.75	<2.25
Nitrate	<0.75	<2.25	<0.75	<2.25
Chloride	<0.75	<2.25	<0.75	<2.25
pH (units)	5.57	5.57	4.97(4.93)[c]	4.94 (4.93)[c]
[H+](µeq/bottle)	0.13	0.40	0.54(0.59)[c]	1.72 (1.77)[c]
Conductivity (µS/cm)	1.3	1.3	7.0(7.2)	7.26(7.2)
Number of weeks	52	52	52	52

Notes: [a] Mass/bottle represents the concentration in µg/mL x 50 or 150 mL. Detection limit values are expressed as (the MDL in mg/L)/2 x 50 or 150 mL. [b] FR25 leachate measured mass = (median concentration measured in bottle leachates - target FR25 concentration) x 50 or 150 mL. Detection values are assigned to negative differences. [c] Values in parentheses represent target values for FR25 with no bottle contact.

measured into one of the them and 50 mL of FR25 into the other one. They are covered with large plastic domes and left for 24 hours. Tables IV-23 (1996) and IV-24 (1997), showing the median concentrations from the lid leachates, show that sodium and potassium persist at small amounts. Both of these ions exceed the MDL for DI water and the FR25 control limits. Excess calcium is also in more than 50 percent of the FR25 leachates. This weekly lid blank represents an extreme case for a field sample. It is believed that small volume samples under normal field handling conditions rarely come into contact with the lid and larger volumes of precipitation would sufficiently dilute the ions so that they would not be a contamination factor in the actual samples.

6. AIRMoN Bottles

AIRMoN bottles are 250-mL wide-mouth HDPE bottles into which are poured the daily samples collected in the same type of 13-liter buckets used for the NADP/NTN weekly samples. These bottles are rinsed with DI water prior to shipment and are used only once, as the samples are shipped and then stored in them at the CAL. Tables IV-25 (1996) and IV-26 (1997) show that the bottles are clean and the control limits are rarely exceeded.

TABLE IV-23. Median Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Snap-on Lids, 1996

Analyte	*DI Water (50 mL)*	*FR25 (50 mL)*	*FR25 target conc.*
Calcium	<0.009	0.105	0.097
Magnesium	<0.003	0.020	0.019
Sodium	0.005	0.078	0.072
Potassium	0.003	0.020	0.013
Ammonium	<0.02	0.09	0.08
Sulfate	<0.03	0.60	0.60
Nitrate	<0.03	0.48	0.48
Chloride	<0.03	0.18	0.17
pH (units)	5.65	5.01	4.94
Conductivity (µS/cm)	1.3	7.0	7.3
Number of weeks	47	47 (46 for NH_4)	

TABLE IV-24. Median Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Snap-on Lids, 1997

Analyte	*DI Water (50 mL)*	*FR25 (50 mL)*	*FR25 target conc.*
Calcium	<0.009	0.098	0.094
Magnesium	<0.003	0.017	0.016
Sodium	0.005	0.051	0.048
Potassium	0.003	0.017	0.014
Ammonium	<0.02	0.09	0.09
Sulfate	<0.03	0.60	0.59
Nitrate	<0.03	0.48	0.47
Chloride	<0.03	0.18	0.17
pH (units)	5.62	4.97	4.93
Conductivity (µS/cm)	1.31	7.1	7.2
Number of weeks	52	52	

TABLE IV-25. Median Analyte Concentrations (mg/L) Found in Monthly Simulated Rain (FR25)
AIRMoN 250-mL HDPE Bottle Leachates, 1996

Analyte	*FR25 (50 mL)*	*FR25 (150 mL)*	*FR25 Target Values*
Calcium	0.098	0.099	0.097
Magnesium	0.019	0.018	0.019
Sodium	0.072	0.072	0.072
Potassium	0.015	0.014	0.013
Ammonium	0.08	0.07	0.083
Sulfate	0.60	0.59	0.60
Nitrate	0.48	0.47	0.48
Chloride	0.17	0.17	0.17
pH (units)	4.96	4.96	4.94
Conductivity (µS/cm)	7.2	7.2	7.31
Number of weeks	12	12	

TABLE IV-26 Median Analyte Concentrations (mg/L) Found in Monthly Simulated Rain (FR25) AIRMoN 250-mL HDPE Bottle Leaches, 1997

Analyte	*FR25 (50 mL)*	*FR25 (150 mL)*	*FR25 target conc.*
Calcium	0.094	0.092	0.094
Magnesium	0.017	0.017	0.016
Sodium	0.047	0.047	0.048
Potassium	0.013	0.013	0.014
Ammonium	0.09	0.09	0.09
Sulfate	0.60	0.60	0.59
Nitrate	0.47	0.48	0.47
Chloride	0.17	0.17	0.17
pH (units)	4.94	4.94	4.93
Conductivity (μS/cm)	7.4	7.3	7.2
Number of weeks	11	11	

V. MONTHLY QUALITY ASSURANCE PROCEDURES

Monthly NADP/NTN and AIRMoN QA activities include the evaluation of the control charts summarizing the daily QCS analyses to determine if there is any change occurring with each analytical instrument, review of the printouts containing internal blind samples data, reanalysis of samples flagged for either an ion or conductivity imbalance or both, and AIRMoN field blanks. Data for samples analyzed in the USGS laboratory intercomparison study are summarized and reviewed prior to transmission to the USGS on a quarterly basis.

A. Reanalysis Procedures

The analytical results of network samples are transmitted to the data processing staff approximately twice a month in sets of 400 or 500 samples. These analytical data are submitted to a reanalysis selection test. A sample is flagged if the ion balance or conductivity percent difference exceeds set limits. The computer algorithm for selection has been the same since 1987.

1. Ion Percent Difference (IPD)

Ion concentrations are measured in milligrams per liter (mg/L). These concentrations are converted to microequivalents per liter (μeq/L) using factors listed in Table V-1 (17,18). The measured ion values as well as pH and 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:

$$\text{IPD} = \frac{\text{Anion Sum - Cation Sum}}{\text{IS}} \times 100$$

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

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

Samples are flagged for reanalysis if:

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

TABLE V-1. Conversion Factors for Reanalysis Calculations

Analyte	*Milligrams/Liter (mg/L) to Microequivalents/L (µe/L)*[a] *for Ion Percent Difference, Multiply by:*	*Microequivalent/L (µe/L) to Equivalent Conductance*[b] *for Conductance Percent Difference Multiply by:*
Calcium	49.90	59.5
Magnesium	82.26	53.0
Sodium	43.50	50.1
Potassium	25.57	73.5
Ammonium	55.44	73.5
Sulfate	20.83	80.0
Nitrate	16.13	71.4
Chloride	28.21	76.3
ortho-Phosphate	31.59	69.0
Hydrogen	992.2	350
Bicarbonate	16.39	44.5
Hydroxide	58.8	198

Notes: [a] *Standard Methods for the Examination of Water and Wastewater* (17). [b] *CRC Handbook of Chemistry and Physics* (18)

2. Conductance Percent Difference (CPD)

Conductance percent difference (CPD) compares the calculated and measured conductivity. Ion concentrations as μeq/L are multiplied by conductance conversions factors listed in Table V-1 (17), summed, and then divided by 1000 in order to calculate the theoretical conductivity. This value is compared to the measured conductivity. The CPD is calculated as follows:

$$\text{CPD} = \frac{(\text{Calculated Conductivity - Measured Conductivity})}{\text{Measured Conductivity}} \text{ X } 100$$

Samples are flagged for reanalysis if:

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

The samples selected are reanalyzed unless they are flagged for contamination and exhibit excessive ion concentrations or the volume is insufficient. The final list of samples is compiled and sent to the laboratory and the samples are analyzed again. The analysts then submit the results to the QA Specialist with suggestions for changes to the database. The final decision is then made and sent to the database manager. 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 CAL's computerized database along with the original analyses values.

3. IPD and CPD histograms

In 1996, 10,451 samples were logged in, and 6917 were classified as "W" or wet, which would make them eligible for the reanalysis program. In 1997, 10,447 samples were logged in at the CAL and 7029 were classified as "W". In 1996, 430 samples were flagged for reanalysis with 170 individual measurement changes made to 161 samples. In 1997, 328 samples were flagged with 194 individual measurements changes made to 120 samples. Figures V-1 and V-2 are the histograms of the IPD and CPD values obtained for 1996 and 1997, respectively, for sample volumes exceeding 35 mL. Each figure presents the mean, standard deviation, median, and number of wet samples.

The 1979-1993 IPD mean and median values fluctuated between zero and 5.6. Both values have fallen below zero in each year since 1993. A negative value indicates a cation excess, which was not observed while the samples were being shipped to the laboratory in the buckets with the pound-on lids containing the butadiene rubber o-rings. These lids were used to ensure a watertight seal, but the o-rings were a source of sample contamination and alteration as many studies showed throughout the time period these lids were used. It was noted that the pH of solutions in contact with the o-ring rose and that an ion exchange reaction seemed to have taken place. Since January 1994, samples have been shipped to the laboratory in 1-liter wide-mouth HDPE bottles with screw-on lids and no gaskets. Since the 1994 bucket/bottle protocol change, laboratory pH and field pH are more similar. The hydrogen ion concentrations are more stable and probably account for a cation excess not seen since the first year, 1978, during which only 239 samples were collected.

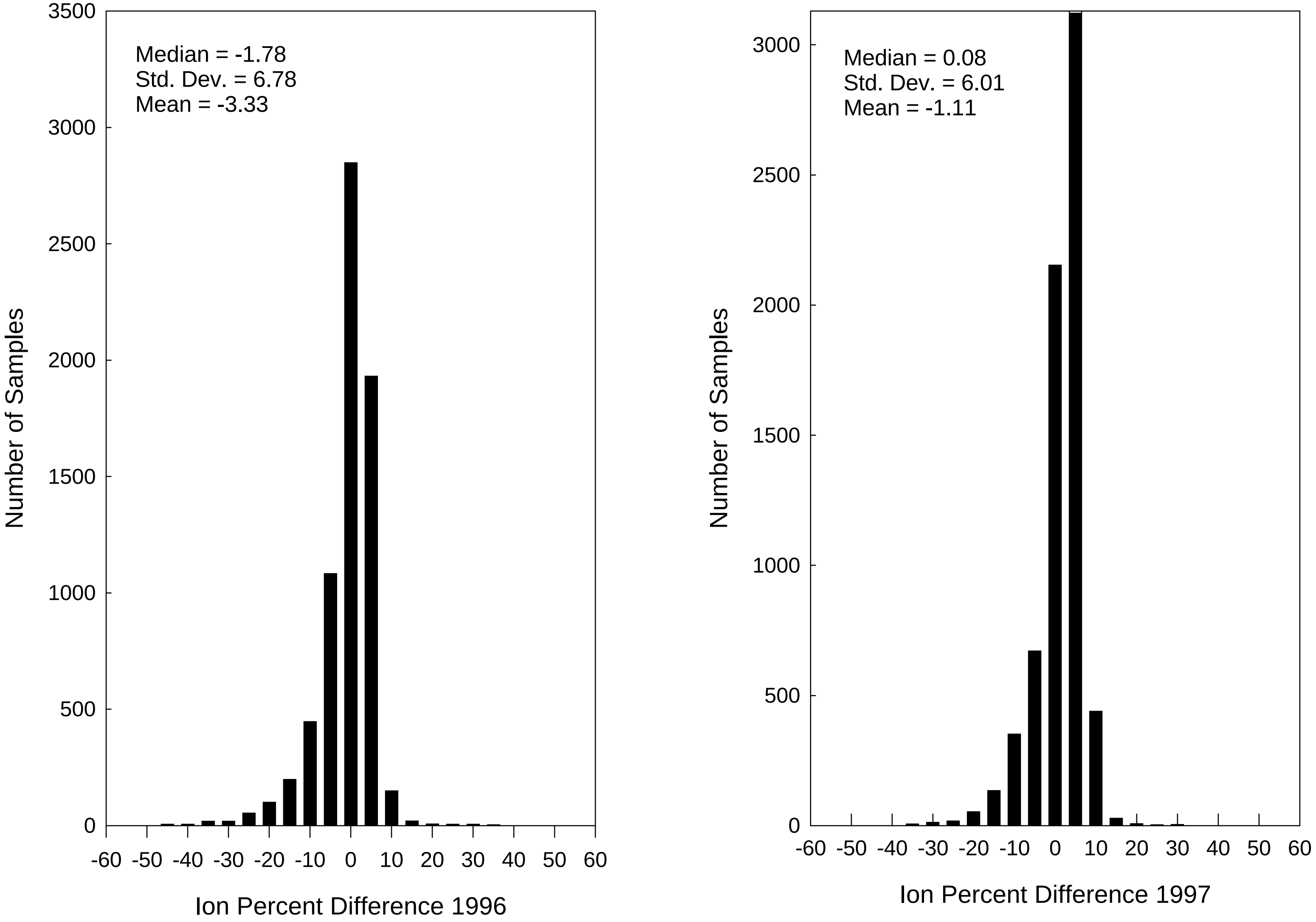


Figure V-1. Ion Percent Difference for NADP/NTN wet-side samples. The number of samples for 1996 was 6917 and 7029 for 1997.

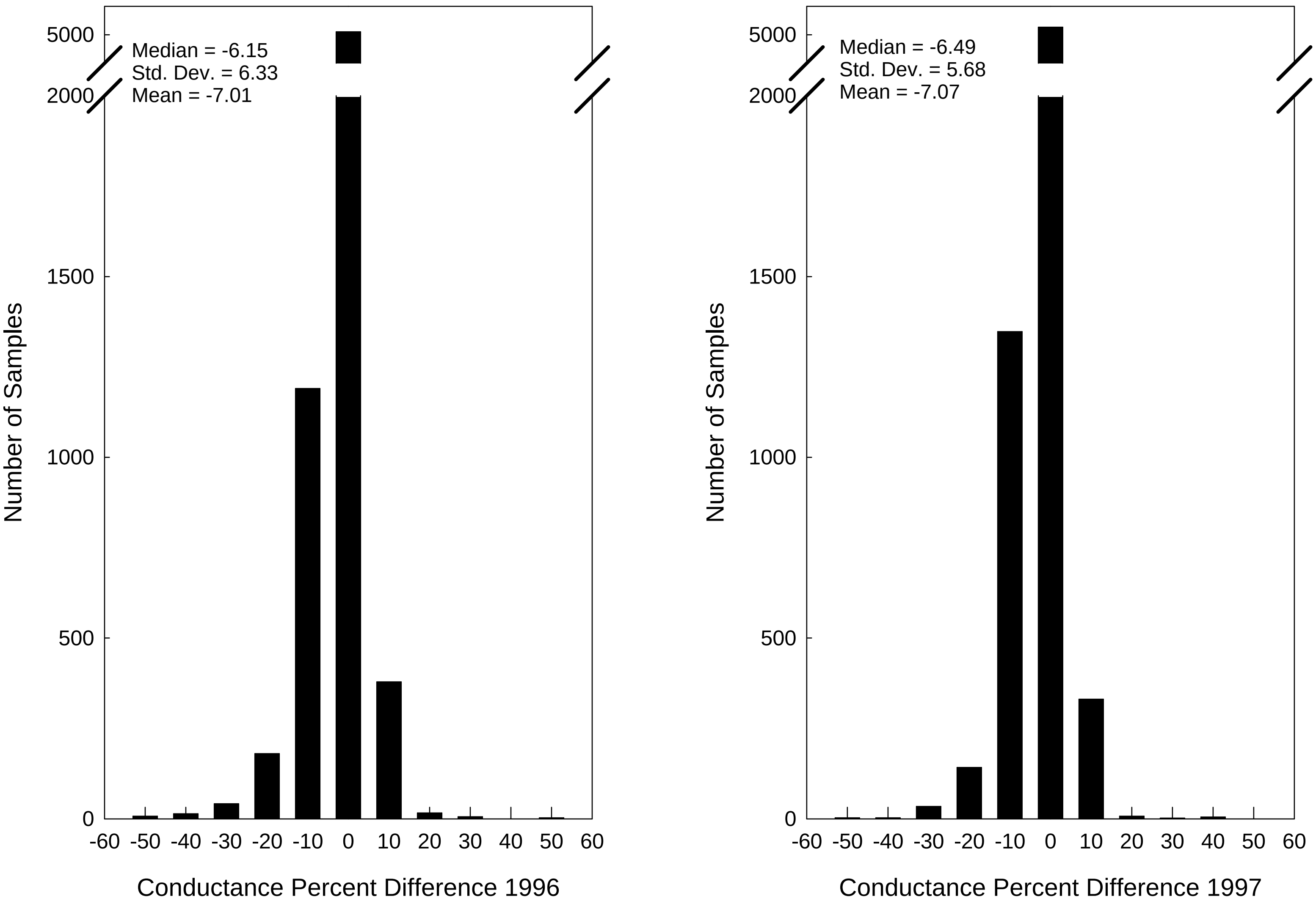


Figure V-2. Conductance Percent Difference for NADP/NTN wet-side samples. The total number of samples for 1996 was 6917 and 7029 for 1997.

The CPD has exhibited a negative skew consistently since 1979. The 1996 mean (-7.01) and median (-6.15) compare favorably with the 1997 mean (-7.07) and median (-6.49) although they are both slightly higher than the 1995 mean (-6.25) and median (-5.39). Negative CPD indicates that the measured conductivity exceeds the calculated conductivity. This is expected due to the nature of the NADP analyses, i.e., only the major ions are analyzed. There are undoubtedly parameters, such as trace metals and organic species, that are not analyzed that contribute to the measured conductivity.

B. AIRMoN Field Blanks

AIRMoN field blanks are collected monthly, as are AIRMoN bottle blanks. On the first Tuesday of each month when there has been no precipitation in the last 26 hours and fewer than six lid openings since the last bucket change, the bucket is removed from the collector and approximately 125 mL of solution is poured into it from a bottle sent from the CAL. The bucket is covered with a snap-on lid and brought back to the field laboratory. The remainder of the bottle containing approximately 125 mL of solution is recapped and also taken back to the field laboratory. The sample remaining in the original bottle is given the designation “DK” and is not analyzed by the field operators. The bucket containing the CAL solution is agitated and allowed to stand overnight or for at least two hours. After the field blank is allowed to remain in the bucket, it is decanted into a 250 mL shipping bottle and field pH and conductivity are measured and recorded on the AIRMoN Field Observer Form (FOF). This bottle is given the designation “DF”. Both the “DF” and “DK” bottles are shipped to the CAL for complete chemical analysis.

Five different solutions were used in the AIRMoN field blank program in 1996, and four were used in 1997. The solutions used in 1996 were DI water, pH 4.3 nitric acid QCS (the AIRMoN pH QCS solution), FR25 (simulated rain emulating the 25th percentile concentration of the NADP/NTN, FR75 (simulated rain emulating the 75th percentile concentration of the NADP/NTN), and pH 4.9 nitric acid/sodium chloride QCS (the NADP/NTN pH QCS solution). No pH 4.9 QCS solution was used in 1997. The pH and conductivity of these solutions are similar to those of precipitation samples. DI water is used to compare the data to the bucket blanks from the CAL. Both the site personnel and the CAL analysts know that the solutions are field blanks used for evaluating the effects of the collection bucket, shipping bottle, and handling.

Tables V-2 and V-3, respectively, summarize the results of the AIRMoN field blank study for 1996 and 1997. The top number for each parameter for each solution is the Median Absolute Difference (MAD) x 1.48, a nonparametric estimator of the variance from duplicate determinations. The second line for each parameter for each solution is the standard deviation estimated from paired measurements. Comparing the “DF”/”DK” numbers in Tables V-2 and V-3 with the replicate numbers found in Tables IV-11 (1996) and IV-12 (1997), the field blanks show a higher variance and a higher standard deviation for all solutions except the DI water for 1996. Calcium and sodium appear to be especially high consistent with possible dry deposition being deposited in the bucket during nonevent periods. This means that the amount of dry deposition in the collection buckets has a greater variability than the replicate analyses in the laboratory. This also means that a real component in the wet samples is derived from nonprecipitation periods. Because the time the buckets are in the field varies from 24 hours to one week, the variability in the amount of deposition is large but consistent across all parameters.

TABLE V-2.
AIRMoN Field Blanks Median Absolute Differences of Bucket Minus Bottle (DF-DK) and Standard Deviations, 1996

Solution	SO_4	NO_3	*Cl*	NH_4	PO_4	*Ca*	*Mg*	*Na*	*K*	*Cond.*	*pH*	*H*	*n*
DI	0.0006[a]	0.001	0.0001	0.0	0.0	0.00006	0.0	0.00004	0.0	0.55	0.006	0.34	10
Water	0.02[b]	0.02	0.05	0.01	0.0	0.014	0.003	0.026	0.003	0.21	0.08	0.55	
pH 4.3	0.04	0.04	0.03	0.0	0.0	0.013	0.003	0.009	0.004	0.6	0.01	1.66	7
HNO_3	0.04	0.03	0.04	0.008	0.002	0.016	0.003	0.021	0.009	0.4	0.02	1.71	
FR25	0.01	0.01	0.01	0.01	0.0	0.007	0.001	0.006	0.003	0.6	0.7	1.73	23
	0.06	0.01	0.11	0.01	0.002	0.035	0.003	1.1	0.036	3.71	0.3	2.28	
FR75	0.03	0.03	0.01	0.03	0.0	0.018	0.003	0.007	0.007	1.2	0.06	5.40	11
	0.04	0.07	0.02	0.02	0.002	0.077	0.002	0.006	0.007	1.3	0.05	4.49	
pH 4.9	0.03	0.03	0.06	0.0	0.0	0.018	0.001	0.040	0.001	0.3	0.04	1.20	11
NaCl/HNO_3	0.02	0.02	0.04	0.01	0.0	0.038	0.002	0.022	0.005	0.6	0.08	2.01	

Notes: [a] The first set of values for each parameter for each solution is the Median Absolute Difference x 1.48. [b] The second set of values for each parameter for each solution is the standard deviation estimated from paired measurements (defined in the glossary, Appendix A). Solutions are shipped to AIRMoN sites in bottles from the CAL, 125 mL are poured into the collection bucket (DF) following sample protocol, and the remaining portion is returned in the original bottle (DK). Returned samples undergo complete chemical analyses.

TABLE V-3.

AIRMoN Field Blanks Median Absolute Differences of Bucket Minus Bottle (DF-DK) and Standard Deviations, 1997

Solution	SO_4	NO_3	*Cl*	NH_4	PO_4	*Ca*	*Mg*	*Na*	*K*	*Cond.*	*pH*	*H*	*n*
DI	0.06[a]	0.09	0.09	0.00	0.00	0.030	0.001	0.016	0.00	1.52	0.21	2.81	2
Water	0.04[b]	0.06	0.06	0.00	0.00	0.017	0.0007	0.010	0.00	0.76	0.13	1.51	
pH 4.3	0.03	0.09	0.03	0.03	0.00	0.013	0.001	0.006	0.003	0.96	0.01	1.75	10
HNO_3	0.03	0.05	0.02	0.02	0.003	0.007	0.001	0.015	0.009	1.1	0.02	2.76	
FR25	0.03	0.03	0.03	0.03	0.00	0.012	0.001	0.009	0.003	0.40	0.04	1.36	42
	0.03	0.04	0.03	0.03	0.001	0.020	0.003	0.010	0.013	1.13	0.06	2.30	
FR75	0.03	0.04	0.03	0.03	0.00	0.010	0.001	0.010	0.006	0.74	0.01	1.54	35
	0.04	0.05	0.05	0.02	0.002	0.017	0.003	0.028	0.017	0.69	0.02	1.98	

Notes: [a] The first set of values for each parameter for each solution is the Median Absolute Difference x 1.48. [b] The second set of values for each parameter for each solution is the standard deviation estimated from paired measurements (defined in the glossary, Appendix A). Solutions are shipped to AIRMoN sites in bottles from the CAL, 125 mL are poured into the collection bucket (DF), following sample protocol, and the remaining aliquot is returned in the original bottle (DK). Returned samples undergo complete chemical analyses.

C. USGS Interlaboratory Comparison

The interlaboratory comparison conducted by the U.S. Geological Survey (USGS), primary external auditor of the NADP/NTN, began in the fall of 1982 as a portion of the external audit of the CAL. The USGS mails several sets of blind samples of differing matrices to participating laboratories each month. The audit has been designed to determine if the laboratories are producing comparable results.

The 1996 and 1997 interlaboratory comparison program included five laboratories: (1) the Illinois State Water Survey (CAL), (2) Atmospheric Environment Service (AES), (3) Environmental Science and Engineering (ESE), (4) Ontario Ministry of the Environment (MOE), and (5) Global Geochemistry Corporation (GGC).

The samples are shipped to the laboratories approximately every two weeks throughout the year. Samples used in 1996 and 1997 were (1) certified samples prepared and certified by the National Institute of Standards and Technology (NIST), (2) uncertified synthetic precipitation samples prepared and bottled by the USGS, (3) natural deposition samples collected at the NADP/NTN sites and composited and bottled at the CAL, and (4) ultrapure DI water samples prepared by the USGS. Data reports from the participating laboratories are submitted quarterly to the USGS.

Tables V-4 (1996) and V-5 (1997) show the 50th and 90th percentile absolute differences of replicate samples obtained by the five participating laboratories. Figures V-3 and V-4 (1996) and V-5 and V-6 (1997) graphically show these same results. The CAL had the best results for sulfate in 1996 and the best results for hydrogen in 1997. Overall, the CAL had excellent results for both years. The complete results of the 1996 and 1997 studies will be published by John Gordon of the USGS.

TABLE V-4. 50th and 90th Percentile Absolute Differences for Analysis of Replicate Samples in the 1996 Interlaboratory Comparison Program

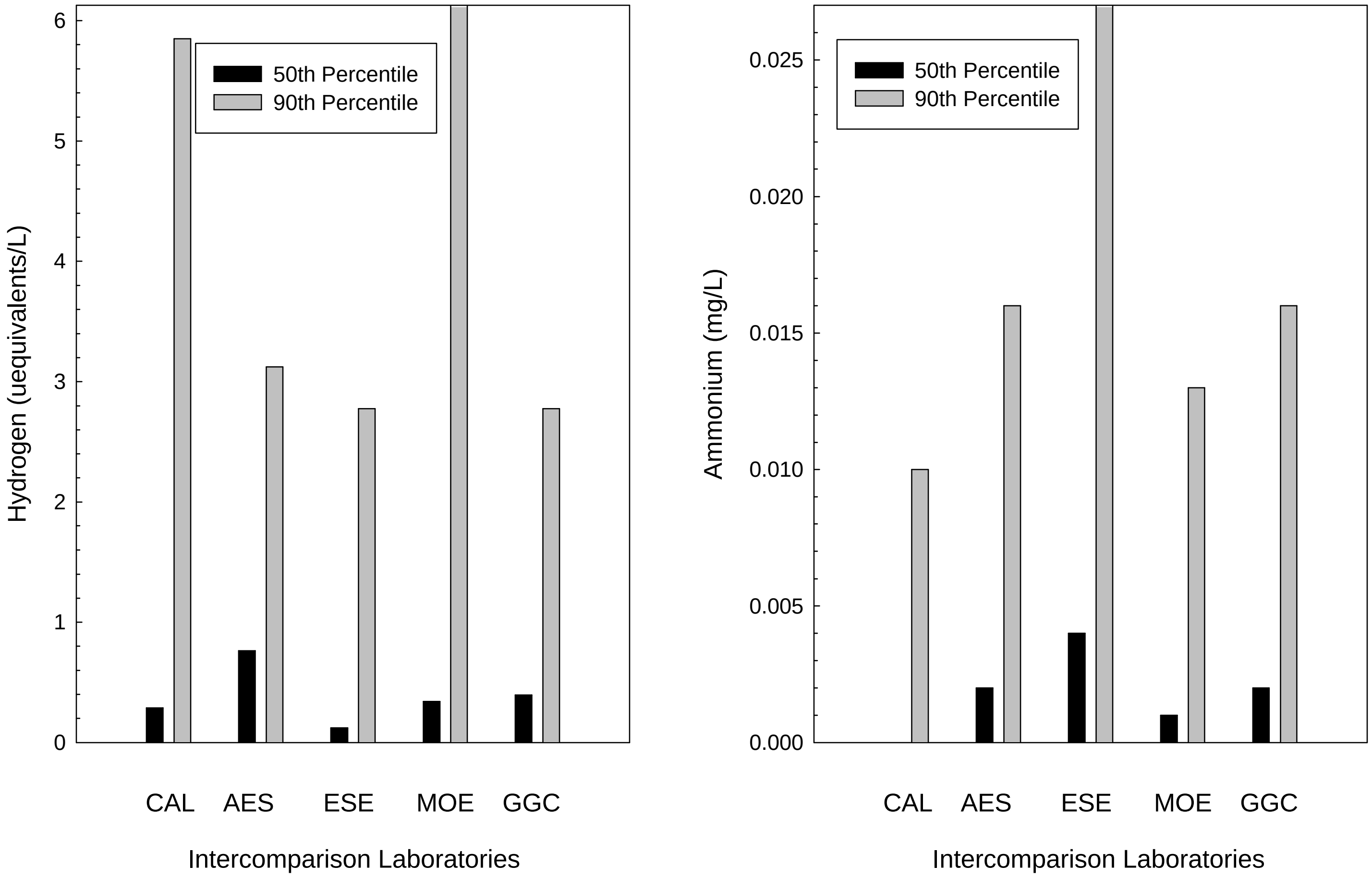
Analyte	*[a]CAL*		*[b]AES*		*[c]ESE*		*[d]MOE*		*[e]GGC*	
	50th	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*
Calcium	0.000	0.010	0.003	0.010	0.001	0.006	0.001	0.009	0.002	0.016
Magnesium	0.000	0.001	0.000	0.002	0.000	0.002	0.001	0.005	0.001	0.014
Sodium	0.001	0.006	0.002	0.007	0.001	0.008	0.003	0.010	0.003	0.011
Potassium	0.001	0.002	0.001	0.007	0.000	0.009	0.001	0.005	0.001	0.005
Ammonium	0.000	0.010	0.002	0.016	0.004	0.027	0.001	0.013	0.002	0.016
Sulfate	0.010	0.030	0.007	0.043	0.008	0.055	0.010	0.100	0.026	0.143
Nitrate	0.005	0.040	0.011	0.052	0.004	0.018	0.000	0.089	0.014	0.075
Chloride	0.000	0.010	0.005	0.016	0.002	0.021	0.000	0.010	0.003	0.016
Hydrogen Ion	0.289	5.851	0.764	3.122	0.122	2.775	0.342	6.127	0.396	2.775
Specific Conductance	0.100	1.300	---	---	0.100	1.500	0.100	1.000	0.100	1.400

Note: The five laboratories participating were [a] Illinois State Water Survey Central Analytical Laboratory, [b] Atmospheric Environment Service, Canada, [c] Environmental Science and Engineering, [d] Ontario Ministry of the Environment, Canada, and [e] Global Geochemistry Corporation.

TABLE V-5. 50th and 90th Percentile Absolute Differences for Analysis of Replicate Samples Determined in the 1997 Interlaboratory Comparison Program

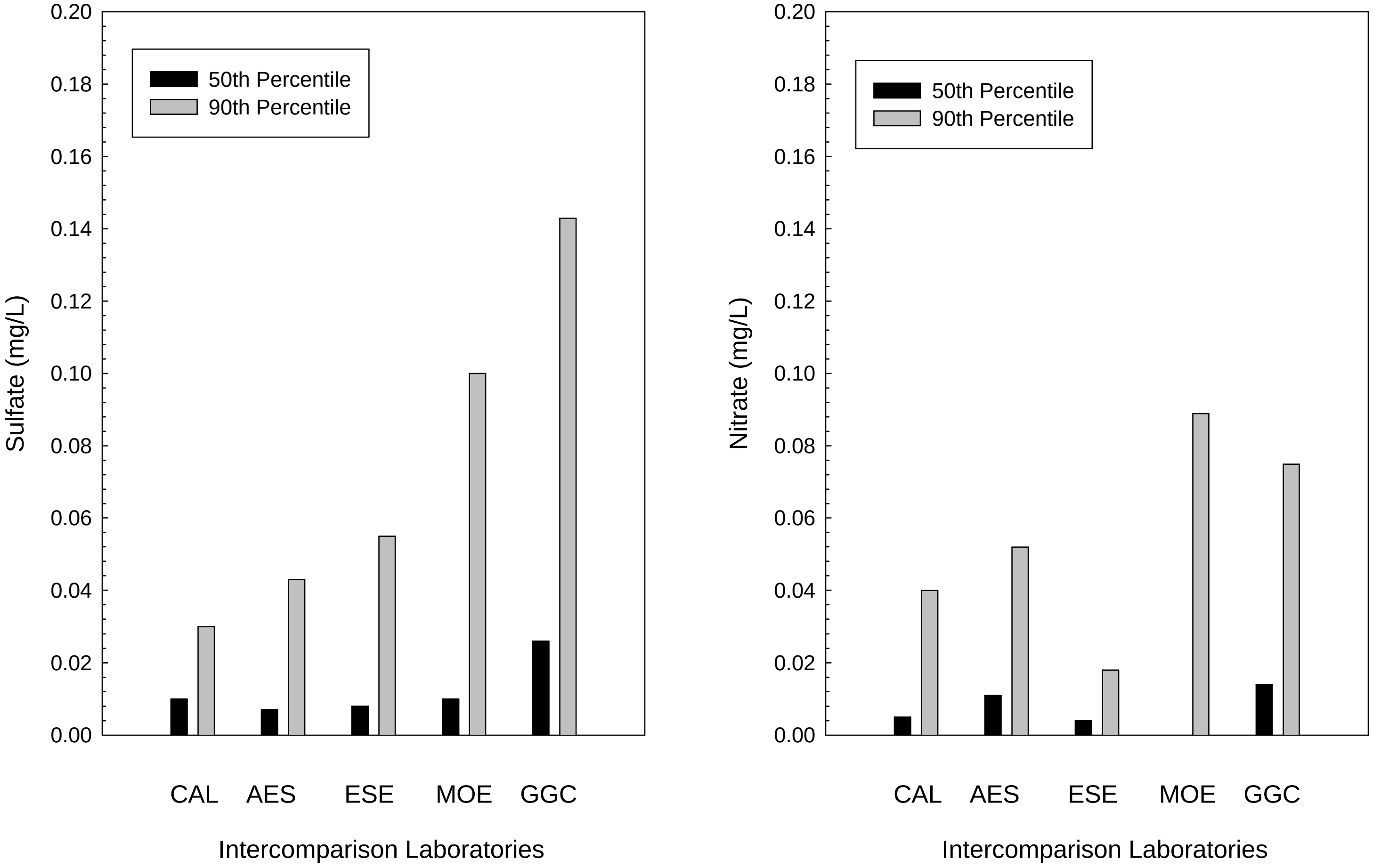
Analyte	*[a]CAL*		*[b]AES*		*[c]ESE*		*[d]MOE*		*[e]GGC*	
	50th	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*
Calcium	0.000	0.010	0.002	0.010	0.001	0.007	0.000	0.020	0.001	0.009
Magnesium	0.001	0.007	0.000	0.001	0.000	0.004	0.000	0.005	0.000	0.003
Sodium	0.001	0.007	0.001	0.005	0.001	0.004	0.002	0.010	0.002	0.005
Potassium	0.001	0.002	0.001	0.002	0.000	0.001	0.000	0.005	0.001	0.003
Ammonium	0.000	0.010	0.001	0.007	0.005	0.021	0.003	0.014	0.004	0.015
Sulfate	0.010	0.040	0.005	0.032	0.005	0.030	0.050	0.100	0.012	0.033
Nitrate	0.010	0.040	0.006	0.025	0.004	0.035	0.011	0.071	0.009	0.030
Chloride	0.000	0.010	0.003	0.041	0.002	0.006	0.010	0.020	0.002	0.007
Hydrogen Ion	0.030	1.529	0.720	3.269	0.369	6.415	0.853	12.10	0.411	1.876
Specific Conductance	0.100	1.100	---	---	0.200	0.900	0.200	0.800	0.065	0.500

Note: The five laboratories participating were [a] Illinois State Water Survey Central Analytical Laboratory, [b] Atmospheric Environment Service, Canada, [c] Environmental Science and Engineering, [d] Ontario Ministry of the Environment, and Canada, [e] Global Geochemistry Corporation.



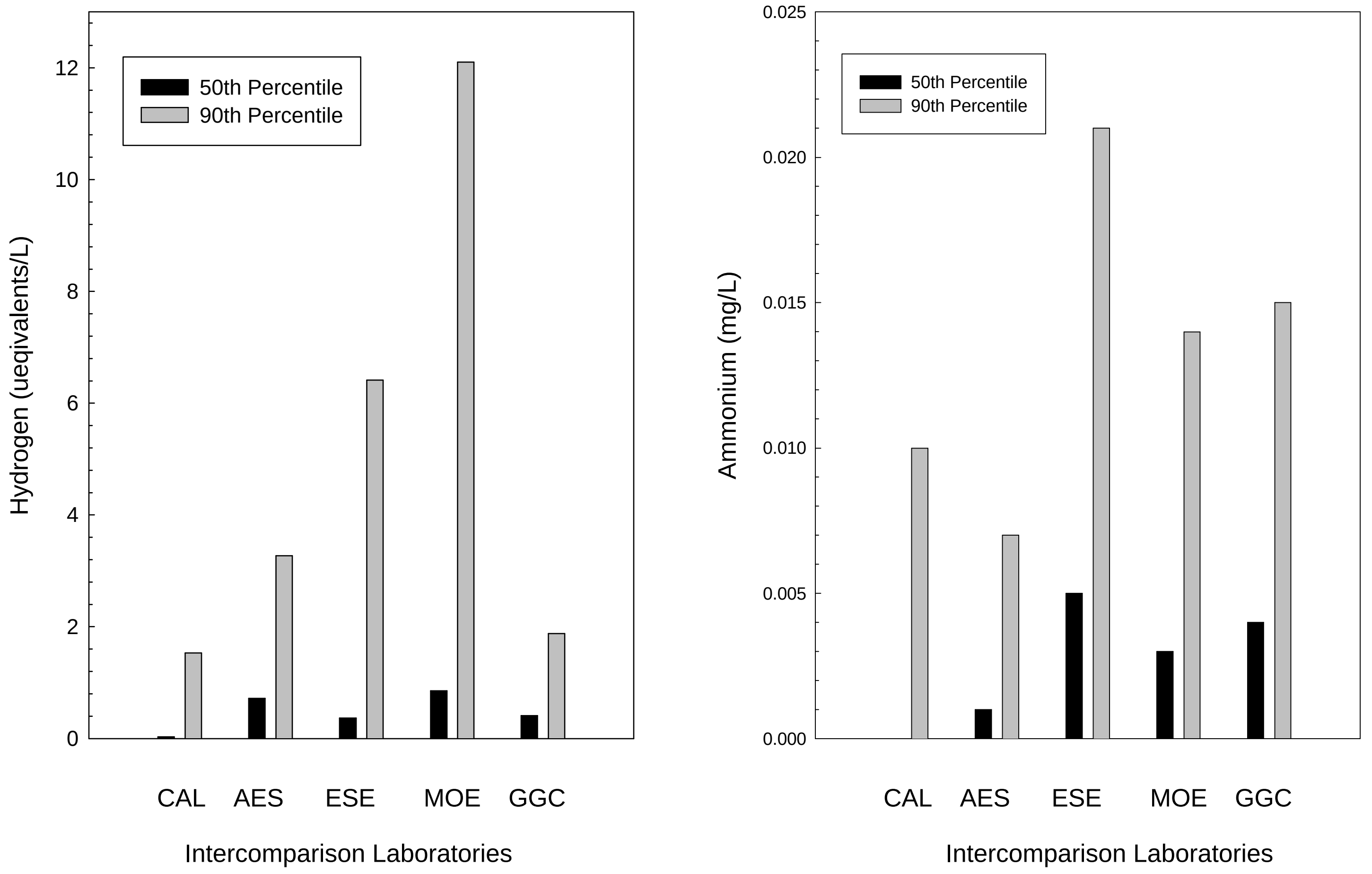
Note: The laboratories involved in the intercomparison study were the NADP Central Analytical Laboratory (CAL), Atmospheric Environment Service (AES), Environmental Science and Engineering (ESE), the Ontario Ministry of the Environment (MOE), and the Global Geochemistry Corporation (GGC).

Figure V-3. 50th and 90th percentile absolute differences for the five laboratories used in the USGS Intercomparison Study for hydrogen and ammonium, 1996.



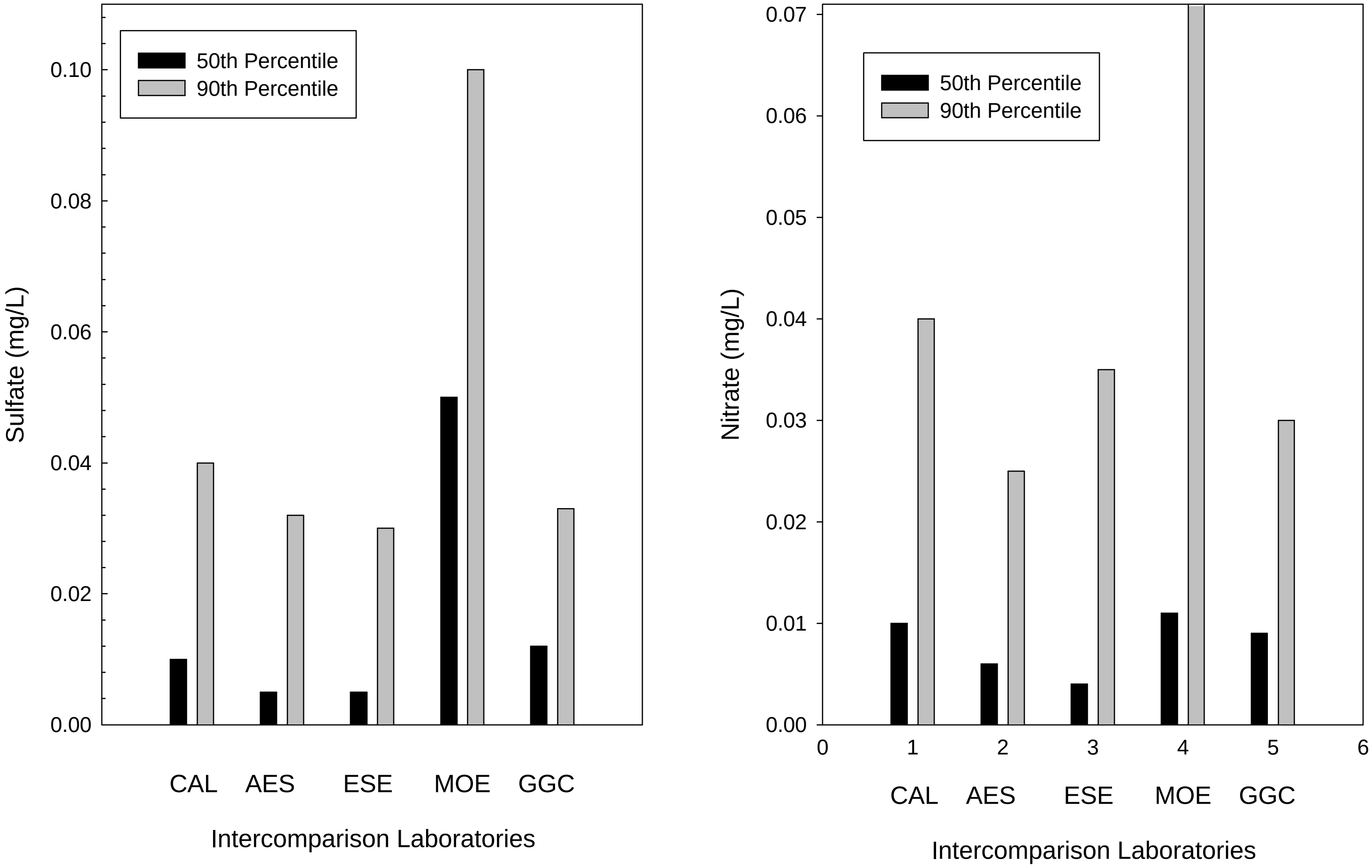
Note: The laboratories involved in the intercomparison study were the NADP Central Analytical Laboratory (CAL), Atmospheric Environment Service (AES), Environmental Science and Engineering (ESE), the Ontario Ministry of the Environment (MOE), and the Global Geochemistry Corporation (GGC).

Figure V-4. 50th and 90th percentile absolute differences for the five laboratories used in the USGS Intercomparison Study for sulfate and nitrate, 1996.



Note: The laboratories involved in the intercomparison study were the NADP Central Analytical Laboratory (CAL), Atmospheric Environment Service (AES), Environmental Science andEngineering (ESE), the Ontario Ministry of the Environment (MOE), and the Global Geochemistry Corporation (GGC).

Figure V-5. 50th and 90th percentile absolute differences for the five laboratories used in the USGS Intercomparison Study for hydrogen and ammonium, 1997.



Note: The laboratories involved in the intercomparison study were the NADP Central Analytical Laboratory (CAL), Atmosperic Environment Service (AES), Environmental Science and Engineering (ESE), the Ontario Ministry of the Environment (MOE), and the Global Geochemistry Corporation (GGC).

Figure V-6. 50th and 90th percentile absolute differences for the five laboratories used in the USGS Intercomparison Study for sulfate and nitrate, 1997.

VI. SEMIANNUAL AND ANNUAL QUALITY ASSURANCE PROCEDURES

The annual report is written each year as the information from the previous year is summarized and interpreted. The network database contains the analyses of the replicate samples and the internal blind samples, and the information summaries are usually the final computer product needed for the completion of the report. Blanks and QCS information are stored on Personal Computer (PC) files and are available in mid-January. These reports are edited both internally at the Illinois State Water Survey and externally by scientists associated with NADP/NTN and AIRMoN. The QA and other NADP information are summarized regularly for reports and for semiannual NADP meetings.

Each year the CAL participates in several interlaboratory comparisons outside the NADP protocol. There were three studies in 1996: one for the World Meteorological Organization (WMO) in Geneva, Switzerland, and two for the National Water Research Institute, Burlington, Ontario, Canada. The CAL participated in these same studies in 1997 and in a study by the Norwegian Institute for Air Research in Lillestrom, Norway.

A. World Meteorological Organization

The 20th set of reference precipitation samples was shipped to participating laboratories in July 1997. Samples were also shipped to participating laboratories in July 1996. Beginning in 1996, the CAL was the contractual laboratory designated to prepare simulated precipitation samples to be sent out worldwide. Ninety-five laboratories requested samples 58 reported their analytical results. In 1997, 61 of the 92 laboratories to which samples were sent returned their analytical results. The 1997 samples were shipped in their diluted concentrations, eliminating one potential source of bias for the participating laboratories (19, 20). Because the samples were prepared at the CAL and the CAL analysts helped define the target values, the CAL did not send in their analytical results. However, Tables VI-1 (1996) and VI-2 (1997) present the target values and the actual CAL analytical results for the samples. Because the CAL did not submit values, the CAL samples were not ranked; however, there is exceptionally close agreement with the target values, which were the theoretical concentrations of the analytes in the solutions.

B. Norwegian Institute for Air Research

Samples for the 16th intercomparison of analytical methods within the European Monitoring and Evaluation Programme (EMEP) reached the CAL in July 1997. No EMEP samples were received in 1996. The samples arrive ready for analysis, i.e., no dilutions or preparations are necessary. The CAL results are listed in Table VI-3. The absolute mean percent difference for all three samples is about 2 percent.

TABLE VI-1. World Meteorological Organization Acid Rain Performance Survey, 1996

Analyte	*Units*	*Sample 1*		*Sample 2*		*Sample 3*	
		Expected	*CAL*	*Expected*	*CAL*	*Expected*	*CAL*
Calcium	mg/L	0.055	0.054	0.136	0.133	0.006	0.009
Magnesium	mg/L	0.041	0.039	0.020	0.020	0.081	0.076
Sodium	mg/L	0.185	0.189	0.250	0.246	0.490	0.477
Potassium	mg/L	0.070	0.072	0.085	0.088	0.097	0.095
Ammonium	mg NH_4/L as N	0.079	0.080	0.62	0.66	0.79	0.83
Sulfate	mg SO_4/L as S	0.92	0.93	2.64	2.62	3.81	3.81
Nitrate	mg NO_3/L as N	0.11	0.16	0.12	0.11	1.39	1.37
Chloride	mg/L	0.296	0.30	0.64	0.65	0.94	0.96
pH	pH units	4.26	4.30	3.88	3.94	3.53	3.6
H	mg/L	54.95	50.12	131.83	125.89	295.12	251.19
Conductivity	µS/cm	26.3	26.4	65.7	64.9	137.1	134.1

Note: The expected values are based on the theoretical concentrations of the solutions.

TABLE VI-2. World Meteorological Organization Acid Rain Performance Survey, 1997

Analyte	*Units*	*Sample 1*		*Sample 2*		*Sample 3*	
		Expected	*CAL*	*Expected*	*CAL*	*Expected*	*CAL*
Calcium	mg/L	0.055	0.052	0.055	0.053	0.150	0.145
Magnesium	mg/L	0.041	0.039	0.020	0.019	0.097	0.089
Sodium	mg/L	0.196	0.190	0.251	0.245	1.345	1.305
Potassium	mg/L	0.086	0.082	0.078	0.074	0.534	0.514
Ammonium	mg NH_4/L as N	0.079	0.080	0.610	0.590	0.342	0.340
Sulfate	mg SO_4/L as S	0.695	0.70	4.14	4.21	2.18	2.19
Nitrate	mg NO_3/L as N	0.11	0.11	0.11	0.11	0.864	0.89
Chloride	mg/L	0.297	0.29	0.362	0.39	1.13	1.15
pH	pH units	4.39	4.43	3.65	3.72	3.89	3.95
H	mg/L	40.74	37.15	223.87	190.55	128.82	112.20
Conductivity	µS/cm	20.3	20.5	104.5	102.1	69.5	69.1

Note: The expected concentrations are based on the theoretical concentrations in the solutions.

TABLE VI-3. European Monitoring and Evaluation Programme Sixteenth Intercomparison of Methods, 1997

Analyte	*Units*	*Sample G-1*		*Sample G-2*		*Sample G-3*		*Sample G-4*	
		Expected	*CAL*	*Expected*	*CAL*	*Expected*	*CAL*	*Expected*	*CAL*
Calcium	mg/L	0.287	0.283	0.326	0.325	0.421	0.41	0.383	0.378
Magnesium	mg/L	0.155	0.152	0.17	0.165	0.248	0.24	0.232	0.228
Sodium	mg/L	0.3	0.298	0.451	0.447	0.488	0.481	0.263	0.26
Potassium	mg/L	0.178	0.177	0.255	0.251	0.306	0.301	0.153	0.15
Ammonium	mg/L	0.642	0.64	0.361	0.36	0.401	0.41	0.602	0.6
Sulfate	mg/L	1.04	1.05	1.03	1.04	2.01	2.01	1.9	1.9
Nitrate	mg/L	0.705	0.72	0.452	0.45	0.51	0.52	0.656	0.66
Chloride	mg/L	0.463	0.47	0.695	0.69	0.753	0.75	0.405	0.4
pH	pH units	4.42	4.46	4.469	4.54	4.076	4.13	4.097	4.14
H	mg/L	38.02	34.67	33.96	28.84	83.95	74.13	79.98	71.44
Conductivity	µS/cm	29	29	25.9	25.8	49.6	49	47.8	47.1
Absolute Mean Percent Difference		1.83		2.36		2.64		2.04	

C. Canada National Water Research Institute (NWRI)

The CAL participated in two studies sponsored by the Canada National Water Research Institute in both 1996 and 1997 . Begun in 1982 as the Long-Range Transport of Atmospheric Pollutants (LRTAP), the studies for 1996 and 1997 were numbers 68, 69, 70, and 71 (21-24). The NWRI samples include selected major ions, nutrients, and physical parameters in natural waters. Median concentrations are used as target values. Most of the samples are surface waters or precipitation samples for which calculated or certified values are not known. Results that are "high", "very high", "low" or "very low" are noted. These flags are based on the biases observed from the calculated target values and the biases of the other labs. A score is computed from these flagged samples. Zero, therefore, denotes the optimum score indicating that all parameters were within the expected range of the target values.

The CAL continues to score high due to high or very high flags for pH. Efforts continue to be made to improve the pH measurements of these high pH and high conductivity samples. Study No. 71, September-October 1997, shows that these efforts are paying off. The ranking for Study No. 71 was 4 out of 40 laboratories with a score of 2.17 and only two pH measurement flagged high. These high pH measurements will continue to be monitored by the CAL in an effort to improve the CAL's score and in turn improve the pH measurements for the NADP/NTN. The data for these studies can be found in Tables VI-4 (1996), VI-5 (1996), VI-6 (1997), and VI-7 (1997).

TABLE VI-4. National Water Research Institute Rain and Soft Water Interlaboratory Study No. 68, April 1996

		Sample 1		*Sample 2*		*Sample 3*		*Sample 4*		*Sample 5*	
Analyte	*Units*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	mg/L	0.900	0.905	0.140	0.144	1.890	1.967	2.284	2.273	3.220	3.180
Magnesium	mg/L	0.318	0.319	0.035	0.034	0.550	0.567	0.650	0.650	0.902	0.898
Sodium	mg/L	0.040	0.035	0.107	0.105	0.220	0.219	0.122	0.125	0.382	0.389
Potassium	mg/L	0.034	0.034	0.030	0.026	0.062	0.063	0.110	0.105	0.163	0.163
Ammonium	mg NH_4/L as N	0.16	0.15	0.18	0.17	0.28	0.28	0.59	0.59	0.01	<0.02
Sulfate	mg/L	1.80	1.82	1.30	1.28	2.69	2.72	5.05	5.09	4.58	4.63
Nitrate	mg NO_3/L as N	0.35	0.35	0.21	0.20	0.40	0.39	1.01	0.99	1.18	1.19
Chloride	mg/L	0.10	0.09	0.20	0.19	0.41	0.43	0.31	0.30	0.71	0.74
pH	units	6.04	6.33	4.71	4.72	6.45	6.92	6.00	6.55	6.23	6.80
Conductivity	µS/cm	11.2	11.3	12.0	12.6	20.0	21.6	28.3	28.8	32.0	32.0

		Sample 6		*Sample 7*		*Sample 8*		*Sample 9*		*Sample 10*	
Analyte	*Units*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	mg/L	3.310	3.260	4.100	3.990	4.590	4.431	6.670	6.444	6.800	6.616
Magnesium	mg/L	0.719	0.713	0.612	0.600	0.790	0.773	1.390	1.361	0.730	0.724
Sodium	mg/L	1.60	1.62	2.590	2.616	2.530	2.576	0.690	0.691	0.858	0.867
Potassium	mg/L	0.220	0.220	0.371	0.370	0.577	0.574	0.260	0.260	0.248	0.251
Ammonium	mg NH_4/L as N	0.01	<0.02	0.01	<0.02	0.01	<0.02	0.01	<0.02	0.02	0.02
Sulfate	mg/L	3.01	3.06	3.78	3.81	4.52	4.58	1.72	1.75	6.33	6.33
Nitrate	mg NO_3/L as N	0.10	0.10	0.21	0.21	0.26	0.27	0.14	0.14	0.07	0.07
Chloride	mg/L	1.57	1.56	3.48	3.48	1.84	1.84	0.74	0.74	0.31	0.32
pH	units	6.84	7.28	6.81	7.19	7.03	7.36	7.44	7.65	7.30	7.56
Conductivity	µS/cm	32.3	32.8	42.0	42.1	45.0	45.1	49.7	50.0	48.0	48.5

TABLE VI-5. National Water Research Institute Rain and Soft Water Interlaboratory Study No. 69, October 1996

		Sample 1		*Sample 2*		*Sample 3*		*Sample 4*		*Sample 5*	
Analyte	*Units*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	mg/L	1.582	1.573	1.518	1.507	3.234	2.863	1.534	1.504	3.314	2.917
Magnesium	mg/L	0.280	0.272	0.277	0.268	0.920	0.825	0.277	0.267	0.920	0.837
Sodium	mg/L	0.06	0.053	0.063	0.059	0.387	0.384	0.058	0.055	0.397	0.394
Potassium	mg/L	0.025	0.024	0.031	0.031	0.159	0.162	0.024	0.024	0.167	0.167
Ammonium	mg/L NH_4 as N	0.17	0.18	0.18	0.18	0.01	<0.02	0.17	0.17	0.01	<0.02
Sulfate	mg/L	1.43	1.43	1.53	1.53	4.60	4.63	5.66	5.63	8.87	8.86
Nitrate	mg/L NO_3 as N	0.28	0.27	0.30	0.30	1.20	1.23	0.58	0.58	1.47	1.47
Chloride	mg/L	0.130	0.13	0.16	0.16	0.71	0.71	0.15	0.16	0.73	0.75
pH	units	6.65	6.84	6.60	6.79	6.37	6.69	4.34	4.35	4.33	4.36
Conductivity	µS/cm	13.8	12.5	13.6	12.3	31.6	28.3	34.5	36.7	53.1	48.4

		Sample 6		*Sample 7*		*Sample 8*		*Sample 9*		*Sample 10*	
Analyte	*Units*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	mg/L	2.972	2.668	6.100	5.44	1.988	1.952	2.910	2.62	4.81	4.27
Magnesium	mg/L	0.472	0.453	0.570	0.544	0.480	0.461	0.700	0.632	0.823	0.750
Sodium	mg/L	0.549	0.540	0.679	0.673	0.615	0.604	0.963	0.956	2.86	2.60
Potassium	mg/L	0.204	0.204	0.221	0.222	0.230	0.231	0.475	0.478	0.410	0.419
Ammonium	mg/L NH_4 as N	0.10	0.10	0.04	0.04	0.03	0.02	0.02	0.017	0.00	<0.02
Sulfate	mg/L	5.19	5.23	5.76	5.78	6.08	6.03	6.93	6.85	3.53	3.57
Nitrate	mg/L NO_3 as N	0.52	0.52	0.75	0.77	0.00	0.01	0.05	0.05	0.21	0.21
Chloride	mg/L	0.23	0.23	0.25	0.25	0.51	0.51	1.04	1.04	2.46	2.41
pH	units	6.29	6.66	6.96	7.24	6.30	6.32	6.71	6.80	7.31	7.42
Conductivity	µS/cm	26.5	24.2	43.2	38.8	22.0	19.9	31.0	28.0	47.3	42.9

TABLE VI-6. National Water Research Institute Soft Water Interlaboratory Study FP70, March and April 1997

		Sample 1		*Sample 2*		*Sample 3*		*Sample 4*		*Sample 5*	
Analyte	*Units*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	mg/L	0.606	0.606	1.38	1.386	1.91	1.887	0.708	0.703	2.640	2.436
Magnesium	mg/L	0.1735	0.166	0.434	0.420	0.55	0.538	0.16	0.154	0.998	0.948
Sodium	mg/L	0.069	0.069	0.100	0.106	0.216	0.219	0.05	0.050	0.280	0.284
Potassium	mg/L	0.025	0.019	0.060	0.059	0.060	0.062	0.016	0.013	0.159	0.158
Ammonium	mg/L NH_4 as N	0.168	0.17	0.003	<0.02	0.0023	<0.02	0.170	0.18	0.355	0.37
Sulfate	mg/L	1.3625	1.35	2.4035	2.45	5.537	5.55	4.039	4.05	3.81	3.85
Nitrate	mg/L NO_3 as N	0.24	0.23	0.65	0.67	1.50	1.52	0.847	0.86	0.57	0.57
Chloride	mg/L	0.15	0.15	0.22	0.22	0.414	0.42	0.117	0.12	0.4875	0.48
pH	units	5.96	6.61	5.81	6.01	4.10	4.15	4.10	4.15	6.91	7.25
Conductivity	µS/cm	8.535	8.7	15.0	15.5	53.9	55.7	43.4	44.4	29.9	30.3

		Sample 6		*Sample 7*		*Sample 8*		*Sample 9*		*Sample 10*	
Analyte	*Units*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	mg/L	1.98	1.947	0.50	0.495	0.80	0.802	2.5	2.308	4.55	4.196
Magnesium	mg/L	0.31	0.300	0.36	0.344	0.385	0.371	0.600	0.572	0.8300	0.804
Sodium	mg/L	0.60	0.598	2.62	2.556	2.937	2.796	2.20	2.128	0.5561	0.556
Potassium	mg/L	0.41	0.407	0.23	0.229	0.293	0.290	0.51	0.505	0.200	0.198
Ammonium	mg/L NH_4 as N	0.018	0.02	0.003	<0.02	0.005	<0.02	0.026	0.02	0.305	0.33
Sulfate	mg/L	5.43	5.49	3.70	3.73	2.221	2.26	4.723	4.72	5.86	5.87
Nitrate	mg/L NO_3 as N	0.41	0.41	0.1240	0.12	0.032	0.04	0.070	0.07	0.860	0.87
Chloride	mg/L	0.45	0.44	4.1075	4.05	4.6535	4.55	1.705	1.69	0.5200	0.51
pH	units	5.34	5.33	4.585	4.61	5.445	5.53	6.80	7.01	6.99	7.25
Conductivity	µS/cm	23.55	24.6	34.05	35.1	26.95	27.4	31.85	32.2	40.75	41.4

TABLE VI-7. National Water Research Institute Soft Water Interlaboratory Study FP71, September and October 1997

		Sample 1		*Sample 2*		*Sample 3*		*Sample 4*		*Sample 5*	
Analyte	*Units*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	mg/L	0.700	0.684	0.9100	0.892	1.99	1.938	2.140	2.087	1.915	1.868
Magnesium	mg/L	0.1600	0.154	0.3200	0.306	0.4800	0.455	0.5800	0.55	0.5600	0.53
Sodium	mg/L	0.050	0.048	0.0360	0.037	0.6200	0.6	1.195	1.181	0.2200	0.216
Potassium	mg/L	0.013	0.013	0.037	0.039	0.2335	0.231	0.270	0.27	0.064	0.063
Ammonium	mg/L NH_4 as N	0.170	0.16	0.0045	<0.02	0.0275	0.02	0.0045	<0.02	0.0040	<0.02
Sulfate	mg/L	2.1300	2.15	1.8050	1.82	6.060	6.14	2.6025	2.68	2.6596	2.72
Nitrate	mg/L NO_3 as N	0.2630	0.26	0.5200	0.54	0.0070	0.01	0.0040	<0.00	0.700	0.73
Chloride	mg/L	0.1200	0.12	0.095	0.1	0.510	0.51	1.810	1.79	0.4100	0.43
pH	units	5.35	5.3	5.28	5.3	6.226	6.32	6.835	6.95	6.429	6.53
Conductivity	µS/cm	10.900	11.3	12.10	13.1	22.25	22.5	24.50	24.7	19.1	19.

		Sample 6		*Sample 7*		*Sample 8*		*Sample 9*		*Sample 10*	
Analyte	*Units*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	mg/L	4.79	4.61	2.600	2.5	2.96	2.84	2.68	2.554	3.50	3.389
Magnesium	mg/L	0.5700	0.54	0.9100	0.879	0.5500	0.533	0.9260	0.88	0.9000	0.86
Sodium	mg/L	0.1520	0.15	0.2760	0.269	2.020	2.02	0.1500	0.145	1.7725	1.76
Potassium	mg/L	0.145	0.144	0.154	0.154	0.3595	0.359	0.1700	0.168	0.2560	0.258
Ammonium	mg/L NH_4 as N	0.0050	<0.02	0.1890	0.18	0.0050	<0.02	0.0030	<0.02	0.0050	<0.02
Sulfate	mg/L	3.7475	3.84	3.8560	3.94	3.750	3.87	5.960	6.02	4.640	4.76
Nitrate	mg/L NO_3 as N	1.431	1.44	0.6700	0.69	0.1600	0.16	0.9500	0.98	0.8600	0.9
Chloride	mg/L	0.2864	0.29	0.5100	0.52	2.1000	2.14	0.3874	0.39	3.1400	3.12
pH	units	6.810	7.02	6.8100	6.95	6.815	7.	6.092	6.23	6.66	6.89
Conductivity	µS/cm	35.15	36.1	27.80	27.9	32.55	32.3	28.70	28.3	40.00	38.0

VII. SUMMARY

This report summarizes the results from the quality assurance program in place at the Central Analytical Laboratory (CAL) of the NADP/NTN/AIRMoN in 1996 and 1997. Due to personnel changes and the move of the Coordination Office from Colorado State University to the Program Office at the Illinois State Water Survey, the two years were combined. Information is presented in the form of tables, figures, and brief written explanations. Appendices A and B provide supplemental information.

Those quality assurance activities that occur on a daily basis are the operation, standardization, and maintenance of the scientific instrumentation used to analyze samples and provide data for the data user. Daily records document reagent and standard preparation and instrument performance and maintenance. Standardization curves are verified using internally formulated CAL rain samples simulating the 25th and 75th percentile concentration levels of the NADP network. The analytical values of these Quality Control Samples (QCS) are recorded and used to construct daily and weekly control charts. QCS data indicate that all parameters measured at the CAL are within the bias and precision target specifications as written in the Network Quality Assurance Plan (1) for both 1996 and 1997.

The internal blinds program provides bias and precision values that more closely approximate those values for real samples and evaluates the contribution of the filtration process to the sample chemistry. Bias and precision numbers are higher for the internal blinds than for the QCS, which has been explained by the random location of the samples in the sample queue and the ion concentrations. Internal blinds that consist of deionized (DI) water and pH 4.3 nitric acid indicate little or no sample carryover during the analysis or no false positives. Filtration lends variability to all samples as well as a positive bias for sodium and a slight negative bias for sulfate for both years.

Replicate network samples serve to verify the precision of real sample analyses. Comparison of variance to that of the QCS and internal blinds shows the replicate samples to be comparable or slightly better for all the parameters measured at the CAL.

Deionized (DI) water and filter and container leachates are analyzed weekly to determine the presence of contamination or whether the sample chemistry is compromised by either the filtration process or any of the containers that the samples contact. Three sources throughout the laboratory provide DI water that is generally ion-free with pH in the mid-5 range and conductivity less than one. Filters leached with DI water and FR25 show both initial filtrates to contain measurable sodium and raised conductivity. The second leachate contains less sodium. Filter leachates do not exhibit the sulfate reduction seen in the internal blind program, but the concentrations used are different. Bucket leachates show slight elevations in calcium, sodium, potassium, and chloride in both 1996 and 1997. A dilution effect is seen when larger leachate volumes are used. One-liter bottle leachates are virtually clean except for potassium in both years although there was less potassium in 1997 than in 1996. Snap-on lids appear to contribute some sodium, calcium, and potassium similar to the buckets for both 1996 and 1997. Normal operations at most sites provide little or no contact of the sample with the lid used to cap the bucket for transport to the laboratory. AIRMoN bottles were clean.

The AIRMoN internal blind program is a cooperative project with the Bondville, Illinois Site Operator and the AIRMoN Coordinator. The results for the analyses of these samples show that the relative standard deviations (RSD) for the solutions used in 1996 and 1997 (FR25, FR75, and pH 4.3 nitric acid QCS) are within the data quality objectives of the Network QA Plan for all parameters except for ammonium in FR25 in 1997. Ammonium is not stable and these solutions are not stored in a refrigerator prior to use. Some loss of ammonium occurs between the time the solution is prepared and the time it is analyzed. The RSD of the pH 4.3 nitric acid QCS is comparable to, if not better than, that same solution, unfiltered, in the NADP/NTN internal blind program.

When the weekly NADP samples have been analyzed, the data are transferred in batches to the data management section, which compiles semimonthly printouts containing the data for 400 to 500 samples. Those samples with volumes greater than 35 milliliters, designated "Wet" or "W", undergo complete chemical analyses for all parameters. Results are submitted for an ion balance and a calculated versus measured conductance test. Samples not meeting the required criteria are flagged and reanalyzed. In 1996, of the 6917 "W" samples, 430 were flagged for reanalysis with 170 changes made to the database for 161 samples. In 1997, 328 samples were flagged of 7029 "W" samples with 194 changes to the database for 120 samples. Once again for both years, the Ion Percent Difference (IPD) mean was negative, as was the median for 1996. The median for 1997 was 0.08 or slightly positive. This indicates an excess of cations in half or more of the samples analyzed. This is a reverse of what was seen prior to the 1994 change in the shipping protocols, now shipping the samples in bottles rather than in the collection bucket, and is believed to be due to the absence of the butadiene rubber gasket in the lid previously used on network samples. The Conductance Percent Difference (CPD) has been skewed negatively since 1979, and it continued to be so in both 1996 and 1997. This means that the measured conductivity exceeds the calculated conductivity, indicating that not all of the parameters are being measured individually in the samples.

The AIRMoN field blanks program was begun in 1994, and field blanks are collected monthly at each site. Five different solutions were used in 1996 and four solutions were used in 1997. Six 250-mL bottles of field blank solutions are sent to the sites twice a year to be used on the first Tuesday of each month with no precipitation in the previous 26 hours and not more than six lid openings without precipitation. A field blank bottle is taken to the site from the field laboratory when the conditions are met and half of the 250 mL sample is poured into the bucket ("DF"). The rest of the solution remains in the original bottle, which is immediately recapped and returned to the CAL without further opening ("DK"). The solution that was poured into the bucket is kept in the bucket for at least two hours or overnight and is then treated like a normal precipitation sample. Both "DK" and "DF" bottles are returned to the CAL along with a Field Observer Form filled out for the "DK" sample. The difference in concentrations found in the "DF" and "DK" bottles indicates a large variability in the amount of dry deposition entering the buckets. The variability of the median absolute difference, when compared to replicate analyses of the same sample, indicates a larger difference between the two solutions than can be explained by repeat analyses alone. Higher sodium and calcium indicates that dry deposition is entering the sample bucket. The numbers, however, are still low compared to the concentration of the average precipitation sample.

The USGS Interlaboratory Comparison study once again included five laboratories in both 1996 and 1997. Four different sample matrices were used and shipped to the laboratories every two weeks. The 50th and 90th percentile absolute differences for these replicate samples indicate that the CAL had excellent ammonium and sulfate results for 1996 and, considering all the analytes, the CAL was rated as one of the best of the five laboratories. Considering all of the analytes for 1997, the CAL was again one of the best, if not the best, laboratory. The CAL again had excellent results for pH.

In both 1996 and 1997, the CAL participated in three interlaboratory comparisons: the World Meteorological Organization (WMO) and two studies from the Canada National Water Research Institute (NWRI). In 1997, the CAL also participated in the Norwegian Institute for Air Research (EMEP), which did not have a study in 1996. The results were good for all the studies. Fifty-eight laboratories participated in the 1996 WMO study and 61 laboratories in the 1997 WMO study. The CAL did not actually submit their results for the WMO samples for official inclusion in the study as those samples were prepared at the CAL. However, in comparing the numbers measured at the CAL to the theoretical values, the CAL results were excellent. The EMEP mean absolute percent difference was higher in 1997 than in 1995, but still quite low, although the 1995 results remain the lowest that the CAL has attained. The NWRI results still show that the CAL has a problem with high pH and high conductivity samples although the second study in 1997 was again typical of previous results. The CAL received several high and very high pH results in the other three studies putting the CAL in the middle of the laboratories participating. The scores from the 1996 and 1997 studies indicate that the CAL compares favorably with its peers throughout the world.

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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 homogeneous 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 (25).
Critical Concentration		A calculated concentration used to determine whether the measured bias is statistically significant (26). $\mathit{Critical\ Concentration} = t * s_{sp} * \sqrt{1/n_1 + 1/n_2}$

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 the analysts. These data are valuable in assessing bias and precision for network samples.

Term	Abbreviation	Definition
Mean	$\bar{x}$	The average obtained by dividing a sum by the number of its addends. $\bar{x} = \sum_{i=1}^{n} x_i / n$
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 (27).
Percent Bias		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. $\%Bias = 100 * [(V_m - V_t)/V_t]$ where: V_m = measured value V_t = true value
Precision		The degree of agreement of repeated measurements of a homogeneous 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 Deviation	**RSD**	The standard deviation expressed as a percentage: RSD = 100 * $(s/\bar{x})$ where: s = sample standard deviation $\bar{x}$ =mean value

Term	Abbreviation	Definition
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 Deviations		The number representing the dispersion of values around their mean. $s = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n-1}}$ where: x_i = each individual value $\bar{x}$ = the mean of all values n = number of values
Standard Deviation Estimated from Measurements		The standard deviation may be estimated from the differences of several sets of paired Paired measurements using the equation (25): $s = \sqrt{\frac{\sum d^2}{2k}}$ where: d = difference of duplicate measurements k = number of sets of duplicate measurements

Term	Abbreviation	Definition
Variance	s^2	The best measure of the dispersion of repeated results (precision) (26). $s^2 = \frac{\Sigma d^2}{2n}$ where d = X_i - X'_i, the difference between value 1 and 2 of pair i n = the number of pair of data

APPENDIX B

WEEKLY QC/QA PROCEDURES: TABLES AND FIGURES

1996 and 1997

TABLE B-1. Comparison of Filtered and Unfiltered Internal Blind Samples, High Purity Standards Simulated Rainwater I (HPS-SRI), 1996

Parameter	*Target Concentration[a] (mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias %*	*Precision (mg/L)*	*Precision (%)*
Calcium	0.015	0.015[b]	24	0.000	-1.4	0.005	33.6
		0.021[c]	12	0.006	42.8	0.008	39.8
Magnesium	0.026	0.026	24	0.000	-0.8	0.001	3.5
		0.026	12	0.000	0.3	0.002	7.9
Sodium	0.200	0.203	24	0.003	1.5	0.010	5.0
		0.287	12	0.087	43.5	0.038	13.2
Potassium	0.050	0.054	24	0.004	7.9	0.005	10.1
		0.052	12	0.002	4.5	0.007	12.7
Ammonium	0.10	0.10	24	0.00	-4.6	0.01	14.5
		0.18	12	0.08	80.0	0.06	34.8
Sulfate	2.50	2.63	24	0.13	5.3	0.03	1.0
		2.52	12	0.02	0.6	0.06	2.5
Nitrate	0.50	0.51	24	0.01	2.2	0.01	1.7
		0.55	12	0.05	9.2	0.03	4.7
Chloride	0.25	0.25	24	0.00	-1.0	0.01	4.4
		0.33	12	0.08	32.7	0.05	15.9
pH (units)	4.40(39.81)	4.29(50.8)	24	-0.11(11.0)	-2.4(27.7)	0.02(2.17)	0.4(4.3)
µeq/L		4.30(50.7)[d]	12	-0.10(10.9)	-2.4(27.5)	0.02(2.47)	0.5(4.9)
Conductivity	23.2	25.8	24	2.6	11.2	0.60	2.3
µS/cm		25.8[d]	12	2.6	11.4	0.51	2.0

Notes: [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 filtered samples. [d] pH and conductivity are measured on unfiltered sample prior to filtering .

TABLE B-2. Comparison of Filtered and Unfiltered Internal Blind Samples
High-Purity Standards Simulated Rainwater I (HPS-SRI), Lot # 690826, 1997

Parameter	*Target Concentration[a] (mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias %*	*Precision (mg/L)*	*Precision (%)*
Calcium	0.015	0.016[b]	25	0.001	6.7	0.003	18.8
		0.025[c]	13	0.010	66.7	0.008	32.0
Magnesium	0.025	0.025	25	0.0	0.0	0.001	4.0
		0.026	13	0.001	4.0	0.001	3.8
Sodium	0.21	0.227	25	0.017	8.1	0.013	5.7
		0.264	13	0.054	25.7	0.017	6.4
Potassium	0.050	0.046	25	-0.004	-8.0	0.002	4.3
		0.044	13	-0.006	-12.0	0.001	2.3
Ammonium	0.100	0.09	25	-0.01	-10.	0.01	10.6
		0.10	13	0.0	0.0	0.01	13.0
Sulfate	2.5	2.71	25	0.21	8.4	0.03	1.1
		2.62	13	0.12	4.8	0.03	1.1
Nitrate	0.50	0.54	25	0.04	8.0	0.02	3.1
		0.58	13	0.08	16	0.02	4.3
Chloride	0.25	0.25	25	0.0	0.0	0.01	5.6
		0.27	13	0.02	8.0	0.02	8.5
pH (units)	4.30(50.1)	4.29(51.6)[d]	25	-0.01(1.5)	-0.2(3.0)	0.02(2.64)	0.51(5.1)
H^+ (µeq/L)		4.28(52.4)[d]	13	-0.02(2.3)	-0.5(4.6)	0.02(2.95)	0.47(5.6)
Conductivity	25.9	26.2[d]	25	0.3	1.2	0.62	2.4
(µS/cm)		26.1[d]	13	0.2	0.8	0.77	3.0

Notes: [a] Target values provided by High-Purity Standards for Simulated Rainwater I, lot # 690826. [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. [d] pH and conductivity are measured on unfiltered sample prior to filtering.

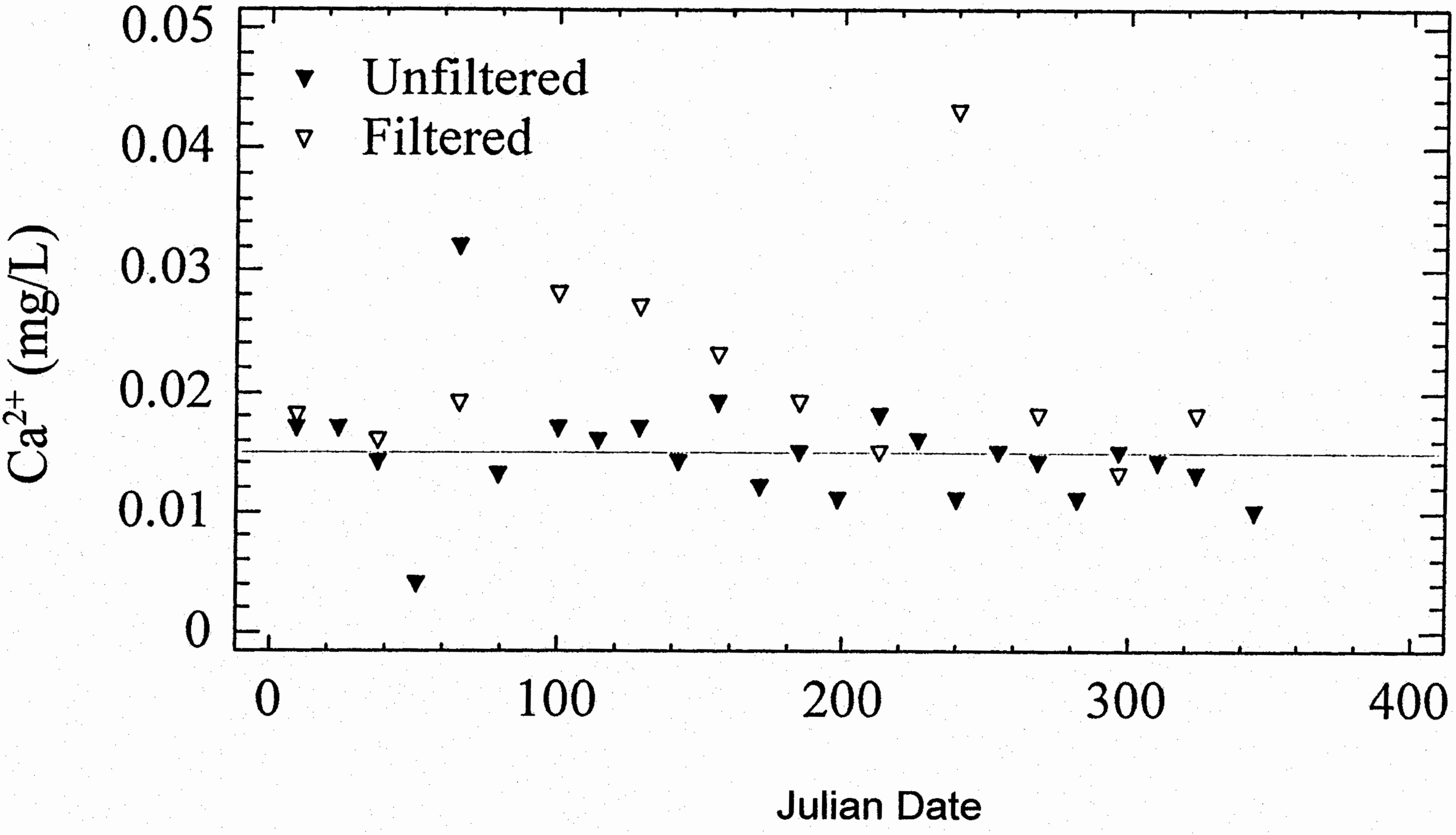


FIGURE B-1. Comparison of filtered and unfiltered internal blind samples (calcium HPS-SRI), 1996.

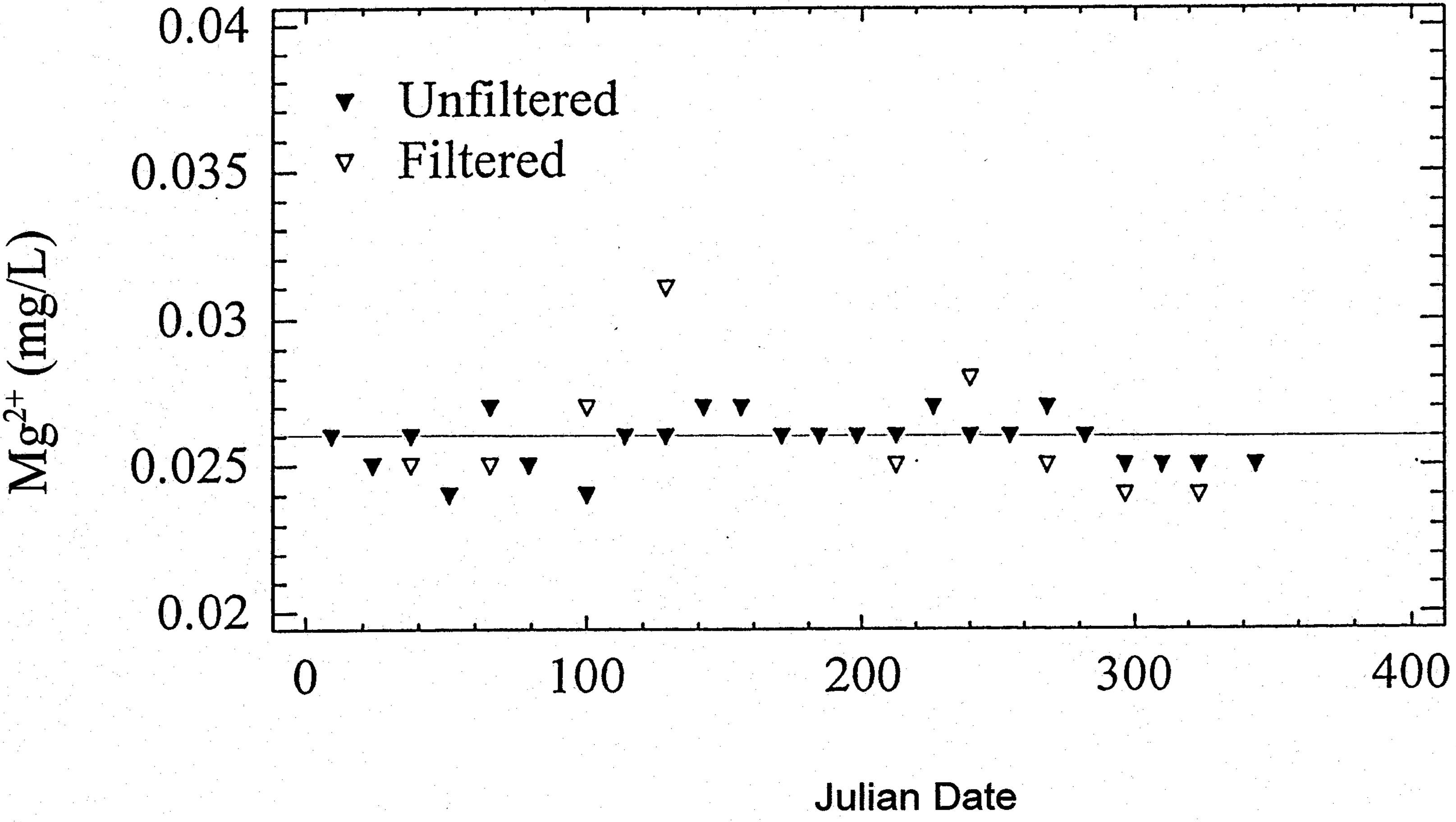


FIGURE B-2. Comparison of filtered and unfiltered internal blind samples (magnesium HPS-SRI), 1996.

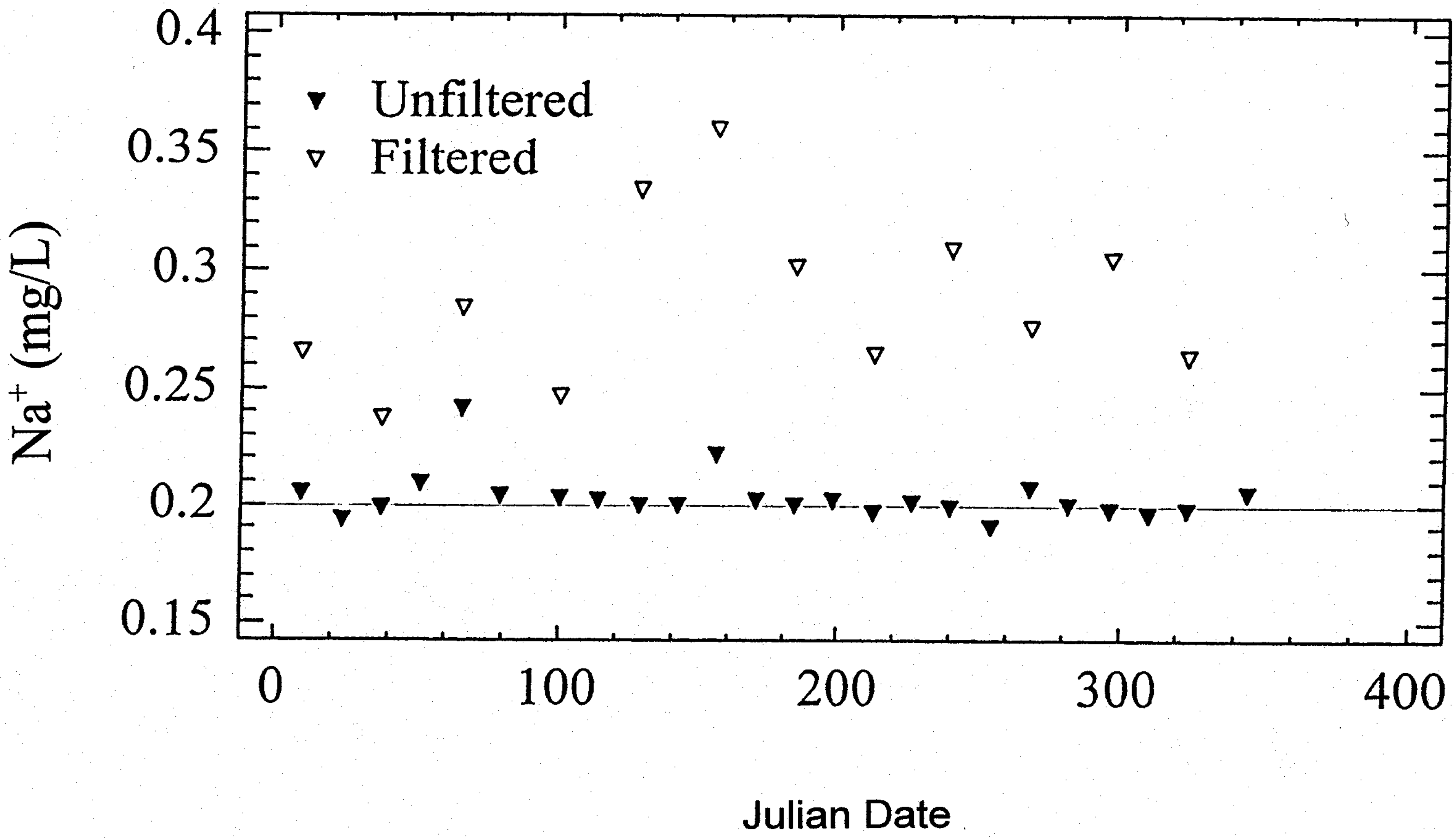


FIGURE B-3. Comparison of filtered and unfiltered internal blind samples (sodium HPS-SRI), 1996.

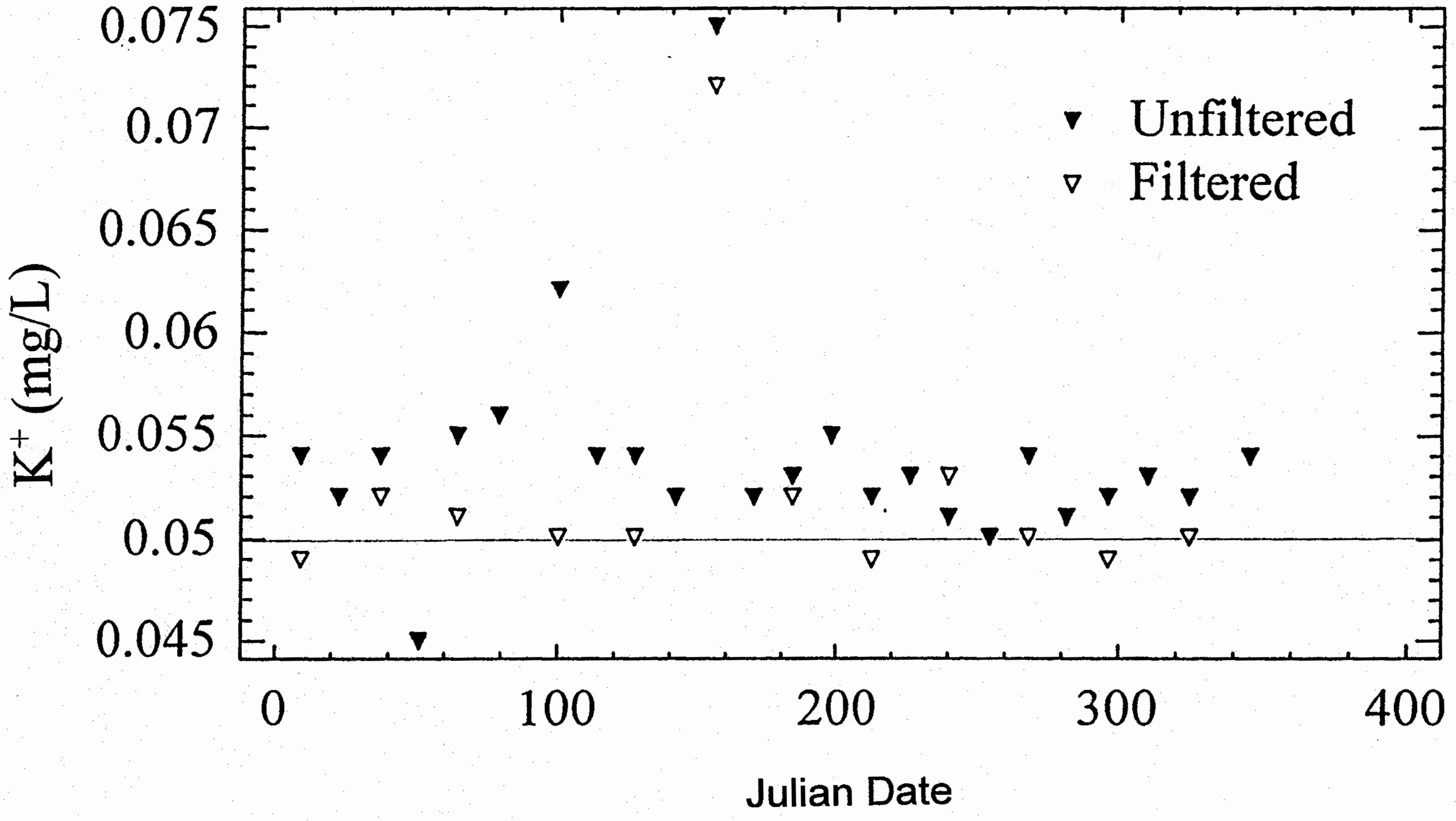


FIGURE B-4. Comparison of filtered and unfiltered internal blind samples (potassium HPS-SRI), 1996.

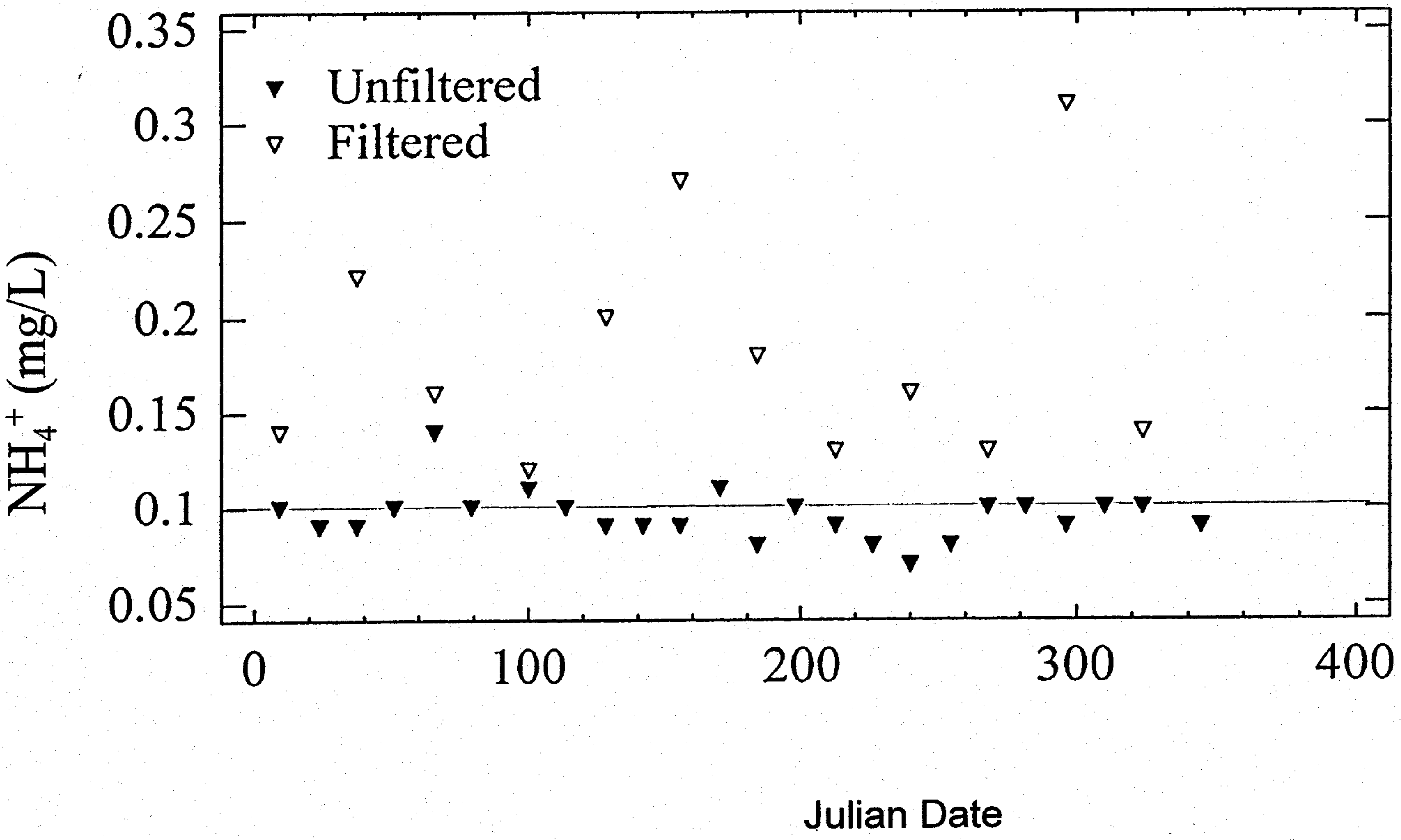


FIGURE B-5. Comparison of filtered and unfiltered internal blind samples (ammonium HPS-SRI), 1996.

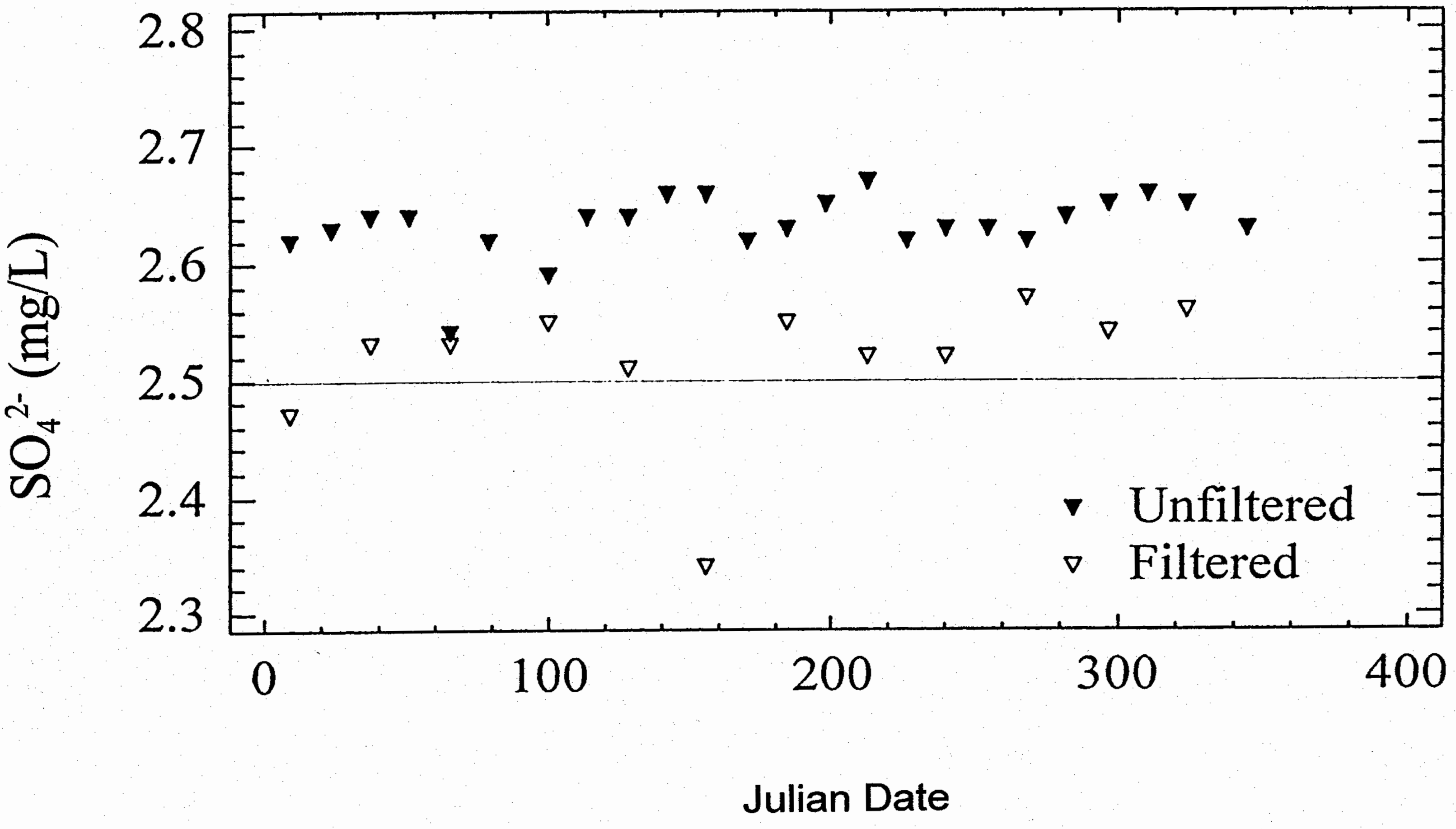


FIGURE B-6. Comparison of filtered and unfiltered internal blind samples (sulfate HPS-SRI), 1996.

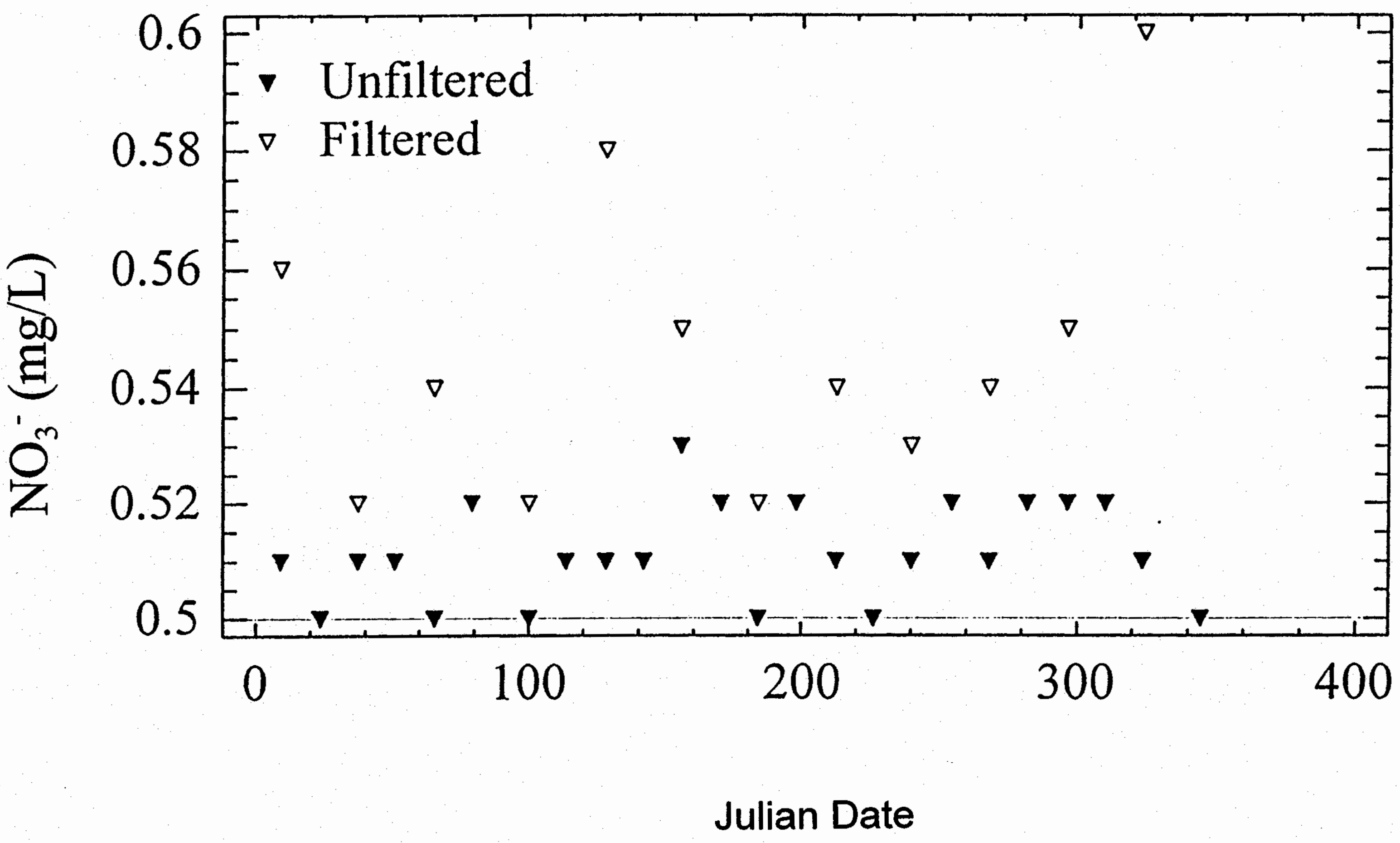


FIGURE B-7. Comparison of filtered and unfiltered internal blind samples (nitrate HPS-SRI), 1996.

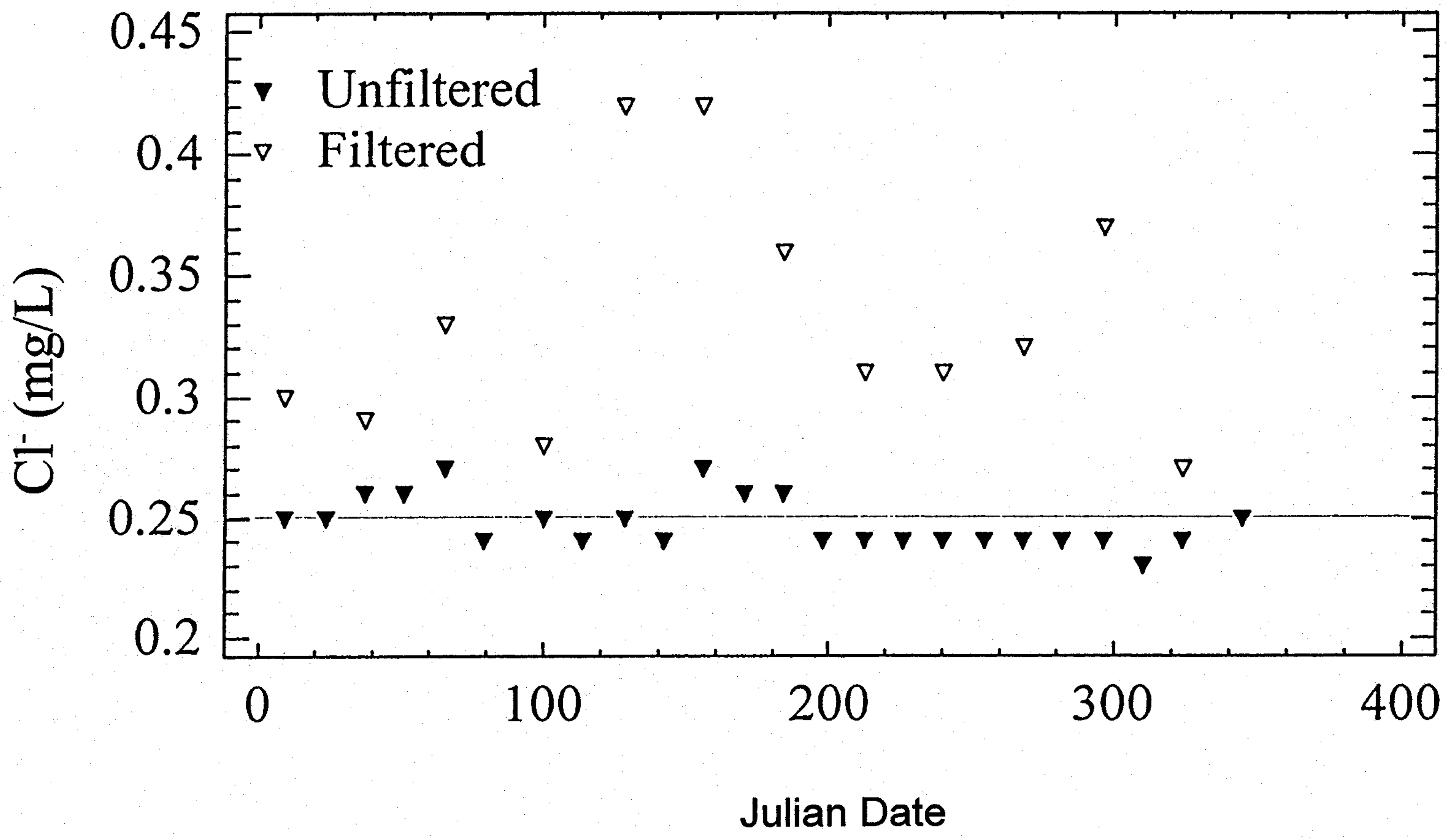


FIGURE B-8. Comparison of filtered and unfiltered internal blind samples (chloride HPS-SRI), 1996.

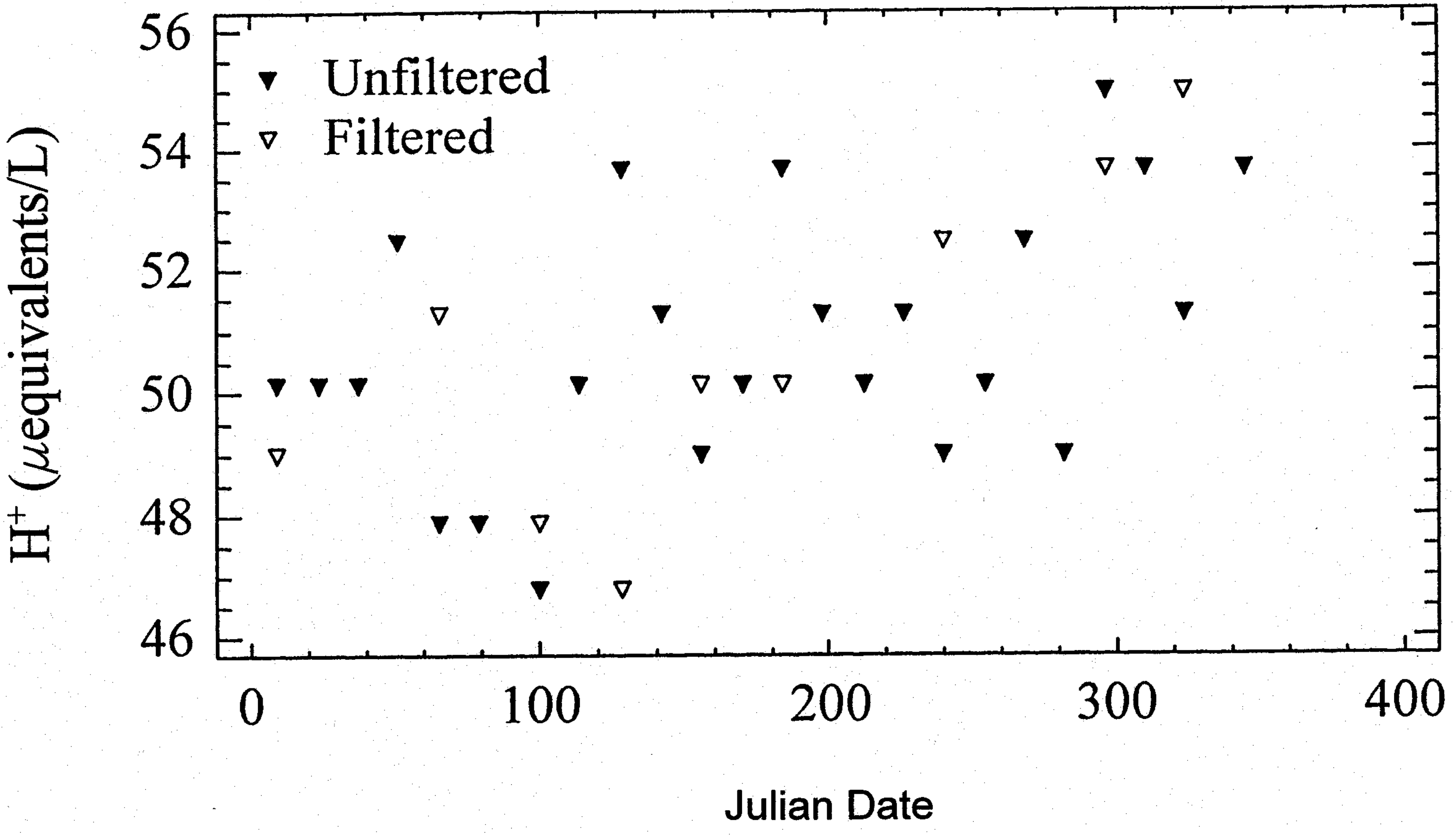


FIGURE B-9. Comparison of filtered and unfiltered internal blind samples (H^+ HPS-SRI), 1996.

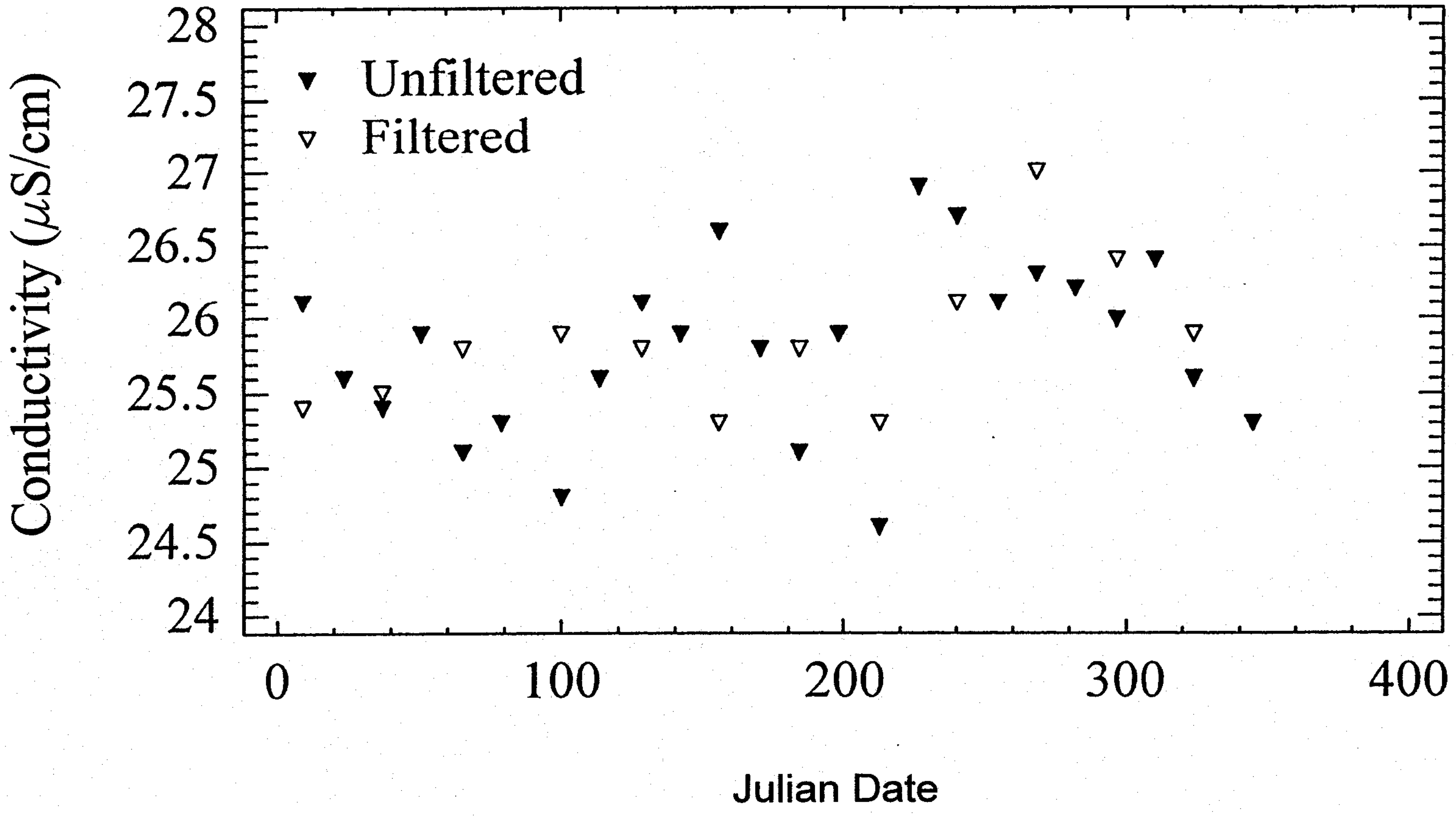


FIGURE B-10. Comparison of filtered and unfiltered internal blind samples (conductivity HPS-SRI), 1996.

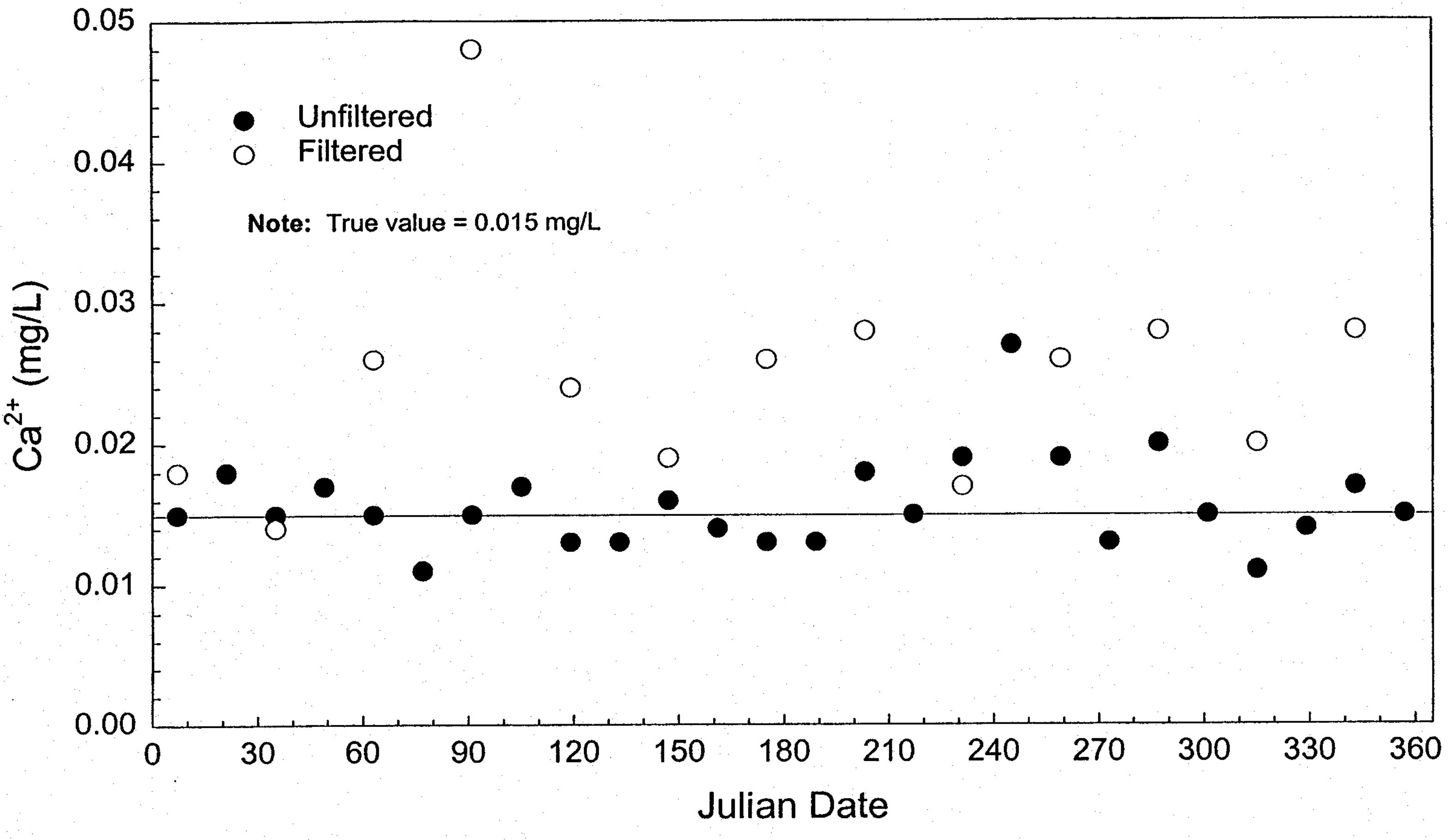


FIGURE B-11. Comparison of filtered and unfiltered internal blind samples (calcium HPS-SRI), 1997.

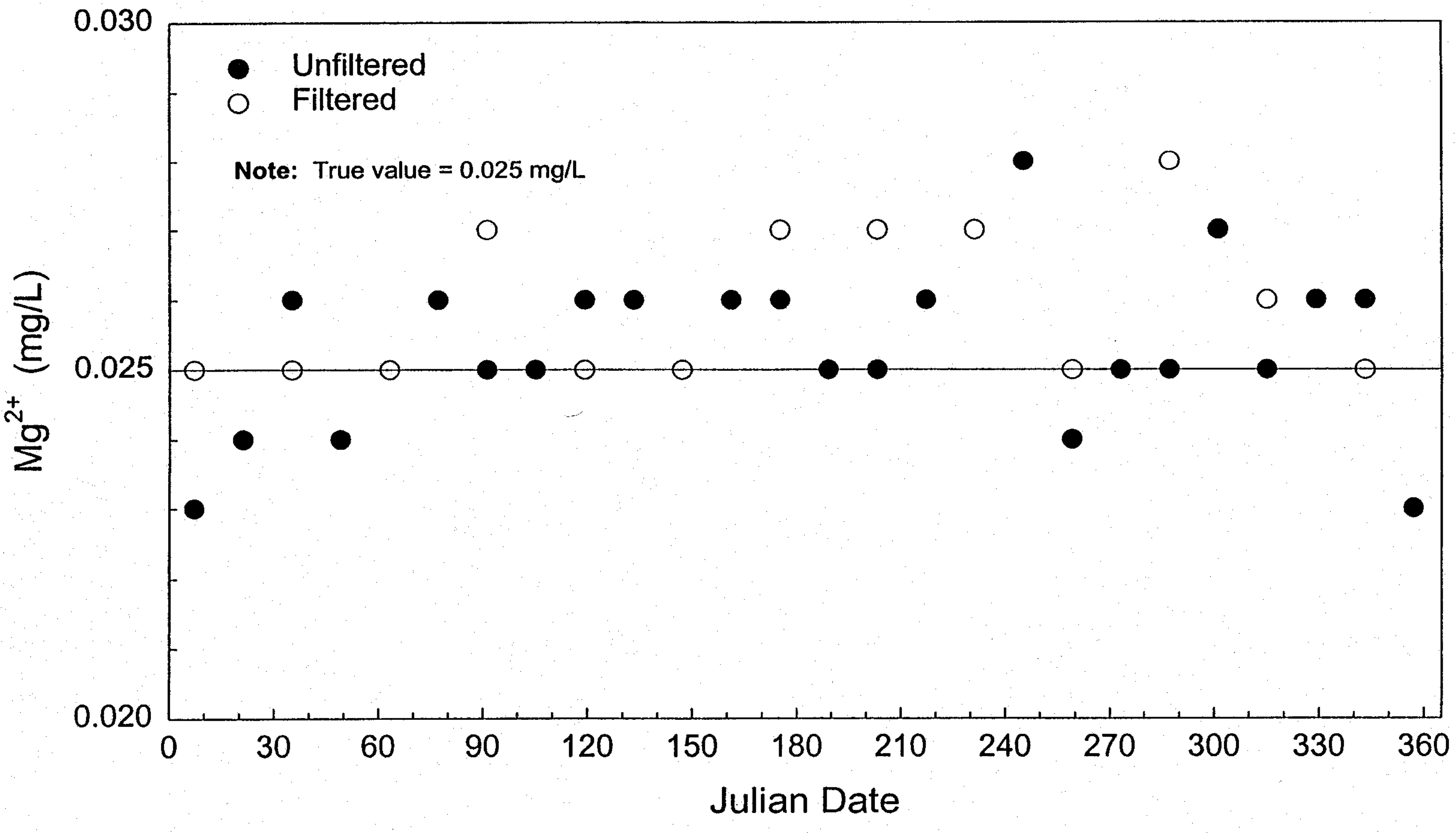


FIGURE B-12. Comparison of filtered and unfiltered internal blind samples (magnesium HPS-SRI), 1997.

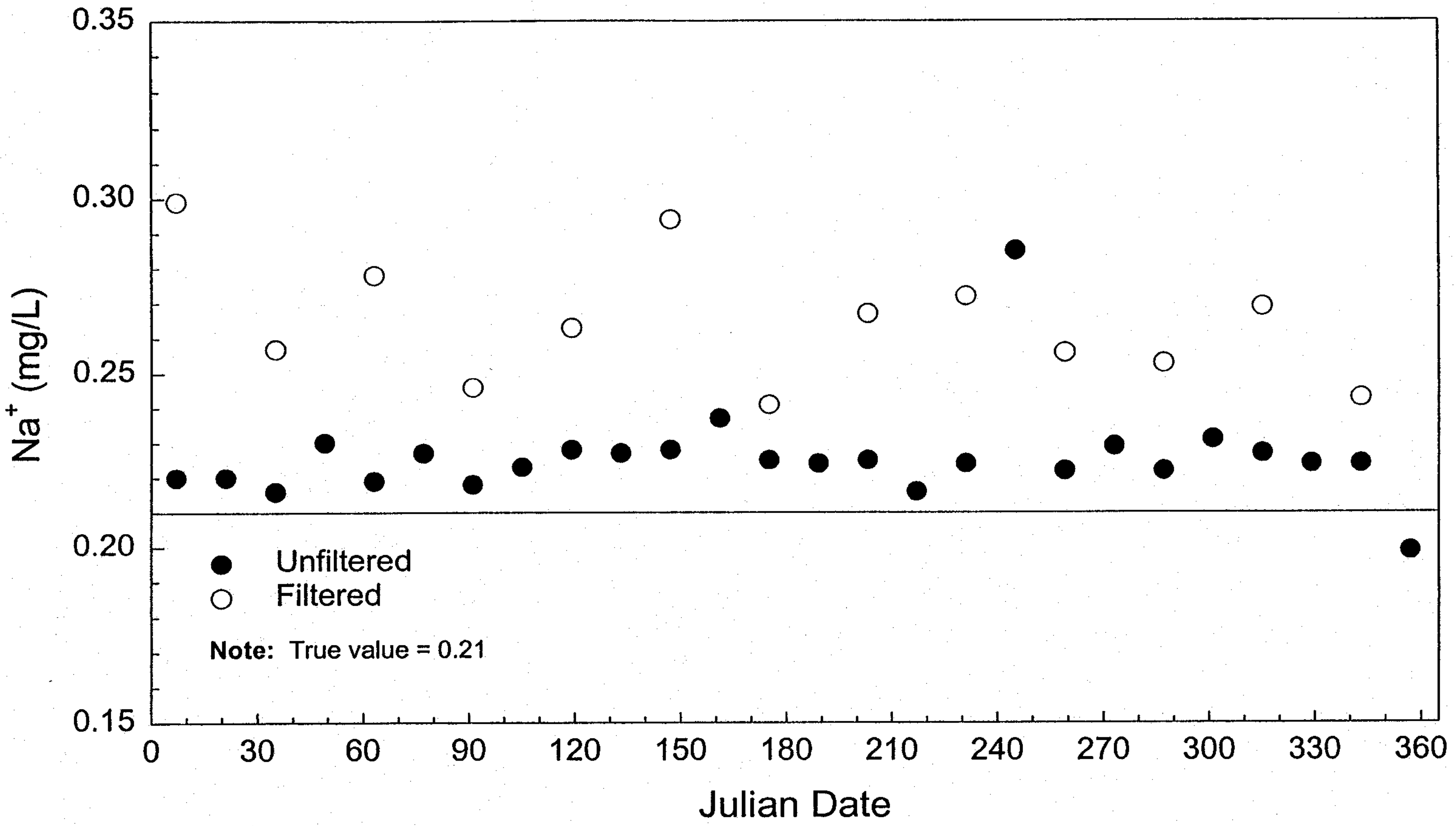


FIGURE B-13. Comparison of filtered and unfiltered internal blind samples (sodium HPS-SRI), 1997.

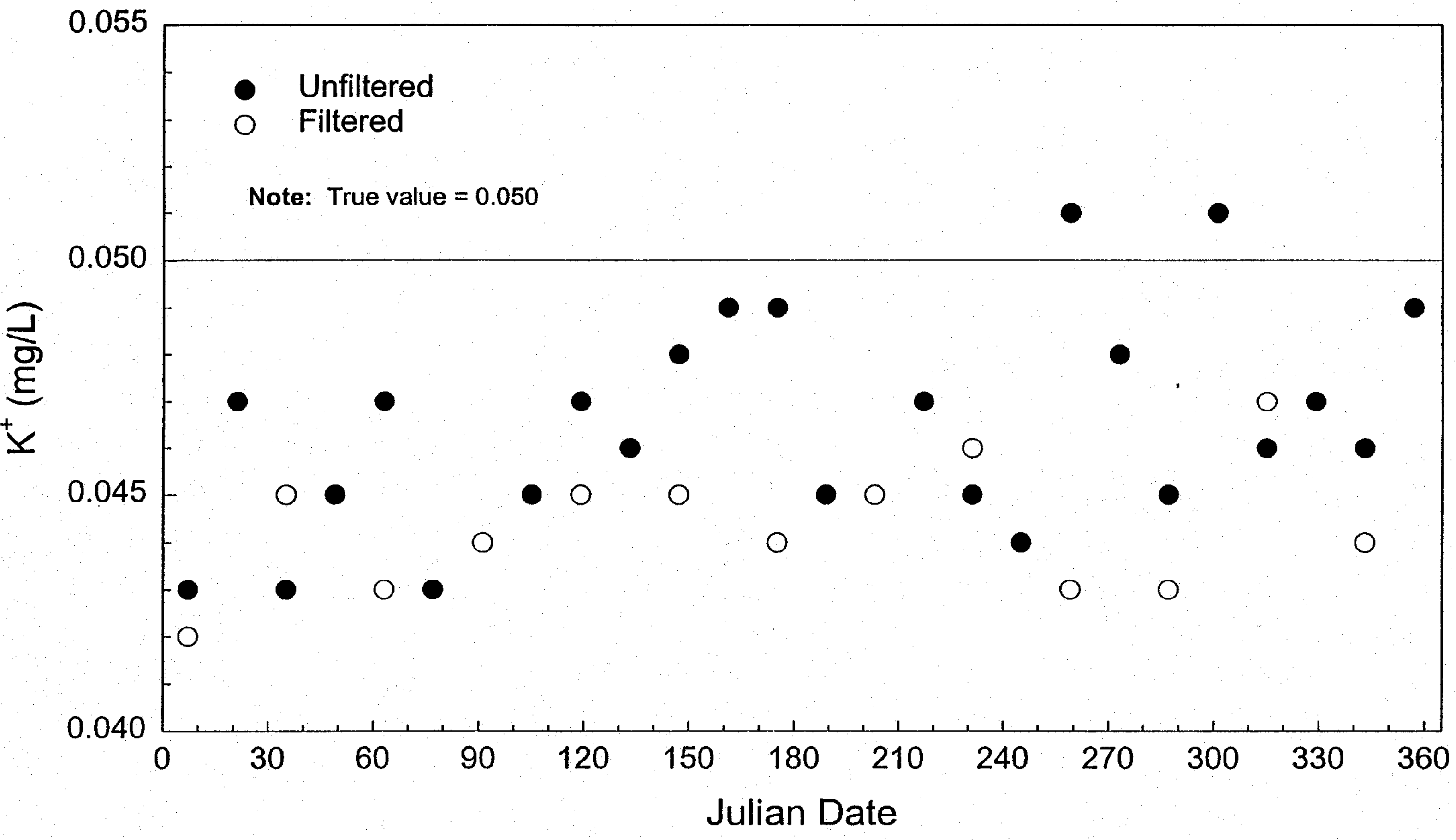


FIGURE B-14. Comparison of filtered and unfiltered internal blind samples (potassium HPS-SRI), 1997.

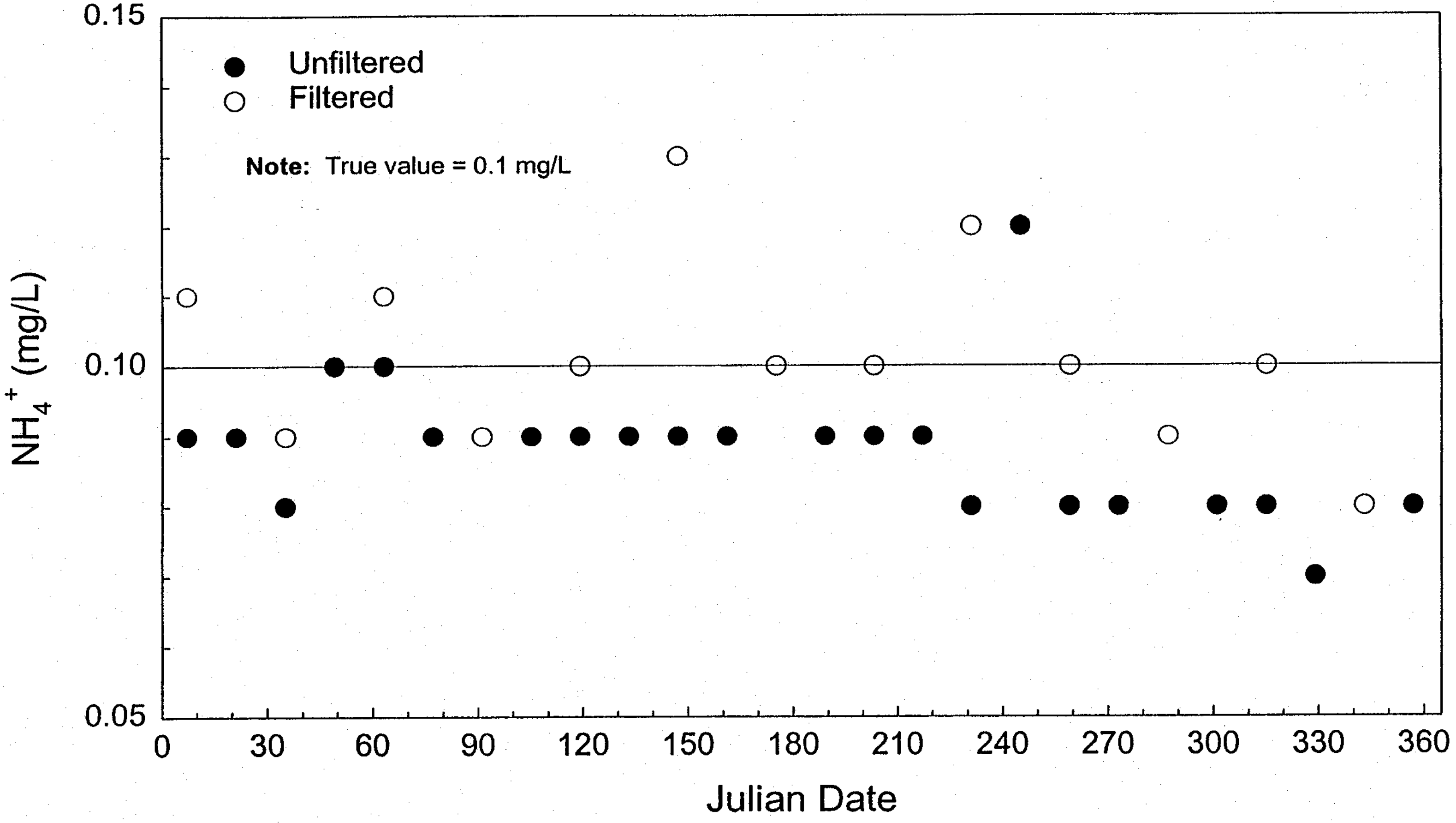
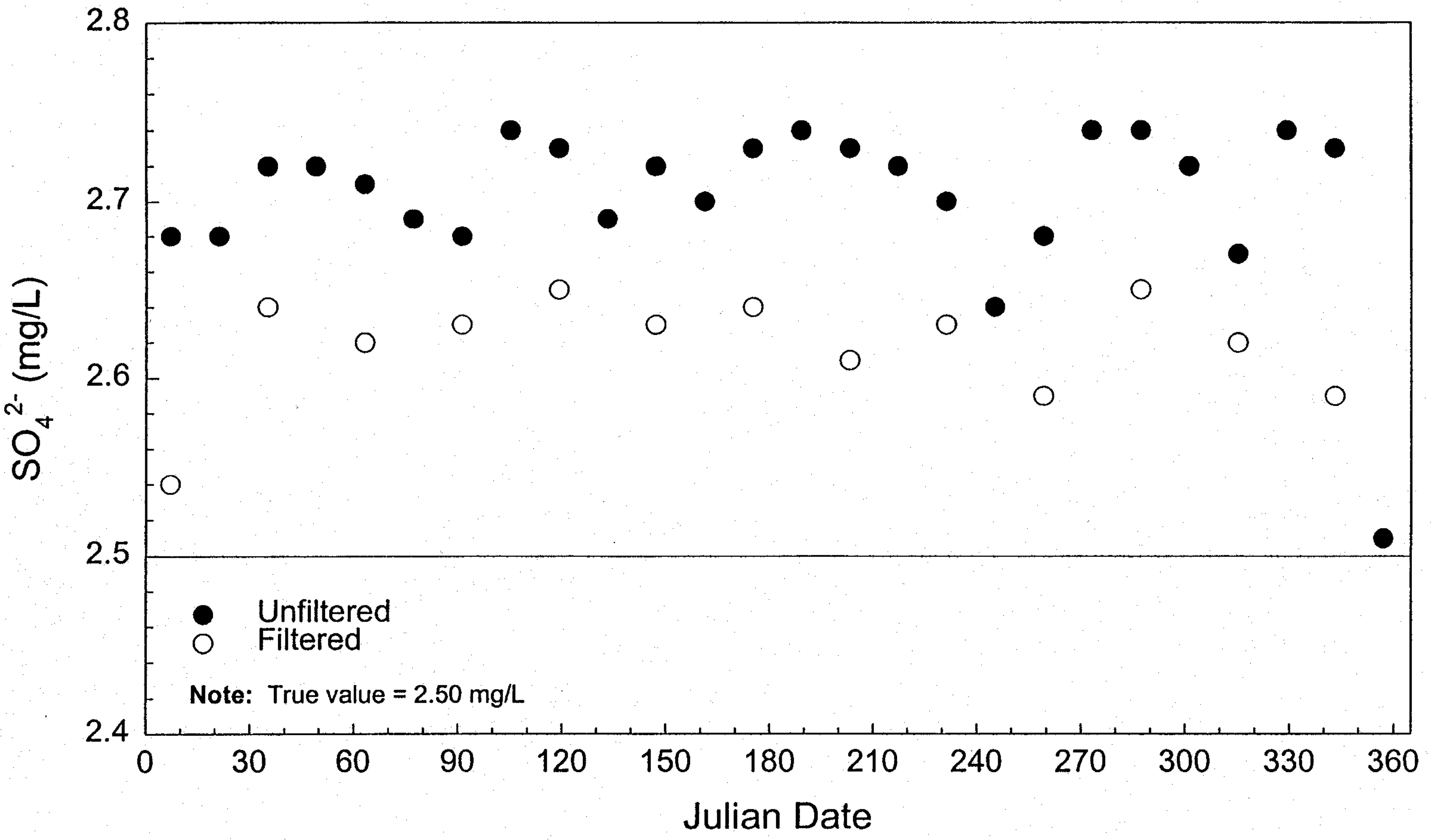


FIGURE B-15. Comparison of filtered and unfiltered internal blind samples (ammonium HPS-SRI), 1997.



Note: True value = 2.50 mg/L

FIGURE B-16. Comparison of filtered and unfiltered internal blind samples (sulfate HPS-SRI), 1997.

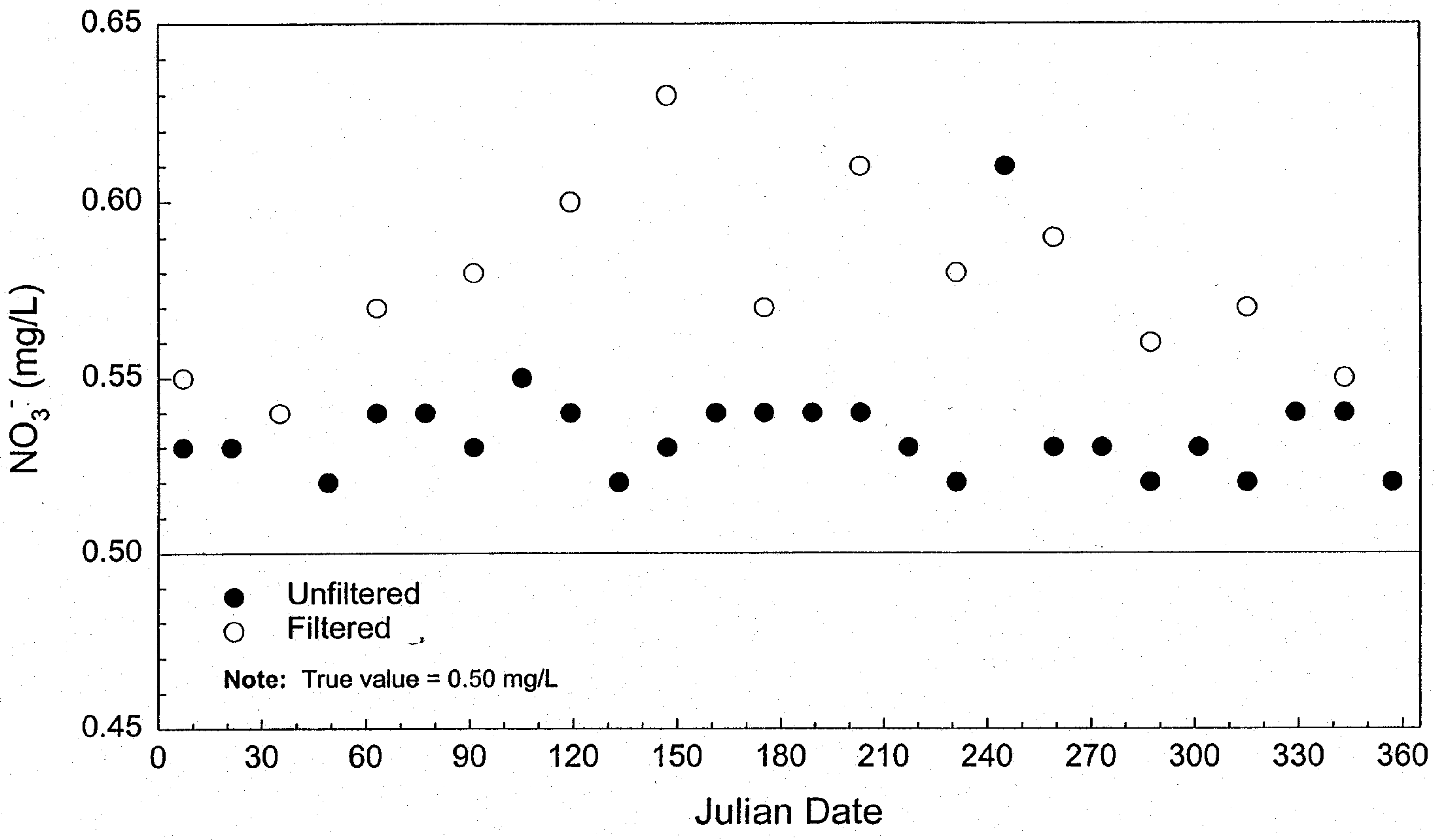


FIGURE B-17. Comparison of filtered and unfiltered internal blind samples (nitrate HPS-SRI), 1997.

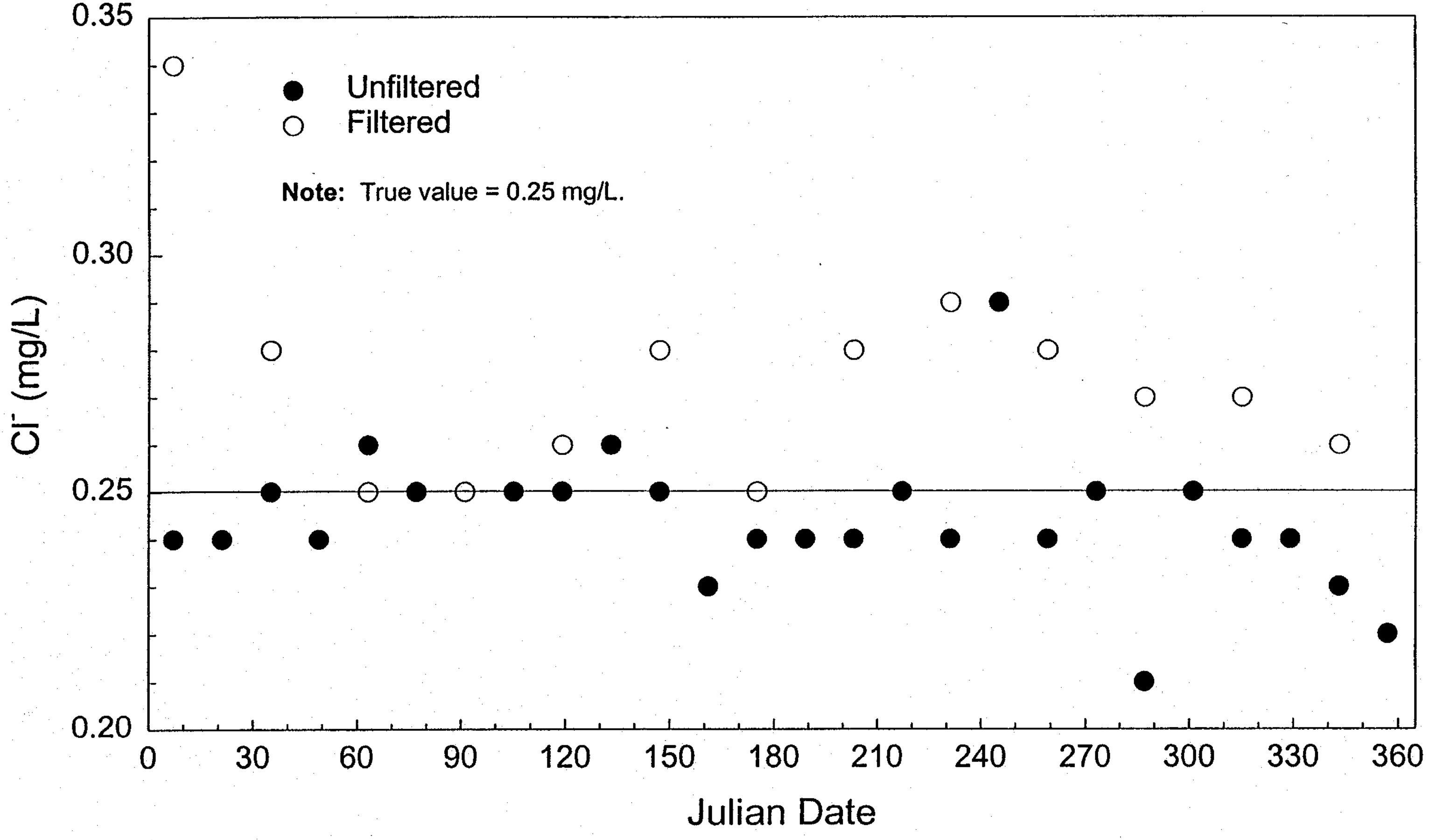


FIGURE B-18. Comparison of filtered and unfiltered internal blind samples (chloride HPS-SRI), 1997.

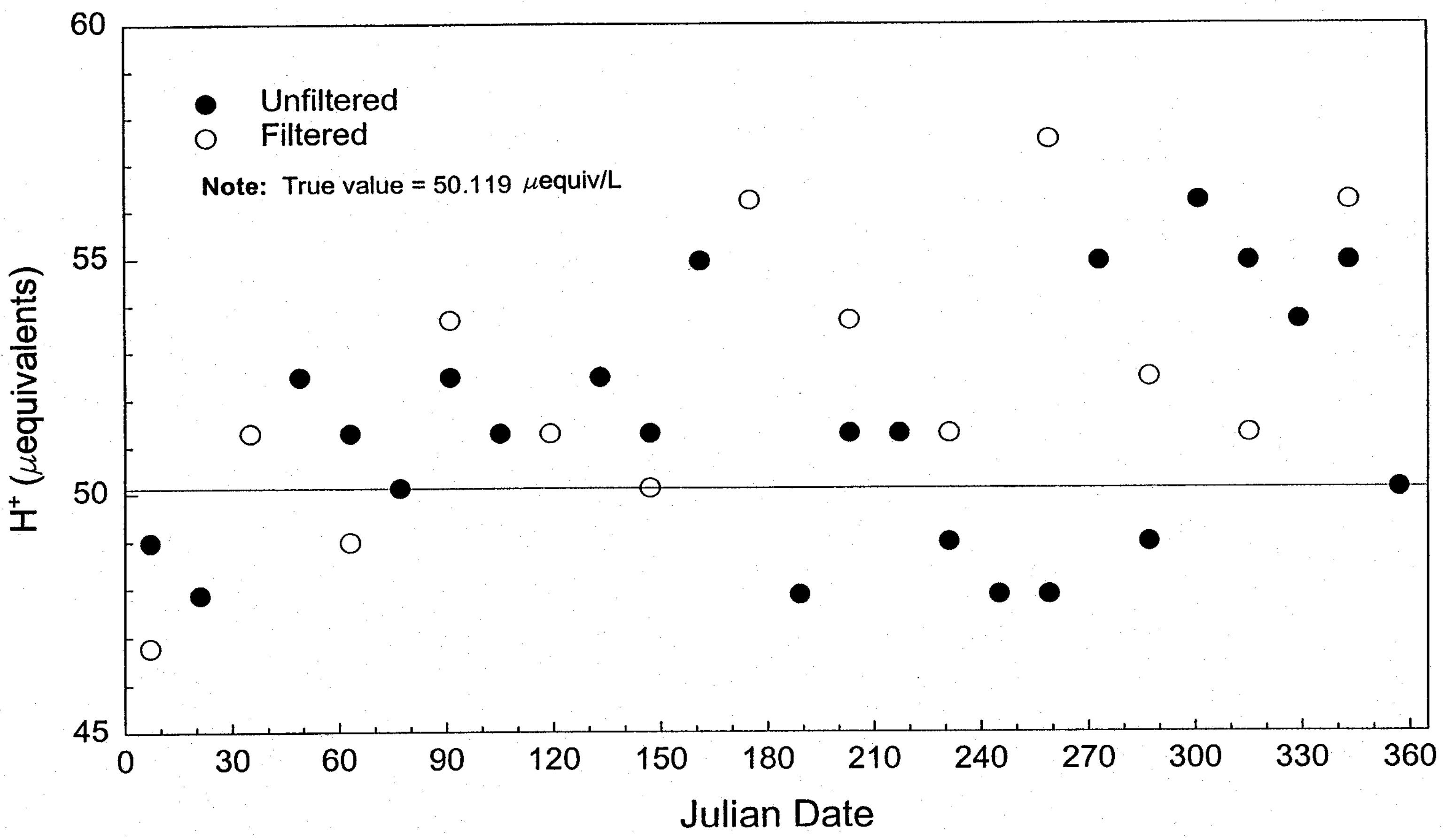


FIGURE B-19. Comparison of filtered and unfiltered blind samples (H^+ HPS-SRI), 1997.

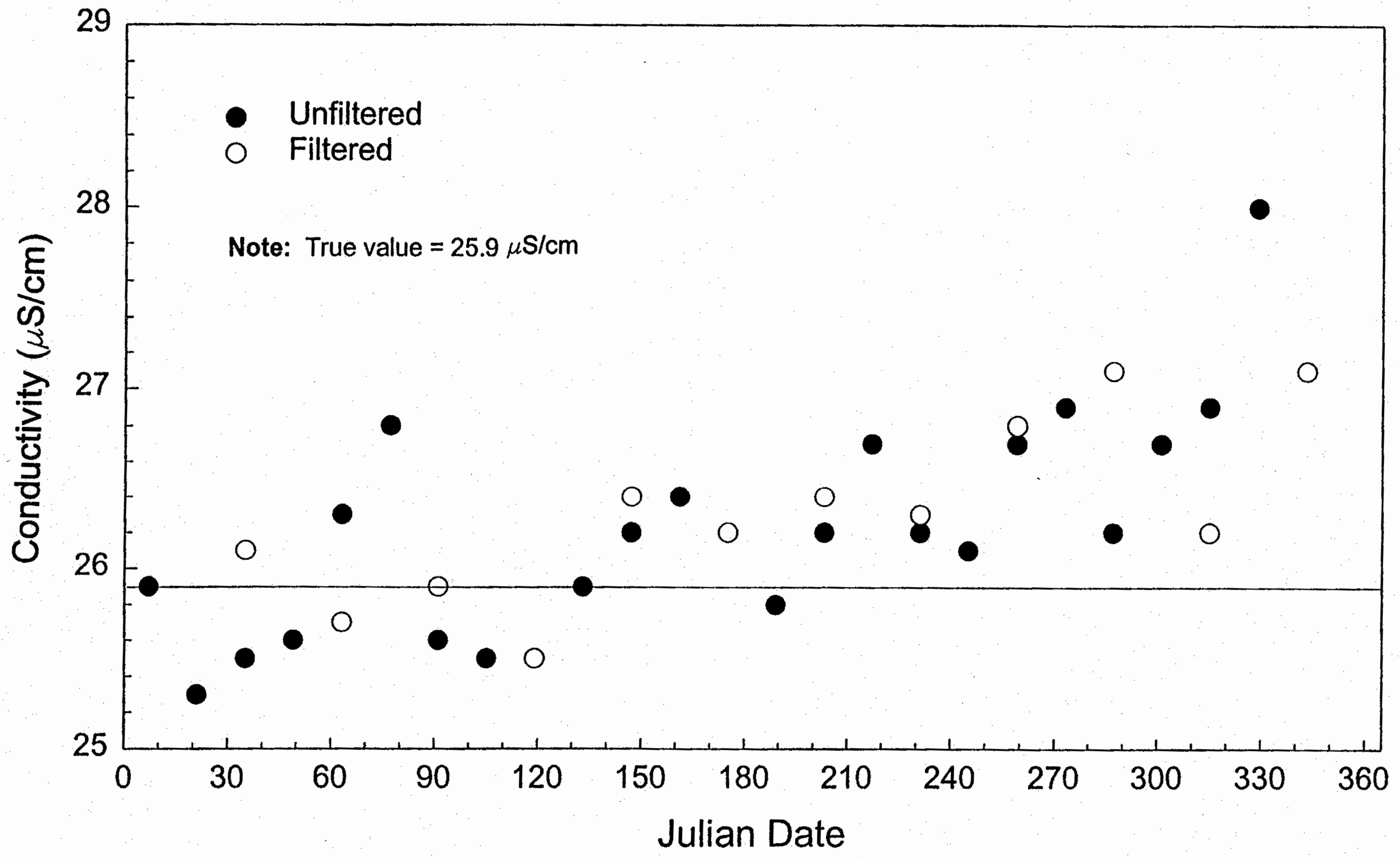


FIGURE B-20. Comparison of filtered and unfiltered internal blind samples (conductivity HPS-SRI), 1997.

TABLE B-3. Comparison of Filtered and Unfiltered Internal Blind Samples, High-Purity Standards Simulated Rainwater II (HPS-SRII), 1996

Parameter	*Target Concentration[a] (mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias %*	*Precision (mg/L)*	*Precision (%)*
Calcium	0.049	0.055[b]	24	0.006	12.7	0.004	7.8
		0.085[c]	12	0.036	72.6	0.037	43.3
Magnesium	0.050	0.048	24	-0.002	-3.8	0.001	2.2
		0.059	12	0.009	18.0	0.022	36.6
Sodium	0.390	0.414	24	0.024	6.3	0.023	5.5
		0.524	12	0.134	34.3	0.065	12.4
Potassium	0.100	0.107	24	0.007	7.2	0.012	10.8
		0.102	12	0.002	2.0	0.004	4.4
Ammonium	1.00	1.01	24	0.01	0.7	0.05	5.3
		1.04	12	0.04	4.3	0.06	5.7
Sulfate	10.10	10.33	24	0.23	2.3	0.25	2.4
		9.90	12	-0.20	-2.0	0.19	1.9
Nitrate	7.10	7.18	24	0.08	1.8	0.16	2.3
		7.01	12	-0.09	-1.3	0.16	2.2
Chloride	0.97	1.03	24	0.06	6.1	0.03	2.5
		1.09	12	0.12	12.4	0.06	5.1
pH (units)	3.42(380.19)	3.61(247.51)	24	0.19(-132.68)	5.5(-34.9)	0.03(14.25)	0.7(5.8)
μeq/L		3.60(251.51)[d]	12	0.18(-128.68)	5.3(-33.8)	0.02(13.82)	0.7(5.5)
Conductivity	128.0	128.7	24	0.7	0.6	3.27	2.5
μS/cm		129.2[d]	12	1.2	0.9	2.55	2.0

Notes: [a] Target values provided by High-Purity Standards 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. [d] pH and conductivity are measured on unfiltered sample prior to filtering .

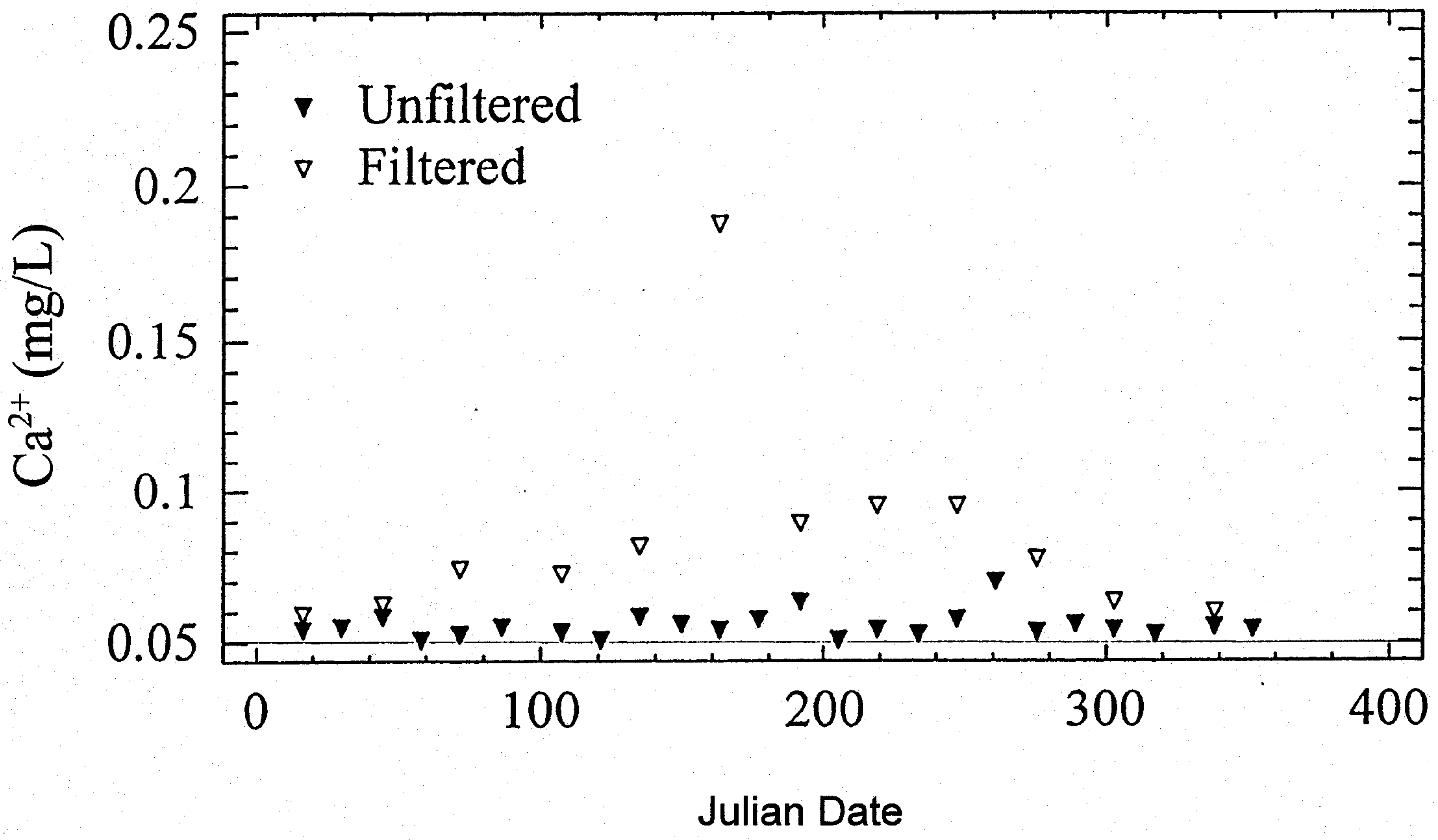


FIGURE B-21. Comparison of filtered and unfiltered internal blind samples (calcium HPS-SRII), 1996.

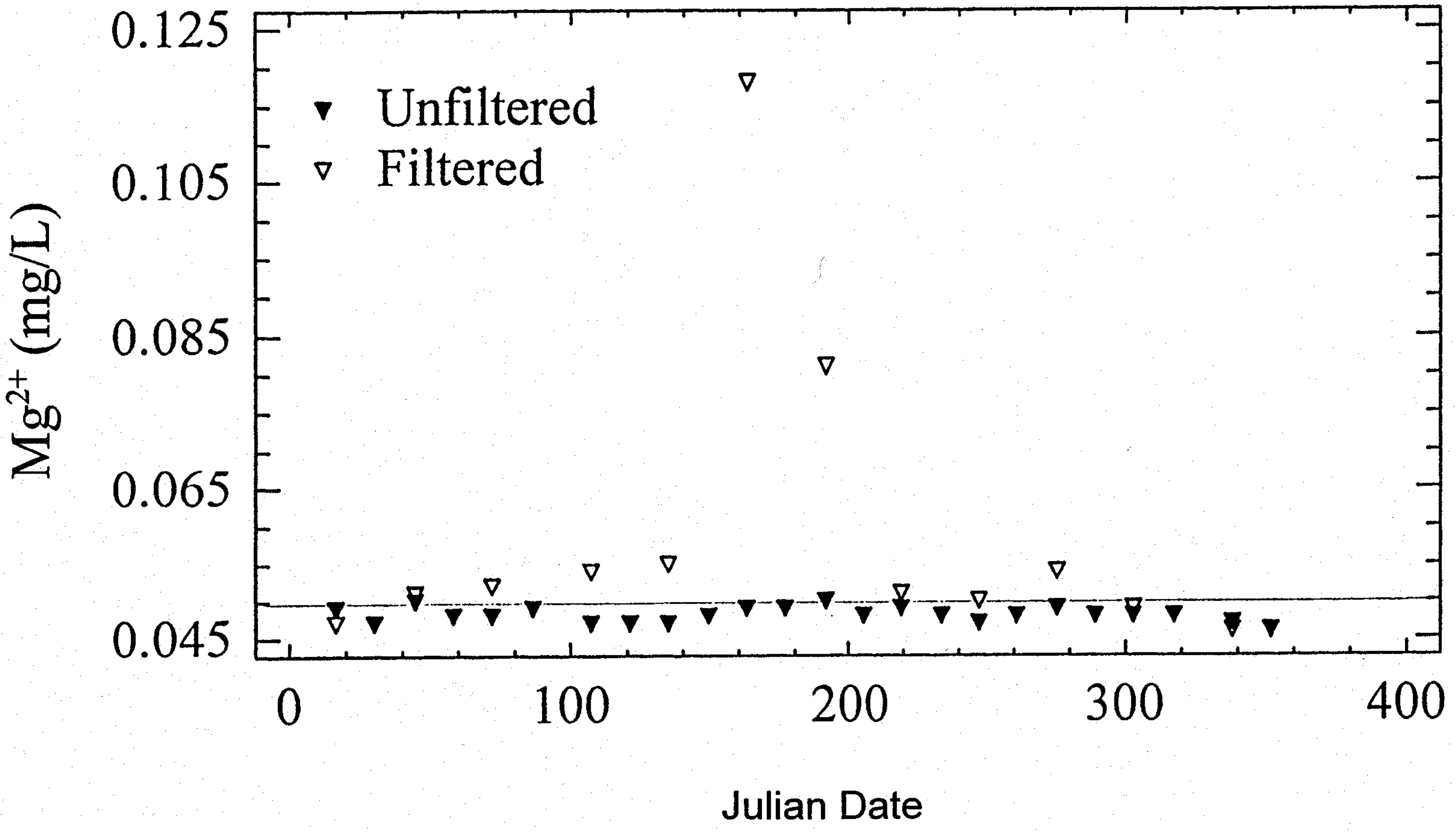


FIGURE B-22. Comparison of filtered and unfiltered internal blind samples (magnesium HPS-SRII), 1996.

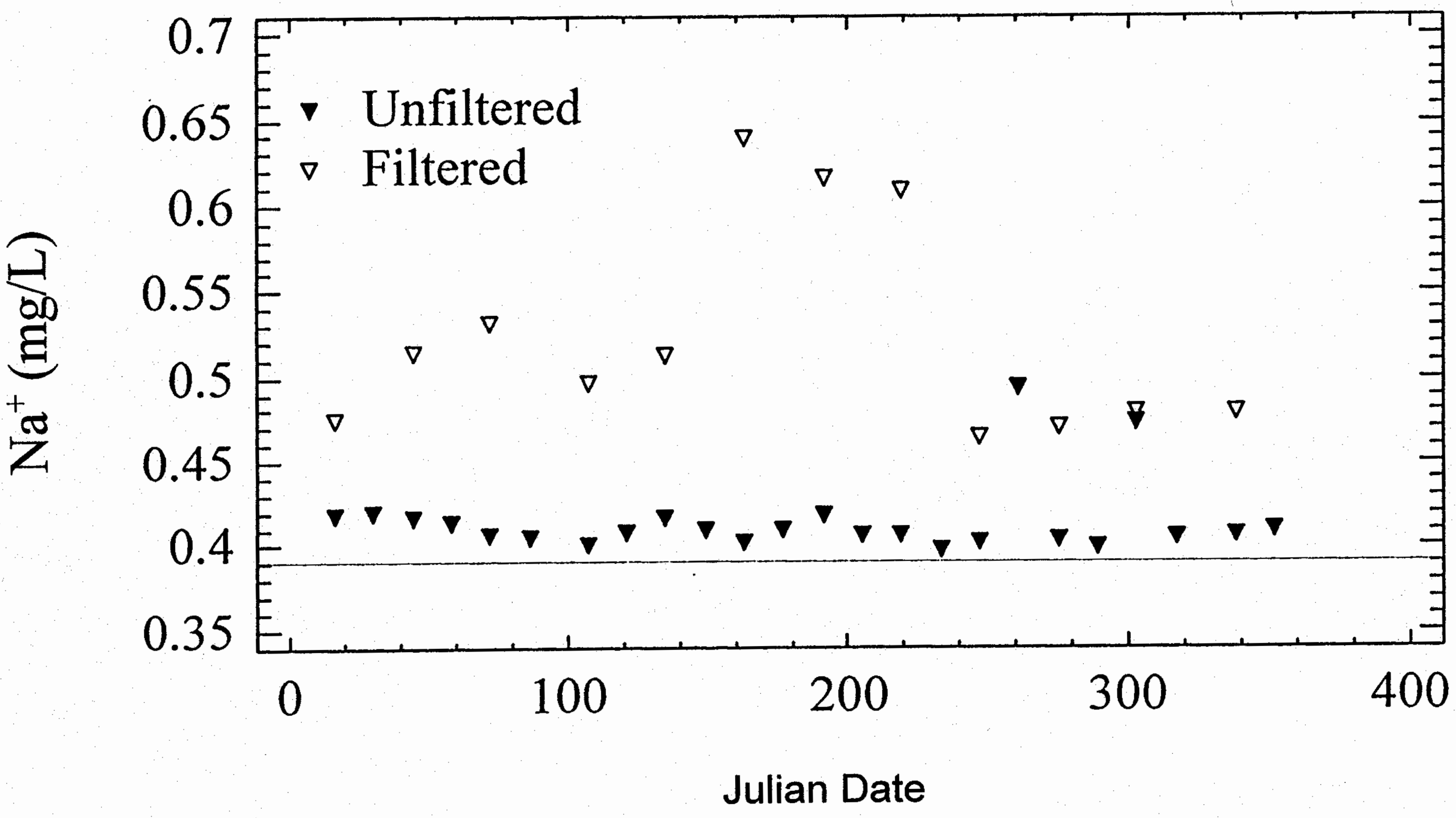


FIGURE B-23. Comparison of filtered and unfiltered internal blind samples (sodium HPS-SRII), 1996.

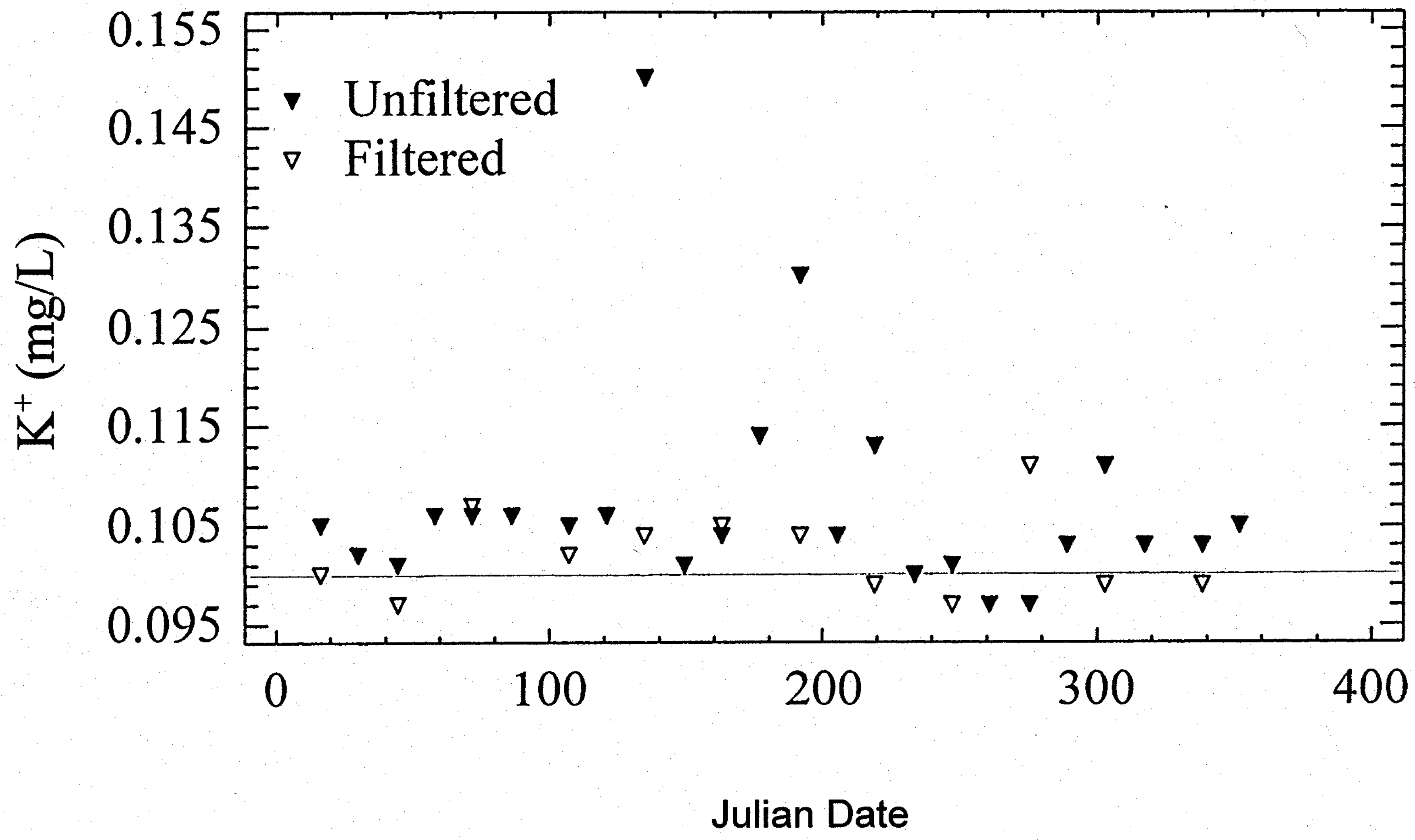


FIGURE B-24. Comparison of filtered and unfiltered internal blind samples (potassium HPS-SRII), 1996.

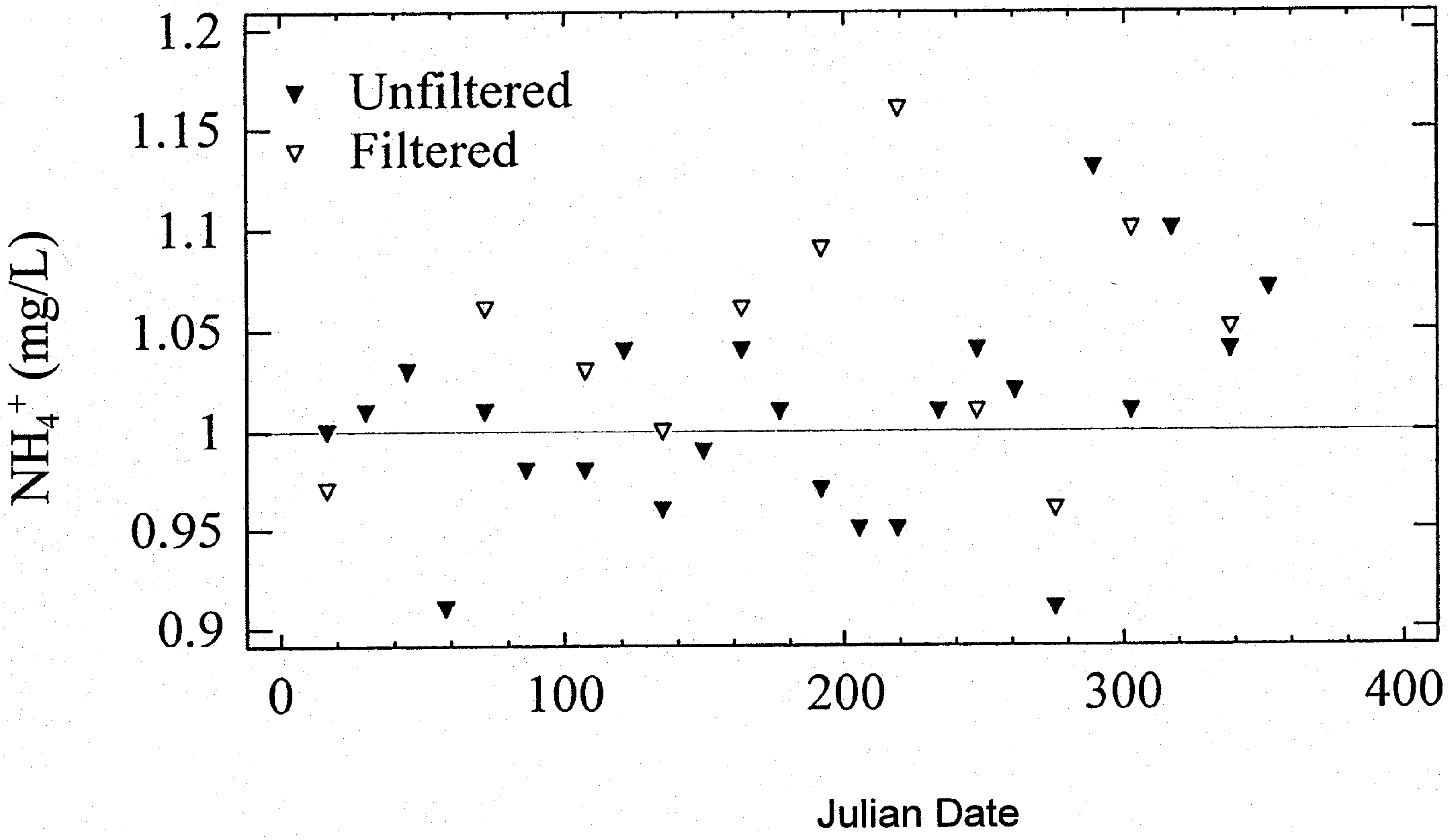


FIGURE B-25. Comparison of filtered and unfiltered internal blind samples (ammonium HPS-SRII), 1996.

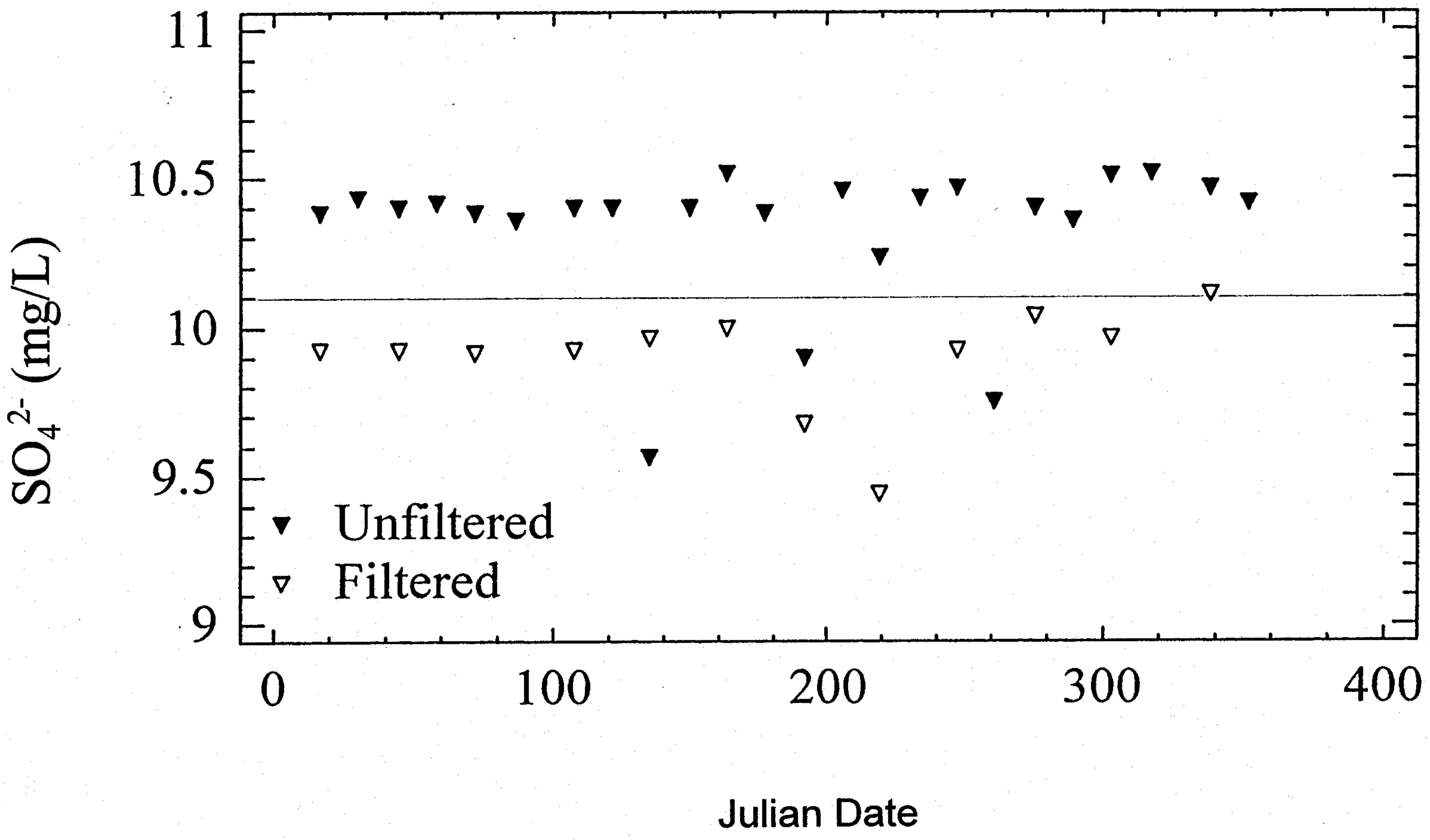


FIGURE B-26. Comparison of filtered and unfiltered internal blind samples (sulfate HPS-SRII), 1996.

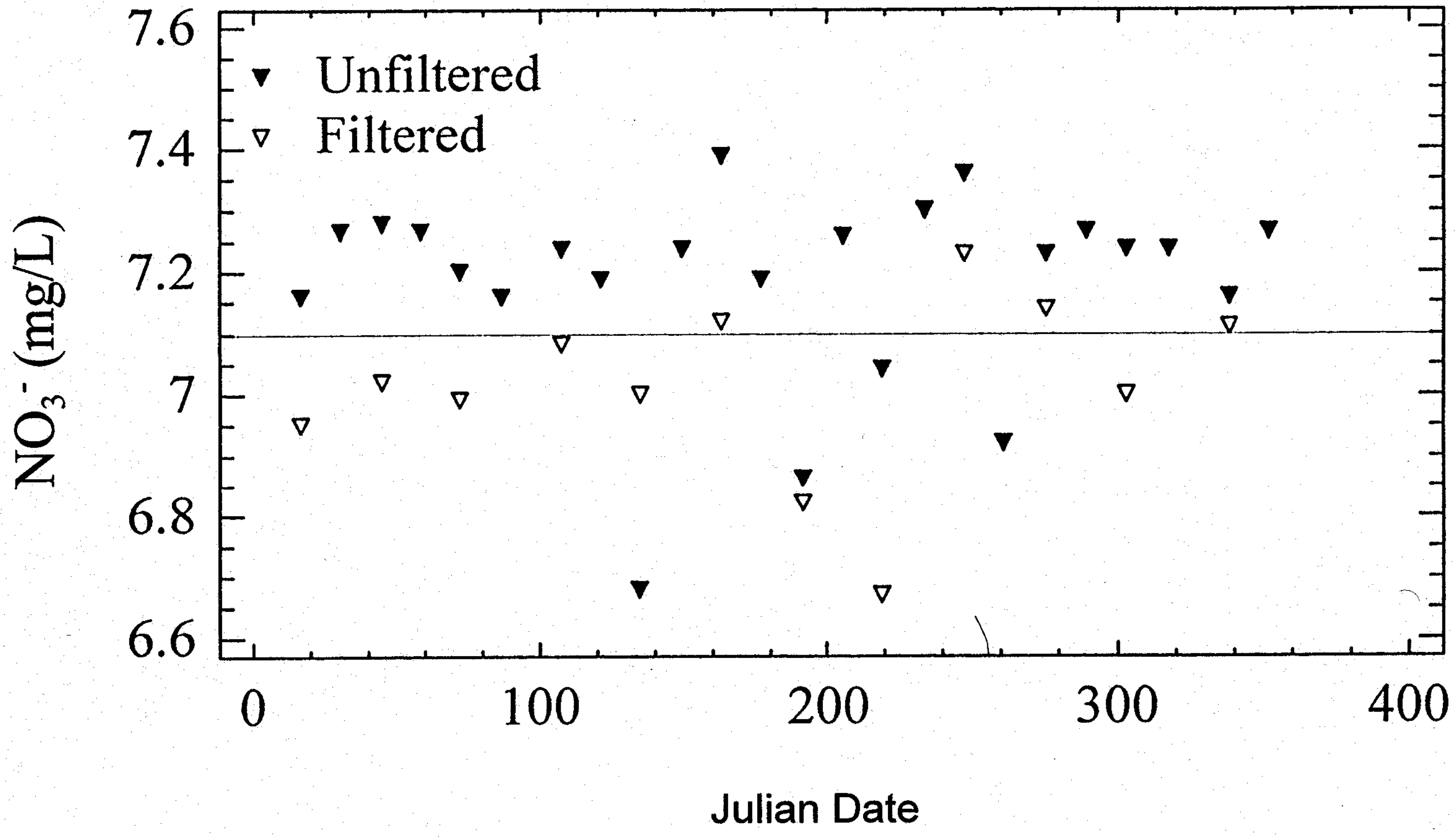


FIGURE B-27. Comparison of filtered and unfiltered internal blind samples (nitrate HPS-SRII), 1996.

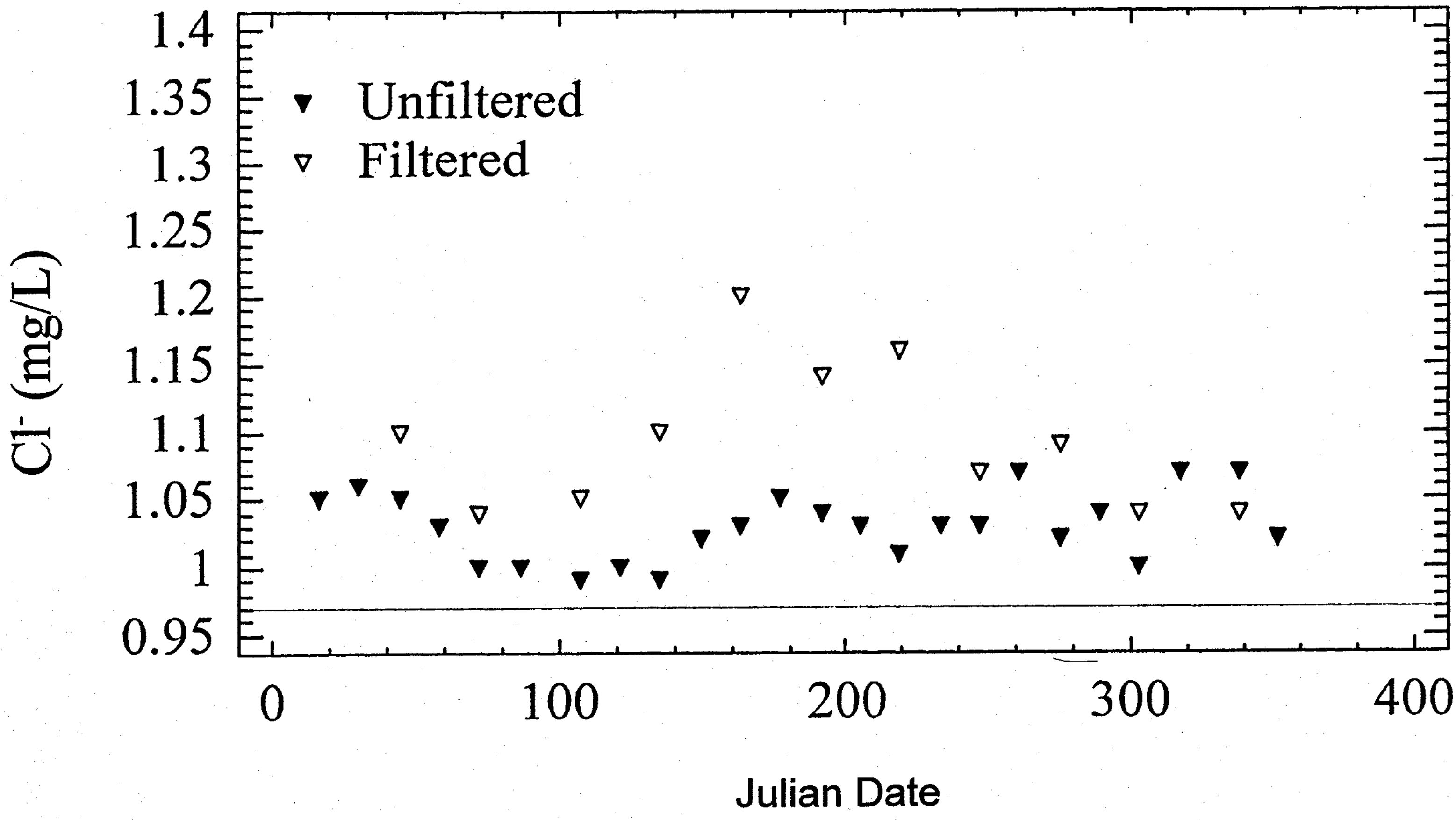


FIGURE B-28. Comparison of filtered and unfiltered internal blind samples (chloride HPS-SRII), 1996.

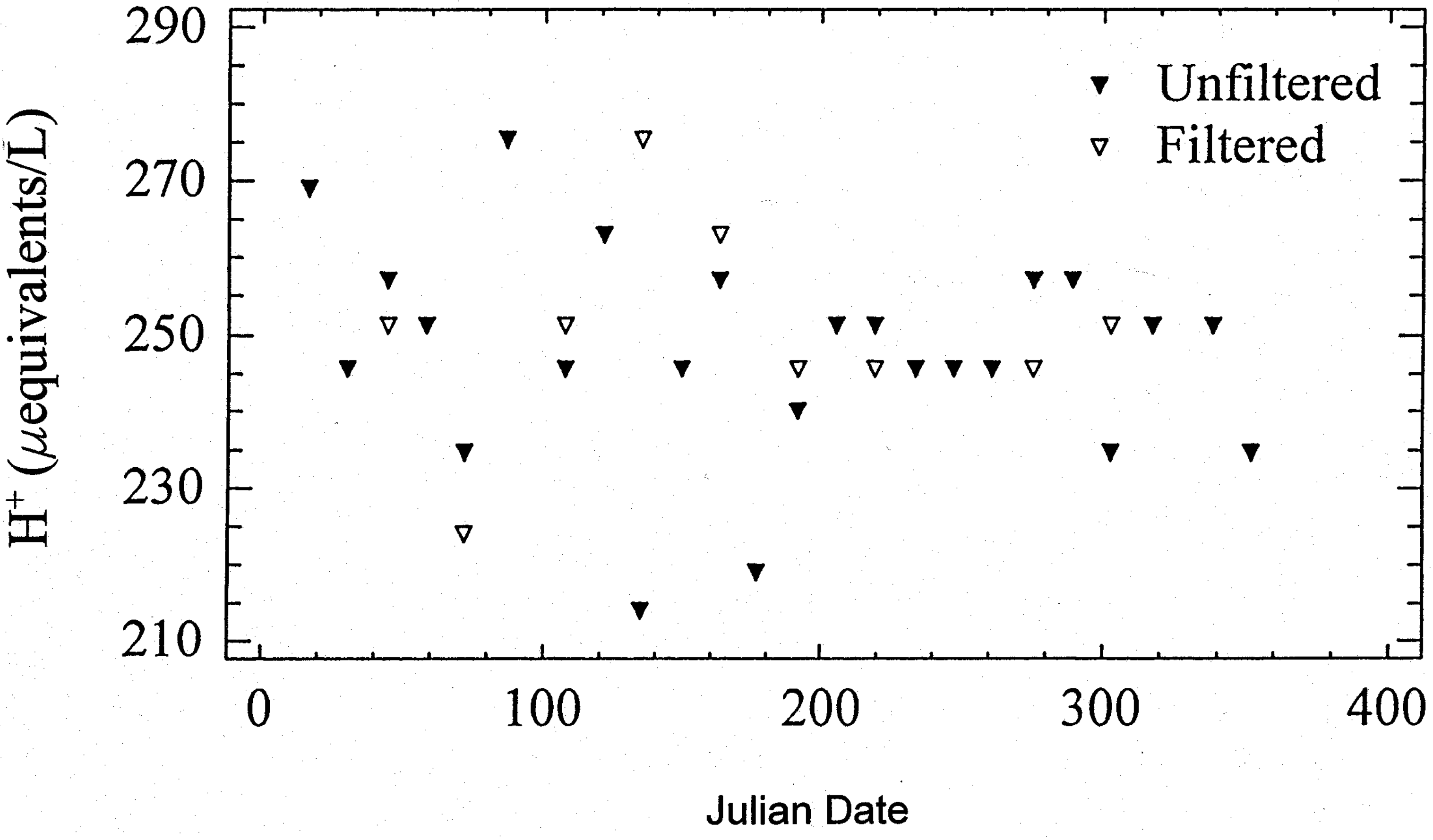


FIGURE B-29. Comparison of filtered and unfiltered internal blind samples (H^+ HPS-SRII), 1996.

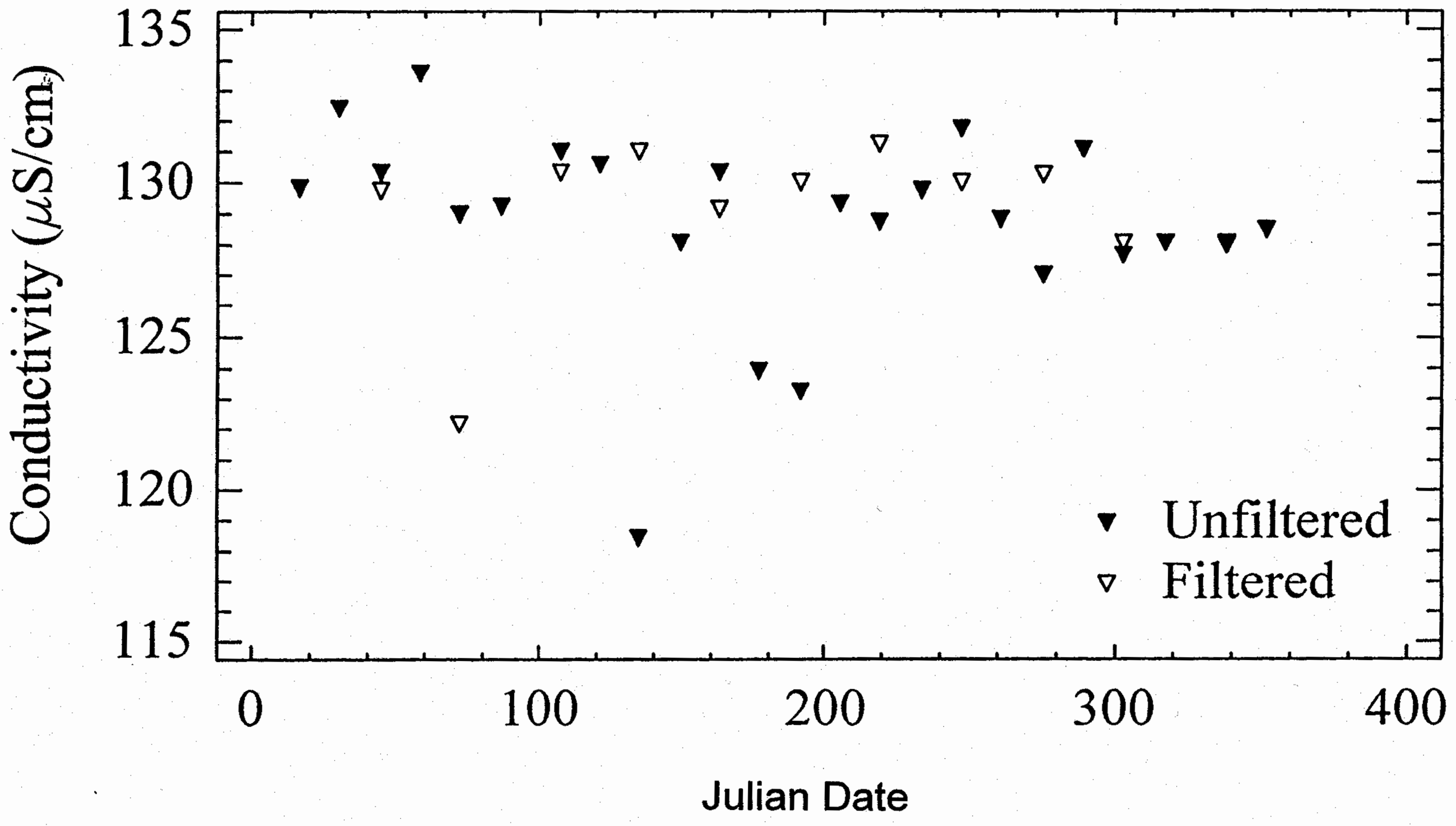


FIGURE B-30. Comparison of filtered and unfiltered internal blind samples (conductivity HPS-SRII), 1996.

TABLE B-4a. Comparison of Filtered and Unfiltered Internal Blind Samples
High-Purity Standards Simulated Rainwater II (HPS-SRII), Lot # 691025, 1997

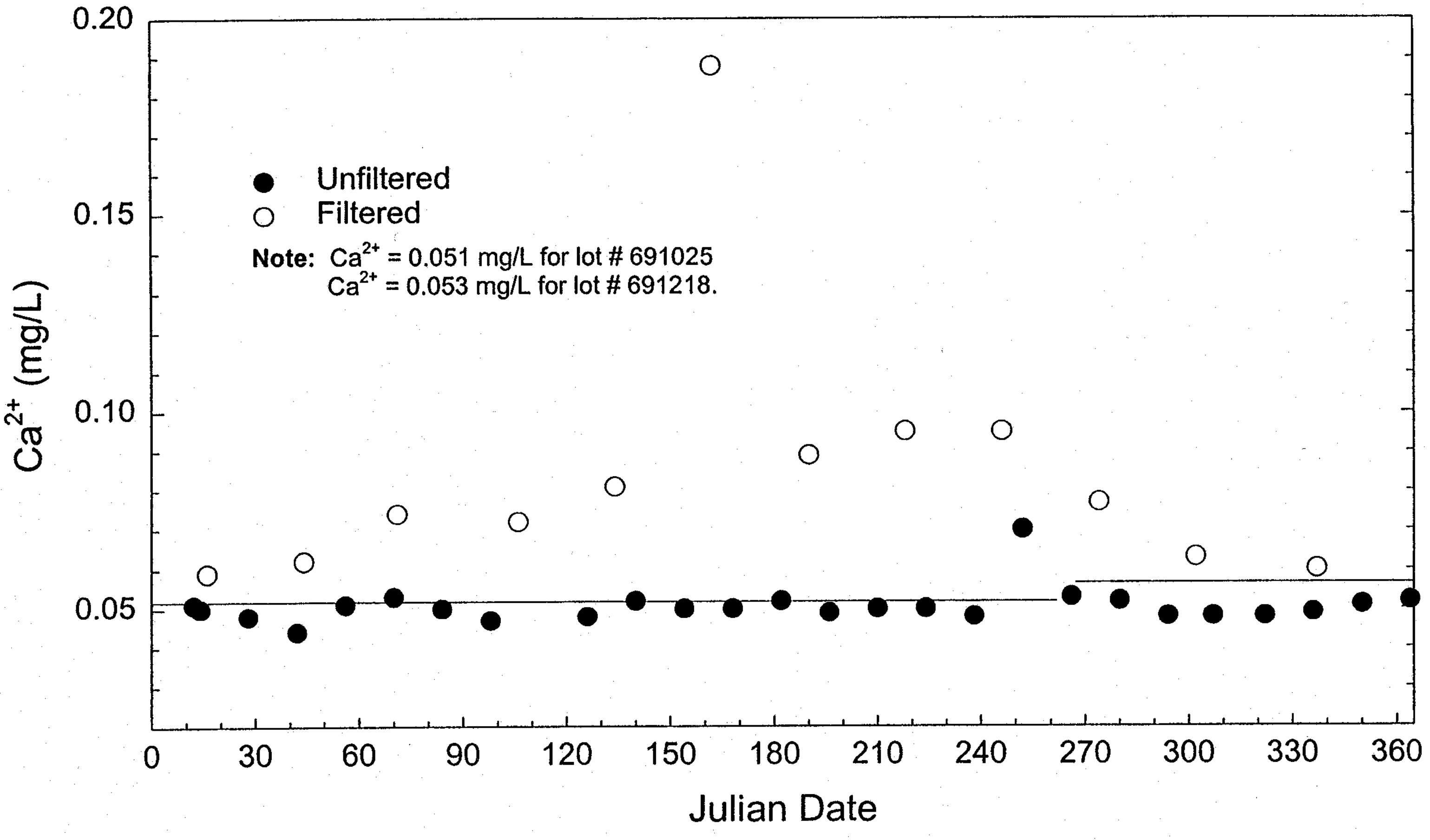
Parameter	*Target Concentration*[a] *(mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias %*	*Precision (mg/L)*	Precision (%)
Calcium	0.051	0.050[b]	17	-0.001	-1.96	0.002	4.0
		0.067[c]	10	0.016	31.4	0.014	20.9
Magnesium	0.051	0.046	17	-0.005	-9.80	0.0008	1.74
		0.048	10	-0.003	-5.88	0.004	8.33
Sodium	0.37	0.387	17	0.017	4.59	0.011	2.84
		0.428	10	0.058	15.7	0.020	4.67
Potassium	0.099	0.100	17	0.001	1.01	0.003	3.0
		0.097	10	-0.002	-2.02	0.003	3.09
Ammonium	1.0	0.98	17	-0.02	-2.0	0.044	4.49
		0.99	10	-0.01	-1.0	0.042	4.24
Sulfate	10.1	10.1	17	0.0	0.0	0.12	1.12
		9.74	10	-0.36	-3.56	0.10	1.03
Nitrate	7.0	7.05	17	0.05	0.71	0.06	0.85
		6.94	10	-0.06	-0.86	0.05	0.72
Chloride	0.98	1.00	17	0.02	2.04	0.02	2.0
		1.01	10	0.03	3.06	0.02	1.98
pH (units)	3.33(467.7)	3.62(242.7)[d]	17	0.29(-225)	8.7(-48.1)	0.02(9.11)	0.55(3.8)
H^+ (μeq/L)		3.62(237.4)[d]	10	0.29(-230.3)	8.7(-49.2)	0.02(10.8)	0.55(4.5)
Conductivity	130.6	125.6[d]	17	-5.0	-3.83	1.29	1.0
(μS/cm)		125.3[d]	10	-5.3	-4.06	1.88	1.5

Notes: [a] Target values provided by High-Purity Standards for Simulated Rainwater II, lot # 691025. [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. [d] pH and conductivity are measured on unfiltered sample prior to filtering.

TABLE B-4b. Comparison of Filtered and Unfiltered Internal Blind Samples
High-Purity Standards Simulated Rainwater II (HPS-SRII), Lot # 691218, 1997

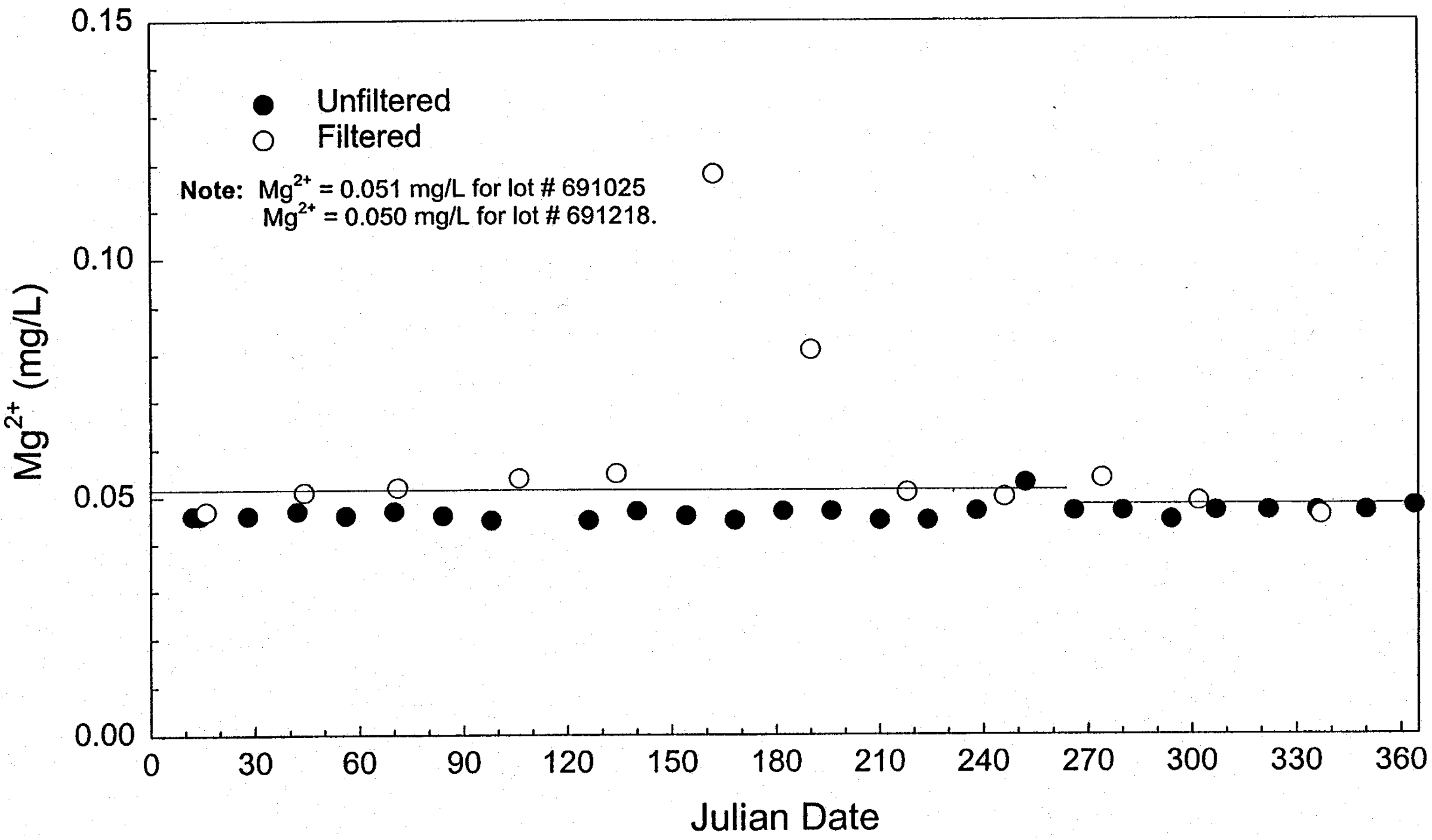
Parameter	*Target Concentration*[a] *(mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias %*	*Precision (mg/L)*	*Precision (%)*
Calcium	0.053	0.052[b]	9	-0.001	-1.89	0.007	13.5
		0.072[c]	3	0.019	35.8	0.015	20.8
Magnesium	0.050	0.048	9	-0.002	-4.0	0.002	4.17
		0.052	3	0.002	4.00	0.004	7.69
Sodium	0.37	0.400	9	0.03	8.11	0.018	4.5
		0.435	3	0.065	17.6	0.012	2.76
Potassium	0.099	0.100	9	0.001	1.01	0.002	2.0
		0.096	3	-0.003	-3.03	0.001	1.04
Ammonium	1.0	0.96	9	-0.04	-4.0	0.022	2.29
		0.94	3	-0.06	-6.0	0.024	2.55
Sulfate	10.1	10.0	9	0.1	0.99	0.12	1.2
		9.67	3	-0.43	-4.26	0.07	0.72
Nitrate	7.0	7.09	9	0.09	1.29	0.09	1.27
		6.96	3	-0.04	-0.57	0.08	1.15
Chloride	0.98	1.02	9	0.04	4.08	0.06	5.88
		1.02	3	0.04	4.08	0.02	1.96
pH (units) H^+ (μeq/L)	3.43(371.5)	3.62(238.9)[d]	9	0.19(-132.6)	5.5(-35.7)	0.02(10.6)	0.55(4.4)
		3.62(241.7)[d]	3	0.19(-129.8)	5.5(-34.9)	0.005(2.63)	0.14(1.1)
Conductivity (μS/cm)	116.5	125.6[d]	9	9.1	3.29	1.44	1.1
		126.5[d]	3	10.0	8.58	1.60	1.3

Notes: [a] Target values provided by High-Purity Standards for Simulated Rainwater II, lot # 691218. [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. [d] pH and conductivity are measured on unfiltered sample prior to filtering.



Note: Ca^{2+} = 0.051 mg/L for lot # 691025
Ca^{2+} = 0.053 mg/L for lot # 691218.

FIGURE B-31. Comparison of filtered and unfiltered internal blind samples (calcium HPS-SRII), 1997.



Note: Mg^{2+} = 0.051 mg/L for lot # 691025
Mg^{2+} = 0.050 mg/L for lot # 691218.

FIGURE B-32. Comparison of filtered and unfiltered internal blind samples (magnesium HPS-SRII), 1997.

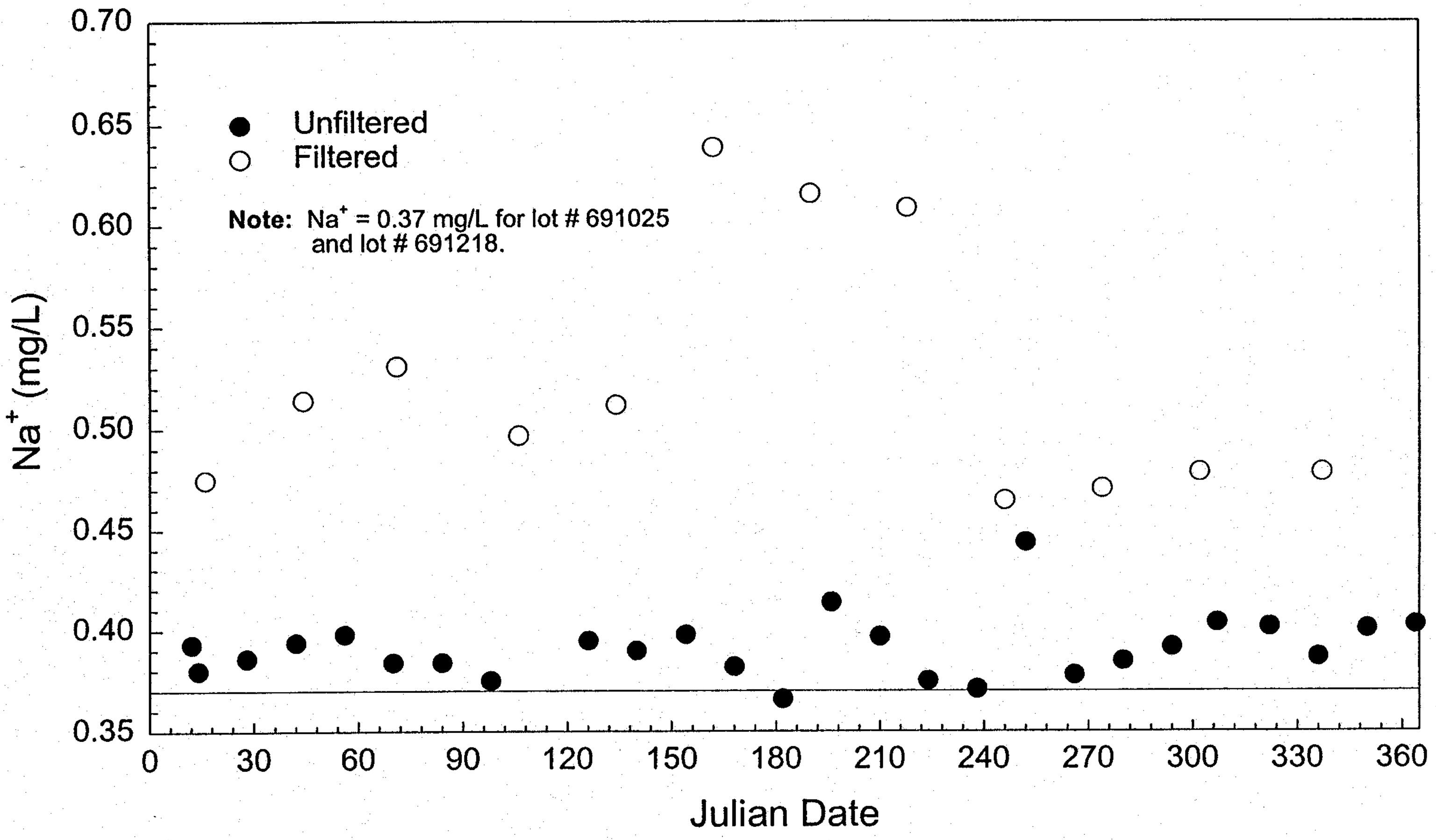


FIGURE B-33. Comparison of filtered and unfiltered internal blind samples (sodium HPS-SRII), 1997.

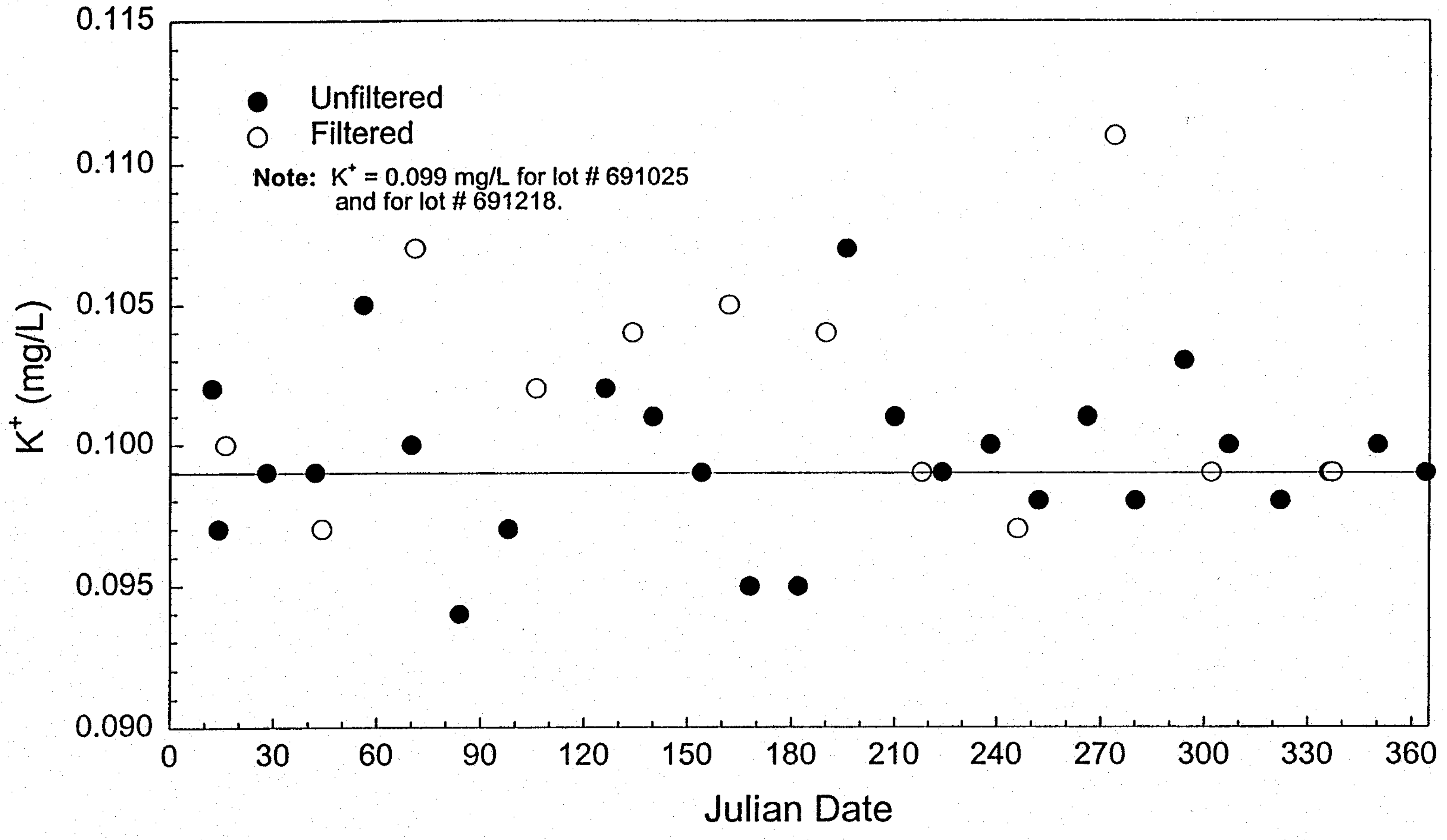


FIGURE B-34. Comparison of filtered and unfiltered internal blind samples (potassium HPS-SRII), 1997.

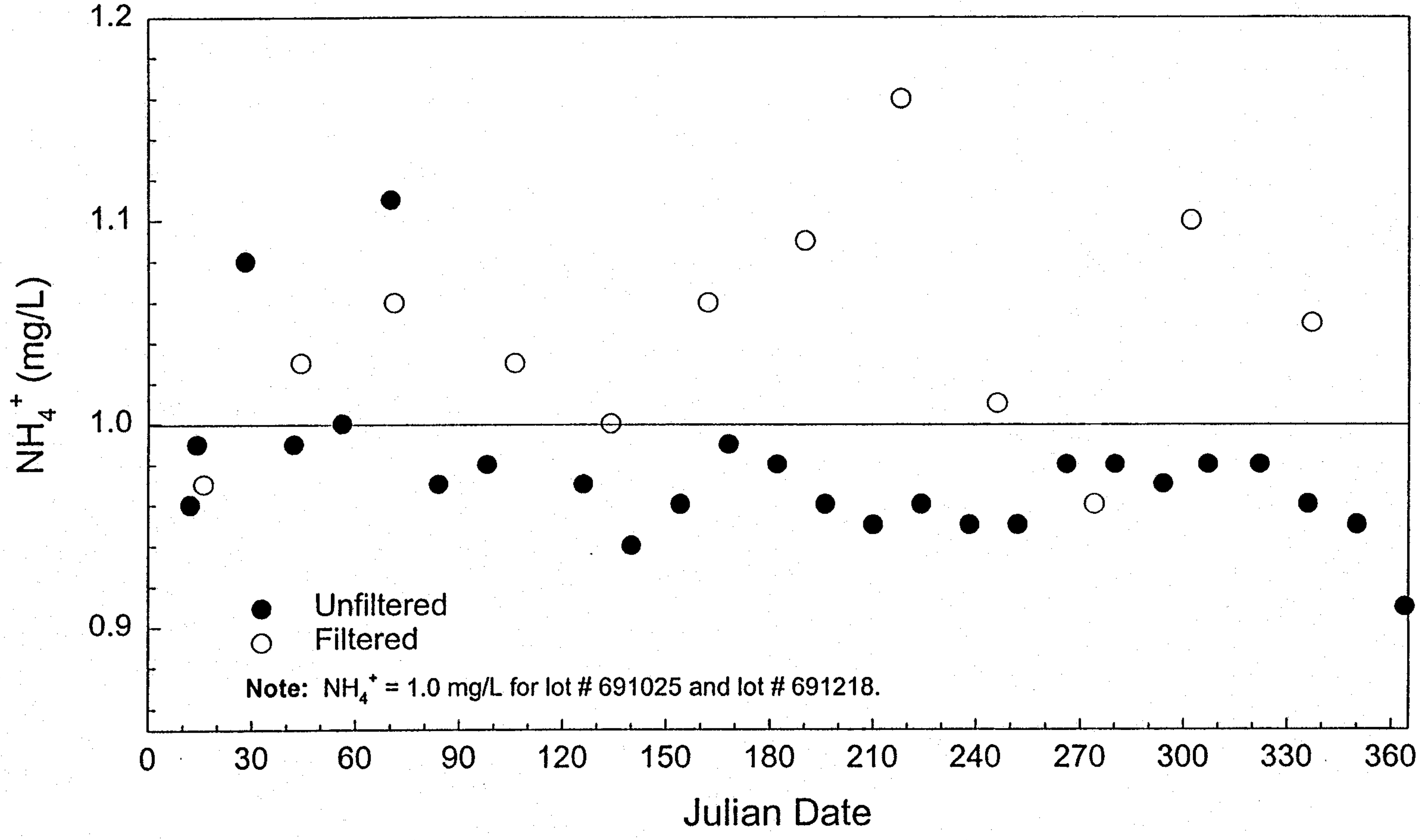
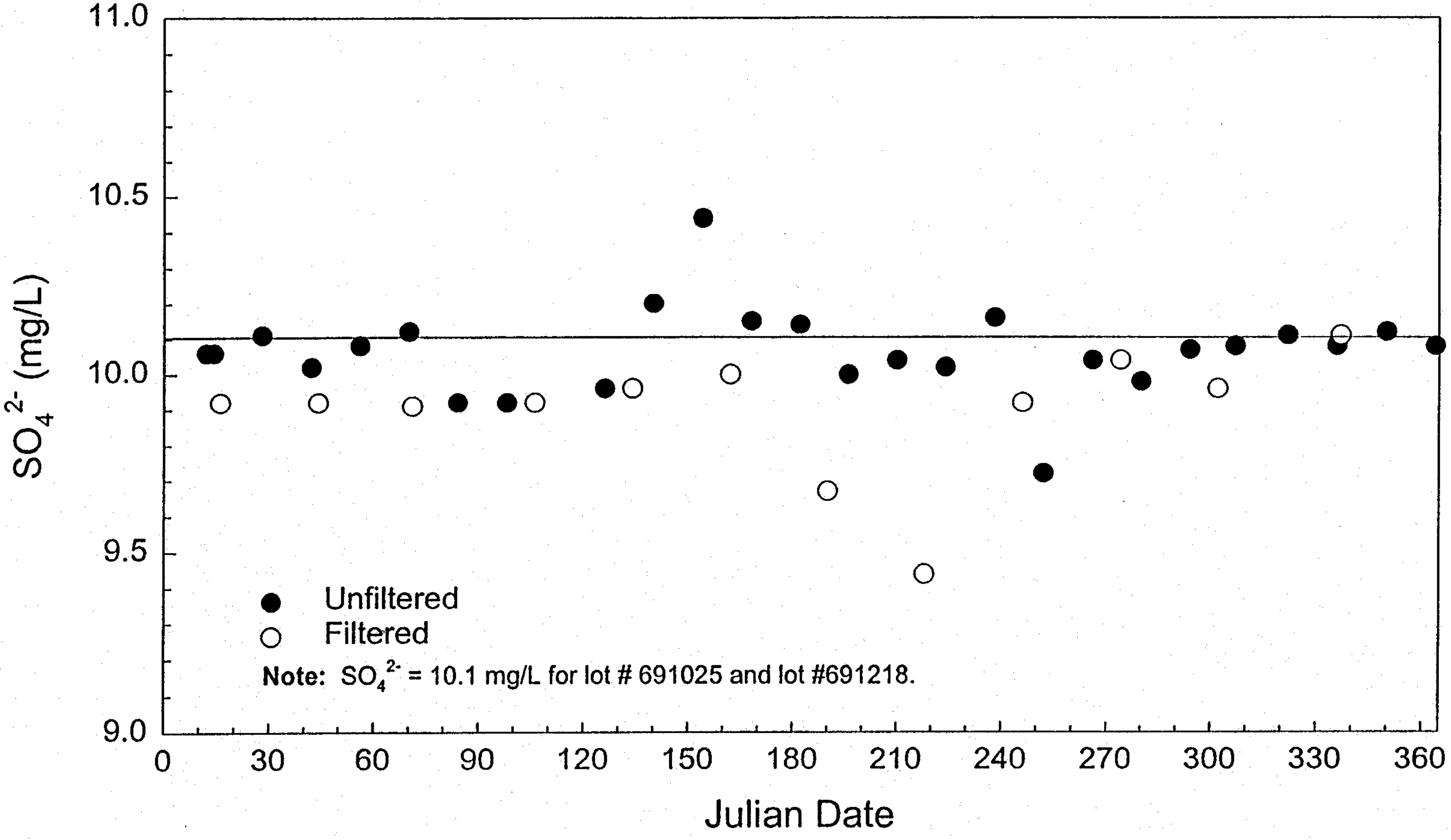


FIGURE B-35. Comparison of filtered and unfiltered internal blind samples (ammonium HPS-SRII), 1997.



Note: SO_4^{2-} = 10.1 mg/L for lot # 691025 and lot #691218.

FIGURE B-36. Comparison of filtered and unfiltered internal blind samples (sulfate HPS-SRII), 1997.

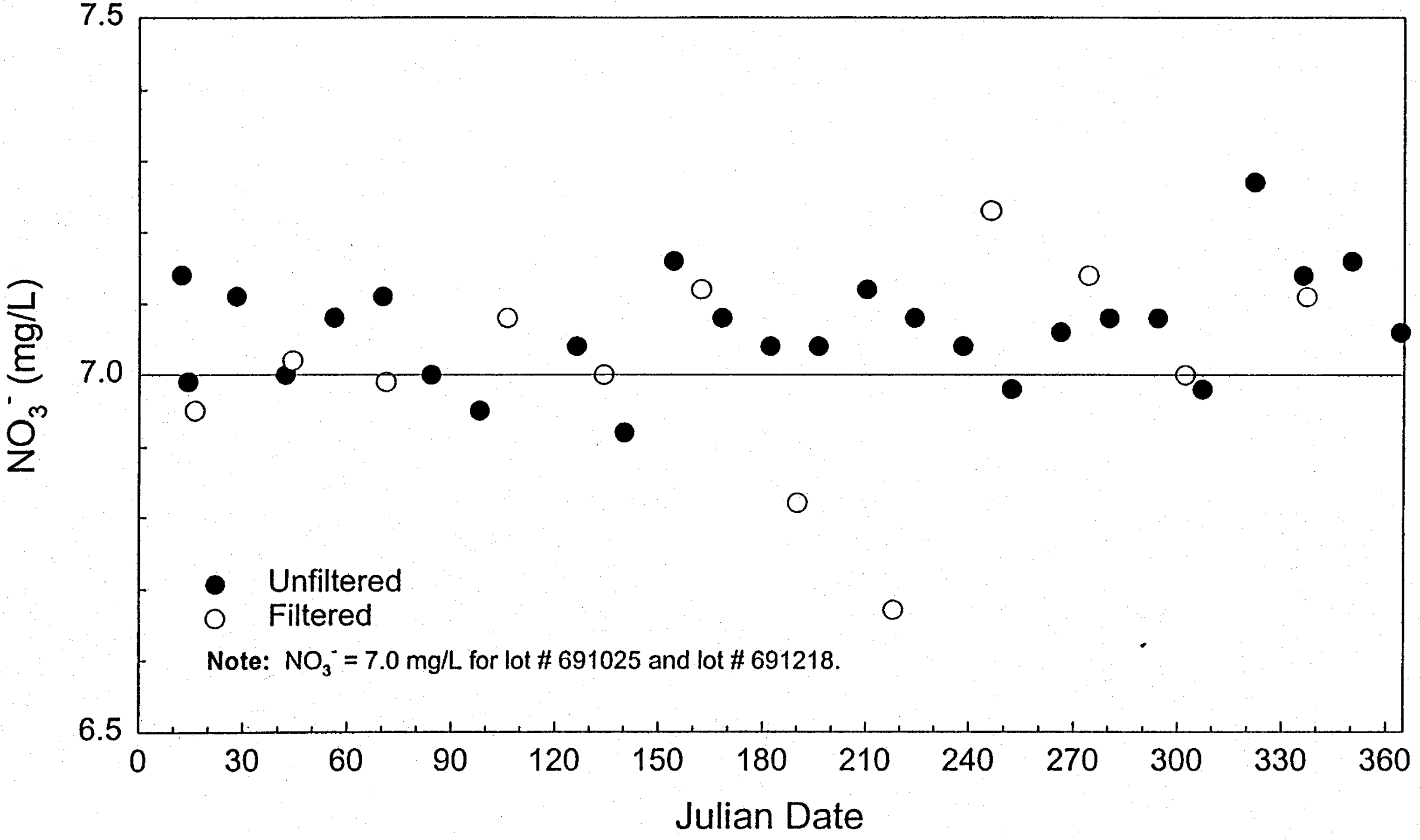


FIGURE B-37. Comparison of filtered and unfiltered internal blind samples (nitrate HPS-SRII), 1997.

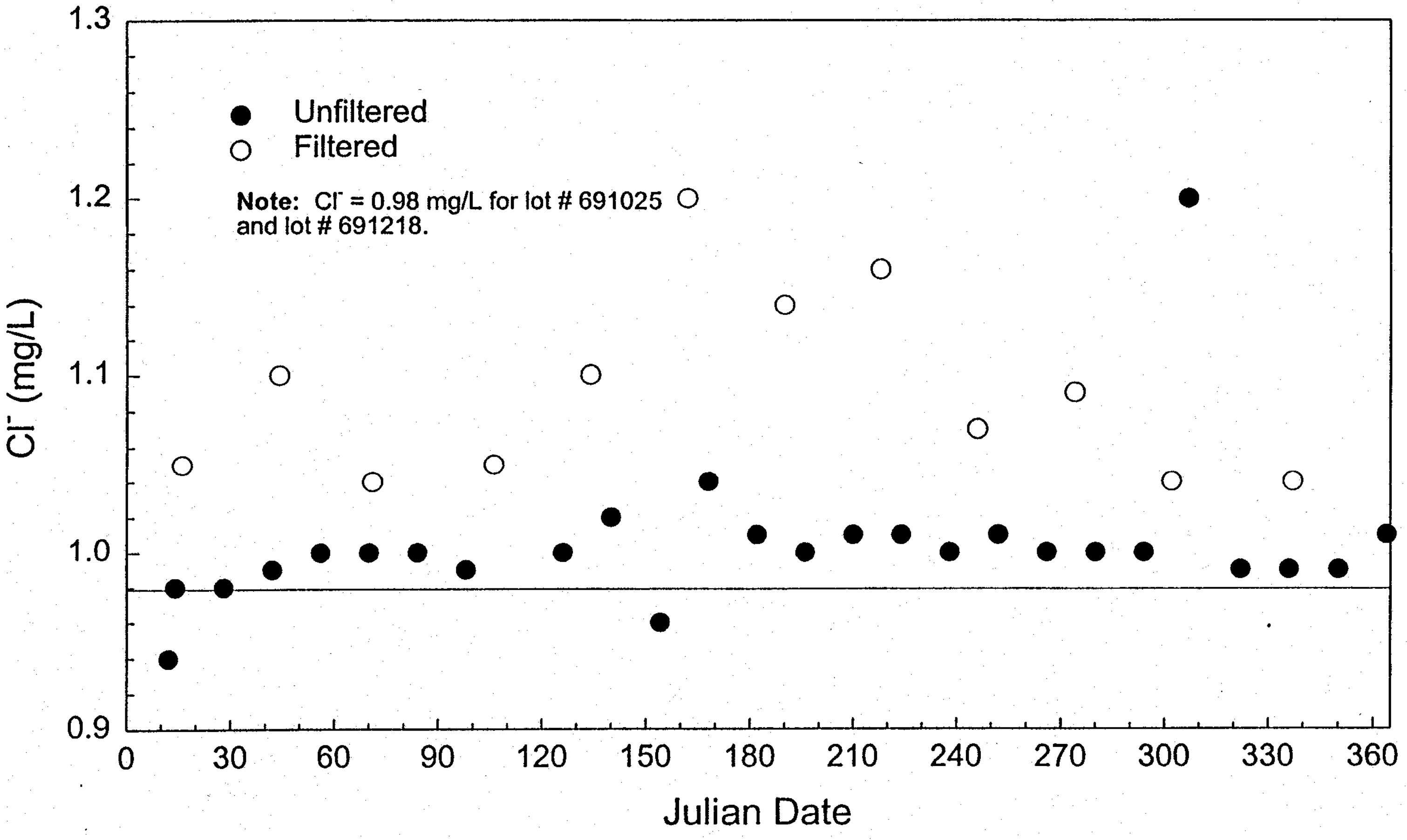


FIGURE B-38. Comparison of filtered and unfiltered internal blind samples (chloride HPS-SRII), 1997.

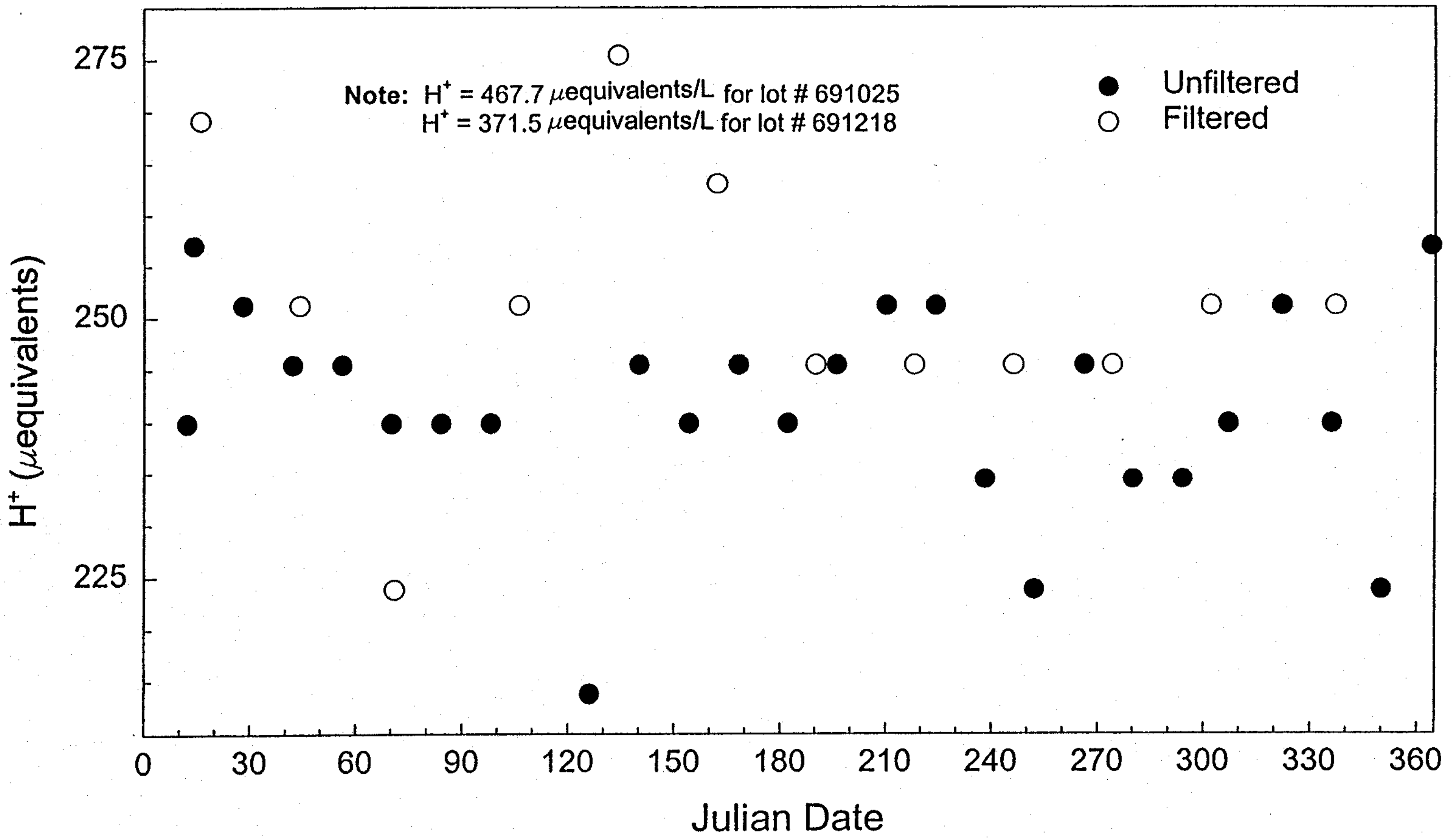
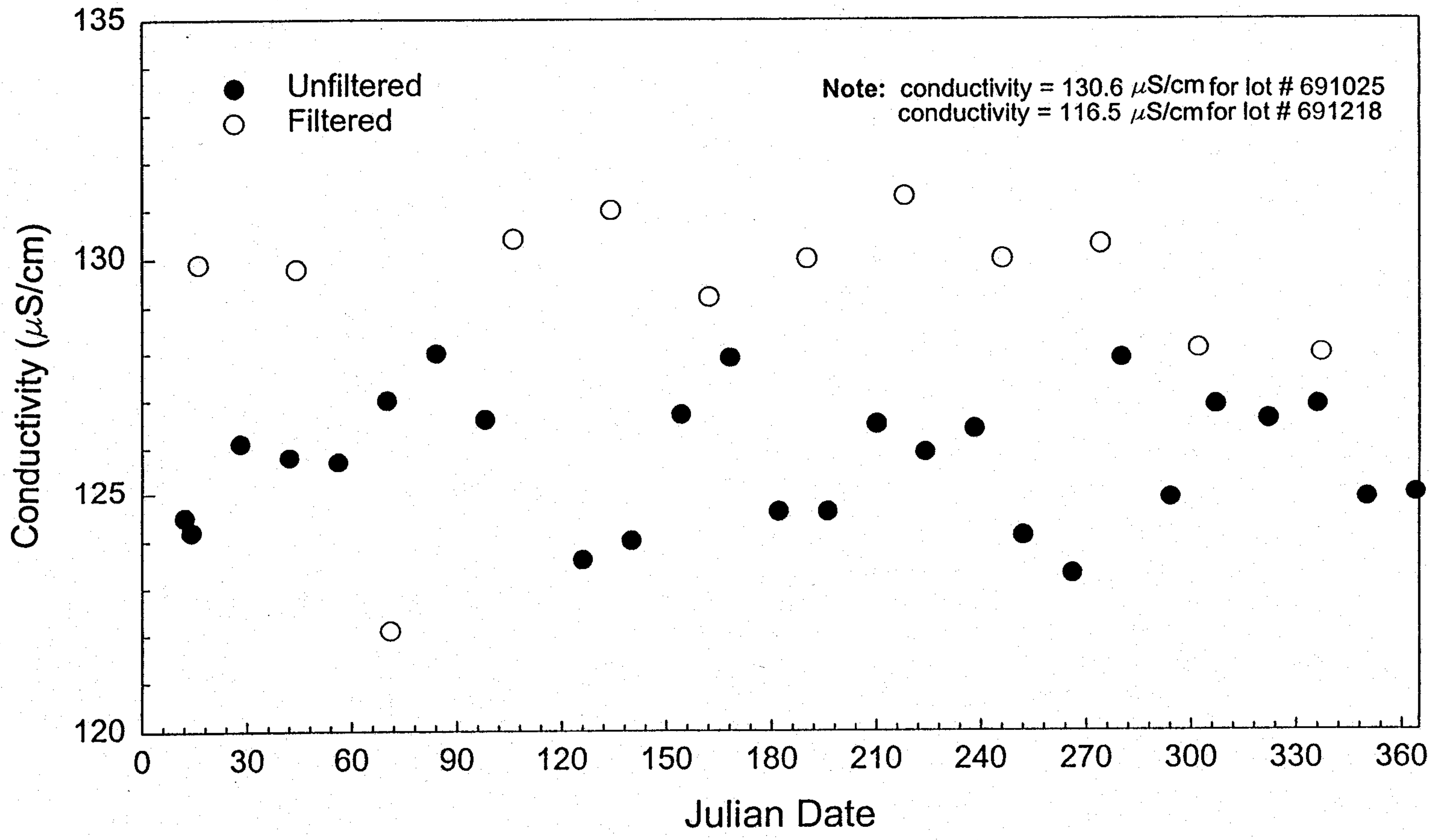


FIGURE B-39. Comparison of filtered and unfiltered internal blind samples (H^+ HPS-SRII), 1997.



Note: conductivity = 130.6 μS/cm for lot # 691025
conductivity = 116.5 μS/cm for lot # 691218

FIGURE B-40. Comparison of filtered and unfiltered internal blind samples (conductivity HPS-SRII), 1997.

Table B-5. 50th and 95th Percentile Concentration Values of Parameters Measured in Replicate (S/Q) Samples, 1996

	Percentile Concentration Values (mg/L)	
Parameter	*50th*	*95th*
Calcium	0.084	0.481
Magnesium	0.020	0.176
Sodium	0.067	1.430
Potassium	0.015	0.094
Ammonium	0.16	0.72
Sulfate	0.88	3.95
Nitrate	0.81	2.90
Chloride	0.13	1.34
pH (units)	4.87	6.28
H^+ (μeq/L)	13.18	64.56
Conductivity (μS/cm)	11.1	42.1

Table B-6. 50th and 95th Percentile Concentration Values of Parameters Measured in Replicate (S/Q) Samples, 1997

	Percentile Concentration Values (mg/L)	
Parameter	*50th*	*95th*
Calcium	0.09	0.548
Magnesium	0.018	0.101
Sodium	0.048	0.595
Potassium	0.016	0.082
Ammonium	0.200	0.619
Sulfate	1.13	3.57
Nitrate	1.02	3.12
Chloride	0.11	1.02
pH (units)	4.67	5.70
H^+ (μeq/L)	21.4	472.3
Conductivity (μS/cm)	14.0	41.6

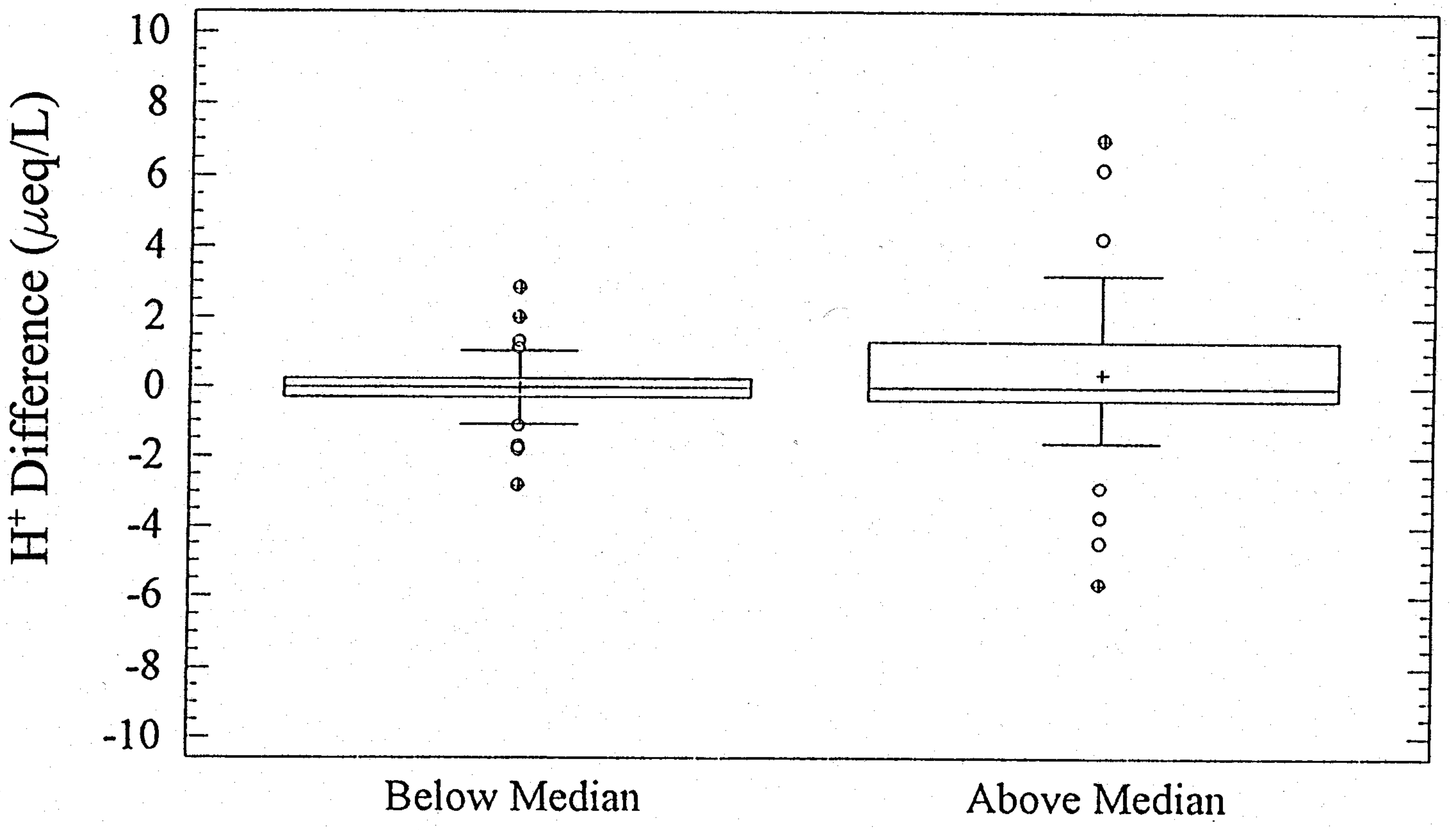


FIGURE B-41. Results of S/Q replicate analysis, H^+, 1996.

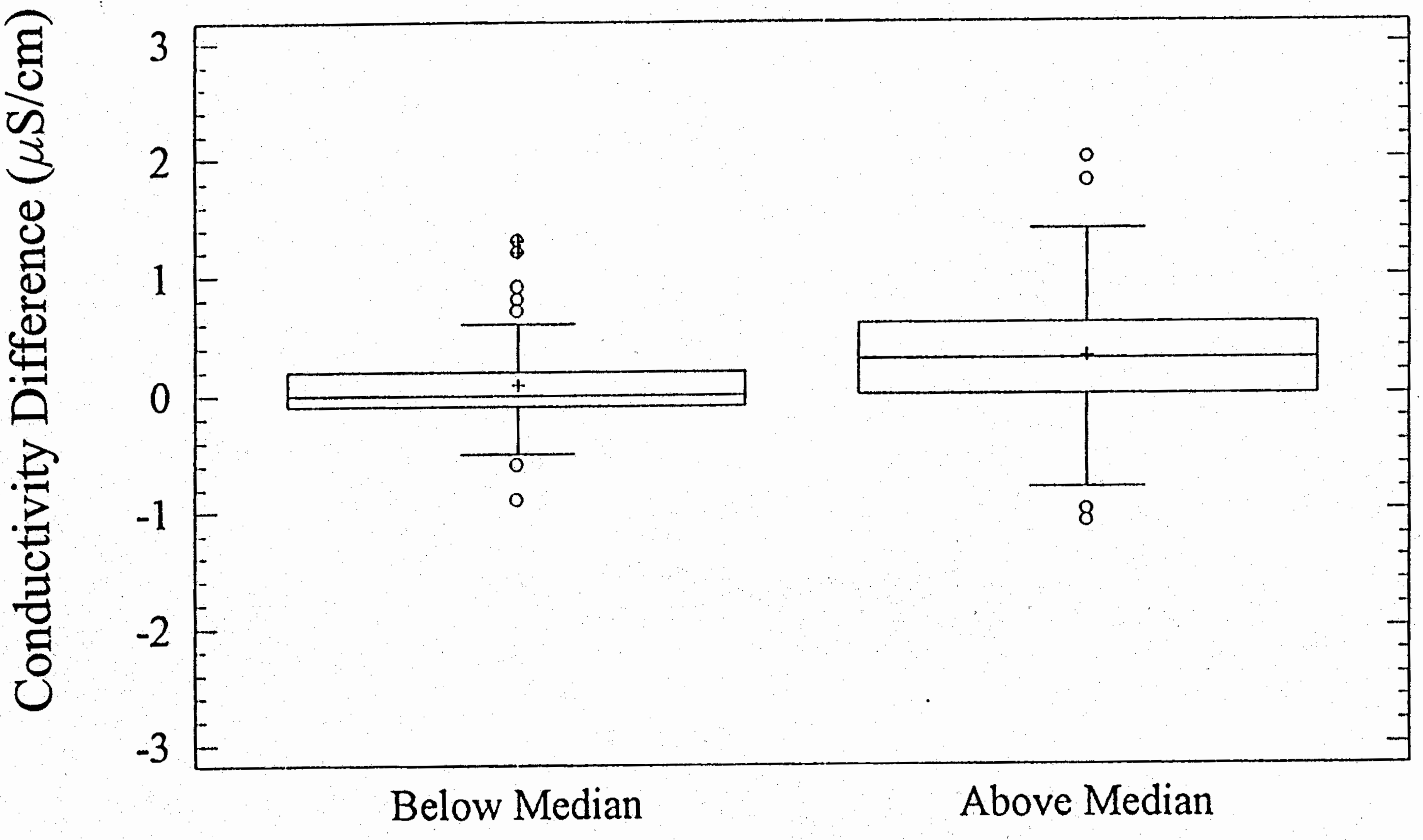


FIGURE B-42. Results of S/Q replicate analysis, conductivity, 1996.

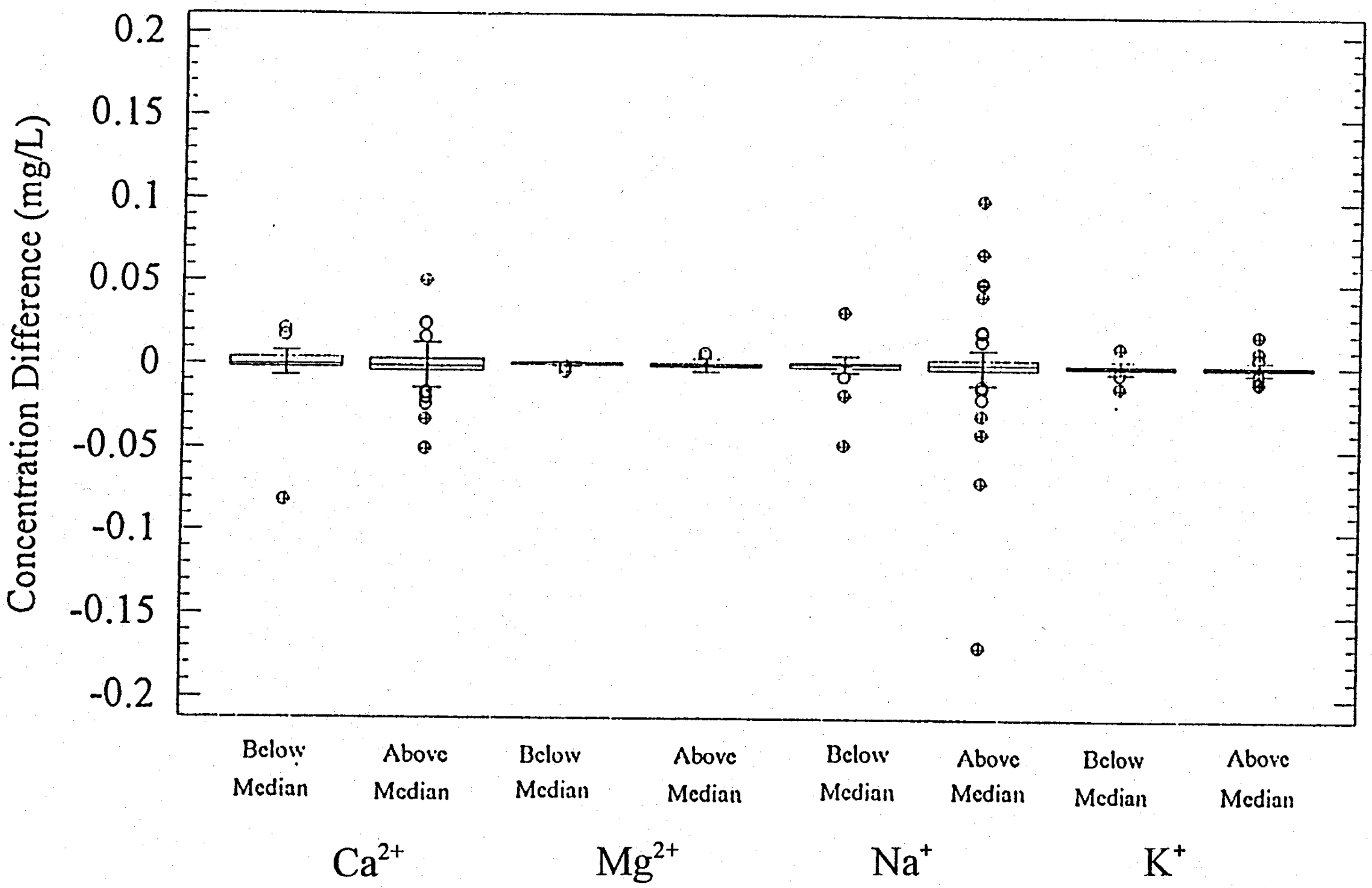


FIGURE B-43. Results of S/Q replicate analysis, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}), 1996.

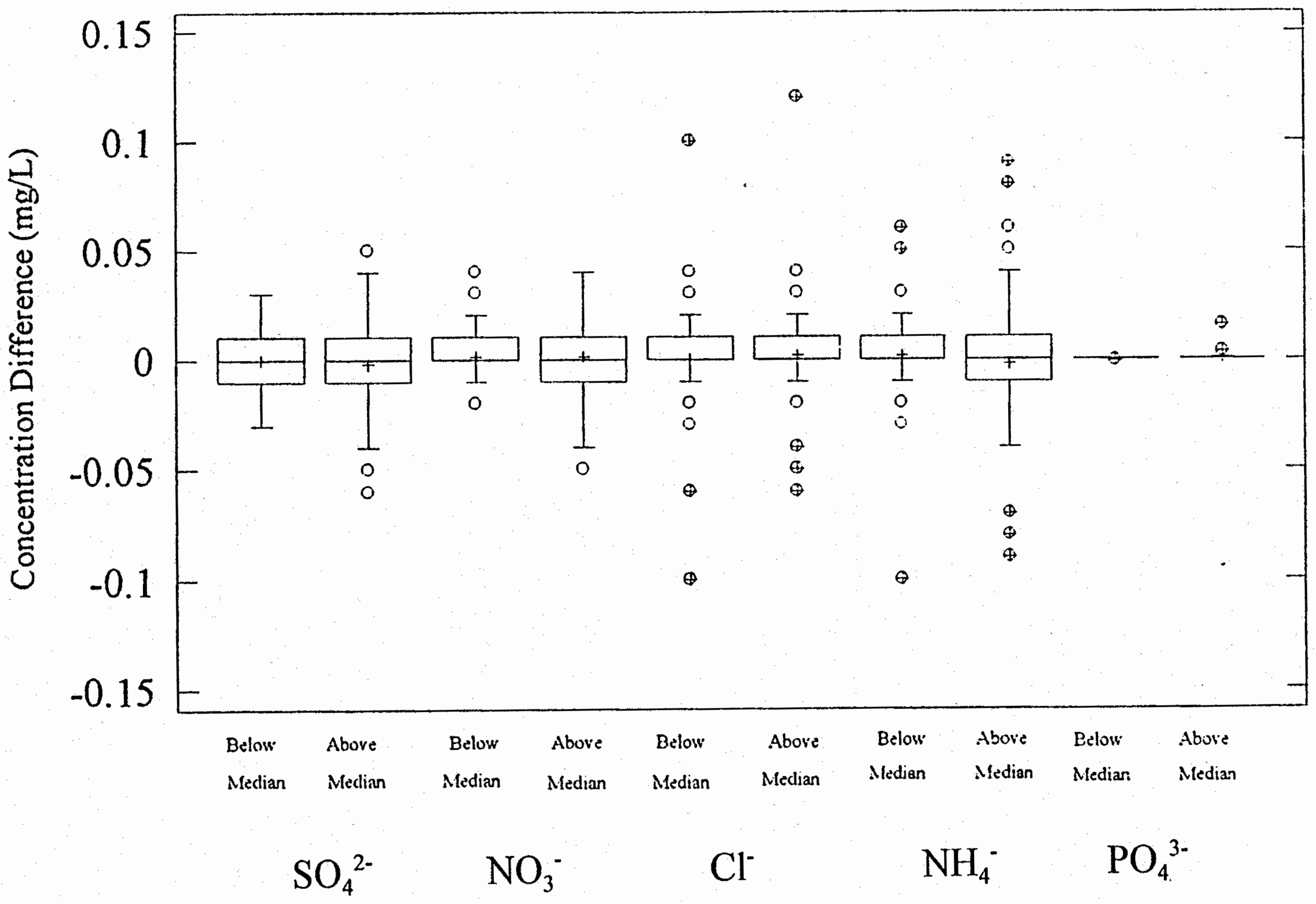


FIGURE B-44. Results of S/Q replicate analysis, sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^-), and phosphate (PO_4^{3-}), 1996.

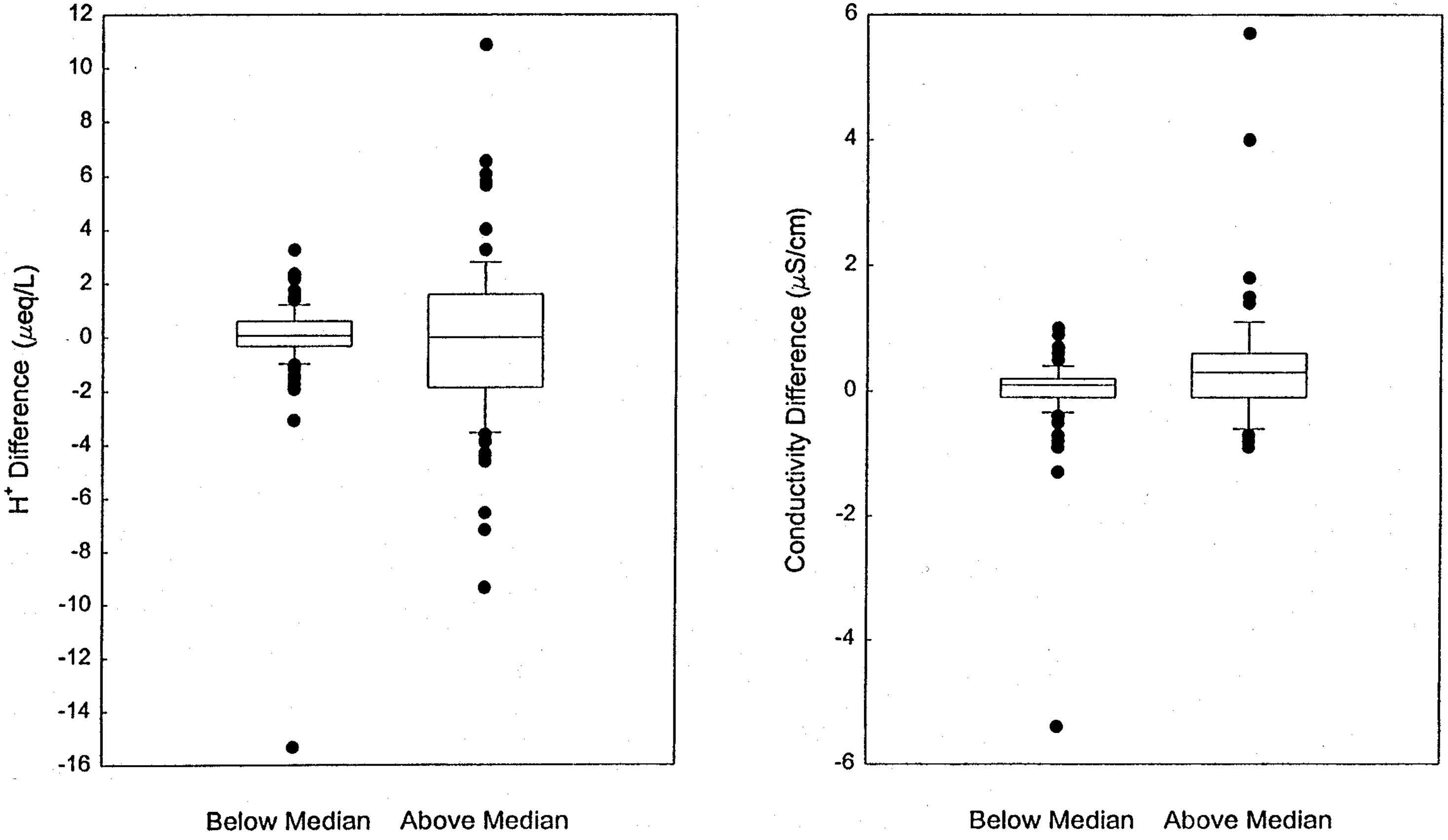


FIGURE B-45. Results of S/Q replicate analysis, H^+ and conductivity, 1997.

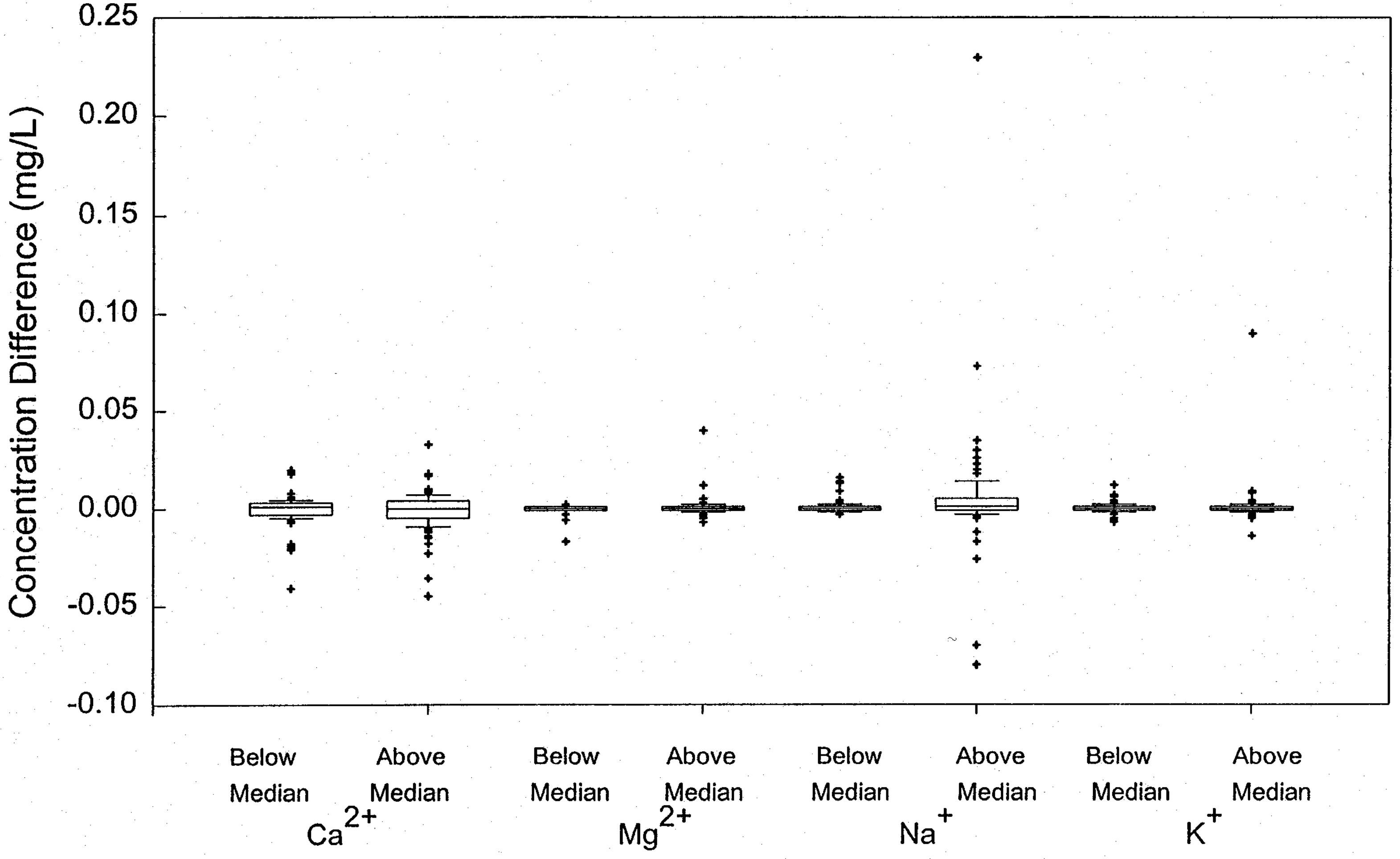


FIGURE B-46. Results of S/Q replicate analysis, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}), 1997.

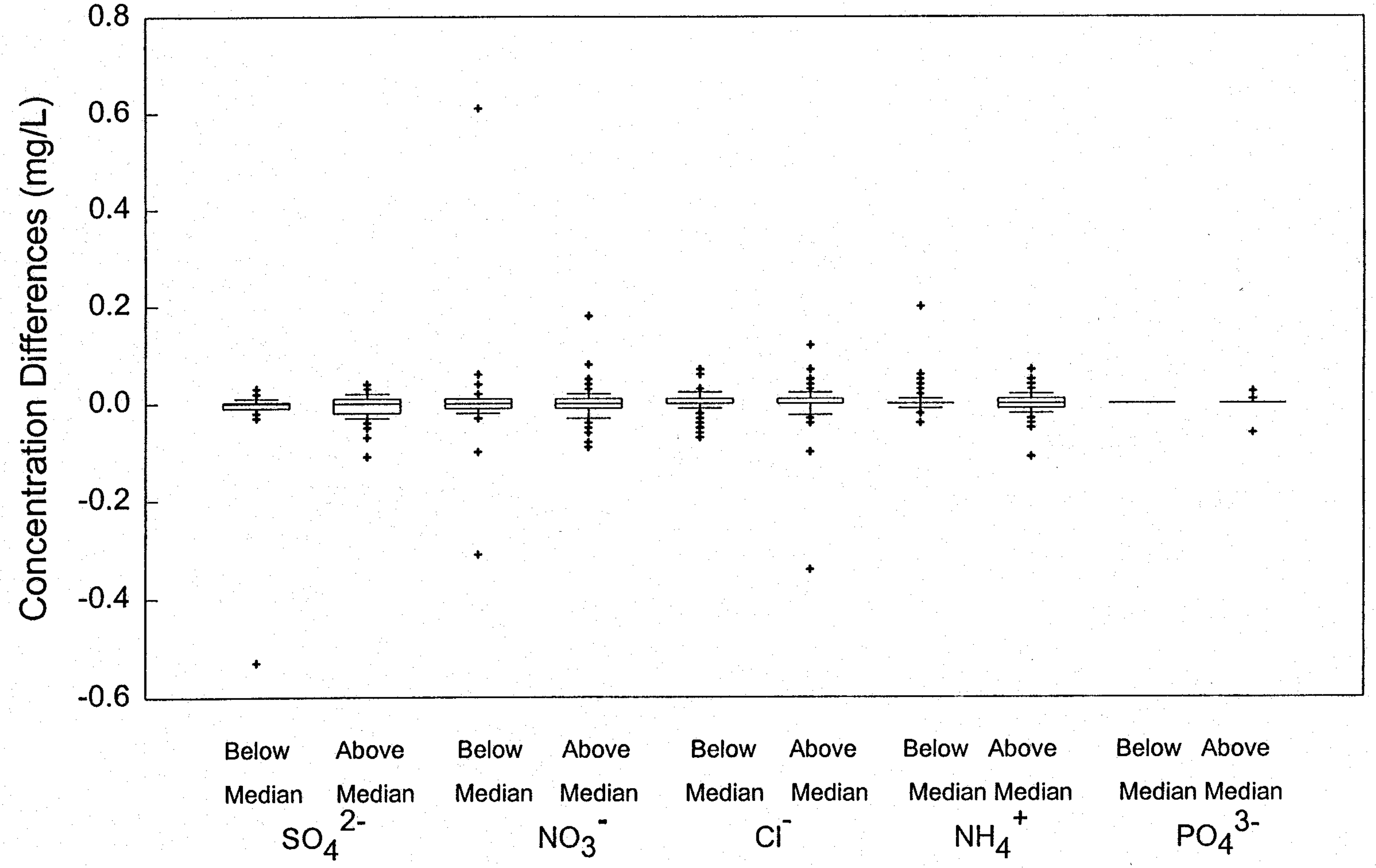


FIGURE B-47. Results of S/Q replicate analysis, sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), and ortho-phosphate (PO_4^{3-}), 1997.

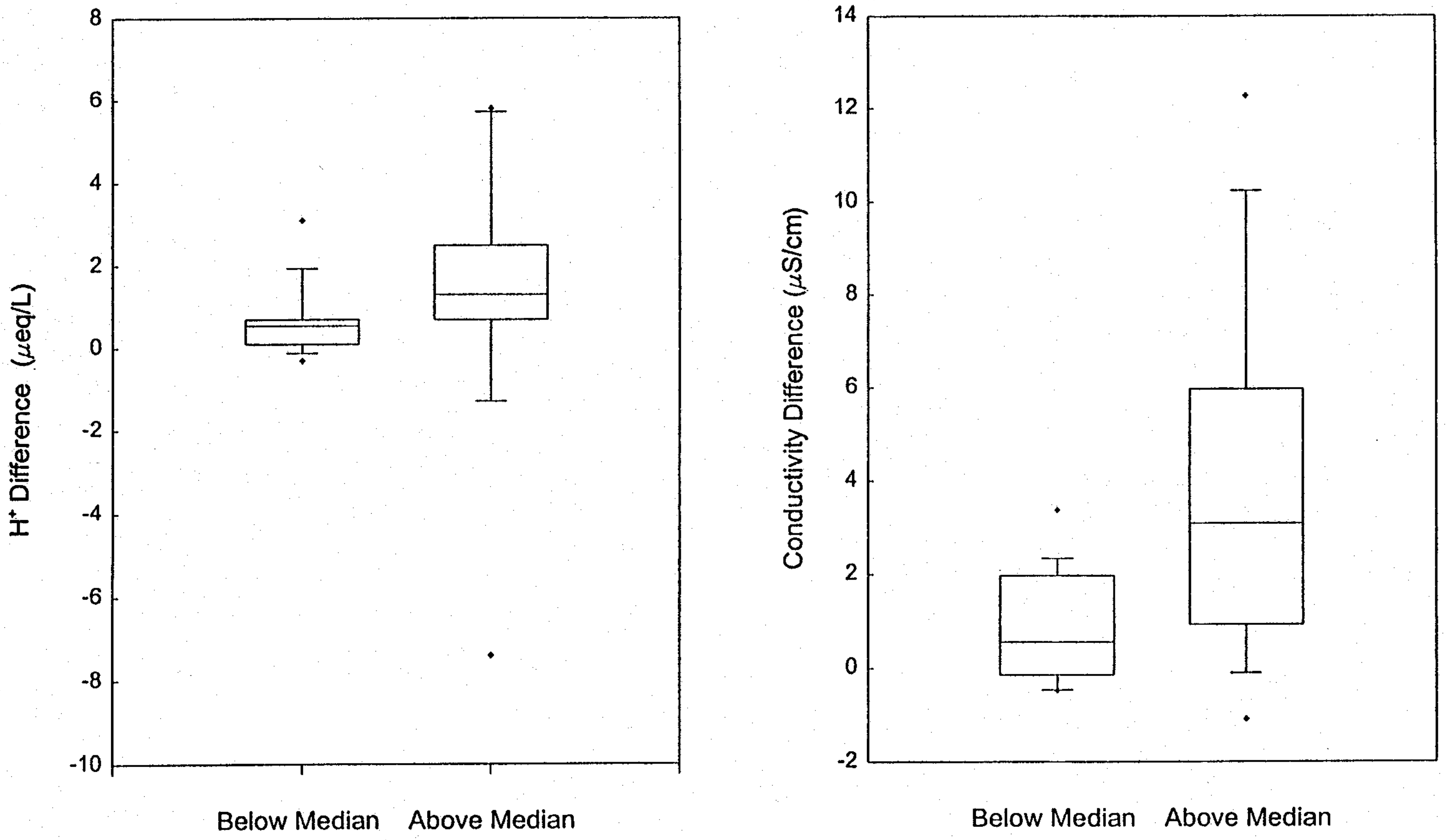


FIGURE B-48. Results of AIRMoN L/Q replicate analysis, H$^+$ and conductivity, 1996.

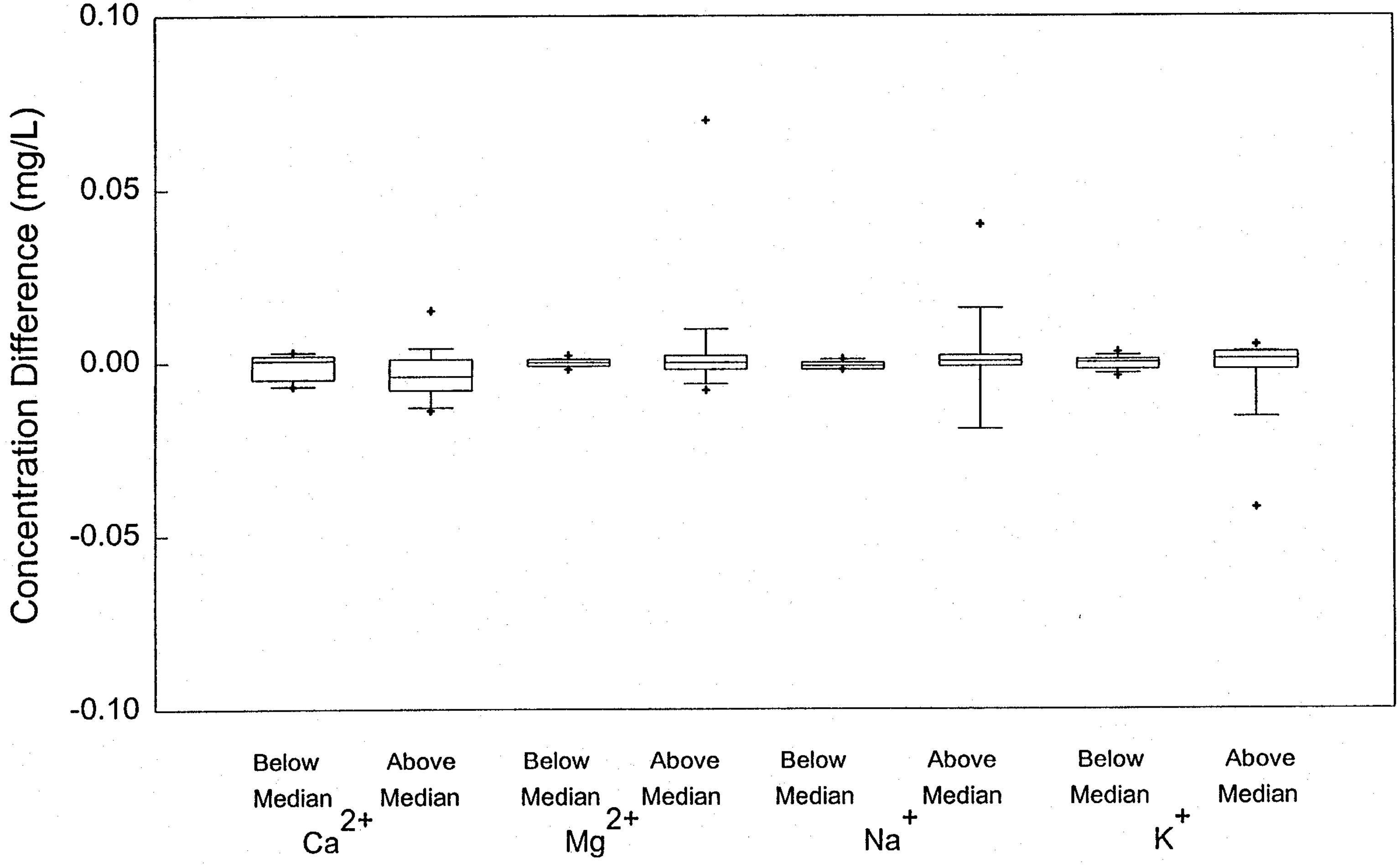


FIGURE B-49. Results of AIRMoN L/Q replicate analysis, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}), 1996.

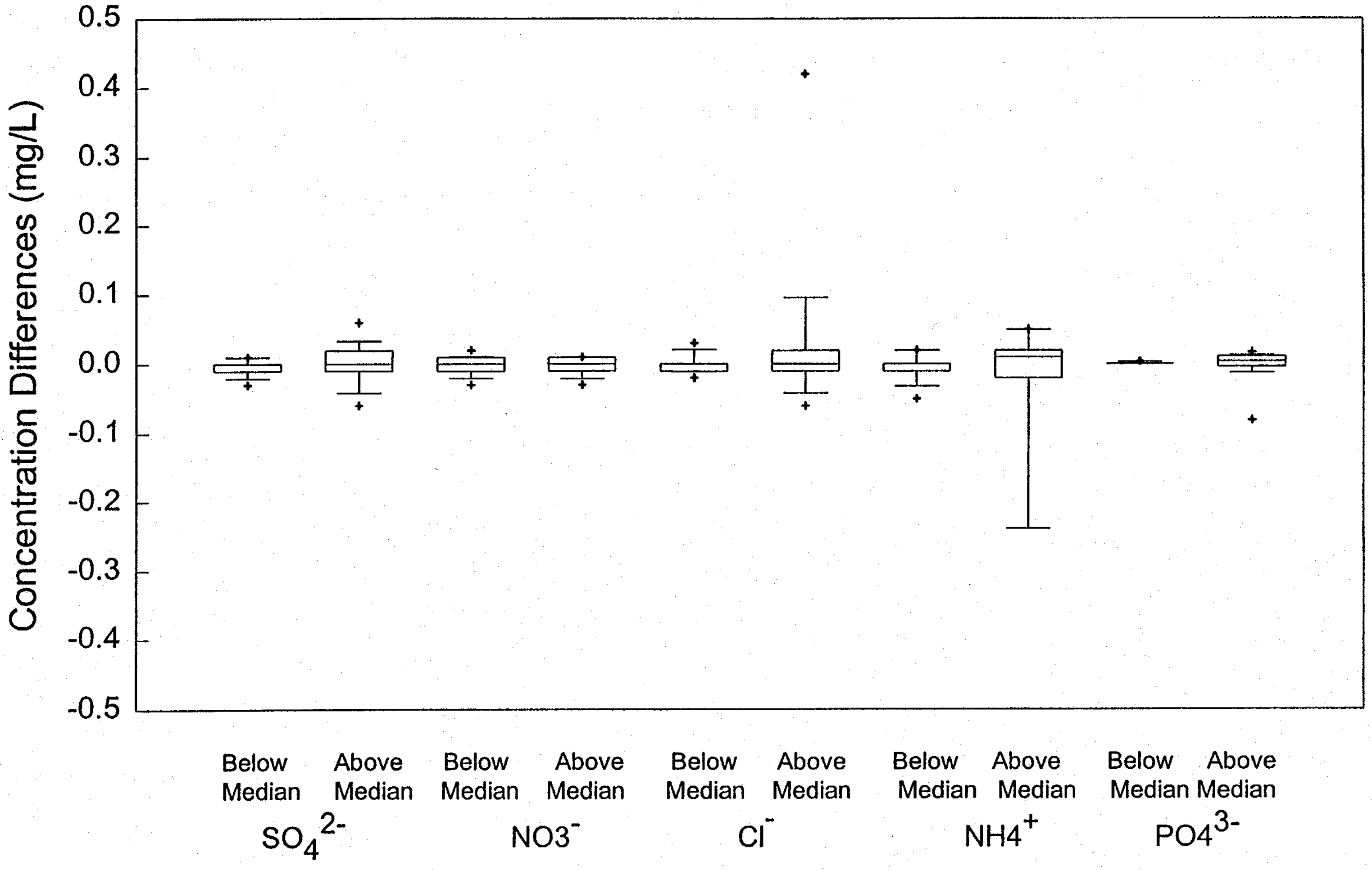


Figure B-50. Results of AIRMoN L/Q replicate analysis, sulfate (SO_4^{2-}), nitrate ($NO3^-$), chloride (Cl^-), ammonium ($NH4^+$), and ortho-phosphate ($PO4^{3-}$), 1996.

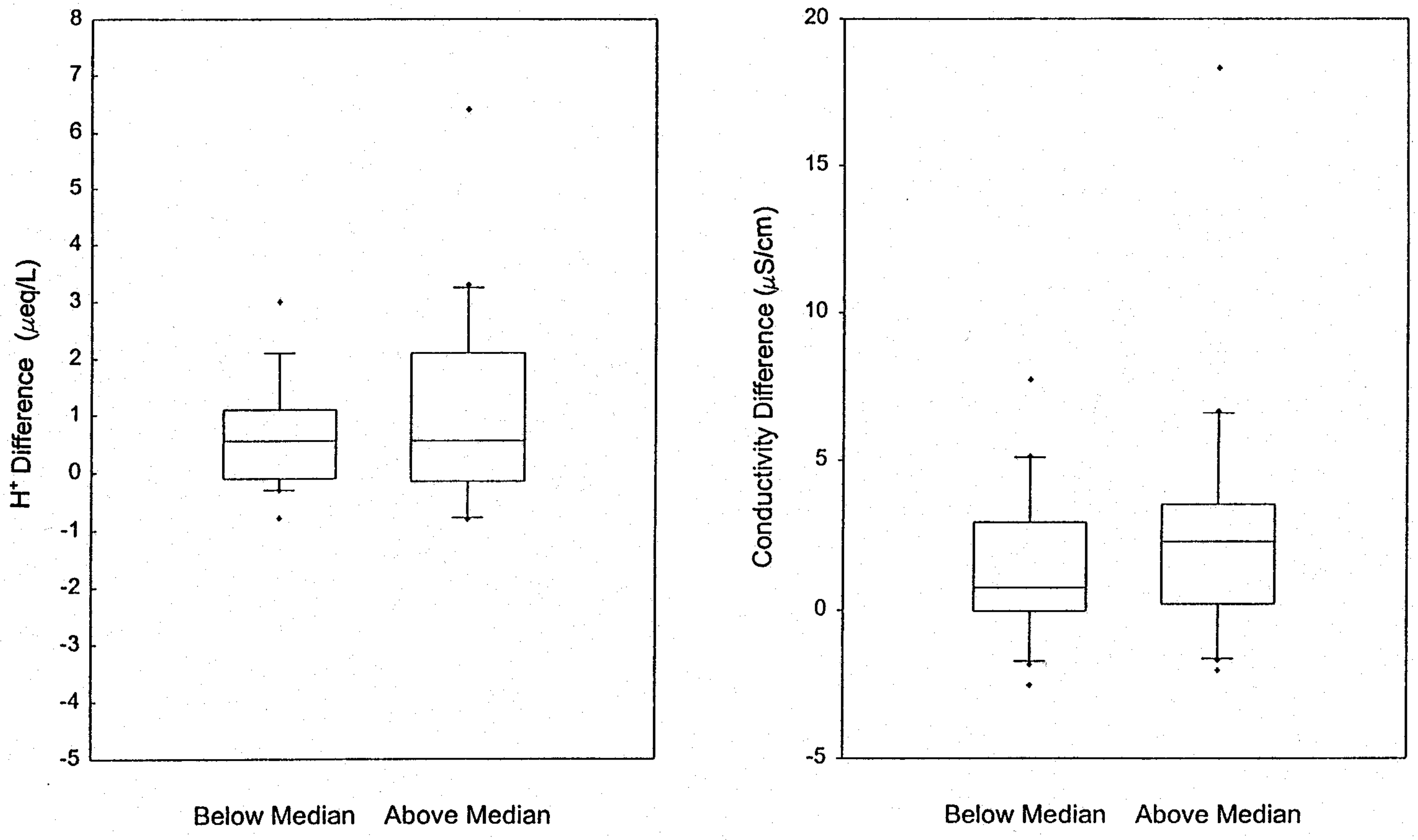


FIGURE B-51. Results of AIRMoN L/Q replicate analysis, H^+ and conductivity, 1997.

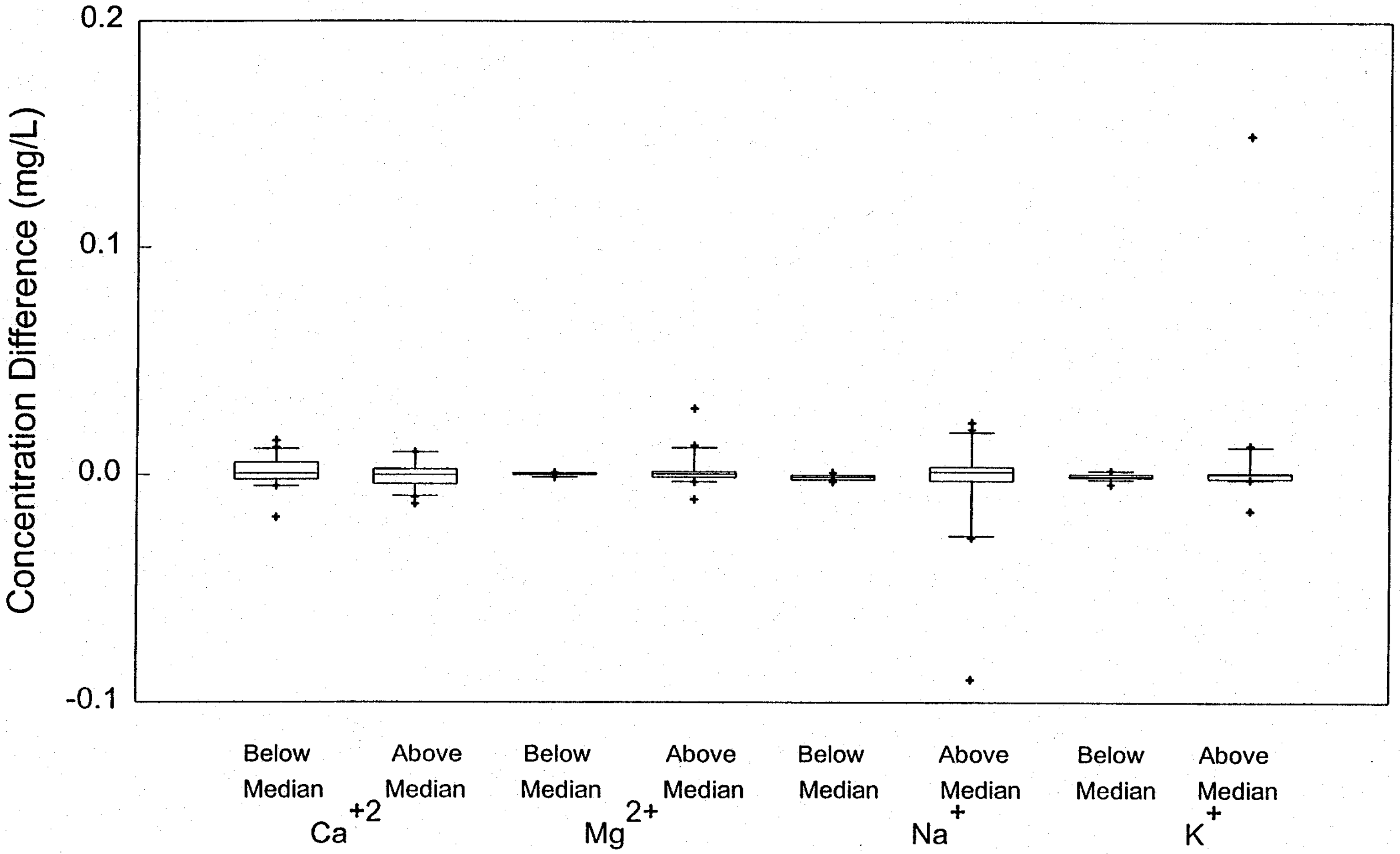


FIGURE B-52. Results of AIRMoN L/Q replicate analysis, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+), 1997.

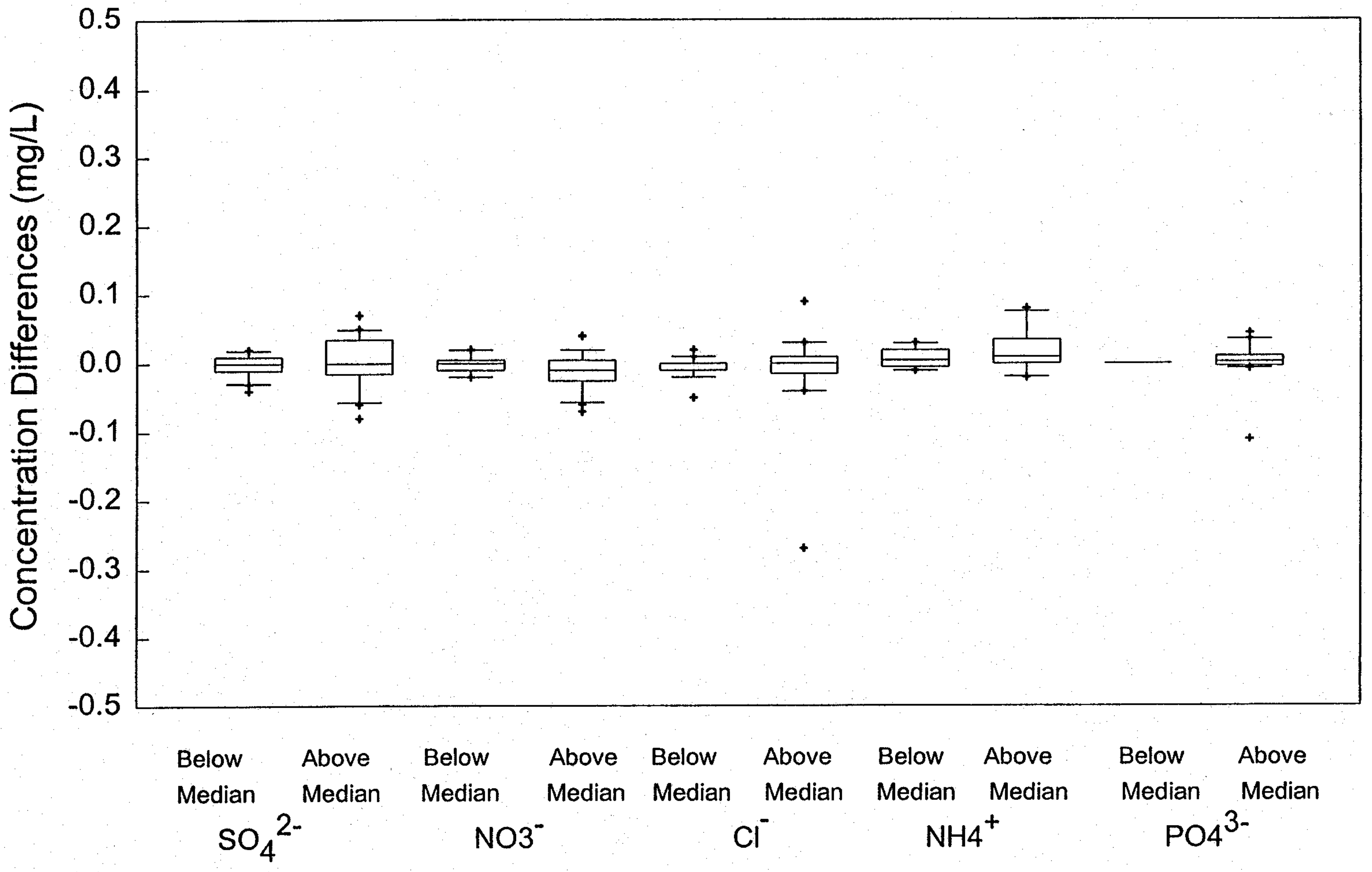


FIGURE B-53. Results of AIRMoN L/Q replicate analysis, sulfate (SO_4^{2-}), nitrate ($NO3^-$), chloride (Cl^-), ammonium ($NH4^+$), and ortho-phosphate ($PO4^{3-}$), 1997.

Table B-7. Percent of Ion Concentrations above MDLs Found in Weekly Deionized (DI) Water Blanks and Leachates, 1996

Blank	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Ammonium*	*Sulfate*	*Nitrate*	*Chloride*	*Phosphate*
DI-(209)	2	0	9	4	0	0	0	0	0
DI-(304)	0	0	4	4	0	0	0	2	6
DI-(323)	4	2	9	6	2	0	0	2	6
Filter A	9	6	98	4	30	0	91	85	0
Filter B	2	2	96	4	2	1	6	9	0
Bucket 50	72	28	96	94	19	0	23	62	4
Bucket 150	26	9	89	70	4	0	2	15	0
Bottle 50	13	21	23	87	2	4	0	0	4
Bottle 150	2	2	4	45	0	0	0	0	4
Lid 50	23	13	79	57	26	0	9	11	0

Note: 47 weekly blanks were analyzed.

TABLE B-8. Percent of Ion Concentrations above MDL's found in Weekly Deionized (DI) Water Blanks and Leachates, 1997

Blank	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Ammonium*	*Sulfate*	*Nitrate*	*Chloride*	*Phosphate*
DI-(209)	6	0	2	0	4	0	0	0	2
DI-(304)	0	0	4	2	0	0	0	0	2
DI-(323)	6	4	8	2	2	0	2	4	2
Filter A	8	0	100	10	6	0	98	73	4
Filter B	2	0	100	10	0	0	17	12	4
Bucket 50	50	27	90	75	29	2	31	71	8
Bucket 150	21	4	62	42	4	2	6	29	2
Bottle 50	8	8	17	60	2	4	0	4	6
Bottle 150	8	2	8	21	4	0	2	0	2
Lid 50	23	8	75	58	12	2	8	36	2

Note: 52 weekly blanks were analyzed.

Table B-9. Percent of Ion Concentrations Above Control Limits Found in Weekly Simulated Rain (FR25) Blanks and Leachates, 1996

Blank	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Ammonium*	*Sulfate*	*Nitrate*	*Chloride*	*Phosphate*
Filter A	11	2	100	17	32	0	32	74	2
Filter B	13	2	77	11	6	0	0	0	2
Bucket 50	34	11	62	94	9	0	2	12	4
Bucket 150	47	2	36	83	0	0	0	9	2
Bottle 50	13	15	4	72	0	4	0	2	13
Bottle 150	11	2	2	36	0	0	0	0	4
Lid 50	62	4	30	79	11	0	4	15	0
AIRMoN 50	18	0	9	9	0	0	0	0	0
AIRMoN 150	0	0	0	0	0	0	0	0	0

Note: 47 NADP/NTN weekly blanks and 12 AIRMoN weekly blanks were analyzed.

TABLE B-10. Percent of Ion Concentrations Above Control Limits Found in Weekly Simulated Rain (FR25) Blanks and Leachate, 1997

Blank	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Ammonium*	*Sulfate*	*Nitrate*	*Chloride*	*Phosphate*
Filter A	4	4	100	2	0	0	60	37	2
Filter B	6	6	56	2	0	0	0	0	2
Bucket 50	15	15	46	44	12	6	12	42	0
Bucket 150	10	8	23	17	2	0	0	17	0
Bottle 50	2	13	6	23	2	4	0	0	4
Bottle 150	4	4	2	2	0	0	0	0	2
Lid 50	13	6	21	31	4	4	4	17	4
AIRMoN	0	0	0	0	0	0	0	0	0
AIRMoN	0	0	0	0	0	0	0	0	0

Note:47 weekly NADP/NTN blanks and 12 weekly AIRMoN blanks were analyzed.

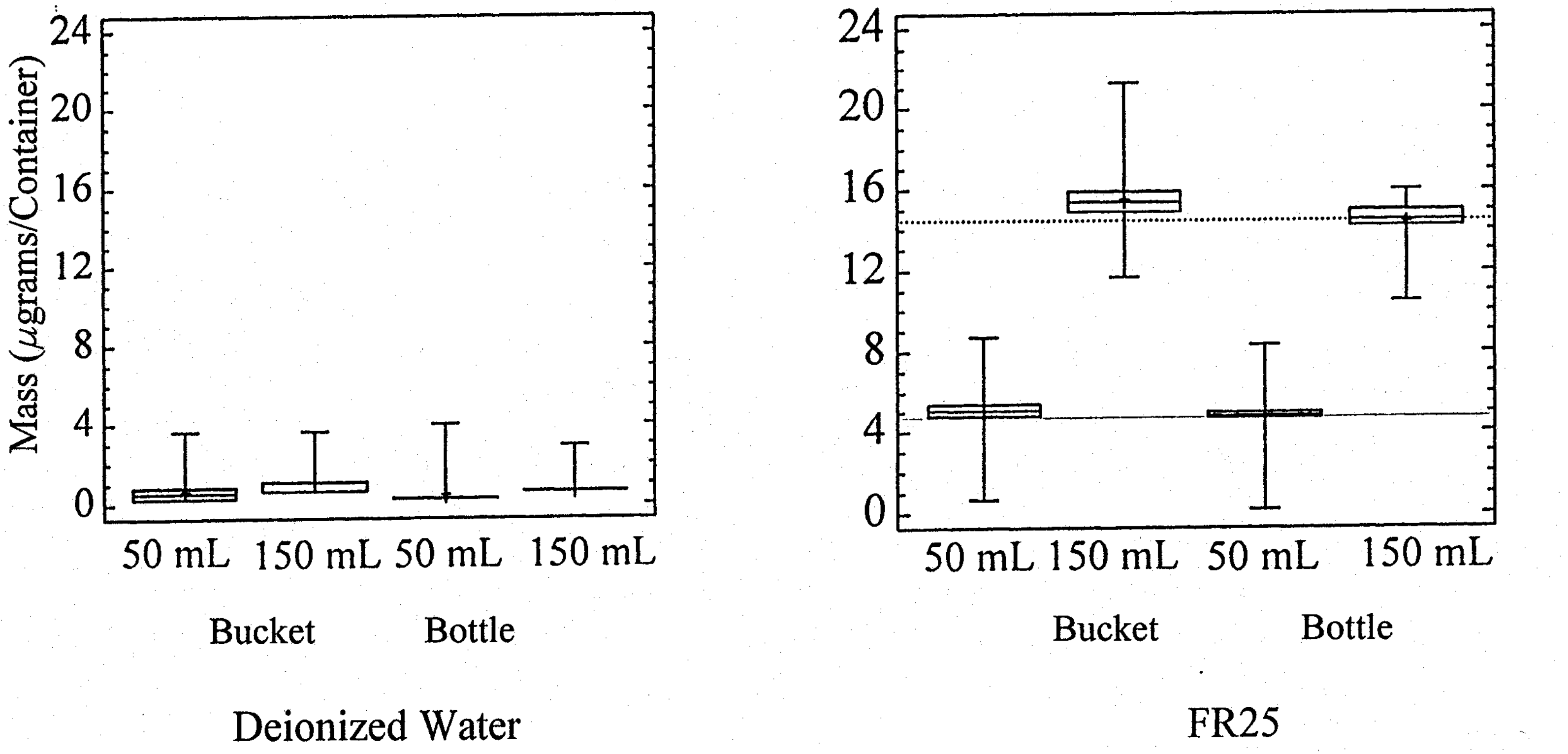


FIGURE B-54. Calcium found in upright bucket blanks and 1 liter bottles, using DI water and FR25 QCS as leaching agents, 1996. FR25 baseline values shown as solid line (50 mL) and dotted line (150 mL).

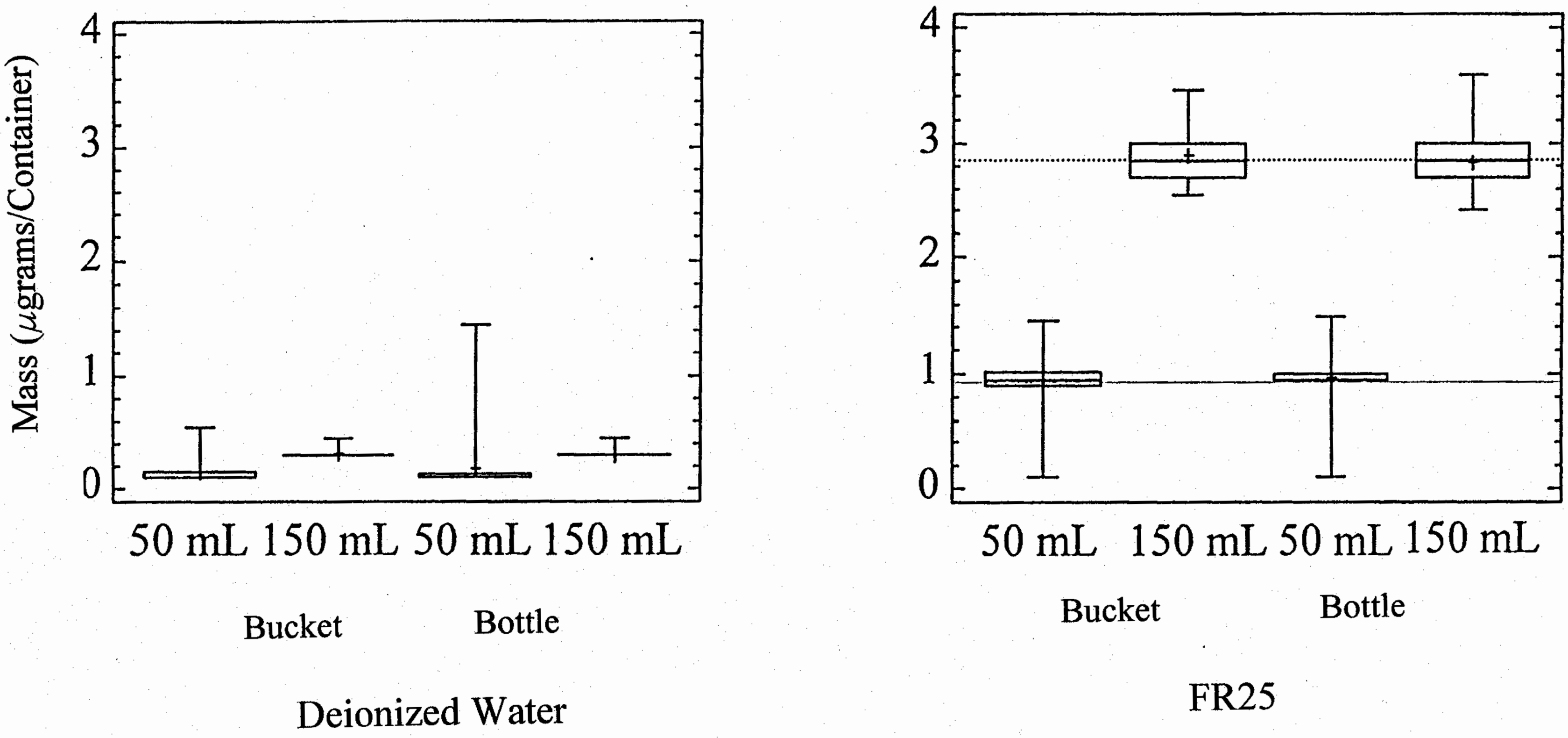


FIGURE B-55. Magnesium found in upright bucket blanks and 1 liter bottles, using DI water and FR25 QCS as leaching agents, 1996. FR25 baseline values shown as solid line (50 mL) and dotted line (150 mL).

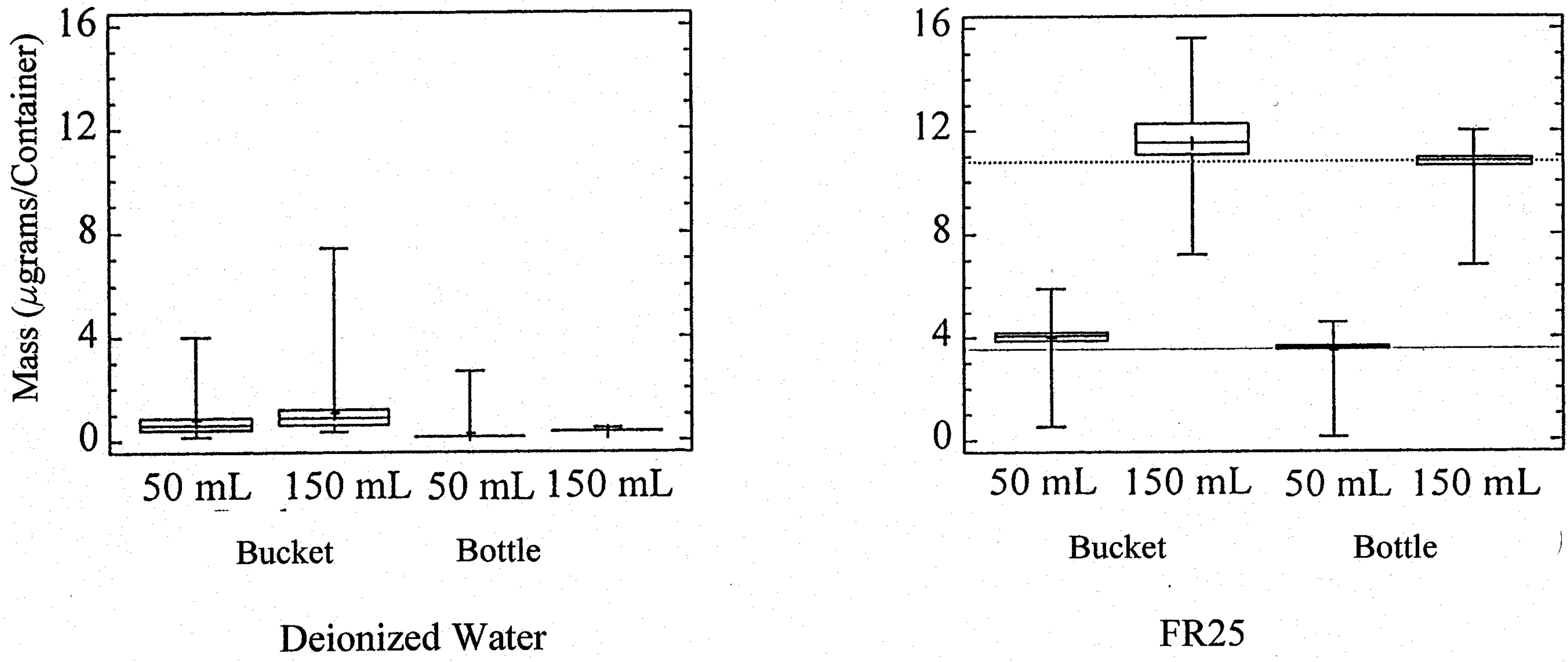


FIGURE B-56. Sodium found in upright bucket blanks and 1 liter bottles, using DI water and FR25 QCS as leaching agents, 1996. FR25 baseline values shown as solid line (50 mL) and dotted line (150 mL).

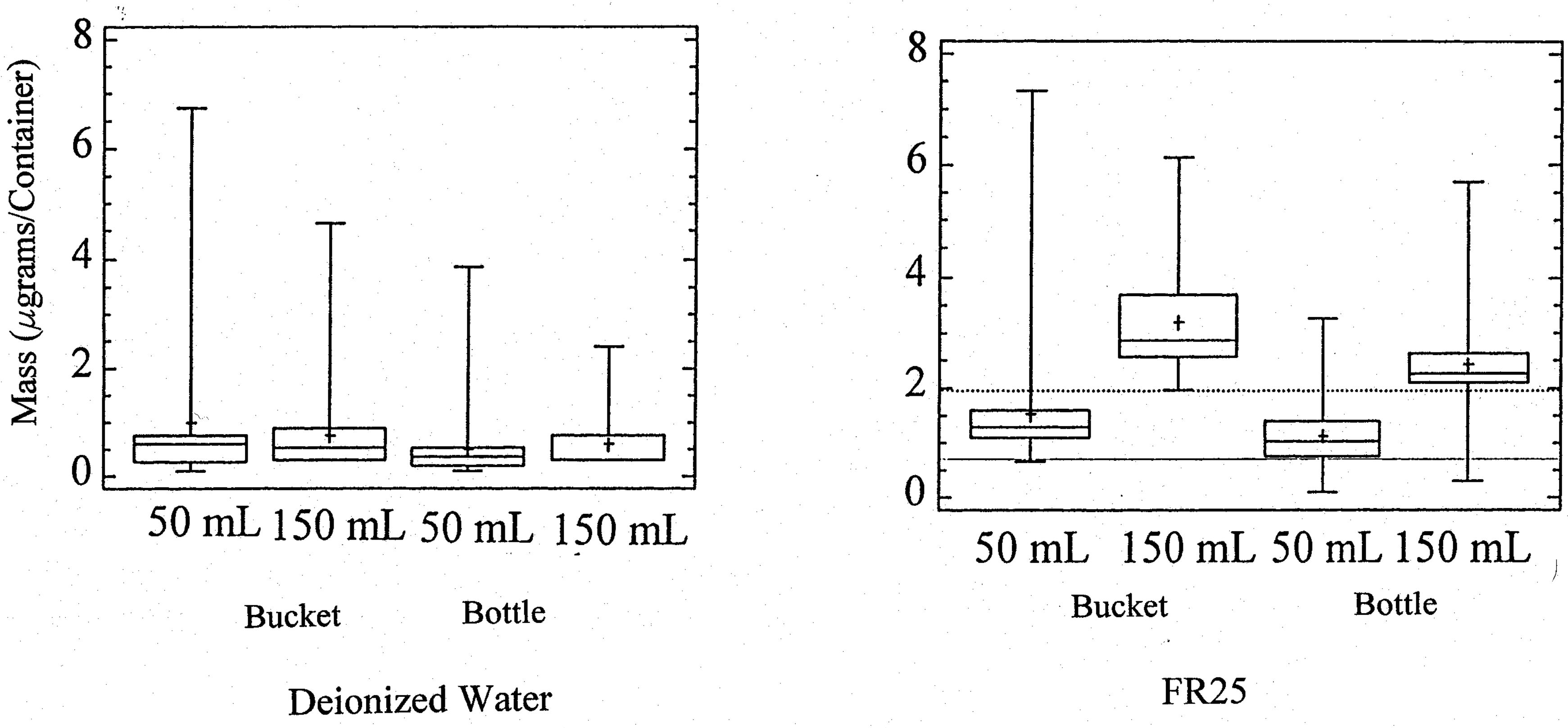


FIGURE B-57. Potassium found in upright bucket blanks and 1 liter bottles, using DI water and FR25 QCS as leaching agents, 1996. FR25 baseline values shown as solid line (50 mL) and dotted line (150 mL).

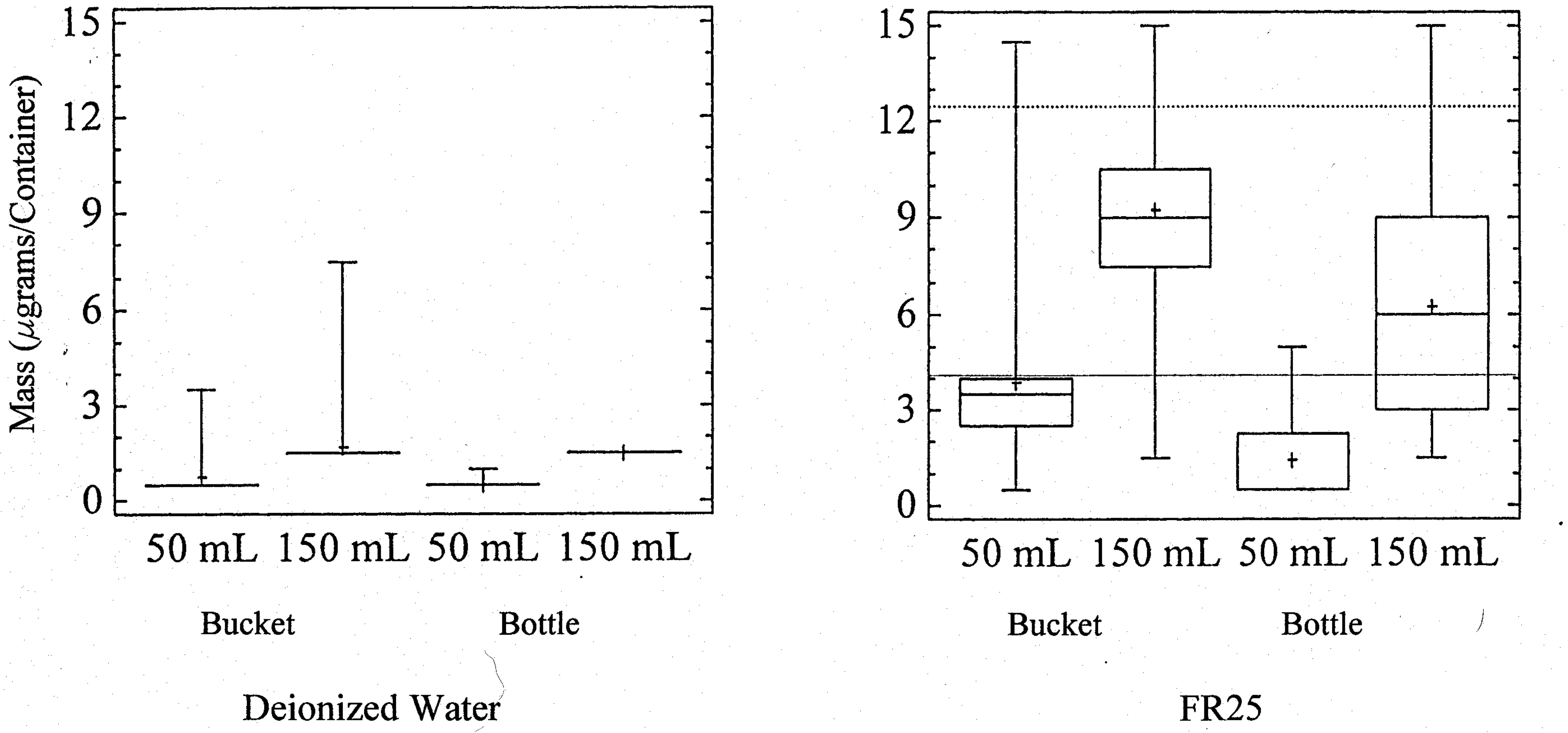


FIGURE B-58. Ammonium found in upright bucket blanks and 1 liter bottles, using DI water and FR25 QCS as leaching agents, 1996. FR25 baseline values shown as solid line (50 mL) and dotted line (150 mL).

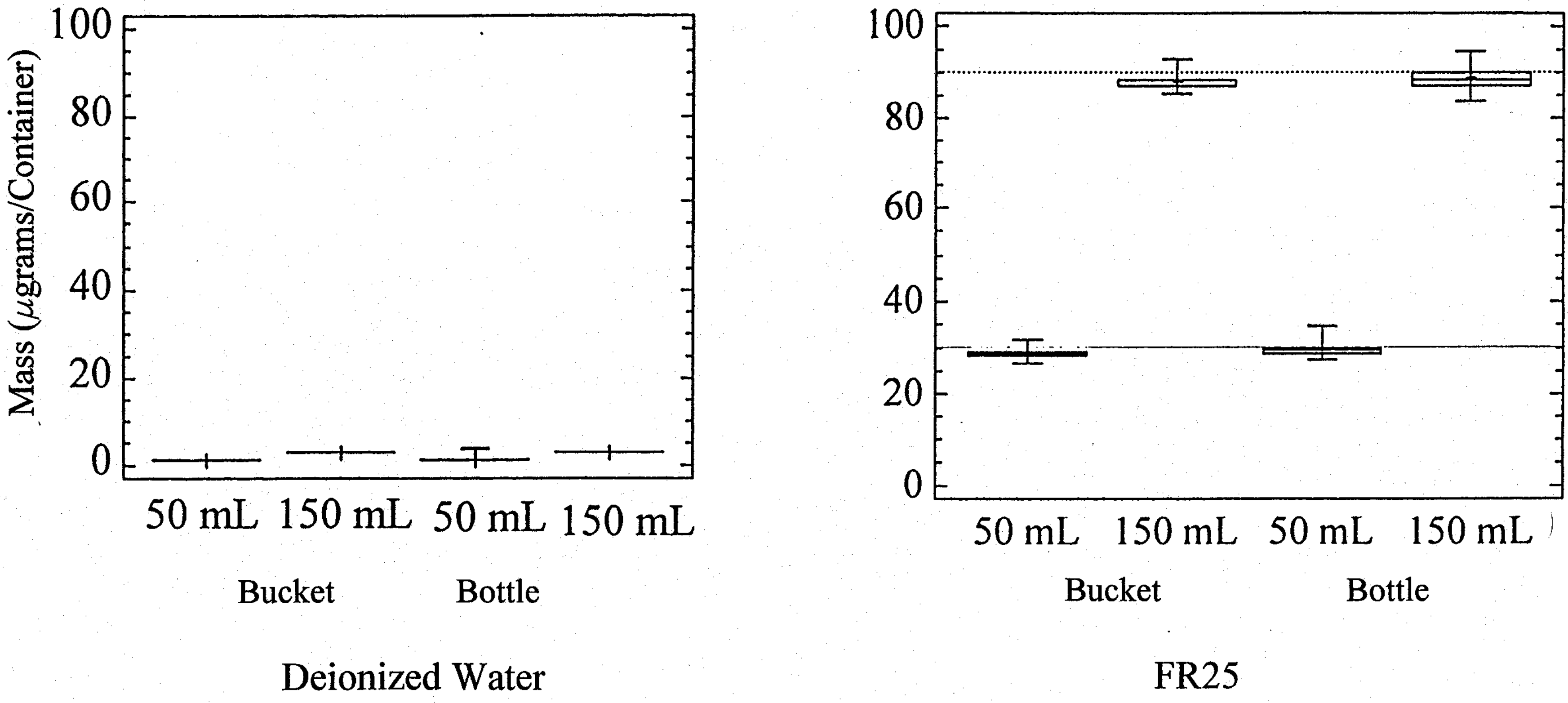


FIGURE B-59. Sulfate found in upright bucket blanks and 1 liter bottles, using DI water and FR25 QCS as leaching agents, 1996. FR25 baseline values shown as solid line (50 mL) and dotted line (150 mL).

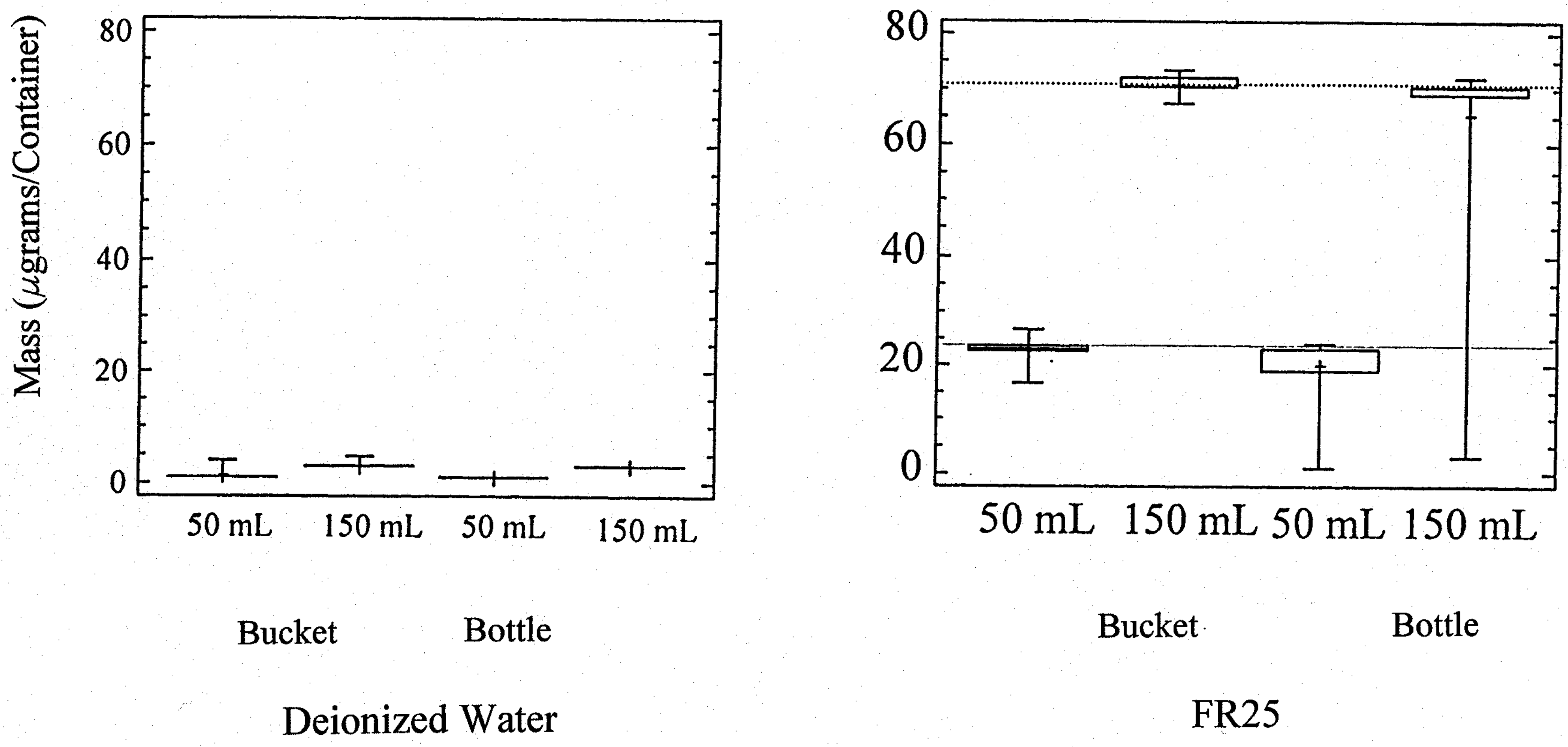


FIGURE B-60. Nitrate found in upright bucket blanks and 1 liter bottles, using DI water and FR25 QCS as leaching agents, 1996. FR25 baseline values shown as solid line (50 mL) and dotted line (150 mL).

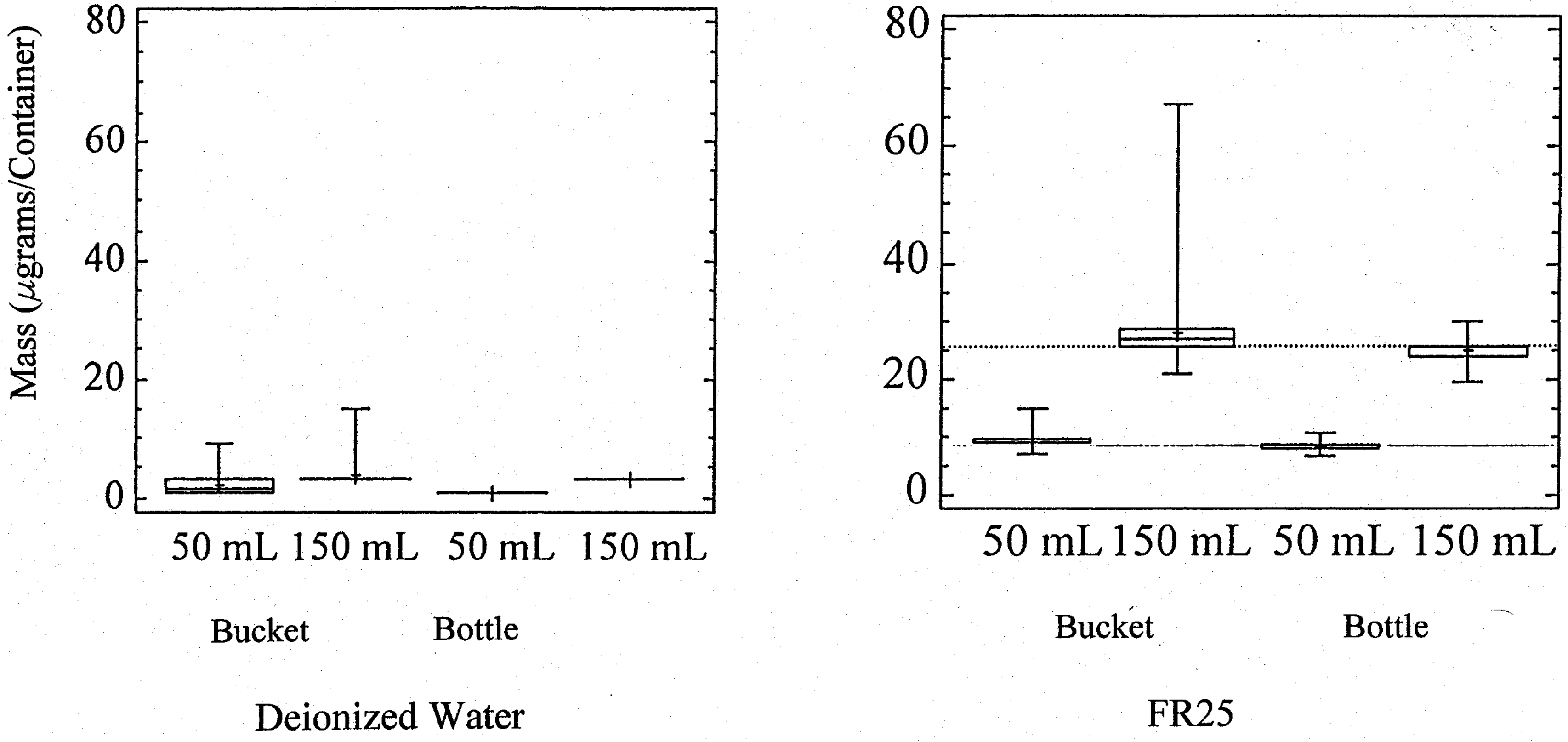


FIGURE B-61. Chloride found in upright bucket blanks and 1 liter bottles, using DI water and FR25 QCS as leaching agents, 1996. FR25 baseline values shown as solid line (50 mL) and dotted line (150 mL).

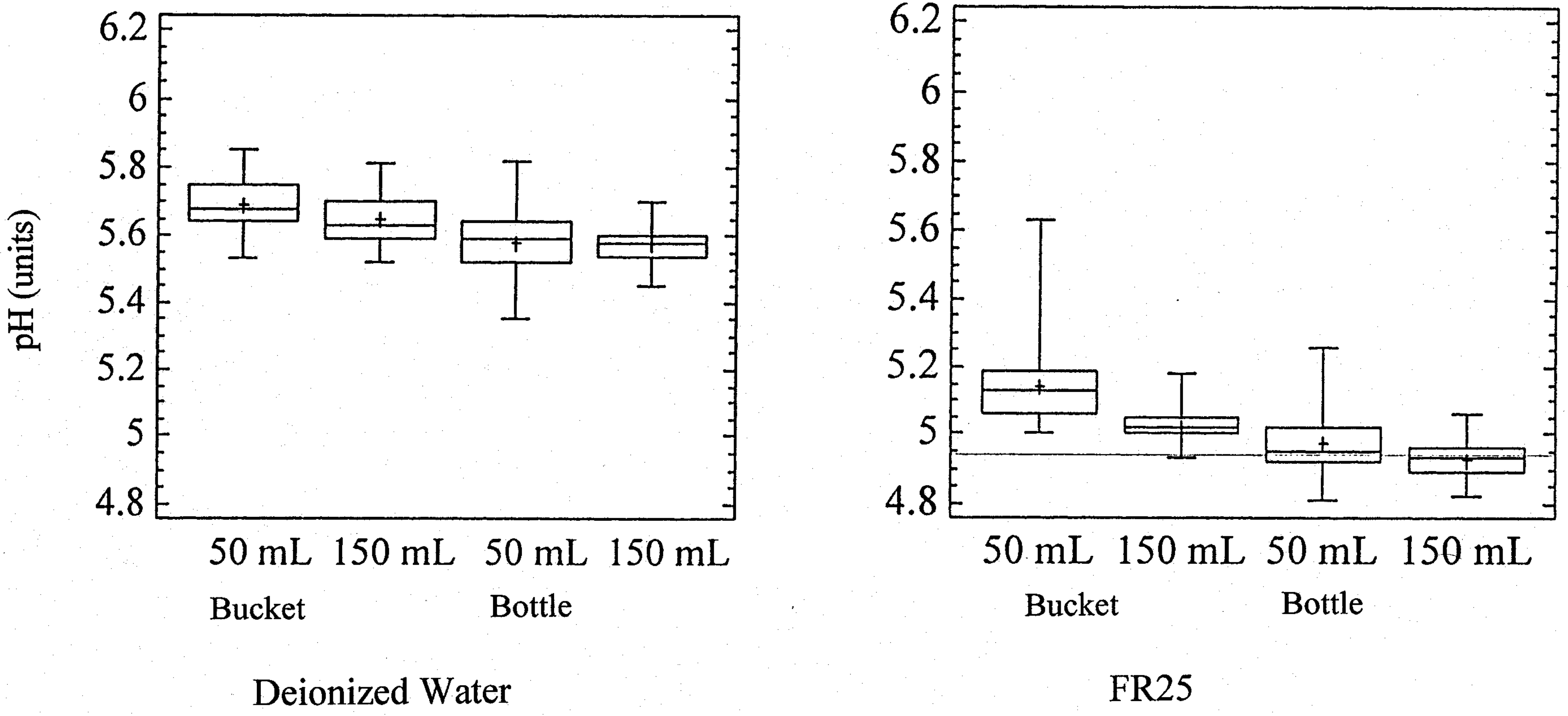


FIGURE B-62. pH of upright bucket blanks and 1 liter bottles, using DI water and FR25 QCS as leaching agents, 1996. FR25 baseline values shown as solid line.

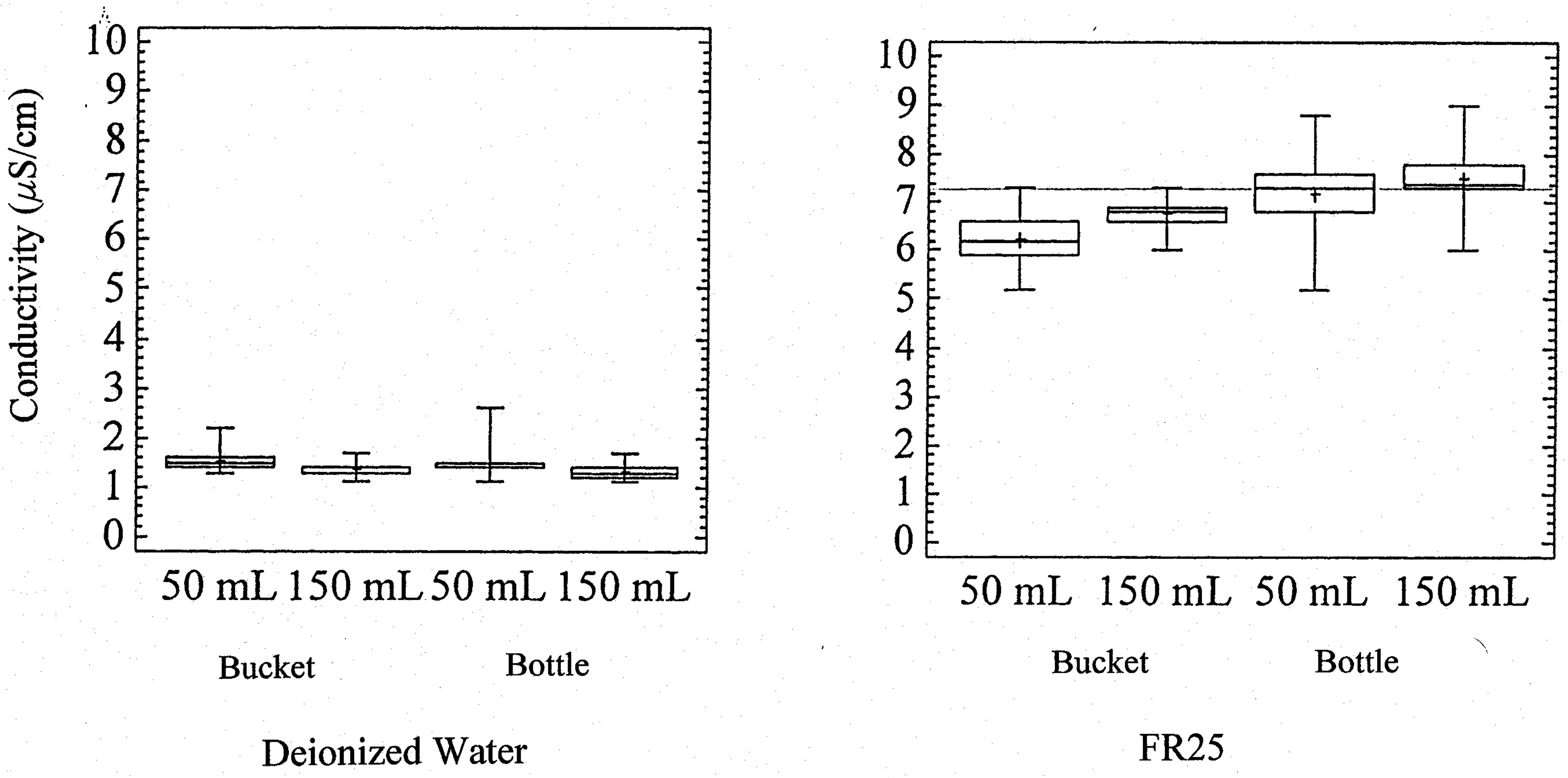


FIGURE B-63. Conductivity of upright bucket blanks and 1 liter bottles, using DI water and FR25 QCS as leaching agents, 1996. FR25 baseline values shown as solid line.

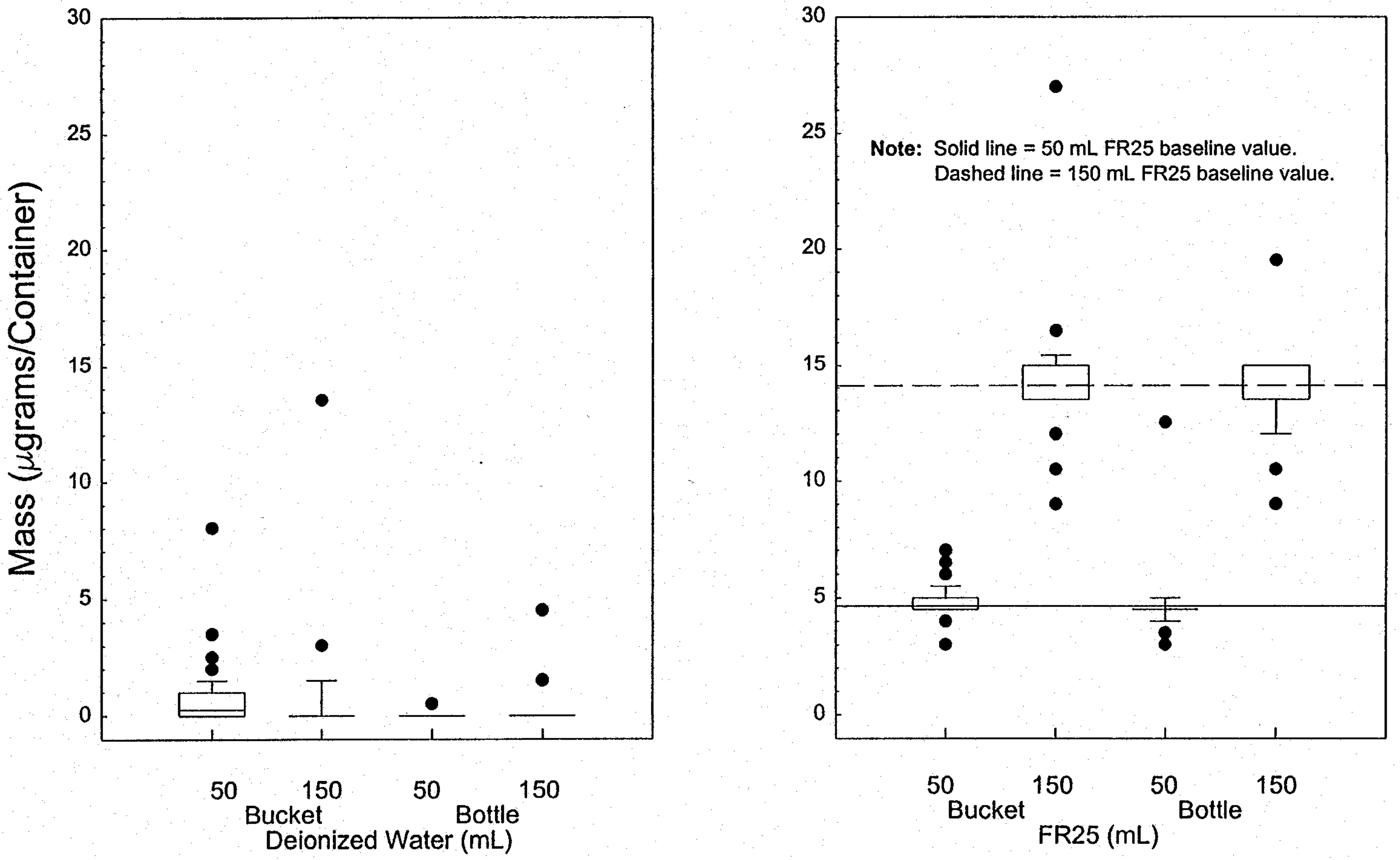
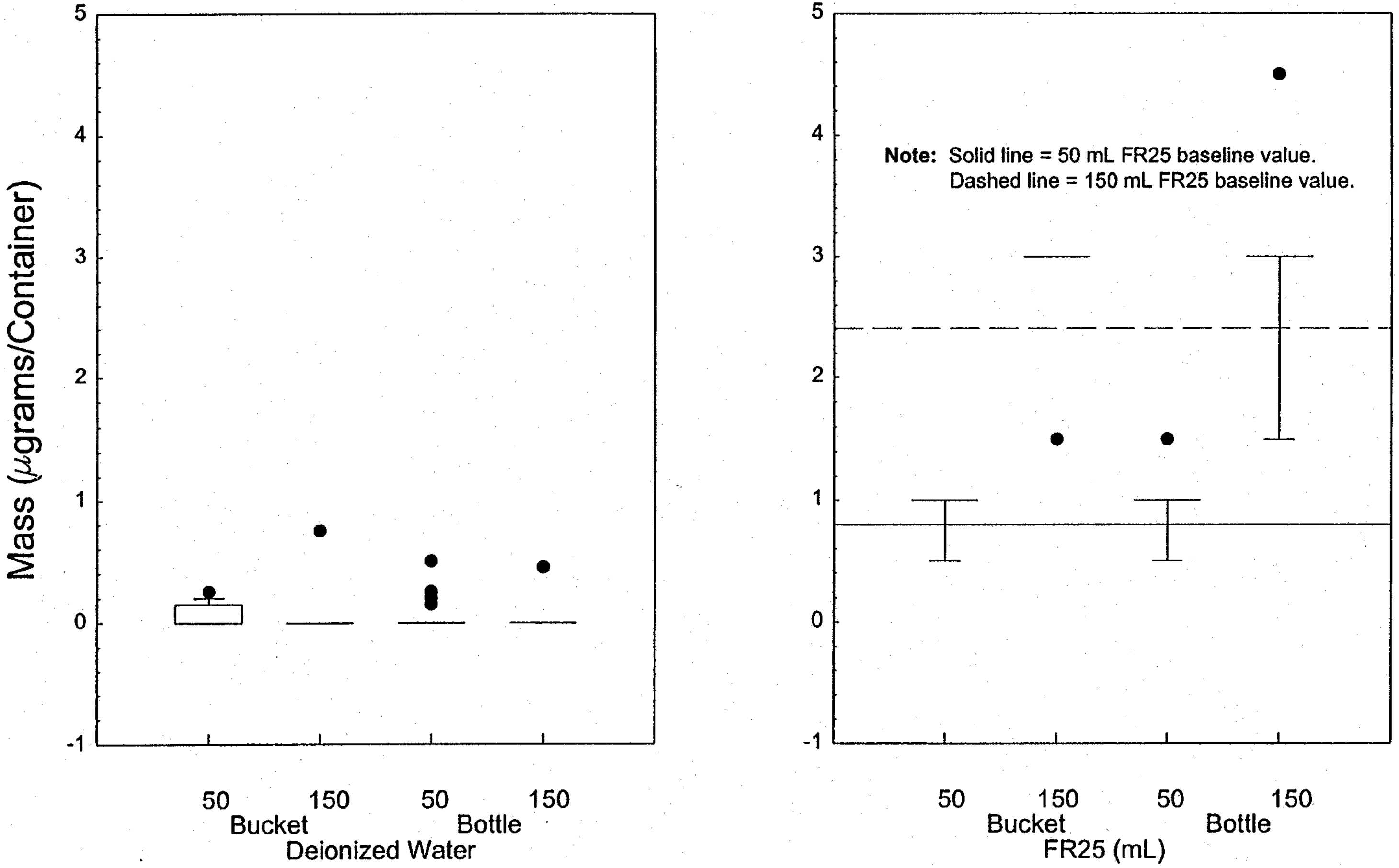


FIGURE B-64. Calcium found in upright bucket and 1-liter bottle blanks using DI water and FR25 QCS as leaching agents, 1997.



Note: Solid line = 50 mL FR25 baseline value.
Dashed line = 150 mL FR25 baseline value.

FIGURE B-65. Magnesium found in upright bucket and 1-liter bottle blanks, using DI water and FR25 QCS as leaching agents, 1997.

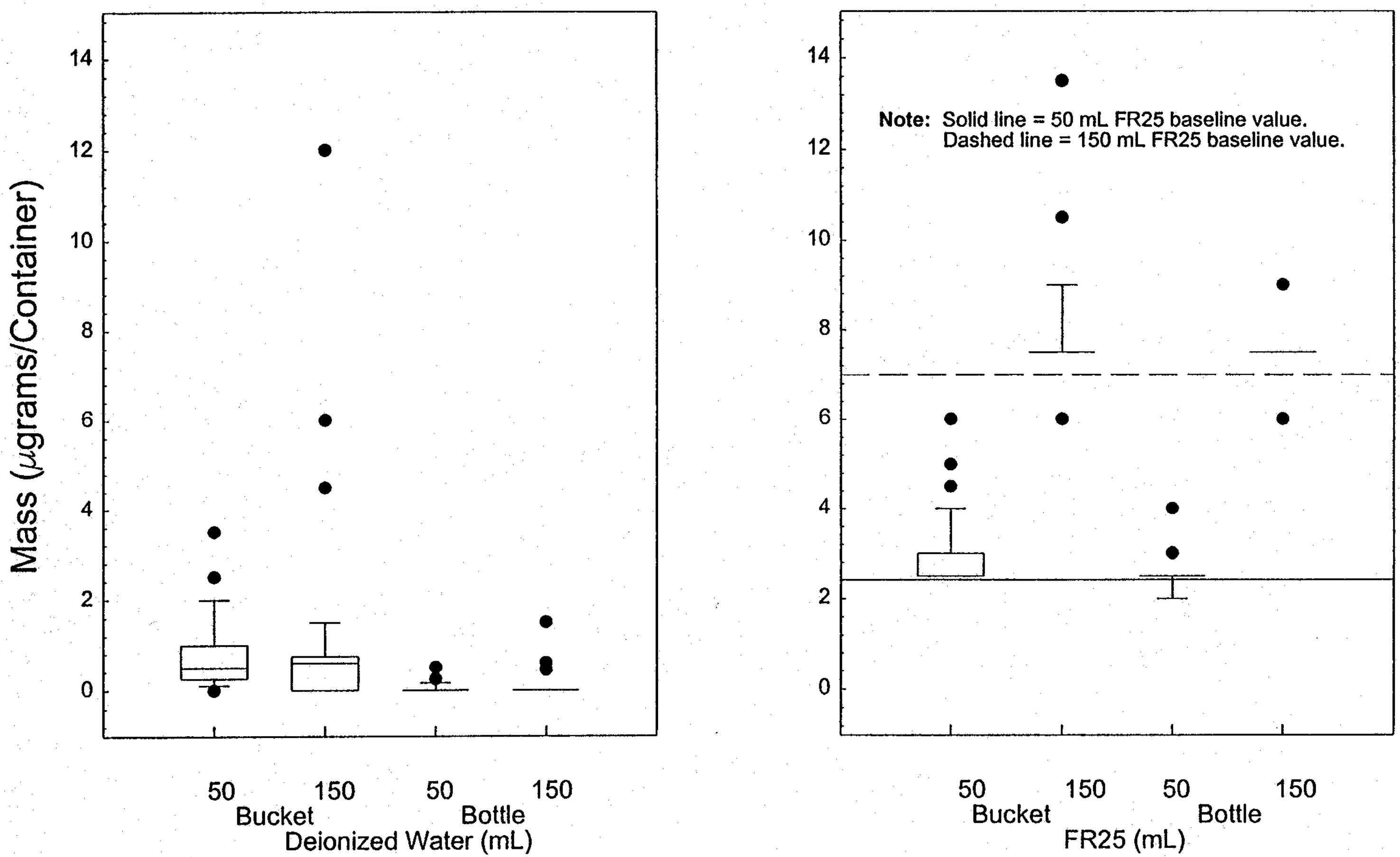


FIGURE B-66. Sodium found in upright bucket and 1-liter bottle blanks using DI water and FR25 QCS as leaching agents, 1997.

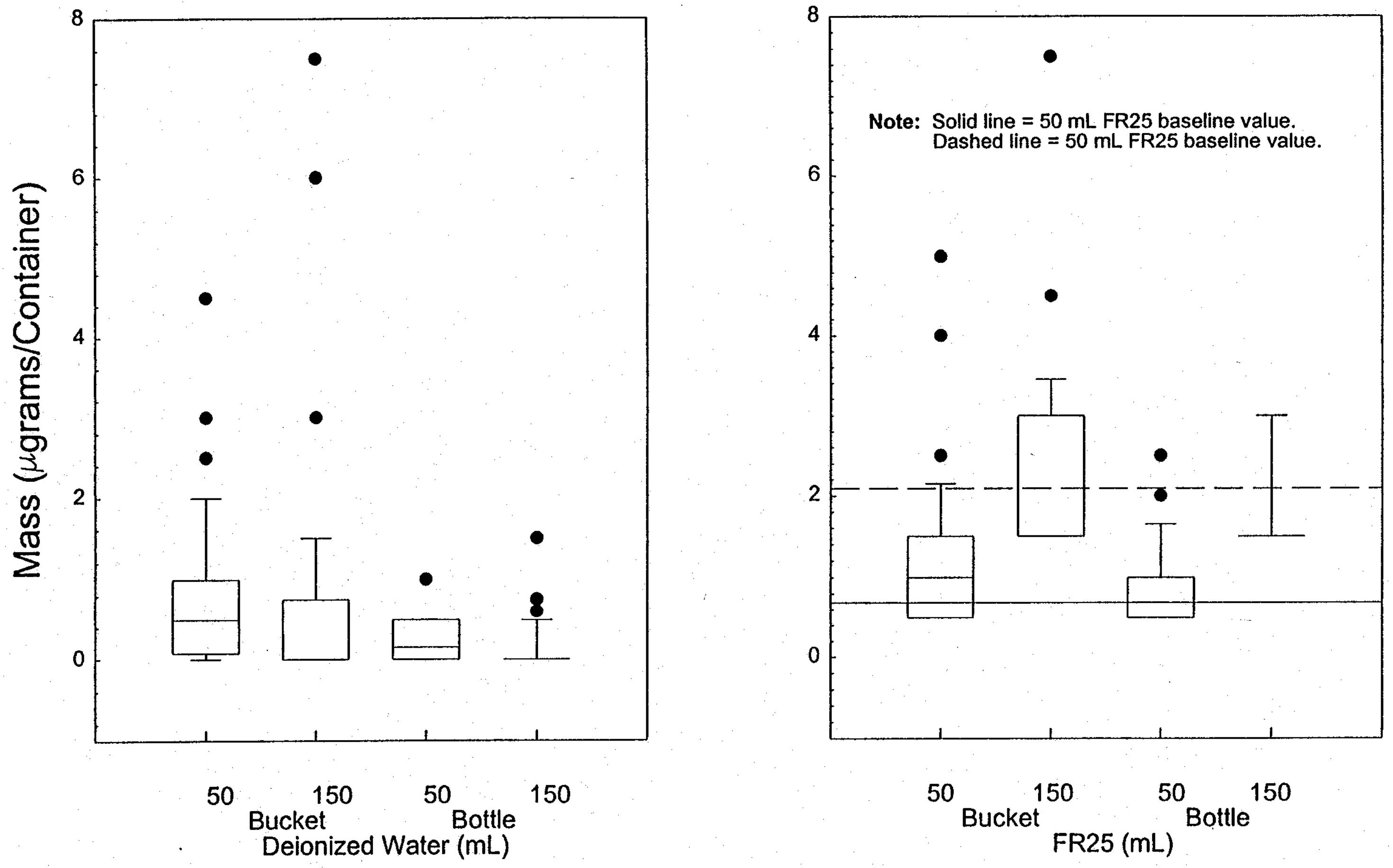


FIGURE B-67. Potassium found in upright bucket and 1-liter bottle blanks using DI water and FR25 QCS as leaching agents, 1997.

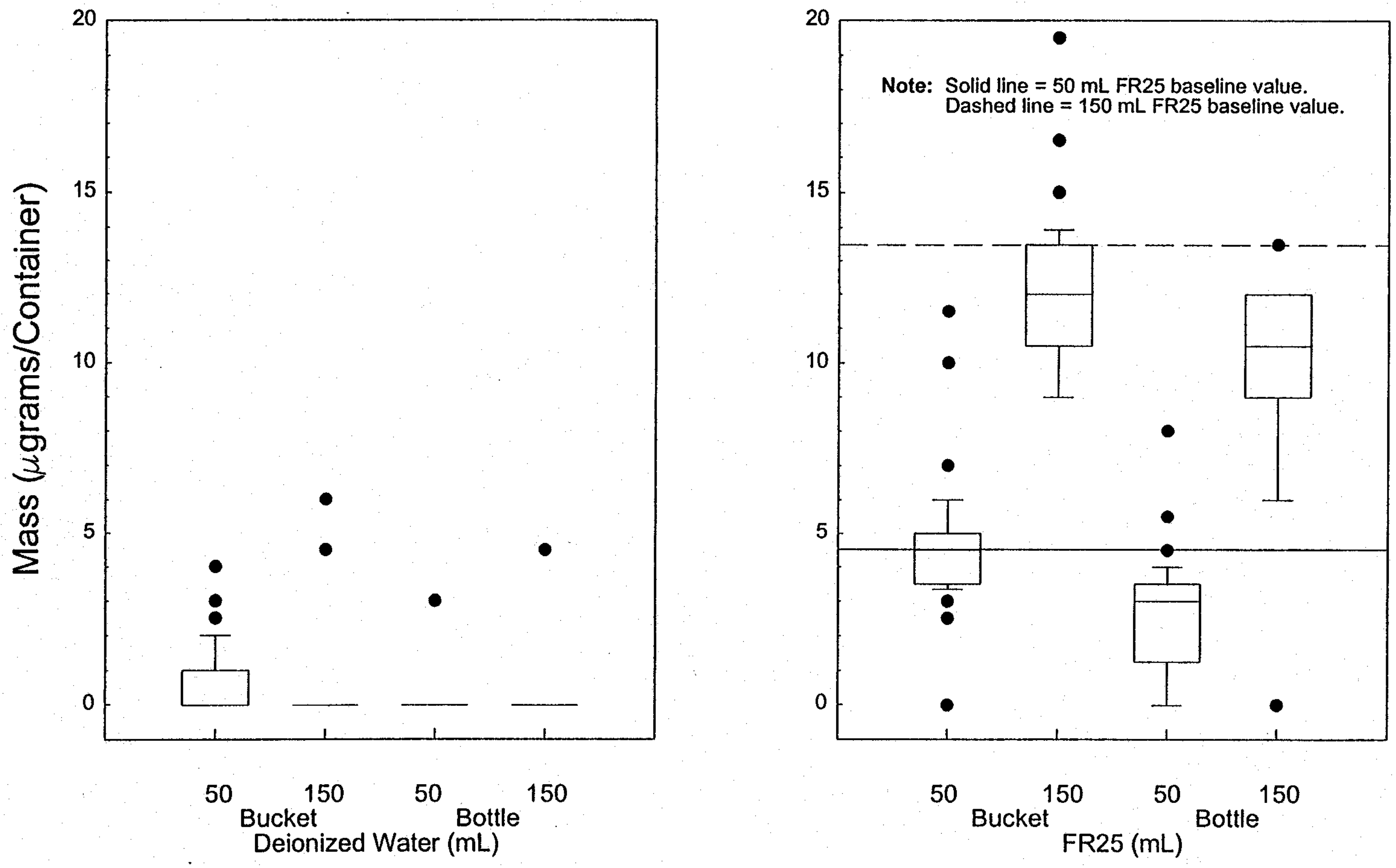
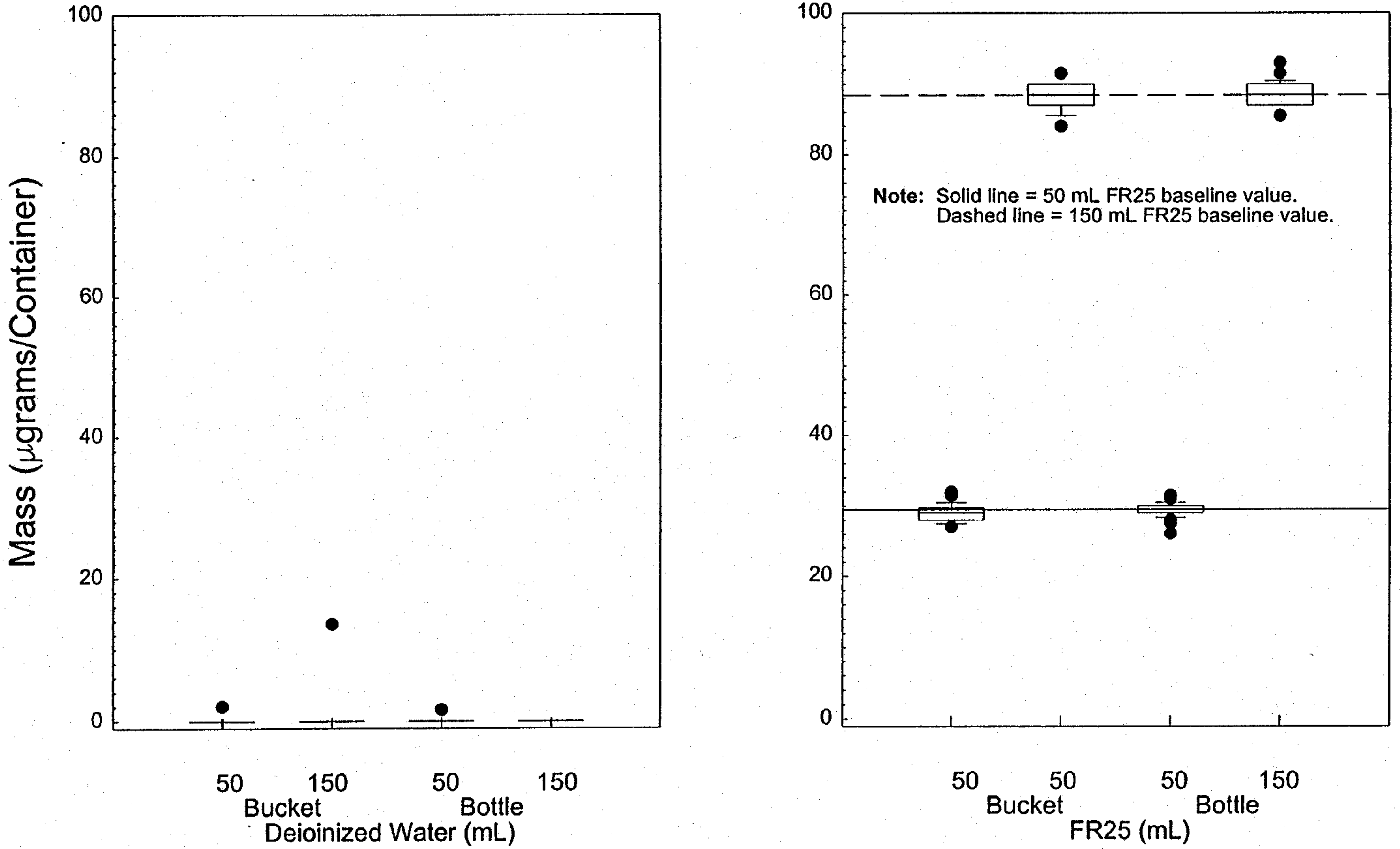


FIGURE B-68. Ammonium found in upright bucket and 1-liter bottle blanks using DI water and FR25 QCS as leaching agents, 1997.



Note: Solid line = 50 mL FR25 baseline value.
Dashed line = 150 mL FR25 baseline value.

FIGURE B-69. Sulfate found in upright bucket and 1-liter bottle blanks using DI water and FR25 QCS as leaching agents, 1997.

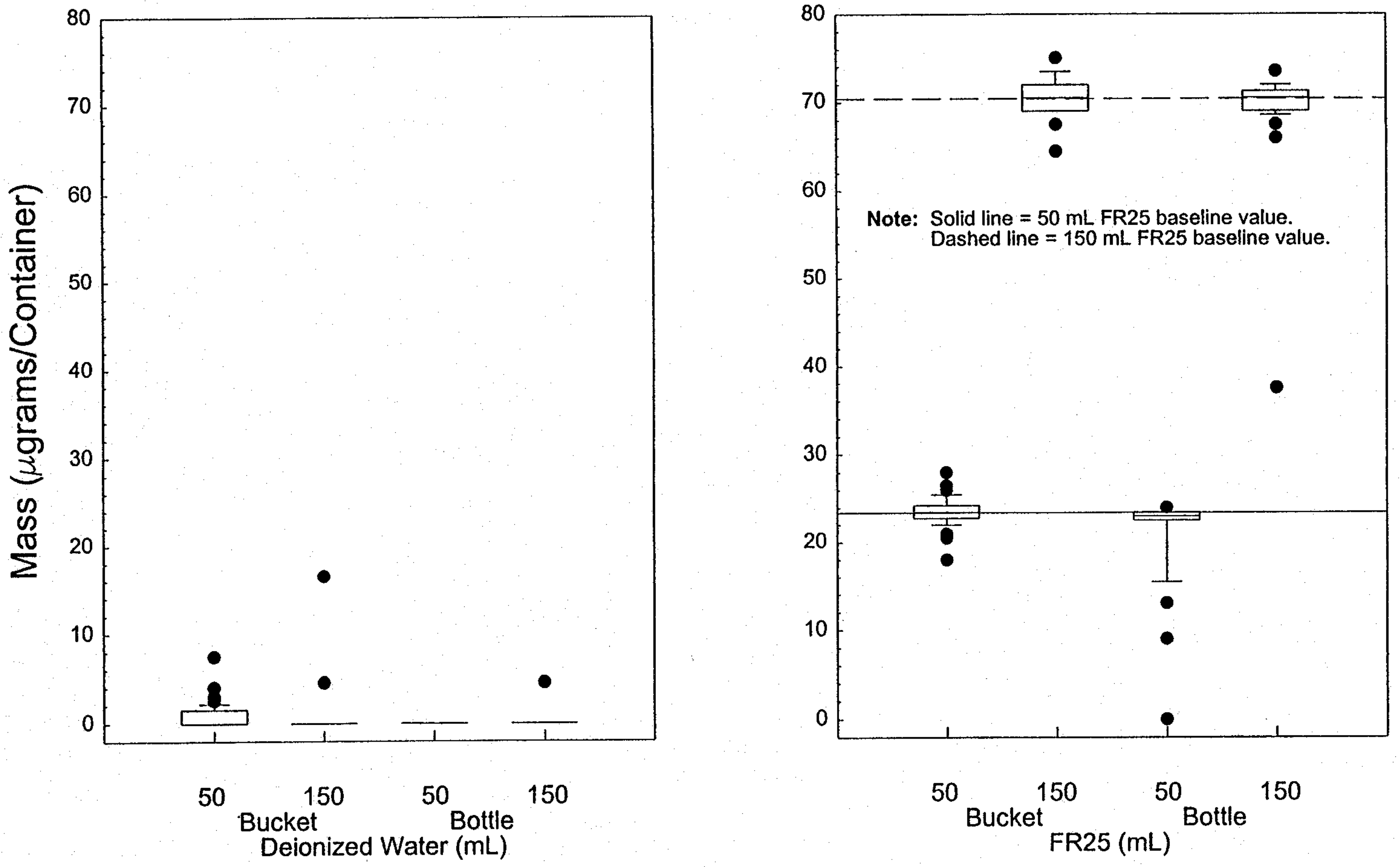


FIGURE B-70. Nitrate found in upright bucket and 1-liter bottle blanks using DI water and FR25 QCS as leaching agents, 1997.

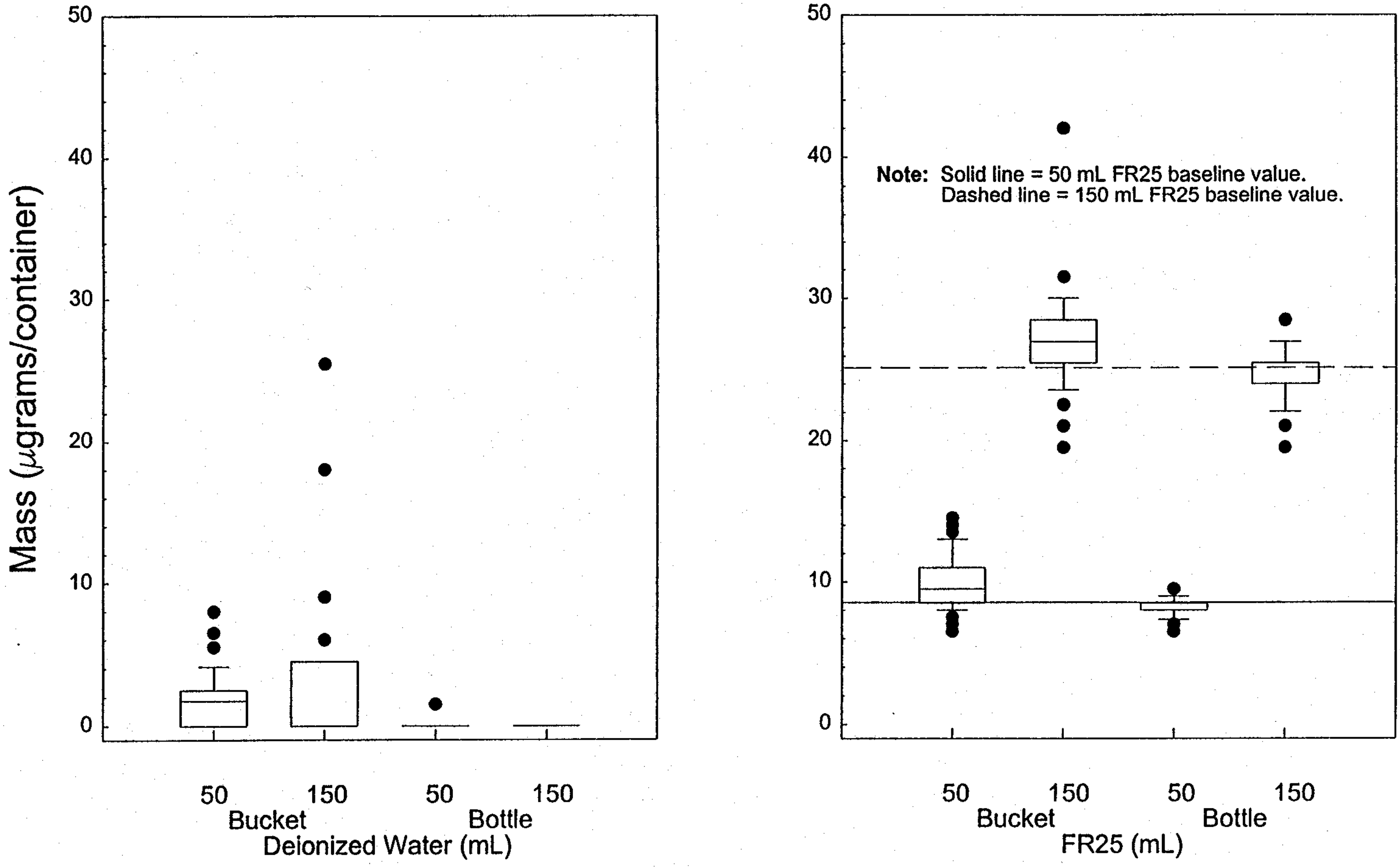


FIGURE B-71. Chloride found in upright bucket and 1-liter bottle blanks using DI water and FR25 QCS as leaching agents, 1997.

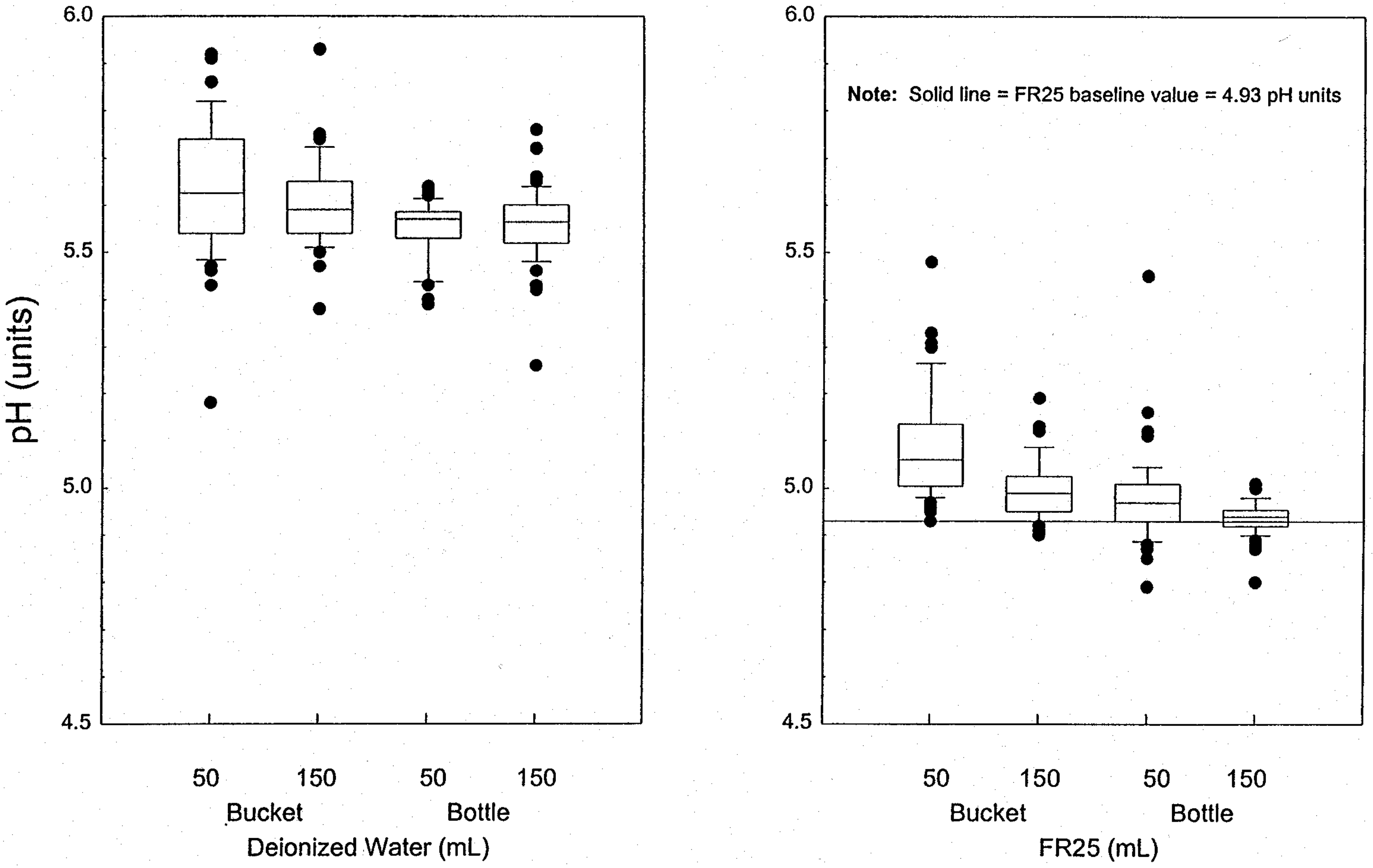


FIGURE B-72. pH of upright bucket and 1-liter bottle blanks leached with DI water and FR25 QCS, 1997.

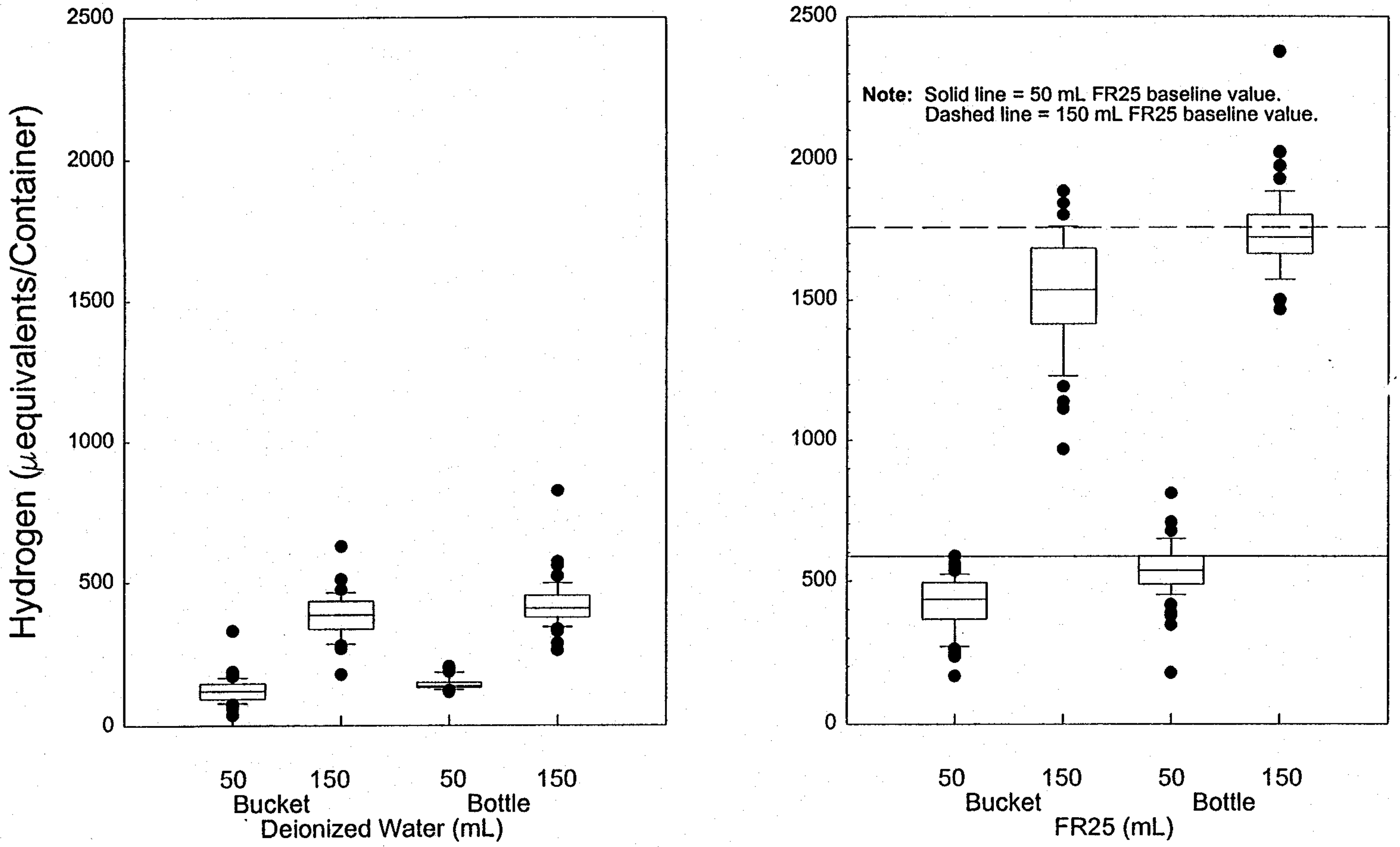
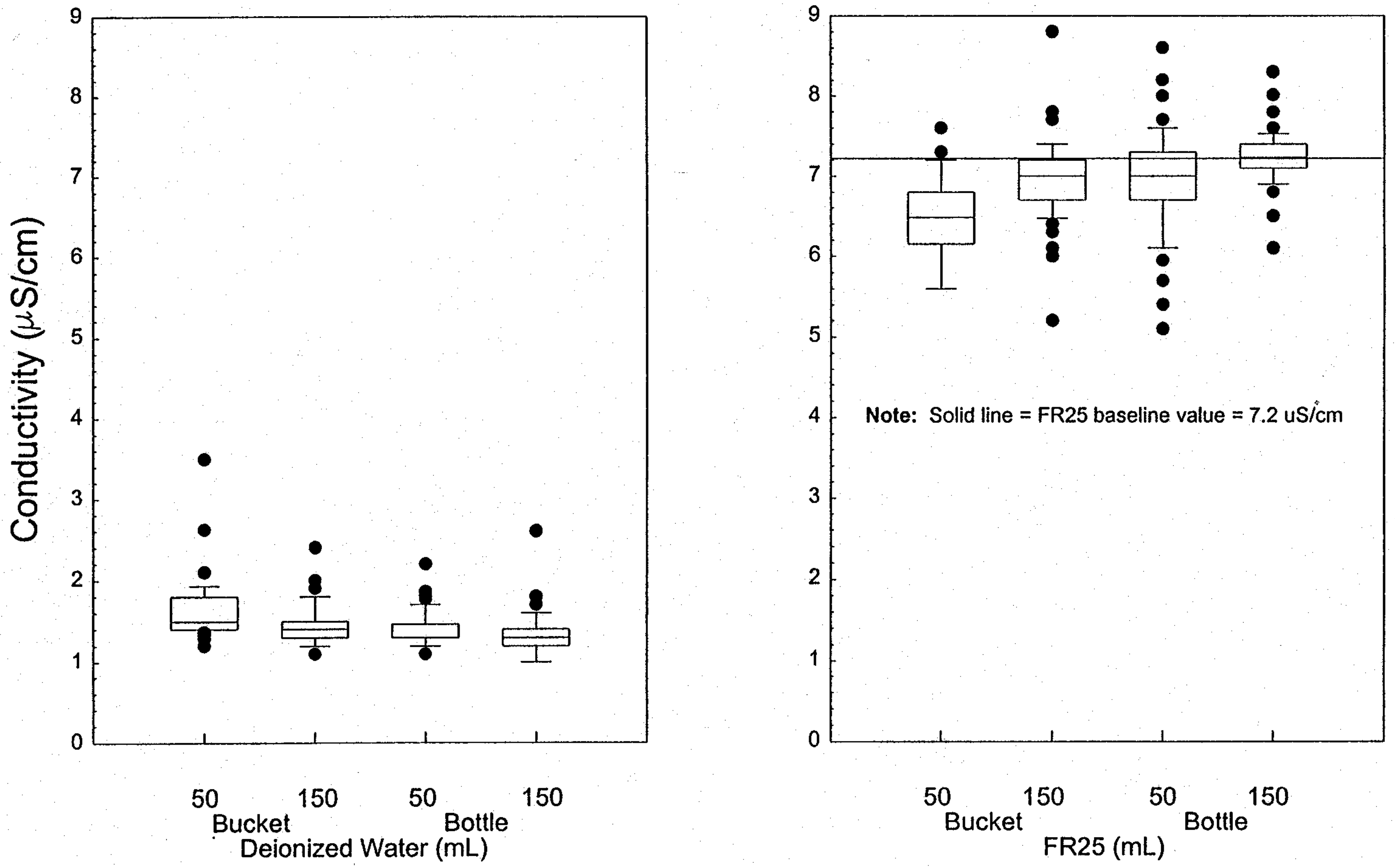


FIGURE B-73. Hydrogen found in upright bucket and 1-liter bottle blanks using DI water and FR25 QCS as leaching agents, 1997.



Note: Solid line = FR25 baseline value = 7.2 uS/cm

FIGURE B-74. Conductivity of upright bucket and 1-liter bottle blanks leached with DI water and FR25 QCS, 1997.