QUALITY ASSURANCE REPORT
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM, 2000

Laboratory Operations
Central Analytical Laboratory

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ABSTRACT

The National Atmospheric Deposition Program (NADP) has been in operation since 1978, and quality assurance always has been of paramount importance. The *Quality Assurance Report, National Atmospheric Deposition Program, 2000*, 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) to ensure that the data produced are of the highest possible caliber. Information about the quality of the data generated is presented in the form of tables, figures, graphs, and brief written explanations. The CAL was within the quality control objectives for the networks in 2000.

ACKNOWLEDGMENTS

The *Quality Assurance Report, National Atmospheric Deposition Program 2000, Laboratory Operations, Central Analytical Laboratory*, 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 Branch of Quality Systems coordinates the external interlaboratory comparison program. Karen Harlin and Van Bowersox, NADP Program Office, provide ongoing input and support throughout the year. Dedicated analytical staff analyze 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; without them this report could not be completed: Karen Harlin, NADP/CAL, Eva Kingston, Illinois State Water Survey (ISWS), Christopher Lehmann, NADP/Program Office, Mark Peden, ISWS, and John Sherwell, State of Maryland.

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EXECUTIVE SUMMARY

The Quality Assurance Plan NADP/NTN Deposition Monitoring (Simmons et al., 1990, revised 1993), defines the quality assurance (QA) goals of the National Atmospheric Deposition Program (NADP). 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 2000, the CAL was in compliance with the NADP QAP.

More samples were processed and analyzed in 2000 than in any other year in NADP history. Daily procedures include charting instrument standardization and maintenance, and ensuring that the instruments are in 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 2000.

Weekly QA procedures included ensuring that all materials coming into contact with precipitation samples did not contaminate the samples. Any problems were investigated and eliminated. All blank analyses, internal blind analyses for NTN and AIRMoN, and replicate analyses for 2000 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 CAL performance in relation to that of other laboratories doing similar work around the world. In 2000, the CAL participated in four different studies. The U.S. Geological Survey (USGS), external auditor for the NADP/NTN, conducted an intercomparison study with seven laboratories in 2000. The CAL was ranked first for sulfate and was tied for first for nitrate, chloride, and specific conductance. The CAL was ranked second for pH, was tied for second for calcium and ammonium, was tied for third for sodium and potassium, and was ranked fifth for magnesium. The CAL ranked second overall due in part to increased sample load and in part to aging equipment.

In 2000, the CAL was contracted to prepare the samples for the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) intercomparison study. Although the CAL also participated in the study, CAL results were not included in the final study rankings. However, when compared with results for other participating laboratories, CAL results were excellent. The National Water Research Institute (NWRI) of Canada conducted two intercomparison studies in 2000. The CAL ranked fourth or "good" out of the 38 participating laboratories in the first study and 13th or "satisfactory" out of 38 laboratories due to a low bias for both ammonium and magnesium in the second study. Over the past ten years of CAL participation in NWRI studies, the CAL has averaged a ranking of seventh out of 37 ranked laboratories with an overall ranking of "good".

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 2000. 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 2000, the CAL analyzed samples from more than 200 NADP/National Trends Network (NTN) sites that collect weekly precipitation samples throughout the United States and parts of Canada. Samples were collected in buckets using a specified sampler. Buckets are removed each Tuesday morning, and the samples are decanted into 1-liter, wide-mouthed, high-density polyethylene (HDPE) bottles and shipped with the sampling buckets 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 and analytical methodologies are different from those of NTN, but both maintain the same high quality control (QC) objectives.

Table I-1 lists staff responsibilities for samples from their arrival at the ISWS until analytical data are sent to the CAL data management group. Approximately half the staff have been employed at the ISWS and associated with the CAL for more than ten years. There were no analytical staff changes at the CAL in 2000.

Data management staff at the CAL (Table I-2) are responsible for screening and reviewing the analytical data after transmittal from the laboratory and before they are sent to the Program Office. Data management staff did not change in 2000.

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 2000. Detection limits for 2000 changed, reflecting the improved capabilities of the ion chromatograph. 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 course of the program and which samples these changes have affected. The MDLs are calculated annually or when there is a significant change in instrumentation or analyst using the method given in Appendix B. Laboratory MDLs then are maintained at or below the MDLs listed in the *NADP Quality Assurance Plan* (Simmons et al., 1990, revised 1993).

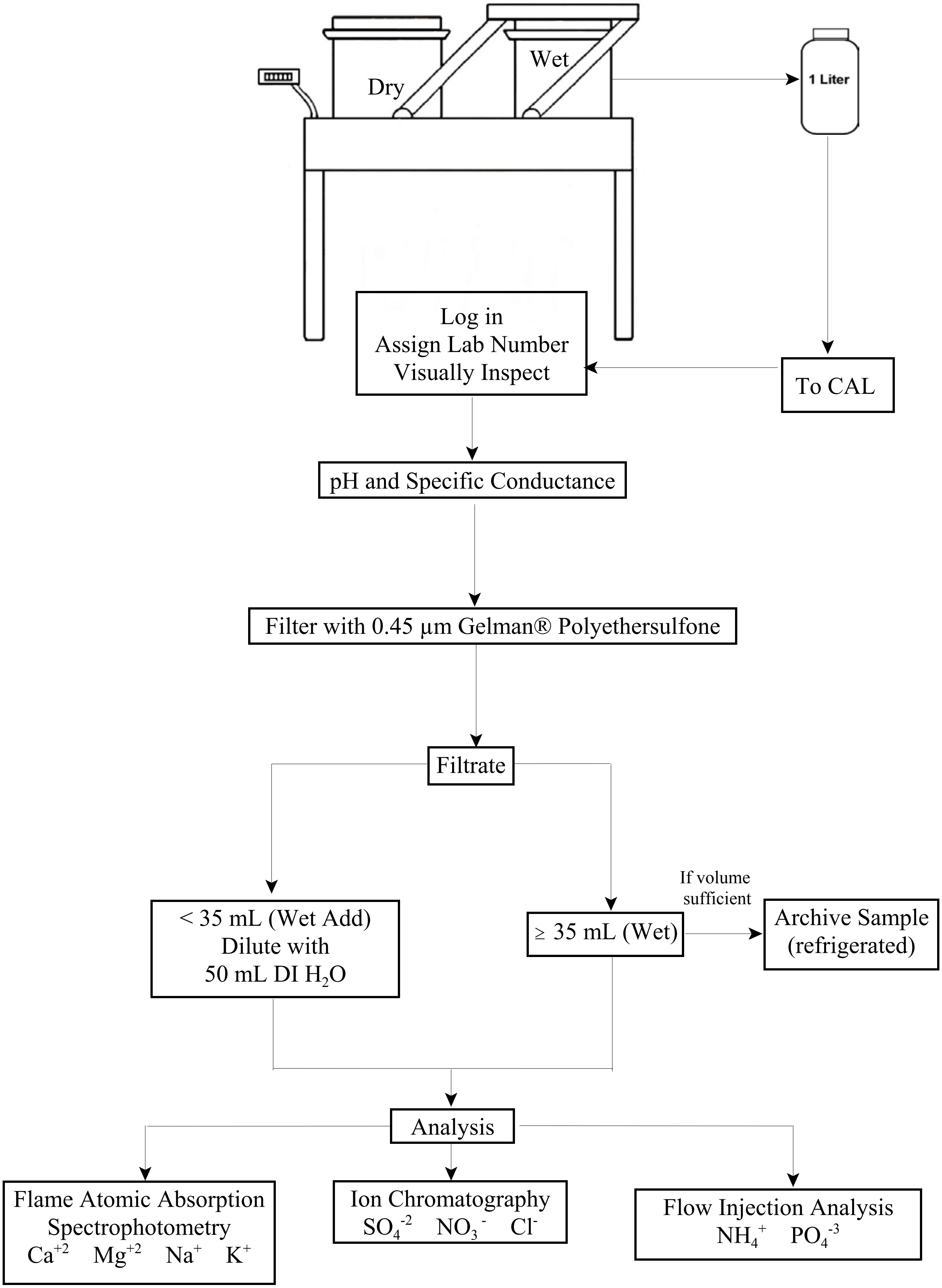

Figure I-1. Sample processing flow chart, January 2000 - December 2000.

Table I-1. Central Analytical Laboratory Analytical Staff, 2000

Staff member	*Job function*	*Period of employment*[*]
Sue Bachman	Analysis of ammonium	08/80 - 12/00
	Analysis of calcium, sodium, magnesium, and potassium	11/88 - 12/00
	Analysis of orthophosphate	01/94 - 12/00
	Sample processing coordinator	09/98 - 12/00
Phyllis Ballard	Bucket and bottle cleaning	09/97 - 04/00
	Sample receipt and processing	04/98 - 12/00
	AIRMoN sample receipt	06/99 - 12/00
Brigita Demir	Analysis of chloride, sulfate, and nitrate	09/81 - 12/00
Karen Harlin	Office of Atmospheric Chemistry Laboratory Supervisor	06/97 - 12/00
	NADP Central Analytical Laboratory Manager and NADP Assistant Coordinator	09/98 - 8/00
	NADP Assistant Coordinator and CAL Director	09/00 - 12/00
Theresa Ingersoll	Sample receipt and processing	03/85 - 12/00
Tracie Patten	Analysis of pH and conductivity, and sample processing	09/98 - 12/00
Jeffrey Pribble	Sample receipt	07/87 - 12/00
	Supply procurement	07/87 - 12/00
	Backup site liaison	07/87 - 12/00
Jane Rothert	AIRMoN Coordinator	05/92 - 12/00
	CAL Quality Assurance Specialist	07/97 - 12/00
Kaye Surratt	Sample processing	08/96 - 04/97
	AIRMoN sample processing	11/98 - 06/99
	AIRMoN analysis of ammonium, orthophosphate, calcium, magnesium, sodium, and potassium	11/98 - 12/00
	AIRMoN analysis of chloride, nitrate, and sulfate	06/99 - 12/00
Angela Weddle	Sample processing	06/95 - 12/97
	Analysis of pH and conductivity	10/89 - 12/00

Note:
[*] The reporting period ended in December 2000. 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, 2000

Staff member	*Job function*	*Period of employment**
Tom Bergerhouse	Computer systems support	07/98 - 12/00
Scotty Dossett	NTN site liaison	09/81 - 12/00
Kathy Douglas	Database manager	04/80 - 12/00
Greg Dzurisin	Computer programer	09/83 - 12/00
Karen Harlin	Final data review	07/97 - 12/00
Sarah Milton	Data screening	01/98 - 12/00
Angela Kwon Rakow	Data review	11/99 - 12/00
Jane Rothert	Data quality assurance	07/97 - 12/00

Note:
*The reporting period ended in December 2000.

Table I-3. Method Detection Limits (MDLs) for Precipitation Analysis, 2000

Analyte	*Field sampling dates*	*Lab ID sequence (LABNO)*	*Method Detection Limit (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 00	NA6544 - NU7202	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 00	NA7300 - NU7202	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 00	NA7742 - NU7202	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 00	NA6001 - NU7202	0.003	Flame Atomic Absorption Spectrometry
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 00	NH6701 - NU7202	0.02	Phenate (Flow Injection Colorimetry)

Table I-3 (concluded)

Analyte	*Field sampling dates*	*Lab ID sequence (LABNO)*	*Method Detection Limit (mg/L)*	*Analytical methodology*
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
	Jan 00 - Dec 00	NS3701 - NU7202	0.005	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
	Jan 00 - Dec 00	NS3701 - NU7202	0.010	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
	Jan 00 - Dec 00	NS3701 - NU7202	0.010	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)
	Jan 00 - Dec 00	NS3700 - NU7202	0.004	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.

From the beginning of the network in 1978, analytical data have been entered into a large central database. Initially data were hand-entered using a double-entry system as a means of verification. Data from the atomic absorption spectrophotometer, the ion chromatograph, and the flow injection analyzer were electronically transferred to the database in 2000. The pH and conductivity measurements were double-entered manually. Once data have been 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 120 days for NTN and about 90 days for AIRMoN. Table I-4 lists the percentile concentration values for all NADP/NTN samples of volume greater than 35 milliliters (mL) and with minimal contamination that were analyzed by the CAL in 2000. A sample is considered "contaminated" if it contains observable extraneous contamination that exhibits anomalous chemistry based on that particular site's chemical history or if there are serious field or laboratory handling violations of that sample. There were 7442 "wet" (W) samples in 2000 with a mean precipitation volume of 1421.8 mL and a median precipitation volume of 915.1 mL. Table I-5 lists the percentile concentration values for AIRMoN samples having a sample volume large enough for a complete chemical analysis in 2000. There were 914 samples with a mean volume of 660.0 mL and a median volume of 385.4 mL. Table I-6 (NTN) and Table I-7 (AIRMoN) show the sample percentile concentration values from 1995 until the end of 2000. For NTN, 42,240 wet-only samples had no severe contamination, a mean sample volume of 1527.57 mL, and a median sample volume of 959.8 mL. For AIRMoN, 5113 samples had no severe contamination, a mean sample volume of 705 mL, and a median sample volume of 390.6 mL. Compared to the long-term averages in Table I-6, median NADP cation concentrations were generally higher in 2000, and anion concentrations were 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 for these low ionic strength samples. The *NADP Quality Assurance Plan* (Simmons et al., 1990, revised 1993) 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 and external laboratory intercomparison studies.

The CAL developed intralaboratory QA procedures to address the difficulties related to analyzing low ionic strength solutions. 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.

Table I-4. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/NTN Precipitation, 2000

					Percentile concentration values (mg/L)					
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*99th*	*Maximum*
Calcium	-0.009	0.019	0.028	0.054	0.117	0.261	0.529	0.812	1.763	61.680
Magnesium	-0.003	0.003	0.005	0.009	0.020	0.043	0.079	0.125	0.292	3.880
Sodium	-0.003	0.006	0.009	0.020	0.047	0.129	0.339	0.643	2.396	15.640
Potassium	-0.003	-0.003	0.004	0.009	0.019	0.037	0.070	0.108	0.282	2.830
Ammonium	-0.02	-0.02	0.03	0.09	0.23	0.45	0.74	1.015	1.68	6.24
Sulfate	-0.010	0.148	0.237	0.523	1.063	1.875	2.941	3.807	6.184	125.480
Nitrate	-0.010	0.219	0.331	0.638	1.174	1.964	3.032	3.953	6.430	20.056
Chloride	-0.005	0.022	0.030	0.052	0.102	0.228	0.563	1.078	3.797	25.260
Orthophosphate	-0.009	-0.009	-0.009	-0.009	-0.009	-0.009	-0.009	-0.009	0.018	0.621
Lab pH(units)	3.41	4.13	4.26	4.49	4.84	5.29	5.98	6.34	6.77	7.95
Lab specific conductance (µS/cm)	1.6	3.6	4.6	7.6	13.0	21.8	33.5	43.2	69.1	464.0

Notes:
Only wet-only samples were used. Samples with severe contamination were not used to tabulate any of the values. All QC samples were removed. Total number of samples = 7442; mean sample volume = 1421.8 mL; and median sample volume = 915.1 mL. Negative numbers in this table represent the method detection limits (MDLs) for each parameter.

Table I-5. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/AIRMoN Precipitation Wet-only Samples, 2000

	Percentile concentration values (mg/L)								
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*Maximum*
Calcium	-0.005	0.010	0.017	0.036	0.089	0.193	0.375	0.580	3.320
Magnesium	0.000	0.002	0.004	0.007	0.019	0.051	0.120	0.180	3.298
Sodium	-0.001	0.003	0.006	0.015	0.050	0.262	0.814	1.288	30.150
Potassium	-0.002	0.003	0.004	0.009	0.020	0.040	0.075	0.107	1.170
Ammonium	-0.02	0.03	0.05	0.13	0.26	0.47	0.87	1.12	4.108
Sulfate	0.100	0.303	0.474	0.939	1.688	2.904	4.691	5.742	19.420
Nitrate	0.087	0.293	0.456	0.817	1.435	2.523	4.278	5.783	17.680
Chloride	0.000	0.024	0.033	0.066	0.156	0.524	1.477	2.319	62.800
Orthophosphate	0.000	0.000	0.000	0.000	0.005	0.014	0.027	0.046	0.208
Lab pH (units)	3.44	3.88	3.97	4.20	4.42	4.63	4.88	5.06	6.38
Lab specific conductance (µS/cm)	2.9	7.3	9.9	15.5	24.2	37.8	58.5	71.4	237.4

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 = 914; mean sample volume = 660.0 mL; and median sample volume = 385.0 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/NTN Precipitation Wet-only Samples, 1995 - 2000

	Percentile concentration values (mg/L)								
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*Maximum*
Calcium	MDL	0.016	0.024	0.049	0.111	0.249	0.512	0.779	61.680
Magnesium	MDL	0.003	0.005	0.010	0.021	0.043	0.081	0.123	3.880
Sodium	MDL	0.009	0.014	0.029	0.060	0.140	0.338	0.613	16.850
Potassium	MDL	MDL	0.004	0.009	0.018	0.036	0.069	0.105	5.870
Ammonium	MDL	MDL	0.03	0.08	0.21	0.43	0.73	0.99	6.93
Sulfate	MDL	0.134	0.227	0.510	1.050	1.890	3.010	3.900	125.480
Nitrate	MDL	0.180	0.290	0.590	1.100	1.870	2.909	3.790	22.400
Chloride	MDL	0.030	0.040	0.112	0.240	0.570	1.050	3.329	25.430
Orthophosphate	MDL	MDL	MDL	MDL	MDL	MDL	MDL	MDL	1.580
Lab pH (units)	3.41	4.13	4.25	4.48	4.82	5.27	5.85	6.24	8.00
Lab specific conductance (µS/cm)	1.3	3.3	4.4	7.4	12.6	21.5	33.6	43.3	464.0

Notes:
Only wet-only samples were used. Samples with severe contamination were not used to tabulate any of the values. All QC samples were removed. Total number of samples = 42240; mean sample volume = 1527.57 mL; and median sample volume = 959.8 mL. The Method Detection Limit (MDL) changed during this six-year period. See Table I-2 for the appropriate MDLs.

Table I-7. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/AIRMoN Precipitation Wet-only Samples, 1995 - 2000

	Percentile concentration values (mg/L)								
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*Maximum*
Calcium	-0.006	0.011	0.019	0.043	0.097	0.216	0.440	0.716	3.990
Magnesium	-0.001	0.002	0.003	0.008	0.021	0.056	0.132	0.201	3.298
Sodium	-0.002	0.005	0.008	0.017	0.048	0.233	0.812	1.399	30.150
Potassium	-0.004	0.003	0.005	0.010	0.020	0.040	0.075	0.106	1.170
Ammonium	-0.02	0.03	0.06	0.13	0.27	0.52	0.87	1.15	4.48
Sulfate	0.030	0.340	0.550	1.040	1.820	3.158	4.962	6.200	19.420
Nitrate	0.020	0.296	0.430	0.830	1.539	2.752	4.443	5.874	21.880
Chloride	0.000	0.030	0.040	0.080	0.170	0.510	1.560	2.697	62.800
Orthophosphate	-0.006	0.000	0.000	0.000	0.003	0.010	0.021	0.035	1.516
Lab pH (units)	3.36	3.85	3.96	4.15	4.37	4.61	4.90	5.13	6.85
Lab specific conductance (µS/cm)	1.6	7.3	10.2	16.4	25.8	40.8	61.4	79.1	237.4

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 = 5113; mean sample volume = 705.0 mL; and median sample volume = 390.6 mL. Negative numbers represent actual values measured, not Method Detection Limits, for each parameter.

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 that of 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, 2000, 2001). This report presents and discusses summaries of the results of QA programs in place in 2000.

II. LABORATORY QUALITY ASSURANCE - A GENERAL DESCRIPTION

This report summarizes the results of the quality assurance (QA) programs in effect at the CAL for 2000. 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 following field protocols soon after sample collection and prior to shipping. Site operators use quality control standard (QCS) solutions as weekly check samples. These solutions are formulated and prepared at the CAL and then shipped to the sites. For NTN and AIRMoN, the QCS solution used in 2000 to calibrate the conductivity cell and to correct the conductivity readings to ambient temperatures was a potassium chloride (KCl) solution with a specific conductance of 75 microsiemens per centimeter (µS/cm). A dilute nitric acid/sodium chloride (HNO_3/NaCl) solution with a pH of 4.9 and a specific conductance of 14 µS/cm (NTN) or a dilute nitric acid (HNO_3) solution with a pH of 4.3 and a specific conductance of 21.8 µS/cm (AIRMoN) was used as the QCS for the pH and conductivity measurements. Because calibration buffer solutions are of high ionic strength, the QCS 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 transported to sample processing, assigned a sequential number, and 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 about 4°C 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, revised 1993) 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/NTN and NADP/AIRMoN Laboratory QA/QC Program Summary, 2000

- 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.
  - C. Inspect control charts generated from QCS measurements.

- 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.
      - d. Storage and shipping bags.
  - 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 a simulated rainwater sample representing approximately the 10th percentile of the NTN samples (FR10), unfiltered.
    - 3. SWS3: Use all four of the above solutions in rotation, filtered.
  - C. Split 2 percent of NTN samples for replicate analysis.
  - D. Split 2 percent of AIRMoN samples for replicate 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. Evaluate internal blind audit and replicate data from printouts.
  - C. Select samples for reanalysis by computer-based ion percent and conductivity percent differences.
    - 1. Evaluate reanalysis data.
    - 2. Edit data record as needed.
  - D. Measure USGS interlaboratory comparison samples every two weeks and send to the USGS, Water Research Division, Branch of Quality Systems in Denver every three months.
  - E. Validate QCS for field chemistry 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 analytical laboratory for analysis of the major ions. The AIRMoN samples are stored on trays in a walk-in cooler (approximately 4°C) 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 volume for complete analysis; therefore, highest priority measurements are made first.

The NTN protocol specifies weekly collection; therefore, 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 than 35 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 consecutive 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 standardization range 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 plotted on 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.

Solutions collected from multiple sources are submitted to the CAL each week 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 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 replicate samples. Two percent of the total NTN sample load are split and processed so that the originals and replicates are separated for analysis. Replicates are submitted with new sample identification numbers, unknown to the analysts, and are analyzed in numerical order, approximately 100 sample numbers away from the original sample number. The replicates, therefore, are analyzed at a different time than the original samples, usually on a separate day, with new calibration standards and check samples. The AIRMoN split sample protocol is similar to that for the NTN replicate program. The AIRMoN also has an internal blind program in which a sample of known concentration is submitted by the IL11 site operator as a real precipitation sample four times a month (48 samples per year). 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, which results in reanalysis of one percent of the NTN samples and 2.5 percent of the AIRMoN samples. This same program also calculates the ion percent and conductance percent difference for each wet ("W") sample. Samples with either difference greater than allowed by the NADP QAP (see Chapter V of this report) are tabulated. Reanalysis lists are generated by the QA Specialist based on the computer-generated lists and distributed to 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 four 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. Those 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 SOP and are followed by the measurement of the QCS to confirm the validity of the calibration curve. Both FR25 and FR75 solutions are used to verify the standard curves at the two concentration levels. Each QCS is measured throughout the sample run, and the values are recorded and graphed on a daily control chart located near the instrument. These 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 known to the analysts, rather than precipitation or blind samples. The QCS are stable solutions, whereas the actual precipitation samples are susceptible to chemical change. The QCS 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 2000, they were comparable with previous years' data and fall within the QA specifications of the NADP QAP (Simmons et al., 1990, revised 1993). 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, revised 1993) for more information.

Table III-1. Analytical Bias and Precision Determined from Analysis of Simulated Rainwater QCS, 2000

Parameter	*Target concentrations (mg/L)*	*Measured mean concentrations (mg/L)*	*Number of analyses*	*Bias (mg/L)*	*Bias (%)*	*Standard deviation (mg/L)*	*RSD (%)*	*Critical concentration (mg/L)*	*Statistically significant bias?*
Ca	0.074[a]	0.075	1557	0.001	1.4	0.002	2.7	0.001	no
	0.300[b]	0.298	498	-0.002	-0.7	0.006	2.0	0.004	no
Mg	0.017	0.017	1606	0.000	0.0	0.0006	3.5	0.0004	no
	0.066	0.066	524	0.000	0.0	0.002	3.0	0.001	no
Na	0.049	0.049	1708	0.000	0.0	0.001	2.0	0.0007	no
	0.192	0.192	309	0.000	0.0	0.002	1.0	0.001	no
K	0.014	0.014	1676	0.000	0.0	0.001	7.1	0.0007	no
	0.056	0.055	526	-0.001	-1.8	0.002	3.6	0.001	no
NH_4	0.09	0.08	1135	-0.01	-11.1	0.01	12.5	0.003	yes
	0.36	0.34	637	-0.02	-5.6	0.01	2.9	0.007	yes
Cl	0.127	0.129	1335	0.002	1.6	0.002	1.6	0.001	yes
	0.525	0.527	1287	0.002	0.4	0.005	0.9	0.003	no
NO_3	0.469	0.467	1317	-0.002	-0.4	0.005	1.1	0.003	no
	1.903	1.884	1163	-0.019	-1.0	0.012	0.6	0.006	yes
SO_4	0.617	0.617	1331	0.000	0.0	0.006	1.0	0.003	no
	2.489	2.483	1280	-0.006	-0.2	0.014	0.6	0.007	no
PO_4	0.035	0.032	2413	-0.003	-8.6	0.003	9.4	0.008	no
	0.089	0.084	1057	-0.005	-5.6	0.006	7.1	0.0011	no
pH	4.96 (11.0)[c]	4.95 (11.2)	1310	-0.01 (0.2)	-0.2 (1.8)	0.02 (0.41)	0.4 (3.7)	0.01 (0.3)	no (no)
units (µeq/L)	4.40 (39.8)	4.38 (41.9)	818	-0.02 (2.1)	-0.5 (5.3)	0.01 (1.0)	0.2 (2.4)	0.01 (0.7)	yes (yes)
Specific conductance (µS/cm)	7.16	7.18	1009	0.02	0.3	0.15	2.1	0.09	no
	27.0	27.0	878	0.0	0.0	0.2	0.7	0.13	no

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: 1) three solutions were submitted as internal blind samples for which only the QA Specialist knew the concentrations; 2) two percent of the network samples were split and analyzed in replicate; and 3) 20 blanks and container leachates were prepared and analyzed. The AIRMoN internal blinds also were submitted weekly, 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 completed Field Observer Report Forms (FORFs) 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 are unfiltered to monitor for possible filter contamination. These samples are identified as SWS1, SWS2, and SWS3. In 2000, 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 a synthetic rain sample made in house that approximated the 10th percentile of the NTN samples (FR10) and also alternated weekly. The SWS1 and SWS2 samples were not filtered. The filtered SWS3 samples were H-PS SR1, H-PS SR2, DI water, and FR10 submitted in rotation.

Tables IV-1 – IV- 4 summarize the 2000 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.) The filtered internally formulated synthetic precipitation samples (FR10) and the filtered DI water also show less bias than the filtered High-Purity Standards samples,

For the SWS1 samples (Table IV-1), certified solutions of two different concentrations from High-Purity Standards were used in 2000. These samples, H-PS SR1 (lot #934925), and H-PS SR2 (lot #935013), were of similar concentrations to those used in previous years and slightly higher than the internal QCS made at the CAL. The H-PS SR1 sample is more similar in concentration to the higher concentration FR75 QCS for all but calcium, magnesium, chloride, and sulfate. The H-PS SR2 samples have still higher concentrations for all but calcium and magnesium. The percent bias was higher for the High-Purity Standards samples than for the

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[1] HIGH-PURITY STANDARDS, P.O. Box 41727, Charleston, SC 29423, catalog numbers 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 SR-1) and II (H-PS SR-2), Unfiltered, 2000

Parameter	*Target concentration [a] (mg/L)*	*Measured concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard deviation (mg/L)*	*RSD (%)*
Calcium	0.014 [b]	0.011	-0.003	-21.4	0.005	45.5
	0.055 [c]	0.053	-0.002	-3.6	0.004	7.5
Magnesium	0.019	0.019	0.000	0.0	0.0008	4.2
	0.051	0.049	-0.002	-3.9	0.002	4.1
Sodium	0.20	0.206	0.006	3.0	0.005	2.4
	0.400	0.407	0.007	1.8	0.008	2.0
Potassium	0.051	0.049	-0.002	-3.9	0.002	4.1
	0.095	0.100	0.005	5.3	0.002	2.0
Ammonium [d]	0.100	0.08	-0.02	-20.0	0.02	25.0
	1.00	0.92	-0.08	-8.0	0.04	4.3
Sulfate	2.5	2.523	0.023	0.9	0.016	0.6
	10.1	10.059	-0.041	- 0.4	0.069	0.7
Nitrate	0.50	0.504	0.004	0.8	0.006	1.2
	7.0	7.071	0.071	1.0	0.050	0.7
Chloride	0.25	0.216	-0.034	-13.6	0.003	1.4
	0.98	0.993	0.013	1.3	0.010	1.0
pH	4.29	4.33	0.04	0.9	0.02	0.5
(units)	3.58	3.62	0.04	1.1	0.03	0.8
H	51.3	47.0	-4.3	-8.4	1.7	3.6
(µeq/L)	263.0	240.8	-22.2	-8.4	13.6	5.6
Specific conductance	24	24.6	0.6	2.5	0.9	3.7
(µS/cm)	122	125.2	3.2	2.6	2.0	1.6

Notes:

There were 26 samples in each set.

[a] Target concentrations are those reported by High-Purity Standards.

[b] Concentration values for H-PS SR-1.

[c] Concentration values for H-PS SR-2.

[d] "Ammonium has been found to not be stable. These values are provided for information only," Theodore C. Rains, Ph.D., President, High-Purity Standards.

Table IV-2. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS2), Deionized Water (DI), and Internally Formulated Simulated Rainwater (00FR10), Unfiltered, 2000

Parameter	*Target concentration* [a] *(mg/L)*	*Measured concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	<0.009 [b]	0.000	0.000		0.003	
	0.031 [c]	0.031	0.000	0.0	0.003	9.7
Magnesium	<0.003	0.000	0.000		0.0006	
	0.007	0.007	0.000	0.0	0.0006	8.6
Sodium	<0.003	0.000	0.000		0.003	
	0.020	0.019	-0.001	-5.0	0.001	5.3
Potassium	<0.003	-0.001	-0.001		0.002	
	0.005	0.004	-0.001	-20.0	0.001	25.
Ammonium	<0.02	0.00	0.00		0.01	
	0.03	0.03	0.00	0.0	0.01	33.3
Sulfate	<0.010	0.000	0.000		0.000	
	0.250	0.250	0.000	0.0	0.003	1.2
Nitrate	<0.010	0.000	0.000		0.003	
	0.190	0.190	0.000	0.0	0.003	1.6
Chloride	<0.006	0.001	0.001		0.003	
	0.052	0.062 (0.053) [d]	0.010 (0.001)[d]	19.2 (1.9)[d]	0.047 (0.002)[d]	75.8 (3.8)[d]
pH	5.65	5.59	-0.06	-1.1	0.08	1.4
(units)	5.23	5.23	0.00	0.0	0.04	0.8
H	2.24	2.63	0.39	17.4	0.5	19.0
(µeq/L)	5.89	5.97	0.08	1.4	0.6	10.0
Specific conductance	0.8	1.2	0.4	50.	0.3	25.0
(µS/cm)	3.6	3.6	0.0	0.0	0.2	5.6

Notes:

There were 26 samples in each set.

[a] The concentration values for the 00FR10 sample are the mean of 7-11 analyses done immediately after sample preparation.

[b] Concentration values for DI water.

[c] Concentration values for internally formulated simulated rainwater (00FR10).

[d] Numbers in parentheses were calculated with the outlier concentration excluded.

Table IV-3. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS3), High-Purity Standards Simulated Rainwater I (H-PS SR-1) and II (H-PS SR-2), Filtered, 2000

Parameter	*Target concentration [a] (mg/L)*	*Measured concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	0.014 [b]	0.046	0.032 [c]	228.6	0.018	39.1
	0.055 [d]	0.098	0.043	78.2	0.010	10.2
Magnesium	0.019	0.014	-0.005	-26.3	0.003	21.4
	0.051	0.049	-0.002	-3.9	0.008	16.3
Sodium	0.20	0.197	-0.003	-1.5	0.003	1.5
	0.400	0.395	-0.005	-1.2	0.008	2.0
Potassium	0.051	0.047	-0.004	-7.8	0.002	4.3
	0.095	0.098	0.003	3.2	0.004	4.1
Ammonium [e]	0.100	0.10	0.00	0.0	0.01	10.0
	1.00	0.93	-0.07	-7.0	0.05	5.4
Sulfate	2.5	2.444	-0.056	-2.2	0.023	0.9
	10.1	9.685	-0.415	-4.1	0.063	0.7
Nitrate	0.50	0.491	-0.009	-1.8	0.006	1.2
	7.0	6.856	-0.144	-2.1	0.046	0.7
Chloride	0.25	0.212	-0.038	-15.2	0.003	1.4
	0.98	0.971	-0.009	-0.9	0.012	1.2
pH	4.29	4.34	0.05	1.2	0.03	0.7
(units)	3.58	3.62	0.04	1.1	0.02	0.6
H	51.3	46.4	-4.9	-9.6	3.3	7.1
(µeq/L)	263.0	239.7	-23.3	-8.9	11.5	4.8
Specific conductance	24	24.8	0.8	3.3	0.6	2.4
(µS/cm)	122	124.7	2.7	2.2	3.1	2.5

Notes:

There were 12 samples for H-PS SR-1 and 13 samples for H-PS SR-2.

[a] Target Concentrations are those reported by High-Purity Standards.

[b] Concentration values for H-PS SR-1.

[c] See “Internal Blind Audit” section for a discussion of this bias.

[d] Concentration values for H-PS SR-2.

[e] The 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 (SWS3), Deionized Water (DI) and Internally Formulated Simulated Rainwater (00FR10), Filtered, 2000

Parameter	*Target concentration [a] (mg/L)*	*Measured concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	<0.009 [b]	0.002	0.000		0.005	
	0.031 [c]	0.031	0.000	0.0	0.013	41.9
Magnesium	<0.003	0.000	0.000		0.0006	
	0.007	0.005	-0.002	-28.6	0.001	20.0
Sodium	<0.003	0.001	0.001		0.001	
	0.020	0.019	-0.001	-5.0	0.001	5.3
Potassium	<0.003	-0.001	-0.001		0.003	
	0.005	0.005	0.000	0.0	0.001	20.0
Ammonium	<0.02	0.00	0.00		0.01	
	0.03	0.03	0.00	0.0	0.01	33.3
Sulfate	<0.010	0.000	0.000		0.000	
	0.250	0.246	-0.004	-1.6	0.004	1.6
Nitrate	<0.010	0.000	0.000		0.000	
	0.190	0.186	-0.004	-2.1	0.004	2.2
Chloride	<0.006	0.000	0.000		0.000	
	0.052	0.053	0.001	1.9	0.002	3.8
pH	5.65	5.60	-0.05	-0.9	0.11	2.0
(units)	5.23	5.22	-0.01	-0.2	0.04	0.8
H	2.24	2.56	0.32	14.3	0.6	23.4
(µeq/L)	5.89	6.03	0.14	2.4	0.6	10.0
Specific conductance	0.8	1.2	0.4	50.	0.3	25.0
(µS/cm)	3.6	3.8	0.2	5.6	0.5	13.2

Notes:

There were 13 samples in each set.

[a] The concentration values for the 00FR10 sample are the mean of 7-11 analyses done immediately after sample preparation.

[b] Concentration values for DI water.

[c] Concentration values for internally formulated simulated rainwater (00FR10).

QCS (Table IV-2). A similar difference between the High-Purity Standards samples and the QCS was seen when the percent relative Standard Deviation (RSD) was compared. The QCS had a lower percent RSD than did the High-Purity Standards samples, which would be expected as the QCS concentrations were established by the CAL. The sulfate and chloride values for the lower QCS concentrations 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. High-Purity Standards does not certify the ammonium concentrations in their simulated rainwater samples. "Ammonium has been found not to be stable. These values are for information only" is stated on each simulated rainwater sample.

A large positive bias between the laboratory measurements and the target concentration for calcium was determined for the filtered samples with a negative bias determined for the unfiltered samples. The ammonium concentration in the High-Purity Standards 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 the lowest concentration QCS used at the CAL (Table IV-2). One solution was DI water, and the other was a synthetic rainwater sample approximating the 10th percentile values of the NTN samples (FR10). 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 indicate that the measured concentrations for DI water solutions were below the method detection limit (MDL) in 2000. For the 00FR10 solution, both sodium and potassium showed a small negative bias for both the filtered and unfiltered solutions. The bias for both sodium and potassium is less than the MDL. The concentration for both potassium and sodium in 00FR00 is less than ten times the MDL. Small biases at these levels may be indicative of instrument noise at this concentration level. The chloride numbers for 00FR00, unfiltered, contained a sample that was determined to have been contaminated, causing a large bias in the data set when that number was included. This contamination was found to be from the accidental addition of the atomic absorption modifier to the sample. The modifier contains chloride, lanthanum, and cesium. A large chloride concentration was found in the sample, and the specific conductance had increased from the initial measurement. An external laboratory with an inductively coupled plasma emission instrument found a stoichiometric amount of cesium when compared to the chloride found at the CAL. This confirmed the source of the contamination and resulted in a change in laboratory procedures to minimize this contamination from occurring again. This new procedure used in the laboratory is described in laboratory SOP AA-01. With this outlier removed, there is no further bias. For the filtered samples, magnesium, sodium, sulfate, and nitrate showed a negative bias, implying a slight loss in concentration of these ions during the filtration process. In all cases, the bias was less than the detection limit. The percent bias loss for magnesium was large compared to the initial concentration, which was only slightly above the MDL. Chloride showed a slight positive bias in the filtered samples equal to that found in the unfiltered samples with the outlier removed.

The SWS3 High-Purity Standard samples, Table IV-3, had larger biases and relative Standard Deviations than most unfiltered SWS1 samples, Table IV-1. Some variation is normal and expected in a system and was observed in the differences between filtered and unfiltered samples in 2000. The RSD for the High-Purity Standards SR1 solution for calcium in 2000 was again larger than in 1999, as were the RSD for both magnesium concentrations, the lower ammonium concentration, the higher chloride concentration, and the pH for both High-Purity Standards solutions. The RSD for all other measurements was lower. Even those samples with higher RSDs were not significantly different from those found in 1999. The sodium bias from filtration seen prior to 1998 and before the laboratory protocol change to the Gelman® filters was not found in 2000. There is, though, a large calcium bias in filtered samples compared with unfiltered samples. This appears to be unrelated to the initial concentration but more like a constant calcium increase in each sample of about 0.03 to 0.04 mg/L, although this did not appear to be the case for the internally prepared simulated rainwater sample (00FR00) or DI water.

Tables B-1 and B-2 (Appendix B) are tabular comparisons of the filtered and unfiltered High-Purity Standards 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 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 and without using the sample bucket on the collector. 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 and delivers the sample to the CAL. 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 reflect 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 2000 were simulated rainwater prepared for the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) intercomparison study for 1998 (Coleman et al., 1999). These samples are prepared at the CAL for the WMO/GAW intercomparison study. The WMO/GAW compares their samples to a calculated concentration

Table IV-5. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, AIRMoN, 2000

Parameter	*Mean WMO/GAW concentration*[a] *(mg/L)*	*CAL mean concentration*[b] *(mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Precision (mg/L)*	*RSD*[c] *(%)*	*Critical concentration*	*Statistical bias*
Calcium	0.062	0.058	-0.004	-6.5	0.003	5.2	0.007	no
Magnesium	0.024	0.023	-0.001	-4.2	0.0008	3.5	0.002	no
Sodium	0.240	0.249	0.009	3.8	0.005	2.0	0.010	no
Potassium	0.075	0.076	0.001	1.3	0.002	2.6	0.007	no
Ammonium	0.14	0.13	-0.01	-7.1	0.05	38.5	0.02	no
Sulfate	1.58	1.590	0.010	0.6	0.012	1.0	0.015	no
Nitrate	0.62	0.610	-0.010	-1.6	0.007	1.1	0.014	no
Chloride	0.40	0.385	-0.015	-3.8	0.005	1.3	0.035	no
pH units	4.52	4.52	0.00	0.0	0.02	0.4	0.03	no
Hydrogen ion (μeq/L)	30.2	30.2	0.0	0.0	1.2	4.0		no
Specific conductance (μS/cm)	16.6	17.5	0.9	5.4	0.33	1.9	0.31	yes

Notes:
This tabulation included 48 internal blinds. Samples were simulated rainwater prepared for the 1998 World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) intercomparison study.

[a] Mean concentration used by the WMO/GAW in their analysis of the data in the 1998 WMO/GAW intercomparison study.

[b] Mean concentration obtained by the CAL from the AIRMoN internal blind samples for 2000.

[c] RSD is Relative Standard Deviation.

(considered the true value) and a mean established from the results of the participating laboratories. Table IV-5 summarizes the results of the AIRMoN internal blind samples using the mean WMO/GAW results. True values similar to the mean values could be used instead, but the author chose to use the mean values. Mean concentrations from the intercomparison study and mean concentrations from the blind samples are used to calculate bias and precision. Sixty-seven laboratories worldwide participated in the 2000 WMO/GAW intercomparison study.

The percent bias of samples in the AIRMoN internal blind program was about the same as for H-PS SR2 solutions used for the NTN internal blind program for 2000 and for the AIRMoN internal blind study for 1999. For ammonium, there was a lower bias for the CAL for the WMO sample (WMO/GAW 1998 Sample #2) than for the H-PS SR1 solution, further supporting the theory that the difference seen in the High-Purity Standards solution was probably due to sample instability. 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, which may indicate no true bias, but random variations in the analyses. Statistically there was no bias for any ions measured although there was a bias for specific conductance.

B. Replicate Samples

Two percent of the NTN and AIRMoN samples are split for replicate analysis. The splits are separated in the analysis queue and are analyzed at different times than the original samples. The NTN samples are divided at the time of filtration into three 60-mL aliquots: one is put on the tray for transfer to the laboratory for initial analysis at its regular place in the queue, one is filtered for archival purposes, and one is sent back to sample processing to be assigned a new and higher laboratory identification number and submitted for analysis later. Samples chosen for splits must have sufficient volume to fill three 60-mL bottles after filtration. The original and the split sample analyses 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 change the laboratory identification number for the replicate to 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 replicate 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 completed FOF accompanies 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. Because 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 2000 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. Because 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 median values used to split the samples into different categories are calculated on the complete set of data. The Standard Deviation estimated from replicate 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 replicate determinations, where 1.48 times the Median Absolute Difference (MAD) is the estimator of dispersion (Helsel and Hirsch, 1992). A comparison of the Standard Deviations for the QCS solutions (Table III-1), SWS1 (Table IV-1), and SWS3 (Table IV-3) to 1.48 × MAD shows comparable cation and anion precision of the split samples.

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 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 2000, two solutions were used to leach filters, bottles, buckets, and lids: DI water from the sample processing laboratory and an FR25 QCS. The DI water blanks from the sample processing, atomic absorption, and the bucket-washing service laboratories are also included in the weekly blank analytical scheme.

1. Deionized Water Blanks

The specific conductance of DI water used for rinsing, leaching, and making reagents and standards is 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

Table IV-6. Variance Estimated from Analysis of Replicate NADP/NTN Precipitation Samples, 2000

	Standard Deviation Estimated from Paired Measurements[a] (mg/L)			
Parameter	*Low*	*High*	*Total*	*(1.48) × MAD[b]*
Calcium	0.005	0.013	0.010	0.007
Magnesium	0.001	0.003	0.002	0.001
Sodium	0.002	0.024	0.017	0.001
Potassium	0.002	0.008	0.006	0.003
Ammonium	0.01	0.03	0.02	0.01
Sulfate	0.007	0.019	0.014	0.013
Nitrate	0.039	0.016	0.030	0.009
Chloride	0.002	0.062	0.044	0.003
Orthophosphate	0.000	0.022	0.016	0.000
pH (units)	0.02	0.06	0.05	0.03
Hydrogen ion (µeq/L)	1.74	0.48	1.28	0.99
Specific Conductance (µS/cm)	0.47	0.50	0.49	0.30
Number of pairs	106	106	212	212

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, 2000

	Standard Deviation Estimated from Paired Measurements [a] *(mg/L)*			
Parameter	*Low*	*High*	*Total*	*(1.48) × MAD* [b]
Calcium	0.003	0.149	0.104	0.006
Magnesium	0.0005	0.018	0.012	0.001
Sodium	0.0008	0.041	0.029	0.001
Potassium	0.001	0.018	0.012	0.003
Ammonium	0.01	0.06	0.05	0.02
Sulfate	0.011	0.017	0.014	0.016
Nitrate	0.006	0.017	0.013	0.010
Chloride	0.002	0.023	0.016	0.003
Orthophosphate	0.017	0.021	0.019	0.004
pH (units)	0.03	0.08	0.06	0.03
Hydrogen ion (µeq/L)	2.37	4.12	3.38	2.65
Specific Conductance (µS/cm)	1.3	1.7	1.5	1.6
Number of pairs	17	16	33	33

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-8. Median pH and Conductivity Values for Weekly Deionized (DI) Water Blanks, 2000

Laboratory	*pH (units)*	*Conductivity (µS/cm)*	*Period (weeks)*
Sample Processing Laboratory	5.55	1.3	52
Atomic Absorption Laboratory	5.57	1.3	51
Service Laboratory	5.57	1.3	51

concentrations. These DI water blanks are also used to evaluate the cleaning efficacy of the 60-mL bottles used as sample storage bottles in NTN. No contamination problem was noted.

2. Filter Leachates

Table IV-9 shows the results of the filter leachates for 2000. 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. All samples with a volume greater than 35 mL then 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 as the leachate.

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, and sodium contamination from the filters was a recurring problem. There is no sodium contamination with the Gelman filters. All parameters approximate the target concentrations. This is in some ways contrary to the results of the filtered vs. unfiltered internal blind samples where the filtered samples show a higher concentration of calcium, a slight positive bias, and a lower concentration for sulfate and nitrate, a slight negative bias. There currently is no explanation for this difference.

Table IV-9. Median Analyte Concentrations Found in Filter Leachates, 2000

	DI Water		*FR25*		*Target*
Analyte	*A*[a] *(mg/L)*	*B*[b] *(mg/L)*	*A*[a] *(mg/L)*	*B*[b] *(mg/L)*	*concentration (mg/L)*
Calcium	<0.009	<0.009	0.078	0.076	0.074
Magnesium	<0.003	<0.003	0.014	0.017	0.017
Sodium	<0.003	<0.003	0.047	0.049	0.048
Potassium	<0.003	<0.003	0.012	0.012	0.013
Ammonium	<0.02	<0.02	0.08	0.08	0.09
Sulfate	<0.010	<0.010	0.593	0.610	0.613
Nitrate	<0.010	<0.010	0.449	0.462	0.465
Chloride	<0.005	<0.005	0.126	0.128	0.126
pH	5.55	5.55	4.94	4.93	4.96
Hydrogen ion (μeq/L)	2.82	2.82	11.5	11.7	11.0
Specific conductance (μS/cm)	1.4	1.4	7.4	7.3	7.2

Notes:

A total of 49 blank samples were collected.

[a] First 50-mL filtrate.

[b] Second 50-mL filtrate.

3. Bucket Blanks

Sample collection buckets of HDPE 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 any precipitation that 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 for both networks.

The weekly procedure for “bucket blanks” includes leaching five buckets for five days with two different volumes of two different solutions: two DI water blanks at 50-mL and one DI water blank at 150-mL and one each FR25 in 50- and 150-mL portions. 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 then were 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 concentration times the number of milliliters used for the leachate. For the DI water blanks, sodium in the 50-mL samples and chloride in all three volumes were the only ions above the MDL. Ammonium concentrations in the buckets were less than the concentration expected in the QCS solutions. This may be as much an artifact of the instability of the ammonium ion as it was to the uptake of ammonium by the bucket. Chemical reaction causing the decrease in ammonium from a reaction with something in or on the bucket also may be the cause for this loss of ammonium. Precipitation samples with low volumes generally had higher concentrations of analytes and, therefore, should not have been affected by the small amount of possible sodium contamination.

4. Bottle Blanks

One-liter HDPE wide-mouth bottles have been used as shipping containers for NTN samples since January 1994. Sample collected in the bucket is transported 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 then are poured into small vials for measuring pH and specific conductance. The remaining bottled sample, the 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 with DI water 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, although there was some loss of ammonium, probably due to instability of the ammonium ion.

Table IV-10. Median Measured Mass as Micrograms (µg)/Bucket[a] Found in Weekly Deionized (DI) Water and Simulated Rainwater (00FR25) in Upright Bucket Leachates, 2000

Analyte	*DI water (50 mL)*	*DI water (150 mL)*	*DI water (50 mL)*	*00FR25[b] (50 mL)*	*00FR25[b] (150 mL)*
Calcium	<0.225[a]	<0.675	<0.225	<0.225	<0.675
Magnesium	<0.075	<0.225	<0.075	<0.075	<0.225
Sodium	0.150	<0.225	0.100	0.075	<0.225
Potassium	<0.075	<0.225	<0.075	<0.075	<0.225
Ammonium	<0.50	<1.50	<0.50	-1.00[c]	-3.45[c]
Sulfate	<0.250	<0.750	<0.250	<0.250	<0.750
Nitrate	<0.250	<0.750	<0.250	<0.250	<0.750
Chloride	0.800	0.375	0.700	0.350	0.900
pH (units)	5.58	5.60	5.58	5.00(4.96)[d]	4.96(4.96)[d]
Hydrogen ion (µeq/bucket)	0.133	0.377	0.132	0.048	0.001
Specific conductance (µS/cm)	1.5	1.4	1.6	6.9(7.2)[c]	7.3(7.2)[c]

Notes:

There were 52 blind sample weeks in 2000.

The 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] The 00FR25 measured mass represents (median concentration measured in upright bucket leachates - target 00FR25 concentration) ×50 or 150 mL.

[c] The negative values shown for ammonium indicate the loss of ammonium in the FR QCS solutions.

[d] Values in parentheses represent mean values for 00FR25 with no bucket contact.

Table IV-11. Median Measured Mass as Micrograms (µg)/Bottle[a] Found in Weekly Deionized (DI) Water and Simulated Rainwater (00FR25) in HDPE 1-Liter Bottle Leachates, 2000

	DI water		*00FR25*[b]	
Analyte	*(50 mL)*	*(150 mL)*	*(50 mL)*	*(150 mL)*
Calcium	<0.225[a]	<0.675	<0.225	<0.675
Magnesium	<0.075	<0.225	<0.075	<0.225
Sodium	<0.075	<0.225	<0.075	<0.225
Potassium	<0.075	<0.225	<0.075	<0.225
Ammonium	<0.50	<1.5	-0.85	-1.8
Sulfate	<0.250	<0.750	-0.450	<0.750
Nitrate	<0.250	<0.750	-0.500	-0.900
Chloride	<0.125	<0.375	<0.125	<0.375
pH (units)	5.56	5.59	4.97(4.96)[c]	4.95(4.96)[c]
Hydrogen ion (µeq/bucket)	0.14	0.39	-0.01	0.04
Specific conductance (µS/cm)	1.4	1.3	7.1(7.2)[c]	7.3(7.2)[c]

Notes:

There were 52 blind sample weeks in 2000.

[a] Mass/bottle 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.

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 to prevent dry deposition contamination. Table IV-12 shows the median concentrations found on the snap-on lid “blanks”. Magnesium and sodium were found in the DI water blanks, but both were near the MDL for those ions. No other ions were found to be above the MDL.

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 as used for 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 blanks. Although only two bottles are tested each month, the same ratio of bottle blank to bottles used for samples is used for AIRMoN and NTN, 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 significant 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.

7. Bag Blanks

Bag blanks were added to the blanks regime in January 2000. The presence of sodium, chloride, magnesium, and occasional other ions in the bucket blanks resulted in the QA Specialist and Laboratory Director looking once again at the bags used to store the buckets and lids prior to and during shipping, and at the sites. The company furnishing the CAL with bags changed their supplier, resulting in a change in the bags used at the CAL. The bag chosen was not 100 percent clean, necessitating the use of bag blanks.

Two bags are selected each week from a different shipping box and used for blanks. One bag has 50-mL of DI water poured into it, and the second bag has 50-mL of FR25 poured into it. The leachate remains in the bags for five days and then it is decanted into appropriately labeled 60-mL HPDE bottles.

Table IV-14 shows that both the DI water blanks and the FR25 blanks contained a small amount of chloride in the bags. Approximately the same amount of chloride was found in the DI water blanks as was found in the FR25 blanks. There is a statistical difference between the chloride found in the bags and the chloride in the FR25 solutions. There is also a statistical difference at the 99 percent confidence level in the amount of calcium, magnesium, sodium, sulfate, and nitrate in the bags versus what was originally in the FR25 solutions. There is no statistical difference for potassium, ammonium, pH, and specific conductance.

Table IV-12. Median Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rainwater (00FR25) Used to Leach Snap-on Lids, 2000

Analyte	*DI water (50 mL)*	*00FR25 (50 mL)*	*00FR25 target concentration (mg/L)*
Calcium	<0.050	0.075	0.074
Magnesium	0.050	0.017	0.017
Sodium	0.050	0.049	0.048
Potassium	<0.003	0.013	0.013
Ammonium	<0.02	0.08	0.09
Sulfate	<0.010	0.613	0.613
Nitrate	<0.010	0.465	0.465
Chloride	<0.005	0.130	0.126
pH (units)	5.56	4.95	4.96
Hydrogen ion (µeq/L)	2.75	11.2	11.0
Specific conductance (µS/cm)	1.4	7.4	7.2

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

Table IV-13. Median Analyte Concentration (mg/L) Found in Monthly Simulated Rainwater (00FR25) AIRMoN 250-mL HDPE Bottle Leachates, 2000

Analyte	*00FR25 (50 mL)*	*00FR25 (150 mL)*	*00FR25 target concentration (mg/L)*
Calcium	0.074	0.074	0.074
Magnesium	0.017	0.017	0.017
Sodium	0.048	0.049	0.048
Potassium	0.014	0.013	0.013
Ammonium	0.08	0.08	0.09
Sulfate	0.613	0.614	0.613
Nitrate	0.470	0.464	0.465
Chloride	0.128	0.128	0.126
pH (units)	4.92	4.94	4.96
Hydrogen ion (µeq/L)	12.0	11.5	11.0
Specific conductance (µS/cm)	7.6	7.4	7.2

Note:
There were 11 months of AIRMoN bottle blanks.

Table IV-14. Median Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rainwater (00FR25) Used to Leach Bags, 2000

Analyte	*DI water (50 mL)*	*00FR25 (50 mL)*	*00FR25 target concentration (mg/L)*
Calcium	<0.009	0.080	0.074
Magnesium	<0.003	0.018	0.017
Sodium	0.004	0.052	0.048
Potassium	<0.003	0.013	0.013
Ammonium	<0.02	0.08	0.09
Sulfate	<0.010	0.586	0.613
Nitrate	<0.010	0.470	0.465
Chloride	0.016	0.137	0.126
pH (units)	5.51	4.97	4.96
Hydrogen ion (µeq/L)	3.1	10.8	11.0
Specific conductance (µS/cm)	1.8	7.3	7.2

Notes:
There were 50 weeks of bag blanks in 2000.
The concentrations for the analytes preceded by < symbols had less than the MDLs found in the blanks.

V. MONTHLY QUALITY ASSURANCE PROCEDURES

Monthly NADP/NTN and NADP/AIRMoN-wet QA activities include: 1) evaluation by the QA Specialist of the control charts summarizing the daily QCS analyses to determine any change occurred in CAL analytical instrument performance, 2) review of the computer printouts containing internal blind sample data, and 3) review of the reanalyses of samples flagged either for 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 NTN samples are transmitted to the data processing staff approximately twice a month in sets of 500 to 600 samples. Data for AIRMoN-wet samples are processed once a month for sets of about 120 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:

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

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%
$50 \leq$ IS < 100 µeq/L	and	IPD > + 30% or IPD < -30%
IS $\geq$ 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-wet. Ion concentrations as μeq/L are multiplied by conductance conversions factors listed in Table V-1 (1987), summed, and then divided by 1000 to calculate the conductivity. This value is compared to the measured conductivity. The CPD is calculated as follows:

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

Samples are flagged for reanalysis if:

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

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. After review by the QA Specialist and data specialists, a final decision is made and the data are edited as needed. When no explanation can be found for differences between the original and reanalysis values, a second reanalysis of the original sample is recommended. For NTN, analysis of the refrigerated archive sample also may be required. Reanalysis values are maintained in the CAL computerized database along with the original analysis values.

3. IPD and CPD Histograms

In 2000, approximately 12,163 samples were logged in and 7443 samples 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 419 samples flagged for reanalysis, and 269 individual measurement changes were made to 175 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 – 2000 median IPDs were positive. A negative value indicates a measured cation excess. Before January 1, 1994, samples were shipped in the collection buckets using lids that contained a butadiene rubber o-ring. Sample pH increased due to an ion exchange reaction at the o-ring/ sample interface. Beginning in January 1994, the NADP began using snap-on lids that do not contain an o-ring. These lids are not water-tight so the buckets cannot be used to ship samples to the CAL. The NTN samples, therefore, are decanted at the field site into 1-L wide-mouth HDPE bottles with screw-on lids and without gaskets before shipping to the CAL. Since the change in shipping protocol, the laboratory pH and field pH are in better agreement. The NADP does not measure organic acids, which could account for some of the excess cations measured. In 1998, the filters used for the NTN samples were changed from a Millipore™ type HAWP, 0.45-micrometer (µm) filter to a Gelman Supor® 450, 0.45-µm polyethersulfone filter. When Millipore™ filters were used, there was a positive 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 some other factors could be at work here as well. Further study is needed to determine the cause of these shifts in the median IPD.

The CPD has consistently exhibited a negative skew since 1979, with 2000 being similar to previous years. Negative CPD indicates that the measured conductivity exceeds the calculated conductivity. This is expected because only major ions in samples are analyzed. There are undoubtedly constituents, such as trace metals and organic species, that contribute to the measured conductivity.

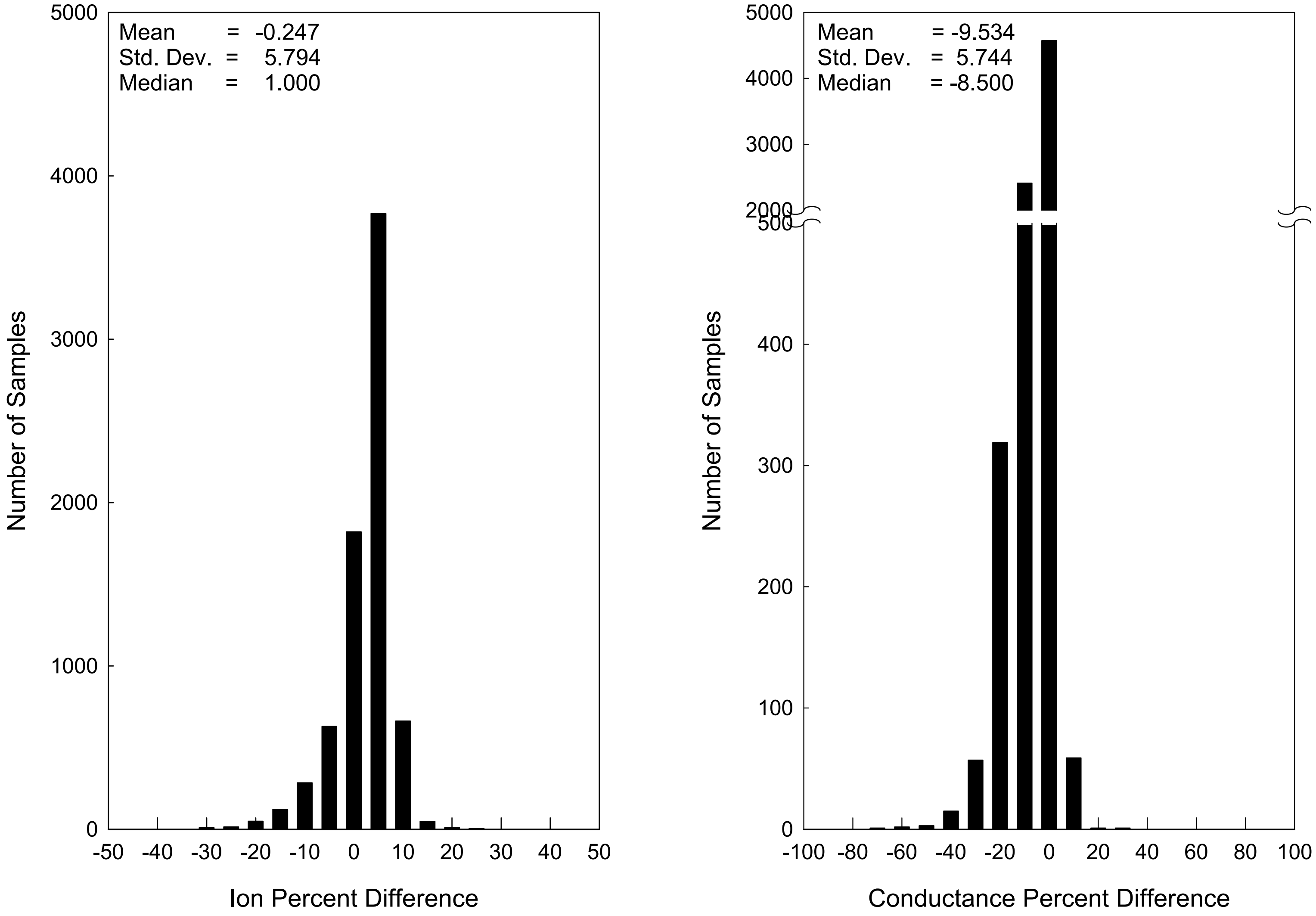


Figure V-1. Ion Percent Difference and Conductance Percent Difference for 7443 NADP/NTN wet samples, 2000.

B. USGS Interlaboratory Comparison

The interlaboratory comparison conducted by the U.S. Geological Survey (USGS), which has a contract with the NADP/NTN to provide for external QA, began in the fall of 1982 as a portion of the external audit of the CAL. The USGS mails several sets of blind samples of differing matrices to participating laboratories each month. If a laboratory participates in the study for an entire year, it receives a total of 104 samples in 26 biweekly mailings. The audit has been designed to determine if the laboratories are producing comparable results.

The interlaboratory comparison program included seven laboratories in 2000: (1) Illinois State Water Survey Central Analytical Laboratory (CAL), Champaign, Illinois; (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; (5) Shepard Analytical (SA), Simi Valley, California, (6) Acid Deposition and Oxidant Research Center (ADOR), Niigata-shi, Japan; and (7) Norwegian Institute for Air Research (NILU), Kjeller, Norway. All laboratories participated for the entire year in 2000.

Samples were shipped to the laboratories approximately every two weeks throughout the year. Samples used in 2000 were (1) National Institute of Standards and Technology (NIST) traceable samples prepared and certified by High-Purity Standards, (2) natural deposition samples collected at the NADP/NTN sites and composited and bottled at the CAL, and (4) ultrapure DI water samples prepared by the USGS. Data reports from the participating laboratories are submitted monthly, quarterly, or semi-annually to the USGS.

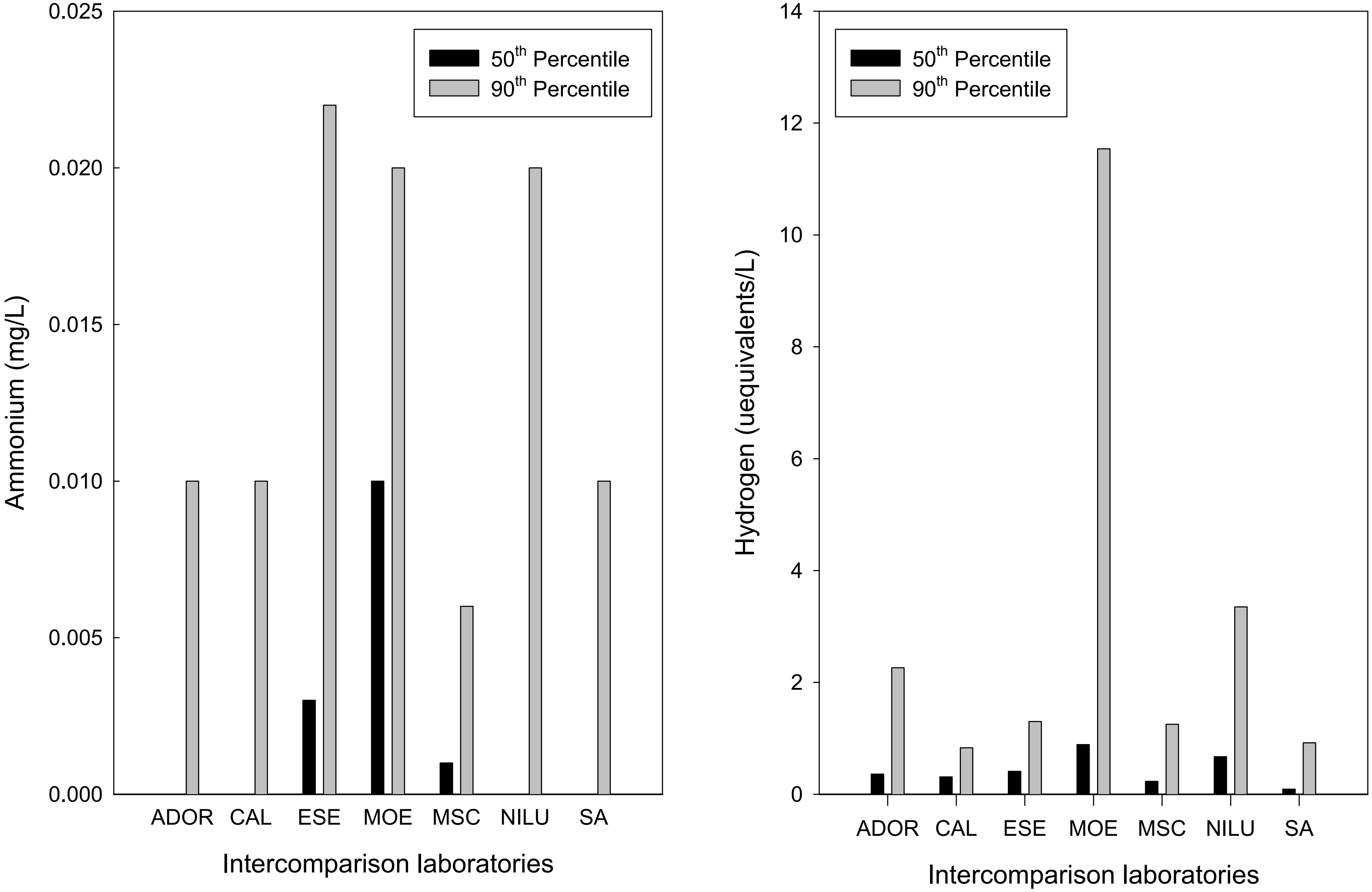
Table V-2 shows the 50th and 90th percentile absolute differences of replicate samples obtained by the seven laboratories participating in 2000. Figures V-1 and V-2 are graphs showing these same results. For comparison, laboratory rankings were determined by summing the 50th and 90th percentile absolute differences (Table V-3). The CAL was ranked first for sulfate and was tied for first with one or more laboratories for nitrate, chloride, and specific conductance in 2000. The CAL was ranked second for pH and tied for second for calcium and ammonium among participating laboratories. The CAL was tied for third for sodium and potassium, and was ranked fifth for magnesium. Overall, the CAL once again had excellent results in 2000. The USGS will publish the complete results of the 2000 study.

Table V-2. 50th and 90th Percentile Absolute Differences for Analysis of Replicate Samples in the 2000 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	0.001	0.004	0.002	0.006	0.001	0.002	0.020	0.040	0.001	0.004	0.001	0.005	0.00	0.01
Magnesium	0.001	0.001	0.000	0.001	0.000	0.001	0.000	0.010	0.000	0.001	0.000	0.001	0.00	0.01
Sodium	0.001	0.006	0.001	0.003	0.001	0.005	0.005	0.075	0.001	0.006	0.000	0.003	0.00	0.02
Potassium	0.001	0.002	0.000	0.003	0.001	0.003	0.005	0.095	0.000	0.002	0.001	0.002	0.00	0.00
Ammonium	0.00	0.01	0.001	0.006	0.003	0.022	0.01	0.02	0.00	0.01	0.00	0.01	0.00	0.02
Sulfate	0.000	0.010	0.003	0.009	0.010	0.020	0.00	0.05	0.00	0.02	0.01	0.03	0.01	0.05
Nitrate	0.000	0.010	0.003	0.013	0.009	0.031	0.01	0.47	0.00	0.01	0.01	0.02	0.02	0.05
Chloride	0.000	0.010	0.002	0.008	0.002	0.014	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.03
Hydrogen Ion (µeq/L)	0.31	0.83	0.23	1.25	0.41	1.30	0.89	11.54	0.09	0.92	0.36	2.268	0.67	3.35
Specific conductance (µS/cm)	0.10	0.30	–	–	0.13	0.70	0.60	5.20	0.10	0.30	0.10	0.30	0.10	0.50

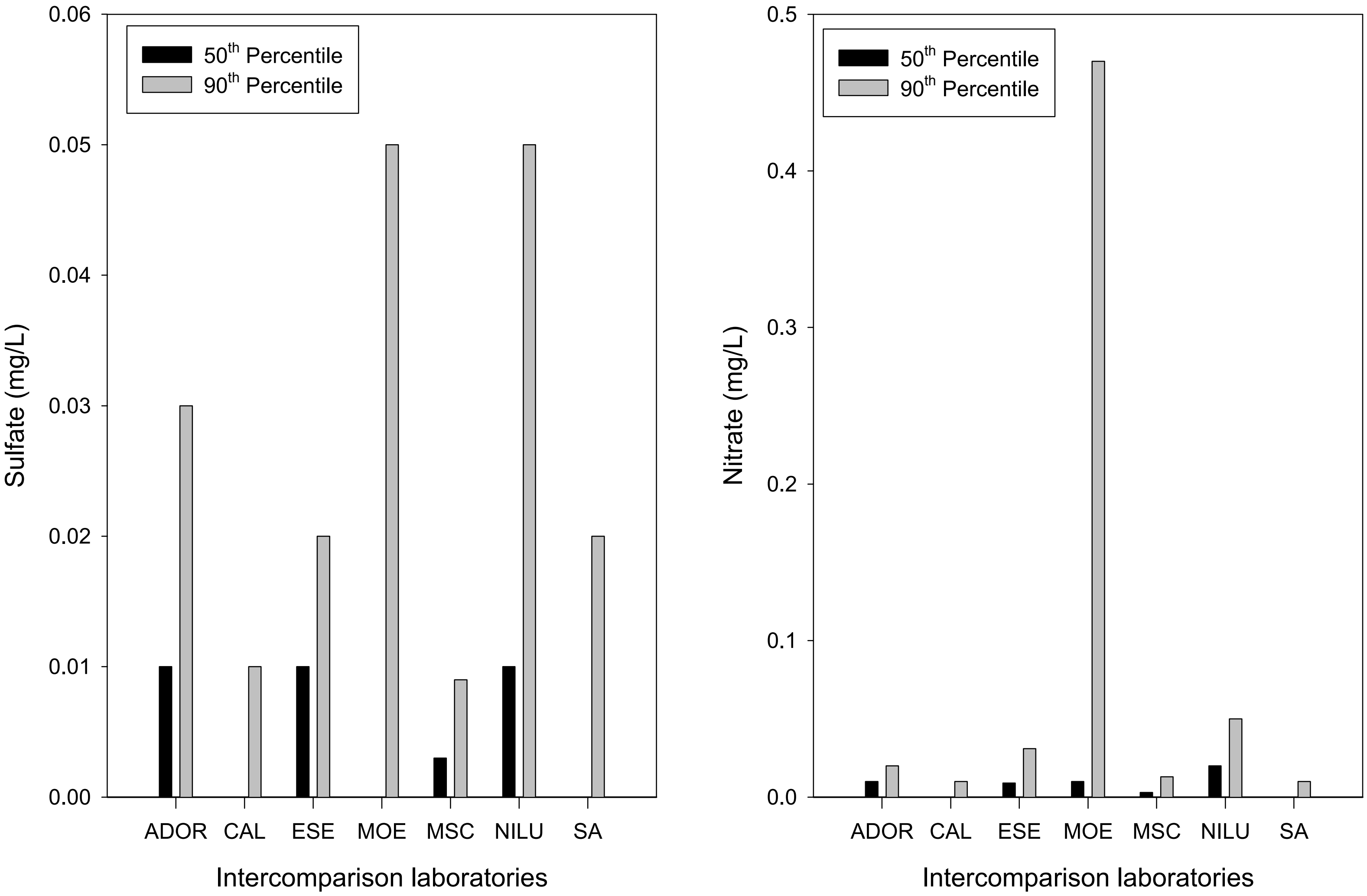
Source: USGS, Water Research Division, Branch of Quality Systems

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, Inc.
[d] Ontario Ministry of the Environment, Canada.
[e] Shepard Analytical.
[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 – December 31, 2000.



Note: The laboratories involved in the intercomparions 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 (SA), the Acid Deposition and Oxidant Research Center of Japan (ADOR), and the Norwegian Institute for Air Research (NILU). Data were provided by USGS Water Research Division Branch of Quality Systems.

Figure V-2. Ammonium and hydrogen 50th and 90th percentile absolute differences for the seven laboratories in the USGS intercomparison study, 2000.



Note: The laboratories involved in the intercomparions 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 (SA), the Acid Deposition and Oxidant Research Center of Japan (ADOR), and the Norwegian Institute for Air Research (NILU). Data were provided by USGS Water Research Division Branch of Quality Systems.

Figure V-3. Sulfate and nitrate 50th and 90th percentile absolute differences for the seven laboratories in the USGS intercomparison study, 2000.

Table V-3. USGS Intercomparison Study Ranking Summary, 2000

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	0.005	2 tie	0.008	5	0.003	1	0.060	7	0.005	2 tie	0.006	4	0.01	6
Magnesium	0.002	5	0.001	1 tie	0.001	1 tie	0.010	6 tie	0.001	1 tie	0.001	1 tie	0.01	6 tie
Sodium	0.007	3 tie	0.009	5	0.006	2	0.080	7	0.007	3 tie	0.003	1	0.02	6
Potassium	0.003	3 tie	0.003	3 tie	0.003	3 tie	0.100	7	0.002	2	0.003	3 tie	0.00	1
Ammonium	0.01	2 tie	0.007	1	0.025	7	0.02	5 tie	0.01	2 tie	0.01	2 tie	0.02	5 tie
Sulfate	0.010	1	0.016	2	0.030	4	0.05	6	0.02	3	0.04	5	0.06	7
Nitrate	0.010	1 tie	0.021	3	0.040	5	0.48	7	0.01	1 tie	0.03	4	0.07	6
Chloride	0.010	1 tie	0.02	5 tie	0.016	4	0.02	5 tie	0.01	1 tie	0.01	1 tie	0.04	7
Hydrogen ion (μeq/L)	1.14	2	1.48	3	1.71	4	12.43	7	1.01	1	2.62	5	4.02	6
Specific Conductance (μS.cm)	0.40	1 tie	not available		0.83	5	5.8	6	0.40	1 tie	0.40	1 tie	0.60	4
Ranking without specific conductance	2		4		5		7		1		3		6	
Overall ranking	2		incomplete		4		6		1		3		5	

Source: USGS, Water Research Division, Branch of Quality Systems

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.

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

[g] Norwegian Institute for Air Research, Norway.

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 from three to five interlaboratory comparison studies not sponsored by the NADP. There were three studies in 2000: 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 23rd set of WMO/GAW reference precipitation samples was shipped to participating laboratories in December 2000. In 2000, the CAL was contracted to prepare the simulated precipitation samples used in this study. Samples were shipped to 96 laboratories, and 67 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 participating laboratories with outliers statistically evaluated and removed, and concentrations measured at the CAL during the actual study. Because the CAL was not included with the study laboratories, the CAL results were not ranked; however, CAL results agreed very closely with the study means and target values.

B. National Water Research Institute

The CAL has been participating in the National Water Research Institute (NWRI) studies since 1989. The CAL participated in both studies sponsored by the NWRI in Burlington, Ontario, Canada. Begun in 1982 as the Long-Range Transport of Atmospheric Pollutants (LRTAP) program, the studies for 2000 were FP76 and FP77 (Blum and Alkema, 2000a, 2000b). The NWRI samples included selected major ions, nutrients, and physical parameters in natural waters. Median concentrations from all reporting laboratories were used as target values. Most samples were surface waters or precipitation samples for which calculated or certified values were not known. High, very high, low, or very low results were noted. These flags were based on the biases observed from the median values found in the study and the biases of the other laboratories. A score was computed from these flagged samples. Zero, therefore, denoted the optimum score, indicating that all parameters were within the expected range of the target values.

Table VI-1. World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) Acid Rain Performance Survey, 2000

Analyte	*Units*	*Sample 1*			*Sample 2*			*Sample 3*		
		Target	*Mean*	*CAL*	*Target*	*Mean*	*CAL*	*Target*	*Mean*	*CAL*
Calcium	mg Ca/L	0.270	0.267	0.261	0.114	0.114	0.111	0.465	0.462	0.452
Magnesium	mg Mg/L	0.117	0.115	0.109	0.033	0.032	0.032	0.211	0.208	0.198
Sodium	mg Na/L	1.123	1.110	1.105	0.148	0.142	0.150	1.431	1.414	1.430
Potassium	mg K/L	0.219	0.214	0.215	0.030	0.033	0.030	0.292	0.284	0.287
Ammonium	mg NH_4/L as N	0.297	0.299	0.29	0.172	0.173	0.17	0.543	0.545	0.53
Sulfate	mg SO_4/L as S	0.646	0.634	0.647	0.447	0.446	0.448	0.921	0.914	0.929
Nitrate	mg NO_3/L as N	0.221	0.217	0.219	0.293	0.239	0.239	0.388	0.386	0.388
Chloride	mg Cl/L	2.030	2.000	2.040	0.280	0.275	0.278	2.278	2.276	2.300
pH	pH units	4.76	4.80	4.76	4.56	4.61	4.57	5.61	6.31	5.27
H	µequiv/L	17.4	15.8	17.4	27.5	24.5	26.9	2.5	4.9	5.4
Specific conductance	µS/cm	20.5	20.2	21.7	15.5	15.2	16.9	21.2	22.1	23.1

Note:
Target values are based on the theoretical concentrations of the solutions. 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 concentration calculations.

Tables VI-2 and VI-3 show the median results and the CAL results for both studies. For Study FP76, the CAL had one high specific conductance value and one high sodium value. The CAL also had one low value for ammonium, nitrate, and pH, and one very low value for ammonium. Although magnesium had no high or low flags, overall the values found at the CAL had a statistically low bias according to the study. Overall, the CAL was rated "good", and the overall percent bias improved over the 1999 Study FP75. For Study FP77, the CAL received no flags for any parameters. Ammonia, though, had a statistically low bias as did magnesium, resulting in an overall CAL rating of "satisfactory".

The NWRI summarizes the performance results for the past ten studies (Studies 0068 – 0077). The CAL received a median score of 5.4 based on the percentage of biased parameters and flagged results on the studies. This was ranked seventh of the 37 ranked laboratories and was rated "satisfactory". The ten studies cover the time period from spring 1996 through fall 2000. To achieve a ranking of "good", the median for the ten studies needed to be under five percent, putting the CAL just barely out of the "good" category and into a "satisfactory" ranking.

C. The Acid Deposition Monitoring Network in East Asia

In 2000, the CAL participated in the Acid Deposition Monitoring Network in East Asia's (EANET) intercomparison study. There were two samples in the study. Results will be reported in the 2001 QA Report (results of the study weren't made available until late 2001.) Study participants included 24 East Asian countries and several others outside East Asia. The study looked at ten parameters: chloride, nitrate, sulfate, ammonium, calcium, magnesium, potassium, sodium, pH, and specific conductance.

Table VI-2. National Water Research Institute Soft Water Interlaboratory Study FP76, March and April 2000

		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	2.940	2.940	3.352	3.370	0.510	0.520	2.662	2.704	2.985	3.043
Magnesium	mg/L	0.480	0.459	0.727	0.705	0.369	0.349	0.930	0.896	0.930	0.897
Sodium	mg/L	0.557	0.568	1.600	1.695	2.665	2.770	0.154	0.156	1.256	1.352
Potassium	mg/L	0.208	0.208	0.218	0.217	0.231	0.231	0.160	0.163	0.545	0.545
Ammonium	mg NH_4/L as N	0.054	0.05	0.004	<0.02	0.003	<0.02	0.004	<0.02	0.005	<0.02
Sulfate	mg SO_4/L as S	5.270	5.270	2.990	3.057	3.750	3.772	6.031	6.031	7.610	7.435
Nitrate	mg NO_3/L as N	0.597	0.606	0.078	0.076	0.135	0.136	0.941	0.945	0.000	<0.015
Chloride	mg/L	0.240	0.230	1.585	1.599	4.114	4.149	0.390	0.386	1.260	1.274
pH	pH units	6.50	6.65	7.03	7.20	4.59	4.60	6.12	6.28	6.77	6.89
Specific conductance	µS/cm	26.7	26.8	32.0	32.4	33.3	34.4	28.5	28.6	34.8	35.0

		Sample 6		*Sample 7*		*Sample 8*		*Sample 9*		*Sample 10*	
Analyte	*units*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	mg/L	4.513	4.597	2.890	2.946	2.350	2.369	0.120	0.122	1.434	1.453
Magnesium	mg/L	0.790	0.783	0.660	0.644	0.626	0.606	0.039	0.036	0.297	0.279
Sodium	mg/L	2.550	2.667	0.154	0.158	0.080	0.079	0.170	0.176	0.147	0.152
Potassium	mg/L	0.560	0.565	0.280	0.276	0.120	0.122	0.030	0.030	0.055	0.056
Ammonium	mg NH_4/L as N	0.003	<0.02	0.259	0.21	0.216	0.064	0.123	0.114	0.002	<0.02
Sulfate	mg SO_4/L as S	4.550	4.608	4.980	5.003	4.000	3.987	1.320	1.301	7.000	6.851
Nitrate	mg NO_3/L as N	0.296	0.261	1.880	1.899	1.505	1.512	0.251	0.253	0.033	0.033
Chloride	mg/L	1.850	1.849	0.520	0.523	0.400	0.399	0.300	0.298	0.155	0.152
pH	pH units	7.25	7.36	4.66	4.62	4.88	4.67	4.59	4.59	4.37	4.37
Specific conductance	µS/cm	44.9	45.6	38.8	40.3	30.5	33.0	14.6	15.3	32.2	33.5

Table VI-3. National Water Research Institute Soft Water Interlaboratory Study FP 77, Fall 2000

		Sample 1		*Sample 2*		*Sample 3*		*Sample 4*		*Sample 5*	
Analyte	*units*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	mg/L	0.9600	0.984	0.6040	0.620	0.4030	0.411	0.1745	0.178	4.5200	4.462
Magnesium	mg/L	0.2000	0.196	0.1800	0.169	0.4000	0.380	0.0330	0.032	0.8600	0.811
Sodium	mg/L	0.1000	0.101	0.0695	0.069	2.7820	2.785	0.1100	0.111	1.0560	1.074
Potassium	mg/L	0.0395	0.039	0.0200	0.017	0.2400	0.245	0.0330	0.037	0.4400	0.450
Ammonium	mg NH_4/L as N	0.0050	<0.02	0.0692	0.064	0.0090	<0.02	0.1900	0.171	0.0050	<0.02
Sulfate	mg/L	0.2521	0.247	1.3714	1.373	2.2860	2.321	1.5700	1.572	4.4125	4.495
Nitrate	mg NO_3/L as N	0.0220	0.023	0.3400	0.343	0.0740	0.075	0.2100	0.211	0.1375	0.138
Chloride	mg/L	0.1032	0.104	0.1500	0.150	4.3545	4.431	0.2025	0.205	0.8230	0.854
pH	pH units	6.7400	6.82	5.3100	5.29	5.5200	5.52	4.6700	4.66	7.1000	7.24
Specific conductance	µS/cm	7.5630	7.4	9.2150	9.8	24.100	24.5	13.410	14.5	36.900	37.4

		Sample 6		*Sample 7*		*Sample 8*		*Sample 9*		*Sample 10*	
Analyte	*units*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	mg/L	2.9600	2.976	3.6540	3.654	3.5635	3.520	4.6410	4.700	2.5000	2.474
Magnesium	mg/L	0.5600	0.530	0.9400	0.898	0.9120	0.866	0.8600	0.821	0.6200	0.586
Sodium	mg/L	2.0320	2.076	1.2800	1.291	1.7850	1.806	0.5800	0.584	2.2200	2.231
Potassium	mg/L	0.3500	0.369	0.4000	0.416	0.2540	0.262	0.2010	0.204	0.5000	0.510
Ammonium	mg NH_4/L as N	0.0050	<0.02	0.0400	0.036	0.0050	<0.02	0.2988	0.272	0.0380	0.034
Sulfate	mg/L	3.7900	3.888	5.8100	5.897	4.6720	4.764	5.9670	6.040	4.6800	4.767
Nitrate	mg NO_3/L as N	0.1670	0.169	0.0280	0.028	0.8735	0.901	0.8680	0.891	0.0700	0.072
Chloride	mg/L	2.1036	2.161	0.8295	0.853	3.1045	3.164	0.5410	0.552	1.6650	1.689
pH	pH units	6.8900	7.02	7.1100	7.17	6.7300	6.81	7.0800	7.14	6.8950	6.96
Specific conductance	µS/cm	32.300	33.0	36.100	37.50	39.800	40.2	41.200	41.3	31.850	33.0

VII. SUMMARY

This report summarizes the results from the quality assurance program in place at the Central Analytical Laboratory (CAL) of the NADP/NTN and NADP/AIRMoN-wet in 2000. Information about the quality of the data generated at the CAL is presented in the form of tables, figures, and brief written explanations. Appendices A and B provide supplemental information.

Quality assurance activities that occurred on a daily basis included the operation, standardization, and maintenance of the scientific instrumentation used to analyze samples and provide data. Daily records documented reagent and standards preparation and instrument performance and maintenance. Standardization curves were verified using internally formulated CAL synthetic rainwater 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, revised 1993).

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 random location of the blinds in the sample queue. The analysts knew the QCS sample concentrations and analysis location, but they did not know the concentrations and locations in the analysis queue of internal blind samples.

In 2000, internal blind solutions of DI water and an internally formulated CAL synthetic rainwater sample approximating the 10th percentile concentration level of the NTN network (FR10) indicated little or no sample carryover during the analysis or no false positives. Also in 2000, it was observed that filtration increased variability in the chemistry of all samples. Unlike 1999, there was no evidence of calcium bias in the filtered internal blind solutions. 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 except for chloride, nitrate, and sulfate. Year 2000 was the first year that these parameters were reported to three decimal places. Previously, data were reported only to two decimal places, and little variability was seen in the QA data. The increased ability to see the true noise of the analytical procedure could account for larger biases than previously seen in these parameters.

The DI water and filter and container leachates were analyzed weekly to detect contamination and to 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 around 1 µS/cm. Filters leached with DI water and 00FR25 showed that the filtrates contained no measurable amount of any of the parameters measured. Bucket leachates show slight elevations for sodium and chloride and a negative bias for ammonium. These biases were traced to the bucket storage bags. Bags were introduced to the weekly analysis scheme and were determined to have a slight calcium, sodium, sulfate, and chloride bias. One-liter NTN bottle leachates and 250-mL AIRMoN-wet bottle blanks contained no contamination.

The AIRMoN-wet internal blind program was a cooperative project with the Bondville, Illinois site operator and the AIRMoN-wet coordinator. Analytical results for these samples showed that the precision for the solution used in 2000, the WMO-GAW 1998 sample #2, was within the data quality objectives of the network QAP for all parameters. Of all the parameters measured, only specific conductance had a statistical bias.

After completion of analyses, sample data were transferred in batches to data management staff, who compiled semimonthly printouts containing the data for 500 – 600 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, revised 1993) were flagged and reanalyzed. Of the 7443 "W" samples, 419 samples were flagged for reanalysis. After evaluation of the original and reanalysis measurements, 269 original measurements from 175 samples were changed. The ion percent difference (IPD) mean and the median were negative for 2000. This indicated an excess of cations in half or more of the wet samples analyzed. The conductance percent difference (CPD) has been skewed negatively since 1979 and continued to be so in 2000. This means that the measured conductivity exceeds the calculated conductivity, indicating that components may be present in the precipitation samples that are not being measured.

The USGS interlaboratory comparison study included seven laboratories in 2000. 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 were 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 second overall of the seven participating laboratories. The CAL ranked first or was tied for that position for sulfate, nitrate, chloride, and specific conductance.

In 2000, 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-seven laboratories participated in the WMO-GAW study, but CAL did not submit WMO-GAW sample results for official inclusion in the study because it prepared those samples and verified the target values. However, in comparing the numbers measured at the CAL obtained during the study to theoretical values and median values from the other 67 laboratories, the CAL results were good. The NWRI results over the last ten studies indicate that the CAL is ranked seventh overall of 37 ranked laboratories. The CAL received one high specific conductance and one high sodium flag, one low flag for ammonium, nitrate, and pH, and one very low flag for ammonium for Study FP76. Although magnesium received no flags, the concentrations of all samples were on the low side, resulting in a negative bias for magnesium. These results gave the CAL a "good" rating. The CAL received no flags for Study FP77, but ammonium and magnesium had statistically low bias resulting in an overall rating for the CAL of "satisfactory".

A comparison of the last ten studies resulted in a median score for the CAL of 5.4 percent or a "satisfactory" rating (5 or less is required for a "good" rating). The CAL continues to compare favorably with its peers throughout the world.

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APPENDIX A

GLOSSARY OF TERMS

GLOSSARY OF TERMS

Term	Abbreviation	Definition
Accuracy		The degree of agreement between an observed value and an accepted reference value. The concept of accuracy includes both bias (systematic error) and precision (random error).
Bias		A persistent positive or negative deviation of the measured value from the true value. In practice, it is expressed as the difference between the value obtained from analysis of a homogeneous sample and the accepted true value. Bias = True value - Measured mean value
Box Plot		A graphical summary representation of the distribution of a set of data, the top and bottom of the box representing the 25th and 75th percentile. The horizontal line represents the median concentration, and the lower and upper Ts extend to the 10th and 90th percentile concentrations.
Control Chart		A graphical plot of test results with respect to time or sequence of measurement, together with limits within which they are expected to lie when the system is in a state of statistical control (Taylor, 1987).
Critical Concentration		A calculated concentration used to determine whether the measured bias is statistically significant (Anderson, 1987). Critical Concentration = $t * s_{sp} * \sqrt{1/n_1 + 1/n_2}$

Term	Abbreviation	Definition
		where: $s_{sp} = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}$ s_{sp} = pooled standard deviation s_1 = Standard Deviation of reference solution measurements s_2 = Standard Deviation of daily QCS measurements n = number of values t = t statistic at the 95% confidence level and $(n_1 + n_2) - 2$ degrees of freedom
External Blind Sample		A Quality Assurance sample of known analyte concentrations submitted to the laboratory by an external agency. These samples arrive at the CAL as normal weekly rain samples and undergo routine processing and analysis. The identity of the sample is unknown to the CAL until all analyses are complete. Data are used to assess contamination potential from handling and shipping.
Internal Blind Sample		A Quality Assurance sample of known analyte concentrations submitted to the laboratory by the QA Specialist. The identity of the sample is known to the processing staff only. The analyte concentrations are unknown to the analysts. These data are valuable in assessing bias and precision for network samples.

Term	Abbreviation	Definition
Mean	$\bar{x}$	The average obtained by dividing a sum by the number of its addends. $\bar{x} = \sum_{i=1}^{n} x_i / n$ where: n = number of values x_i = values
Mean Bias		The sum of the bias for each sample divided by the total number of replicates (n).
Mean Percent Recovery		The sum of the percent recovery for each sample divided by the number of replicates (n).
Median		The median is the middle item when the values are arranged in order of magnitude. For symmetrical distributions, the median is an estimate of the mean.
Method Detection Limit	**MDL**	The minimum concentration of an analyte that can be reported with 99 percent confidence that the value is greater than zero (Glaser et al., 1981).
Percent Bias		The difference between the mean value obtained by repeated analysis of a homogeneous sample and the accepted true value expressed as a percentage of the true value. $\% \, Bias = 100 * [(V_m - V_t)/V_t]$ where: V_m = mean measured value V_t = true value

Term	Abbreviation	Definition
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).
Quality Assessment		The system of procedures that ensures that QC practices are achieving the desired goal in terms of data quality. Included is a continuous evaluation of analytical performance data.
Quality Assurance	**QA**	An integrated system of activities involving planning, QC, reporting, and remedial action to ensure that a product or service meets defined standards of quality.
Quality Control	**QC**	The system of procedures designed to eliminate analytical error. These procedures determine potential sources of sample contamination and monitor analytical procedures to produce data within prescribed tolerance limits.
Quality Control Solution	**QCS**	A solution containing known concentrations of analytes used by the analysts to verify calibration curves and validate sample data. The values obtained from the analyses of these samples are used for calculation of bias and precision and for the monthly control charts.
Relative Standard Deviation	**RSD**	The Standard Deviation expressed as a percentage: $RSD = 100 * (s/\bar{x})$ where: s = sample Standard Deviation $\bar{x}$ = mean value

Term	Abbreviation	Definition
Replicates (Splits)		Two aliquots of the same sample treated identically throughout the laboratory analytical procedure. Analyses of laboratory replicates are beneficial when assessing precision associated with laboratory procedures but not with collection and handling. Also referred to as splits.
Sensitivity		The method signal response per unit of analyte.
Standard Deviations		The number representing the dispersion of values around their mean. $s = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n-1}}$ where: x_i = each individual value $\bar{x}$ = the mean of all values n = number of values
Standard Deviation Estimated from 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). $s^2 = \frac{\Sigma d^2}{2n}$ 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, 2000

Table B-1. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, High-Purity Standards Simulated Rainwater-1 (H-PS SR-1), 2000

Parameter	*Target concentration*[a] *(mg/L)*	*Measured concentrations (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	0.014	0.011[b]	-0.003	-21.4	0.005	45.5
		0.046[c]	0.032	228.6	0.018	39.1
Magnesium	0.019	0.019	0.000	0.0	0.0008	4.2
		0.014	-0.005	-26.3	0.003	21.4
Sodium	0.20	0.206	0.006	3.0	0.005	2.4
		0.197	-0.003	-1.5	0.003	1.5
Potassium	0.051	0.049	-0.002	-3.9	0.002	4.1
		0.047	-0.004	-7.8	0.002	4.3
Ammonium	0.100	0.08	-0.02	-20.0	0.02	25.0
		0.10	0.00	0.0	0.01	10.0
Sulfate	2.5	2.523	0.023	0.9	0.016	0.6
		2.444	-0.056	-2.2	0.023	0.9
Nitrate	0.50	0.504	0.004	0.8	0.006	1.2
		0.491	-0.009	-1.8	0.006	1.2
Chloride	0.25	0.216	-0.034	-13.6	0.003	1.4
		0.212	-0.038	-15.2	0.003	1.4
pH[d]	4.29	4.33	0.04	0.9	0.02	0.5
		4.34	0.05	1.2	0.03	0.7
Hydrogen ion (µeq/L)	51.3	47.0	-4.3	-8.4	1.7	3.6
		46.4	-4.9	-9.6	3.3	7.1
Specific conductance[d] (µS/cm)	24	24.6	0.6	2.5	0.9	3.7
		24.8	0.8	3.3	0.6	2.4

Notes:

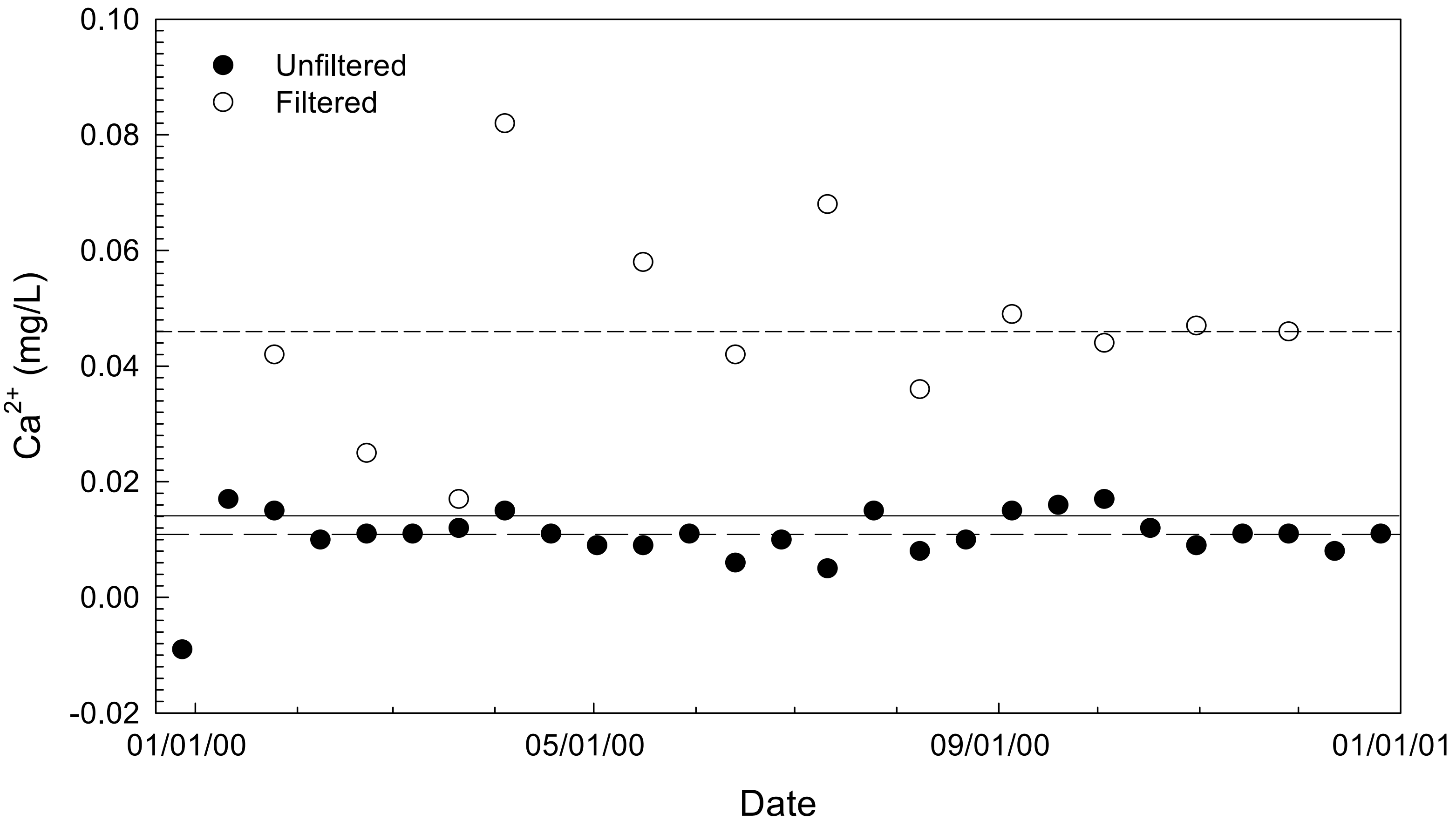
There were 26 unfiltered samples and 13 filtered samples in each set.

[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.

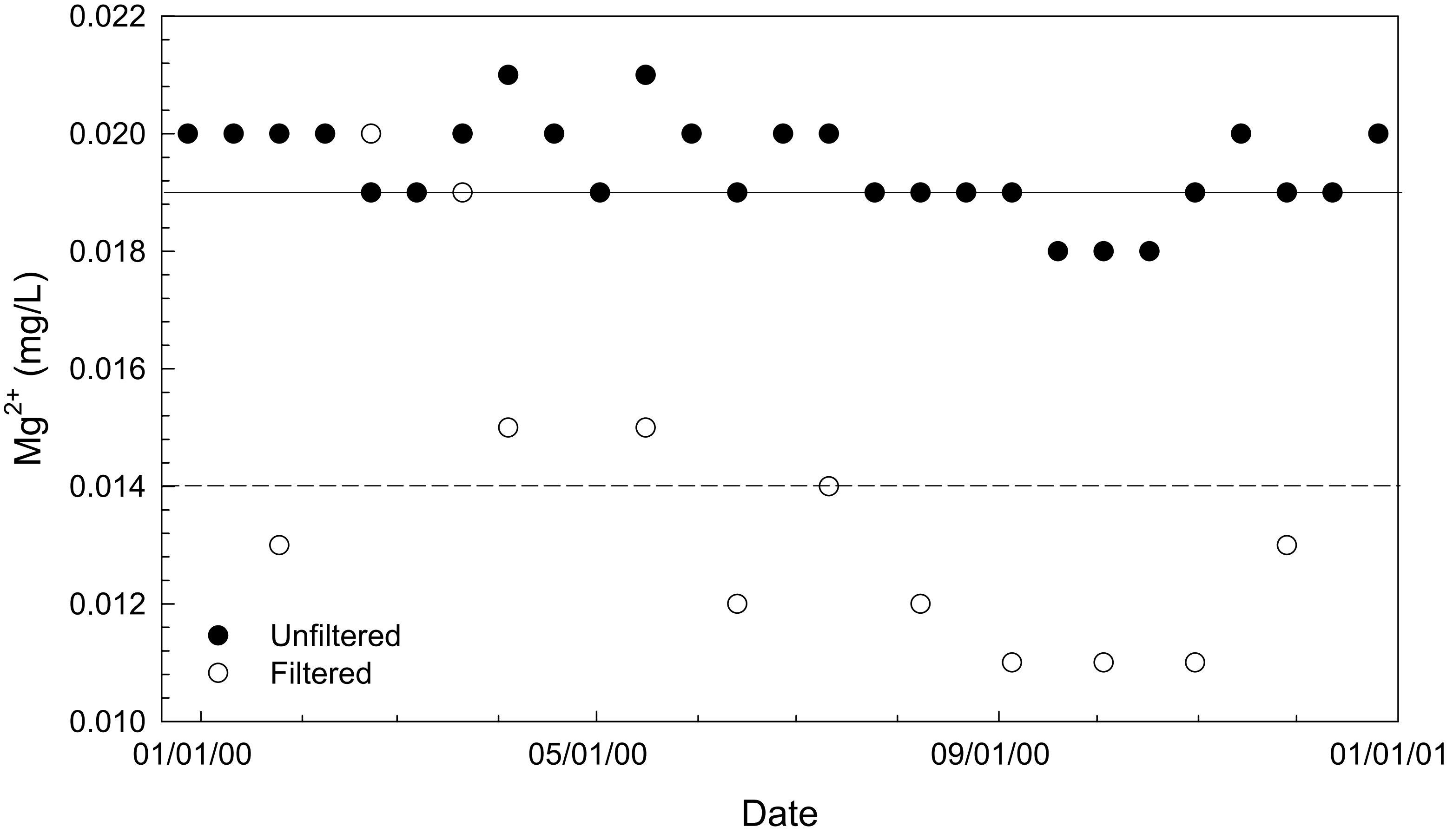
[c] The second set of values for each parameter is for filtered samples.

[d] Both pH and specific conductance are measured on unfiltered samples prior to filtering.



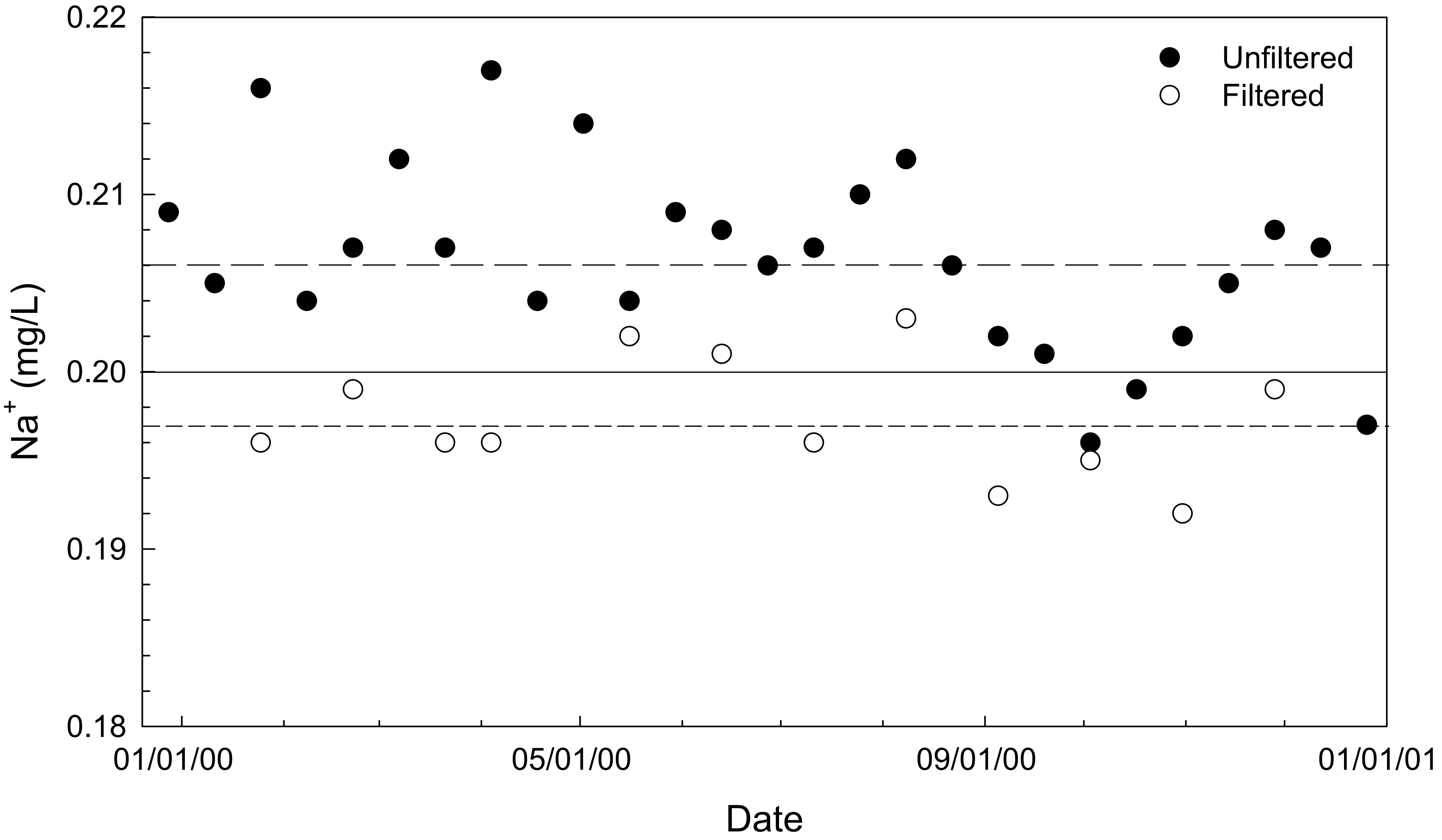
Note: Solid line denotes H-PS target Ca^{2+} concentration: 0.014 mg/L; long dashed line denotes mean unfiltered Ca^{2+} concentration: 0.011 mg/L; and short dashed line denotes mean filtered Ca^{2+} concentration: 0.046 mg/L.

Figure B-1. Comparison of filtered and unfiltered internal blind samples, (calcium), High-Purity Standards, SR1, 2000.



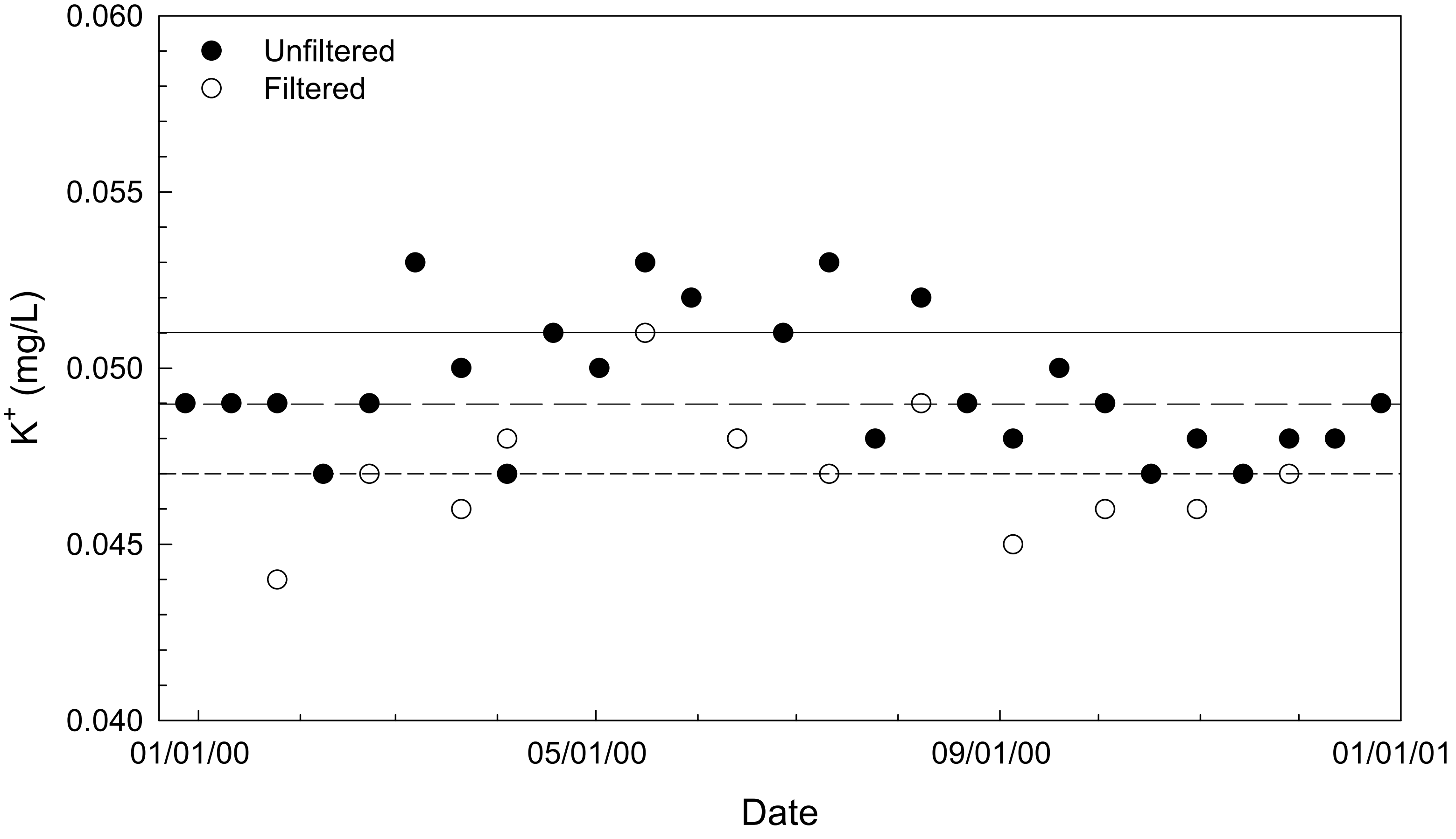
Note: Solid line denotes H-PS target and mean unfiltered Mg^{2+} concentration: 0.019 mg/L; and short dashed line denotes mean filtered Mg^{2+} concentration: 0.014 mg/L.

Figure B-2. Comparison of filtered and unfiltered internal blind samples, (magnesium), High-Purity Standards, SR1, 2000.



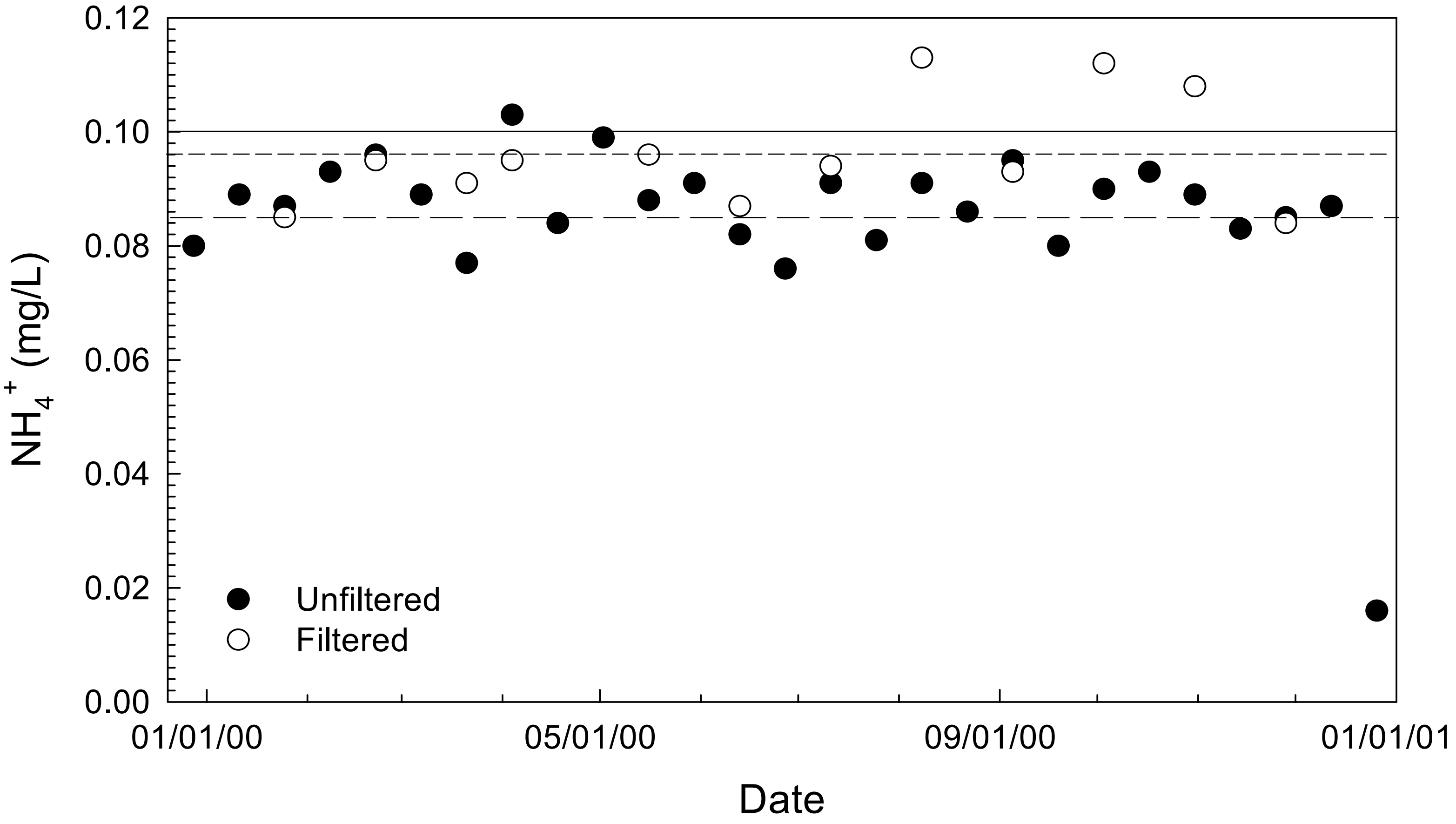
Note: Solid line denotes H-PS target Na$^+$ concentration: 0.20 mg/L; long dashed line denotes mean unfiltered Na$^+$ concentration: 0.206 mg/L; and short dashed line denotes mean filtered Na$^+$ concentration: 0.197 mg/L.

Figure B-3. Comparison of filtered and unfiltered internal blind samples, (sodium), High-Purity Standards, SR1, 2000.



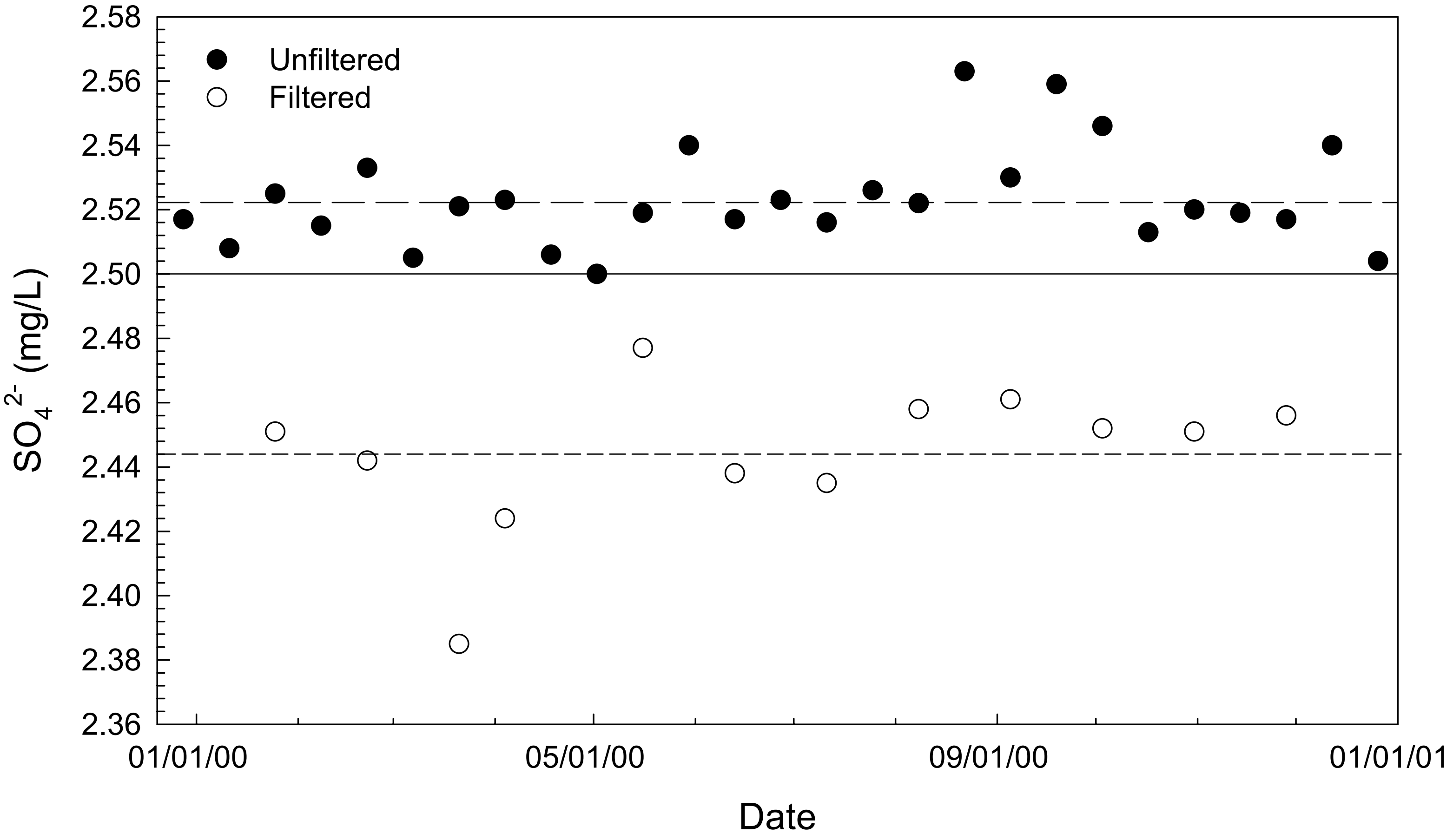
Note: Solid line denotes H-PS target K^+ concentration: 0.051 mg/L; long dashed line denotes mean unfiltered K^+ concentration: 0.049 mg/L; and short dashed line denotes mean filtered K^+ concentration: 0.047 mg/L.

Figure B-4. Comparison of filtered and unfiltered internal blind samples, (potassium), High-Purity Standards, SR1, 2000.



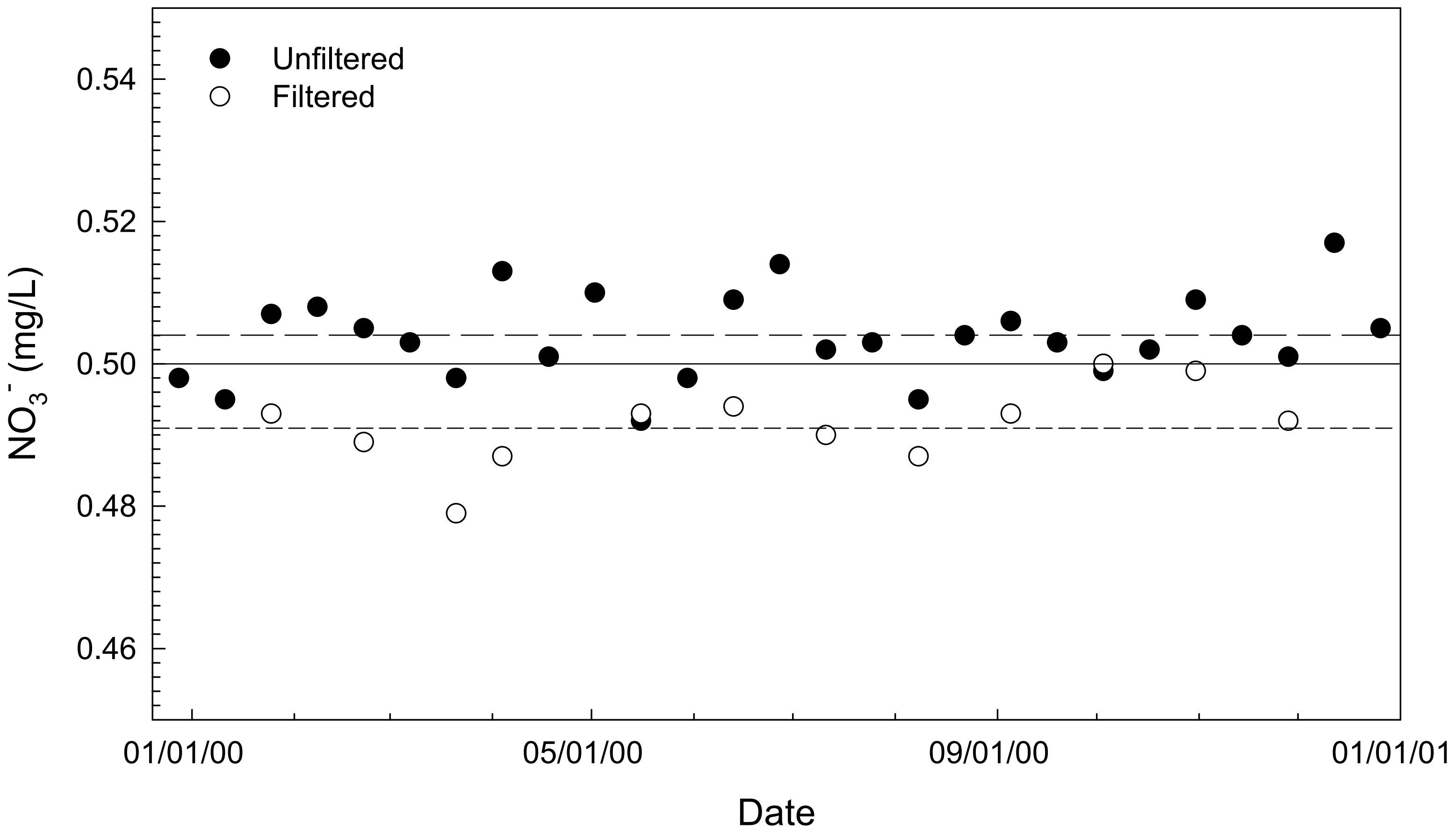
Note: Solid line denotes H-PS target NH_4^+ concentration: 0.100 mg/L; long dashed line denotes mean unfiltered NH_4^+ concentration: 0.085 mg/L; and short dashed line denotes mean filtered NH_4^+ concentration: 0.096 mg/L.

Figure B-5. Comparison of filtered and unfiltered internal blind samples, (ammonium), High-Purity Standards, SR1, 2000.



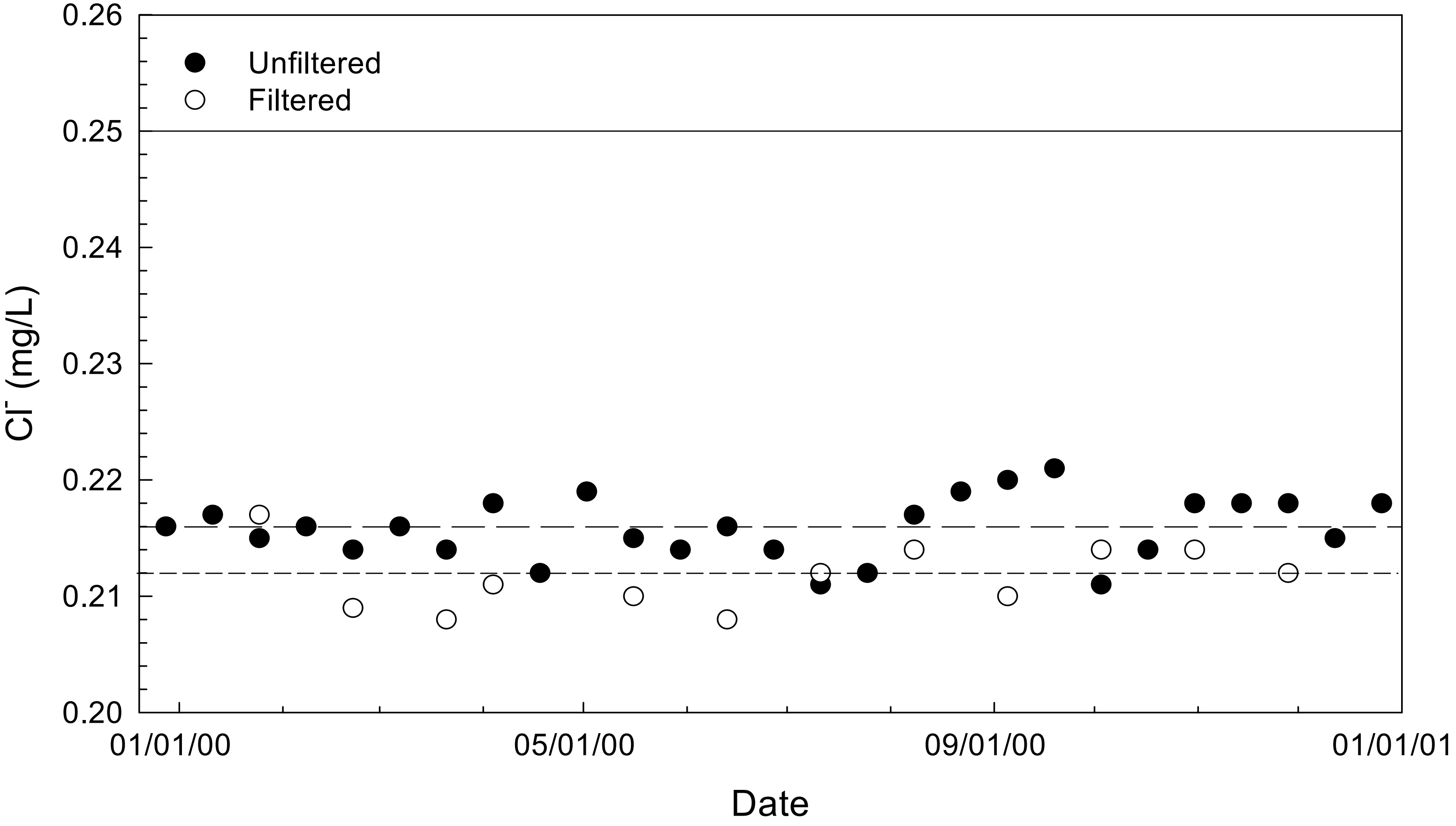
Note: Solid line denotes H-PS target SO_4^{2-} concentration: 2.5 mg/L; long dashed line denotes mean unfiltered SO_4^{2-} concentration: 2.523 mg/L; and short dashed line denotes mean filtered SO_4^{2-} concentration: 2.444 mg/L.

Figure B-6. Comparison of filtered and unfiltered internal blind samples, (sulfate), High-Purity Standards, SR1, 2000.



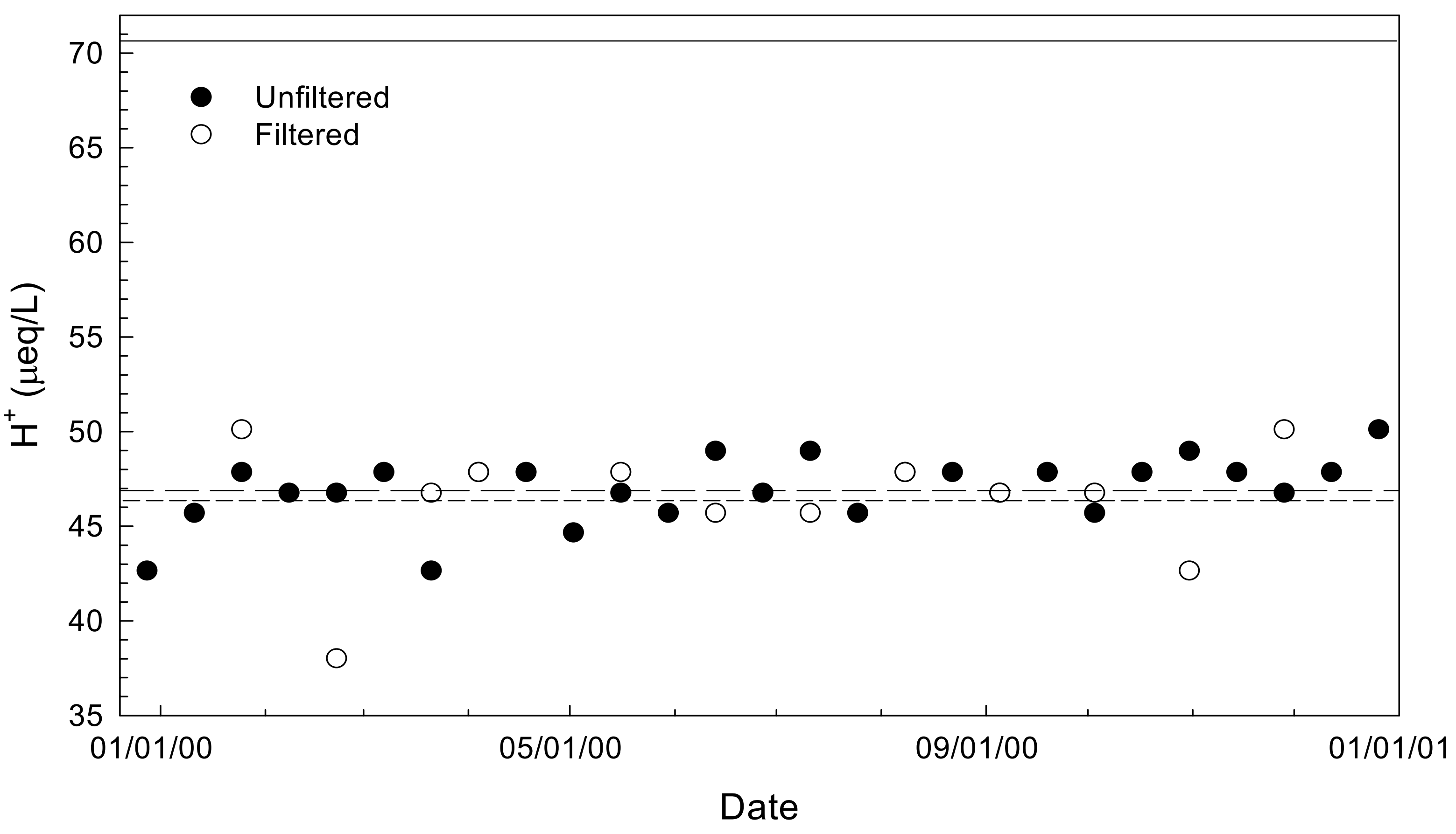
Note: Solid line denotes H-PS target NO_3^- concentration: 0.50 mg/L; long dashed line denotes mean unfiltered NO_3^- concentration: 0.504 mg/L; and short dashed line denotes mean filtered NO_3^- concentration: 0.491 mg/L.

Figure B-7. Comparison of filtered and unfiltered internal blind samples, (nitrate), High-Purity Standards, SR1, 2000.



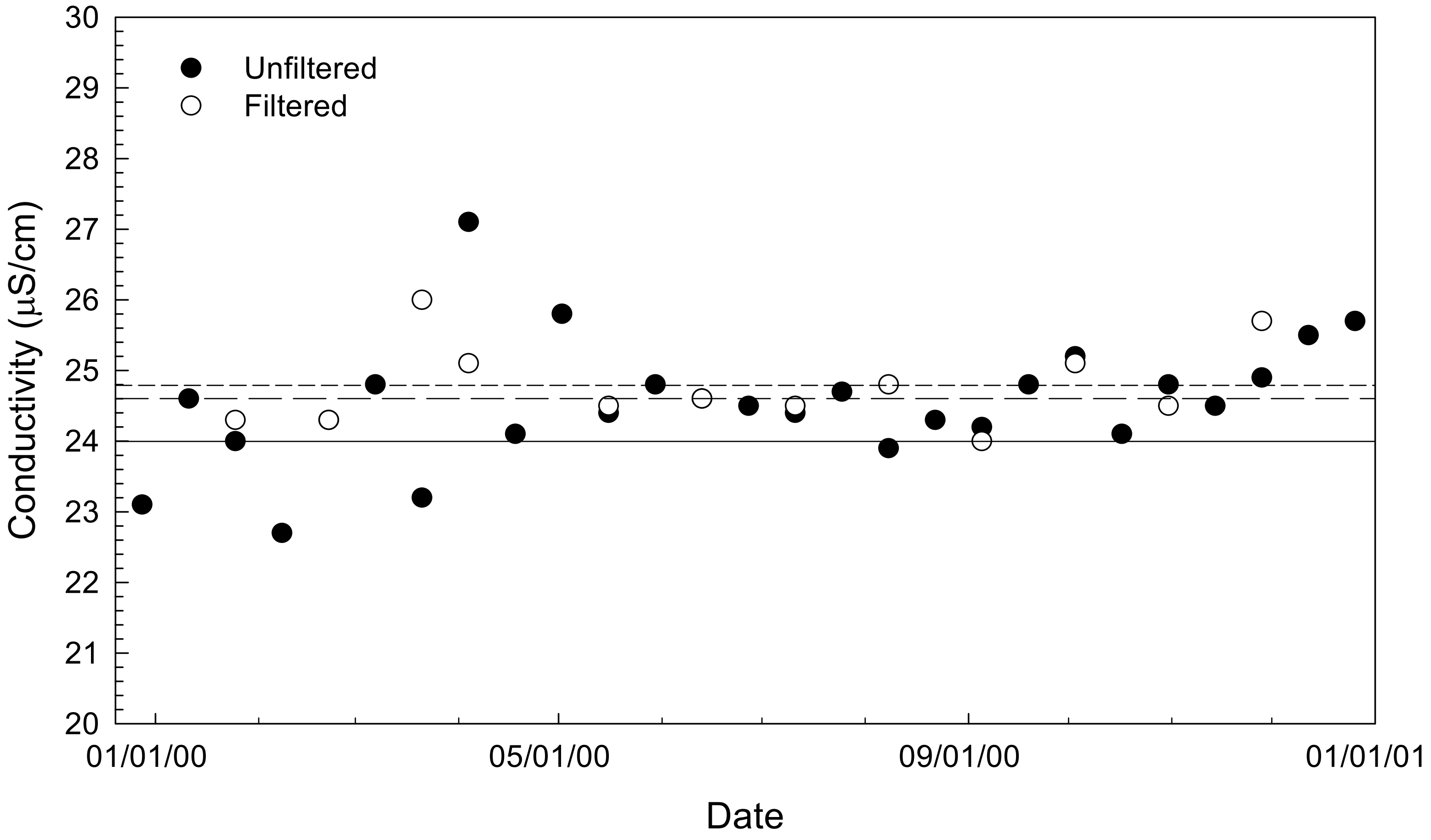
Note: Solid line denotes H-PS target Cl^- concentration: 0.25 mg/L; long dashed line denotes mean unfiltered Cl^- concentration: 0.216 mg/L; and short dashed line denotes mean filtered Cl^- concentration: 0.212 mg/L.

Figure B-8. Comparison of filtered and unfiltered internal blind samples, (chloride), High-Purity Standards, SR1, 2000.



Note: Solid line denotes H-PS target H^+ concentration: 70.8 µeq/L; long dashed line denotes mean unfiltered H^+ concentration: 47.0 µeq/L; and short dashed line denotes mean filtered H^+ concentration: 46.4 µeq/L.

Figure B-9. Comparison of filtered and unfiltered internal blind samples, (hydrogen ion), High-Purity Standards, SR1, 2000.



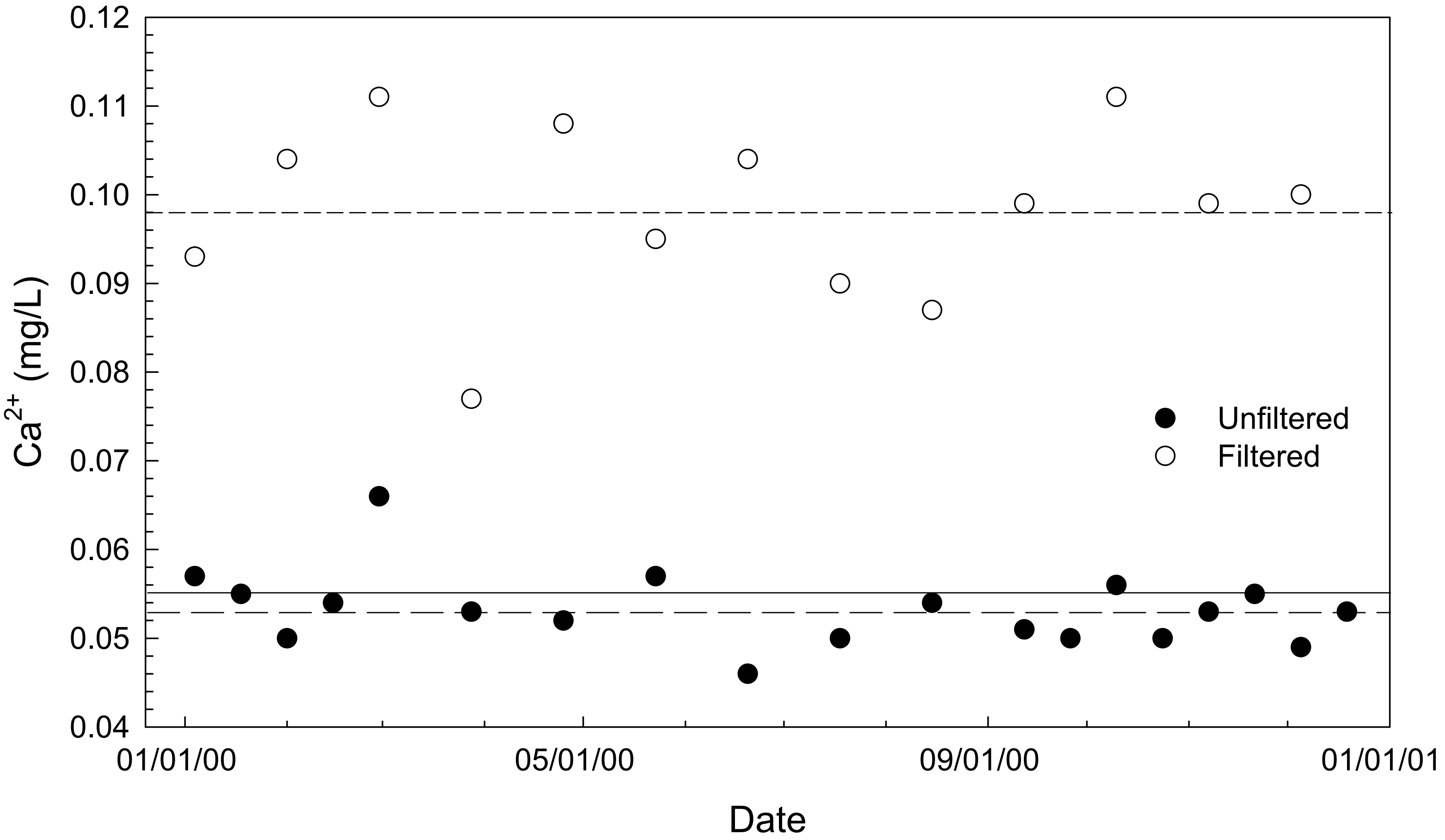
Note: Solid line denotes H-PS target conductivity: 24 µS/cm; long dashed line denotes mean unfiltered conductivity: 24.6 µS/cm; and short dashed line denotes mean filtered conductivity: 24.8 µS/cm.

Figure B-10. Comparison of filtered and unfiltered internal blind samples, (conductivity), High-Purity Standards, SR1, 2000.

Table B-2. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, High-Purity Standards Simulated Rainwater-2 (H-PS SR-2), 2000

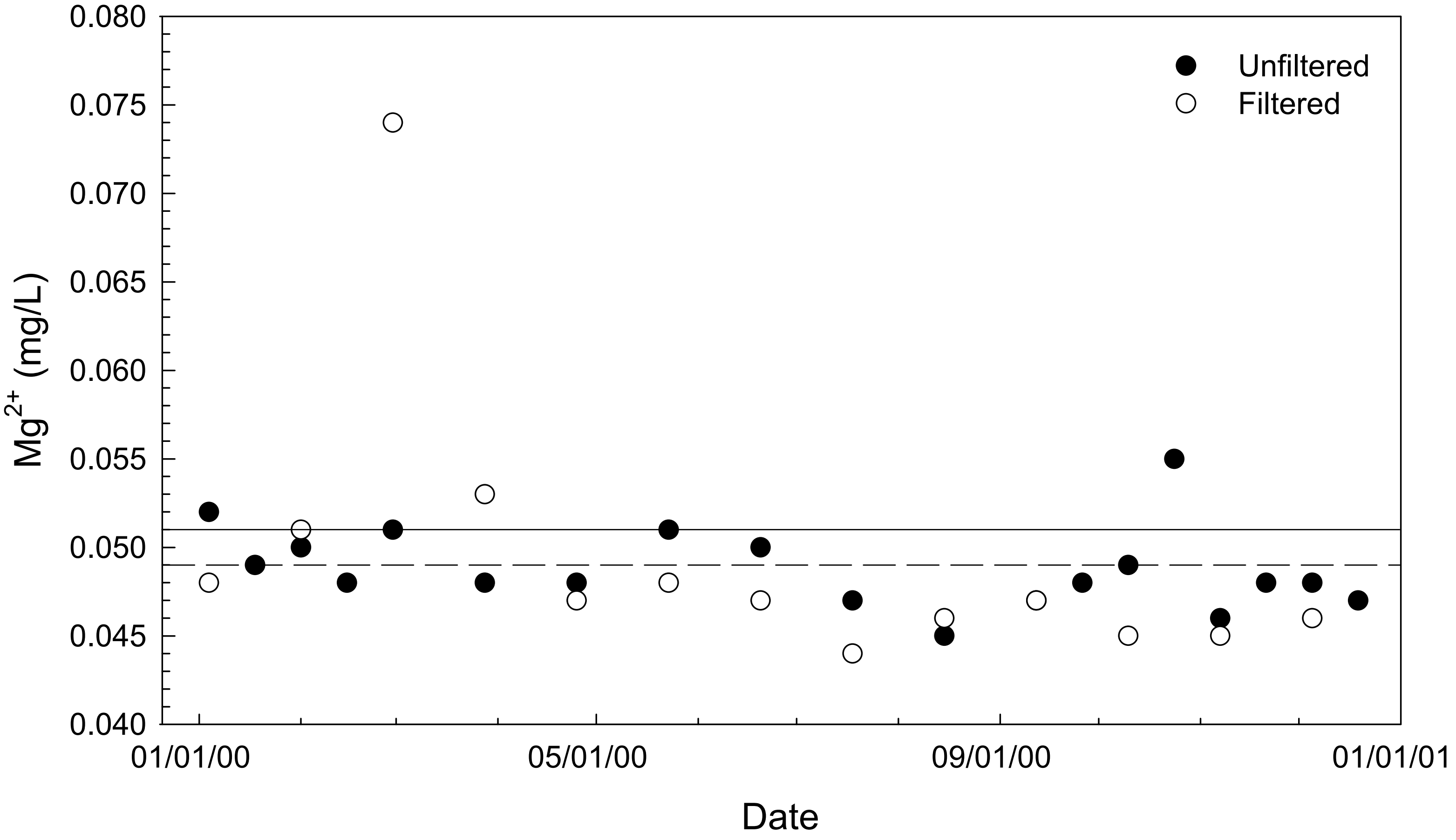
Parameter	*Target concentration[a] (mg/L)*	*Measured concentrations (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	0.055	0.053[b]	-0.002	-3.6	0.004	7.5
		0.098[c]	0.043	78.2	0.010	10.2
Magnesium	0.051	0.049	-0.002	-3.9	0.002	4.1
		0.049	-0.002	-3.9	0.008	16.3
Sodium	0.400	0.407	0.007	1.8	0.008	2.0
		0.395	-0.005	-1.2	0.008	2.0
Potassium	0.095	0.100	0.005	5.3	0.002	2.0
		0.098	0.003	3.2	0.004	4.1
Ammonium	1.00	0.92	-0.08	-8.0	0.04	4.3
		0.93	-0.07	-7.0	0.05	5.4
Sulfate	10.1	10.059	-0.041	-0.4	0.069	0.7
		9.685	-0.415	-4.1	0.063	0.7
Nitrate	7.0	7.071	0.071	1.0	0.050	0.7
		6.856	-0.144	-2.1	0.046	0.7
Chloride	0.98	0.993	0.013	1.3	0.010	1.0
		0.971	-0.009	-0.9	0.012	1.2
pH[d]	3.58	3.62	0.04	1.1	0.03	0.8
		3.62	0.04	1.1	0.02	0.6
Hydrogen ion (µeq/L)	263	240.8	-22.2	-8.4	13.6	5.6
		239.7	-23.3	-8.9	11.5	4.8
Specific conductance[d] (µS/cm)	122	125.2	3.2	2.6	2.0	1.6
		124.7	2.7	2.2	3.1	2.5

Notes:
There were 26 unfiltered samples and 13 filtered samples in each 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 specific conductance are measured on unfiltered samples prior to filtering.



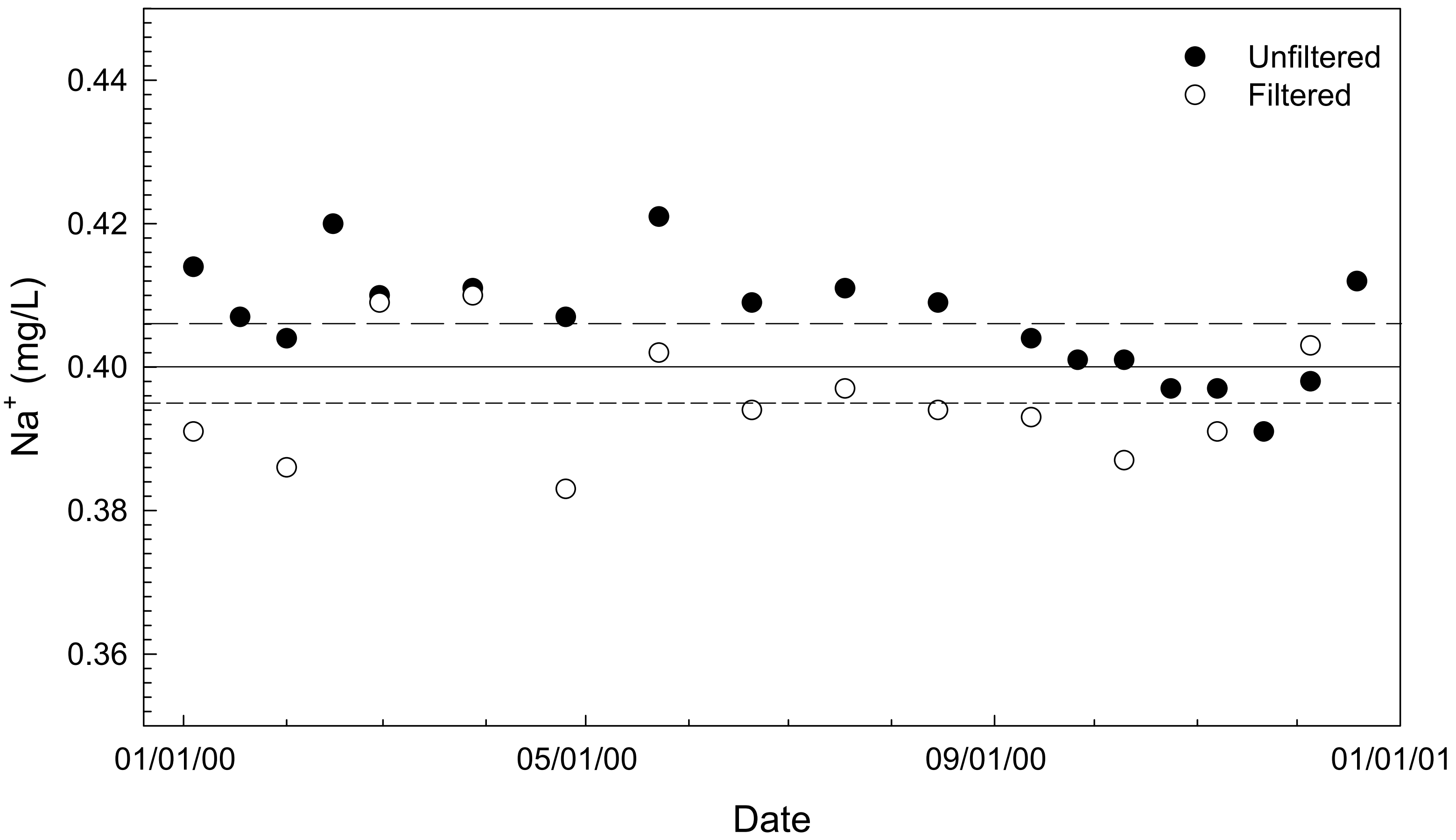
Note: Solid line denotes H-PS target Ca^{2+} concentration: 0.055 mg/L; long dashed line denotes mean unfiltered Ca^{2+} concentration: 0.053 mg/L; and short dashed line denotes mean filtered Ca^{2+} concentration: 0.098 mg/L.

Figure B-11. Comparison of filtered and unfiltered internal blind samples, (calcium), High-Purity Standards, SR2, 2000.



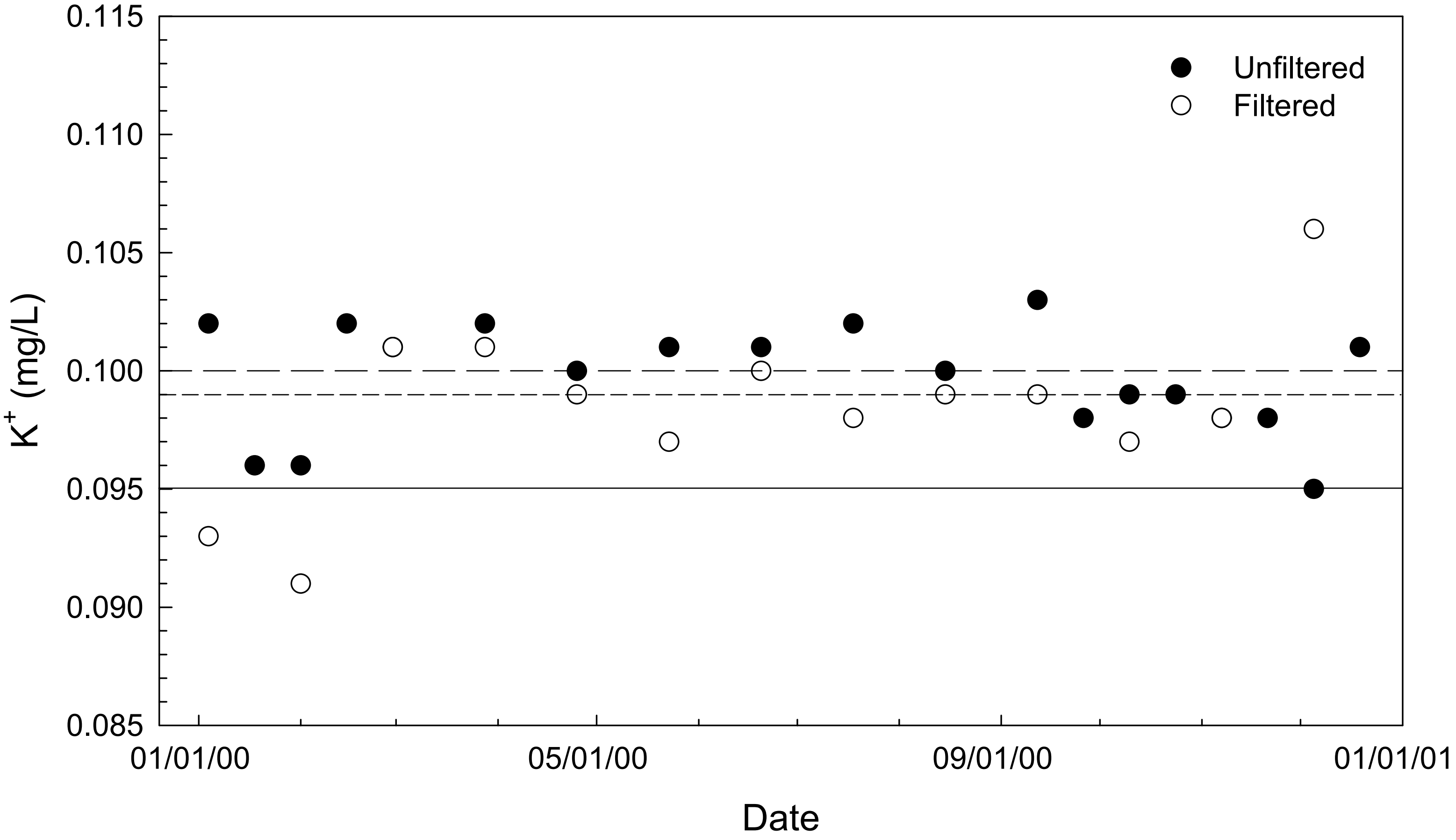
Note: Solid line denotes H-PS target Mg^{2+} concentration: 0.051mg/L; and dashed line denotes mean filtered and unfiltered Mg^{2+} concentration: 0.049 mg/L.

Figure B-12. Comparison of filtered and unfiltered internal blind samples, (magnesium), High-Purity Standards, SR2, 2000.



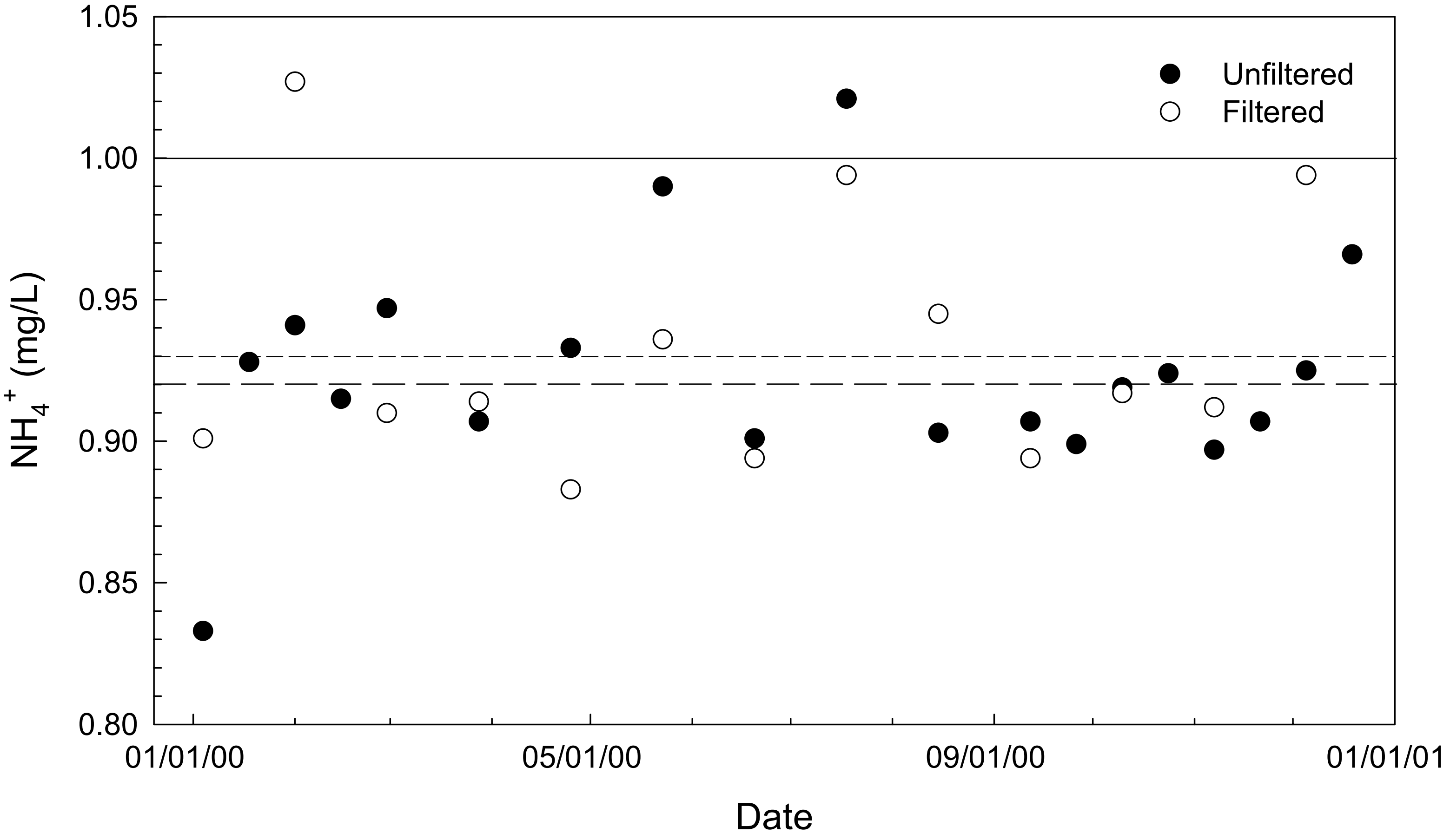
Note: Solid line denotes H-PS target Na^+ concentration: 0.40 mg/L; long dashed line denotes mean unfiltered Na^+ concentration: 0.406 mg/L; and short dashed line denotes mean filtered Na^+ concentration: 0.395 mg/L.

Figure B-13. Comparison of filtered and unfiltered internal blind samples, (sodium), High-Purity Standards, SR2, 2000.



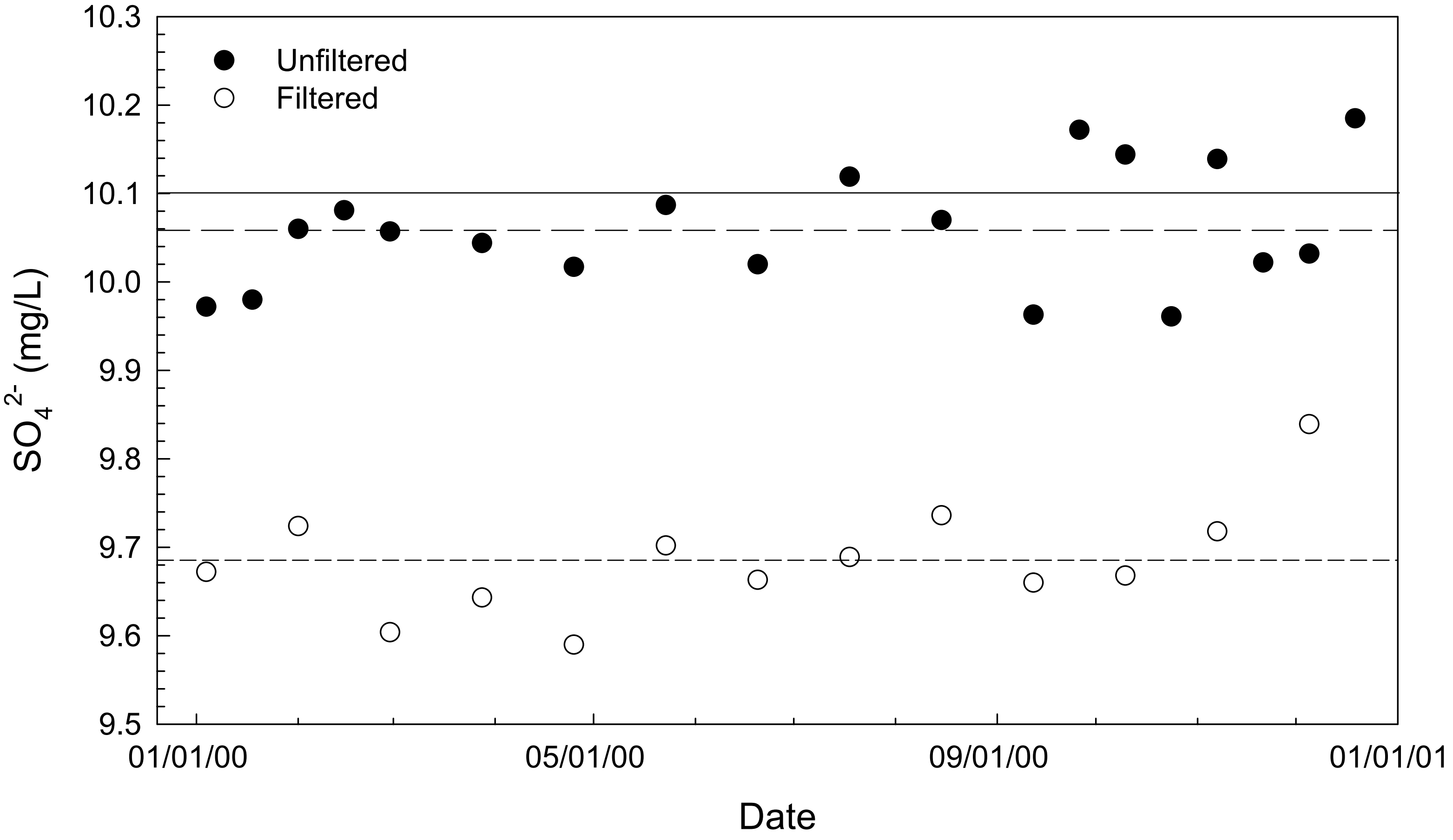
Note: Sold line denotes H-PS target K^+ concentration: 0.095 mg/L; long dashed line denotes mean unfiltered K^+ concentration: 0.100 mg/L; and short dashed line denotes mean filtered K^+ concentration: 0.098 mg/L.

Figure B-14. Comparison of filtered and unfiltered internal blind samples, (potassium), High-Purity Standards, SR2, 2000.



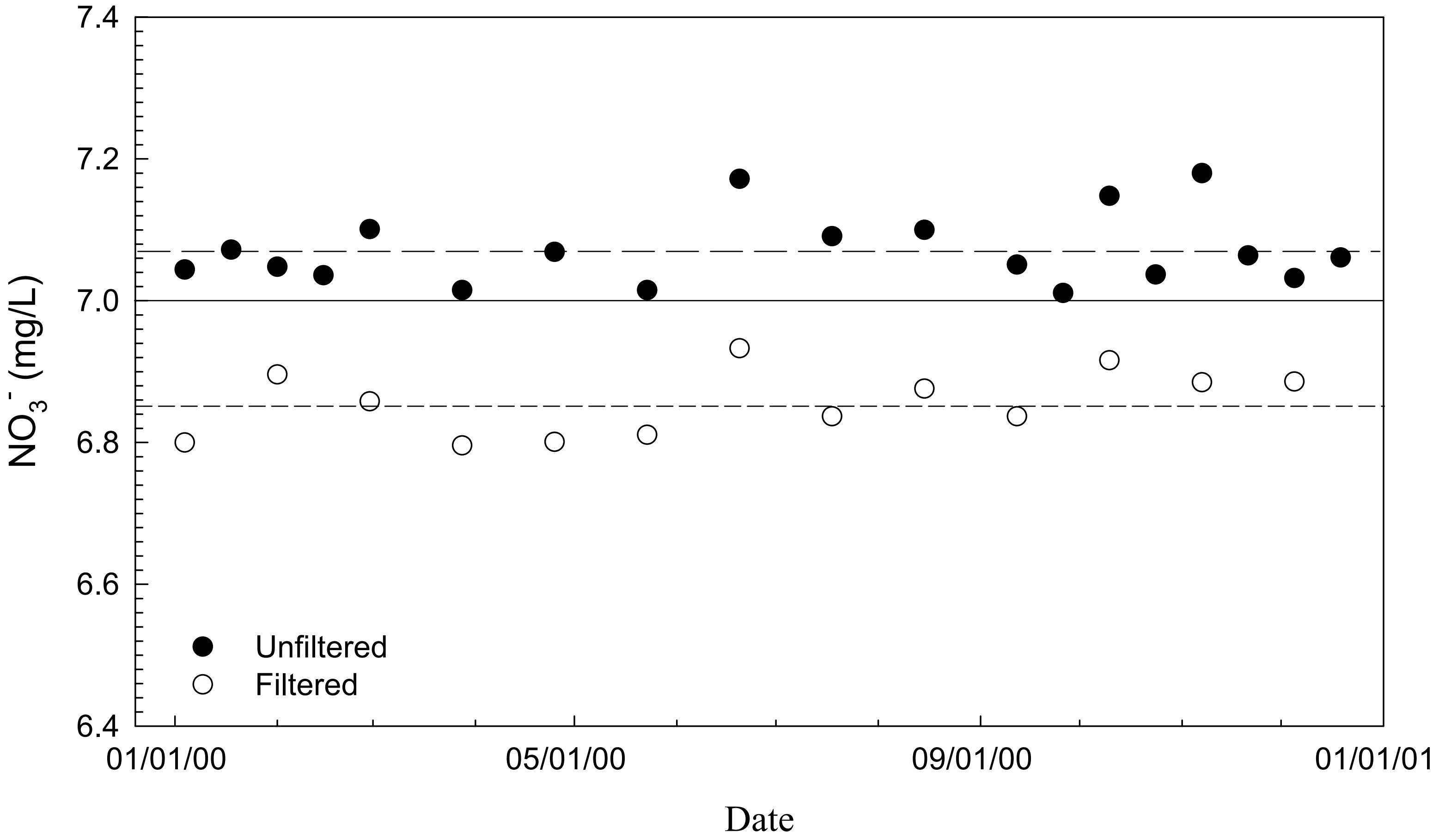
Note: Solid line denotes H-PS target NH_4^+ concentration: 1.00 mg/L; long dashed line denotes mean unfiltered NH_4^+ concentration: 0.92 mg/L; and short dashed line denotes mean filtered NH_4^+ concentration: 0.93 mg/L.

Figure B-15. Comparison of filtered and unfiltered internal blind samples, (ammonium), High-Purity Standards, SR2, 2000.



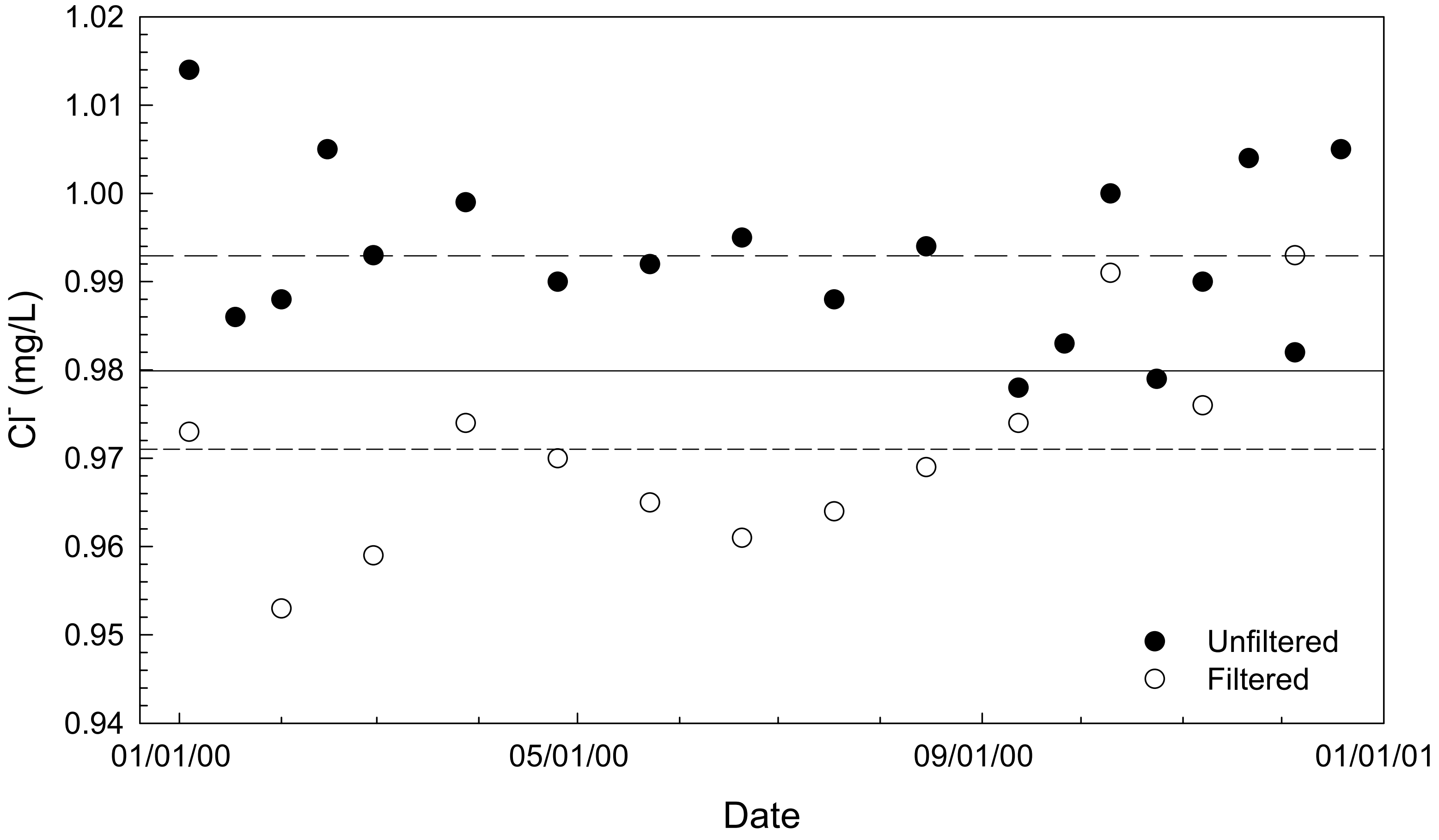
Note: Solid line denotes H-PS target SO_4^{2-} concentration: 10.1 mg/L; long dashed line denotes mean unfiltered SO_4^{2-} concentration: 10.059 mg/L; and short dashed line denotes mean filtered SO_4^{2-} concentration: 9.685 mg/L.

Figure B-16. Comparison of filtered and unfiltered internal blind samples, (sulfate), High-Purity Standards, SR2, 2000.



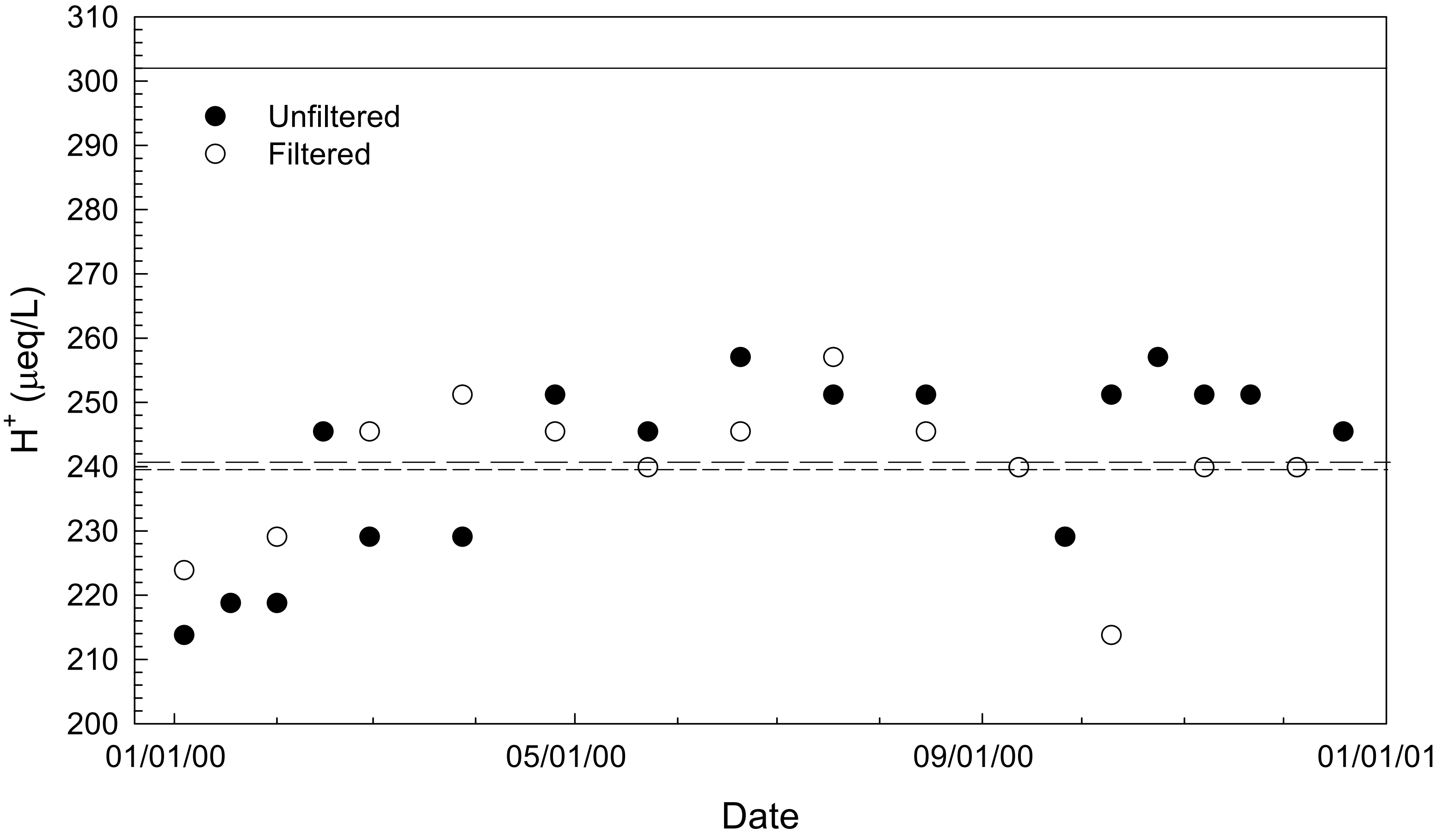
Note: Solid line denotes H-PS target NO_3^- concentration: 7.0 mg/L; long dashed line denotes mean unfiltered NO_3^- concentration: 7.071 mg/L; and short dashed line denotes mean filtered NO_3^- concentration: 6.856 mg/L.

Figure B-17. Comparison of filtered and unfiltered internal blind samples, (nitrate), High-Purity Standards, SR2, 2000.



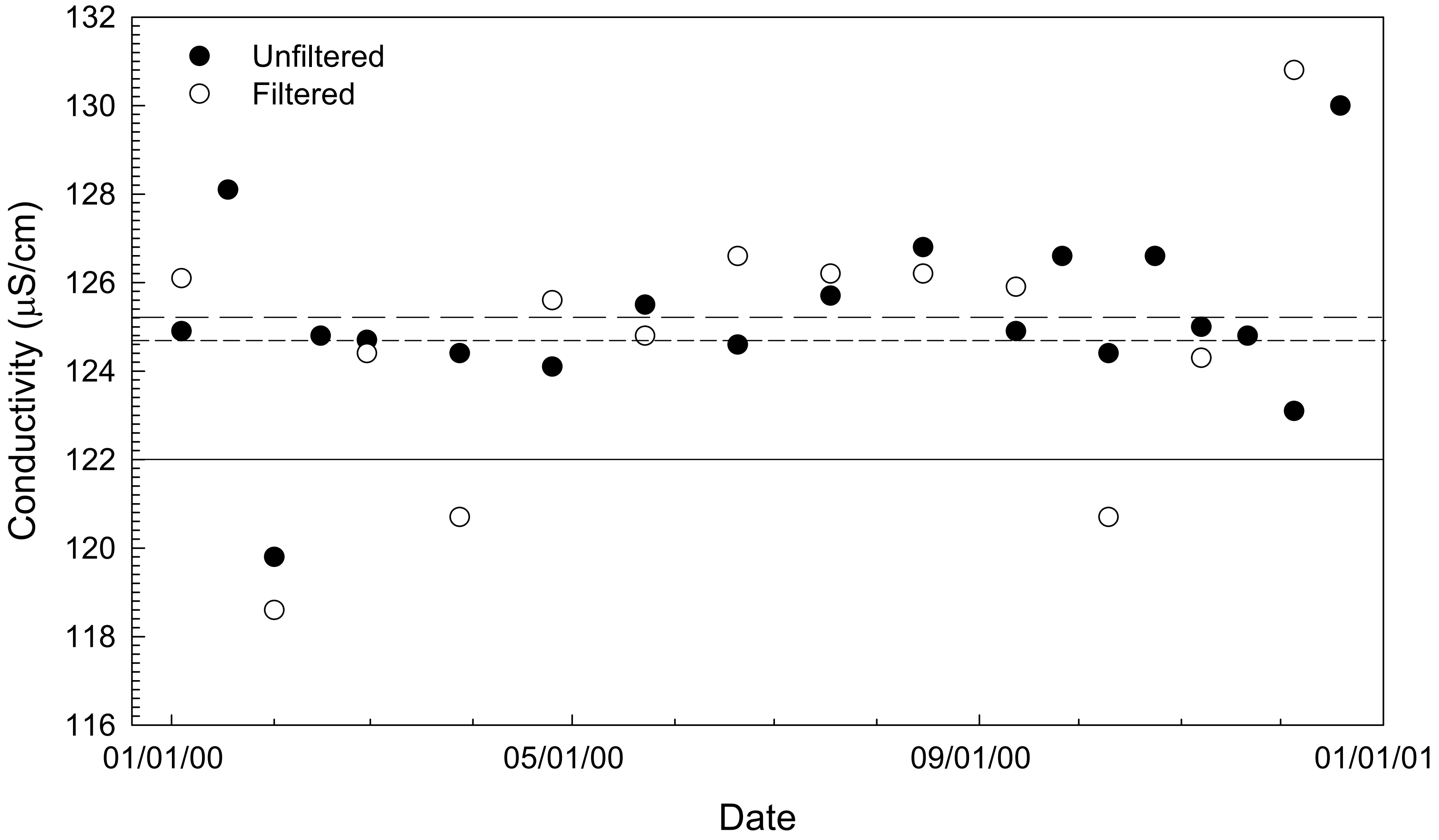
Note: Solid line denotes H-PS target Cl$^-$ concentration: 0.98 mg/L; long dashed line denotes mean unfiltered Cl$^-$ concentration: 0.993 mg/L; and short dashed line denotes mean filtered Cl$^-$ concentration: 0.971 mg/L.

Figure B-18. Comparison of filtered and unfiltered internal blind samples, (chloride), High-Purity Standards, SR2, 2000.



Note: Solid line denotes H-PS target H^+ concentration: 302 µeq/L; long dashed line denotes mean unfiltered H^+ concentration: 240.8 µeq/L; and short dashed line denotes mean filtered H^+ concentration: 239.7 µeq/L.

Figure B-19. Comparison of filtered and unfiltered internal blind samples, (hydrogen ion), High-Purity Standards, SR2, 2000.



Note: Solid line denotes H-PS target conductivity: 122 µS/cm; long dashed line denotes mean unfiltered conductivity: 125.2 µS/cm; and short dashed line denotes mean filtered conductivity: 124.7 µS/cm.

Figure B-20. Comparison of filtered and unfiltered internal blind samples, (conductivity), High-Purity Standards SR2, 2000.

Table B-3. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, Internally Formulated Simulated Rainwater (00FR10), 2000

Parameter	*Target concentration* [a] *(mg/L)*	*Measured concentrations (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	0.031	0.031[b]	0.000	0.0	0.003	9.7
		0.031[c]	0.000	0.0	0.013	41.9
Magnesium	0.007	0.007	0.000	0.0	0.0006	8.6
		0.005	-0.002	-28.6	0.001	20.0
Sodium	0.020	0.019	-0.001	-5.0	0.001	5.3
		0.019	-0.001	-5.0	0.001	5.3
Potassium	0.005	0.004	-0.001	-20.0	0.001	25.0
		0.005	0.000	0.0	0.001	20.0
Ammonium	0.03	0.03	0.00	0.0	0.01	33.3
		0.03	0.00	0.0	0.01	33.3
Sulfate	0.250	0.250	0.000	0.0	0.003	1.2
		0.246	-0.004	-1.6	0.004	1.6
Nitrate	0.190	0.190	0.000	0.0	0.003	1.6
		0.186	-0.004	-2.1	0.004	2.2
Chloride	0.052	0.062 (0.053) [d]	0.010 (0.001) [d]	19.2 (1.9) [d]	0.047 (0.002) [d]	75.8 (3.8) [d]
		0.053	0.001	1.9	0.002	3.8
pH [e]	5.23	5.23	0.00	0.0	0.04	0.8
		5.22	-0.01	-0.2	0.04	0.8
Hydrogen ion (µeq/L)	5.89	5.97	0.08	1.4	0.6	10.1
		6.03	0.14	2.4	0.6	10.0
Specific conductance [e] (µS/cm)	3.6	3.6	0.0	0.0	0.2	5.6
		3.8	0.2	5.6	0.5	13.2

Notes:

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

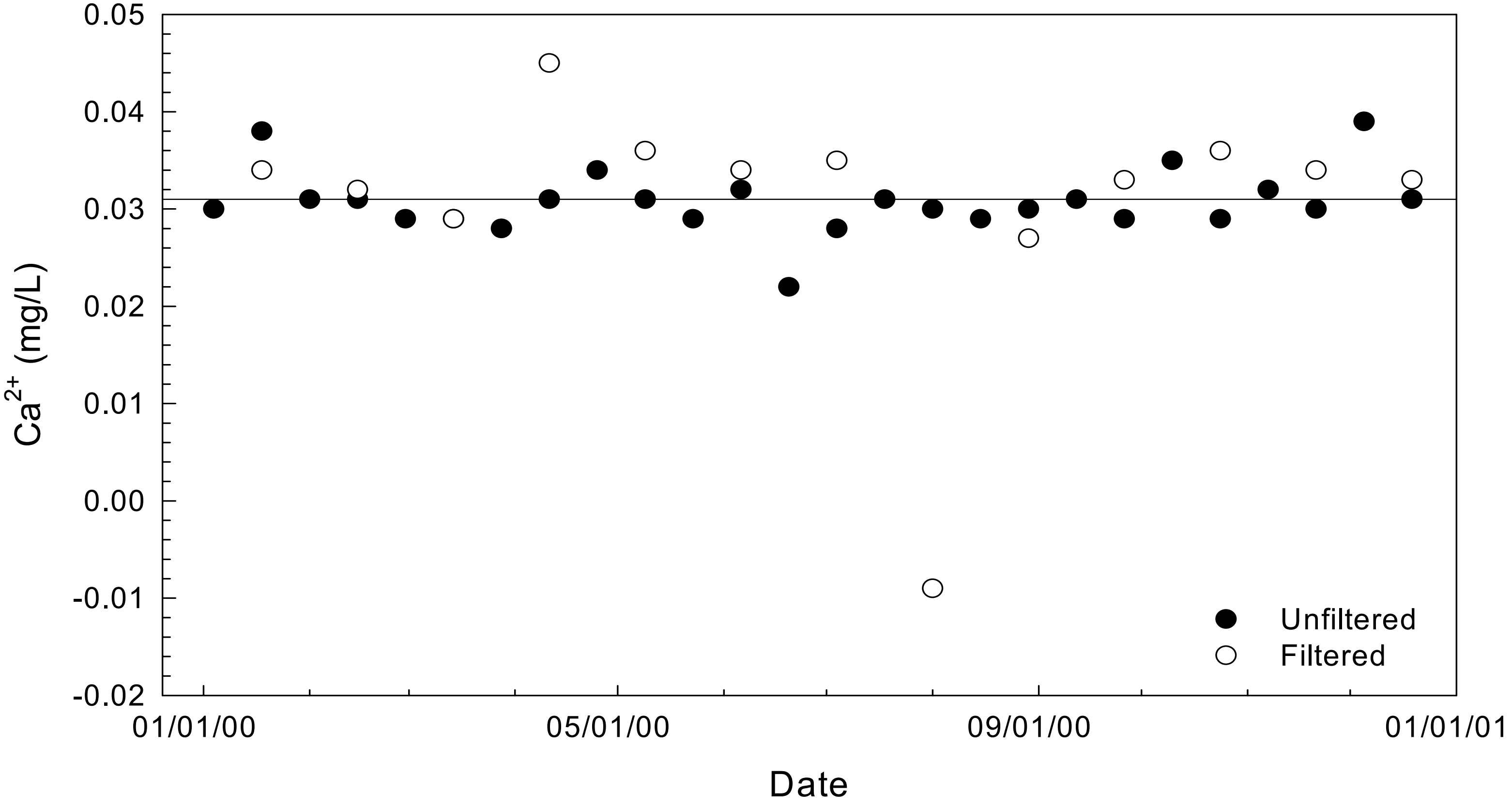
[a] Target values are the mean of 7-11 analyses done immediately after sample preparation.

[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.

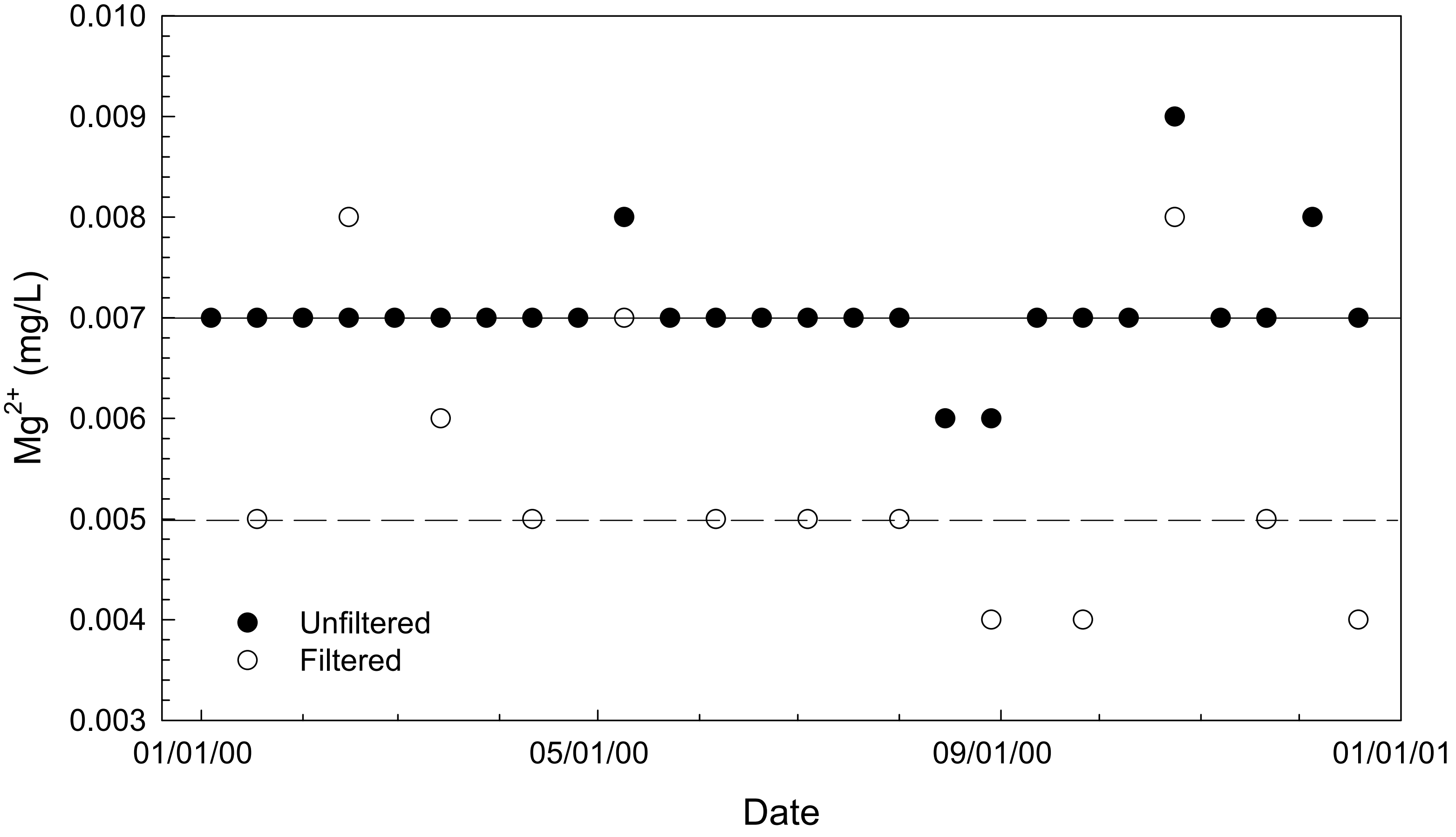
[d] Numbers in parentheses are calculated with the outlier excluded.

[e] Both pH and specific conductance are measured on unfiltered samples prior to filtering.



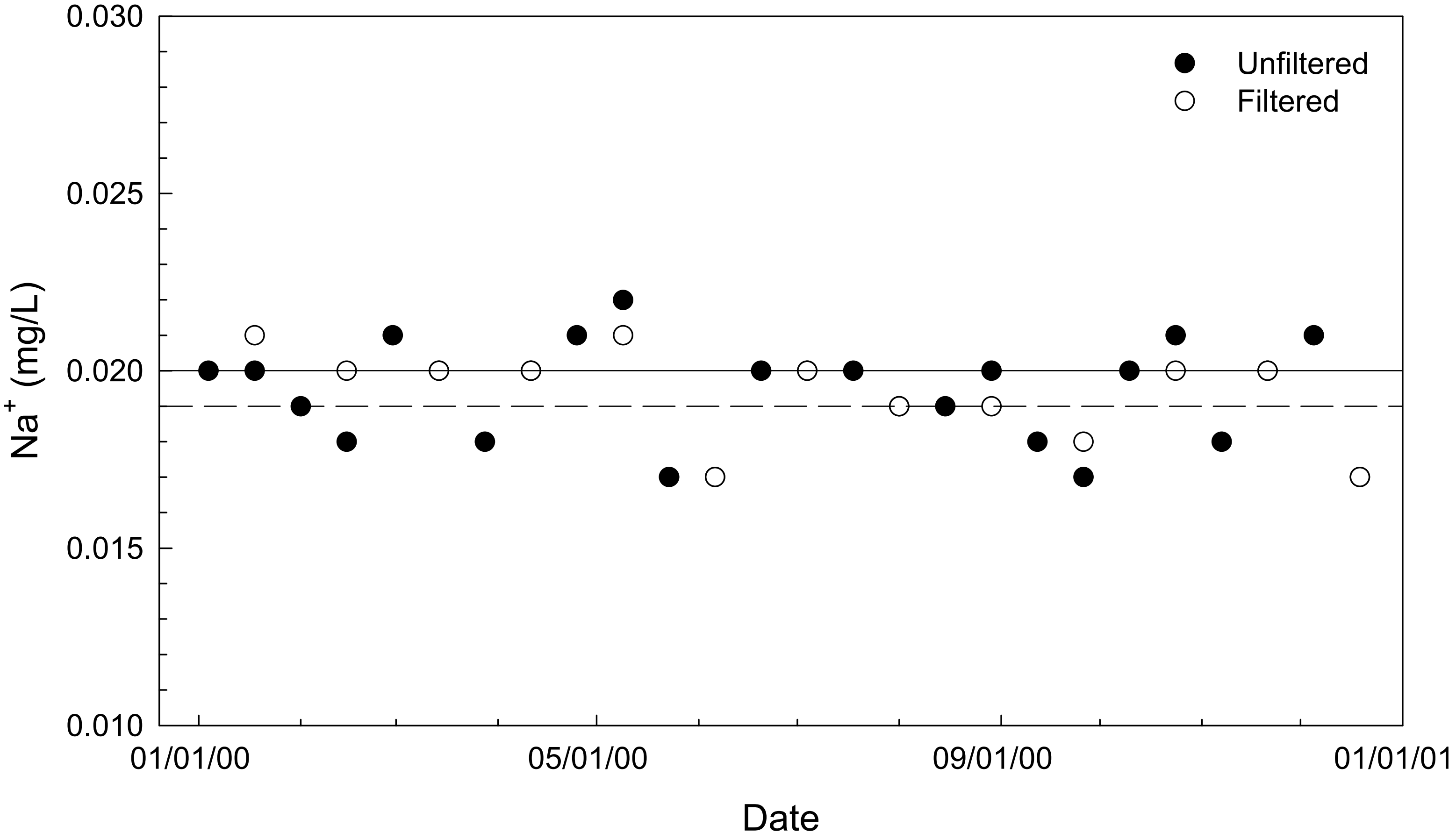
Note: Line denotes target, mean filtered, and mean unfiltered Ca^{2+} concentration: 0.031 mg/L.

Figure B-21. Comparison of filtered and unfiltered internal blind samples, (calcium), internally formulated simulated rainwater (00FR10), 2000.



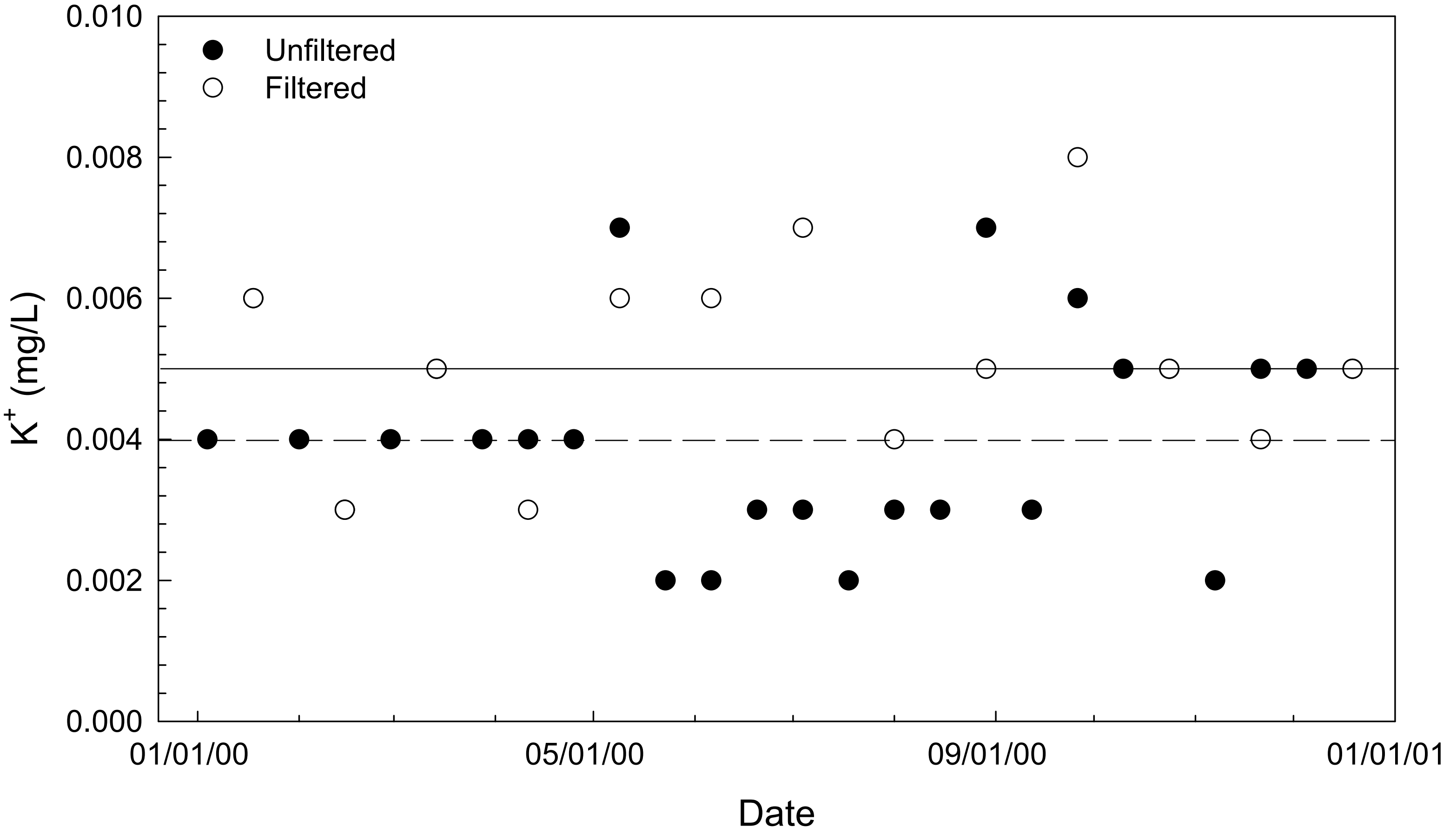
Note: Solid line denotes both target and mean unfiltered Mg^{2+} concentration: 0.007 mg/L; and long dashed line denotes mean filtered Mg^{2+} concentration: 0.005 mg/L.

Figure B-22. Comparison of filtered and unfiltered internal blind samples, (magnesium), internally formulated simulated rainwater (00FR10), 2000.



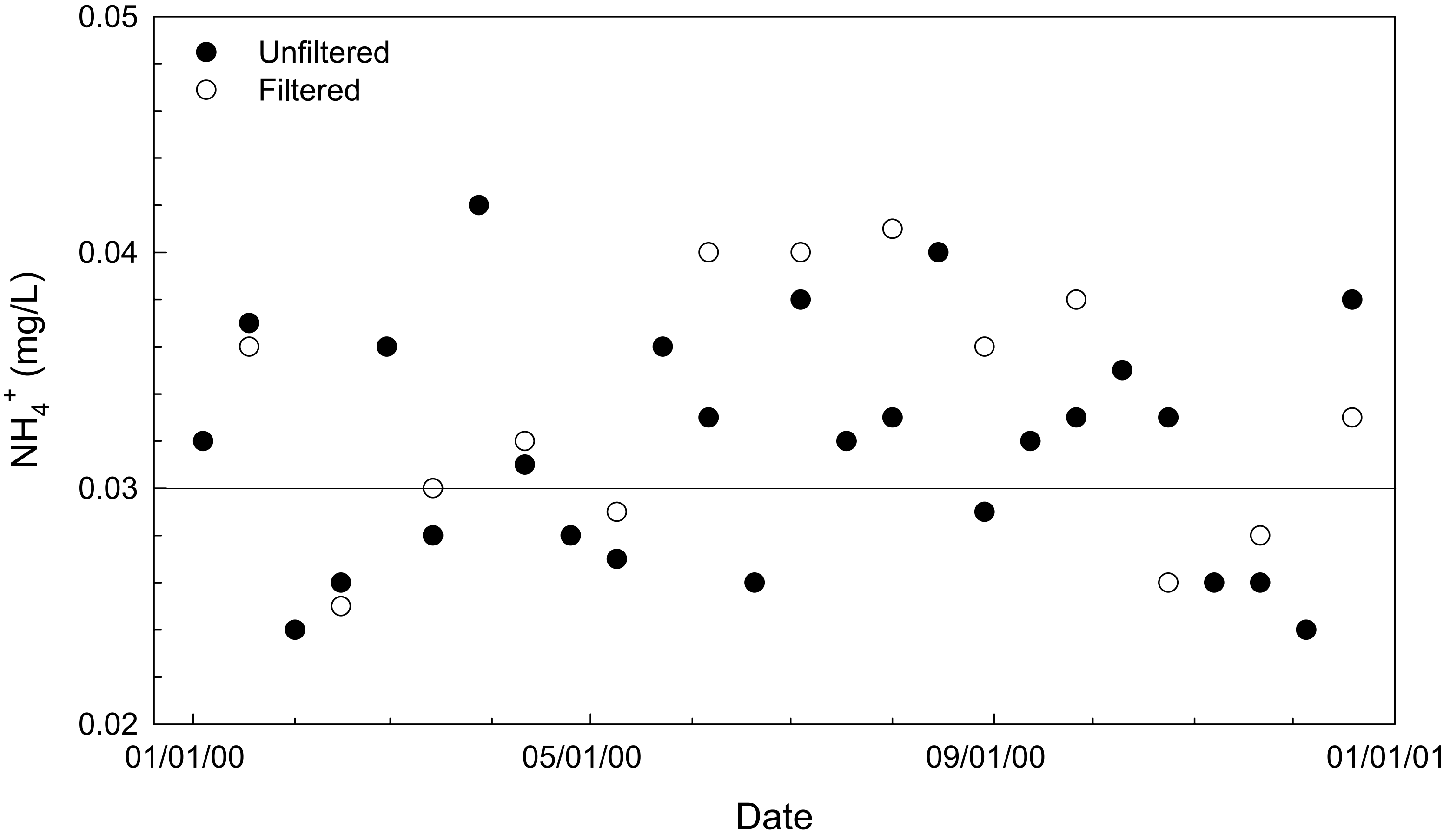
Note: Solid line denotes target Na^+ concentration: 0.020 mg/L; and long dashed line denotes mean filtered and mean unfiltered Na^+ concentration: 0.019 mg/L.

Figure B-23. Comparison of filtered and unfiltered internal blind samples, (sodium), internally formulated simulated rainwater (00FR10), 2000.



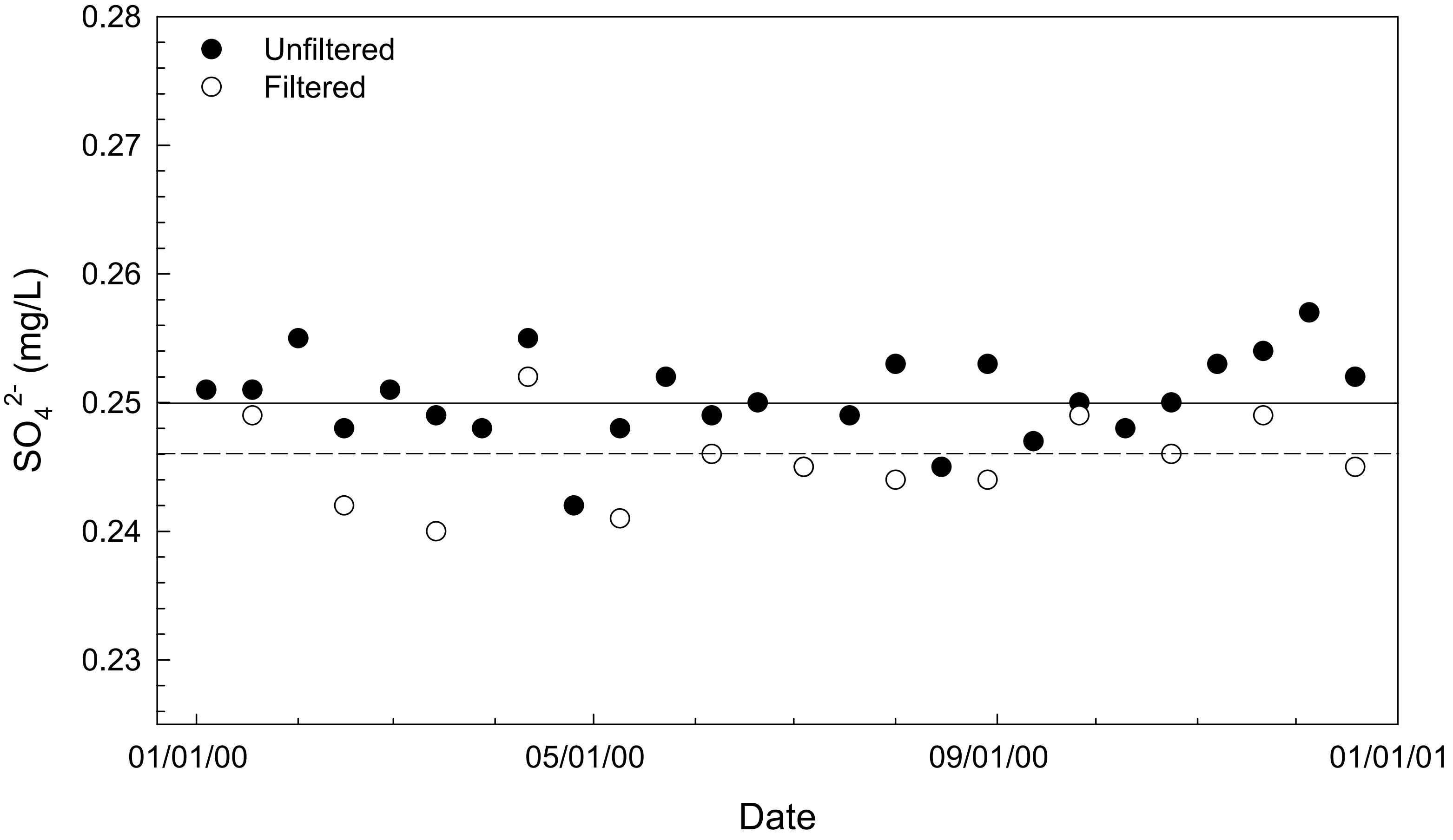
Note: Solid line denotes target and mean unfiltered K^+ concentration: 0.005 mg/L; and long dashed line denotes mean filtered K^+ concentration: 0.004 mg/L.

Figure B-24. Comparison of filtered and unfiltered internal blind samples, (potassium), internally formulated simulated rainwater (00FR10), 2000.



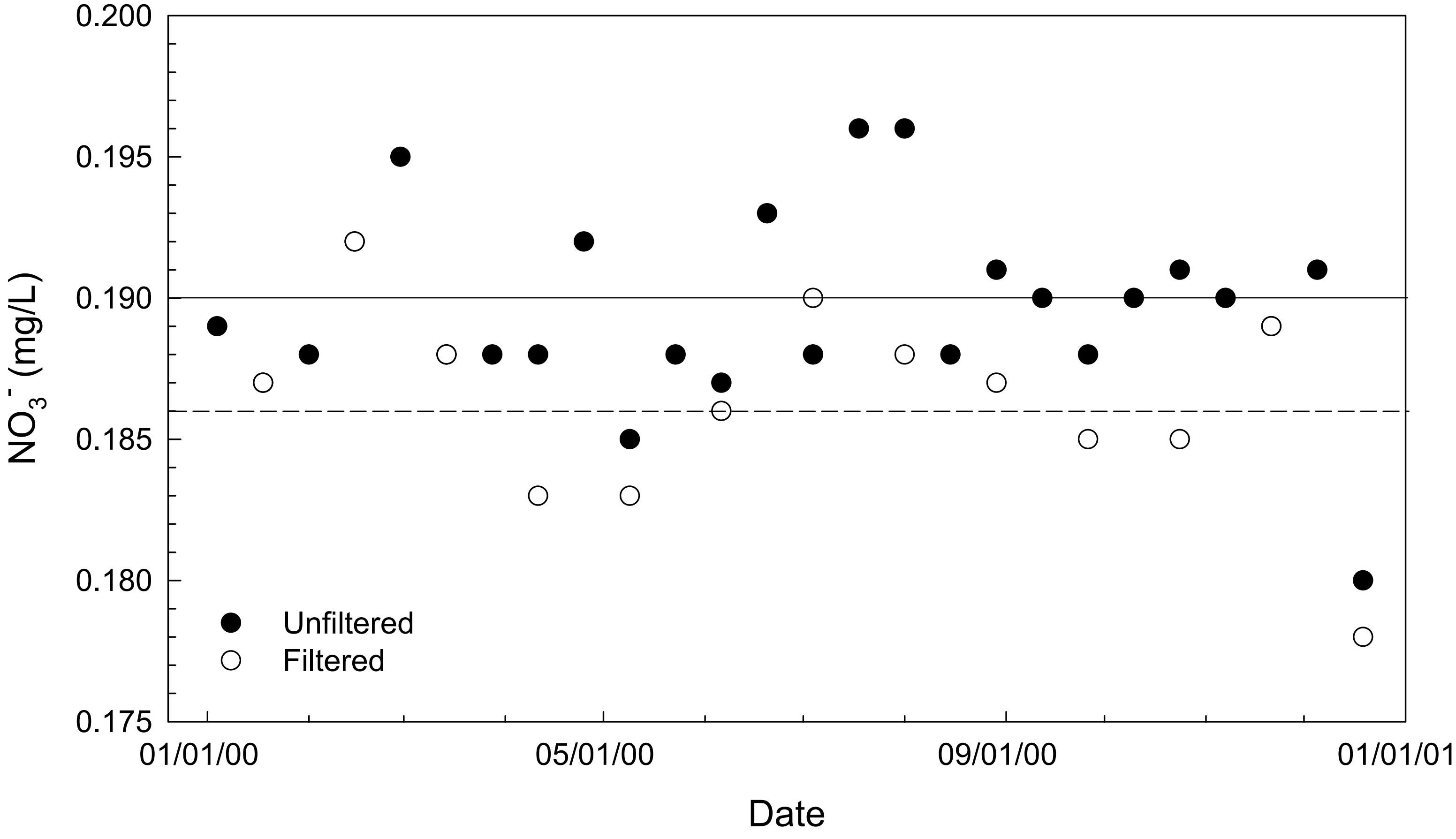
Note: Solid line denotes target, mean unfiltered, and mean filtered NH_4^+ concentration: 0.03 mg/L.

Figure B-25. Comparison of filtered and unfiltered internal blind samples, (ammonium), internally formulated simulated rainwater (00FR10), 2000.



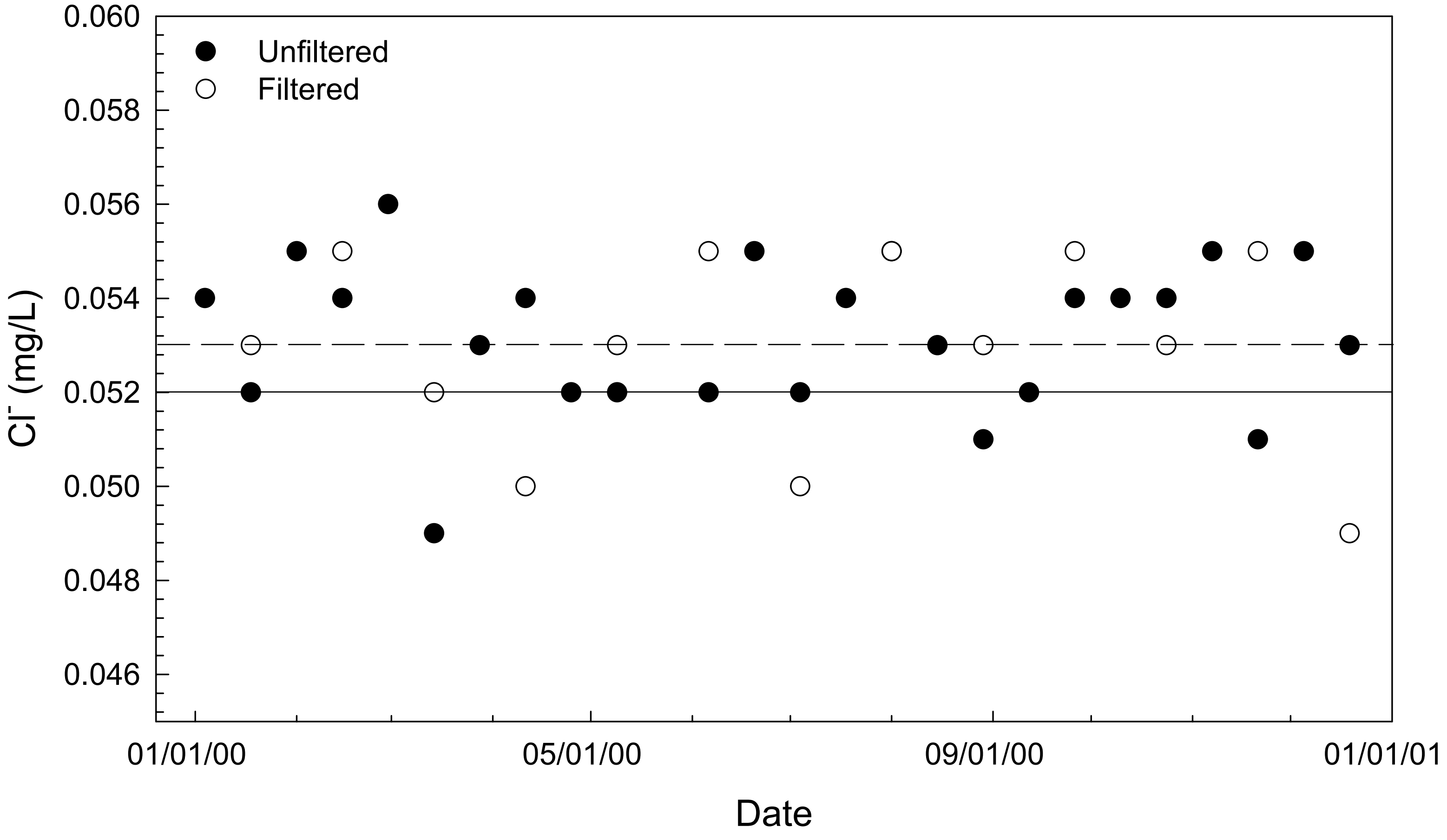
Note: Solid line denotes target and mean unfiltered SO_4^{2-} concentration: 0.250 mg/L; and short dashed line denotes mean filtered SO_4^{2-} concentration: 0.246 mg/L.

Figure B-26. Comparison of filtered and unfiltered internal blind samples, (sulfate), internally formulated simulated rainwater (00FR10), 2000.



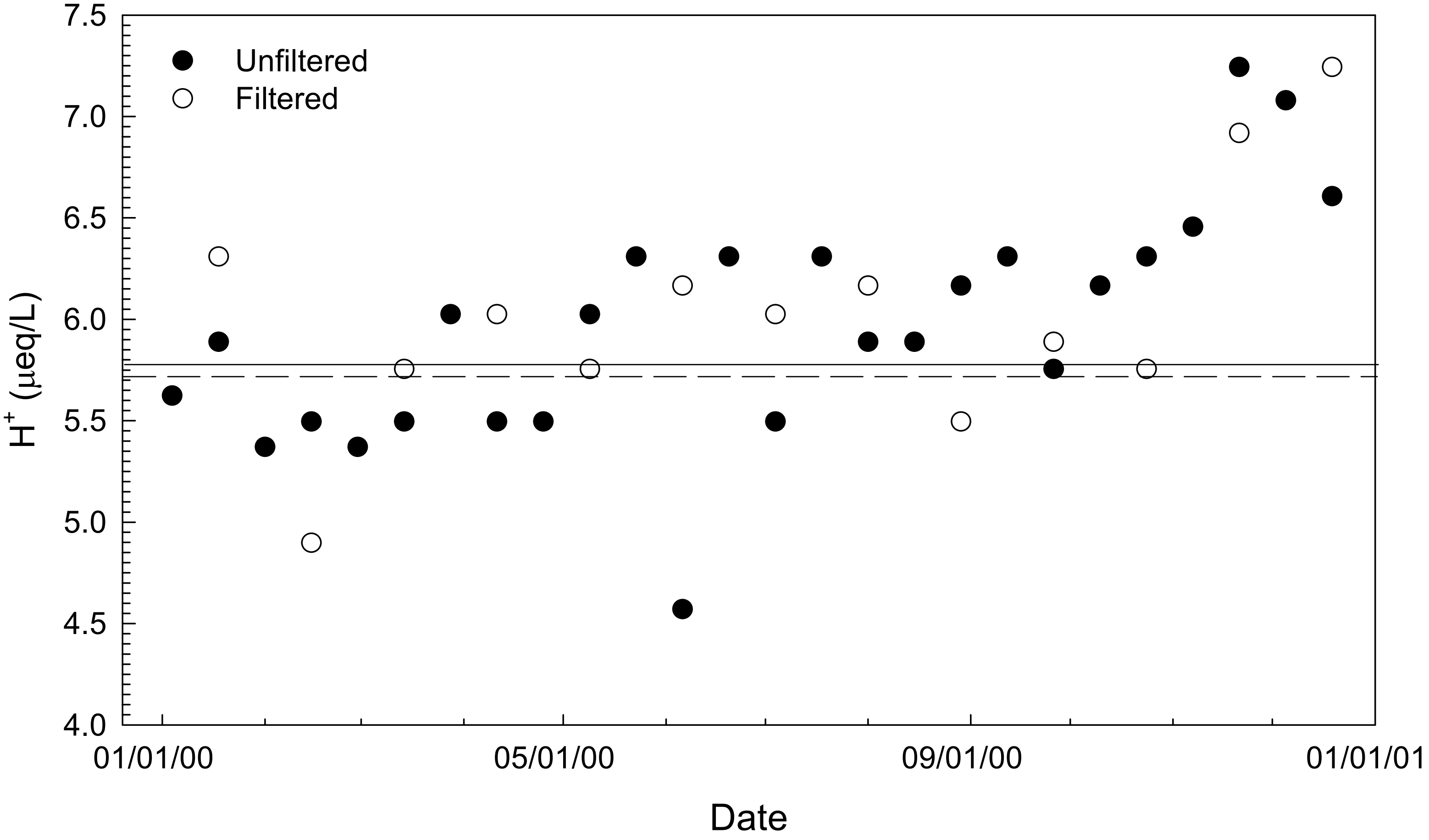
Note: Solid line denotes target and mean unfiltered NO$_3^-$ concentration: 0.190 mg/L; and short dashed line denotes mean filtered NO$_3^-$ concentration: 0.186 mg/L.

Figure B-27. Comparison of filtered and unfiltered internal blind samples, (nitrate), internally formulated simulated rainwater (00FR10), 2000.



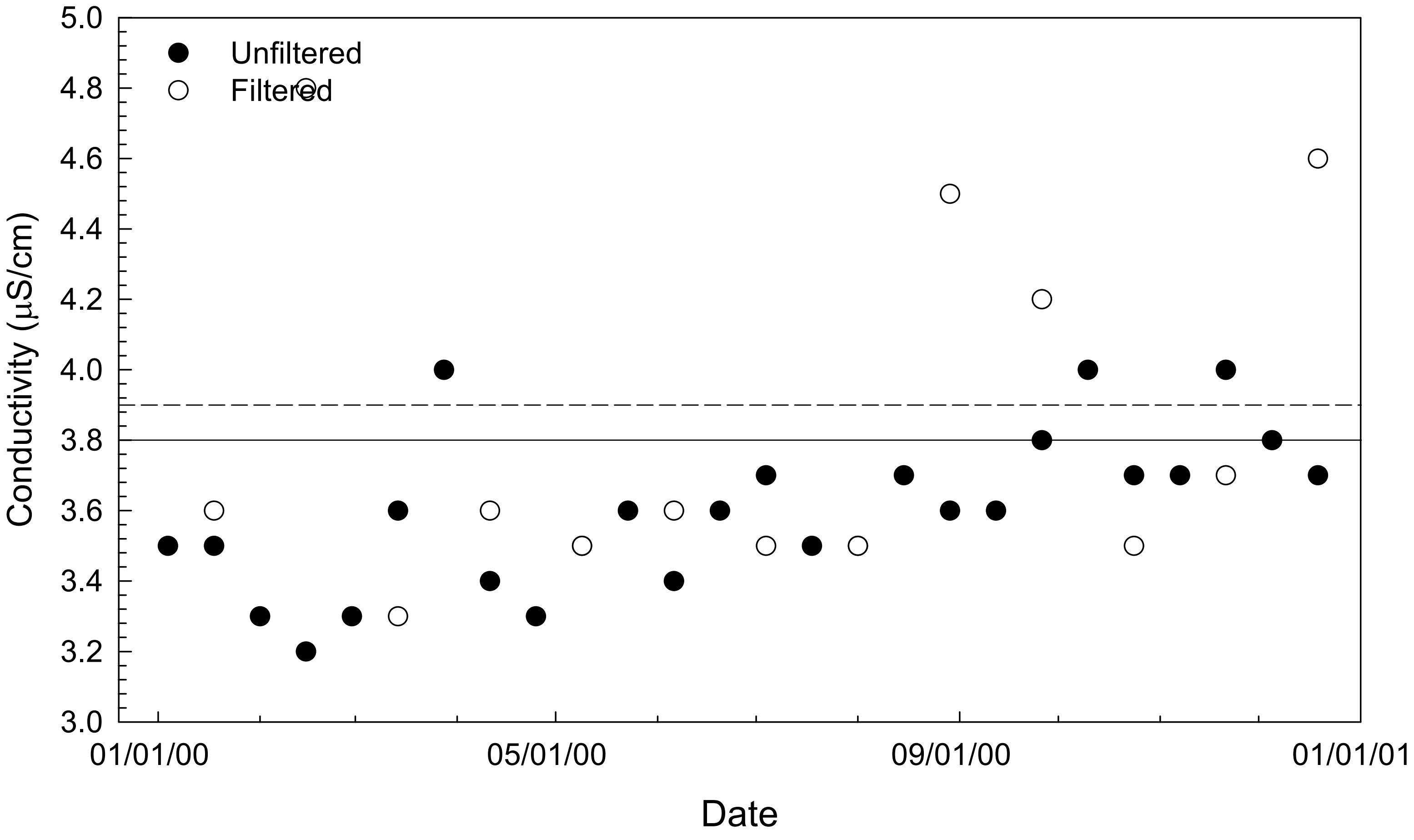
Note: Solid line denotes target Cl$^-$ concentration: 0.052 mg/L; and long dashed line denotes mean unfiltered and filtered Cl$^-$ concentration: 0.053 mg/L.

Figure B-28. Comparison of filtered and unfiltered internal blind samples, (chloride), internally formulated simulated rainwater (00FR10), 2000.



Note: Solid line denotes target and mean filtered H^+ concentration: 6.03 µeq/L; and long dashed line denotes mean unfiltered H^+ concentration: 5.97 µeq/L.

Figure B-29. Comparison of filtered and unfiltered internal blind samples, (hydrogen ion), internally formulated simulated rainwater (00FR10), 2000.



Note: Solid line denotes target and mean unfiltered conductvity: 3.6 μS/cm; and short dashed line denotes mean filtered conductivity: 3.8 μS/cm.

Figure B-30. Comparison of filtered and unfiltered internal blind samples, (conductivity), internally formulated simulated rainwater (00FR10), 2000.

Table B-4. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, Deionized Water, 2000

Parameter	*Target concentration [a] (mg/L)*	*Measured concentrations (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	0.000	0.000[b]	0.000		0.003	
		0.002[c]	0.000		0.005	
Magnesium	0.000	0.000	0.000		0.0006	
		0.000	0.000		0.0006	
Sodium	0.000	0.000	0.000		0.003	
		0.001	0.001		0.001	
Potassium	0.000	-0.001	-0.001		0.002	
		-0.001	-0.001		0.003	
Ammonium	0.00	0.00	0.00		0.01	
		0.00	0.00		0.01	
Sulfate	0.000	0.000	0.000		0.000	
		0.000	0.000		0.000	
Nitrate	0.000	0.000	0.000		0.003	
		0.000	0.000		0.000	
Chloride	0.000	0.001	0.001		0.003	
		0.000	0.000		0.000	
pH [d]	5.65	5.59	-0.06	-1.1	0.08	1.4
		5.60	-0.05	-0.9	0.11	2.0
Hydrogen ion (μeq/L)	2.24	2.63	0.39	17.4	0.5	19.0
		2.56	0.32	14.3	0.6	23.4
Specific conductance [d] (μS/cm)	0.8	1.2	0.4	50.	0.3	25.0
		1.2	0.4	50.	0.3	25.0

Notes:

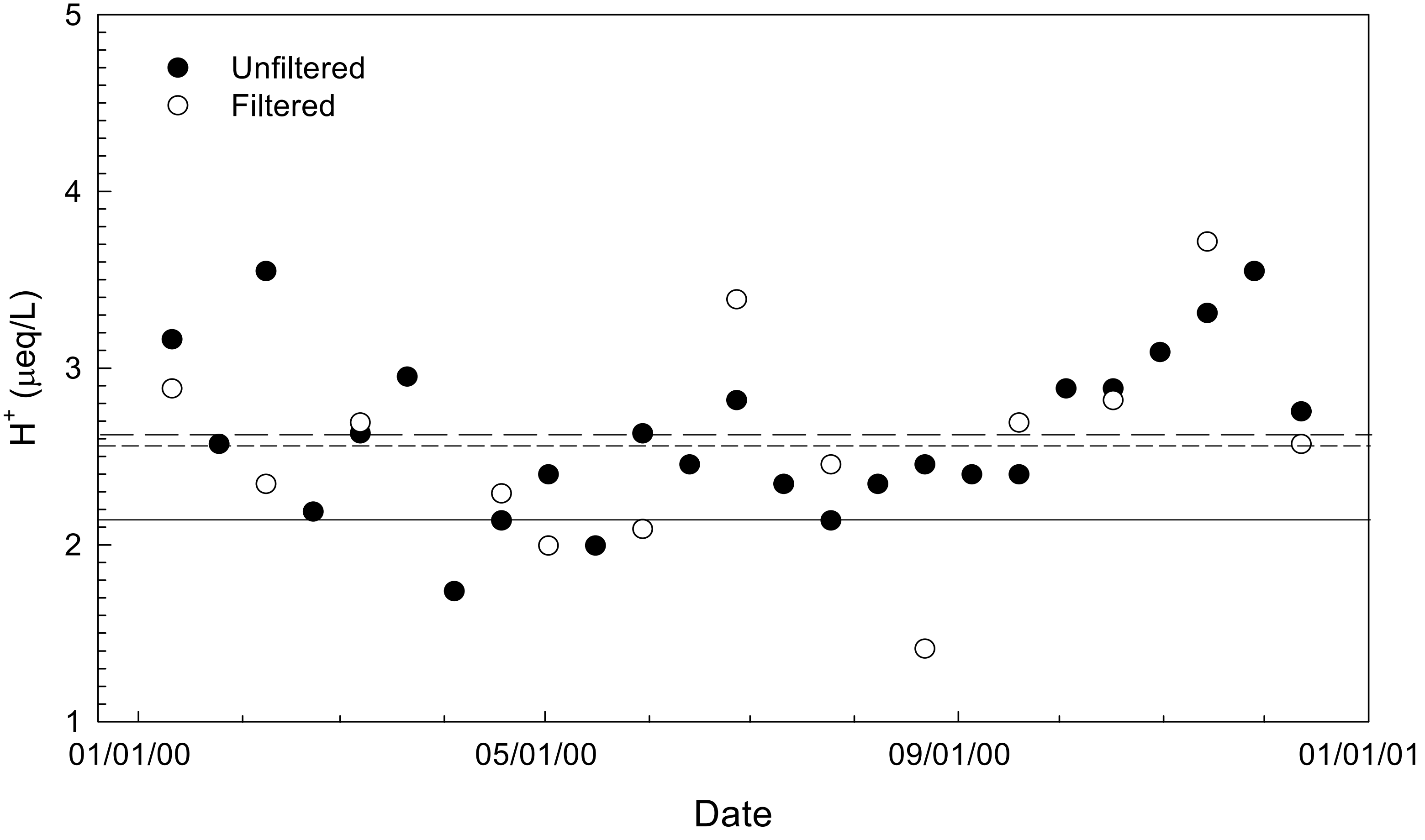
There were 26 unfiltered samples and 13 filtered samples in each set.

[a] Target values are for DI water samples.

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

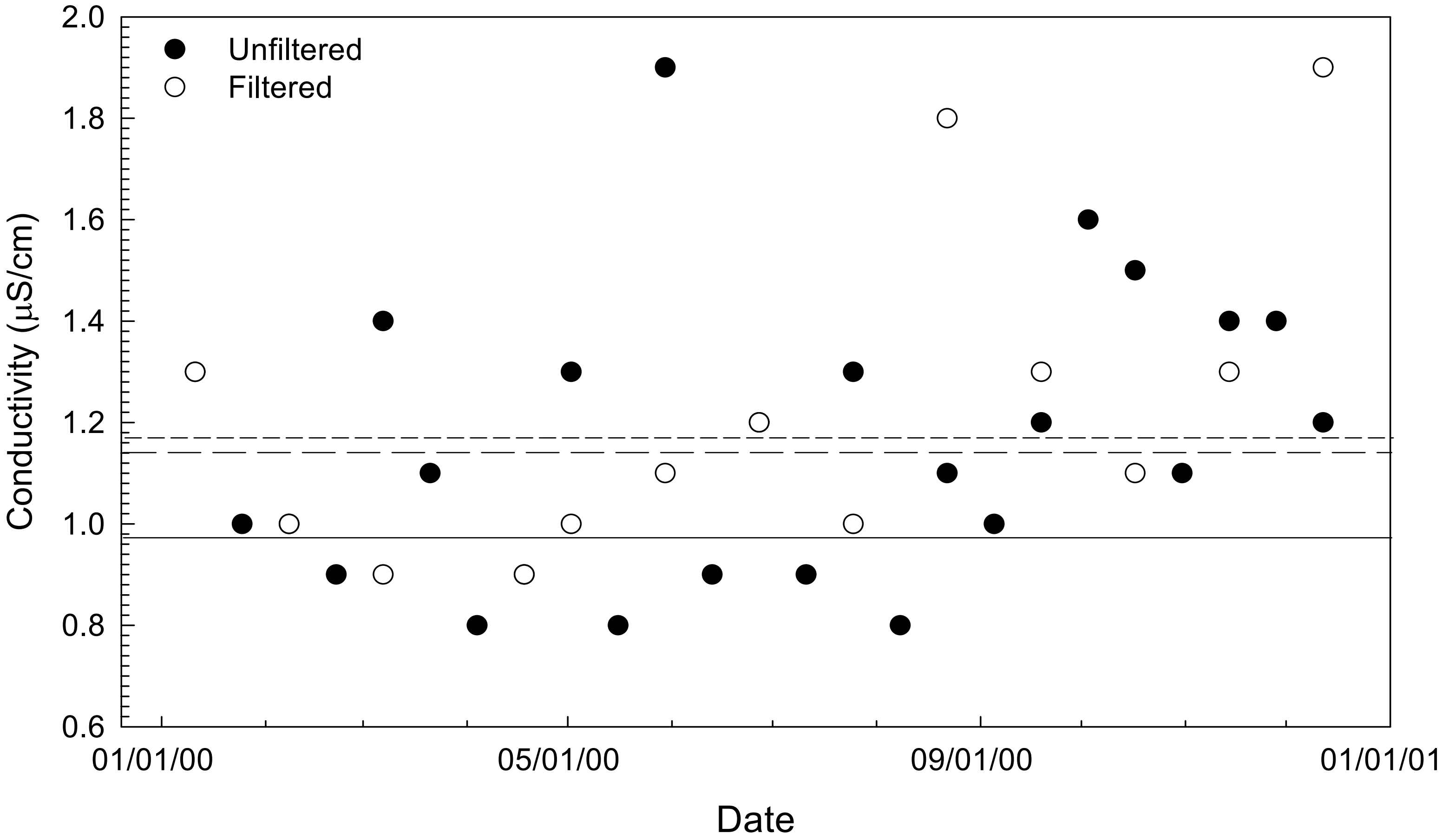
[c] The second set of values for each parameter is for filtered samples.

[d] Both pH and specific conductance are measured on unfiltered samples prior to filtering.



Note: Solid line denotes expected deionized water H^+ concentration: 2.24 μeq/L; long dashed line denotes mean unfiltered H^+ concentration: 2.63 μeq/L; and short dashed line denotes mean filtered H^+ concentration: 2.57 μeq/L.

Figure B-31. Comparison of filtered and unfiltered internal blind samples, (hydrogen), deionized water, 2000.



Note: Solid line denotes theoretical deionized water conductivity: 0.8 μS/cm; long dashed line denotes mean unfiltered conductivity: 1.16 μS/cm; and short dashed line denotes mean filtered conductivity: 1.22μS/cm.

Figure B-32. Comparison of filtered and unfiltered internal blind samples, (conductivity), deionized water, 2000.

Table B-5. 5th, 50th, and 95th Percentile Concentration Values of Parameters Measured in Replicate Samples, NTN, 2000

	Percentile concentration values (mg/L)		
Parameter	*5th*	*50th*	*95th*
Calcium	0.014	0.096	0.557
Magnesium	0.003	0.021	0.158
Sodium	0.008	0.056	0.819
Potassium	0.003	0.017	0.152
Ammonium	<0.02	0.19	0.86
Sulfate	0.110	0.960	3.772
Nitrate	0.111	0.935	2.915
Chloride	0.023	0.116	1.666
pH (units)	4.16	4.90	6.24
Hydrogen ion (µeq/L)	0.58	12.59	69.03
Specific conductance (µS/cm)	3.2	11.8	41.3

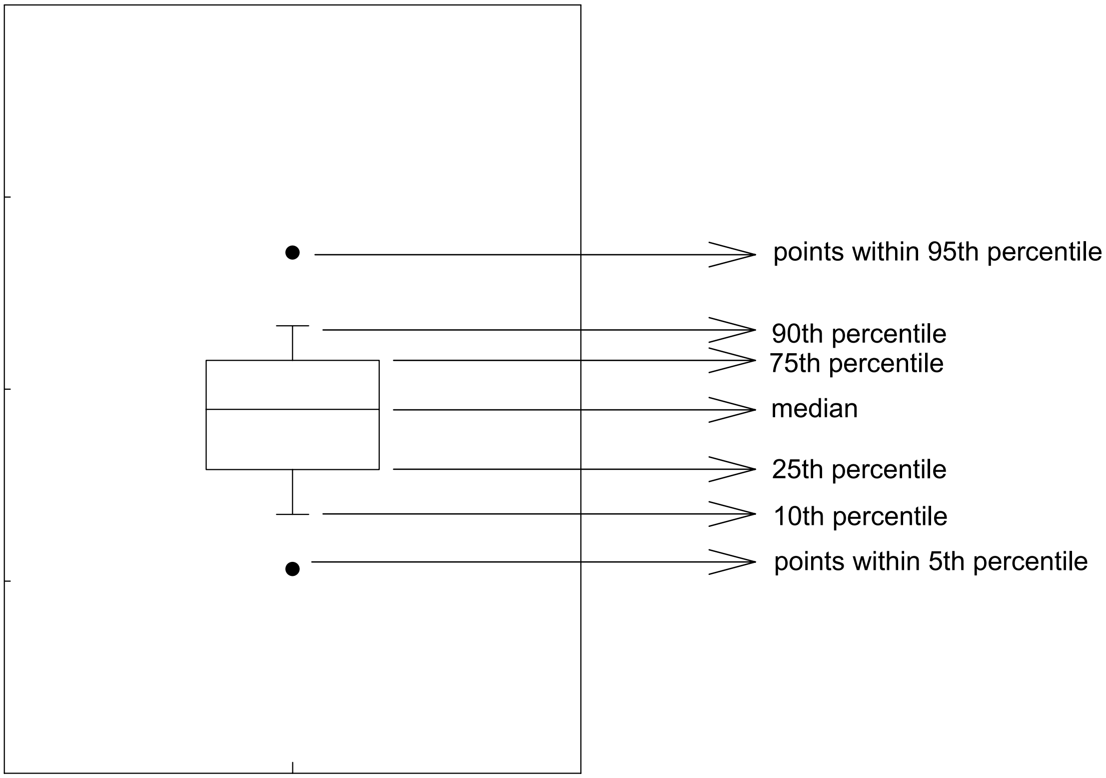


Figure B-33. Explanation of box and whisker plots.

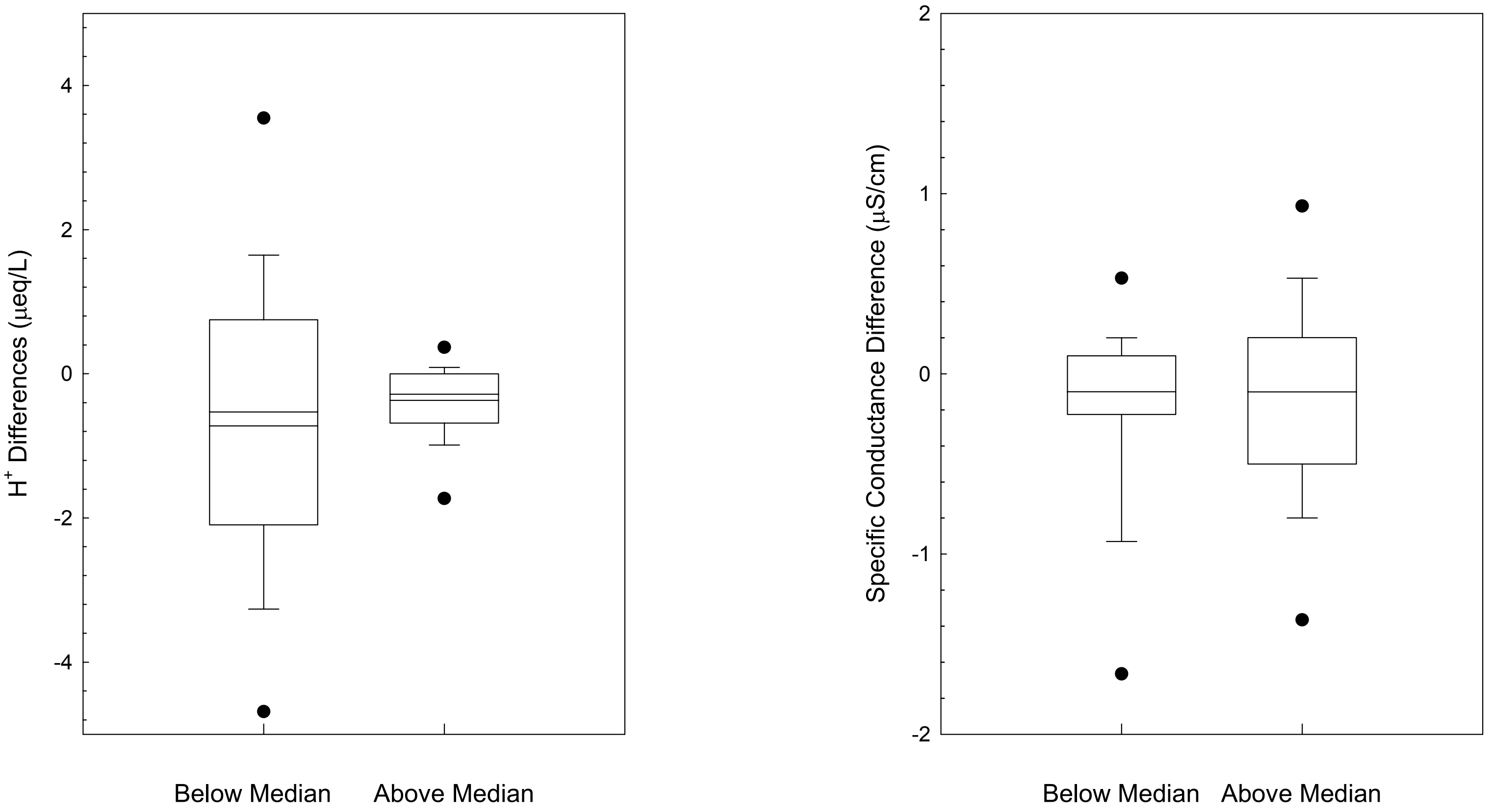


Figure B-34. Results of NTN replicate analysis, hydrogen ion (H^+) and specific conductance, 2000.

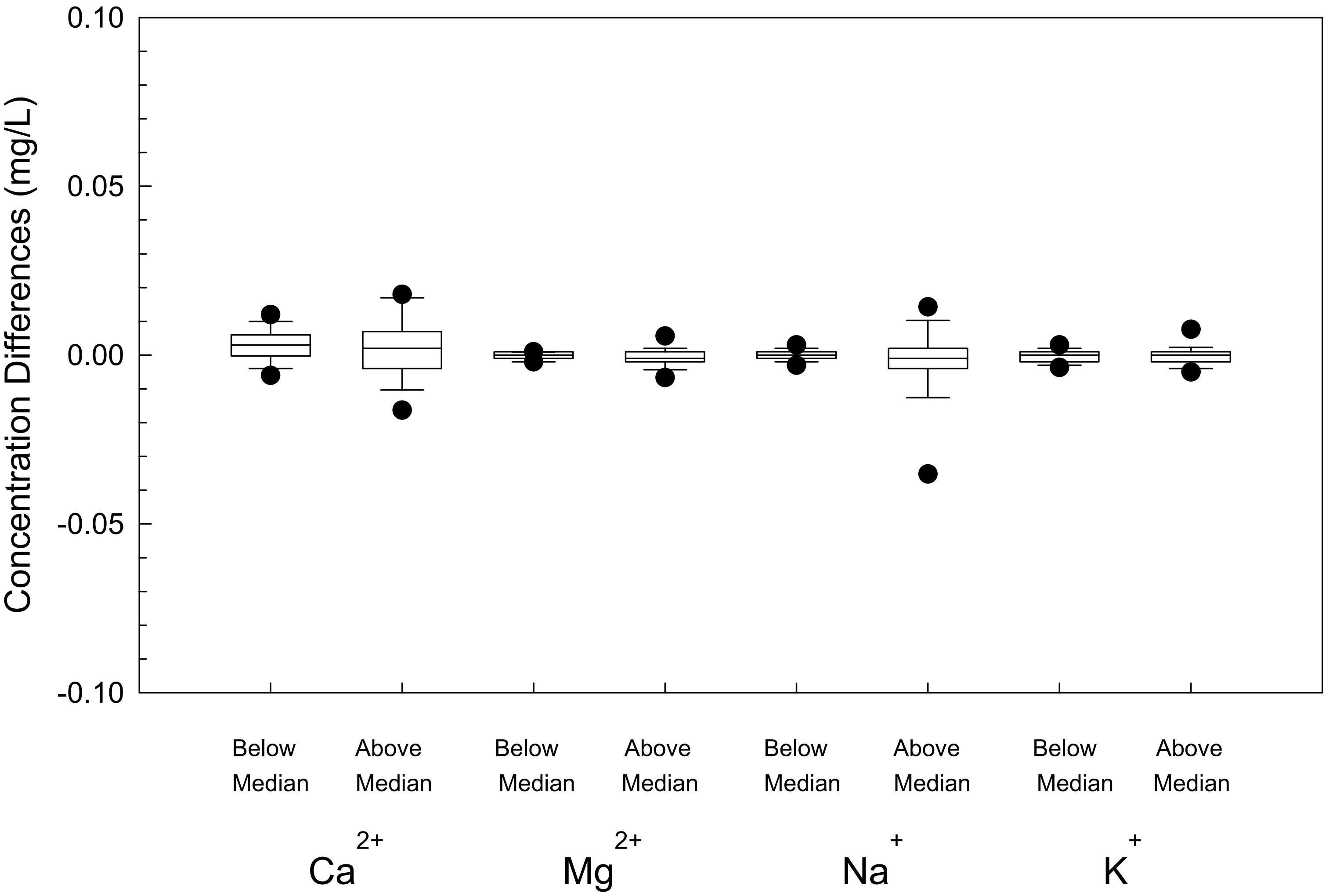


Figure B-35. Results of NTN replicate analysis, calcium (Ca^{2+}) magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}), 2000.

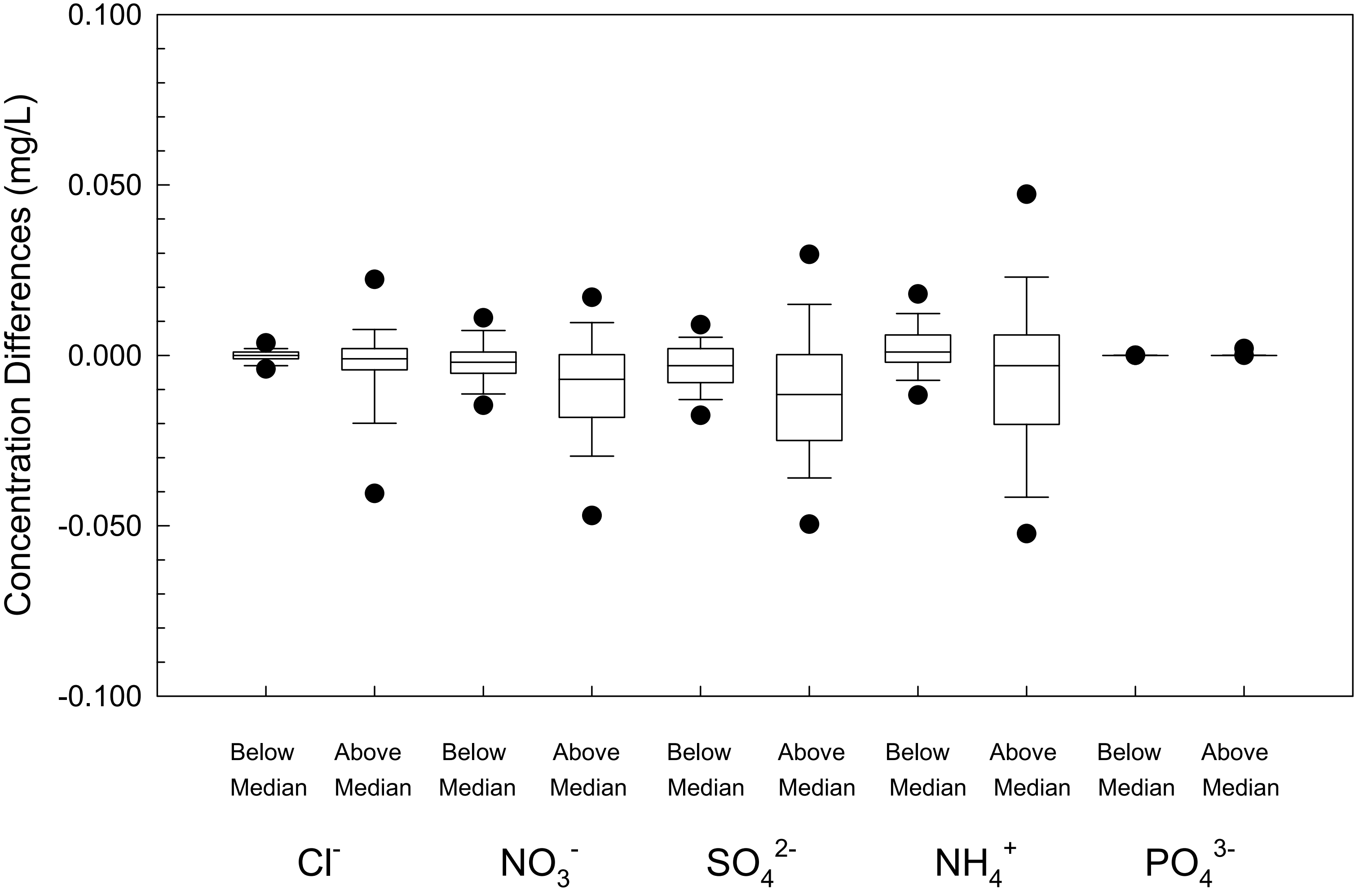


Figure B-36. Results of NTN replicate analysis, sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), and orthophosphate (PO_4^{3-}), 2000.

Table B-6. 5th, 50th, and 95th Percentile Concentration Values of Parameters Measured in Replicate Samples, AIRMoN, 2000

	Percentile concentration values (mg/L)		
Parameter	*5th*	*50th*	*95th*
Calcium	0.003	0.081	1.022
Magnesium	0.001	0.021	0.261
Sodium	0.003	0.029	1.187
Potassium	0.004	0.020	0.144
Ammonium	0.01	0.27	1.30
Sulfate	0.273	1.872	5.050
Nitrate	0.160	1.234	4.172
Chloride	0.020	0.116	2.590
pH (units)	4.10	4.44	5.23
Hydrogen ion (µeq/L)	6.07	36.31	79.23
Specific conductance (µS/cm)	6.4	24.9	44.5

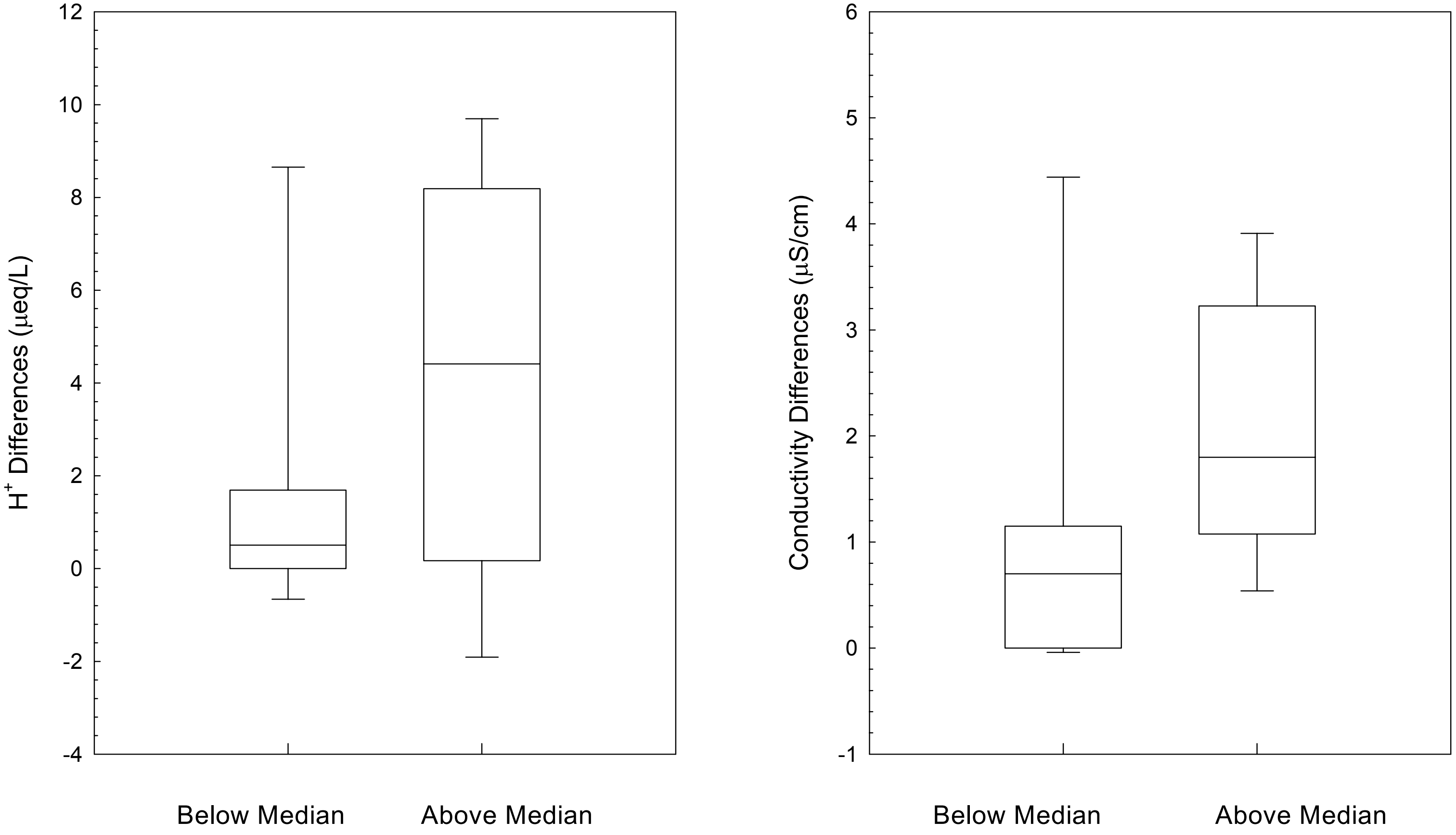


Figure B-37. Results of AIRMoN replicate analysis, hydrogen ion (H^+) and conductivity, 2000.

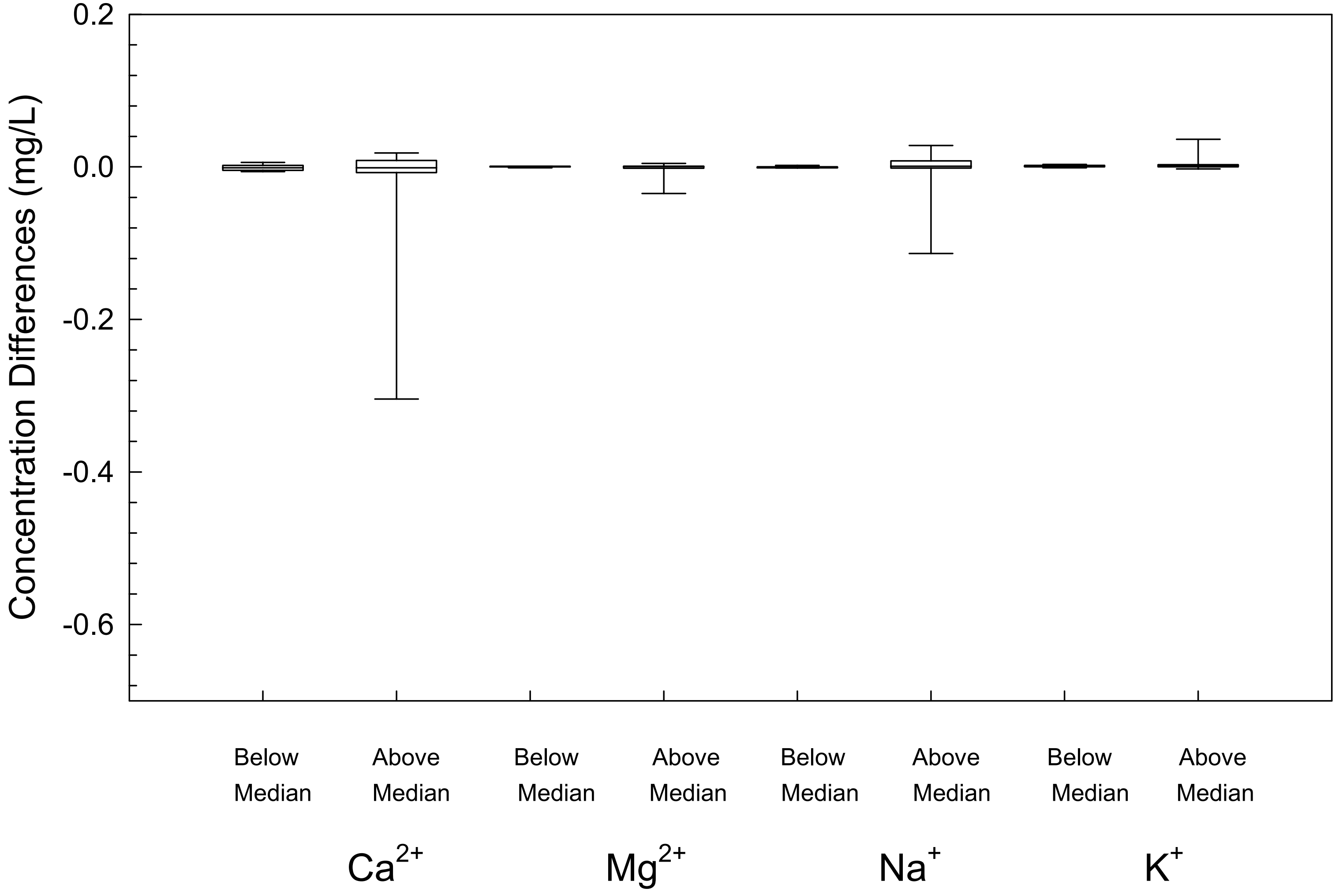


Figure B-38. Results of AIRMoN replicate analysis, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}), 2000.

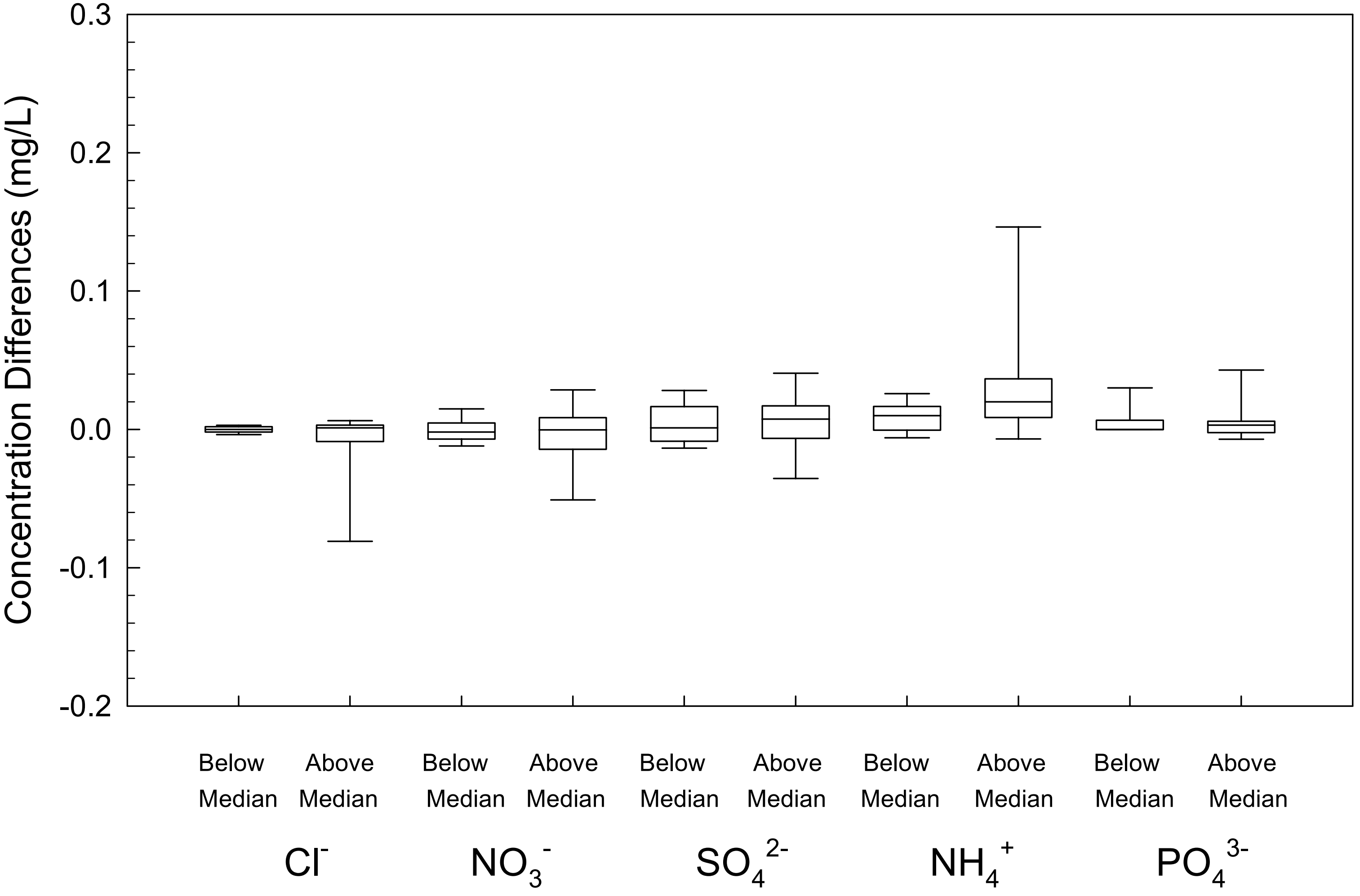


Figure B-39. Results of AIRMoN replicate analysis, sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), and orthophosphate (PO_4^{3-}), 2000.

Table B-7. Percent of Ion Concentrations above MDL Found in Weekly Deionized (DI) Water Blanks and Leachates, 2000

Blank	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Ammonium*	*Phosphate*	*Chloride*	*Nitrate*	*Sulfate*
DI (Rm 209)	5.8	0.0	3.8	0.0	1.9	0.0	0.0	0.0	0.0
DI (Rm 304)	2.0	0.0	11.8	2.0	0.0	0.0	3.9	2.0	0.0
DI (Rm 323)	0.0	0.0	2.0	3.9	0.0	0.0	0.0	0.0	0.0
Filter A	4.1	0.0	6.1	2.0	0.0	0.0	6.1	2.0	2.0
Filter B	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bucket - 50 mL	21.2	3.8	26.9	11.5	7.7	0.0	62.7	37.3	2.0
Bucket - 150 mL	3.8	1.9	5.8	3.8	1.9	0.0	11.8	5.9	2.0
Bucket - 50 mL	13.5	1.9	34.6	9.6	19.2	0.0	54.9	29.4	0.0
Bottle - 50 mL	1.9	0.0	5.8	1.9	0.0	0.0	0.0	0.0	0.0
Bottle - 150 mL	1.9	0.0	1.9	0.0	0.0	0.0	0.0	0.0	2.0
Lid - 50 mL	7.7	1.9	3.8	3.8	5.8	0.0	2.0	0.0	2.0

Note:
There were 52 weeks of blank samples but only 51 samples of Cl^-, NO_3^-, and SO_4^{2-}.

Table B-8. Percent of Ion Concentrations above and below Control Limits Found in Weekly Simulated Rainwater (FR25) Leachates, 2000

Blank	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Ammonium*	*Chloride*	*Nitrate*	*Sulfate*
Filter A	53.1[a]	0.0	2.0	0.0	2.0	0.0	0.0	0.0
	0.0[b]	65.3	0.0	0.0	51.0	0.0	89.8	85.7
Filter B	32.7	2.0	2.0	2.0	4.1	4.1	4.1	6.1
	8.2	0.0	0.0	0.0	46.9	0.0	14.3	6.1
Bucket - 50 mL	13.5	1.9	19.2	1.9	5.8	25.5	25.5	2.0
	25.0	0.0	0.0	0.0	71.2	0.0	39.2	56.9
Bucket - 150 mL	21.2	0.0	13.5	3.8	1.9	11.8	19.6	3.8
	5.8	0.0	0.0	0.0	90.4	0.0	29.4	42.3
Bottle - 50 mL	0.0	1.9	0.0	0.0	3.8	0.0	0.0	0.0
	21.2	0.0	0.0	1.9	75.0	0.0	68.6	25.5
Bottle - 150 mL	3.8	0.0	3.8	0.0	0.0	0.0	2.0	2.0
	13.5	0.0	0.0	0.0	59.6	0.0	49.0	5.9
Lid - 50 mL	21.6	0.0	7.8	2.0	9.8	3.8	11.8	9.8
	3.9	0.0	2.0	0.0	45.1	0.0	19.2	2.0
AIRMoN Bottle - 50 mL	0.0	0.0	8.3	0.0	0.0	8.3	0.0	8.3
	0.0	0.0	0.0	0.0	66.7	0.0	33.3	0.0
AIRMoN Bottle - 150 mL	8.3	0.0	8.3	0.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	66.7	0.0	16.7	0.0

Notes:

Fifty-two NTN blanks and 12 monthly AIRMoN blanks were analyzed.

[a] Top numbers are the percent of samples above the upper control limit.

[b] Bottom numbers are the percent of samples below the bottom control limit.

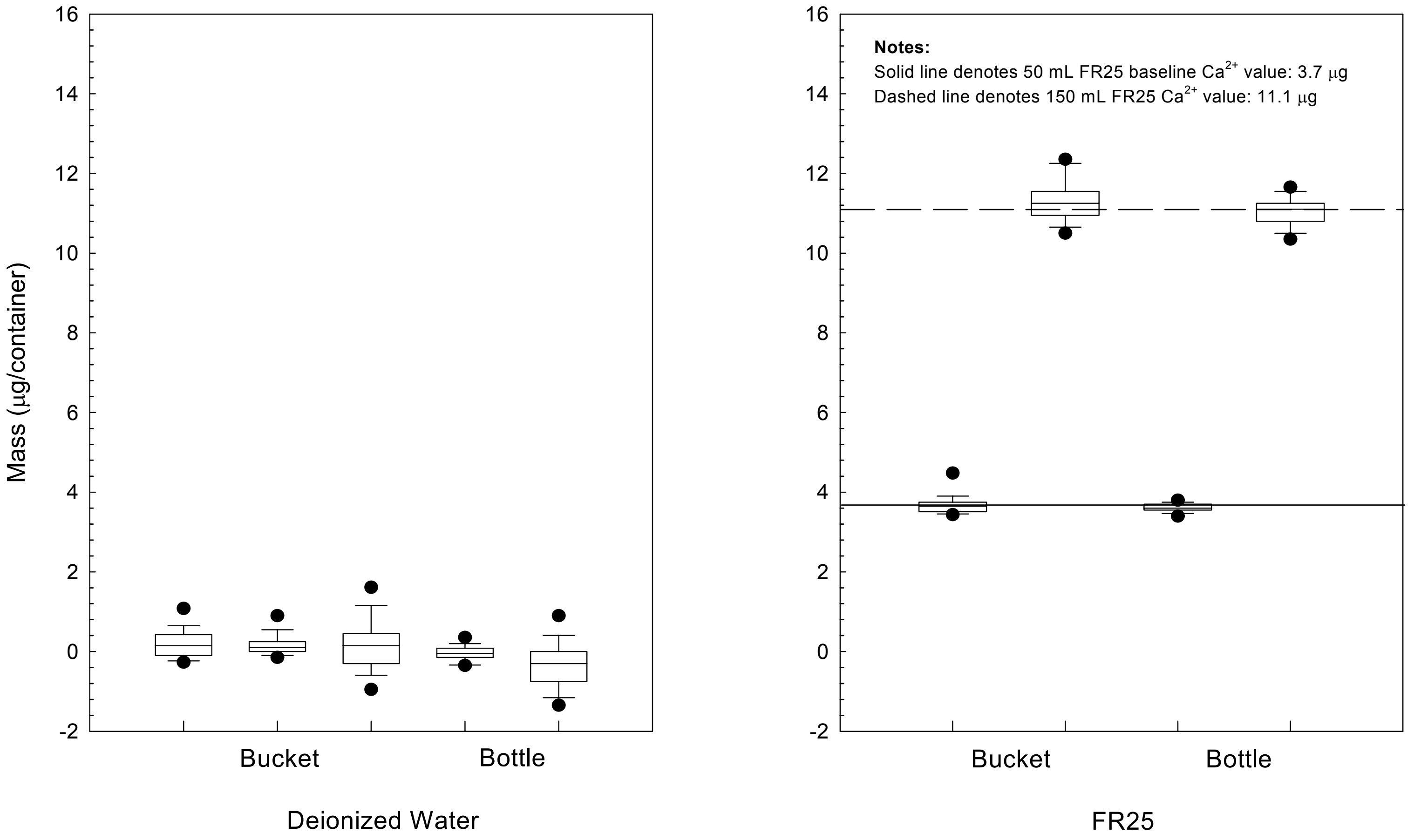


Figure B-40. Calcium found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 2000.

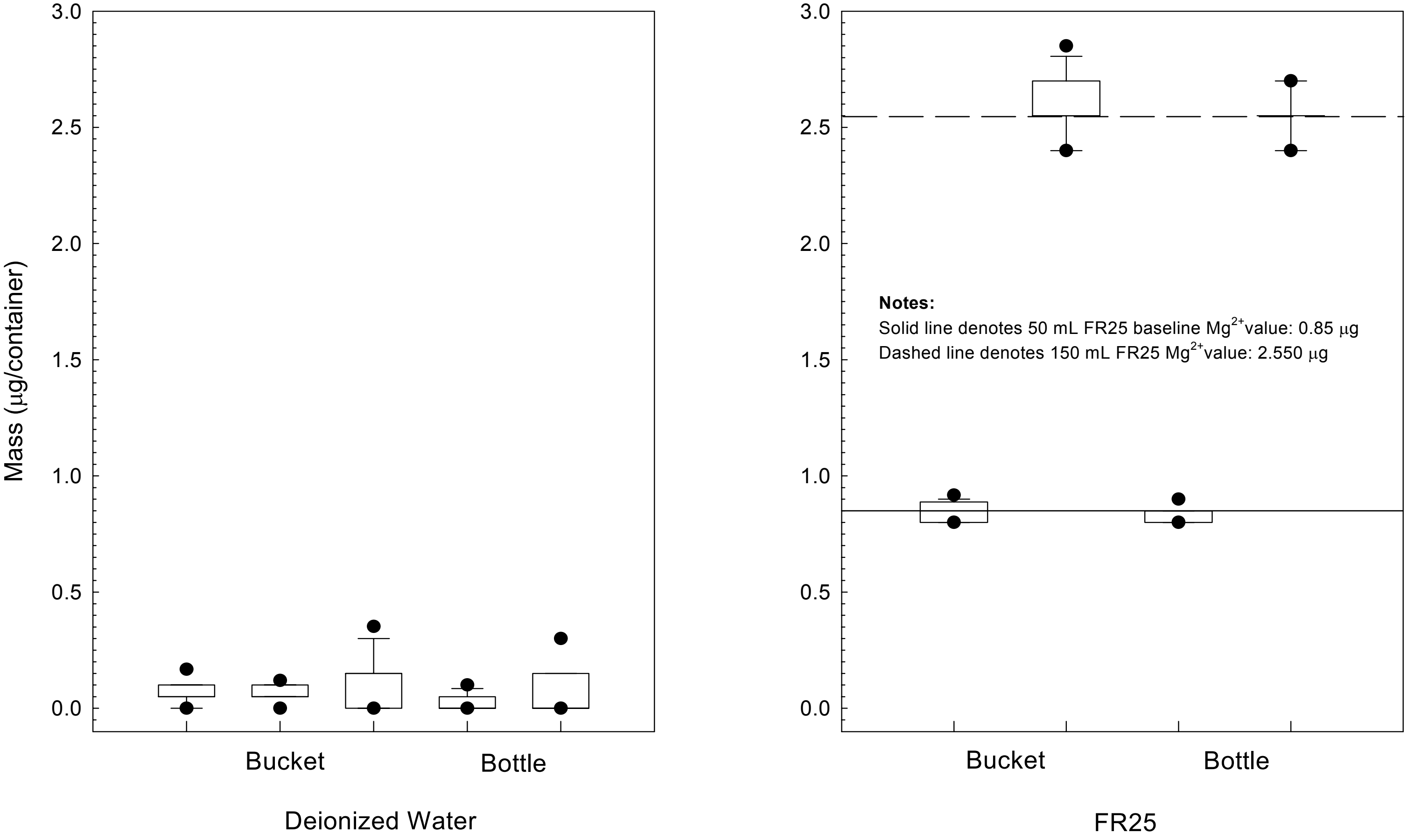


Figure B-41. Magnesium found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 2000.

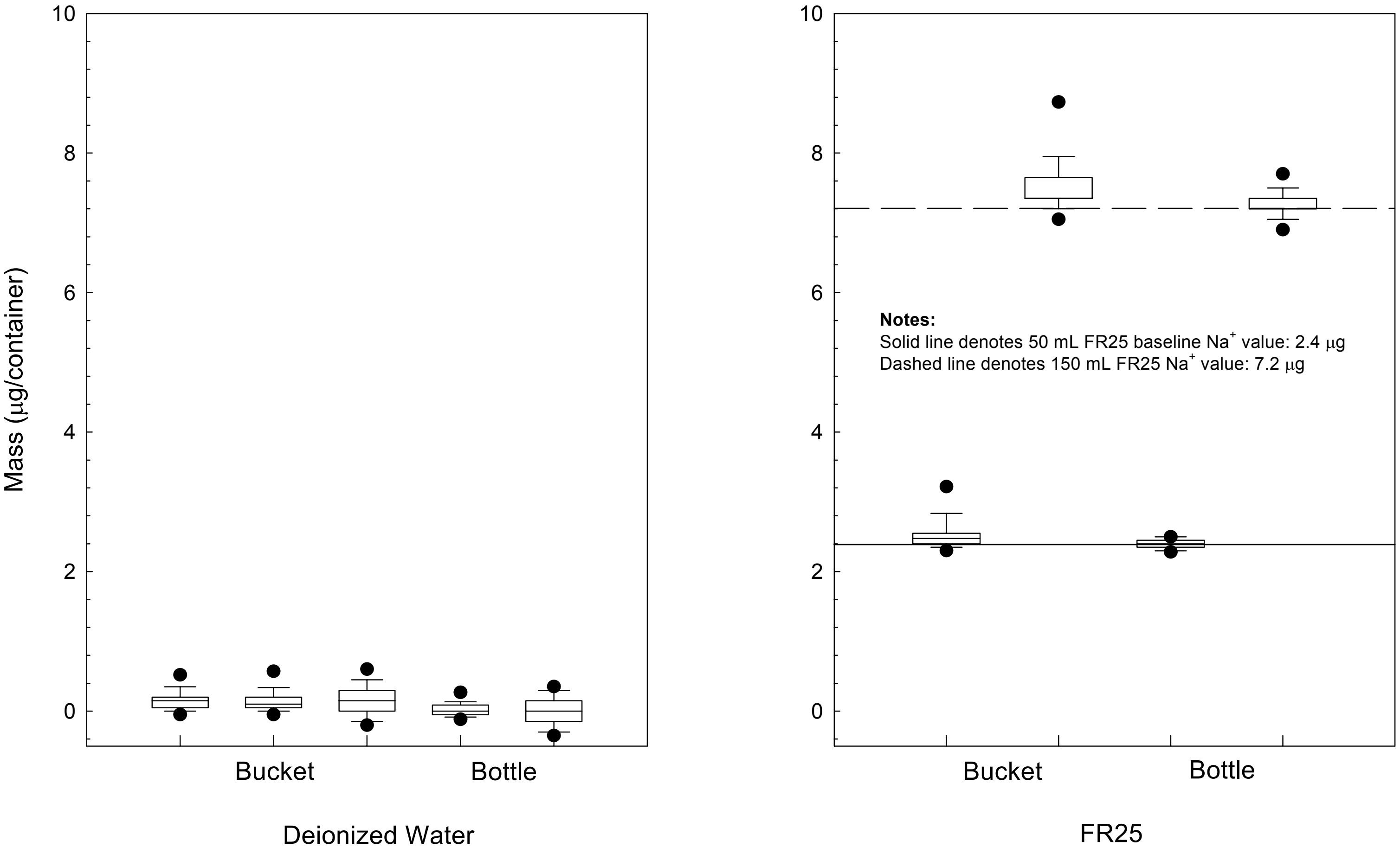


Figure B-42. Sodium found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 2000.

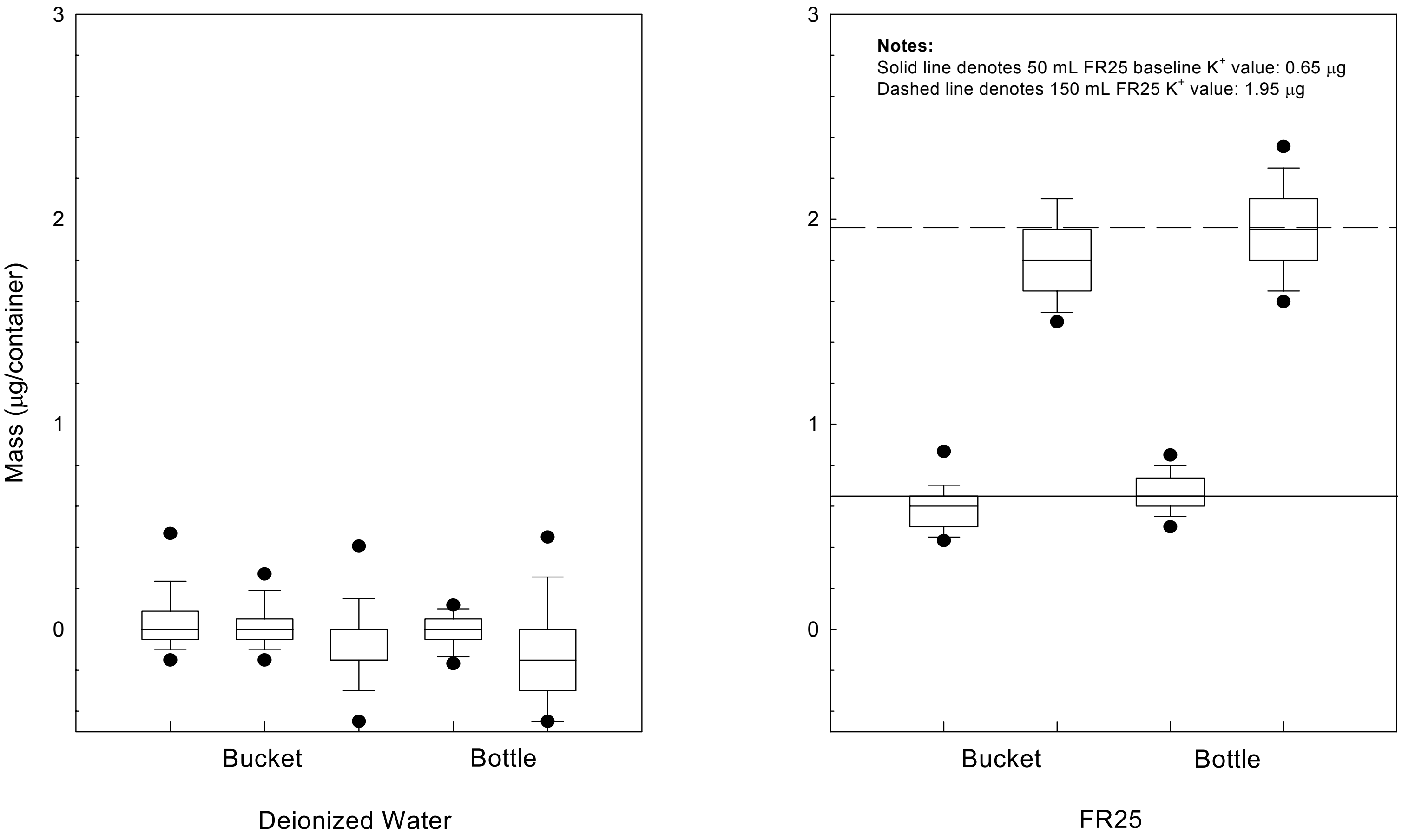


Figure B-43. Potassium found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 2000.

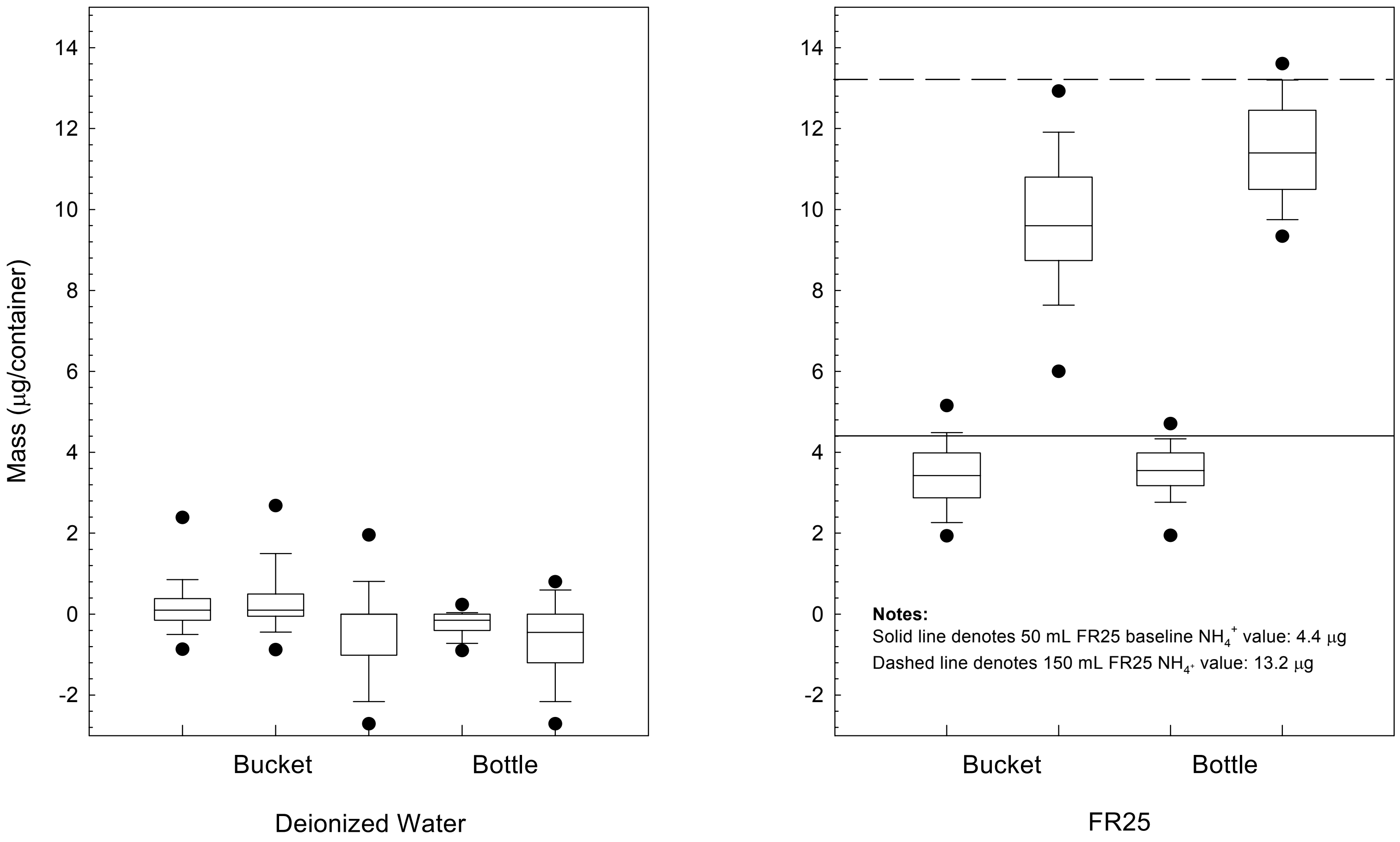
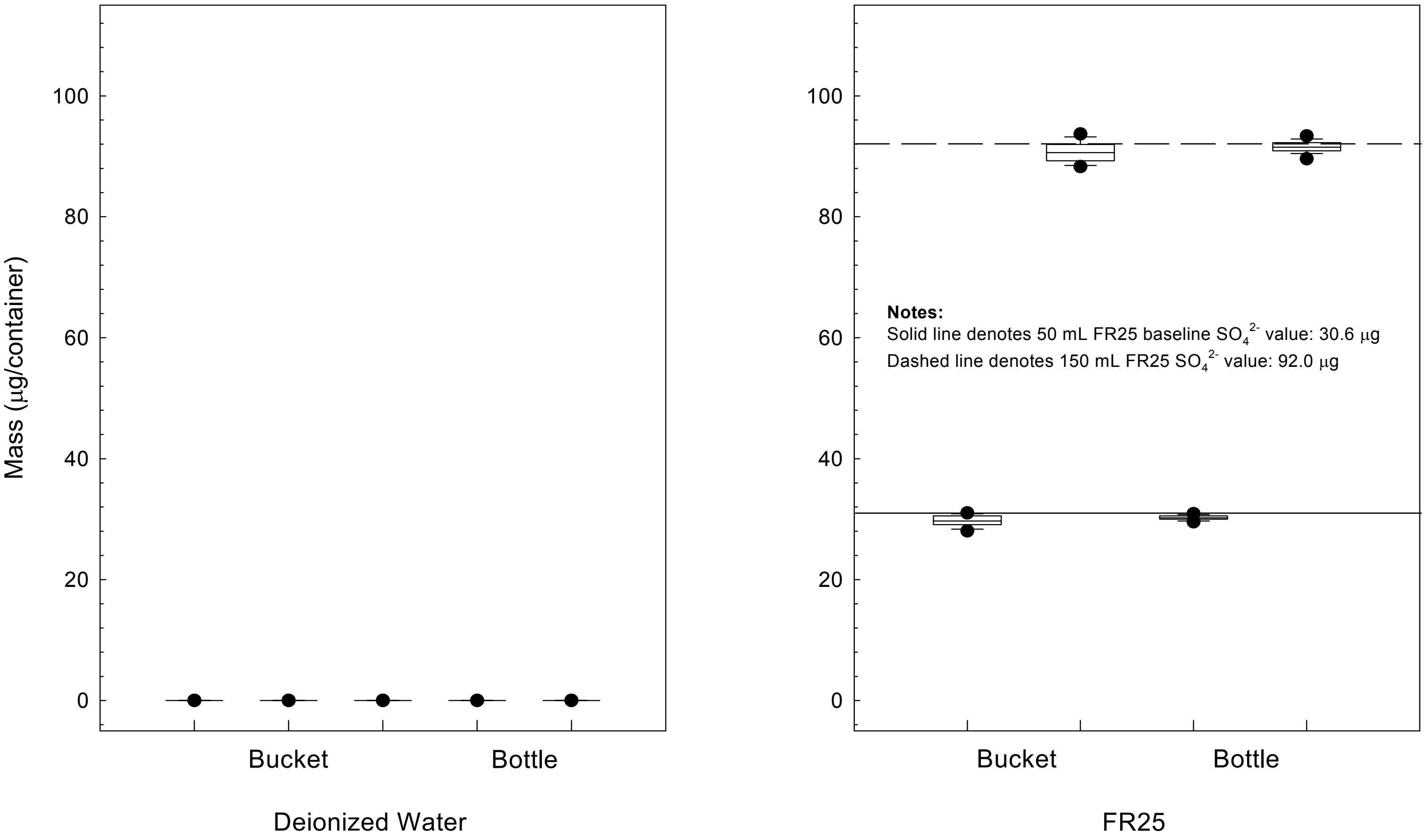


Figure B-44. Ammonium found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 2000.



Notes:

Solid line denotes 50 mL FR25 baseline SO_4^{2-} value: 30.6 µg

Dashed line denotes 150 mL FR25 SO_4^{2-} value: 92.0 µg

Figure B-45. Sulfate found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 2000.

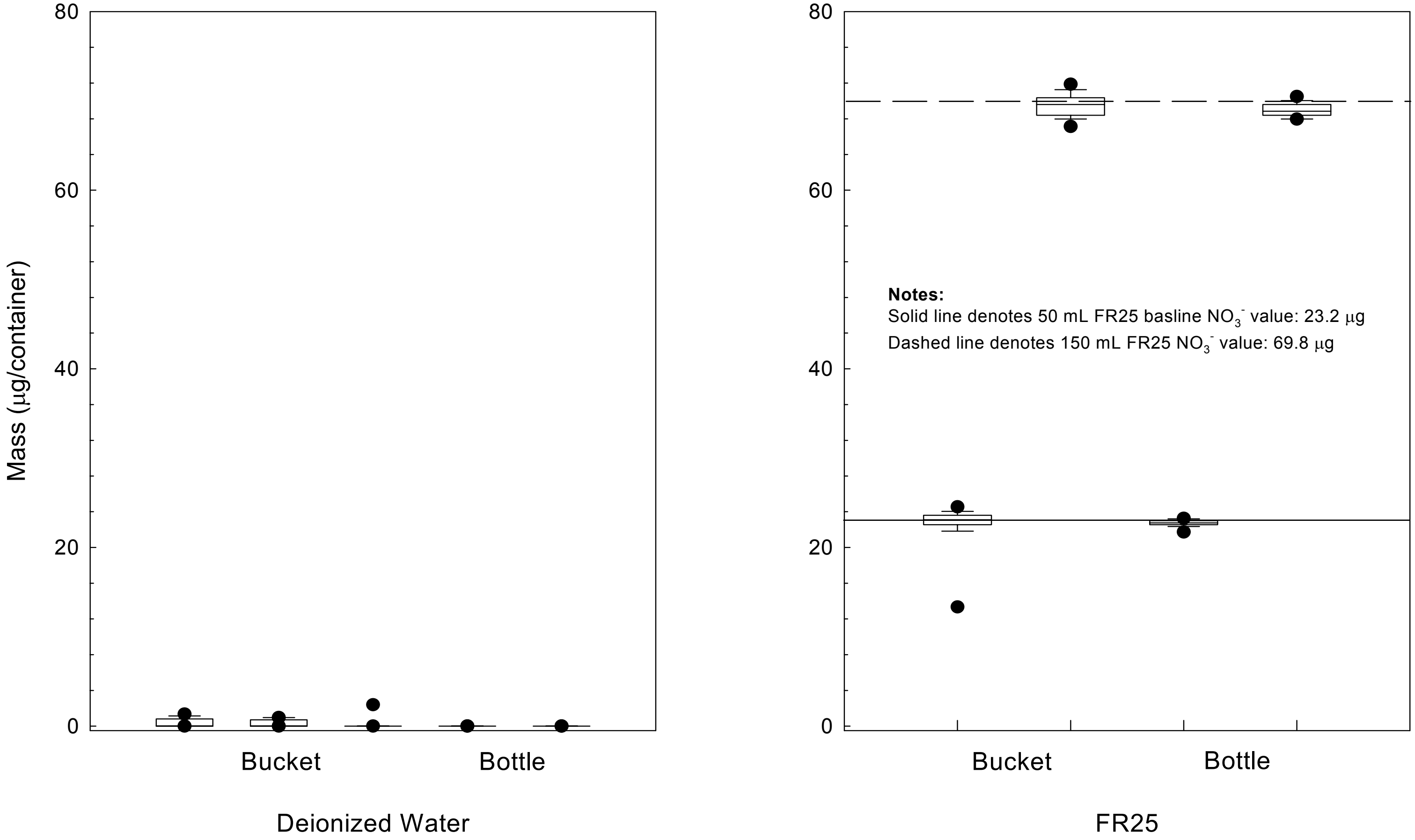
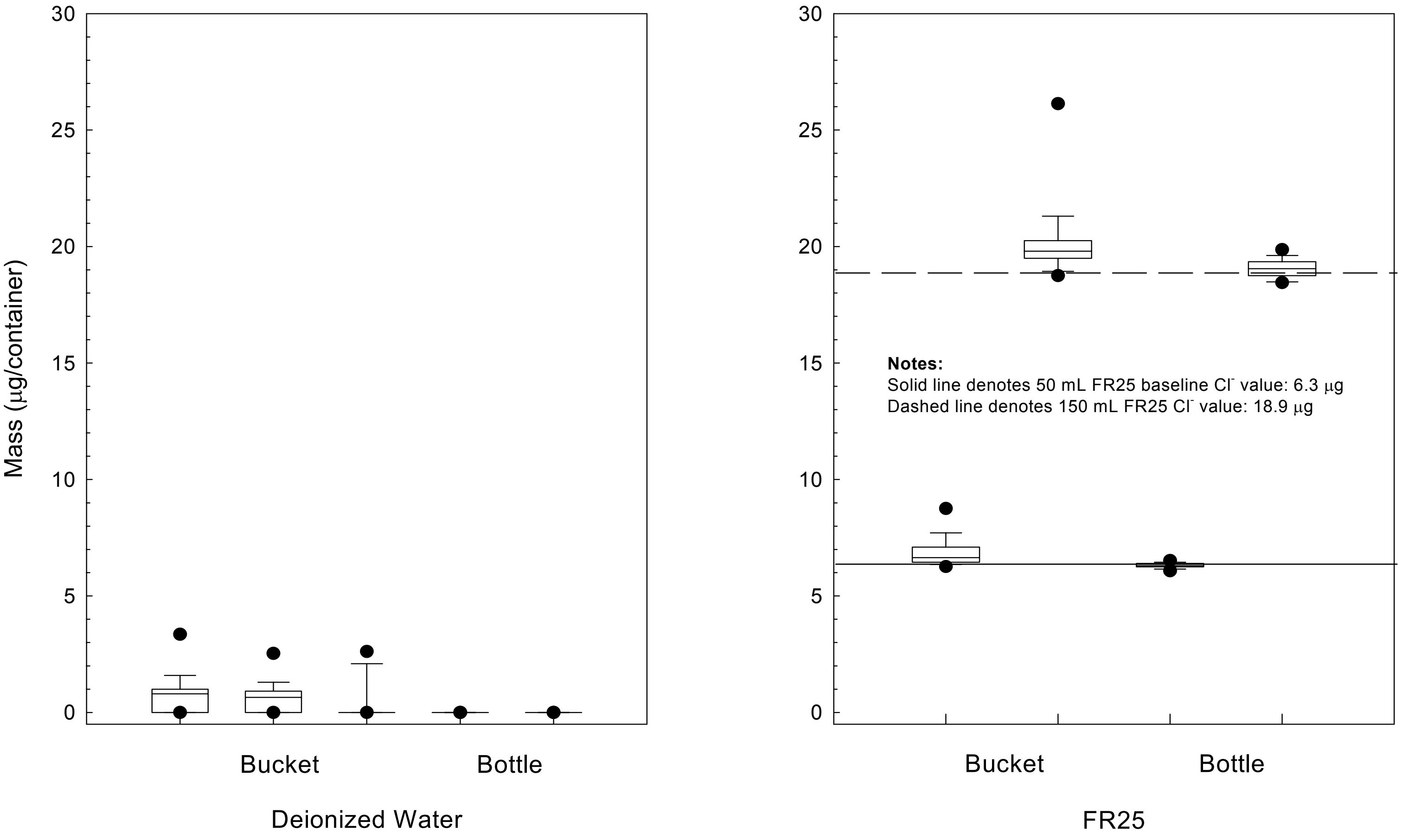
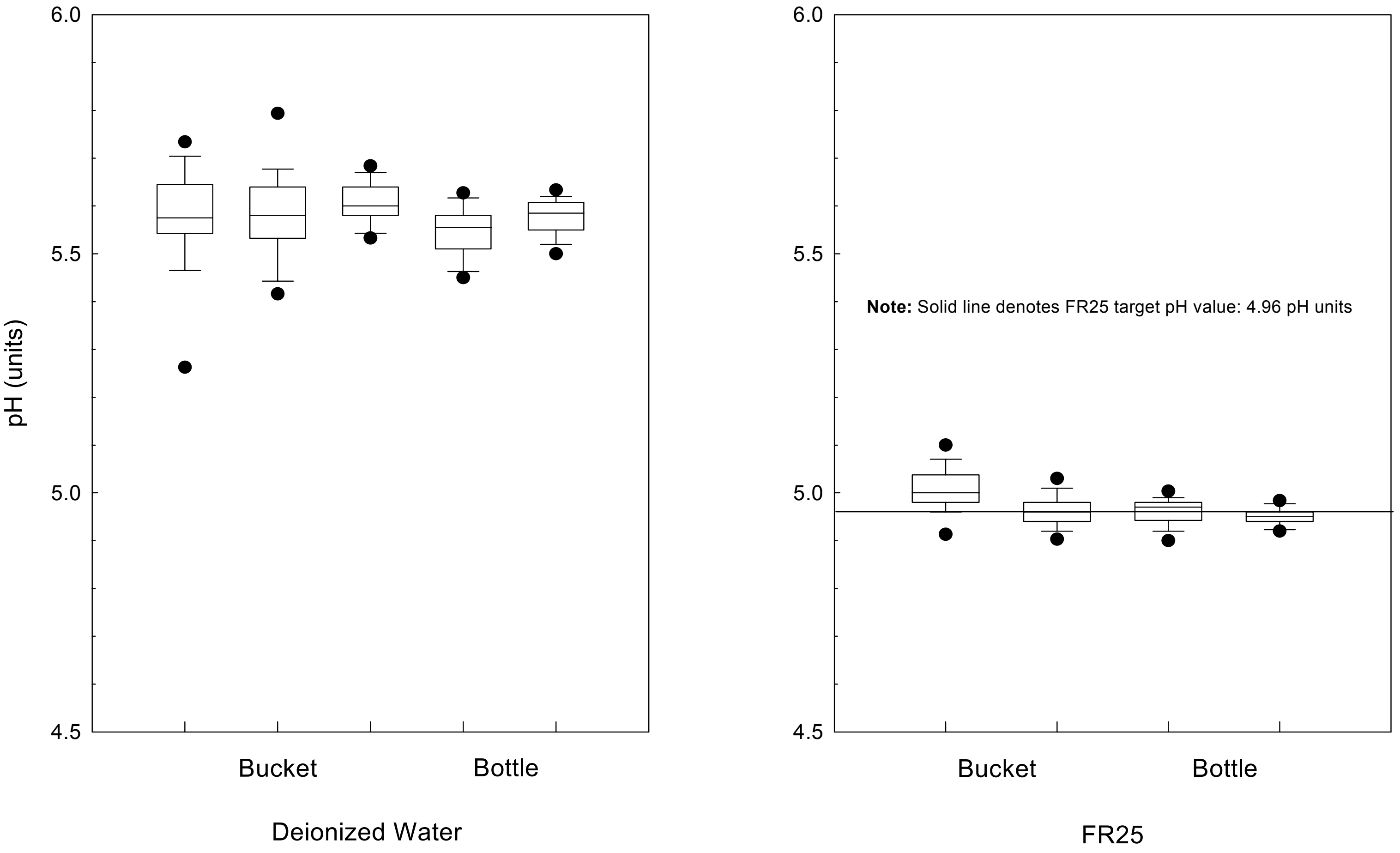


Figure B-46. Nitrate found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCs as leaching agents, 2000.



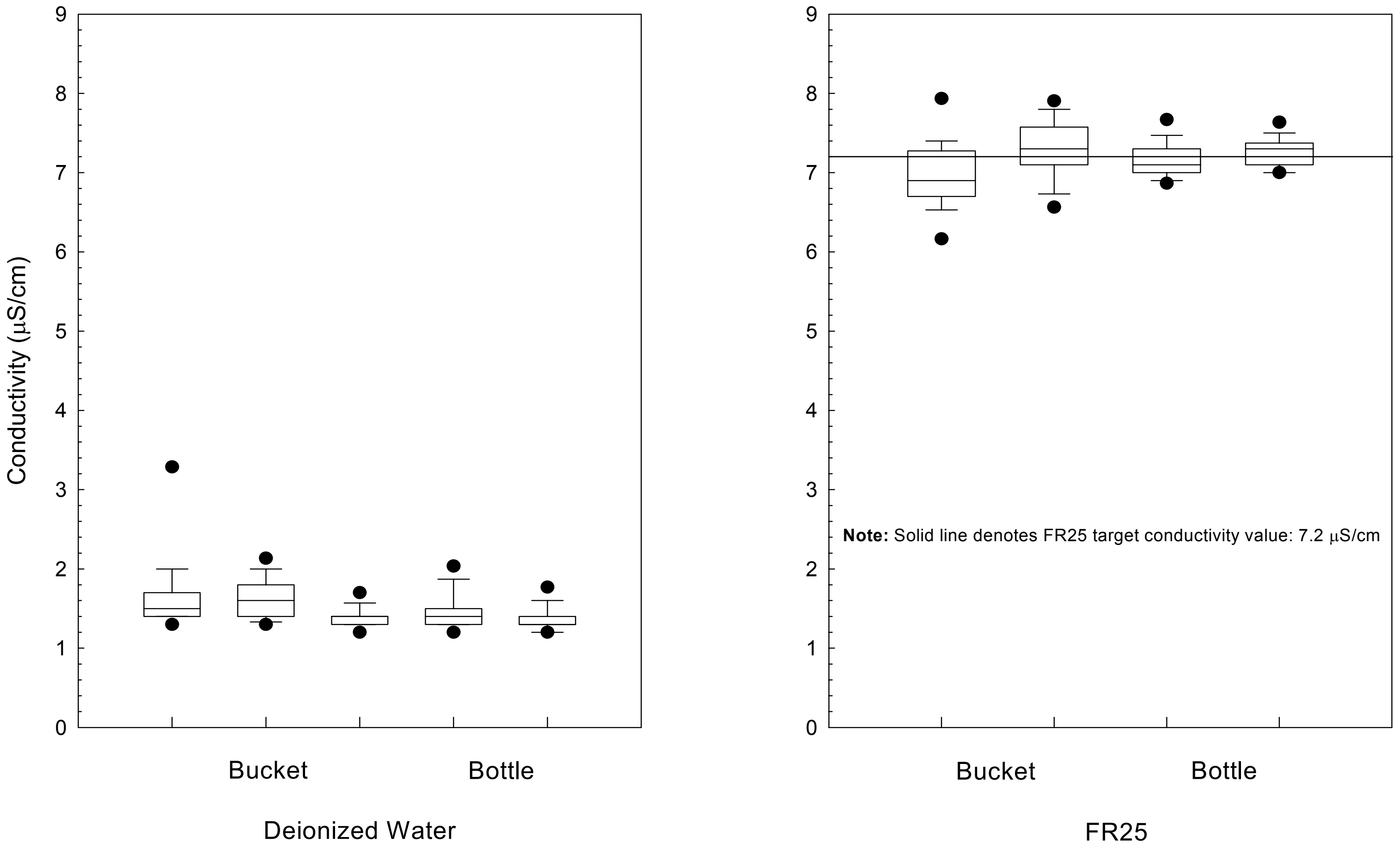
Notes:
Solid line denotes 50 mL FR25 baseline Cl^- value: 6.3 µg
Dashed line denotes 150 mL FR25 Cl^- value: 18.9 µg

Figure B-47. Chloride found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 2000.



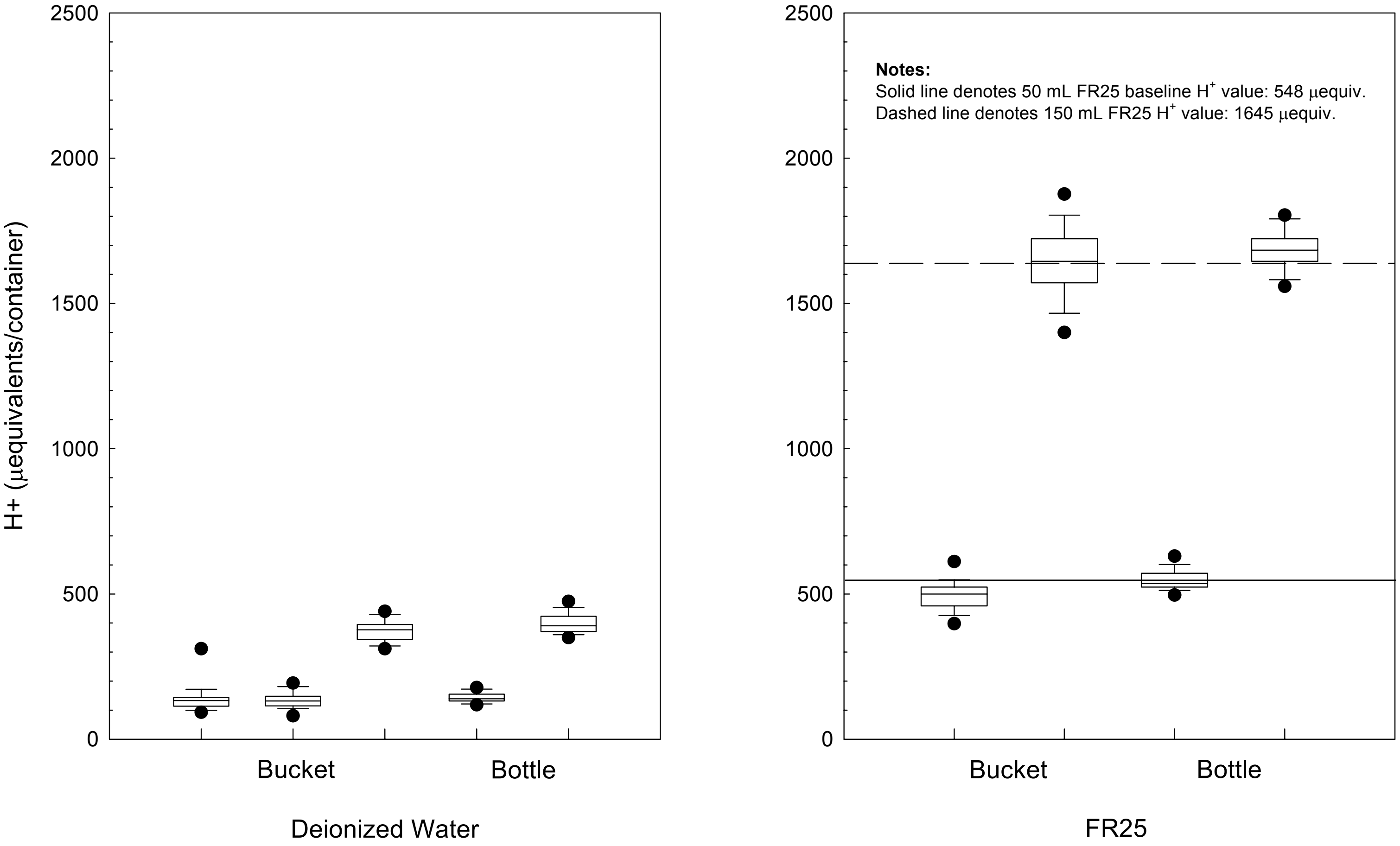
Note: Solid line denotes FR25 target pH value: 4.96 pH units

Figure B-48. pH found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 2000.



Note: Solid line denotes FR25 target conductivity value: 7.2 µS/cm

Figure B-49. Conductivity found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 2000.



Notes:
Solid line denotes 50 mL FR25 baseline H^+ value: 548 μequiv.
Dashed line denotes 150 mL FR25 H^+ value: 1645 μequiv.

Figure B-50. Hydrogen ion found in upright bucket and 1-L bottle blanks using deionized water and FR25 QCS as leaching agents, 2000.