NADP QA Report 2000-01a

QUALITY ASSURANCE REPORT
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM, 1998

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

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Laboratory Operations
Central Analytical Laboratory

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ABSTRACT

The National Atmospheric Deposition Program (NADP) has been in operation since 1978. Since the beginning of the Network, quality assurance has been of paramount importance. The *Quality Assurance Report, National Atmospheric Deposition Program, 1998*, describes the quality assurance/quality control measures used at the Central Analytical Laboratory (CAL) of the NADP/National Trends Network and NADP/Atmospheric Integrated Research Monitoring Network in order to ensure that the quality of the data produced is of the highest possible caliber. Information about the quality of the data generated is presented in the form of tables, figures, graphs, and brief written explanations. The CAL was within the quality control objectives for the network in 1998.

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 the NADP/Atmospheric Integrated Research Monitory 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 and Van Bowersox of the NADP Program Office provide ongoing input and support throughout the year. A dedicated analytical staff analyzes thousands of samples with the support of conscientious sample receiving and processing personnel. Pam Bedient helped compile and format the text, tables, and files. The following reviewers and editors contributed their time and input to the final report, and without them this report could not be completed: John Gordon, Karen Harlin, Eva Kingston, Mark Peden, John Sherwell, and John Shimshock.

I. INTRODUCTION

This Quality Assurance Report describes and summarizes the results of the National Atmospheric Deposition Program (NADP) Central Analytical Laboratory (CAL) quality assurance program for 1998. 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 bias 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—a role it has held ever since. The CAL operations began on October 1, 1978, analyzing the samples from 14 NADP sites. In 1998, the CAL analyzed samples from approximately 200 NADP/National Trends Network (NTN) sites collecting precipitation throughout the United States and parts of Canada. The samples are collected in buckets using a specified sampler. The buckets are removed each Tuesday morning. Each sample is decanted from the collection bucket into a 1-liter, wide-mouthed, high-density polyethylene (HDPE) bottle and shipped with the sampling bucket to the CAL each week for processing. Figure I-1 illustrates the sample's journey after its arrival at the CAL.

The Atmospheric Integrated Research Monitoring Network (AIRMoN) protocol was implemented in 1992, and its Quality Assurance (QA) program was put into place at that time. Since then, the NADP/NTN and the NADP/AIRMoN have shared the same analytical staff and methodology. The AIRMoN sample protocol differs in that samples are collected daily if a precipitation event occurs and then are chilled and shipped in an insulated container. Sample pH and conductivity are measured upon receipt at the CAL. The sample remains in its original 250 milliliter (mL) HDPE shipping bottle and is refrigerated at all times except when portions are decanted for analysis. The parameters are analyzed in a specified order: pH and conductivity are measured first followed in order by ammonium and orthophosphate (NH_4^+ and PO_4^{3-}), the anions, sulfate, nitrate, and chloride (SO_4^{2-}, NO_3^-, and Cl^-), and finally the remaining cations calcium, magnesium, sodium, and potassium (Ca^{2+}, Mg^{2+}, Na^+, and K^+).

By 1998, the Program Office for the NADP was relocated from Colorado State University to the ISWS. This did not affect the day-to-day operations for most people at the CAL. For some, it meant that their time would be shared between the CAL and the Program Office. The analytical staff maintained their full-time commitment to the laboratory and the analysis of the data. Some data staff work for both the CAL and the Program Office.

Table I-1 lists the staff who were responsible for samples from the time they reach the ISWS until the analytical data are sent to the CAL data management group. Approximately half the staff have been employed at the ISWS and associated with the CAL for more than ten years. There were several changes to the CAL staff in 1998, which included new jobs for several employees. Tracie Klotz was hired in September to replace Laura Zangori who moved to Boston, MA. Tracie is currently working in sample processing and analyzing samples for pH and specific conductance.

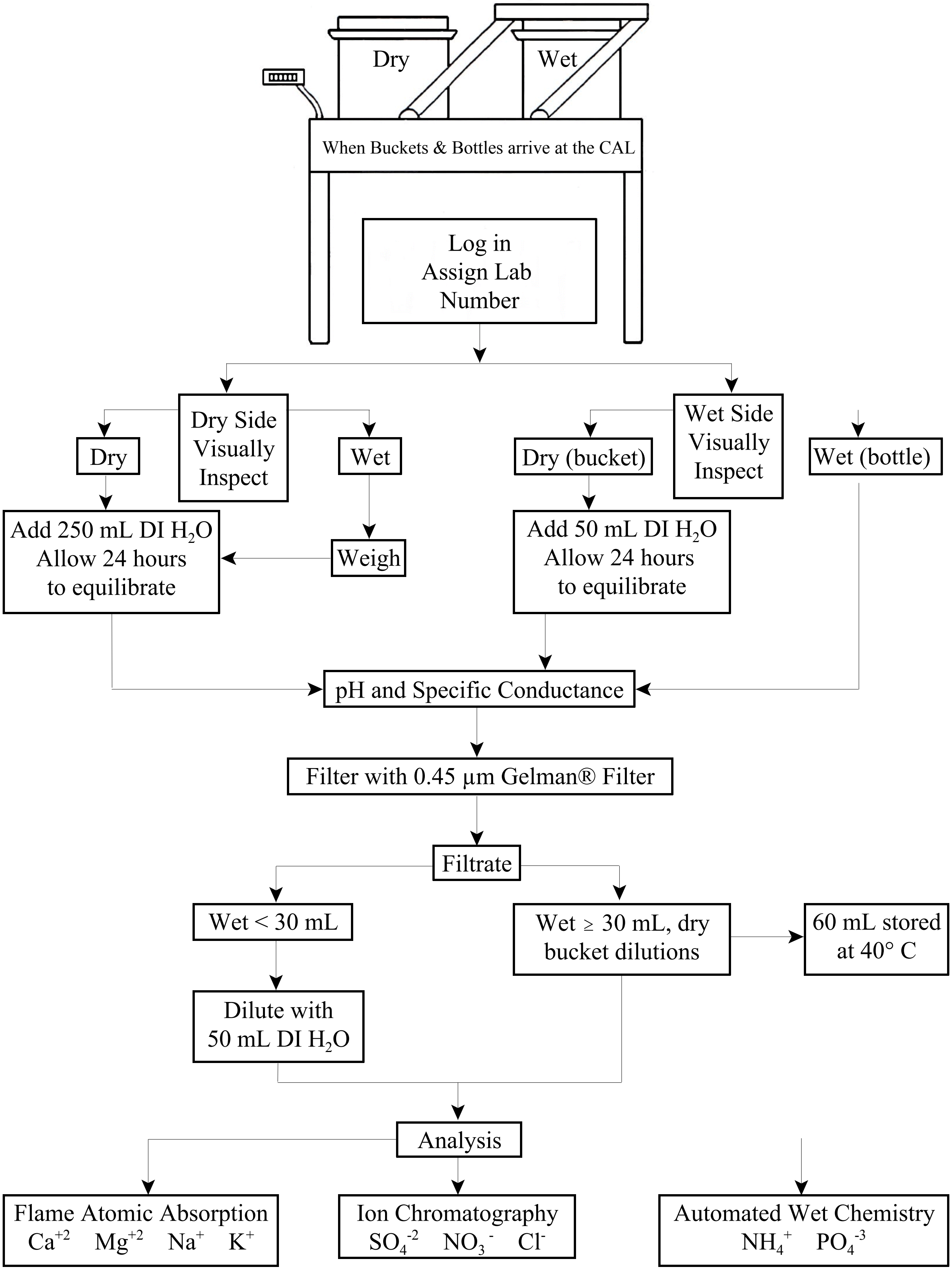

Figure I-1. Sample processing flowchart, January 1998 - December 1998.

Table I-1. Central Analytical Laboratory Analytical Staff, 1998

Staff Member	*Job Function*	*Period of Employment*
Sue Bachman	Analysis of ammonium	08/80 - 12/98
	Analysis of calcium, sodium, magnesium, and potassium	11/88 - 12/98
	Analysis of orthophosphate	01/94 - 12/98
	Sample Processing Laboratory Coordinator	09/98 - 12/98
Phyllis Ballard	Bucket and bottle cleaning	09/97 - 04/98
	Sample receipt and processing	04/98 - 12/98
Brigita Demir	Analysis of chloride, sulfate, and nitrate	09/81 - 12/98
Karen Harlin	Office of Atmospheric Chemistry Laboratory Supervisor	06/97 - 10/98
	NADP Central Analytical Laboratory Manager and NADP Assistant Coordinator	09/98 - 12/98
Lori Henry	AIRMoN sample processing and analysis of ammonium, orthophosphate, calcium, magnesium, sodium, and potassium	08/92 - 12/98
Theresa Ingersoll	Sample receipt and processing	03/85 - 12/98
Tracie Klotz	Analysis of pH and conductivity and sample processing	09/98 - 12/98
Mark Peden	Central Analytical Laboratory Manager	01/98 - 09/98
Jeffrey Pribble	Sample receipt	07/87 - 12/98
	Supply procurement	
	Backup site liaison	
Jane Rothert	AIRMoN coordinator	05/92 - 12/98
	Quality Assurance specialist	07/97 - 12/98
Kaye Surratt	Sample processing	08/96 - 04/97
	AIRMoN sample processing and analysis of ammonium, orthophosphate, calcium, magnesium, sodium, and potassium	11/98 - 12/98
Angela Weddle	Analysis of pH and conductivity	10/89 - 12/98
	Sample processing	06/95 - 12/97
Laura Zangori	Analysis of pH and conductivity and sample processing	12/97 - 09/98

Kaye Surratt replaced Lori Henry as the AIRMoN sample processor and analyst. Mark Peden, although still at the State Water Survey, is no longer part of the NADP but is the Director of Quality Assurance and External Relations for the ISWS. Sue Bachman added more duties to her schedule by becoming the sample processing coordinator in September, 1998. Phyllis Ballard began working in sample receipt and processing in April, 1998. Karen Harlin became the NADP CAL Director in September 1998.

The data management staff at the CAL is responsible for screening and reviewing the analytical data once they are transmitted from the laboratory and before they are sent to the Program Office. There were several changes with the data staff as well in 1998 (Table I-2). Although most of the data staff have been with the CAL for many years, two new positions were filled in 1998. Tom Bergerhouse transferred from another job at the ISWS to become the computer systems specialist in charge of upgrading and maintaining the computers used in the laboratories to collect the data. Sarah Milton joined the CAL staff in 1998 doing first round data screening and editing. Karen Harlin, in addition to her job as the CAL manager, also began conducting final data screening for the data management team. Jane Rothert, in her capacity as QA specialist, screens the NTN data for reanalysis. Scotty Dossett and Kathy Douglas are employed part time by the Program Office and part time by the CAL, splitting their time and duties between the two parts of the NADP.

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. No instrument updates occurred in 1998. Detection limits for 1998 did not change. Table I-3 lists the CAL method detection limits (MDLs) for the ions of interest as well as the methods used. This table also gives an historic perspective of how the analytical techniques and MDLs have changed over the course of the program.

From the beginning of the network in 1978, the analytical data have been entered into a large central database. The data were hand-entered using a double-entry system as a means of verification in the early years. Currently, data from the atomic absorption spectrophotometer, the ion chromatograph, and the flow injection analyzer are transferred electronically to the database. The pH and conductivity measurements are still double-entered manually. Once the data are verified and validated by data management at the CAL, they are sent to the Program Office for additional screening and coding before being loaded onto an Internet server where they are then available for general usage. Table I-4 lists the percentile concentration values for all NADP/NTN samples of volume greater than 35 mL analyzed by the CAL in 1998. The total number of “wet” (W) samples for 1998 was 6799 with a mean volume of 1577.3 mL and median volume of 978.2 mL. For a historical comparison, Table I-5, a percentile chart for 1983, was originally published in the 1983 QA Report (Lockard, 1987). Some of the parameters have decreased in concentration; others have stayed the same or increased. Ammonium concentrations at the 50th percentile were the same in 1998 as they were in 1983. Sulfate concentrations were lower. The number of samples was slightly greater in 1998 than in 1983. Table I-6 lists the percentile concentration values for the AIRMoN samples for 1998 where sample volume (wet only samples) was large enough for a complete chemical analysis.

Table I-2. Central Analytical Laboratory Data Staff, 1998

Staff Member	*Job Function*	*Period of Employment*
Tom Bergerhouse	Computer systems support	07/98 - 12/98
Scotty Dossett	NTN site liaison	09/81 - 12/98
Kathy Douglas	Database manager	04/80 - 12/98
Greg Dzurisin	Computer programmer	09/83 - 12/98
Karen Harlin	Final data review	07/97 - 12/98
Sarah Milton	Data screening	01/98 - 12/98
Jane Rothert	Data quality assurance	07/97 - 12/98

Table I-3. Method Detection Limits (MDLs) for Precipitation Analysis, 1998

Ion	*MDL (mg/L)*	*Dates*	*Method*
Calcium	0.02	07/78 - 10/80	Flame Atomic Absorption
	0.009	10/80 - 12/98	Flame Atomic Absorption
Magnesium	0.002	07/78 - 10/80	Flame Atomic Absorption
	0.003	10/80 - 12/98	Flame Atomic Absorption
Sodium	0.004	07/78 - 10/80	Flame Atomic Absorption
	0.003	10/80 - 12/98	Flame Atomic Absorption
Potassium	0.004	07/78 - 10/80	Flame Atomic Absorption
	0.003	10/80 - 12/98	Flame Atomic Absorption
Ammonium	0.02	07/78 - 12/98	Automated Phenate, colorimetric
Sulfate	0.10	07/78 - 05/85	Automated Methyl Thymol Blue, colorimetric
	0.03	05/85 - 12/98	Ion Chromatography
Nitrate/Nitrite	0.02	07/78 - 05/85	Automated Cadmium Reduction, colorimetric
Nitrate	0.03	05/85 - 12/98	Ion Chromatography
Chloride	0.05	07/78 - 03/81	Automated Ferricyanide, colorimetric
	0.02	03/81 - 05/85	Automated Ferricyanide, colorimetric
	0.03	05/85 - 12/98	Ion Chromatography
Orthophosphate	0.003	07/78 - 02/86	Automated Ascorbic Acid, colorimetric
	0.01	02/86 - 07/87	Automated Ascorbic Acid, colorimetric
	0.02	07/87 - 12/93	Ion Chromatography
	0.003	12/93 - 12/98	Automated Ascorbic Acid, colorimetric

Table I-4. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/NTN Precipitation Samples, 1998

	Percentile Concentration Values (mg/L)									
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*99th*	*Maximum*
Calcium	-0.009	0.016	0.023	0.047	0.105	0.239	0.493	0.775	1.692	20.600
Magnesium	-0.003	0.003	0.004	0.009	0.020	0.042	0.080	0.122	0.280	1.860
Sodium	-0.003	0.006	0.009	0.017	0.041	0.115	0.306	0.579	2.000	16.850
Potassium	-0.003	-0.003	0.004	0.008	0.017	0.035	0.068	0.102	0.269	1.650
Ammonium	-0.02	-0.02	-0.02	0.07	0.20	0.45	0.78	1.10	1.88	5.72
Sulfate	-0.03	0.14	0.23	0.51	1.09	1.97	3.13	4.21	6.82	40.56
Nitrate	-0.03	0.17	0.28	0.58	1.09	1.85	2.92	3.80	6.16	16.90
Chloride	-0.03	-0.03	0.03	0.05	0.10	0.22	0.54	1.02	3.07	25.43
Orthophosphate	-0.003	-0.003	-0.003	-0.003	-0.003	-0.003	-0.003	-0.003	0.025	0.572
pH (units)	3.49	4.10	4.24	4.48	4.84	5.27	5.80	6.22	6.71	8.00
Specific Conductance (µS/cm)	1.5	3.3	4.4	7.3	12.8	21.5	34.2	44.7	76.0	183.2

Notes:
Number of wet samples = 6799; mean sample volume = 1577.3 mL; and median sample volume = 978.2 mL. Negative numbers in this table are the method detection limits (MDLs) for each parameter.

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 for 1983

	Percentile Concentration Values (mg/L)			
Parameter	*25th*	*50th*	*75th*	*95th*
Calcium	0.070	0.100	0.36	0.500
Magnesium	0.021	0.025	0.082	0.125
Sodium	0.048	0.100	0.238	0.500
Potassium	0.016	0.025	0.060	0.125
Ammonium	0.06	0.20	0.40	1.00
Sulfate	0.78	1.50	2.59	7.50
Nitrate	0.51	1.00	1.86	5.00
Chloride	0.10	0.30	0.36	1.50
Orthophosphate	-0.003	------	-0.003	------
pH (units)	4.42	4.50	5.37	6.50
Specific Conductance (µS/cm)	8.3	15.0	26.0	75.0

Note:
A total of 4308 "wet" (W) samples were analyzed in 1983.

TABLE I-6. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/AIRMoN Precipitation Samples, 1998

	Percentile Concentration Values (mg/L)								
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*Maximum*
Calcium	-0.003	0.010	0.020	0.046	0.095	0.199	0.419	0.695	3.390
Magnesium	0.000	0.002	0.003	0.009	0.021	0.060	0.136	0.197	0.596
Sodium	0.000	0.005	0.007	0.016	0.045	0.222	0.787	1.450	4.790
Potassium	-0.001	0.003	0.005	0.011	0.022	0.042	0.078	0.109	1.050
Ammonium	0.00	0.03	0.06	0.13	0.30	0.59	0.94	1.26	2.94
Sulfate	0.04	0.41	0.60	1.14	2.02	3.49	5.23	6.54	18.51
Nitrate	0.09	0.27	0.40	0.86	1.60	2.86	4.53	6.20	14.94
Chloride	0.00	0.03	0.04	0.08	0.17	0.57	1.60	2.48	8.81
Orthophosphate	-0.006	0.000	0.000	0.000	0.005	0.013	0.026	0.040	0.393
pH (units)	3.37	3.82	3.92	4.11	4.32	4.58	4.89	5.07	6.36
Specific Conductance (µS/cm)	2.6	7.3	10.5	16.9	27.7	43.6	64.8	83.2	216.2

Notes:
Number of wet-only samples = 876; mean sample volume = 720.8 mL; and median sample volume = 404.5 mL. Negative numbers in this table are actual values measured, not method detection limits (MDLs).

The ion concentrations displayed in Tables I-4 and I-6 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 (Simmons et al., 1990) 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 standard (QCS) 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 and NADP/AIRMoN daily queue. Extensive analyses 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 external quality assurance studies performed by the U.S. Geological Survey (USGS) as an official part of network operations enables the CAL to evaluate the quality of its work compared with peer laboratories throughout the United States, Canada, and Europe. The history of the CAL program is described in the Laboratory QA reports published annually since 1986 and available from the CAL or the Program Office (Stensland et al., 1980; Lockard, 1987; Peden, 1988; James, 1988 - 1997; Rothert, 1999). This report presents and discusses summaries of the results of QA programs in place in 1998.

II. LABORATORY QUALITY ASSURANCE - A GENERAL DESCRIPTION

This report summarizes the results of the quality assurance (QA) program in effect at the CAL for 1998. 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 measured soon after sample collection and prior to shipping. Quality Control Standard (QCS) solutions are formulated and prepared at the CAL are shipped to the sites and used as weekly check samples by site operators. The two QCS solutions used in 1998 were a potassium chloride (KCl) solution with a specific conductance of 75 microSiemens per centimeter (µS/cm) and a dilute nitric acid/sodium chloride (HNO_3/NaCl) solution with a pH of 4.9 and a specific conductance of 14 µS/cm. The first solution, was used to calibrate the conductivity cell and to correct the conductivity readings to ambient temperature; the second solution was used as the QCS for the pH and conductivity measurements. Since calibration buffer solutions are of high ionic strength, it is necessary to verify that the pH probe will measure solutions that are similar in ionic strength to the precipitation samples.

When precipitation samples reach the CAL, they are unpacked carefully. The information and requests written on the field forms are noted and logged into a database. The samples are then transported to sample processing where they are assigned sequential numbers. After the identifying laboratory number is assigned, the 1-liter shipping bottles are taken to the laboratory where they are visually inspected and pH and conductivity are measured. After the samples are measured for pH and conductivity, they are filtered into pre-washed 60-mL high density polyethylene (HDPE) round bottles using 0.45 micrometer (µm) pore-size filters. These sample aliquots are used to obtain the chemistry of the weekly samples and are also used for further analyses. When there is sufficient volume, a second sample aliquot is filtered into a square bottle for archival purposes. Samples from the Atmospheric Integrated Research Monitoring Network (AIRMoN) are never filtered per the AIRMoN protocols, but are kept at 4 degrees Celsius in the 250-mL shipping bottles into which they were decanted at the site.

The pH meter is calibrated with commercial 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 simulating the 25th and 75th percentile concentrations of the NTN. These solutions are prepared in-house and are tested extensively prior to being made available for use as QCS solutions. These solutions, referred to as FR25 and FR75, are used as QCS solutions for the entire suite of measurements except for orthophosphate, which is too unstable, especially at the low concentrations found in NTN and AIRMoN samples (Ridder et al., 1985) to be made up and used for any extended period of time.) The U.S. Environmental Protection Agency (USEPA) nutrient concentrates are diluted and used for orthophosphate QCS.

After filtration, the samples in the round 60-mL bottles are placed on a tray that is taken to the main laboratory building and placed with other sample trays containing samples awaiting analysis of the major ions. The 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

Table II-1. NADP Laboratory QA/QC Program Summary
1998

I. Daily
  A. Standardize instruments and verify standardization curves using QCS.
    1. Use CAL-formulated solutions of simulated rainwater, quality control which 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. Use deionized (DI) water.
    2. Filter leachates using DI water and simulated rainwater.
    3. Use DI water and simulated rainwater for
      a. Sample collection bucket
      b. Snap-on lids for sample collection bucket
      c. One-liter sample bottles
    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.
    2. SWS1: Use High-Purity Standards (H-PS) simulated rainwater I and II, unfiltered.
    3. SWS2: Use DI water and pH 4.3 nitric acid, unfiltered.
    4. SWS3: Use 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.

III. Monthly
  A. Leach AIRMoN 250-mL HDPE bottles with simulated rainwater and analyze leachates with weekly blanks.
  B. Collect AIRMoN field blanks and analyze with weekly blanks.
  C. Inspect control charts generated from QCS measurements.
  D. Evaluate internal blind audit and replicate data from printouts.
  E. Select samples for reanalysis by computer-based ion percent and conductivity percent differences.
    1. Evaluate reanalysis data.
    2. Suggest 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 reports for spring and fall NADP subcommittee meetings.
  B. Participate in additional interlaboratory comparisons.

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

and orthophosphate; chloride, nitrate, and sulfate; and finally calcium, magnesium, sodium, and potassium. This order of analysis was mandated in order to analyze the least stable parameters first. Samples are collected within 26 hours of precipitation start, refrigerated continuously after collection, and shipped within 7 days to the CAL via next day air. Measurement of the least stable parameters is important in keeping with the timely collection and analysis required for the AIRMoN. Since low volume AIRMoN samples are not diluted there is not always sufficient sample for complete analysis. Highest priority measurements are made first. The NTN samples are in the field for up to one week and shipped via ground transportation. Once pH and conductivity are complete, the order of analyses is not prioritized. Low volume NTN samples, those less than 30 mL, are diluted to ensure sufficient sample for a complete analysis on each sample. Analysts select the samples with numbers in the next sequence and analyze them 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 expected range of the standardization are diluted and reanalyzed using the diluted value to calculate the concentration of that parameter. The standardization curve is verified with the two QCS solutions, FR25 and FR75. The values of these two solutions are recorded daily and summarized monthly for control charts. Monthly means and standard deviations are calculated for the QCS solutions. These statistics represent optimum analytical conditions. These QCS solutions are analyzed immediately after standardization solutions and blanks have been analyzed and then regularly throughout the run. The analyst is fully aware of the concentration of these solutions and uses them to evaluate whether or not the instrument initially is standardized properly and whether it is maintaining its standardized analytical curve throughout the day.

Each week solutions are collected from multiple sources and submitted to the laboratory for analysis as blank samples. These samples are used to evaluate possible contamination sources both from the sample collection and shipping activity and the processing procedures 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 of DI water are collected weekly 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 or more 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 include 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 100 samples removed 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. The AIRMoN split sample protocol is very similar to the NTN 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.

Monthly reanalysis lists are distributed to the laboratory so that randomly selected samples and samples with an ion percent or conductance percent difference greater than allowed by the NADP QAP can be reanalyzed. Archival samples, if available, are used to support either the original values or the reanalysis values when discrepancies in the analytical results occur. Every two weeks, the USGS ships the CAL interlaboratory comparison 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, CO.

Other external agencies conducting 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 worldwide.

III. DAILY QUALITY CONTROL PROCEDURES

Each morning prior to analysis, the analysts prepare reagents and standards, if needed, and evaluate the performance of the analytical instrumentation. Standards preparation and instrument maintenance information are recorded in notebooks kept in the individual laboratories. Calibration standards are analyzed according to the method standard operating procedure and are followed by the measurement of the QCS solutions to confirm the validity of the calibration curve. Both FR25 and FR75 solutions are used to test the standard curves at two concentration levels. Each QCS solution is measured throughout the sample run. The values are recorded and graphed on a daily control chart located near the instrument. The same data are compiled and summarized at the end of the calendar year (Table III-1).

The data presented in Table III-1 represent bias and precision estimates under optimum conditions. The data in this table were generated using QCS solutions known to the analysts, rather than precipitation or blind samples. Because of this, they represent the optimum precision and bias to be expected from the analysis of samples and should be used in that context as data quality indicators. They are comparable with previous years' data and fall within the QA specifications of the NADP QAP (Simmons et al., 1990). When the absolute bias exceeds the critical concentration, the bias (see Appendix A, Glossary of Terms) is considered to be statistically significant. Refer to the laboratory portion of the NADP QA Plan (Simmons et al., 1990) for more information.

Table III-1. Analytical Bias and Precision Determined from Analysis of Simulated Rain QCS, 1998

Parameter	*Target Concentrations (mg/L)*	*Measured Mean Concentrations (mg/L)*	*Number of Replicates*	*Bias (mg/L)*	*Bias (%)*	*Precision (mg/L)*	*Precision (%)*	*Critical Concentration (mg/L)*	*Statistically Significant Bias?*
Ca	0.075[a]	0.074	1325	-0.001	-1.3	0.003	4.1	0.002	no
	0.290[b]	0.293	505	0.003	1.0	0.006	2.0	0.003	no
Mg	0.017	0.017	1278	0.0003	0.0	0.0006	3.5	0.0003	no
	0.065	0.067	471	0.002	3.1	0.001	1.5	0.0005	yes
Na	0.046	0.047	1362	-0.0005	0.0	0.001	2.1	0.0005	no
	0.188	0.189	486	0.001	0.5	0.004	2.1	0.002	no
K	0.015	0.014	1370	-0.001	-6.7	0.001	7.1	0.0005	yes
	0.054	0.055	489	0.001	1.9	0.002	3.6	0.001	no
NH_4	0.084	0.080	1507	-0.004	-4.8	0.01	12.5	0.005	no
	0.34	0.35	677	0.009	2.6	0.01	2.9	0.005	yes
Cl	0.12	0.13	1055	-0.007	-5.7	0.003	2.3	0.002	yes
	0.53	0.52	1212	-0.005	-0.9	0.007	1.3	0.003	yes
NO_3	0.46	0.47	1055	0.004	1.3	0.006	1.3	0.003	yes
	1.93	1.94	1203	0.01	0.5	0.01	0.5	0.005	yes
SO_4	0.62	0.62	1053	-0.005	-0.8	0.006	1.0	0.003	yes
	2.54	2.54	1209	0.0	0.0	0.01	0.4	0.005	no
PO_4	0.024	0.021	516	-0.003	-12.5	0.003	14.3	0.002	yes
	0.060	0.055	355	-0.005	-8.3	0.005	9.1	0.002	yes
pH	4.91(12.3)[c]	4.91(12.2)	1366	0.0(-0.1)	0.0(-0.8)	0.02(0.54)	0.4(4.4)	0.01(0.34)	no (no)
units (μeq/L)	4.34(45.7)	4.35(44.5)	1366	0.01(-1.2)	0.2(-2.6)	0.01(1.4)	0.2(3.1)	0.005(0.90)	yes (yes)
Specific Conductance	7.31	7.33	850	0.02	0.3	0.17	2.3	0.06	no
(μS/cm)	27.8	27.6	850	-0.2	-0.7	0.26	0.9	0.12	yes

Notes:

See Appendix A for definitions and formulas for Bias, Standard Deviation, Precision, and Critical Concentrations.

[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 (μeq/L).

IV. WEEKLY QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES

Three Quality Assurance (QA) activities occurred on a weekly basis: three solutions were submitted as internal blind samples for which only the QA specialist knew the concentrations; 2 percent of the network samples were split and analyzed in duplicate; and 19 blanks and container leachates were bottled and analyzed. The AIRMoN internal blinds also were submitted on a weekly schedule, and the AIRMoN bottle blanks and leachates were submitted monthly**.**

A. Internal Blind Audit

1. NADP/NTN

Each week the QA specialist submits three solutions of known concentrations with accompanying field forms to the sample processing area where laboratory identification numbers are assigned. These samples are processed with the network samples and treated as such except that two of the three samples bypass the filtering process in order to separate out possible filter contaminations. The sites for these samples are coded as SWS1, SWS2, and SWS3. In 1998, SWS1 samples were High-Purity Standards Simulated Rainwater 1 (H-PS SR1) and 2 (H-PS SR2), which were alternated weekly. The SWS2 samples were DI water from the ion chromatography laboratory and pH 4.3 nitric acid QCS solution, which were also alternated weekly. The SWS1 and SWS2 samples are not filtered. The SWS3 samples were H-PS SR1, H-PS SR2, DI water, and pH 4.3 nitric acid QCS samples submitted in rotation. SWS3 samples are filtered.

Tables IV-1 – IV-4 summarize the 1998 data from the weekly internal blind audit samples for NTN. It is important to remember that the blind sample population is considerably smaller than that of the QCS solutions. 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 representative of precipitation sample measurements. The SWS1 and SWS2 samples show fewer contaminants and less variability than the filtered the SWS3 (which have an even smaller sample population for each solution.)

For the SWS1 samples (Table IV-1), certified solutions of two different concentrations from High-Purity Standards[1] were used in 1998. These samples, H-PS SR1 (Lot #800925), and H-PS SR2 (Lot #800915), were of similar concentrations as those used in previous years and slightly higher than the internal QCS made at the CAL. H-PS SR1 is more similar in concentration to the higher concentration FR75 QCS with H-PS SR2 having still higher concentrations. The percent bias for most of the parameters was higher for the H-PS solutions than the QCS. The exceptions were potassium, nitrate, sulfate, and conductivity. A similar difference between the H-PS solutions and the QCS was seen when the percent relative standard deviation (RSD) was compared. The QCS had a lower percent RSD than did the H-PS solutions. The potassium values of both of the QCS and the chloride value for the FR25 QCS appeared to have higher percent RSDs than the blinds; however, the concentrations for potassium

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[1] HIGH-PURITY STANDARDS, P.O. Box 80609, Charleston, SC 29416, catalog #s SR-1 and SR-2

Table IV-1. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS1), High-Purity Standards Simulated Rainwater 1(H-PS SR1) and 2 (H-PS SR2), Unfiltered, 1998

Parameter	*Target Concentration*[a] *(mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias %*	*Standard Deviation (mg/L)*	*RSD*[e] *(%)*
Calcium	0.015[b]	0.031	27	0.016	109.6	0.010	31.7
	0.048[c]	0.064	25	0.016	32.4	0.015	24.3
Magnesium	0.020	0.026	27	0.006	30.0	0.003	10.5
	0.052	0.049	25	-0.003	-5.8	0.002	3.3
Sodium	0.20	0.195	27	-0.005	-2.5	0.007	3.6
	0.39	0.395	25	0.005	1.4	0.011	2.7
Potassium	0.050	0.048	27	-0.002	-3.3	0.002	4.3
	0.093	0.101	25	0.008	8.1	0.002	2.1
Ammonium[d]	0.1	0.034	27	-0.066	-65.9	0.043	127.4
	1	0.956	25	-0.044	-4.4	0.032	3.3
Sulfate	2.5	2.49	27	-0.01	-0.6	0.03	1.1
	10.1	10.04	25	-0.06	-0.6	0.10	1.0
Nitrate	0.5	0.50	27	0.00	0.5	0.02	4.0
	7.0	7.10	25	0.10	1.4	0.07	1.0
Chloride	0.25	0.22	27	-0.03	-11.9	0.00	1.5
	0.98	0.99	25	0.01	0.9	0.02	2.0
pH	4.32	4.32	27	0.00	0.0	0.03	0.6
(units)	3.56	3.63	25	0.07	1.9	0.02	0.5
Hydrogen ion	47.9	47.9	27	0.00	0.0	2.79	5.8
(µeq/L)	275.4	236.6	25	-38.83	-14.1	10.0	1.4
Specific Conductance	24.4	24.4	27	0.00	0.0	0.9	3.5
(µS/cm)	126.6	124.7	25	-1.9	-1.5	1.7	1.4

Notes:

[a] Certified concentrations as reported by High-Purity Standards.

[b] Concentration values for H-PS SR1, Lot# 800925.

[c] Concentration values for H-PS SR2, Lot #800915.

[d] NH_4 concentrations have been found to be unstable and are provided for information purposes only.

[e] RSD = Relative Standard Deviation.

Table IV-2. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS2), Deionized Water (DI) and pH 4.3 Quality Control Sample (QCS), Unfiltered, 1998

Parameter	*Target Concentration (mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias %*	*Standard Deviation (mg/L)*	*RSD[d] (%)*
Calcium	<0.009 [a]	<0.009	26			0.024	
	<0.009 [b]	<0.009	25			0.011	
Magnesium	<0.003	<0.003	26			0.003	
	<0.003	<0.003	25			0.000	
Sodium	<0.003	<0.003	26			0.000	
	<0.003	<0.003	25			0.002	
Potassium	<0.003	<0.003	26			0.000	
	<0.003	<0.003	25			0.001	
Ammonium	<0.02	<0.02	26			0.00	
	<0.02	<0.02	25			0.00	
Sulfate	<0.03	<0.03	26			0.00	
	<0.03	<0.03	25			0.02	
Nitrate	<0.03	<0.03	26			0.00	
	3.12 [c]	3.23	25	0.11	3.4	0.04	1.2
Chloride	<0.03	<0.03	26			0.00	
	<0.03	<0.03	25			0.00	
pH	5.65	5.56	26	-0.09	-1.5	0.14	2.4
(units)	4.30	4.32	25	0.02	0.4	0.02	0.4
Hydrogen ion	2.24	2.87	26	0.63	28.3	1.04	36.0
(µeq/L)	50.12	48.39	25	-1.73	-3.4	2.01	4.2
Specific Conductance	1	1.1	26	0.1	10.0	0.32	29.1
(µS/cm)	21.1	21.5	25	0.4	2.0	0.59	2.7

Notes:

[a] Concentration values for DI water.

[b] Concentration values for pH 4.3 Quality Control Sample (QCS).

[c] Concentration values for the pH 4.3 QCS are based on theoretical values. Concentrations for each prepared solution may vary slightly from ideal values.

[d] RSD = Relative Standard Deviation.

Table IV-3. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS3), High-Purity Standards Simulated Rainwater 1(H-PS SR1) and 2 (H-PS SR2), Filtered, 1998

Parameter	*Target Concentration*[a] *(mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD*[e] *(%)*
Calcium	0.015[b]	0.047	11	0.032	215.2	0.009	19.7
	0.048[c]	0.089	13	0.041	85.9	0.016	17.6
Magnesium	0.020	0.028	12	0.008	40.0	0.004	15.6
	0.052	0.050	13	-0.002	-3.8	0.004	7.2
Sodium	0.20	0.189	12	-0.011	-5.5	0.004	1.9
	0.39	0.385	13	-0.005	-1.4	0.011	2.8
Potassium	0.050	0.046	12	-0.004	-9.0	0.001	2.8
	0.093	0.097	13	0.004	4.5	0.003	3.4
Ammonium[d]	0.1	0.052	12	-0.048	-48.3	0.036	70.6
	1	0.925	13	-0.075	-7.5	0.027	2.9
Sulfate	2.5	2.40	12	-0.10	-4.1	0.03	1.1
	10.1	9.61	13	-0.49	-4.8	0.17	1.8
Nitrate	0.5	0.49	12	-0.01	-1.7	0.01	1.8
	7.0	6.84	13	-0.16	-2.2	0.13	2.0
Chloride	0.25	0.21	12	-0.04	-14.3	0.00	2.3
	0.98	0.96	13	-0.02	-1.6	0.02	2.2
pH	4.32	4.32	12	0.00	0.0	0.03	0.6
(units)	3.56	3.62	13	0.06	1.8	0.01	0.4
Hydrogen ion	47.9	47.9	12	0.00	0.0	2.91	6.1
(µeq/L)	275.4	237.9	13	-37.52	-13.6	7.92	3.3
Specific Conductance	24.4	24.6	12	0.2	0.9	0.66	2.7
(µS/cm)	126.6	124.1	13	-2.5	-1.9	1.6	1.3

Notes:

[a] Certified concentrations as reported by High-Purity Standards.

[b] Concentration values for HPS SR1, Lot #800925

[c] Concentration values for HPS SR2, Lot #800915

[d] Concentrations of ammonium have been found to be unstable and are provided for information purposes only.

[e] RSD = Relative Standard Deviation.

TABLE IV-4. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS2), DI Water and pH 4.3 Quality Control Sample (QCS), Filtered, 1998

Parameter	*Target Concentration (mg/L)*	*Measured Concentration (mg/L)*	*Number of Samples*	*Bias (mg/L)*	*Bias (%)*	*Standaard Deviation (mg/L)*	*RSD[d] (%)*
Calcium	<0.009[a]	<0.009	13			0.010	
	<0.009[b]	<0.009	12			0.023	
Magnesium	<0.003	<0.003	13			0.000	
	<0.003	<0.003	12			0.003	
Sodium	<0.003	<0.003	13			0.002	
	<0.003	<0.003	12			0.003	
Potassium	<0.003	<0.003	13			0.000	
	<0.003	<0.003	12			0.008	
Ammonium	<0.02	<0.02	13			0.00	
	<0.02	<0.02	12			0.00	
Sulfate	<0.03	<0.03	13			0.00	
	<0.03	<0.03	12			0.02	
Nitrate	<0.03	<0.03	13			0.00	
	3.12[c]	3.14	12	0.02	0.5	0.05	1.5
Chloride	<0.03	<0.03	13			0.00	
	<0.03	<0.03	12			0.00	
pH	5.65	5.62	13	-0.03	-0.4	0.15	2.7
(units)	4.30	4.31	12	0.01	0.3	0.01	0.3
Hydrogen ion	2.24	2.50	13	0.26	11.5	0.67	26.7
(µeq/L)	50.12	48.81	12	-1.30	-2.6	1.54	3.1
Specific Conductance	1.0	1.1	13	0.05	5.0	0.18	16.9
(µS/cm)	21.1	21.6	12	0.48	2.3	0.32	1.5

Notes:

[a] Concentration values for DI Water.

[b] Concentration values for 4.3 Quality Control Sample (QCS).

[c] Concentration values for the 4.3 QCS are based on theoretical values. Concentrations for each prepared solution may vary slightly from ideal values.

[d] RSD = Relative Standard Deviation.

and chloride were considerably lower for the QCS than for the blinds. The RSDs for potassium and chloride for QCS FR75 were lower that the RSDs for the same ions for H-PS SR1. These two solutions have similar concentrations of potassium and chloride.

A large positive bias between the laboratory measurements and the target concentration for calcium was determined. An outside laboratory, Environmental Science and Engineering (ESE), was asked to measure the calcium concentration in the H-PS solutions. The calcium concentration obtained by ESE (0.022 mg/L) was within the range of the CAL measurements and outside the certified limits set by H-PS. The ammonium concentration in the H-PS solutions is not certified and is included for information only. The apparent large bias and precision shown by the CAL measurements for ammonium in H-PS SR 1 may be indicative of this parameter's instability.

The SWS2 solutions are, for the most part, blanks. One was DI water and the other was acidified DI water. These solutions are placed randomly among the network samples so that their analytical results can indicate possible problems with sample carryover or false positives. Two tables show that the measured concentrations for DI water solutions were below the method detection limit (MDL). A small positive bias for nitrate was found in the nitric acid solution. This could have been due to a low initial target value. The nitrate bias for the filtered samples was less than for the unfiltered samples. This may have been an artifact of the analyses or may have indicated a slight loss of nitrate by the filters.

The SWS3 samples, Table IV-3, had larger biases and relative standard deviations than the unfiltered SWS1 samples for the H-PS solutions. Although the 1998 bias for calcium was greater than the biases found in 1996 or 1997, the relative standard deviation was less. Part of this bias may be explained as an error in the printed certified value. Calcium measurements by the CAL and Environmental Science & Engineering (ESE) were in agreement, and both are much above the certified H-PS values. The smaller RSD for 1998 indicated that the CAL measured the calcium in the samples with greater precision. The RSD for the other parameters indicated that the precision of the CAL measurements was about the same or slightly better in 1998 than in 1997. The only ion that appeared to have a much larger percent RSD in 1998 than in 1997 was the ammonium ion and evidence indicated that the lower concentration solution was not stable for ammonium. The percent bias for magnesium for 1998 was also greater than for 1997. The large sodium biases seen in previous years decreased dramatically in 1998 with the use of the Gelman® filters. Although there was a slightly lower bias in the filtered samples compared with the unfiltered samples, -5.5 percent vs. -2.5 percent, both biases were negative indicating no addition of sodium from the filtration process. In 1997, the sodium bias in the filtered samples was 25.7 percent.

Tables B-1 and B-2 (Appendix B) are tabular comparisons of the filtered and unfiltered H-PS solutions. Tables B-3 and B-4 are comparisons of the DI water and nitric acid acidified DI water solutions. Figures displaying the data for each parameter follow the tables.

2. AIRMoN

Four times per month, the IL11 (Bondville, Illinois) site operator submits an internal blind sample for inclusion in the AIRMoN analysis queue. At the beginning of each month, the site operator receives these samples in an AIRMoN-type 250-mL sample bottle enclosed in a plastic bag. The weight of the empty bottle and the type of solution are written on the bag. The site operator submits the QA samples only on days when no wet deposition was collected. The sample bucket on the collector is not affected in any way. An AIRMoN Field Observer Form (FOF) accompanies each sample. The site operator weighs the sealed QA sample and records the sample volume and a corresponding precipitation amount on the FOF. "On" and "Off" dates and times are recorded on the FOF and bottle as if the sample were a real wet deposition sample. In addition, the operator reports the target pH and conductivity values in the field chemistry section of the FOF, although the sample is not actually measured. Throughout these steps, the site operator never opens the bottle. The site operator ships the sample to the CAL. The sample receiving person at the CAL has no indication that this is not a real precipitation sample. Every effort is made to ensure that the sample is "blind" to the analytical and receiving staff. After submitting the sample to the AIRMoN receiving staff, the site operator submits a copy of the FOF to the AIRMoN liaison so that the database can be edited to show the true identity of the sample and the date and time "on" can be corrected for the real sample submitted immediately after the QA sample. These samples are processed in the laboratory as AIRMoN precipitation samples.

The internal blind samples used in 1998 were dilute nitric acid, pH = 4.3 (4.3 QCS), and a solution of simulated rainwater prepared for the World Meteorological Organization (WMO) intercomparison study. Tables IV-5a and IV-5b summarize the results of the AIRMoN internal blind samples. The AIRMoN reports all values, including those below the MDL and negative values. No samples had a negative mean value, and most of them had a mean value of zero. Percent bias and RSD were not included in the tables for any of the parameters that were not present in the solution. The percent bias was similar for nitrate and pH in the AIRMoN internal blind 4.3 QCS and the NTN SWS2 4.3 QCS. This is a good indication that the values for the NADP/AIRMoN samples were comparable to the NADP/NTN analytical results, with no contamination in either sample.

The WMO solution used in 1998 as an internal blind was one of the solutions used in the WMO/Global Atmospheric Watch (GAW) intercomparison study for 1998. The values measured for the study by the CAL are included in Table IV-5 along with the target and mean concentrations for the intercomparison study and the mean concentrations from the blind samples. The bias calculations for the internal blind study used the mean concentration for the intercomparison study. There were 64 laboratories world-wide participating in the 1998 WMO/GAW Intercomparison Study. The percent bias of the CAL internal blind study was about the same as for the H-PS SR solutions. In some cases, notably calcium and ammonium, the bias for the CAL was considerably less for the WMO sample than for the H-PS SR solutions, emphasizing the possibility of erroneously reported concentrations of the H-PS SR solutions. Both calcium and ammonium concentrations indicated that although the CAL was biased high, the difference between the biases of the two samples, 109.6 percent vs. 5.2 percent for calcium and -65.9 percent vs.18.2 percent for ammonium for H-PS solutions and internal blind samples

Table IV-5a. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (4.3 Quality Control Check Sample) - AIRMoN, 1998

Parameter	*Target Concentration (mg/L)*	*Mean Concentration (mg/L)*	*Bias (mg/L)*	*Bias %*	*Standard Deviation (mg/L)*	*RSD*[a] (%)
Calcium	0.0	0.00	0.00		0.003	
Magnesium	0.0	0.00	0.00		0.0005	
Sodium	0.0	0.00	0.00		0.0007	
Potassium	0.0	0.00	0.00		0.001	
Ammonium	0.0	0.00	0.00		0.008	
Sulfate	0.0	0.01	0.01		0.01	
Nitrate	3.15	3.23	0.08	2.5	0.02	0.62
Chloride	0.0	0.00	0.00		0.0	
pH units	4.30	4.30	0.00		0.02	0.47
Hydrogen ion (µeq/L)	50.12	50.52	0.40	0.8	2.51	5.0
Specific Conductance (µS/cm)	21.8	22.2	0.4	1.8	0.39	1.76

Note:
Twenty-seven internal blinds were included in this tabulation.
[a] RSD = Relative Standard Deviation.

Table IV-5. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples - AIRMoN, 1998

Parameter	*Theoretical Concentration*[a] *(mg/L)*	*Mean WMO/GAW Concentration*[b] (mg/L)	*CAL Study Concentration*[c]	*CAL Mean Concentration*[d]	*Bias (mg/L)*	*Bias %*	*Standard Deviation (mg/L)*	*RSD*[e] *(%)*
Calcium	0.050	0.058	0.060	0.061	0.003	5.2	0.002	3.28
Magnesium	0.024	0.024	0.024	0.023	0.0	0.0	0.000	0.0
Sodium	0.235	0.244	0.241	0.244	0.0	0.0	0.003	1.23
Potassium	0.078	0.072	0.077	0.079	0.007	9.7	0.002	2.53
Ammonium	0.11	0.11	0.13	0.13	0.02	18.2	0.01	7.69
Sulfate	1.65	1.62	1.59	1.59	-0.06	-3.6	0.01	0.63
Nitrate	0.62	0.62	0.62	0.61	-0.01	-1.61	0.00	0.0
Chloride	0.39	0.40	0.38	0.39	-0.01	-2.5	0.01	2.56
pH units	4.51	4.52	4.52	4.53	0.01	0.22	0.01	0.22
Hydrogen ion (µeq/L)	30.9	30.2	30.2	29.3	-0.9	-3.0	0.62	2.12
Specific Conductance (µS/cm)	17.0	16.7	17.1	17.0	0.3	1.8	0.25	1.47

Note:
Sixteen internal blinds were included in this tabulation. These samples were a solution of simulated rainwater prepared for the 1998 World Meteorological Organization intercomparison study.

[a] Theoretical concentration based on calculated values.

[b] Mean concentration used by the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) in their analysis of the data in the 1998 WMO intercomparison study.

[c] The concentration reported to the WMO/GAW by the CAL during the 1998 WMO intercomparison study.

[d] The mean concentration obtained by the CAL from the AIRMoN internal blind samples.

[e] RSD = Relative Standard Deviation.

respectively, was sufficiently high to question the certified concentrations of the H-PS SR solutions. The percent RSD for the AIRMoN blind samples was better than for the replicate NTN blind samples, but this could have been due to fewer samples being measured in the AIRMoN program.

B. Replicate Samples

Two percent of the NTN and AIRMoN samples are split for duplicate analysis. The splits are separated in the analysis queue and are analyzed at different times than the original samples. The NTN samples are divided at the time of filtration into three 60-mL aliquots: one is put on the tray for transfer to the laboratory for initial analysis at its regular place in the queue, one is filtered for archival purposes, and one is sent back to sample processing to be assigned a new and higher laboratory identification number and submitted for analysis at a later time. Samples chosen for splits must have sufficient volume to fill three filtered 60-mL bottles. The original and the split sample analysis may be on the same day or several days apart depending on their location on the sample trays, but never one immediately after the other. After analysis, the data management staff recodes the duplicate with the original sample identification number followed by a “Q” (quality control sample) to distinguish it from the original identification number that included the letter “S” for standard sample. With a common numeric sample identification number, the original and duplicate analytical results appear consecutively on data printouts. The AIRMoN samples are split in a similar manner to the NTN samples although they are not filtered. An AIRMoN sample with a full or almost full sample bottle near the middle of a sample tray is chosen as the sample to be split. A second sample bottle is prepared with the same sample information on the bottle and half of the sample is poured from the original sample bottle into the split sample bottle. When the next tray is about half full, the split sample is placed on the tray and assigned a new number, with a Field Observer Form filled out to go along with it. The sample identification number of the second bottle is changed to the original number after analysis is complete but instead of an “L” designating the original sample, a “Q” is placed at the end of the sample identification number.

Replicate samples serve as another estimator of sample precision. Since these are blind, real precipitation samples, their concentration values should produce representative precision data. Tables IV-6 and IV-7, respectively, summarize the analyses of replicate samples analyzed in 1998 for NTN and AIRMoN. Differences are calculated by subtracting the reanalysis value from the original value. The annual summaries of each ion have been split into two sections. Since these samples are actual precipitation samples, the concentration of the split samples can cover the entire range of concentrations found in precipitation. The median concentration of the split samples for the year is determined for each analyte (Appendix B, Table B-5). The box plots (Appendix B, Figures B-24 to B-27 for NTN and Figures B-28 to B-30 for AIRMoN) are constructed to show the differences for the low concentrations (from zero to the median values) and the high concentrations (from the median values to the highest concentrations). The standard deviation estimated from duplicate measurements, defined in the Glossary (Appendix A), was used to calculate the standard deviations for three categories: concentrations below the median, concentrations above the median, and the entire population. The fourth column in Tables IV-6 and IV-7 shows a nonparametric estimator of variability from duplicate determinations, where 1.48 times the Median Absolute Difference (MAD) is the estimator of dispersion (Helsel and

Table IV-6. Variance Estimated from Analysis of Replicate NADP/NTN Precipitation Samples, 1998

Parameter	*Standard Deviation Estimated from Paired Measurements[a] (mg/L)* *Low*	 *High*	 *Total*	 *(1.48) x MAD[b]*
Calcium	0.004	0.008	0.006	0.005
Magnesium	0.001	0.006	0.004	0.001
Sodium	0.001	0.036	0.026	0.001
Potassium	0.001	0.003	0.002	0.001
Ammonium	0.01	0.05	0.03	0.01
Sulfate	0.01	0.03	0.02	0.01
Nitrate	0.01	0.02	0.02	0.01
Chloride	0.01	0.02	0.02	0.00
Orthophosphate	0.000	0.016	0.01	0.000
Hydrogen ion (µeq/L)	3.92	0.60	2.81	0.95
Specific Conductance (µS/cm)	0.20	0.48	0.36	0.30
Number of pairs	89	88	177	177

Notes:

[a] Standard Deviation Estimated from Paired Measurements is defined in the Glossary of Terms, Appendix A.

[b] MAD = Median Absolute Difference.

TABLE IV-7. Variance Estimated from Analysis of Replicate AIRMoN Precipitation Samples, 1998

	Standard Deviation Estimated from Paired Measurements [a] (mg/L)			
Parameter	*Low*	*High*	*Total*	*(1.48) x MAD [b]*
Calcium	0.002	0.005	0.004	0.005
Magnesium	0.001	0.001	0.001	0.001
Sodium	0.001	0.065	0.035	0.001
Potassium	0.001	0.004	0.003	0.003
Ammonium	0.01	0.04	0.03	0.01
Sulfate	0.01	0.03	0.02	0.01
Nitrate	0.01	0.04	0.03	0.01
Chloride	0.00	0.01	0.01	0.00
Orthophosphate	0.003	0.007	0.006	0.001
pH (units)	0.02	0.06	0.04	0.04
Hydrogen ion (µeq/L)	6.98	2.54	5.26	6.05
Specific Conductance (µS/cm)	1.6	1.8	1.7	1.6
Number of pairs	16	16	32	32

Notes:

[a] Defined in glossary with equation.

[b] MAD = Median Absolute Difference.

Hirsch, 1992). This value is F-pseudosigma. A comparison of the RSD for the QCS (Table III-1), SWS1 (Table IV-1) and SWS3 (Table IV-3) to F-pseudosigma shows the cation and anion precision of the split samples to be comparable.

C. Blanks

Solutions referred to as “blanks” are known to the analysts and are identified as such by sample 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 the samples being taken to the ion chromatography, atomic absorption, and flow injection analysis laboratories. The “blanks” are analyzed as a weekly set by the analysts, and the week they are collected is included in the “blank” identification number. In 1998, two solutions were used to leach filters, bottles, buckets, and lids: DI water from the sample processing laboratory and the FR25 QCS. The DI water blanks from the sample processing, atomic absorption, and the bucket-washing service laboratories are also included in the weekly blank analytical scheme.

1. Deionized Water Blanks

The conductivity or resistance of DI water used for rinsing, leaching, and making reagents and standards is monitored routinely in each of the laboratories. There is an in-line resistivity meter at the source of the DI water in the laboratory building and in all individual laboratories at their wall-mounted polishing units. Once a week, 60-mL samples are collected from three sources for analysis: the atomic absorption laboratory, the bucket-washing service laboratory, and the sample processing laboratory. These DI water samples are analyzed for all parameters. The DI water blanks showed no median values above the MDLs. Table IV-8 shows the median pH and conductivity for the DI water from these three laboratories. The pH is slightly lower with slightly higher corresponding conductivity readings than in the past two years, but it is still similar to past measurements. The DI water blanks are also used to evaluate the cleaning efficacy of the 60-mL bottles used as sample storage bottles in NTN. No contamination problem was noted.

2. Filter Leachates

Prior to filtering an NTN sample, the Gelman Supor® 450, 0.45-micrometer (μm) polysulfone filters are rinsed with 250-300 mL of DI water. Following the DI water rinse, all samples with a volume greater than 35 mL are poured from their 1-liter (1-L) shipping bottle through the filter into a 60-mL wide-mouth High Density Polyethylene (HDPE) Boston-round 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 with 250-300 mL of DI water and then 50 mL of DI water is filtered into a sample bottle 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. The Gelman filters were first used in 1998. Prior to this, Millipore™ HAWP filters were used.

Table IV-9 shows the median concentration for the four filter leachate “blanks”. Neither the DI water leachates nor the FR25 leachates show any evidence of contamination by the filter.

Table IV-8. Median pH and Conductivity Values for Weekly Deionized (DI) Water Blanks, 1998

Parameter	*Sample Processing Laboratory*	*Atomic Absorption Laboratory*	*Service Laboratory*
pH (units)	5.59	5.62	5.62
Conductivity (µS/cm)	1.00	1.08	0.95
Number of weeks	48	48	48

Table IV-9. Median Analyte Concentrations Found in Filter Leachates, 1998

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 Concentration (mg/L)*
Calcium	<0.009	<0.009	0.076	0.076	0.075
Magnesium	<0.003	<0.003	0.016	0.017	0.017
Sodium	<0.003	<0.003	0.047	0.048	0.047
Potassium	<0.003	<0.003	0.012	0.012	0.014
Ammonium	<0.02	<0.02	0.07	0.08	0.085
Sulfate	<0.03	<0.03	0.60	0.62	0.63
Nitrate	<0.03	<0.03	0.46	0.47	0.48
Chloride	<0.03	<0.03	0.13	0.13	0.13
pH (units)	5.58	5.59	4.91	4.92	4.92
Hydrogen ion (µeq/L)	2.66	2.60	11.9	12.3	12.0
Specific Conductance (µS/cm)	1.3	1.2	7.2	7.4	7.4

Note:

[a] First 50-mL filtrate.

[b] Second 50-mL filtrate.

Forty-eight blanks were collected. Calcium and magnesium calculations only include 46 values and sodium and potassium calculations only include 47 values. All others included the 48 measurements.

Before the use of the Gelman filters, sodium contamination from the filters was a recurring problem. There is no sodium contamination with the Gelman filters. All parameters are close to the target concentrations.

3. Bucket Blanks

Sample collection buckets are made of HDPE and have a 13-L capacity. These buckets are washed at the CAL, bagged upon removal from the dishwashing machine, and shipped to sites for weekly (NTN) or daily (AIRMoN) placement on the samplers. Buckets on the "wet" side remain on the collector for one week for NTN and collect whatever precipitation falls from Tuesday to Tuesday. The AIRMoN buckets are changed only if there was a precipitation event within the last 24 hours or once a week if there was 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 external QA blind audit study where a portion of a sample of known concentration is poured from a bottle into a bucket at the NTN site and submitted as a network sample. A portion of the bottled sample is saved and returned to the CAL. The bucket and bottle sample results are sent to the USGS for statistical analysis. The CAL has performed blind audit studies since the network began.

The weekly procedure for "bucket blanks" included leaching four buckets for five days with two different volumes of two different solutions: DI water and FR25 in 50- and 150-mL portions. The solutions were measured into the buckets, covered with snap-on lids, and stored for five days in the sample processing laboratory. The four solutions were then poured into appropriately labeled 60-mL bottles for analysis.

Table IV-10 shows the median mass per bucket found in the weekly leachates. Note that for the DI water leachates, these values are the leachate concentrations in micrograms/mL (µg/mL) times the number of milliliters of leachate. For the FR25 solutions, the values are the median concentrations found in the "blanks" minus the FR25 target concentrations times the number of milliliters used for the leachate. For the DI water "blanks", sodium was the only parameter that was present in a measurable amount and only in the lower volume (50-mL) "blanks". Precipitation samples with low volumes generally had higher concentrations of analytes, and, therefore, should not have been affected by the small amount of possible sodium contamination.

4. Bottle Blanks

One-liter HDPE wide-mouth bottles have been used as shipping containers for the 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 measuring 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. At the CAL, portions of the samples are removed for pH and conductivity measurements, filtered, and collected in 60-mL bottles. Any excess sample is discarded. The shipping bottles are washed at the CAL and sent back to the NTN sites for reuse.

Table IV-10. Median Measured Mass as Micrograms (μg)/Bucket[a] Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in Upright Bucket Leachates, 1998

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	<0.225
Sodium	0.15	<0.225	0.10	0.30
Potassium	<0.075	<0.225	0.10	0.30
Ammonium	<0.50	<1.50	<0.75	<2.25
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)	5.56	5.57	4.98(4.92)[c]	4.94(4.92)[c]
Hydrogen ion (μeq/bucket)	0.139	0.404	0.525(0.601)[c]	1.72(1.80)[c]
Specific Conductance (μS/cm)	1.5	1.4	7.0(7.4)[c]	7.4(7.4)[c]

Notes:

There were 48 sample blind weeks in 1998 but only 46 Ca and Mg values and 47 K and Na values.

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

[b] The FR25 measured mass represents (median concentration measured in upright bucket leachates - target FR25 concentration) x 50 or 150 mL.

[c] Values in parentheses represent mean values for FR25 with no bucket contact.

Table IV-11. Median Measured Mass as Micrograms (μg)/Bottle[a] Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in HDPE 1-Liter Bottle Leachates, 1998

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	<0.225
Sodium	<0.075	<0.225	<0.075	<0.225
Potassium	0.15	<0.225	<0.075	<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)	5.52	5.55	4.93(4.92)[c]	4.91(4.92)[c]
Hydrogen ion (μeq/bucket)	0.15	0.42	0.59(0.60)[c]	1.85(1.80)[c]
Specific Conductance (μS/cm)	1.4	1.3	7.3(7.4)[c]	7.4(7.4)[c]

Notes:

There were 48 sample blind weeks in 1998 but only 46 Ca and Mg values and 47 K and Na values.

[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] The FR25 measured mass represents (median concentration measured in upright bucket leachates- target FR25 concentration) x 50 or 150 mL.

[c] Values in parentheses represent mean values for FR25 with no bucket contact.

Table IV-11 shows the median measured mass found in bottle leachates. From this table, it can be seen that the 1-L shipping bottles contained no contaminants.

5. Snap-on Lid Blanks

Snap-on lids are used to contain the sample in the bucket between the collector and the site field laboratory. At the CAL two lids are inverted on the laboratory bench and 50 mL of DI water is measured onto one of the them and 50 mL of FR25 onto the other one. They are covered with large plastic domes and left for 24 hours. Table IV-12 shows the median concentrations found on the snap-on lid "blanks". The median sodium value found in the DI water "blank" was at the detection limit of sodium. All values found in the FR25 "blank" were essentially the same as the target concentrations. No contamination due to the lids was determined.

6. AIRMoN Bottles

Shipping and storage bottles for AIRMoN are 250-mL wide-mouth HDPE bottles. These bottles are washed at the CAL with DI water prior to shipment to the sites. They are not reused. The AIRMoN daily samples are collected in the same type of 13-L buckets used for the NTN weekly samples. Once the AIRMoN samples are taken to the field laboratories, they are poured into the 250-mL sample shipping bottles and sent to the CAL. Unlike NTN samples, AIRMoN samples are stored in these shipping bottles and are not filtered or transferred into smaller, 60-mL storage bottles.

Once a month, two AIRMoN 250-mL bottles are used for AIRMoN bottle blanks. Although only two bottles are tested each month, the same ratio of bottle blanks to bottles is used for AIRMoN sample storage and NTN sample storage, or about 1 blank bottle per 50 - 60 samples. The leachate used for the AIRMoN bottle blanks was the FR25 solution. One bottle had a 50-mL aliquot; the other a 150-mL aliquot. Table IV-13 shows no difference between the leachate values of the FR25 in the AIRMoN bottle blanks and the target FR25 concentrations used for either the 50-mL aliquot or the 150-mL aliquot.

Table IV-12. Median Analyte Concentrations (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Snap-on Lids, 1998

Analyte	*DI Water (50 mL)*	*FR25 (50 mL)*	*FR25 Target Concentration (mg/L)*
Calcium	<0.009	0.077	0.075
Magnesium	<0.003	0.017	0.017
Sodium	0.003	0.049	0.047
Potassium	<0.003	0.016	0.014
Ammonium	<0.02	0.08	0.085
Sulfate	<0.03	0.62	0.63
Nitrate	<0.03	0.47	0.48
Chloride	<0.03	0.14	0.13
pH (units)	5.60	4.96	4.92
Specific Conductance (µS/cm)	1.4	7.2	7.4

Notes:
There were 46 weeks of snap-on lid blanks with DI water but only 44 weeks with Ca and Mg measured and 45 weeks with Na and K measured. There were 47 weeks of snap-on lid blanks with FR25 but only 45 weeks with Ca and Mg measured and 46 weeks with Na and K measured.

Table IV-13. Median Analyte Concentrations (mg/L) Found in Monthly Simulated Rain (FR25) AIRMoN 250-mL HDPE Bottle Leachates, 1998

Analyte	*DI Water (50 mL)*	*FR25 (50 mL)*	*FR25 Target Concentration (mg/L)*
Calcium	0.074	0.074	0.075
Magnesium	0.017	0.017	0.017
Sodium	0.048	0.048	0.047
Potassium	0.012	0.013	0.014
Ammonium	0.080	0.080	0.085
Sulfate	0.63	0.63	0.63
Nitrate	0.48	0.47	0.48
Chloride	0.13	0.13	0.13
pH (units)	4.90	4.90	4.92
Specific Conductance (µS/cm)	7.4	7.4	7.4

Notes:
There were 12 months of AIRMoN bottle blanks but only 11 months of Ca and Mg analyses for 50-mL samples and 11 months of Ca, Mg, Na, K, and NH_4 analyses for 150-mL samples.

V. MONTHLY QUALITY ASSURANCE PROCEDURES

Monthly NADP/NTN and NADP/AIRMoN QA activities include evaluation of the control charts summarizing the daily QCS analyses to determine if any change has occurred with each analytical instrument, review of the printouts containing internal blind sample 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 the 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. All samples including internal blinds, field blanks, and collocated program samples are included in the 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 (1976, 1987). The measured concentration of the ions 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:

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

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

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

Samples are flagged for reanalysis if:

$IS < 50$ µeq/L and $-60\% \geq IPD \geq \pm 60\%$

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

$IS \geq 100$ µeq/L and $-15\% \geq IPD \geq \pm 15\%$

Table V-1. Conversion Factors for Reanalysis Calculations

Analyte	*Milligrams/Liter (mg/L) to Microequivalents/L (µequiv/L)[a] for Ion Percent Difference, Multiply by:*	*Microequivalent/L (µequiv/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
orthophosphate	31.59	69.0
Hydrogen	992.2	350.0
Bicarbonate	16.39	44.5
Hydroxide	58.8	198.0

Notes:

[a] **Source:** *Standard Methods for the Examination of Water and Wastewater* (1976).

[b] **Source:** *CRC Handbook of Chemistry and Physics* (1987).

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, summed, and then divided by 1000 in order to calculate the 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 for reanalysis. The analysts then submit the results to the QA Specialist with suggestions for changes. 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, a second reanalysis of the original sample and/or analysis of the archived sample is requested. Reanalysis values are maintained in the CAL’s computerized database along with the original analyses values.

3. IPD and CPD Histograms

In 1998, approximately 10,800 samples were logged in and 6731 were classified as “W” (wet), which would make them eligible for the reanalysis program. These samples had volumes of 35 mL or more. In all, 416 samples were flagged for reanalysis with 224 individual measurement changes made to 124 samples. Figure V-1 depicts the histograms for the IPD and CPD values and includes the mean, the standard deviation, and the median.

Between 1979 and 1993, the IPD mean and median values were positive. Since 1993, the mean values have been negative. The 1994-1997 medians were also negative, but the 1998 median IPD was positive. A negative value indicates a cation excess. Before January 1, 1994, samples were shipped in the collection buckets using lids that contained a butadiene rubber o-ring. The pH of the samples increased due to an ion exchange reaction at the o-ring/sample interface. Beginning in January 1994, the NADP began using snap-on lids that do not contain an o-ring. These lids are not water-tight so the buckets cannot be used to ship samples to the CAL. The NTN samples, therefore, are decanted at the field site into 1-L wide-mouth HDPE bottles with screw-on lids and without gaskets before shipping to the CAL. Since the change in shipping protocol, the laboratory pH and field pH are in better agreement. The NADP does not measure organic acids, which could account for some of the excess cations measured. In 1998, the filters used for filtering the NTN samples were changed from a Millipore ™ type HAWP, 0.45 micrometer (µm) filter to a Gelman Supor® 450, 0.45 µm polysulfone filter. When the Millipore™ filters were used, there was a high bias for sodium in filter blank and leachates. In 1998, that bias disappeared with the use of the Gelman filters. This may, in part, account for the

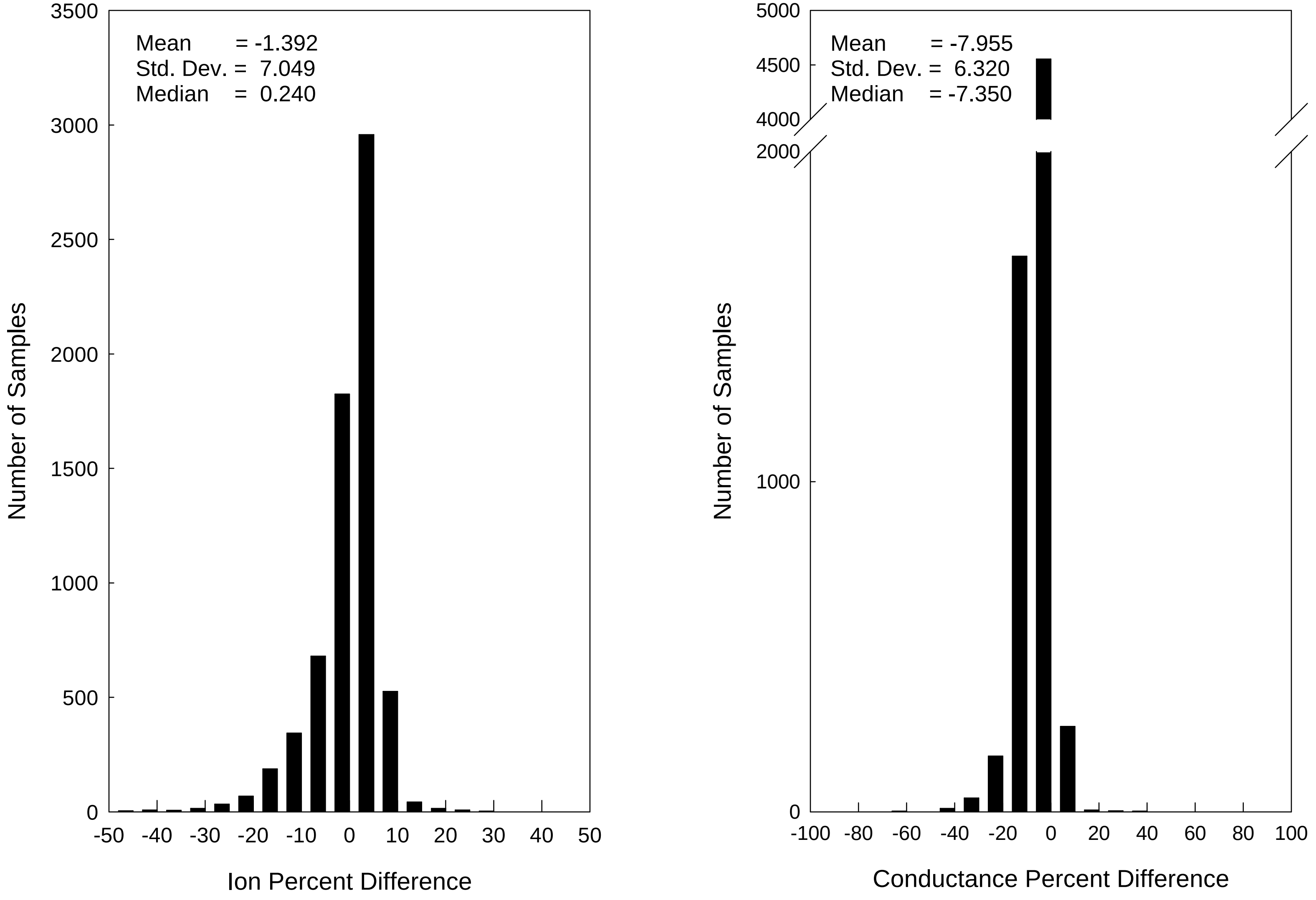


Figure V-1. Ion Percent Difference and Conductance Percent Difference for 6731 NADP/NTN wet samples, 1998.

positive IPD median and the low mean. Similar values, however, were seen in 1997 so there could be some other factors at work here as well. Further study is needed to determine the cause of these shifts in the median IDP.

The CPD has consistently exhibited a negative skew since 1979 with 1998 being similar to previous years. Negative CPD indicates that the measured conductivity exceeds the calculated conductivity. This is expected since only the major ions in the samples are analyzed. There are undoubtedly constituents, such as trace metals and organic species that contribute to the measured conductivity.

B. AIRMoN Field Blanks

AIRMoN field blanks are collected monthly. On the first Tuesday of the 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 specially marked bottle sent from the CAL. This bottle contains the field blank solution and is identified with the sample matrix on the bottle, a field blank number, and a large red circle on the lid. The remainder of the solution, approximately 125 mL, is left in the original bottle, which is recapped and taken back to the field laboratory. The sample remaining in the original bottle is returned to the CAL without being reopened for field measurements and is designated “DK”. The bucket containing the decanted field blank solution is agitated and then allowed to stand overnight or for at least two hours. The solution is then poured into a 250-mL shipping bottle and the field pH and conductivity are measured and recorded on an AIRMoN Field Observer Form (FOF). This bottle is given the designation “DF”. Both the “DF” and the ”DK” bottles are shipped to the CAL for complete chemical analysis.

In 1998, four different solutions were used in the AIRMoN field blank program: DI water, pH 4.3 nitric acid, FR25, and FR75. The pH of all but the DI water is similar to samples collected in the network. Both the site personnel and the CAL analysts knew that the solutions were field blank solutions being used for evaluating the effects of the collection bucket in the field, potential shipping bottle contamination, and handling. Other solutions, such as AIRMoN replicates, were used to evaluate the chemical analysis.

Table V-2 summarizes the results of the AIRMoN field blanks program for 1998. The top number 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. The field blank samples overall have a higher variance and a higher standard deviation than do the replicates, when comparing the “DF”/”DK” numbers in Table V-2 with the replicate numbers found in Table IV-7. Calcium was noticeably higher in the field blank numbers, which is to be expected.

Calcium is a large component of wind-blown dry deposition contaminants, which could be expected in buckets that are in the field during dry deposition periods. These numbers indicate that dry deposition in the collection buckets has a greater variability than the replicate analyses of the samples in the laboratory. This also means that a real component in the wet

Table V-2. AIRMoN Field Blanks Median Absolute Difference of Bucket Minus Bottle (DF-DK)[a] and Paired Standard Deviations, 1998

Analyte	*DI Water*	*pH 4.3 HNO_3*	*FR25*	*FR75*
Sulfate	0.00[b] 0.02[c]	0.04 0.03	0.03 0.04	0.06 0.07
Nitrate	0.03 0.02	0.06 0.04	0.04 0.03	0.06 0.04
Chloride	0.03 0.02	0.01 0.03	0.01 0.06	0.03 0.02
Ammonium	0.01 0.01	0.01 0.01	0.01 0.02	0.01 0.02
Calcium	0.009 0.006	0.007 0.007	0.007 0.010	0.016 0.018
Magnesium	0.001 0.002	0.001 0.002	0.001 0.002	0.003 0.002
Sodium	0.006 0.008	0.004 0.012	0.004 0.013	0.007 0.008
Potassium	0.003 0.002	0.002 0.007	0.001 0.006	0.004 0.003
Conductivity (µS/cm)	0.59 1.04	0.74 0.54	0.74 1.13	0.89 2.26
pH (pH units)	0.06 0.05	0.03 0.01	0.01 0.05	0.03 0.02
H (µeq/L)	0.40 0.43	3.26 1.63	0.45 1.80	3.12 2.37
n	27	18	10	27

Notes:

All measurements are in mg/L unless otherwise indicated.

[a] Solutions are shipped to AIRMoN sites in bottles from the CAL. Sample protocol is followed in pouring 125 mL into a collection bucket (DF). The remaining solution is returned in the original bottle (DK). Returned samples undergo complete chemical analyses.

[b] The first set of values for each analyte for each solution is the Median Absolute Difference X 1.48.

[c] The second set of values for each analyte for each solution is the standard deviation estimated from paired measurements (defined in the glossary, Appendix A).

samples may be derived from nonprecipitation periods. Because the time the buckets are in the field varies from 24 hours to one week, the variability of the dry deposition contribution to the samples is large but consistent across all parameters.

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 program. The USGS mails samples of different chemical matrices to participating laboratories twice each month. This audit is designed to determine if the laboratories produce comparable results.

The 1998 interlaboratory comparison program included five laboratories: (1) NADP/CAL, (2) Atmospheric Environment Service (AES), (3) Environmental Science and Engineering (ESE), (4) Ontario Ministry of the Environment (MOE), and (5) Shepard Analytical Services (SA).

The samples were shipped to the laboratories approximately every two weeks throughout the year. Samples used in 1998 were (1) National Institute of Standards and Technology (NIST) traceable solutions prepared and certified by H-PS, (2) uncertified synthetic precipitation samples prepared and bottled by the USGS, (3) natural deposition samples collected at NTN sites and composited and bottled at the CAL, and (4) ultrapure DI water prepared by the USGS. Data reports from participating laboratories were submitted monthly or quarterly to the USGS. Although the natural deposition samples were prepared at the CAL, the CAL analysts did not know the target concentrations nor when these samples were being measured.

Table V-3 shows the 50th and 90th percentile absolute differences of replicate samples obtained by the five participating laboratories in 1998. Figures V-2 and V-3 graphically show these same results. For comparison, laboratory rankings were determined by summing the 50th and 90th percentile absolute differences, included in Table V-4. The CAL was ranked first for sulfate and sodium and tied for first with one or more laboratories in terms of having the best results for ammonium, chloride, magnesium, nitrate and potassium in 1998. The CAL was ranked second for calcium and third for pH and specific conductance among participating laboratories. An overall ranking done for the five laboratories indicated that the CAL ranked number 1 overall in 1998. The USGS will publish the complete report for the 1998 study.

Table V-3. 50th and 90th Percentile Absolute Differences for Analysis of Replicate Samples in the 1998 Interlaboratory Comparison Program

	CAL[a]		*AES*[b]		*ESE*[c]		*MOE*[d]		*SA*[e]	
Analyte	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*
Calcium	0.001	0.010	0.000	0.010	0.010	0.320	0.000	0.010	0.000	0.010
Magnesium	0.000	0.001	0.000	0.004	0.000	0.004	0.000	0.000	0.000	0.001
Sodium	0.001	0.002	0.001	0.006	0.001	0.008	0.000	0.005	0.002	0.004
Potassium	0.001	0.003	0.001	0.011	0.001	0.016	0.000	0.005	0.001	0.003
Ammonium	0.000	0.010	0.000	0.010	0.010	0.320	0.000	0.010	0.000	0.010
Sulfate	0.000	0.010	0.010	0.020	0.010	0.030	0.000	0.050	0.010	0.020
Nitrate	0.010	0.010	0.010	0.020	0.000	0.020	0.010	0.040	0.010	0.020
Chloride	0.000	0.010	0.000	0.010	0.000	0.020	0.000	0.010	0.000	0.010
Hydrogen Ion (µeq/L)	0.248	1.834	0.667	2.650	1.10	4.226	0.263	1.340	0.429	1.340
Specific Conductance (µS/cm)	0.100	0.600	–	–	0.100	2.900	0.000	0.400	0.050	0.200

Notes:

All measurements are in mg/L unless otherwise indicated.

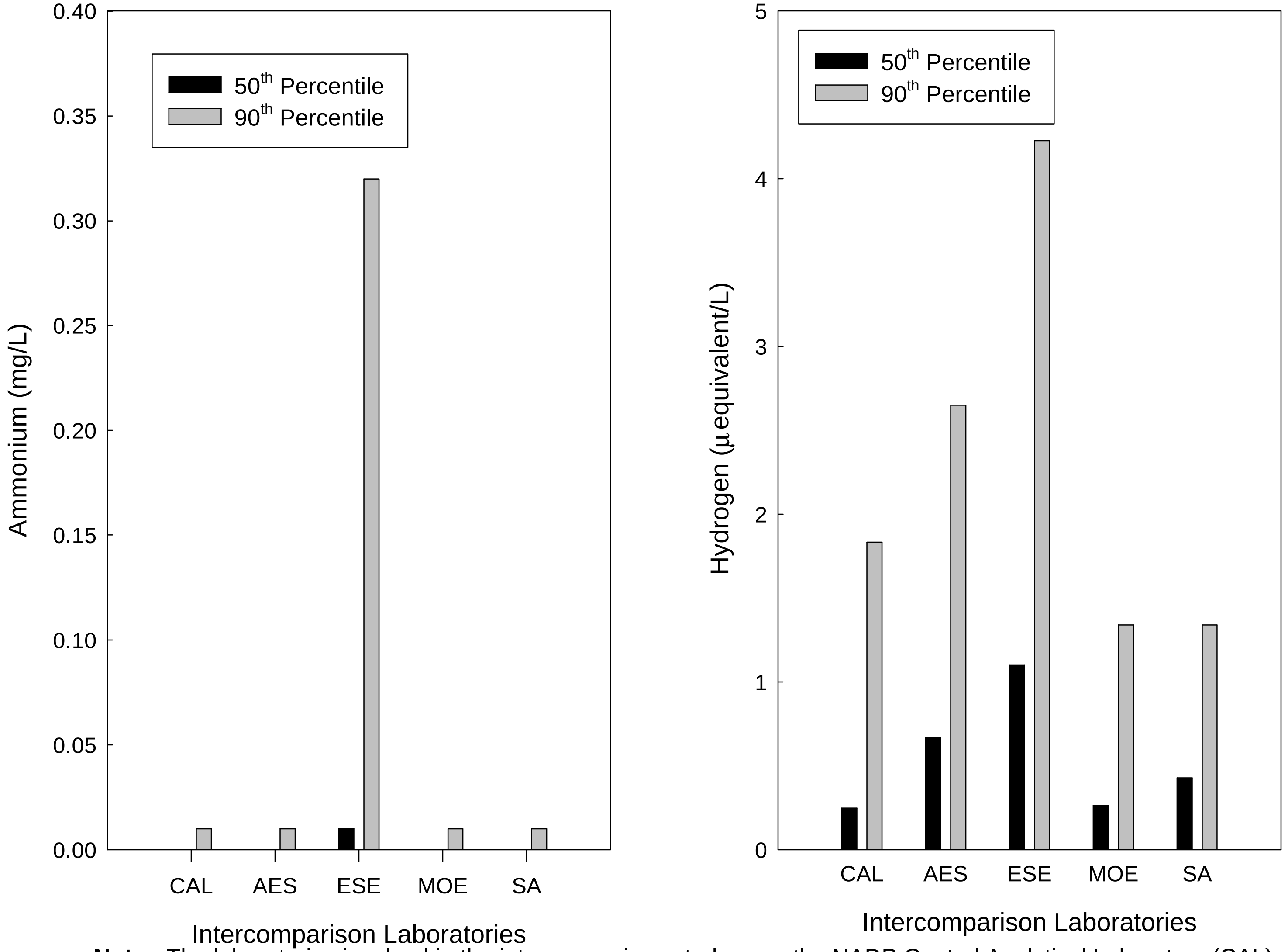
[a] Illinois State Water Survey.

[b] Atmospheric Environment Service, Canada.

[c] Environmental Science and Engineering.

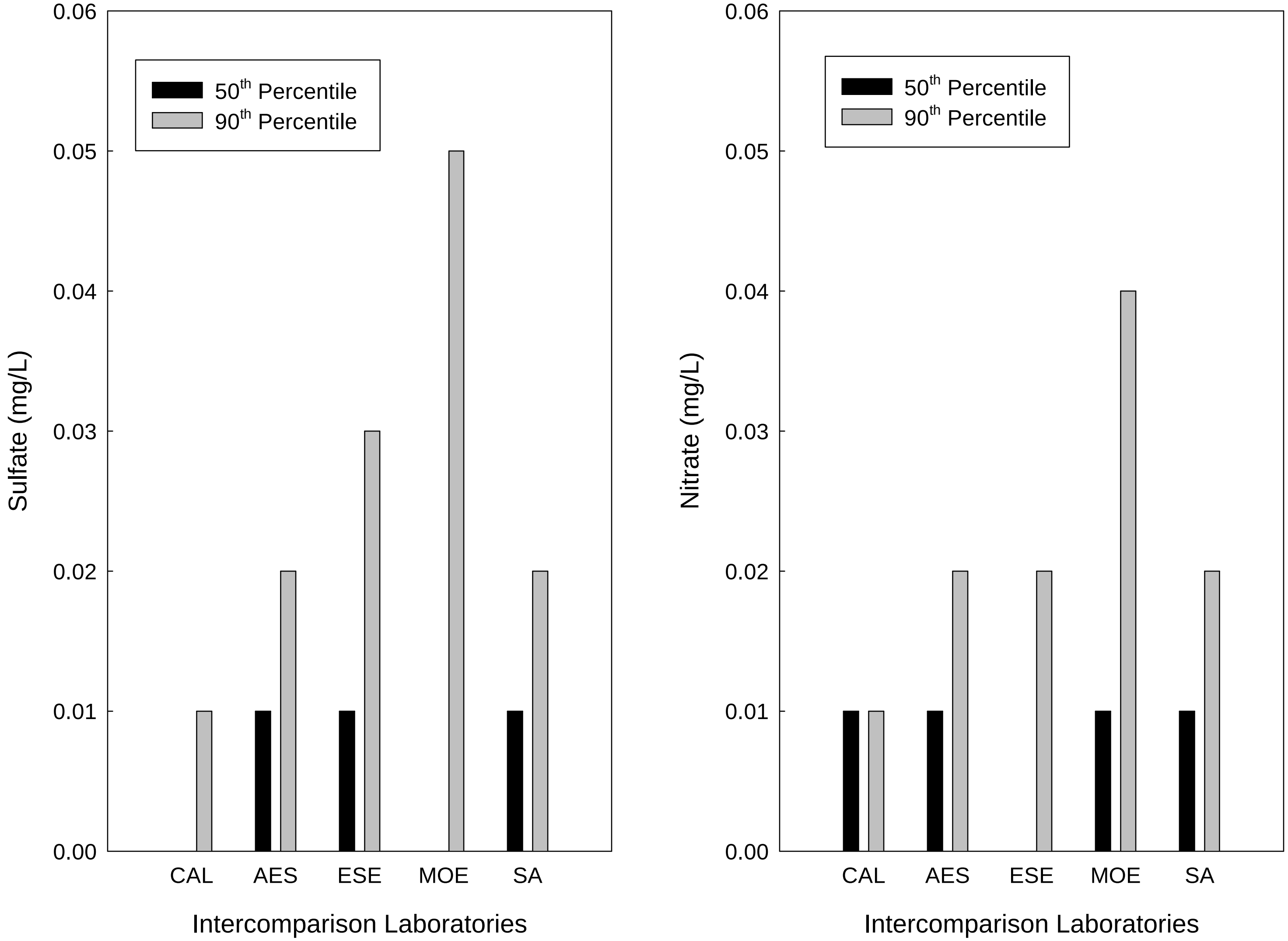
[d] Ontario Ministry of the Environment, Canada.

[e] Shepard Analytical Services.



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 Envronment (MOE), and Shepard Analytical Services (SA).

Figure V-2. Ammonium and hydrogen 50th and 90th percentile absolute differences for the five laboratories in the USGS Intercomparison Study, 1998.



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 Shepard Analytical Services (SA).

Figure V-3. Sulfate and nitrate 50th and 90th percentile absolute differences for the five laboratories in the USGS Intercomparison Study, 1998.

TABLE V-4. USGS Intercomparison Study Ranking Summary for 1998

Analyte	*CAL*[a]		*AES*[b]		*ESE*[c]		*MOE*[d]		*SA*[e]	
	Sum	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*
Calcium	0.006	2	0.005	1	0.012	4	0.020	5	0.010	3
Magnesium	0.001	2 tie	0.004	4 tie	0.004	4 tie	0.000	1	0.001	2 tie
Sodium	0.003	1	0.007	4	0.009	5	0.005	2	0.006	3
Potassium	0.004	1 tie	0.012	4	0.017	5	0.005	3	0.004	1 tie
Ammonium	0.010	1 tie	0.010	1 tie	0.330	5	0.010	1 tie	0.010	1 tie
Sulfate	0.010	1	0.030	2 tie	0.040	4	0.050	5	0.030	2 tie
Nitrate	0.020	1 tie	0.030	3 tie	0.020	1 tie	0.050	5	0.030	3 tie
Chloride	0.010	1 tie	0.010	1 tie	0.020	5	0.010	1 tie	0.010	1 tie
Hydrogen ion (µeq/L)	2.082	3	3.317	4	5.326	5	1.603	1	1.769	2
Specific Conductance (µS/cm)	0.700	3	not available		3.000	4	0.400	2	0.250	1
Overall Ranking	1		4		5		3		2	

Note:
All measurements are in mg/L unless otherwise indicated. Laboratory rankings were determined by summing the 50th and 90th percentile absolute differences for replicate samples analyzed as part of the USGS Interlaboratory Comparison Program.

[a] NADP/CAL.

[b] Atmospheric Environment Service.

[c] Environmental Science and Engineering.

[d] Ontario Ministry of the Environment.

[e] Shepard Analytical Services.

VI. SEMIANNUAL AND ANNUAL QUALITY ASSURANCE PROCEDURES

Each year a report is prepared summarizing the previous year's QA data. The CAL database contains the analyses of the replicate samples and the internal blind samples as well as the network precipitation samples. Blank and QCS measurements are stored on personal computer (PC) files. The annual report is reviewed internally at the Illinois State Water Survey and externally by NADP scientists. The QA and NADP information is summarized and presented regularly in reports and at semiannual NADP meetings by scientists worldwide.

Each year the CAL participates in three to five interlaboratory comparison studies not sponsored by the NADP. There were three studies in 1998: the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) intercomparison study, Geneva, Switzerland and two intercomparisons conducted by the National Water Research Institute (NWRI), Burlington, Ontario, Canada.

A. World Meteorological Organization/Global Atmospheric Watch

The 21st set of WMO/GAW reference precipitation samples was shipped to participating laboratories in July 1998. In 1998, the CAL was the contracted to prepare the simulated precipitation samples used in this study. Samples were shipped to 96 laboratories, and 64 laboratories reported results to the WMO Quality Assurance/Science Activity Center for the Americas located at the Atmospheric Science Research Center in Albany, NY (Coleman et al., 1999). Because the samples were prepared at the CAL and the CAL analysts confirmed the target concentrations, the analytical results obtained by the CAL during the actual study were not included in the study's final report. Table VI-1 presents the target values, the mean obtained by all the participating laboratories with outliers statistically identified and removed, and the concentrations measured at the CAL during the actual study. Because the CAL was not included with the study laboratories, the results from the CAL were not ranked; however, the CAL results agreed very closely with the mean found in the study and with 82 percent of the target values.

B. National Water Research Institute

The CAL participated in both studies sponsored by the NWRI in Burlington, Ontario, Canada. Begun in 1982 as the Long-Range Transport of Atmospheric Pollutants (LRTAP) program, the studies for 1998 were numbers 0072 and 0073 (Alkema and Hjelm, 1998; Alkema, 1998). The NWRI samples included selected major ions, nutrients, and physical parameters in natural waters. Median concentrations from all reporting laboratories were used as target values. Most samples were surface waters or precipitation samples for which calculated or certified values were not known. Results that were high, very high, low, or very low were noted. These flags were based on the biases observed from the calculated target values and the biases of the other laboratories. A score was computed from these flagged samples. Zero, therefore, denoted the optimum score indicating that all parameters were within the expected range of the target values.

Table VI-1. World Meteorological Organization/Global Atmospheric Watch (WMO-GAW) Acid Rain Performance Survey, 1998

Analyte	*Units*	*Sample 1*			*Sample 2*			*Sample 3*		
		Target	*Mean*	*CAL*	*Target*	*Mean*	*CAL*	*Target*	*Mean*	*CAL*
Calcium	mg Ca/L	0.136	0.139	0.133	0.060	0.058	0.060	0.056	0.053	0.055
Magnesium	mg Mg/L	0.020	0.021	0.020	0.024	0.024	0.024	0.020	0.021	0.020
Sodium	mg Na/L	0.252	0.248	0.249	0.248	0.244	0.241	0.252	0.243	0.246
Potassium	mg K/L	0.084	0.084	0.085	0.076	0.072	0.077	0.076	0.073	0.078
Ammonium	mg NH_4/L (as N)	0.62	0.63	0.61	0.11	0.11	0.11	0.61	0.61	0.61
Sulfate	mg SO_4/L (as S)	2.65	2.60	2.61	0.55	0.54	0.53	4.14	4.06	4.08
Nitrate	mg NO_3/L (as N)	0.12	0.12	0.11	0.14	0.14	0.14	0.11	0.11	0.11
Chloride	mg Cl/L	0.64	0.64	0.64	0.39	0.40	0.38	0.36	0.36	0.35
pH	pH units	3.92	3.91	3.95	4.51	4.52	4.52	3.71	3.68	3.73
Hydrogen ion	µequiv/L	120.2	123.0	112.2	30.9	30.2	30.2	195.0	208.9	186.2
Specific Conductance	µS/cm	63.5	61.4	62.4	17.0	16.7	17.1	99.6	97.1	98.2

Note:
Target values are based on theoretical concentrations of solutions. Mean values are based on participating laboratories with the WMO/GAW Acid Rain Performance Survey. The CAL values were not included in the mean concentrations calculations, since the CAL prepared the samples and confirmed the concentrations.

Tables VI-2 and VI-3 show the median results and the CAL results for both studies. For Study 0072, the CAL had one high pH flag out of the ten samples, ten parameters per sample reported. For laboratories reporting more than two parameters, the CAL had the fewest percentage of results flagged. For Study 0073 the CAL had five results flagged: one low magnesium, two low and one very low calcium, and one low sodium. The low sodium, low magnesium, and one of the low calcium flags were all for the same sample. This sample was a precipitation/river water mix. These five flags gave the CAL a 5.32 percentage of results flagged making the CAL the 9th best laboratory out of 39 laboratories participating. Some laboratories only measure three parameters; others measure twenty per sample, which is why the percentage of flags was used.

The NWRI summarized the performance results for the past ten studies (Studies 0064–0073). The CAL received a median score of 2.6 based on the percentage of biased parameters and flagged results on the studies. This was the second lowest score based on the 37 laboratories ranked and was rated “good”.

Table VI-2. National Water Research Institute Soft Water Interlaboratory Study FP72, March and April 1998

		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	0.617	0.610	0.913	0.918	0.173	0.169	0.276	0.271	0.122	0.122
Magnesium	mg/L	0.170	0.170	0.320	0.319	0.033	0.033	0.068	0.067	0.038	0.037
Sodium	mg/L	0.074	0.073	0.036	0.036	0.107	0.104	0.068	0.068	0.166	0.164
Potassium	mg/L	0.020	0.016	0.036	0.035	0.025	0.026	0.030	0.028	0.030	0.030
Ammonium	mg NH_4/L (as N)	0.17	0.16	0.003	<0.02	0.18	0.17	0.22	0.21	0.13	0.12
Sulfate	mg SO_4/L (as S)	1.31	1.31	1.81	1.81	1.59	1.56	1.61	1.60	8.99	8.75
Nitrate	mg NO_3/L (as N)	0.27	0.27	0.52	0.54	0.21	0.21	0.24	0.24	2.77	2.82
Chloride	mg/L	0.15	0.15	0.10	0.10	0.19	0.19	0.14	0.14	0.31	0.30
pH	pH units	5.96	5.92	5.34	5.27	4.63	4.63	4.80	4.80	3.45	3.49
conductivity	µS/cm	17.0	18.4	19.0	19.1	33.7	34.6	22.0	22.5	42.8	43.0

		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	0.162	0.164	1.900	1.905	0.510	0.510	2.810	2.820	2.960	2.997
Magnesium	mg/L	0.030	0.029	0.550	0.554	0.365	0.359	0.575	0.578	0.670	0.678
Sodium	mg/L	0.070	0.065	0.220	0.221	2.625	2.578	0.111	0.108	3.929	3.867
Potassium	mg/L	0.028	0.027	0.060	0.064	0.230	0.232	0.170	0.178	0.381	0.387
Ammonium	mg NH_4/L (as N)	0.17	0.16	0.005	<0.02	0.004	<0.02	0.002	<0.02	0.005	<0.02
Sulfate	mg SO_4/L (as S)	1.86	1.82	2.69	2.73	3.70	3.75	1.88	1.89	1.98	1.98
Nitrate	mg NO_3/L (as N)	0.24	0.24	0.70	0.73	0.13	0.13	0.45	0.46	0.13	0.13
Chloride	mg/L	0.12	0.12	0.41	0.42	4.16	4.12	0.20	0.20	6.14	6.13
pH	pH units	4.51	4.50	6.39	6.45	4.59	4.60	6.95	7.00	6.69	6.95
Conductivity	µS/cm	8.6	8.7	12.0	13.0	14.0	14.9	12.2	13.2	152.0	157.2

Table VI-3. National Water Research Institute Soft Water Interlaboratory Study FP73, September and October 1998

		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	1.980	1.879	2.620	2.380	4.650	4.175	0.401	0.385	0.960	0.924
Magnesium	mg/L	0.310	0.302	0.922	0.880	0.834	0.782	0.398	0.400	0.200	0.195
Sodium	mg/L	0.596	0.600	0.268	0.272	0.552	0.555	2.700	2.633	0.098	0.097
Potassium	mg/L	0.410	0.418	0.142	0.159	0.196	0.202	0.230	0.241	0.040	0.039
Ammonium	mg/NH$_4$/L (as N)	0.01	<0.02	0.18	0.17	0.30	0.30	0.004	<0.02	0.002	<0.02
Sulfate	mg/SO$_4$/L (as S)	5.50	5.54	5.27	5.27	5.92	5.95	2.28	2.30	0.24	0.24
Nitrate	mg/NO$_3$/L (as N)	0.41	0.42	2.07	2.10	0.87	0.89	0.07	0.07	0.02	0.02
Chloride	mg/L	0.45	0.44	0.52	0.52	0.52	0.52	4.39	4.43	0.10	0.10
pH	units	5.38	5.35	4.49	4.51	7.00	7.13	5.50	5.51	6.70	6.56
conductivity	µS/cm	23.5	23.5	43.4	43.8	40.8	39.8	24.2	24.2	7.4	7.3

		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	0.610	0.589	1.510	1.445	3.550	3.242	1.420	1.344	0.359	0.343
Magnesium	mg/L	0.176	0.172	0.270	0.263	0.900	0.832	0.290	0.282	0.200	0.194
Sodium	mg/L	0.067	0.068	0.056	0.056	1.73	1.615	0.141	0.142	1.320	1.280
Potassium	mg/L	0.018	0.017	0.022	0.024	0.250	0.256	0.054	0.055	0.124	0.130
Ammonium	mg/NH$_4$/L (as N)	0.09	0.08	0.002	<0.02	0.002	<0.02	0.004	<0.02	0.11	0.10
Sulfate	mg/SO$_4$/L (as S)	1.38	1.37	1.55	1.54	4.70	4.75	6.98	6.86	1.72	1.72
Nitrate	mg/NO$_3$/L (as N)	0.32	0.32	0.48	0.49	0.86	0.90	0.03	0.03	0.09	0.09
Chloride	mg/L	0.16	0.15	0.15	0.15	3.12	3.15	0.16	0.15	2.03	2.03
pH	units	5.47	5.49	6.43	6.52	6.67	6.77	4.35	4.36	5.36	5.38
conductivity	µS/cm	8.9	8.9	12.6	12.4	39.9	39.2	32.3	31.9	15.3	15.2

VII. SUMMARY

This report summarizes the results from the QA program in place at the Central Analytical Laboratory (CAL) of the NADP/NTN and NADP/AIRMoN in 1998. Information about the quality of the data generated at the CAL is presented in the form of tables, figures, and brief written explanations. Appendices A and B provide supplemental information.

Quality assurance activities that occurred on a daily basis included the operation, standardization, and maintenance of the scientific instrumentation used to analyze samples and provide data. Daily records documented reagent and standards preparation and instrument performance and maintenance. Standardization curves were verified using internally formulated CAL synthetic rain samples approximating the 25th and 75th percentile concentration levels of the NADP network (FR25 and FR75). The analytical values of these and other QCS solutions were recorded and used to construct daily and weekly control charts. The QCS data indicated that all parameters measured at the CAL were within the bias and precision target specifications as written in the NADP Quality Assurance Plan (Simmons et al., 1990).

The internal blinds program provided bias and precision data that more closely represent wet deposition data and evaluate the contribution of the sample handling, filtration, and measurement processes to the sample chemistry. Bias and precision numbers were higher for the internal blinds than for the QCS samples which was due in part to random location of the blinds in the sample queue. The analysts knew the QCS sample concentrations and analysis location, but they did not know the concentrations and locations in the analysis queue of internal blind samples.

In 1998, internal blind solutions that consisted of DI water and pH 4.3 nitric acid indicated little or no sample carryover during the analysis or no false positives. Also in 1998, it was observed that filtration increased variability in the chemistry of all samples and generated a slight positive calcium bias. The sodium bias caused by Millipore™ filters was eliminated with the change to Gelman® filters.

Replicate network samples served to monitor the precision of precipitation sample analyses. Comparison of replicate samples with QCS and internal blind solutions showed that the replicate samples had equal or slightly less variation for all the parameters measured at the CAL.

The DI water and filter and container leachates were analyzed weekly to detect the presence of contamination and determine whether the sample chemistry was compromised by either the filtration process or contact with any of the containers. Three sources throughout the laboratory provided DI water with pH of about 5.6 pH units and conductivity near 1 µS/cm. Filters leached with DI water and FR25 showed that the filtrates contained no measurable amount of any of the parameters measured. Bucket leachates showed slight elevations only for sodium. This is in contrast with the results for 1996-1997 when bucket leachates showed slight elevations in calcium, sodium, and potassium. A dilution effect was seen when larger leachate volumes were used. One-liter bottle leachates were virtually clean except for potassium. The snap-on lids may have contributed to the sodium concentrations causing a positive bias. Normal operations at most sites provide little or no sample contact with the lid used to cap the bucket for transport to the laboratory. The AIRMoN bottle blanks contained no contamination.

The AIRMoN internal blind program is a cooperative project between the Bondville, Illinois site operator and the AIRMoN coordinator. The results for the analyses of these samples showed that the precision for the solutions used in 1998, pH 4.3 nitric acid QCS and the WMO/GAW sample #2, were within the data quality objectives of the Network QAP for all parameters. The precision of the pH 4.3 nitric acid QCS was comparable to that same solution, unfiltered, in the NADP/NTN internal blind program.

After analyses, sample data were transferred in batches to data management, which compiled semimonthly printouts containing the data for 400 or 500 samples. Those samples designated "wet" ("W", volume greater than 35 mL) or "wet-add" ("WA", volume greater than or equal to 10 mL and less than 35 mL) underwent complete chemical analyses for all parameters. Results were submitted for an ion balance and a calculated versus measured conductance comparison. Samples not meeting the required criteria (Simmons et al., 1990) were flagged and reanalyzed. Of the 6731 "W" samples, 416 were flagged for reanalysis. After evaluation of the original and reanalysis measurements, 224 original measurements from 214 samples were changed. The Ion Percent Difference (IPD) mean was negative for 1998. The median for 1998 was 0.24. This indicated an excess of cations in half or more of the wet samples analyzed. This was the reverse of what was seen prior to the 1994 change in the sample shipping protocols. Beginning in January 1994, the samples were shipped in bottles rather than in the collection bucket. It is believed that the use of a butadiene rubber gasket in the lid previously used on network samples resulted in a positive cation bias in the samples, resulting in a mean positive IPD. The Conductance Percent Difference (CPD) has been skewed negatively since 1979 and continued to be so in 1998. This means that the measured conductivity exceeds the calculated conductivity, indicating that components may be present in the precipitation samples not being measured.

The AIRMoN field blank program began in 1994, and field blanks are collected monthly at all sites. Four solutions (DI water, pH 4.3 nitric acid, FR25, and FR75) were used in 1998. Twelve 250-mL bottles of field blank solutions were sent to the sites. Field blanks were used on the first Tuesday of each month when there was no precipitation in the previous 26 hours and no more than six lid openings without precipitation. A field blank bottle was taken to the site from the field laboratory when the conditions were met and half of the 250 mL sample was poured into the bucket ("DF"). The original bottle with the remaining solution was immediately recapped and returned to the CAL without further opening ("DK"). The solution that was poured into the bucket was kept in the bucket for at least two hours or overnight and was then treated like a normal precipitation sample. Both "DK" and "DF" samples were returned to the CAL along with a completed Field Observer Form for the "DF" sample. The difference in concentrations found in the "DF" and "DK" samples indicated 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, indicated a larger difference between the two solutions than could be explained by repeat analyses alone. Higher calcium variances indicated that dry deposition is entering the sample bucket. The numbers, however, were still low compared with the concentration of the average precipitation sample.

The USGS Interlaboratory Comparison study included five laboratories in 1998. Four different sample matrices were used and shipped to the laboratories every two weeks. Half of all samples sent to the laboratories in this study are natural precipitation samples prepared (without verification of the target values) by the CAL. The 50th and 90th percentile absolute differences for these samples indicated that the CAL had excellent results, ranking first overall of the five participating laboratories. The CAL ranked first or was tied for that position for sodium, potassium, ammonium, sulfate, nitrate, and chloride analyses.

In 1998, the CAL participated in three additional interlaboratory comparisons: the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) and two studies from the Canada National Water Research Institute (NWRI). The results were good for all the studies. Sixty-four laboratories participated in the WMO/GAW study. The CAL did not submit results for the WMO/GAW samples for official inclusion in the study because the CAL prepared those samples and verified the target values. However, in comparing the numbers measured at the CAL obtained during the study to the theoretical values and the median values found from the other 64 laboratories, the CAL results were excellent. The NWRI results over the last ten studies indicate that the CAL is ranked second overall of 37 reporting laboratories. The CAL received one high pH flag for Study 0072 giving the CAL the fewest number of flags assigned for all laboratories reporting more than two parameters. For Study 0073, the CAL received five low or very low flags of which three flags were for the same solution. All flags were for cations measured by atomic absorption. These flags resulted in the CAL being ranked ninth out of 39 laboratories based on the number of flags received. The CAL continues to compare 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 = True value - Measured mean 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 (Taylor, 1987).
Critical Concentration		A calculated concentration used to determine whether the measured bias is statistically significant (Anderson, 1987). 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 Quality Assurance 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 Quality Assurance 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. $\bar{x} = \sum_{i=1}^{n} x_i / n$ where: n = number of values x_i = values
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 (Glaser et al; 1981).
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 = mean 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: $RSD = 100 * (s/\overline{x})$ where: s = sample standard deviation $\overline{x}$ = 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 Paired Measurements		The standard deviation may be estimated from the differences of several sets of paired measurements using the equation (Taylor, 1987): $s = \sqrt{\frac{\sum d^2}{2k}}$ 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). $s^2 = \frac{\sum d^2}{2n}$ where d = $X_i - X'_i$, the difference between value 1 and 2 of pair i n = the number of pairs of data

APPENDIX B

WEEKLY QA/QC PROCEDURES: TABLES AND FIGURES

1998

Table B-1. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, High Purity Standards Simulated Rainwater I (H-PS SRI), 1998

Parameter	*Target Concentrations*[a] *(mg/L)*	*Measured Concentrations (mg/L)*	*Bias (mg/L)*	*Bias %*	*Standard Deviation (mg/L)*	*RSD %*
Calcium	0.015	0.031[b]	0.016	109.6	0.010	31.7
		0.047[c]	0.032	215.2	0.009	19.7
Magnesium	0.019	0.026	0.007	39.2	0.003	10.5
		0.028	0.009	45.2	0.004	15.6
Sodium	0.20	0.195	-0.005	-2.5	0.007	3.6
		0.189	-0.011	-5.5	0.004	1.9
Potassium	0.050	0.048	-0.002	-3.3	0.002	4.3
		0.046	-0.004	-9.0	0.001	2.8
Ammonium	0.100	0.03	-0.07	-65.9	0.04	127.4
		0.05	-0.05	-48.3	0.04	70.6
Sulfate	2.5	2.49	-0.01	-0.6	0.03	1.1
		2.40	-0.10	-4.1	0.03	1.1
Nitrate	0.50	0.50	0.00	0.5	0.02	4.0
		0.49	-0.01	-1.7	0.01	1.8
Chloride	0.25	0.22	-0.03	-11.9	0.003	1.5
		0.21	-0.04	-14.3	0.005	2.3
pH[d]	4.32	4.32	0.0	0.0	0.03	0.6
		4.32	0.0	0.0	0.03	0.6
Hydrogen ion (μeq/L)	47.9	47.9	0.0	0.0	2.79	5.8
		47.9	0.0	0.0	2.91	6.1
Conductivity[d] (μS/cm)	24.4	24.4	0.0	0.0	0.85	3.5
		24.6	0.2	0.9	0.66	2.7

Notes:

There were 27 unfiltered and 12 filtered samples, but only 11 filtered samples for calcium.

[a] Target values provided by High-Purity Standards 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 samples prior to filtering.

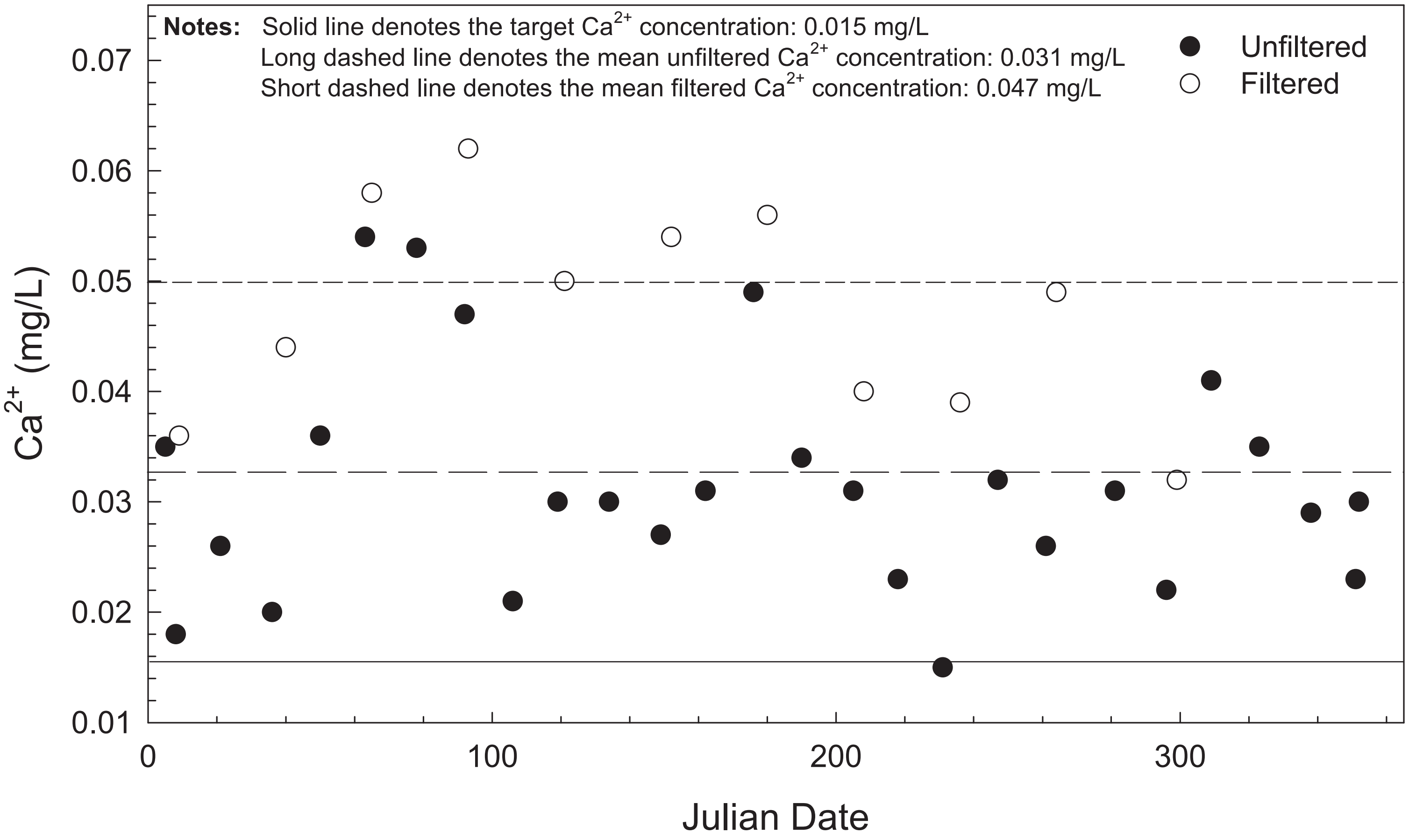
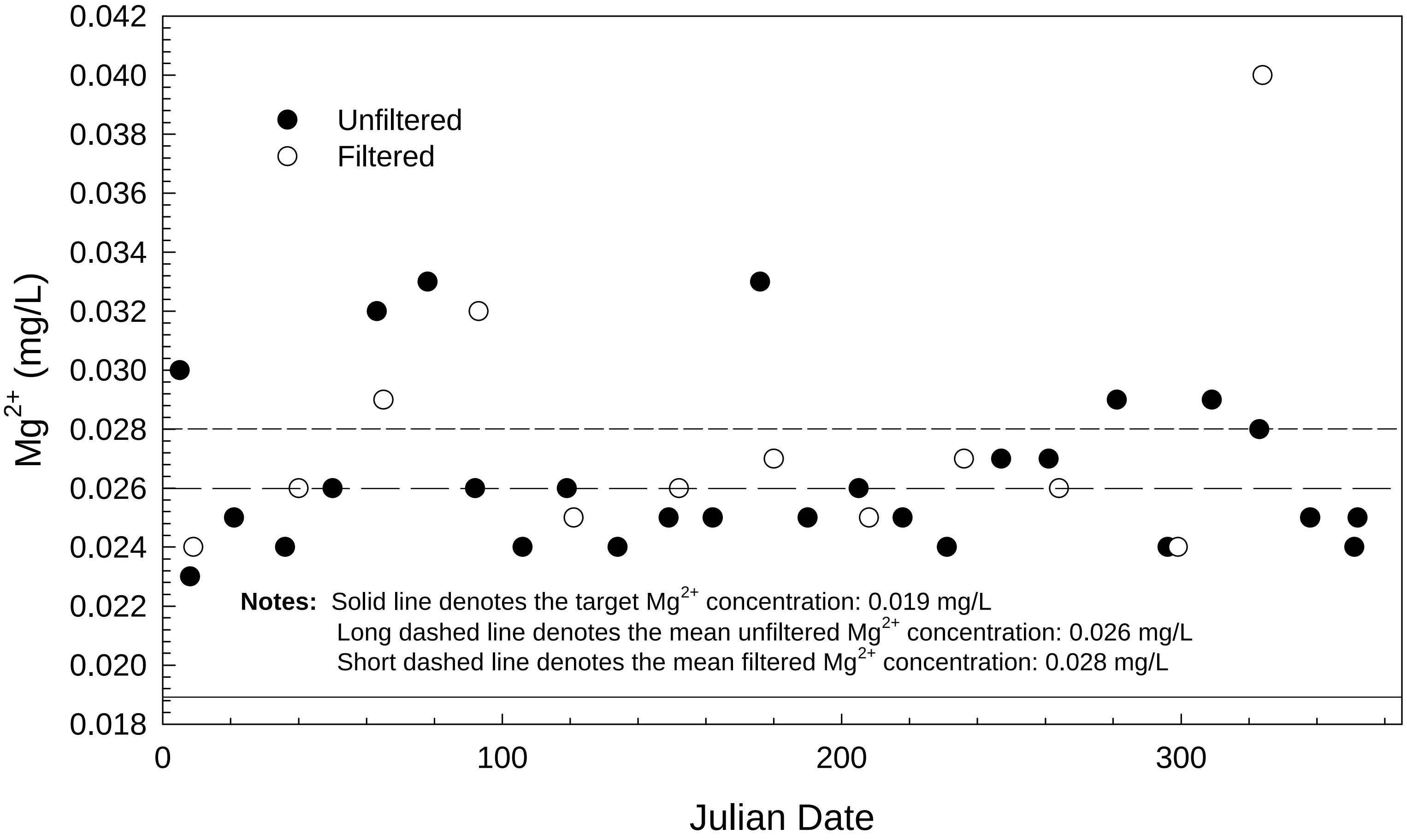
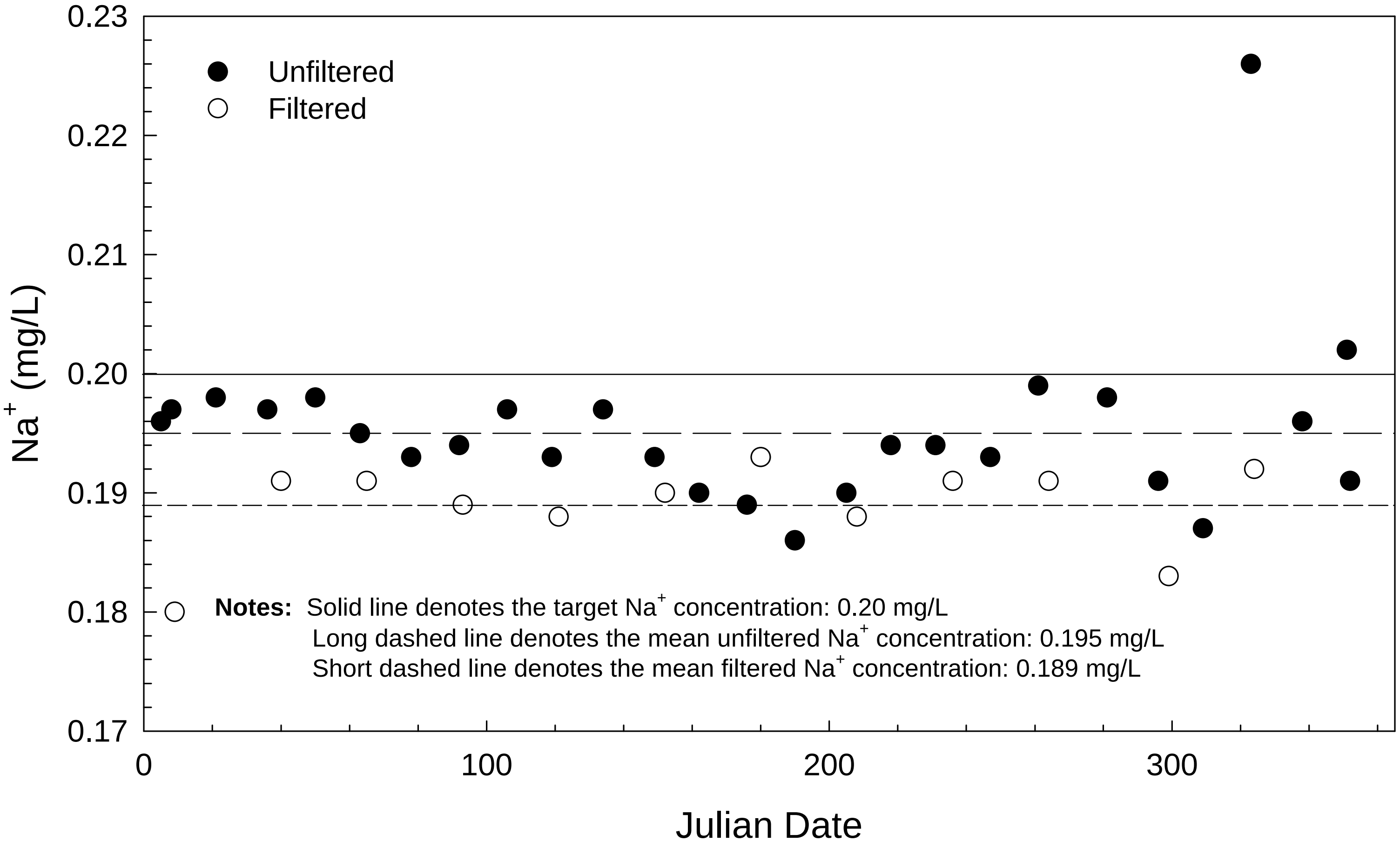


Figure B-1. Comparison of filtered and unfiltered internal blind samples, (calcium), High-Purity Standards, SR1, 1998.



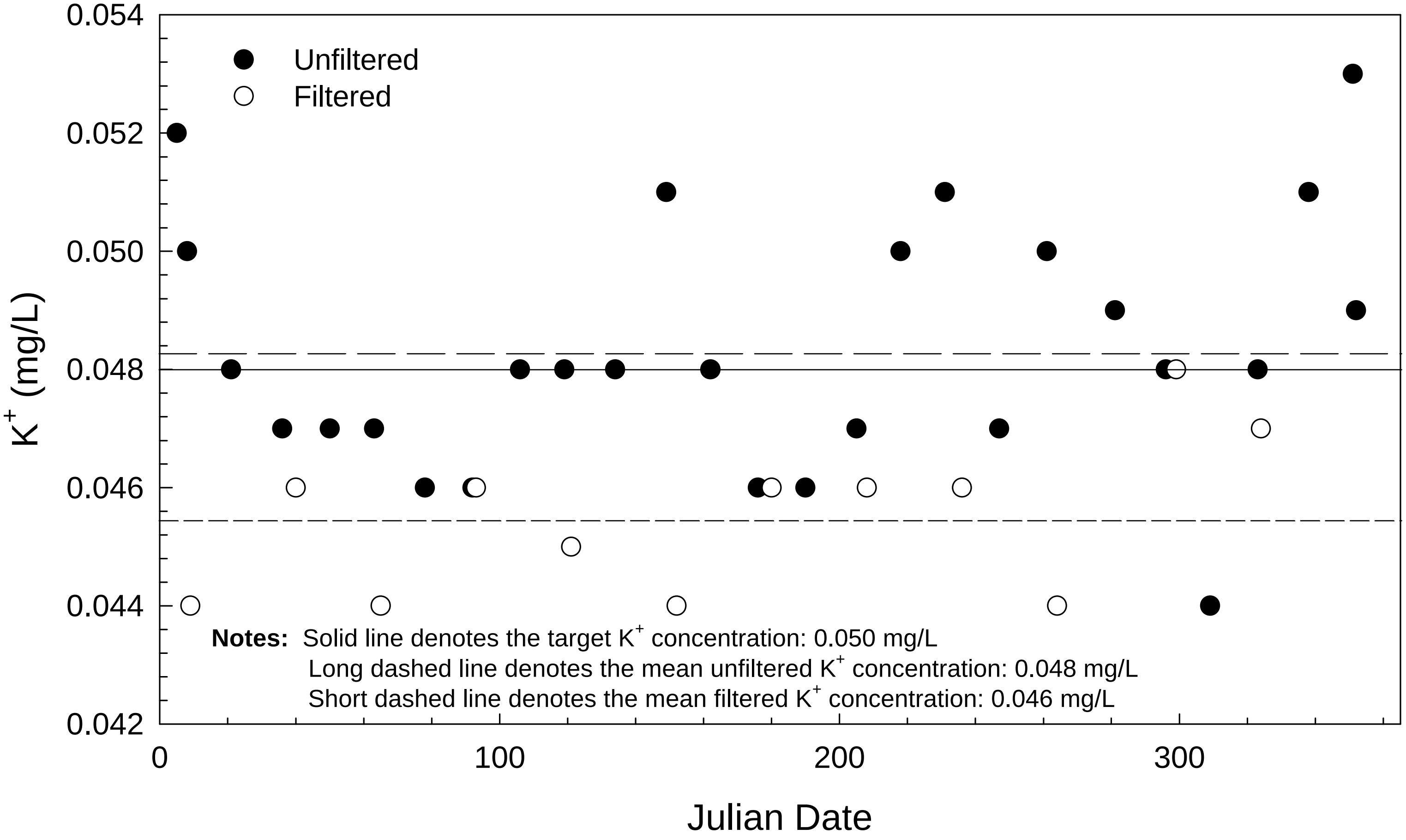
Notes: Solid line denotes the target Mg^{2+} concentration: 0.019 mg/L
Long dashed line denotes the mean unfiltered Mg^{2+} concentration: 0.026 mg/L
Short dashed line denotes the mean filtered Mg^{2+} concentration: 0.028 mg/L

Figure B-2. Comparison of filtered and unfiltered internal blind samples, (magnesium), High-Purity Standards, SR1, 1998.



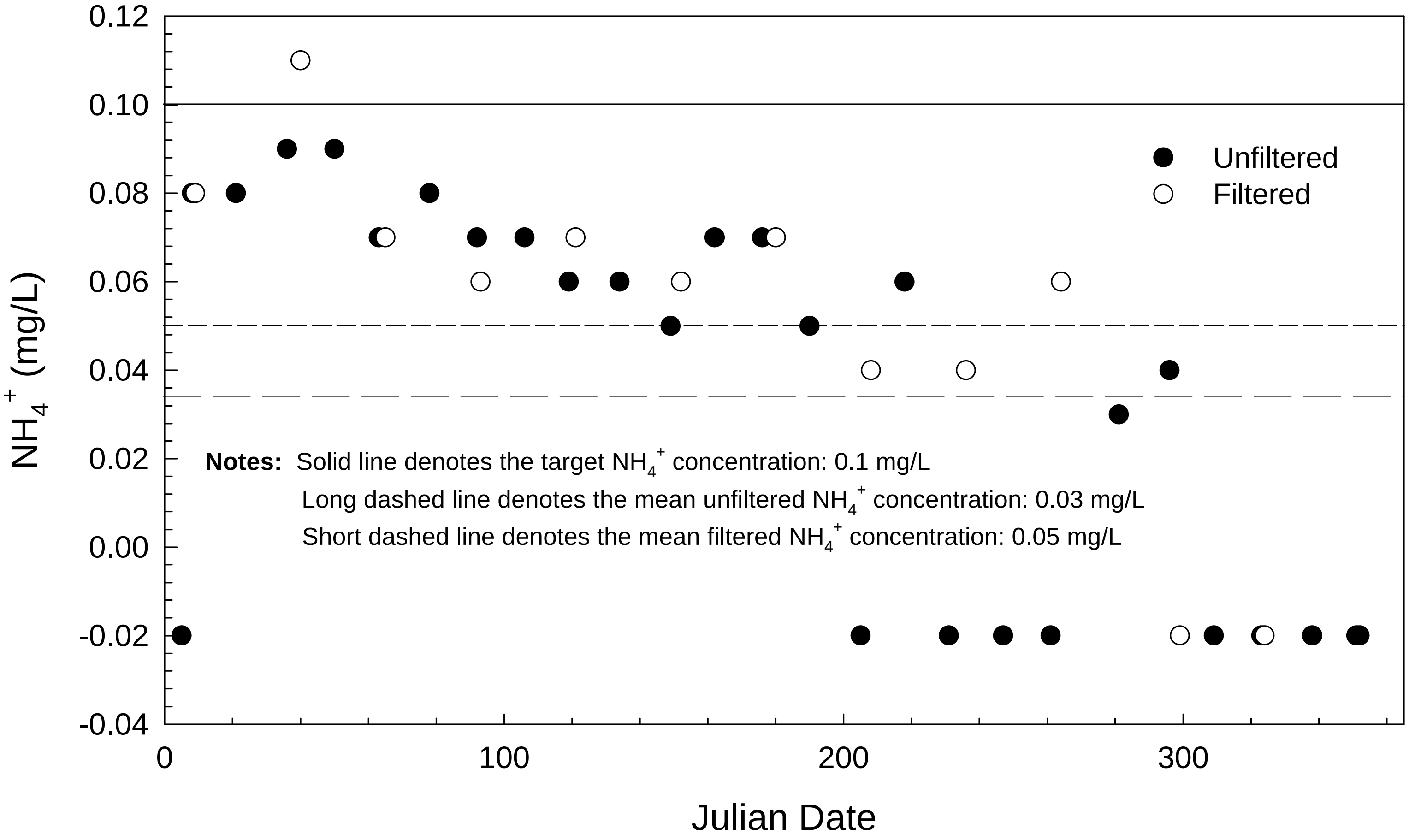
Notes: Solid line denotes the target Na^+ concentration: 0.20 mg/L
Long dashed line denotes the mean unfiltered Na^+ concentration: 0.195 mg/L
Short dashed line denotes the mean filtered Na^+ concentration: 0.189 mg/L

Figure B-3. Comparison of filtered and unfiltered internal blind samples, (sodium), High-Purity Standards, SR1, 1998.



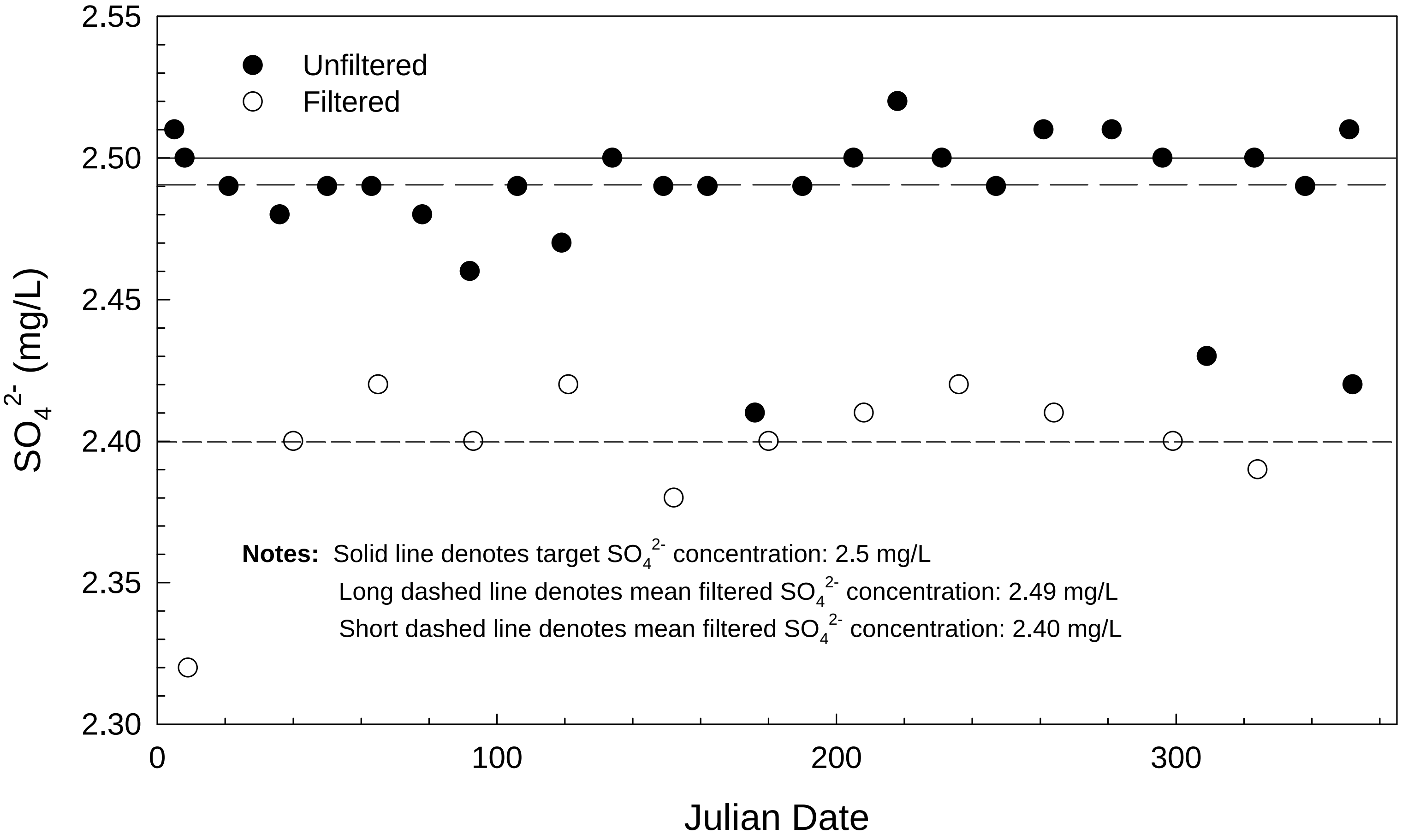
Notes: Solid line denotes the target K^+ concentration: 0.050 mg/L
Long dashed line denotes the mean unfiltered K^+ concentration: 0.048 mg/L
Short dashed line denotes the mean filtered K^+ concentration: 0.046 mg/L

Figure B-4. Comparison of fitered and unfiltered internal blind samples, (potassium), High-Purity Standards, SR1, 1998.



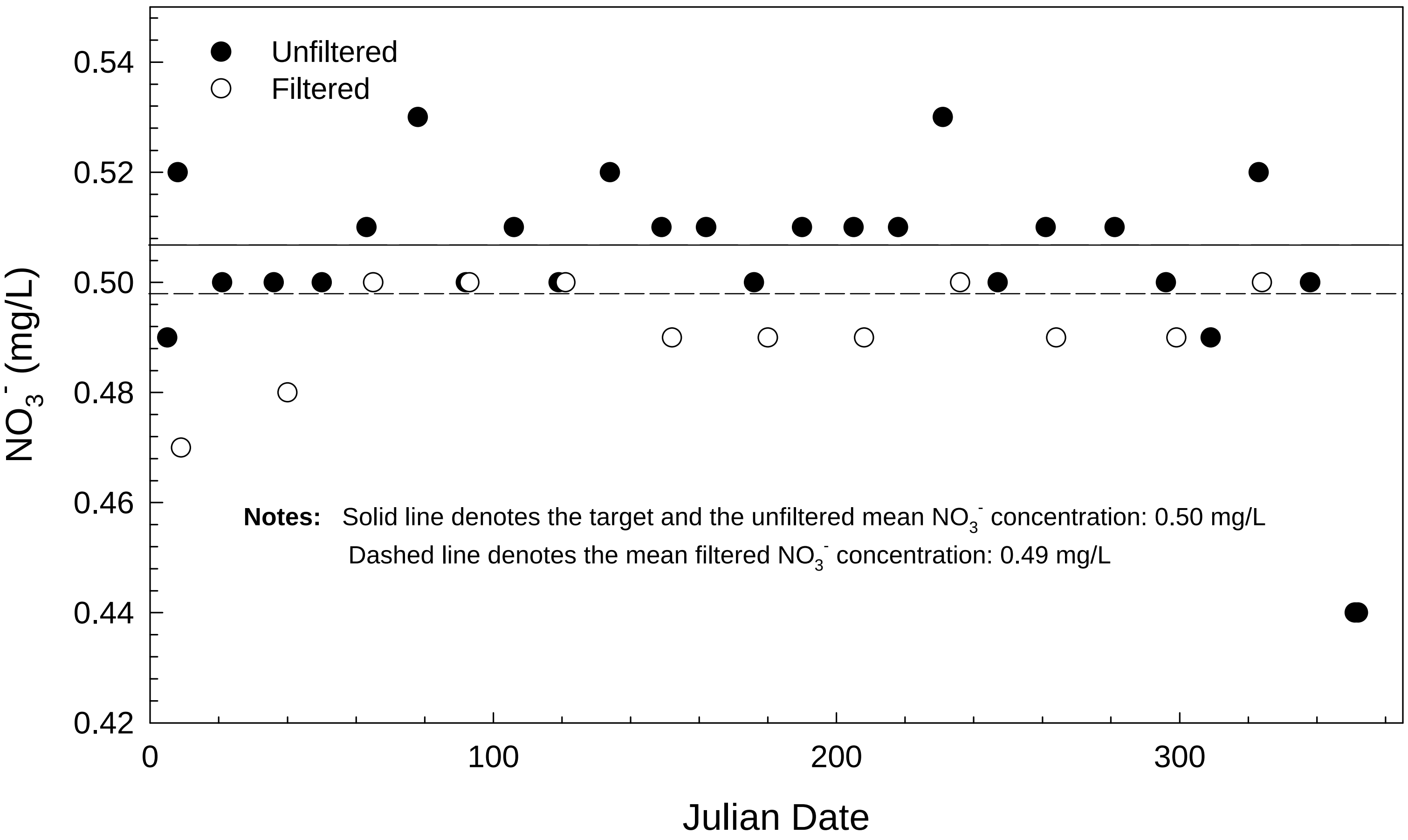
Notes: Solid line denotes the target NH_4^+ concentration: 0.1 mg/L
Long dashed line denotes the mean unfiltered NH_4^+ concentration: 0.03 mg/L
Short dashed line denotes the mean filtered NH_4^+ concentration: 0.05 mg/L

Figure B-5. Comparison of filtered and unfiltered internal blind samples, (ammonium), High-Purity Standards, SR1, 1998.



Notes: Solid line denotes target SO_4^{2-} concentration: 2.5 mg/L
Long dashed line denotes mean filtered SO_4^{2-} concentration: 2.49 mg/L
Short dashed line denotes mean filtered SO_4^{2-} concentration: 2.40 mg/L

Figure B-6. Comparison of filtered and unfiltered internal blind samples, (sulfate), High-Purity Standards, SR1, 1998.



Notes: Solid line denotes the target and the unfiltered mean NO_3^- concentration: 0.50 mg/L
Dashed line denotes the mean filtered NO_3^- concentration: 0.49 mg/L

Figure B-7. Comparison of filtered and unfiltered internal blind samples, (nitrate), High-Purity Standards, SR1, 1998.

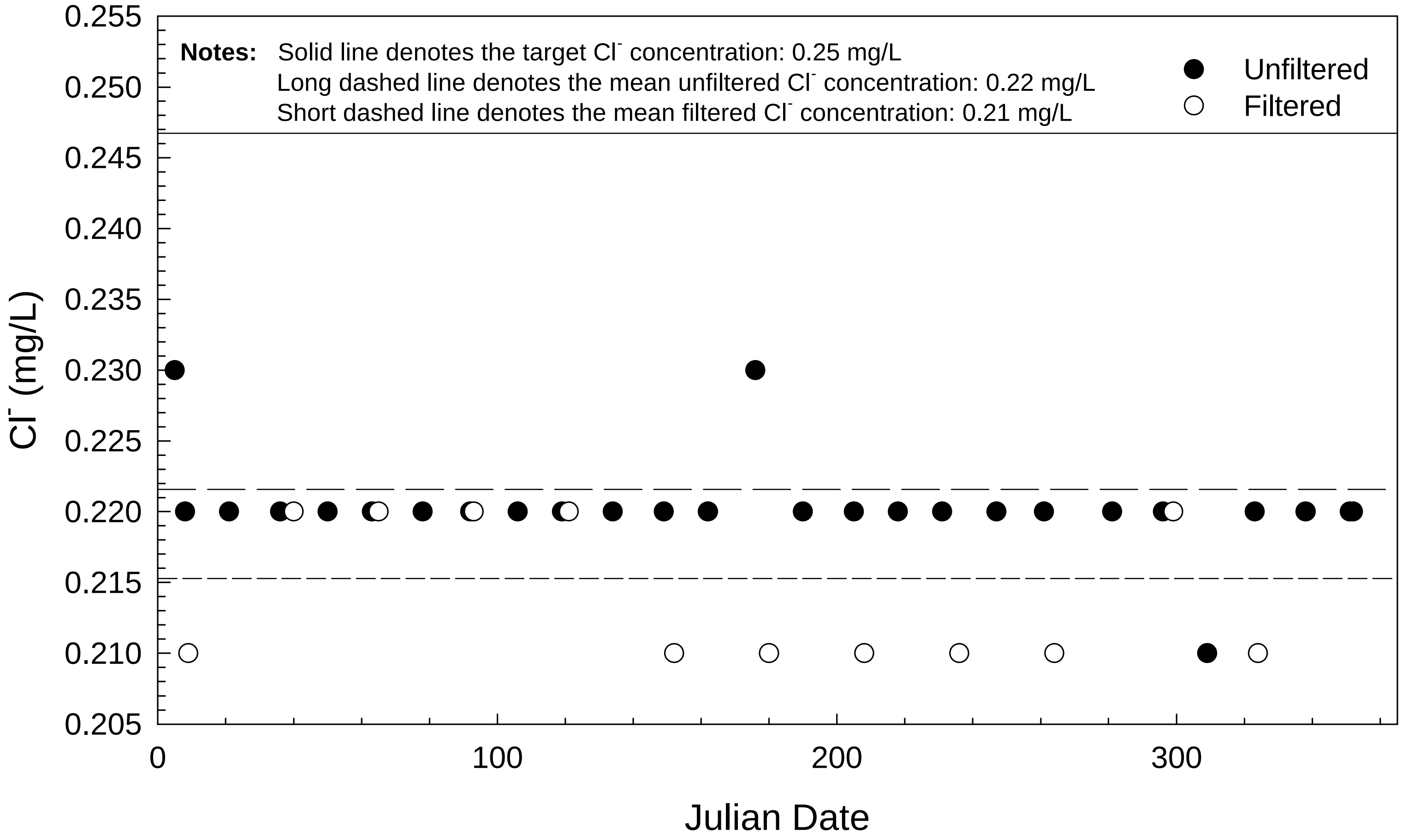


Figure B-8. Comparison of filtered and unfiltered internal blind samples, (chloride), High-Purity Standards, SR1, 1998.

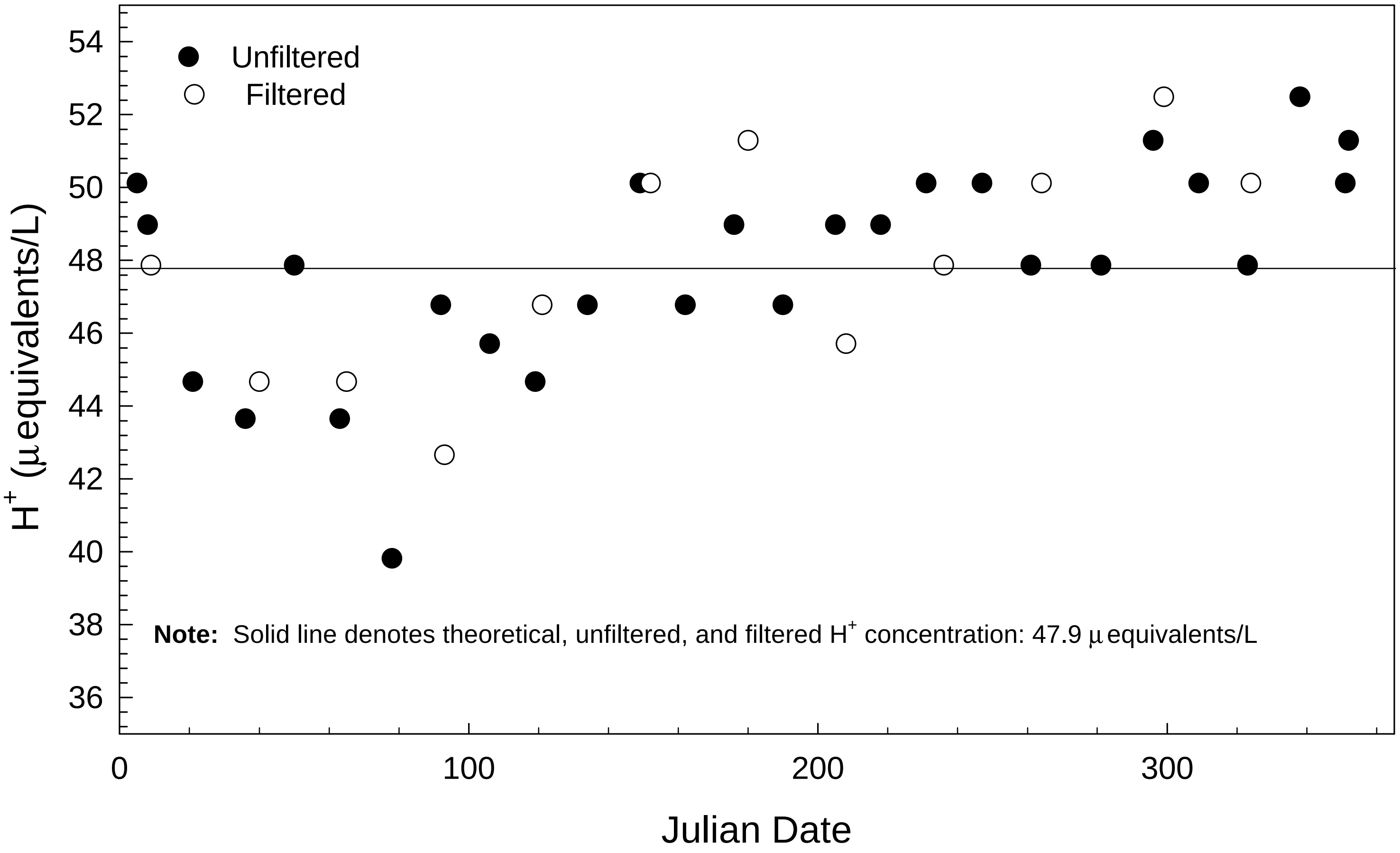


Figure B-9. Comparison of filtered and unfiltered internal blind samples, (hydrogen ion), High-Purity Standards, SR1, 1998.

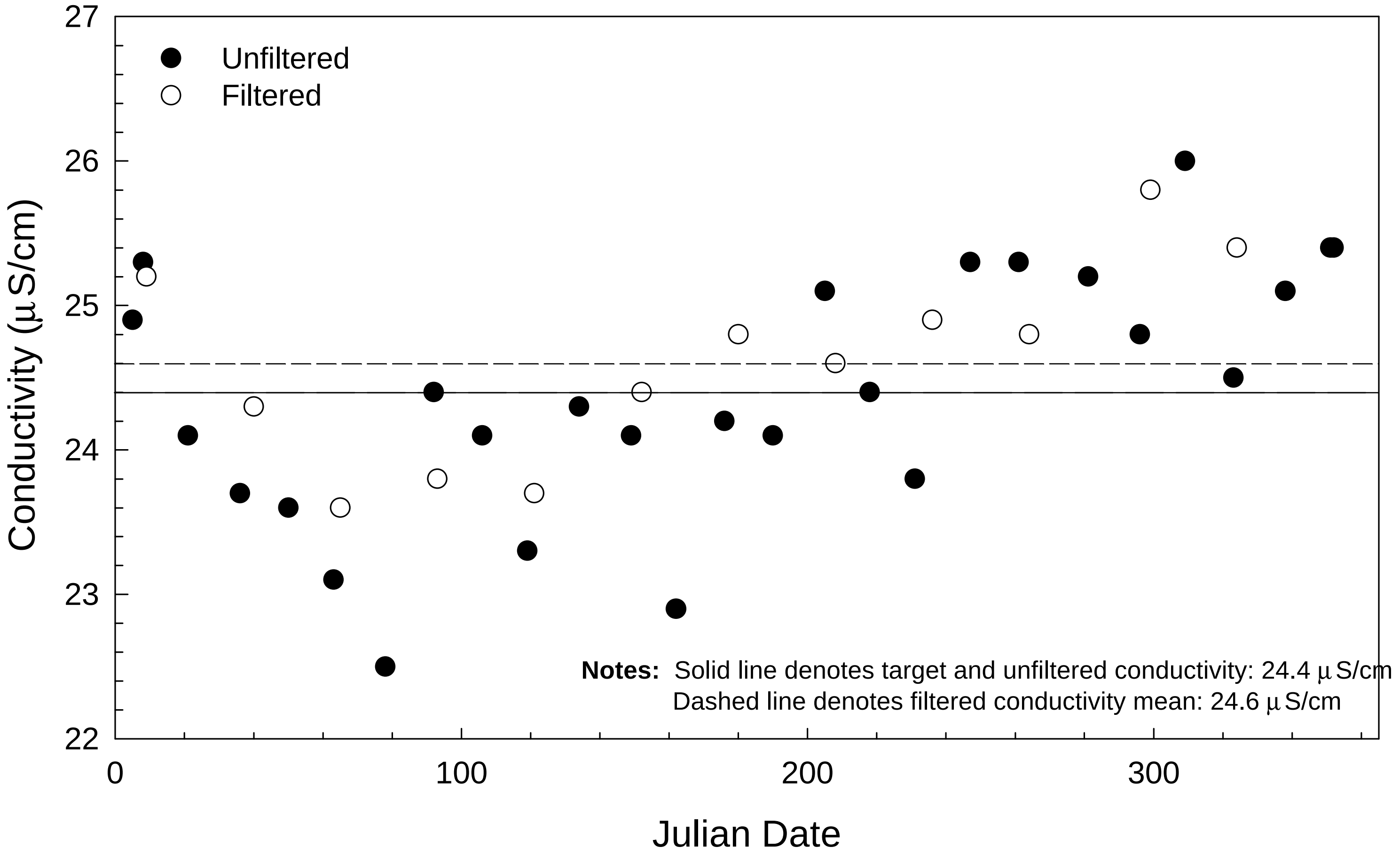


Figure B-10. Comparison of filtered and unfiltered internal blind samples, (conductivity) High-Purity Standards, SR1, 1998.

Table B-2. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, 1998

Parameter	*Target Concentrations*[a] *(mg/L)*	*Measured Concentrations (mg/L)*	*Bias (mg/L)*	*Bias %*	*Standard Deviation (mg/L)*	*RSD %*
Calcium	0.048	0.064[b]	0.016	32.4	0.015	24.3
		0.089[c]	0.041	85.9	0.016	17.6
Magnesium	0.051	0.049	-0.002	-4.6	0.002	3.3
		0.050	-0.001	-2.3	0.004	7.2
Sodium	0.39	0.395	0.005	1.4	0.011	2.7
		0.385	-0.005	-1.4	0.011	2.8
Potassium	0.093	0.101	0.008	8.1	0.002	2.1
		0.097	0.004	4.5	0.003	3.4
Ammonium	1.0	0.96	-0.04	-4.4	0.03	3.3
		0.92	-0.08	-7.5	0.03	2.9
Sulfate	10.1	10.04	-0.06	-0.6	0.10	1.0
		9.61	-0.49	-4.8	0.17	1.8
Nitrate	7.0	7.10	0.1	1.4	0.07	1.0
		6.84	-0.16	-2.2	0.13	2.0
Chloride	0.98	0.99	0.01	0.9	0.02	2.0
		0.96	-0.02	-1.6	0.02	2.2
pH[d]	3.56	3.63	0.07	1.9	0.02	0.5
		3.62	0.06	1.8	0.01	0.4
Hydrogen ion	275.4	236.6	-38.8	-14.1	9.99	4.2
(µeq/L)		237.9	-37.5	-13.6	7.92	3.3
Conductivity[d]	126.6	124.7	-1.9	-1.5	1.73	1.4
(µS/cm)		124.1	-2.5	-1.9	1.61	1.3

Notes:

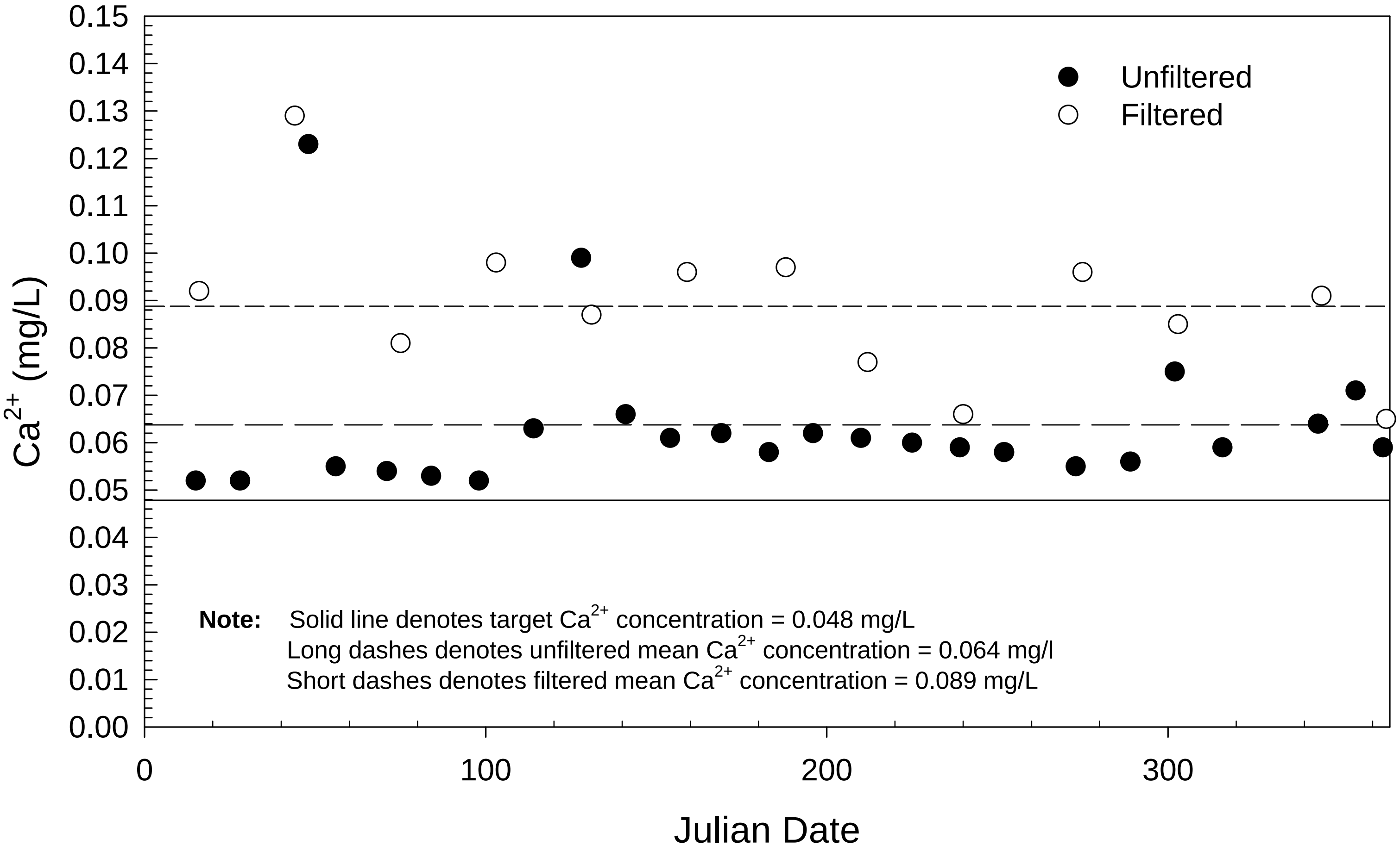
There were 25 unfiltered and 13 filtered samples, but only 11 filtered samples for calcium.

[a] Target values provided by High-Purity Standards for Simulated Rainwater 2.

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

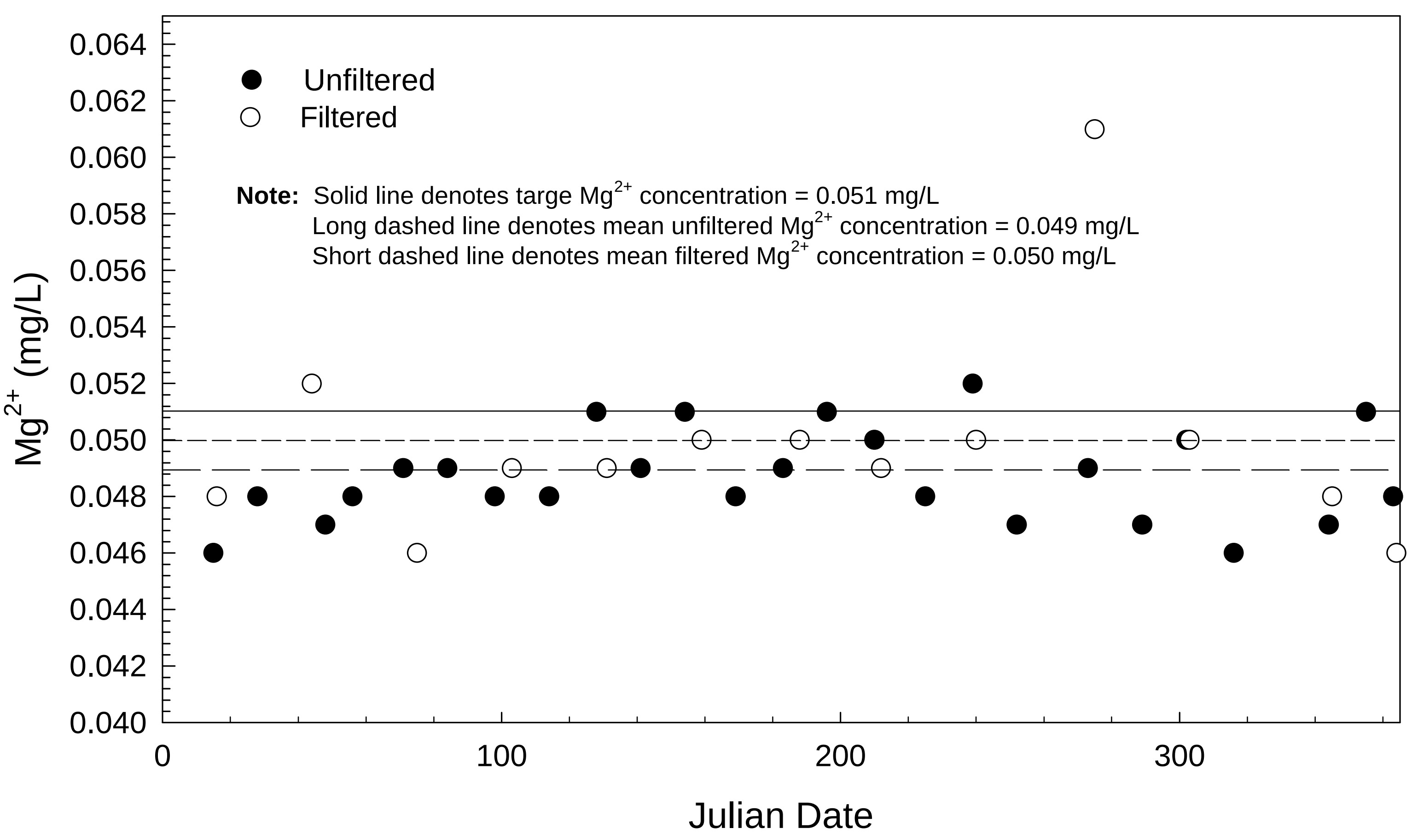
[c] The second set of values for each parameter is for filtered samples.

[d] pH and conductivity are measured on unfiltered samples prior to filtering.



Note: Solid line denotes target Ca^{2+} concentration = 0.048 mg/L
Long dashes denotes unfiltered mean Ca^{2+} concentration = 0.064 mg/l
Short dashes denotes filtered mean Ca^{2+} concentration = 0.089 mg/L

FIGURE B-11. Comparison of filtered and unfiltered internal blind samples, (calcium), High-Purity Standards, SR2, 1998.



Note: Solid line denotes targe Mg^{2+} concentration = 0.051 mg/L
Long dashed line denotes mean unfiltered Mg^{2+} concentration = 0.049 mg/L
Short dashed line denotes mean filtered Mg^{2+} concentration = 0.050 mg/L

FIGURE B-12. Comparison of filtered and unfiltered internal blind samples (magnesium), High-Purity Standards, SR2, 1998.

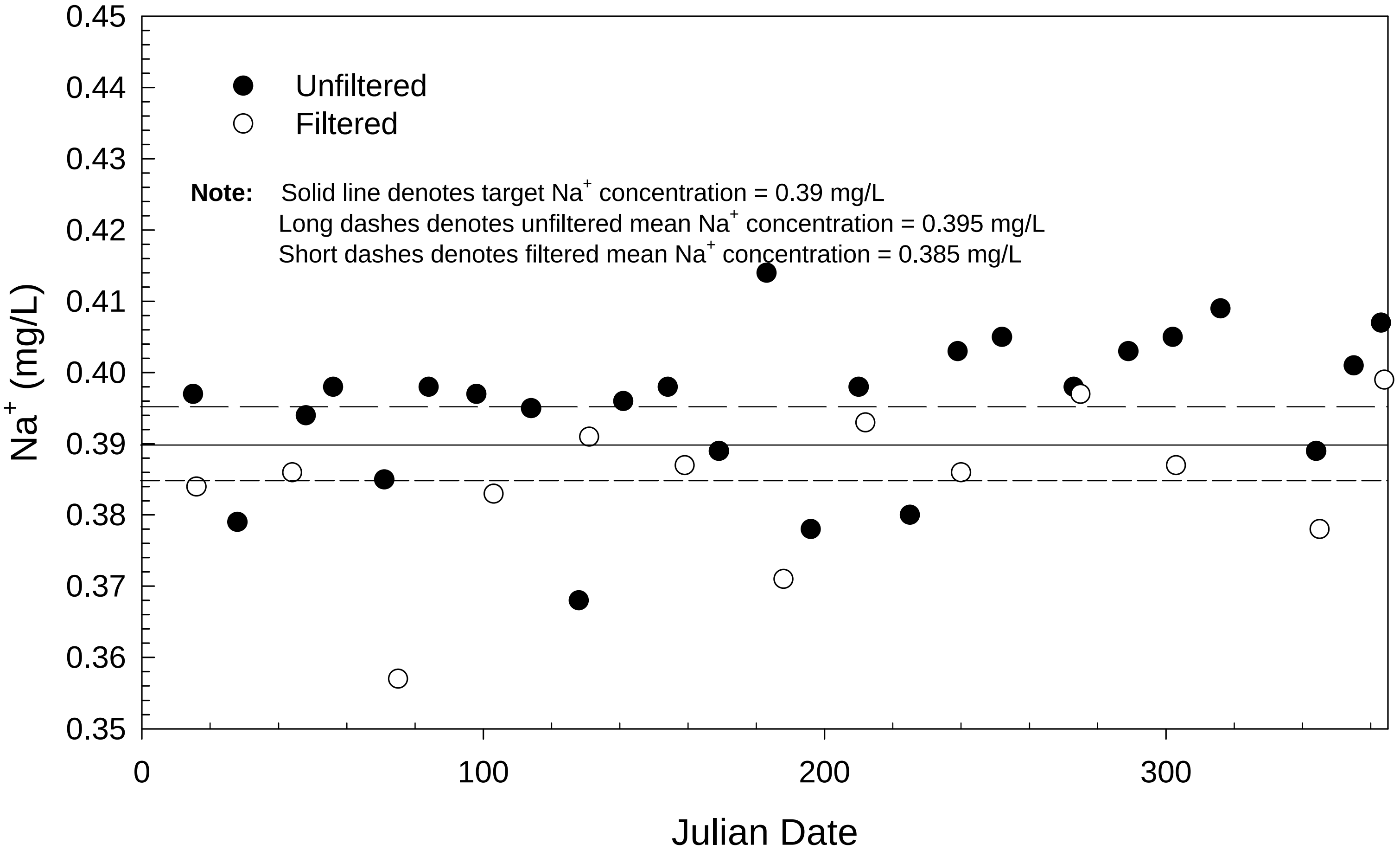
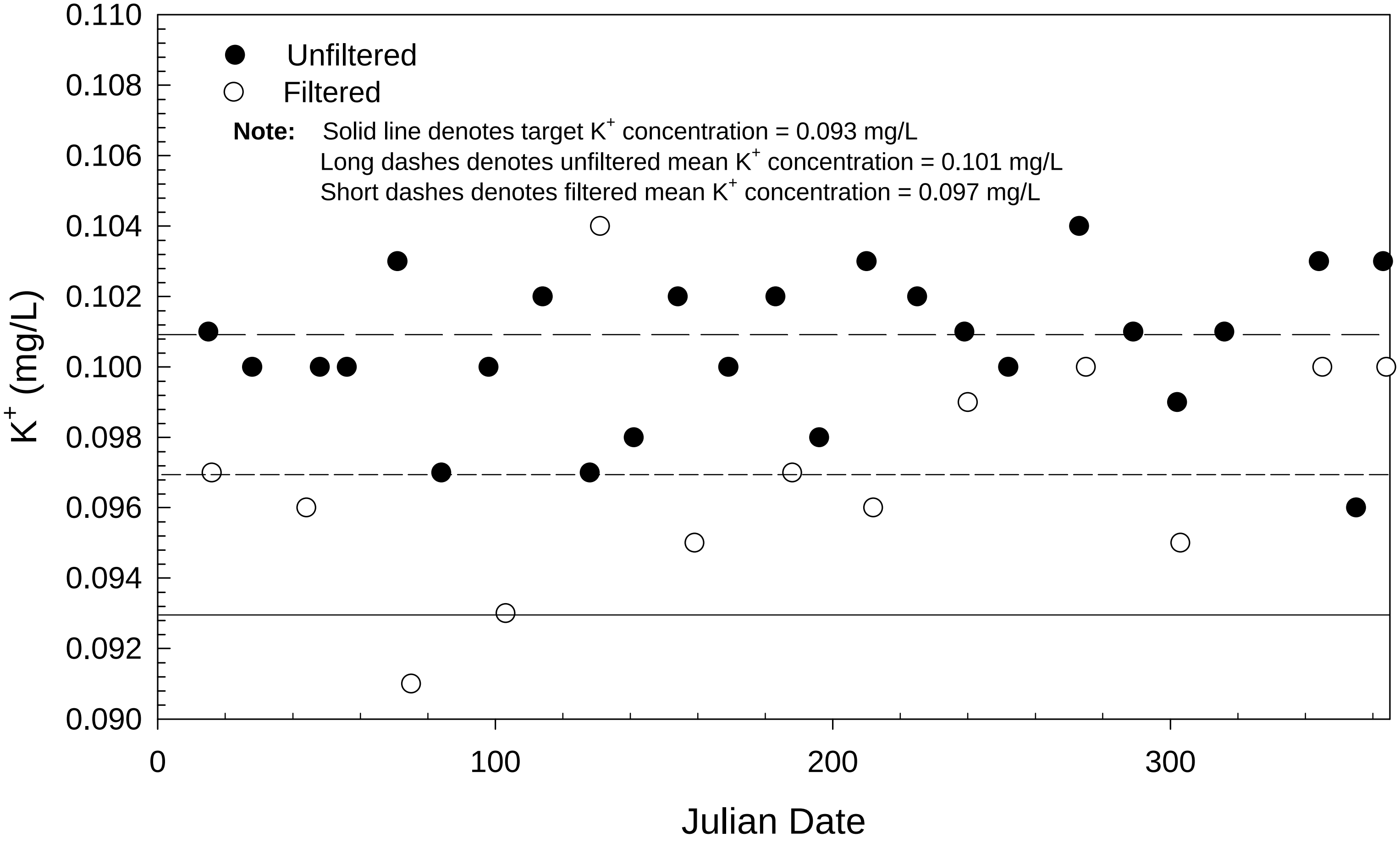


FIGURE B-13. Comparison of filtered and unfiltered internal blind samples, (sodium), High-Purity Standards, SR2, 1998.



Note: Solid line denotes target K^+ concentration = 0.093 mg/L
Long dashes denotes unfiltered mean K^+ concentration = 0.101 mg/L
Short dashes denotes filtered mean K^+ concentration = 0.097 mg/L

FIGURE B-14. Comparison of filtered and unfiltered internal blind samples, (potassium), High-Purity Standards, SR2, 1998.

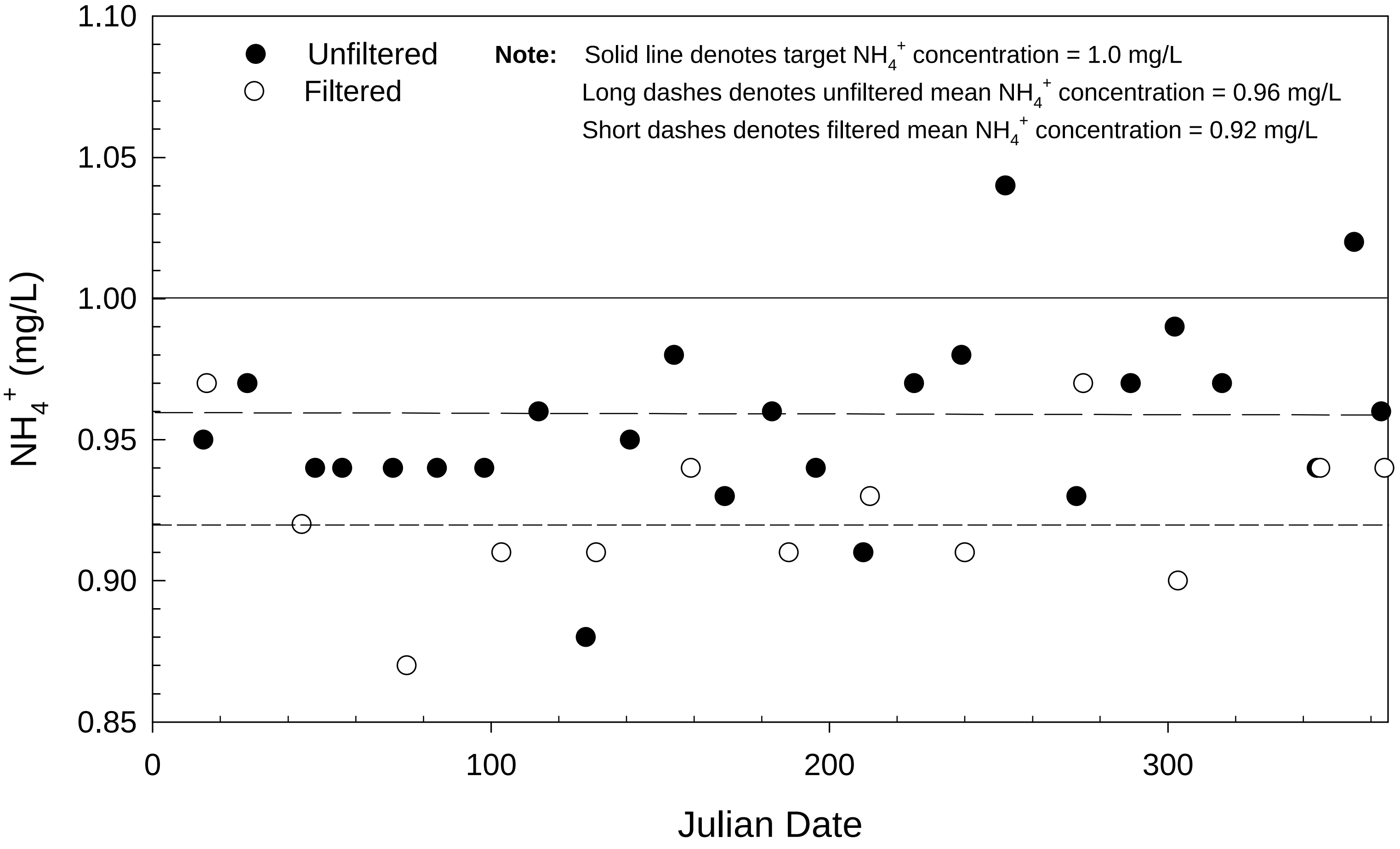


FIGURE B-15. Comparison of filtered and unfiltered internal blind samples, (ammonium), High-Purity Standards, SR2, 1998.

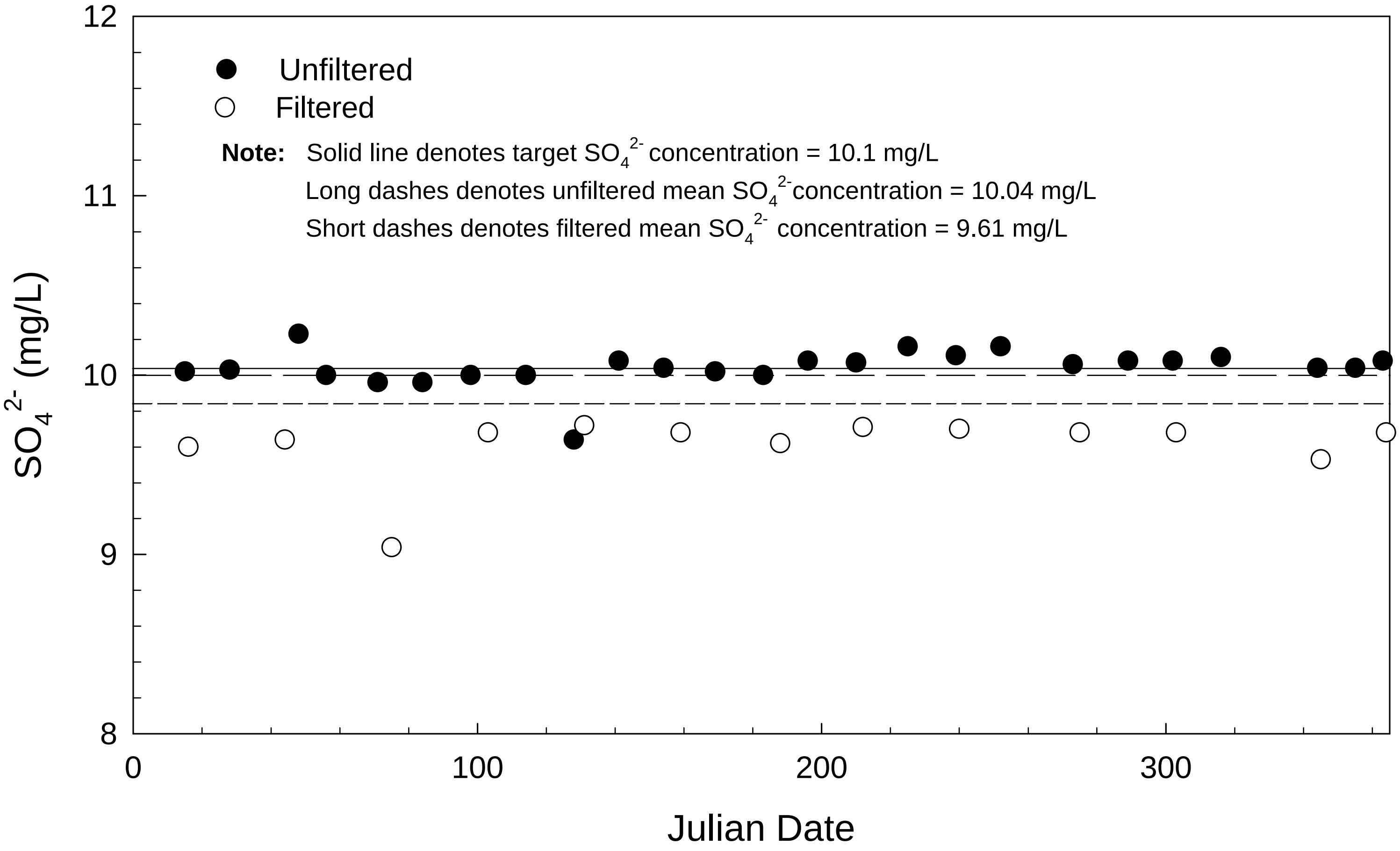
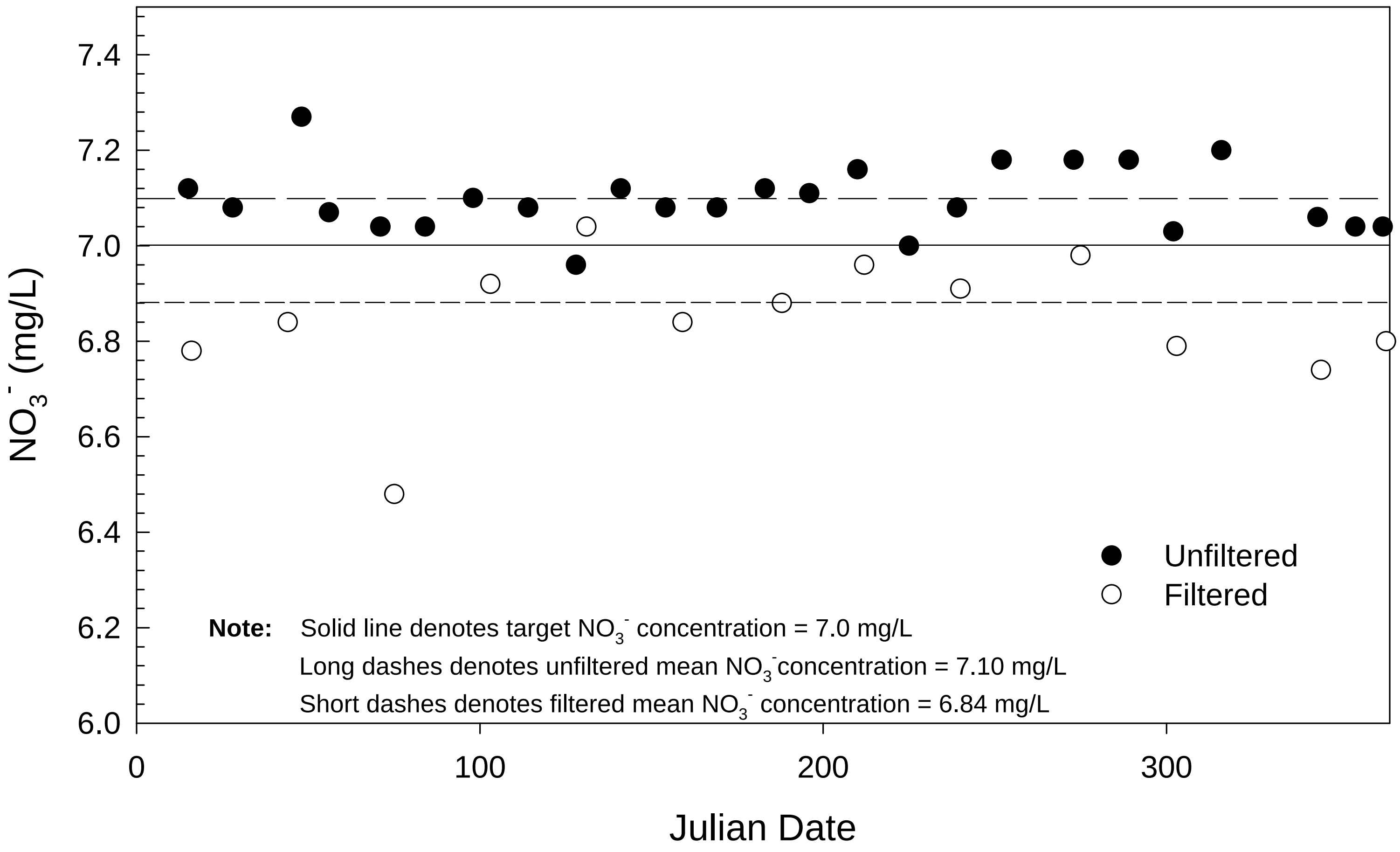
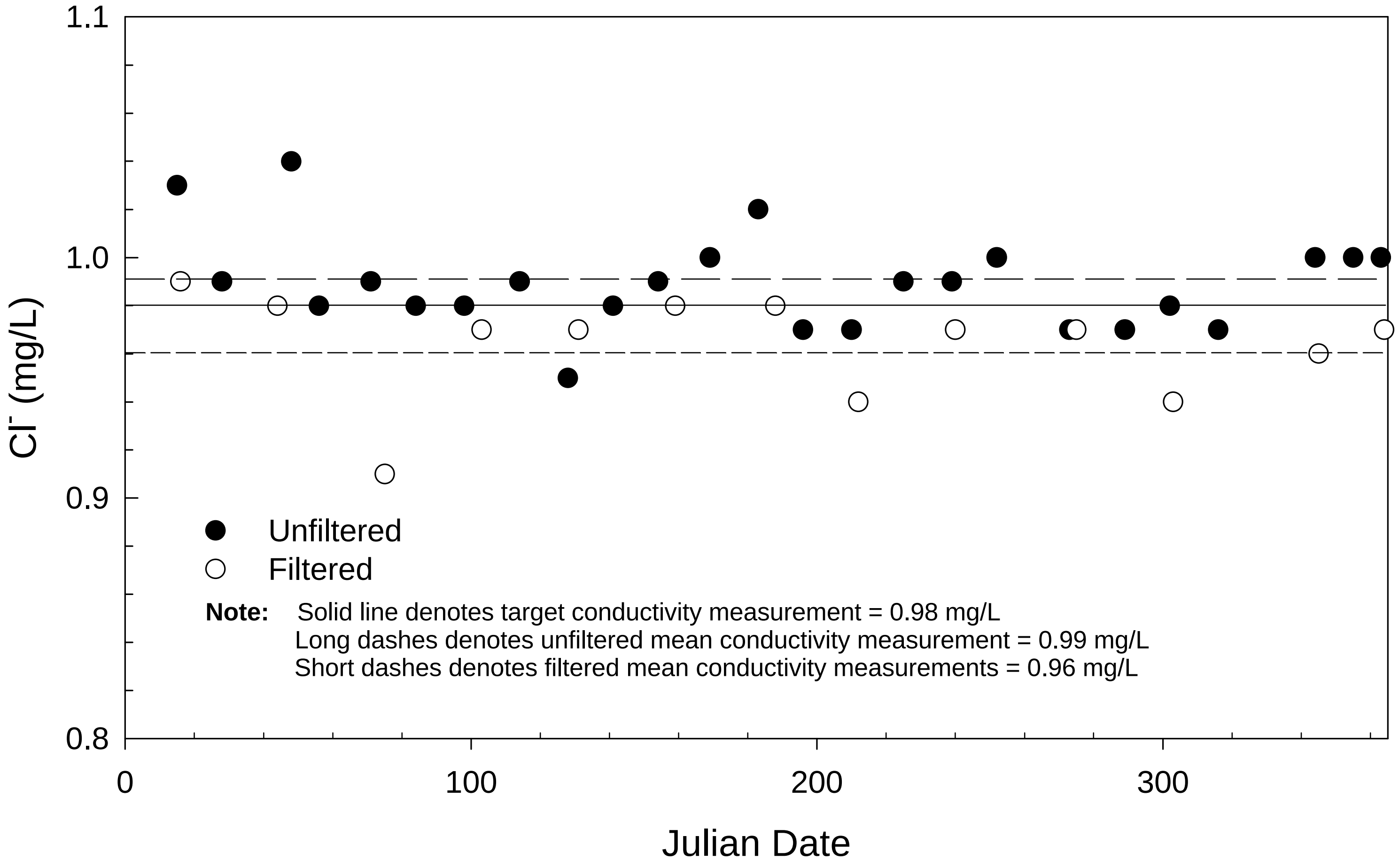


FIGURE B-16. Comparison of filtered and unfiltered internal blind samples, (sulfate), High-Purity Standards, SR2, 1998.



Note: Solid line denotes target NO_3^- concentration = 7.0 mg/L
Long dashes denotes unfiltered mean NO_3^- concentration = 7.10 mg/L
Short dashes denotes filtered mean NO_3^- concentration = 6.84 mg/L

FIGURE B-17. Comparison of filtered and unfiltered internal blind samples (nitrate), High-Purity Standards, SR2, 1998.



Note: Solid line denotes target conductivity measurement = 0.98 mg/L
Long dashes denotes unfiltered mean conductivity measurement = 0.99 mg/L
Short dashes denotes filtered mean conductivity measurements = 0.96 mg/L

FIGURE B-18. Comparison of filtered and unfiltered blind samples (chloride), High-Purity Standards, SRII, 1998.

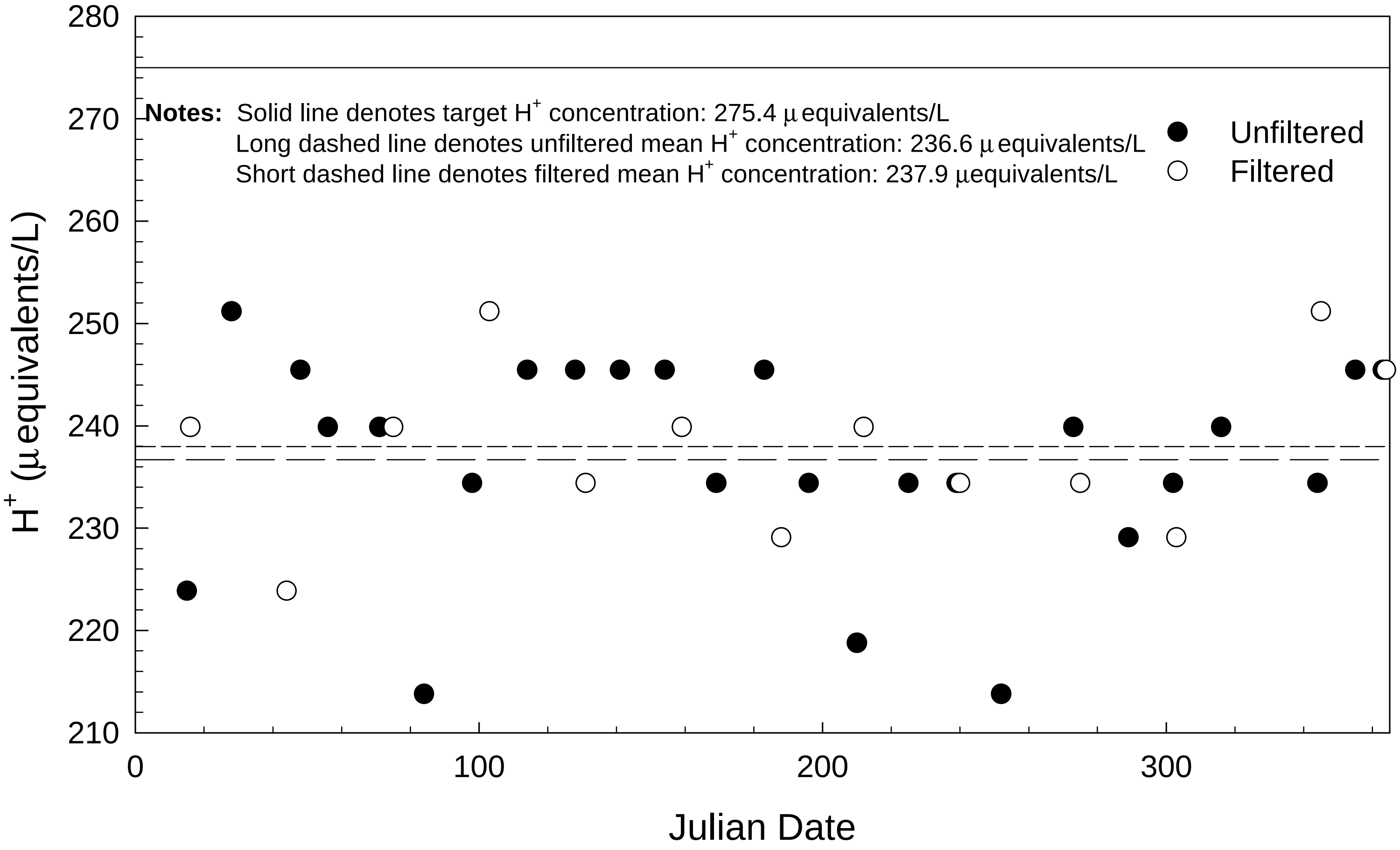
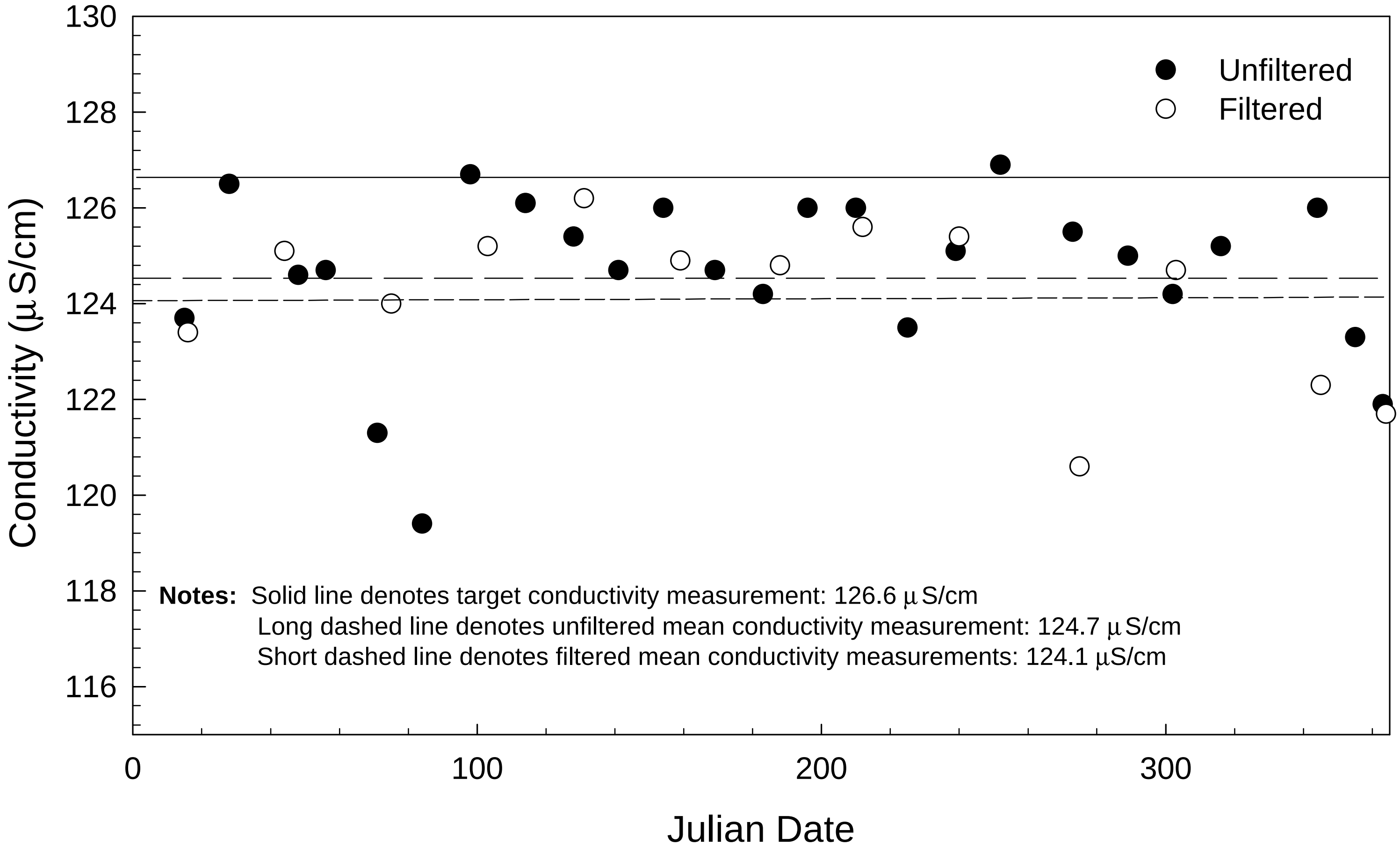


Figure B-19. Comparison of filtered and unfiltered blind samples (H^+),
High-Purity Standards -SR2, 1998.



Notes: Solid line denotes target conductivity measurement: 126.6 µS/cm
Long dashed line denotes unfiltered mean conductivity measurement: 124.7 µS/cm
Short dashed line denotes filtered mean conductivity measurements: 124.1 µS/cm

Figure B-20. Comparison of filtered and unfiltered internal blind samples (conductivity), High-Purity Standard SR2, 1998.

Table B-3. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, 1998

Parameter	*Target Concentrations*[a] *(mg/L)*	*Measured Concentrations (mg/L)*	*Bias (mg/L)*	*Bias %*	*Standard Deviation (mg/L)*	*RSD %*
Calcium	0.0					
Magnesium	0.0					
Sodium	0.0					
Potassium	0.0					
Ammonium	0.0					
Sulfate	0.0					
Nitrate	3.12	3.23[b]	0.11	3.4	0.04	1.2
		3.14[c]	0.02	0.5	0.05	1.6
Chloride	0.0					
pH[d]	4.30	4.32	0.02	0.4	0.02	0.4
		4.31	0.01	0.3	0.01	0.3
Hydrogen ion	50.12	48.39	-1.73	-3.4	2.00	4.2
(µeq/L)		48.81	-1.30	-2.6	1.54	3.1
Conductivity[d]	21.1	21.5	0.4	2.0	0.59	2.7
(µS/cm)		21.6	0.5	2.3	0.32	1.5

Notes:
There were 25 unfiltered samples and 12 filtered samples.
All concentrations that are blank were below the method detection limit.
[a] Target values are for the CAL prepared pH 4.3 Quality Control Solution.
[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 samples prior to filtering.

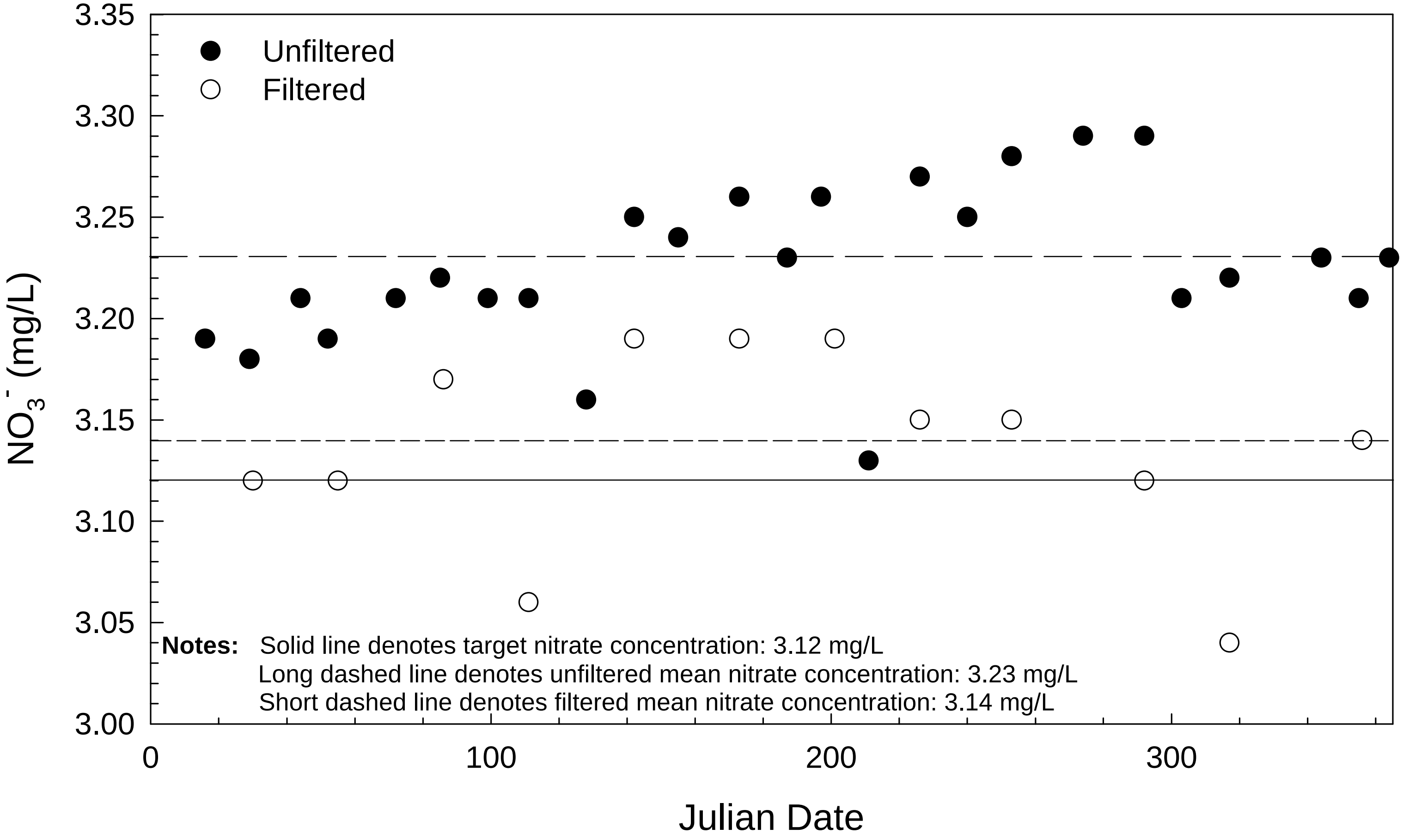
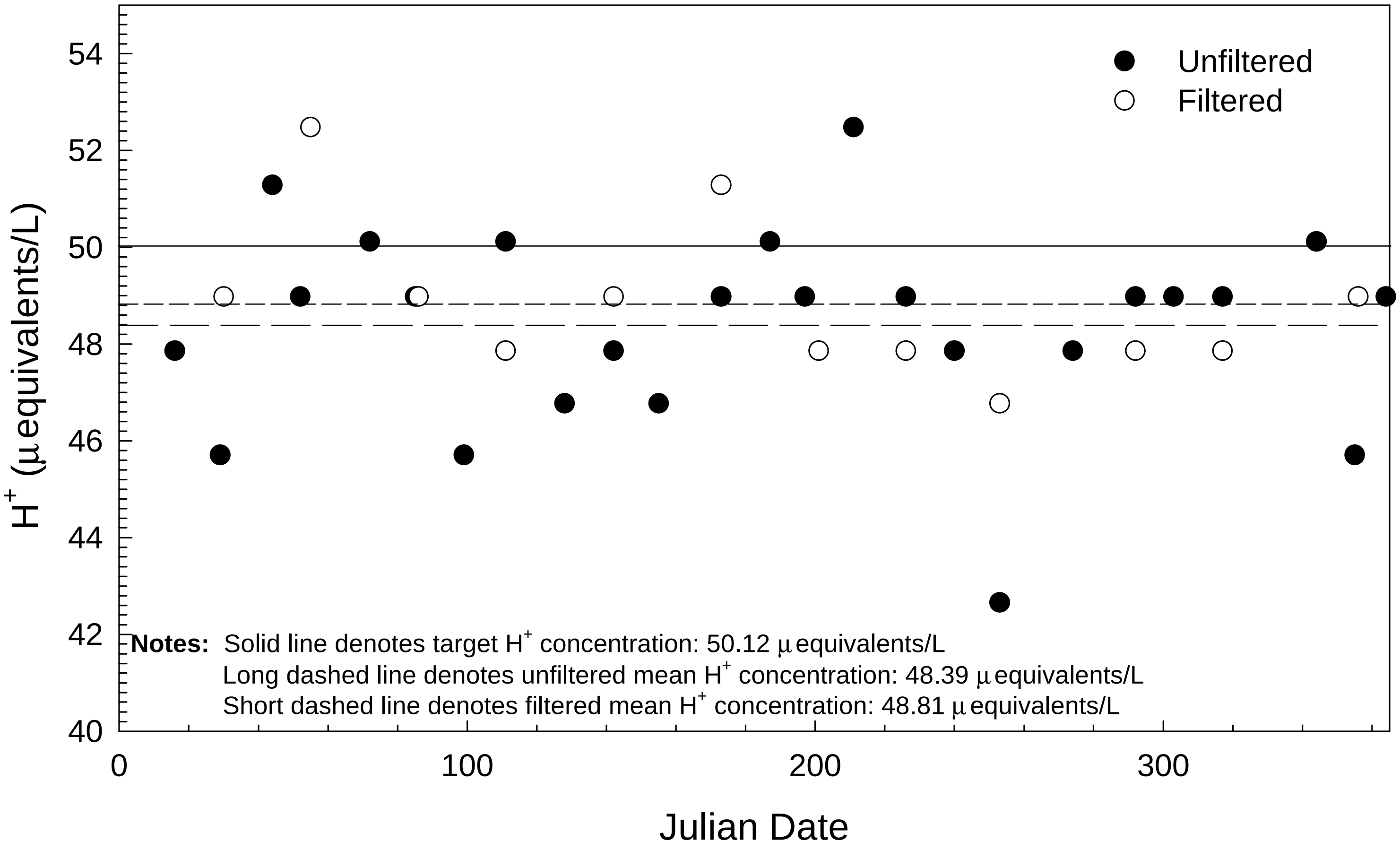
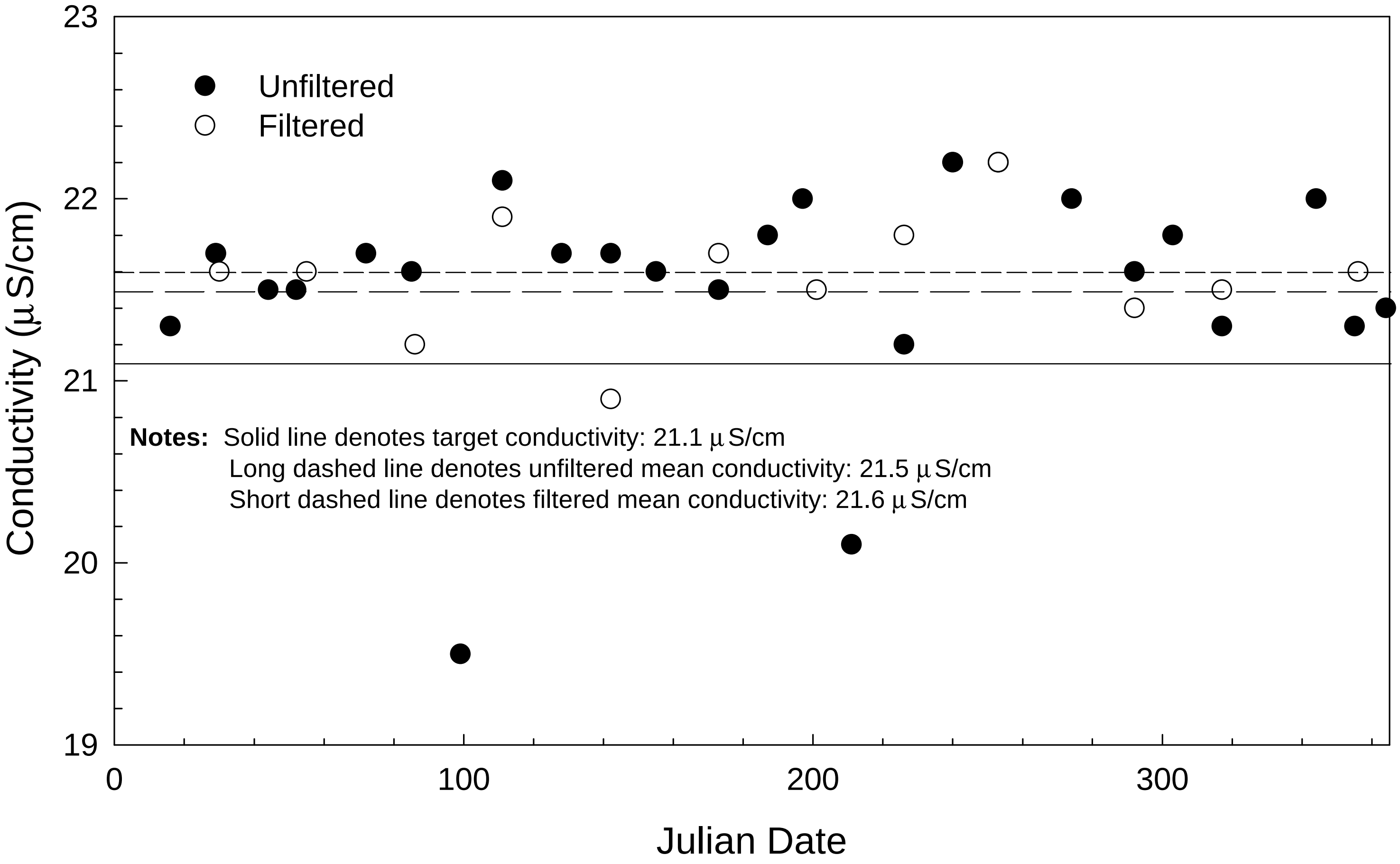


Figure B-21. Comparison of filtered and unfiltered internal blind samples, (nitrate), pH 4.3 Quality Control Solution, 1998.



Notes: Solid line denotes target H^+ concentration: 50.12 µequivalents/L
Long dashed line denotes unfiltered mean H^+ concentration: 48.39 µequivalents/L
Short dashed line denotes filtered mean H^+ concentration: 48.81 µequivalents/L

Figure B-22. Comparison of filtered and unfiltered internal blind samples, (hydrogen ion), pH 4.3 Quality Control Standard Solution, 1998.



Notes: Solid line denotes target conductivity: 21.1 µS/cm
Long dashed line denotes unfiltered mean conductivity: 21.5 µS/cm
Short dashed line denotes filtered mean conductivity: 21.6 µS/cm

Figure B-23. Comparison of filtered and unfiltered internal blind samples, (conductivity), pH 4.3 Quality Control Standard Solution, 1998.

Table B-4. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, 1998

Parameter	*Target Concentrations*[a] *(mg/L)*	*Measured Concentrations (mg/L)*	*Bias (mg/L)*	*Bias %*	*Standard Deviation (mg/L)*	*RSD %*
Calcium	0.0					
Magnesium	0.0					
Sodium	0.0					
Potassium	0.0					
Ammonium	0.0					
Sulfate	0.0					
Nitrate	0.0					
Chloride	0.0					
pH[d]	5.65	5.56	-0.09	-1.5	0.14	2.4
		5.62	0.03	-0.4	0.15	2.7
H	2.24	2.87	0.63	28.3	1.04	36.0
(µeq/L)		2.50	-0.26	-11.5	0.67	26.7
Conductivity[d]	0.9	1.1	0.2	22.2	0.32	29.2
(µS/cm)		1.1	0.2	17.1	0.18	16.9

Notes:
There were 26 unfiltered samples and 13 filtered samples.
All concentrations that are blank were below the method detection limit.
[a] Target values are for DI water samples.
[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 samples prior to filtering.

Table B-5. 5th, 50th, and 95th Percentile Concentration Values of Parameters Measured in Replicate Samples, 1998

	Percentile Concentration Values (mg/L)		
Parameter	*5th*	*50th*	*95th*
Calcium	0.012	0.069	0.472
Magnesium	<0.003	0.016	0.102
Sodium	0.005	0.043	0.666
Potassium	<0.003	0.014	0.076
Ammonium	<0.02	0.15	0.84
Sulfate	0.11	0.93	3.83
Nitrate	0.12	0.92	2.72
Chloride	<0.03	0.10	1.17
pH(units)	4.11	4.77	5.98
Hydrogen ion µeq/L)	1.06	16.98	77.01
Conductivity (µS/cm)	2.6	11.7	42.5

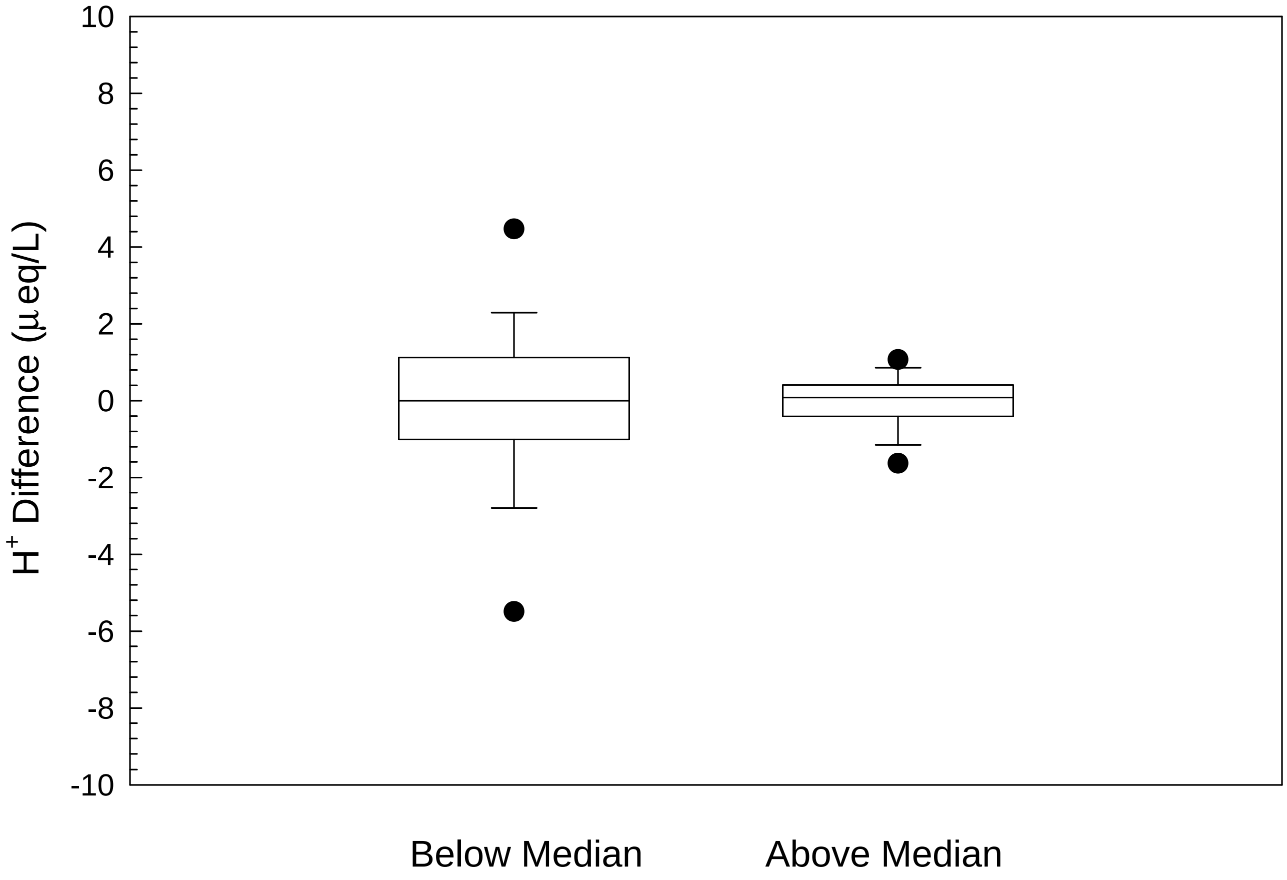


Figure B-24. Results of NTN replicate analysis, H^+, 1998.

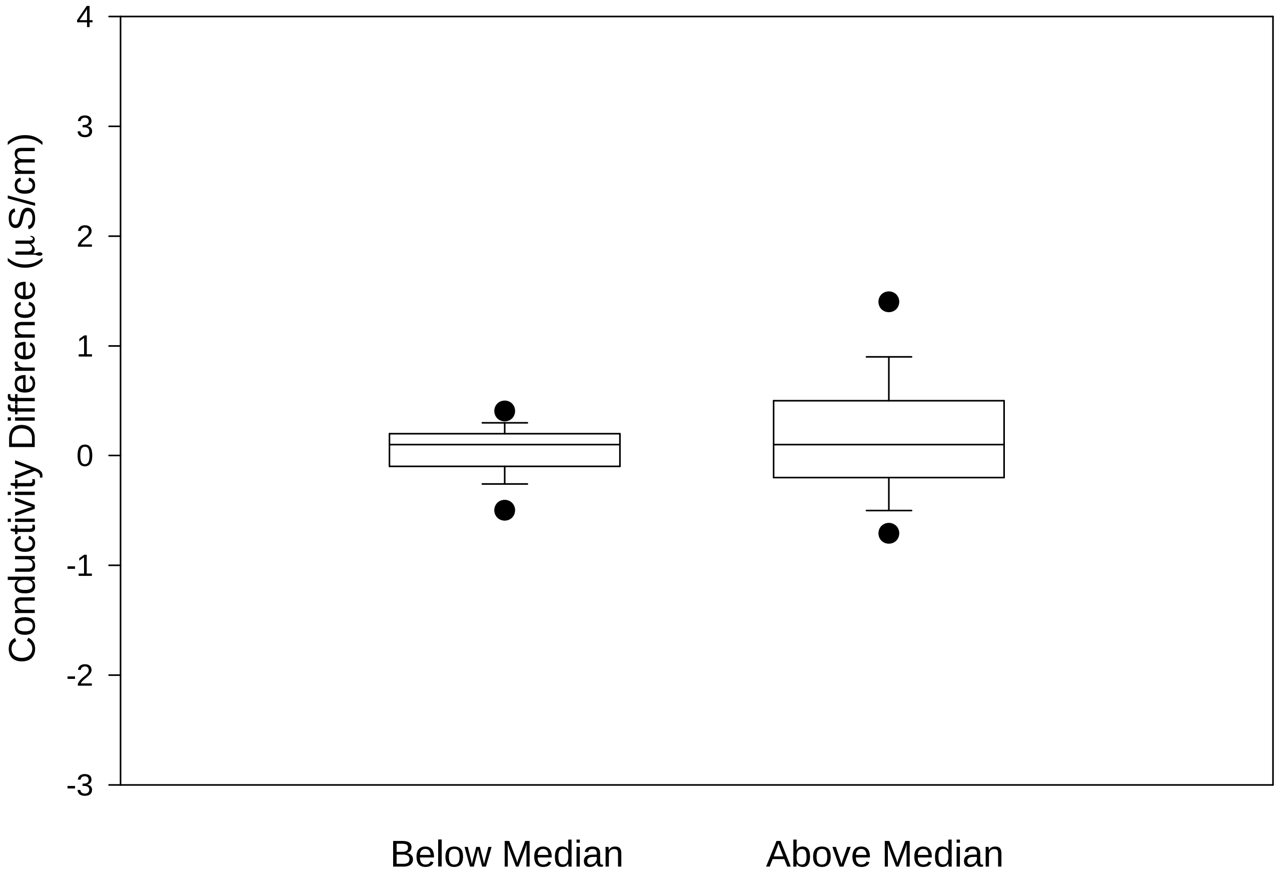


Figure B-25. Results of NTN replicate analysis, conductivity, 1998.

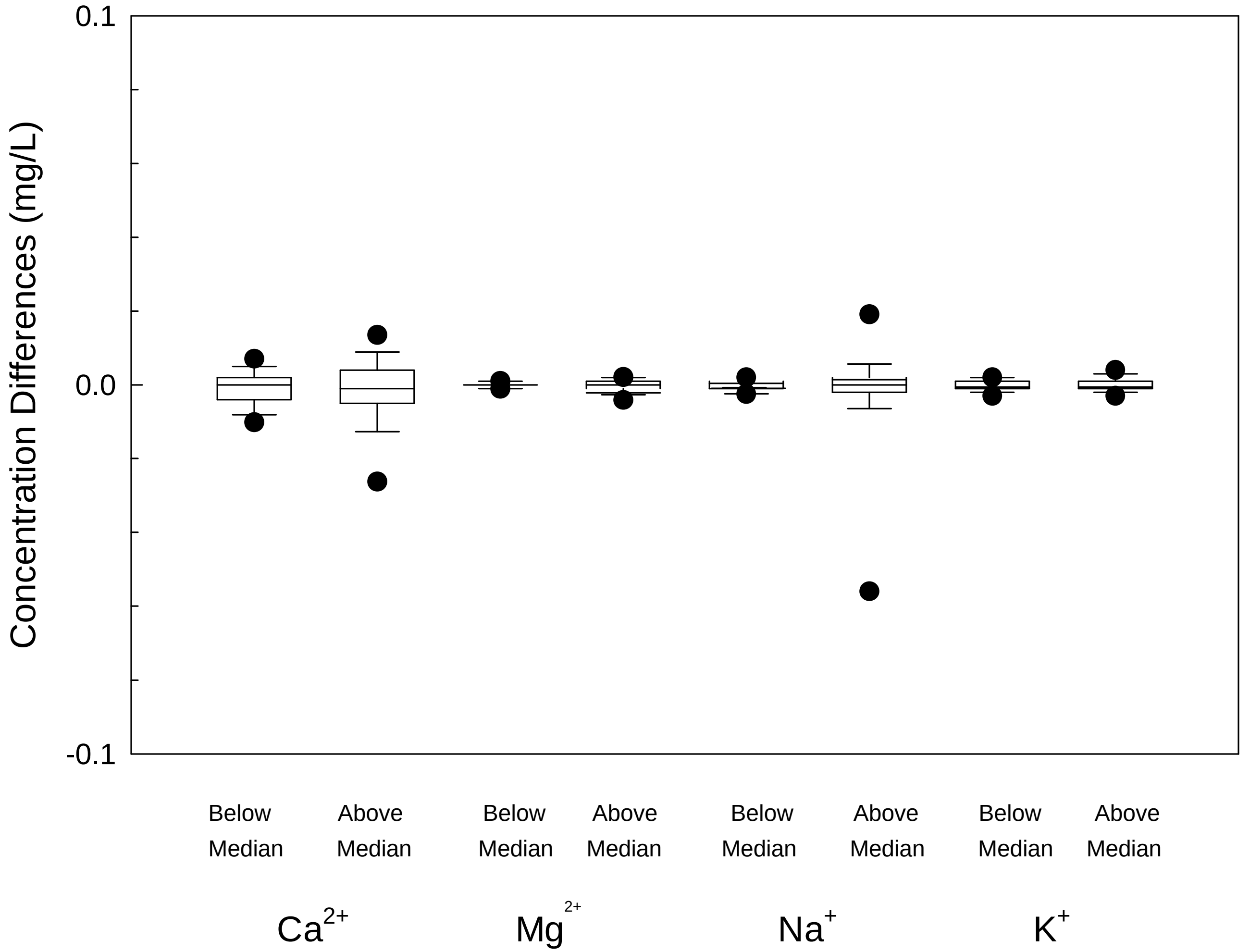


Figure B-26. Results of NTN replicate analysis, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}), 1998.

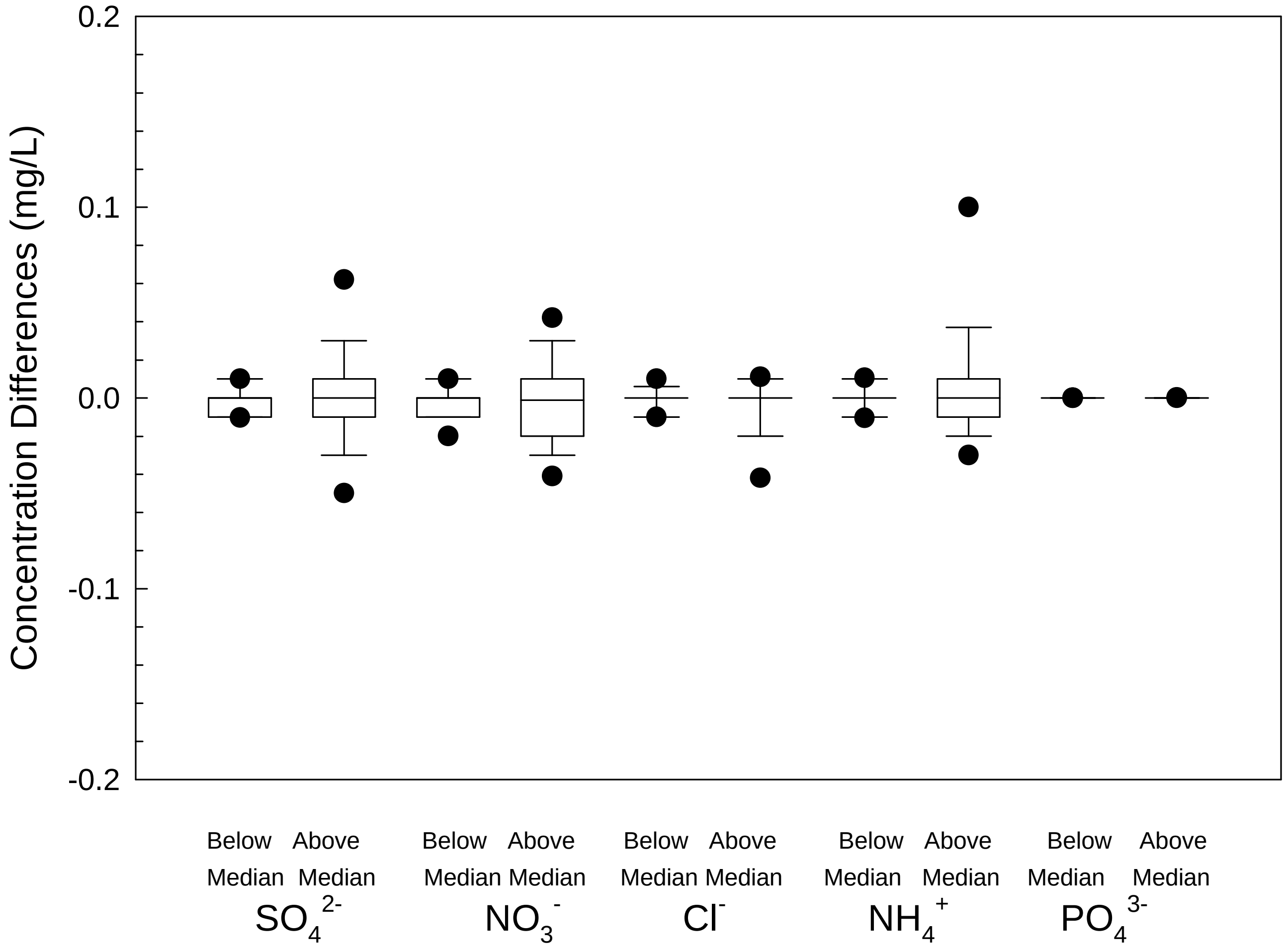


Figure B-27. Results of NTN replicate analysis, sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), and ortho-phosphate (PO_4^{3-}), 1998.

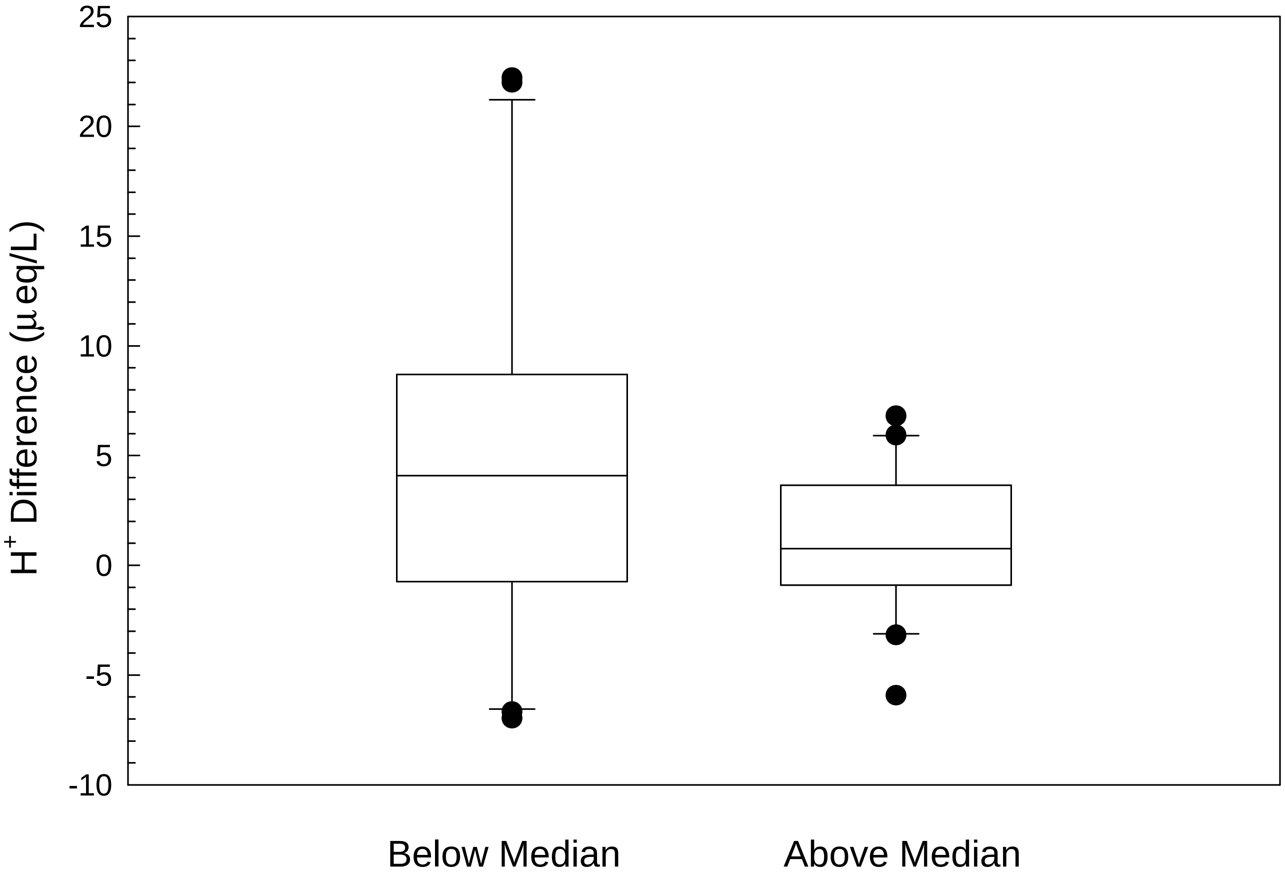


Figure B-28. Results of AIRMoN replicate analysis, H^+, 1998.

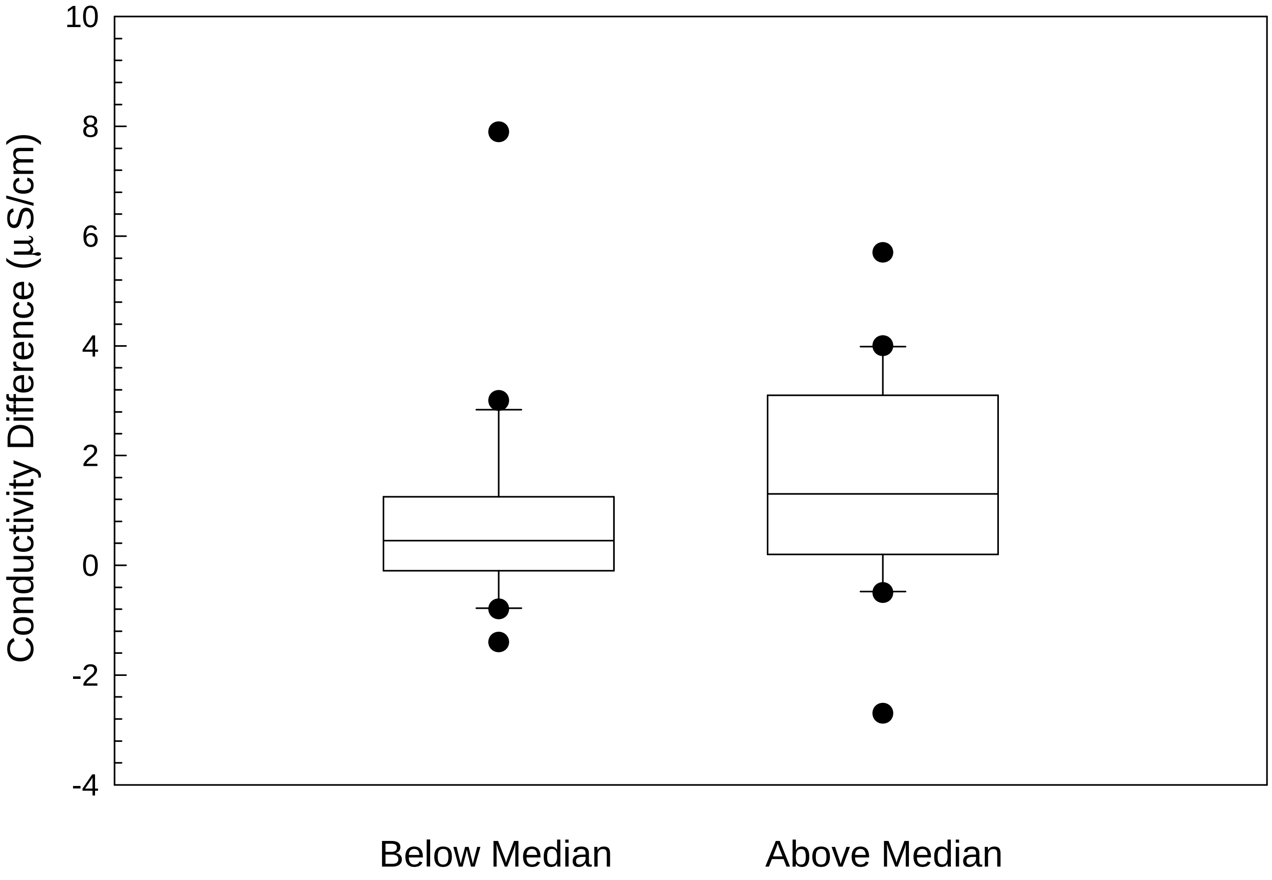


Figure B-29. Results of AIRMoN replicate analysis, conductivity, 1998.

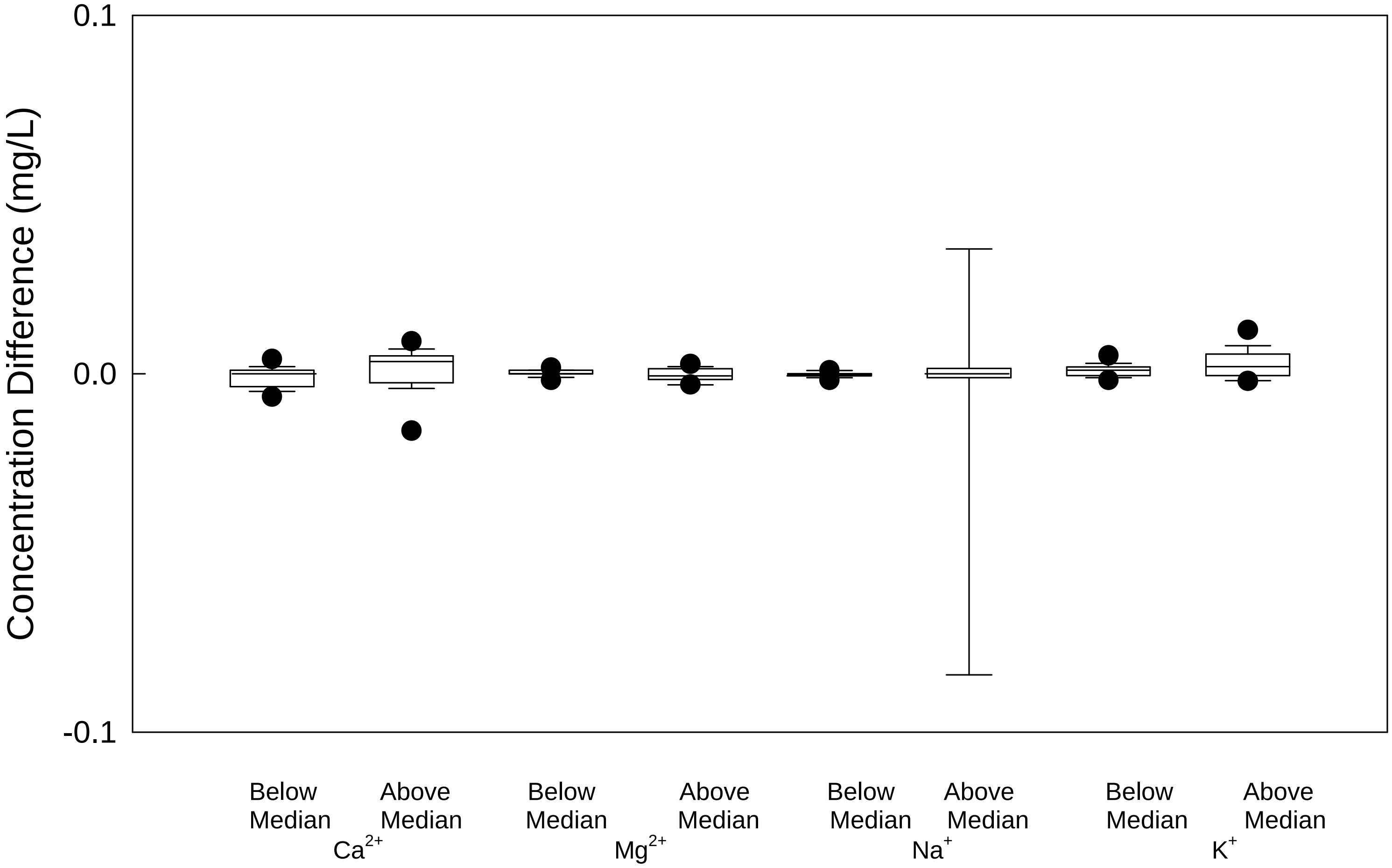


Figure B-30. Results of AIRMoN replicate analysis, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}), 1998.

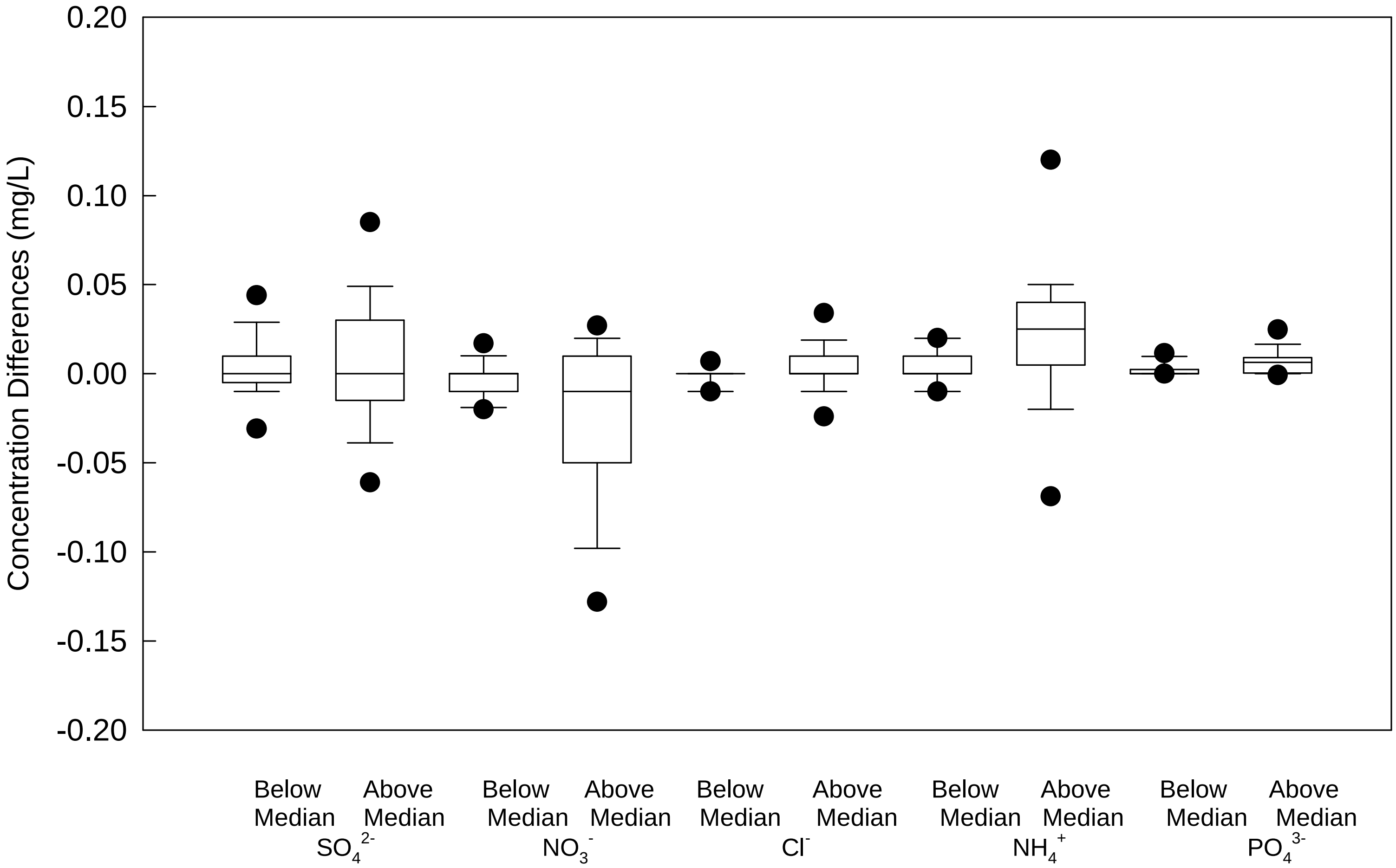


Figure B-31. Results of AIRMoN replicate analysis, sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), and orthophosphate (PO_4^{3-}), 1998.

Table B-6. Percent of Ion Concentrations above MDL's Found in Weekly Deionized (DI) Water Blanks and Leachates, 1998

Blank	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Ammonium*	*Phosphate*	*Chloride*	*Nitrate*	*Sulfate*
DI (Rm 209)	2.2	0.0	2.1	0.0	0.0	2.1	0.0	0.0	0.0
DI (Rm 304)	0.0	0.0	10.6	2.1	6.2	2.1	0.0	0.0	0.0
DI (Rm 323)	0.0	0.0	4.3	2.1	2.1	2.1	0.0	0.0	0.0
Filter A	13.0	0.0	17.0	0.0	2.1	2.1	2.1	0.0	0.0
Filter B	8.7	0.0	4.3	0.0	0.0	2.1	0.0	0.0	0.0
Bucket 50	43.5	10.9	51.1	38.3	14.6	2.1	41.7	4.2	0.0
Bucket 150	15.2	0.0	17.0	14.9	2.1	4.2	4.2	0.0	0.0
Bottle 50	17.4	8.7	8.5	53.2	0.0	8.3	0.0	0.0	2.1
Bottle 150	4.3	0.0	0.0	21.3	0.0	8.3	0.0	0.0	2.1
Lid 50	13.6	0.0	48.9	40.0	6.5	4.3	21.7	0.0	0.0

Notes:
The number of blanks ranges from 44 weeks where lids were leached and measured for calcium and magnesium to 48 weeks for most other blanks for chloride, nitrate, and sulfate.

TABLE B-7. Percent of Ion Concentrations above Control Limits Found in Weekly Simulated Rain (FR25) Leachates, 1998

Blank	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Ammonium*	*Phosphate*	*Chloride*	*Nitrate*	*Sulfate*
Filter A	19.6	2.2	4.3	2.1	0.0	2.1	0.0	0.0	0.0
Filter B	13.0	0.0	0.0	0.0	0.0	2.1	0.0	0.0	0.0
Bucket - 50	21.7	0.0	31.9	12.8	4.2	2.1	2.1	0.0	0.0
Bucket - 150	8.7	4.3	21.3	14.9	2.1	2.1	2.1	0.0	0.0
Bottle - 50	6.5	0.0	0.0	14.9	0.0	2.1	0.0	0.0	2.1
Bottle - 150	8.9	0.0	4.3	6.5	0.0	2.1	0.0	0.0	0.0
Lid - 50	6.7	0.0	26.1	19.6	4.3	2.1	8.5	0.0	0.0
AIRMoN Bottle - 50	0.0	0.0	0.0	0.0	8.3	0.0	0.0	0.0	0.0
AIRMoN Bottle - 150	0.0	0.0	0.0	0.0	9.1	0.0	0.0	0.0	0.0

Notes:

From 45 to 48 weekly NTN blanks and 11 or 12 monthly AIRMoN blanks were analyzed.

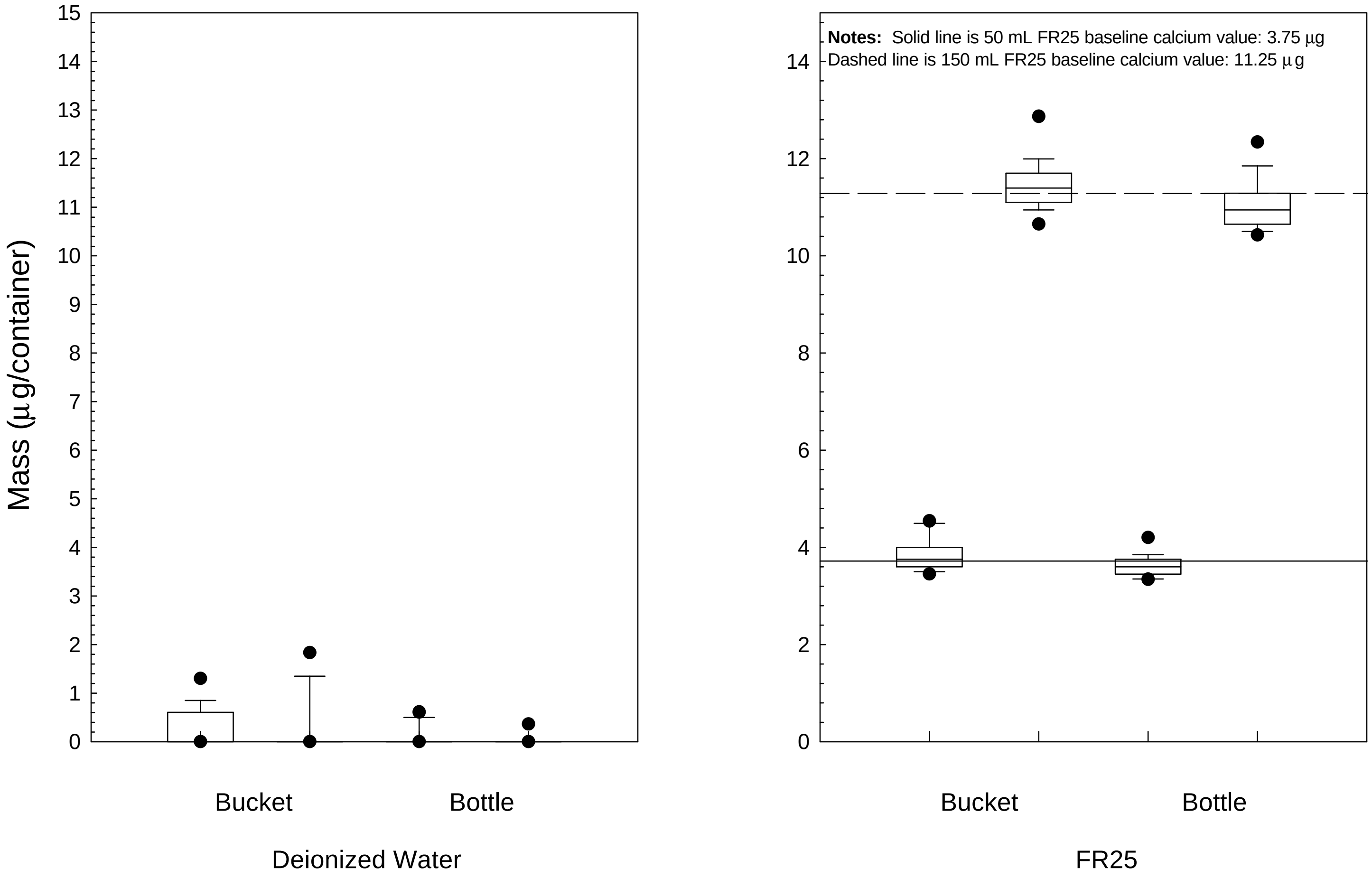


Figure B-32. Calcium found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 1998.

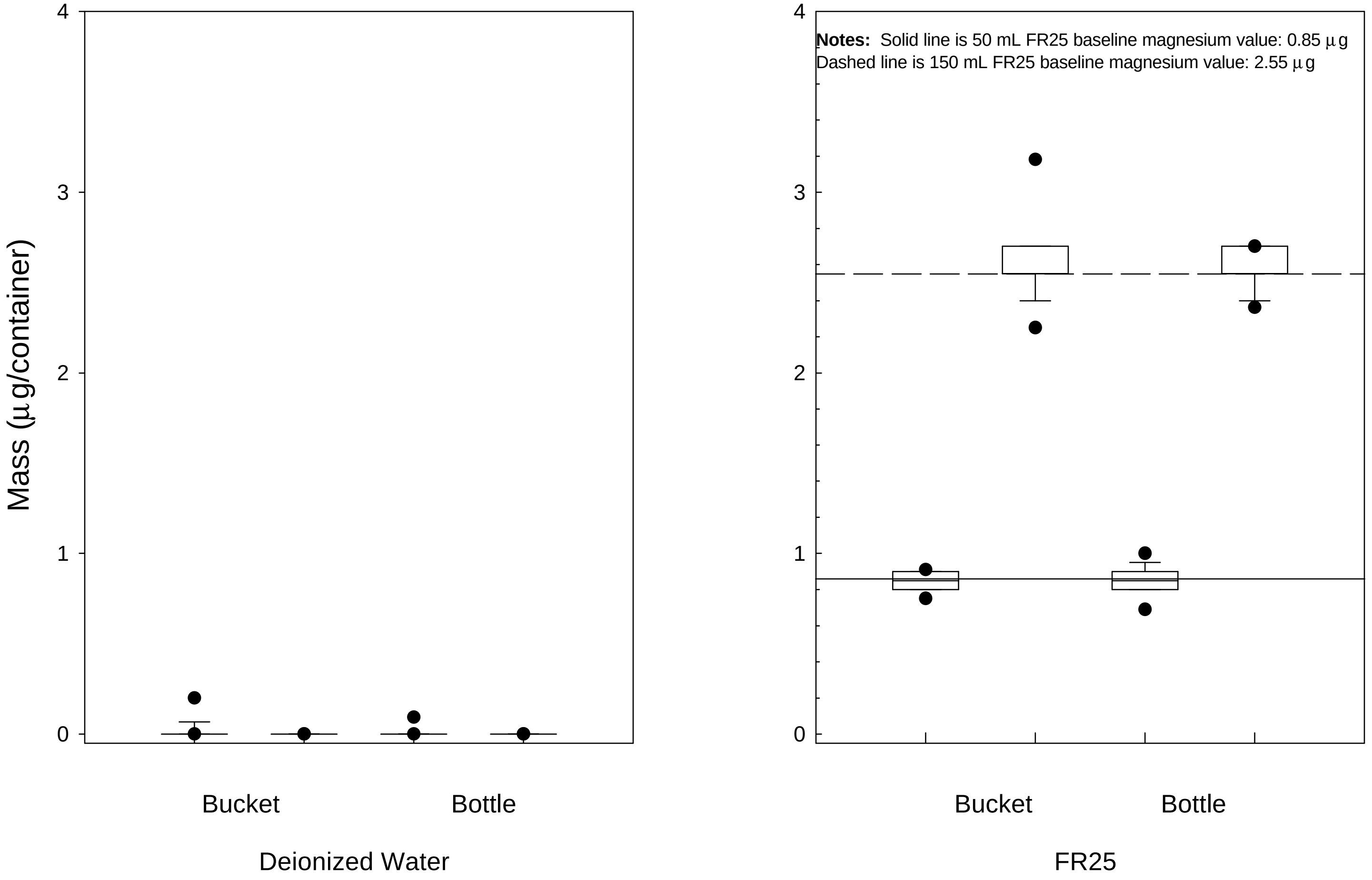


Figure B-33. Magnesium found in upright bucket blanks and 1-L bottles using deionized water and FR25 QCS as leaching agents, 1998.

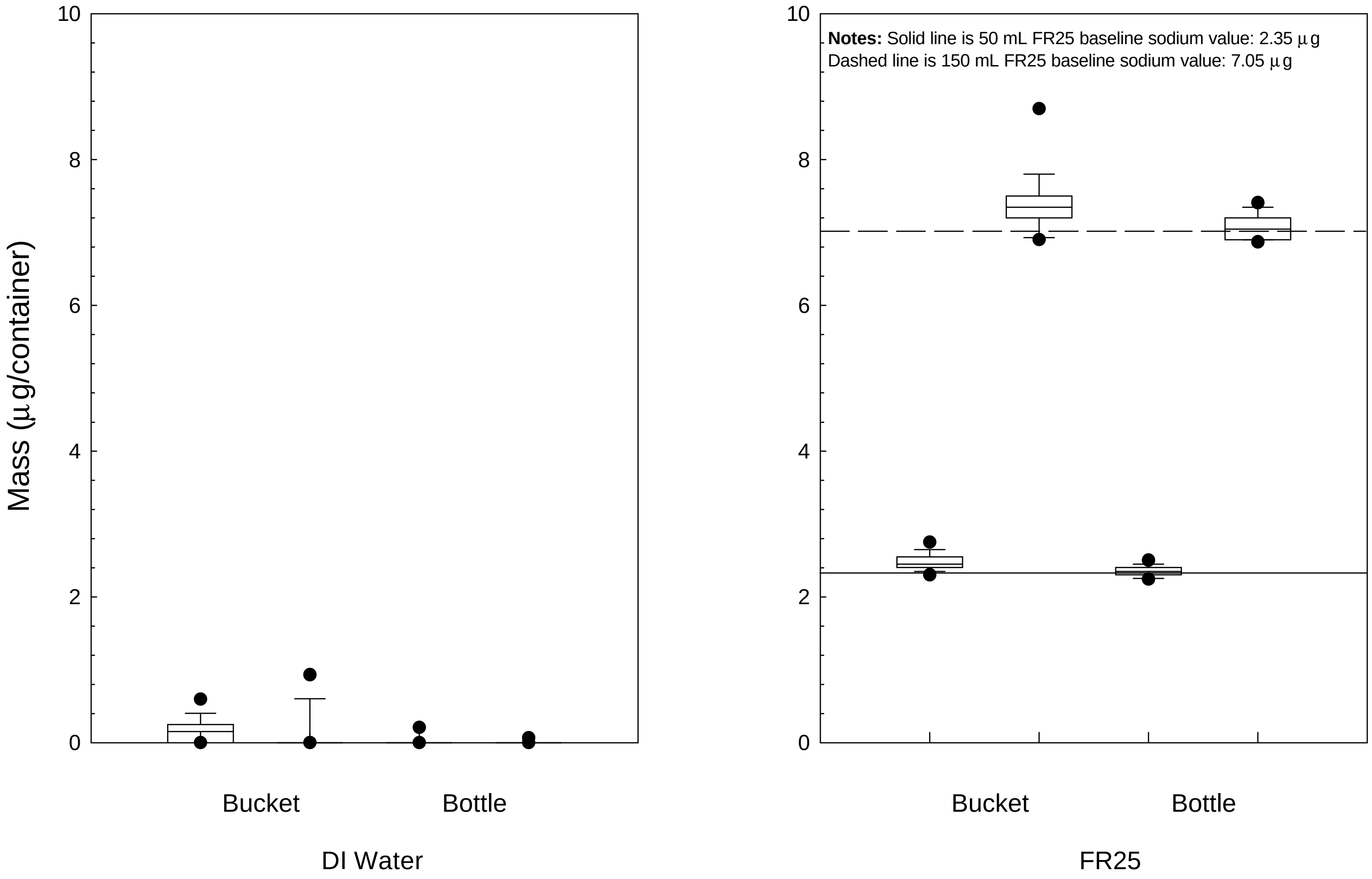


Figure B-34. Sodium found in upright bucket blanks and 1-L bottles using deionized water and FR25 QCS as leaching agents, 1998.

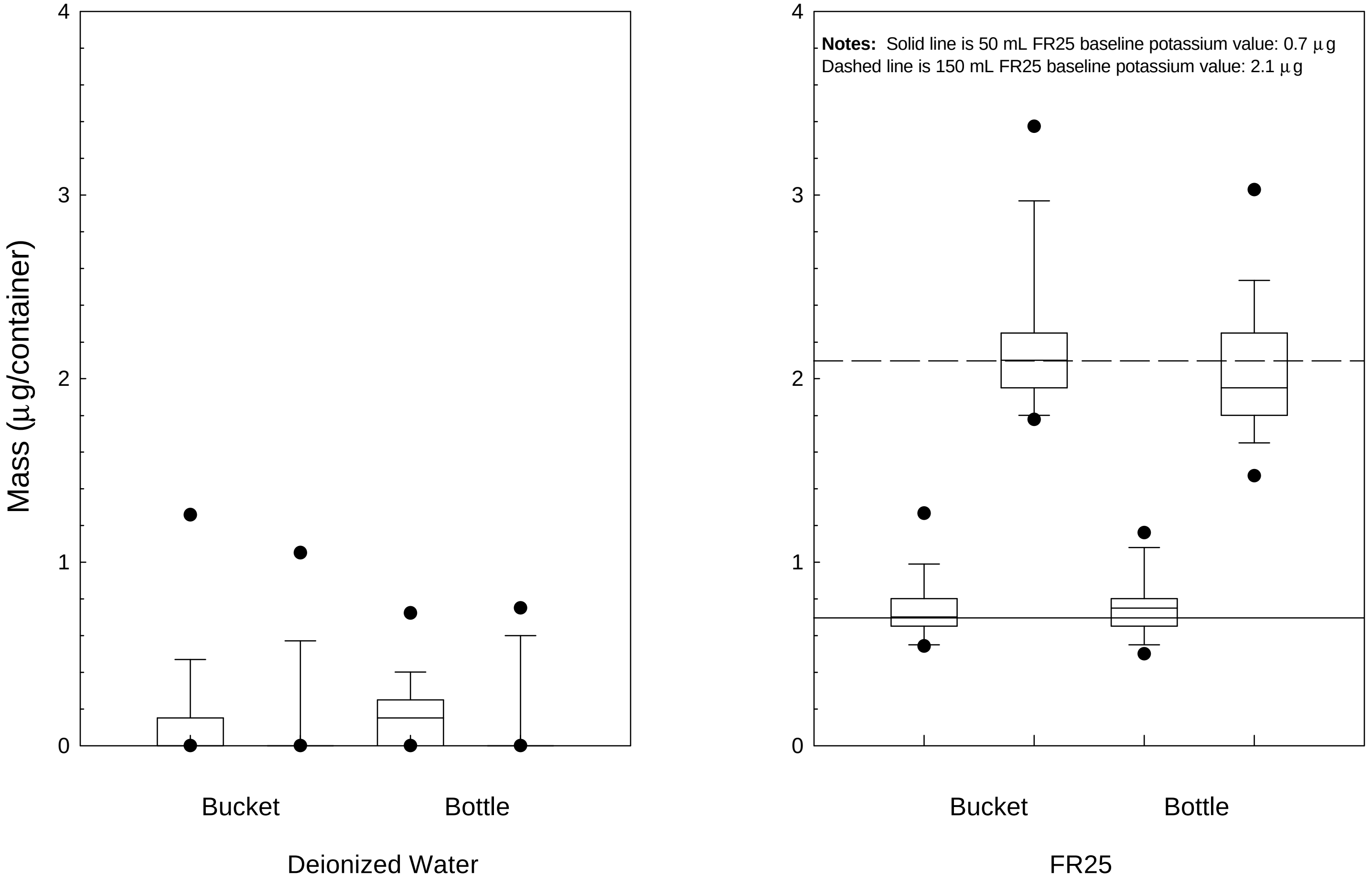
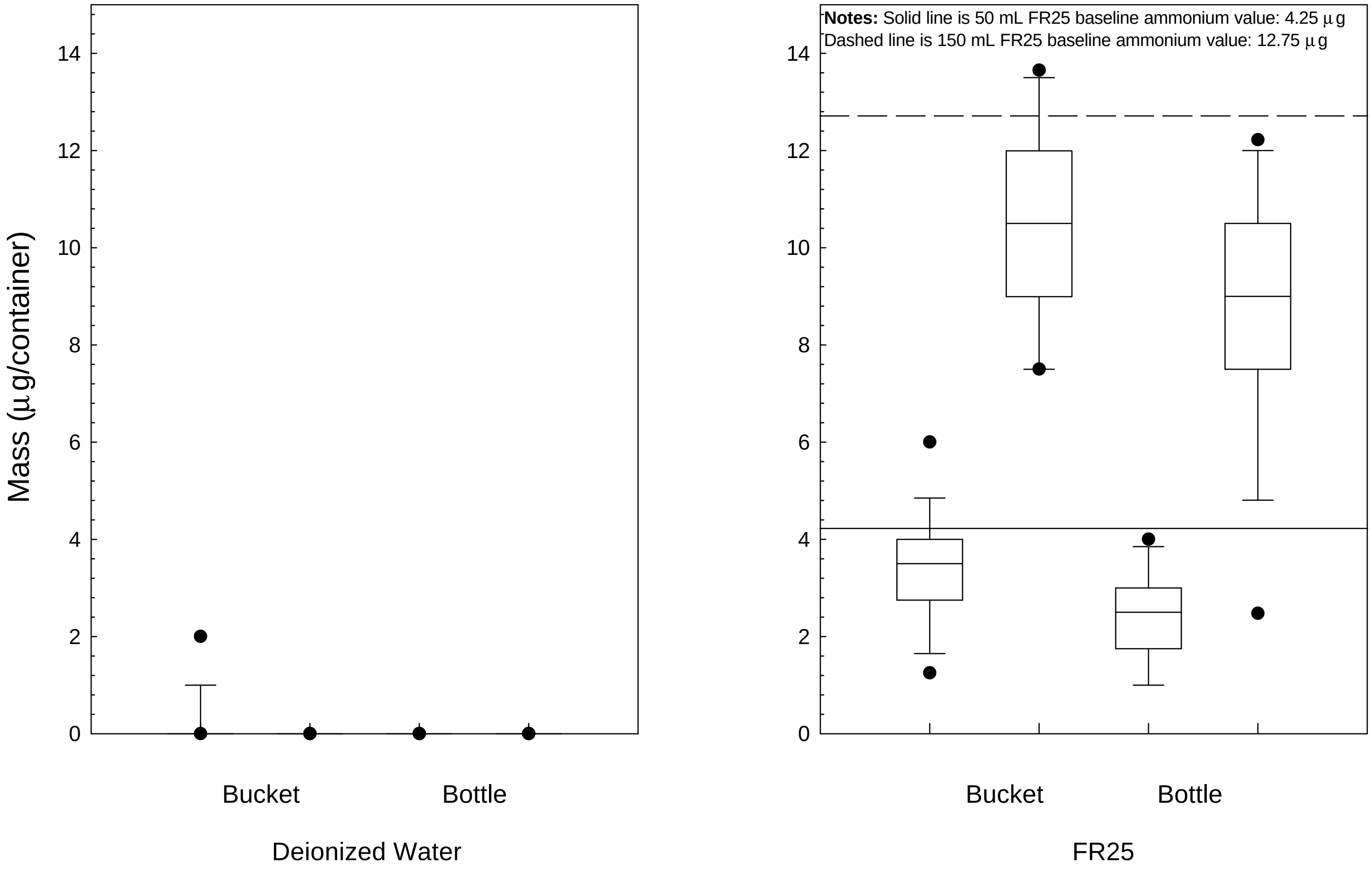


Figure B-35. Potassium found in upright bucket blanks and 1-L bottles, using deionized water and FR25 QCS as leaching agents, 1998.



Notes: Solid line is 50 mL FR25 baseline ammonium value: 4.25 µg
Dashed line is 150 mL FR25 baseline ammonium value: 12.75 µg

Figure B-36. Ammonium found in upright bucket blanks and 1-L bottles using deioinized water and FR25 QCS as leaching agents, 1998.

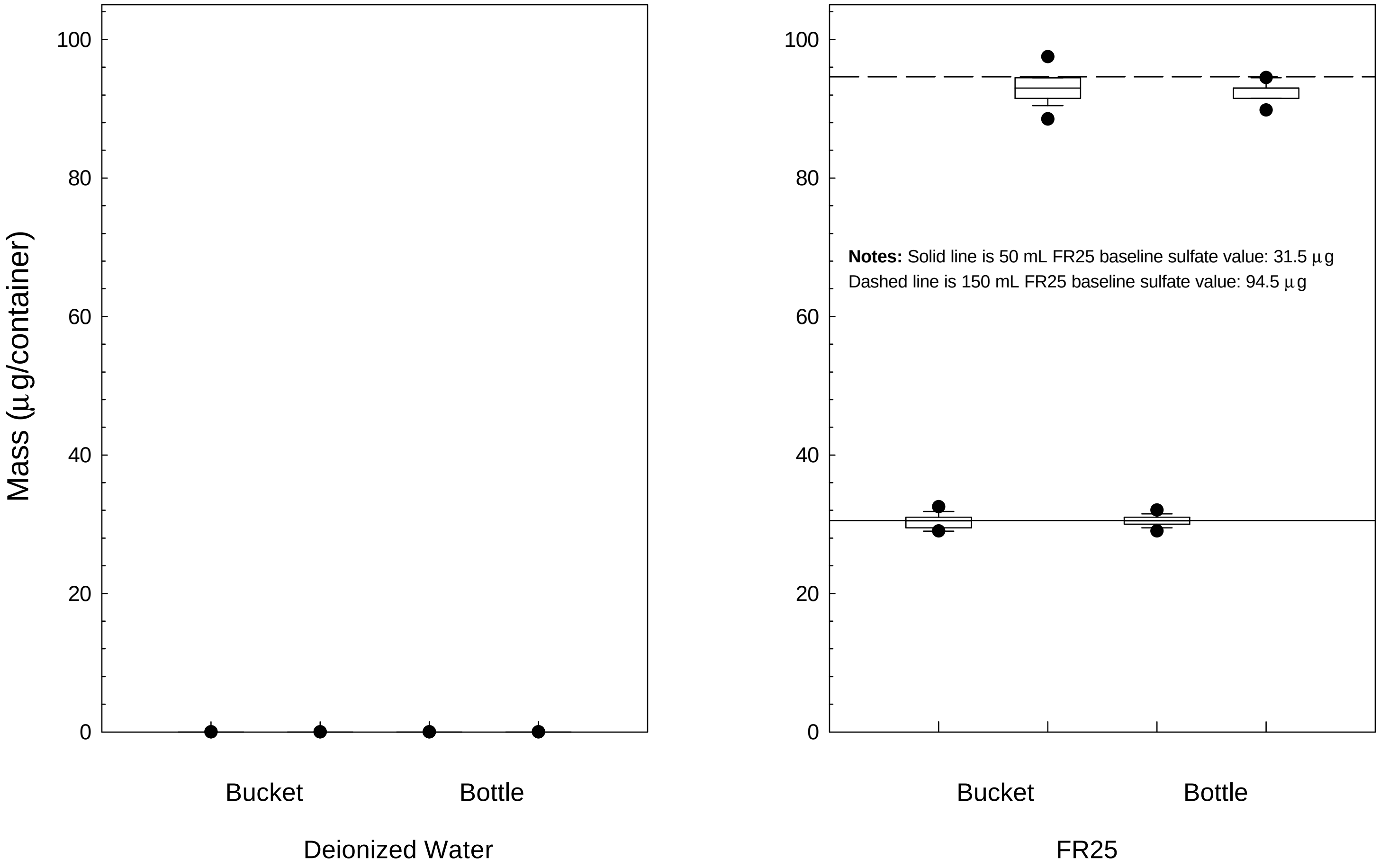


Figure B-37. Sulfate found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 1998.

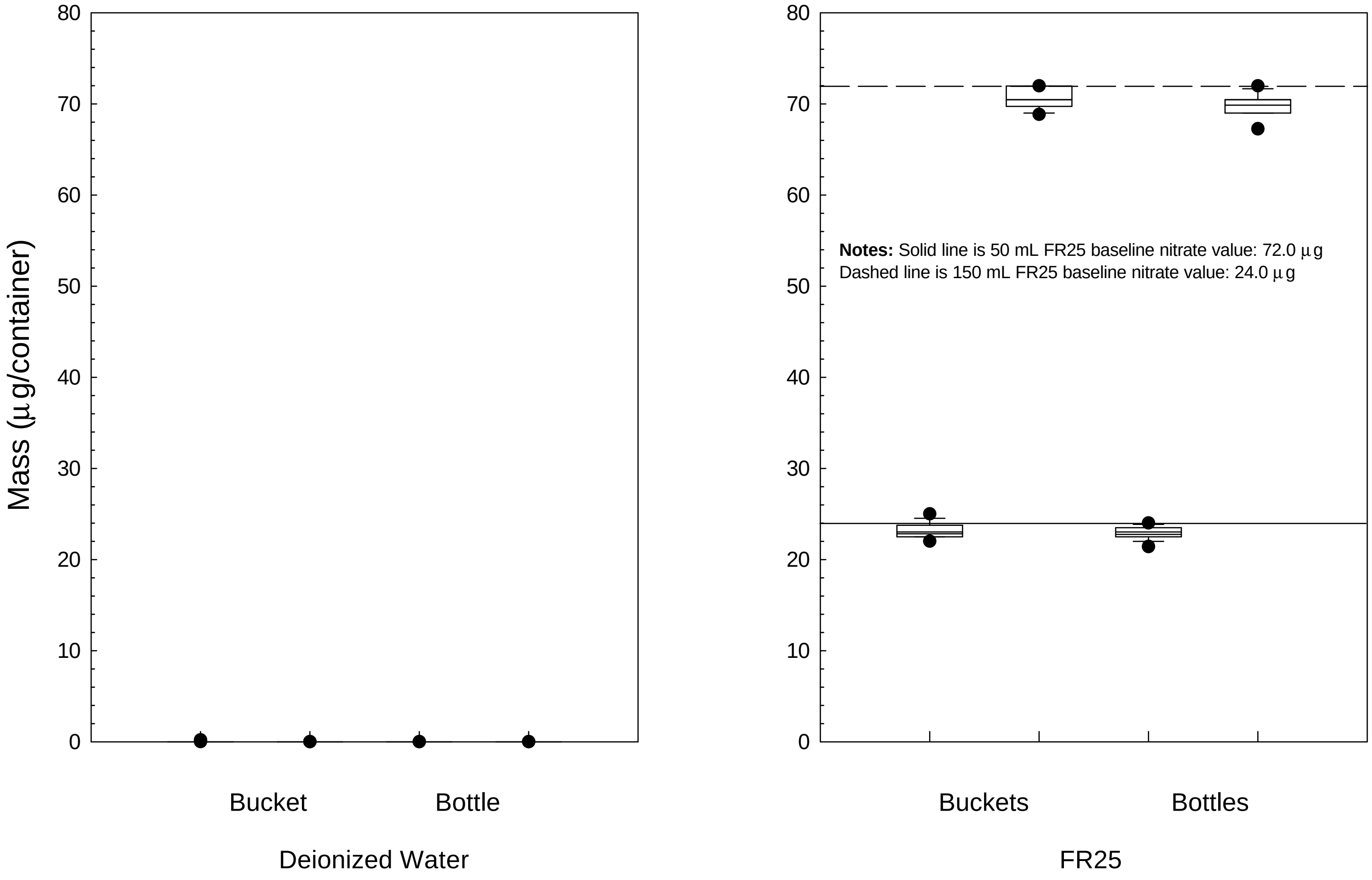
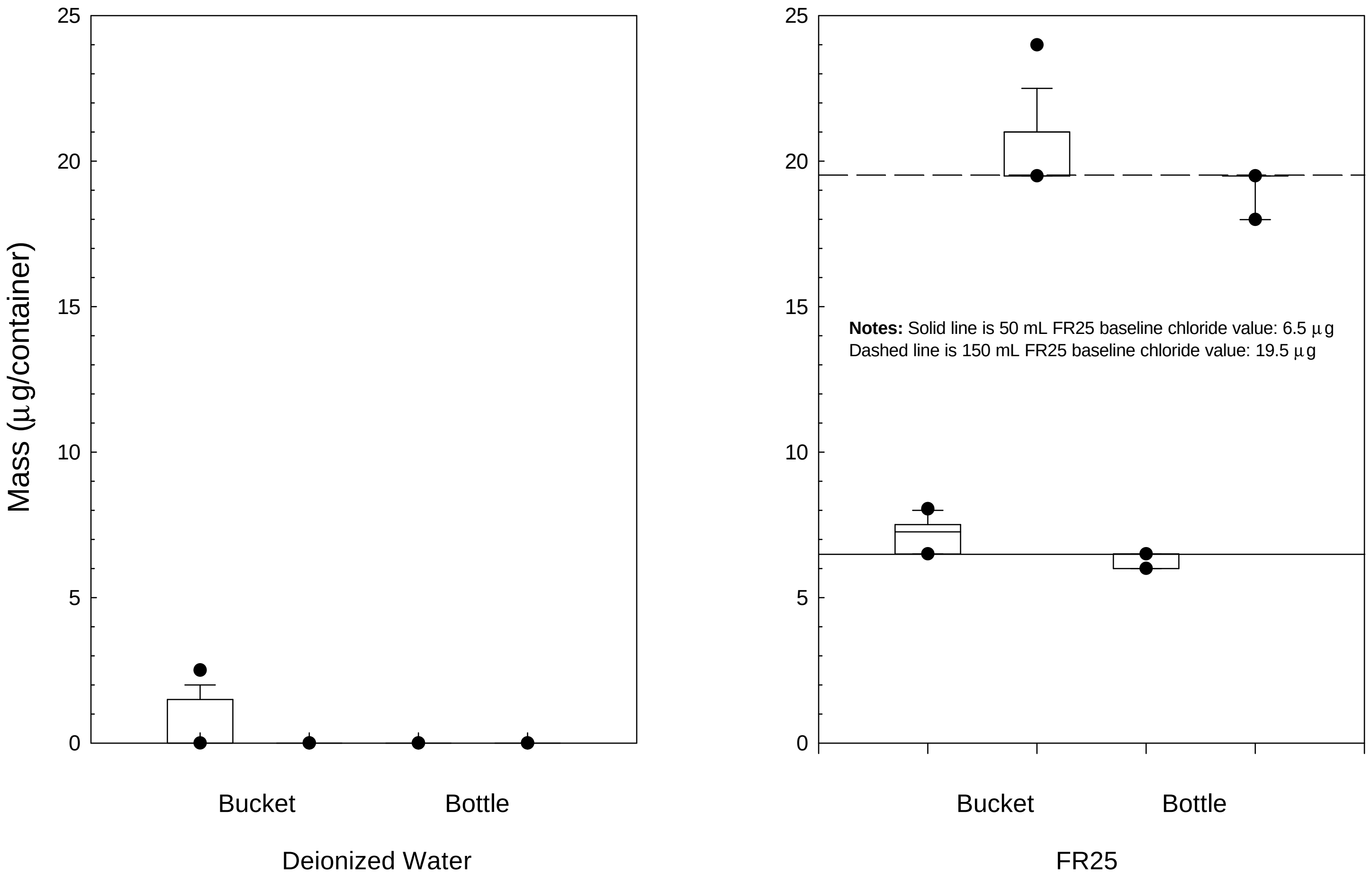


Figure B-38. Nitrate found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 1998.



Notes: Solid line is 50 mL FR25 baseline chloride value: 6.5 µg
Dashed line is 150 mL FR25 baseline chloride value: 19.5 µg

Figure B-39. Chloride found in upright bucket blanks and 1-L bottles using deionized water and FR25 QCS as leaching agents, 1998.

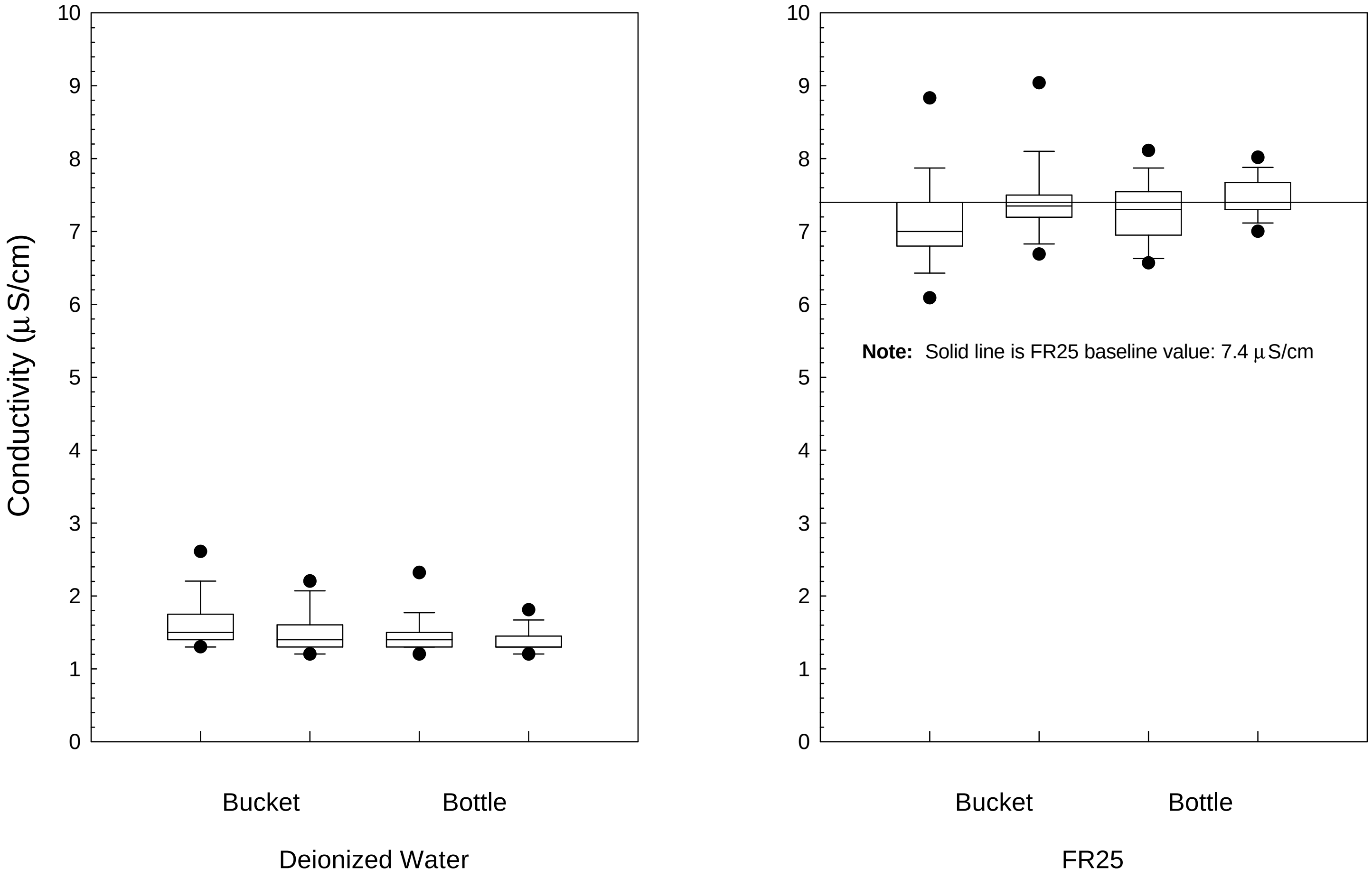


Figure B-41. Conductivity of upright bucket and 1-L bottle blanks leached with deionized water and FR25 QCS, 1998.