QUALITY ASSURANCE REPORT
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM,
1999

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, 1999*, describes the quality assurance/quality control measures used at the Central Analytical Laboratory (CAL) of the NADP/National Trends Network (NTN) and NADP/Atmospheric Integrated Research Monitoring Network (AIRMoN) and reports the results of these programs. The goal of the CAL quality assurance program is to provide reliable, consistent, high-quality data that fulfills the needs of researchers and other data users. This is achieved by incorporating quality checks throughout the sample flow process. System blanks and control checks are included at strategic sample and data flow points. Results are compiled to generate information about the quality of the data generated and presented as tables, figures, graphs, or brief written explanations. The CAL was within the quality control objectives for the networks in 1999.

ACKNOWLEDGMENTS

This *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 Monitoring Network (NADP/AIRMoN), is the product of many individuals. The U.S. Geological Survey (USGS) 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, USGS; Karen Harlin, NADP/CAL; Eva Kingston, Illinois State Water Survey (ISWS); Mark Peden, ISWS; Dave MacTavish, Meteorological Service of Canada; and John Shimshock, Advanced Technology Systems, Inc.

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EXECUTIVE SUMMARY

The *Quality Assurance Plan NADP/NTN Deposition Monitoring* (Simmons et al., 1990) defines the quality assurance (QA) goals of the National Atmospheric Deposition Network (NADP). The precipitation samples collected by the National Trends Network (NTN) and the Atmospheric Integrated Research Monitoring Network (AIRMoN) of NADP are analyzed at the Central Analytical Laboratory (CAL) located at the Illinois State Water Survey in Champaign, Illinois. As the CAL for NADP, the laboratory must comply with all QA mandates in the NADP Quality Assurance Plan (QAP). In 1999, the CAL was in compliance with the NADP QAP.

More samples were processed and analyzed in 1999 than in any other year in the history of NADP. Daily procedures include charting instrument standardization and maintenance and ensuring that the instruments are operating in statistical control. Following strict standard operating procedures from sample arrival at the CAL to data archival with the Program Office ensures sample integrity and quality data. The Quality Control Sample (QCS) solutions used at the CAL show the instrumentation to be in control for 1999.

Weekly QA procedures include ensuring that all materials coming into contact with the precipitation samples do not contaminate the samples. Any problems that arise must be investigated and eliminated. All blank analyses, internal blind analyses for NTN and AIRMoN, and replicate analyses for 1999 were in compliance with the NADP QAP.

Monthly evaluation of laboratory control charts, reanalysis samples, Ion Percent Differences, and Conductance Percent Differences showed the CAL to be in compliance with the NADP QAP.

Interlaboratory comparison studies are vital in determining how the CAL is performing compared with other laboratories around the world doing similar work. In 1999, the CAL participated in four different studies. The U.S. Geological Survey (USGS), the external auditor for the NADP/NTN, conducted an intercomparison study with seven laboratories in 1999. The CAL ranked first overall. In 1999, the CAL was contracted to prepare the samples for the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) intercomparison study. Although the CAL did participate in the study, the CAL results were not included in the final study rankings because the samples were made and initially tested at the CAL. The CAL results, when compared with those from the other participating laboratories, were excellent. The National Water Research Institute of Canada conducted two intercomparison studies in 1999. In the first study, the CAL ranked first among the 37 participating laboratories. In the second study, the CAL ranked 16th out of 45 due to high pH results. The CAL was ranked “good” in the first study and “satisfactory” in the second.

I. INTRODUCTION

This Quality Assurance (QA) Report describes and summarizes the results of the National Atmospheric Deposition Program (NADP) Central Analytical Laboratory (CAL) QA program for 1999. The procedures for supporting reliable data are demonstrated through a QA program. This report, through text, figures, and tables, defines the QA 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 spring of 1978 to be the CAL for the NADP – a role it has held ever since. The CAL operations began by analyzing samples from 14 NADP sites in 1978. In 1999, the CAL analyzed samples from approximately 200 NADP/National Trends Network (NTN) sites collecting weekly precipitation samples throughout the United States and parts of Canada. Samples were collected in buckets using a specified sampler. The buckets were removed each Tuesday morning. Each sample was 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 QA program was put into place. Since then, NADP/NTN and NADP/AIRMoN have shared the same analytical staff and methodology. The AIRMoN sample protocol is different from the NTN sample protocol, but both maintain the same high quality control (QC) objectives.

Table I-1 lists the staff 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. Analytical staff changes at the CAL included Lori Henry leaving the Water Survey in December 1998, and Phyllis Ballard expanding her duties to include AIRMoN sample receipt in 1999.

Data management staff at the CAL (Table I-2) are responsible for screening and reviewing the analytical data once they are transmitted from the laboratory and before they are sent to the Program Office. Angela Kwon was hired in 1999 to help with sample screening. Scott 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.

Employees performing the sample analyses are responsible for implementing QC procedures within their analytical scheme. Analytical methods are revised and validated as technology improves and as new instruments are purchased. No instrument updates occurred in 1999. Detection limits for 1999 did not change. Table I-3 lists the CAL method detection limits (MDLs) for the analytes of interest and the methods used. This table also gives an historic perspective of how the analytical techniques and MDLs have changed over the

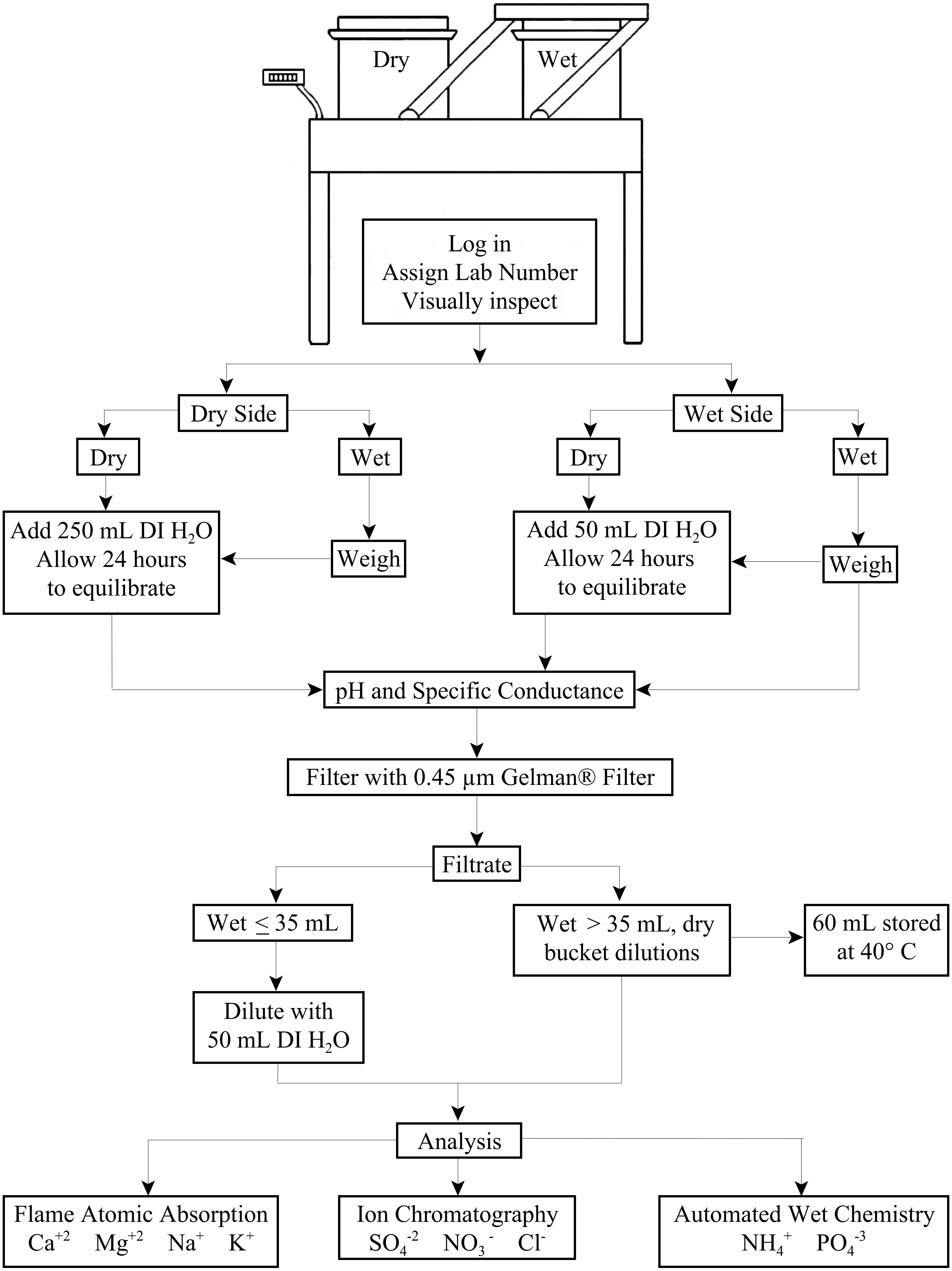

FIGURE I-1. Sample processing flowchart, January 1999 - December 1999.

Table I-1. Central Analytical Laboratory Analytical Staff, 1999

Staff Member	*Job Function*	*Period of Employment*[*]
Sue Bachman	Analysis of ammonium	08/80 - 12/99
	Analysis of calcium, sodium, magnesium, and potassium	11/88 - 12/99
	Analysis of orthophosphate	01/94 - 12/99
	Sample processing coordinator	09/98 - 12/99
Phyllis Ballard	Bucket and bottle cleaning	09/97 - 04/99
	Sample receipt and processing	04/98 - 12/99
	AIRMoN sample receipt	06/99-12/99
Brigita Demir	Analysis of chloride, sulfate, and nitrate	09/81 - 12/99
Karen Harlin	Office of Atmospheric Chemistry Laboratory Supervisor	06/97 - 10/99
	NADP Central Analytical Laboratory Manager and NADP Assistant Coordinator	09/98 - 12/99
Theresa Ingersoll	Sample receipt and processing	03/85 - 12/99
Tracie Patten	Analysis of pH and conductivity, and sample processing	09/98 - 12/99
Jeffrey Pribble	Sample receipt Supply procurement Backup site liaison	07/87 - 12/99
Jane Rothert	AIRMoN coordinator	05/92 - 12/99
	Quality Assurance specialist	07/97 - 12/99
Kaye Surratt	Sample processing	08/96 - 04/97
	AIRMoN sample processing and analysis of ammonium, orthophosphate, calcium, magnesium, sodium, and potassium	11/98 - 12/99
Angela Weddle	Sample processing	06/95 - 12/97
	Analysis of pH and conductivity	10/89 - 12/99

Note:

[*] The reporting period ended in December 1999. Other end dates indicate the last date on which a staff member was responsible for a particular duty.

Table I-2. Central Analytical Laboratory Data Staff, 1999

Staff Member	*Job Function*	*Period of Employment**
Tom Bergerhouse	Computer systems support	07/98 - 12/99
Scotty Dossett	NTN site liaison	09/81 - 12/99
Kathy Douglas	Database manager	04/80 - 12/99
Greg Dzurisin	Computer programer	09/83 - 12/99
Karen Harlin	Final data review	07/97 - 12/99
Angela Kwon	Data review	11/99 - 12/99
Sarah Milton	Data screening	01/98 - 12/99
Jane Rothert	Data quality assurance	07/97 - 12/99

Note:
*The reporting period ended in December 1999.

Table I-3. Method Detection Limits (MDLs) for Precipitation Analysis, 1999

Analyte	*Field Sampling Dates*	*Lab ID Sequence (LABNO)*	*Method Detection Limit (MDL) (mg/L)*	*Analytical Methodology*
Calcium	Jul 78 - Dec 78	NA0001 - NA0221	0.01	Flame Atomic Absorption Spectrometry
	Dec 78 - Jan 79	NA0222 - NA0335	0.02	Flame Atomic Absorption Spectrometry
	Jan 79 - Apr 79	NA0336 - NA0668	0.01	Flame Atomic Absorption Spectrometry
	Apr 79 - Aug 80	NA0669 - NA3361	0.02	Flame Atomic Absorption Spectrometry
	Aug 80 - Sep 80	NA3362 - NA3695	0.008	Flame Atomic Absorption Spectrometry
	Sep 80 - Oct 80	NA3696 - NA4254	0.006	Flame Atomic Absorption Spectrometry
	Oct 80 - Apr 81	NA4255 - NA6328	0.008	Flame Atomic Absorption Spectrometry
	Apr 81 - May 81	NA6329 - NA6543	0.024	Flame Atomic Absorption Spectrometry
	May 81 - Dec 99	NA6544 - NS3700	0.009	Flame Atomic Absorption Spectrometry
Magnesium	Jul 78 - Apr 81	NA0001 - NA6328	0.002	Flame Atomic Absorption Spectrometry
	Apr 81 - May 81	NA6329 - NA6543	0.009	Flame Atomic Absorption Spectrometry
	May 81 - Jul 81	NA6544 - NA7299	0.002	Flame Atomic Absorption Spectrometry
	Jul 81 - Dec 99	NA7300 - NS3700	0.003	Flame Atomic Absorption Spectrometry
Sodium	Jul 78 - Aug 80	NA0001 - NA3475	0.004	Flame Atomic Absorption Spectrometry
	Aug 80 - Aug 81	NA3476 - NA7741	0.002	Flame Atomic Absorption Spectrometry
	Aug 81 - Dec 99	NA7742 - NS3700	0.003	Flame Atomic Absorption Spectrometry
Potassium	Jul 78 - Jan 79	NA0001 - NA0335	0.002	Flame Atomic Absorption Spectrometry
	Jan 79 - Feb 79	NA0336 - NA0446	0.004	Flame Atomic Absorption Spectrometry
	Feb 79 - Sep 79	NA0447 - NA1331	0.002	Flame Atomic Absorption Spectrometry
	Sep 79 - Nov 79	NA1332 - NA1675	0.004	Flame Atomic Absorption Spectrometry
	Nov 79 - Dec 79	NA1676 - NA1800	0.002	Flame Atomic Absorption Spectrometry
	Dec 79 - Aug 80	NA1801 - NA3475	0.004	Flame Atomic Absorption Spectrometry
	Aug 80 - Apr 81	NA3476 - NA6000	0.002	Flame Atomic Absorption Spectrometry
	Apr 81 - Dec 99	NA6001 - NS3700	0.003	Flame Atomic Absorption Spectrometry

Table I-3 (concluded)

Analyte	*Field Sampling Dates*	*Lab ID Sequence (LABNO)*	*Method Detection Limit (MDL) (mg/L)*	*Analytical Methodology*
Ammonium	Jul 78 - Oct 78	NA0001 - NA0104	0.03	Phenate (Segmented Flow Colorimetry)
	Oct 78 - Apr 81	NA0105 - NA6000	0.02	Phenate (Segmented Flow Colorimetry)
	Apr 81 - May 81	NA6001 - NA6650	0.01	Phenate (Segmented Flow Colorimetry)
	May 81 - Jun 89	NA6651 - NH6700	0.02	Phenate (Segmented Flow Colorimetry)
	Jun 89 - Dec 99	NH6701 - NS3700	0.02	Phenate (Flow Injection Colorimetry)
Chloride	July 78 - Apr 81	NA0001 - NA6000[1]	0.05	Ferricyanide (Segmented Flow Colorimetry)
	Apr 81 - Apr 85	NA6001 - ND1937	0.02	
	Apr 85 - Dec 99	ND1938 - NS3700	0.03	Ion Chromatography
Nitrate + Nitrite	Jul 78 - Oct 78	NA0001 - NA0080	0.03	Cadmium Reduction (Segmented Flow Colorimetry)
	Oct 78 - Apr 85	NA0081 - ND1938	0.02	
Nitrate	Apr 85 - Dec 99	ND1939 - NS3700	0.03	Ion Chromatography
Sulfate	Jul 78 - Apr 85	NA0001 - ND1938[2]	0.10	Methylthymol Blue (Segmented Flow Colorimetry)
	Apr 85 - Dec 99	ND1939 - NS3700	0.03	Ion Chromatography
Orthophosphate	Jul 78 - Oct 78	NA0001 - NA0067	0.005	Ascorbic Acid Reduction (Segmented Flow Colorimetry)
	Oct 78 - Feb 79	NA0068 - NA0452	0.004	
	Feb 79 - Apr 85	NA0453 - ND2633	0.003	Ascorbic Acid Reduction (Segmented Flow Colorimetry)
	Apr 85 - Jun 87	ND2634 - NF4630[3]	0.01	
	Jun 87 - Nov 93	NF4631 - NM6824[4]	0.02	Ion Chromatography
	Nov 93 - Dec 99	NM6825 - NS3700	0.003	Ascorbic Acid Reduction (Flow Injection Colorimetry)

Notes:

[1] Sample NA5766 had a detection limit of 0.020 mg Cl$^-$/L.

[2] Sample NB1415 had a detection limit of 0.06 mg SO_4^{2-}/L, and samples NB2015 and NB2254 had detection limits of 0.05 mg SO_4^{2-}/L.

[3] Samples NF4532Q and NF4558Q had detection limits less than 0.020 mg PO_4^{3-}/L.

[4] Sample NM6394 had a detection limit of 0.006 mg PO_4^{3-}/L, sample NM6764Q had a detection limit of 0.009 mg PO_4^{3-}/L, and sample NM6816Q had a detection limit of less than 0.003 mg PO_4^{3-}/L.

course of the program and which samples these changes affect. The MDLs are calculated annually or when there is a change in instrumentation or analyst using the method given in Appendix B. Laboratory MDLs are then maintained at or below the MDLs listed in the *NADP Quality Assurance Plan* (Simmons et al., 1990).

From the beginning of the network in 1978, analytical data have been entered into a large central database. Initially the data were hand-entered using a double-entry system as a means of verification. Currently, data from the atomic absorption spectrophotometer, the ion chromatograph, and the flow injection analyzer are electronically transferred to the database. The pH and conductivity measurements are still double-entered manually. Once the data are verified and validated by CAL data management staff, they are sent to the Program Office for additional screening and coding before being made available for general usage on the Internet. Turnaround time for sample analysis and data processing is 180 days for NTN. Table I-4 lists the percentile concentration values for all NADP/NTN samples of volume greater than 35 milliliters (mL) analyzed by the CAL in 1999. There were 6910 “wet” (W) samples in 1999 with a mean volume of 1519.3 mL and a median volume of 948.3 mL. Table I-5 lists the percentile concentration values for those 1999 AIRMoN samples having a sample volume large enough for a complete chemical analysis. There were 835 samples with a mean volume of 748.0 mL and a median volume of 419.4 mL. Table I-6 shows the AIRMoN sample percentile concentration values from the fall of 1992 until the end of 1999 for 5737 samples with a mean volume of 710.6 mL and a median volume of 398.5 mL. Compared to the long-term averages, median NADP cation concentrations were generally higher in 1999 and anion concentrations were generally about the same.

The ion concentrations displayed in Tables I-4 and I-6 indicate the dilute nature of the precipitation samples analyzed in the laboratory. An extensive laboratory QA program ensures meaningful data.. The Network Quality Assurance Plan (Simmons et al., 1990) summarizes the methods used to document the analysis of each sample. Various facets of the program have been modified and refined over the years. The CAL uses two types of QC procedures: intralaboratory QC procedures and external laboratory intercomparison studies.

The CAL developed intralaboratory QA procedures to address the difficulties related to low ionic strength solution. Internal QC standard (QCS) samples used in the laboratory 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 analysts and are valuable ways of assessing sample bias and/or precision in the NADP/NTN and NADP/AIRMoN daily queue. Extensive analyses of blank solutions every week help identify and/or eliminate sources of contamination.

In addition to external QA studies performed by the U.S. Geological Survey (USGS) as an official part of network operations, the CAL participates in several international laboratory intercomparison studies. These studies allow the CAL to evaluate the quality of its work compared with peer laboratories throughout the United States, Canada, and worldwide. Laboratory QA reports published annually since 1986 and available from the CAL or the Program Office present the history of the CAL program (Stensland et al., 1980; Lockard, 1987; Peden, 1988; James, 1988 - 1997; Rothert, 1999; Rothert, 2000). This report presents and discusses summaries of the results of QA programs in place in 1999.

Table I-4. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/NTN Precipitation Samples, 1999

Parameter	*Percentile Concentration Values (mg/L)*									
	Minimum	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*99th*	*Maximum*
Calcium	-0.009	0.022	0.032	0.064	0.139	0.297	0.581	0.849	1.940	18.050
Magnesium	-0.003	0.004	0.006	0.012	0.024	0.049	0.089	0.137	0.296	1.800
Sodium	-0.003	0.006	0.010	0.020	0.049	0.138	0.377	0.703	2.440	11.520
Potassium	-0.003	-0.003	0.004	0.009	0.019	0.039	0.072	0.108	0.281	5.870
Ammonium	-0.02	-0.02	0.02	0.08	0.22	0.43	0.71	0.97	1.61	5.15
Sulfate	-0.03	0.15	0.25	0.54	1.09	2.00	3.13	3.95	6.68	20.28
Nitrate	-0.03	0.18	0.30	0.62	1.14	1.93	2.96	3.81	6.00	15.96
Chloride	-0.03	0.03	0.04	0.06	0.11	0.25	0.64	1.25	3.74	18.87
Orthophosphate	-0.003	-0.003	-0.003	-0.003	-0.003	-0.003	-0.003	-0.003	0.031	0.677
pH (units)	3.48	4.15	4.25	4.48	4.84	5.34	5.94	6.29	6.81	7.84
Specific Conductance (µS/cm)	1.5	3.4	4.5	7.5	12.9	22.3	34.7	44.0	70.0	212.9

Notes:
Number of samples = 6910, mean sample volume = 1519.3 mL, and median sample volume = 948.3 mL. Negative numbers represent the method detection limits for each parameter.

Table I-5. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/AIRMoN Precipitation Wet-only Samples, 1999

	Percentile Concentration Values (mg/L)								
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*Maximum*
Calcium	-0.001	0.019	0.031	0.063	0.149	0.296	0.644	0.915	3.990
Magnesium	0.000	0.003	0.005	0.011	0.028	0.073	0.162	0.246	1.060
Sodium	-0.002	0.005	0.008	0.022	0.079	0.432	0.937	1.443	15.440
Potassium	-0.004	0.002	0.004	0.009	0.020	0.043	0.083	0.121	0.553
Ammonium	-0.01	0.03	0.04	0.11	0.26	0.50	0.78	1.02	2.84
Sulfate	0.06	0.34	0.48	1.03	1.89	3.32	5.09	6.18	15.68
Nitrate	0.05	0.25	0.40	0.77	1.53	2.75	4.30	5.34	13.68
Chloride	0.00	0.03	0.05	0.10	0.22	0.91	2.12	3.64	22.75
Orthophosphate	-0.004	0.000	0.000	0.000	0.000	0.010	0.024	0.041	1.516
pH (units)	3.42	3.88	3.98	4.16	4.40	4.69	5.01	5.26	6.85
Specific Conductance (µS/cm)	2.0	6.7	9.4	16.2	26.1	42.2	62.7	79.8	187.1

Notes:
Only wet-only samples were used. Samples with a quality rating of C, signifying severe contamination, were not used to tabulate any of the values. Total number of samples = 835. Mean sample volume = 748.0 mL. Median sample volume = 419.4 mL. Maximum sample volume = 8962.2 mL. Minimum sample volume = 25.5 mL. Negative numbers represent actual values measured, not method detection limits for each parameter.

Table I-6. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/AIRMoN Precipitation Wet-only Samples, 1992 - 1999

	Percentile Concentration Values (mg/L)								
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*Maximum*
Calcium	-0.006	0.011	0.018	0.042	0.094	0.214	0.446	0.691	6.700
Magnesium	-0.002	0.002	0.003	0.007	0.019	0.051	0.120	0.196	2.870
Sodium	-0.002	0.005	0.008	0.017	0.044	0.174	0.703	1.290	24.800
Potassium	-0.004	0.002	0.004	0.009	0.019	0.039	0.072	0.102	2.070
Ammonium	-0.01	0.04	0.06	0.13	0.27	0.51	0.85	1.14	4.59
Sulfate	0.03	0.37	0.59	1.10	1.92	3.30	5.18	6.47	25.84
Nitrate	0.02	0.31	0.45	0.86	1.56	2.85	4.50	5.88	21.88
Chloride	0.00	0.03	0.04	0.08	0.16	0.42	1.40	2.52	43.95
Orthophosphate	-0.006	0.000	0.000	0.000	0.000	0.008	0.017	0.029	1.516
pH (units)	3.19	3.82	3.93	4.12	4.34	4.58	4.87	5.11	7.43
Specific Conductance (µS/cm)	1.6	7.4	10.5	16.6	26.7	42.3	64.1	82.4	291.8

Notes:
Only wet-only samples were used. Samples with a quality rating of C, signifying severe contamination, were not used to tabulate any of the values. All QC samples were removed. Total number of samples = 5737. Mean sample volume = 710.6 mL. Median sample volume = 398.5 mL. Maximum sample volume = 9285.9 mL. Minimum sample volume = 13.6 mL. Negative numbers represent actual values measured, not method detection limits for each parameter.

II. LABORATORY QUALITY ASSURANCE - A GENERAL DESCRIPTION

This report summarizes the results of the quality assurance (QA) program in effect at the CAL for 1999. Table II-1 summarizes the various QA/Quality Control (QC) components and their frequency of occurrence.

A. Field QA Program

The QA of chemical and physical measurements begins in the field where pH and specific conductance are measured soon after sample collection and prior to shipping. Site operators use quality control standard (QCS) solutions formulated and prepared at the CAL and shipped to the sites as weekly check samples. The two QCS solutions used in 1999 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 KCl solution was used to calibrate the conductivity cell and to correct the conductivity readings to ambient temperature; the HNO_3/NaCl 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 that of the precipitation samples.

B. Laboratory QA Program

Precipitation samples are unpacked carefully upon arrival at the CAL. Information and requests written on the field forms are noted and logged into a database. Samples are then transported to sample processing where the 1-liter shipping bottles are assigned sequential numbers. Samples are then visually inspected. Following pH and conductivity measurements, samples are filtered into pre-washed 60-mL high density polyethylene (HDPE) round bottles using 0.45 micrometer (μm) pore-size polyethersulfone filters. These sample aliquots are used to obtain the chemistry of the weekly samples. 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, but they 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 commercially prepared buffer solutions of pH 7 and 4. The ability of the electrode to measure low ionic strength precipitation solutions is verified by measuring two solutions of simulated rainwater at ionic strengths simulating the 25th and 75th percentile concentrations of the NTN. These solutions are prepared in-house and are tested (Simmons et al., 1990) prior to use as QCS solutions. These solutions, referred to as FR25 and FR75, are used as QCS solutions for all measurements except for orthophosphate [orthophosphate is not stable, especially at the low concentrations found in NADP samples (Ridder, et al., 1985)]. Instead, U.S. Environmental Protection Agency (USEPA) nutrient concentrates are diluted and used for orthophosphate QCS.

Table II-1. NADP Laboratory QC/QA Program Summary, 1999

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

II. Weekly
   A. Analyze blanks.
      1. Analyze the laboratory's deionized (DI) water.
      2. Use DI water and simulated rainwater for filter leaching.
      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.
   B. Analyze internal blind audit samples from sites SWS1, SWS2, and SWS3.
      1. SWS1: Use High-Purity Standards (H-PS) simulated rainwater 1 and 2, unfiltered.
      2. SWS2: Use DI water and pH 4.3 nitric acid, unfiltered.
      3. 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. Inspect control charts generated from QCS measurements.
   C. Evaluate internal blind audit and replicate data from printouts.
   D. Select samples for reanalysis by computer-based ion percent and conductivity percent differences.
      1. Evaluate reanalysis data.
      2. Suggest data changes to data management.
   E. Measure USGS interlaboratory comparison samples every 2 weeks and send to the USGS in Denver every 3 months.
   F. Validate QCS prior to shipment to sites as needed.

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.

After filtration, samples in the round 60-mL bottles are placed on a tray and transported to the main laboratory for analysis of the major ions. The AIRMoN samples are stored on trays in a walk-in cooler in the sample processing area for analysis in a specified order: pH and conductivity; ammonium and orthophosphate; chloride, nitrate, and sulfate; and 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). Because low volume AIRMoN samples are not diluted, there is not always sufficient sample for complete analysis; therefore, highest priority measurements are made first.

The NTN samples are in the field for up to one week and then shipped via ground transportation to the CAL. Once pH and conductivity are complete, the order of analyses is not prioritized. Low volume NTN samples (less then 30 mL) are diluted after pH and conductivity are determined to ensure sufficient volume for a complete analysis of each sample. Analysts select the samples with numbers in the next sequence for analysis by atomic absorption, ion chromatography, or flow injection automated colorimetry. These instruments are standardized using solutions encompassing the expected concentration range of samples. Samples with concentrations greater than the expected range of 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. Values are recorded daily and summarized monthly for control charts. These QCS solutions are analyzed immediately after analysis of standardization solutions and blanks and then periodically throughout the run. The analyst is fully aware of the concentration of these solutions and uses them to evaluate initial standardization of the instrument and whether it is maintaining its standardized analytical curve throughout the day.

Each week solutions collected from multiple sources are submitted to the CAL for analysis as blank samples. These samples are used to evaluate possible contamination both from sample collection and shipping activities and from 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, the sample preparation, and the bucket washing laboratories. 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 blind samples and four or five samples that are split so that the originals and duplicates are separated for analysis. Duplicates are submitted with new sample identification numbers, which are unknown to the analysts, and are analyzed in numerical order, approximately 100 samples away from the original sample. The duplicates, therefore, are analyzed at a different time than the original samples, possibly on a separate day, with new calibration standards and check samples. The AIRMoN split sample protocol is similar to the NTN duplicate program. A sample of known concentration is submitted by the IL11 site operator as a real precipitation sample on a weekly basis. This internal blind sample undergoes the entire AIRMoN system of sample log-in through final analysis to monitor all laboratory systems.

Each month a computer program generates a random selection of samples for reanalysis. This same program also calculates the ion percent and conductance percent difference for each wet ("W") sample and wet-add samples with volumes less than 35 mL but greater than 10 mL ("WA"). Samples with an ion percent or conductance percent difference greater than allowed by the NADP QAP are tabulated. Reanalysis lists are generated by the QA specialist based on the computer-generated lists and distributed to the laboratory analysts. 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, Colorado. 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 the United States, Canada, and worldwide.

III. DAILY QUALITY CONTROL PROCEDURES

Each morning, prior to analysis, the analysts prepare reagents and standards, as required in the standard operating procedure (SOP) for each instrument, and evaluate the performance of the analytical instrumentation. Standards preparation and instrument maintenance information are recorded in notebooks kept in 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 the 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).

Data presented in Table III-1 represent bias and precision estimates under optimum conditions. The data were generated using QCS solutions known to the analysts, rather than precipitation or blind samples. The QCS solutions are stable solutions, whereas the actual precipitation samples are potentially still chemically changing. The QCS solutions 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. In 1999, they were 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. This bias could reflect instrument changes over the course of the year or could indicate that the original mean determined for that parameter was biased. Refer to the laboratory portion of the NADP QAP (Simmons et al., 1990) for more information.

Table III-1. Analytical Bias and Precision Determined from Analysis of Simulated Rain QCS, 1999

Parameter	*Target Concentrations (mg/L)*	*Measured Mean Concentrations (mg/L)*	*Number of Replicates*	*Bias (mg/L)*	*Bias (%)*	*Precision (mg/L)*	*RSD (%)*	*Critical Concentration (mg/L)*	*Statistically Significant Bias?*
Ca	0.076[a]	0.076	1038	0.0	0.0	0.002	2.6	0.001	no
	0.296[b]	0.297	745	0.001	0.3	0.006	2.0	0.004	no
Mg	0.017	0.018	1075	0.001	5.9	0.0007	3.9	0.005	no
	0.066	0.068	732	0.002	3.0	0.002	2.9	0.001	yes
Na	0.048	0.048	1147	0.0	0.0	0.001	2.1	0.0007	no
	0.189	0.189	825	0.0	0.0	0.005	2.6	0.003	no
K	0.013	0.013	1102	0.0	0.0	0.001	7.7	0.0007	no
	0.057	0.057	794	0.0	0.0	0.002	3.5	0.001	no
NH_4	0.08	0.08	1041	0.0	0.0	0.01	12.5	0.004	no
	0.35	0.35	843	0.0	0.0	0.01	2.9	0.010	no
Cl	0.13	0.13	1282	0.0	0.0	0.004	3.1	0.002	no
	0.53	0.53	1232	0.0	0.0	0.007	1.3	0.004	no
NO_3	0.46	0.47	1280	0.01	2.2	0.006	1.3	0.004	yes
	1.91	1.91	1277	0.0	0.0	0.02	1.0	0.011	no
SO_4	0.61	0.61	1275	0.0	0.0	0.008	1.3	0.005	no
	2.50	2.51	1225	0.01	0.4	0.01	0.4	0.008	yes
PO_4	0.035	0.034	495	-0.001	-3.5	0.004	11.4	0.008	no
	0.089	0.085	211	-0.004	-4.1	0.006	7.1	0.0011	no
pH	4.94(11.6)[c]	4.94(11.6)	1513	0.0(0.0)	0.0(0.0)	0.03(0.54)	0.6(4.4)	0.02(0.34)	no(no)
units (µeq/L)	4.36(43.2)	4.37(42.8)	1370	0.01(-0.4)	0.2(-0.9)	0.02(1.7)	0.5(3.9)	0.01 (1.0)	no(no)
Specific Conductance	7.1	7.2	1023	0.1	1.4	0.1	1.4	0.08	no
(µS/cm)	26.9	27.1	957	0.2	0.7	0.2	0.7	0.13	yes

Notes:

See Appendix A for definitions and formulas for Bias, Precision, RSD, 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 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 to monitor for possible filter contamination. The sites for these samples are coded as SWS1, SWS2, and SWS3. In 1999, the SWS1 samples were High-Purity Standards[1] 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. The SWS3 samples are filtered.

Tables IV-1 – IV-4 summarize the 1999 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 occur at any point 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 SWS3 samples (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 were used in 1999. These samples, H-PS SR1 (lot #821825), and H-PS SR2 (lot #821806), were of similar concentrations as those used in previous years and slightly higher than the internal QCS solutions made at the CAL. The H-PS SR1 sample is more similar in concentration to the higher concentration FR75 QCS solution with the H-PS SR2 sample having still higher concentrations. The percent bias for most of the parameters was higher for the H-PS samples than the QCS. The exceptions were nitrate and conductivity. A similar difference between the H-PS samples and the QCS was

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

Disclaimer: The use of trade or manufacturer's names does not constitute an endorsement by the Illinois State Water Survey, the NADP, or the CAL.

Table IV-1. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS1) High-Purity Standards Simulated Rainwater I (H-PS SR1) and II (H-PS SR2), Unfiltered, 1999

Parameter	*Target Concentration [a] (mg/L)*	*Measured Concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Precision (mg/L)*	*RSD (%)*
Calcium	0.015 [b]	0.025	0.010	66.7	0.011	44.0
	0.048 [c]	0.055	0.007	14.6	0.005	9.1
Magnesium	0.019	0.024	0.005	26.3	0.001	4.2
	0.049	0.047	-0.002	-4.1	0.001	2.1
Sodium	0.20	0.198	-0.002	-1.0	0.005	2.5
	0.40	0.399	-0.001	-0.25	0.010	2.5
Potassium	0.050	0.050	0.00	0.0	0.001	2.0
	0.093	0.102	0.008	8.6	0.003	2.9
Ammonium [d]	0.100	0.045	-0.06	-60.0	0.008	17.8
	1.0	0.956	-0.04	-4.4	0.071	7.4
Sulfate	2.5	2.49	-0.01	-0.4	0.02	0.8
	10.1	10.04	-0.06	-0.6	0.17	1.7
Nitrate	0.50	0.50	0.00	0.0	0.01	2.0
	7.0	7.10	0.10	1.4	0.07	1.0
Chloride	0.25	0.22	-0.03	-12.0	0.00	0.0
	0.98	0.99	0.01	1.0	0.01	1.0
pH	4.29	4.34	0.04	0.9	0.03	0.7
(units)	3.55	3.64	0.09	2.5	0.03	0.8
H	50.9	46.3	-4.6	-9.0	3.02	6.5
(µeq/L)	281.8	228.7	-53.1	-18.8	17.1	7.5
Specific Conductance	24.7	24.2	-0.5	-2.0	0.9	3.7
(µS/cm)	125.0	124.3	-0.7	-0.6	1.7	2.8

Notes:
There were 26 samples in each set.

[a] Target concentrations are those reported by High-Purity Standards and may not be correct.

[b] Concentration values for H-PS SR1, Lot #821825.

[c] Concentration values for H-PS SR2, Lot #821806.

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

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, 1999

Parameter	*Target Concentration (mg/L)*	*Measured Concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Precision (mg/L)*	*RSD (%)*
Calcium	<0.009 [a]	<0.009			0.004	
	<0.009 [b]	<0.009			0.004	
Magnesium	<0.003	<0.003			0.000	
	<0.003	<0.003			0.000	
Sodium	<0.003	<0.003			0.000	
	<0.003	<0.003			0.000	
Potassium	<0.003	<0.003			0.000	
	<0.003	<0.003			0.000	
Ammonium	<0.02	<0.02			0.00	
	<0.02	<0.02			0.00	
Sulfate	<0.03	<0.03			0.00	
	<0.03	<0.03			0.00	
Nitrate	<0.03	<0.03			0.00	
	3.12 [c]	3.25	0.13	4.2	0.04	1.2
Chloride	<0.03	<0.03			0.01	
	<0.03	<0.03			0.00	
pH	5.65	5.60	-0.05	-0.9	0.15	2.7
(units)	4.30	4.33	0.03	0.7	0.02	0.5
H	2.24	2.67	0.44	19.6	0.8	30.0
(µeq/L)	50.1	46.7	-3.4	-6.8	2.1	4.5
Specific Conductance	0.9	1.1	0.2	22.2	0.24	21.8
(µS/cm)	21.1	21.5	0.4	1.9	0.81	3.8

Notes:

There were 26 samples in each set.

[a] Concentration values for deionized (DI) water.

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

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

Table IV-3. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS1), High-Purity Standards Simulated Rainwater I (H-PS SR1), and II (H-PS SR2), Filtered, 1999

Parameter	*Target Concentration* [a] *(mg/L)*	*Measured Concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Precision (mg/L)*	*RSD (%)*
Calcium	0.015 [b]	0.037	0.022	146.7	0.011	29.7
	0.048 [c]	0.089	0.041	85.4	0.036	40.4
Magnesium	0.019	0.025	0.006	31.62	0.004	16.0
	0.049	0.049	0.000	0.0	0.004	8.2
Sodium	0.20	0.193	-0.007	-3.5	0.004	2.1
	0.40	0.389	-0.011	-2.8	0.008	2.1
Potassium	0.050	0.047	-0.003	-6.0	0.002	4.3
	0.093	0.098	0.005	5.4	0.004	4.1
Ammonium [d]	0.100	0.05	-0.05	-50.0	0.01	20.0
	1.0	0.92	-0.08	-8.0	0.03	3.3
Sulfate	2.5	2.39	-0.11	-4.4	0.03	1.3
	10.1	9.67	-0.43	-4.3	0.15	1.6
Nitrate	0.50	0.49	-0.01	-2.0	0.01	2.0
	7.0	6.87	-0.13	-1.9	0.14	2.0
Chloride	0.25	0.21	-0.04	-16.0	0.00	0.0
	0.98	0.95	-0.03	-3.1	0.02	2.1
pH	4.29	4.33	0.04	0.9	0.02	0.5
(units)	3.55	3.65	0.10	2.8	0.02	0.5
H	50.9	46.6	-4.3	-8.4	1.7	3.6
(µeq/L)	281.8	226.5	-55.3	-19.6	10.7	4.7
Specific Conductance	24.7	24.4	-0.3	-1.2	0.6	2.5
(µS/cm)	125	123.9	-1.1	-0.9	3.8	3.1

Notes:

There were 13 samples in each set.

[a] Target Concentrations are those reported by High Purity Standards and are not necessarily correct.

[b] Concentration values for H-PS SR1, Lot #821825.

[c] Concentration values for H-PS SR2, Lot #821806.

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

Table IV-4. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS2), Deionized Water (DI) and pH 4.3 Quality Control Sample (QCS), Filtered, 1999

Parameter	*Target Concentration (mg/L)*	*Measured Concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Precision (mg/L)*	*RSD (%)*
Calcium	<0.009 [a]	<0.009			0.000	
	<0.009 [b]	<0.009			0.013	
Magnesium	<0.003	<0.003			0.000	
	<0.003	<0.003			0.002	
Sodium	<0.003	<0.003			0.002	
	<0.003	<0.003			0.000	
Potassium	<0.003	<0.003			0.000	
	<0.003	<0.003			0.000	
Ammonium	<0.02	<0.02			0.00	
	<0.02	<0.02			0.00	
Sulfate	<0.03	<0.03			0.01	
	<0.03	<0.03			0.00	
Nitrate	<0.03	<0.03			0.00	
	3.12 [c]	3.14	0.02	0.6	0.08	2.5
Chloride	<0.03	<0.03			0.00	
	<0.03	<0.03			0.00	
pH	5.65	5.56	-0.09	-1.6	0.06	1.1
(units)	4.30	4.33	0.03	0.7	0.02	0.5
H	2.24	2.75	0.51	22.8	0.35	12.7
(µeq/L)	50.12	46.3	-3.8	-7.6	2.15	4.6
Specific Conductance	0.9	1.1	0.2	22.2	0.21	19.1
(µS/cm)	21.1	21.6	0.5	2.4	0.59	2.7

Notes:
There were 13 samples in each set.
[a] Concentration values for deionized (DI) water.
[b] Concentration values for pH 4.3 Quality Control Sample (QCS).
[c] Concentration values for pH 4.3 QCS are based on theoretical values. Concentrations for each prepared solution may vary slightly from ideal values.

seen when the percent relative standard deviation (RSD) was compared. The QCS solutions had a lower percent RSD than did the H-PS samples. The potassium and chloride values of both QCS solutions appeared to have higher percent RSDs than the internal blinds; however, the concentrations for potassium and chloride were considerably lower for the QCS solutions than for the blinds.

A large positive bias between the laboratory measurements and the target concentration for calcium was determined. In 1998, an outside laboratory, Environmental Science and Engineering (ESE), was asked to measure the calcium concentration in the H-PS solutions to determine the bias. The calcium concentration obtained by ESE in 1998 (0.022 mg/L) was within the range of the CAL measurements and outside the certified limits set by H-PS. This intercomparison between ESE and the CAL was not done in 1999, but the bias between the CAL and the certified limits set by H-PS is the same. The ammonium concentration in the H-PS samples is not certified and is included for information only. The apparent large bias and precision shown by CAL measurements for ammonium in H-PS SR1 may be indicative of this parameter’s instability.

The SWS2 solutions are, for the most part, blanks. One solution 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. Tables IV-2 and IV-4 show measured concentrations for DI water solutions below the method detection limit (MDL). A small positive bias for nitrate was found in the nitric acid solution, which 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 most of the unfiltered SWS1 samples for the H-PS solutions. The systematic bias observed prior to 1998 has been eliminated. Some variation is normal and expected in a system and was observed in the differences between filtered and unfiltered samples in 1999. The RSD for calcium in 1999 was larger than in 1998, but the values in 1998 were much lower than previous values. The 1999 RSD seems more indicative of the values obtained at the CAL. The RSD for the other parameters indicated that the precision of the CAL measurements was about the same in 1999 as in 1998. The only ion that appeared to have a much larger difference in percent RSD in 1999 than in 1998 was the ammonium ion. The RSD for ammonium in 1999 was also more indicative of values CAL has obtained. The large sodium biases seen prior to 1998, before the use of the Gelman® filters, were not found in 1999. Although there was a slightly lower bias in the unfiltered samples compared with the filtered samples for sodium, both biases were negative, indicating no addition of sodium from the filtration process.

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 250-mL sample bottle that is 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 involved 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 site 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 delivers the sample to the CAL. The sample receiving staff at the CAL have 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 1999 were simulated rainwater prepared for the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) intercomparison study for 1998 (Coleman et al., 1999). Table IV-5 summarizes the results of the AIRMoN internal blind samples. The values measured for the study by the CAL are included in Table IV-5 along with the target concentrations and the 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 samples in the AIRMoN internal blind program was about the same as for H-PS SR solutions used for the NTN internal blind program for 1999 and for the AIRMoN internal blind study for 1998. In some cases, notably calcium, magnesium, and ammonium, there was no bias for the CAL for the WMO #2 sample. Whereas for the H-PS SR solutions, the bias was 66.7 percent for calcium, 26.3 percent for magnesium, and -60.0 percent for ammonium. This emphasizes the possibility of erroneously reported concentrations of the H-PS solutions. The percent RSD for the AIRMoN blind samples was better for some parameters, the same for others, and worse for still other parameters compared to the NTN blind samples. 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

Table IV-5. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, AIRMoN, 1999

Parameter	*Theoretical Concentration*[a] *(mg/L)*	*Mean WMO/GAW Concentration*[b] *(mg/L)*	*CAL Study Concentration*[c] *(mg/L)*	*CAL Mean Concentration*[d] *(mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Precision (mg/L)*	*RSD*[e] *(%)*
Calcium	0.060	0.058	0.060	0.060	0.0	0.0	0.006	1.0
Magnesium	0.024	0.024	0.024	0.024	0.0	0.0	0.002	8.3
Sodium	0.248	0.244	0.241	0.240	-0.008	-3.2	0.006	2.5
Potassium	0.076	0.072	0.077	0.077	0.001	1.3	0.002	2.6
Ammonium	0.14	0.14	0.14	0.14	0.0	0.0	0.03	21.4
Sulfate	1.65	1.62	1.59	1.58	-0.07	-4.2	0.01	0.6
Nitrate	0.62	0.62	0.62	0.61	-0.01	-1.6	0.01	1.6
Chloride	0.39	0.40	0.38	0.38	-0.01	-2.6	0.01	2.6
pH units	4.51	4.52	4.52	4.53	0.02	0.44	0.02	0.4
Hydrogen ion (µeq/L)	30.9	30.2	30.2	29.9	-1.0	-3.2	1.5	5.0
Specific Conductance (µS/cm)	17.0	16.7	17.1	17.4	0.4	2.4	0.94	5.4

Notes:
This tabulation included 48 internal blinds. Samples were 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] Concentration reported to the WMO/GAW by the CAL during the 1998 WMO intercomparison study.
[d] Mean concentration obtained by the CAL from the AIRMoN internal blind samples for 1999.
[e] RSD is Relative Standard Deviation.

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 later. 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 recode 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, 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 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, and a Field Observer Form is filled out to accompany 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 1999 for NTN and AIRMoN. Differences are calculated by subtracting the reanalysis value from the original value. 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 5th, 50th, and 95th percentile concentrations of the replicate samples for the year are determined for each analyte (Appendix B, Table B-5). The box plots (Appendix B, Figures B-24 – B-26 for NTN and Figures B-27 – B-29 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 concentration, concentrations above the median concentration, 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 Hirsch, 1992). A comparison of the RSD for the QCS solutions (Table III-1), SWS1 (Table IV-1) and SWS3 (Table IV-3) to 1.48 × MAD 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. Solutions are collected and

Table IV-6. Variance Estimated from Analysis Replicate NADP/NTN Precipitation Samples, 1999

Parameter	*Standard Deviation Estimated from Paired Measurements*[a] *(mg/L)* *Low*	*High*	*Total*	*(1.48) × MAD*[b]
Calcium	0.005	0.040	0.029	0.006
Magnesium	0.001	0.010	0.007	0.001
Sodium	0.001	0.152	0.108	0.002
Potassium	0.002	0.002	0.002	0.001
Ammonium	0.01	0.03	0.02	0.01
Sulfate	0.01	0.02	0.01	0.01
Nitrate	0.02	0.01	0.02	0.01
Chloride	0.01	0.03	0.02	0.00
Orthophosphate	0.000	0.001	0.000	0.000
pH (units)	0.02	0.09	0.07	0.03
Hydrogen ion (µeq/L)	2.22	0.85	1.68	0.98
Specific Conductance (µS/cm)	0.31	0.67	0.52	0.30
Number of pairs	96	96	192	192

Notes:

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

[b] MAD is Median Absolute Difference.

Table IV-7. Variance Estimated from Analysis of Replicate AIRMoN Precipitation Samples, 1999

	Standard Deviation Estimated from Paired Measurements [a] *(mg/L)*			
Parameter	*Low*	*High*	*Total*	*(1.48) × MAD* [b]
Calcium	0.002	0.005	0.004	0.006
Magnesium	0.001	0.001	0.001	0.001
Sodium	0.001	0.051	0.036	0.001
Potassium	0.002	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	0.00	0.04	0.03	0.01
Chloride	0.00	0.01	0.01	0.00
Orthophosphate	0.001	0.008	0.006	0.0001
pH (units)	0.02	0.05	0.04	0.04
Hydrogen ion (µeq/L)	2.41	7.24	5.40	6.10
Specific Conductance (µS/cm)	1.6	1.8	1.7	1.6
Number of pairs	15	15	30	30

Notes:

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

[b] MAD is Median Absolute Difference.

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 analysts analyze the "blanks" as a weekly set, and the week they are collected is included in the "blank" identification number. In 1999, two solutions were used to leach filters, bottles, buckets, and lids: DI water from the sample processing laboratory and the FR25 QCS solution. 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 specific conductance of DI water used for rinsing, leaching, and making reagents and standards is indirectly monitored weekly in each laboratory. Resistivity, the inverse of conductivity, is measured with an in-line resistivity meter at the source of the DI water in the laboratory building and in all individual laboratories. 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 and conductivity readings are similar to past measurements and approximate readings for uncontaminated DI water concentrations. The DI water blanks also are 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, Gelman Supor® 450, 0.45-micrometer (µm) hydrophylic polyethersulfone 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.

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. Gelman polyethersulfone filters were first used in January 1998. Prior to this, Millipore™ HAWP filters were used. 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 approximate the target concentrations.

Table IV-8. Median pH and Conductivity Values for Weekly Deionized (DI) Water Blanks, 1999

Laboratory	*pH (units)*	*Conductivity (µS/cm)*	*Period (weeks)*
Sample Processing Laboratory	5.64	1.0	50
Atomic Absorption Laboratory	5.68	0.9	52
Service Laboratory	5.67	0.9	52

Table IV-9. Median Analyte Concentrations Found in Filter Leachates, 1999

	DI Water		*FR25*		
Analyte	*A*[a] *(mg/L)*	*B*[b] *(mg/L)*	*A*[a] *(mg/L)*	*B*[b] *(mg/L)*	*Target Concentration (mg/L)*
Calcium	<0.009	<0.009	0.076	0.076	0.076
Magnesium	<0.003	<0.003	0.016	0.017	0.017
Sodium	<0.003	<0.003	0.047	0.048	0.048
Potassium	<0.003	<0.003	0.013	0.013	0.014
Ammonium	<0.02	<0.02	0.08	0.08	0.08
Sulfate	<0.03	<0.03	0.59	0.62	0.61
Nitrate	<0.03	<0.03	0.45	0.47	0.46
Chloride	<0.03	<0.03	0.13	0.13	0.13
pH	5.60	5.60	4.94	4.93	4.93
Hydrogen ion (µeq/L)	2.51	2.51	11.6	11.7	11.7
Specific Conductance (µS/cm)	1.2	1.2	7.2	7.3	7.2

Notes:
A total of 52 blank samples were collected.
[a] First 50-mL filtrate.
[b] Second 50-mL filtrate.

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 dishwasher, 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 beginning of NADP.

The weekly procedure for "bucket blanks" includes leaching four buckets for five days with two different volumes of two different solutions: DI water and FR25 in 50- and 150-mL portions. Beginning October 12, 1999, a fifth bucket using DI water for the leachate was added because of the increased number of buckets being used on the two networks. The solutions were measured into the buckets which were covered with snap-on lids and stored for five days in the sample processing laboratory. The five 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, calcium, sodium, and ammonium were present in measurable amounts in the lower volume (50-mL) blanks and calcium was found in the higher volume blanks. Sodium was also found in the second set of DI water blanks started toward the end of 1999 . 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.

The calcium in the bucket blanks was a cause for concern, and a study was initiated to determine the source. Calcium in the samples used to be caused by the butadiene rubber o-ring in the lid, but use of shipping bottles and lids without o-rings had eliminated this problem. In February 1999, the clean bucket and lid shipping bag manufacturer changed the process for making the bags used by the CAL. Random spikes were noted in bucket blanks throughout 1999, but not until early fall was a pattern seen. Beginning in October 1999, after determining that the releasing agent used in the bags was the source of the calcium contamination, the CAL once again began using bags without added releasing agent. In October, November, and December, several new sources of bags were investigated in order to find bags with the least potential for contamination. Bag blanks were added to the blanks regime in January 2000.

Table IV-10. Median Measured Mass as Micrograms (mg)/Bucket[a] Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in Upright Bucket Leachates, 1999

Analyte	*DI Water (50 mL)*	*DI Water (150 mL)*	*DI Water[b] (50 mL)*	*FR25[c] (50 mL)*	*FR25[c] (150 mL)*
Calcium	0.325[d]	0.975[d]	<0.225	0.725[d]	1.35
Magnesium	<0.075	<0.225	<0.075	<0.075	<0.225
Sodium	0.15	<0.225	0.075	0.125	0.30
Potassium	<0.075	<0.225	<0.075	<0.075	0.30
Ammonium	0.50	<1.50	0.50	1.0	<2.25
Sulfate	<0.75	<2.25	<0.75	<0.75	<2.25
Nitrate	<0.75	<2.25	<0.75	<0.75	<2.25
Chloride	<0.75	<2.25	<0.75	0.75	<2.25
pH (units)	5.66	5.66	5.71	5.03(4.93)[e]	4.99(4.93)[e]
Hydrogen ion (µeq/bucket)	0.109	0.328	0.098	0.467(0.587)[d]	1.53(1.76)[d]
Specific Conductance (µS/cm)	1.5	1.3	1.5	6.7(7.4)[c]	7.0(7.4)[c]

Notes:
There were 52 blind sample weeks in 1999.
MDLs are reported in Table I-3.

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

[b] There were 11 sample blind weeks for a second bucket with 50 mL DI water.

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

[d] The high calcium in the bucket blanks was due to manufacturer change in bag preparation. These bags were used between February and September 1999.

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

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. Upon sample arrival at the CAL, portions of sample are removed for pH and conductivity measurements, filtered, and collected in 60-mL bottles. Excess sample is discarded. Shipping bottles are washed at the CAL and sent back to the NTN sites for reuse.

Table IV-11 shows the median measured mass found in bottle leachates. The 1-L shipping bottles contained no analyte concentrations above the MDL.

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 are measured onto one lid and 50 mL of FR25 onto the other lid. They are covered with large plastic domes for 24 hours. Table IV-12 shows the median concentrations found on the snap-on lid “blanks”. There were no analyte concentrations above the MDLs found on the lids.

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 AIRMoN samples are taken to the field laboratories, they are poured into 250-mL sample shipping bottles and sent to the CAL.

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

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, 1999

	DI Water		*FR25*[b]	
Analyte	*(50 mL)*	*(150 mL)*	*(50 mL)*	*(150 mL)*
Calcium	<0.225	<0.675	<0.150	<0.300
Magnesium	<0.075	<0.225	<0.075	<0.225
Sodium	<0.075	<0.225	0.075	<0.225
Potassium	<0.075	<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)	5.58	5.59	4.98(4.93)[c]	4.96(4.93)[c]
Hydrogen ion (µeq/bucket)	0.13	0.39	0.52(0.59)[c]	1.66(1.76)[c]
Specific Conductance (µS/cm)	1.3	1.3	7.0(7.2)[c]	7.1(7.2)[c]

Notes:

There were 52 blind sample weeks in 1999.

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

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

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

Table IV-12. Median Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Snap-on Lids, 1999

Analyte	*DI Water (50 mL)*	*FR25 (50 mL)*	*FR25 Target Concentration (mg/L)*
Calcium	<0.009	0.081	0.076
Magnesium	<0.003	0.018	0.017
Sodium	<0.003	0.049	0.048
Potassium	<0.003	0.015	0.014
Ammonium	<0.02	0.10	0.08
Sulfate	<0.03	0.62	0.61
Nitrate	<0.03	0.47	0.46
Chloride	<0.03	0.13	0.13
pH (units)	5.65	4.99	4.93
Hydrogen Ion (µeq/L)	2.24	10.2	11.7
Specific Conductance (µS/cm)	1.3	7.0	7.2

Note:
There were 52 weeks of snap-on lid blanks.

Table IV-13. Median Analyte Concentration (mg/L) Found in Monthly Simulated Rain (FR25) AIRMoN 250-mL HDPE Bottle Leachates, 1999

Analyte	*FR25 (50 mL)*	*FR25 (150 mL)*	*FR25 Target Concentration (mg/L)*
Calcium	0.076	0.074	0.076
Magnesium	0.017	0.017	0.017
Sodium	0.049	0.049	0.048
Potassium	0.014	0.014	0.014
Ammonium	0.09	0.09	0.08
Sulfate	0.61	0.61	0.61
Nitrate	0.47	0.47	0.46
Chloride	0.13	0.13	0.13
pH (units)	4.93	4.94	4.93
Hydrogen ion (µeq/L)	11.7	11.5	11.7
Specific Conductance (µS/cm)	7.4	7.2	7.2

Notes:
There were 11 months of AIRMoN bottle blanks.

V. MONTHLY QUALITY ASSURANCE PROCEDURES

Monthly NADP/NTN and NADP/AIRMoN QA activities include the evaluation of the control charts summarizing the daily QCS analyses to determine if there was any change in the analytical instruments used at the CAL, the review of the computer printouts containing internal blind sample data, and the review of the reanalysis of samples flagged for either an ion or conductivity imbalance or both. 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 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:

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

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

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

Samples are flagged for reanalysis if:

IS < 50 μeq/L	and	IPD > + 60% or IPD < -60%
50 ≤ IS < 100 μeq/L	and	IPD > + 30% or IPD < -30%
IS ≥ 100 μeq/L	and	IPD > + 15% or IPD < -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.
Bicarbonate	16.39	44.5
Hydroxide	58.8	198.

Notes: [a] *Standard Methods for the Examination of Water and Wastewater* (1976).
[b] *CRC Handbook of Chemistry and Physics* (1987).

2. Conductance Percent Difference (CPD)

Conductance percent difference (CPD) compares the calculated and measured conductivity of the precipitation samples of both NTN and AIRMoN. Ion concentrations as µeq/L are multiplied by conductance conversions factors listed in Table V-1 (1976), 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:

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

Samples are flagged for reanalysis if:

$$\text{CPD} < -40\% \text{ or CPD} > +10\%$$

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. After reanalyzing the samples and reviewing the results, analysts submit the results to the QA specialist with suggested changes. A 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 computerized database along with the original analysis values.

3. IPD and CPD Histograms

In 1999, approximately 11,400 samples were logged in, and 6990 were classified as "W" (wet), which would make them eligible for the reanalysis program. These samples had volumes of 35 mL or more. There were 335 samples flagged for reanalysis with 284 individual measurement changes made to 150 samples. Figure V-1 contains 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 and 1999 median IPDs were 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 taking place 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

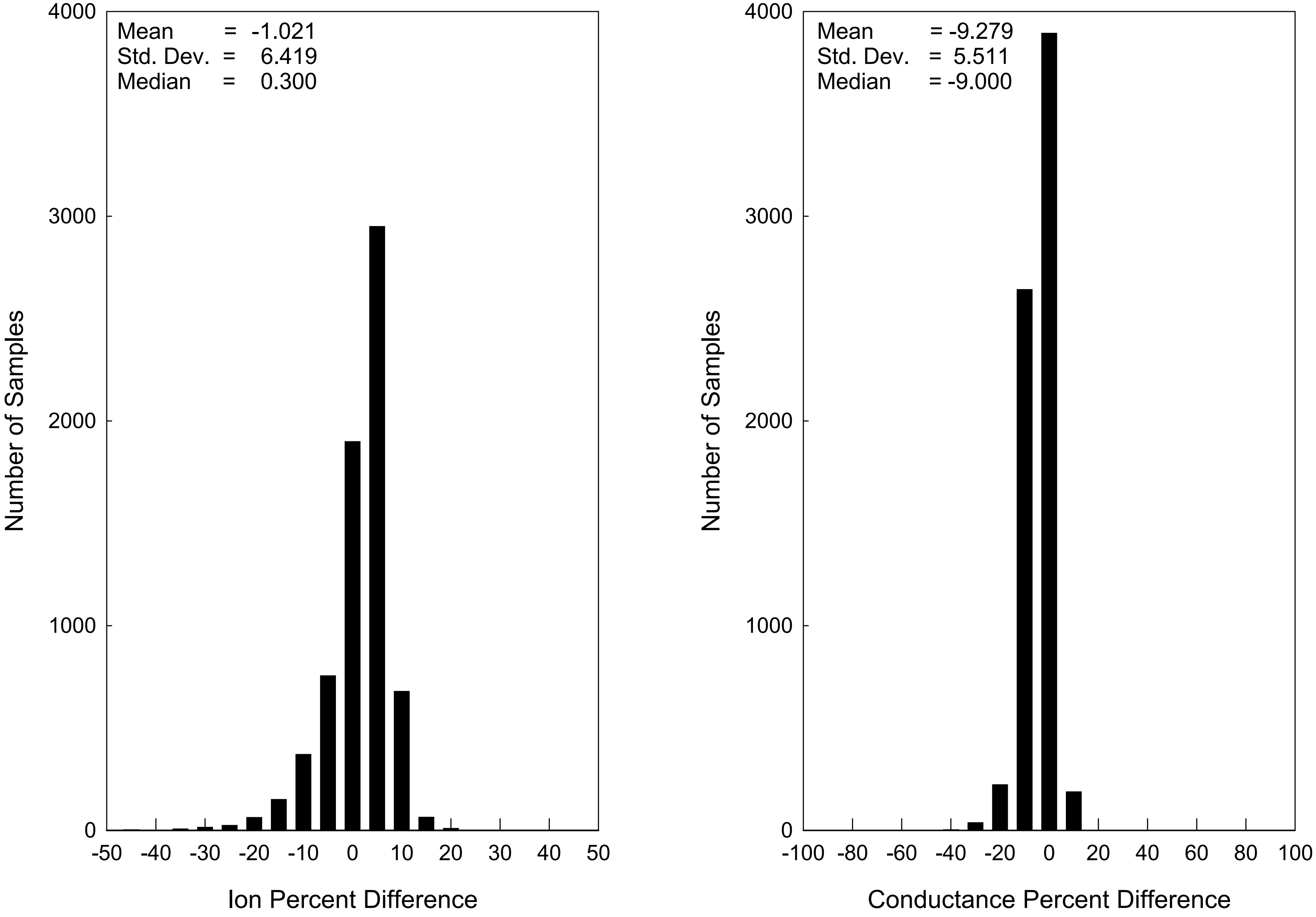


Figure V-1. Ion Percent Difference and Conductance Percent Difference for 6990 NADP/NTN wet samples, 1999.

Supor® 450, 0.45-µm polyethersulfone filter. When the Millipore™ filters were used, there was a high bias for sodium in filter blanks and leachates. In 1998, that bias disappeared with the use of the Gelman filters. This may, in part, account for the 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 1999 being similar to previous years. Negative CPD indicates that the measured conductivity exceeds the calculated conductivity. This is expected since only major ions in samples are analyzed. There are undoubtedly constituents, such as trace metals and organic species, that contribute to the measured conductivity.

B. 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 1999 interlaboratory comparison program included seven laboratories. Five laboratories have participated previously: (1) NADP/CAL; (2) Meteorological Service of Canada (MSC), Ontario, Canada; (3) Environmental Science and Engineering, Inc. (ESE), Gainesville, Florida; (4) Ontario Ministry of the Environment, Water Quality Section (MOE), Ontario, Canada; and (5) Shepard Analytical Services (SAS), Simi Valley, California. The MSC was formerly known as the Atmospheric Environment Service. Two new laboratories joined the study in June 1999: Acid Deposition and Oxidant Research Center (ADOR), Niigata-shi, Japan and (7) Norwegian Institute for Air Research (NILU), Kjeller, Norway. Participation of ESE was temporarily discontinued from January 15 to June 2, 1999.

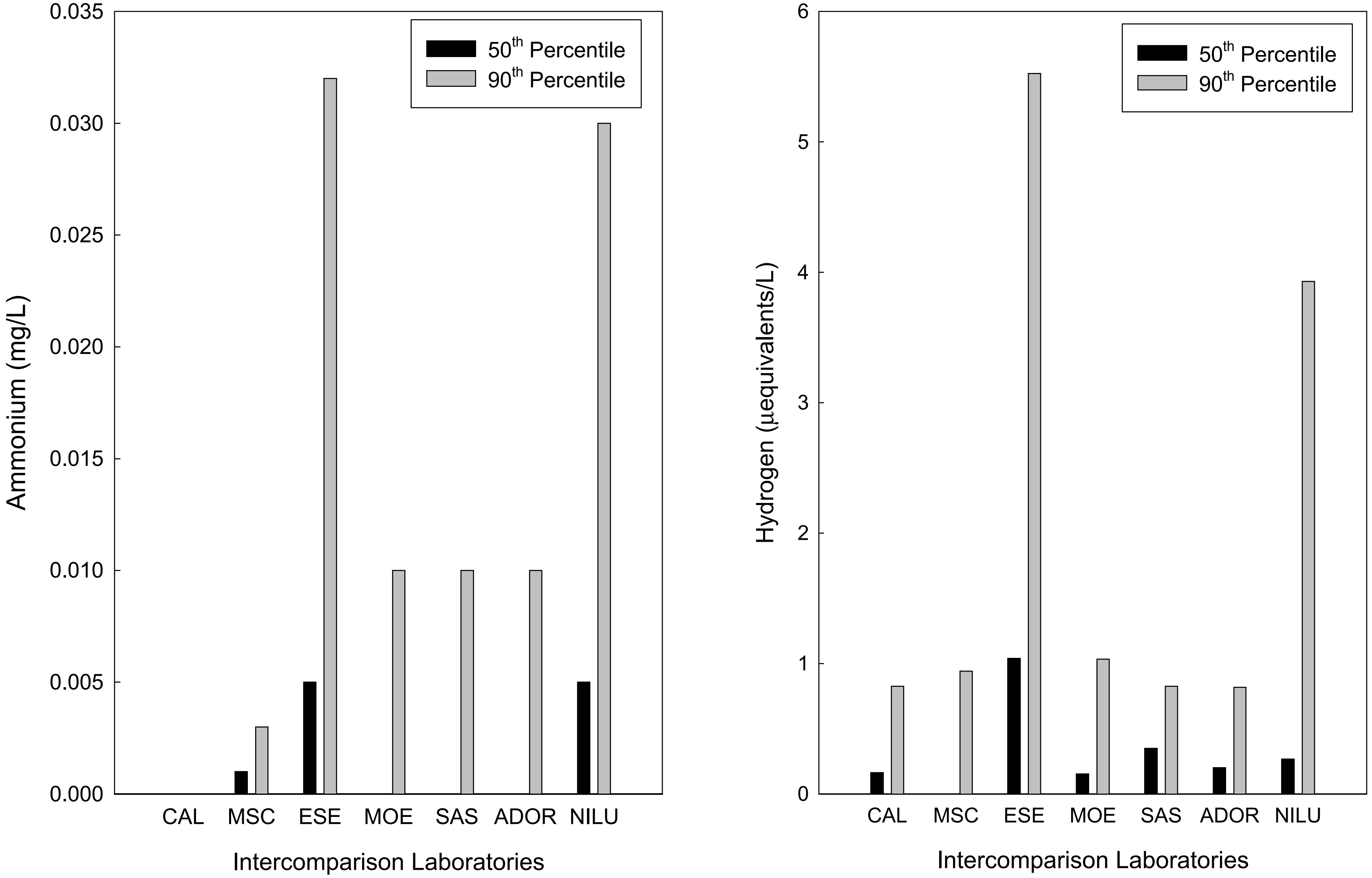
The samples are shipped to the laboratories approximately every two weeks throughout the year. Samples used in 1999 were (1) National Institute of Standards and Technology (NIST) traceable samples prepared and certified by High-Purity Standards, (2) uncertified synthetic precipitation samples prepared and bottled by the USGS, (3) natural precipitation samples collected at the NADP/NTN sites and composited and bottled at the CAL then shipped to the USGS, and (4) ultrapure DI water samples prepared by the USGS. Data reports from the participating laboratories are submitted monthly or quarterly to the USGS. Although the natural deposition samples were prepared by the CAL, CAL analysts did not know the target values nor did they know when the samples were analyzed.

Table V-2 shows the 50th and 90th percentile absolute differences of replicate samples obtained by the five participating laboratories in 1999. Figures V-2 and V-3 are bar graphs of these same results. For comparison, laboratory rankings were determined by summing the 50th and 90th percentile absolute differences, Table V-3. The CAL was ranked

Table V-2. 50th and 90th Percentile Absolute Differences for Analysis of Replicate Samples in the 1999 Interlaboratory Comparison Program

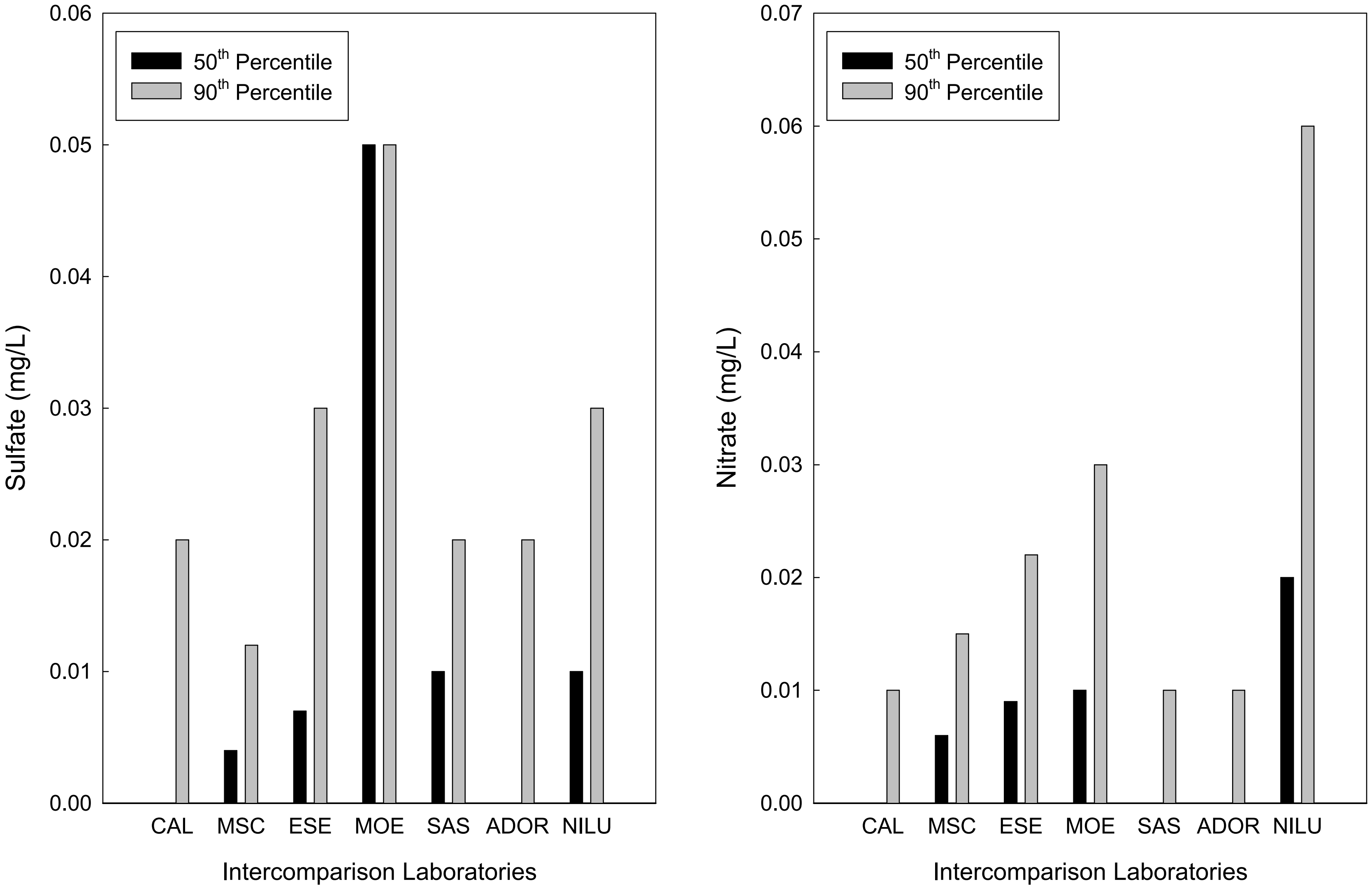
	CAL[a]		*MSC*[b]		*ESE*[c,h]		*MOE*[d]		*SAS*[e]		*ADOR*[f]		*NILU*[g]	
Analyte	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*
Calcium	0.002	0.006	0.001	0.006	0.001	0.020	0.000	0.020	0.001	0.003	0.001	0.004	0.00	0.01
Magnesium	0.000	0.001	0.000	0.001	0.000	0.001	0.000	0.005	0.000	0.001	0.000	0.002	0.00	0.01
Sodium	0.001	0.006	0.001	0.008	0.001	0.004	0.005	0.025	0.001	0.004	0.000	0.003	0.00	0.01
Potassium	0.000	0.002	0.000	0.003	0.001	0.002	0.005	0.020	0.001	0.002	0.000	0.002	0.00	0.01
Ammonium	0.00	0.00	0.001	0.003	0.005	0.032	0.000	0.010	0.000	0.010	0.00	0.01	0.005	0.030
Sulfate	0.000	0.02	0.004	0.012	0.007	0.030	0.05	0.05	0.01	0.02	0.00	0.02	0.01	0.03
Nitrate	0.00	0.01	0.006	0.015	0.009	0.022	0.01	0.03	0.00	0.01	0.00	0.01	0.02	0.06
Chloride	0.00	0.01	0.002	0.006	0.003	0.009	0.01	0.04	0.00	0.01	0.00	0.01	0.00	0.01
Hydrogen Ion (µeq/L)	0.163	0.826	0.000	0.942	1.039	5.524	0.153	1.034	0.350	0.826	0.201	0.818	0.267	3.93
Specific Conductance (µS/cm)	0.1	0.2	–	–	0.3	1.3	0.2	1.6	0.0	0.2	0.1	0.4	0.10	0.32

Notes:
All measurements are in mg/L unless otherwise indicated.
[a] NADP Central Analytical Laboratory.
[b] Meteorological Service of Canada, Canada.
[c] Environmental Science and Engineering.
[d] Ontario Ministry of the Environment, Canada.
[e] Shepard Analytical Services.
[f] Acid Deposition and Oxidant Research Center, Japan.
[g] Norwegian Institute for Air Research, Norway.
[h] Interlaboratory comparison program participant from January 1-15 and June 2 through December 31, 1999.



Note: The laboratories involved in the intercomparison study were the NADP Central Analytical Laboratory (CAL), the Meteorological Service of Canada (MSC), Environmental Science and Engineering (ESE), the Ontario Ministry of the Environment (MOE), Shepard Analytical Services (SAS), the Acid Deposition and Oxidant Research Center of Japan (ADOR), and the Norwegian Institute for Air Research (NILU).

Figure V-2. Ammonium and hydrogen 50th and 90th percentile absolute differences for the seven laboratories in the USGS Intercomparison Study, 1999.



Note: The laboratories involved in the intercomparison study were the NADP Central Analytical Laboratory (CAL), the Meteorological Service of Canada (MSC), Environmental Science and Engineering (ESE), the Ontario Ministry of the Environment (MOE), Shepard Analytical Services (SAS), the Acid Deposition and Oxidant Research Center of Japan (ADOR), and the Norwegian Institute of Air Research (NILU).

Figure V-3. Sulfate and nitrate 50th and 90th percentile absolute differences for the seven laboratories in the USGS Intercomparison Study, 1999.

Table V-3. USGS Intercomparison Study Ranking Summary, 1999

Analyte	*CAL*[a]		*MSC*[b]		*ESE*[c]		*MOE*[d]		*SAS*[e]		*ADOR*[f]		*NILU*[g]	
	Sum	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*
Calcium	0.008	4	0.007	3	0.021	7	0.020	6	0.004	1	0.005	2	0.01	5
Magnesium	0.001	1 tie	0.001	1 tie	0.001	1 tie	0.005	6	0.001	1 tie	0.002	5	0.01	7
Sodium	0.007	4	0.009	5	0.005	2 tie	0.030	7	0.005	2 tie	0.003	1	0.01	6
Potassium	0.002	1 tie	0.003	3 tie	0.003	3 tie	0.025	7	0.003	3 tie	0.002	1 tie	0.01	6
Ammonium	0.00	1	0.004	2	0.037	7	0.010	3 tie	0.010	3 tie	0.01	3 tie	0.035	6
Sulfate	0.02	2 tie	0.016	1	0.037	5	0.100	7	0.03	4	0.02	2 tie	0.04	6
Nitrate	0.01	1 tie	0.021	4	0.031	5	0.04	6	0.01	1 tie	0.01	1 tie	0.08	7
Chloride	0.01	2 tie	0.008	1	0.012	6	0.05	7	0.01	2 tie	0.01	2 tie	0.01	2 tie
Hydrogen ion (µeq/L)	0.989	2	0.942	1	6.563	7	1.187	5	1.176	4	1.019	3	4.197	6
Specific Conductance (µS/cm)	0.3	2	not available		1.6	5	1.8	6	0.2	1	0.5	4	0.42	3
Ranking without Specific Conductance	1		3		5		7		3		2		6	
Overall Ranking	1		incomplete		4		6		2		3		5	

Notes:

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 Central Analytical Laboratory.

[b] Meteorological Service of Canada, Canada.

[c] Environmental Science and Engineering.

[d] Ontario Ministry of the Environment, Canada.

[e] Shepard Analytical Services.

[f] Acid Deposition and Oxidant Research Center, Japan.

[g] Norwegian Institute for Air Research, Norway.

first for ammonium and tied for first with one or more laboratories for magnesium, nitrate, and potassium in 1999. The CAL was ranked second for chloride, pH, sulfate and specific conductance among participating laboratories, and fourth for calcium and sodium. Overall, the CAL had excellent results in 1999 with the lowest median rank when the ranks for each laboratory for all 10 analytes were totaled. The USGS will publish the complete results of the 1999 study.

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, the internal blind samples, and the network precipitation samples. Blanks 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 1999: the World Meteorological/Global Atmospheric Watch Intercomparison Study, Geneva, Switzerland, and two intercomparisons conducted by the National Water Research Institute, Burlington, Ontario, Canada.

A. World Meteorological Organization/Global Atmospheric Watch

The 22nd set of WMO/GAW reference precipitation samples was shipped to participating laboratories in July 1999. In 1999, the CAL was 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, New York (Coleman et al., 2000). 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 evaluated 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 study means and target values.

B. Norwegian Institute for Air Research

Samples for the 17th European Monitoring and Evaluation Programme (EMEP) Intercomparison of Methods study were analyzed at the CAL in July 1999. The samples arrived ready for analysis; no dilutions or preparations were necessary. The CAL results are listed in Table VI-2. The absolute mean percent difference is between 2.49 and 2.77 percent.

C. National Water Research Institute

The CAL participated in both studies sponsored by the National Water Research Institute (NWRI) in Burlington, Ontario, Canada. Begun in 1982 as the Long-Range Transport of Atmospheric Pollutants (LRTAP) program, the studies for 1999 were FP 74 and FP 75 (Alkema, 1999; Blum and Alkema, 1999). The NWRI samples included selected major ions, nutrients, and physical parameters in natural waters. Median concentrations from

Table VI-1. World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) Acid Rain Performance Survey, 1999

Analyte	*Units*	*Sample 1*			*Sample 2*			*Sample 3*		
		Target	*Mean*	*CAL*	*Target*	*Mean*	*CAL*	*Target*	*Mean*	*CAL*
Calcium	mg Ca/L	0.401	0.399	0.382	0.005	0.028	<0.009	0.150	0.144	0.146
Magnesium	mg Mg/L	0.122	0.117	0.116	0.086	0.077	0.076	0.097	0.093	0.094
Sodium	mg Na/L	1.847	1.830	1.823	0.493	0.474	0.479	1.345	1.327	1.337
Potassium	mg K/L	0.782	0.770	0.778	0.097	0.093	0.097	0.534	0.520	0.533
Ammonium	mg NH_4/L as N	0.844	0.850	0.78	0.790	0.785	0.73	0.342	0.346	0.32
Sulfate	mg SO_4/L as S	4.010	4.107	4.09	3.800	3.857	3.83	2.280	2.228	2.21
Nitrate	mg NO_3/L as N	2.160	2.163	2.17	1.390	1.394	1.40	0.860	0.859	0.88
Chloride	mg Cl/L	2.843	2.819	2.86	0.938	0.931	0.95	1.130	1.108	1.15
pH	pH units	3.49	3.52	3.58	3.53	3.57	3.61	3.89	3.92	3.89
H	µequiv/L	323.6	302.0	263.0	295.1	269.2	245.5	128.8	120.2	128.8
Specific Conductance	µS/cm	161.6	154.0	158.0	136.5	129.8	135.0	69.0	68.3	70.3

Note: The target values are based on the theoretical concentrations of the solutions. The mean values are based on the participating laboratories with the WMO/GAW Acid Rain Performance Survey. The CAL values were not included in the mean concentrations calculations.

Table VI-2. European Monitoring and Evaluation Programme, Seventeenth Intercomparison of Methods, 1999

		Sample G-1		*Sample G-2*		*Sample G-3*		*Sample G-4*	
Analyte	*Units*	*Expected*	*CAL*	*Expected*	*CAL*	*Expected*	*CAL*	*Expected*	*CAL*
Calcium	mg Ca/L	0.364	0.372	0.249	0.247	0.402	0.402	0.287	0.286
Magnesium	mg Mg/L	0.124	0.120	0.217	0.207	0.201	0.194	0.139	0.135
Sodium	mg Na/L	0.258	0.265	0.698	0.691	0.827	0.826	0.322	0.332
Potassium	mg K/L	0.153	0.155	0.280	0.280	0.102	0.103	0.331	0.335
Ammonium	mg NH_4/L as N	0.281	0.27	0.561	0.54	0.481	0.46	0.241	0.24
Sulfate	mg SO_4/L as S	0.936	0.94	1.93	1.95	1.00	1.03	1.73	1.75
Nitrate	mg NO_3/L as N	0.401	0.40	0.858	0.87	0.747	0.76	0.441	0.44
Chloride	mg Cl/L	0.232	0.23	0.579	0.59	0.695	0.70	0.290	0.30
pH	pH units	4.52	4.58	4.05	4.11	4.59	4.63	4.09	4.15
H	µequiv/L	30	26	90	78	26	23	71	71
Conductivity	µS/cm	21.6	21.9	53.3	53.1	26.0	26.8	44.2	44.3
Absolute Mean Percent Difference		2.77		2.76		2.49		2.51	

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.

Tables VI-3 and VI-4 show the median results and the CAL results for both studies. For Study FP 74, the CAL had one very high pH flag out of the ten samples. For all other parameters, the CAL was rated as “good”. For laboratories reporting more than two parameters, the CAL ranked first overall because it had the fewest percentage of results flagged. For Study FP 75, the CAL had five pH results flagged high or very high, indicating a high pH bias for this study. These five flags gave the CAL a 5.2 percentage of results flagged, making the CAL the 16th best laboratory out of 45 participating laboratories. The CAL’s overall ranking for Study FP 75 was satisfactory. All pH values where the CAL was ranked high or very high were greater than 6 pH units. A pH value of 6 or greater is outside the normal pH range of precipitation for the NADP.

The NWRI summarized the performance results for the past ten studies (Studies 0066 – 0075). The CAL received a median score of 4.4 based on the percentage of biased parameters and flagged results on the studies. This was the 7th lowest score of the 39 ranked laboratories and was rated “good”.

Table VI-3. National Water Research Institute Soft Water Interlaboratory Study FP 74, March and April 1999

		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	2.917	2.829	3.270	3.180	0.706	0.688	0.280	0.266	0.800	0.783
Magnesium	mg/L	0.678	0.655	0.730	0.708	0.160	0.158	0.070	0.066	0.390	0.375
Sodium	mg/L	4.000	3.892	1.600	1.641	0.050	0.052	0.070	0.071	2.960	2.870
Potassium	mg/L	0.393	0.398	0.220	0.225	0.016	0.014	0.029	0.029	0.290	0.300
Ammonium	mg NH$_4$/L as N	0.015	<0.02	0.005	<0.02	0.17	0.16	0.22	0.21	0.007	<0.02
Sulfate	mg SO$_4$/L as S	2.01	2.02	2.99	3.05	2.15	2.16	1.64	1.61	2.26	2.26
Nitrate	mg NO$_3$/L as N	0.13	0.13	0.08	0.08	0.26	0.27	0.24	0.24	0.04	0.04
Chloride	mg/L	6.15	6.03	1.60	1.60	0.13	0.12	0.14	0.14	4.60	4.67
pH	pH units	6.76	6.95	6.93	7.23	5.34	5.28	4.82	4.78	5.46	5.49
conductivity	µS/cm	42.5	42.7	32.2	32.4	10.6	11.1	11.8	12.5	26.3	26.8

		Sample 6		*Sample 7*		*Sample 8*		*Sample 9*		*Sample 10*	
Analyte	*units*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	mg/L	2.630	2.604	2.156	2.007	2.450	2.388	1.990	1.933	0.124	0.121
Magnesium	mg/L	1.027	0.989	0.550	0.531	0.613	0.588	0.490	0.489	0.040	0.037
Sodium	mg/L	0.289	0.291	0.774	0.772	2.210	2.147	0.630	0.633	0.164	0.171
Potassium	mg/L	0.160	0.169	0.200	0.211	0.510	0.519	0.240	0.248	0.030	0.031
Ammonium	mg NH$_4$/L as N	0.37	0.35	0.01	<0.02	0.03	0.02	0.03	0.03	0.13	0.12
Sulfate	mg SO$_4$/L as S	3.82	3.90	6.91	6.90	4.69	4.75	6.19	6.16	1.32	1.29
Nitrate	mg NO$_3$/L as N	0.57	0.59	0.05	0.05	0.07	0.07	0.004	0.006	0.25	0.26
Chloride	mg/L	0.49	0.50	0.74	0.76	1.70	1.71	0.53	0.53	0.30	0.31
pH	pH units	6.90	7.08	5.42	5.40	6.74	6.91	6.22	6.32	4.59	4.59
Conductivity	µS/cm	30.0	30.4	25.8	26.1	31.6	31.7	22.4	22.4	14.6	14.8

Table VI-4. National Water Research Institute Soft Water Interlaboratory Study FP 75, September and October 1999

		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	3.100	3.086	2.187	2.144	1.590	1.610	2.640	2.592	0.357	0.363
Magnesium	mg/L	0.738	0.728	0.600	0.555	0.280	0.265	0.935	0.887	0.200	0.194
Sodium	mg/L	1.020	1.008	1.200	1.217	0.056	0.052	0.280	0.277	1.365	1.381
Potassium	mg/L	0.510	0.515	0.275	0.280	0.022	0.021	0.155	0.157	0.130	0.134
Ammonium	mg NH_4/L as N	0.04	0.04	0.003	<0.02	0.003	<0.02	0.18	0.17	0.11	0.10
Sulfate	mg SO_4/L as S	7.41	7.33	2.66	2.72	1.42	1.45	5.31	5.30	1.72	1.74
Nitrate	mg NO_3/L as N	0.06	0.06	0.001	<0.01	0.46	0.47	2.08	2.08	0.10	0.09
Chloride	mg/L	1.10	1.13	1.83	1.83	0.12	0.12	0.51	0.53	2.03	2.03
pH	pH units	6.73	7.02	6.91	7.18	6.51	6.88	4.51	4.53	5.39	5.45
Conductivity	µS/cm	33.1	33.0	24.9	24.5	12.8	11.0	43.8	44.5	15.2	15.3

		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	0.160	0.167	2.800	2.780	2.820	2.783	1.800	1.835	2.120	2.092
Magnesium	mg/L	0.030	0.028	0.580	0.556	0.834	0.829	0.456	0.435	0.636	0.633
Sodium	mg/L	0.070	0.066	0.110	0.109	0.330	0.330	0.063	0.062	0.057	0.053
Potassium	mg/L	0.030	0.026	0.176	0.182	0.202	0.211	0.107	0.109	0.100	0.104
Ammonium	mg NH_4/L as N	0.16	0.16	0.003	<0.02	0.02	0.02	0.20	0.20	0.02	0.02
Sulfate	mg SO_4/L as S	1.82	1.82	1.87	1.91	6.83	6.76	3.11	3.12	3.20	3.22
Nitrate	mg NO_3/L as N	0.24	0.24	0.46	0.47	0.63	0.64	1.15	1.16	1.48	1.47
Chloride	mg/L	0.12	0.12	0.20	0.20	0.47	0.48	0.30	0.31	0.31	0.31
pH	pH units	4.53	4.55	6.95	7.24	6.28	6.60	5.07	5.10	4.81	4.84
Conductivity	µS/cm	16.6	17.4	22.0	22.0	29.2	29.2	23.0	23.5	27.7	28.5

VII. SUMMARY

This report summarizes the results from the quality assurance program in place at the Central Analytical Laboratory (CAL) of the NADP/NTN and NADP/AIRMoN in 1999. Information about the quality of the data generated at the CAL is presented in the form of tables, figures, and text. 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 process to the sample chemistry. Bias and precision numbers were higher for the internal blinds than for the QCS samples due to the random location of 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 1999, 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 1999, it was observed that filtration increased variability in the chemistry of all samples and generated a noticeable, although slight, positive calcium bias. The sodium bias caused by the Millipore™ filters was eliminated with the change to Gelman® filters in 1998.

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 show slight elevations for sodium and calcium in contrast with the 1998 results when bucket leachates showed slight elevations in sodium only. The calcium was attributed to the bags in which the buckets were stored after leaching. A dilution effect was seen when larger leachate volumes were used. One-liter bottle leachates were clean. The AIRMoN bottle blanks contained no contamination.

The AIRMoN internal blind program was a cooperative project with the Bondville, Illinois site operator and the AIRMoN coordinator. The results for the analyses of these samples showed that the precision for the solution used in 1999, the WMO/GAW 1998 sample #2, was within the data quality objectives of the network QAP for all parameters.

After analyses, sample data were transferred in batches to data management, which compiled semimonthly printouts containing the data for 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 6990 "W" samples, 335 samples were flagged for reanalysis. After evaluation of the original and reanalysis measurements, 284 original measurements from 150 samples were changed. The Ion Percent Difference (IPD) mean was negative for 1999. The median for 1999 was 0.300. The Conductance Percent Difference (CPD) has been skewed negatively since 1979 and continued to be so in 1999. This means that the measured conductivity exceeds the calculated conductivity, indicating that components, such as organic acids and trace metals, may be present in the precipitation samples that are not being measured.

The USGS Interlaboratory Comparison study included seven laboratories in 1999. 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 out of the seven participating laboratories. The CAL ranked first or was tied for that position for magnesium, potassium, ammonium, and nitrate analyses.

In 1999, 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 good. The NWRI results over the last ten studies indicate that the CAL is ranked 7th overall of 39 ranked laboratories. The CAL received one high pH flag for Study FP 74 giving the CAL the fewest number of flags assigned for all laboratories reporting more than two parameters. For Study FP 75, the CAL received three high and two very high flags for pH. These flags resulted in the CAL being ranked 16th out of 45 laboratories based on the number of flags received. The CAL continues to compare favorably with its peers throughout the world.

REFERENCES

Alkema, H.: *Ecosystem Interlaboratory Quality Assurance Program Study FP 74 - Rain and Soft Waters (March and April 1999), Report No. NWRI-QA-99-01.* National Water Research Institute National Laboratory for Environmental Testing, Burlington, Ontario, Canada, June 1999.

Anderson, R.L.: *Practical Statistics for Analytical Chemists*. Van Nostrand Reinhold Company, New York, NY, pp. 36, 37, 74, 75, 79, and 303, 1987.

Blum, J., and H. Alkema: *Ecosystem Interlaboratory Quality Assurance Program Study FP 75 - Rain and Soft Waters (September and October 1999), Report No. NWRI-QA-99-309*. National Water Research Institute National Laboratory for Environmental Testing, Burlington, Ontario, Canada, December 1999.

Coleman, T.L., P.J. Galvin, and V.A. Mohnen: *Report of the 21st Intercomparison of WMO/GAW Precipitation Chemistry Laboratories*. World Meteorological Organization/Global Atmospheric Watch, Atmospheric Sciences Research Center, University of Albany, State University of New York, Albany, NY, March 1999.

Coleman, T.L., P.J. Galvin, and V.A. Mohnen: *Report of the 22nd Intercomparison of WMO/GAW Precipitation Chemistry*. World Meteorological Organization/Global Atmospheric Watch, Atmospheric Sciences Research Center, University of Albany, State University of New York, Albany, NY, February 2000.

CRC Handbook of Chemistry and Physics (67th edition). CRC Press, Inc., Boca Raton, FL, pp. D-167 and D-168, 1987.

Glaser, J.A., D.L. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde: "Trace Analyses for Wastewaters." *Environmental Science and Technology*, Vol. 15, No. 12, pp. 1426-1435, 1981.

Helsel, D.R. and R.M. Hirsch: *Statistical Methods in Water Resources*. Elsevier Science Publishers; Amsterdam,The Netherlands, 1992.

James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1986 through December 1986*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, October 1988.

James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1987 through December 1987*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, October 1989.

James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1988 through December 1988*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, March 1990.

James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1989 through December 1989*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, April 1991.

James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1990 through December 1990*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, April 1992.

James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1991 through December 1991*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, June 1993.

James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1992 through December 1992*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, June 1994.

James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1993 through December 1993*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, June 1995.

James, K.O.W.:*Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1994 through December 1994*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, June 1996.

James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1995 through December 1995*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, June 1997.

Lockard, J.M.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, July 1978 through December 1983*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, May 1987.

Peden, J.M.L.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1984 through December 1985*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, May 1988.

Ridder, T.B., T.A. Buishand, H.F.R. Reignders, M.J. t'Hart, and J. Slanina: "Effects of Storage on the Composition of Main Components in Rainwater Samples," *Atmospheric Environment*, Vol. 19, No. 5., pp. 759-762, 1985.

Rothert, J.E.: *Quality Assurance Report, National Atmospheric Deposition Program, 1996 and 1997, Laboratory Operations, Central Analytical Laboratory*. NADP Program Office, Illinois State Water Survey, Champaign, IL, April 1999.

Rothert, J.E.: *Quality Assurance Report, National Atmospheric Deposition Program, 1998, Laboratory Operations, Central Analytical Laboratory*. NADP Program Office, Illinois State Water Survey, Champaign, IL, April 2000.

Simmons, C.L., S.R. Dossett, W.C. Eaton, B.A. Malo, M.E. Peden, and D.S. Bigelow: *Quality Assurance Plan NADP/NTN Deposition Monitoring.* NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory; Colorado State University, Fort Collins, CO, October 1990. Figure 3-1, page 3-9, was revised in June 1991.

Standard Methods for the Examination of Water and Wastewater (14th edition), American Public Health Association; Washington, D.C., p. 35, 1976.

Stensland, G.J, R.G. Semonin, M.E. Peden, V.C. Bowersox, F.F. McGurk, L.M. Skowron, M.J. Slater, and R.K. Stahlhut: *NADP Quality Assurance Report - Central Analytical Laboratory, January 1979 through December 1979*. Champaign, IL, 1980.

Taylor, J.K.: *Quality Assurance of Chemical Measurements*. Lewis Publishers, Inc.; Chelsea, MI, pp. 22, 123, and 247, 1987.

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. $\% \mathit{Bias} = 100 * [(V_m - V_t)/V_t]$ 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 Deviation		The number representing the dispersion of values around their mean. $s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}}$ where: x_i = each individual value $\bar{x}$ = the mean of all values n = number of values
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) (Anderson, 1987). $s^2 = \frac{\sum d^2}{2n}$ 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,

1999

Table B-1. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, High-Purity Standards Simulated Rainwater 1 (H-PS SR1), 1999

Parameter	*Target Concentrations*[a] *(mg/L)*	*Measured Concentrations (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	0.015	0.025[b]	0.010	69.7	0.011	44.7
		0.037[c]	0.022	147.2	0.011	29.0
Magnesium	0.019	0.024	0.005	28.3	0.001	5.9
		0.025	0.006	32.0	0.004	14.7
Sodium	0.20	0.198	-0.002	-0.8	0.005	2.3
		0.193	-0.007	-3.4	0.004	2.2
Potassium	0.05	0.050	0.000	-0.2	0.001	2.9
		0.047	-0.003	-5.4	0.002	4.2
Ammonium	0.1	0.04	-0.06	-55.0	0.01	187.5
		0.05	-0.05	-52.3	0.01	16.8
Sulfate	2.5	2.49	-0.01	-0.5	0.02	0.9
		2.39	-0.11	-4.5	0.03	1.4
Nitrate	0.50	0.50	0.00	0.8	0.01	1.2
		0.49	-0.01	-2.6	0.01	1.5
Chloride	0.25	0.22	-0.03	-11.4	0.00	1.7
		0.21	-0.04	-14.5	0.00	2.2
pH[d]	4.293	4.34	0.04	1.0	0.03	0.7
		4.33	0.04	0.9	0.02	0.4
Hydrogen ion (µeq/L)	50.9	46.3	-4.6	-9.1	3.02	6.5
		46.6	-4.3	-8.4	1.78	3.8
Conductivity[d] (µS/cm)	24.7	24.2	-0.6	-2.2	0.89	3.7
		24.4	-0.3	-1.2	0.64	2.6

Notes:

There were 26 unfiltered samples and 13 filtered samples in each set.

[a] Target values provided by High-Purity Standards for Simulated Rainwater 1.

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

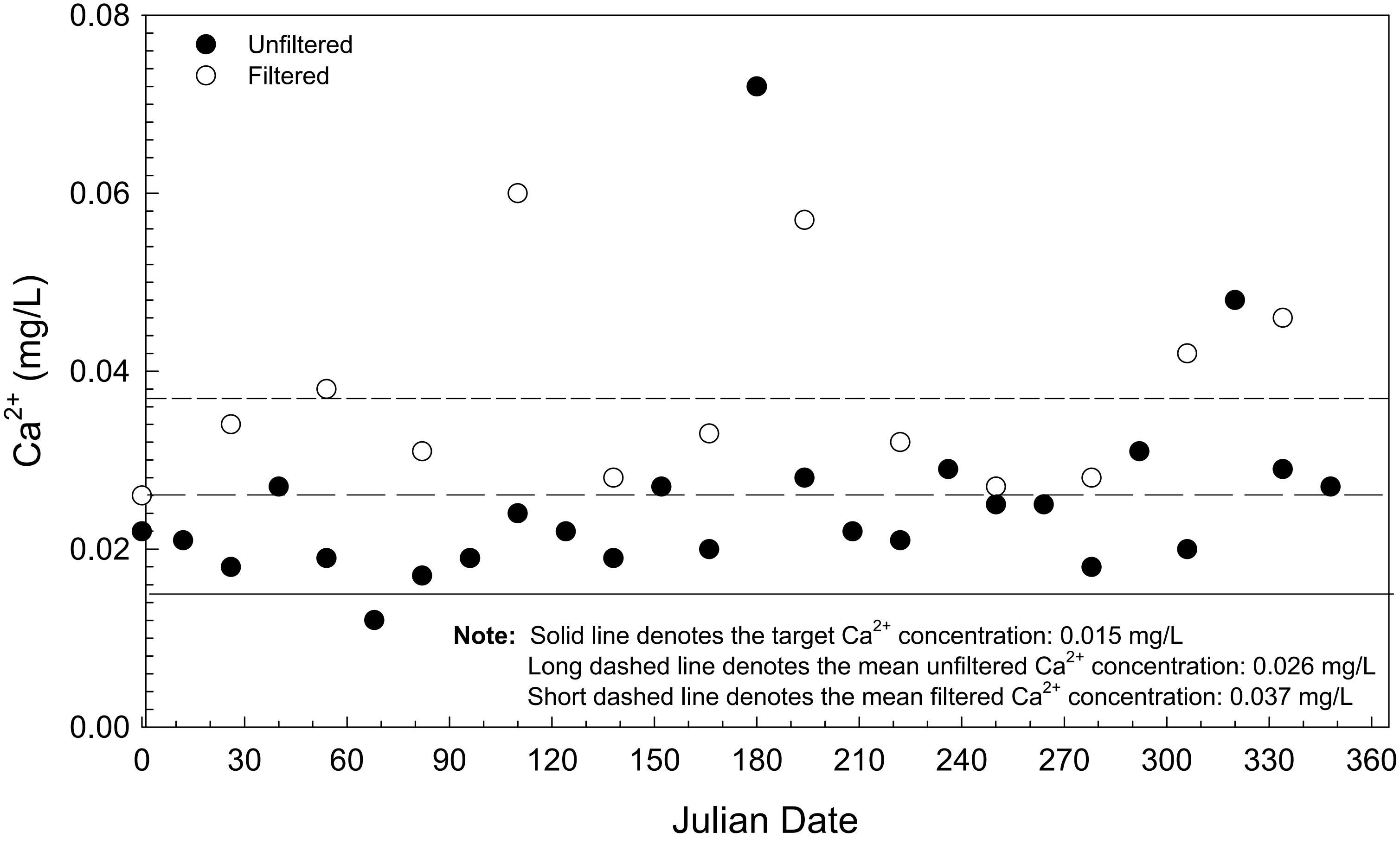
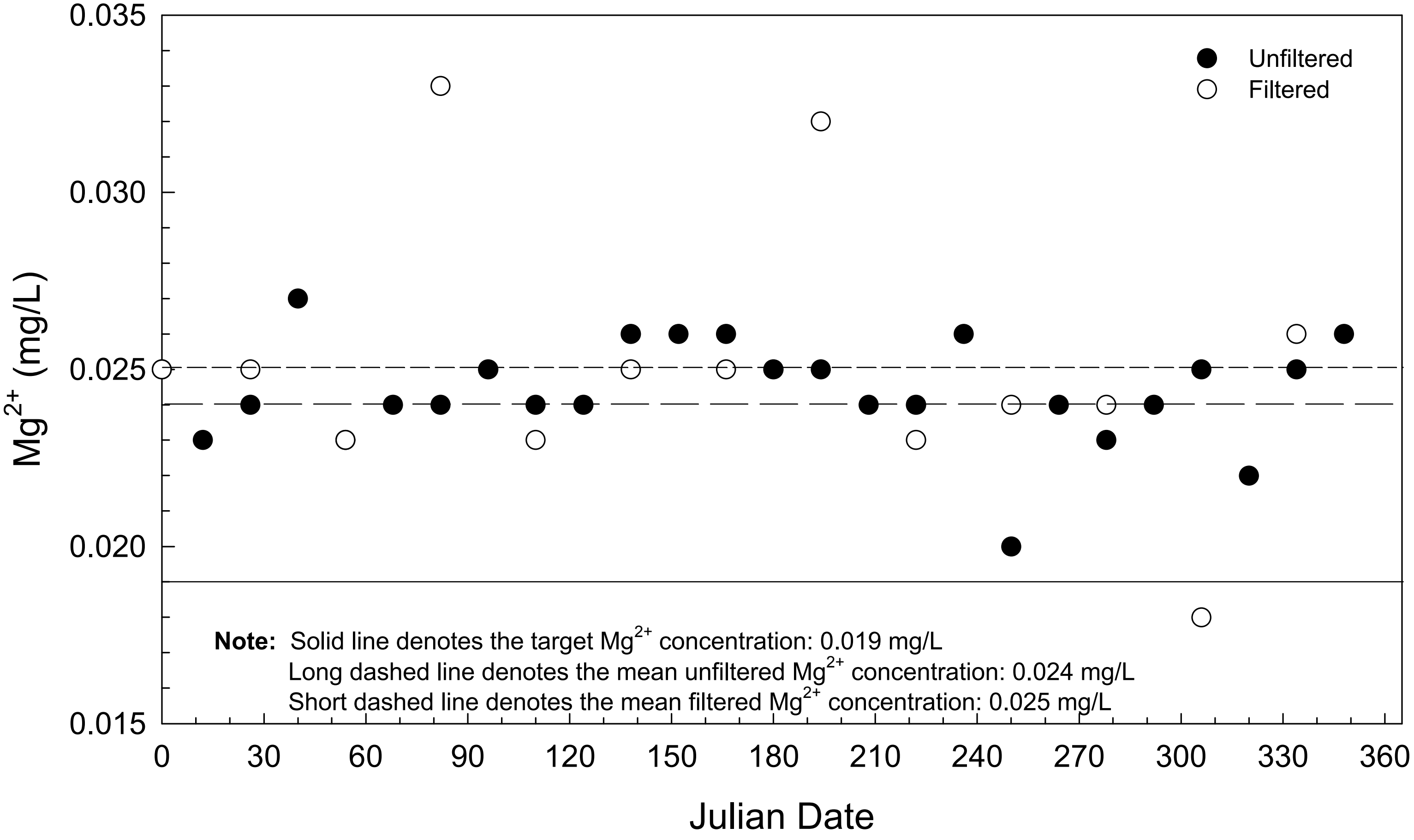
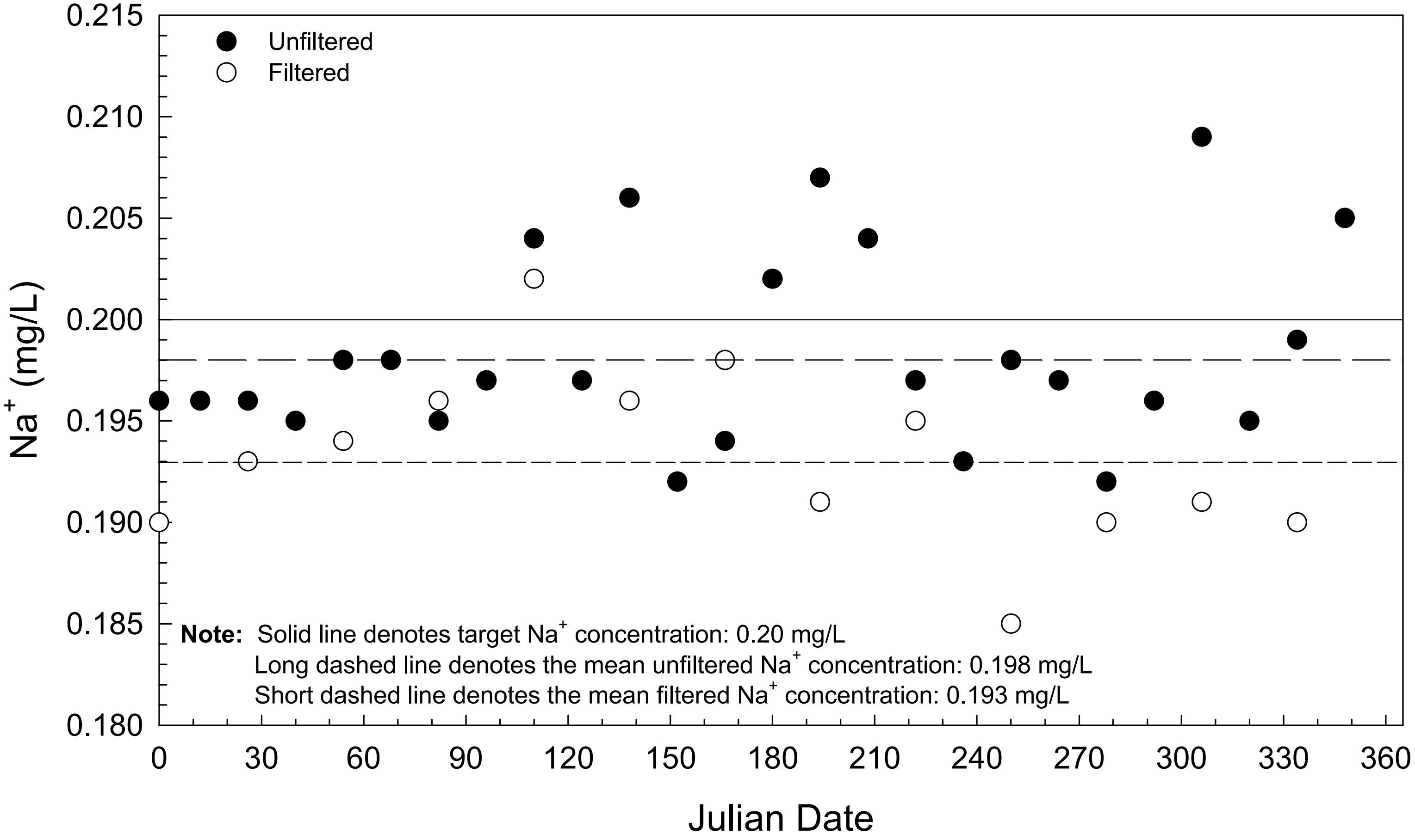


Figure B-1. Comparison of filtered and unfiltered internal blind samples, (calcium), High-Purity Standards, SR1, 1999.



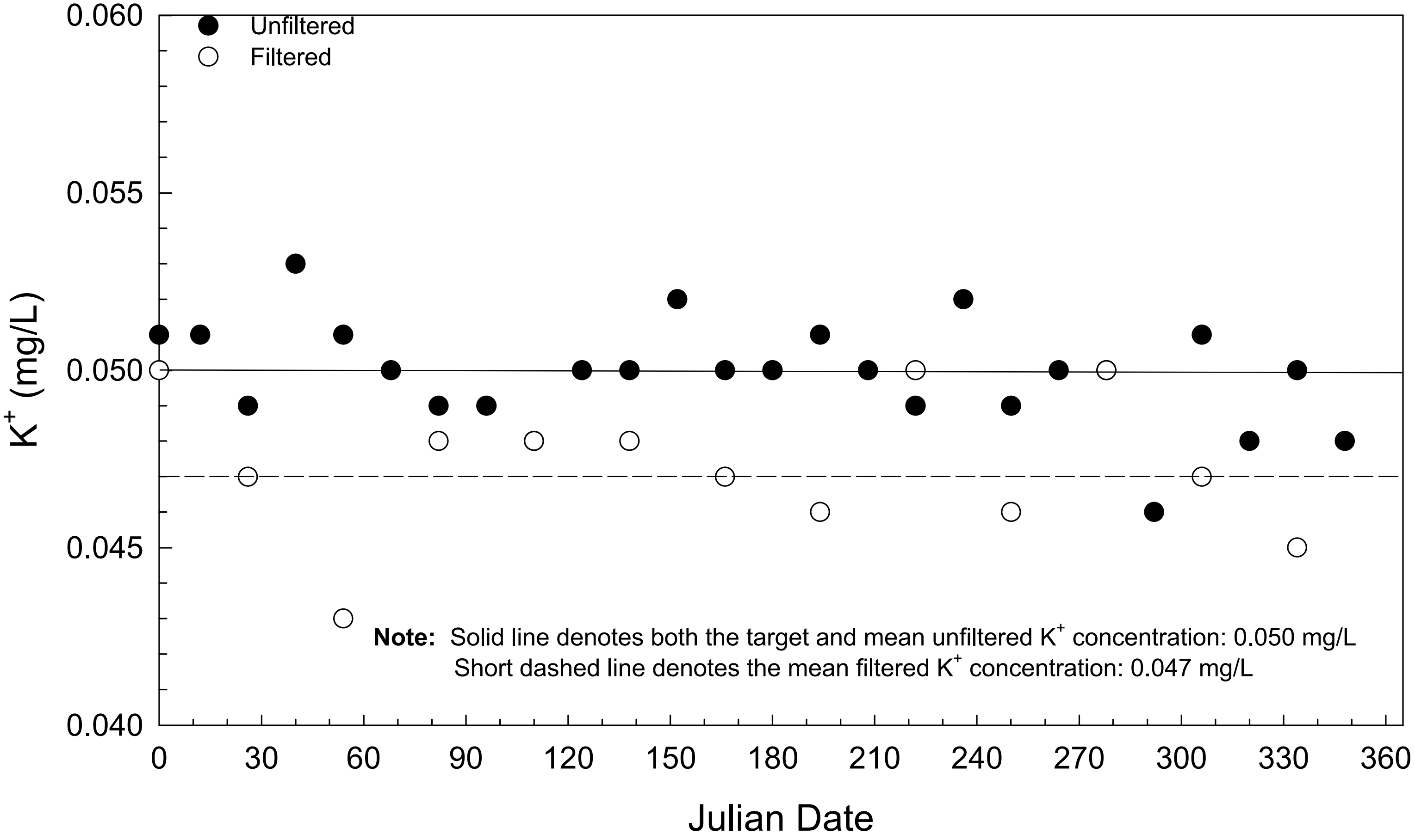
Note: Solid line denotes the target Mg^{2+} concentration: 0.019 mg/L
Long dashed line denotes the mean unfiltered Mg^{2+} concentration: 0.024 mg/L
Short dashed line denotes the mean filtered Mg^{2+} concentration: 0.025 mg/L

Figure B-2. Comparison of filtered and unfiltered internal blind samples, (magnesium), High-Purity Standards, SR1, 1999.



Note: Solid line denotes target Na^+ concentration: 0.20 mg/L
Long dashed line denotes the mean unfiltered Na^+ concentration: 0.198 mg/L
Short dashed line denotes the mean filtered Na^+ concentration: 0.193 mg/L

Figure B-3. Comparison of filtered and unfiltered internal blind samples (sodium), High-Purity Standards, SR1, 1999.



Note: Solid line denotes both the target and mean unfiltered K^+ concentration: 0.050 mg/L
Short dashed line denotes the mean filtered K^+ concentration: 0.047 mg/L

Figure B-4. Comparison of filtered and unfiltered internal blind samples, (potassium), High-Purity Standards, SR1, 1999.

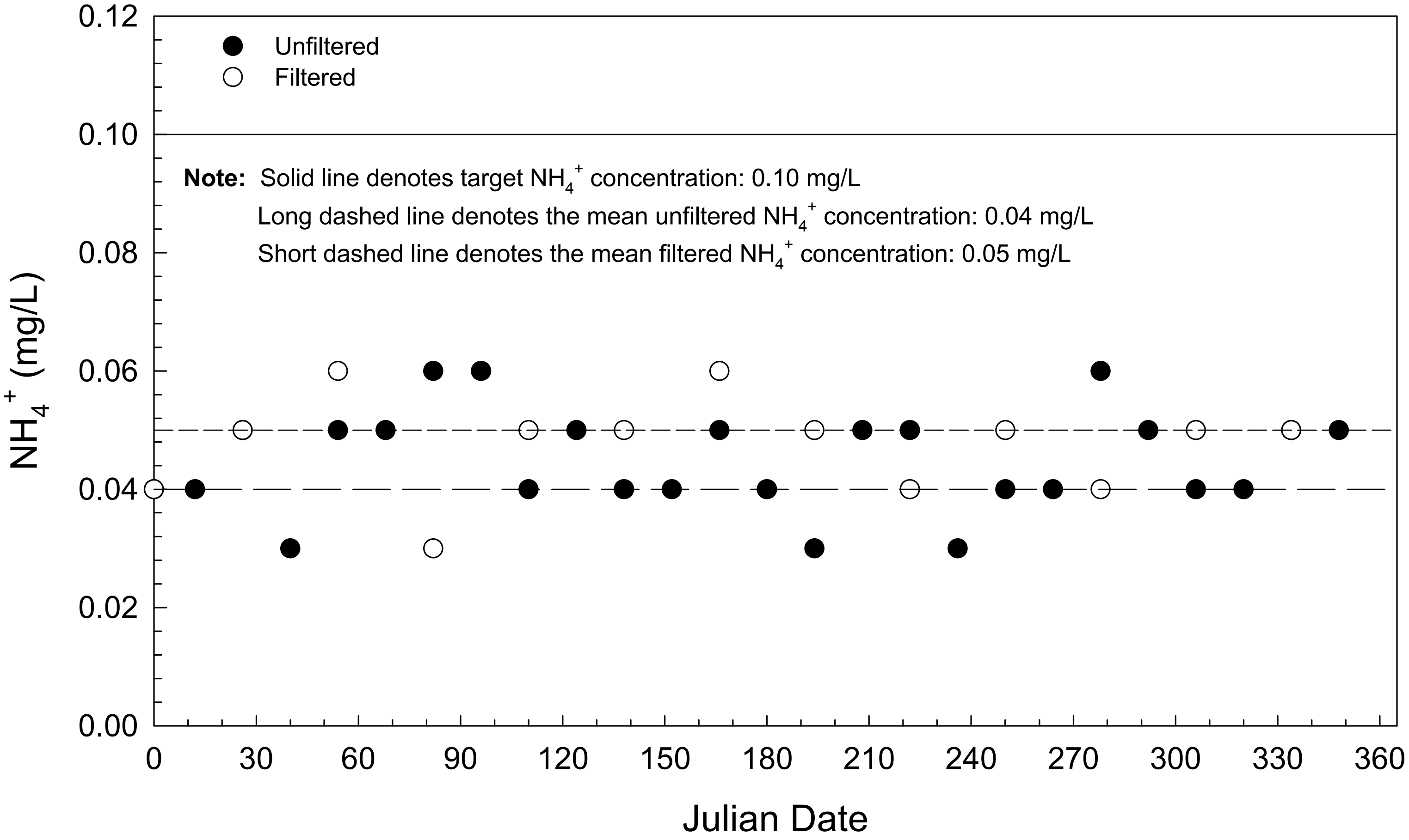


Figure B-5. Comparison of filtered and unfiltered internal blind samples, (ammonium), High-Purity Standards, SRI, 1999.

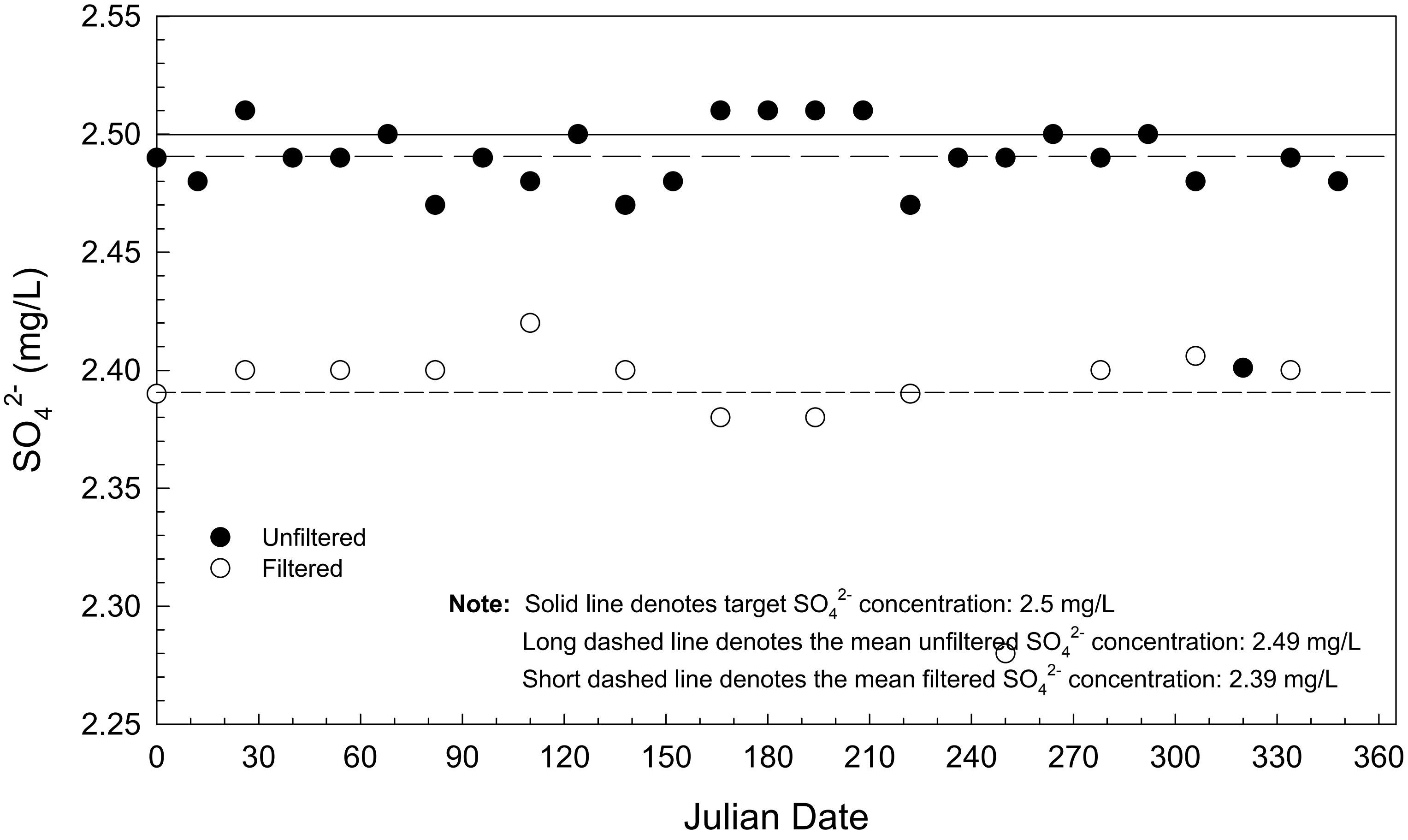


Figure B-6. Comparison of filtered and unfiltered internal blind samples, (sulfate), High-Purity Standards, SRI, 1999.

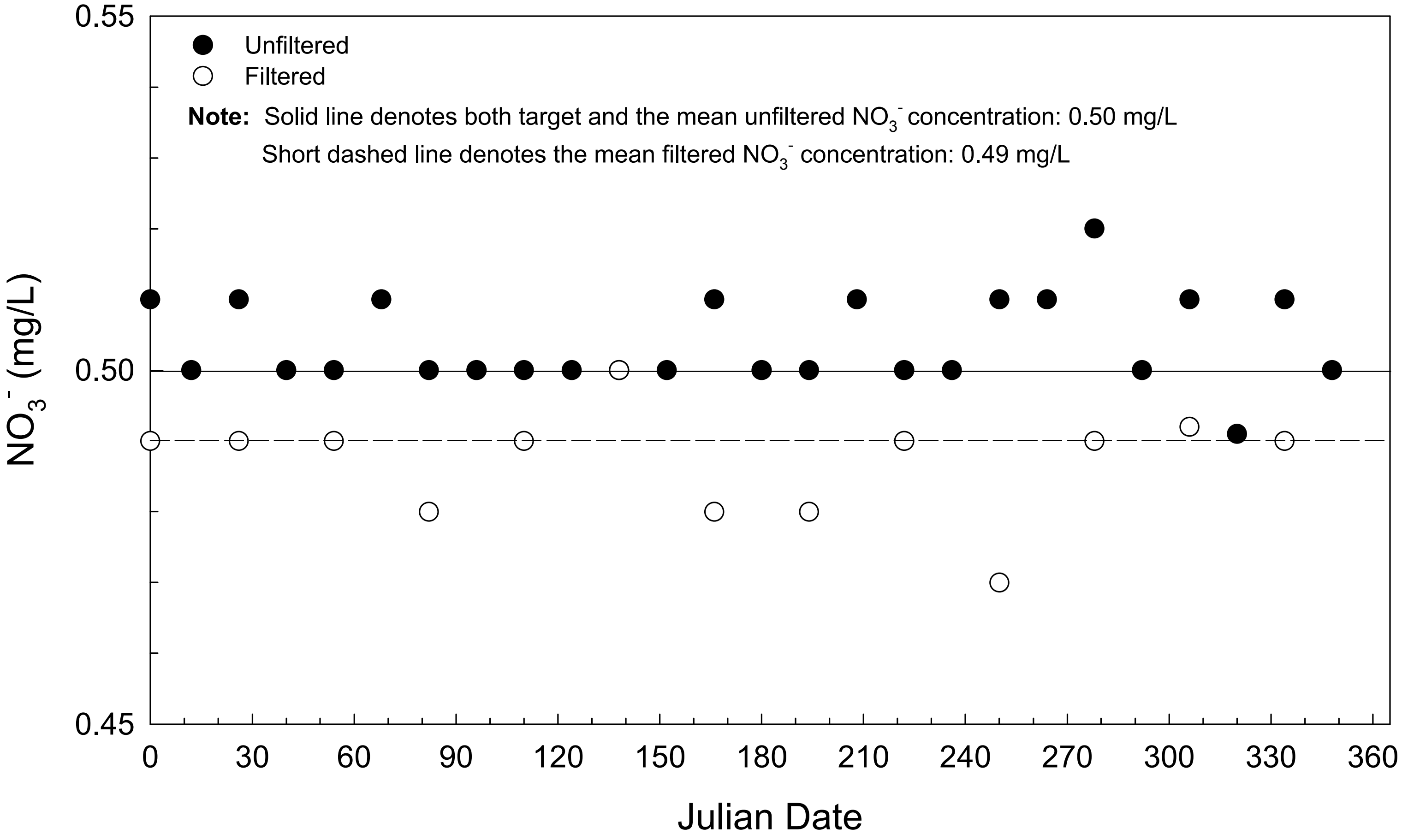
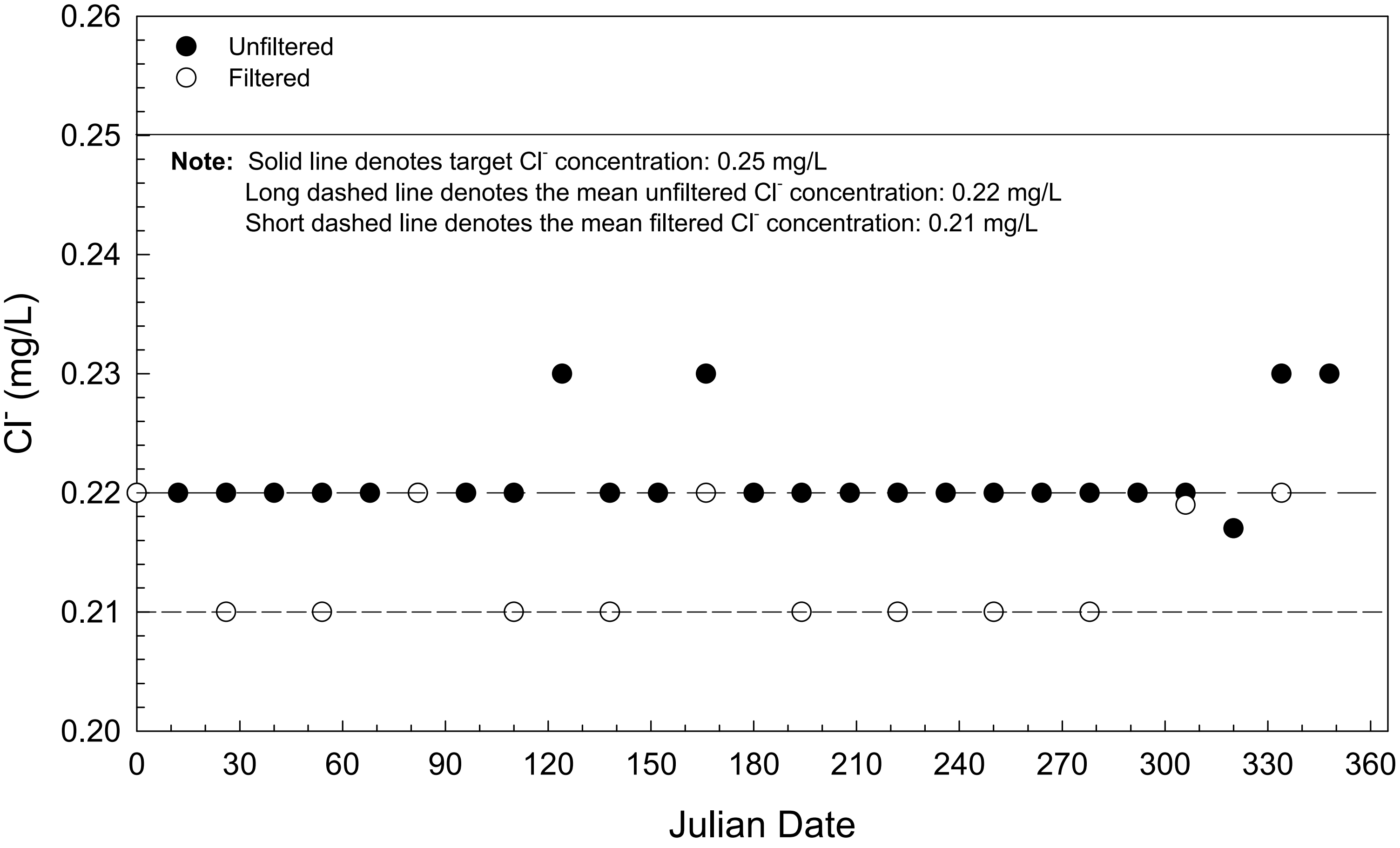
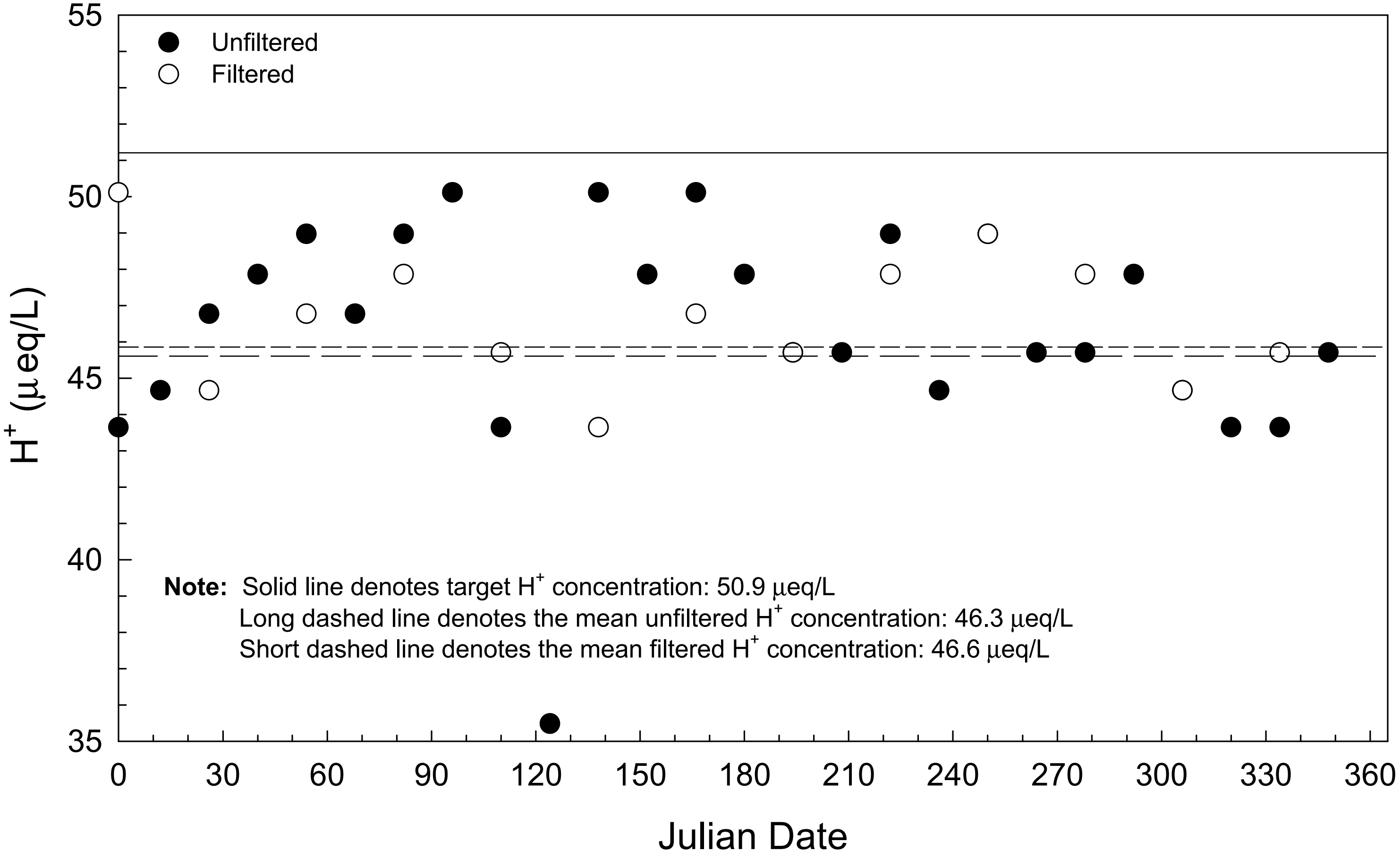


Figure B-7. Comparison of filtered and unfiltered internal blind samples, (nitrate), High-Purity Standards, SRI, 1999.



Note: Solid line denotes target Cl^- concentration: 0.25 mg/L
Long dashed line denotes the mean unfiltered Cl^- concentration: 0.22 mg/L
Short dashed line denotes the mean filtered Cl^- concentration: 0.21 mg/L

Figure B-8. Comparison of filtered and unfiltered internal blind samples, (chloride), High-Purity Standards, SRI, 1999.



Note: Solid line denotes target H^+ concentration: 50.9 µeq/L
Long dashed line denotes the mean unfiltered H^+ concentration: 46.3 µeq/L
Short dashed line denotes the mean filtered H^+ concentration: 46.6 µeq/L

Figure B-9. Comparison of filtered and unfiltered internal blind samples, (hydrogen), High-Purity Standards, SRI, 1999.

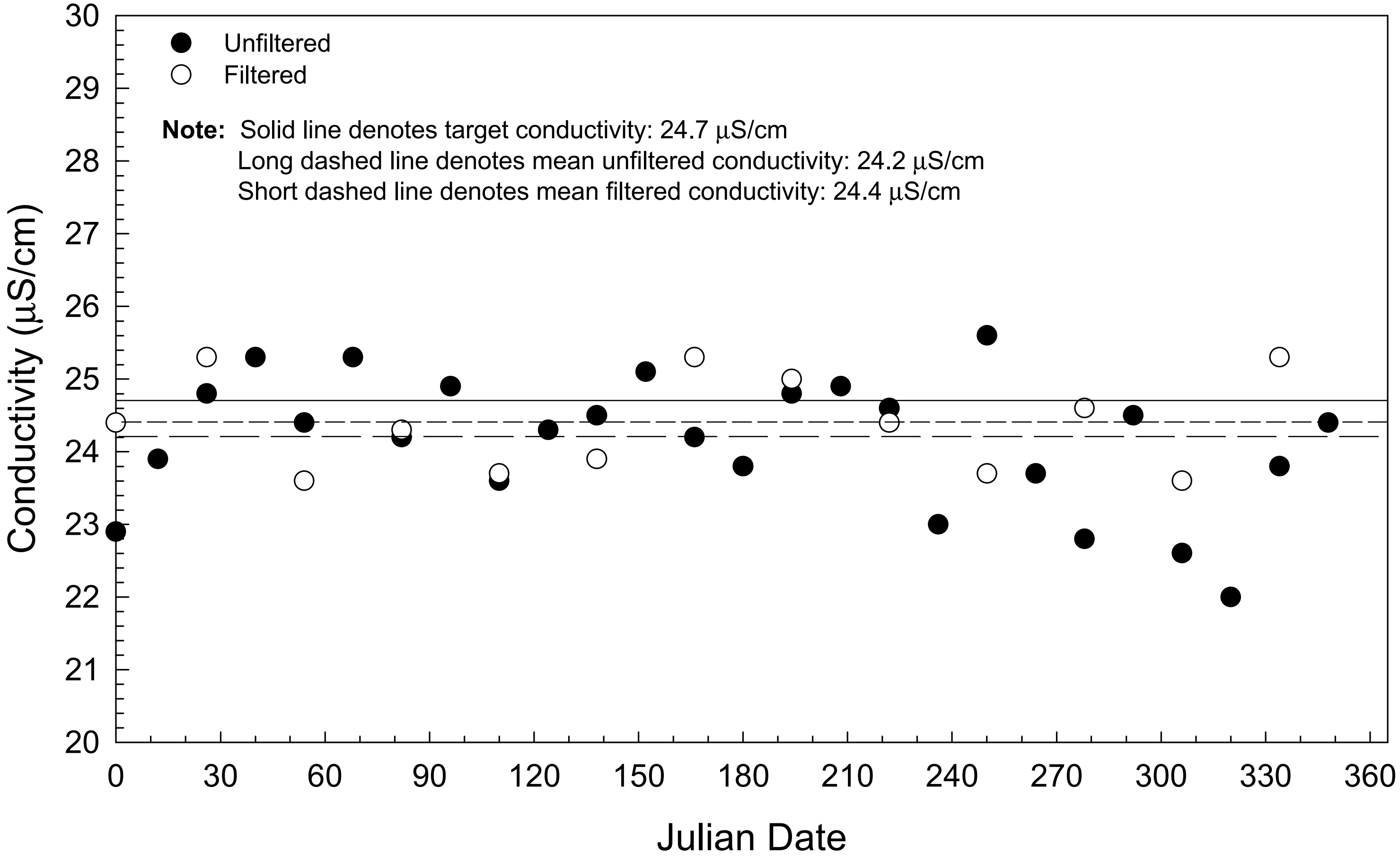


Figure B-10. Comparison of filtered and unfiltered internal blind samples, (conductivity), High-Purity Standards, SRI, 1999.

Table B-2. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, High-Purity Standards Simulated Rainwater 2 (H-PS SR2), 1999

Parameter	*Target Concentrations*[a] *(mg/L)*	*Measured Concentrations (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	0.048	0.055[b]	0.007	15.3	0.005	9.9
		0.089[c]	0.041	86.4	0.036	39.9
Magnesium	0.049	0.047	-0.002	-3.1	0.001	2.4
		0.049	0.00	-0.9	0.004	7.3
Sodium	0.4	0.399	-0.001	-0.3	0.010	2.4
		0.389	-0.011	-2.8	0.008	2.2
Potassium	0.093	0.102	0.008	9.1	0.003	3.0
		0.098	0.004	5.1	0.004	3.7
Ammonium	1.0	0.96	-0.04	-4.4	0.07	7.4
		0.92	-0.08	-7.5	0.03	3.7
Sulfate	10.1	10.04	-0.06	-0.6	0.17	1.7
		9.67	-0.43	-4.3	0.15	1.5
Nitrate	7.0	7.10	0.10	1.5	0.07	1.0
		6.87	-0.13	-1.9	0.14	2.1
Chloride	0.98	0.98	0.01	0.8	0.01	1.2
		0.95	-0.03	-2.7	0.02	2.2
pH[d]	3.55	3.64	0.09	2.6	0.03	0.9
		3.65	0.10	2.7	0.02	0.6
Hydrogen ion (µeq/L)	281.8	228.7	-53.1	-18.8	17.1	7.5
		226.5	-55.3	-19.6	10.7	4.7
Conductivity[d] (µS/cm)	125	124.3	-0.7	-0.6	3.5	2.8
		123.9	-1.1	-0.9	3.8	3.1

Notes:

There were 26 unfiltered samples and 13 filtered samples in this set.

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

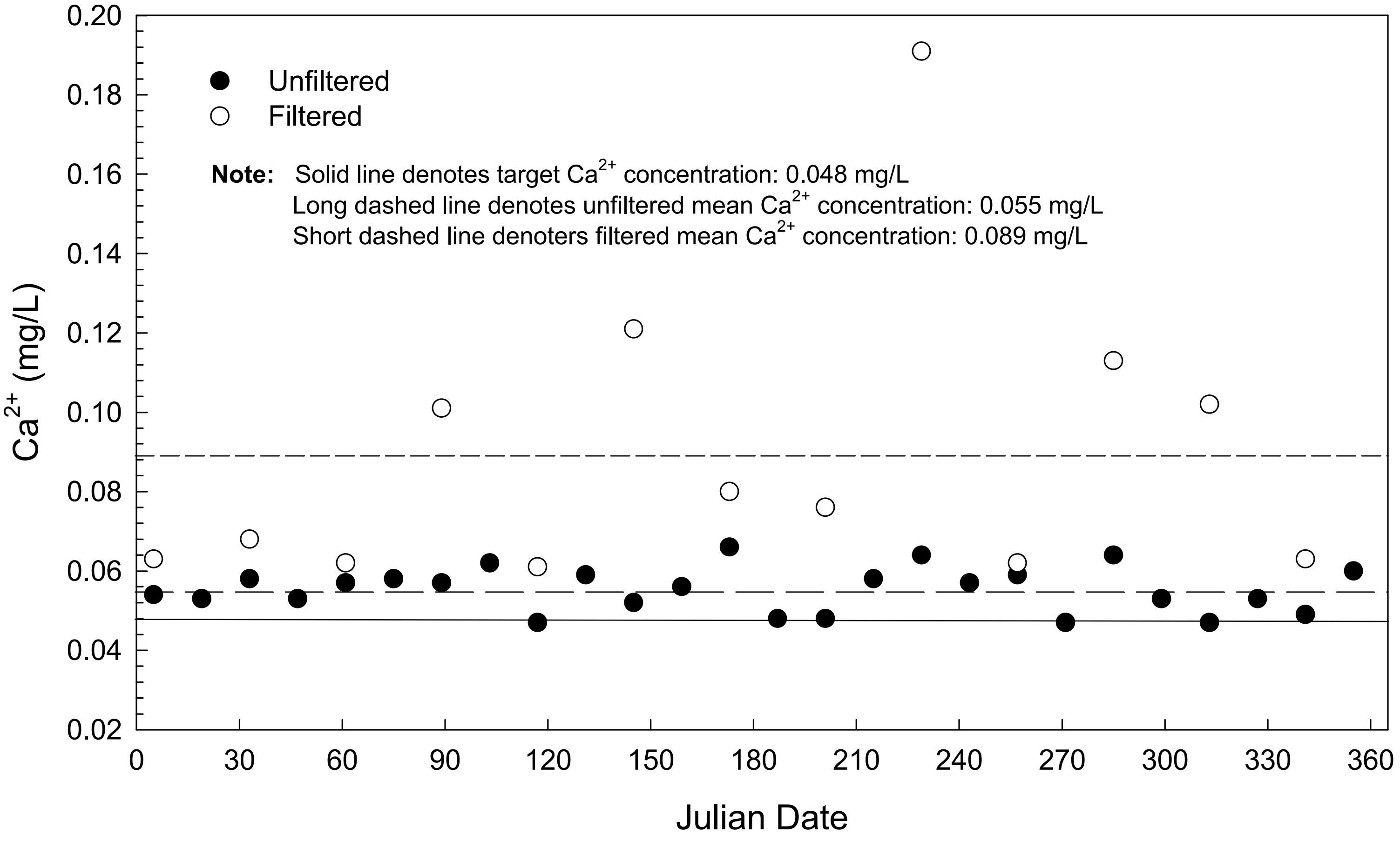
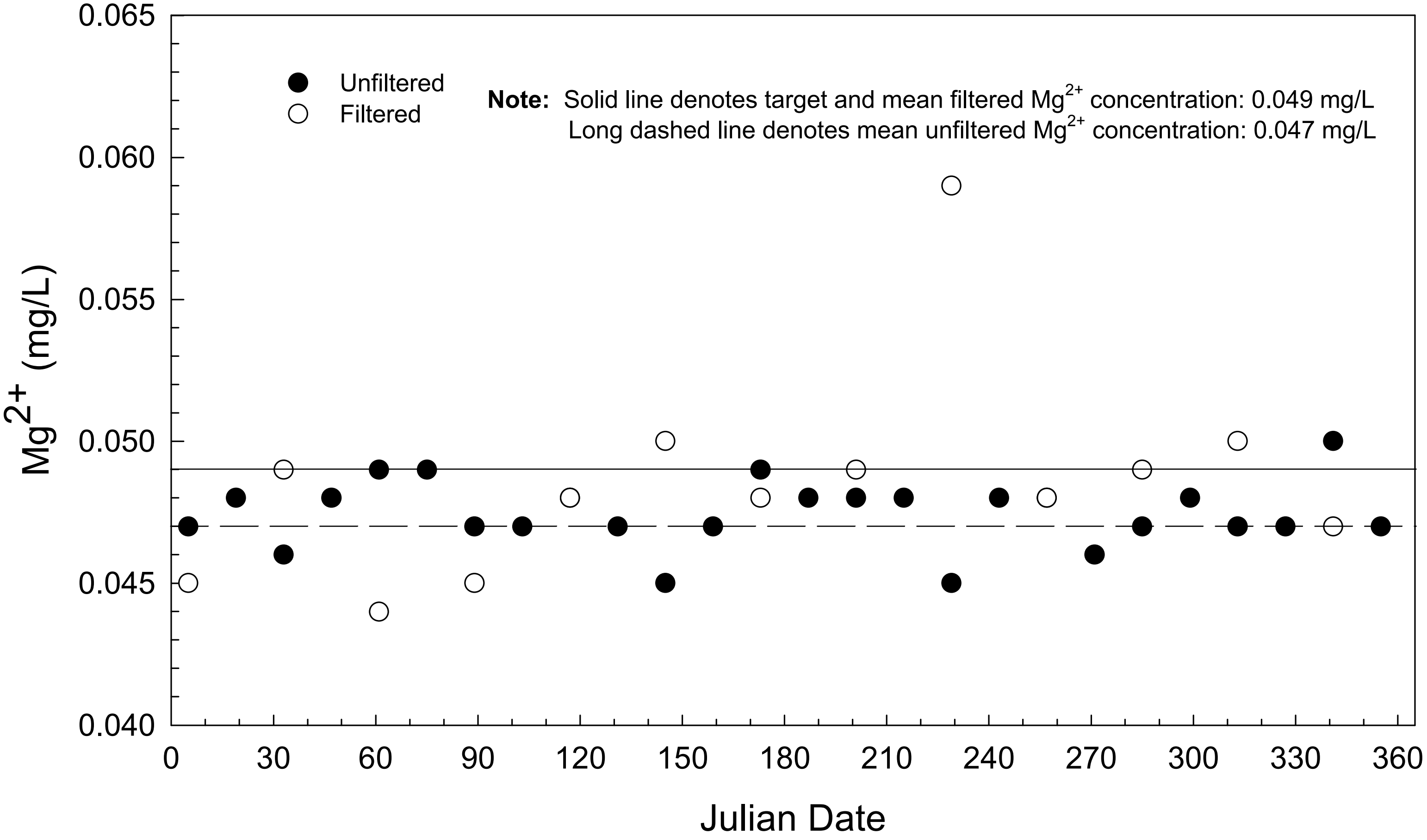
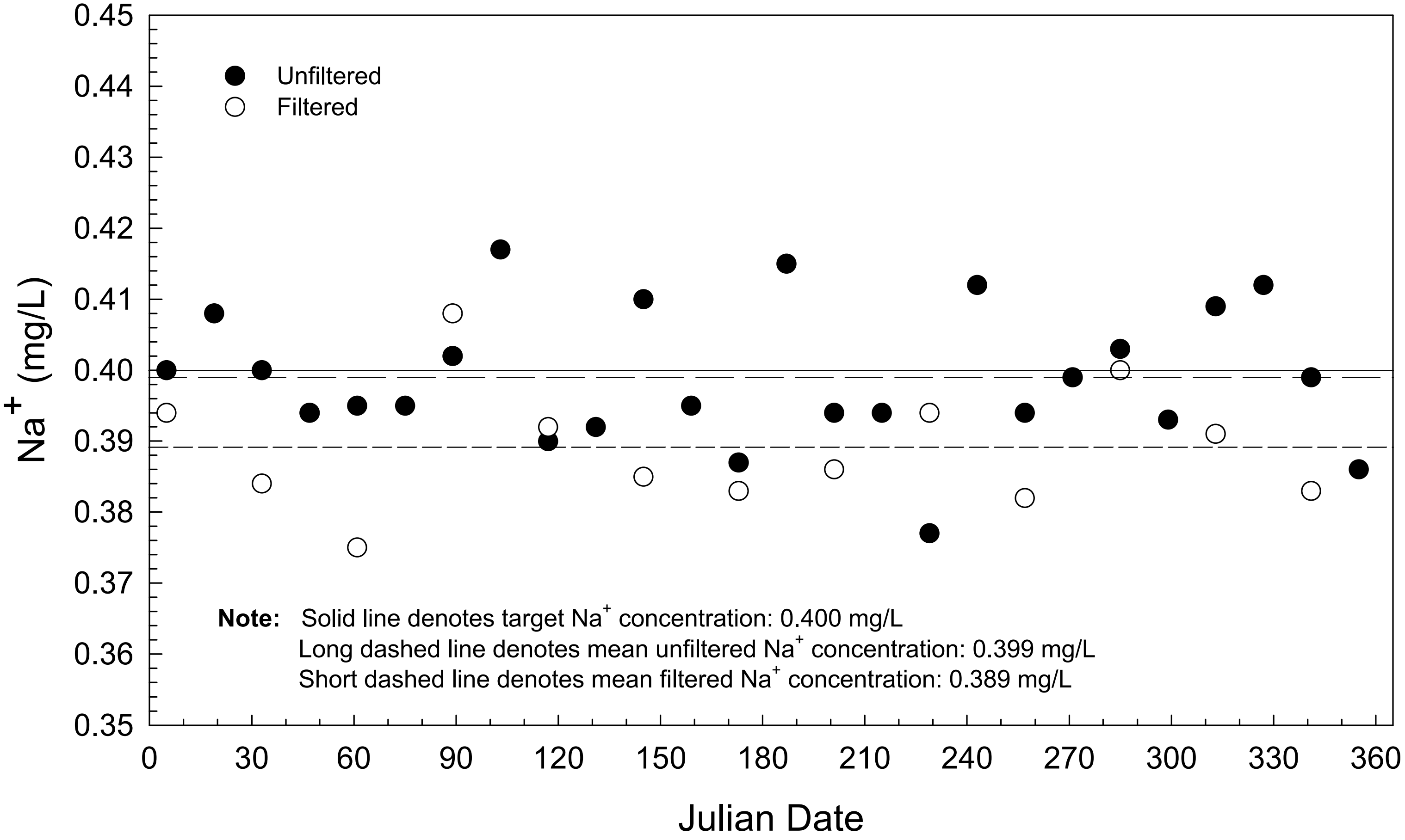


Figure B-11. Comparison of filtered and unfiltered internal blind samples, (calcium), High-Purity Standards, SR2, 1999.



Note: Solid line denotes target and mean filtered Mg^{2+} concentration: 0.049 mg/L
Long dashed line denotes mean unfiltered Mg^{2+} concentration: 0.047 mg/L

Figure B-12. Comparison of filtered and unfiltered internal blind samples, (magnesium), High-Purity Standards, SR2, 1999.



Note: Solid line denotes target Na$^+$ concentration: 0.400 mg/L
Long dashed line denotes mean unfiltered Na$^+$ concentration: 0.399 mg/L
Short dashed line denotes mean filtered Na$^+$ concentration: 0.389 mg/L

Figure B-13. Comparison of filtered and unfiltered internal blind samples, (sodium), High-Purity Standards, SR2, 1999.

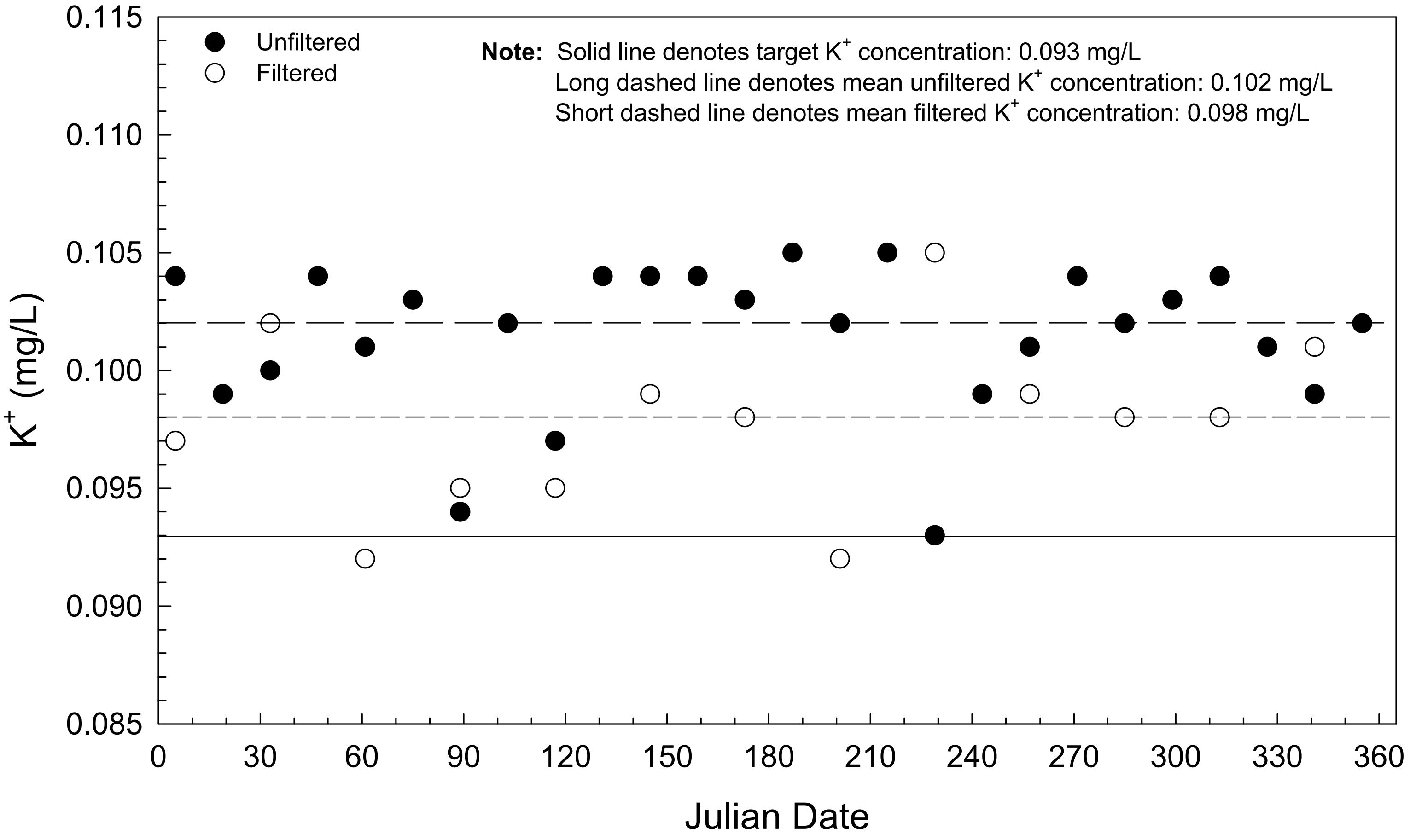
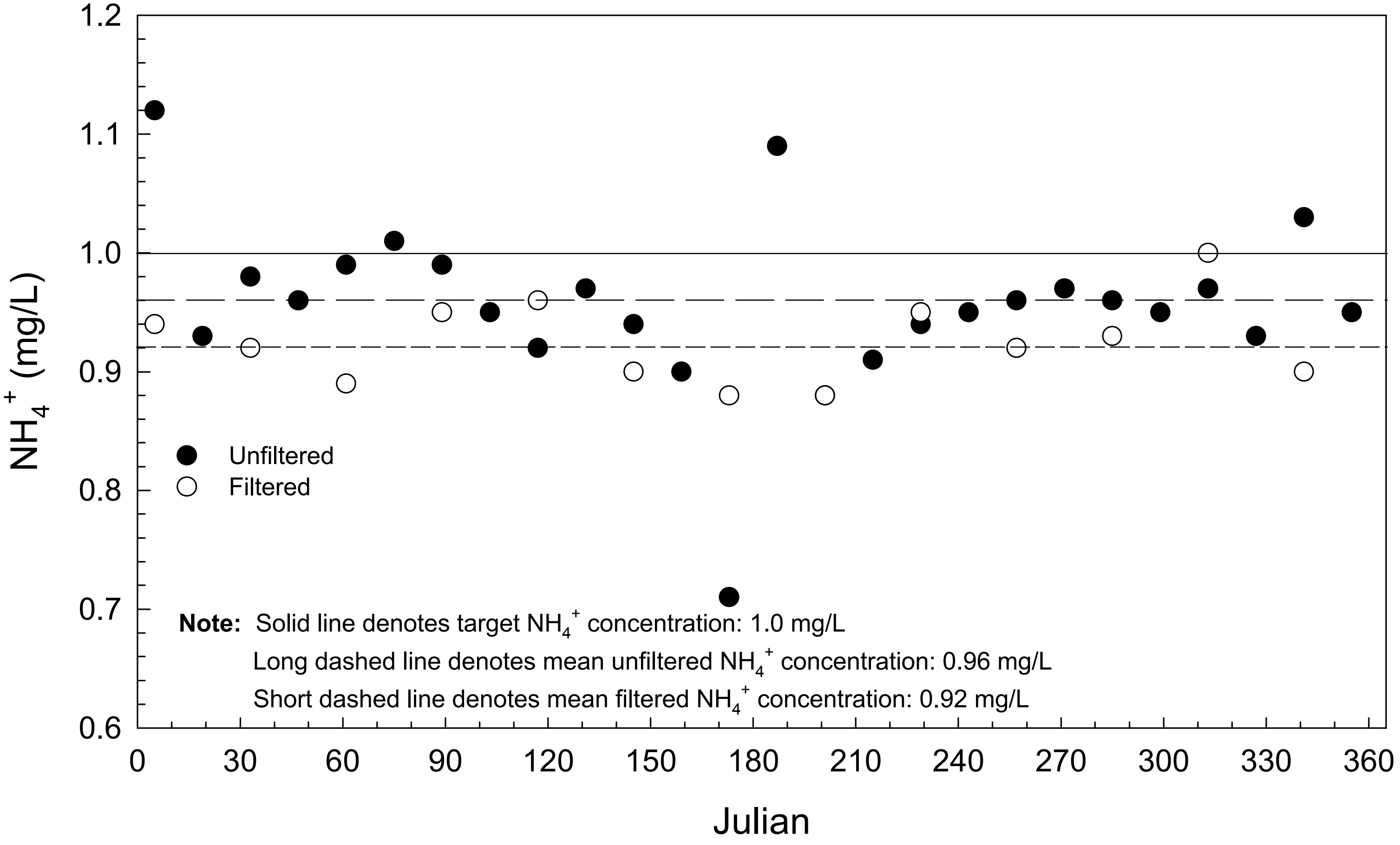


Figure B-14. Comparison of filtered and unfiltered blind samples, (potassium), High-Purity Standards, SR2, 1999.

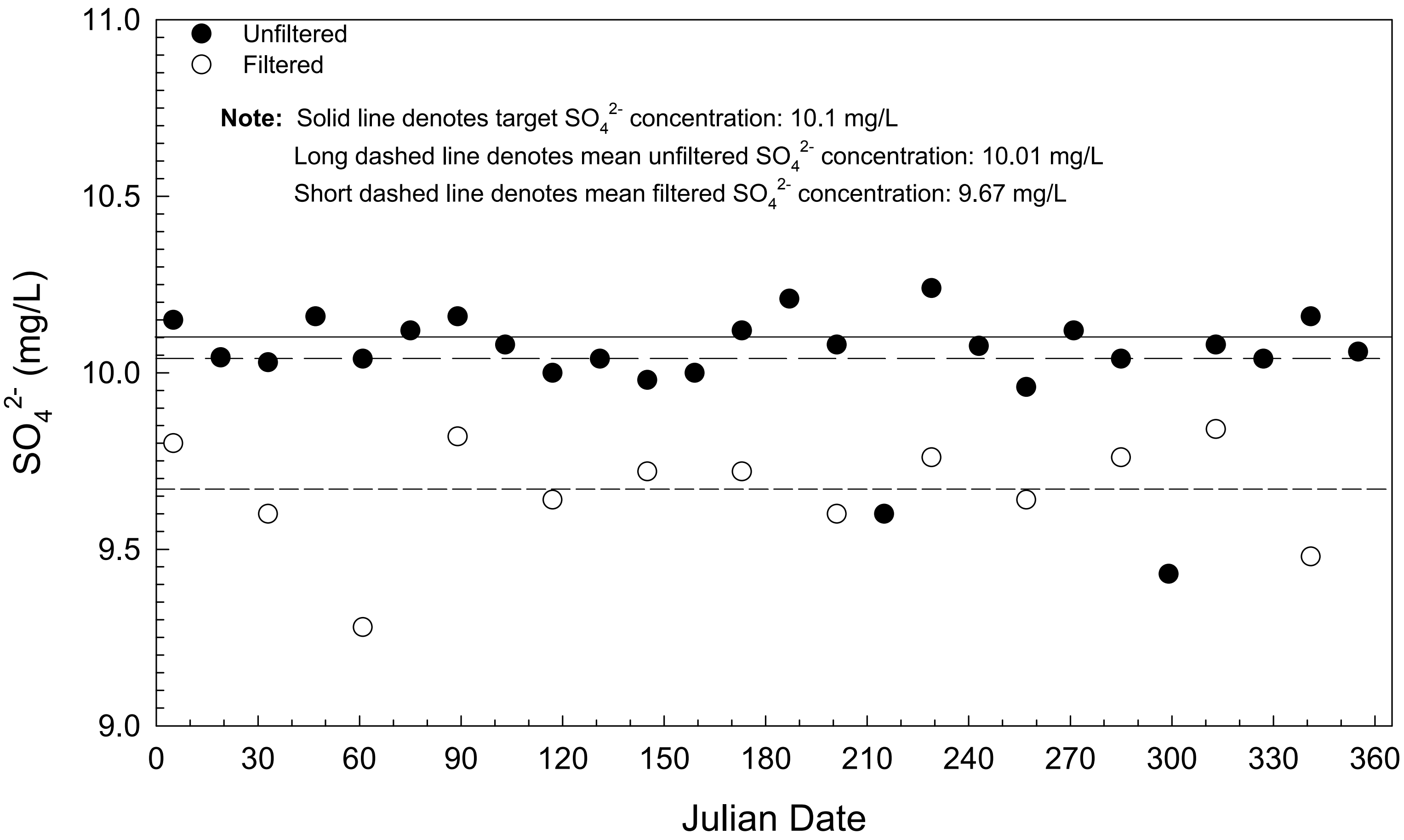


Note: Solid line denotes target NH_4^+ concentration: 1.0 mg/L

Long dashed line denotes mean unfiltered NH_4^+ concentration: 0.96 mg/L

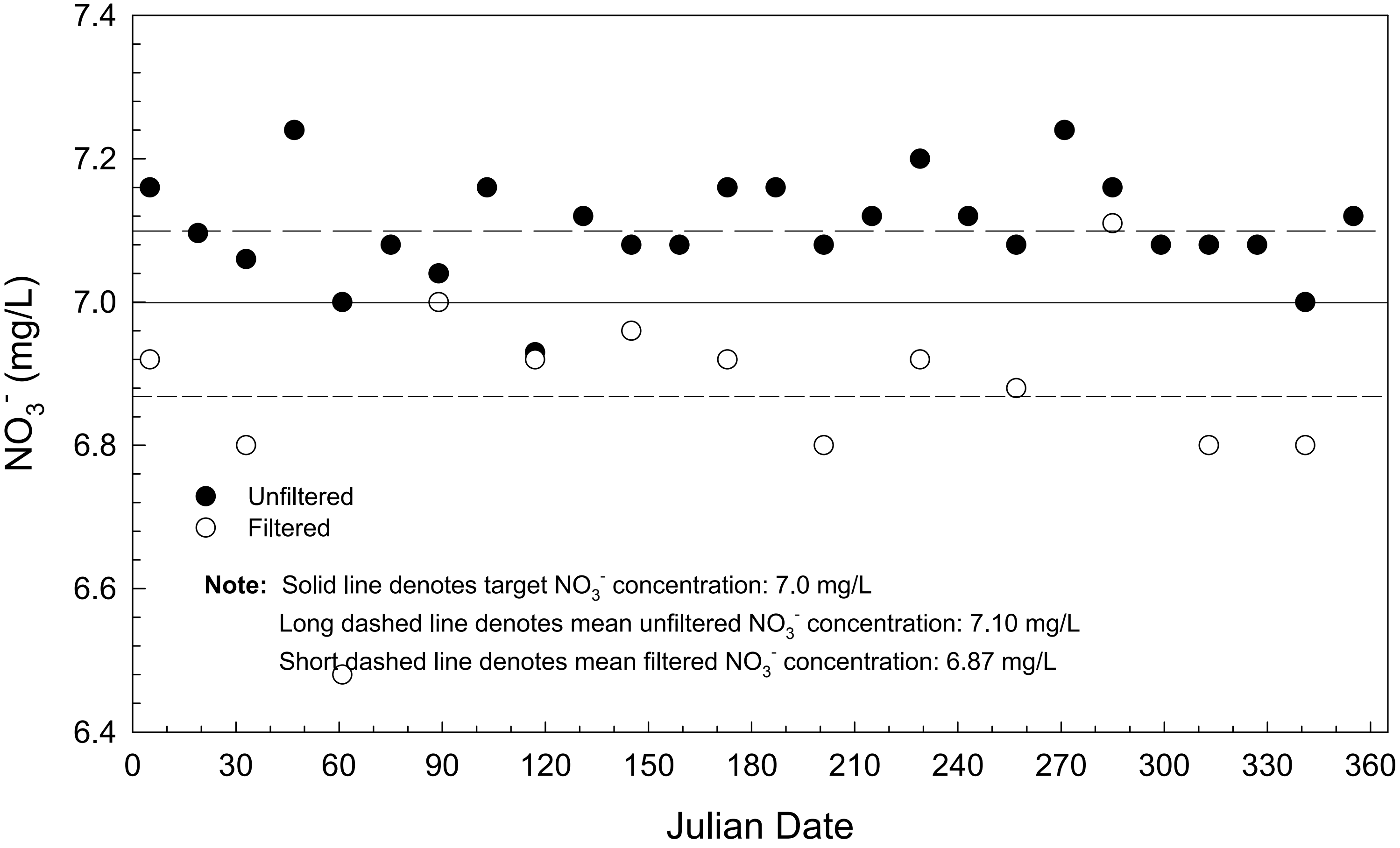
Short dashed line denotes mean filtered NH_4^+ concentration: 0.92 mg/L

Figure B-15. Comparison of filtered and unfiltered internal blind samples, (ammonium), High-Purity Standards, SR2, 1999.



Note: Solid line denotes target SO$_4^{2-}$ concentration: 10.1 mg/L
Long dashed line denotes mean unfiltered SO$_4^{2-}$ concentration: 10.01 mg/L
Short dashed line denotes mean filtered SO$_4^{2-}$ concentration: 9.67 mg/L

Figure B-16. Comparison of filtered and unfiltered internal blind samples, (sulfate), High-Purity Standards, SR2, 1999.



Note: Solid line denotes target NO_3^- concentration: 7.0 mg/L
Long dashed line denotes mean unfiltered NO_3^- concentration: 7.10 mg/L
Short dashed line denotes mean filtered NO_3^- concentration: 6.87 mg/L

Figure B17. Comparison of filtered and unfiltered internal blind samples, (nitrate), High-Purity Standards, SR2, 1999.

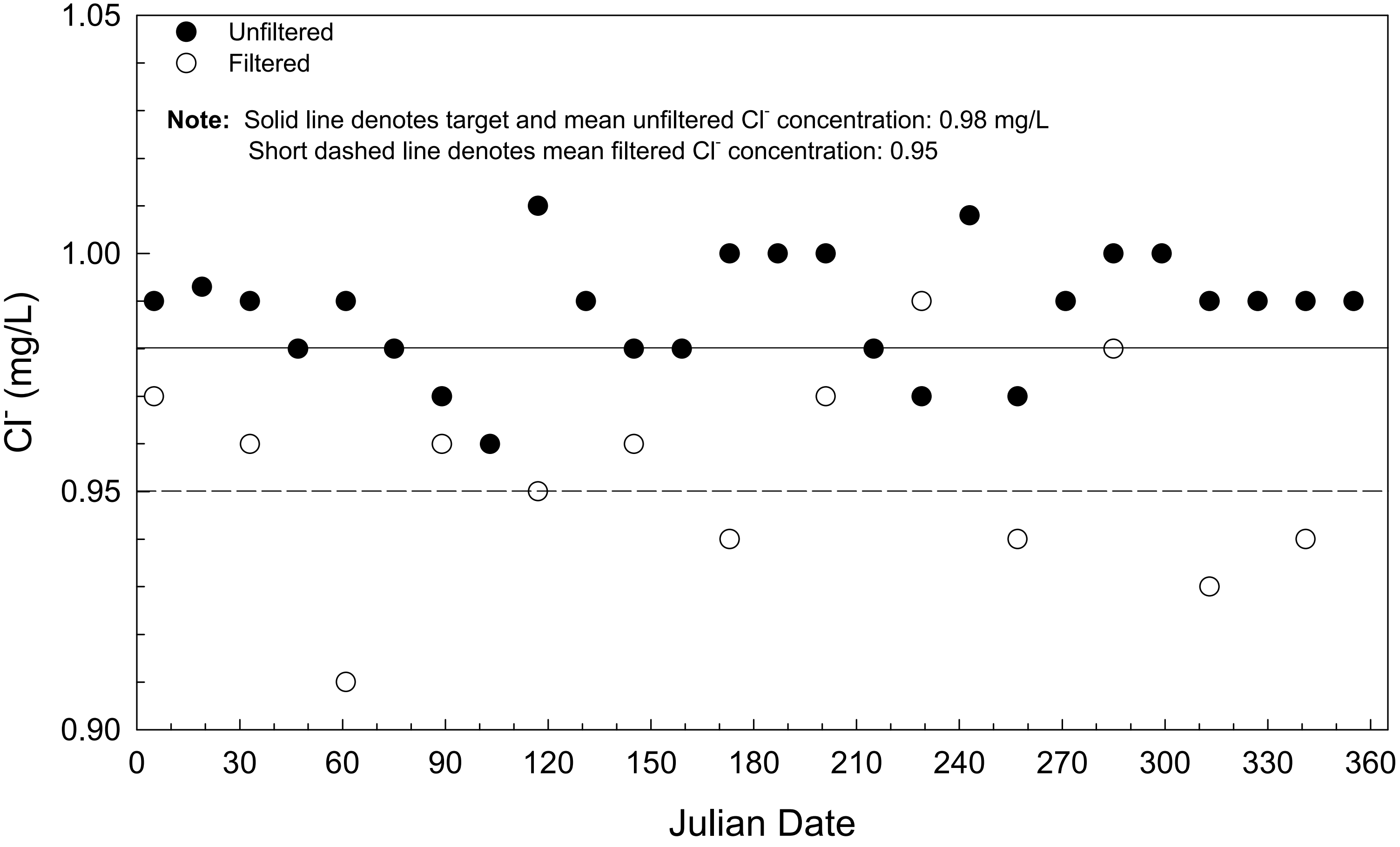


Figure B-18. Comparison of filtered and unfiltered internal blind samples, (chloride), High-Purity Standards, SR2, 1999.

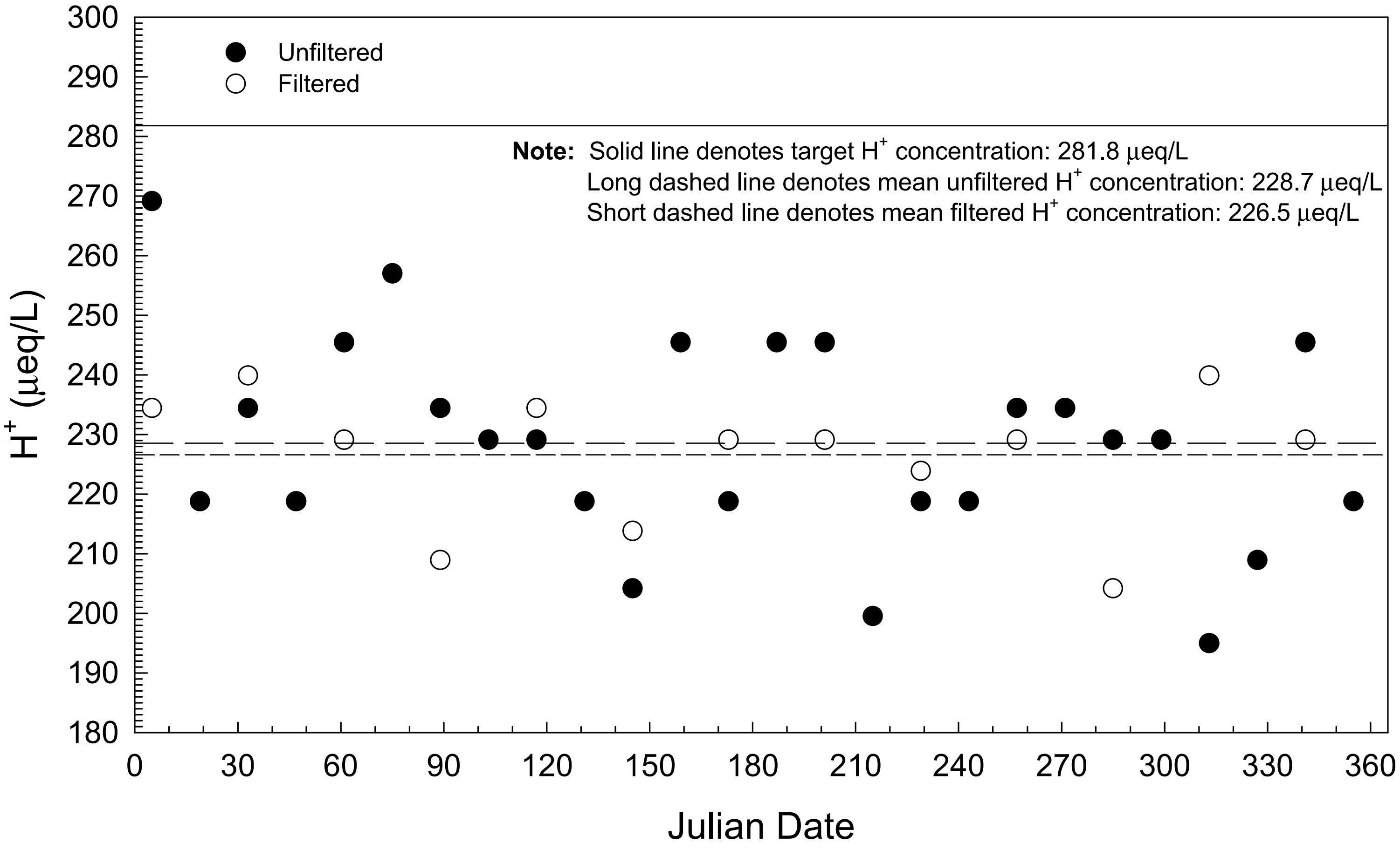
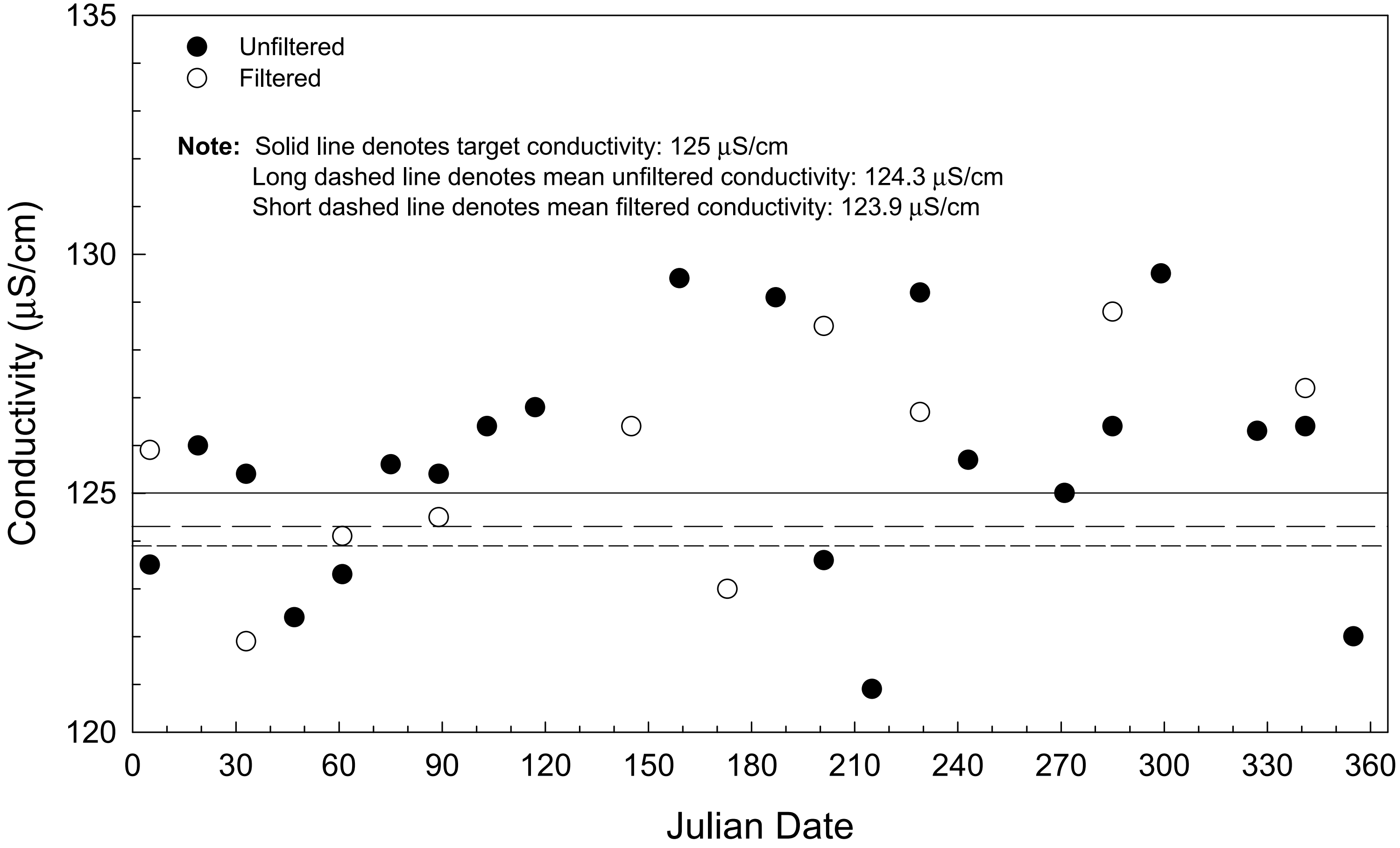


Figure B-19. Comparison of filtered and unfiltered internal blind samples, (hydrogen ion), High-Purity Standards, SR2, 1999.



Note: Solid line denotes target conductivity: 125 µS/cm
Long dashed line denotes mean unfiltered conductivity: 124.3 µS/cm
Short dashed line denotes mean filtered conductivity: 123.9 µS/cm

Figure B-20. Comparison of filtered and unfiltered internal blind samples (conductivity), High-Purity Standards, SR2, 1999.

Table B-3. Comparison of Filtered and Unfiltered Internal Blind Audit Samples Using 4.3 Quality Assurance Check Sample, 1999

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	3.25[b]	0.15	4.1	0.04	1.3
		3.14[c]	0.02	0.7	0.08	2.5
Chloride	0.0					
pH[d]	4.30	4.33	0.03	0.7	0.02	0.5
		4.33	0.03	0.8	0.02	0.5
Hydrogen ion (µeq/L)	50.12	47.9	-2.3	-6.8	2.1	4.6
		46.3	-3.8	-7.6	2.1	4.6
Conductivity[d] (µS/cm)	21.1	21.3	0.2	2.0	0.81	3.7
		21.6	0.5	2.3	0.59	2.7

Notes:
There were 26 unfiltered samples and 13 filtered samples in this set.
All concentrations that are blank above were below the method detection limit for that parameter.
[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] Both pH and conductivity are measured on unfiltered samples prior to filtering.

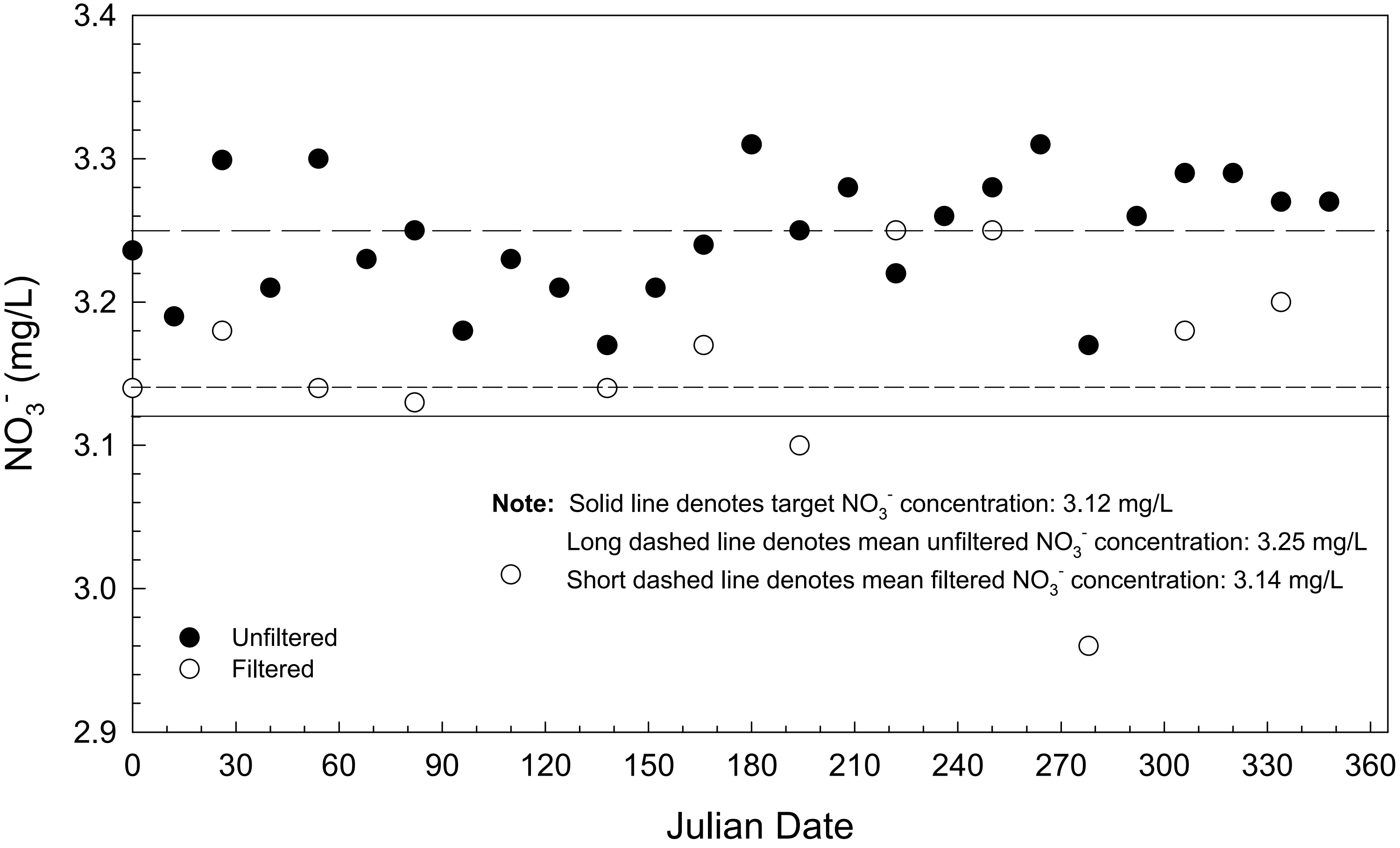


Figure B-21. Comparison of filtered and unfiltered internal blind samples (nitrate), pH 4.3 nitric acid check sample, 1999.

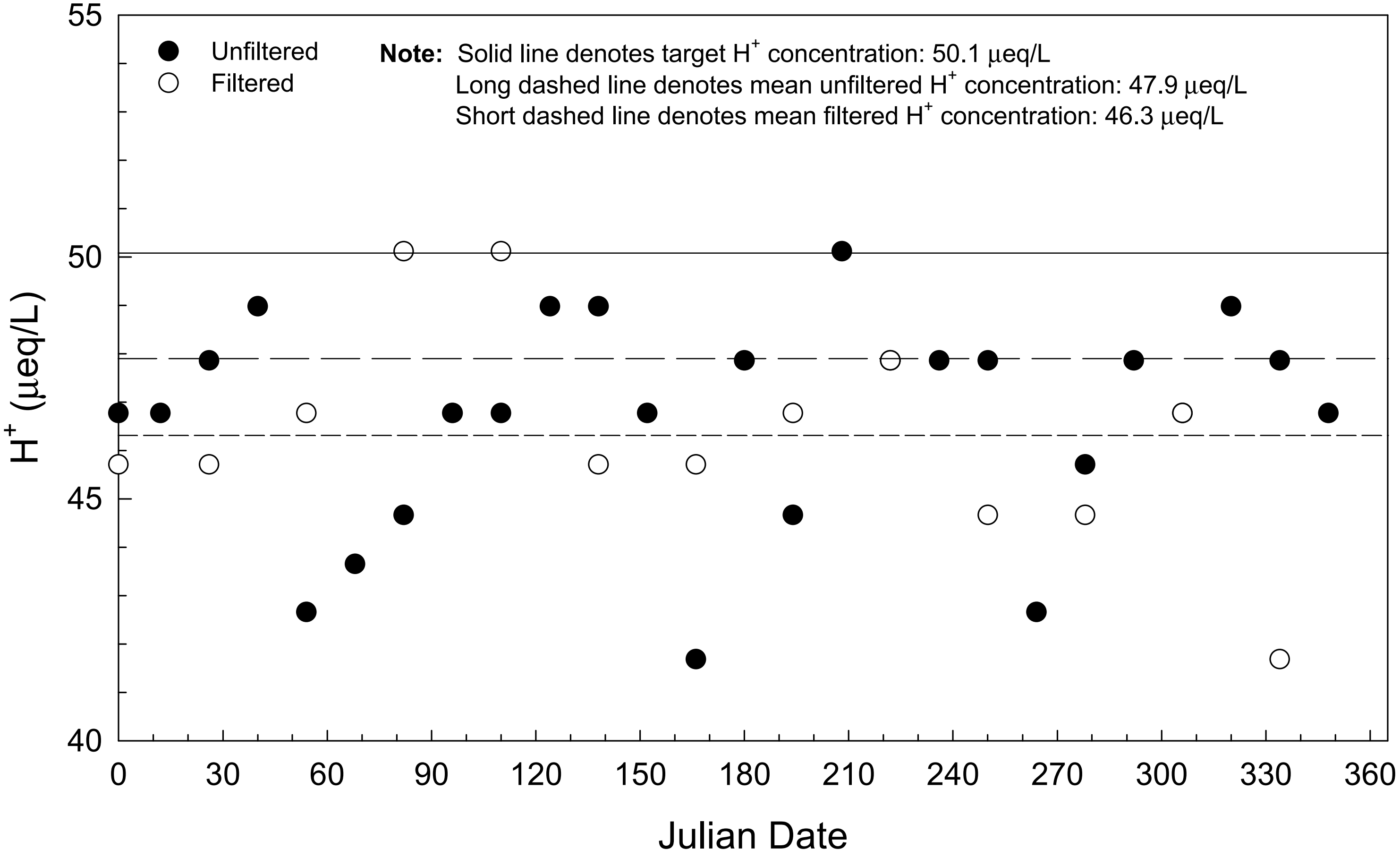


Figure B-22. Comparison of filtered and unfiltered internal blind samples (hydrogen ion), pH 4.3 nitric acid check sample, 1999.

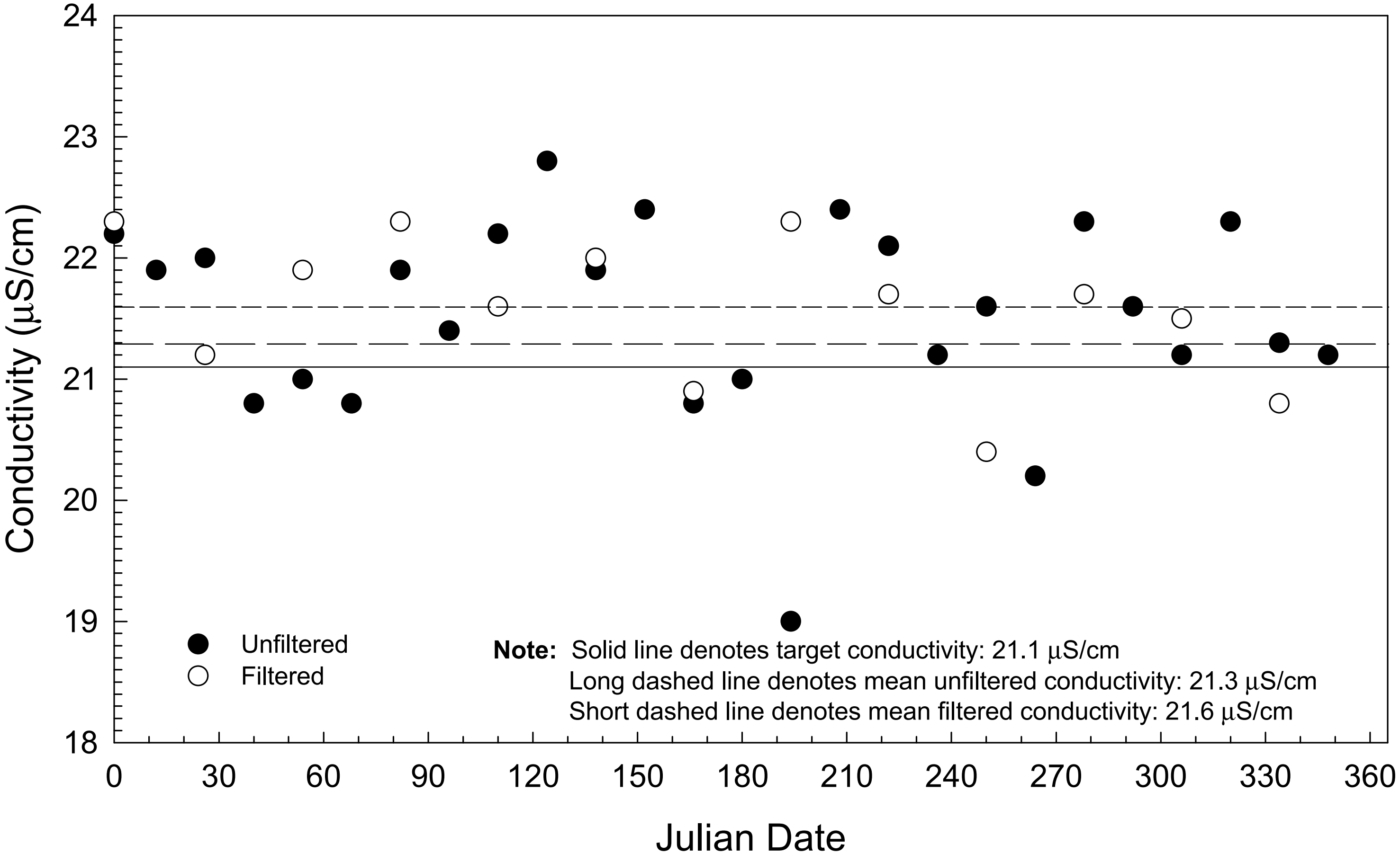


Figure B-23. Comparison of filtered and unfiltered internal blind samples (conductivity), pH 4.3 nitric acid check sample, 1999.

Table B-4. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, Deionized Water, 1999

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	5.60[b]	-0.05	-1.0	0.15	2.7
		5.56[c]	-0.09	-1.5	0.06	1.0
Hydrogen ion (µeq/L)	2.24	2.67	0.44	19.4	0.79	29.7
		2.75	0.51	23.0	0.35	12.7
Conductivity[d] (µS/cm)	0.9	1.1	0.2	27.4	0.24	21.1
		1.1	0.2	23.9	0.21	18.6

Notes:

There were 26 unfiltered samples and 13 filtered samples in this set.

All concentrations that are blank above 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] Both 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 NTN Samples, 1999

	Percentile Concentration Values (mg/L)		
Parameter	*5th*	*50th*	*95th*
Calcium	0.012	0.153	0.537
Magnesium	0.003	0.039	0.157
Sodium	0.005	0.256	1.430
Potassium	<0.003	0.031	0.079
Ammonium	<0.02	0.21	0.64
Sulfate	0.14	1.28	3.57
Nitrate	0.08	1.01	2.54
Chloride	0.03	0.43	2.15
pH (units)	4.14	4.91	5.92
Hydrogen ion (μeq/L)	1.21	22.12	72.12
Specific Conductance (μS/cm)	2.9	15.4	42.3

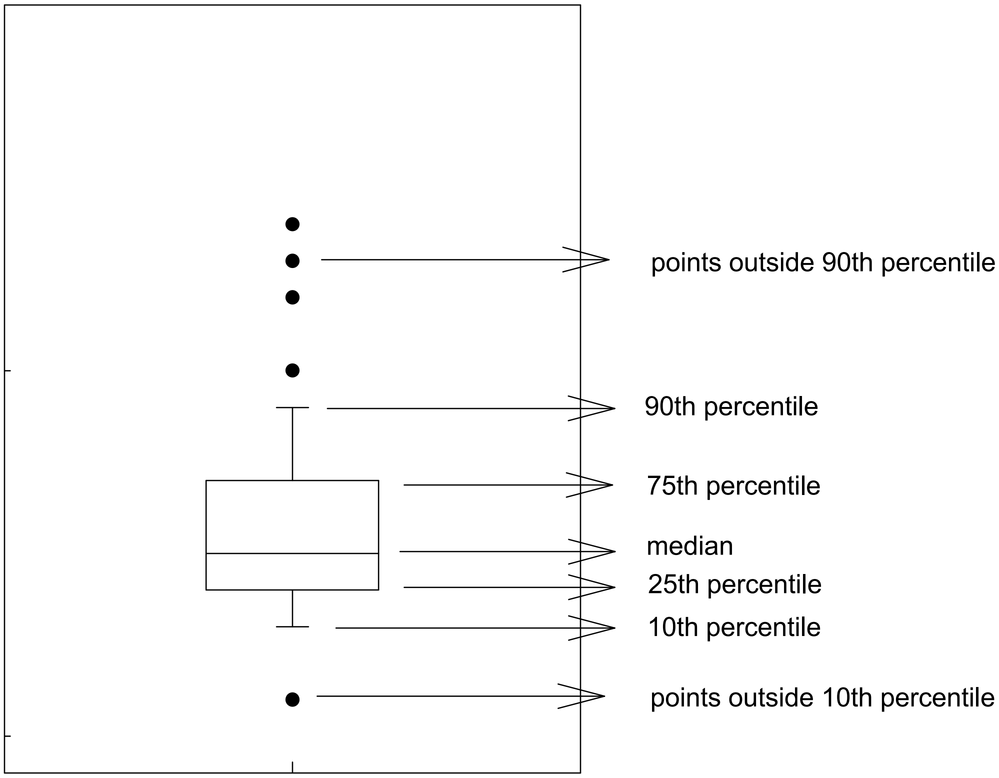


Figure B-24. Explanation of box and whisker plots.

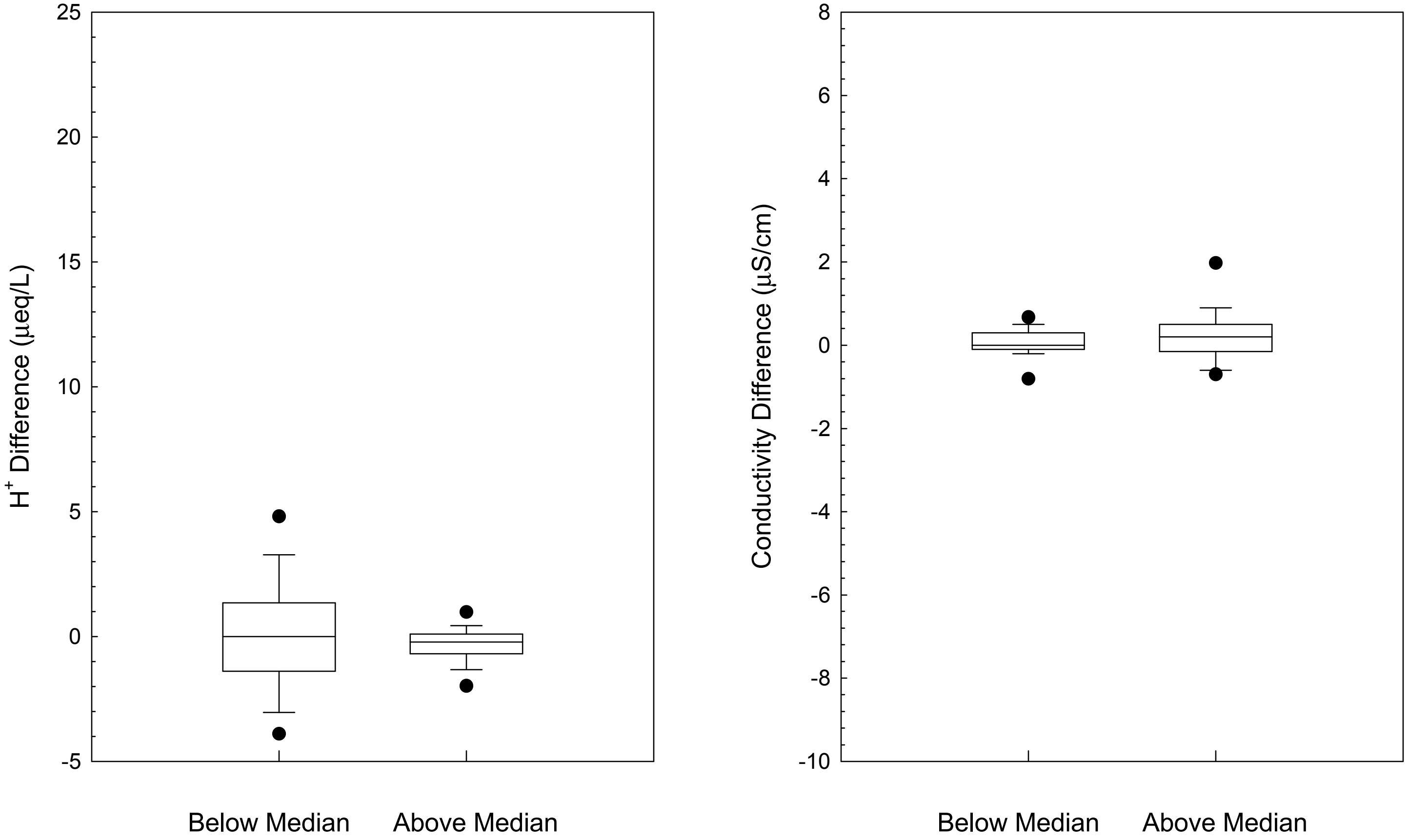


Figure B-25. Results of NTN replicate analysis, hydrogen ion (H$^+$) and conductivity, 1999.

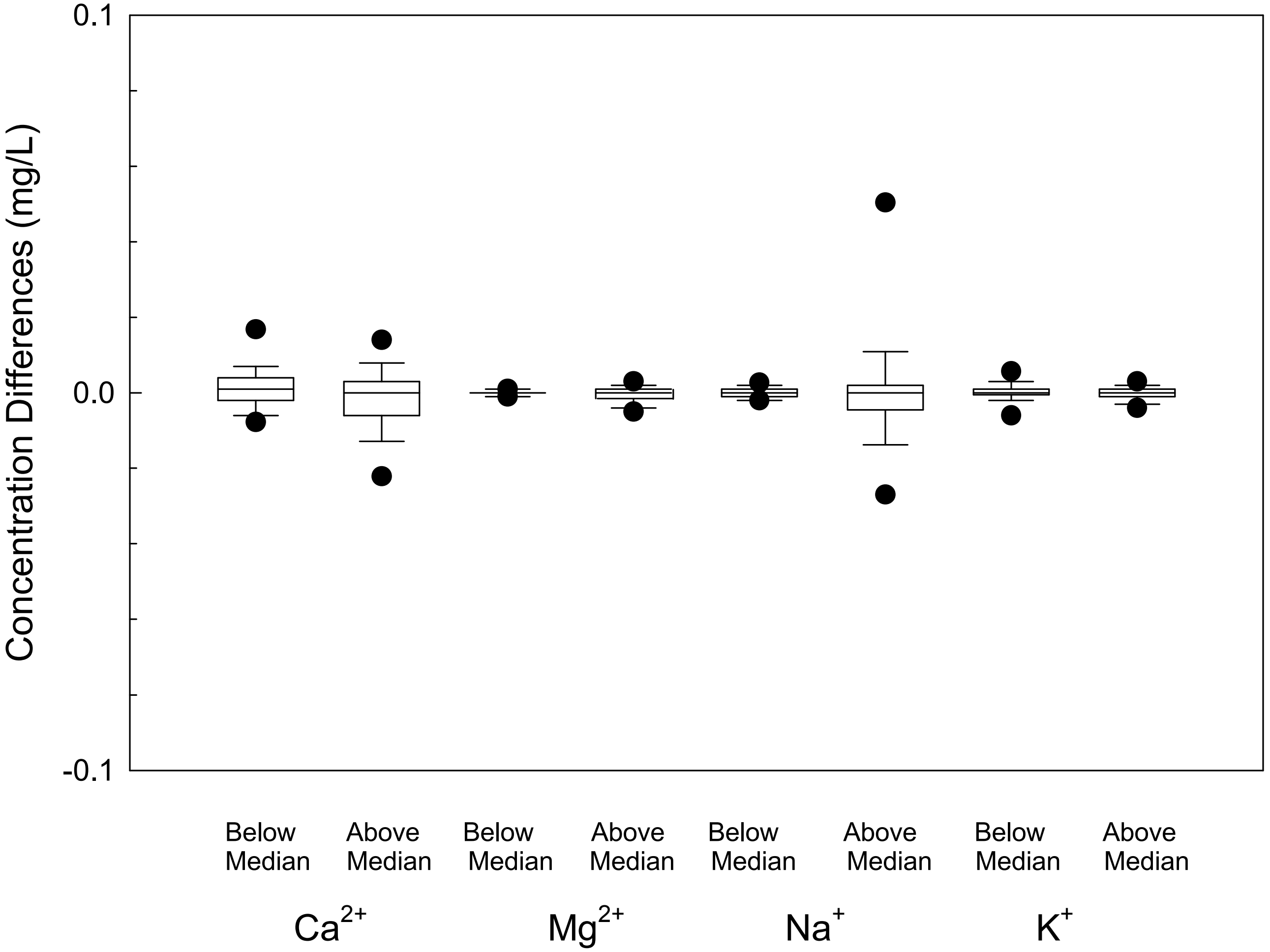


Figure B-26. Results of NTN replicate analysis, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}), 1999.

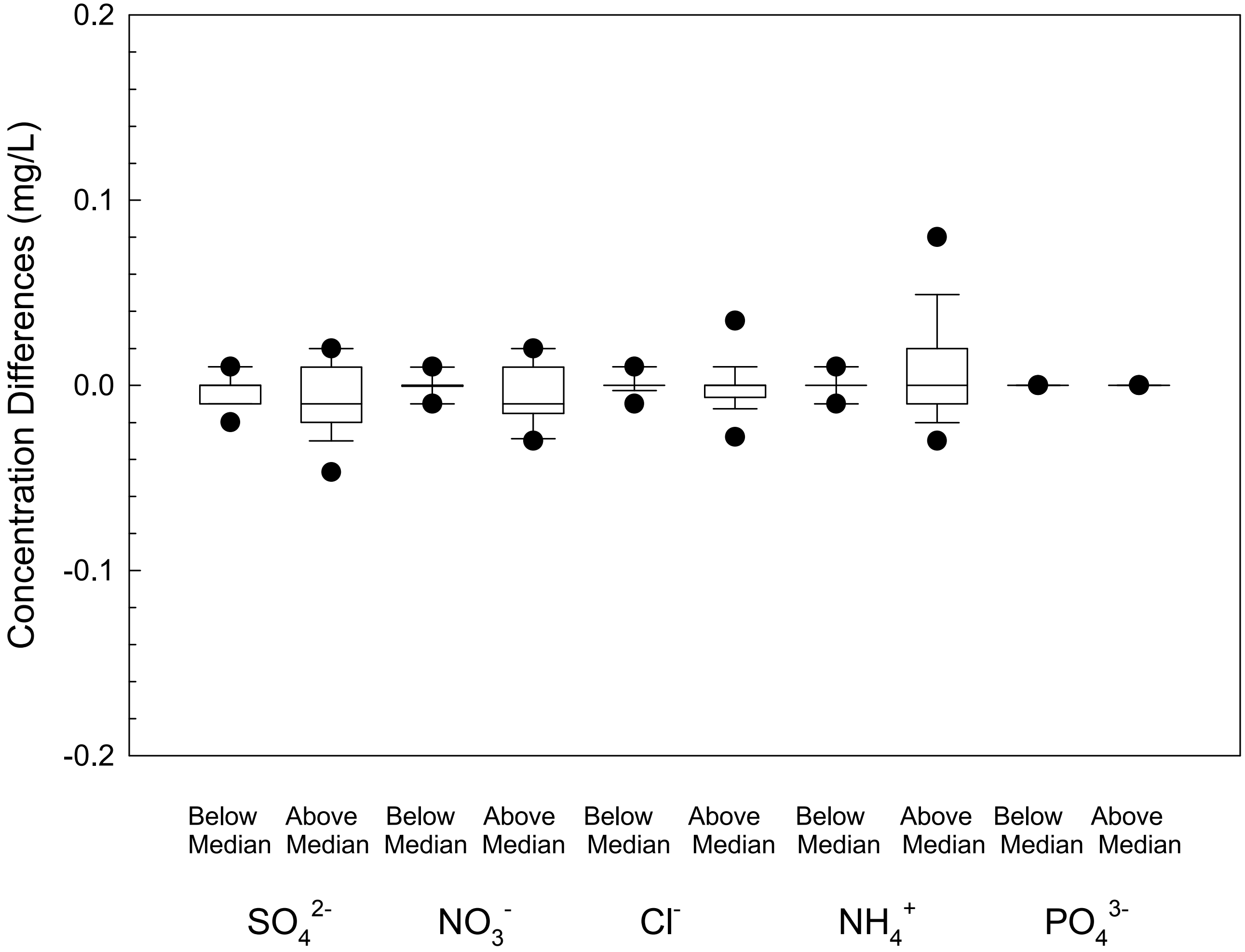


Figure B-27. Results of NTN replicate analysis, sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), and orthophosphate (PO_4^{3-}), 1999.

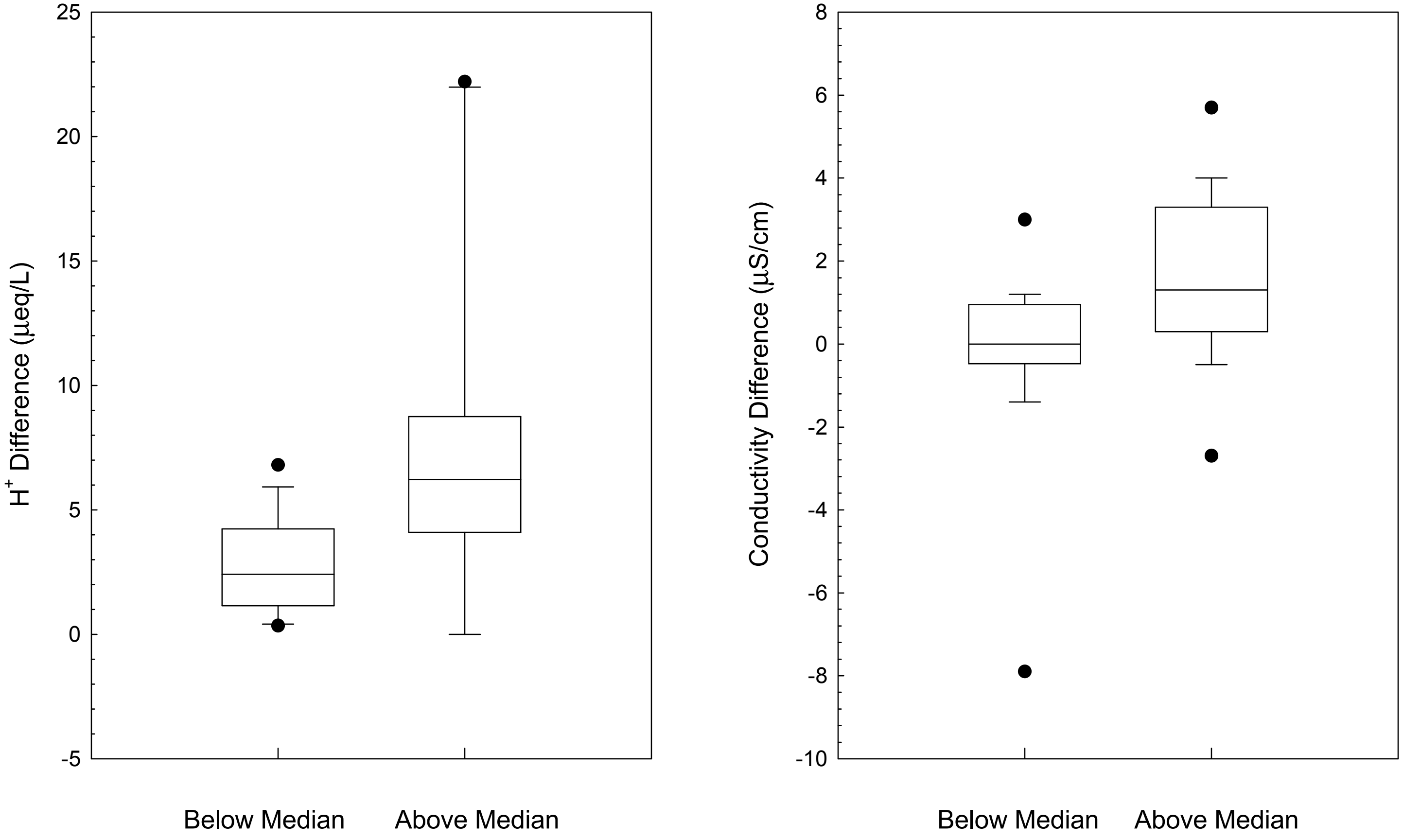


Figure B-28. Results of AIRMoN replicate analysis, hydrogen ion (H^+) and conductivity, 1999.

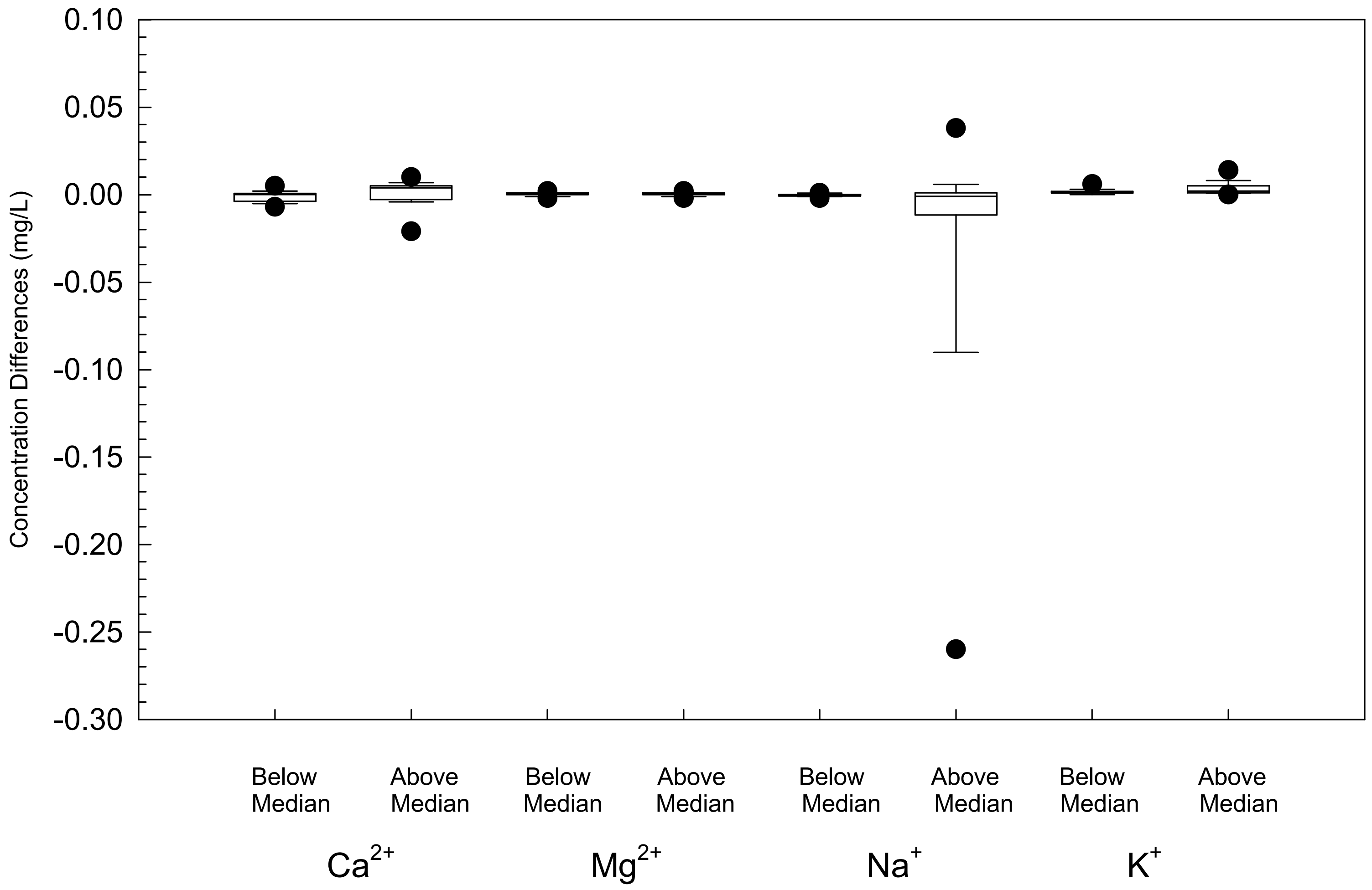


Figure B-29. Results of AIRMoN replicate analysis, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}) and potassium (K^{+}), 1999.

Table B-6. Percent of Ion Concentrations above MDL Found in Weekly Deionized (DI) Water Blanks and Leachates, 1999

Blank	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Ammonium*	*Phosphate*	*Chloride*	*Nitrate*	*Sulfate*
DI (Rm 209)	0.0	0.0	2.0	2.0	0.0	0.0	0.0	2.0	0.0
DI (Rm 304)	3.8	0.0	11.5	0.0	0.0	0.0	0.0	1.9	1.9
DI (Rm 323)	0.0	0.0	1.9	1.9	0.0	0.0	0.0	1.9	0.0
Filter A	5.8	1.9	5.8	1.9	0.0	1.9	0.0	1.9	0.0
Filter B	1.9	0.0	1.9	0.0	0.0	0.0	0.0	1.9	0.0
Bucket - 50 mL	59.6	7.6	34.6	13.5	53.8	1.9	23.1	19.2	0.0
Bucket - 150 mL	63.5	3.8	21.2	9.6	19.2	0.0	13.5	1.9	0.0
Bucket - 50 mL	27.3	0.0	63.6	9.0	54.5	0.0	18.2	36.4	0.0
Bottle - 50 mL	7.7	7.7	3.8	36.5	1.9	1.9	0.0	1.9	1.9
Bottle - 150 mL	1.9	1.9	5.8	7.7	0.0	0.0	0.0	1.9	0.0
Lid - 50 mL	32.7	7.7	11.5	7.7	19.2	0.0	13.5	0.0	0.0

Note:
There were 52 weeks of blank samples.

Table B-7. Percent of Ion Concentrations above Control Limits Found in Weekly Simulated Rain (FR25) Leachates, 1999

Blank	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Ammonium*	*Phosphate*	*Chloride*	*Nitrate*	*Sulfate*
Filter A	28.8	0.0	1.9	1.9	0.0	0.0	0.0	0.0	0.0
Filter B	34.6	0.0	1.9	0.0	0.0	0.0	0.0	0.0	0.0
Bucket - 50 mL	75.0	7.7	42.3	13.5	30.8	0.0	13.5	28.8	19.2
Bucket - 150 mL	71.2	0.0	21.2	1.9	1.9	0.0	7.7	5.8	9.6
Bottle - 50 mL	9.6	9.6	7.7	28.8	0.0	1.9	0.0	0.0	3.8
Bottle - 150 mL	5.8	0.0	0.0	11.5	0.0	1.9	0.0	0.0	0.0
Lid - 50 mL	59.6	1.9	15.4	7.8	7.7	0.0	1.9	0.0	0.0
AIRMoN Bottle - 50 mL	18.2	0.0	9.1	9.1	0.0	0.0	0.0	0.0	0.0
AIRMoN Bottle - 150 mL	9.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Note:
Fifty-two NTN blanks and 11 monthly AIRMoN blanks were analyzed.

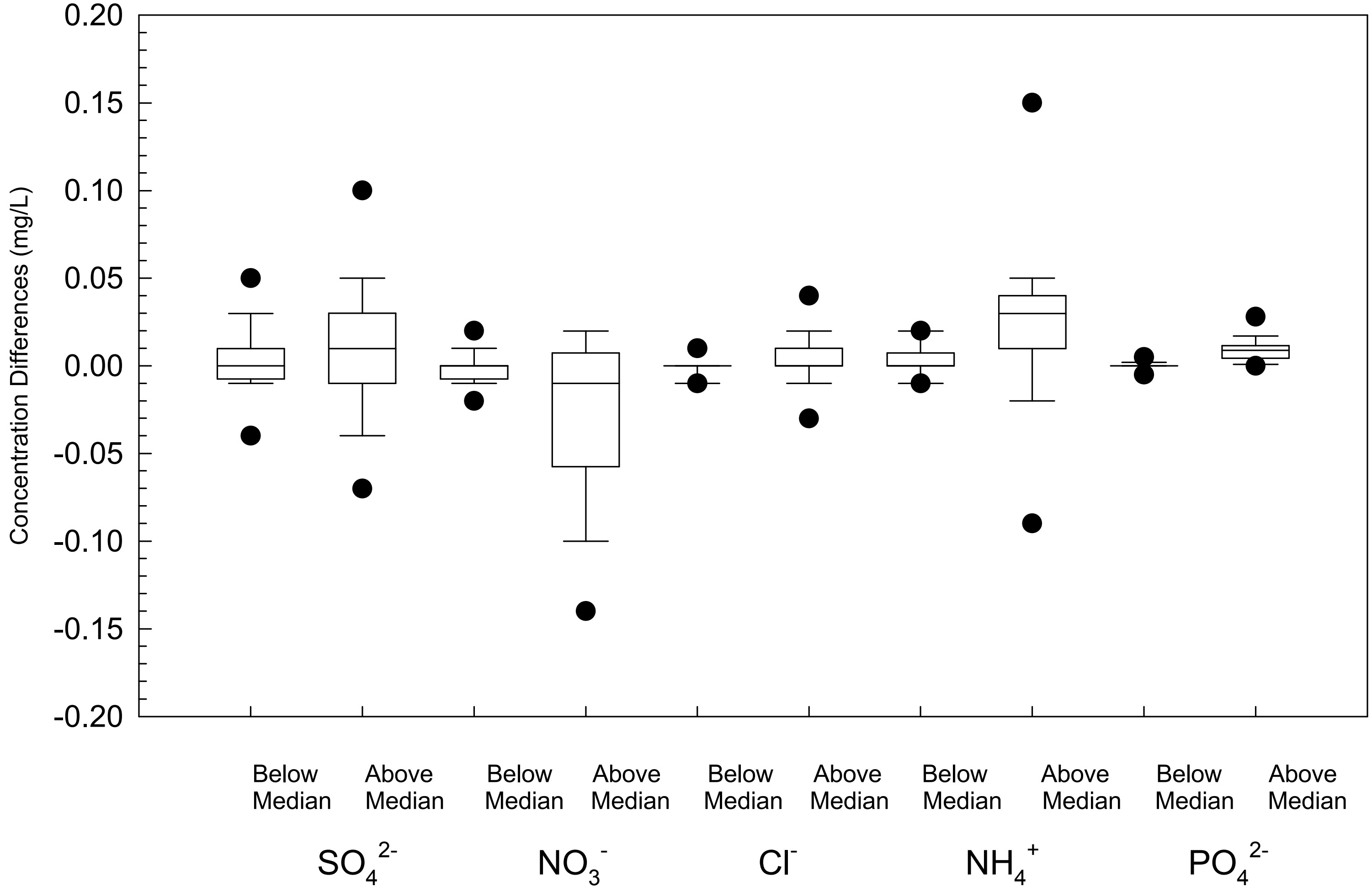
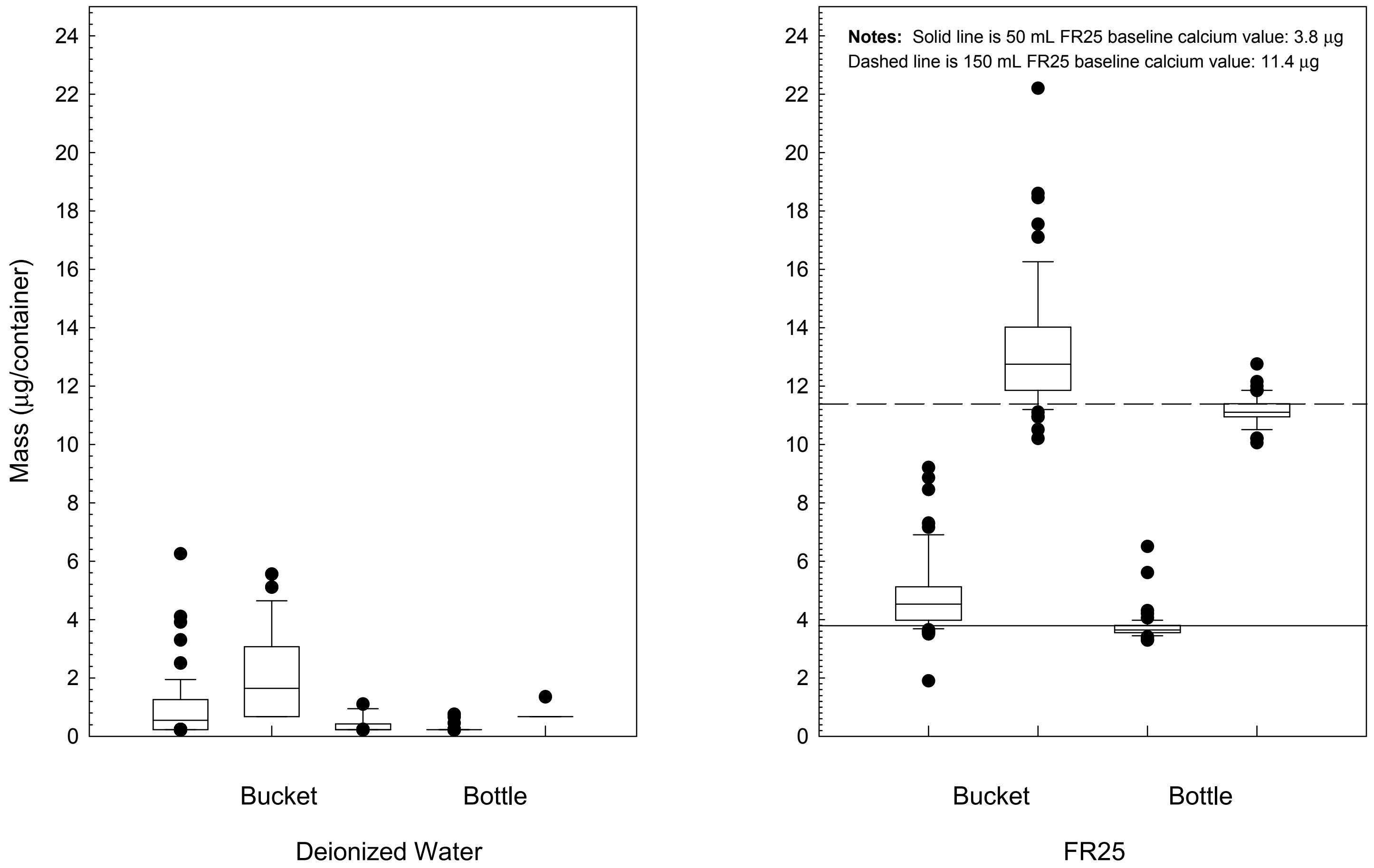


Figure B-30. Results of AIRMoN replicate analysis, sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), and orthophosphate (PO_4^{3-}), 1999.



Notes: Solid line is 50 mL FR25 baseline calcium value: 3.8 µg
Dashed line is 150 mL FR25 baseline calcium value: 11.4 µg

Figure B-31. Calcium found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 1999.

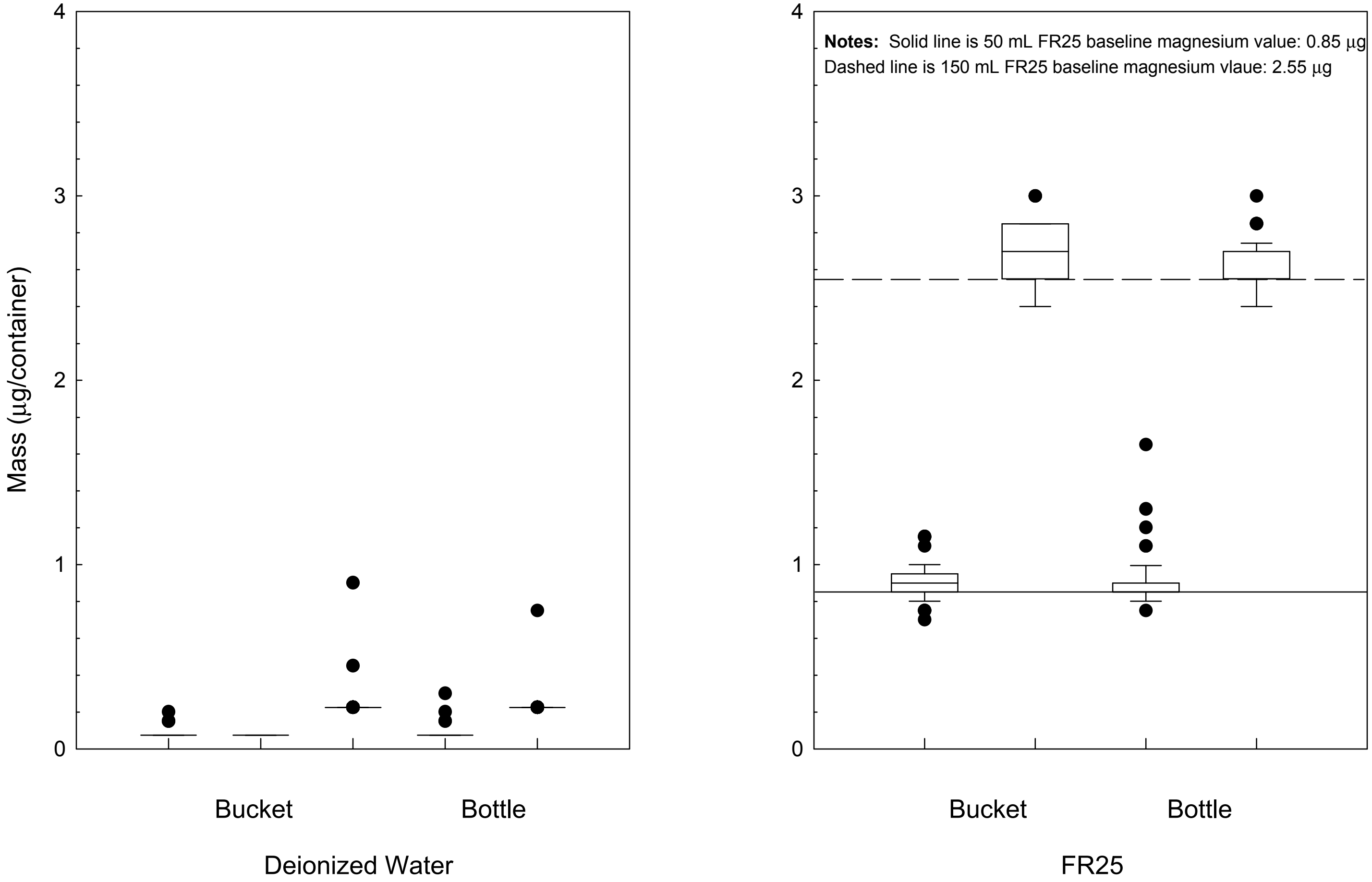


Figure B-32. Magnesium found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 1999.

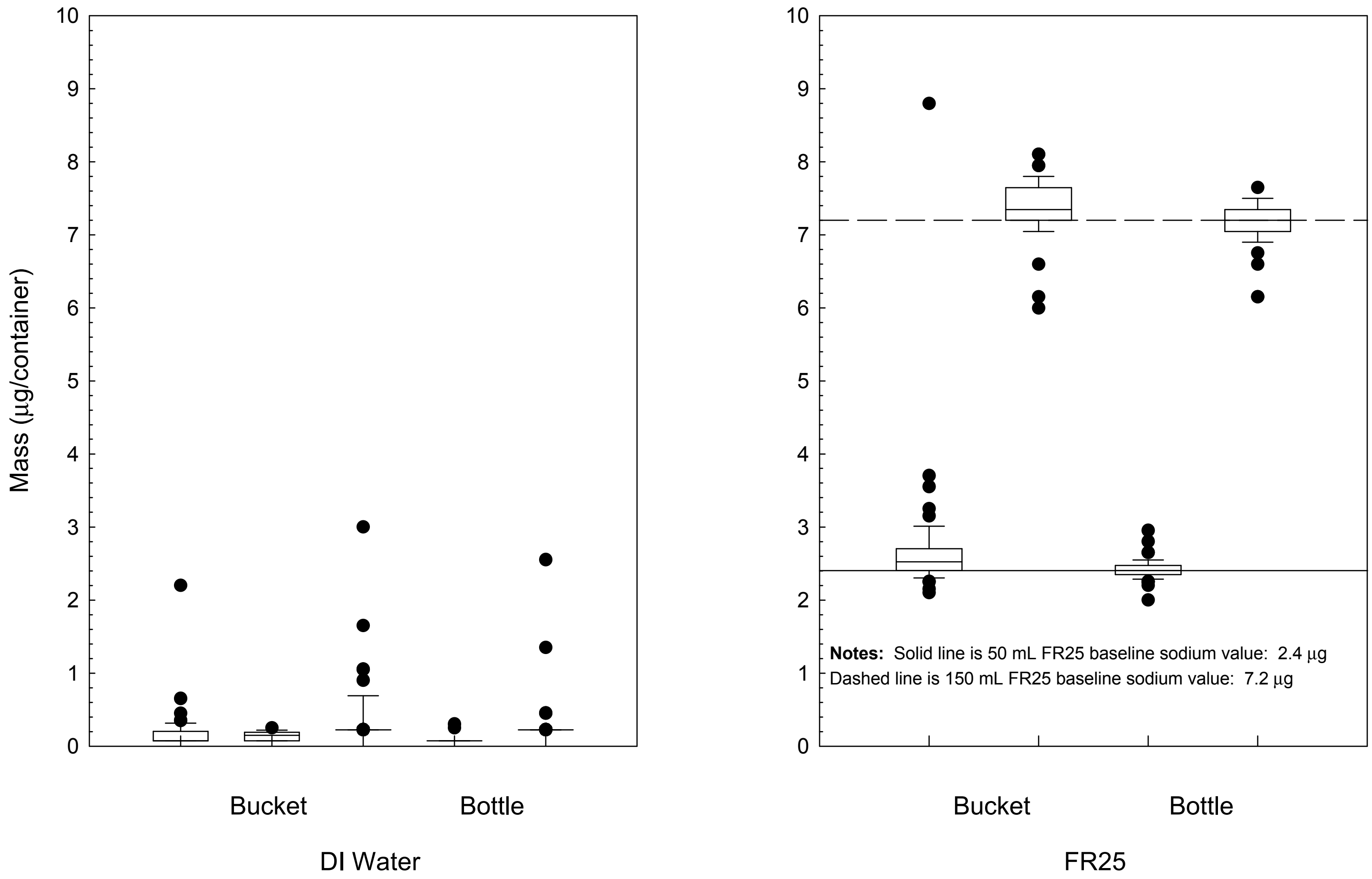


Figure B-33. Sodium found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 1999.

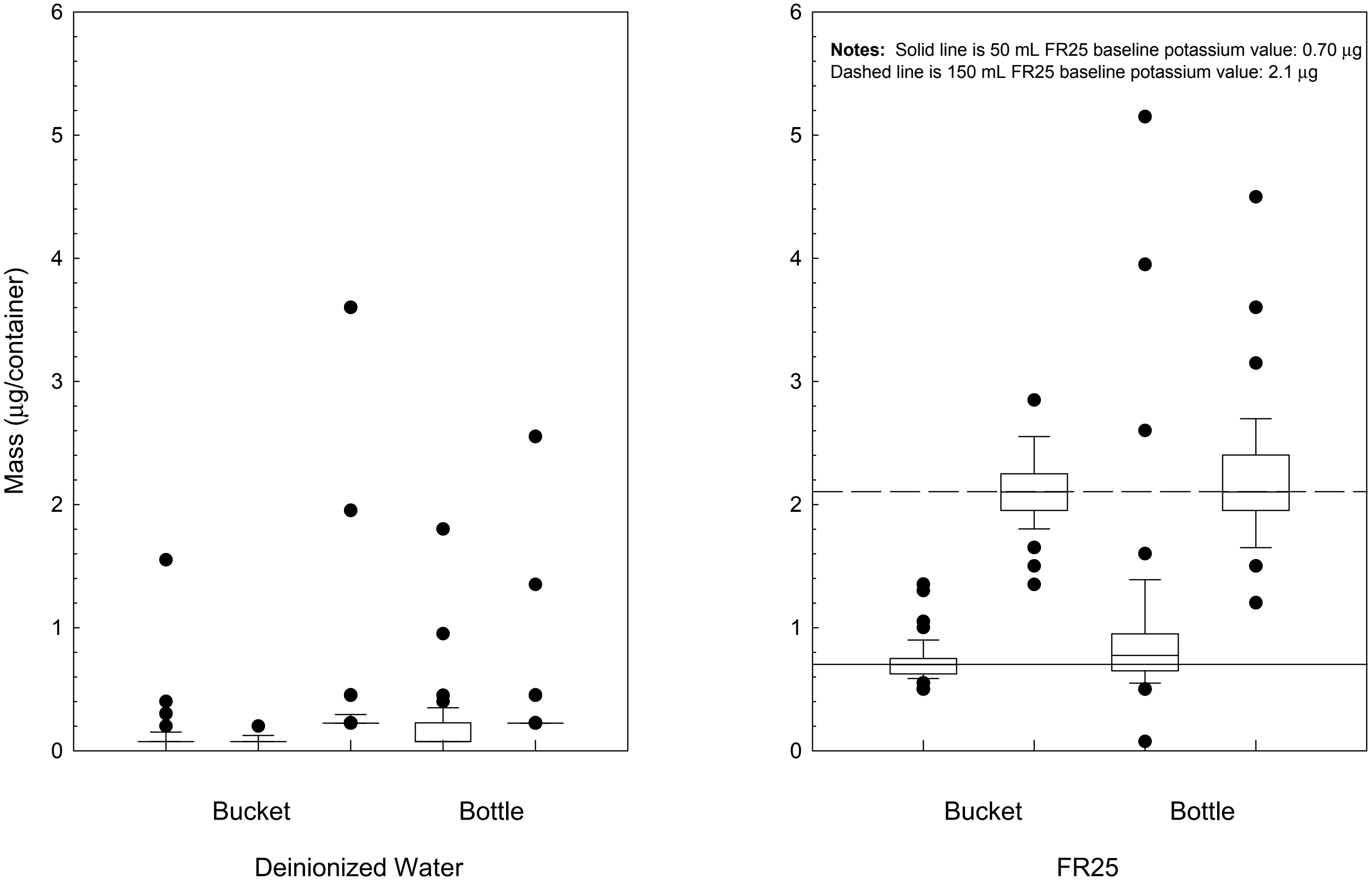


Figure B-34. Potassium found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 1999.

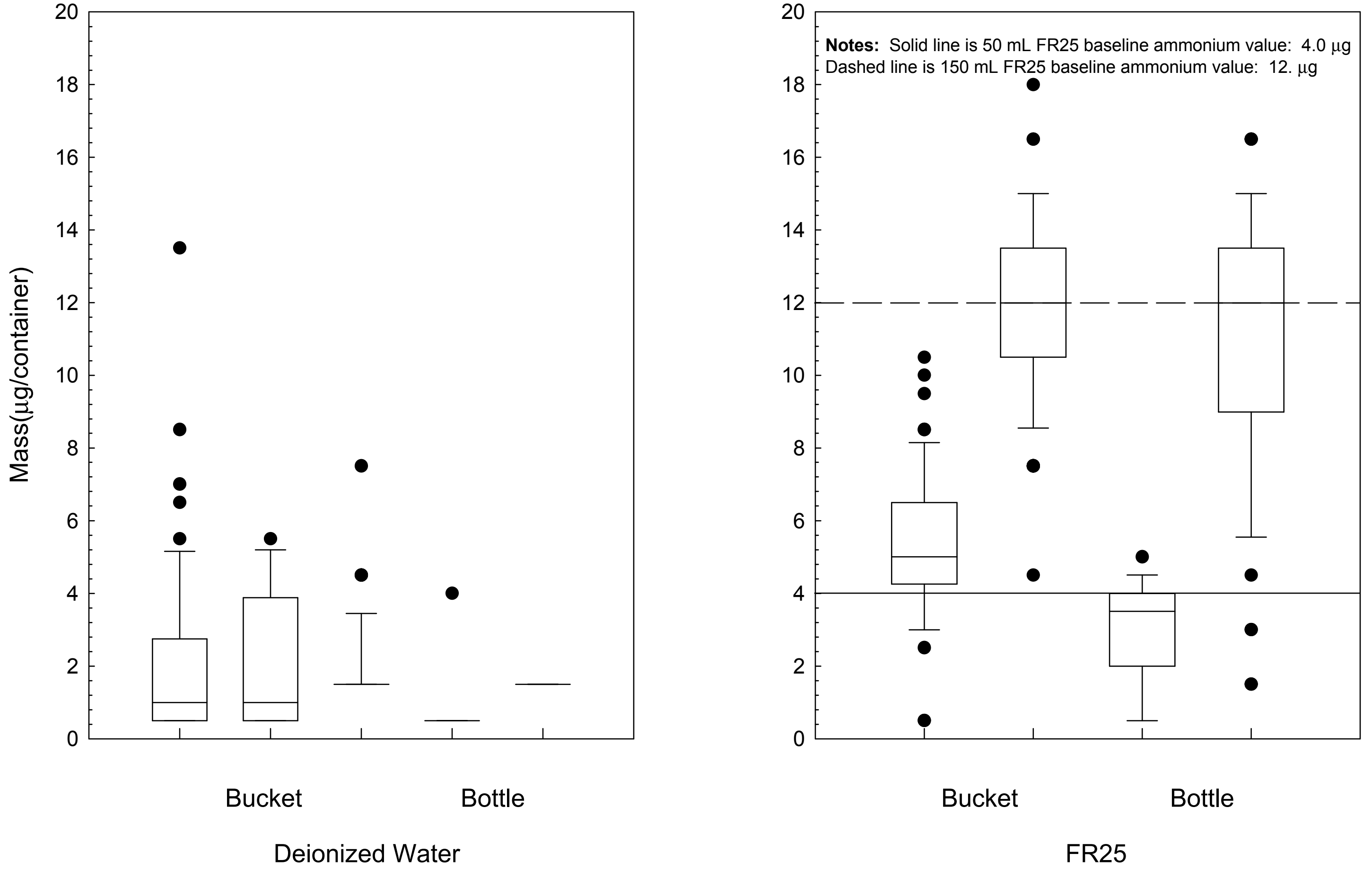
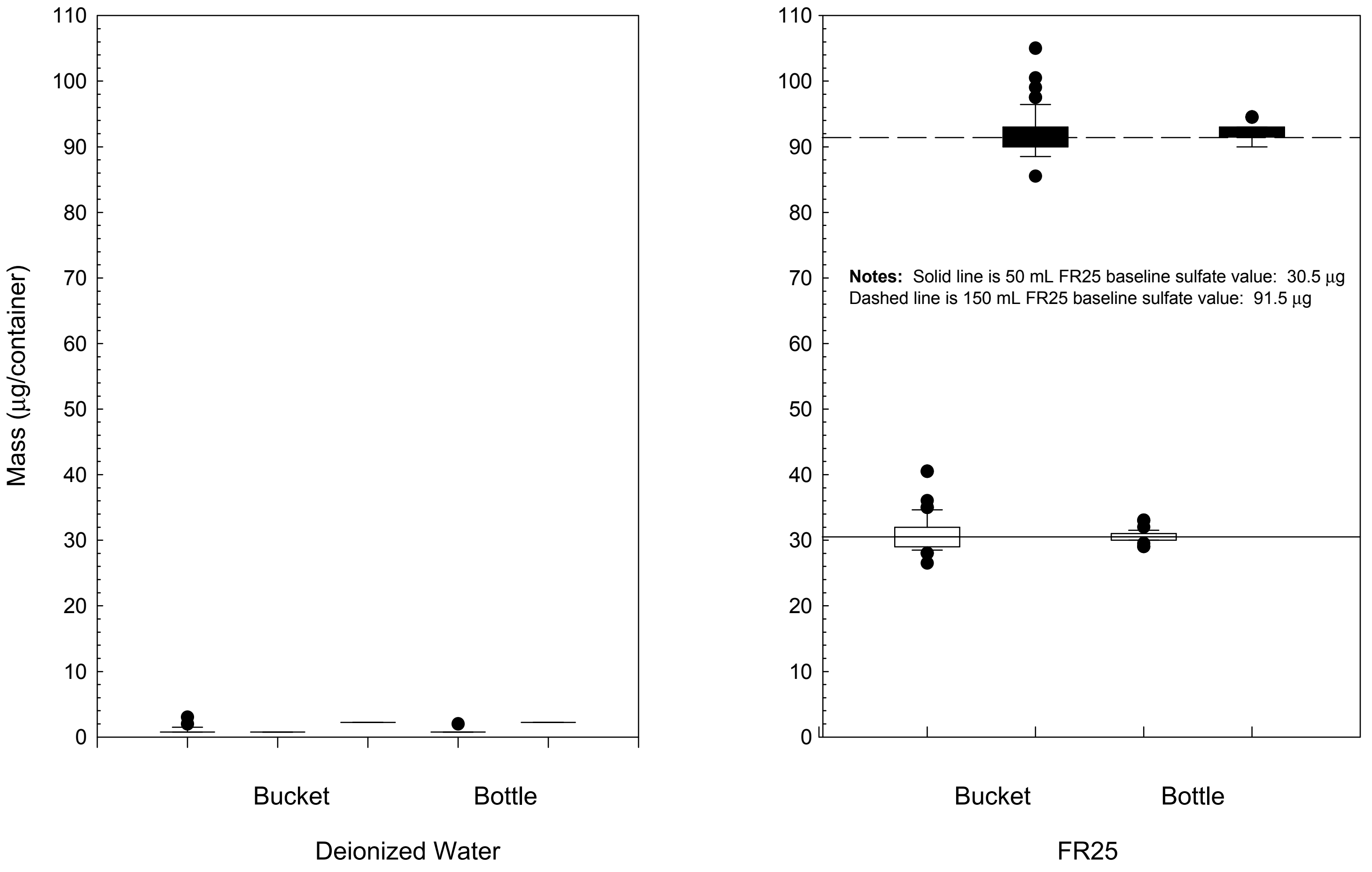


Figure B-35. Ammonium found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 1999.



Notes: Solid line is 50 mL FR25 baseline sulfate value: 30.5 µg
Dashed line is 150 mL FR25 baseline sulfate value: 91.5 µg

Figure B-36. Sulfate found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 1999.

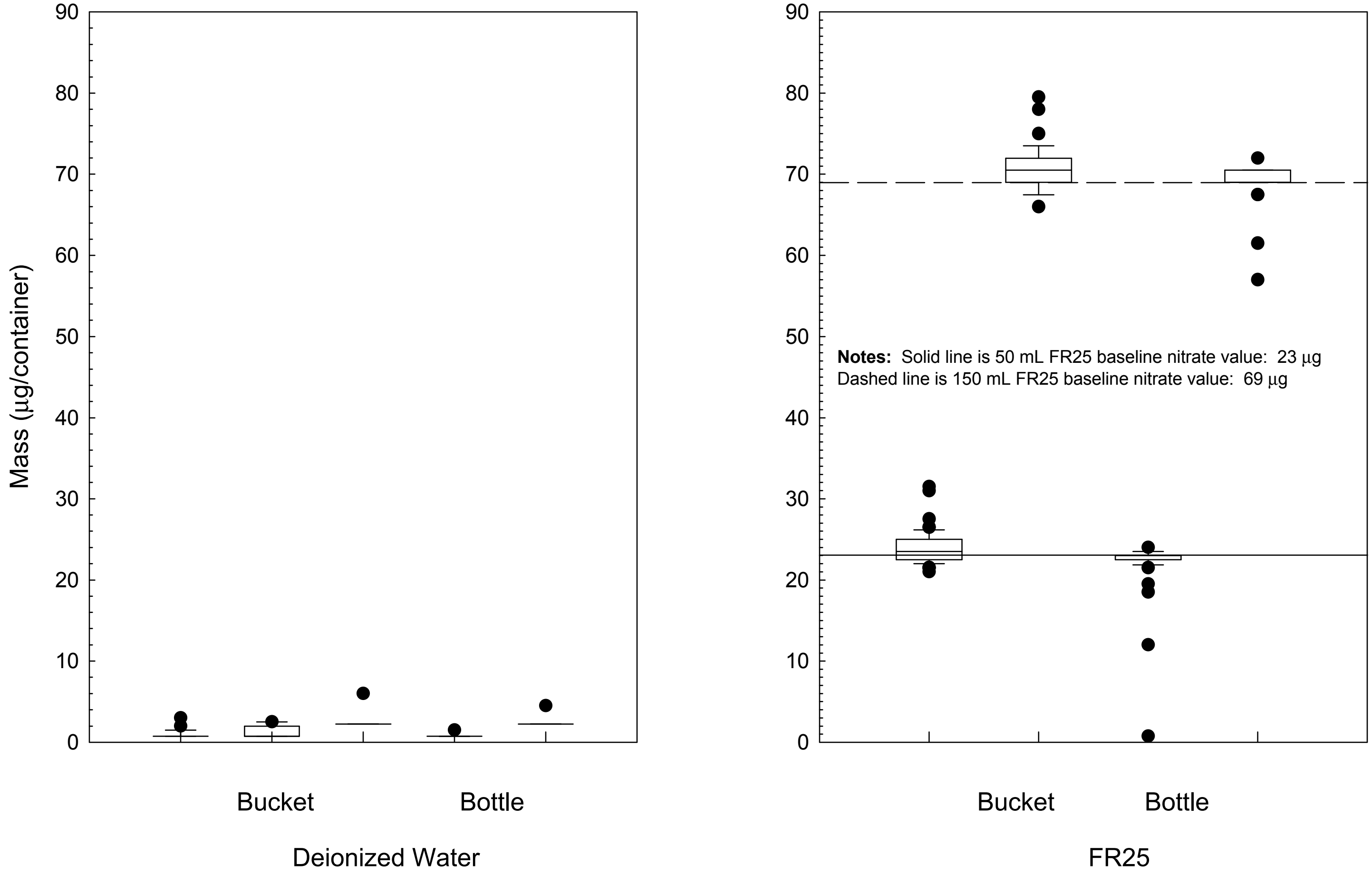


Figure B-37. Nitrate found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 1999.

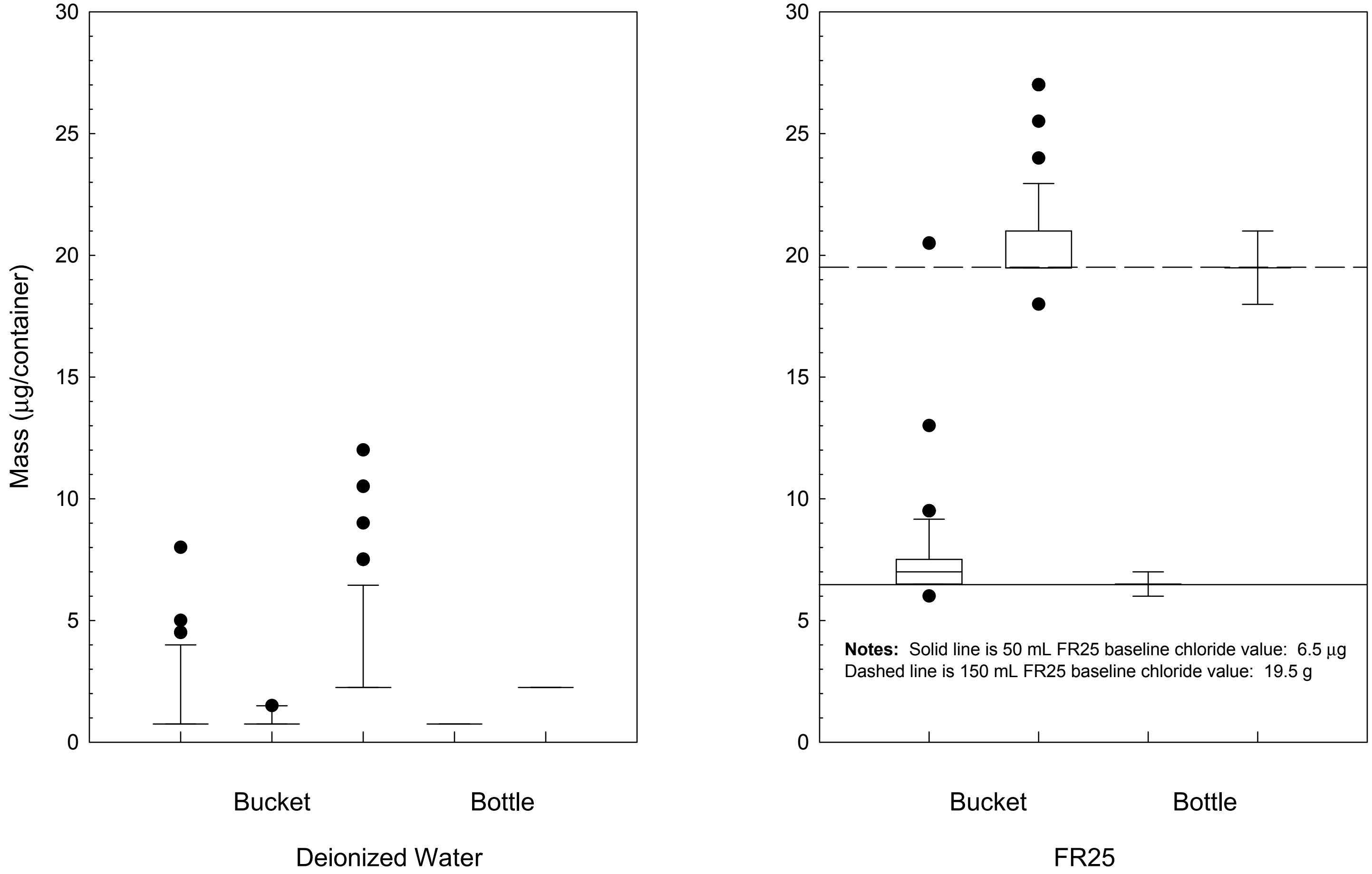
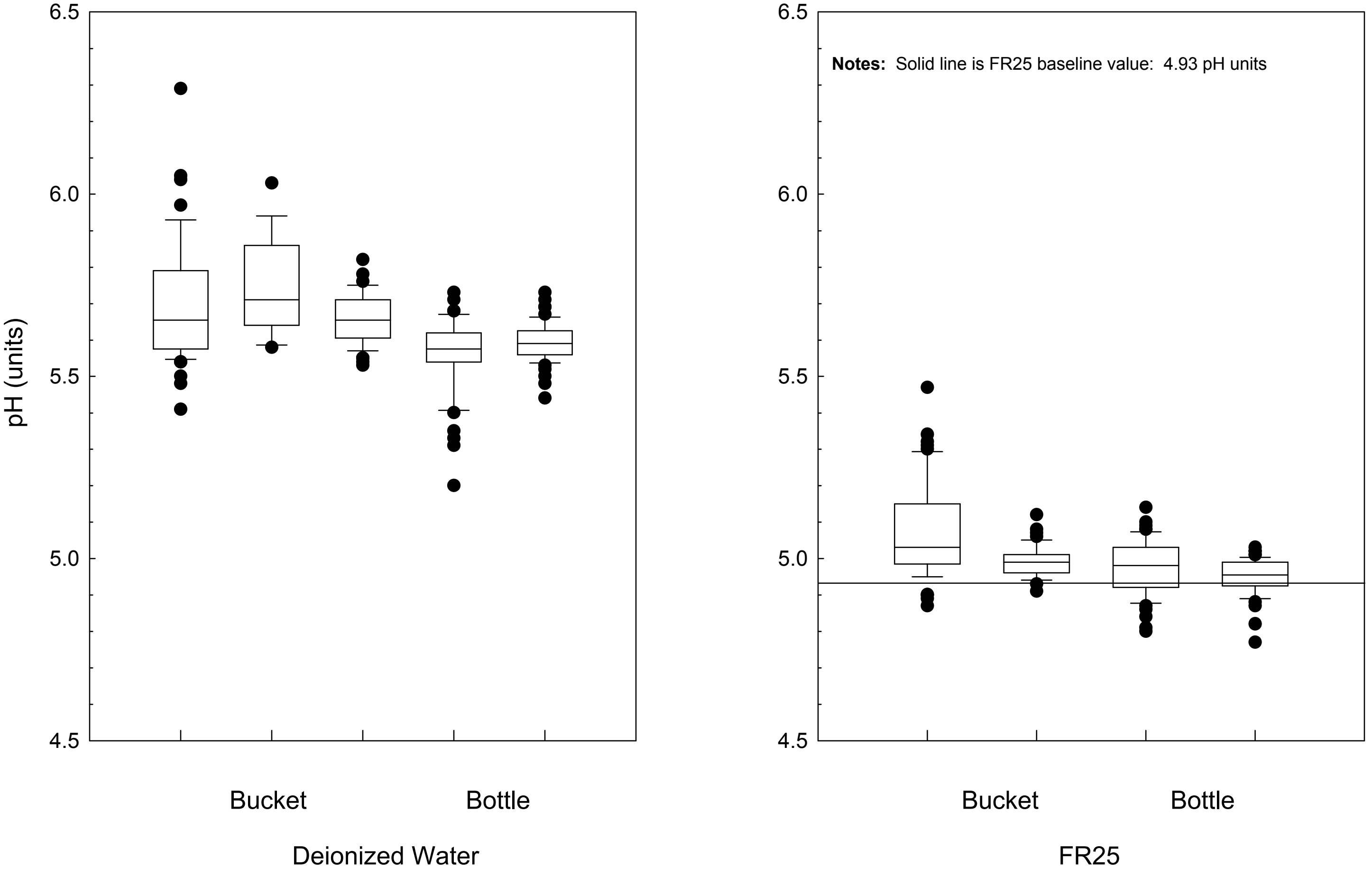
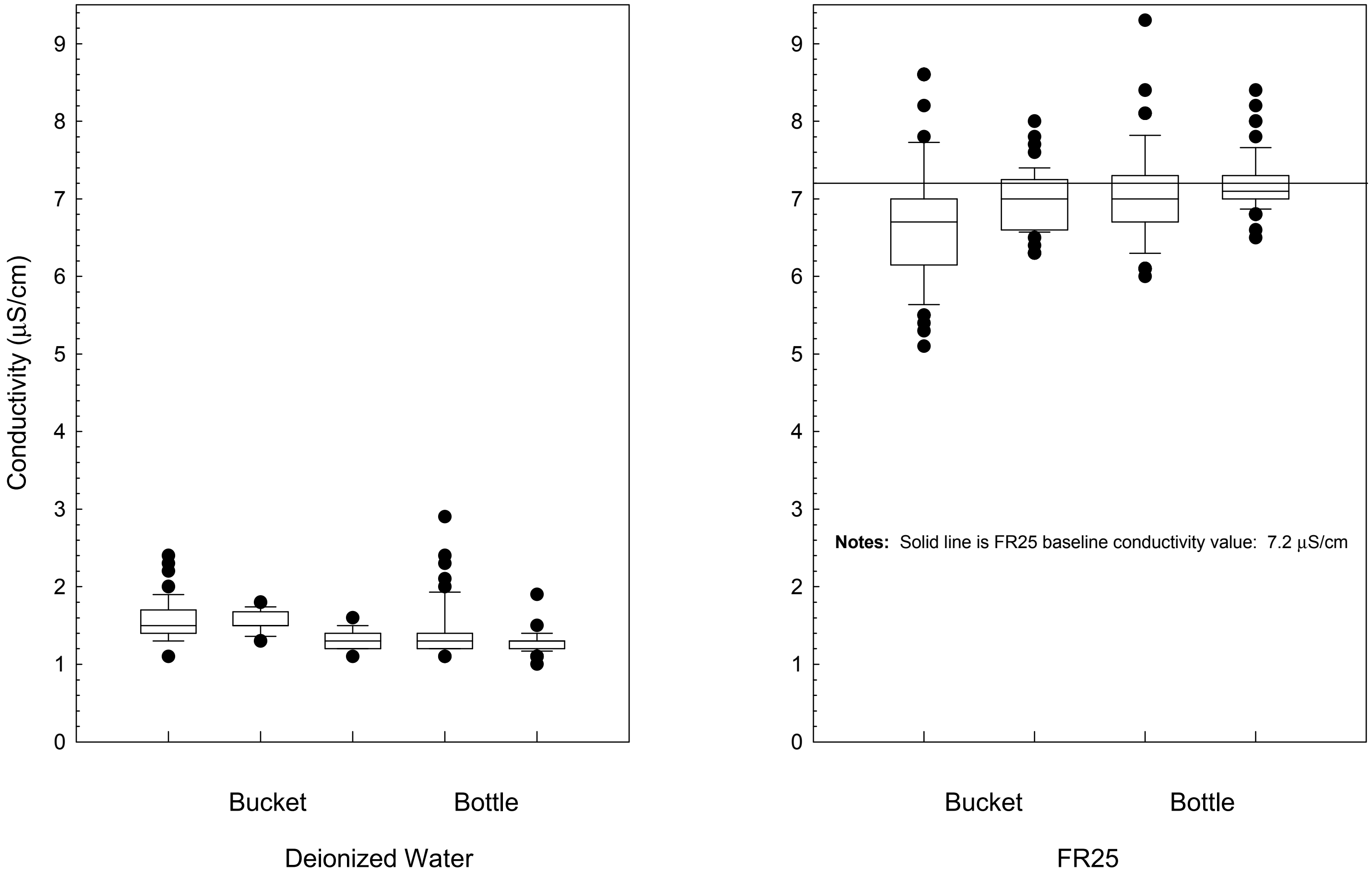


Figure B-38. Chloride found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 1999.



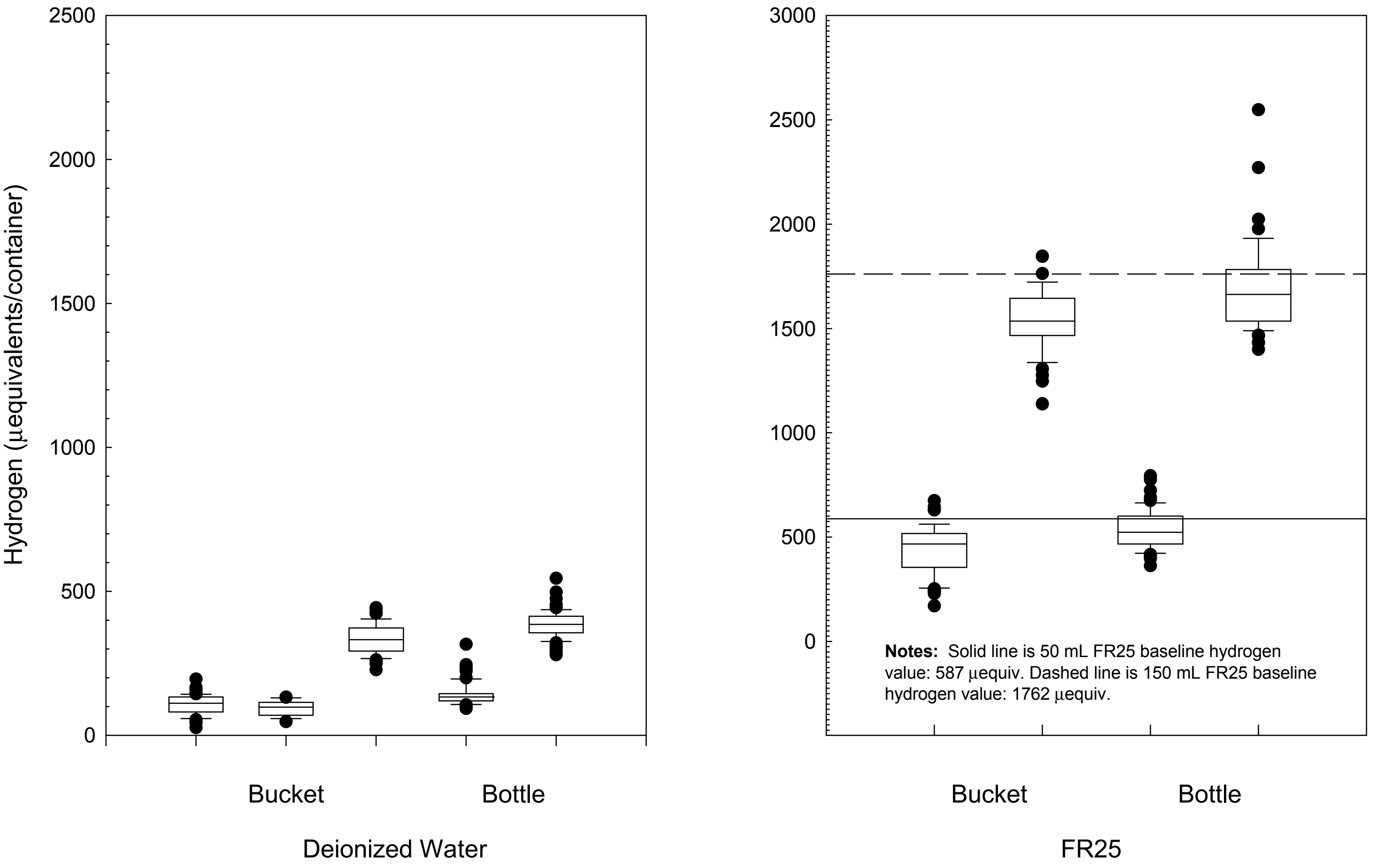
Notes: Solid line is FR25 baseline value: 4.93 pH units

Figure B-39. pH found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 1999.



Notes: Solid line is FR25 baseline conductivity value: 7.2 µS/cm

Figure B-40. Conductivity found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 1999.



Notes: Solid line is 50 mL FR25 baseline hydrogen value: 587 µequiv. Dashed line is 150 mL FR25 baseline hydrogen value: 1762 µequiv.

Figure B-41. Hydrogen ion found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 1999.