NADP QA Report 2006-01
ISWS Data/Case Study 2006-01

QUALITY ASSURANCE REPORT
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM, 2002

Laboratory Operations
Central Analytical Laboratory

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

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

In 2005, scientists, students, educators, and others interested in the National Atmospheric Deposition Program (NADP) logged more than 310,000 sessions and viewed nearly 93,000 maps on the NADP Web site. Users downloaded 18,564 data files from this site, which now annually receives more than 1.2 million hits. These data are used to address important questions about the impact of the wet deposition of nutrients on eutrophication in coastal estuarine environments; the relationship between wet deposition, the health of unmanaged forests, and the depletion of base cations from forest soils; the impact of pollutant emissions changes on precipitation chemistry; and the rate at which precipitation delivers mercury to remote lakes and streams.

The NADP was organized in 1977 under State Agricultural Experiment Station (SAES) leadership to address the problem of atmospheric deposition and its effects on agricultural crops, forests, rangelands, surface waters, and other natural and cultural resources. In 1978, sites in the NADP precipitation chemistry network first began collecting one-week, wet-only deposition samples analyzed by the Central Analytical Laboratory (CAL) at the Illinois State Water Survey. The network was established to provide data on amounts, temporal trends, and geographic distributions of the atmospheric deposition of acids, nutrients, and base cations by precipitation. The NADP initially was organized as SAES North Central Regional Project NC-141, which all four SAES regions endorsed as Interregional Project IR-7 in 1982. A decade later, IR-7 was reclassified as National Research Support Project NRSP-3, which it remains.

In October 1981, the federally supported National Acid Precipitation Assessment Program (NAPAP) was established to increase understanding of the causes and effects of acidic precipitation. This program sought to establish a long-term precipitation chemistry network of sampling sites distant from point source influences. Because of its experience in organizing and operating a national-scale network, the NADP agreed to coordinate operation of NAPAP's National Trends Network (NTN). To benefit from identical siting criteria and operating procedures and a shared analytical laboratory, NADP and NTN merged with the designation NADP/NTN. Many NADP/NTN sites were supported by the U.S. Geological Survey, NAPAP's lead federal agency for deposition monitoring. Under Title IX of the federal Clean Air Act Amendments of 1990, NAPAP continues. Today there are more than 250 sites in the network, and the network designation has been shortened to NTN.

In October 1992, the Atmospheric Integrated Research Monitoring Network (AIRMoN), currently with seven sites, joined the NADP. AIRMoN sites collect samples daily when precipitation occurs. Samples are refrigerated until analysis at the CAL for the same constituents measured in NTN samples. The AIRMoN seeks to investigate pollutant source/receptor relationships and the effect of emissions changes on precipitation chemistry, combining measurements with atmospheric models. The AIRMoN also evaluates sample collection and preservation methods.

In January 1996, the Mercury Deposition Network (MDN), currently with more than 90 sites, joined the NADP. MDN sites collect wet-only deposition samples that are sent to the MDN analytical laboratory at Frontier Geosciences, Inc. The MDN was formed to provide data on the wet deposition of mercury to surface waters, forested watersheds, and other receptors. Forty-five states and eight Canadian provinces have advisories against consuming fish from lakes with high mercury concentrations in fish tissues. MDN data enable researchers to investigate the link between mercury in precipitation and this problem.

The NADP receives support from the U.S. Geological Survey; Environmental Protection Agency; National Park Service; National Oceanic and Atmospheric Administration; U.S. Department of Agriculture - Forest Service; U.S. Fish & Wildlife Service; Tennessee Valley Authority; Bureau of Land Management; and U.S. Department of Agriculture - Cooperative State Research, Education, and Extension Service under agreement 2002-39138-11964. Additional support is provided by other federal, state, local, and tribal agencies, State Agricultural Experiment Stations, universities, and nongovernmental organizations. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the U.S. Department of Agriculture or any other sponsor.

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Laboratory Operations
Central Analytical Laboratory

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Abstract

The National Atmospheric Deposition Program (NADP) and the Central Analytical Laboratory (CAL) have been in operation since 1978. Since the beginning of the network, quality assurance has been of paramount importance. The *Quality Assurance Report, National Atmospheric Deposition Program, 2002*, describes the quality assurance/quality control measures used at the CAL of the NADP/National Trends Network (NTN) and NADP/Atmospheric Integrated Research Monitoring Network (AIRMoN), and reports the results of these programs. The goal of the CAL quality assurance program is to provide reliable, consistent, high-quality data that fulfill the needs of researchers and other data users. This is achieved by incorporating quality checks throughout the sample flow process. System blanks and control checks are included at strategic sample and data flow points. Results are compiled to generate information about the quality of the data, which are presented in tables, figures, or brief written explanations. The CAL was within the quality control objectives for the networks in 2002.

Acknowledgments

This *Quality Assurance Report*, a product of many individuals, summarizes the quality control/quality assurance measures 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). The U.S. Geological Survey (USGS) 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 editor contributed their time and input to the final report: Karen Harlin, NADP/CAL; Eva Kingston, Illinois State Water Survey (ISWS); and Christopher Lehmann, ISWS.

The NADP is a cooperative research support program entitled National Research Support Project - 3: A Long-Term Monitoring Program in Support of Atmospheric Chemical Deposition. State Agricultural Experiment Stations, federal, state, and local government agencies, universities, and nongovernmental organizations support the NADP, as does the Cooperative State Research, Education, and Extension Service, U.S. Department of Agriculture, under Agreement No. 2002-39138-11964. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the author and do not necessarily reflect the view of the U.S. Department of Agriculture or any other sponsor.

Executive Summary

The *Quality Assurance Plan NADP/NTN Deposition Monitoring* 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). The CAL was in compliance with the NADP QAP in 2002.

More samples were processed and analyzed in 2002 than in any other year in the history of NADP. Daily procedures include charting instrument standardization and maintenance and ensuring that the instruments operate in statistical control. Following strict standard operating procedures from sample arrival at the CAL to data archival with the Program Office ensures sample integrity and quality data. Data obtained from the laboratory analysis of the Quality Control Sample (QCS) solutions used at the CAL show the instrumentation to be in statistical control for 2002.

Weekly QA procedures ensure that all materials coming into contact with the precipitation samples do not contaminate the samples. Any problems that arise must be investigated, documented, and eliminated if possible or practical. All blank analyses, matrix-spiked analyses, internal blind sample analyses for NTN and AIRMoN, and replicate analyses for 2002 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 and that of other laboratories around the world doing similar work. In 2002, the CAL participated in five different independent studies in addition to the U.S. Geological Survey (USGS) laboratory intercomparison study program. The USGS operates the QA program for the NADP/NTN. The CAL ranked fourth overall in the USGS intercomparison study, although the differences between the eight participating laboratories were minor and within the detection limits of the CAL. In 2002, the CAL was under contract to prepare samples for the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) intercomparison studies. Although the CAL participated in the studies, the CAL results were not included in the final study rankings because samples were made and initially tested at the CAL. The CAL results were favorable, when unofficially compared with those from other participating laboratories. The National Water Research Institute (NWRI) of Canada conducted two intercomparison studies in 2002. The CAL ranked "satisfactory" in both. The fifth intercomparison study was with the Norwegian Institute for Air Research (NILU), the 20th European Monitoring and Evaluation Programme (EMEP) intercomparison of analytical methods for atmospheric precipitation. All results were within the standard expected variation for the analyte.

Overall the CAL has performed well in all intercomparison studies during 2002 based on the parameters established by each study for evaluating the participating laboratories. Based on these intercomparison studies, the CAL continues to be one of the best atmospheric precipitation laboratories in the world.

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 2002. 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 2002, 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 from a specified sampler are collected in buckets . These buckets are removed each Tuesday morning, and the samples are decanted into 1-liter, wide-mouthed, high-density polyethylene (HDPE) bottles and both are shipped to the CAL each week for processing. Figure I-1 illustrates the sample's journey after arrival at the CAL.

The Atmospheric Integrated Research Monitoring Network (AIRMoN) protocol was implemented in 1992, and the network's QA program was established. Since then, NADP/NTN and NADP/AIRMoN have shared the same analytical staff and methodology. The AIRMoN sample protocol and analytical methodologies differ from those of NTN, but both maintain the same high quality control (QC) objectives (Figure I-2).

Table I-1 lists staff responsibilities from sample 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 a decade. The CAL employed Tracy Dombek part time in 2002 to help with the Atomic Absorption analyses.

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 2002.

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 2002. Table I-3 lists the CAL method detection limits (MDLs) for the analytes of interest and the methods used. This table also gives historic perspective of how analytical techniques and MDLs have changed over the course of the program and samples affected. The MDLs are calculated annually or when there is a significant change in instrumentation or analyst using methods defined in Appendix A. Laboratory MDLs are maintained at or below the MDLs listed in the *NADP Quality Assurance Plan* (Simmons et al., 1991, revised 1993).

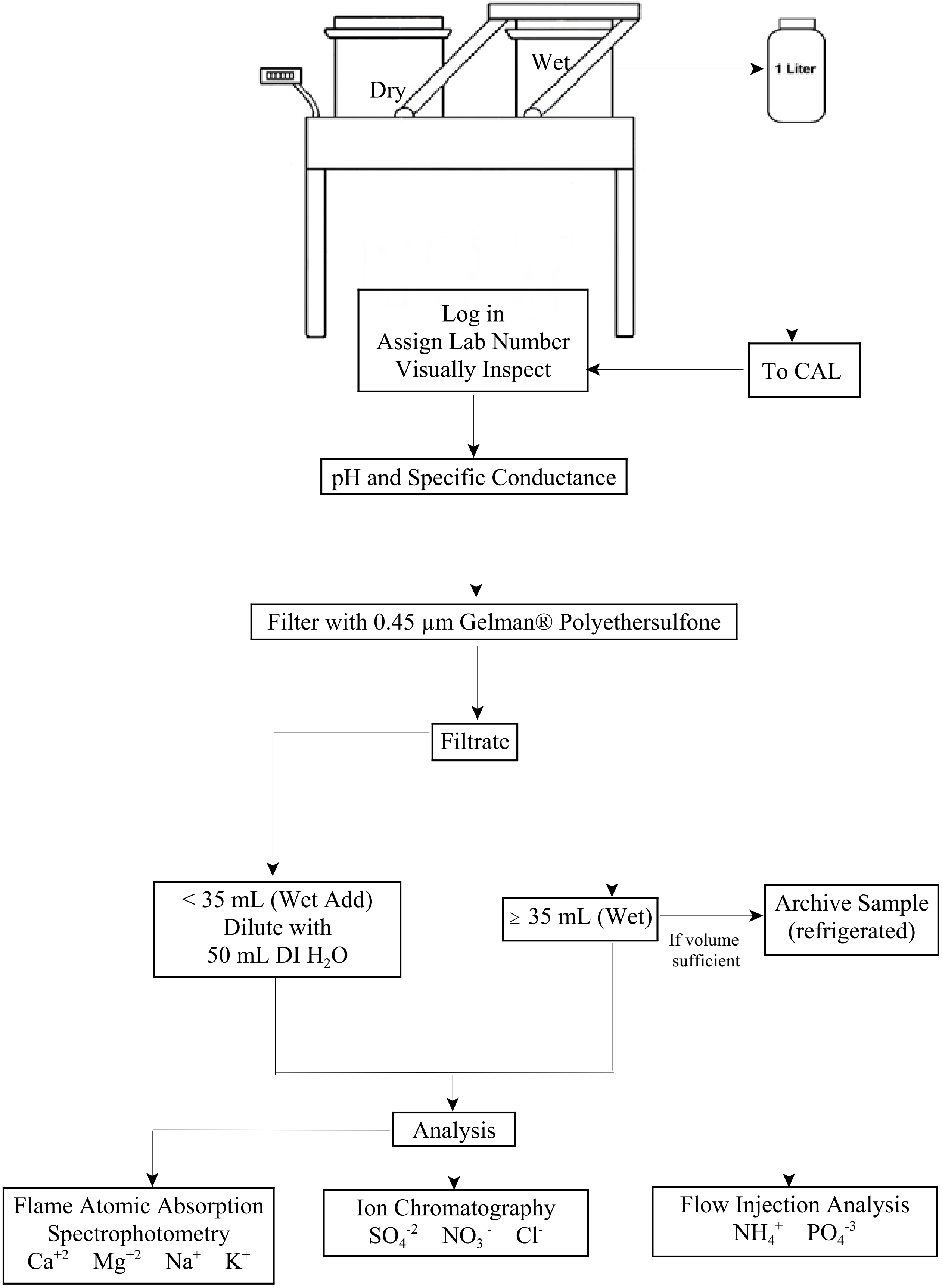

Figure I-1. NADP/NTN sample processing flowchart, January 2002 – December 2002.

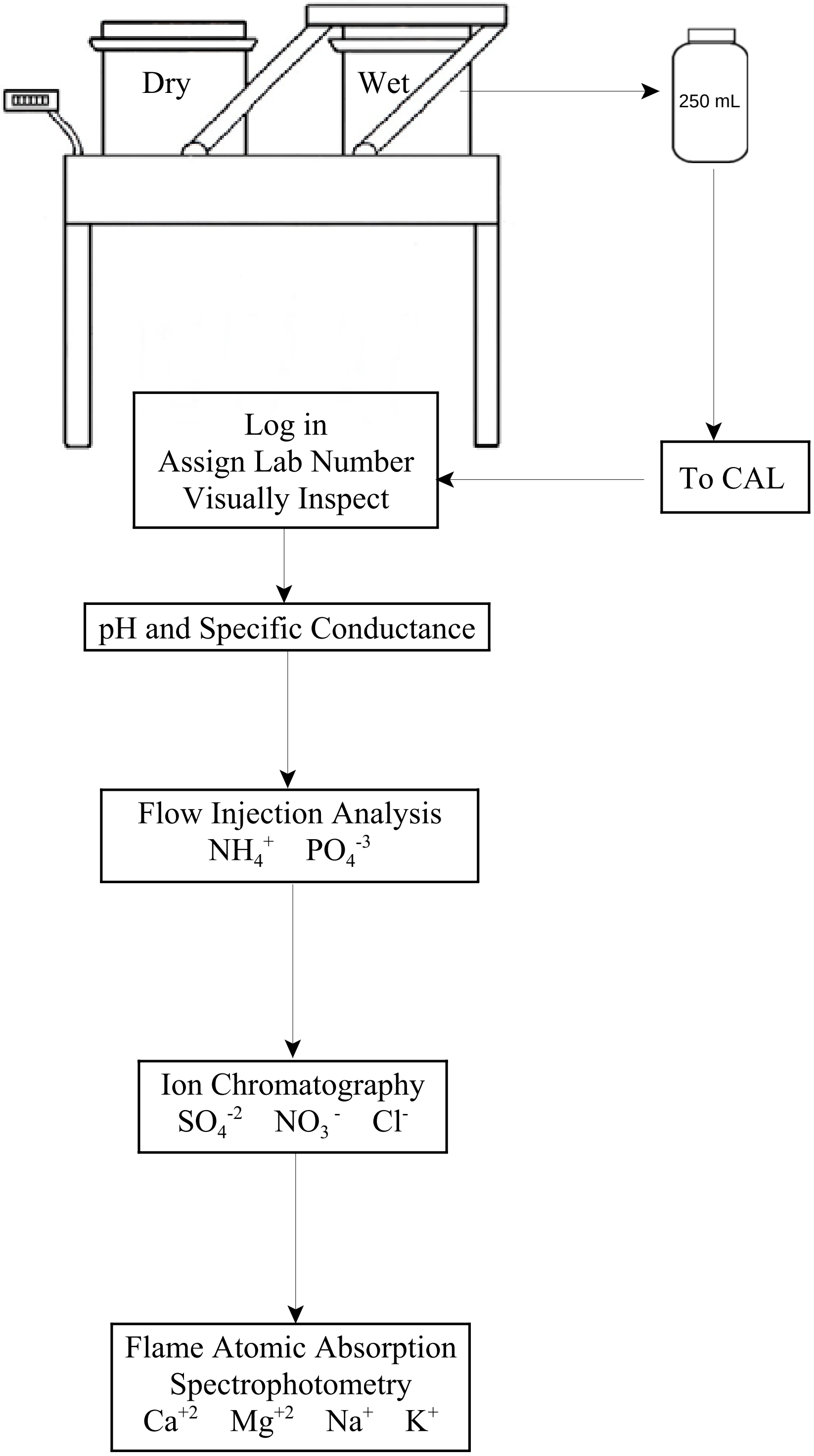

Figure I-2. NADP/AIRMoN sample processing flowchart, January 2002– December 2002.

Table I-1. Central Analytical Laboratory Analytical Staff, 2002

Staff member	*Job function*	*Period of employment*
Sue Bachman	Analysis of ammonium	08/80 - 12/02
	Analysis of calcium, sodium, magnesium, and potassium	11/88 - 12/02
	Analysis of orthophosphate	01/94 - 12/02
	Sample processing coordinator	09/98 - 12/02
Phyllis Ballard	Bucket and bottle cleaning	09/97 - 04/02
	Sample receipt and processing	04/98 - 12/02
	AIRMoN sample receipt	06/99 - 12/02
Brigita Demir	Analysis of chloride, sulfate, and nitrate	09/81 - 12/02
Tracy Dombek	NTN analysis of calcium, sodium, magnesium, and potassium	08/01 - 12/02
Karen Harlin	Office of Atmospheric Chemistry Laboratory Supervisor	06/97 - 09/98
	NADP Assistant Coordinator	09/98 - 12/02
	NADP CAL Manager	09/98 - 09/00
	NADP CAL Director	09/00 - 12/02
Theresa Ingersoll	NTN sample receipt and processing	03/85 - 12/02
Tracie Patten	Analysis of pH and conductivity and NTN sample processing	09/98 - 12/02
	Analysis of ammonium and orthophosphate	03/02 - 12/02
Jeffrey Pribble	NTN sample receipt	07/87 - 12/02
	Supply procurement	07/87 - 12/02
	Backup NTN site liaison	04/02 - 12/02
Jane Rothert	AIRMoN Coordinator	05/92 - 12/02
	CAL Quality Assurance Specialist	07/97 - 12/02
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 - 12/02
	AIRMoN analysis of chloride, nitrate, and sulfate	06/99 - 12/02
	NTN analysis of ammonium and orthophosphate	12/00 - 12/02
Angela Weddle	NTN sample processing	06/95 - 12/97
	Analysis of pH and conductivity	10/89 - 12/02

Note:
The reporting period ended in December 2002. 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, 2002

Staff member	*Job function*	*Period of employment*
Tom Bergerhouse	Computer systems support	07/98 - 12/02
	AIRMoN database manager	05/01 - 12/02
Scotty Dossett	NTN site liaison	09/81 - 12/02
Kathy Douglas	NADP/CAL database manager	04/80 - 05/01
	NTN database manager	05/01 - 12/02
Greg Dzurisin	Computer programer	09/83 - 12/02
Karen Harlin	Final data review	07/97 - 12/99
Sarah Milton	Data screening	01/98 - 12/02
Angela Kwon Rakow	Data review	11/99 - 12/02
Jane Rothert	Data quality assurance	07/97 - 12/02

Note:
The reporting period ended in December 2002.

Table I-3. Method Detection Limits (MDLs) for Precipitation Analysis, 1978 – 2002

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 02	NA6544 - NX3302	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 02	NA7300 - NX3302	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 02	NA7742 - NX3302	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 02	NA6001 - NX3302	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 02	NH6701 - NX3302	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[a]	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 02	NS3701 - NX3302	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 02	NS3701 - NX3302	0.010	Ion Chromatography
Sulfate	Jul 78 - Apr 85	NA0001 - ND1938[b]	0.10	Methylthymol Blue (Segmented Flow Colorimetry)
	Apr 85 - Dec 99	ND1939 - NS3700	0.03	Ion Chromatography
	Jan 00 - Dec 02	NS3701 - NX3302	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[c]	0.01	
	Jun 87 - Nov 93	NF4631 - NM6824[d]	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)
	Jan 01 - Dec 02	NU7203 - X3302	0.009	

Notes:

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

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

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

[d] 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, hand-entered data were verified using a double-entry system. Data from the atomic absorption spectrophotometer, the ion chromatograph, and the flow injection analyzer were transferred electronically to the database in 2002. Manual double entry of pH and conductivity measurements continued through June 20, 2002, when the Laboratory Information Management System (LIMS) for the CAL went on line. Those measurements were recorded automatically in the LIMS and then transferred to the database. Once data have been verified and validated by CAL data management staff, the Program Office does additional screening and coding before data are available for general usage on the Internet (htpp://nadp.sws.uiuc.edu). Turnaround time for sample analysis and data processing is about 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) with minimal contamination analyzed at the CAL in 2002. 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. There were 8445 “wet” (W) samples in 2002 with a mean precipitation volume of 1556.9 mL and a median precipitation volume of 959.9 mL.

Table I-5 lists the percentile concentration values for AIRMoN samples having a sample volume large enough for a complete chemical analysis in 2002. There were 996 samples with a mean volume of 753.4 mL and a median volume of 407.5 mL.

Table I-6 (NTN) and Table I-7 (AIRMoN) show the sample percentile concentration values for a five-year period, from the beginning of 1998 until the end of 2002. For NTN, 39,602 wet-only samples had no severe contamination, a mean sample volume of 1487.5 mL, and a median sample volume of 908.0 mL. For AIRMoN, 4536 wet, nonquality assurance samples had no severe contamination, a mean sample volume of 714.9 mL, and a median sample volume of 407.1 mL. Compared to the long-term averages, median NADP/NTN concentrations were about the same in 2002, and median AIRMoN concentrations were lower than historical values.

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., 1991, revised 1993) summarizes the methods used to document sample analysis. Various facets of the program have been modified and refined over time. 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 analysis of low ionic strength solutions. Internal QC standard (QCS) samples used in the laboratory and known to the analysts as guides to ensure the accuracy of analyses. Other samples unknown or blind to the analysts are valuable ways of assessing sample bias and/or precision in the NADP/NTN and NADP/AIRMoN daily queue. Extensive analyses of blank and deionized (DI) water-spiked solutions every week help identify and/or eliminate sources of contamination.

In addition to external QA studies performed by the U.S. Geological Survey (USGS) as an official part of network operations, the CAL participates in several international laboratory

Table I-4. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/NTN Precipitation Samples, 2002

	Percentile concentration values (mg/L)									
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*99th*	*Maximum*
Calcium	-0.009	0.014	0.023	0.049	0.111	0.261	0.552	0.889	2.391	30.440
Magnesium	-0.003	0.003	0.004	0.010	0.023	0.047	0.093	0.145	0.300	3.120
Sodium	-0.003	0.005	0.008	0.019	0.053	0.151	0.426	0.825	2.330	33.200
Potassium	-0.003	-0.003	0.003	0.007	0.017	0.037	0.076	0.119	0.371	4.800
Ammonium	-0.02	0.02	0.04	0.11	0.24	0.49	0.84	1.21	1.92	6.18
Sulfate	-0.010	0.133	0.222	0.515	0.998	1.706	2.726	3.611	5.824	35.282
Nitrate	-0.010	0.182	0.293	0.580	1.075	1.827	2.900	3.711	6.247	18.146
Chloride	-0.005	0.021	0.028	0.051	0.108	0.259	0.726	1.459	4.023	29.975
Orthophosphate	-0.009	-0.009	-0.009	-0.009	-0.009	-0.009	-0.009	-0.009	0.060	3.174
Lab pH (units)	3.64	4.23	4.36	4.60	4.96	5.46	6.13	6.47	6.92	8.12
Lab specific conductance (µS/cm)	1.6	3.5	4.6	7.5	12.3	19.6	30.2	39.0	63.5	236.5

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 = 8445; mean sample volume = 1556.9 mL; and median sample volume = 959.9 mL. Negative numbers 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, 2002

	Percentile concentration values (mg/L)									
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*99th*	*Maximum*
Calcium	-0.009	0.001	0.008	0.026	0.072	0.171	0.349	0.587	1.281	4.040
Magnesium	-0.003	0.001	0.002	0.008	0.021	0.053	0.128	0.205	0.386	1.296
Sodium	-0.002	0.003	0.006	0.016	0.064	0.287	0.958	1.691	3.339	12.495
Potassium	-0.004	0.002	0.004	0.010	0.020	0.042	0.071	0.104	0.187	0.930
Ammonium	0.00	0.04	0.06	0.13	0.27	0.51	0.77	1.09	1.58	2.12
Sulfate	0.034	0.293	0.468	0.895	1.533	2.624	4.176	5.384	7.860	17.708
Nitrate	0.026	0.236	0.338	0.651	1.211	2.337	3.713	4.983	8.309	16.104
Chloride	0.000	0.021	0.031	0.068	0.165	0.574	1.859	3.267	6.308	25.347
Orthophosphate	0.000	0.000	0.000	0.000	0.008	0.013	0.024	0.039	0.124	0.720
Lab pH (units)	3.45	3.95	4.06	4.25	4.49	4.75	5.03	5.24	6.13	6.64
Lab specific conductance (µS/cm)	2.6	6.0	8.7	13.3	21.8	35.4	52.4	64.6	103.0	213.8

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 = 996; mean sample volume = 753.4 mL; and median sample volume = 407.5 mL. Negative numbers represent actual values measured, not method detection limits, for each parameter.

Table I-6. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/NTN Precipitation Wet-only Samples, 1998–2002

	Percentile concentration values (mg/L)									
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*99th*	*Maximum*
Calcium	MDL	0.017	0.026	0.053	0.118	0.267	0.544	0.807	1.905	61.680
Magnesium	MDL	0.003	0.005	0.010	0.022	0.046	0.090	0.143	0.290	3.880
Sodium	MDL	0.006	0.009	0.019	0.049	0.141	0.400	0.699	2.250	33.200
Potassium	MDL	MDL	0.004	0.009	0.018	0.038	0.074	0.108	0.292	6.080
Ammonium	MDL	MDL	0.03	0.09	0.23	0.46	0.77	1.04	1.79	16.39
Sulfate	MDL	0.136	0.230	0.530	1.070	1.913	3.050	4.000	6.265	125.480
Nitrate	MDL	0.175	0.293	0.598	1.120	1.920	2.940	3.771	6.203	45.430
Chloride	MDL	0.022	0.030	0.052	0.108	0.249	0.663	1.225	3.724	35.000
Orthophosphate	MDL	MDL	MDL	MDL	MDL	MDL	MDL	MDL	0.030	8.703
Lab pH (units)	3.41	4.16	4.28	4.50	4.86	5.34	5.96	6.32	6.79	8.12
Lab specific conductance (µS/cm)	1.1	3.4	4.5	7.5	12.9	21.6	33.6	42.1	68.7	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 = 39602; mean sample volume = 1487.5 mL; and median sample volume = 908.0 mL. The method detection limit (MDL) changed during this five-year period. See Table I-3 for the appropriate MDLs.

Table I-7. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/AIRMoN Precipitation Wet-only Samples, 1998–2002

	Percentile concentration values (mg/L)									
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*99th*	*Maximum*
Calcium	-0.015	0.008	0.016	0.039	0.093	0.207	0.430	0.725	1.524	5.252
Magnesium	-0.003	0.002	0.003	0.008	0.021	0.057	0.135	0.200	0.405	3.298
Sodium	-0.004	0.004	0.007	0.017	0.056	0.281	0.893	1.453	3.214	30.150
Potassium	-0.026	0.002	0.004	0.010	0.020	0.040	0.074	0.109	0.211	1.170
Ammonium	-0.02	0.03	0.06	0.13	0.27	0.51	0.85	1.11	1.87	4.11
Sulfate	0.034	0.340	0.521	0.992	1.751	3.040	4.733	5.975	9.286	19.420
Nitrate	0.019	0.270	0.400	0.765	1.440	2.585	4.250	5.540	8.968	17.680
Chloride	0.000	0.025	0.040	0.077	0.175	0.585	1.740	2.768	5.786	62.800
Orthophosphate	-0.006	0.000	0.000	0.000	0.006	0.013	0.025	0.041	0.125	1.516
Lab pH (units)	3.37	3.88	3.99	4.18	4.41	4.66	4.95	5.15	5.77	7.00
Lab specific conductance (µS/cm)	2.0	6.8	9.6	15.4	24.7	39.7	60.0	74.5	111.7	237.4

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 = 4536; mean sample volume = 714.9 mL; and median sample volume = 407.1 mL. Negative numbers represent actual values measured, not method detection limits for each parameter.

intercomparison studies. These studies allow the CAL to evaluate the quality of its work 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 - 2003). This report presents and discusses summaries of the results of QA programs in place in 2002.

II. Laboratory Quality Assurance - A General Description

The quality of CAL data is assessed and improved through two separate QA programs, field and laboratory. 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 with measurement of pH and specific conductance soon after sample collection and prior to shipping following field protocols . 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 2002 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). The QCS solution used for pH and conductivity-only measurements was 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). Because calibration buffer solutions are of high ionic strength, the QCS is necessary to verify that the pH probe will measure solutions 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 laboratory identification number, and then visually inspected.

The NTN samples are filtered into pre-washed 60-mL high-density polyethylene (HDPE) round bottles using 0.45-micrometer (µm) pore-size polyethersulfone filters following pH and conductivity measurements. These sample aliquots are used to obtain the chemistry of the weekly samples and are coded “W” for sample type. When there is sufficient volume, a second sample aliquot is filtered into a square 60-mL HDPE bottle for archival purposes. 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. Because the NTN protocol specifies weekly collection, samples are in the field for up to a week and then shipped to the CAL. Once pH and conductivity measurements are complete, the order of analyses is not prioritized. Low-volume NTN samples (less than 35 mL) coded “WA” are diluted after pH and conductivity are determined to ensure sufficient volume for complete analysis.

The AIRMoN samples are never filtered, but are kept at about 4°C in the 250-mL shipping bottles into which they were decanted at the site. 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

Table II-1. NADP/NTN and NADP/AIRMoN Laboratory QA/QC Program Summary, 2002

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 solutions every 12-15 samples (depending on instrumentation).
    3. Record and plot QCS solution values on daily control charts.
    4. Repeat standardization as indicated by QCS solution measurements.
  B. Prepare records of standards preparation and update instrument maintenance records.
  C. Inspect control charts generated from QCS solution measurements.

II. Weekly
  A. Evaluate laboratory water and supplies for cleanliness.
    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 designated 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 Resources Division, Branch of Quality Systems in Denver.
  E. Validate QCS solution 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.

mandated 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, sample volume is not always sufficient for complete analysis; therefore, highest priority measurements are made first.

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 FR25 and FR75 solutions are prepared in house and are tested (Simmons et al., 1991, revised 1993) prior to use as QCS solutions. Nutrient concentrates from Environmental Resource Association[1] are diluted and used for orthophosphate[2] QCS solutions.

Analysts select the samples by laboratory identification numbers for analysis by atomic absorption, ion chromatography, or flow injection automated colorimetry. The MDLs for the analytes are recalculated as needed, when a new instrument is purchased, when a critical new part is installed on an existing instrument, or for new analysts using the instruments. The solution used to determine the MDL is the simulated rain sample prepared to be similar to the tenth percentile of the precipitation concentrations (FR10). In addition, these instruments are standardized using solutions encompassing the expected concentration range of samples. These 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 FR25 and FR75 QCS solutions. Values of the QCS solutions are plotted daily on control charts. These QCS solutions are analyzed immediately after instrument standardization and 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 to check for drift throughout the day.

Solutions from multiple sources are submitted to the CAL each week for analysis. These samples are used to evaluate possible contamination both from sample collection and shipping activities and from processing procedures used in the laboratory. There is regular monitoring of the deionized (DI) water used for standards preparation, bucket and bottle washing, rinse water, and filter leaching. The DI water is collected weekly from atomic absorption, sample preparation, and bucket-washing laboratories, and then analyzed for contamination. 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.

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[1] Environmental Resource Association, 5540 Marshall Street, Arvada, CO 80002, Simple Nutrients, catalog number 584. **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.

[2] Orthophosphate is not stable, especially at the low concentrations found in NADP samples (Ridder et al., 1985).

Other weekly components of the program include submission of three samples as internal blinds and replicates. Three internal blind samples, two unfiltered and one filtered, are introduced to the NTN analysis queue weekly. All three samples are introduced into the analysis queue unknown to the analysts although the concentration and the laboratory number of the samples is known to the QA Specialist. Two percent of the total NTN sample load is split and processed, separating originals and replicates for analysis. Replicates are submitted with new sample identification numbers, unknown to the analysts, and are analyzed in numerical order, approximately 100 sample numbers higher than the original sample number. 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 Bondville, Illinois site (IL11) 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: 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 undiluted wet (“W”) sample. Samples with either difference greater than allowed by the *NADP Quality Assurance Plan* or 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.

Samples generated externally to the NADP program are an integral part of the CAL QA. Every two weeks, the USGS ships the CAL four interlaboratory comparison samples, which are analyzed as a group upon arrival. The analysts know that the samples are interlaboratory comparison samples; however, they do not know the concentrations of the parameters in the samples. 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 performance of the CAL in relation to other laboratories in the United States and around the world that also analyze low ionic strength water samples.

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 solutions 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 solution is measured throughout the sample run, and 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 Tables III-1 and III-2 represent bias and precision estimates under optimum conditions. The data were generated using QCS solutions and calibration standards known to the analysts, rather than precipitation or blind samples. The QCS solutions and standards are relatively stable, whereas the actual precipitation samples are susceptible to chemical change. These solutions represent the optimum precision and bias expected from sample analysis and should be used in that context as data quality indicators. In 2002, they were comparable with previous years' data and fell within the QA specifications of the NADP QAP (Simmons et al., 1991, revised 1993). When the absolute bias exceeds the critical concentration at the 95th percentile, the bias (see Appendix A) is considered to be statistically significant. For 2002, ammonium, orthophosphate, chloride, and nitrate showed a statistically significant bias for one or both QCS solutions. This 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., 1991, revised 1993) for more information.

Table III-1. Analytical Bias and Precision Determined from Analysis of Simulated Rain QCS, 2002

Parameter	*Target concentrations (mg/L)*	*Measured mean concentrations (mg/L)*	*Number of replicates*	*Bias (mg/L)*	*Bias (%)*	*Standard deviation (mg/L)*	*RSD (%)*	*Critical concentration (mg/L)*	*Statistically significant bias (95%)*
Calcium	0.071[a]	0.074	1416	-0.001	1.1	0.004	4.8	0.003	no
	0.280[b]	0.285	478	-0.002	-0.5	0.011	3.8	0.005	no
Magnesium	0.016	0.017	1612	-0.000	-0.3	0.001	6.4	0.001	no
	0.065	0.067	478	0.000	-0.2	0.003	4.0	0.001	no
Sodium	0.046	0.047	1600	-0.001	-1.5	0.002	4.6	0.001	no
	0.191	0.187	542	-0.002	-1.0	0.006	3.2	0.004	no
Potassium	0.012	0.013	1544	0.0004	2.7	0.001	8.5	0.001	no
	0.050	0.052	514	0.001	2.4	0.002	3.8	0.001	no
Ammonium	0.079	0.084	1116	0.005	6.9	0.006	6.8	0.003	yes
	0.340	0.343	1016	0.003	0.8	0.006	1.8	0.003	no
Orthophosphate	0.025	0.027	957	0.002	8.6	0.003	9.8	0.001	yes
	0.123	0.115	920	-0.008	-6.3	0.005	4.0	0.003	yes
Chloride	0.131	0.129	1333	-0.002	-1.5	0.003	2.4	0.001	yes
	0.540	0.537	1339	-0.003	-0.6	0.006	1.1	0.002	yes
Nitrate	0.470	0.472	1324	0.002	0.4	0.006	1.2	0.002	no
	1.936	1.930	1287	-0.006	-0.3	0.012	0.6	0.004	yes
Sulfate	0.632	0.633	1187	0.001	0.1	0.006	1.0	0.003	no
	2.579	2.579	1268	0.000	0.0	0.023	0.9	0.008	no
pH units (μeq/L)	4.93 (11.7)[c]	4.94 (11.5)	1811	0.01 (-0.2)	0.2 (-5.8)	0.03 (1.2)	0.6 (10.7)	0.02 (0.28)	no (no)
	4.35 (44.7)	4.36 (43.6)	1329	0.01 (-1.1)	0.25 (-2.3)	0.02 (1.9)	0.5 (4.3)	0.01 (0.94)	no (no)
Specific conductance (μS/cm)	7.3	7.3	1246	0.0	0.0	0.5	6.9	0.3	no
	27.7	27.7	1134	0.0	0.0	0.3	0.9	0.1	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).

Table III-2. Analytical Bias and Precision Determined from Analysis of Analytical Standards, 2002

Parameter	*Target concentrations (mg/L)*	*Measured mean concentrations (mg/L)*	*Number of replicates*	*Bias (mg/L)*	*Bias (%)*	*Standard deviation (mg/L)*	*RSD (%)*
Calcium	0.050[a]	0.046	404	-0.004	-8.2	0.004	8.8
	0.500[b]	0.482	380	-0.018	-3.7	0.014	3.0
Magnesium	0.025	0.024	406	-0.001	-4.6	0.001	4.0
	0.100	0.096	384	-0.004	-3.6	0.003	2.7
Sodium	0.025	0.024	416	-0.001	-3.7	0.002	7.1
	0.250	0.253	397	0.003	1.3	0.009	3.7
Potassium	0.025	0.024	415	-0.001	-2.4	0.002	8.7
	0.100	0.101	391	0.001	0.9	0.003	3.3
Ammonium	0.075	0.074	405	-0.001	-1.9	0.005	6.8
	1.000	1.003	438	0.003	0.1	0.015	1.5
Orthophosphate	0.010	0.009	405	-0.001	-10.1	0.002	20.2
	0.100	0.098	438	-0.001	-1.8	0.006	6.2
Chloride	0.025	0.026	723	0.001	5.3	0.002	9.3
	1.500	1.500	692	0.000	0.0	0.012	0.8
Nitrate	0.050	0.056	722	0.006	11.5	0.004	7.3
	6.000	6.014	692	0.014	0.2	0.041	0.7
Sulfate	0.050	0.055	723	0.005	9.8	0.005	9.8
	6.000	6.011	678	0.011	0.2	0.046	0.8
Specific conductance[c] (µS/cm)	3.4	3.7	256	0.3	8.2	0.4	9.9

Notes:

See Appendix A for definitions and formulas for bias, precision, and RSD.

[a] The first set of values for each parameter is for the low calibration standard for that analyte.

[b] The second set of values for each parameter is for the high calibration standard for that analyte.

[c] The specific conductance values are based on 02FR10, the internally formulated simulated rain solution approximating the tenth percentile concentration.

IV. Weekly Quality Assurance/Quality Control Procedures

Three quality assurance (QA) activities occur on a weekly basis for NTN: 1) three solutions are submitted as internal blind samples for which only the QA Specialist knows the concentrations; 2) two percent of the network samples are split and analyzed in replicate; and 3) blanks and container leachates are prepared and analyzed. The AIRMoN internal blinds also are submitted weekly. The AIRMoN bottle blanks and leachates are submitted monthly but are included in the weekly procedures with the NTN blanks and leachates.

A. Internal Blind Samples

1. NADP/NTN

Each week the QA Specialist submits three solutions with completed Field Observer Report Forms (FORFs) to the sample processing area, and laboratory identification numbers are assigned. These samples are processed with the network samples, but two of the samples are unfiltered to monitor for possible filter bias. These samples are identified as SWS1, SWS2, and SWS3. In 2002, the SWS1 samples were High-Purity Standards[3] Simulated Rainwater 1 (H-PS SR1) and 2 (H-PS SR2), which were alternated weekly. The SWS2 samples were alternated weekly between DI water from the ion chromatography laboratory and a synthetic rain sample made in house that approximated the 10th percentile of NTN sample concentrations (FR10). 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 2002 data from the weekly internal blind 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 solution). The bias and precision estimates derived are, therefore, more representative of precipitation sample measurements than the measurement of the FR25 and FR75 solutions or the standards used as QCS solutions. The SWS1 and SWS2 samples overall show less bias and less variability than the filtered SWS3 samples, which have an even smaller sample population for each solution. For parameters with concentrations near the detection limits, there is a higher standard deviation due to the noise in the instrument and, therefore, the measurement. The filtered, internally formulated synthetic precipitation samples (FR10) and the filtered DI water also show less bias than the filtered High-Purity Standards samples except for parameters close to the detection limits. The lower biases for the blind audit samples prepared in house, both filtered and unfiltered, because the target, measured concentrations for these solutions are determined in the laboratory, eliminating biases caused by the instrument, calibration, or other causes. Smaller biases in the filtered solutions may be due to pH of the solutions. The High-Purity Standards solutions have lower pH than either DI water or the FR10 solution. The lower pH may cause leaching from the filters and, therefore, a bias in those solutions. Also once again, the calcium standard concentration as furnished by High-Purity Standards are considerably different than concentrations found at the CAL. This has been confirmed previously by other laboratories measuring these samples.

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[3] 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 1 (H-PS SR1) and 2 (H-PS SR2), Unfiltered, 2002

Parameter	*Target concentration[a] (mg/L)*	*Measured concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard deviation (mg/L)*	*RSD (%)*
Calcium	0.014[b]	0.009[c]	-0.005	-37.3	0.008	91.8
	0.052[d]	0.050	-0.002	-3.4	0.005	9.0
Magnesium	0.020	0.019	-0.001	-6.5	0.001	7.0
	0.050	0.048	-0.002	-3.8	0.001	2.6
Sodium	0.20	0.198	-0.002	-1.0	0.016	8.0
	0.40	0.398	-0.002	-0.4	0.010	2.5
Potassium	0.051	0.049	-0.002	-3.6	0.002	3.6
	0.095	0.099	0.004	4.7	0.002	1.9
Ammonium[e]	0.100	0.10	0.00	0.0	0.01	12.1
	1.00	0.93	-0.07	-7.5	0.02	2.0
Sulfate	2.47	2.496	0.026	1.1	0.024	0.9
	10.1	10.234	0.134	1.3	0.172	1.7
Nitrate	0.50	0.517	0.017	3.4	0.007	1.4
	7.0	7.176	0.176	2.5	0.067	0.9
Chloride	0.25	0.221	-0.029	-11.6	0.005	2.2
	0.98	1.005	0.025	2.5	0.021	2.1
pH (units)	4.35	4.34	-0.01	-0.3	0.02	0.5
	3.60	3.62	0.02	0.5	0.02	0.6
H (µeq/L)	44.7	45.9	1.2	2.8	2.1	4.5
	251.2	241.5	-9.7	-3.9	12.1	5.0
Specific conductance (µS/cm)	22	24.8	2.8	12.7	0.6	2.6
	123.5	127.4	3.9	3.2	1.4	1.1

Notes:

There were 27 H-PS SR1 samples and 26 H-PS SR2 samples in 2002.

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

[b] Concentration values for H-PS SR1 (lot # 102216).

[c] The MDL for calcium is 0.009, so the concentration for this solution is close to the noise of the instrument.

[d] Concentration values for H-PS SR2 (lot # 129002).

[e] Ammonium concentrations were found to be unstable and are provided for information purposes only.

Table IV-2. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS2), Deionized (DI) Water, and Internally Formulated Simulated Rain (02FR10), Unfiltered, 2002

Parameter	*Target concentration (mg/L)*	*Measured concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard deviation (mg/L)*	*RSD (%)*
Calcium	<0.009[a]	<0.009	-0.004		0.004	
	0.029[b] [c]	0.026	-0.003	-11.9	0.005	20.4
Magnesium	<0.003	<0.003	0.000		0.001	
	0.006	0.007	0.001	9.6	0.001	11.3
Sodium	<0.003	<0.003	-0.001		0.002	
	0.018	0.019	0.001	5.3	0.002	12.8
Potassium	<0.003	<0.003	-0.002		0.002	
	0.004	0.004	0.000	1.0	0.002	41.5
Ammonium	<0.02	<0.02	0.00		0.00	
	0.03	0.03	0.00	6.9	0.01	17.7
Sulfate	<0.010	<0.010	0.000		0.003	
	0.256	0.257	0.001	0.4	0.005	2.0
Nitrate	<0.010	<0.010	0.000		0.000	
	0.192	0.192	0.000	-0.2	0.004	2.1
Chloride	<0.006	<0.006	0.000		0.003	
	0.053	0.051	-0.002	-3.7	0.004	6.9
pH (units)	5.65	5.66	0.01	1.1	0.11	1.6
	5.23	5.23	0.00	-0.1	0.03	0.6
H (µeq/L)	2.2	2.3	0.1	1.7	0.5	19.9
	5.9	6.0	0.1	1.3	0.5	7.8
Specific conductance (µS/cm)	0.9	1.3	0.4	43.2	0.2	10.2
	3.4	3.7	0.3	10.0	0.5	13.6

Notes:

There were 27 DI samples and 26 02FR10 samples in 2002.

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

[b] Concentration values for internally formulated simulated rain (02FR10).

[c] The concentration values for the 02FR10 are the mean of 7-11 analyses immediately after the solution was prepared.

Table IV-3. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS3), High-Purity Standards Simulated Rainwater 1 (H-PS SR1) and 2 (H-PS SR2), Filtered, 2002

Parameter	*Target concentration*[a] *(mg/L)*	*Measured concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard deviation (mg/L)*	*RSD (%)*
Calcium	0.014[b]	0.040	0.026	184.2	0.010	24.4
	0.052[c]	0.096	0.044	83.7	0.012	12.2
Magnesium	0.020	0.017	-0.003	-15.4	0.012	71.0
	0.050	0.050	0.000	0.3	0.007	14.9
Sodium	0.20	0.192	-0.008	-4.2	0.010	5.0
	0.40	0.382	-0.018	-4.5	0.014	3.5
Potassium	0.051	0.048	-0.003	-6.9	0.001	3.0
	0.095	0.096	0.001	1.2	0.003	2.9
Ammonium[d]	0.100	0.10	0.0	-0.9	0.01	13.4
	1.00	0.89	-0.11	-10.8	0.02	2.5
Sulfate	2.47	2.412	-0.058	-2.4	0.027	1.1
	10.1	9.790	-0.300	-3.0	0.154	1.6
Nitrate	0.50	0.505	0.005	-1.0	0.013	2.6
	7.0	6.908	-0.092	-1.3	0.125	1.8
Chloride	0.25	0.217	-0.034	-13.4	0.003	1.5
	0.98	0.964	-0.016	-1.6	0.026	2.7
pH	4.35	4.34	-0.01	-0.2	0.02	0.5
(units)	3.60	3.62	0.02	0.6	0.02	0.6
H	44.7	45.8	1.2	2.6	2.2	4.7
(µeq/L)	251.2	239.7	-11.5	-4.6	11.3	4.7
Specific conductance	22	24.9	2.9	13.2	0.9	3.4
(µS/cm)	123.5	127.7	4.2	3.4	1.1	0.8

Notes:

There were 14 H-PS SR1 and 13 H-PS SR2 samples in 2002.

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

[b] Concentration values for H-PS SR1 (lot #102216).

[c] Concentration values for H-PS SR2 (lot #129002).

[d] The NH_4 concentrations were 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 (DI)Water, and Internally Formulated Simulated Rain (02FR10), Filtered, 2002

Parameter	*Target concentration (mg/L)*	*Measured concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard deviation (mg/L)*	*RSD (%)*
Calcium	<0.009[a]	<0.009			0.013	
	0.029[b] [c]	0.032	0.003	9.0	0.004	13.2
Magnesium	<0.003	<0.003			0.001	
	0.006	0.006	0.000	-3.8	0.003	51.8
Sodium	<0.003	<0.003			0.002	
	0.018	0.018	0.000	-0.9	0.002	8.6
Potassium	<0.003	<0.003			0.003	
	0.004	0.005	0.001	13.5	0.003	55.8
Ammonium	<0.02	<0.02			0.01	
	0.03	0.03	0.005	18.3	0.00	14.2
Sulfate	<0.010	<0.010			0.005	
	0.256	0.252	-0.004	-1.7	0.006	2.2
Nitrate	<0.010	<0.010			0.004	
	0.192	0.187	-0.005	-2.7	0.004	2.4
Chloride	<0.006	<0.006			0.004	
	0.053	0.053	0.000	-0.6	0.004	7.9
pH (units)	5.65	5.62	-0.03	-1.7	0.05	0.6
	5.23	5.24	0.01	0.1	0.06	1.1
H (µeq/L)	2.24	2.48	0.24	25.0	0.3	10.8
	5.89	5.86	-0.03	-0.5	0.7	12.3
Specific conductance (µS/cm)	0.9	1.3	0.4	47.0	0.5	42.7
	3.4	3.7	0.3	9.3	0.5	14.2

Notes:
There were 13 samples in each set.

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

[b] Concentration values for internally formulated simulated rain (02FR10).

[c] The concentration values for the 02FR10 are the mean of 7-11 analyses immediately after sample preparation.

Certified solutions of two different concentrations from High-Purity Standards were used for the SWS1 samples (Table IV-1) in 2002. These samples, H-PS SR1 (lot #102216) and H-PS SR2 (lot #129002), were of similar concentrations to those used in previous years and slightly higher than the internal QCS solutions made at the CAL. The H-PS SR1 sample was similar in concentration to the higher concentration FR75 QCS solution for all analytes except calcium, magnesium, ammonium, chloride, and nitrate. The H-PS SR2 sample had even higher concentrations for all analytes except calcium and magnesium. The overall percent bias was higher for the High-Purity Standards samples than for the DI water and FR10 internal blind samples (Table IV-2). A similar difference between the High-Purity Standards samples and the QCS solutions was observed when the relative standard deviation (RSD) was compared except where the concentration of the analyte approached the detection limit. The QCS solution had a lower percent bias than the High-Purity Standards samples, which would be expected as the CAL established the QCS solution concentrations. High-Purity Standards does not certify the ammonium concentrations in their simulated rainwater samples. A positive bias between the laboratory measurements and the target concentration for calcium was determined for the filtered samples, and a smaller but still positive bias was determined for the unfiltered samples.

The SWS2 solutions were the lowest concentration QCS solutions 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 were placed randomly among the network samples so that their analytical results can indicate possible problems with sample carryover or false positives. The mean measured concentrations for DI water solutions were below the MDL for both unfiltered and filtered samples for all analytes in 2002, as tabulated in Tables IV-2 and IV-4. Chloride and calcium had a negative bias in the SWS1 samples (Table IV-1) with specific conductance having a positive bias. Magnesium and chloride had a negative bias in the filtered solution with calcium and specific conductance having a positive bias. Several parameters had slight positive or negative biases, but the difference between the target and the measured concentrations for these solutions was less than the detection limit in most cases.

The SWS3 H-PS samples (Table IV-3) had larger biases than most unfiltered SWS1 samples (Table IV-1). Some normal and expected variation was observed in the differences between filtered and unfiltered samples in 2002. The RSD for H-PS SR1 solution was smaller for calcium, potassium, and ammonium in 2002 than in 2001. The H-PS SR1 solution had a higher RSD for sodium in 2002 than in 2001 and the H-PS SR2 solution had a higher RSD for magnesium in 2002 than in 2001. Other parameters had similar RSDs in 2002 and 2001. For those parameters with higher RSDs in 2002, the difference was small and probably due to noise differences in the system from year to year. There was a positive calcium bias in filtered samples compared with unfiltered samples for both H-PS SR1 and H-PS SR2. The RSD for the higher concentration H-PS SR2 varied between the ions measured, with most being very similar to the RSD found in 2001. Both the H-PS SR1 and H-PS SR2 had higher acidity than solutions prepared at the CAL, the 02FR10, and DI water.

Tables B-1 and B-4 (Appendix B) are tabular comparisons of the filtered and unfiltered High-Purity Standards solutions. Tables B-2, B-3, B-5, and B-6 are the actual concentrations found for H-PS SR1 and H-PS SR2 filtered and unfiltered solutions. Tables B-7 and B-10 are comparisons of the 02FR10 simulated rainwater solution and DI water, filtered and unfiltered. Tables B-8, B-9, B-11, and B-12 are the tabulated concentrations found in these QC 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. 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. Upon completion of the forms, the site operator sends 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, the site operator submits a copy of the FOF to the AIRMoN liaison so that the database can be corrected to 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.

Internal blind samples used in 2002 were simulated rainwater prepared for the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) intercomparison study for 2001 (Coleman et al., 2001). These samples are prepared at the CAL for the WMO/GAW intercomparison study. The WMO/GAW compares their sample results to a calculated concentration (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 WMO/GAW target concentrations. Sixty-eight laboratories worldwide participated in the 2002 WMO/GAW intercomparison study.

The percent bias of samples in the 2002 AIRMoN internal blind program was higher than in 2001 for all but ammonium and potassium. The bias for all parameters was at or below the MDL for all parameters except nitrate. The percent RSD for the AIRMoN blind samples was higher for all parameters in 2002 than in 2001. Specific conductance was the only parameter with a statistically high bias in 2002.

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 sample is put on the tray for transfer to the laboratory for initial analysis at its regular place in the queue; one sample is filtered for archival purposes; and one sample is sent back to sample processing assigned a new and higher laboratory identification number, and submitted for analysis later. The NTN samples chosen for splits must have sufficient volume to fill three 60-mL bottles after filtration. Original and 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

Table IV-5. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, AIRMoN, 2002

Parameter	*Target WMO/GAW concentration[a] (mg/L)*	*CAL original concentration[b] (mg/L)*	*CAL mean concentration[c] (mg/L)*	*Bias[d] (mg/L)*	*Bias (%)*	*Precision (mg/L)*	*RSD[e] (%)*	*Critical concentration*	*Statistical bias*
Calcium	0.110	0.111	0.113	0.003	3.0	0.029	25.4	0.029	no
Magnesium	0.043	0.039	0.040	-0.003	-6.8	0.005	12.7	0.005	no
Sodium	0.083	0.080	0.084	0.001	0.9	0.026	30.6	0.026	no
Potassium	0.031	0.030	0.030	-0.001	-2.2	0.003	8.3	0.003	no
Ammonium	0.21	0.19	0.21	0.00	0.9	0.10	49.5	0.09	no
Sulfate	1.028	1.013	1.020	-0.008	-0.8	0.077	7.6	0.078	no
Nitrate	1.107	1.151	1.154	0.047	4.2	0.086	7.5	0.087	no
Chloride	0.119	0.116	0.115	-0.004	-3.8	0.022	18.8	0.022	no
pH units	4.75	4.74	4.72	-0.03	-0.6	0.24	5.1	0.24	no
Hydrogen ion (µeq/L)	17.8	18.2	20.1	2.3	12.8	3.0	14.8	3.0	no
Specific conductance (µS/cm)	11.1	12.4	13.2	2.1	18.5	0.5	3.8	0.51	yes

Notes:
This tabulation included 48 internal blinds. Samples were simulated rainwater prepared for the 2001 World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) intercomparison study.

[a] Target concentration used by the WMO/GAW in their analysis of the data in the 2002 WMO/GAW intercomparison study.

[b] Mean concentration obtained by the CAL during the intercomparison study in 2002.

[c] Mean concentration obtained by the CAL from the AIRMoN internal blind samples in 2002.

[d] Bias based on the difference between the CAL mean concentration from the AIRMoN internal blind samples and the WMO/GAW target concentrations.

[e] RSD is relative standard deviation.

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” (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 FOF is completed to accompany it. The sample identification number of the second bottle is changed to the original number after analysis is complete, but instead of an “L” designating the original sample, a “Q” is placed at the end of the sample identification number.

Replicate samples serve as another estimator of sample precision. Because these are blind, real precipitation samples, concentration values should be representative of the precision of the sample analysis for large-volume samples. Tables IV-6 and IV-7, respectively, summarize the analyses of replicate samples analyzed in 2002 for NTN and AIRMoN. Differences are calculated by subtracting the reanalysis value from the original value. Annual summaries of each ion were 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 for each network (see Appendix B, Table B-14 for NTN, and Table B-15 for AIRMoN). The box plots (Appendix B, Figures B-49–B-51 for NTN and Figures B-52–B-54 for AIRMoN) 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). Median values used to split samples into different categories were calculated on the complete set of data. The standard deviation estimated from replicate measurements, defined in the Glossary (Appendix A), was used to calculate standard deviations for three categories: concentrations below the median concentration, concentrations above the median concentration, and the entire population. The last column in Tables IV-6 and IV-7 shows a nonparametric estimator of variability from replicate determinations: 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.

The CAL QAP states that the maximum allowable bias of the analysis in the laboratory is concentration dependent: the smaller the concentration, the larger the percent allowable bias. The following formulation is used to determine the allowable bias for the samples:

- A maximum allowable bias of ± 100 percent at the MDL.
- A ± 20 percent allowable bias at 10 times the MDL.
- A ± 10 percent allowable bias at 100 times the MDL.

Table IV-6. Variance Estimated from Analysis of Replicate NADP/NTN Precipitation Samples, 2002

	Standard deviation estimated from paired measurements[a] (mg/L)			
Parameter	*Low*	*High*	*Total*	*(1.48) × MAD[b]*
Calcium	0.006	0.009	0.007	0.007
Magnesium	0.002	0.002	0.002	0.001
Sodium	0.002	0.013	0.009	0.003
Potassium	0.002	0.010	0.007	0.001
Ammonium	0.005	0.01	0.01	0.00
Sulfate	0.009	0.025	0.019	0.016
Nitrate	0.042	0.052	0.047	0.015
Chloride	0.004	0.047	0.034	0.004
Orthophosphate	0.001	0.003	0.002	0.000
pH (units)	0.02	0.05	0.04	0.03
Hydrogen ion (µeq/L)	0.36	1.36	1.00	0.75
Specific conductance (µS/cm)	0.45	0.66	0.57	0.44
Number of pairs	118	118	236	236

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 NADP/AIRMoN Precipitation Samples, 2002

	Standard deviation estimated from paired measurements[a] *(mg/L)*			
Parameter	*Low*	*High*	*Total*	*(1.48) × MAD*[b]
Calcium	0.003	0.014	0.010	0.006
Magnesium	0.001	0.002	0.002	0.001
Sodium	0.001	0.027	0.019	0.003
Potassium	0.002	0.003	0.003	0.003
Ammonium	0.01	0.02	0.01	0.01
Sulfate	0.016	0.025	0.021	0.021
Nitrate	0.005	0.011	0.009	0.008
Chloride	0.002	0.022	0.016	0.004
Orthophosphate	0.000	0.006	0.005	0.000
pH (units)	0.05	0.15	0.11	0.03
Hydrogen ion (μeq/L)	2.61	3.90	3.32	1.91
Specific conductance (μS/cm)	1.1	1.5	1.3	0.5
Number of pairs	18	18	36	36

Notes:

[a] "Standard deviation estimated from paired measurements" is defined in the "Glossary of Terms, Appendix A."

[b] MAD is median absolute difference.

Figures B-55–B-72 in Appendix B show graphically where the replicate samples fall in this formulation for NTN and AIRMoN for 2002. There were nine specific conductance replicates, one calcium, one magnesium, two sodium, one potassium, one chloride, three nitrate, and one orthophosphate NTN replicate outside control limits of 236 pairs. There were four pH and five specific conductance AIRMoN replicates outside control limits of 36 pairs.

C. Blanks

Solutions referred to as "blanks" are either DI water or simulated rainwater approximating the 25th percentile concentration. These solutions are used to discern the cleanliness of supplies washed and used at the CAL and/or shipped to sites for field use. Blanks are used to leach the cleaned supplies and then are analyzed for contamination. The term "blanks" traditionally has been used at the CAL to refer to both DI water leachates and simulated rainwater leachates. Blanks known to the analysts are identified as such by sample numbers that correspond to their various sources and weeks of collection. Blanks are collected and grouped by the sample processing staff. Both pH and conductivity are measured prior to sample analysis by ion chromatography, atomic absorption, or flow injection analysis. Solutions are not filtered unless they are used to determine cleanliness of the filters. Blanks are analyzed as a weekly set. The DI water blanks from the sample processing, atomic absorption, and bucket-washing service laboratories also are included in this set of samples.

1. Deionized Water Blanks

Each laboratory monitors the specific conductance of DI water used for rinsing, leaching, and making reagents and standards weekly. 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, maximum, and minimum values for pH and conductivity for the DI water from these three laboratories. The pH and conductivity readings were similar to past measurements and were typical of readings for uncontaminated DI water concentrations. These DI water blanks also were used to evaluate the cleaning efficacy of the 60-mL bottles used as sample storage bottles for the NTN. No contamination problem was noted.

2. Filter Leachates

Prior to filtering an NTN sample, Gelman Supor® 450, 0.45-micrometer (µm) hydrophylic polyethersulfone filters are rinsed with 250-300 mL of DI water. 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, two sets of filter leachates are collected and analyzed each week. One filter is rinsed with 250-300 mL of DI water, and then 50 mL of DI water is filtered into a sample bottle. A second DI water-rinsed filter using FR25 as the leachate also is prepared.

Table IV-9 shows the median concentration for the two filter leachates. Magnesium, sodium, sulfate, and nitrate show a slight but statistically relevant negative bias in the FR25 leachate. There is a statistically positive bias for pH in the FR25 leachate. No biases are seen in the DI water leachates. Gelman polyethersulfone filters first were used in January 1998. The filtered internal blind samples show a higher concentration of calcium and a positive bias but a lower concentration for magnesium, sodium, sulfate, nitrate, and a negative bias. It is interesting that the calcium bias so evident in the filtered internal blinds is not evident in the filter blank leachates. This is further evidence that the degree of bias for calcium and other analytes may be pH dependent. Further investigation will be conducted to ascertain if this is true.

3. Bucket Blanks

Sample collection buckets of HDPE have a 13-L capacity. These buckets are washed at the CAL with DI water, 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 the following 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 weekly procedure for "bucket blanks" includes leaching five buckets that had been washed in accordance with the NADP protocol and stored in plastic bags ready for shipping. The buckets are removed randomly from the set ready to be shipped to sites. The buckets are removed from the bags and leached for five days with two different volumes of two different solutions: two DI water blanks in 50-mL and and one DI water blank in 150-mL portions; and one FR25 solutions each 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 DI water leachates, these values are the leachate concentrations in micrograms/mL (µg/mL) times the number of milliliters of leachate. The values for the FR25 solutions are the median concentrations found in the blanks minus the FR25 target concentration times the number of milliliters used for the leachate. The DI water blanks had calcium, ammonium, and chloride in the 50-mL samples above the MDL. Ammonium was the only analyte present above the MDL for the 150-mL DI samples. The FR25 leachates had ammonium, nitrate, and chloride in the 50-mL aliquot. Sodium, nitrate, and chloride were present in both the 50-mL and the 150-mL aliquot. Sulfate concentrations were less than expected (a negative bias). The presence (or absence) of these constituents is believed to be related to bag contamination or absorption. Continued research is being conducted to find a contaminant-free bag material in which to store cleaned buckets and lids.

Table IV-8. pH and Specific Conductance for Weekly DI Water Blanks, 2002

	Sample processing laboratory	*Atomic absorption laboratory*	*Service laboratory*
Median			
pH (units)	5.68	5.71	5.71
Specific conductance (µS/cm)	0.9	0.8	0.9
Maximum			
pH (units)	5.78	5.81	5.83
Specific conductance (µS/cm)	1.3	1.4	1.4
Minimum			
pH (units)	5.55	5.53	5.55
Specific conductance (µS/cm)	0.7	0.6	0.6

Note:
A total of 52 blank samples were collected.

Table IV-9. Median Analyte Concentrations Found in Filter Leachates, 2002

Analyte	*DI water (mg/L)*	*FR25 (mg/L)*	*Target FR25 concentration (mg/L)*	*Statistical bias*
Calcium	<0.009	0.072	0.070	no
Magnesium	<0.003	0.011	0.016	yes
Sodium	<0.003	0.044	0.046	yes
Potassium	<0.003	0.013	0.012	no
Ammonium	<0.02	0.08	0.08	no
Orthophosphate	<0.009	0.000	0.000	no
Sulfate	<0.010	0.603	0.621	yes
Nitrate	<0.010	0.450	0.459	yes
Chloride	<0.005	0.125	0.127	no
pH	5.65	4.96	4.93	yes
Hydrogen ion (µeq/L)	2.24	11.0	11.9	yes
Specific conductance (µS/cm)	1.1	7.1	7.1	no

Note:
A total of 52 blank samples were collected.

Table IV-10. Median Measured Mass as Micrograms (µg)/Bucket[a] Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in Upright Bucket Leachates, 2002

	DI water[a]		*FR25*[b]	
Analyte	*(50 mL)*	*(150 mL)*	*(50 mL)*	*(150 mL)*
Calcium	<0.225	<0.675	<0.250	<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	3.48	3.45	3.15	3.68
Sulfate	<0.250	<0.750	-0.800	-1.725
Nitrate	<0.250	<0.750	0.475	0.750
Chloride	0.600	<0.375	0.400	0.450
pH (units)	5.77	5.72	5.14(4.93)[c]	5.03(4.93)[c]
Hydrogen ion (µeq/bucket)	0.085	0.286	-0.231	-0.381
Specific conductance (µS/cm)	1.5	1.3	6.3(7.1)[c]	6.7(7.1)[c]

Notes:
There were 52 blind sample weeks in 2002 with 104 50-mL DI water bucket blanks. Table I-3 reports MDLs.

[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 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.

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 decanted 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 pH and specific conductance measurements. 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 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 NTN sites for reuse.

Table IV-11 shows the median measured mass found in bottle leachates. The 1-L shipping bottle leachates contained no analyte concentrations above the MDL in the DI water leachates. Loss of sulfate, nitrate, chloride, ammonium, and sodium is evident in the 50-mL aliquots, and loss of sulfate and sodium was evident in the 150-mL aliquots for FR25.

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.” No parameters were above the MDL for the DI water blank and any differences were less than the MDL for the FR25 blank.

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 washed and reused like the NTN 1-L shipment bottles. The AIRMoN daily samples are collected in the same 13-L buckets used for NTN weekly samples. After AIRMoN samples are taken to the field laboratories, they are poured into the 250-mL sample shipping bottles and sent to the CAL. The AIRMoN samples are stored in these same 250-mL bottles in the refrigerator until they are discarded.

Once a month, two AIRMoN 250-mL bottles are used for AIRMoN bottle blanks. Although only two bottles are tested each month, AIRMoN and NTN use the same ratio of bottle blanks to bottles for samples, or about one blank bottle per 50–60 samples. The leachate used for the AIRMoN bottles 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.

Table IV-11. Median Measured Mass as Micrograms (μg)/Bottle[a] Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in HDPE 1-Liter Bottle Leachates, 2002

	DI water		*FR25[b]*	
Analyte	*(50 mL)*	*(150 mL)*	*(50 mL)*	*(150 mL)*
Calcium	<0.225	<0.675	<0.225	<0.675
Magnesium	<0.075	<0.225	<0.075	<0.225
Sodium	<0.075	<0.225	-0.100	-0.300
Potassium	<0.075	<0.225	<0.075	<0.225
Ammonium	<0.50	<1.5	-0.83	<1.5
Sulfate	<0.250	<0.750	-0.650	-0.900
Nitrate	<0.250	<0.750	-0.300	<0.750
Chloride	<0.125	<0.375	-0.125	<0.375
pH (units)	5.60	5.62	4.96(4.93)[c]	4.96(4.93)[c]
Hydrogen ion (μeq/bucket)	0.13	0.36	-0.05	-0.14
Specific conductance (μS/cm)	1.3	1.2	7.2(7.1)[c]	7.2(7.1)[c]

Notes:
There were 52 blind sample weeks in 2002.

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

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

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

Table IV-12. Median Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Snap-on Lids, 2002

Analyte	*DI water (50 mL)*	*FR25 (50 mL)*	*FR25 target concentration (mg/L)*
Calcium	<0.009	0.068	0.070
Magnesium	<0.003	0.016	0.016
Sodium	<0.003	0.046	0.046
Potassium	<0.003	0.012	0.012
Ammonium	<0.02	0.09	0.08
Sulfate	<0.010	0.622	0.621
Nitrate	<0.010	0.466	0.459
Chloride	<0.005	0.130	0.127
pH (units)	5.69	5.00	4.93
Hydrogen ion (µeq/L)	2.04	10.1	11.9
Specific conductance (µS/cm)	1.2	7.0	7.1

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

Table IV-13. Median Analyte Concentration (mg/L) Found in Monthly Simulated Rain (FR25) AIRMoN 250-mL HDPE Bottle Leachates, 2002

Analyte	*FR25 (50 mL)*	*FR25 (150 mL)*	*FR25 target concentration (mg/L)*
Calcium	0.067	0.067	0.070
Magnesium	0.016	0.016	0.016
Sodium	0.045	0.046	0.046
Potassium	0.011	0.012	0.012
Ammonium	0.09	0.09	0.08
Sulfate	0.620	0.618	0.621
Nitrate	0.461	0.465	0.459
Chloride	0.124	0.124	0.127
pH (units)	4.95	4.96	4.93
Hydrogen ion (µeq/L)	11.2	11.0	11.9
Specific conductance (µS/cm)	7.3	7.2	7.1

Notes:
There were 12 months of AIRMoN bottle blanks and spikes.

7. Bag Blanks

Bag blanks were added to the blanks regime in January 2001. The presence of ammonium, chloride, and occasionally other ions in bucket blanks resulted in the QA Specialist and Laboratory Director reviewing the bags used to store the buckets and lids before and after shipping and at sites. The bag blank protocol introduced in 2001 was continued in 2002 and has been incorporated in the blank schedule on a permanent basis because of the continued difficulty in obtaining “clean” bags,

Two bags are selected each week from a different shipping box for contamination evaluation. 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 is decanted into appropriately labeled 60-mL HDPE bottles.

Table IV-14 shows a statistical bias for ammonium, nitrate, chloride, and pH in the FR25 leachates. Both the DI water leachates and the FR25 leachates contained approximately the same amount of excess chloride and ammonium, implying that the contamination was definitely in the bags and was being leached out in the same quantity in both solutions. Although there was a statistically significant bias for nitrate, no nitrate appeared in the DI water blank. The amount of contamination from the bags slightly exceeds the detection limit of the analyte. The sample never comes into direct contact with the bags, so the possibility of contamination above the detection limit is minimal and should fall within the noise level for all samples.

Table IV-14. Median Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Bags, 2002

Analyte	*DI water (50 mL)*	*FR25 (50 mL)*	*FR25 target concentration (mg/L)*	*Statistically significant bias*
Calcium	<0.009	0.070	0.070	no
Magnesium	<0.003	0.017	0.016	no
Sodium	<0.003	0.047	0.046	no
Potassium	<0.003	0.012	0.012	no
Ammonium	0.04	0.12	0.08	yes
Sulfate	<0.010	0.627	0.621	no
Nitrate	<0.010	0.470	0.459	yes
Chloride	0.019	0.142	0.127	yes
pH (units)	5.65	5.02	4.93	yes
Hydrogen ion (µeq/L)	2.24	9.5	11.9	yes
Specific conductance (µS/cm)	1.5	7.0	7.1	no

Note:
There were 51 weeks of bag blanks and bag spikes in 2002.

V. Monthly Quality Assurance Procedures

Monthly NADP/NTN and NADP/AIRMoN QA activities by the QA Specialist include: 1) evaluation of control charts summarizing daily QCS analyses to determine any change in CAL analytical instrument performance, 2) review of computer printouts containing internal blind sample data, and 3) review of reanalyses of samples flagged either for an ion or conductivity imbalance or both. Data for samples analyzed in the USGS laboratory intercomparison study also 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 – 600 samples. Data for AIRMoN samples also are processed once a month in sets of about 120 samples. These analytical data are submitted for a reanalysis selection test that includes all samples (internal blinds, field blanks, and collocated program samples). A sample is flagged if the ion percent difference (IPD) or conductivity percent difference (CPD) exceeds set limits as defined the NADP QAP (Simmons et al., 1991, revised 1993). The computer algorithm for sample selection has been the same since 1987.

1. Ion Percent Difference (IPD)

Ion concentrations are measured in milligrams per liter (mg/L). The 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 IPD. The ion sum (IS) is equal to the sum of the measured cations, measured anions, and calculated anions. The IPD is calculated as follows:

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

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

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

Samples are flagged for reanalysis if:

IS < 50 μeq/L	and	IPD > + 60% or IPD < -60%
50 ≤ IS < 100 μeq/L	and	IPD > + 30% or IPD < -30%
IS ≥ 100 μeq/L	and	IPD > + 15% or IPD < -15%

Table V-1. Conversion Factors for Reanalysis Calculations

Analyte	*Milligrams/liter (mg/L) to microequivalents/L (μeq/L)[a] for ion percent difference, Multiply by:*	*Microequivalent/L (μeq/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	992.20	350.0
Bicarbonate	16.39	44.5
Hydroxide	58.80	198.0

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

2. Conductance Percent Difference (CPD)

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

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

Selected samples are reanalyzed unless they are flagged for contamination and exhibit excessive ion concentrations as defined in the NADP work statement or the volume is insufficient. The final list of samples is compiled and sent 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 the CAL 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, the original sample is reanalyzed a second time. 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 2002, approximately 13,198 NTN samples were logged in, and 9,662 samples were classified as "W" (wet) with 134 field blanks. A total of 9,796 samples were eligible for reanalysis. These samples had volumes of 35 mL or more, by definition of "W" samples. The 566 samples flagged for reanalysis included one percent of the total number of samples chosen randomly. A total of 285 individual measurement changes were made to 182 samples. Figure V-1 contains the histograms for the IPD and CPD values for NTN, and includes the mean, the standard deviation, and the median. About 1,705 samples logged in for AIRMoN with 1,233 "W" samples (samples with enough liquid for a complete analysis) and 186 field blanks, a total of 1,419 samples were eligible for reanalysis. Of this total 71 samples were flagged for reanalysis, including three percent of the total number selected randomly. There were 7 edits on 7 of the 71 samples. Figure V-2 contains the histograms for the IPD and CPD values for AIRMoN, including the mean, the standard deviation, and the median.

Between 1979 and 1993, the IPD mean and median values for NTN were positive. Since 1993, the mean values have been negative. The 1994–1997 medians also were negative, but the 1998–2002 median IPDs were positive for NTN and negative for AIRMoN. A negative value indicates a measured cation excess, a positive value indicates an excess of measured anions, and values close to zero indicate that the majority of anions and cations are being measured.

The IPD mean and median AIRMoN values are both negative, indicating a lack of measured anions or excess measured cations. All AIRMoN samples are kept cold after collection, even during shipping. The negative mean and median may represent organic acids not measured at the CAL. Organic acids are commonly seen with the ion chromatograph but not quantified.

The CPD consistently has exhibited a negative skew since 1979, with 2002 results being similar to those in previous years for both NTN and AIRMoN. Negative CPD indicates that measured conductivity exceeds 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 measured conductivity but are not measured or present in calculated conductivity.

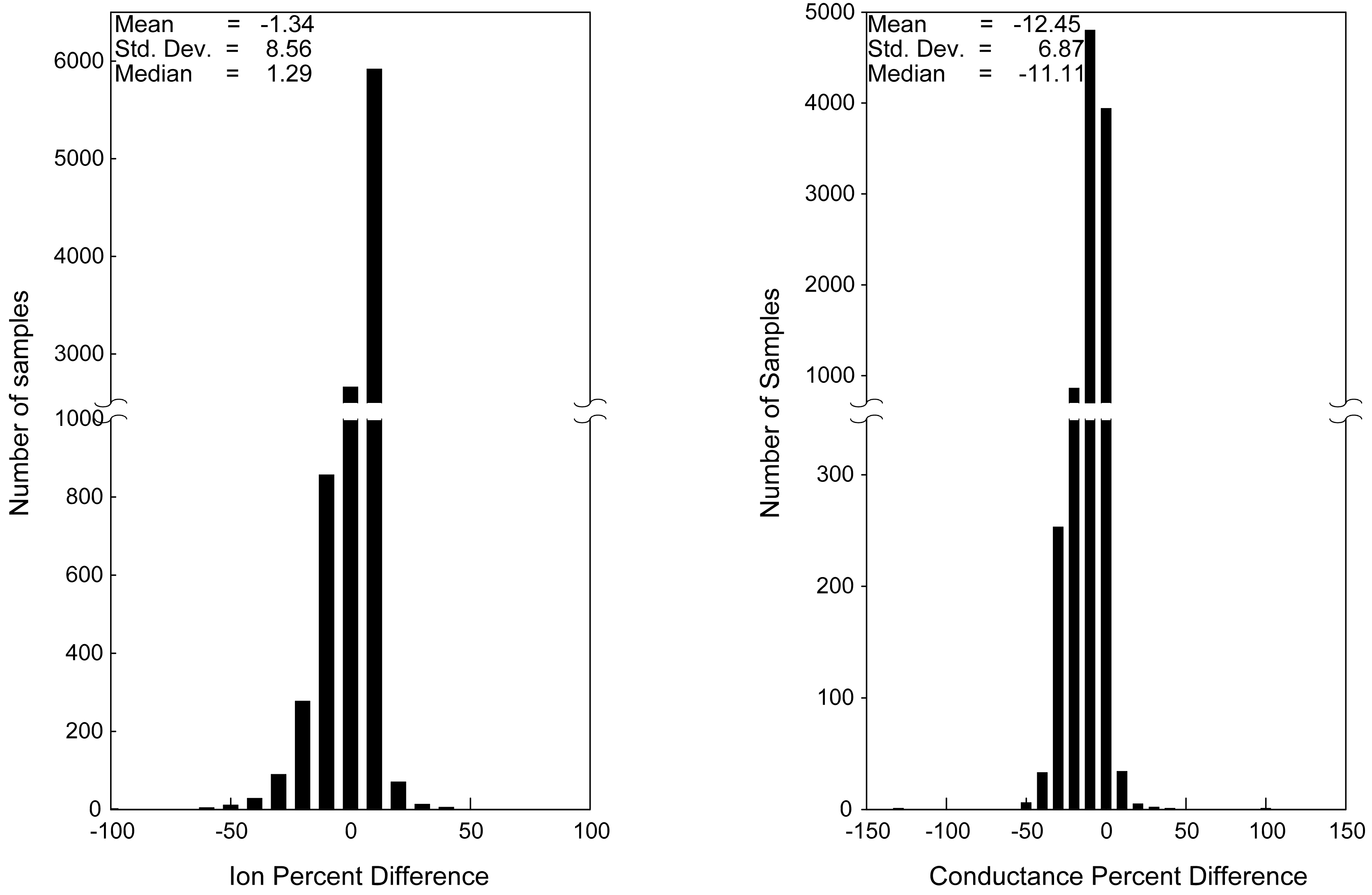

Figure V-1. Ion Percent Difference and Conductance Percent Difference for 9796 NADP/NTN wet samples, 2002.

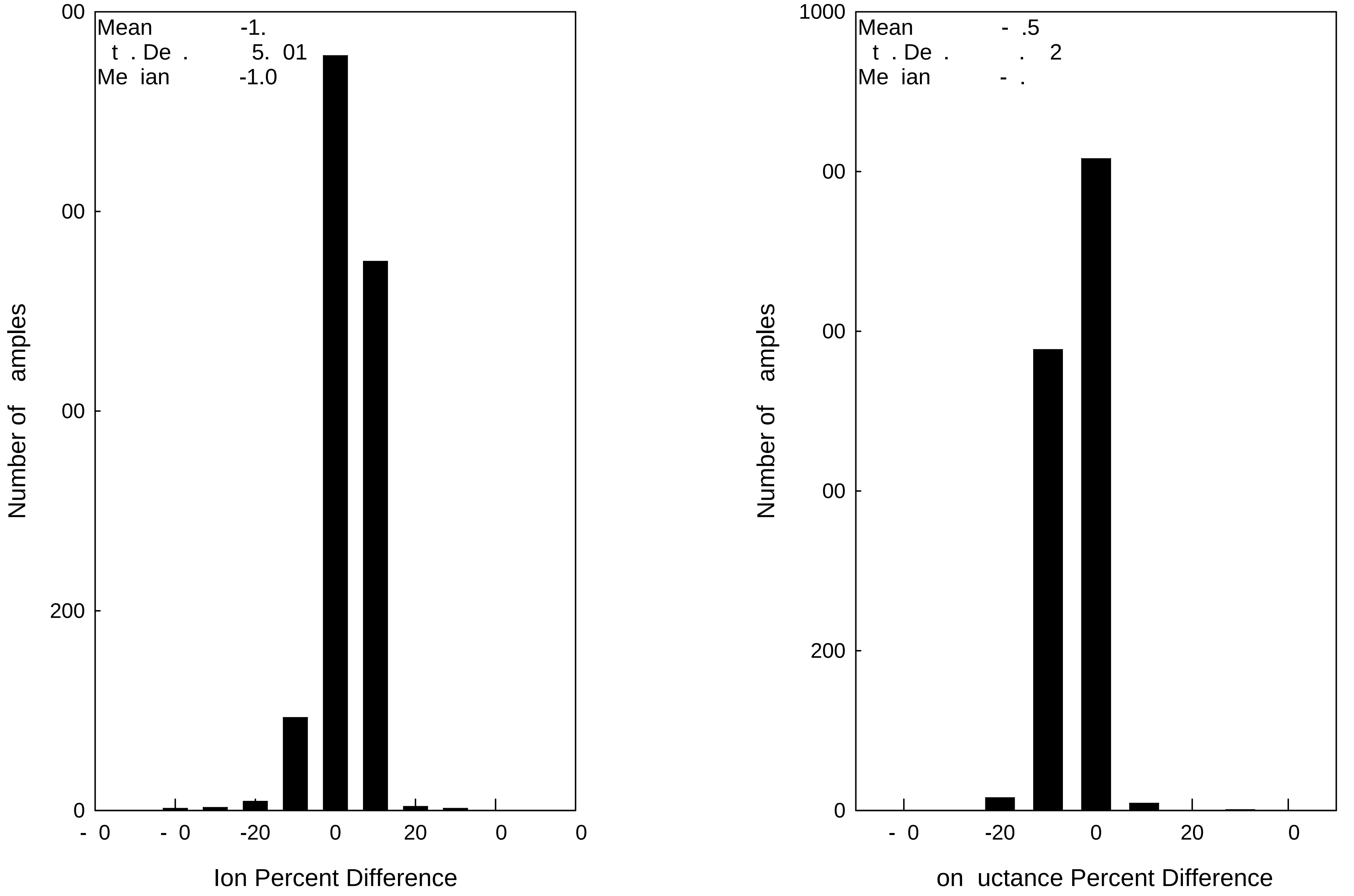

Figure -2. Ion Percent Difference an on uctance Percent Difference for 1 1 NADP/AIRMoN wet samples, 2002.

B. USGS Interlaboratory Comparison

The Interlaboratory Comparison Program conducted by the USGS began in fall 1982 as a portion of the external QA oversight of the CAL for the NADP/NTN. Every two weeks, the USGS mails one set of four blind samples of different matrices to participating laboratories: a total of 104 samples in 26 biweekly mailings. The protocol is designed to determine if the laboratories are producing comparable results.

The Interlaboratory Comparison Program included eight laboratories in 2002:

- NADP Central Analytical Laboratory (CAL), Champaign, Illinois, USA
- Meteorological Service of Canada (MSC), Downsview, Ontario, Canada
- Environmental Science and Engineering, Inc. (ESE), Gainesville, Florida, USA
- Ontario Ministry of Environment and Energy, Water Quality Section (MOE), Dorset, Ontario, Canada
- Shepard Analytical Services (SA), Simi Valley, California, USA
- Acid Deposition and Oxidant Research Center (ADORC), Sowa, Niigata-shi, Japan
- Norwegian Institute for Air Research (NILU), Kjeller, Norway
- New York State Department of Environmental Conservation (NYSDEC), Albany, New York, USA

All laboratories participated for the entire year in 2002.

Samples used in 2002 were comprised of three types: (1) National Institute of Standards and Technology (NIST) traceable solutions prepared by High-Purity Standards (H-PS) and diluted by either the USGS (solutions SP1 and SP5) or by HPS (solutions SP97 and SP98c), (2) natural deposition samples collected at the NADP/NTN sites and composited and bottled at the CAL, and (3) ultrapure DI water samples prepared by the USGS. Data reports from the participating laboratories are submitted monthly, quarterly, or semiannually to the USGS. The USGS makes the data available on the Internet to each participating laboratory. For more information about the program, contact the USGS Branch of Quality Systems (http://bqs.usgs.gov/precip/project_overview/interlab/ilab_intro.htm).

Table V-2 shows the median and F-pseudosigma for the replicate samples obtained from the eight laboratories participating in 2002. For comparison, laboratory rankings for precision were determined by summing the 50th and 90th percentile absolute differences for the replicate results (Table V-3). Table V-4 shows laboratory rankings. The CAL ranked first for hydrogen ion concentration and specific conductance; tied for second for sulfate concentration; tied for third for magnesium, potassium, ammonium, and nitrate concentrations; and ranked fifth for calcium, sodium, and chloride concentrations. By this system, the CAL ranked fourth overall among the eight laboratories participating in the USGS Interlaboratory Comparison Program in 2002 for analytical precision. The CAL's summed 50th and 90th percentile absolute differences of replicate samples were slightly higher during 2002 than in 2001. The USGS publishes complete results of these studies without the laboratory rankings.

Table V-2. CAL Median Values and F-pseudosigma for USGS Intercomparison Samples, 2002

Analyte	*SP1*		*SP2*		*SP5*		*SP97*		*SP98c*	
(mg/L)	*Median*	*F-pseudosigma*	*Median*	*F-pseudosigma*	*Median*	*F-pseudosigma*	*Median*	*F-pseudosigma*	*Median*	*F-pseudosigma*
Ca	0.439	0.007	0.427	0.008	0.553	0.021	0.124	0.004	0.013	0.004
Mg	0.095	0.003	0.069	0.004	0.163	0.010	0.017	0.000	0.035	0.001
Na	0.419	0.007	0.361	0.007	0.458	0.017	0.022	0.000	0.211	0.004
K	0.078	0.002	0.062	0.001	0.084	0.002	0.018	0.001	0.059	0.000
NH_4	0.634	0.004	0.500	0.042	0.665	0.002	0.280	0.013	0.101	0.010
Cl	0.586	0.007	0.445	0.004	0.714	0.020	0.055	0.001	0.228	0.001
NO_3	2.111	0.016	3.022	0.007	2.570	0.022	1.173	0.009	0.565	0.004
SO_4	3.891	0.047	2.337	0.024	4.557	0.045	1.130	0.006	2.431	0.022
pH (pH units)	4.43	0.007	4.53	0.022	4.36	0.017	4.76	0.015	4.40	0.007
Specific conductance (µS/cm)	30.4	0.363	24.6	0.173	35.9	0.490	12.2	0.267	22.7	0.090

Note:
F-pseudosigma is a nonparametric measure of spread.

Table V-3. The 50th and 90th Percentile Absolute Differences for Analysis of Replicate Samples in the 2002 Interlaboratory Comparison Program, 2002

	CAL[a]		MSC[b]		ESE[c]		MOE[d]	
Analyte	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*
Calcium	0.002	0.014	0.003	0.014	0.001	0.005	0.000	0.020
Magnesium	0.001	0.004	0.000	0.002	0.000	0.001	0.000	0.005
Sodium	0.002	0.020	0.001	0.004	0.001	0.006	0.000	0.005
Potassium	0.001	0.003	0.000	0.003	0.000	0.001	0.000	0.005
Ammonium	0.000	0.010	0.001	0.002	0.006	0.012	0.000	0.020
Sulfate	0.000	0.021	0.005	0.012	0.010	0.020	0.000	0.050
Nitrate	0.000	0.015	0.002	0.010	0.004	0.009	0.010	0.110
Chloride	0.000	0.008	0.001	0.004	0.002	0.007	0.010	0.020
Hydrogen ion (µeq/L)	0.00	0.99	0.84	2.37	0.750	4.23	0.89	4.61
Specific conductance (µS/cm)	0.0	0.1	–	–	0.3	1.4	0.2	1.0

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 and Energy, Canada.

[e] Shepard Analytical Services.

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

[g] Norwegian Institute for Air Research, Norway.

[h] New York State Department of Environmental Conservation.

Table V-3. The 50th and 90th Percentile Absolute Differences for Analysis of Replicate Samples in the 2002 Interlaboratory Comparison Program, 2002 (concluded)

	SA[e]		*ADORC*[f]		*NILU*[g]		*NYSDEC*[h]	
Analyte	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*
Calcium	0.002	0.007	0.002	0.005	0.000	0.010	0.003	0.012
Magnesium	0.000	0.001	0.000	0.002	0.000	0.010	0.002	0.006
Sodium	0.001	0.003	0.000	0.003	0.000	0.010	0.001	0.004
Potassium	0.001	0.002	0.001	0.003	0.000	0.010	0.001	0.002
Ammonium	0.00	0.01	0.00	0.00	0.00	0.02	0.00	0.01
Sulfate	0.01	0.02	0.01	0.02	0.03	0.09	0.00	0.04
Nitrate	0.01	0.02	0.01	0.02	0.01	0.09	0.00	0.04
Chloride	0.00	0.01	0.00	0.00	0.01	0.03	0.00	0.01
Hydrogen ion (µeq/L)	0.000	1.195	0.64	2.28	0.61	2.28	0.41	1.88
Specific conductance (µS/cm)	0.1	0.3	0.2	1.1	0.1	0.3	0.2	1.0

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 and Energy, Canada.

[e] Shepard Analytical Services.

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

[g] Norwegian Institute for Air Research, Norway.

[h] New York State Department of Environmental Conservation.

Table V-4. USGS Intercomparison Study Ranking Summary, 2002

Analyte	*CAL*[a]		*MSC*[b]		*ESE*[c]		*MOE*[d]	
	Sum	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*
Calcium	0.016	5	0.017	6	0.006	1	0.02	7 tie
Magnesium	0.005	3 tie	0.002	2 tie	0.001	1 tie	0.005	3 tie
Sodium	0.022	5	0.005	2 tie	0.007	3	0.005	2 tie
Potassium	0.004	3 tie	0.004	3 tie	0.002	1	0.005	4
Ammonium	0.01	3 tie	0.003	2	0.018	5	0.02	6 tie
Sulfate	0.03	2 tie	0.017	6	0.03	2 tie	0.05	3
Nitrate	0.019	3	0.012	1	0.013	2	0.12	7
Chloride	0.011	5	0.005	2	0.009	3	0.03	7
Hydrogen ion (µeq/L)	0.994	1	3.212	5	4.98	7	5.492	8
Specific conductance (µS.cm)	0.118	1	not available		1.7	7	1.2	5
Ranking without specific conductance		4		3		2		6
Overall ranking		3		incomplete		4		6

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, Inc.

[d] Ontario Ministry of the Environment and Energy, Canada.

[e] Shepard Analytical Services.

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

[g] Norwegian Institute for Air Research, Norway.

[h] New York State Department of Environmental Conservation.

Table V-4. USGS Intercomparison Study Ranking Summary, 2002 (concluded)

Analyte	*SA*[e]		*ADORC*[f]		*NILU*[g]		*NYSDEC*[h]	
	Sum	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*
Calcium	0.009	3	0.007	2	0.02	7 tie	0.015	4
Magnesium	0.001	1 tie	0.002	2 tie	0.01	5	0.008	4
Sodium	0.004	1 tie	0.004	1 tie	0.01	4	0.005	2 tie
Potassium	0.003	2	0.004	3 tie	0.01	5	0.013	6
Ammonium	0.01	3	0.0	1	0.02	6 tie	0.011	4
Sulfate	0.03	2 tie	0.03	2 tie	0.115	5	0.058	4
Nitrate	0.03	4 tie	0.03	4 tie	0.1	6	0.051	5
Chloride	0.01	4	0.0	1	0.035	8	0.015	6
Hydrogen ion (µeq/L)	1.195	2	3.556	6	2.893	4	2.281	3
Specific conductance (µS.cm)	0.4	2	1.3	6	0.42	3	1.16	4
Ranking without specific conductance		1 tie		1 tie		7		5
Overall ranking		1		2		7		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, Inc.
[d] Ontario Ministry of the Environment and Energy, Canada.
[e] Shepard Analytical Services.
[f] Acid Deposition and Oxidant Research Center, Japan.
[g] Norwegian Institute for Air Research, Norway.
[h] New York State Department of Environmental Conservation.

Rankings given in this report are relative numbers comparing the eight laboratories and do not necessarily define laboratory quality. Further inspection of the data reveals little difference among the eight laboratories. For the CAL data, the median absolute differences determined for each constituent were all less than the detection limits. The sums of the 50th and 90th percentile absolute differences for each constituent were all less than ten times the CAL's MDLs. Therefore, the differences are not likely environmentally significant to data users.

VI. Semiannual and Annual Quality Assurance Procedures

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 interlaboratory comparison studies not sponsored by the NADP. There were five studies in 2002: two studies conducted by the World Meteorological/Global Atmospheric Watch (WMO/GAW), Geneva, Switzerland; two studies conducted by the National Water Research Institute (NWRI), Burlington, Ontario, Canada; and one study conducted by the the Norwegian Institute for Air Research (NILM), Kjeller, Norway.

A. World Meteorological Organization/Global Atmospheric Watch

The 26th and 27th sets of WMO/GAW reference precipitation samples were shipped to participating laboratories in April and October 2002, respectively. The CAL had a contract to prepare the simulated precipitation samples used in these studies. Samples were shipped to about 100 laboratories. Sixty-three 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., 2002) in the April study and 74 laboratories reported results in the October study. Because the samples were prepared at the CAL and CAL analysts confirmed the target concentrations, the analytical results obtained by the CAL during the actual studies were not included in the study’s final report. Tables VI-1 and VI-2 present 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 among the study’s laboratories, the CAL results were not ranked; however, CAL results agreed favorably with the study’s means and target values when unofficially compared with those from other participating laboratories.

Without benefit of the statistical input of the other laboratories, the CAL data consistently appear to be low for calcium, magnesium, and ammonium concentrations and high for specific conductance. All other parameters vary and have no obvious trend. Whether these biases are statistically significant cannot be determined from these data since the CAL was not an official participant in the studies. These results are intended to complement other data shown in this report.

B. National Water Research Institute

The CAL participated in both studies sponsored by the National Water Research Institute (NWRI) in Burlington, Ontario, Canada. Begun in 1982 as the Long-Range Transport of Atmospheric Pollutants (LRTAP) program, the studies for 2002 were FP80 and FP81 (Blum and Alkema, 2002a, 2002b). 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

Table VI-1. 26th World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) Acid Rain Performance Survey, April 2002

Analyte	*Units*	*Sample 1*			*Sample 2*			*Sample 3*		
		Target	*Mean*	*CAL*	*Target*	*Mean*	*CAL*	*Target*	*Mean*	*CAL*
Calcium	mg Ca/L	0.239	0.244	0.220	0.170	0.174	0.156	0.624	0.617	0.583
Magnesium	mg Mg/L	0.124	0.120	0.114	0.079	0.078	0.072	0.248	0.244	0.234
Sodium	mg Na/L	1.036	1.021	1.069	0.484	0.473	0.495	2.301	2.280	2.361
Potassium	mg K/L	0.183	0.178	0.183	0.112	0.107	0.114	0.390	0.376	0.411
Ammonium	mg NH_4/L as N	0.348	0.352	0.322	0.193	0.192	0.176	0.600	0.611	0.561
Sulfate	mg SO_4/L as S	0.812	0.797	0.806	0.488	0.478	0.485	1.419	1.406	1.429
Nitrate	mg NO_3/L as N	0.277	0.279	0.279	0.143	0.143	0.143	0.485	0.485	0.502
Chloride	mg Cl/L	1.619	1.594	1.601	0.802	0.785	0.807	3.592	3.554	3.648
pH	pH units	4.68	4.73	4.71	4.96	4.95	4.92	4.59	4.64	4.64
Hydrogen ion	µequiv/L	20.9	18.6	19.5	11.0	11.2	12.0	25.7	22.9	22.9
Specific conductance	µS/cm	22.0	20.9	22.5	11.9	12.2	13.0	38.1	36.6	38.3

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.

Table VI-2. 27th World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) Acid Rain Performance Survey, October 2002

Analyte	*Units*	*Sample 1*			*Sample 2*			*Sample 3*		
		Target	*Mean*	*CAL*	*Target*	*Mean*	*CAL*	*Target*	*Mean*	*CAL*
Calcium	mg Ca/L	0.240	0.238	0.225	0.110	0.106	0.104	0.340	0.334	0.317
Magnesium	mg Mg/L	0.123	0.121	0.114	0.043	0.042	0.040	0.100	0.098	0.093
Sodium	mg Na/L	1.035	1.026	1.019	0.083	0.074	0.082	0.421	0.414	0.413
Potassium	mg K/L	0.183	0.180	0.180	0.031	0.031	0.031	0.129	0.123	0.127
Ammonium	mg NH_4/L as N	0.347	0.350	0.324	0.163	0.162	0.153	0.474	0.471	0.452
Sulfate	mg SO_4/L as S	0.811	0.807	0.813	0.343	0.342	0.339	0.840	0.841	0.845
Nitrate	mg NO_3/L as N	0.278	0.276	0.280	0.250	0.252	0.252	0.430	0.436	0.441
Chloride	mg Cl/L	1.619	1.624	1.607	0.119	0.116	0.115	0.781	0.768	0.789
pH	pH units	4.70	4.72	4.71	4.73	4.76	4.75	4.59	4.60	4.61
Hydrogen ion	µequiv/L	20.0	19.1	19.5	18.6	17.4	17.8	25.7	25.1	24.5
Specific conductance	µS/cm	21.6	21.3	22.4	11.4	11.4	12.1	22.2	21.8	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.

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. For a complete explanation of the flagging system used in these studies, refer to the original reports (Blum and Alkema, 2002a, 2002b).

Tables VI-3 and VI-4 show the median results and the CAL results for both studies. For Study FP80, the CAL had one low ammonium value and one high sodium value. Although the magnesium concentrations received no flags, the ranking indicates a slight low bias resulting in a third flagged analyte. The resultant overall ranking for the CAL was 12th out of 34 laboratories reporting numbers and a rating of "satisfactory" (three laboratories ranked above the CAL analyzed less than 10 parameters). For Study FP81, the CAL received four low flags for calcium, which also received a low ranking indicating a low bias. Overall, this gave the CAL a ranking of "satisfactory" for Study FP81 and an overall ranking of ninth of 33 reporting laboratories. For a description of how "flags" are assigned to the NWRI interlaboratory comparison samples, see their summary reports (Blum and Alkema, 2002a, 2002b).

The NWRI summarizes performance results for the past ten studies (Studies 0072–0081). The CAL received a median score of 6.0 based on the percentage of biased parameters and flagged results on the studies. This was the eighth lowest score (the lower the score, the better the laboratory and the ranking) of the 32 ranked laboratories and was rated "satisfactory".

C. Norwegian Institute for Air Research

The Norwegian Institute for Air Research (NILU) sponsored the 20th European Monitoring and Evaluation Programme (EMEP) intercomparison of analytical methods for atmospheric precipitation in late summer 2002. There were four samples in the study. Table VI-5 presents study results. All results were within the standard expected variation for that analyte.

Table VI-3. National Water Research Institute Soft Water Interlaboratory Study FP80, Spring 2002

		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	0.915	0.881	1.580	1.521	0.358	0.344	0.410	0.390	2.133	2.067
Magnesium	mg/L	0.326	0.317	0.280	0.269	0.203	0.196	0.400	0.388	0.644	0.615
Sodium	mg/L	0.037	0.039	0.056	0.058	1.370	1.477H	2.793	2.805	0.054	0.055
Potassium	mg/L	0.035	0.038	0.025	0.027	0.132	0.136	0.240	0.242	0.100	0.106
Ammonium	mg NH_4/L as N	0.005	<0.015	0.002	<0.015	0.003	<0.015	0.003	<0.015	0.038	0.032
Sulfate	mg SO_4/L	1.833	1.833	1.480	1.459	1.730	1.732	2.310	2.329	3.210	3.229
Nitrate	mg NO_3/L as N	0.527	0.547	0.464	0.478	0.212	0.214	0.088	0.086	1.497	1.508
Chloride	mg/L	0.104	0.102	0.130	0.130	2.051	2.052	4.460	4.387	0.310	0.310
pH	pH units	5.28	5.26	6.49	6.49	4.88	4.90	5.43	5.45	4.83	4.86
Specific conductance	µS/cm	12.2	13.4	12.8	13.3	18.0	19.1	24.4	25.2	28.0	29.2

		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	2.490	2.413	0.620	0.597	2.510	2.421	3.036	2.943	4.554	4.296
Magnesium	mg/L	0.610	0.597	0.180	0.172	0.622	0.603	0.900	0.861	1.116	1.055
Sodium	mg/L	2.200	2.178	0.076	0.076	2.706	2.741	2.325	2.345	3.500	3.525
Potassium	mg/L	0.507	0.521	0.020	0.027	0.340	0.362	0.432	0.454	0.572	0.598
Ammonium	mg NH_4/L as N	0.039	0.030	0.064	0.054	0.044	0.033	0.027	0.018	0.029	0.019L
Sulfate	mg SO_4/L	4.710	4.786	1.390	1.372	5.773	5.808	6.120	6.075	10.800	10.639
Nitrate	mg NO_3/L as N	0.072	0.074	0.344	0.350	0.093	0.092	0.086	0.085	0.040	0.039
Chloride	mg/L	1.690	1.698	0.167	0.162	3.971	3.938	3.207	3.247	8.225	8.137
pH	pH units	6.84	6.88	5.31	5.34	6.51	6.56	6.80	6.89	6.33	6.35
Specific conductance	µS/cm	31.6	32.9	9.5	10.3	37.0	37.6	39.3	40.4	61.0	62.5

Table VI-4. National Water Research Institute Soft Water Interlaboratory Study FP 81, Fall 2002

		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	0.991	0.924	0.621	0.580	0.713	0.677	2.972	2.772	3.080	2.876
Magnesium	mg/L	0.201	0.195	0.178	0.170	0.160	0.156	0.470	0.458	0.431	0.424
Sodium	mg/L	0.099	0.096	0.066	0.066	0.050	0.049	0.560	0.544	1.530	1.476
Potassium	mg/L	0.039	0.041	0.018	0.018	0.018	0.017	0.207	0.206	0.367	0.374
Ammonium	mg NH_4/L as N	0.002	<0.015	0.055	0.052	0.154	0.146	0.003	<0.015	0.004	<0.015
Sulfate	mg/L	0.250	0.244	1.370	1.354	2.200	2.189	5.264	5.220	3.244	3.252
Nitrate	mg NO_3/L as N	0.022	0.021	0.350	0.356	0.290	0.292	0.660	0.675	0.228	0.231
Chloride	mg/L	0.109	0.106	0.157	0.153	0.120	0.117	0.232	0.231	0.960	0.979
pH	pH units	6.73	6.73	5.21	5.22	5.09	5.12	6.42	6.45	6.89	6.95
Specific conductance	µS/cm	7.5	7.6	9.5	10.0	11.8	12.3	26.0	26.5	28.3	28.9

		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	2.369	2.193	2.737	2.508L	4.586	4.245L	4.412	4.097L	3.874	3.540L
Magnesium	mg/L	0.620	0.610	0.920	0.883	0.850	0.829	1.226	1.173	1.040	1.009
Sodium	mg/L	0.075	0.074	0.147	0.145	1.071	1.033	1.575	1.518	2.540	2.463
Potassium	mg/L	0.116	0.120	0.163	0.166	0.441	0.452	0.652	0.640	0.480	0.484
Ammonium	mg NH_4/L as N	0.166	0.163	0.003	<0.015	0.003	<0.015	0.010	<0.015	0.017	0.017
Sulfate	mg/L	3.995	4.006	6.088	6.047	4.489	4.511	7.347	7.372	5.600	5.545
Nitrate	mg NO_3/L as N	1.570	1.587	0.937	0.961	0.152	0.154	0.237	0.240	0.108	0.108
Chloride	mg/L	0.410	0.460	0.390	0.390	0.840	0.854	1.108	1.138	3.450	3.479
pH	pH units	4.73	4.78	6.16	6.19	7.13	7.17	6.99	6.98	6.96	6.99
Specific conductance	µS/cm	31.8	32.8	28.0	28.9	36.9	37.4	42.9	43.5	43.6	44.6

Table VI-5. Norwegian Institute for Air Research European Monitoring and Evaluation Programme 20th Intercomparison of Analytical Methods, 2002

		Sample 1		*Sample 2*		*Sample 3*		*Sample 4*	
Analyte	*Units*	*Target*	*CAL*	*Target*	*CAL*	*Target*	*CAL*	*Target*	CAL
Calcium	mg/L	0.335	0.324	0.239	0.230	0.364	0.353	0.259	0.250
Magnesium	mg/L	0.139	0.136	0.085	0.084	0.101	0.098	0.124	0.121
Sodium	mg/L	0.301	0.309	0.499	0.503	0.636	0.638	0.872	0.870
Potassium	mg/L	0.255	0.251	0.204	0.206	0.306	0.317	0.153	0.155
Ammonium	mg N/L	0.401	0.377	0.261	0.245	0.481	0.454	0.221	0.208
Sulfate	mg S/L	1.574	1.600	1.586	1.617	1.025	1.049	1.012	1.031
Nitrate	mg N/L	0.607	0.612	0.546	0.552	0.738	0.752	0.521	0.525
Chloride	mg/L	0.174	0.171	0.232	0.228	0.608	0.607	0.724	0.725
pH	pH units	4.15	4.22	4.10	4.15	4.43	4.47	4.40	4.45
Specific conductance	µS/cm	40.6	40.7	43.1	43.5	29.3	29.9	27.9	28.5

VII. Summary

This report summarizes the results from the quality assurance program in place at the Central Analytical Laboratory (CAL) of the NADP/NTN and NADP/AIRMoN-wet in 2002. 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 measured by 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 bias and precision target specifications.

The internal blinds program provided bias and precision data that more closely represent wet deposition data and evaluate the effects of sample handling, filtration, and measurement process on sample chemistry. Bias and precision numbers were higher for the internal blinds than for the QCS samples. Analysts know the QCS sample concentrations and analysis location and are required to reanalyze if the concentrations are outside specific limits. They do not know the concentrations or positions in the analysis queue of internal blind samples so these are more indicative of the bias and precision of real samples.

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; thus, there were no false positives. It was observed that filtration increased variability in the chemistry of all samples. There was evidence of positive 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. Some pH effect with biases may occur through filtration.

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 parameters measured at the CAL, except chloride, nitrate, and sulfate. Year 2000 was the first year chloride, nitrate, and sulfate 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 apparent bias increase for these parameters may be due to the increased ability to measure the true noise of the analytical procedure. The standard deviation estimated from paired measurements increased for most of the analytes in 2002 compared to that estimated in 2001. Potassium, ammonium, and chloride were improved, nitrate stayed the same, and the standard deviation increased for all other analytes; however, concentration differences were still within the limits set for the CAL by NADP. A few concentrations for the replicate samples were outside the acceptable limits for split and random reanalysis data. A new procedure to review these samples in a timely manner will be adopted at the CAL for future evaluation of replicate samples.

The DI water and filter and container leachates were analyzed weekly to detect contamination and to determine whether 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 ~ 5.6 pH units and conductivity of ~ 1 µS/cm. Filtrates from filters leached in DI water and 02FR25 showed biases for calcium, magnesium, sulfate, and nitrate. Bucket leachates showed slight positive biases for calcium, sodium, ammonium, nitrate, and chloride. Most of these biases were traced to the bucket storage bags. Bag leachates were introduced to the weekly analysis scheme and were determined to have a slight statistically significant bias for calcium, magnesium, and sodium. One-liter NTN bottle leachates and 250-mL AIRMoN-wet bottle blanks contained no measurable contamination.

The AIRMoN-wet internal blind program is a cooperative project with the Bondville, Illinois site operator and the AIRMoN-wet liaison. Analytical results for these internal blind samples showed that the precision calculated for the solution used in 2002, the WMO/GAW 2001, was within the data quality objectives of the network QAP for all parameters. Of all the parameters measured, specific conductance had a statistically significant positive bias and ammonium had a statistically significant negative 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 and pH comparison. Samples not meeting the required criteria 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 2002. 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 this trend continued in 2002. This means that measured conductivity exceeds the calculated conductivity, indicating that anions are present in the precipitation samples that are not being measured under current protocols.

The USGS interlaboratory comparison study included eight laboratories in 2002. Six 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 good results. Although the CAL has dropped in overall ranking in the past few years as seen from the results of the studies compared to the other participating laboratories, CAL results basically have remained the same and well within parameters set out by the NADP. Ammonium was biased low, sulfate and calcium had slight overall positive biases, but all other analytes were within the acceptable limits.

In 2002, the CAL participated in five additional interlaboratory comparisons: two with the WMO/GAW, two studies from the NWRI, and one study with the NILU. The CAL results were good for all the studies for most of the parameters. The only consistent biases were a negative bias for ammonium for the WMO/GAW, NWRI, and NILU samples, and a positive bias for specific conductance for the WMO/GAW and NWRI samples. Sixty-three laboratories participated in the first WMO/GAW study, and 74 participated in the second study, but the CAL did not submit WMO/GAW sample results for official inclusion in the study because it prepared the study samples and verified the target values. However, unofficial comparison of the data from the CAL with theoretical and median values from the other laboratories, indicated that the CAL results were acceptable. The NWRI results over the last ten studies indicate that the CAL is ranked eighth overall of 32 ranked laboratories. The CAL received four low calcium flags in Study FP81 and one low ammonium and one high sodium flag in Study FP80. Magnesium, although no sample was flagged, was determined to be biased low in Study FP80. Both studies rated the CAL "satisfactory." A comparison of the last ten studies resulted in a median score for the CAL of 6.0 percent or "satisfactory." The only apparent bias for the CAL in the NILU study was a possible negative bias for ammonium. The CAL's performance was acceptable for all other parameters. The CAL continues to compare favorably with other laboratories analyzing low ionic strength samples throughout the world.

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APPENDIX A

GLOSSARY OF TERMS

GLOSSARY OF TERMS

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

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

Term	Abbreviation	Definition
Mean	$\bar{x}$	The average obtained by dividing a sum by the number of its addends. $\bar{x} = \sum_{i=1}^{n} x_i / n$ where: n = number of values x_i = values
Mean Bias		The sum of the bias for each sample divided by the total number of replicates (*n*).
Mean Percent Recovery		The sum of the percent recovery for each sample divided by the number of replicates (*n*).
Method Detection Limit	**MDL**	The minimum concentration of an analyte that can be reported with 99 percent confidence that the value is greater than zero (Glaser et al., 1981).
Percent Bias		The difference between the mean value obtained by repeated analysis of a homogeneous sample and the accepted true value expressed as a percentage of the true value. $\%Bias = 100 * [(V_m - V_t)/V_t]$ where: V_m = mean measured value V_t = true value
Precision		The degree of agreement of repeated measurements of a homogeneous sample by a specific procedure, expressed in terms of dispersion of the values obtained about the mean value. It is often reported as the sample standard deviation (*s*).

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

2002

Table B-1. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, High-Purity Standards Simulated Rainwater 1 (H-PS SR1), 2002

Parameter	*Target concentration*[a] *(mg/L)*	*Mean measured concentrations (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard deviation (mg/L)*	*RSD (%)*
Calcium	0.014	0.009[b] 0.040[c]	-0.005 0.026	-37.3 184.2	0.008 0.010	91.8 24.4
Magnesium	0.020	0.019 0.017	-0.001 -0.003	-6.5 -15.4	0.001 0.012	7.0 71.0
Sodium	0.20	0.198 0.192	-0.002 -0.008	-1.0 -4.2	0.016 0.010	8.0 5.0
Potassium	0.051	0.049 0.048	-0.002 -0.003	-3.6 -6.9	0.002 0.001	3.6 3.0
Ammonium	0.100	0.10 0.10	0.00 0.00	0.0 -0.9	0.01 0.01	12.1 13.4
Sulfate	2.47	2.496 2.412	0.026 -0.058	1.1 -2.4	0.024 0.027	0.9 1.1
Nitrate	0.50	0.517 0.505	0.017 0.005	3.4 1.0	0.007 0.013	1.4 2.6
Chloride	0.25	0.221 0.217	-0.029 -0.034	-11.6 -13.4	0.005 0.003	2.2 1.5
pH[d] (pH units)	4.35	4.34 4.34	-0.01 -0.01	-0.3 -0.2	0.02 0.02	0.5 0.5
H (µeq/L)	44.7	45.9 45.8	1.2 1.2	2.8 2.6	2.1 2.2	4.5 4.7
Specific conductance[d] (µS/cm)	22	24.8 24.9	2.8 2.9	12.7 13.2	0.6 0.9	2.6 3.4

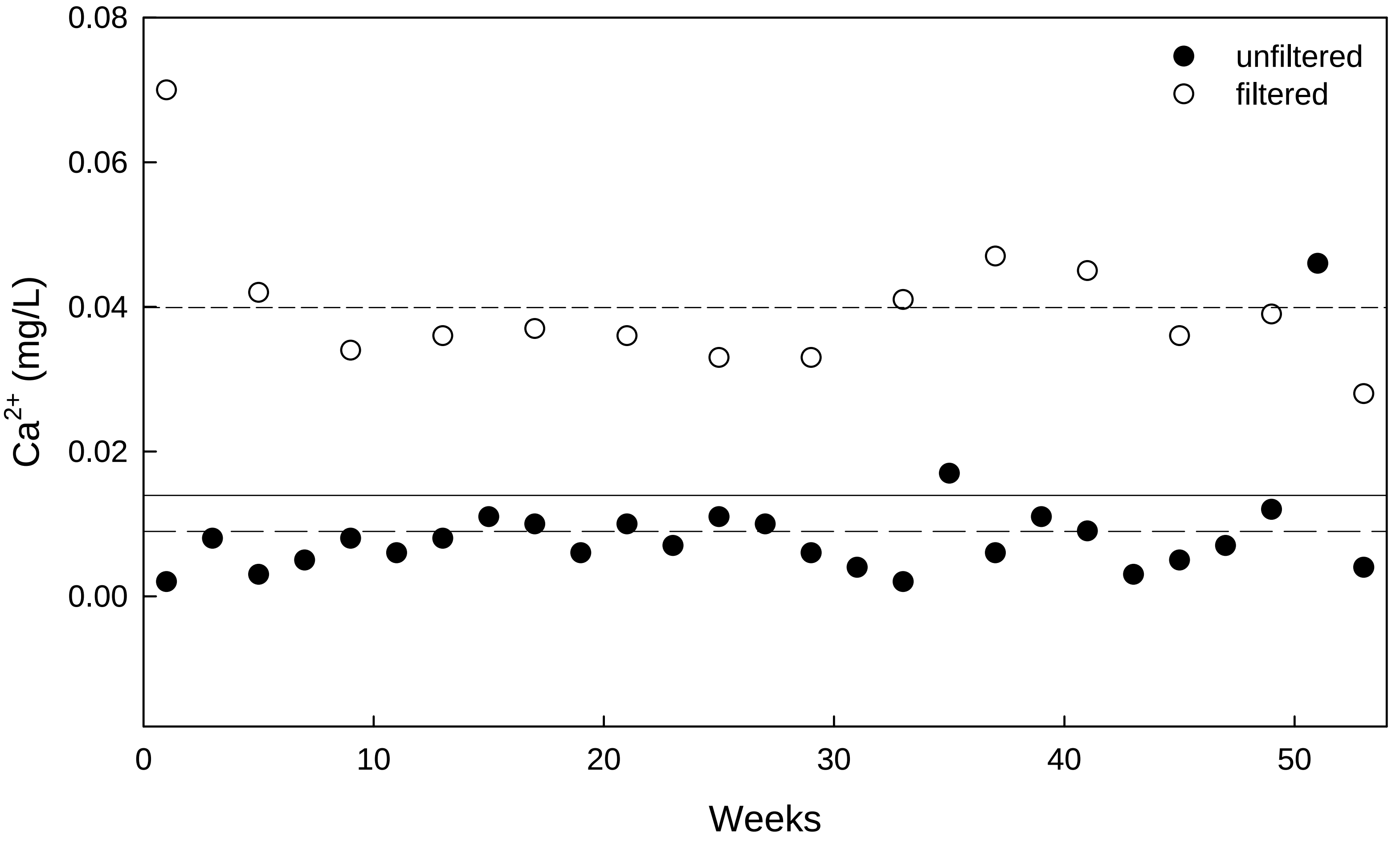
Notes:
There were 27 unfiltered and 14 filtered samples in each set.
[a] Target values provided by High-Purity Standards for Simulated Rainwater 1.
[b] The first set of values for each parameter is for unfiltered samples.
[c] The second set of values for each parameter is for filtered samples.
[d] Both pH and specific conductance are measured on unfiltered samples prior to filtering.

Table B-2. Unfiltered Blind Concentrations for High-Purity Standards Simulated Rainwater 1 (H-PS SR1), 2002

Weeks	*Ca^{2+} (mg/L)*	*Mg^{2+} (mg/L)*	*Na^{+} (mg/L)*	*K^{+} (mg/L)*	*NH_4^{+} (mg/L)*	*SO_4^{2-} (mg/L)*	*NO_3^{-} (mg/L)*	*Cl^{-} (mg/L)*	*pH (pH units)*	*H^{+} (µeq/L)*	*Specific conductance (µS/cm)*
1	0.002	0.019	0.202	0.048	0.102	2.488	0.504	0.218	4.32	47.9	24.9
3	0.008	0.019	0.193	0.046	0.102	2.488	0.514	0.221	4.35	44.7	24.3
5	0.003	0.019	0.202	0.050	0.079	2.572	0.515	0.229	4.36	43.7	24.8
7	0.005	0.019	0.197	0.050	0.108	2.496	0.520	0.221	4.33	46.8	24.8
9	0.008	0.018	0.208	0.050	0.098	2.491	0.513	0.222	4.34	45.7	24.4
11	0.006	0.019	0.274	0.048	0.073	2.509	0.520	0.217	4.35	44.7	24.9
13	0.008	0.018	0.199	0.051	0.105	2.495	0.514	0.224	4.35	44.7	24.2
15	0.011	0.018	0.203	0.054	0.103	2.496	0.511	0.219	4.33	46.8	24.5
17	0.010	0.020	0.195	0.049	0.103	2.507	0.521	0.220	4.35	44.7	24.3
19	0.006	0.018	0.193	0.051	0.087	2.511	0.526	0.223	4.31	49.0	26.1
21	0.010	0.019	0.203	0.048	0.087	2.492	0.518	0.220	4.34	45.7	25.8
23	0.007	0.020	0.200	0.048	0.103	2.533	0.526	0.220	4.32	47.9	24.9
25	0.011	0.018	0.195	0.051	0.086	2.504	0.515	0.213	4.31	49.0	25.3
27	0.010	0.019	0.193	0.048	0.100	2.507	0.514	0.209	4.35	44.7	24.3
29	0.006	0.019	0.202	0.050	0.112	2.486	0.507	0.215	4.34	45.7	24.9
31	0.004	0.019	0.197	0.049	0.105	2.455	0.516	0.236	4.33	46.8	25.0
33	0.002	0.019	0.188	0.047	0.101	2.457	0.512	0.226	4.32	47.9	25.4
35	0.017	0.020	0.193	0.050	0.090	2.496	0.523	0.220	4.31	49.0	23.2
37	0.006	0.019	0.192	0.046	0.104	2.467	0.532	0.220	4.36	43.7	24.8
39	0.011	0.019	0.193	0.052	0.079	2.518	0.526	0.224	4.36	43.7	25.3
41	0.009	0.018	0.191	0.050	0.099	2.481	0.514	0.222	4.32	47.9	24.2
43	0.003	0.018	0.192	0.049	0.067	2.504	0.516	0.227	4.32	47.9	24.6
45	0.005	0.020	0.191	0.047	0.102	2.471	0.516	0.220	4.40	39.8	25.5
47	0.007	0.019	0.193	0.048	0.104	2.491	0.524	0.219	4.35	44.7	24.9
49	0.012	0.020	0.190	0.050	0.111	2.494	0.515	0.219	4.33	46.8	23.4
51	0.046	0.013	0.186	0.049	0.085	2.467	0.498	0.223	4.35	44.7	24.9
53	0.004	0.019	0.183	0.048	0.103	2.519	0.529	0.222	4.34	45.7	25.6
Mean	0.009	0.019	0.198	0.049	0.096	2.496	0.517	0.221	4.34	45.9	24.8
Median	0.007	0.019	0.193	0.049	0.102	2.495	0.516	0.220	4.34	45.7	24.9
Target	0.014	0.020	0.20	0.051	0.100	2.47	0.50	0.25	4.35	44.7	22

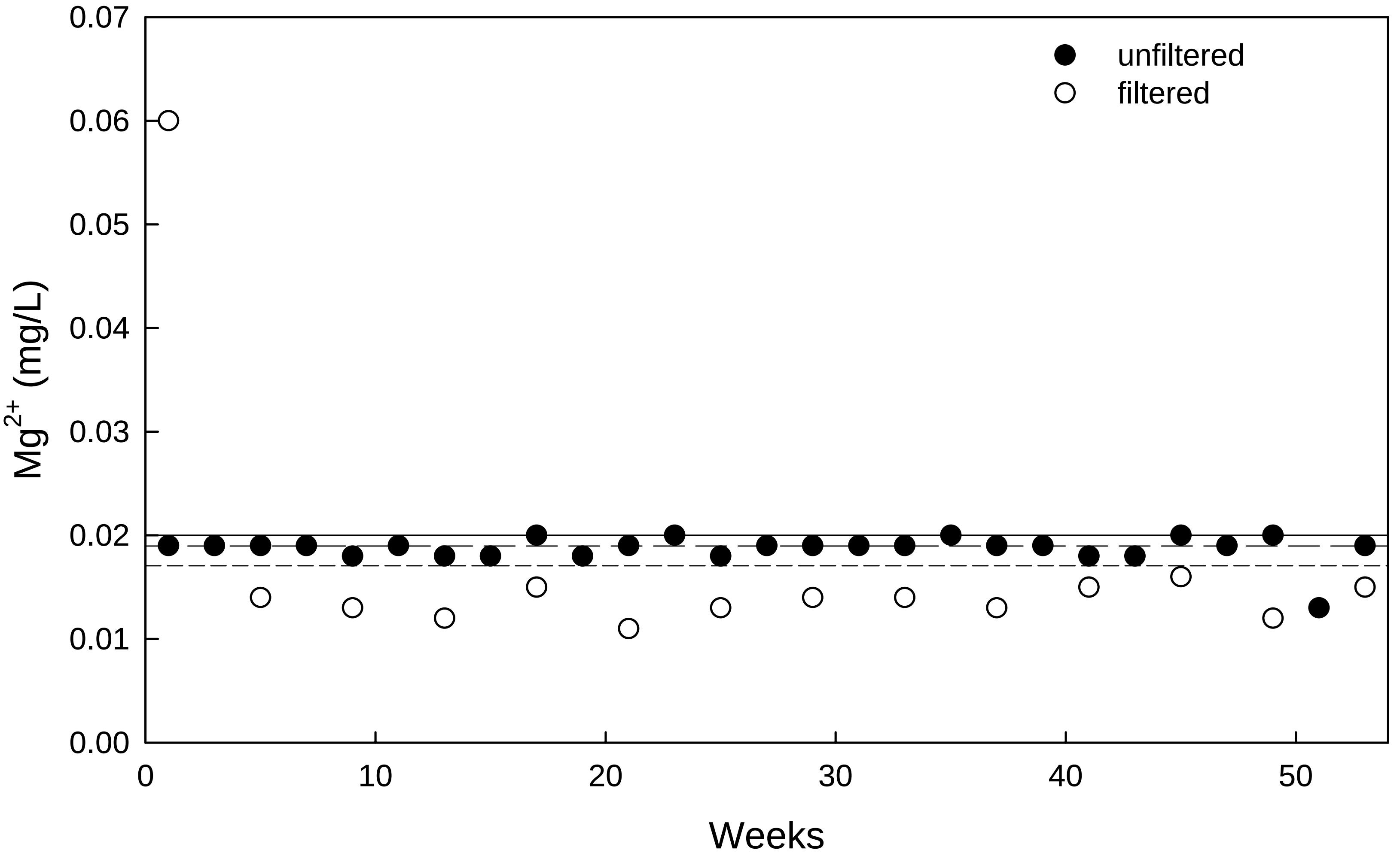
Table B-3. Filtered Blind Concentrations for High-Purity Standards Simulated Rainwater 1 (H-PS SR1), 2002

Weeks	*Ca^{2+} (mg/L)*	*Mg^{2+} (mg/L)*	*Na^{+} (mg/L)*	*K^{+} (mg/L)*	*NH_4^{+} (mg/L)*	*SO_4^{2-} (mg/L)*	*NO_3^{-} (mg/L)*	*Cl^{-} (mg/L)*	*pH (pH units)*	*H^{+} (μeq/L)*	*Specific conductance (μS/cm)*
1	0.070	0.060	0.201	0.050	0.099	2.415	0.491	0.217	4.38	41.7	24.8
5	0.042	0.014	0.190	0.047	0.102	2.401	0.481	0.218	4.37	42.7	24.7
9	0.034	0.013	0.220	0.050	0.071	2.435	0.509	0.218	4.32	47.9	25.7
13	0.036	0.012	0.187	0.048	0.095	2.393	0.506	0.219	4.35	44.7	24.1
17	0.037	0.015	0.184	0.048	0.102	2.366	0.497	0.210	4.33	46.8	25.0
21	0.036	0.011	0.198	0.045	0.128	2.405	0.506	0.220	4.37	42.7	22.7
25	0.033	0.013	0.191	0.047	0.100	2.460	0.501	0.216	4.32	47.9	25.1
29	0.033	0.014	0.194	0.048	0.113	2.427	0.493	0.213	4.34	45.7	25.9
33	0.041	0.014	0.187	0.046	0.106	2.371	0.491	0.215	4.35	44.7	24.8
37	0.047	0.013	0.182	0.047	0.081	2.405	0.525	0.219	4.33	46.8	25.3
41	0.045	0.015	0.183	0.047	0.104	2.393	0.530	0.217	4.31	49.0	24.8
44	0.036	0.016	0.183	0.046	0.095	2.398	0.514	0.214	4.33	46.8	25.3
47	0.039	0.012	0.189	0.047	0.086	2.450	0.510	0.212	4.32	47.9	26.4
51	0.028	0.015	0.193	0.049	0.106	2.443	0.517	0.223	4.33	46.8	24.2
Mean	0.040	0.017	0.192	0.048	0.099	2.412	0.505	0.217	4.34	45.8	24.9
Median	0.037	0.014	0.190	0.047	0.101	2.405	0.506	0.217	4.33	46.8	24.9
Target	0.014	0.020	0.20	0.051	0.100	2.47	0.50	0.25	4.35	44.7	22



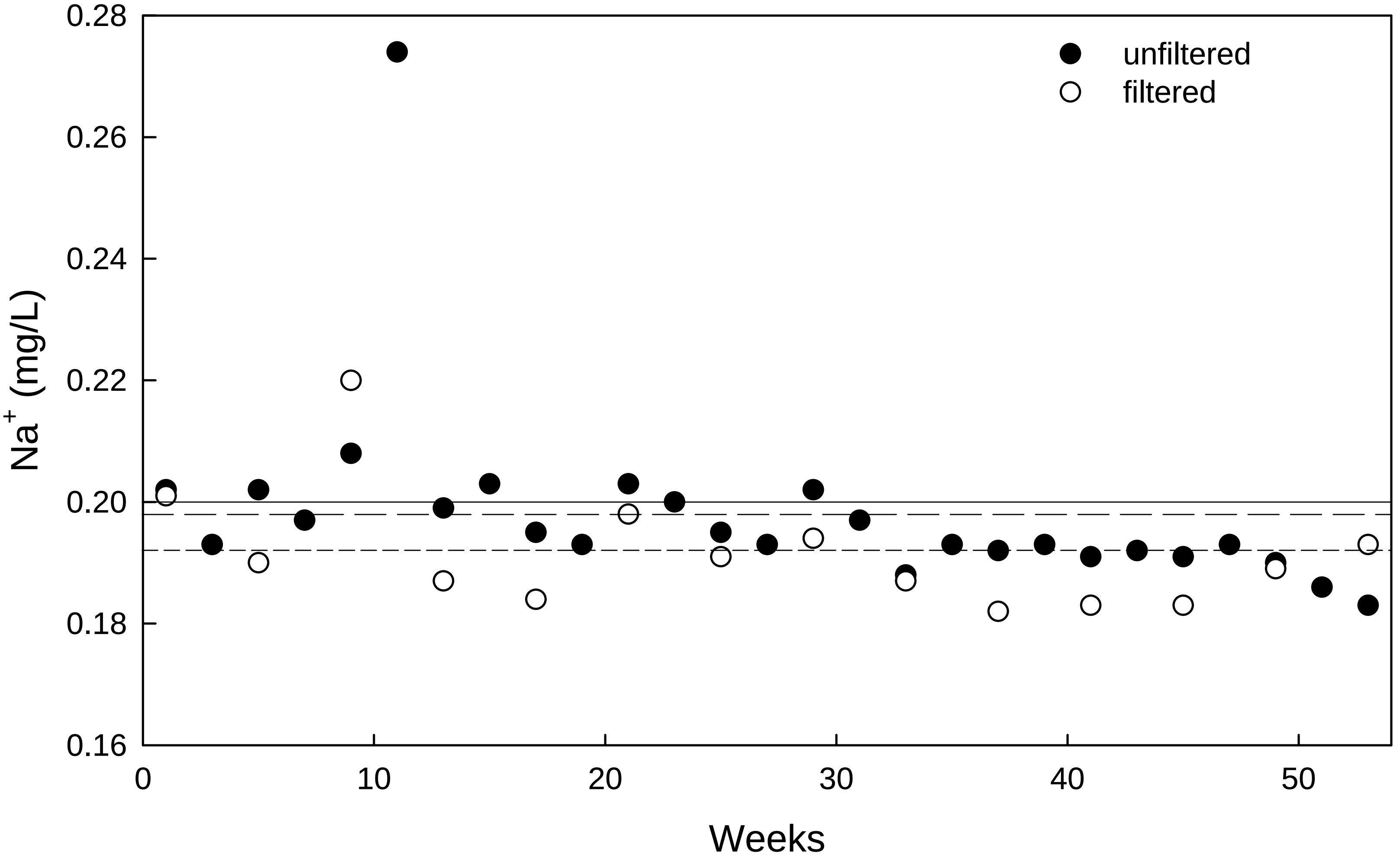
Note:
Solid line denotes target Ca^{2+} concentration: 0.014 mg/L; long dashed line denotes mean unfiltered Ca^{2+} concentration: 0.009; and short dashed line denotes mean filtered Ca^{2+} concentration: 0.040 mg/L.

Figure B-1. Comparison of NTN filtered and unfiltered internal blind samples, (calcium), High-Purity Standards, SR1, 2002.



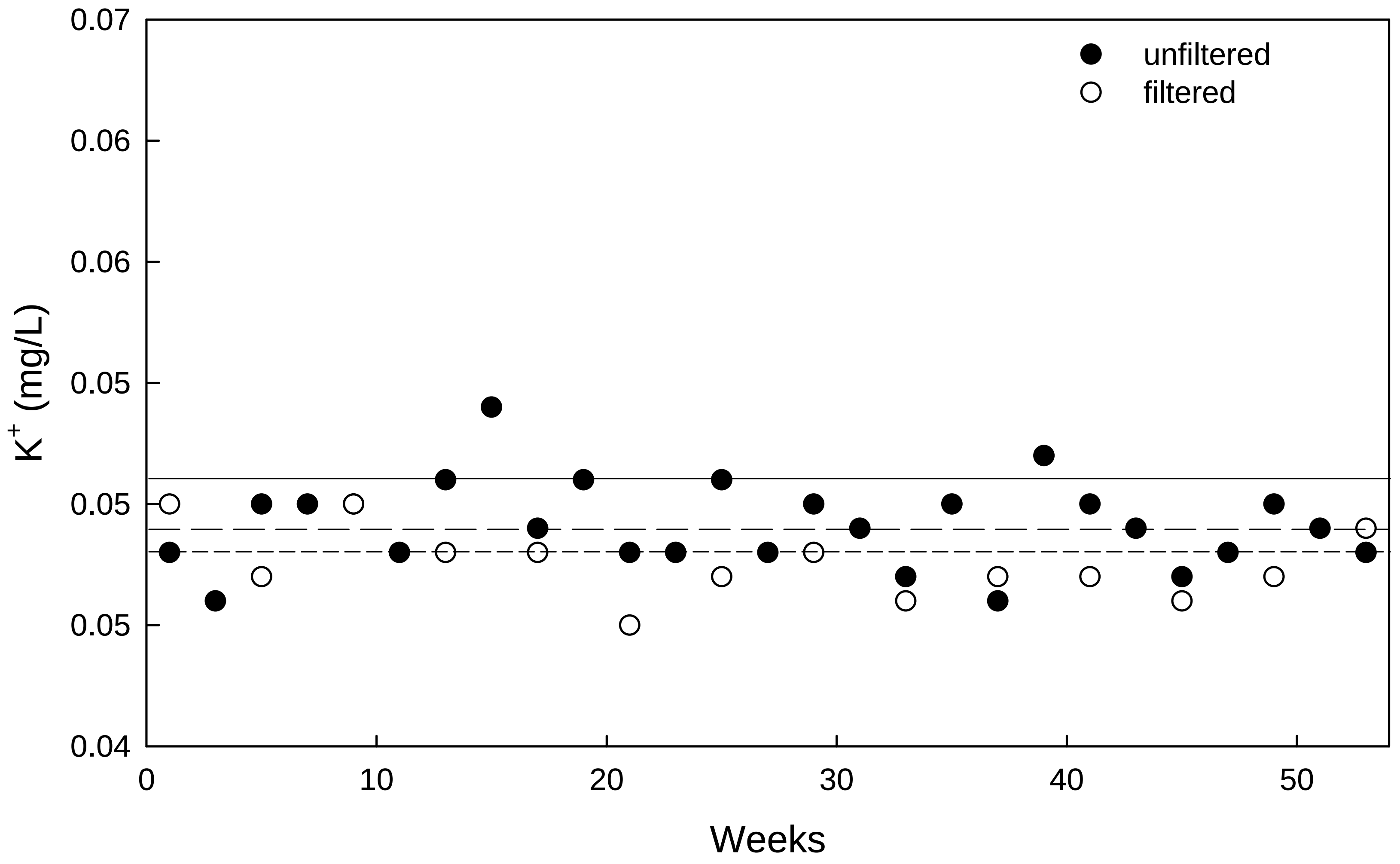
Note:
Solid line denotes target Mg^{2+} concentration: 0.020 mg/L; long dashed line denotes mean unfiltered Mg^{2+} concentration: 0.019 mg/L; and short dashed line denotes mean filtered Mg^{2+} concentration: 0.017 mg/L.

Figure B-2. Comparison of NTN flitered and unfiltered blind samples, (magnesium), High-Purity Standards, SR1, 2002.



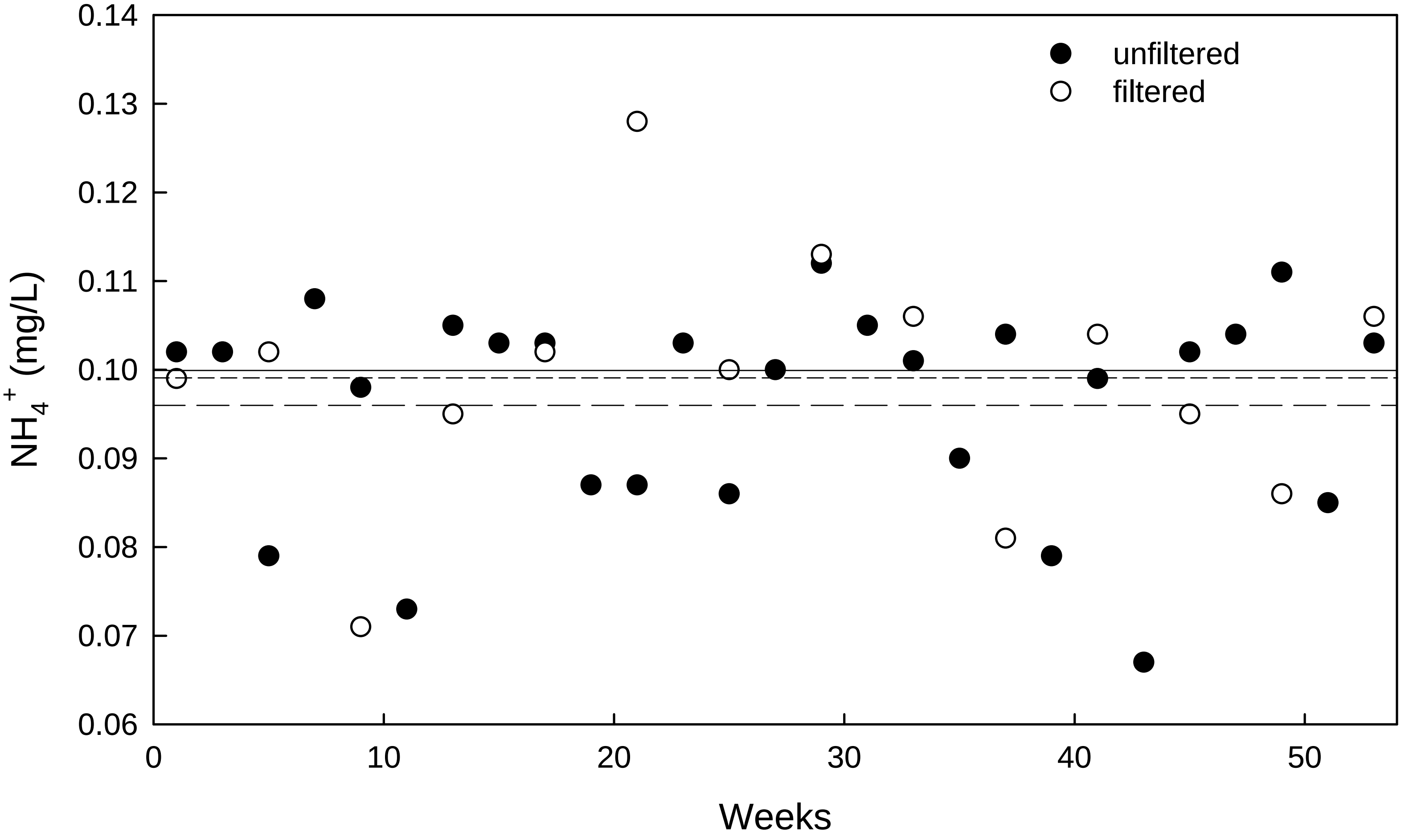
Note:
Solid line denotes target Na$^+$ concentration: 0.20 mg/L; long dashed line dentoes mean unfiltered Na$^+$ concentration: 0.198 mg/L; and short dashed line denotes mean filtered Na$^+$ concentration: 0.192 mg/L.

Figure B-3. Comparison of NTN filtered and unfiltered blind samples, (sodium), High-Purity Standards, SR1, 2002.



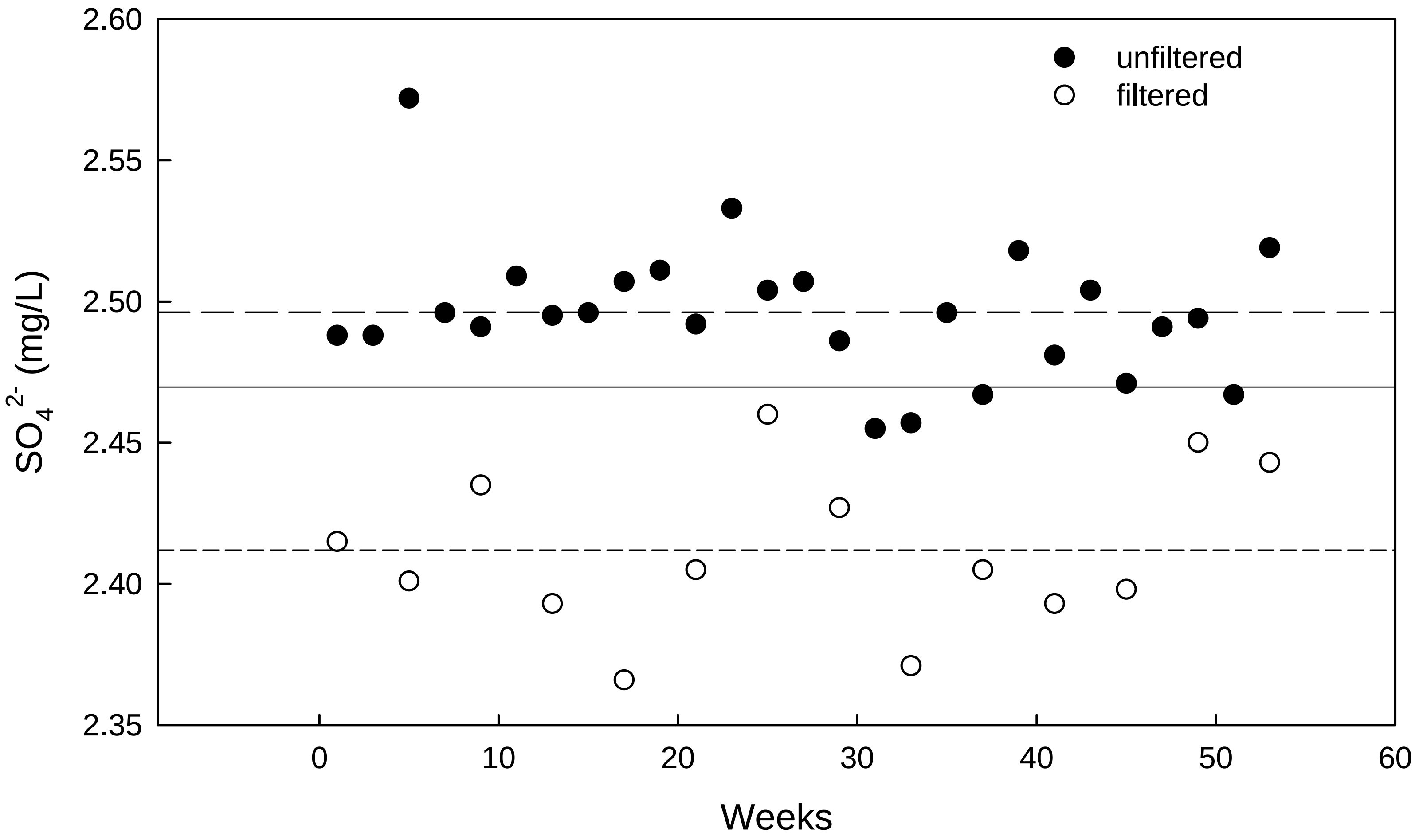
Note:
Solid line denotes target K^+ concentration: 0.051 mg/L; long dashed line denotes mean unfiltered K^+ concentration: 0.049 mg/L; and short dashed line denotes mean filtered K^+ concentration: 0.048 mg/L.

Figure B-4. Comparison of NTN filtered and unfiltered internal blind samples, (potassium), High-Purity Standards, SR1, 2002.



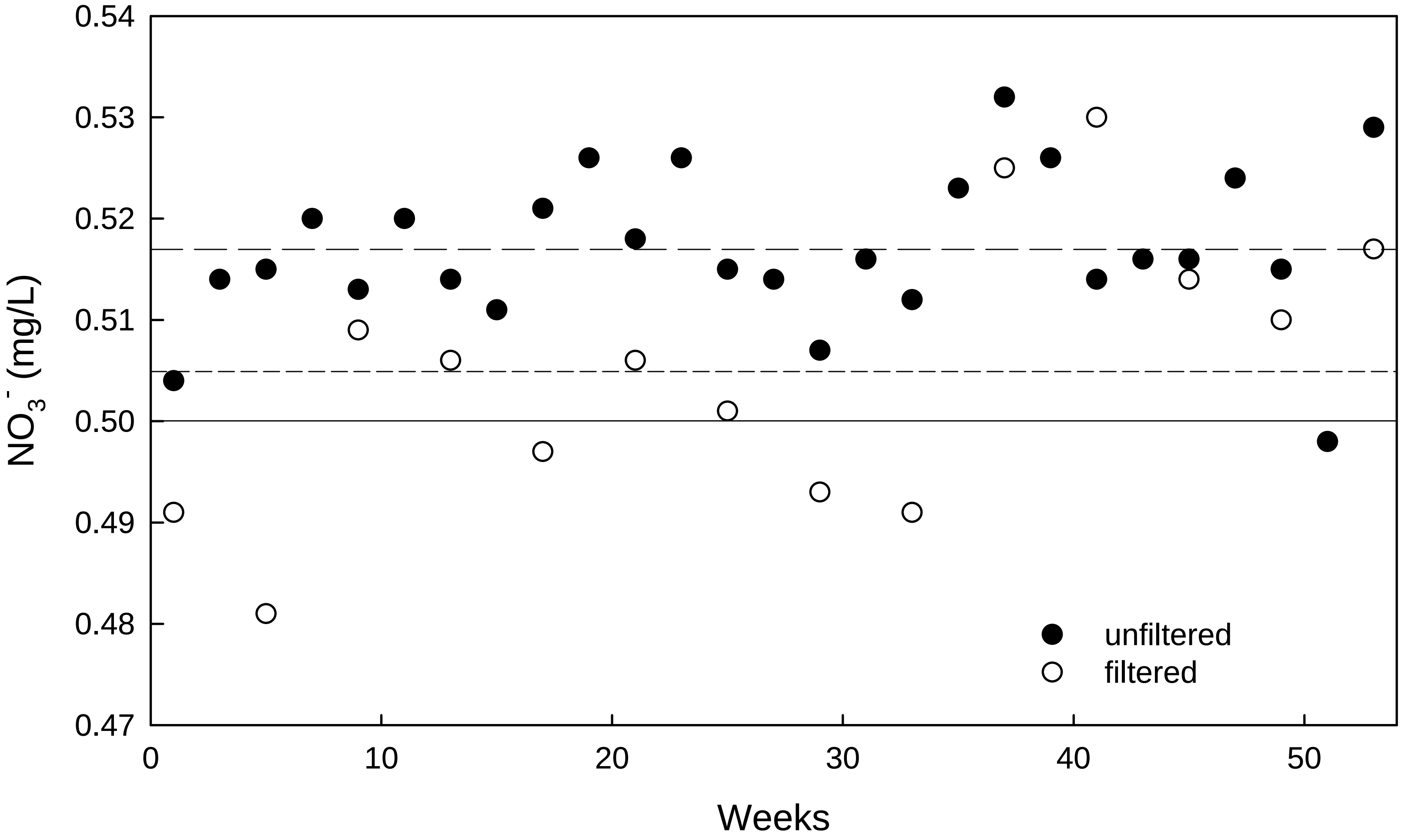
Note:
Solid line denotes target NH$_4^+$ concentration: 0.100 mg/L; long dashed line denotes mean filtered NH$_4^+$ concentration: 0.096 mg/L; and short dashed line denotes mean filtered NH$_4^+$ concentration: 0.099 mg/L.

Figure B-5. Comparison of NTN filtered and unfiltered internal blind samples, (ammonium), High-Purity Standards, SR1, 2002.



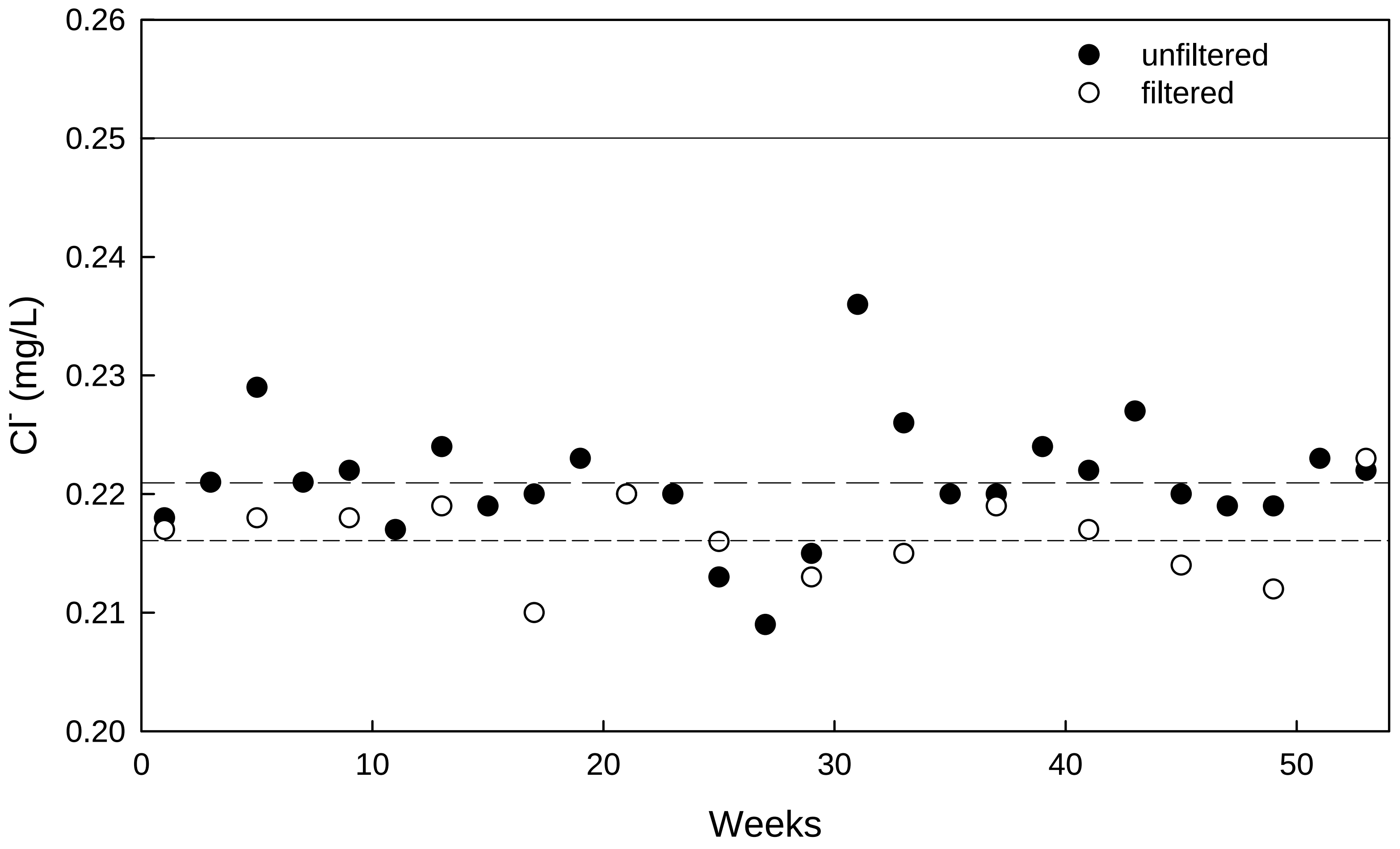
Note:
Solid line denotes target SO_4^{2-} concentration: 2.47 mg/L; long dashed line denotes mean unfiltered SO_4^{2-} concentration: 2.496 mg/L; and short dashed line denotes mean filtered SO_4^{2-} concentration: 2.412 mg/L.

Figure B-6. Comparison of NTN filtered and unfiltered internal blind samples, (sulfate), High-Purity Standards, SR1, 2002.



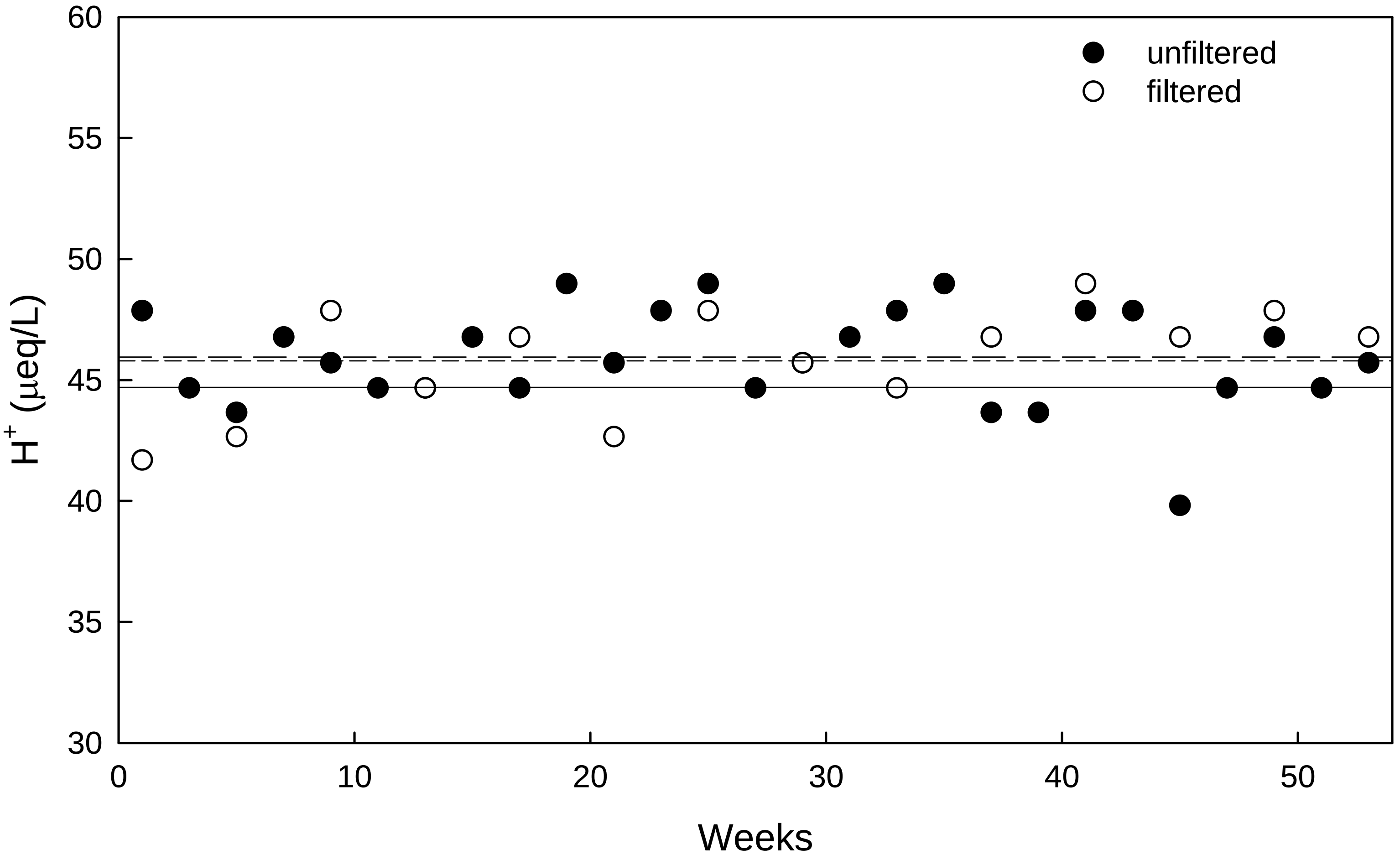
Note:
Solid line denotes target NO_3^- concentration: 0.50 mg/L; long dashed line denotes mean unfiltered NO_3^- concentration: 0.517 mg/L; and short dashed line denotes filtered NO_3^- concentration: 0.505 mg/L.

Figure B-7. Comparison of NTN filtered and unfiltered internal blind samples, (nitrate), High-Purity Standards, SR1, 2002.



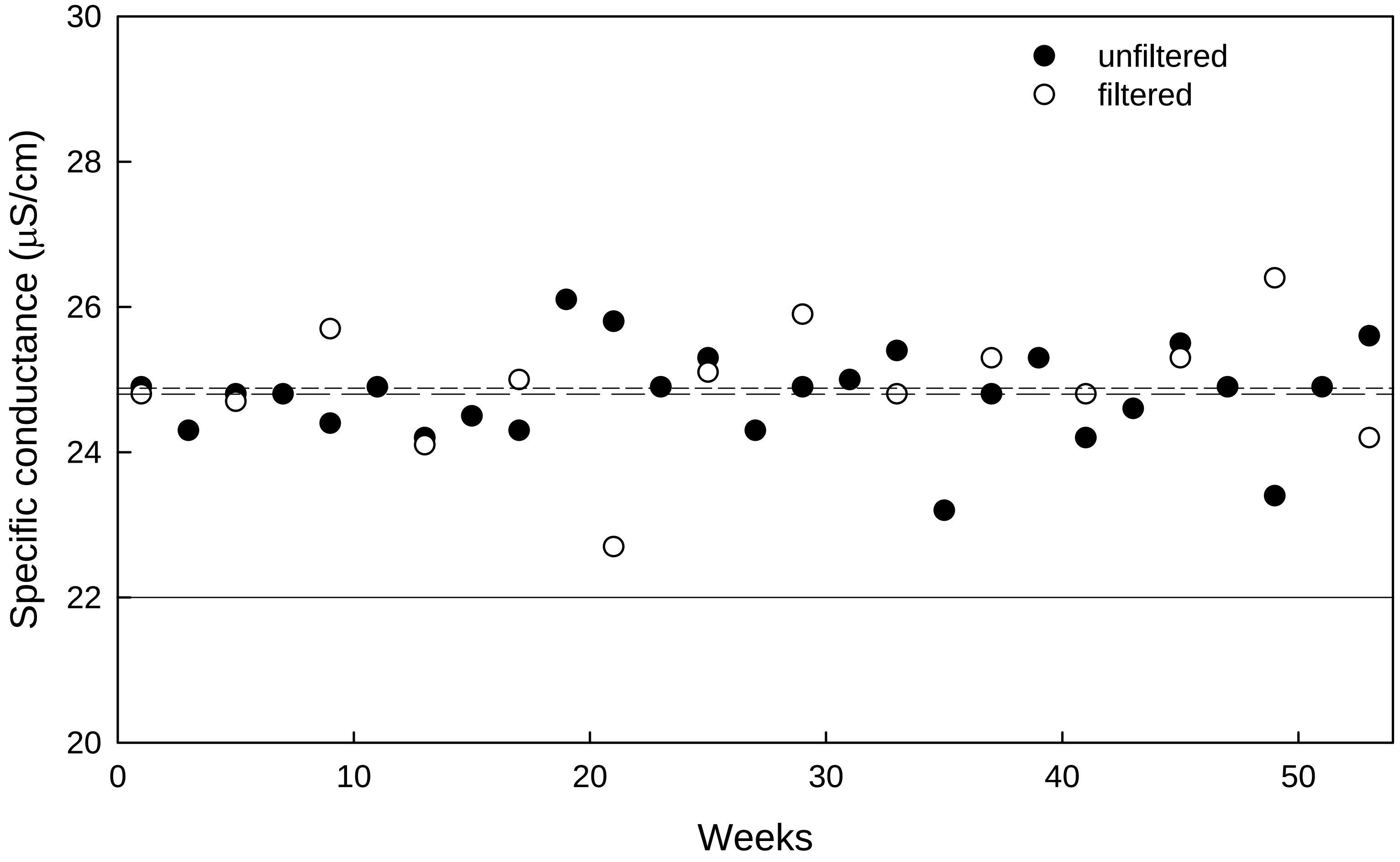
Note:
Solid line denotes target Cl^- concentration: 0.25 mg/L; long dashed line denotes mean unfiltered Cl^- concentration: 0.221 mg/L; and short dashed line denotes mean filtered Cl^- concentration: 0.217 mg/L.

Figure B-8. Comparison of NTN filtered and unfiltered internal blind samples, (chloride), High-Purity Standards, SR1, 2002.



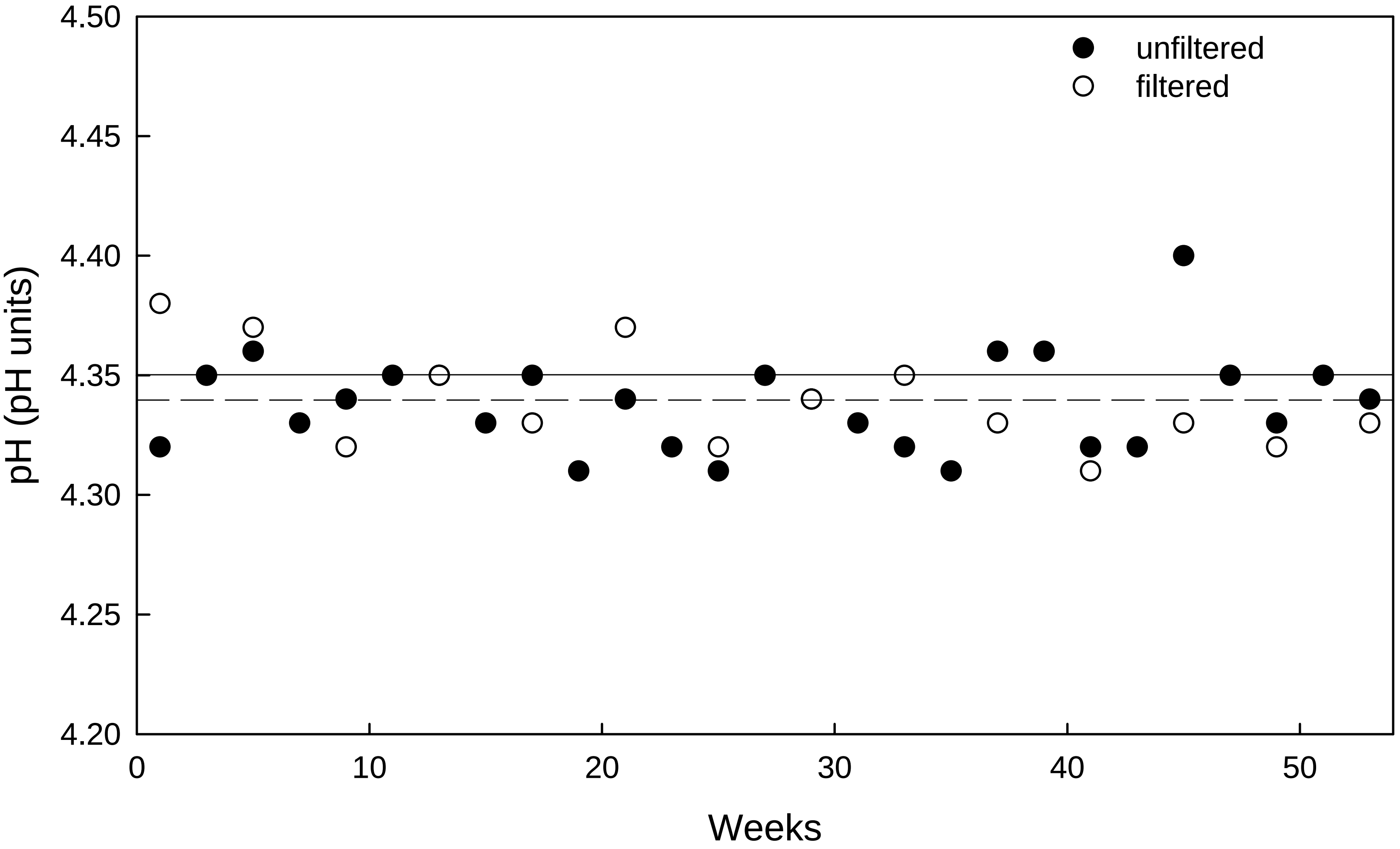
Note:
Solid line denotes target H^+ concentration: 44.7 μeq/L; long dashed line denotes mean unfiltered H^+ concentration: 45.9 μeq/L; and short dashed line denotes mean filtered H^+ concentration: 45.8 μeq/L.

Figure B-9. Comparison of NTN filtered and unfiltered internal blind samples, (hydrogen), High-Purity Standards, SR1, 2002.



Note:
Solid line denotes target specific conductance: 22 µS/cm; long dashed line denotes unfiltered specific conductance: 24.8 µS/cm; and short dashed line denotes mean filtered specific conductance: 24.9 µS/cm.

Figure B-10. Comparison of NTN filtered and unfiltered internal blind samples, (specific conductance), High-Purity Standards, SR1, 2002.



Note:
Solid line denotes target pH: 4.35; and long dashed line denotes mean filtered and unfiltered pH: 4.34.

Figure B-11. Comparison of NTN filtered and unfiltered internal blind samples, (pH), High-Purity Standards, SR1, 2002.

Table B-4. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, High-Purity Standards Simulated Rainwater 2 (H-PS SR2), 2002

Parameter	*Target concentration*[a] *(mg/L)*	*Mean measured concentrations (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard deviation (mg/L)*	*RSD (%)*
Calcium	0.052	0.050[b]	-0.002	-3.4	0.005	9.0
		0.096[c]	0.044	83.7	0.012	12.2
Magnesium	0.050	0.048	-0.002	-3.8	0.001	2.6
		0.050	0.000	0.3	0.007	14.9
Sodium	0.40	0.398	-0.002	-0.4	0.010	2.5
		0.382	-0.018	-4.5	0.014	3.5
Potassium	0.095	0.099	0.004	4.7	0.002	1.9
		0.096	0.001	1.2	0.003	2.9
Ammonium	1.00	0.93	-0.07	-7.5	0.02	2.0
		0.89	-0.11	-10.8	0.02	2.5
Sulfate	10.1	10.234	0.134	1.3	0.172	1.7
		9.790	-0.300	-3.0	0.154	1.6
Nitrate	7.0	7.176	0.176	2.5	0.067	0.9
		6.908	-0.092	-1.3	0.125	1.8
Chloride	0.98	1.005	0.025	2.5	0.021	2.1
		0.964	-0.016	-1.6	0.026	2.7
pH[d] (pH units)	3.60	3.62	0.02	0.5	0.02	0.6
		3.62	0.02	0.6	0.02	0.6
H (µeq/L)	251.2	241.5	-9.7	-3.9	12.1	5.0
		239.7	-11.5	-4.6	11.3	4.7
Specific conductance[d] (µS/cm)	123.5	127.4	3.9	3.2	1.4	1.1
		127.7	4.2	3.4	1.1	0.8

Notes:

There were 26 unfiltered 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.

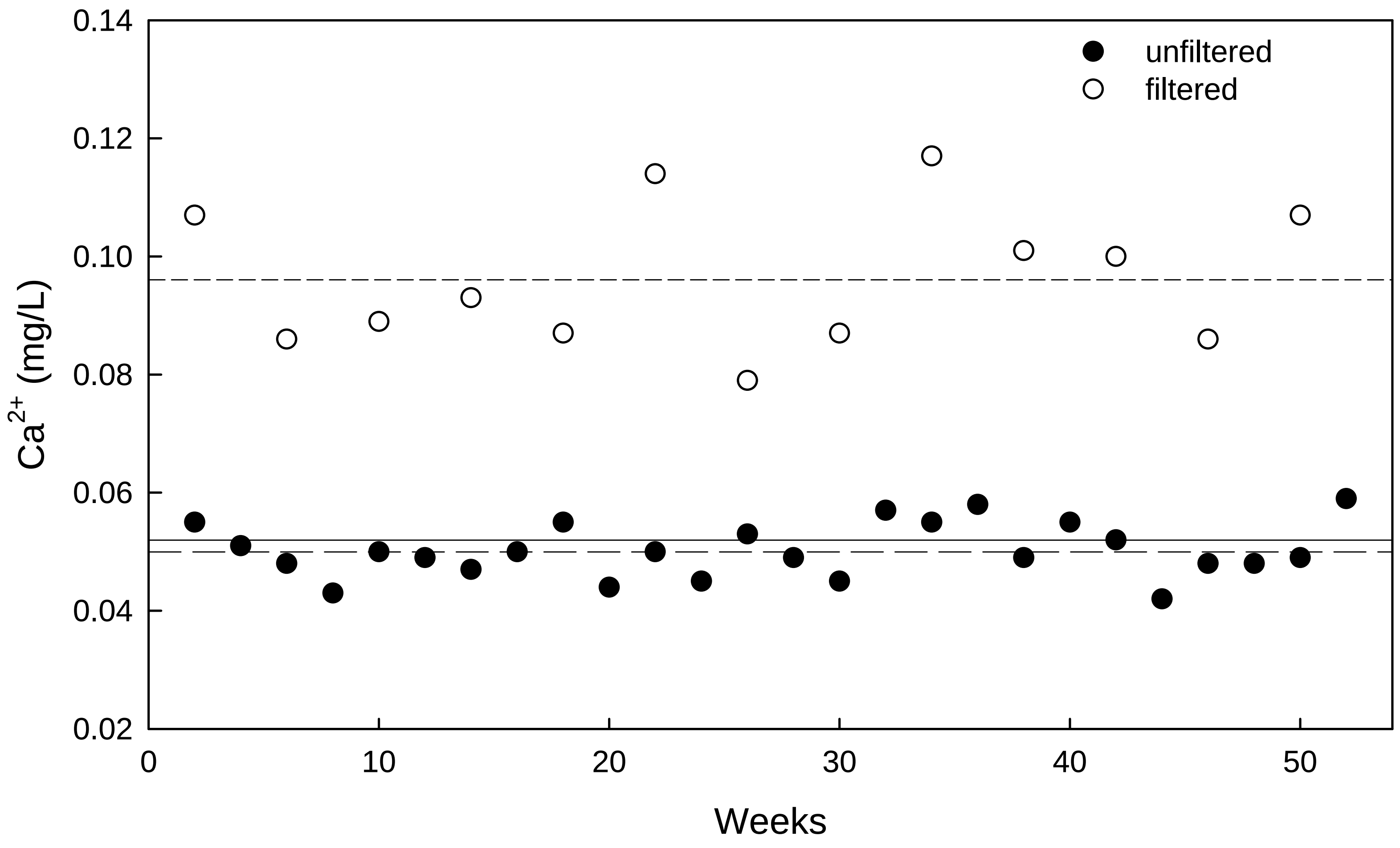
[d] Both pH and specific conductance are measured on unfiltered samples prior to filtering.

Table B-5. Unfiltered Blind Concentrations for High-Purity Standards Simulated Rainwater 2 (H-PS SR2), 2002

Weeks	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	NH_4^{+} (mg/L)	SO_4^{2-} (mg/L)	NO_3^{-} (mg/L)	Cl^{-} (mg/L)	pH (pH units)	H^{+} (μeq/L)	Specific conductance (μS/cm)
2	0.055	0.050	0.408	0.100	0.909	10.226	7.237	1.001	3.61	245.5	129.6
6	0.051	0.047	0.385	0.101	0.918	10.196	7.120	0.999	3.65	223.9	127.4
8	0.048	0.047	0.392	0.099	0.939	10.218	7.272	1.015	3.61	245.5	129.5
10	0.043	0.049	0.414	0.100	0.928	10.179	7.173	1.055	3.58	263.0	128.8
12	0.050	0.046	0.412	0.098	0.922	10.136	7.244	0.991	3.61	245.5	128.1
14	0.049	0.047	0.393	0.098	0.909	10.047	7.148	1.012	3.63	234.4	127.9
16	0.047	0.047	0.408	0.100	0.912	10.239	7.212	1.005	3.62	239.9	125.8
18	0.050	0.048	0.410	0.100	0.891	10.220	7.266	1.006	3.61	245.5	128.6
20	0.055	0.048	0.403	0.100	0.930	10.380	7.144	1.007	3.66	218.8	126.7
22	0.044	0.049	0.406	0.102	0.970	10.383	7.194	1.012	3.59	257.1	129.1
24	0.050	0.049	0.407	0.098	0.934	10.551	7.284	1.036	3.59	257.0	129.0
26	0.045	0.048	0.420	0.098	0.916	10.544	7.200	1.006	3.62	239.9	124.4
28	0.053	0.049	0.400	0.099	0.909	10.328	7.248	1.022	3.59	257.0	129.2
30	0.049	0.050	0.404	0.099	0.949	10.236	7.080	0.992	3.61	245.5	128.0
32	0.045	0.049	0.401	0.101	0.919	10.242	7.109	1.003	3.62	239.9	126.7
34	0.057	0.050	0.393	0.099	0.920	9.597	7.238	0.999	3.62	239.9	129.8
36	0.055	0.049	0.395	0.103	0.951	10.216	7.092	1.050	3.62	239.9	126.5
38	0.058	0.048	0.393	0.097	0.929	10.143	7.039	0.986	3.61	245.5	126.4
40	0.049	0.046	0.396	0.100	0.927	10.245	7.249	0.993	3.64	229.1	127.4
42	0.055	0.049	0.393	0.099	0.944	10.230	7.175	0.957	3.60	251.2	126.9
44	0.052	0.046	0.385	0.101	0.930	10.098	7.110	0.987	3.62	239.9	126.7
46	0.042	0.049	0.381	0.094	0.941	10.156	7.076	0.993	3.68	208.9	125.7
48	0.048	0.048	0.390	0.099	0.920	10.293	7.136	0.989	3.62	239.9	126.0
50	0.048	0.048	0.386	0.102	0.944	10.270	7.183	1.031	3.63	234.4	126.0
52	0.049	0.046	0.394	0.097	0.887	10.339	7.203	0.980	3.63	234.4	126.1
54	0.059	0.049	0.388	0.102	0.902	10.364	7.156	0.995	3.59	257.0	126.6
Mean	0.050	0.048	0.398	0.099	0.925	10.234	7.176	1.005	3.62	241.5	127.4
Median	0.050	0.048	0.396	0.100	0.925	10.233	7.179	1.002	3.62	239.9	127.2
Target	0.052	0.050	0.40	0.095	1.00	10.1	7.0	0.98	3.60	251.2	123.5

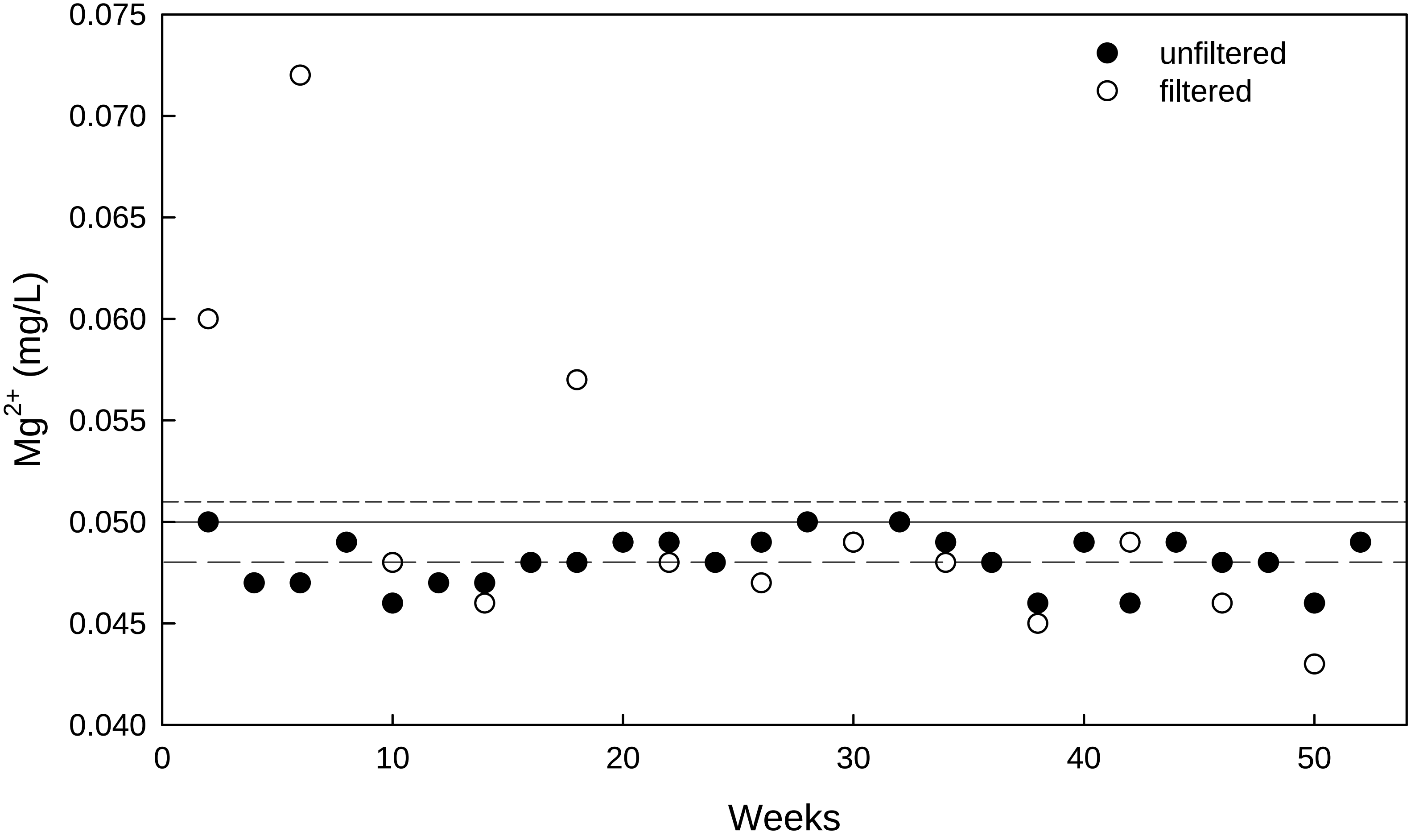
Table B-6. Filtered Blind Concentrations for High-Purity Standards Simulated Rainwater 2 (H-PS SR2), 2002

Weeks	Ca^{2+} *(mg/L)*	Mg^{2+} *(mg/L)*	Na^{+} *(mg/L)*	K^{+} *(mg/L)*	NH_4^{+} *(mg/L)*	SO_4^{2-} *(mg/L)*	NO_3^{-} *(mg/L)*	Cl^{-} *(mg/L)*	*pH (pH units)*	H^{+} *(μeq/L)*	*Specific conductance (μS/cm)*
2	0.107	0.060	0.388	0.084	0.891	9.675	6.912	0.984	3.60	251.2	129.3
6	0.086	0.072	0.388	0.097	0.899	9.834	7.034	0.991	3.67	213.8	127.8
10	0.089	0.048	0.397	0.095	0.917	9.859	7.173	0.992	3.61	245.5	128.4
14	0.093	0.046	0.394	0.099	0.877	9.813	6.954	0.992	3.63	234.4	127.0
18	0.087	0.057	0.363	0.091	0.844	9.432	6.704	0.927	3.61	245.5	128.2
22	0.114	0.048	0.399	0.100	0.881	10.080	6.928	0.944	3.59	257.0	128.9
26	0.079	0.047	0.390	0.094	0.917	9.860	6.908	0.996	3.61	245.5	129.2
30	0.087	0.049	0.390	0.099	0.909	9.828	6.860	0.973	3.60	251.2	128.7
34	0.117	0.048	0.388	0.095	0.919	9.780	6.9123	0.977	3.61	245.5	127.5
38	0.101	0.045	0.377	0.095	0.897	9.900	7.009	0.952	3.62	239.9	127.8
42	0.100	0.049	0.372	0.100	0.880	9.652	6.818	0.933	3.65	223.9	126.5
46	0.086	0.046	0.371	0.096	0.900	9.900	6.880	0.971	3.63	234.4	126.5
50	0.107	0.043	0.355	0.093	0.867	9.656	6.716	0.923	3.62	239.9	125.4
Mean	0.096	0.051	0.382	0.095	0.892	9.790	6.908	0.966	3.62	239.7	127.8
Median	0.091	0.048	0.388	0.095	0.897	9.828	6.908	0.973	3.61	242.7	127.8
Target	0.052	0.050	0.40	0.095	1.00	10.1	7.0	0.98	3.60	251.2	123.5



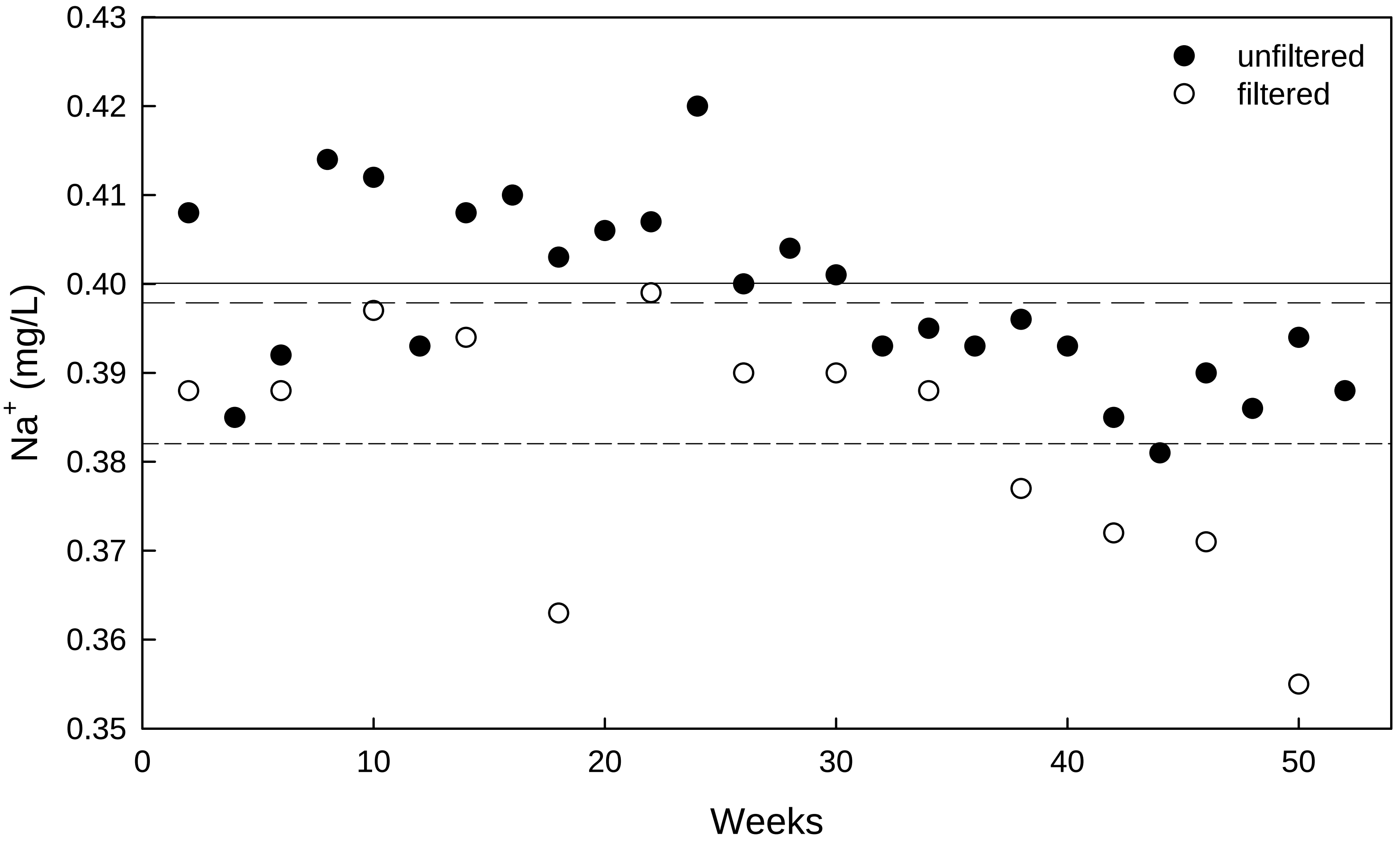
Note:
Solid line denotes target Ca^{2+} concentration: 0.052 mg/L; long dashed line denotes mean unfiltered Ca^{2+} concentration: 0.050 mg/L; and short dashed line denotes mean filtered Ca^{2+} concentration: 0.096 mg/L.

Figure B-12. Comparison of NTN filtered and unfiltered internal blind samples, (calcium), High-Purity Standards, 2002.



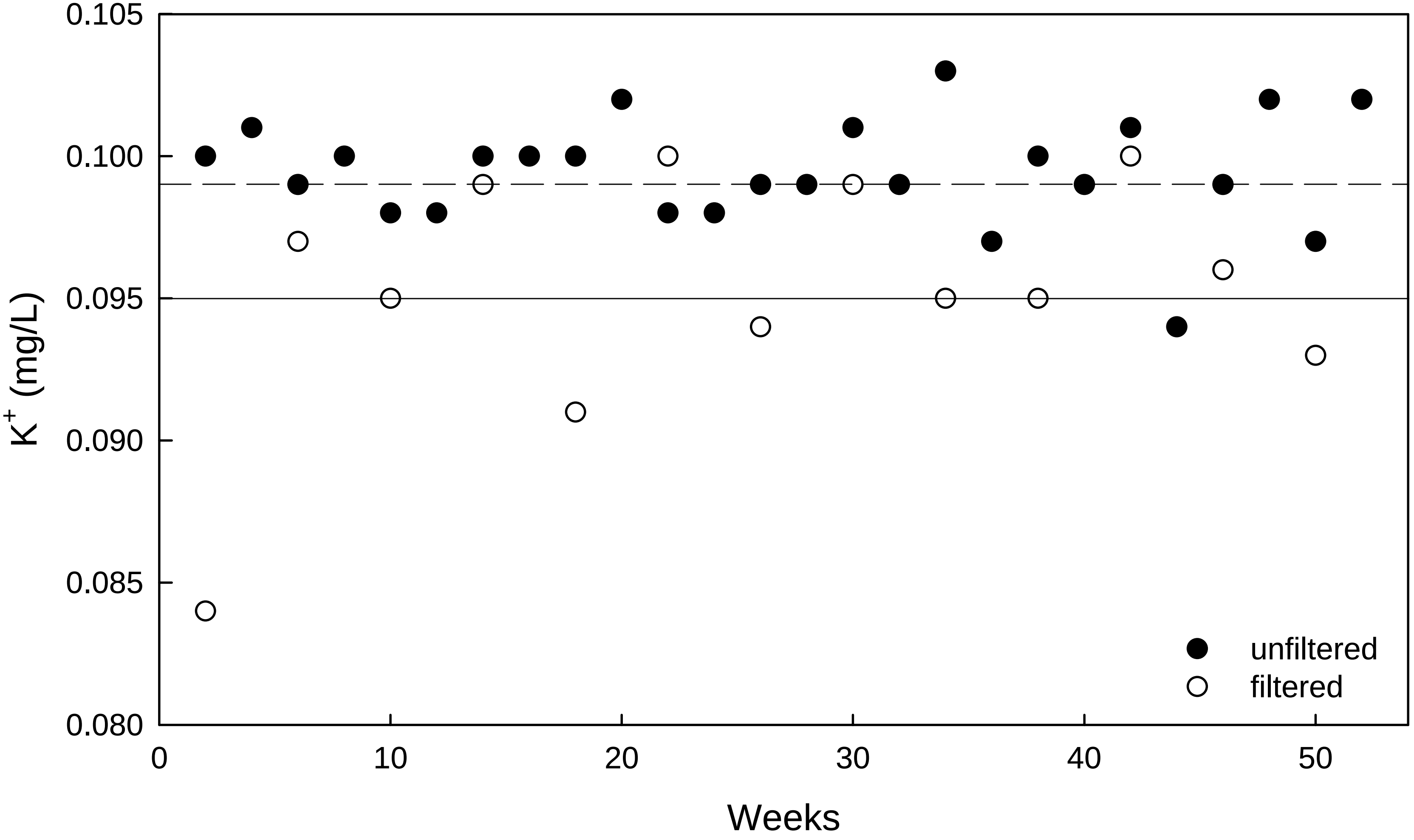
Note:
Solid line denotes target Mg^{2+} concentration: 0.050 mg/L); long dashed line denotes unfiltered Mg^{2+} concentration: 0.048 mg/L; and short dashed line denotes filtered Mg^{2+} concentration: 0.051 mg/L.

Figure B-13. Comparison of NTN filtered and unfiltered internal blind samples, (magnesium), High-Purity Standards, SR2, 2002.



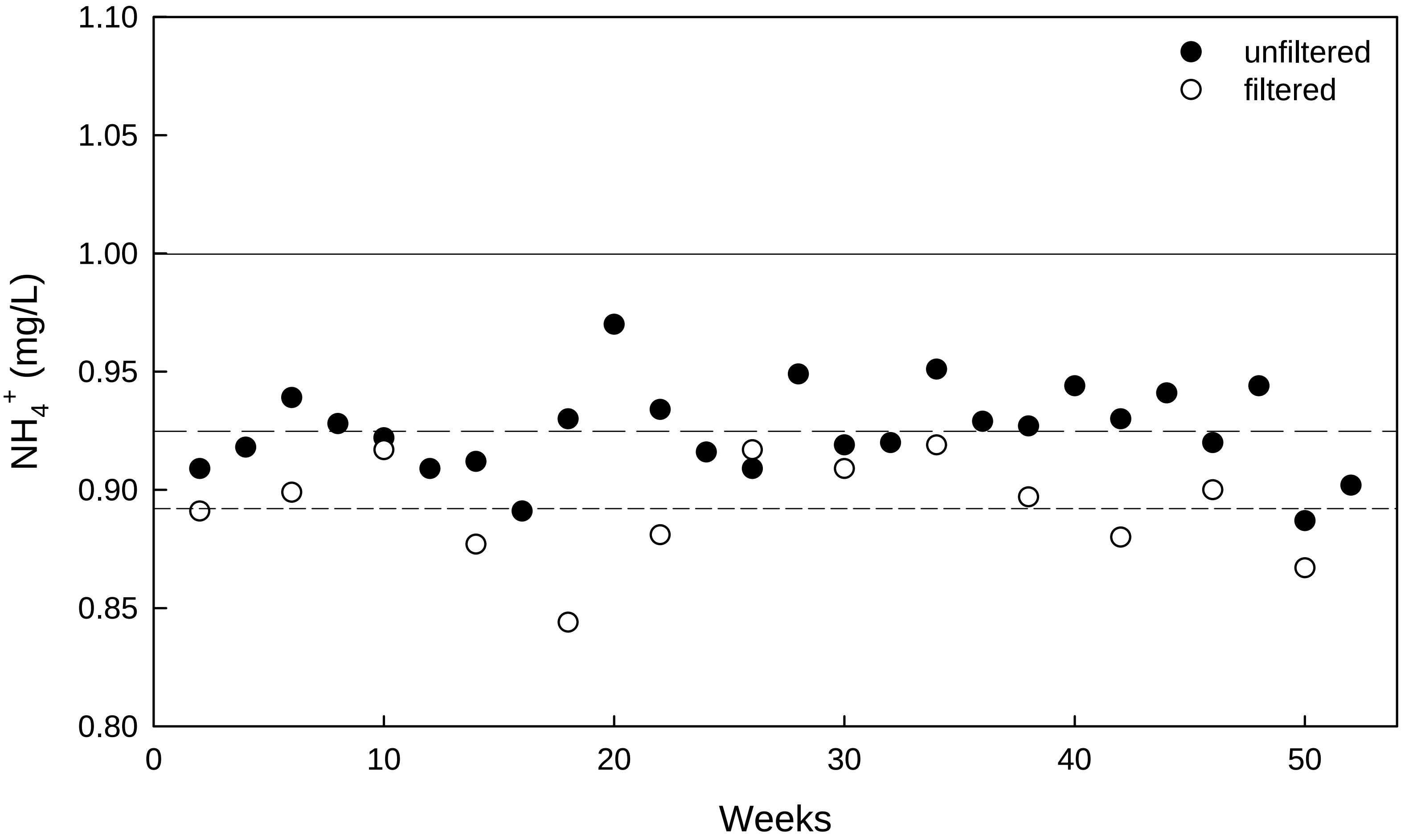
Note:
Solid line denotes target Na^+ concentration: 0.40 mg/L; long dashed line denotes mean unfiltered Na^+ concentration: 0.398 mg/L; and short dashed line denotes mean filtered Na^+ concentration: 0.382 mg/L.

Figure B-14. Comparison of NTN filtered and unfiltered internal blind samples, (sodium), High-Purity Standards, 2002.



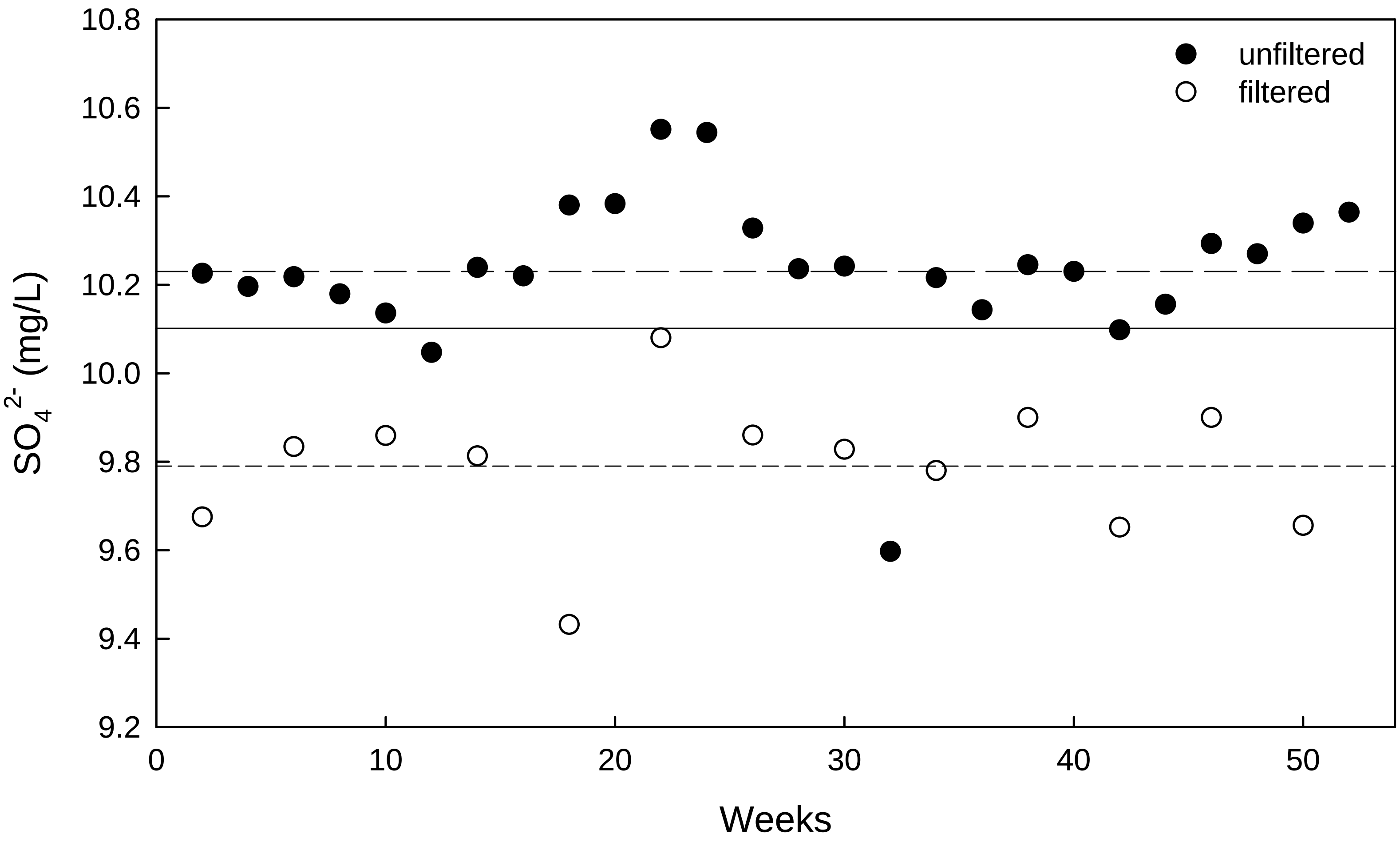
Note:
Solid line denotes target and mean filtered K^+ concentration: 0.095 mg/L; and long dashed line denotes mean unfiltered K^+ concentration: 0.099 mg/L.

Figure B-15. Comparison of NTN filtered and unfiltered internal blind samples, (potassium), High-Purity Standards, SR2, 2002.



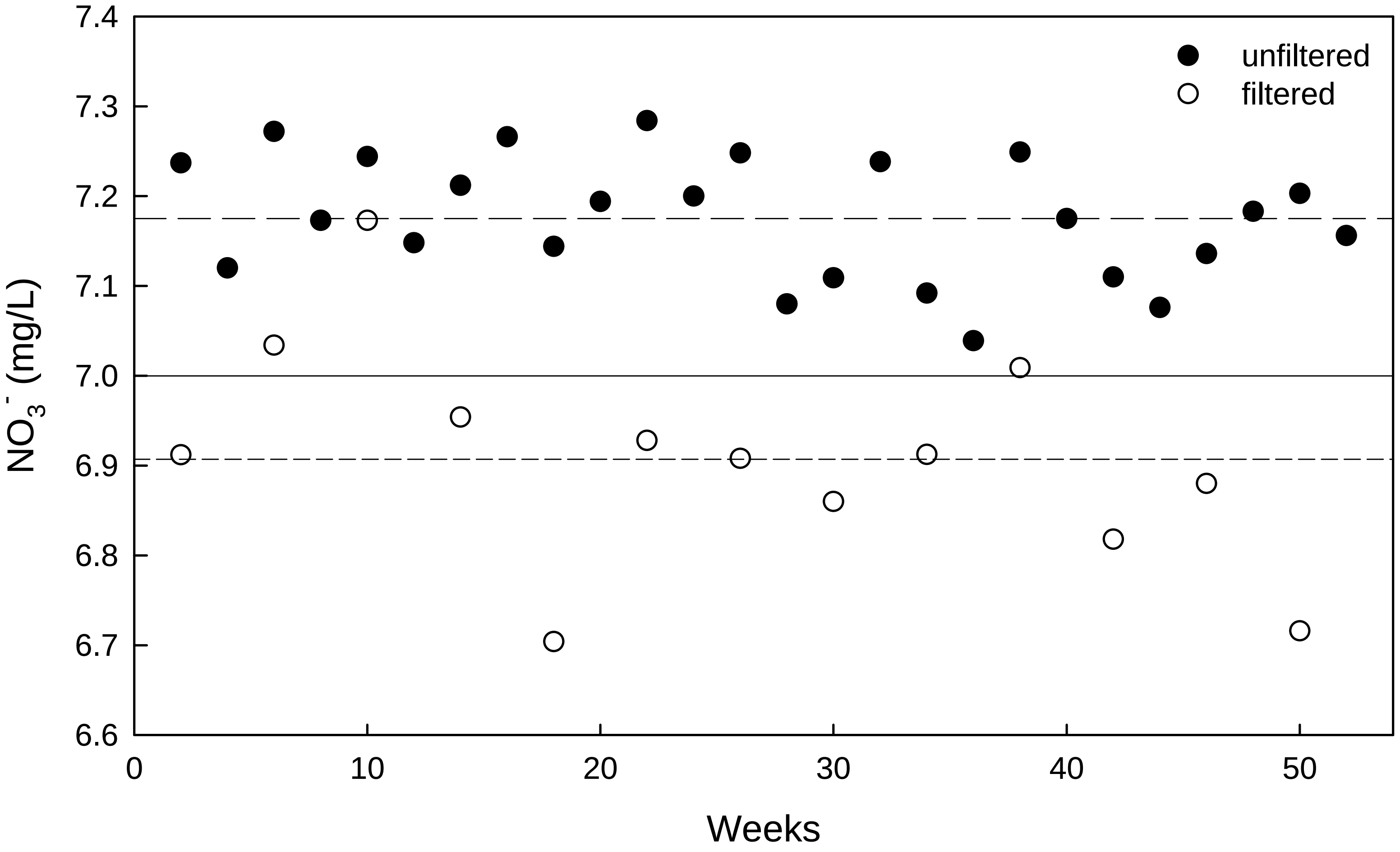
Note:
Solid line denotes target NH_4^+ concentration: 1.00 mg/L; long dashed line denotes mean unfiltered NH_4^+ concentration: 0.925 mg/L; and short dashed line denotes mean filtered NH_4^+ concentration: 0.862 mg/L.

Figure B-16. Comparison of NTN filtered and unfiltered internal blind samples, (ammonium), High-Purity Standards, SR2, 2002.



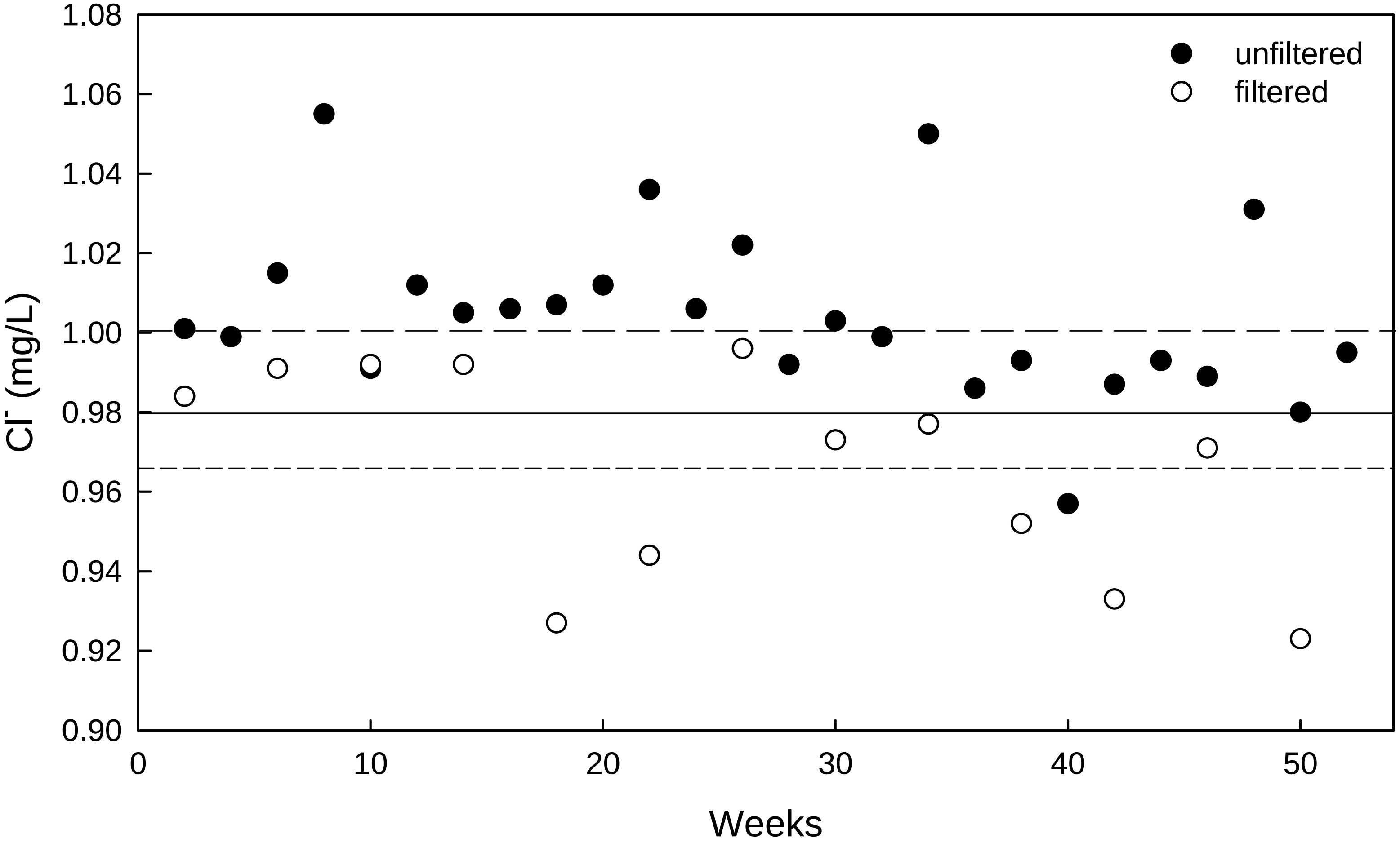
Note:
Solid line denotes target SO_4^{2-} concentration: 10.1 mg/L; long dashed line denotes mean unfiltered SO_4^{2-} concentration: 10.234 mg/L; and short dashed line denotes mean filtered SO_4^{2-} concentration: 9.790 mg/L.

Figure B-17. Comparison of NTN filtered and unfiltered internal blind samples, (sulfate), High-Purity Standards, SR2, 2002.



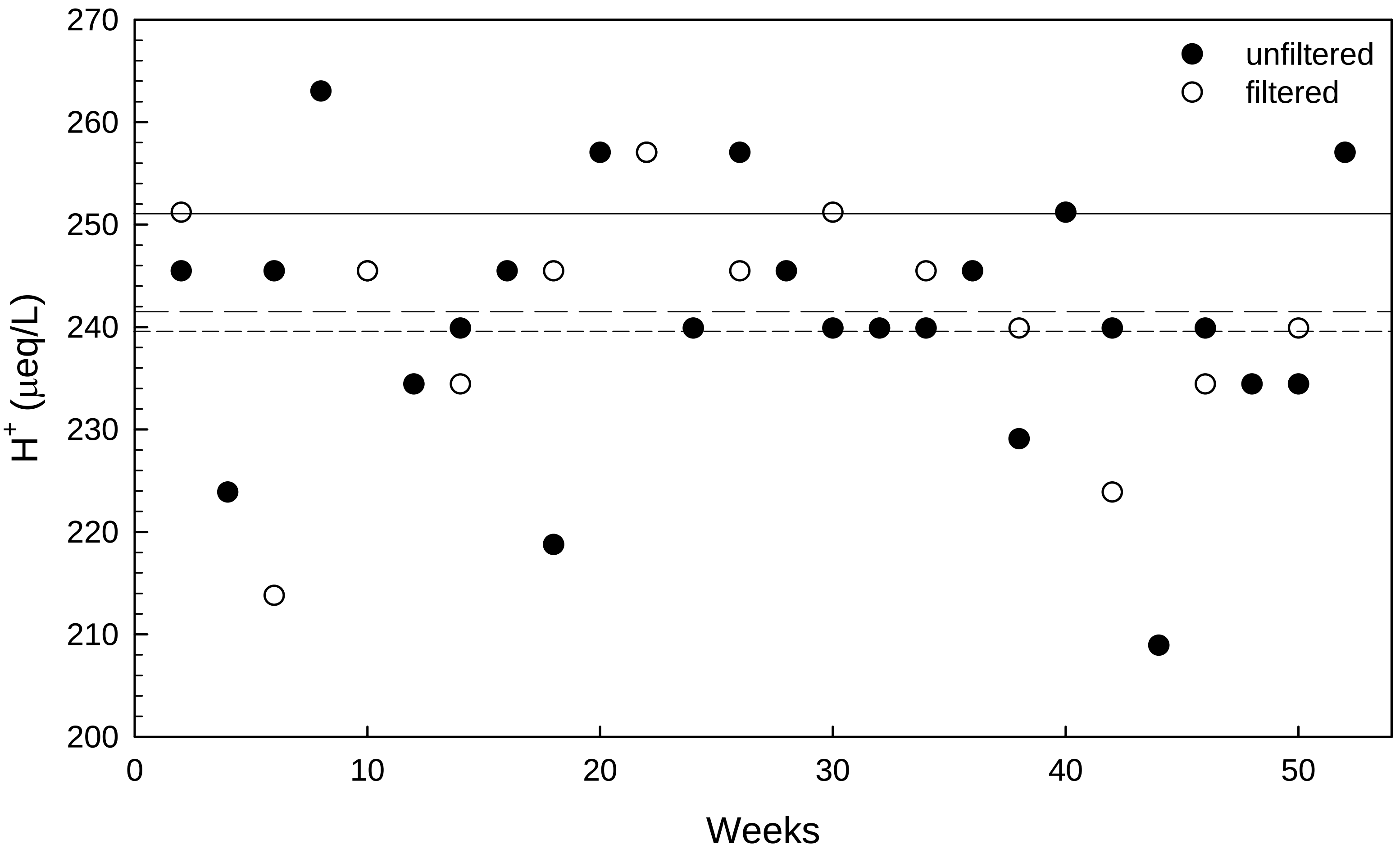
Note:
Solid line denotes target NO_3^- concentration: 7.0 mg/L; long dashed line denotes mean unfiltered NO_3^- concentration: 7.176 mg/L; and short dashed line denotes mean filtered NO_3^- concentration: 6.908 mg/L.

Figure B-18. Comparison of NTN filtered and unfiltered internal blind samples, (nitrate), High-Purity Standards, SR2, 2002.



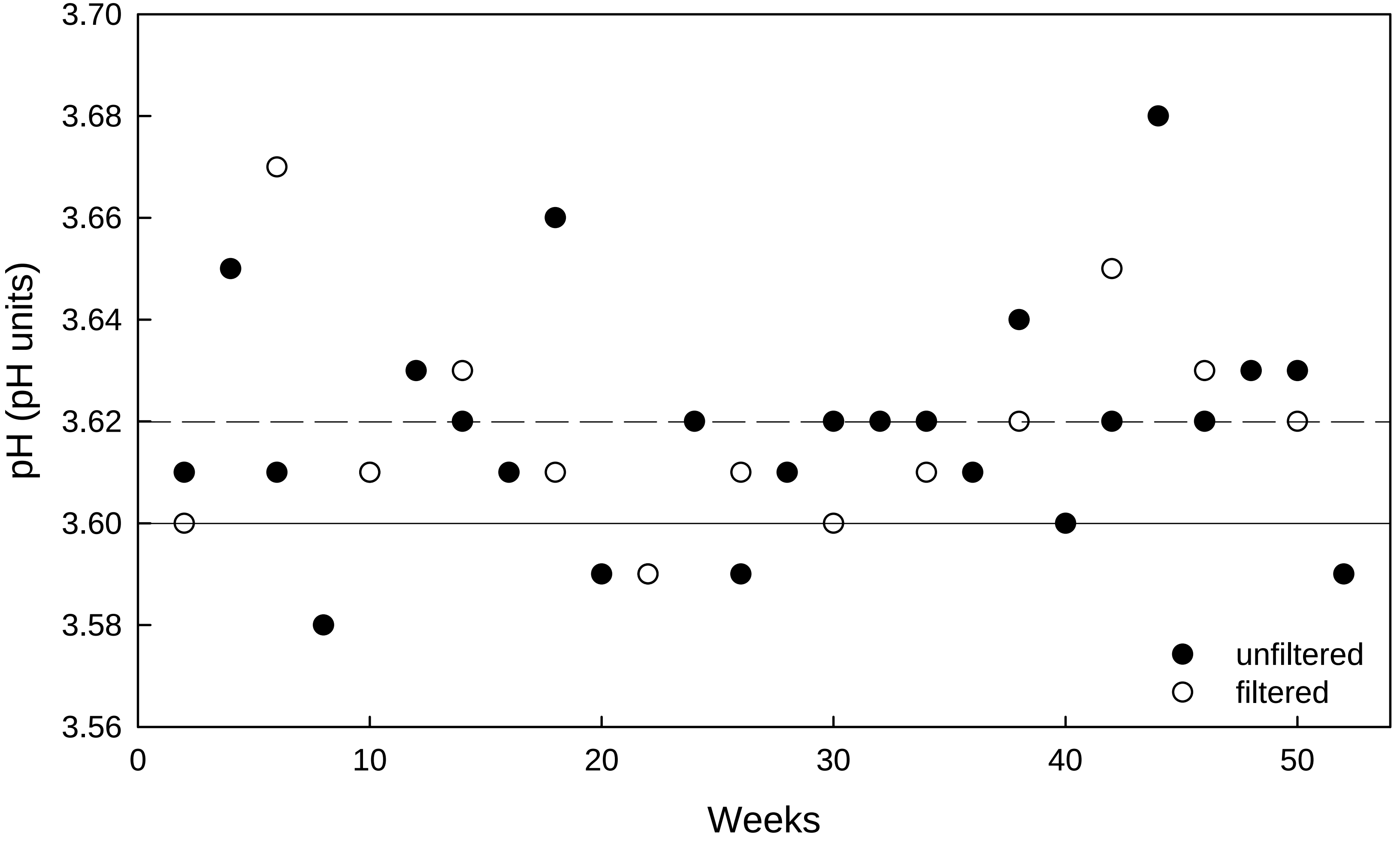
Note:
Solid line denotes target Cl^- concentration: 0.98 mg/L; long dashed line denotes mean unfiltered Cl^- concentration: 1.005 mg/L; and short dashed line denotes mean filtered Cl^- concentration: 0.966 mg/L.

Figure B-19. Comparison of NTN filtered and unfiltered internal blind samples, (chloride), High-Purity Standards, SR2, 2002.



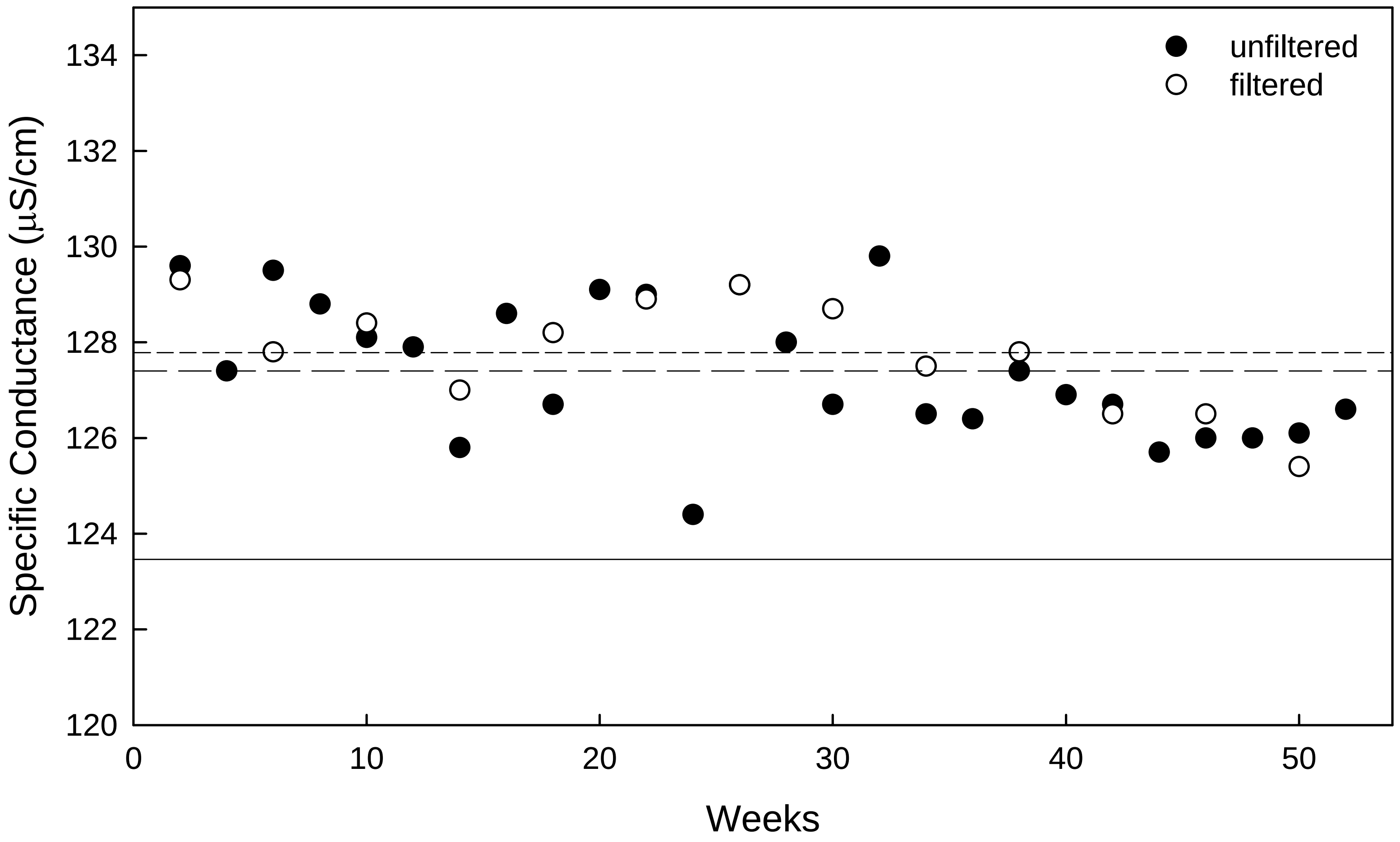
Note:
Solid line denotes target H^+ concentration: 251.2 µeq/L; long dashed line denotes mean unfiltered H^+ concentration: 241.5 µeq/L; and short dashed line denotes mean filtered H^+ concentration: 239.7 µeq/L.

Figure B-20. Comparison of NTN filtered and unfiltered internal blind samples, (hydrogen), High-Purity Standards, SR2, 2002.



Note:
Solid line denotes target pH: 3.60; and long dashed line denotes mean filtered and unfiltered pH: 3.62.

Figure B-21. Comparison of NTN filtered and unfiltered internal blind samples, (pH), High-Purity Standard, SR2, 2002.



Note:
Solid line denotes target specific conductance: 123.5 µS/cm; long dashed line denotes mean unfiltered specific conductance: 127.4 µS/cm; and short dashed line denotes mean filtered specific conductance; 127.8 µS/cm.

Figure B-22. Comparison of NTN filtered and unfiltered internal blind samples, (specific conductance), High-Purity Standards, SR2, 2002.

Table B-7. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, Internally Formulated Simulated Rainwater (02FR10), 2002

Parameter	*Target concentration[a] (mg/L)*	*Mean measured concentrations (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard deviation (mg/L)*	*RSD (%)*
Calcium	0.029	0.026[b]	-0.003	-11.9	0.005	20.4
		0.032[c]	0.003	9.0	0.004	13.2
Magnesium	0.006	0.007	0.001	9.6	0.001	11.3
		0.006	0.000	-3.8	0.003	51.8
Sodium	0.018	0.019	0.001	5.3	0.002	12.8
		0.018	0.000	-0.9	0.002	8.6
Potassium	0.004	0.004	0.000	1.0	0.002	41.5
		0.005	0.001	13.5	0.003	55.8
Ammonium	0.03	0.03	0.00	6.9	0.01	17.7
		0.03	0.005	18.3	0.00	14.2
Sulfate	0.256	0.257	0.001	0.4	0.005	2.0
		0.252	-0.004	-1.7	0.006	2.2
Nitrate	0.192	0.192	0.000	-0.2	0.004	2.1
		0.187	-0.005	-2.7	0.004	2.4
Chloride	0.053	0.051	-0.002	-3.7	0.004	6.9
		0.053	0.000	-0.6	0.004	7.9
pH[d] (pH units)	5.23	5.23	0.00	-0.1	0.03	0.6
		5.24	0.01	0.1	0.06	1.1
H (µeq/L)	5.9	6.0	0.1	1.3	0.5	7.8
		5.9	-0.03	-0.5	0.7	12.3
Specific conductance[d] (µS/cm)	3.4	3.7	0.3	10.0	0.5	13.6
		3.7	0.3	9.3	0.5	14.2

Notes:

There were 27 unfiltered and 14 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.

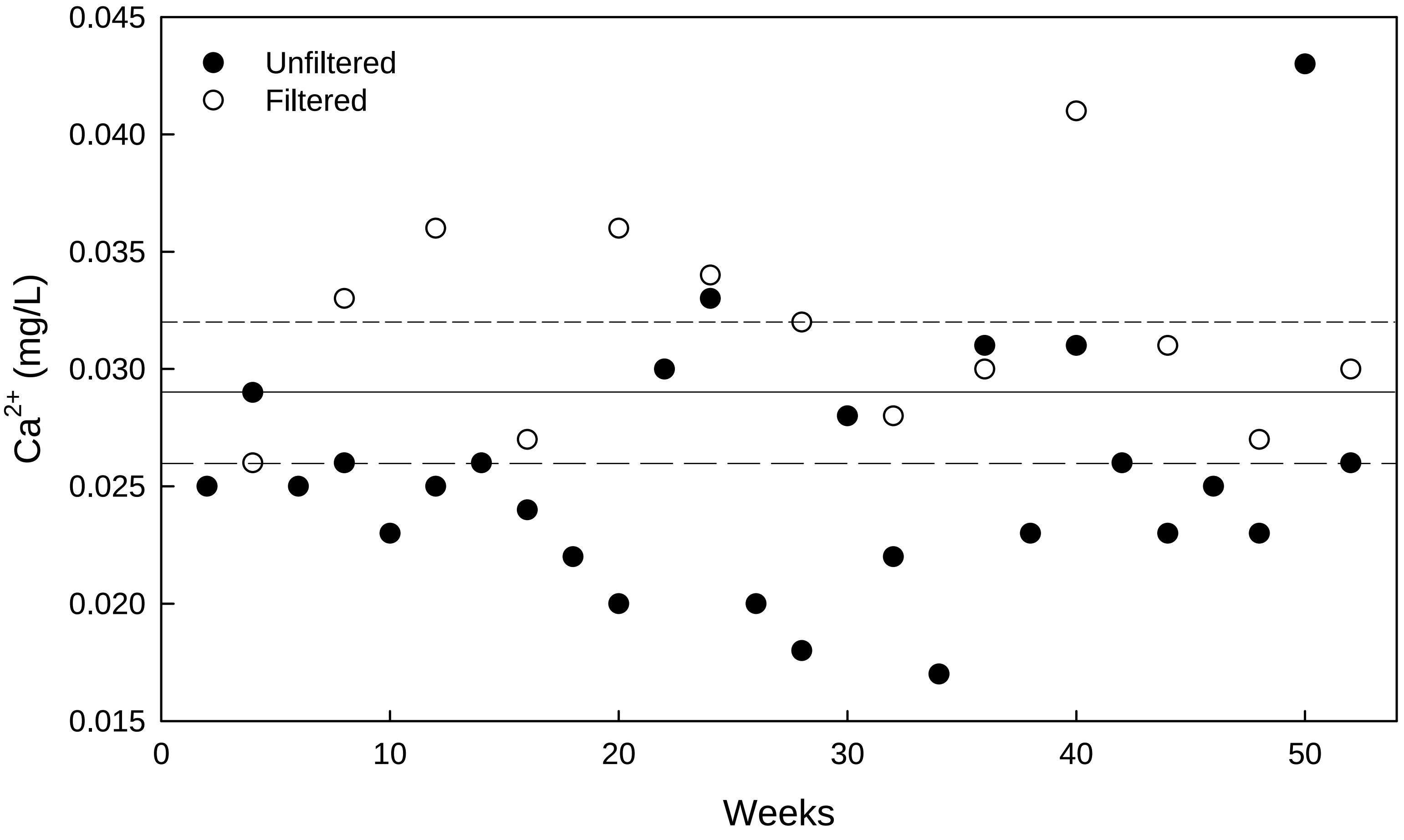
[d] Both pH and specific conductance are measured on unfiltered samples prior to filtering.

Table B-8. Unfiltered Blind Concentrations for Internally Formulated Simulated Rainwater (02FR10), 2002

Weeks	Ca^{2+} *(mg/L)*	Mg^{2+} *(mg/L)*	Na^{+} *(mg/L)*	K^{+} *(mg/L)*	NH_4^{+} *(mg/L)*	SO_4^{2-} *(mg/L)*	NO_3^{-} *(mg/L)*	Cl^{-} *(mg/L)*	*pH (pH units)*	H^{+} *(μeq/L)*	*Specific conductance (μS/cm)*
2	0.025	0.007	0.022	0.003	0.024	0.250	0.188	0.054	5.20	6.3	3.5
4	0.029	0.006	0.018	0.004	0.026	0.252	0.186	0.050	5.24	5.8	3.6
6	0.025	0.007	0.017	0.003	0.032	0.256	0.189	0.048	5.23	5.9	3.9
8	0.026	0.006	0.018	0.003	0.022	0.260	0.198	0.052	5.23	5.9	3.6
10	0.023	0.007	0.019	0.003	0.016	0.258	0.194	0.056	5.23	5.9	3.5
12	0.025	0.007	0.017	0.006	0.024	0.264	0.192	0.049	5.22	6.0	3.8
14	0.026	0.006	0.024	0.000	0.027	0.263	0.190	0.046	5.24	5.8	3.5
16	0.024	0.006	0.019	0.004	0.026	0.262	0.191	0.055	5.22	6.0	3.7
18	0.022	0.007	0.024	0.004	0.035	0.262	0.187	0.051	5.25	5.6	3.5
20	0.020	0.007	0.021	0.001	0.023	0.249	0.198	0.053	5.20	6.3	3.9
22	0.030	0.007	0.020	0.005	0.034	0.261	0.197	0.051	5.21	6.2	4.0
24	0.033	0.008	0.023	0.004	0.030	0.250	0.195	0.052	5.24	5.8	3.5
26	0.020	0.006	0.017	0.004	0.034	0.256	0.201	0.056	5.13	7.4	6.0
28	0.018	0.006	0.017	0.005	0.035	0.265	0.191	0.054	5.26	5.5	3.3
30	0.028	0.007	0.017	0.003	0.033	0.263	0.191	0.045	5.23	5.9	3.5
32	0.022	0.006	0.017	0.001	0.034	0.251	0.185	0.046	5.24	5.8	3.7
34	0.017	0.006	0.017	0.003	0.034	0.256	0.192	0.052	5.19	6.5	3.6
36	0.031	0.007	0.018	0.005	0.035	0.254	0.192	0.051	5.23	5.9	3.7
38	0.023	0.005	0.018	0.006	0.035	0.250	0.191	0.046	5.23	5.9	3.5
40	0.031	0.007	0.017	0.006	0.036	0.258	0.187	0.046	5.22	6.0	3.7
42	0.026	0.007	0.017	0.006	0.034	0.250	0.192	0.049	5.20	6.3	4.0
44	0.023	0.008	0.016	0.006	0.036	0.254	0.190	0.054	5.22	6.0	3.7
46	0.025	0.005	0.019	0.003	0.034	0.252	0.185	0.047	5.23	5.9	3.7
48	0.023	0.007	0.021	0.006	0.037	0.264	0.192	0.052	5.31	4.9	3.2
50	0.043	0.006	0.017	0.006	0.037	0.258	0.196	0.055	5.18	6.6	4.3
52	0.026	0.007	0.023	0.005	0.033	0.262	0.192	0.057	5.29	5.1	3.3
Mean	0.026	0.007	0.019	0.004	0.031	0.257	0.192	0.051	5.23	6.0	3.7
Median	0.025	0.007	0.018	0.004	0.034	0.257	0.192	0.052	5.23	5.9	3.7
Target	0.029	0.006	0.018	0.004	0.029	0.256	0.192	0.053	5.23	5.9	3.4

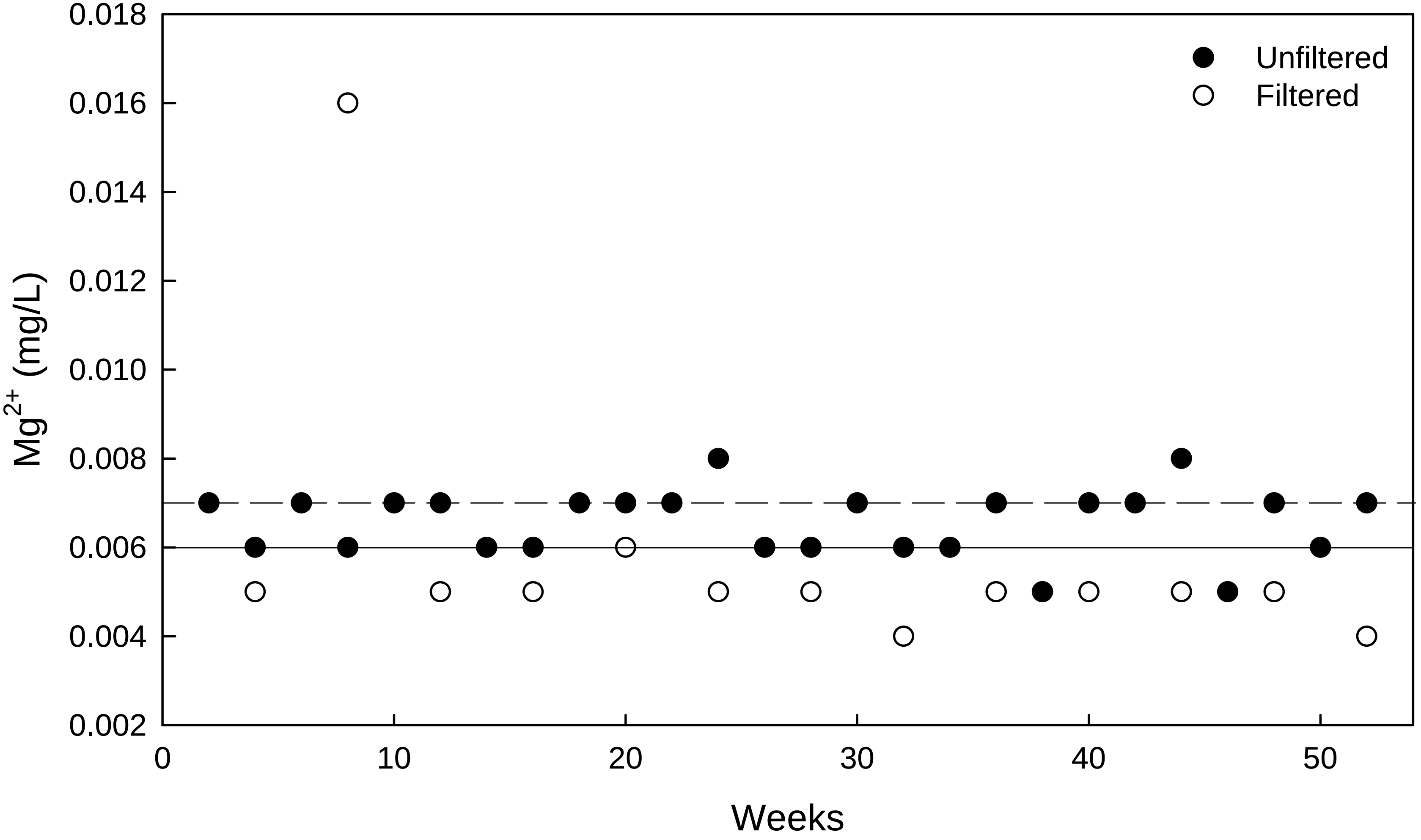
Table B-9. Filtered Blind Concentrations for Internally Formulated Simulated Rainwater (02FR10), 2002

Weeks	*Ca^{2+} (mg/L)*	*Mg^{2+} (mg/L)*	*Na^{+} (mg/L)*	*K^{+} (mg/L)*	*NH_4^{+} (mg/L)*	*SO_4^{2-} (mg/L)*	*NO_3^{-} (mg/L)*	*Cl^{-} (mg/L)*	*pH (pH units)*	*H^{+} (µeq/L)*	*Specific conductance (µS/cm)*
4	0.026	0.005	0.017	0.003	0.027	0.259	0.192	0.055	5.25	5.6	3.5
8	0.033	0.016	0.020	0.011	0.030	0.257	0.193	0.059	5.25	5.6	3.0
12	0.036	0.005	0.021	0.006	0.027	0.260	0.192	0.057	5.21	6.2	5.1
16	0.027	0.005	0.016	0.002	0.030	0.247	0.189	0.052	5.22	6.0	3.1
20	0.036	0.006	0.020	0.001	0.037	0.250	0.191	0.060	5.18	6.6	3.5
24	0.034	0.005	0.017	0.006	0.036	0.251	0.186	0.054	5.25	5.6	3.5
28	0.032	0.005	0.016	0.006	0.036	0.256	0.188	0.047	5.18	6.6	3.8
32	0.028	0.004	0.018	0.001	0.039	0.246	0.186	0.047	5.21	6.2	3.7
36	0.030	0.005	0.019	0.004	0.035	0.244	0.184	0.050	5.22	6.0	4.4
40	0.041	0.005	0.019	0.005	0.035	0.250	0.185	0.051	5.21	6.2	4.0
44	0.031	0.005	0.017	0.005	0.045	0.255	0.184	0.053	5.30	5.0	3.5
48	0.027	0.005	0.019	0.004	0.037	0.255	0.180	0.053	5.18	6.6	3.7
50	0.030	0.004	0.017	0.005	0.032	0.242	0.178	0.047	5.41	3.9	3.5
Mean	0.032	0.006	0.018	0.005	0.034	0.252	0.187	0.053	5.24	5.9	3.7
Median	0.031	0.005	0.018	0.005	0.035	0.251	0.186	0.053	5.22	6.0	3.5
Target	0.029	0.006	0.018	0.004	0.029	0.256	0.192	0.053	5.23	5.9	3.4



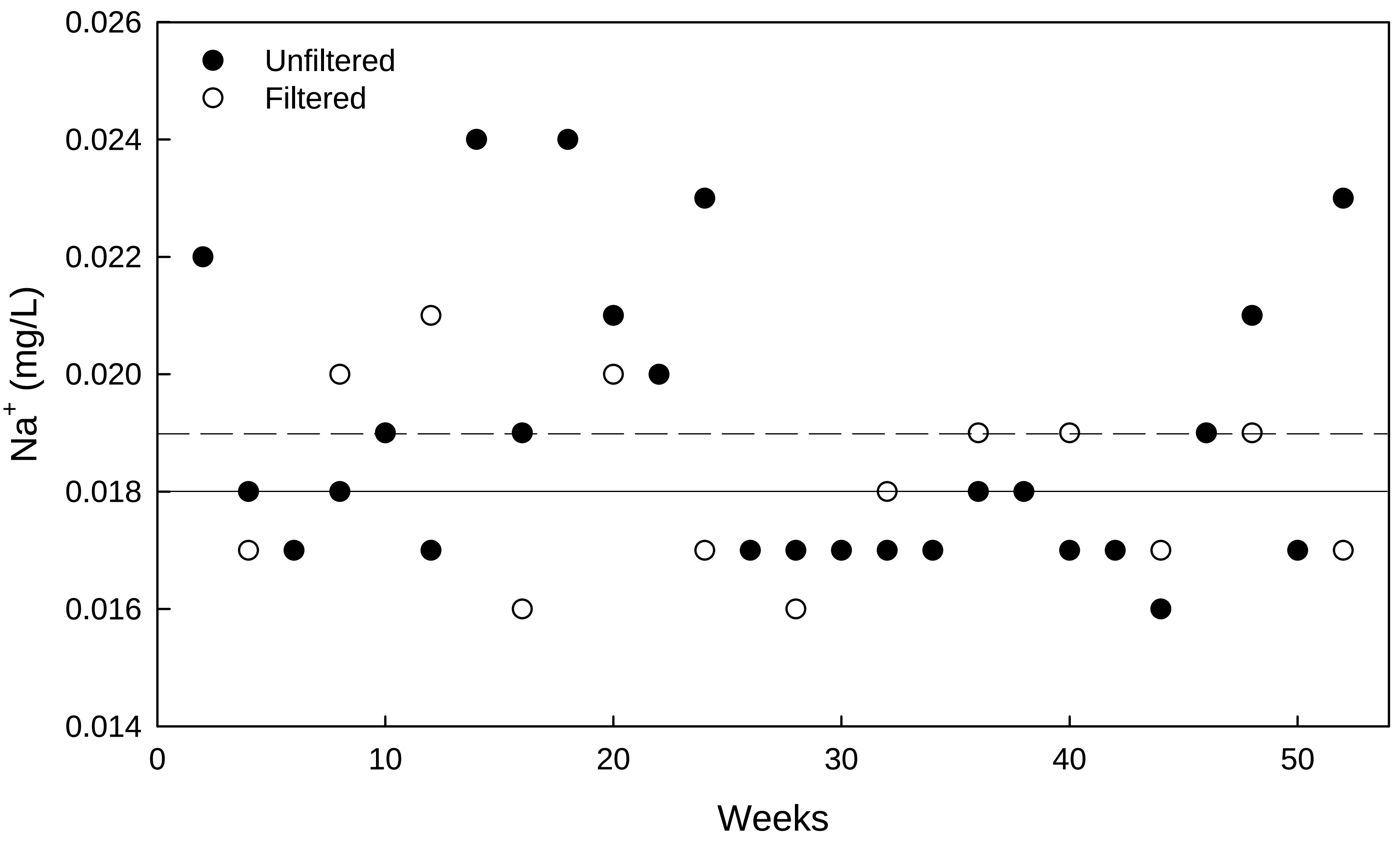
Note:
Solid line denotes target Ca^{2+} concentration: 0.029 mg/L; long dashed line denotes mean unfiltered Ca^{2+} concentration: 0.026 mg/L; and short dashed line denotes mean filtered Ca^{2+} concentration: 0.032 mg/L.

Figure B-23. Comparison of NTN filtered and unfiltered internal blind samples, (calcium), internally formulated simulated rain (02FR10), 2002.



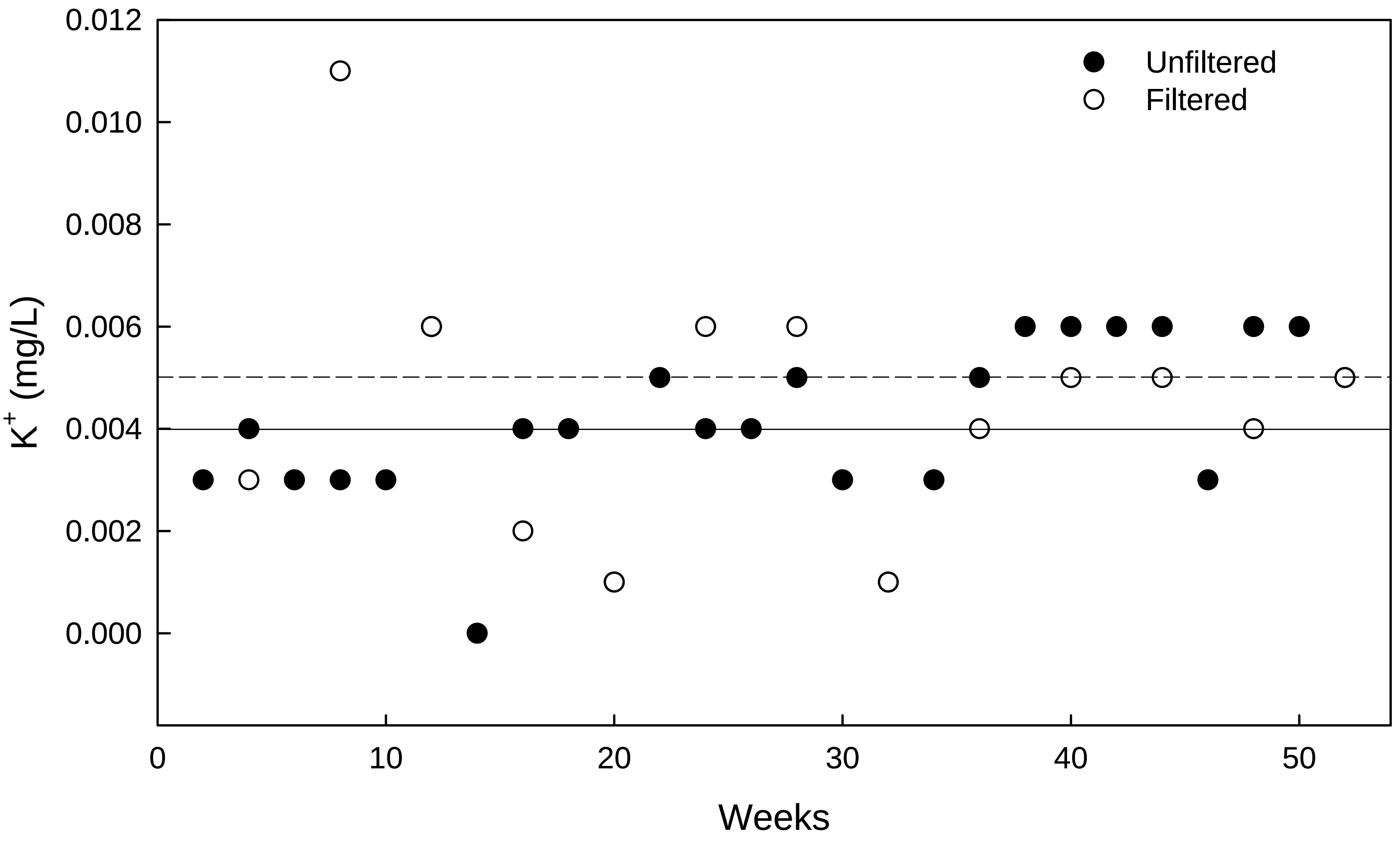
Note:
Solid line denotes target and mean filtered Mg^{2+} concentrations: 0.006 mg/L;
and short dashed line denotes mean unfiltered Mg^{2+} concentration: 0.007 mg/L.

Figure B-24. Comparison of NTN filtered and unfiltered internal blind samples, (magnesium), internally formulated simulated rain (02FR10), 2002.



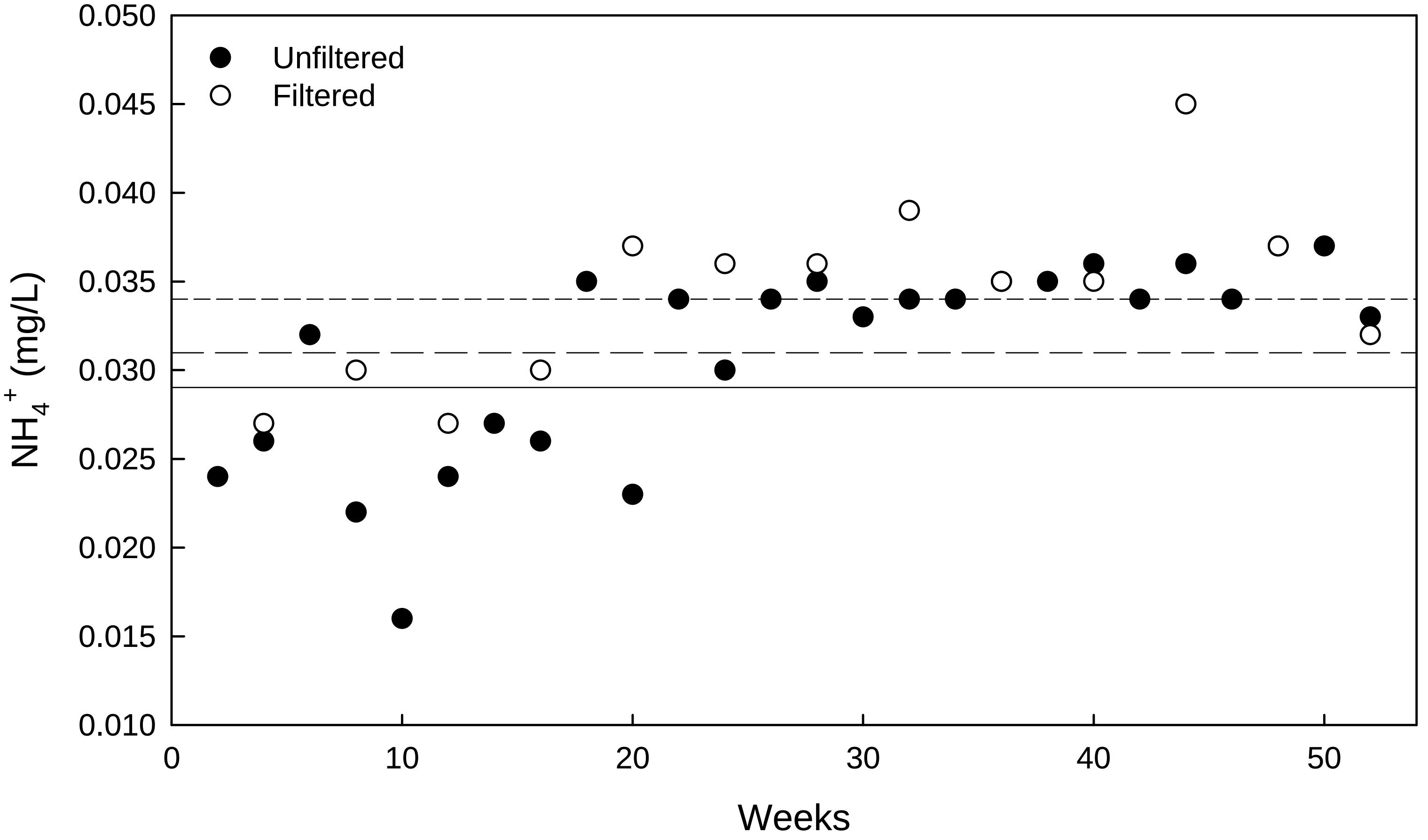
Note:
Solid line denotes target and filtered Na^+ concentrations: 0.018 mg/L;
and long dashed line denotes unfiltered Na^+ concentration: 0.019 mg/L.

Figure B-25. Comparison of NTN filtered and unfiltered internal blind samples, (sodium), internally formulated simulated rain (02FR10), 2002.



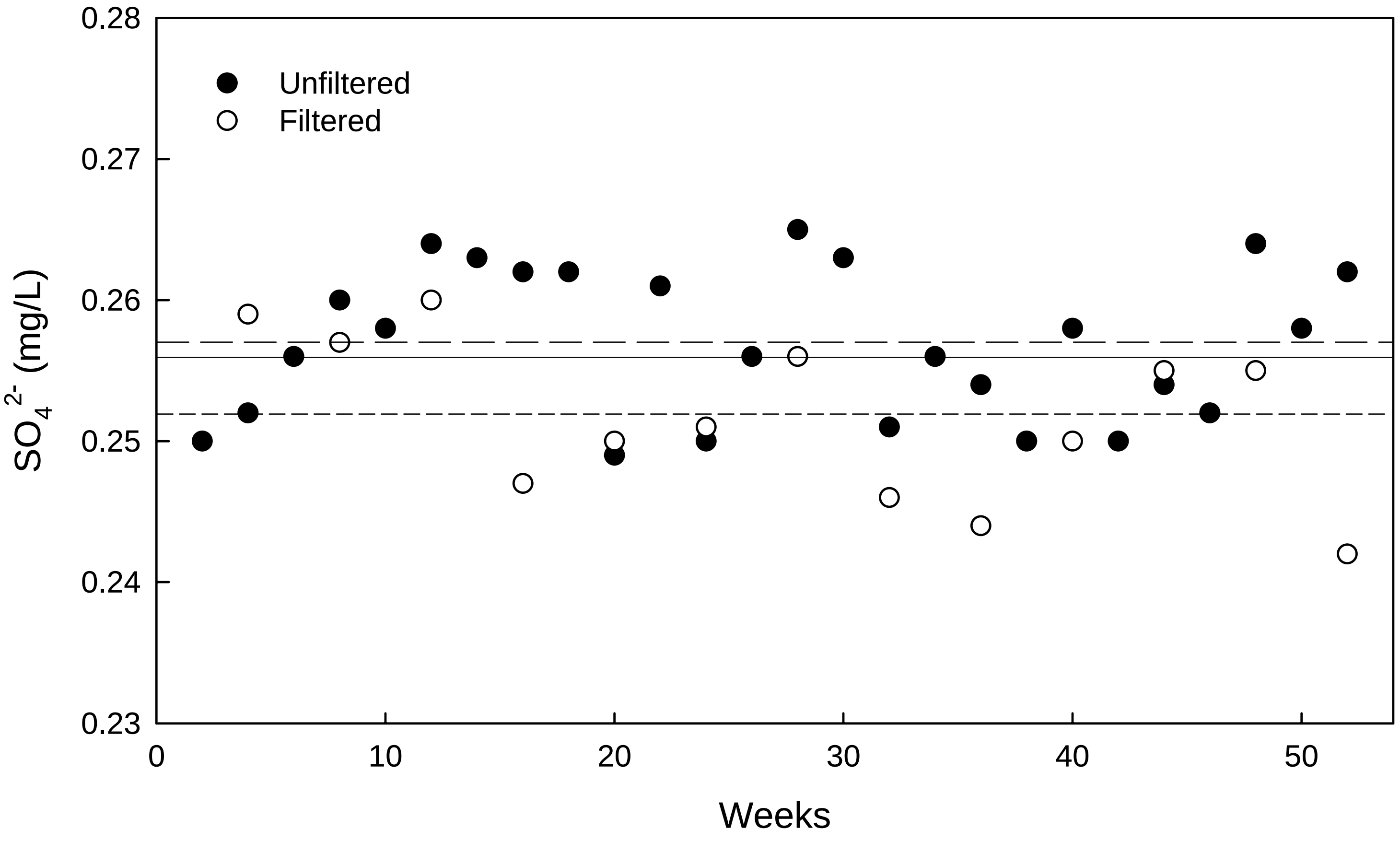
Note:
Solid line denotes target and mean unfiltered K$^+$ concentrations: 0.004 mg/L;
and short dashed line denotes mean filtered K$^+$ concentration: 0.005 mg/L.

Figure B-26. Comparison of NTN filtered and unfiltered internal blind samples, (potassium), internally formulated simulated rain (02FR10), 2002.



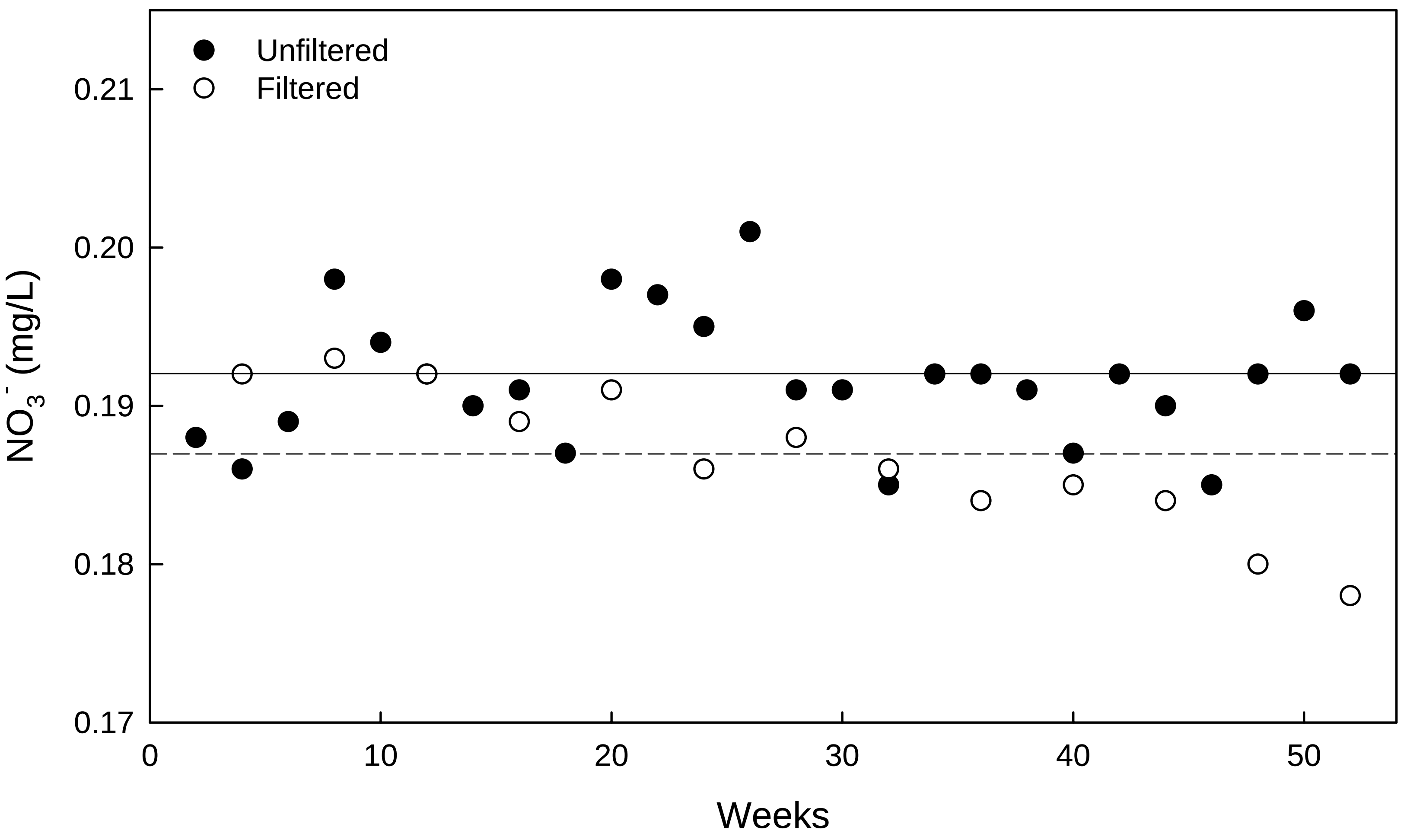
Note:
Solid line denotes target NH_4^+ concentration: 0.029 mg/L; long dashed line denotes mean unfiltered NH_4^+ concentration: 0.031 mg/L; and short dashed line denotes mean filtered NH_4^+ concentration: 0.034 mg/L.

Figure B-27. Comparison of NTN filtered and unfiltered internal blind samples, (ammonium), internally formulated simulated rain (02FR10), 2002.



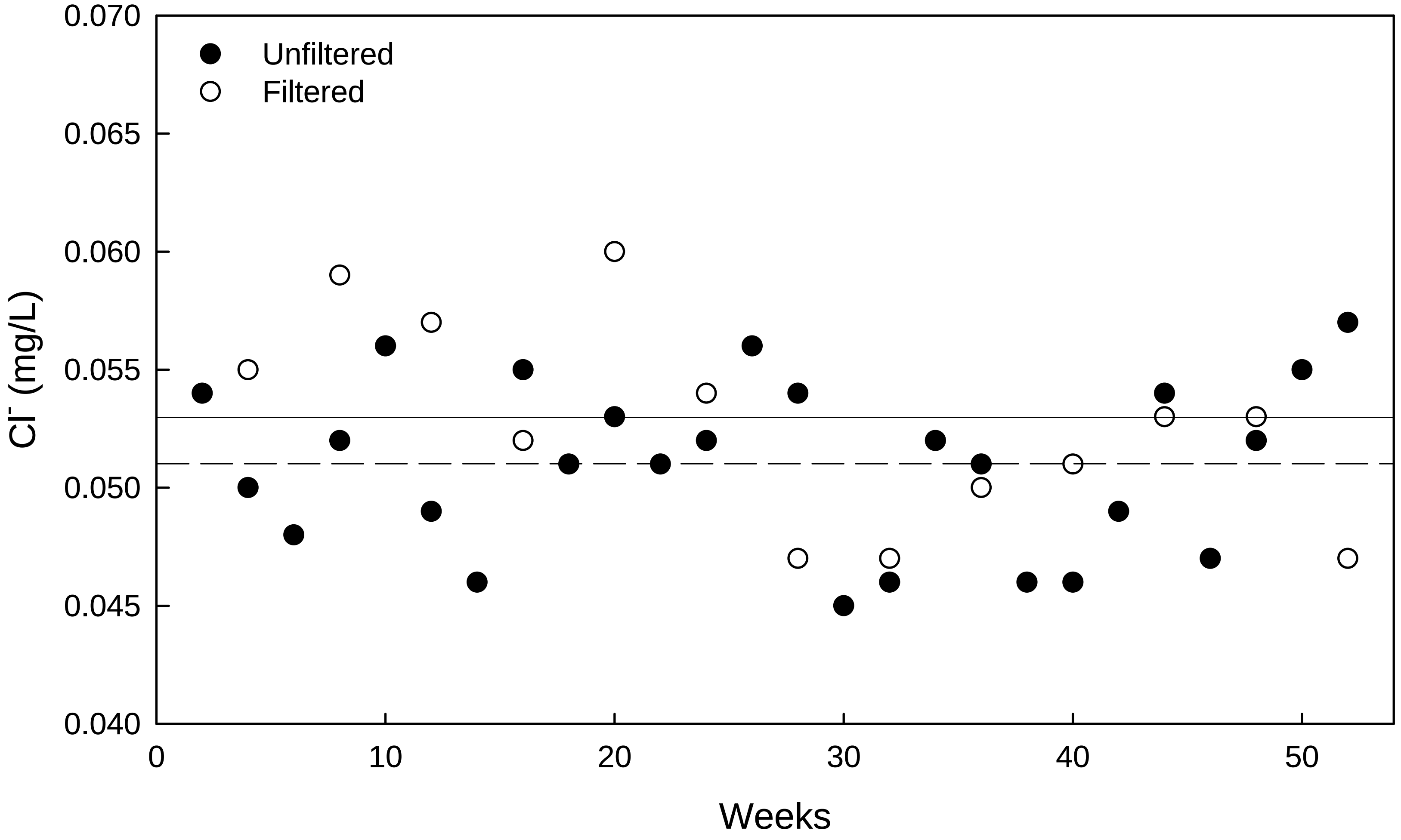
Note:
Solid line denotes target SO_4^{2-} concentration: 0.256 mg/L; long dashed line denotes mean unfiltered SO_4^{2-} concentration: 0.257 mg/L; and short dashed line denotes mean filtered SO_4^{2-} concentration: 0.252 mg/L.

Figure B-28. Comparison of NTN filtered and unfiltered internal blind samples, (sulfate), internally formulated simulated rain (02FR10), 2002.



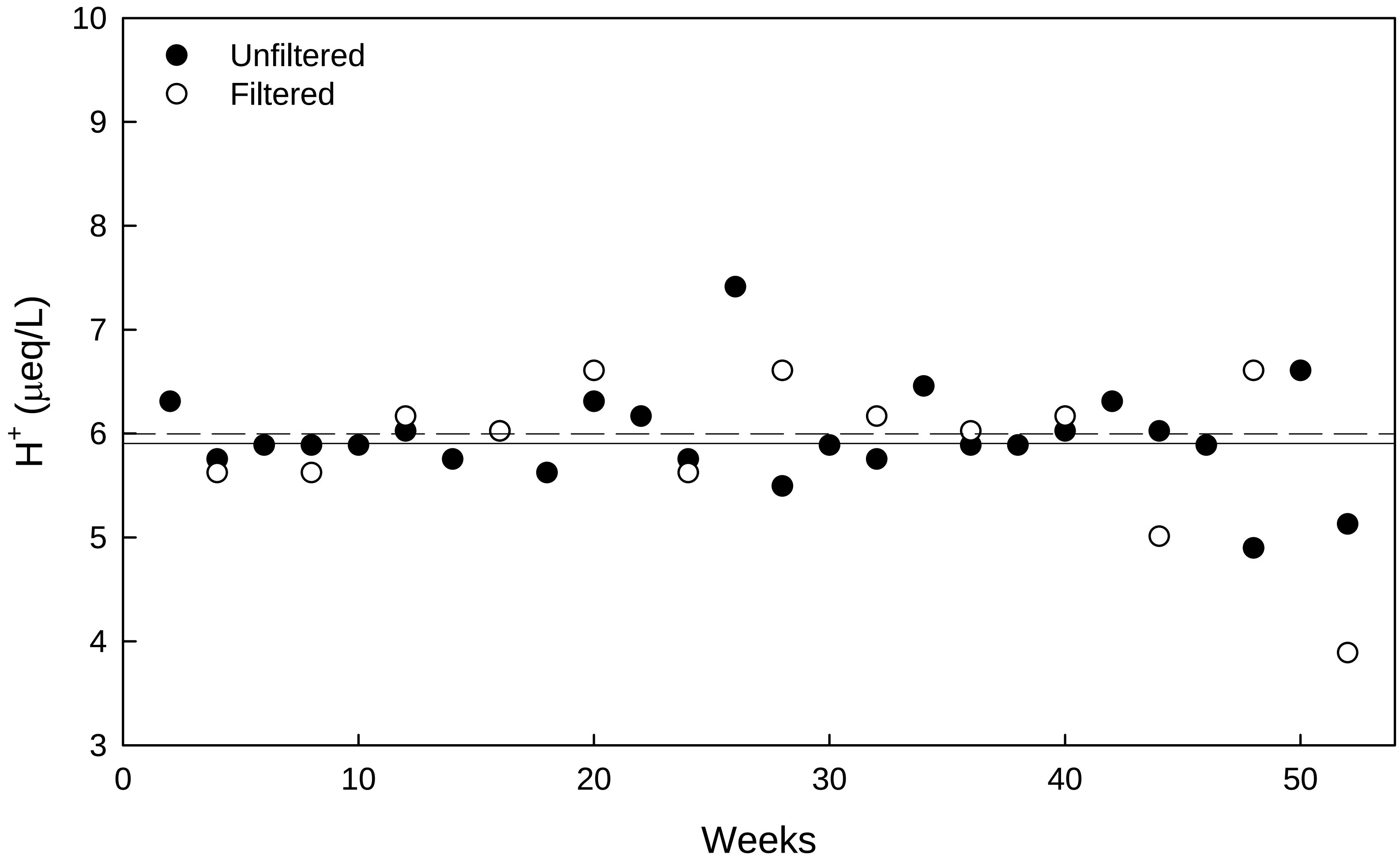
Note:
Solid line denotes target and mean unfiltered NO_3^- concentration: 0.192 mg/L;
and short dashed line denotes mean filtered NO_3^- concentration: 0.187 mg/L.

Figure B-29. Comparison of NTN filtered and unfiltered internal blind samples, (nitrate), internally formulated simulated rain, (02FR10), 2002.



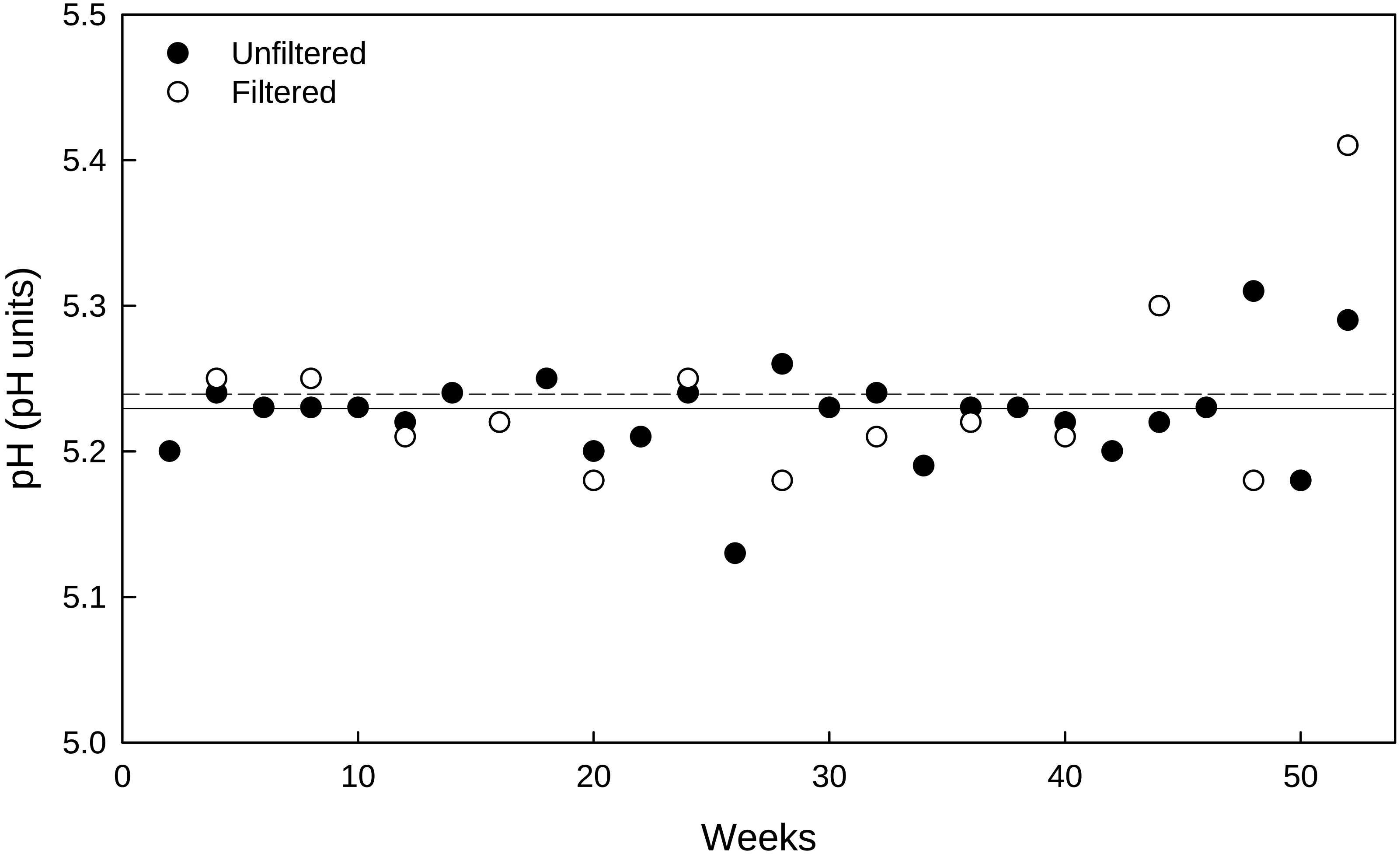
Note:
Solid line denotes target and mean filtered Cl$^-$ concentrations: 0.053 mg/L;
and long dashed line denotes mean unfiltered Cl$^-$ concentration: 0.051 mg/L.

Figure B-30. Comparison of NTN filtered and unfiltered blind samples, (chloride), internally formulated simulated rain (02FR10), 2002.



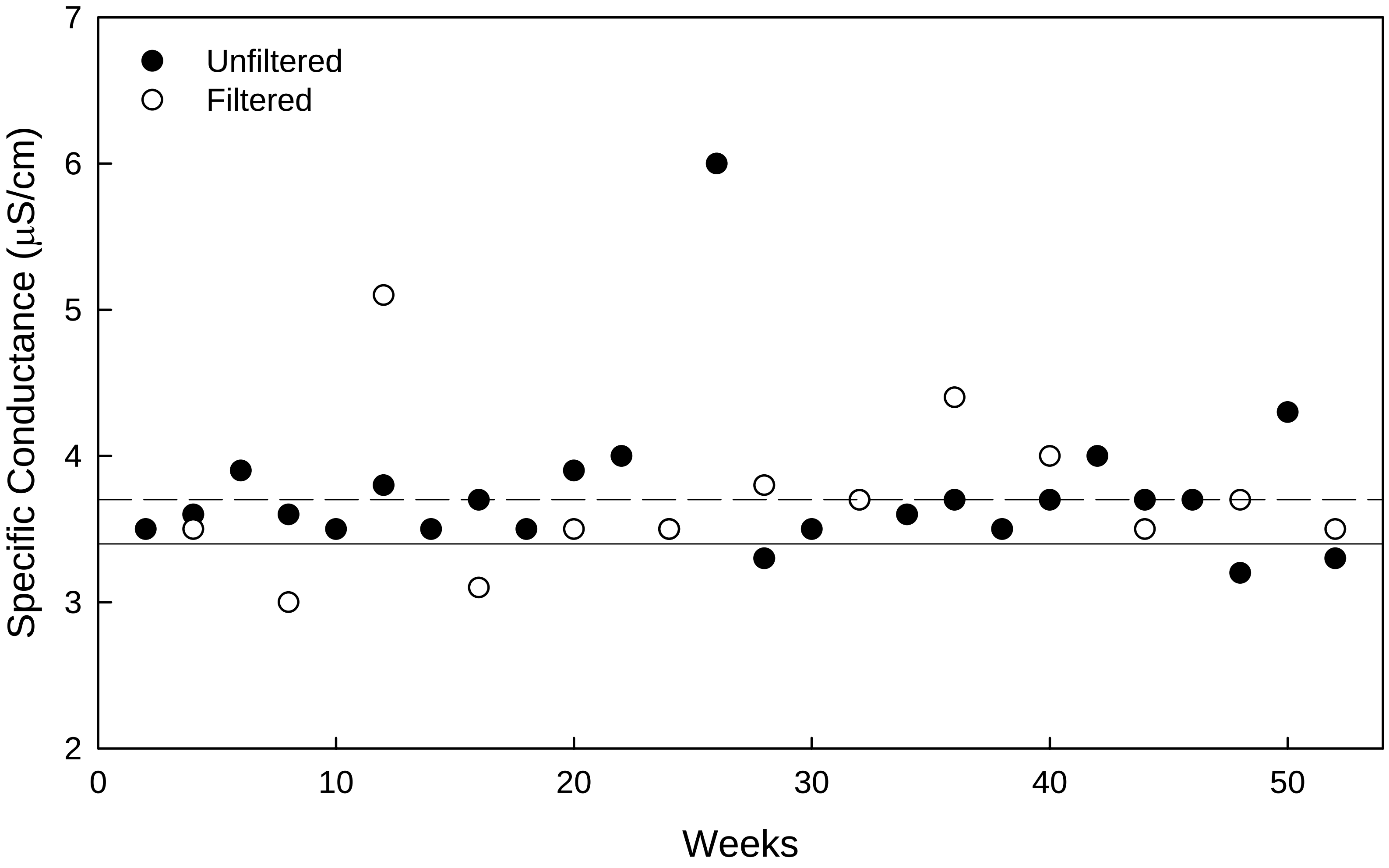
Note:
Solid line denotes target and mean filtered H^+ concentration: 5.9 µeq/L;
and long dashed line denotes mean unfiltered H^+ concentration: 6.0 µeq/L.

Figure B-31. Comparison of NTN filtered and unfiltered internal blind samples, (hydrogen), internally formulated simulated rain (02FR10), 2002.



Note:
Solid line denotes target and mean unfiltered pH: 5.23;
and short dashed line denotes mean filtered pH: 5.24.

Figure B-32. Comparison of NTN filtered and unfiltered internal blind samples, (pH), internally formulated simulated rain (02FR10), 2002.



Note:
Solid line denotes target specific conductance: 3.4 µS/cm; and long dashed line denotes mean filtered and unfiltered conductance: 3.7 µS/cm.

Figure B-33. Comparison of NTN filtered and unfiltered internal blind samples, (specific conductance), internally formulated simulated rain (02FR10), 2002.

Table B-10. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, Deionized (DI) Water, 2002

Parameter	*Target concentration*[a] *(mg/L)*	*Mean measured concentrations (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard deviation (mg/L)*	*RSD (%)*
Calcium	<0.009	<0.009[b] <0.009[c]			0.013 0.004	
Magnesium	<0.003	<0.003 <0.003			0.001 0.001	
Sodium	<0.003	<0.003 <0.003			0.002 0.002	
Potassium	<0.003	<0.003 <0.003			0.002 0.003	
Ammonium	<0.02	<0.02 <0.02			0.00 0.01	
Sulfate	<0.010	<0.010 <0.010			0.003 0.005	
Nitrate	<0.010	<0.010 <0.010			0.000 0.004	
Chloride	<0.006	<0.006 <0.006			0.003 0.004	
pH[d] (pH units)	5.65	5.66 5.62	0.01 -0.03	1.1 -1.7	0.11 0.05	1.6 0.6
H (µeq/L)	2.2	2.3 2.5	0.1 0.3	4.5 13.6	0.5 0.3	19.9 10.8
Specific conductance[d] (µS/cm)	0.9	1.3 1.3	0.4 0.4	43.2 47.0	0.2 0.5	10.2 42.7

Notes:
There were 27 unfiltered and 14 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.

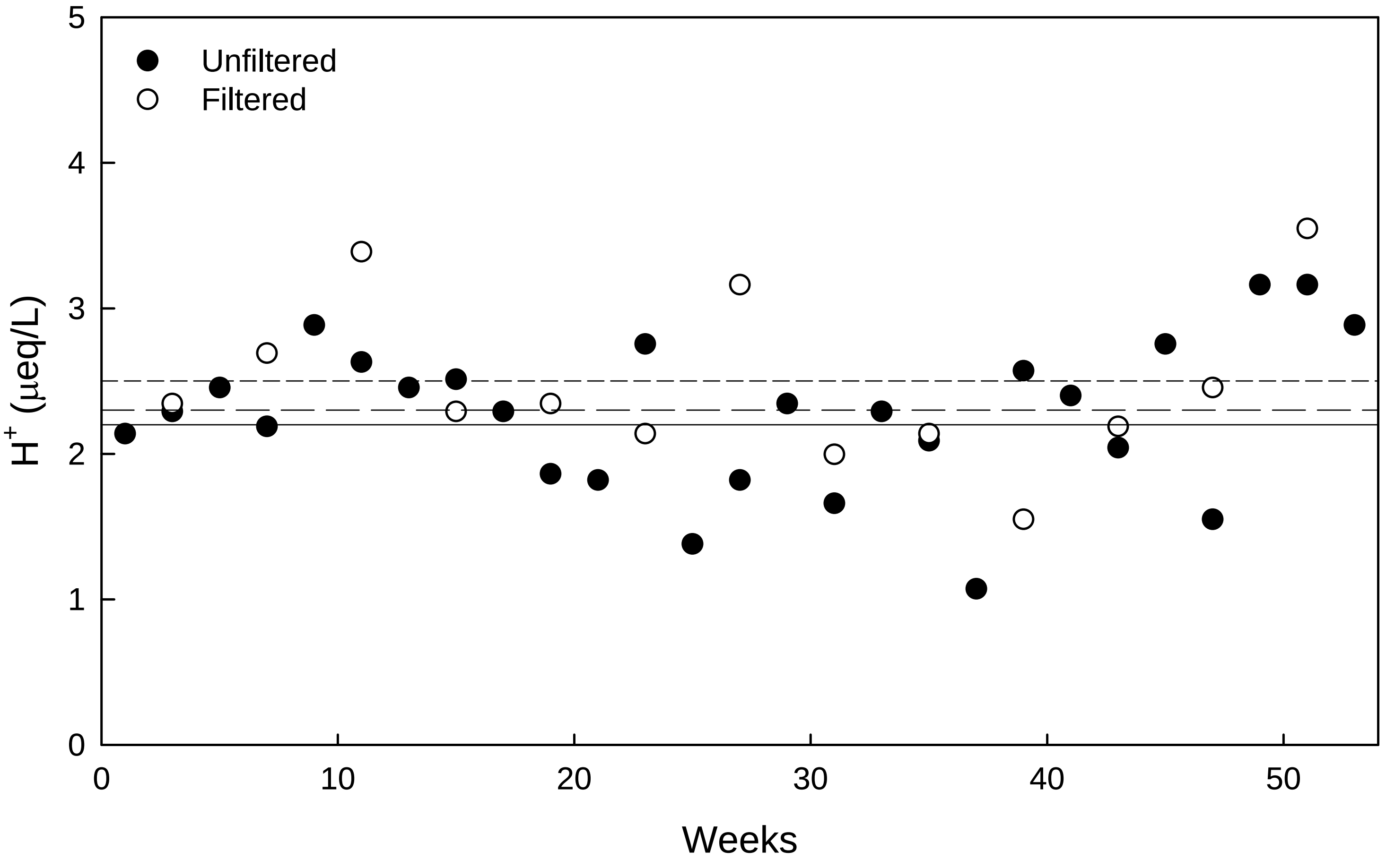
[d] Both pH and specific conductance are measured on unfiltered samples prior to filtering.

Table B-11. Unfiltered Blind Concentrations for Deionized (DI) Water, 2002

Weeks	Ca^{2+} *(mg/L)*	Mg^{2+} *(mg/L)*	Na^{+} *(mg/L)*	K^{+} *(mg/L)*	NH_4^{+} *(mg/L)*	SO_4^{2-} *(mg/L)*	NO_3^{-} *(mg/L)*	Cl^{-} *(mg/L)*	*pH (pH units)*	H^{+} *(µeq/L)*	*Specific conductance (µS/cm)*
1	-0.001	0.00	-0.005	-0.005	-0.006	0.000	0.000	0.000	5.67	2.1	1.2
3	0.000	0.000	-0.003	-0.002	-0.012	0.000	0.000	0.000	5.64	2.3	1.3
5	-0.003	0.000	-0.002	-0.006	-0.006	0.000	0.000	0.000	5.61	2.5	1.1
7	0.004	0.000	-0.002	-0.003	-0.001	0.000	0.000	0.000	5.66	2.2	1.3
9	-0.005	-0.001	0.001	-0.001	-0.001	0.011	0.000	0.000	5.54	2.9	1.2
11	-0.005	-0.002	0.001	-0.002	-0.003	0.014	0.000	0.000	5.58	2.6	1.3
13	-0.005	0.000	0.000	-0.001	-0.005	0.000	0.000	0.000	5.61	2.5	1.3
15	-0.001	0.000	0.002	-0.001	-0.002	0.000	0.000	0.000	5.60	2.5	2.0
17	0.002	0.000	0.001	-0.001	0.000	0.000	0.000	0.000	5.64	2.3	1.1
19	-0.006	-0.001	0.000	0.002	0.000	0.000	0.000	0.000	5.73	1.9	1.2
21	-0.002	0.000	-0.003	-0.001	0.000	0.000	0.000	0.000	5.74	1.8	1.5
23	-0.005	0.000	-0.001	-0.001	0.000	0.000	0.000	0.000	5.56	2.8	1.3
25	-0.003	-0.002	-0.001	-0.001	0.000	0.000	0.000	0.000	5.86	1.4	1.1
27	-0.003	0.000	-0.001	-0.001	0.000	0.000	0.000	0.015	5.74	1.8	1.2
29	-0.007	0.000	-0.005	-0.006	0.000	0.000	0.000	0.000	5.63	2.3	1.3
31	-0.001	0.000	-0.002	-0.001	0.000	0.000	0.000	0.000	5.78	1.7	0.9
33	-0.008	0.000	-0.001	-0.002	0.000	0.000	0.000	0.000	5.64	2.3	1.8
35	-0.002	-0.001	-0.001	0.000	0.000	0.000	0.000	0.000	5.68	2.1	1.3
37	-0.006	0.000	-0.001	-0.003	0.000	0.000	0.000	0.000	5.97	1.1	1.1
39	0.000	-0.001	-0.001	-0.001	0.000	0.000	0.000	0.000	5.59	2.6	1.6
41	0.003	0.000	-0.001	-0.002	0.000	0.000	0.000	0.000	5.62	2.4	1.5
43	-0.007	0.001	0.009	0.000	0.000	0.000	0.000	0.000	5.69	2.0	1.1
45	-0.007	-0.001	-0.001	0.001	0.000	0.000	0.000	0.000	5.56	2.8	1.1
47	-0.014	-0.001	-0.001	-0.001	0.000	0.000	0.000	0.000	5.81	1.5	1.1
49	0.000	0.001	-0.002	-0.001	0.000	0.000	0.000	0.000	5.50	3.2	1.5
51	-0.013	0.000	-0.001	-0.002	0.000	0.000	0.000	0.000	5.50	3.2	1.3
53	-0.011	0.000	-0.002	0.000	0.000	0.000	0.000	0.000	5.54	2.9	1.1
Mean	<0.009	<0.003	<0.003	<0.003	<0.02	<0.010	<0.010	<0.006	5.66	2.3	1.3
Median	<0.009	<0.003	<0.003	<0.003	<0.02	<0.010	<0.010	<0.006	5.64	2.3	1.3
Target	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	5.65	2.2	0.9

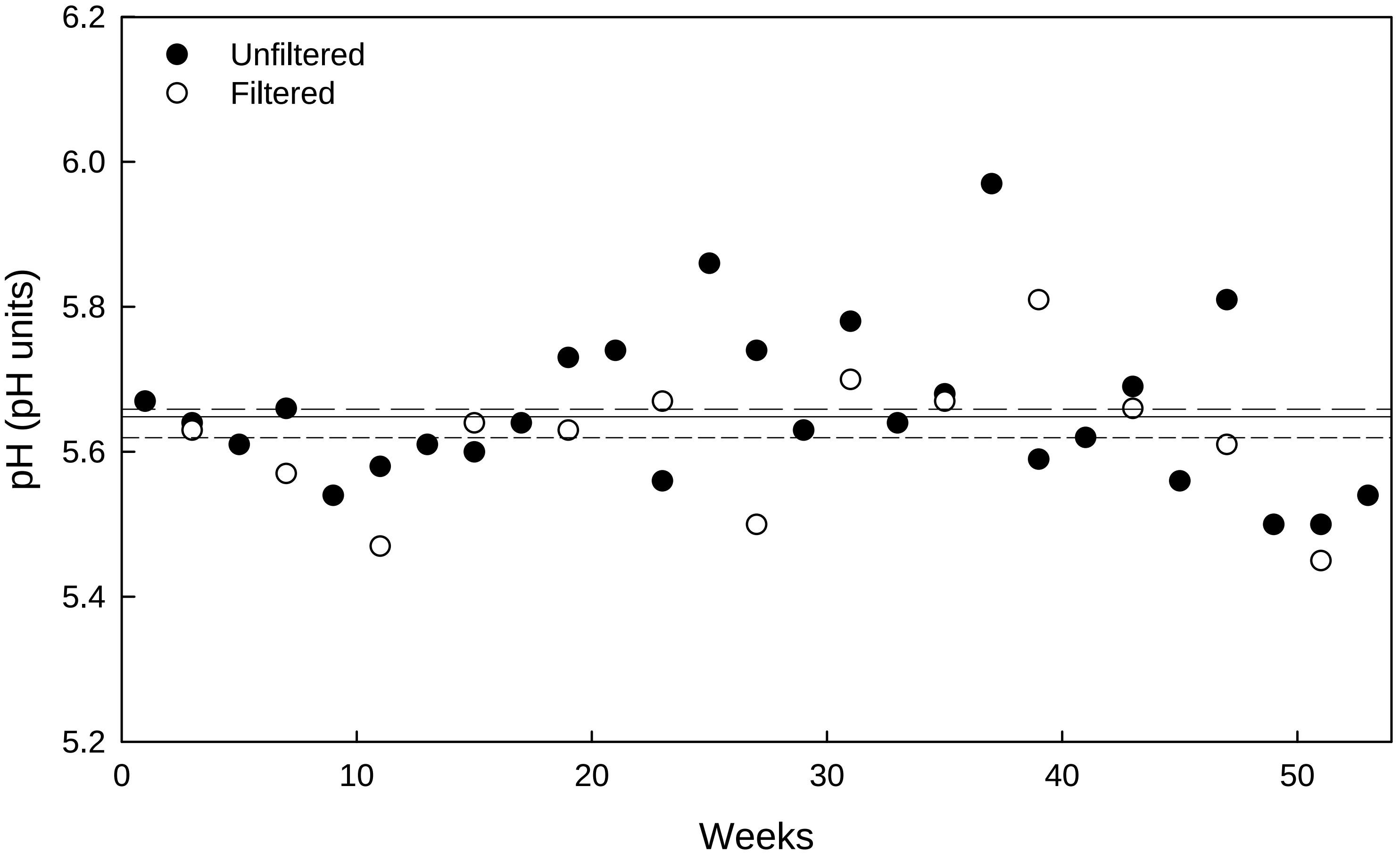
Table B-12. Filtered Blind Concentrations for Deionized (DI) Water, 2002

Weeks	Ca^{2+} *(mg/L)*	Mg^{2+} *(mg/L)*	Na^{+} *(mg/L)*	K^{+} *(mg/L)*	NH_4^{+} *(mg/L)*	SO_4^{2-} *(mg/L)*	NO_3^{-} *(mg/L)*	Cl^{-} *(mg/L)*	*pH (pH units)*	H^{+} *(µeq/L)*	*Specific conductance (µS/cm)*
3	0.000	0.001	-0.003	-0.002	-0.015	0.000	0.000	0.015	5.63	2.3	1.2
7	-0.005	0.000	-0.001	-0.003	-0.001	0.000	0.000	0.000	5.57	2.7	1.3
11	-0.001	0.000	0.006	-0.003	0.001	0.013	0.000	0.000	5.47	3.4	1.9
15	-0.003	0.000	0.001	0.003	0.004	0.011	0.000	0.000	5.64	2.3	1.3
19	0.000	0.000	0.000	-0.005	0.000	0.000	0.000	0.000	5.63	2.3	1.2
23	-0.011	0.001	0.001	-0.001	0.008	0.000	0.000	0.000	5.67	2.1	1.1
27	0.017	0.001	-0.001	-0.001	0.009	0.000	0.000	0.000	5.50	3.2	1.1
31	-0.005	0.000	-0.003	0.000	0.008	0.000	0.000	0.000	5.70	2.0	1.1
35	-0.007	0.000	0.000	0.002	0.005	0.000	0.000	0.000	5.67	2.1	1.1
39	0.008	0.000	0.000	0.001	0.000	0.000	0.000	0.000	5.81	1.5	1.1
43	-0.004	0.000	-0.002	-0.001	0.000	0.000	0.000	0.000	5.66	2.2	1.3
47	-0.003	-0.001	-0.003	-0.001	0.000	0.000	0.000	0.000	5.61	2.5	1.8
51	-0.011	0.000	-0.001	0.000	0.000	0.000	0.000	0.000	5.45	3.5	1.2
Mean	<0.009	<0.003	<0.003	<0.003	<0.02	<0.010	<0.010	<0.006	5.62	2.5	1.3
Median	<0.009	<0.003	<0.003	<0.003	<0.02	<0.010	<0.010	<0.006	5.63	2.3	1.2
Target	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	5.65	2.2	0.9



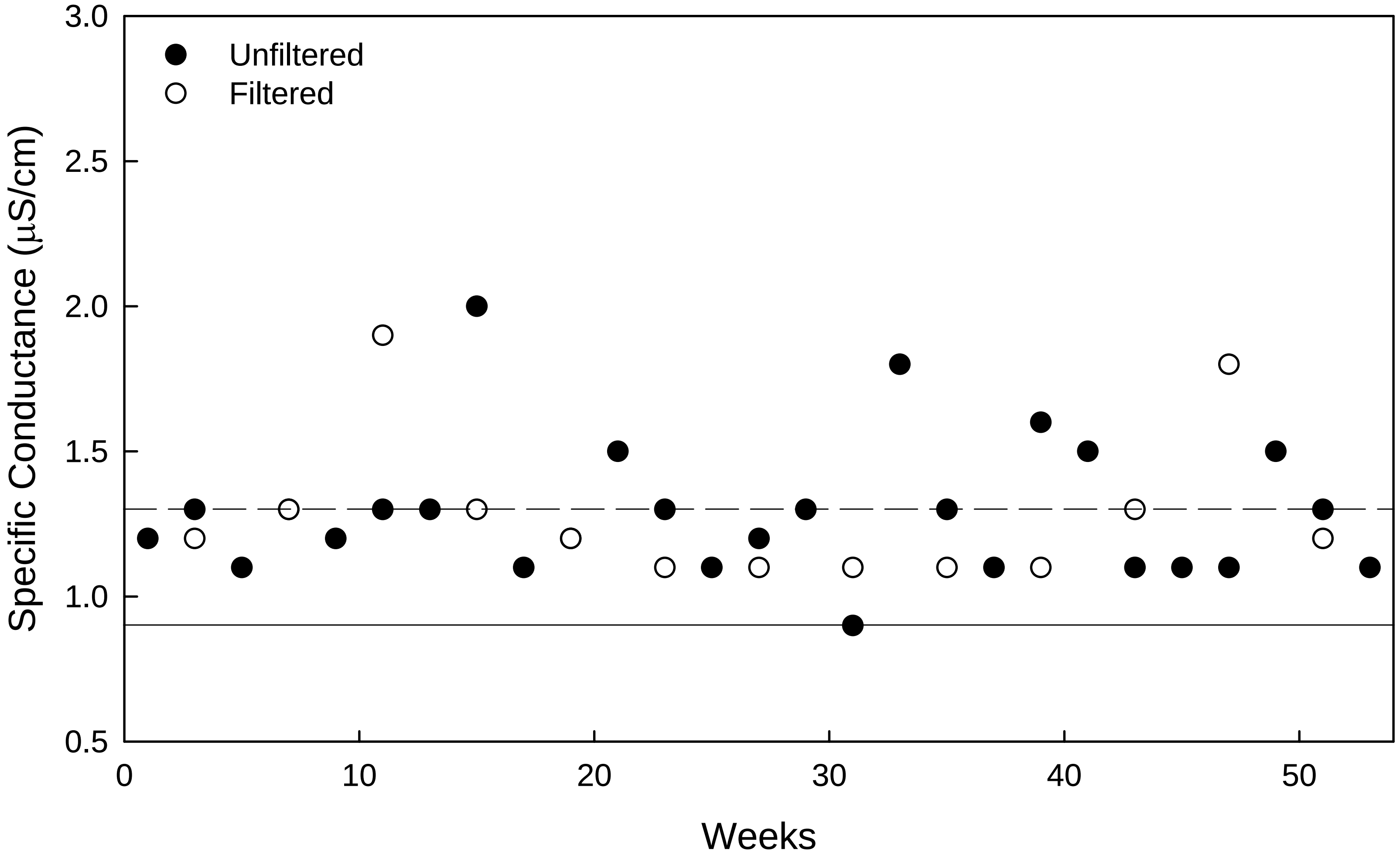
Note:
Solid line denotes target H^+ concentration: 2.2 μeq/L; long dashed line denotes mean unfiltered H^+ concentration: 2.3 μeq/L; and short dashed line denotes mean filtered H^+ concentration: 2.5 μeq/L.

Figure B-34. Comparison of NTN filtered and unfiltered internal blind samples, (hydrogen), deionized (DI) water, 2002.



Note:
Solid line denotes target pH: 5.65; long dashed line denotes mean unfiltered pH: 5.66; and short dashed line denotes mean filtered pH: 5.62.

Figure B-35. Comparison of NTN filtered and unfiltered internal blind samples, (pH), deionized (DI) water, 2002.



Note:
Solid line denotes target specific conductance: 0.9 µS/cm; and long dashed line denotes mean filtered and unfiltered specific conductance: 1.3 µS/cm.

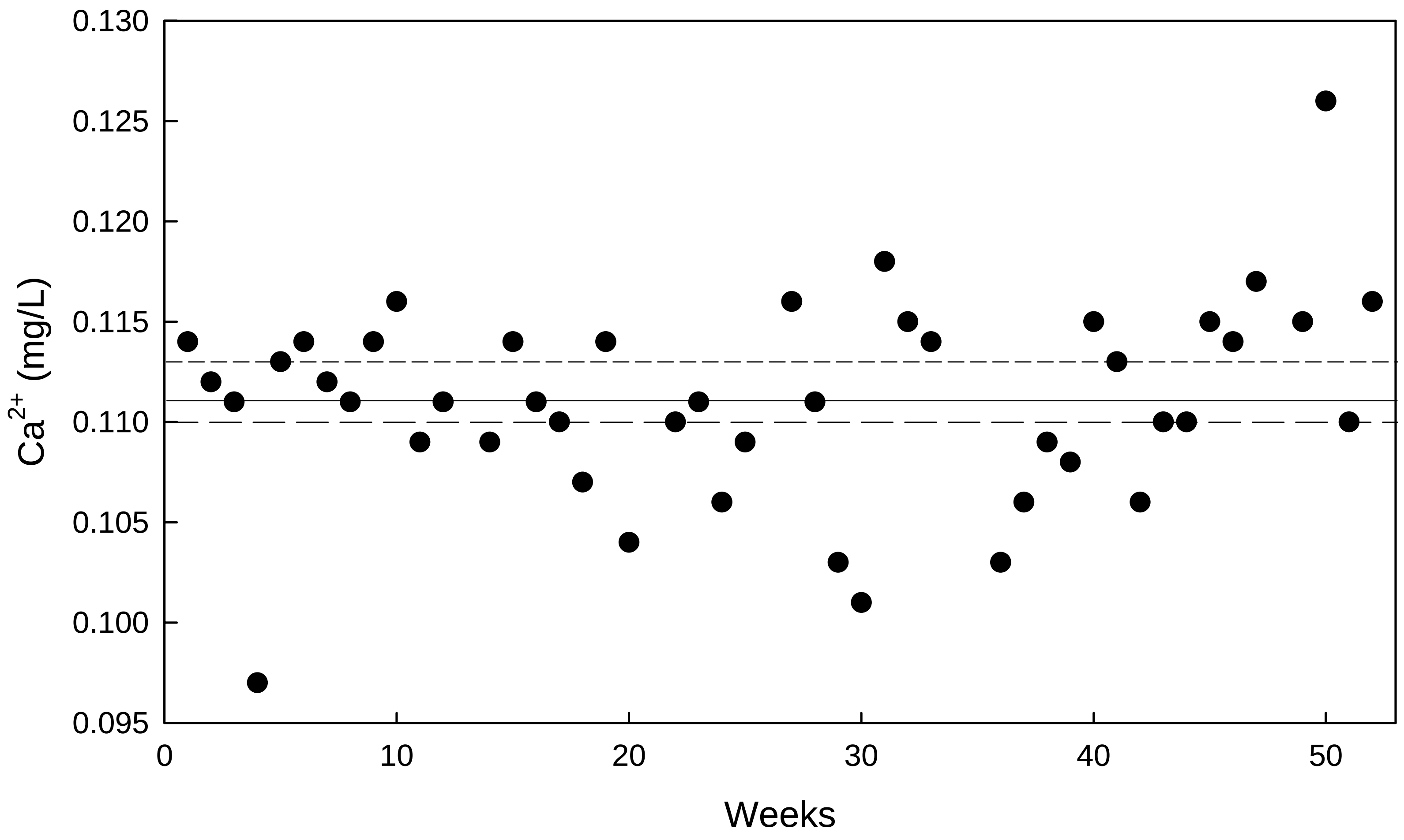
Figure B-36. Comparison of NTN filtered and unfiltered internal blind samples, (specific conductance), deionized (DI) water, 2002.

Table B-13. Internal Blind Sample Concentrations, AIRMoN, WMO/GAW Sample, 2002

Weeks	Ca^{2+} *(mg/L)*	Mg^{2+} *(mg/L)*	Na^{+} *(mg/L)*	K^{+} *(mg/L)*	NH_4^{+} *(mg/L)*	SO_4^{2-} *(mg/L)*	NO_3^{-} *(mg/L)*	Cl^{-} *(mg/L)*	*pH (pH units)*	H^{+} *(µeq/L)*	*Specific conductance (µS/cm)*
1	0.114	0.041	0.084	0.031	0.184	1.028	1.161	0.116	4.70	20.0	13.2
2	0.112	0.040	0.083	0.032	0.185	1.026	1.164	0.115	4.70	20.0	13.2
3	0.111	0.041	0.084	0.030	0.181	1.012	1.159	0.116	4.68	20.9	13.2
4	0.097	0.040	0.083	0.030	0.188	1.025	1.168	0.114	4.70	20.0	12.9
5	0.113	0.039	0.078	0.030	0.181	1.019	1.155	0.112	4.69	20.4	13.3
6	0.114	0.041	0.078	0.027	0.191	1.029	1.168	0.117	4.72	19.1	13.2
7	0.112	0.039	0.077	0.032	0.189	1.018	1.165	0.112	4.68	20.9	13.0
8	0.111	0.041	0.076	0.026	0.191	1.021	1.170	0.114	4.72	19.1	12.9
9	0.114	0.042	0.088	0.031	0.187	1.023	1.162	0.115	4.69	20.4	13.3
10	0.116	0.041	0.083	0.028	0.185	1.015	1.170	0.116	4.67	21.4	13.2
11	0.109	0.041	0.086	0.028	0.188	1.016	1.171	0.115	4.71	19.5	12.9
12	0.111	0.041	0.097	0.031	0.194	1.019	1.165	0.115	4.71	19.5	13.0
14	0.109	0.041	0.085	0.031	0.194	1.026	1.179	0.113	4.69	20.4	13.3
15	0.114	0.041	0.083	0.032	0.191	1.011	1.152	0.115	4.68	20.9	13.5
16	0.111	0.039	0.085	0.035	0.189	1.029	1.164	0.115	4.67	21.4	13.5
17	0.110	0.040	0.082	0.032	0.189	1.022	1.157	0.113	4.68	20.9	13.6
18	0.107	0.041	0.082	0.030	0.192	1.017	1.152	0.112	4.70	20.0	13.3
19	0.114	0.042	0.085	0.031	0.195	1.016	1.178	0.110	4.66	21.9	13.6
20	0.104	0.040	0.082	0.031	0.199	1.015	1.164	0.115	4.68	20.9	13.3
21	0.110	0.040	0.081	0.031	0.197	1.029	1.160	0.117	4.70	20.0	13.1
23	0.111	0.041	0.082	0.032	0.198	1.024	1.156	0.118	4.66	21.9	13.7
24	0.106	0.040	0.081	0.032	0.193	1.022	1.153	0.120	4.75	17.8	12.3
25	0.109	0.040	0.082	0.029	0.193	1.014	1.159	0.124	4.70	20.0	13.2
27	0.116	0.041	0.083	0.030	0.191	1.006	1.174	0.127	4.70	20.0	13.3
28	0.111	0.041	0.082	0.031	0.192	1.047	1.158	0.122	4.70	20.0	13.6
29	0.103	0.042	0.082	0.030	0.198	1.063	1.164	0.116	4.69	20.4	13.1

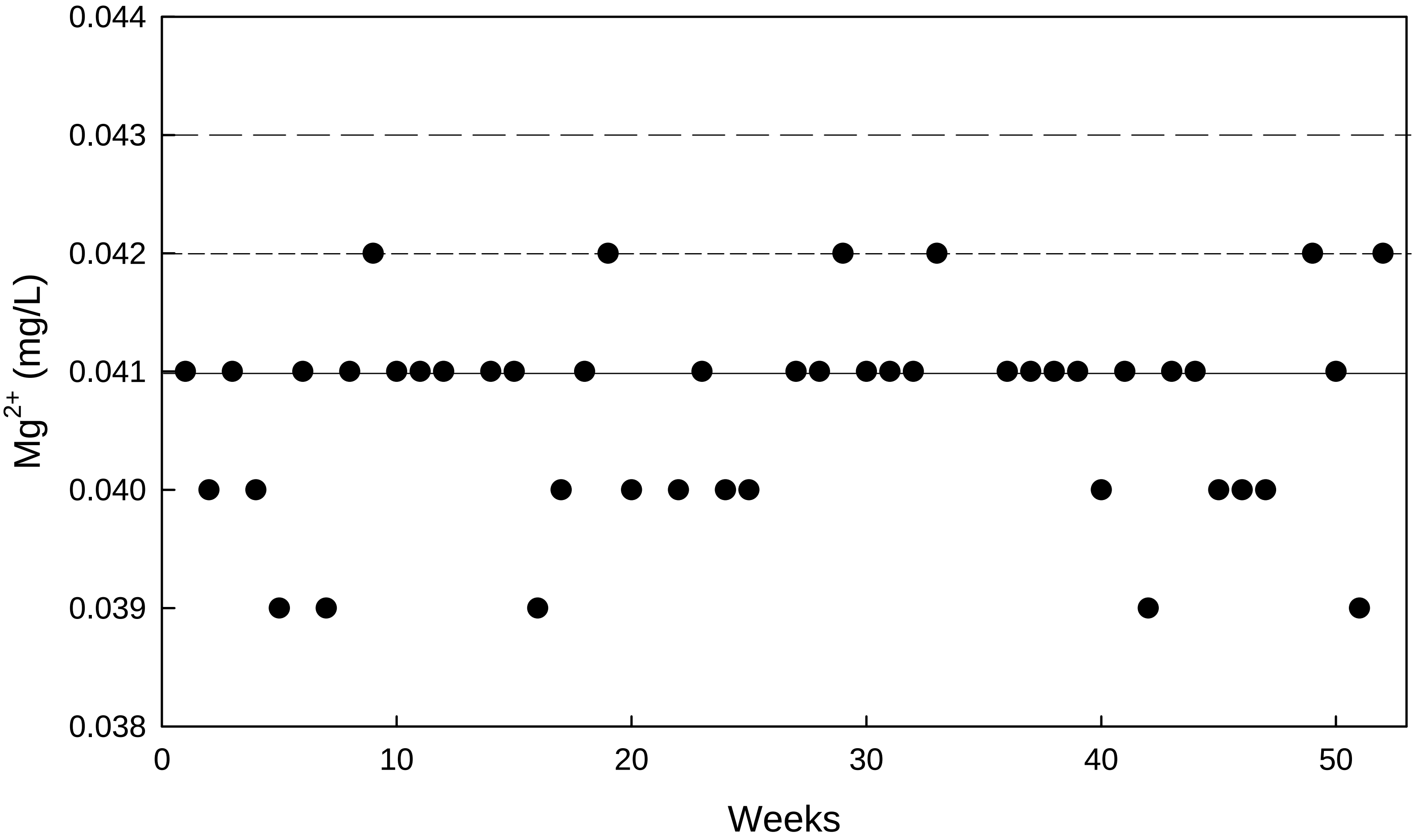
Table B-13. Internal Blind Sample Concentrations, AIRMoN, WMO/GAW Sample, 2002 (concluded)

Weeks	*Ca^{2+} (mg/L)*	*Mg^{2+} (mg/L)*	*Na^{+} (mg/L)*	*K^{+} (mg/L)*	*NH_4^{+} (mg/L)*	*SO_4^{2-} (mg/L)*	*NO_3^{-} (mg/L)*	*Cl^{-} (mg/L)*	*pH (pH units)*	*H^{+} (μeq/L)*	*Specific conductance (μS/cm)*
30	0.101	0.041	0.080	0.030	0.199	1.037	1.163	0.117	4.68	20.9	13.5
31	0.118	0.041	0.082	0.032	0.193	1.038	1.155	0.116	4.68	20.9	13.2
33	0.115	0.041	0.082	0.030	0.196	1.055	1.157	0.117	4.69	20.4	13.5
34	0.114	0.042	0.080	0.031	0.197	1.024	1.157	0.116	4.68	20.9	13.5
36	0.103	0.041	0.082	0.031	0.197	1.025	1.177	0.116	4.68	20.9	13.0
37	0.106	0.041	0.080	0.031	0.197	1.035	1.174	0.118	4.69	20.4	12.3
38	0.109	0.041	0.079	0.032	0.198	1.022	1.178	0.213	4.69	20.4	13.3
39	0.108	0.041	0.080	0.031	0.195	1.036	1.162	0.114	4.68	20.9	13.7
40	0.115	0.040	0.079	0.029	0.200	1.023	1.164	0.113	4.68	20.9	13.1
41	0.113	0.041	0.079	0.035	0.202	1.022	1.164	0.114	4.67	21.4	13.7
42	0.106	0.039	0.079	0.031	0.198	1.034	1.175	0.115	4.68	20.9	13.2
43	0.110	0.041	0.079	0.030	0.199	1.022	1.170	0.113	4.69	20.4	13.0
44	0.110	0.041	0.080	0.032	0.191	1.029	1.153	0.117	4.67	21.4	13.3
45	0.115	0.040	0.080	0.030	0.199	1.025	1.171	0.115	4.67	21.4	13.1
46	0.114	0.040	0.081	0.032	0.199	1.036	1.173	0.114	4.66	21.9	13.9
47	0.117	0.040	0.081	0.029	0.194	1.031	1.169	0.113	4.70	20.0	12.9
48	0.115	0.042	0.082	0.029	0.197	1.032	1.163	0.116	4.71	19.5	13.2
50	0.126	0.041	0.081	0.032	0.198	1.033	1.181	0.115	4.69	20.4	13.1
51	0.110	0.039	0.083	0.031	0.199	1.018	1.161	0.119	4.70	20.0	13.6
52	0.116	0.042	0.079	0.030	0.195	1.032	1.164	0.118	4.68	20.9	12.9
Mean	0.111	0.041	0.082	0.031	0.193	1.026	1.165	0.118	4.59	20.5	13.2
Median	0.111	0.041	0.082	0.031	0.194	1.025	1.164	0.115	4.69	20.4	13.2
Target	0.110	0.043	0.083	0.031	0.206	1.028	1.107	0.119	4.75	17.8	11.1
CAL mean	0.111	0.039	0.080	0.030	0.190	1.013	1.151	0.116	4.74	18.2	12.4



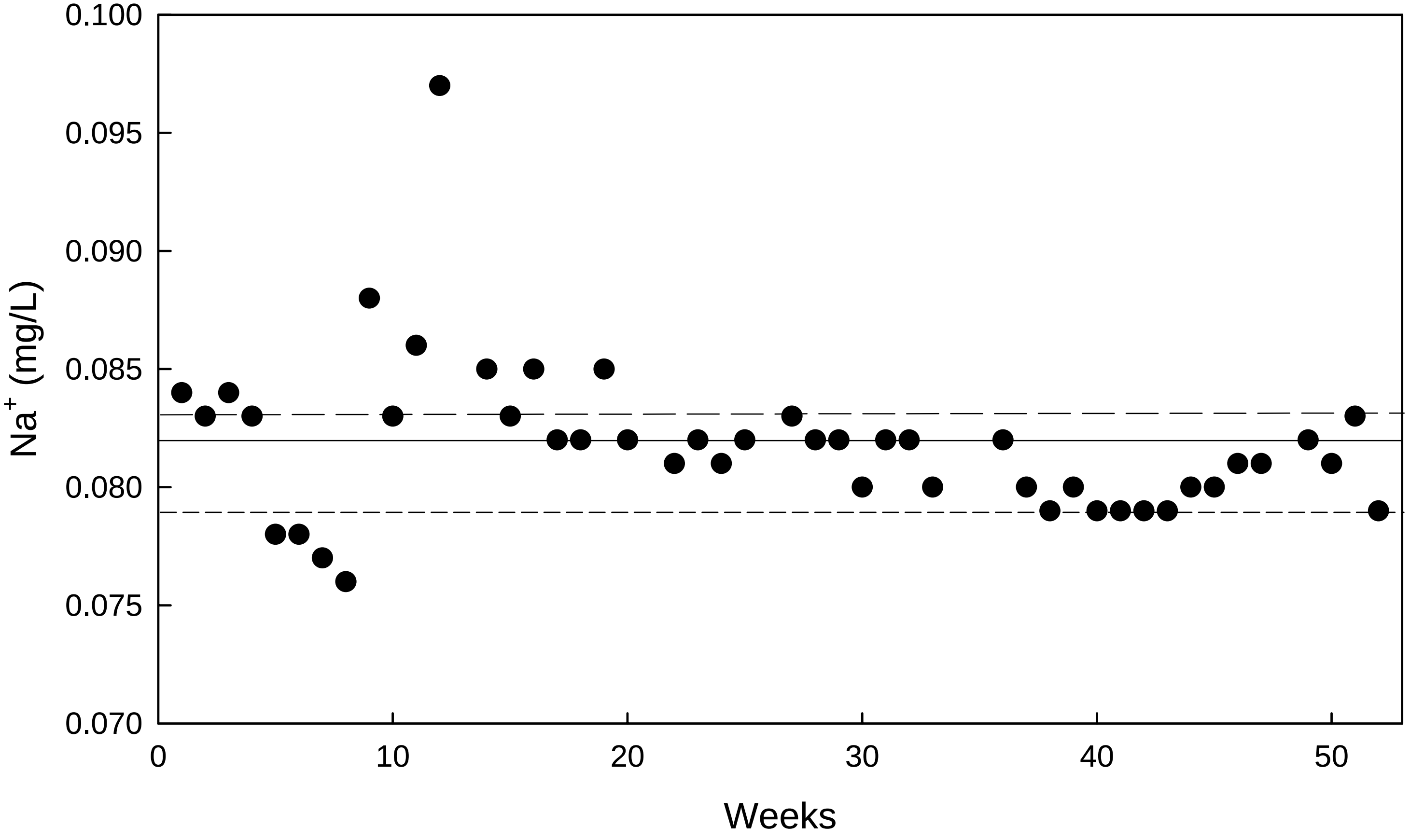
Note:
Solid line denotess mean Ca^{2+} concentration: 0.111 mg/L; long dashed line denotes target Ca^{2+} concentration: 0.110 mg/L; and short dashed line denotes mean Ca^{2+} concentration from the laboratory intercomparison study: 0.113 mg/L.

Figure B-37. AIRMoN internal blind samples, (calcium), WMO/GAW 2001, October study, sample #3, 2002.



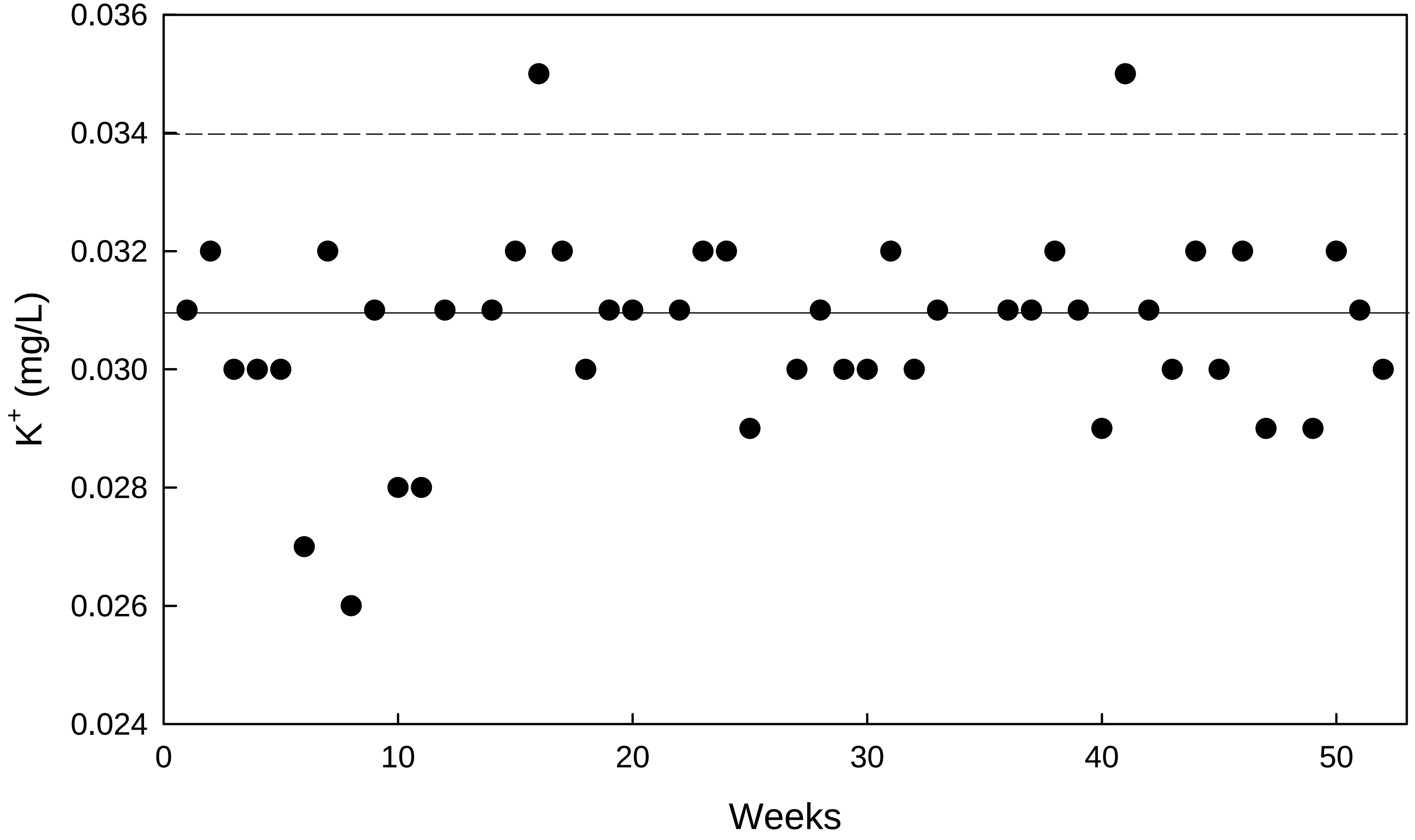
Note:
Solid line denotes mean Mg^{2+} concentration: 0.041 mg/L; long dashed line denotes target Mg^{2+} concentration: 0.043 mg/L; and short dashed line denotes mean Mg^{2+} concentration from the laboratory intercomparison study: 0.042 mg/L.

Figure B-38. AIRMoN internal blind samples, (magnesium), WMO/GAW 2001, October study, sample #3, 2002.



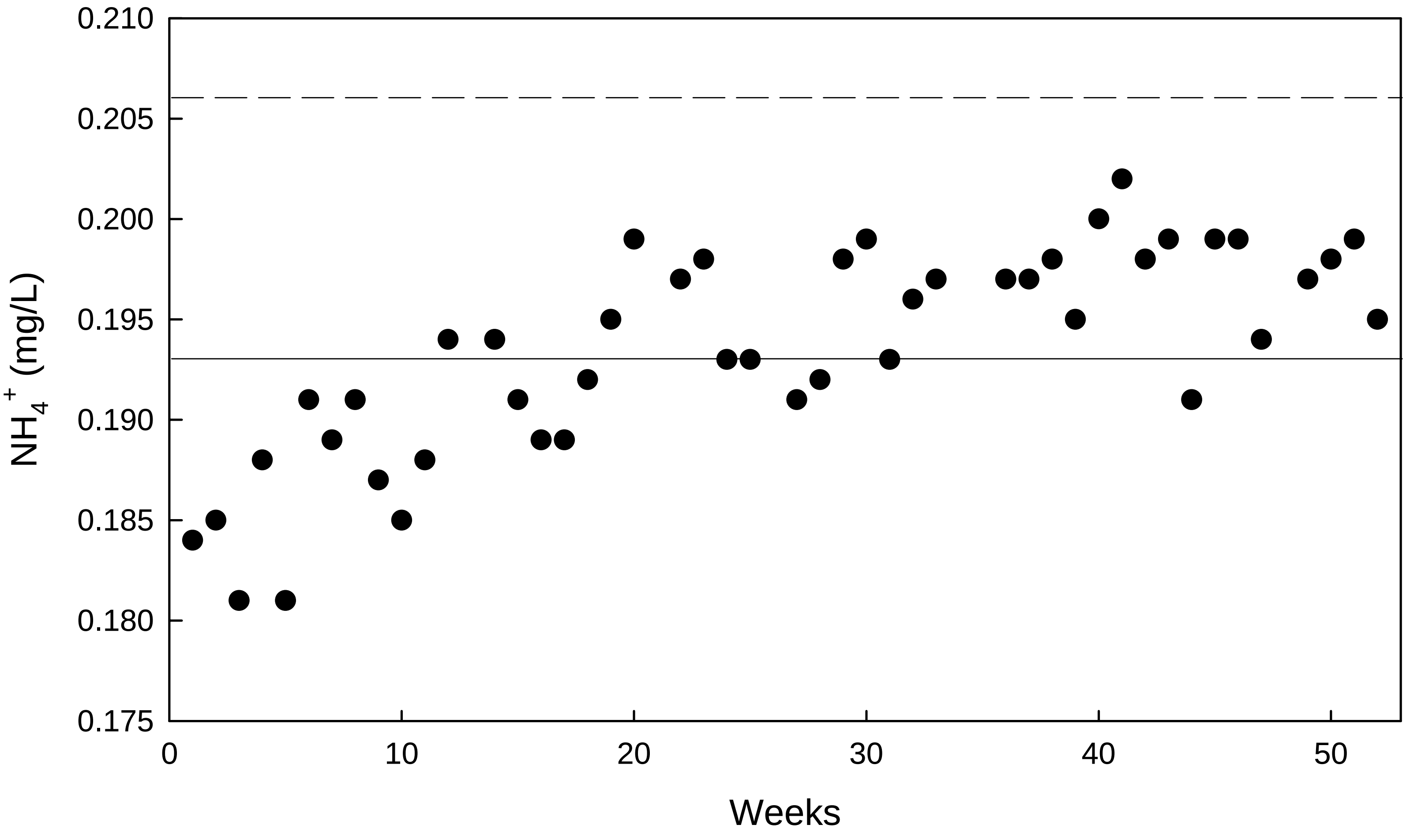
Note:
Solid line denotes mean Na^+ concentration: 0.082 mg/L; long dashed line denotes targe Na^+ concentration: 0.083 mg/L; and short dashed line denotes mean Na^+ concentration from the laboratory intercomparison study: 0.079 mg/L.

Figure B-39. AIRMoN internal blind samples, (sodium), WMO/GAW 2001, October study, sample #3, 2002.



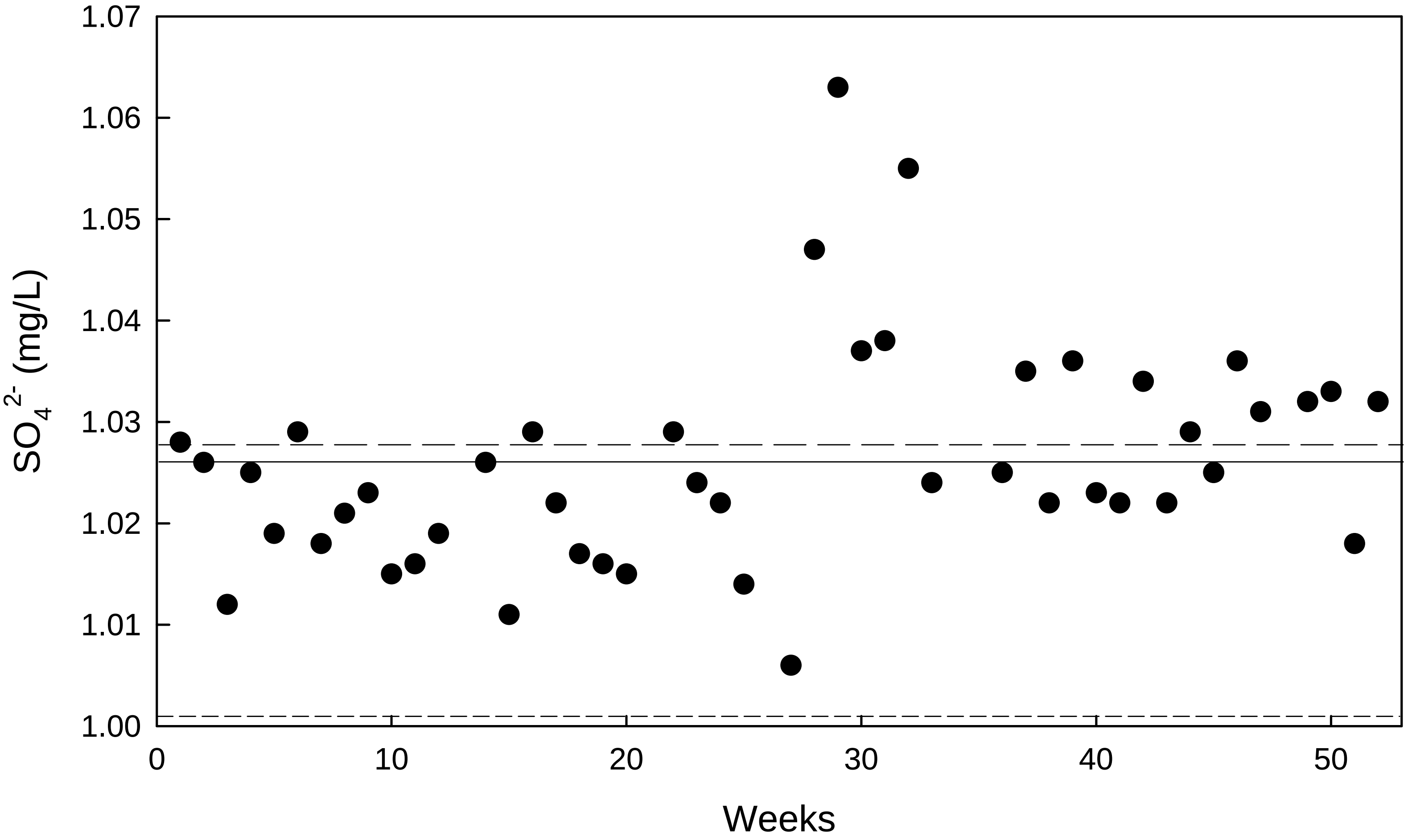
Note:
Solid line denotes mean and target K^+ concentrations: 0.031 mg/L; and short dashed line denotes mean K^+ concentration from the laboratory intercomparison study: 0.034 mg/L.

Figure B-40. AIRMoN internal bind samples, (potassium), WMO/GAW 2001, October study, sample #3, 2002.



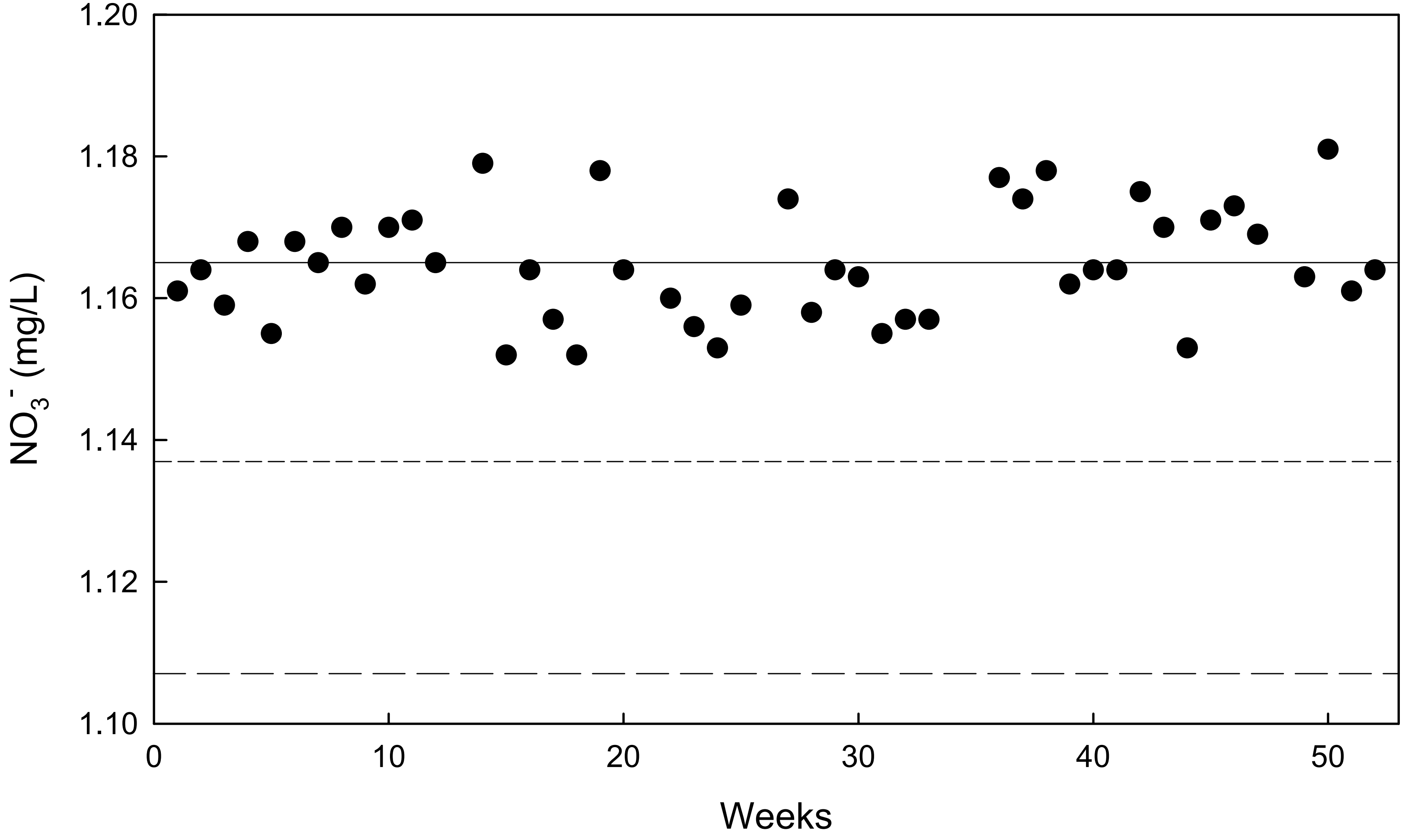
Note:
Solid line denotes mean NH_4^+ concentration: 0.193 mg/L; and long dashed line denotes target and mean NH_4^+ concentrations from the laboratory intercomparison study: 0.206 mg/L.

Figure B-41. AIRMoN internal blind samples, (ammonium), WMO/GAW 2001, October study, sample #3, 2002.



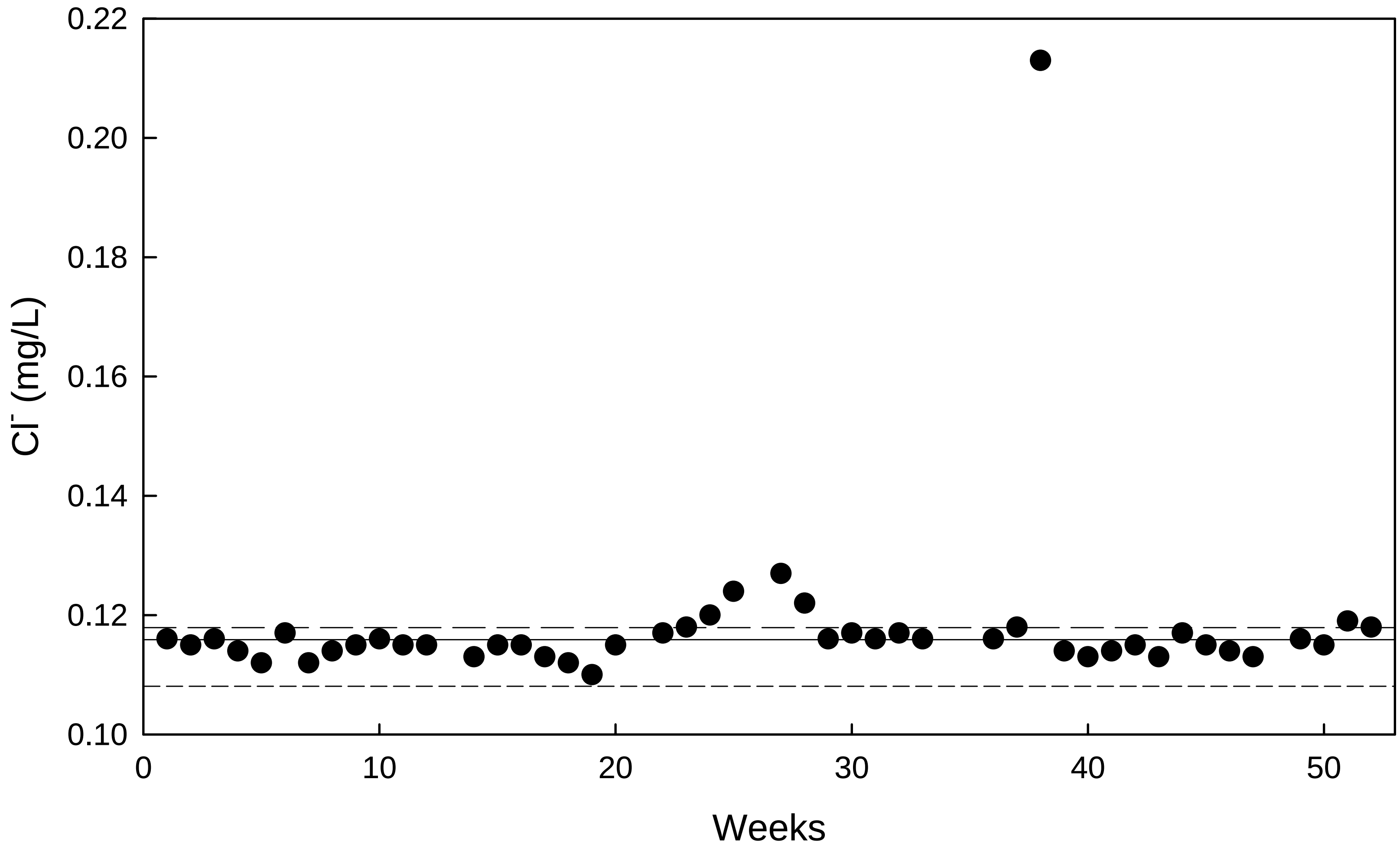
Note:
Solid line denotes mean SO_4^{2-} concentration: 1.026 mg/L; long dashed line denotes the target SO_4^{2-} concentration: 1.028 mg/L; and short dashed line denotes the mean SO_4^{2-} concentration from the laboratory intercomparison study: 1.001 mg/L.

Figure B-42. AIRMoN internal blind samples, (sulfate), WMO/GAW 2001, October study, sample #3, 2002.



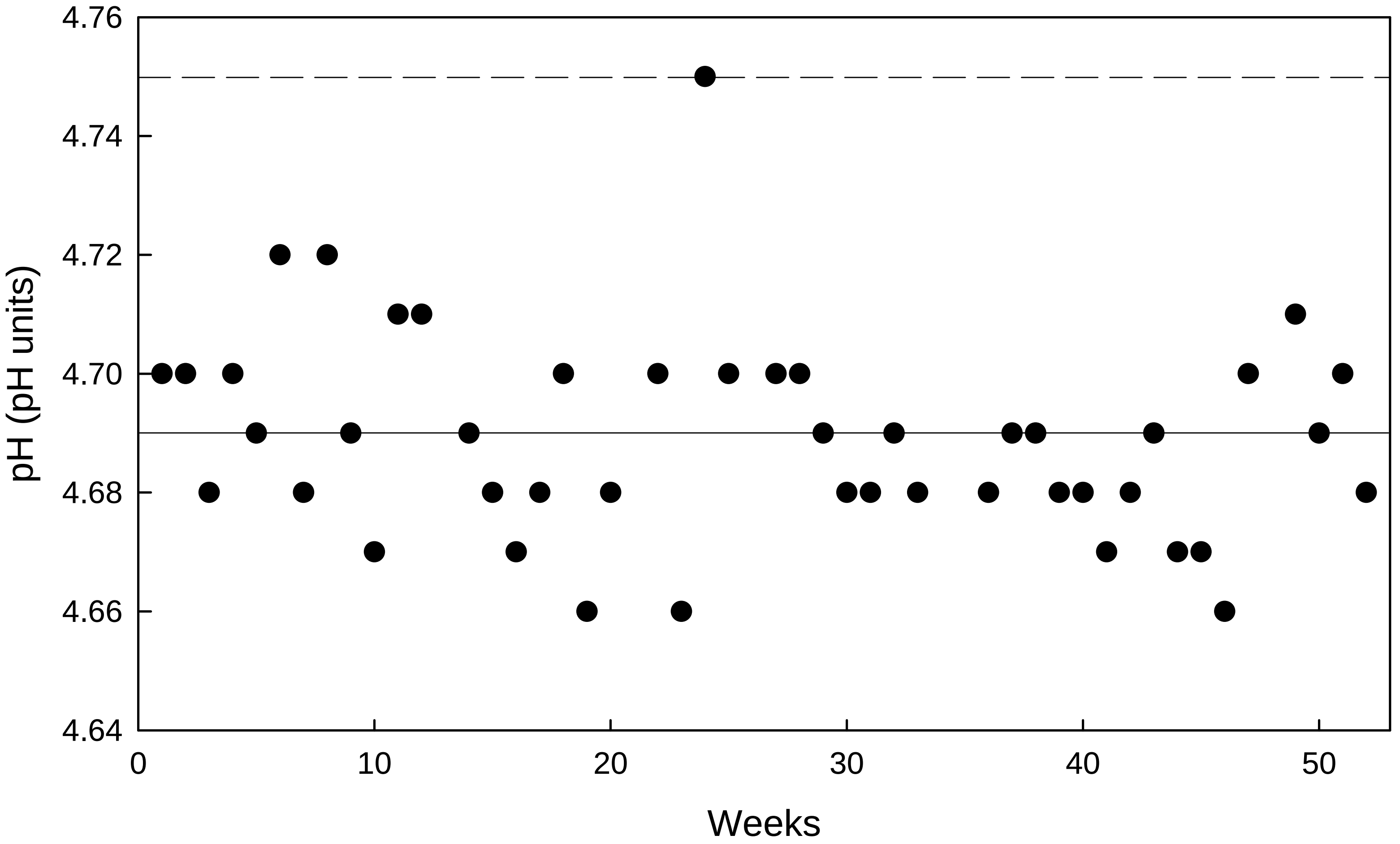
Note:
Solid line denotes mean NO_3^- concentration: 1.165 mg/L; long dashed line denotes the target NO_3^- concentration: 1.107 mg/L; and short dashed line denotes the mean NO_3^- concentration from the laboratory intercomparison study: 1.137 mg/L.

Figure B-43. AIRMoN internal blind samples, (nitrate), WMO/GAW 2001, October study, sample #3, 2002.



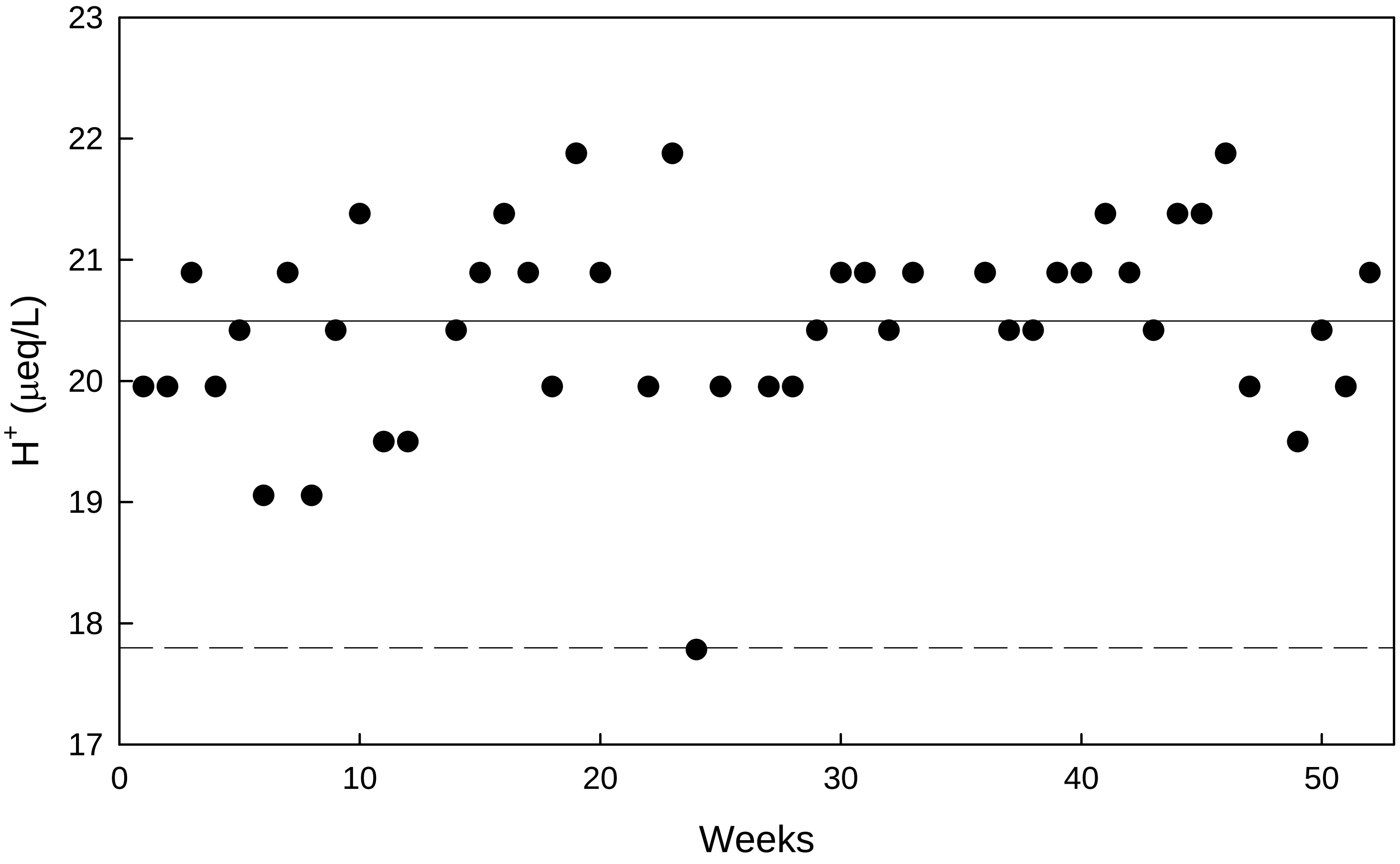
Note:
Solid line denotes mean Cl^- concentration: 0.118 mg/L; long dashed line denotes the target Cl^- concentration: 0.119 mg/L; and short dashed line denotes the mean Cl^- concentration from the laboratory intercomparison study: 0.114 mg/L.

Figure B-44. AIRMoN internal blind samples, (chloride), WMO/GAW 2001, October study, sample #3,2002.



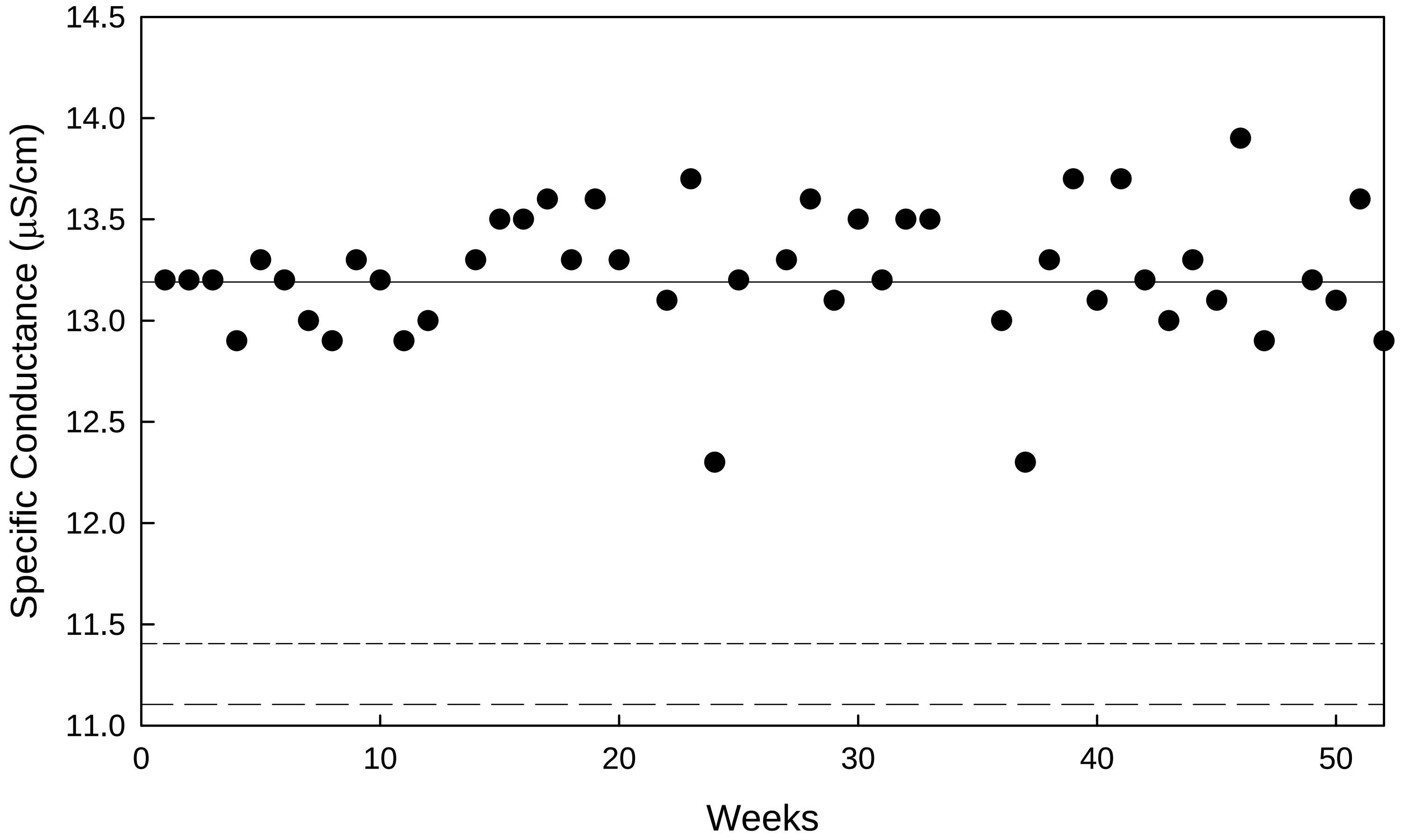
Note:
Solid line denotes mean pH: 4.69; and long dashed line denotes target and mean pH from the laboratory intercomparison study: 4.75.

Figure B-45. AIRMoN internal blind samples, (pH), WMO/GAW 2001, October study, sample #3, 2002.



Note:
Solid line denotes mean H$^+$ concentration: 20.5 μeq/L; and long dashed line denotes target and mean H$^+$ concentrations from the laboratory intercomparison study: 17.8 μeq/L.

Figure B-46. AIRMoN internal blind samples, (H$^+$), WMO/GAW 2001, October study, sample #3, 2002.



Note:
Solid line denotes mean specific conductance: 13.2 μS/cm; long dashed line denotes target specific conductance: 11.1 μS/cm; and short dashed line denotes mean specific conductance from the laboratory intercomparison study: 11.4 μS/cm.

Figure B-47. AIRMoN internal blind samples, (specific conductance), WMO/GAW 2001, October study, sample #3, 2002.

Table B-14. 5th, 50th, and 95th Percentile Concentration Values of Parameters Measured in Replicate Samples, NTN, 2002

	Percentile concentration values (mg/L)		
Parameter	*5th*	*50th*	*95th*
Calcium	0.013	0.086	0.515
Magnesium	<0.003	0.020	0.116
Sodium	0.004	0.062	0.816
Potassium	<0.003	0.016	0.097
Ammonium	<0.02	0.20	0.85
Sulfate	0.145	0.939	3.030
Nitrate	0.122	0.875	2.753
Chloride	0.020	0.114	1.536
pH (units)	4.25	4.89	6.21
Hydrogen ion (µeq/L)	0.62	12.88	56.77
Specific conductance (µS/cm)	3.3	11.8	31.3

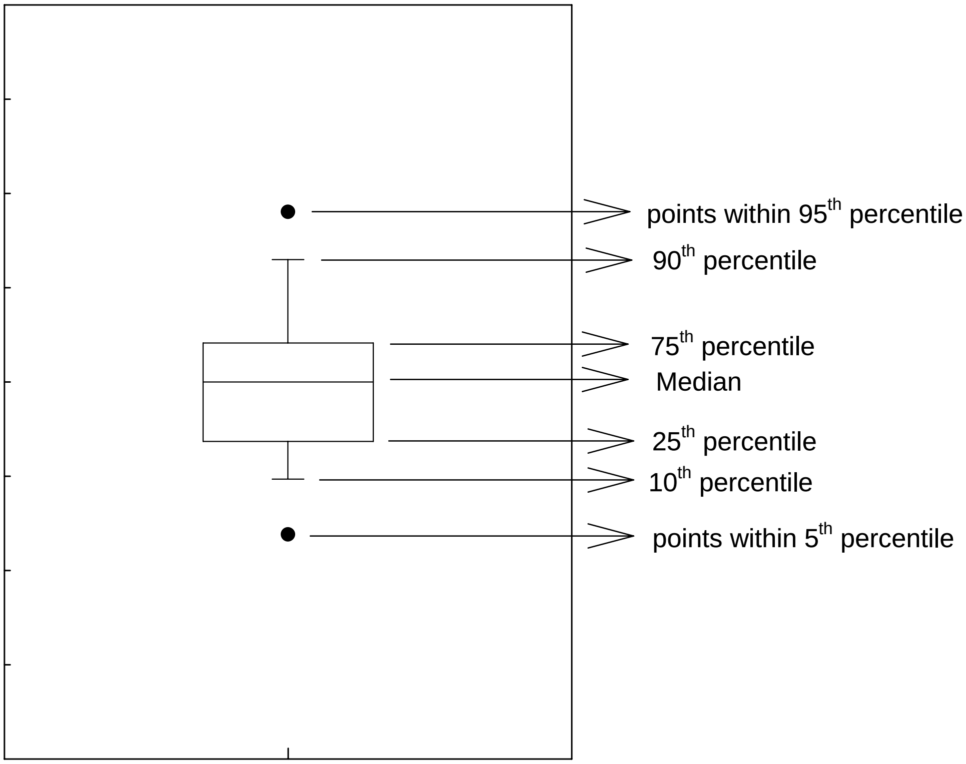


Figure B-48. An explanation of the box and whisker plots used in this report, 2002.

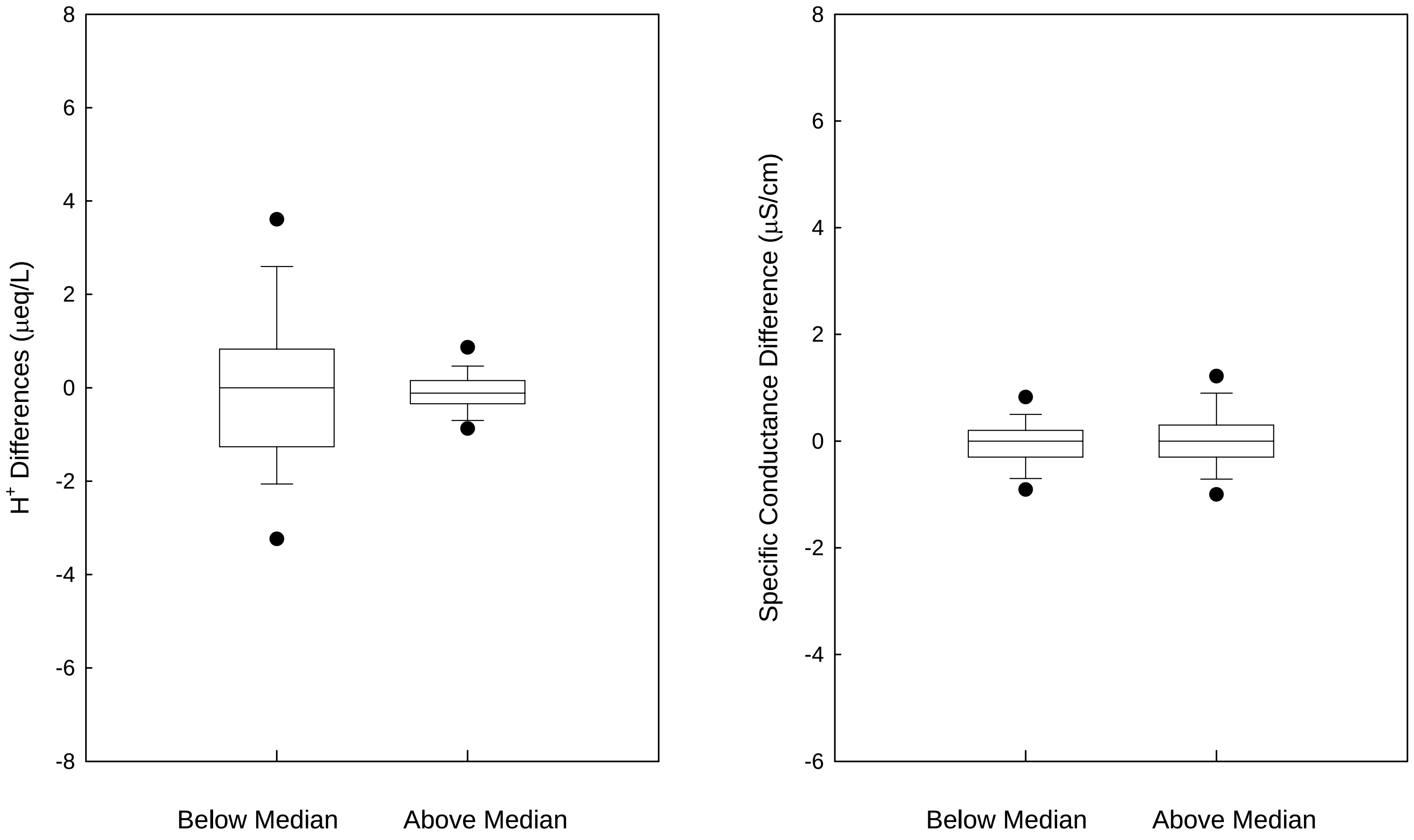


Figure B-49. Results of NTN replicate analysis, hydrogen ion (H^+) and specific conductance, 2002.

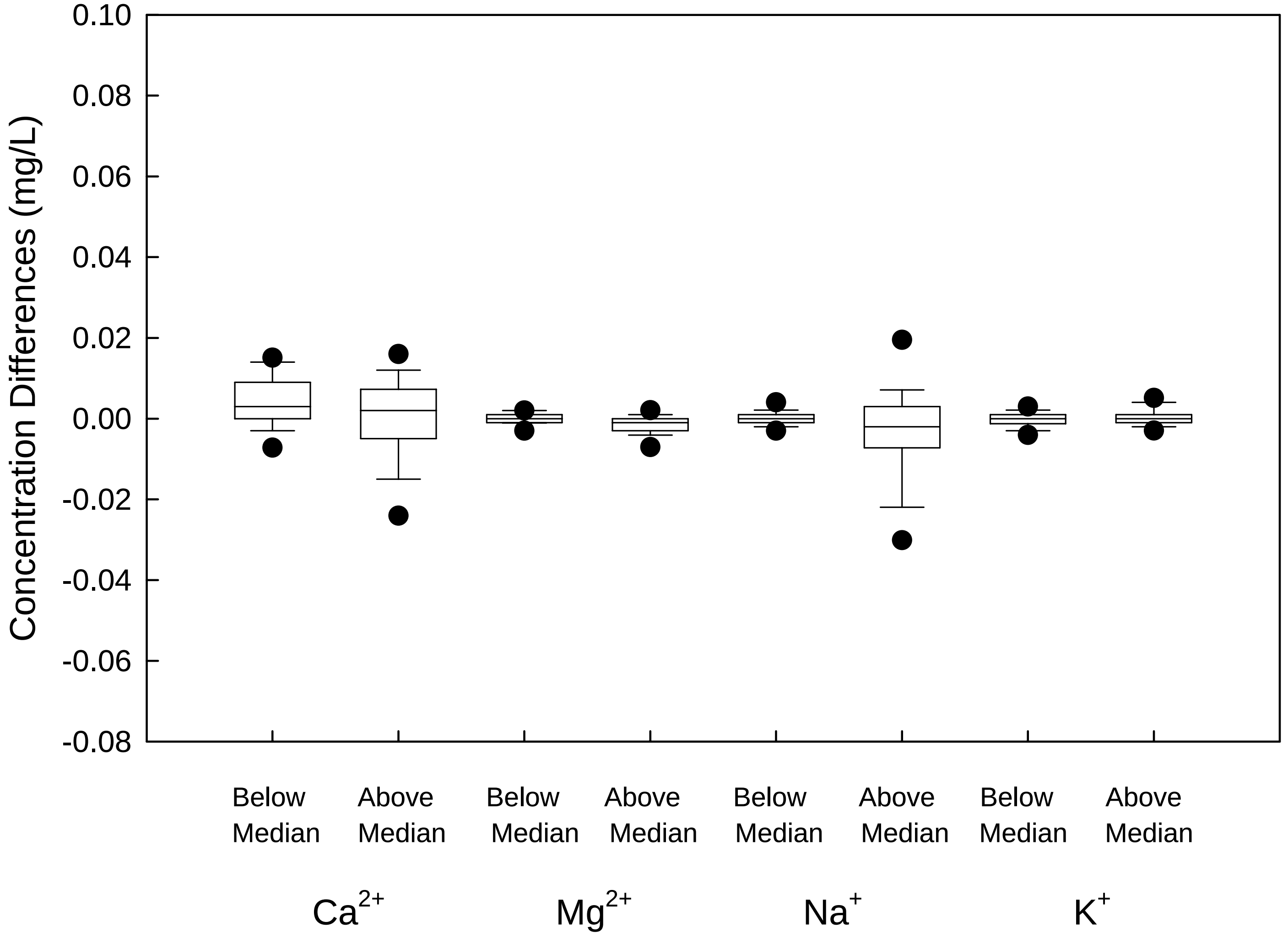


Figure B-50. Results of NTN replicate analysis, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}), 2002.

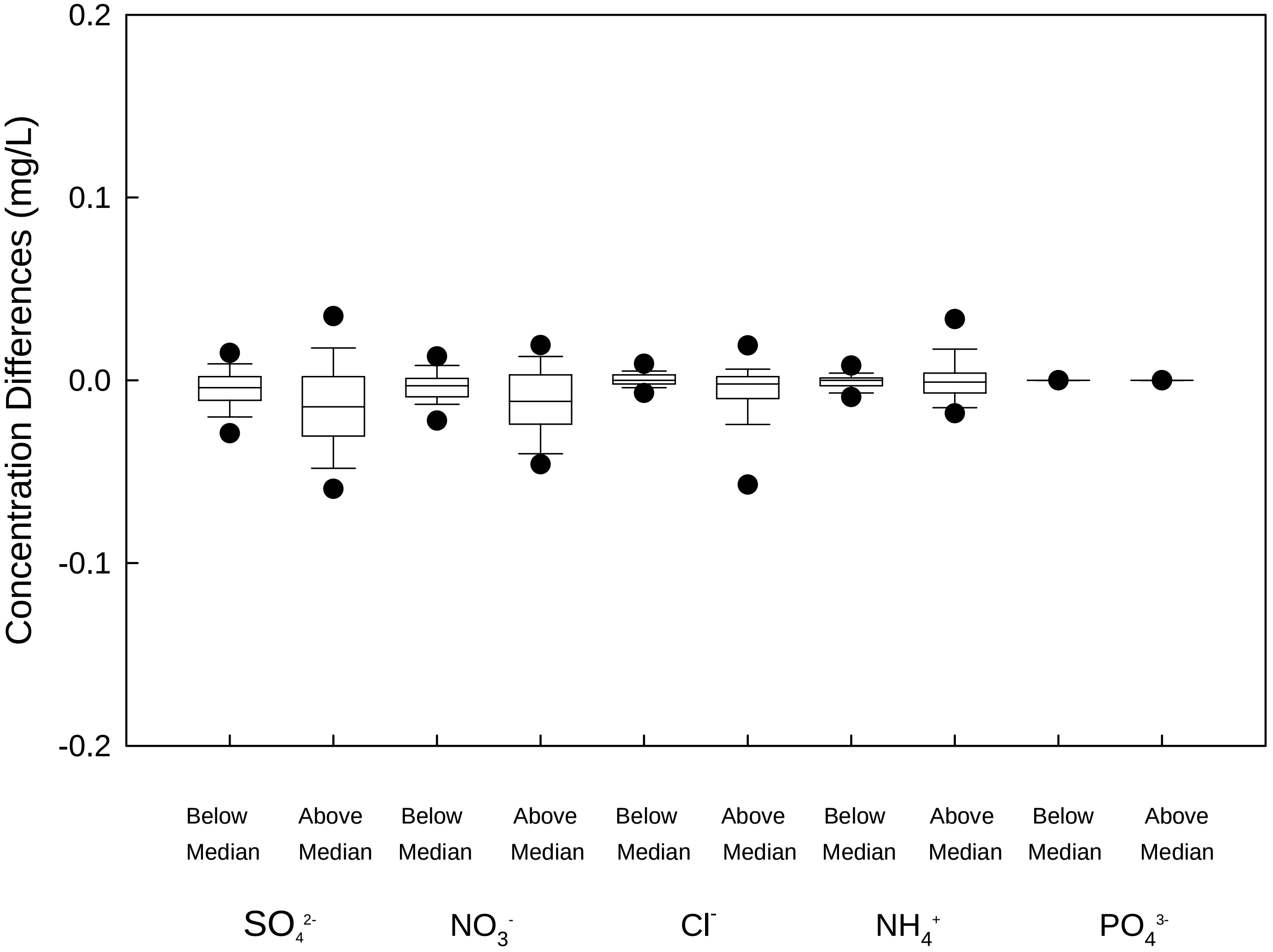


Figure B-51. Results of NTN replicate analysis, sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), and orthophosphate (PO_4^{3-}), 2002.

Table B-15. 5th, 50th, and 95th Percentile Concentration Values of Parameters Measured in Replicate Samples, AIRMoN, 2002

	Percentile concentration values (mg/L)		
Parameter	*5th*	*50th*	*95th*
Calcium	0.000	0.112	0.527
Magnesium	0.000	0.035	0.138
Sodium	0.000	0.204	0.874
Potassium	0.000	0.023	0.086
Ammonium	0.011	0.267	0.728
Orthophosphate	0.000	0.009	0.029
Sulfate	0.232	1.692	4.723
Nitrate	0.191	1.064	3.040
Chloride	0.015	0.415	1.984
pH (units)	4.10	4.60	5.20
Hydrogen ion (µeq/L)	6.30	34.33	79.40
Specific Conductance (µS/cm)	3.8	21.1	51.4

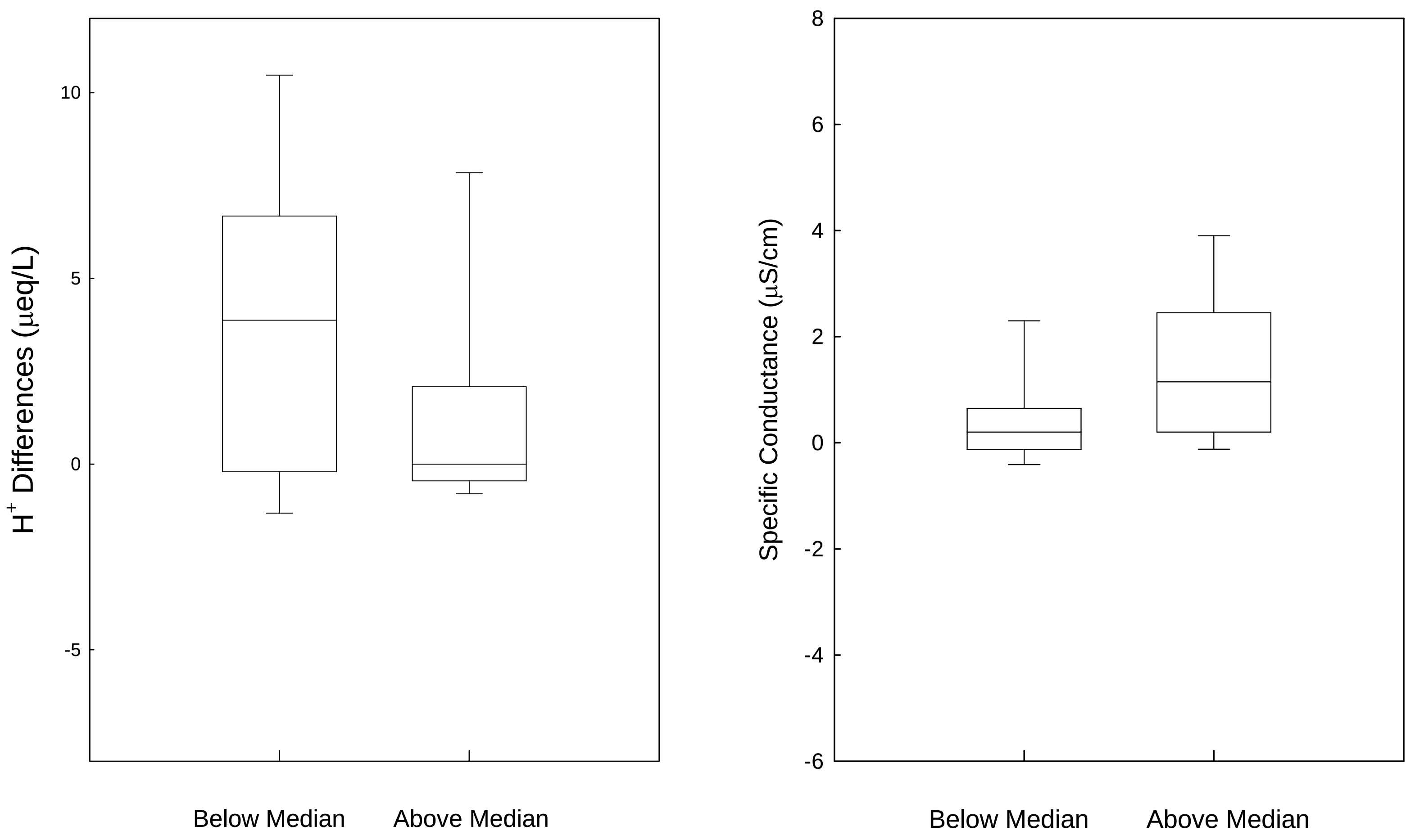


Figure B-52. Results of AIRMoN replicate analysis, hydrogen ion (H^+) and specific conductance, 2002.

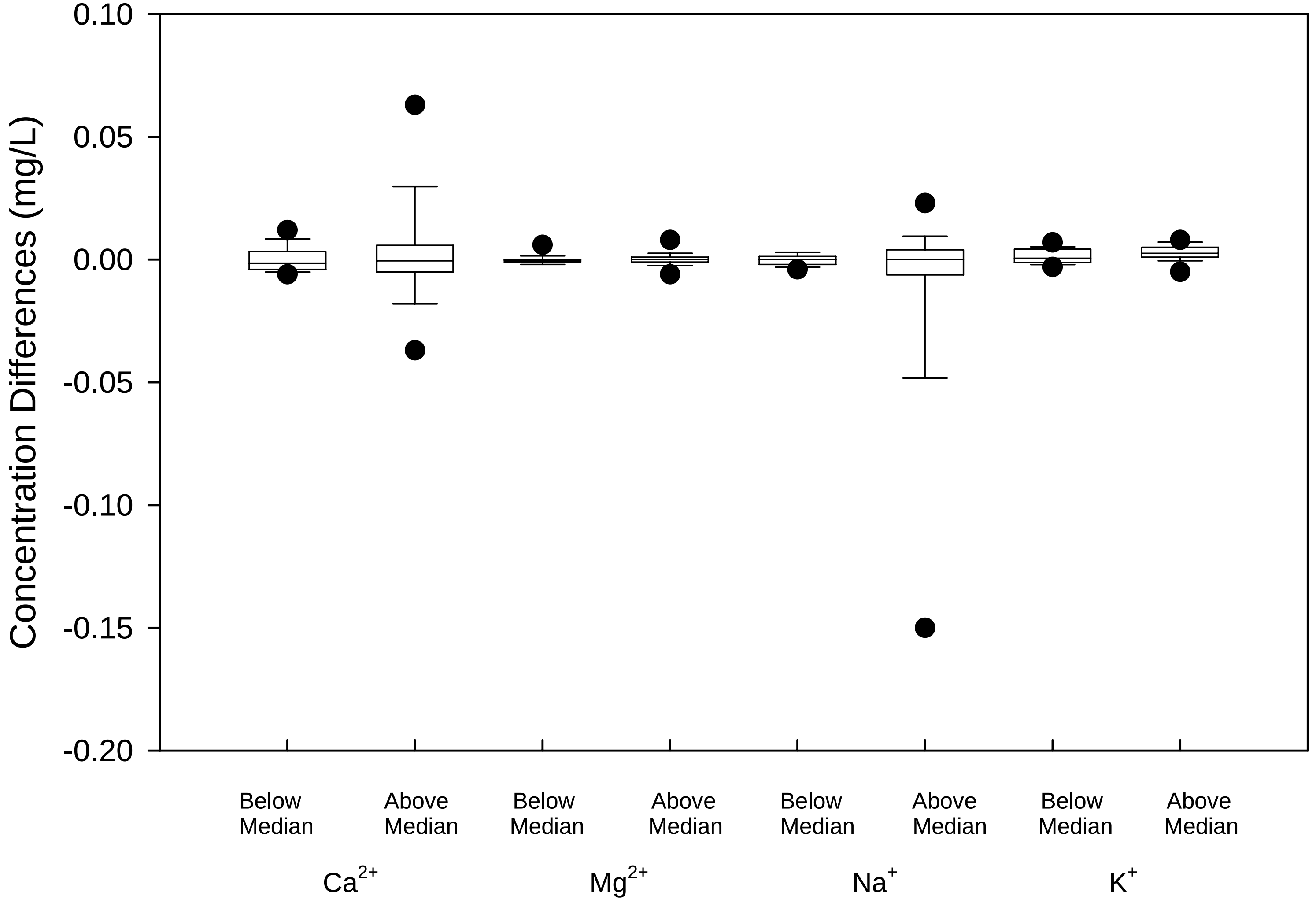


Figure B-53. Results of AIRMoN replicate analysis, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}), 2002.

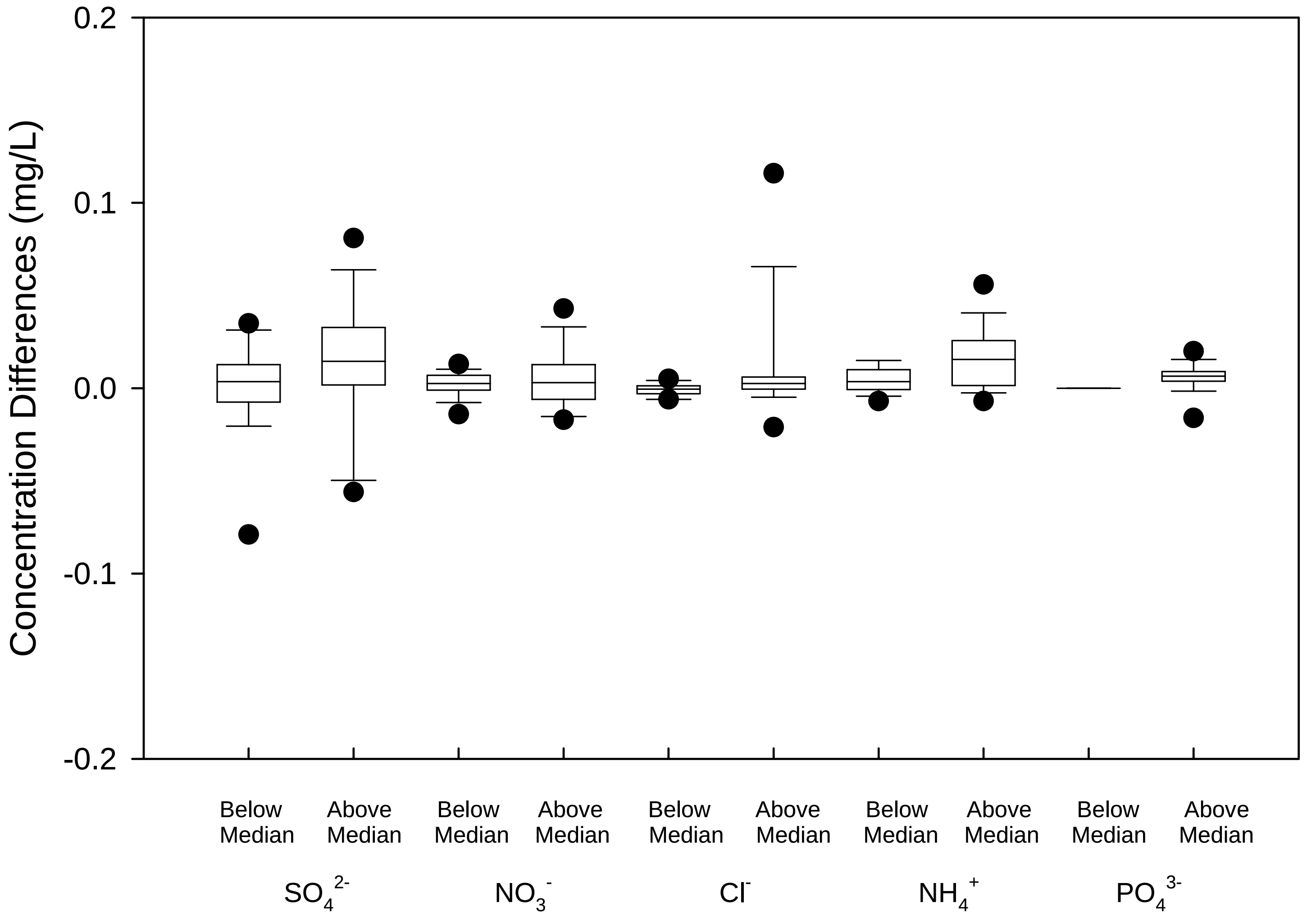


Figure B-54. Results of AIRMoN replicate analysis, sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), and orthophosphate (PO_4^{3-}), 2002.

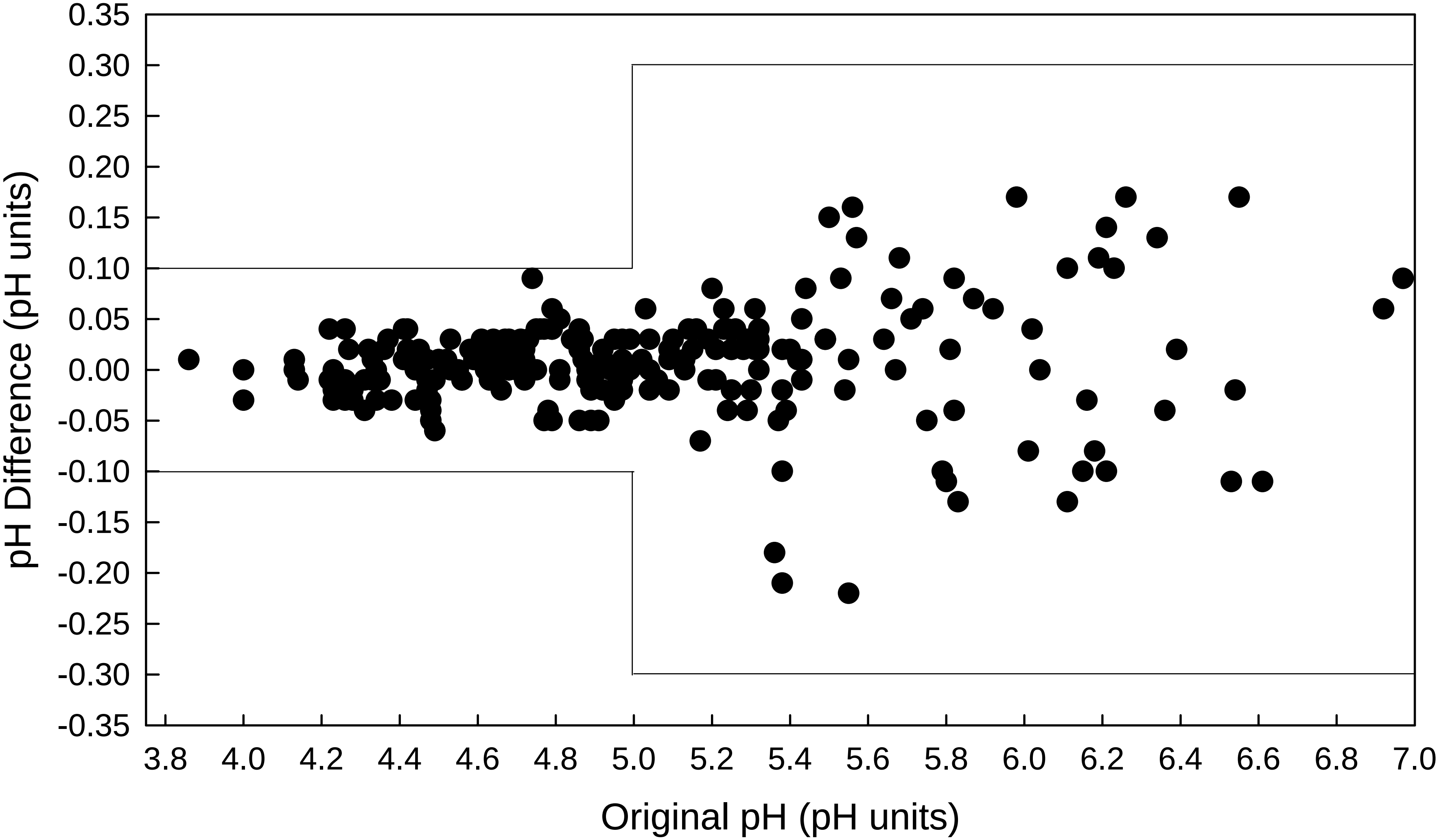


Figure B-56. NTN replicate sample differences (original-replicate) for pH, 2002.

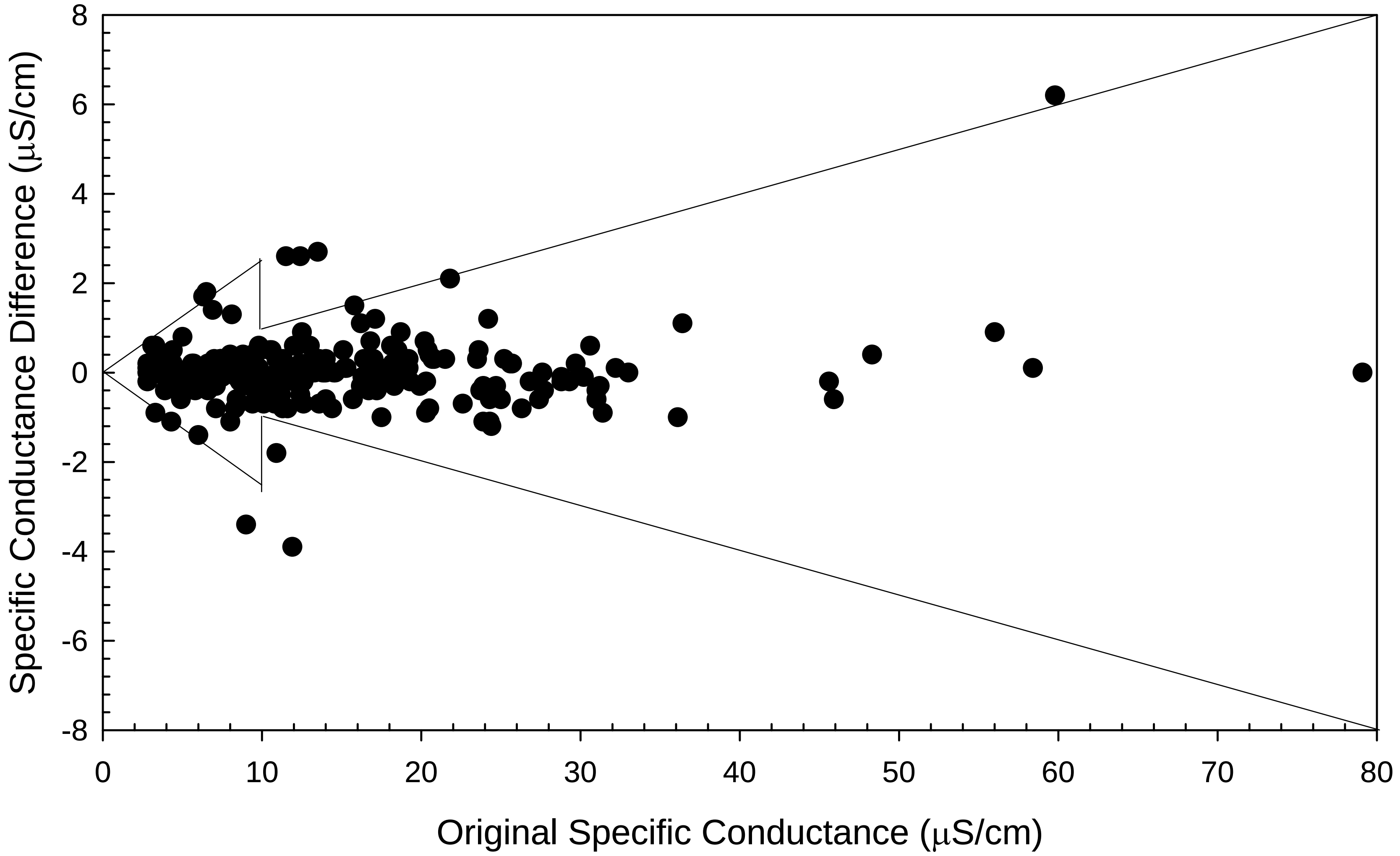


Figure B-57. NTN replicate sample differences (original-replicate) for specific conductance, 2002.

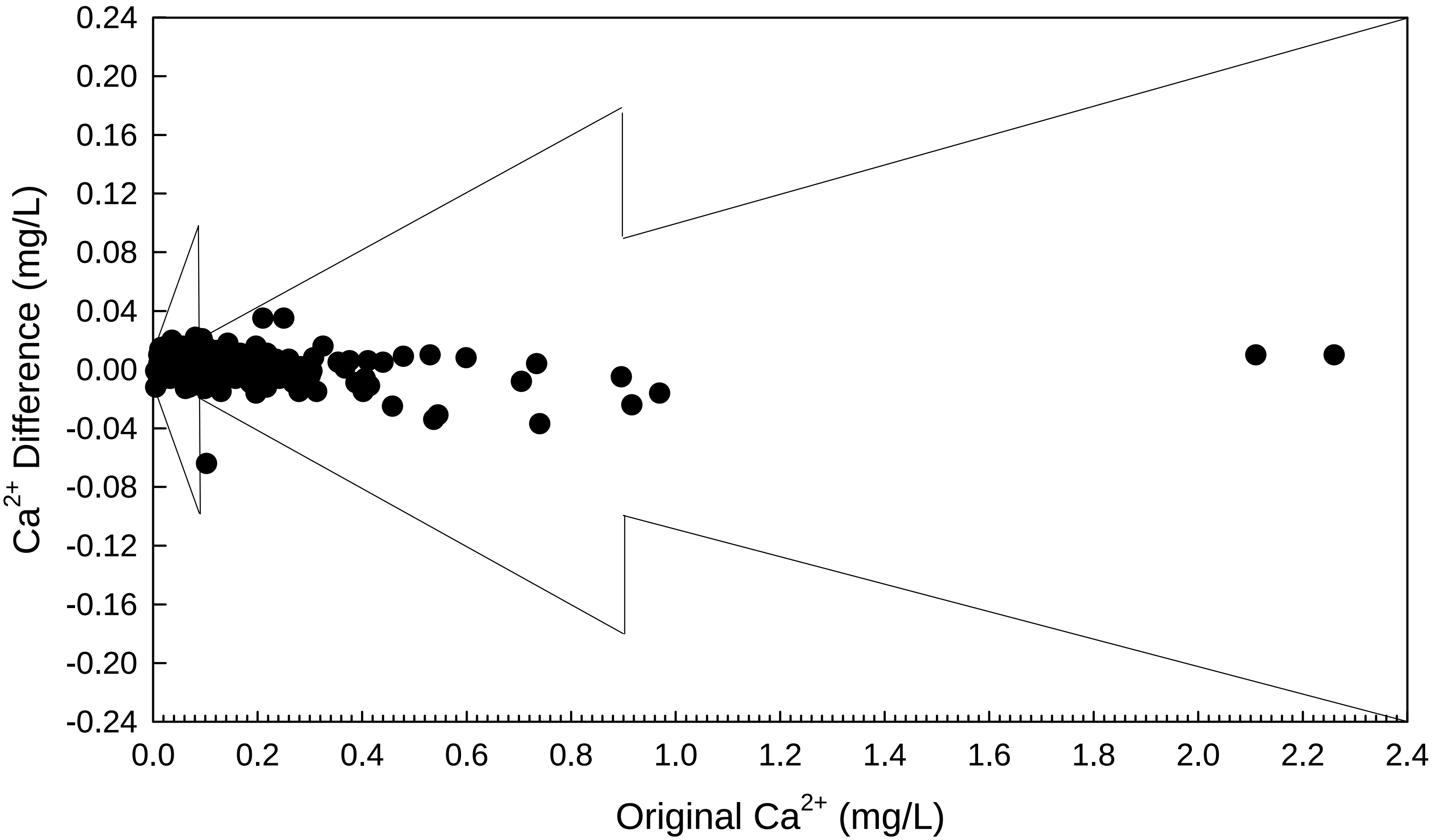


Figure B-58. NTN replicate sample differences (original-replicate) for calcium, 2002.

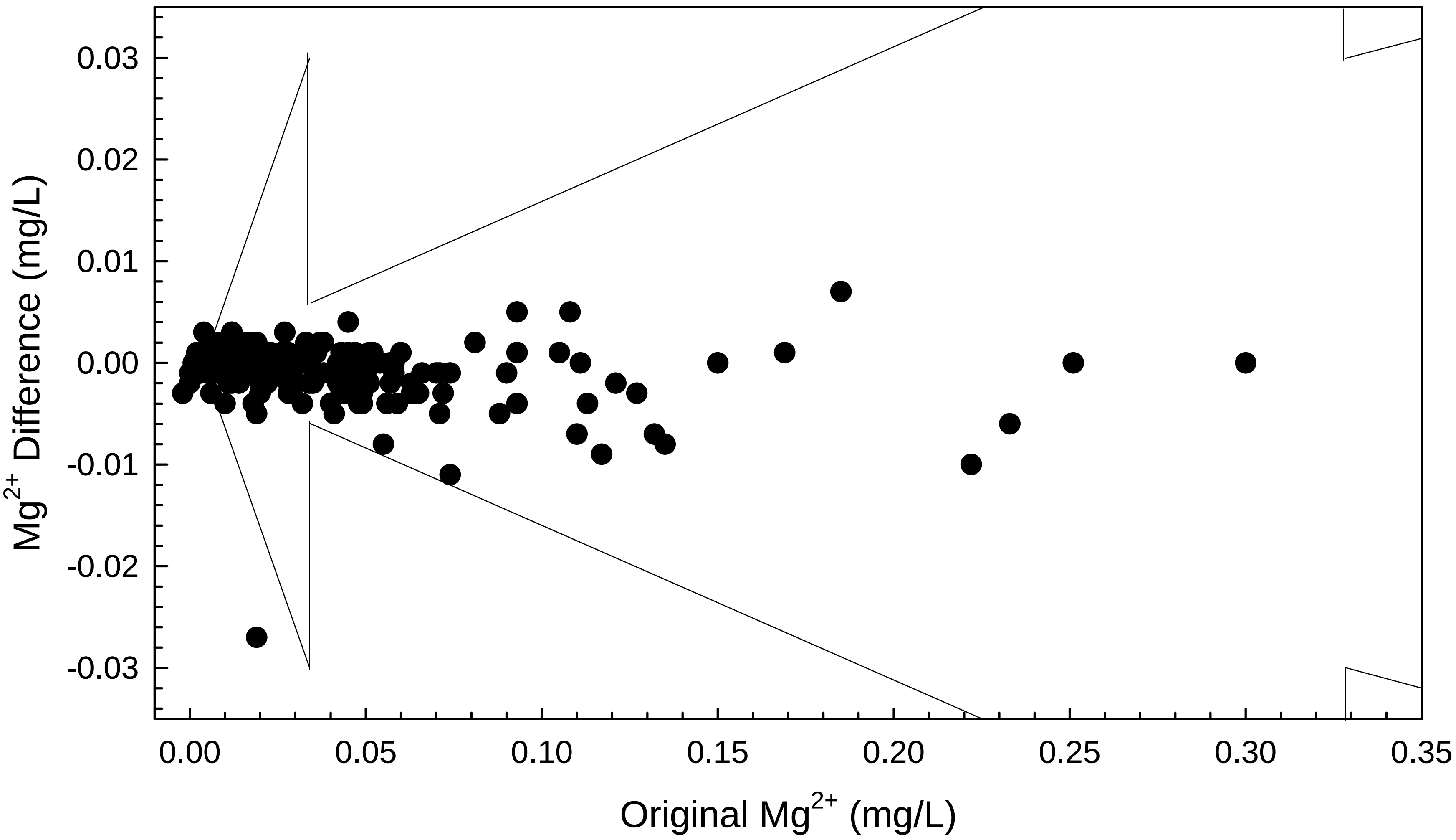


Figure B-59. NTN replicate sample differences (original - replicate) for magnesium, 2002.

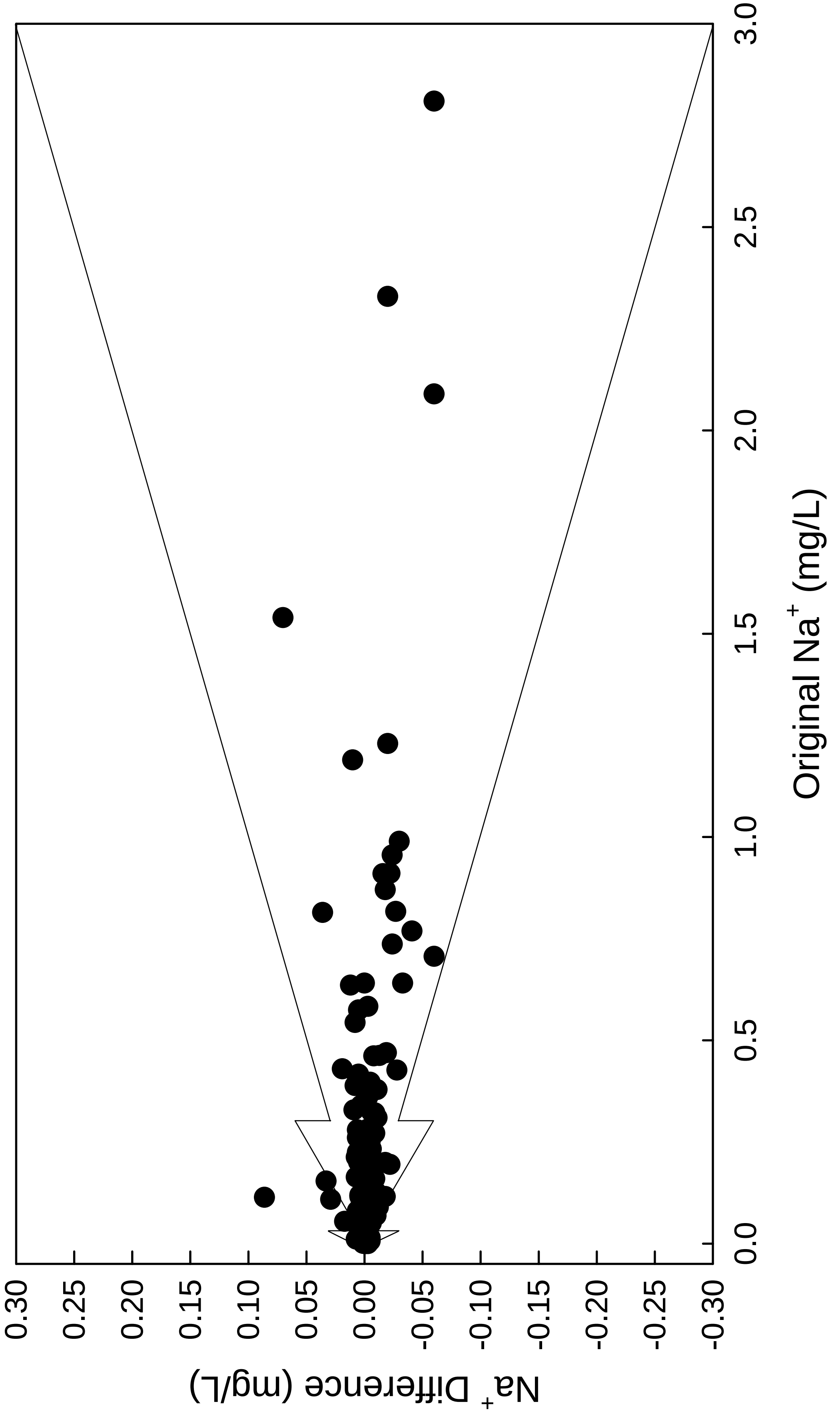


Figure B-60. NTN replicate sample differences (original - replicate) for sodium, 2002.

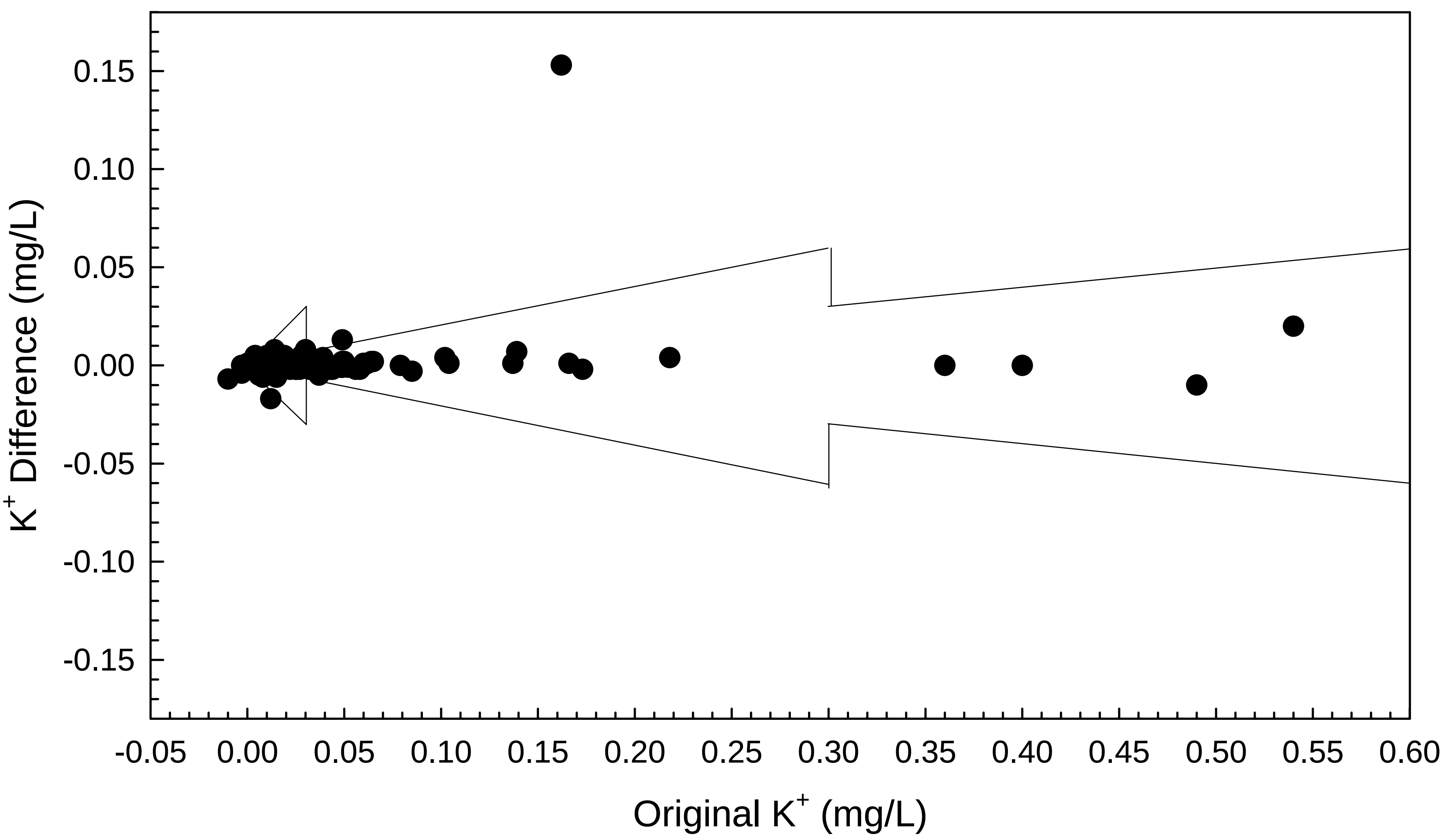


Figure B-61. NTN replicate sample differences (original - replicate) for potassium, 2002.

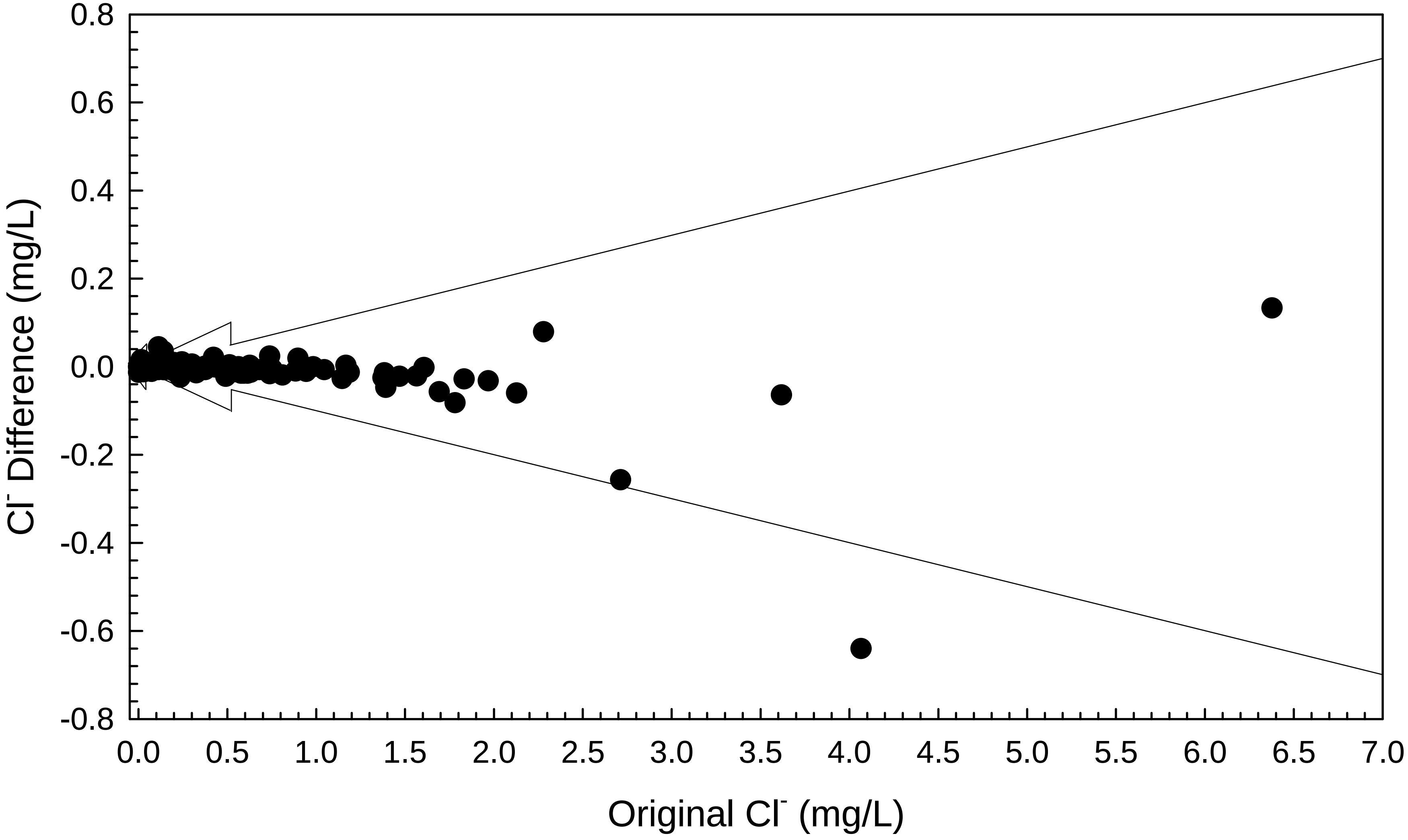


Figure B-62. NTN replicate sample differences (original-replicate) for chloride, 2002.

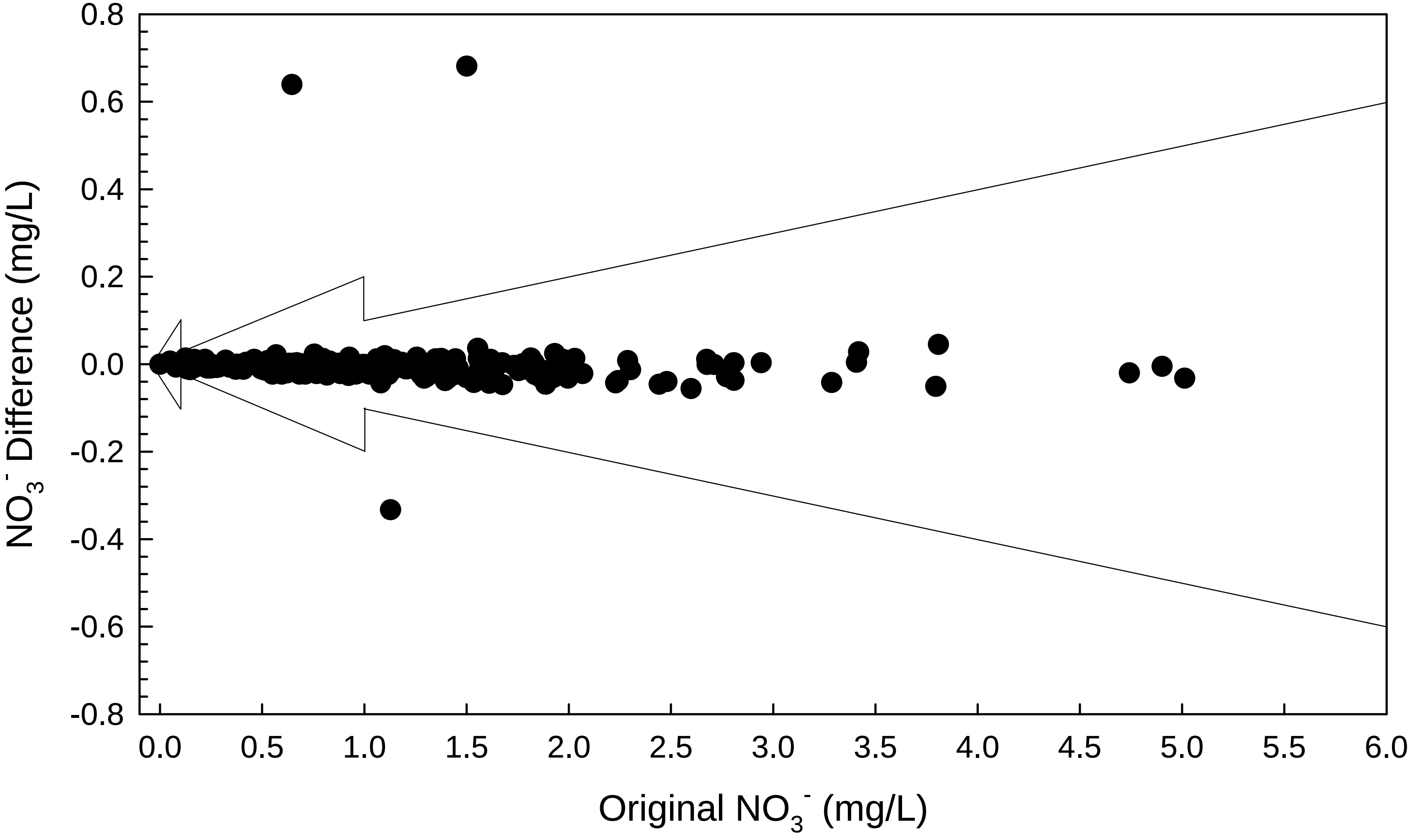


Figure B-63. NTN replicate sample differences (original - replicate) for nitrate, 2002.

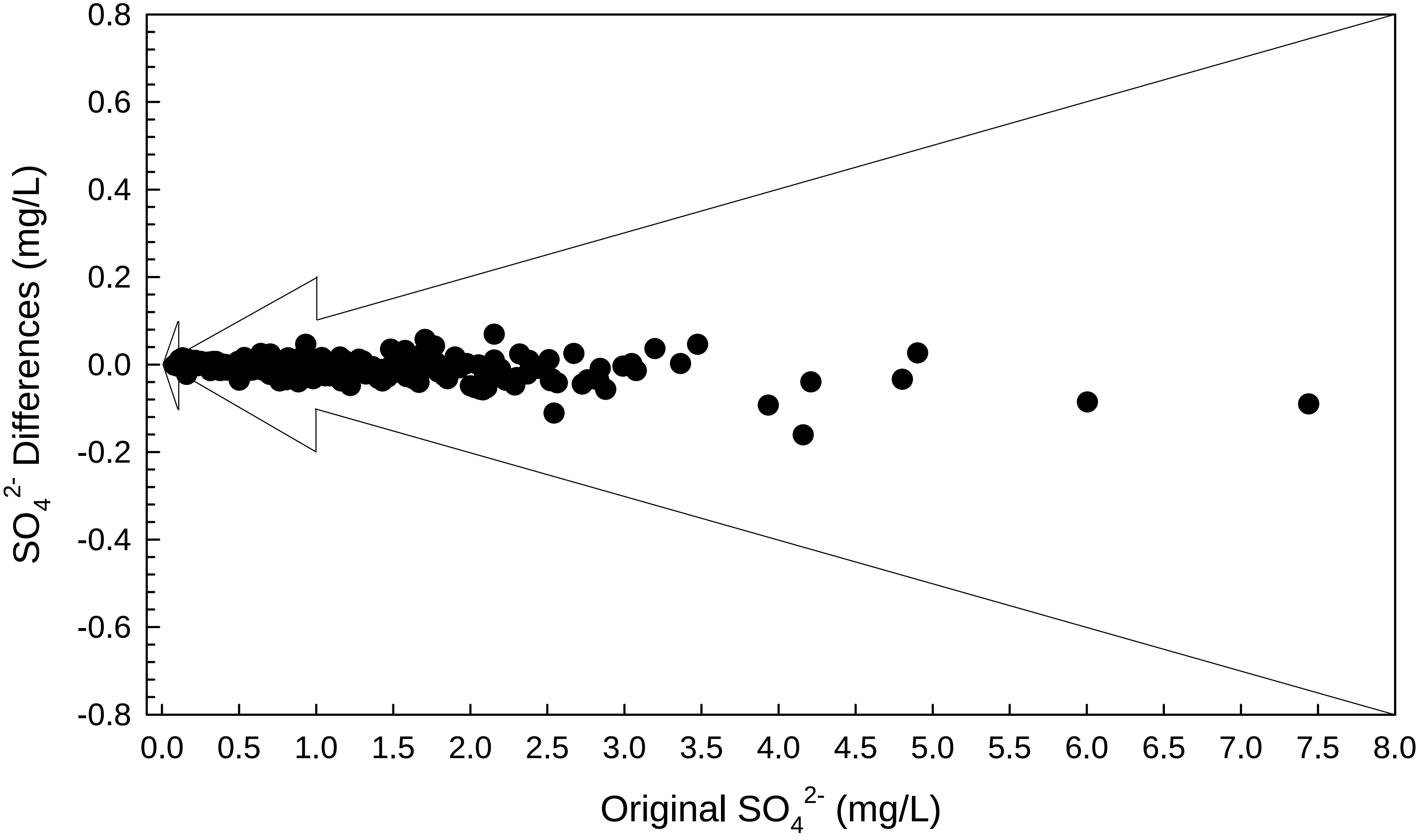


Figure B-64. NTN replicate sample differences (original - replicate) for sulfate, 2002.

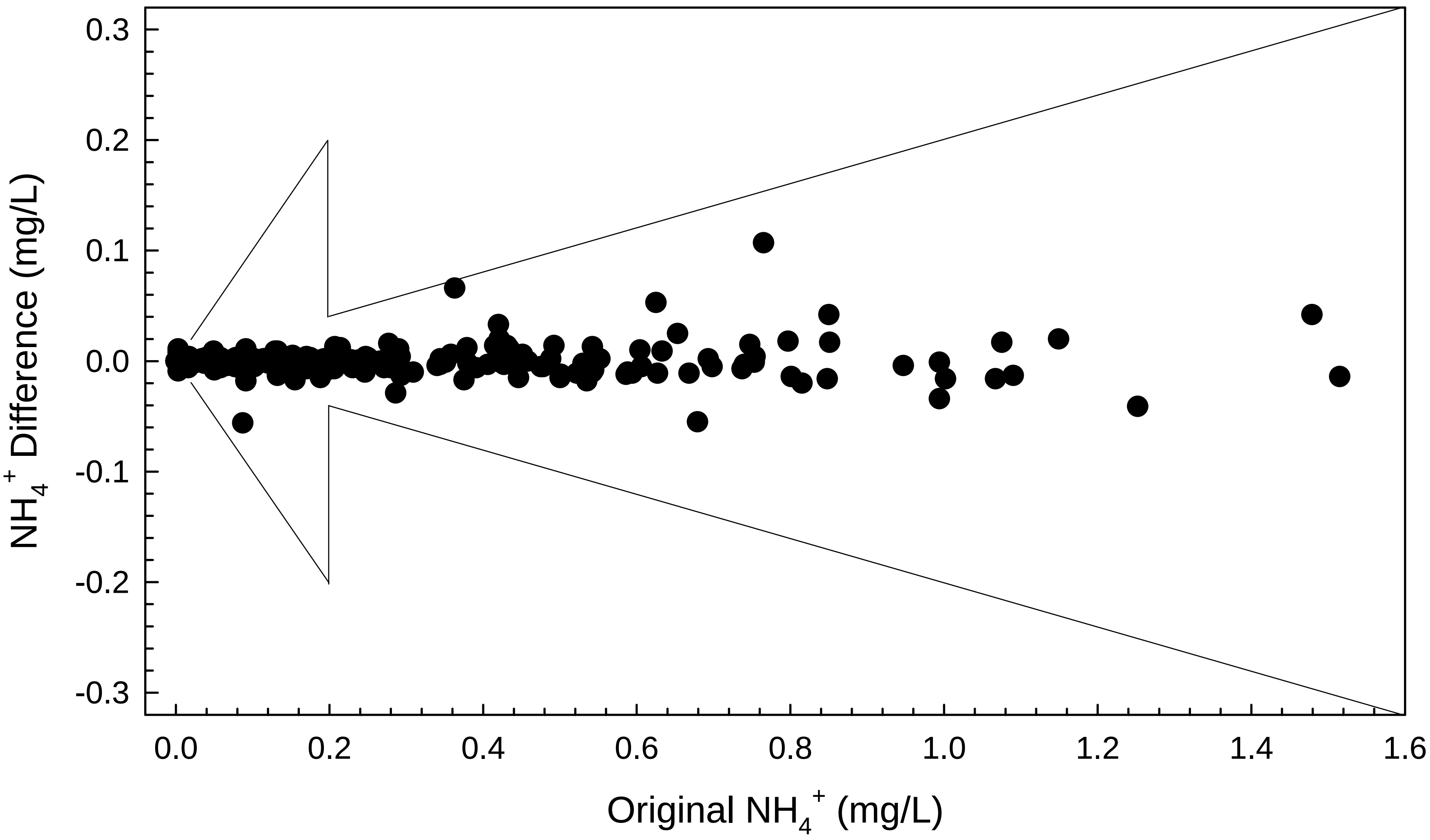


Figure B-65. NTN replicate sample differences (original - replicate) for ammonium, 2002.

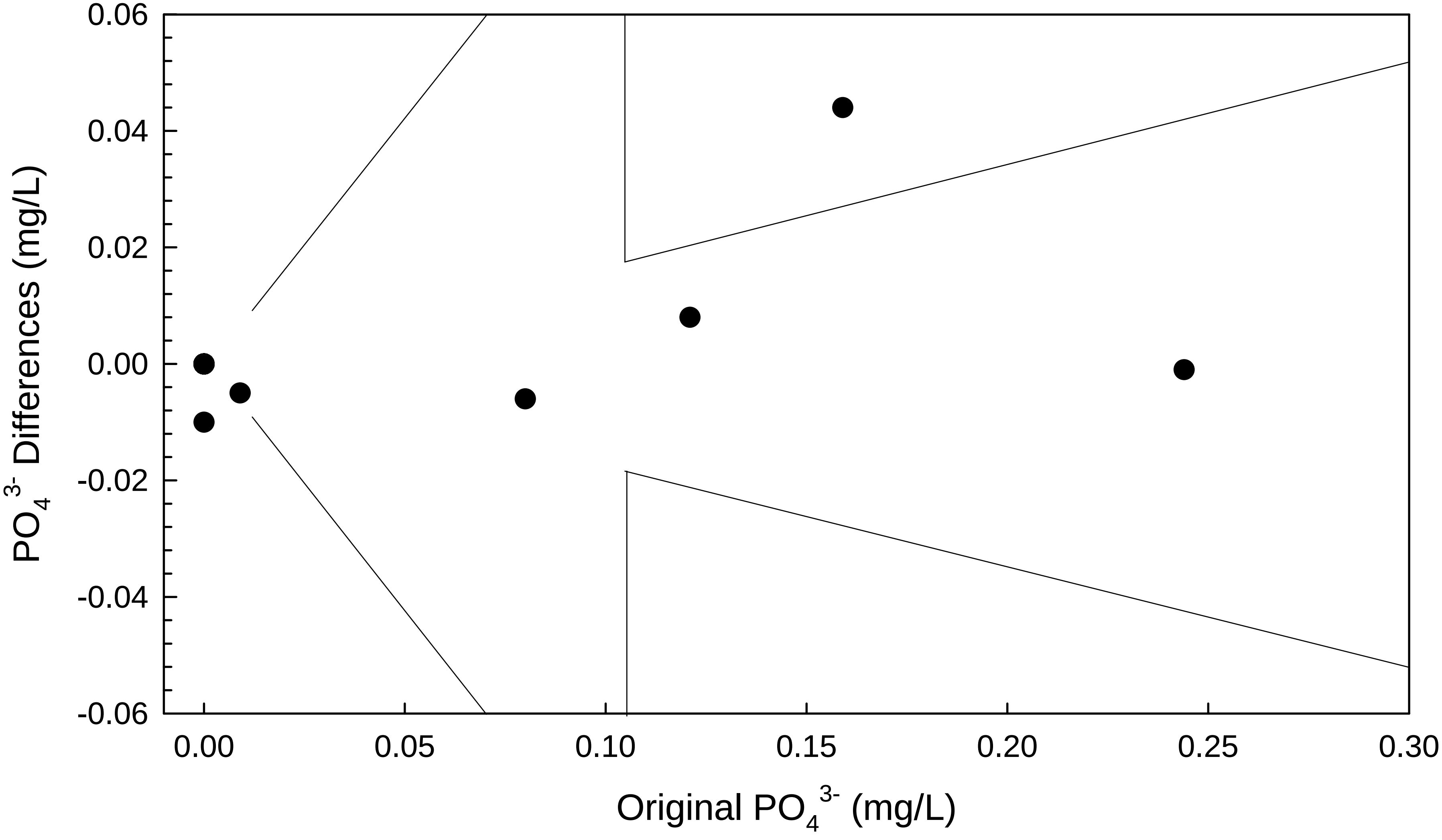


Figure B-66. NTN replicate sample differences (original - replicate) for orthophosphate, 2002.

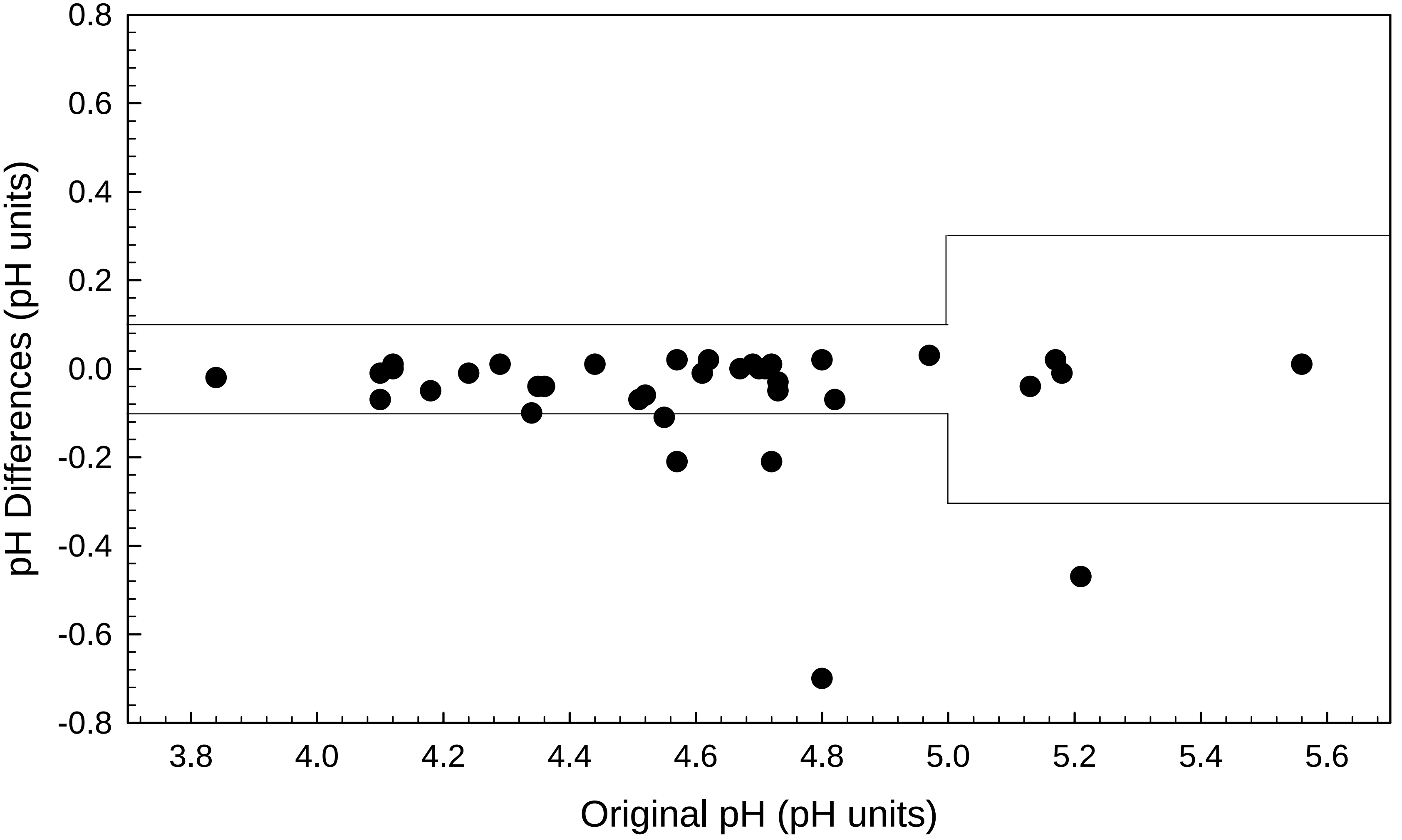


Figure B-67. AIRMoN replicate sample differences (original - replicate) for pH, 2002.

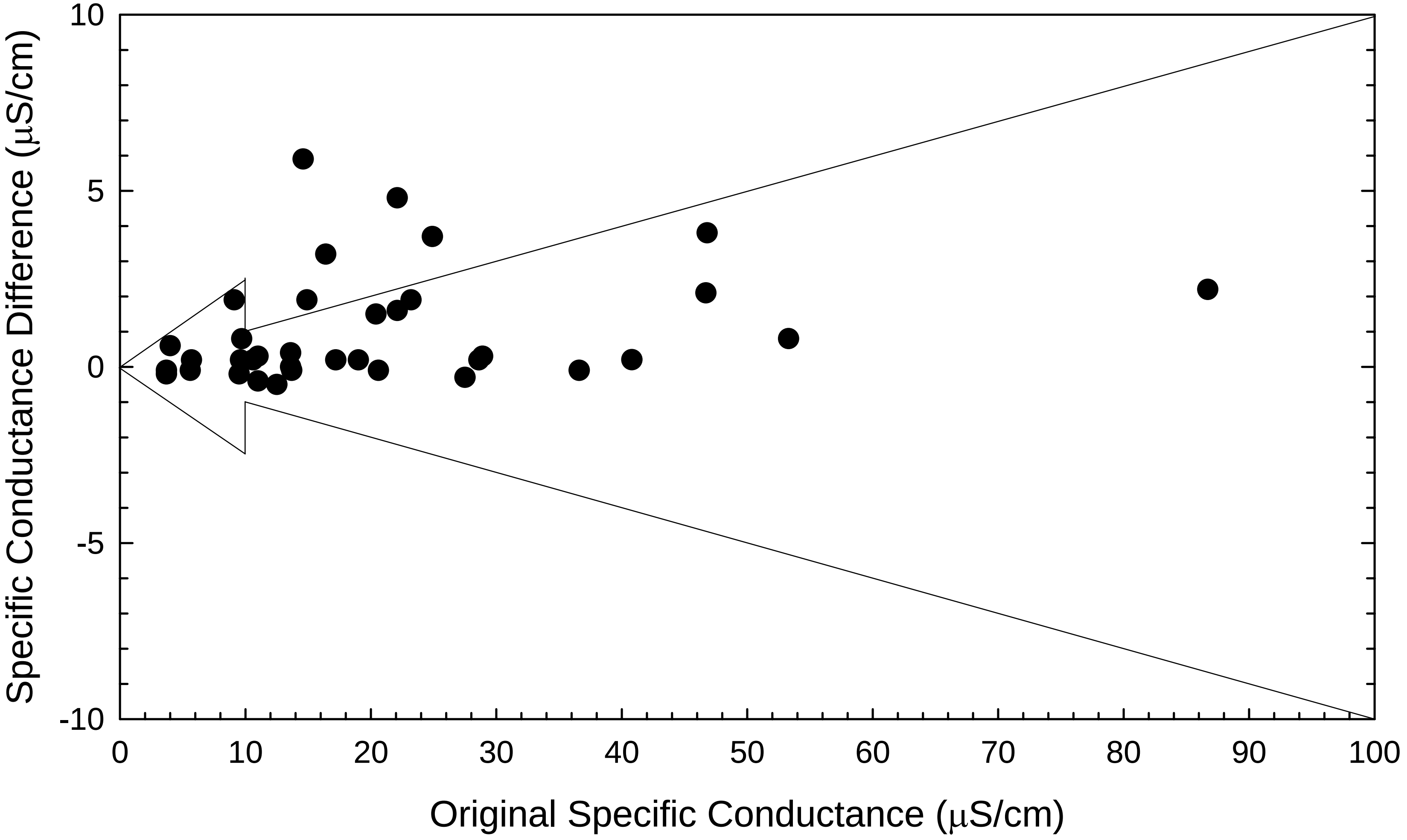


Figure B-68. AIRMoN replicate sample differences (original - replicate) for specific conductance, 2002.

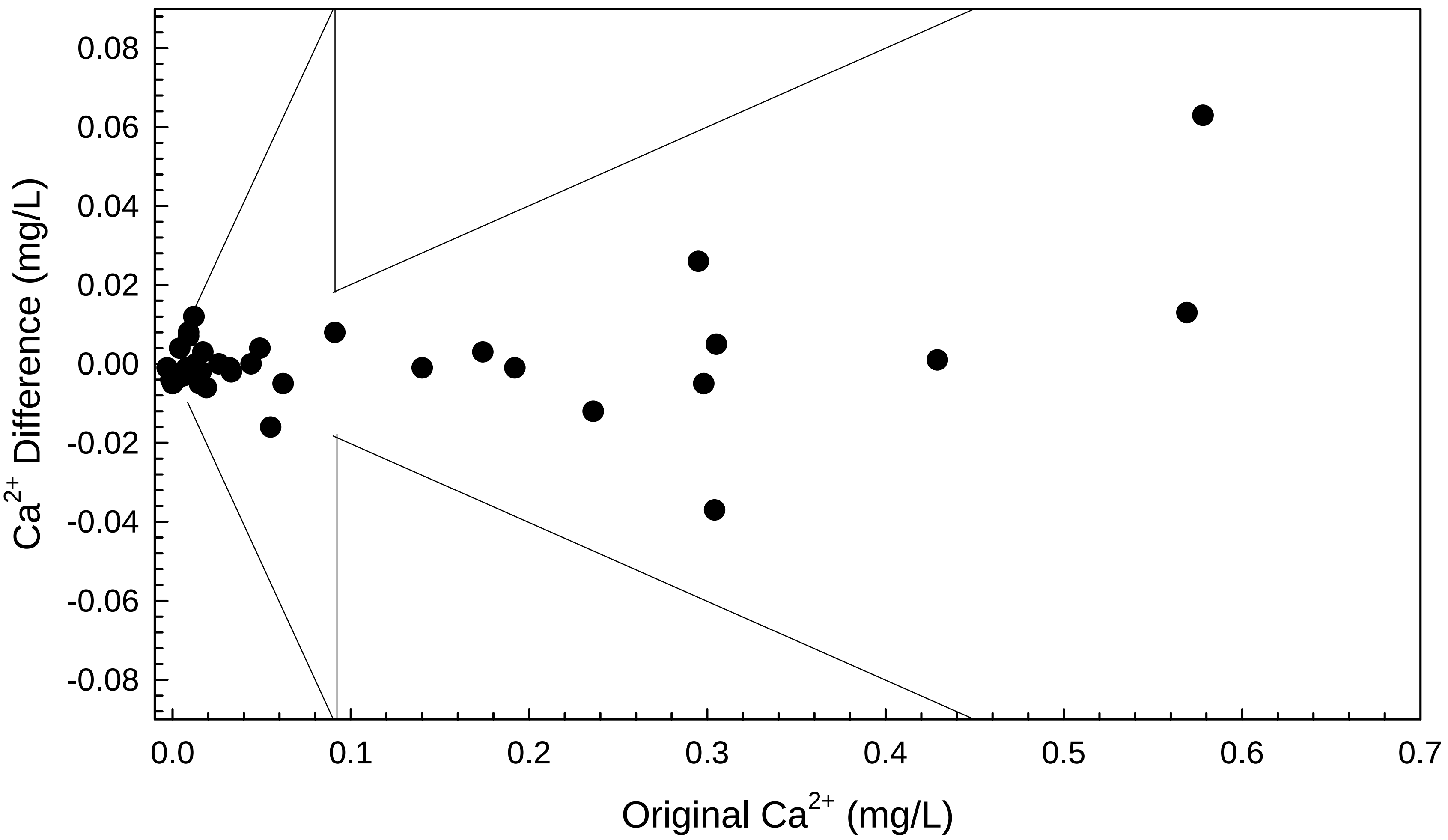


Figure B-69. AIRMoN replicate sample differences (original - replicate) for calcium, 2002.

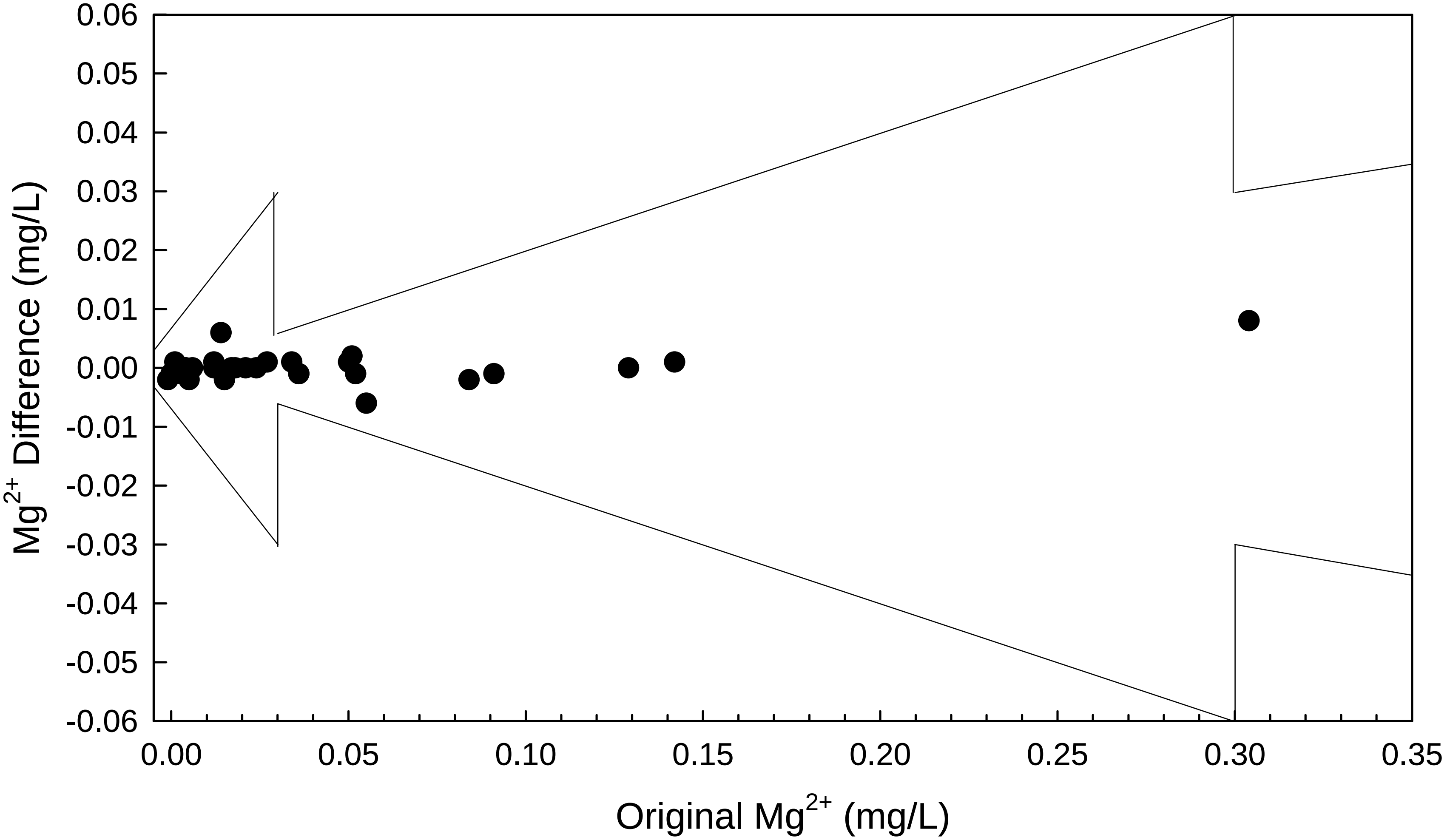


Figure B-70. AIRMoN replicate sample differences (original - replicate) for magnesium, 2002.

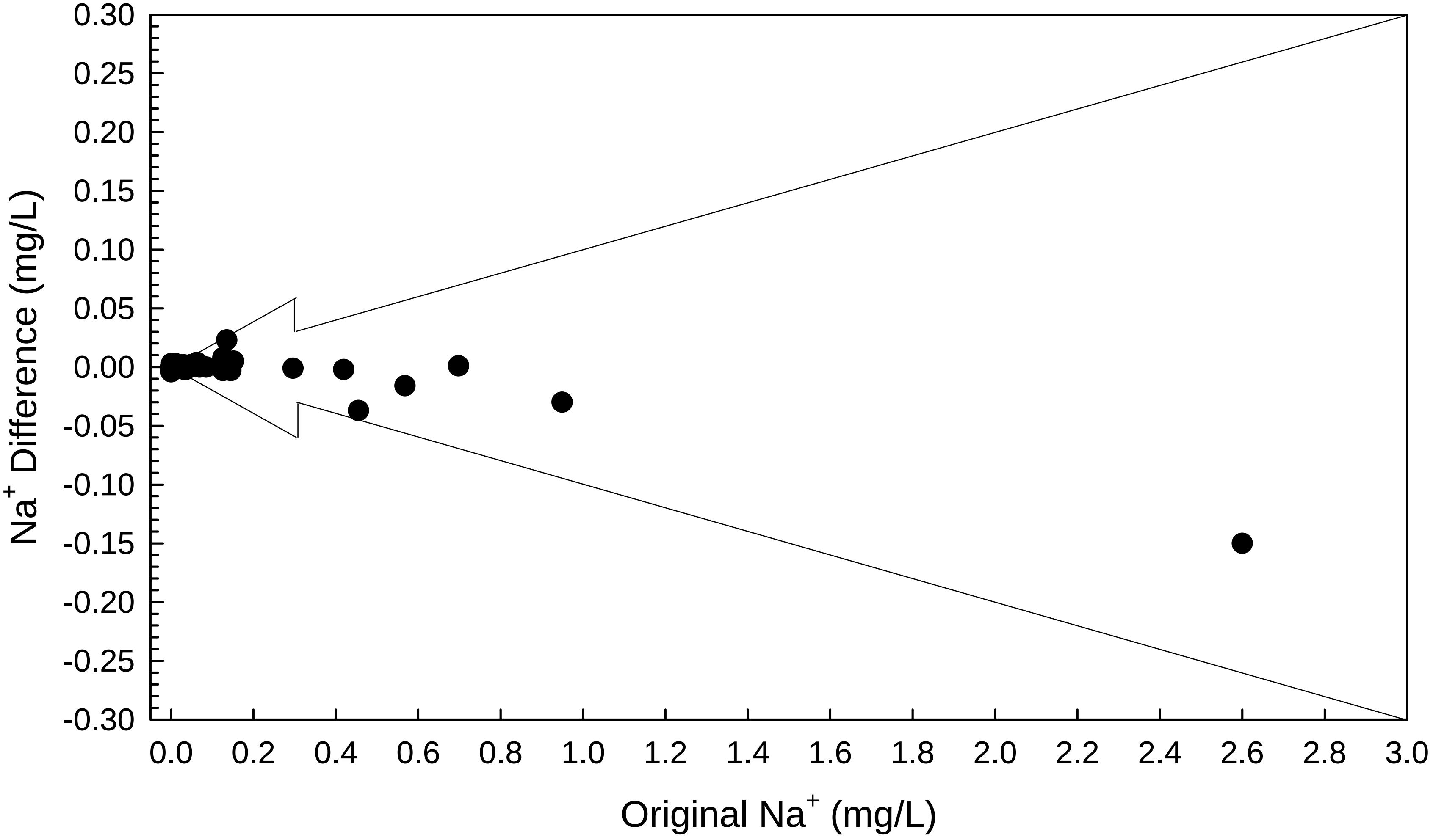


Figure B-71. AIRMoN replicate sample differences (original - replicate) for sodium, 2002.

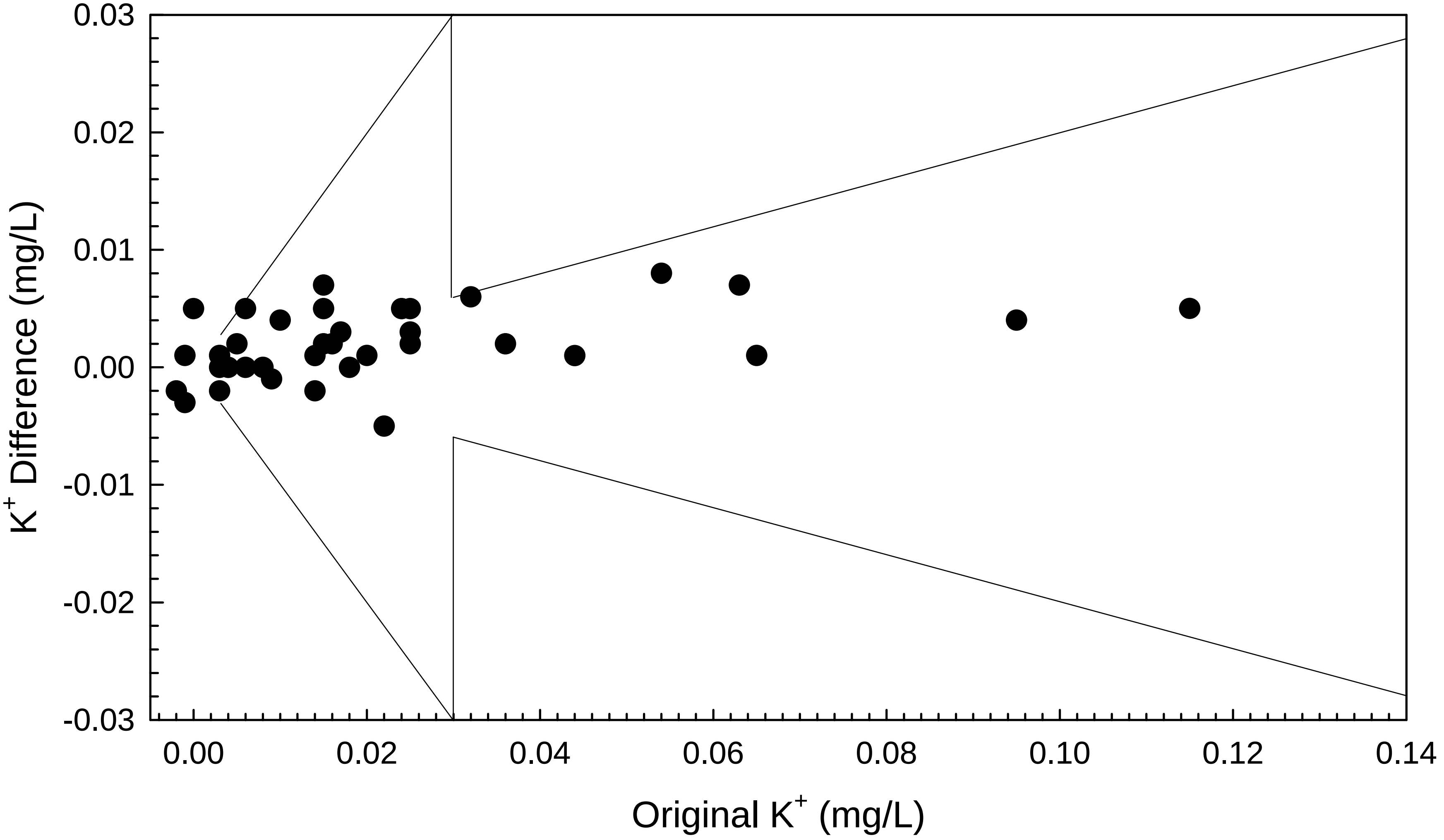


Figure B-72. AIRMoN replicate sample differences (original - replicate) for potassium, 2002.

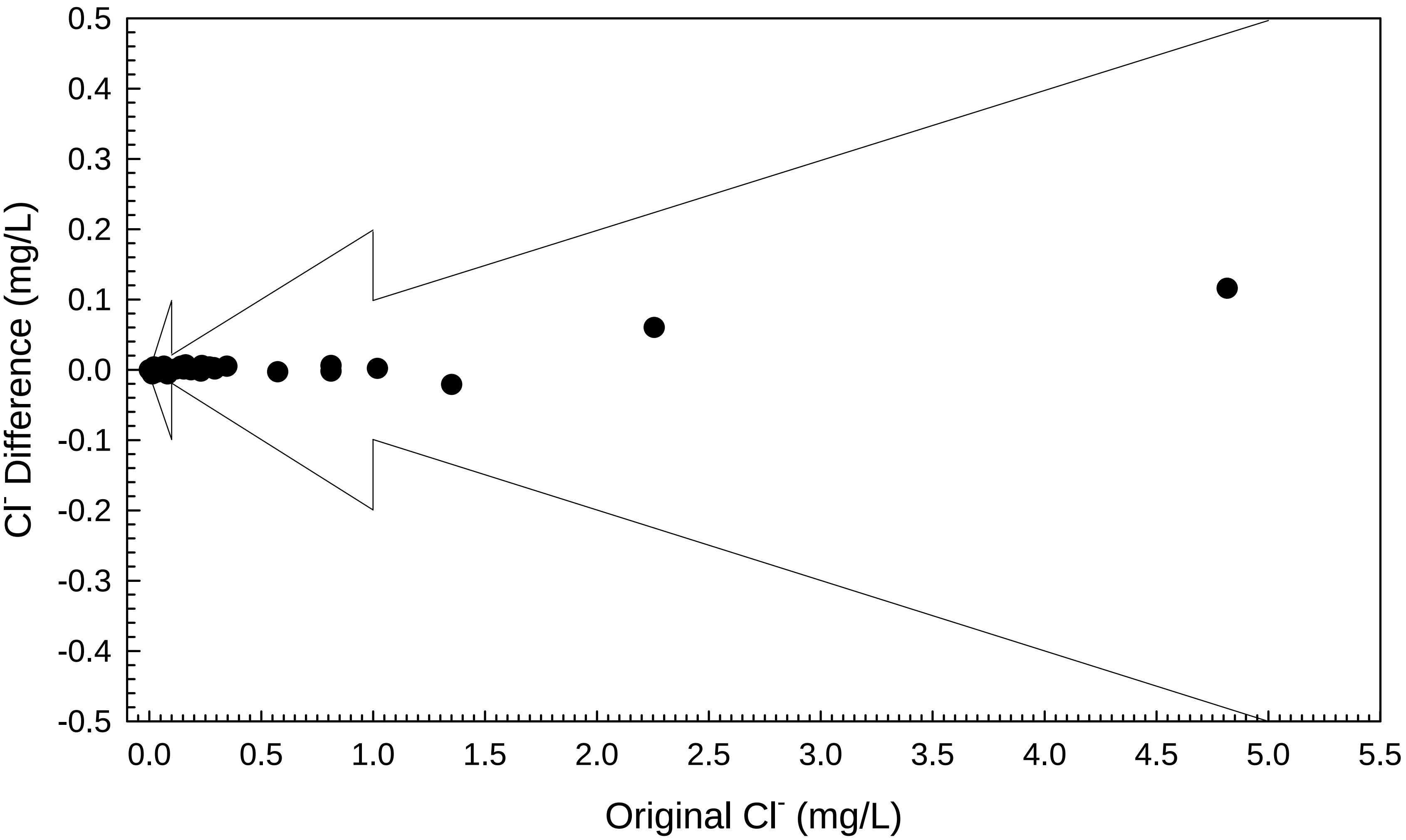


Figure B-73. AIRMoN replicate sample differences (original - replicate) for chloride, 2002.

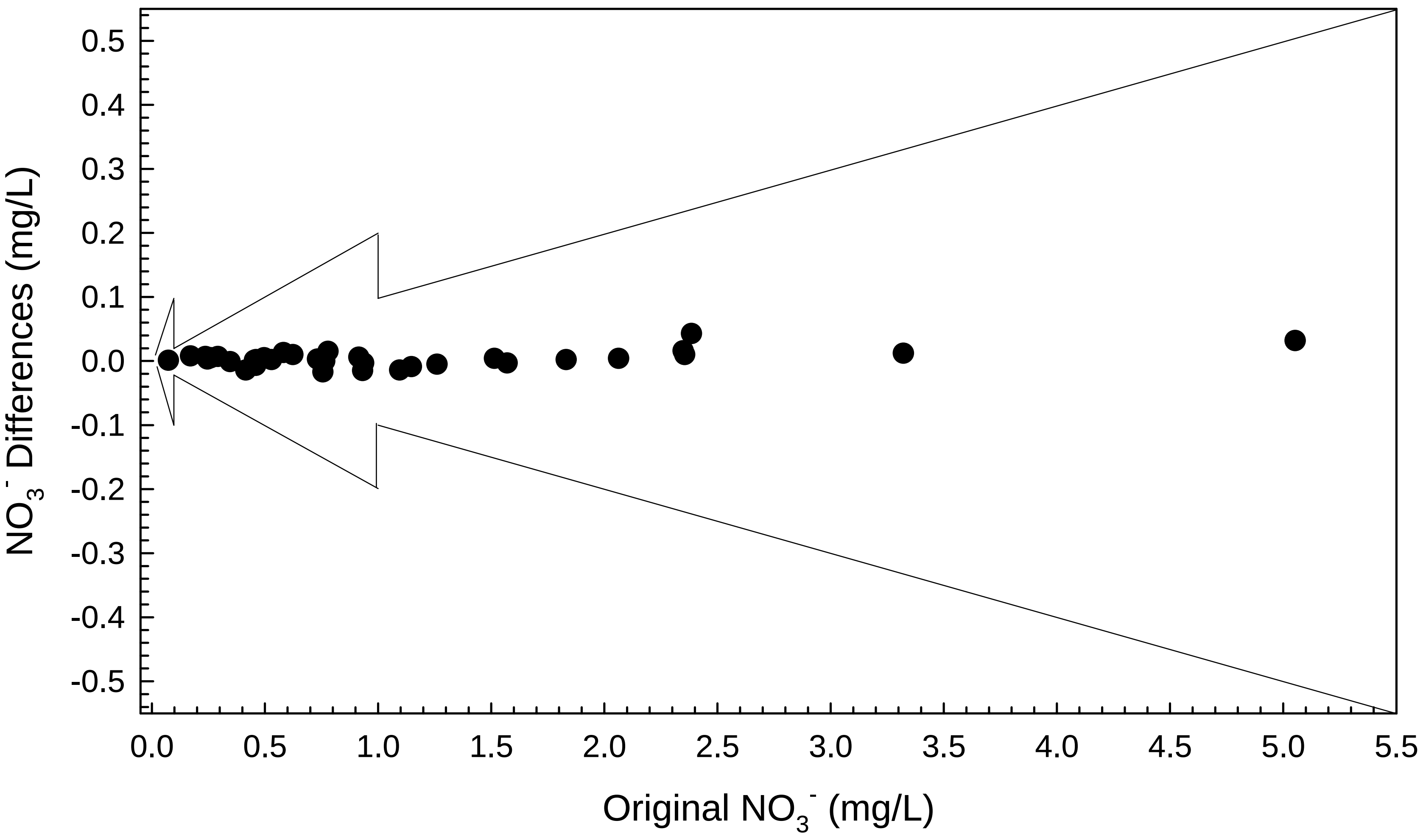


Figure B-74. AIRMoN replicate sample differences (original - replicate) for nitrate, 2002.

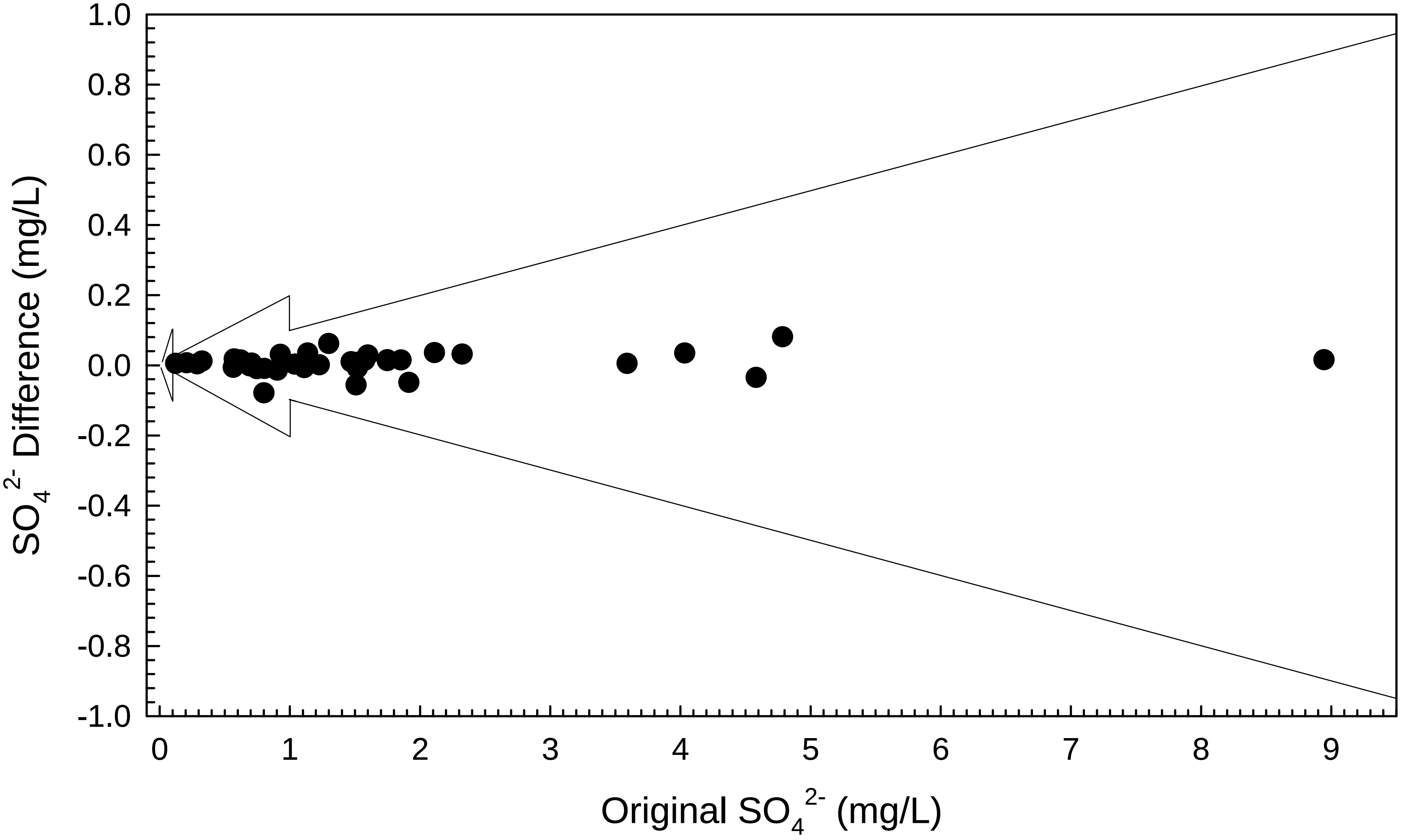


Figure B-75. AIRMoN replicate sample differences (original - replicate) for sulfate, 2002.

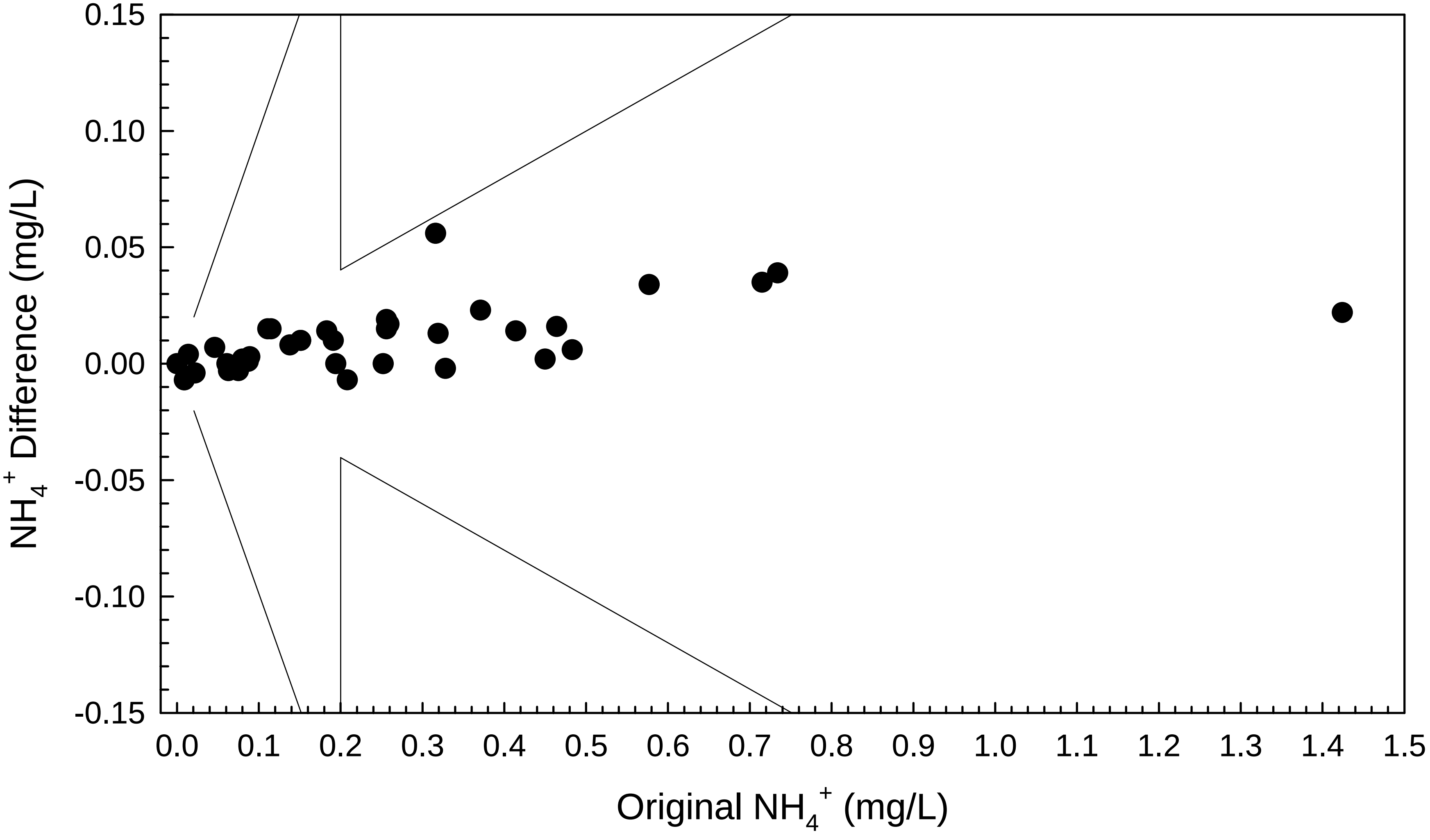


Figure B-76. AIRMoN replicate sample differences (original - replicate) for ammonium, 2002.

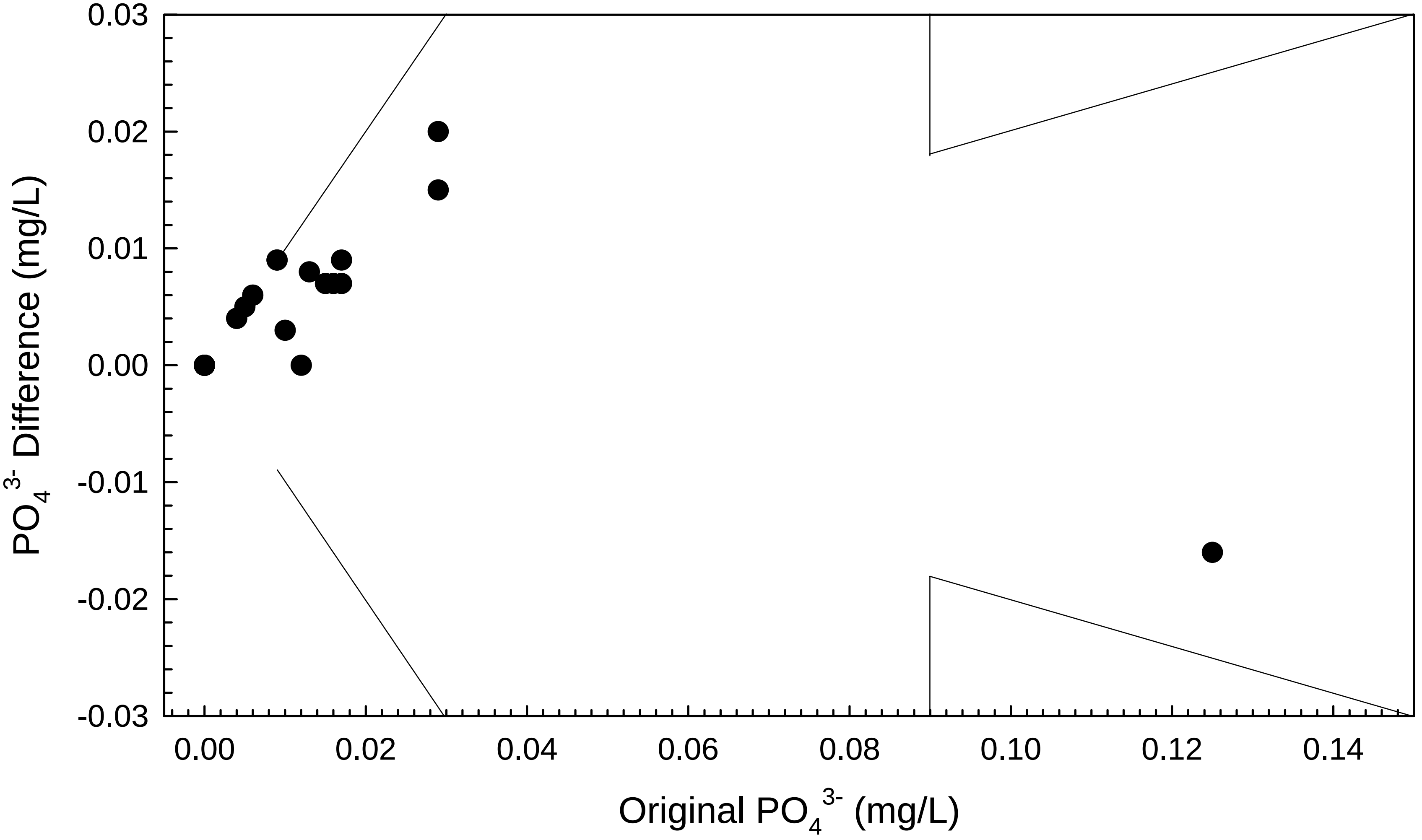


Figure B-77. AIRMoN replicate sample differences (original - replicate) for orthophosphate, 2002.

Table B-16. Percent of Ion Concentrations above MDL Found in Weekly Deionized (DI) Water Blanks and Leachates, 2002

Blank	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Ammonium*	*Orthophosphate*	*Chloride*	*Nitrate*	*Sulfate*
DI (Rm 209)	0.0	0.0	3.9	0.0	0.0	0.0	0.0	0.0	0.0
DI (Rm 304)	0.0	0.0	0.0	3.9	0.0	0.0	1.9	3.8	0.0
DI (Rm 323)	3.8	0.0	3.8	5.8	0.0	0.0	0.0	0.0	0.0
Filter	0.0	0.0	3.8	3.8	1.9	0.0	15.4	1.9	0.0
Bucket - 50 mL	3.8	1.0	11.5	17.3	97.1	0.0	55.8	34.6	1.0
Bucket - 150 mL	5.8	1.9	5.8	9.6	57.7	0.0	13.5	11.5	0.0
Bottle - 50 mL	1.9	0.0	3.8	15.4	0.0	0.0	0.0	0.0	0.0
Bottle - 150 mL	0.0	0.0	5.8	3.8	0.0	0.0	1.9	0.0	1.9
Lid - 50 mL	1.9	0.0	9.6	9.6	11.5	0.0	9.6	0.0	0.0
Bag - 50 mL	7.8	0.0	23.5	21.6	92.2	78.4	78.4	2.0	9.8

Note:
There were 52 weeks of blank samples and 104 50-mL bucket blanks.

Table B-17. Percent of Ion Concentrations Above and Below Control Limits Found in Weekly Simulated Rain (FR25) Leachates, 2002

Blank	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Ammonium*	*Orthophosphate*	*Chloride*	*Nitrate*	*Sulfate*
Filter	0.0[a]	53.8	1.9	1.9	15.4	0.0	9.6	48.1	61.5
	13.5[b]	0.0	0.0	0.0	9.6	0.0	1.9	1.9	0.0
Bucket - 50 mL	13.5	3.8	0.0	5.8	0.0	0.0	0.0	13.5	52.9
	5.8	5.8	9.6	3.8	98.0	0.0	59.6	50.0	21.6
Bucket - 150 mL	0.0	0.0	0.0	1.9	1.9	0.0	1.9	0.0	36.5
	3.8	1.9	0.0	3.8	86.5	1.9	26.9	30.8	1.9
Bottle - 50 mL	3.8	0.0	0.0	11.5	61.5	0.0	13.5	36.5	28.8
	1.9	7.7	3.8	11.5	3.8	1.9	0.0	5.8	0.0
Bottle - 150 mL	3.8	0.0	0.0	0.0	38.5	0.0	5.8	7.7	11.5
	1.9	3.8	1.9	1.9	3.8	0.0	0.0	9.6	0.0
Lid - 50 mL	0.0	0.0	0.0	0.0	2.0	0.0	0.0	3.8	3.8
	9.6	1.9	3.8	3.8	72.0	0.0	7.7	38.5	3.8
Bag - 50 mL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.9
	2.0	5.9	3.9	5.9	100.0	60.8	90.2	58.8	13.7
AIRMoN Bottle - 50 mL	0.0	0.0	0.0	0.0	8.3	0.0	8.3	0.0	8.3
	0.0	0.0	0.0	0.0	25.0	0.0	0.0	0.0	0.0
AIRMoN Bottle - 150 mL	0.0	0.0	0.0	0.0	8.3	0.0	0.0	0.0	0.0
	8.3	0.0	0.0	0.0	16.7	0.0	0.0	25.0	0.0

Note:
Fifty-two NTN matrix spikes were analyzed, 12 monthly AIRMoN matrix spikes were analyzed, and 51 bag matrix spikes 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.

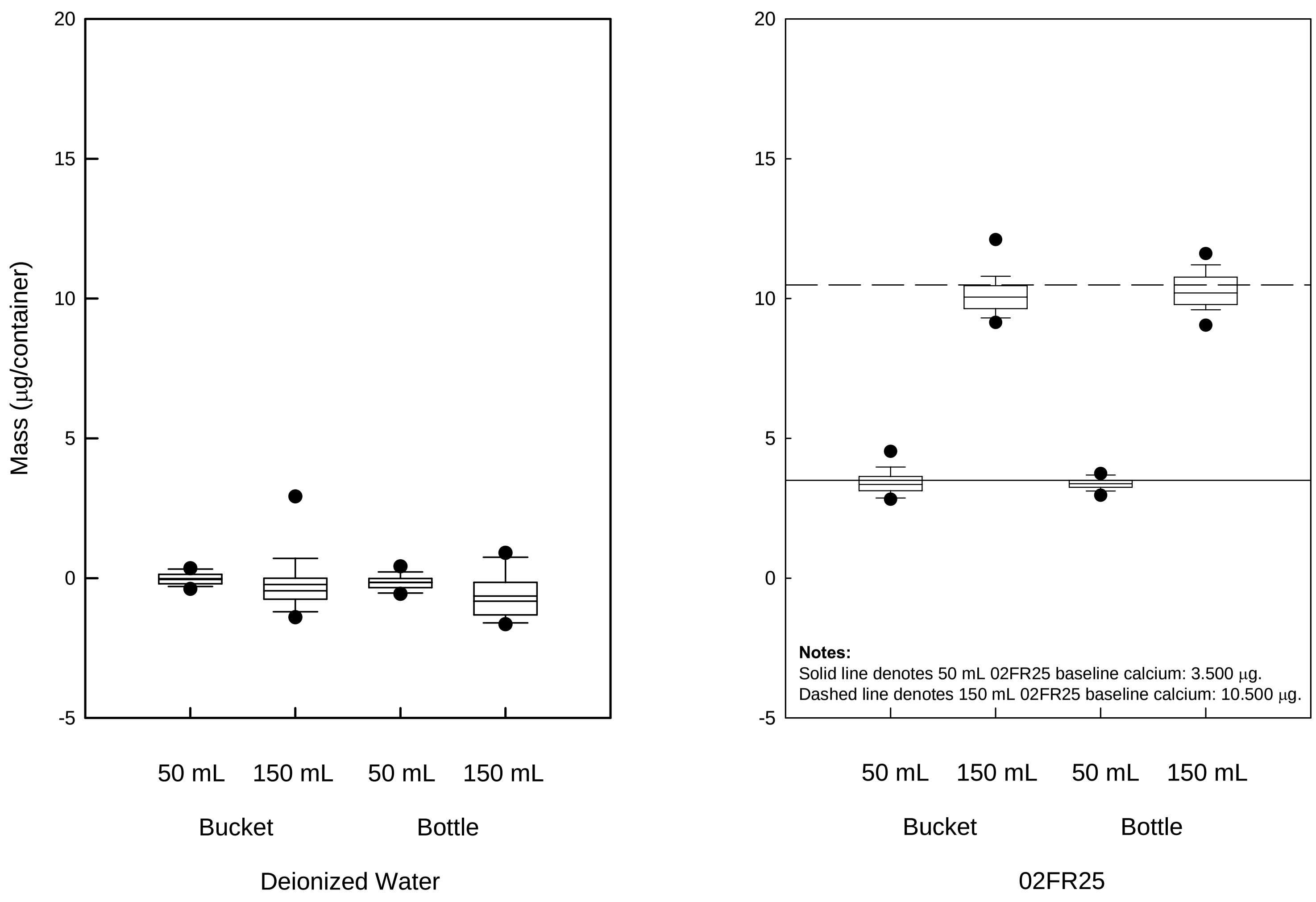
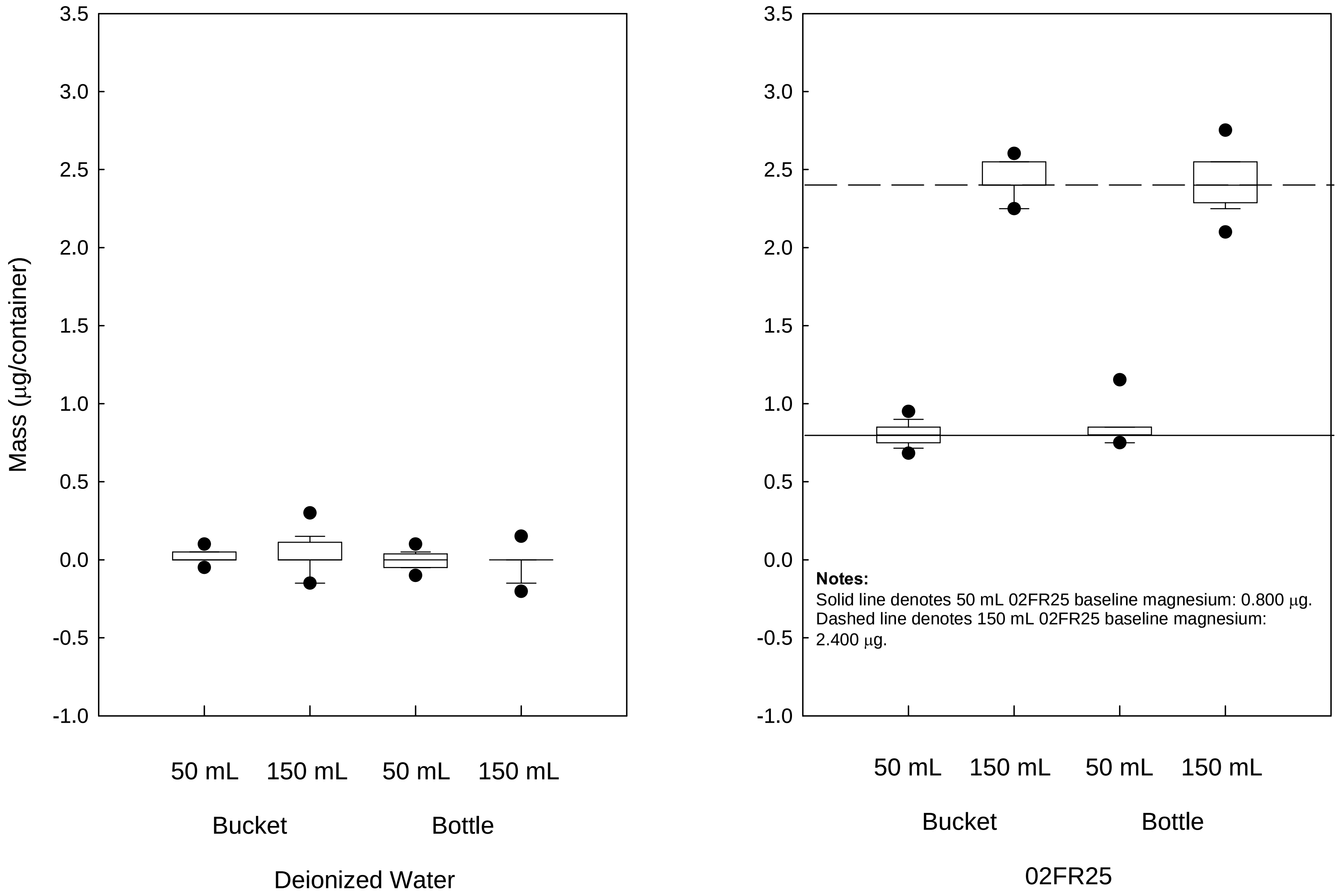


Figure B-78. Calcium found in upright bucket and 1-L NTN bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2002.



Notes:
Solid line denotes 50 mL 02FR25 baseline magnesium: 0.800 µg.
Dashed line denotes 150 mL 02FR25 baseline magnesium: 2.400 µg.

Figure B-79. Magnesium found in upright bucket and 1-L NTN bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2002.

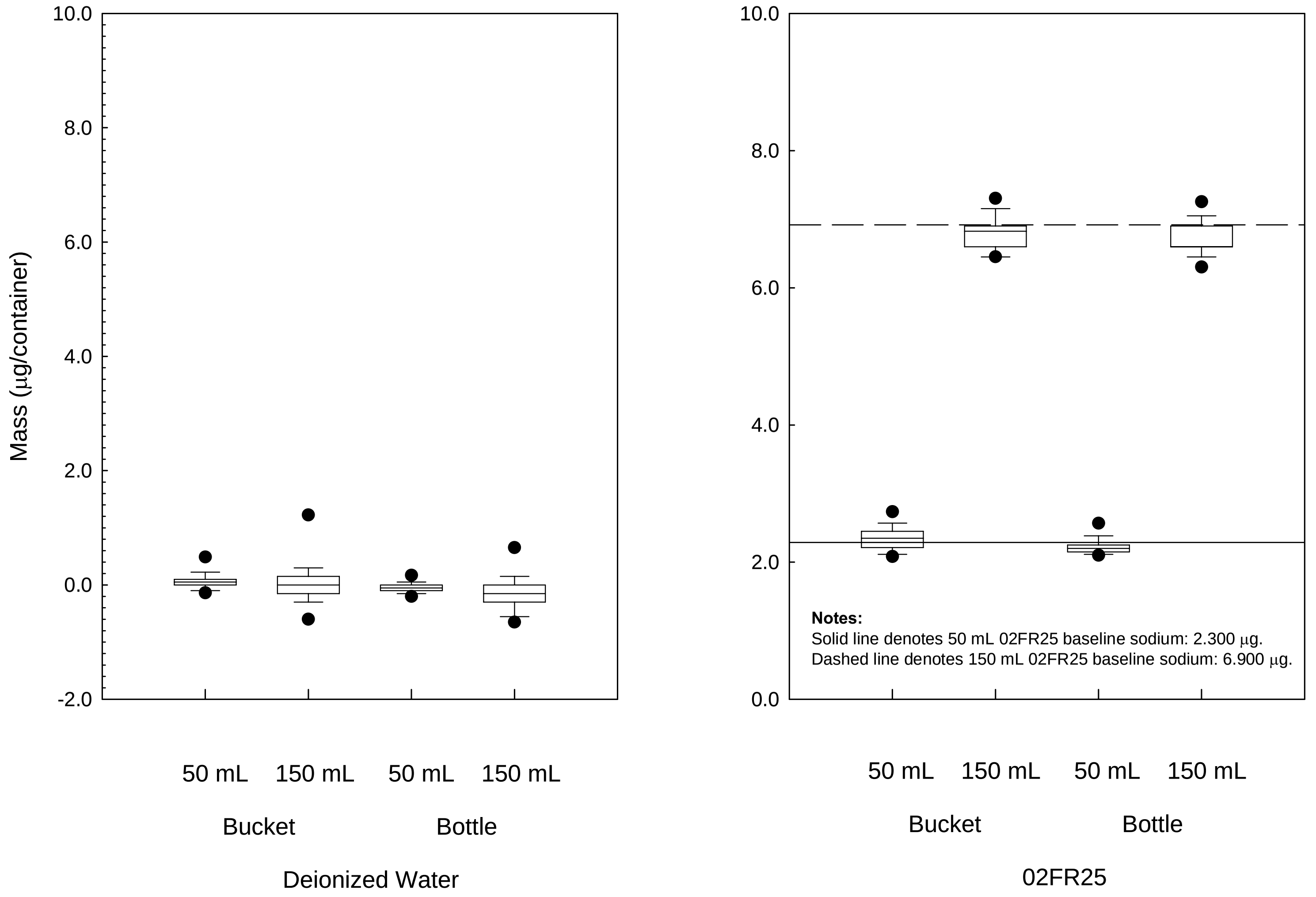
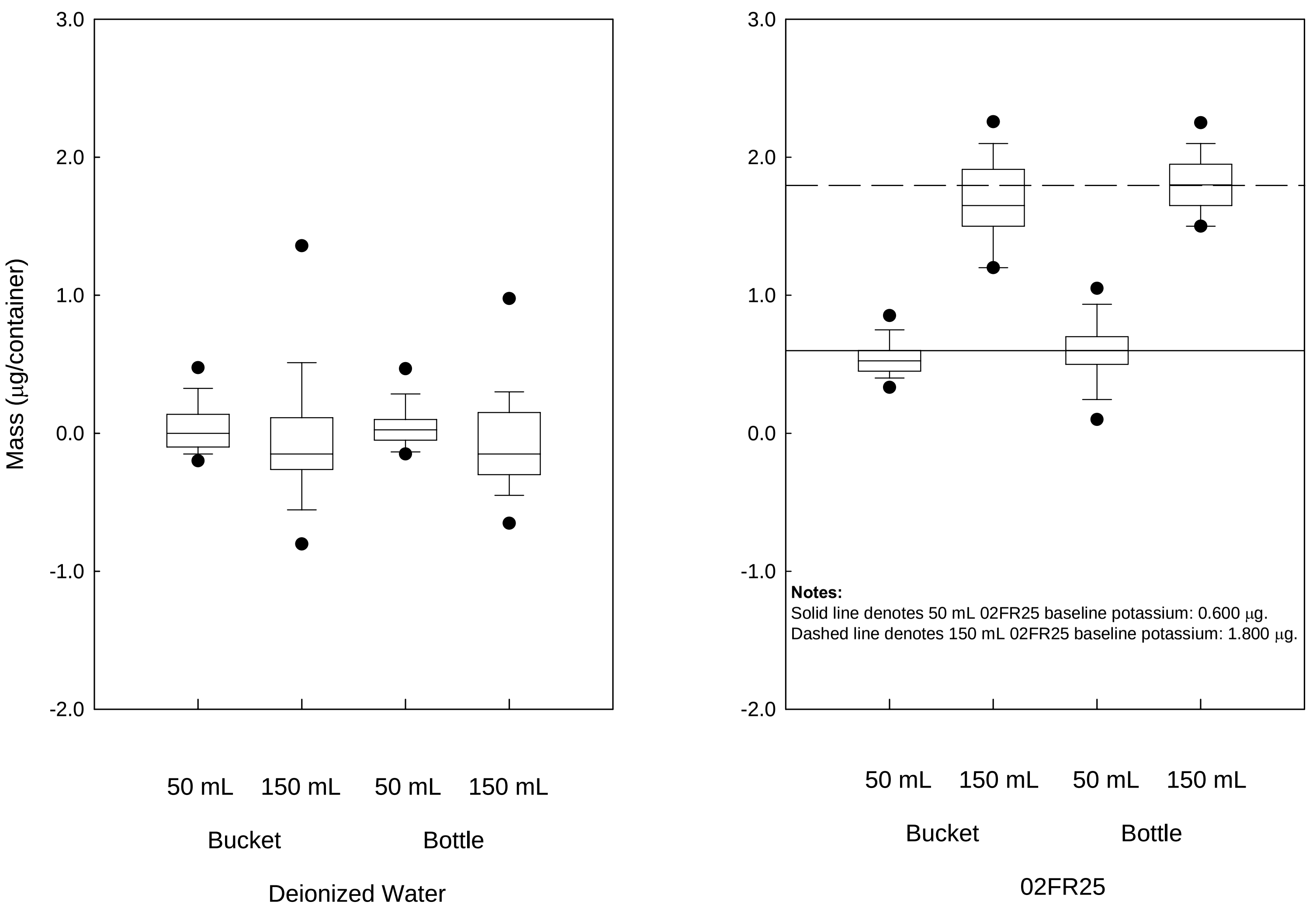


Figure B-80. Sodium found in upright bucket and 1-L NTN bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2002.



Notes:
Solid line denotes 50 mL 02FR25 baseline potassium: 0.600 µg.
Dashed line denotes 150 mL 02FR25 baseline potassium: 1.800 µg.

Figure B-81. Potassium found in upright bucket and 1-L NTN bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2002.

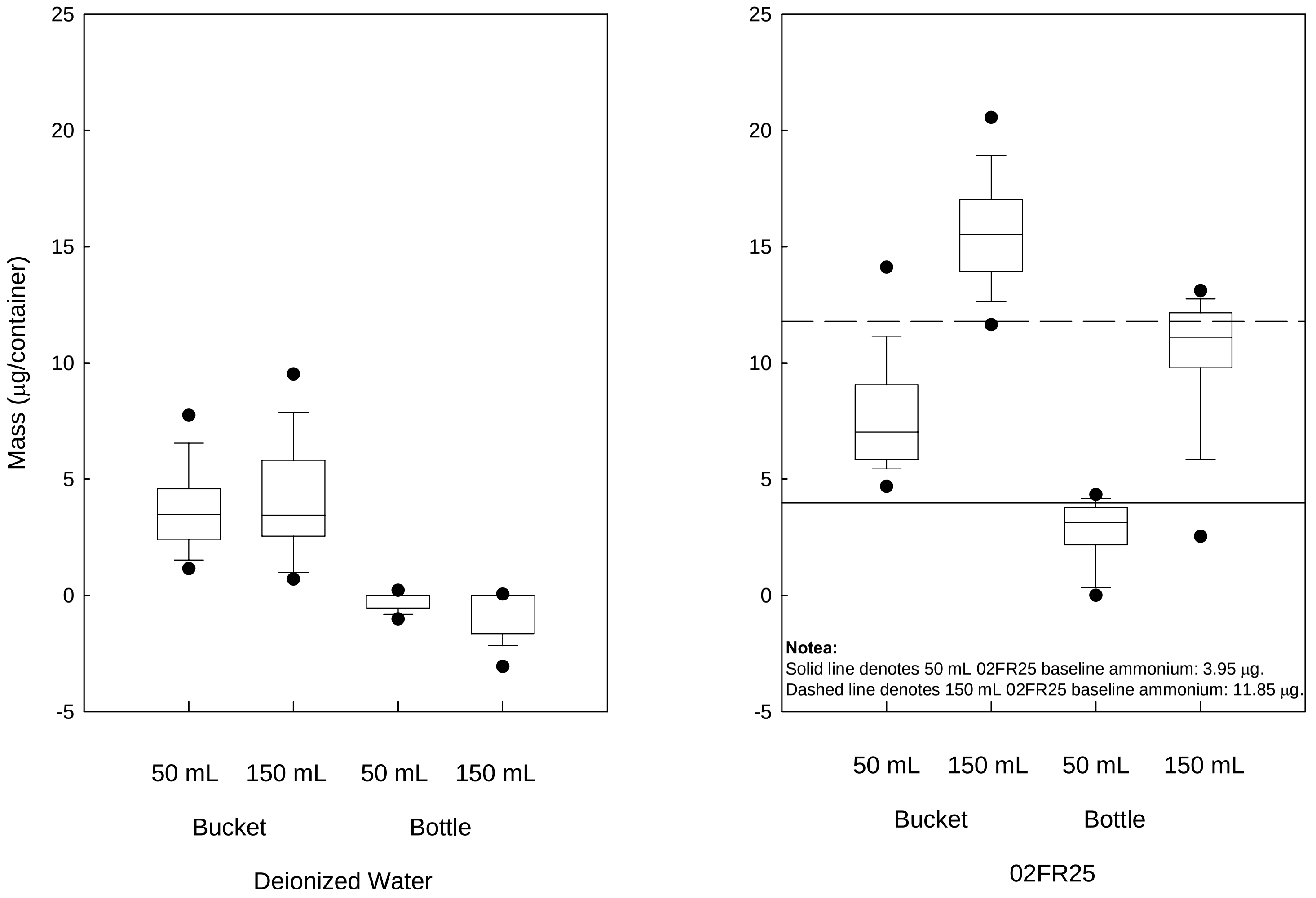


Figure B-82. Ammonium found in upright bucket and 1-L NTN bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2002.

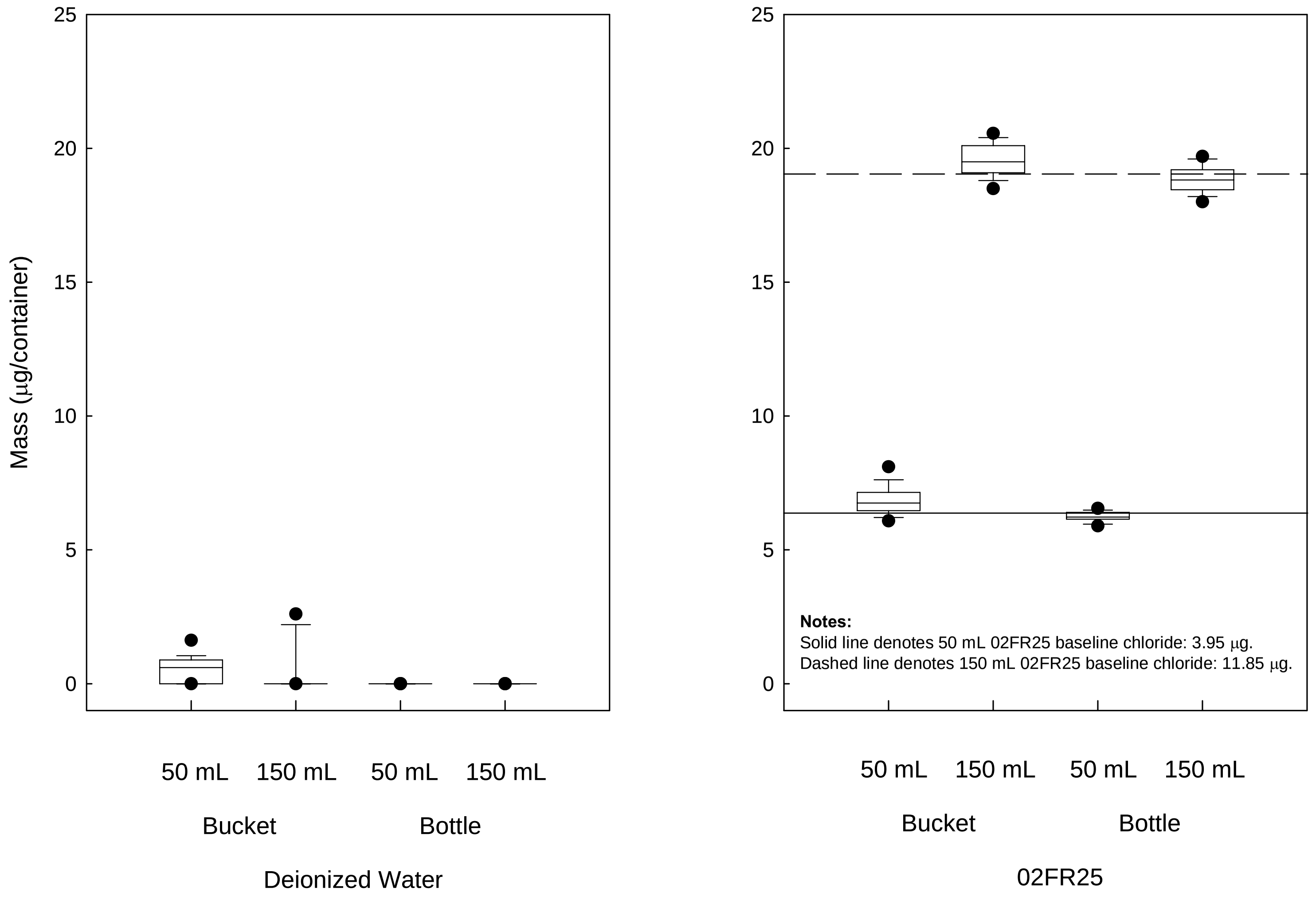


Figure B-83. Chloride found in upright bucket and 1-L NTN bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2002.

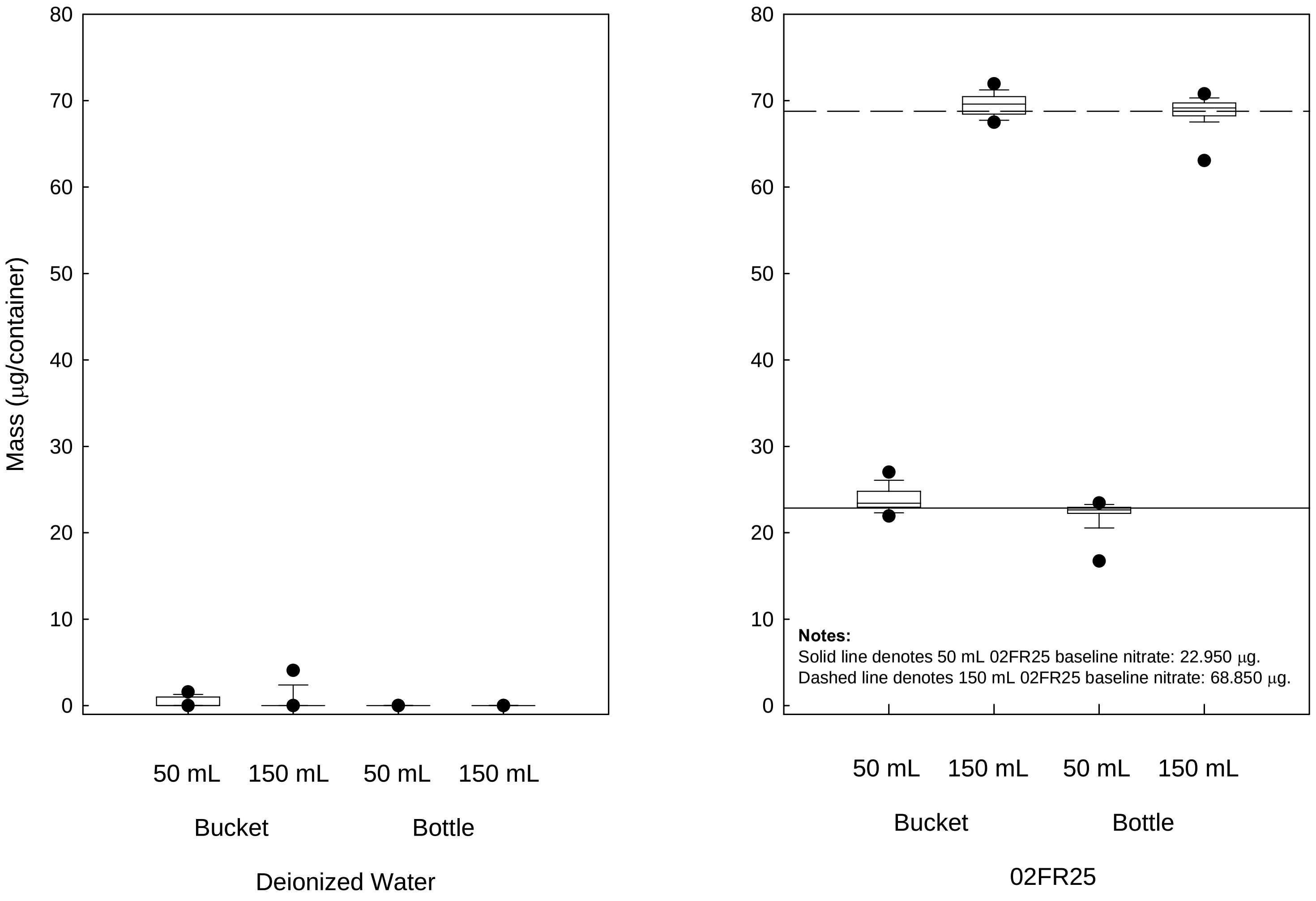


Figure B-84. Nitrate found in upright bucket and 1-L NTN bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2002.

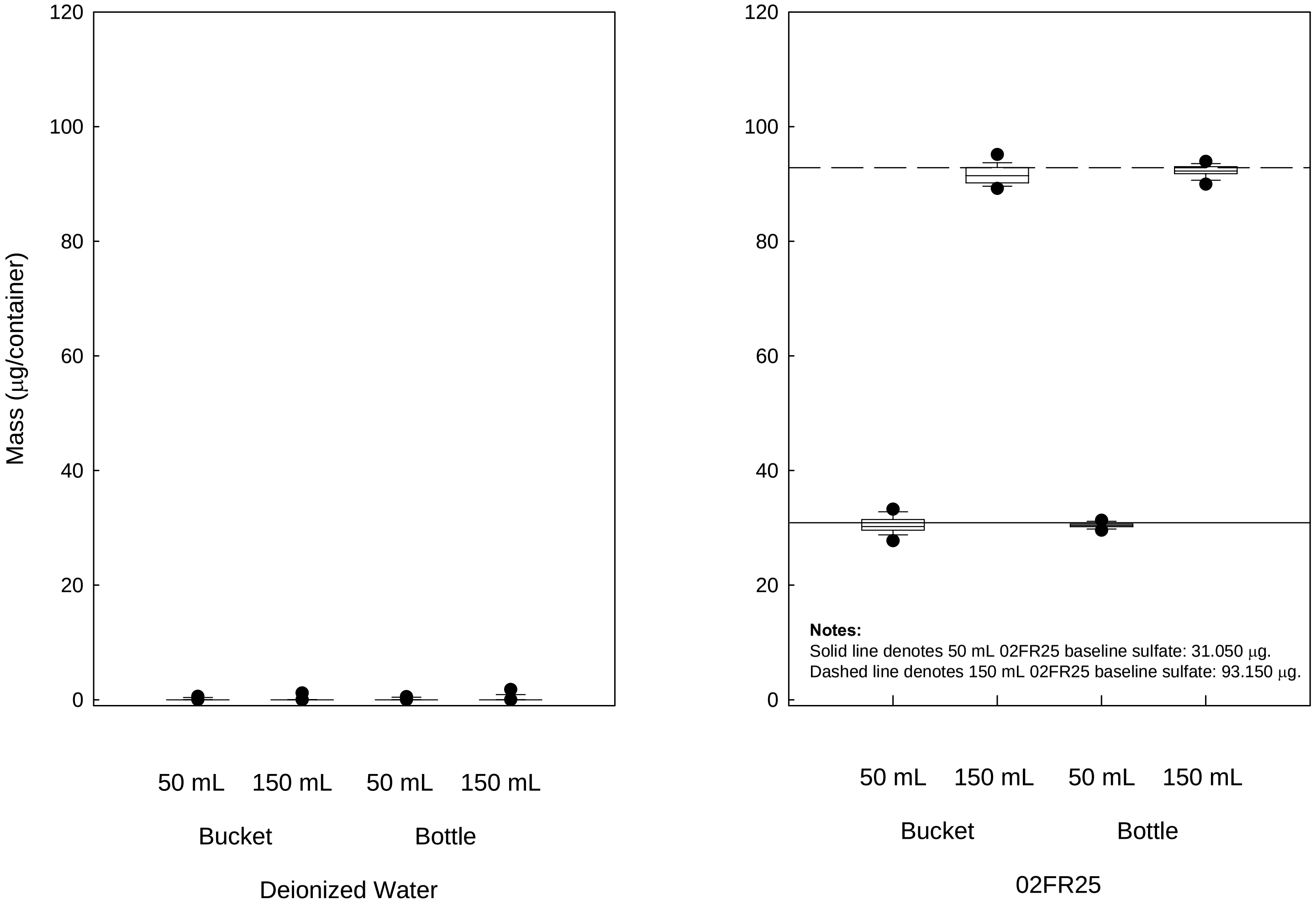


Figure B-85. Sulfate found in upright bucket and 1-L NTN bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2002.

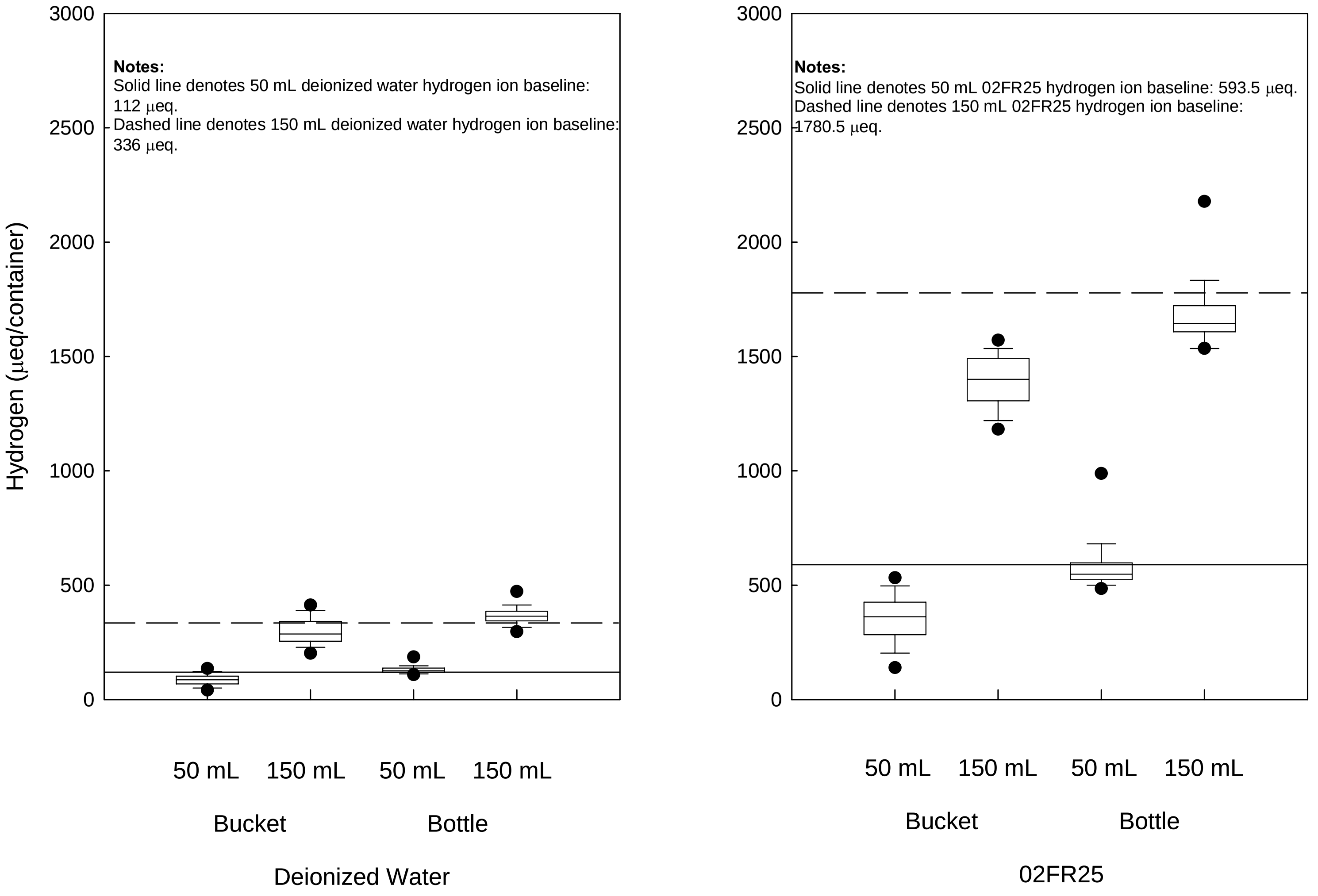


Figure B-86. Hydrogen ion found in upright bucket and 1-L NTN bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2002.

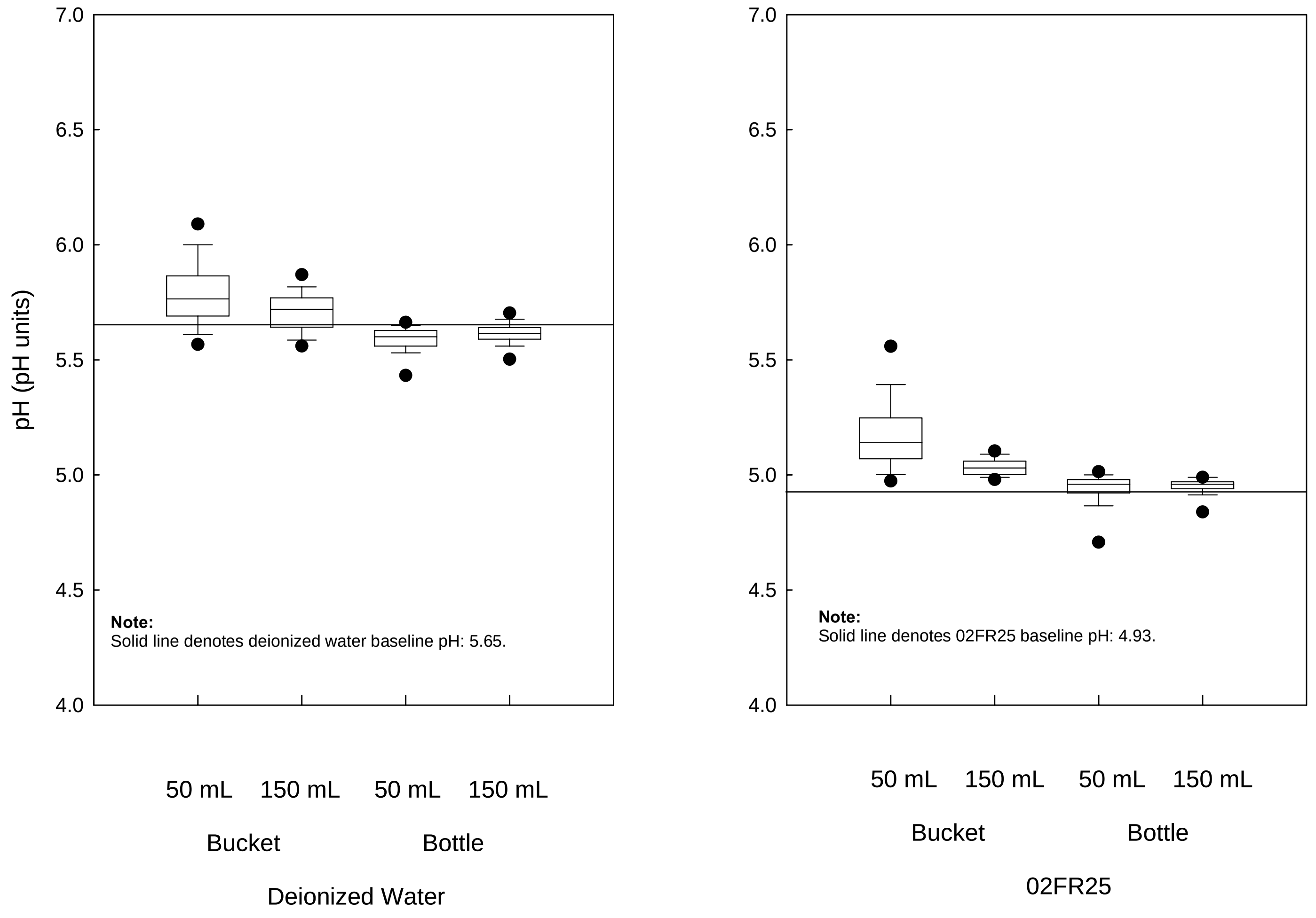
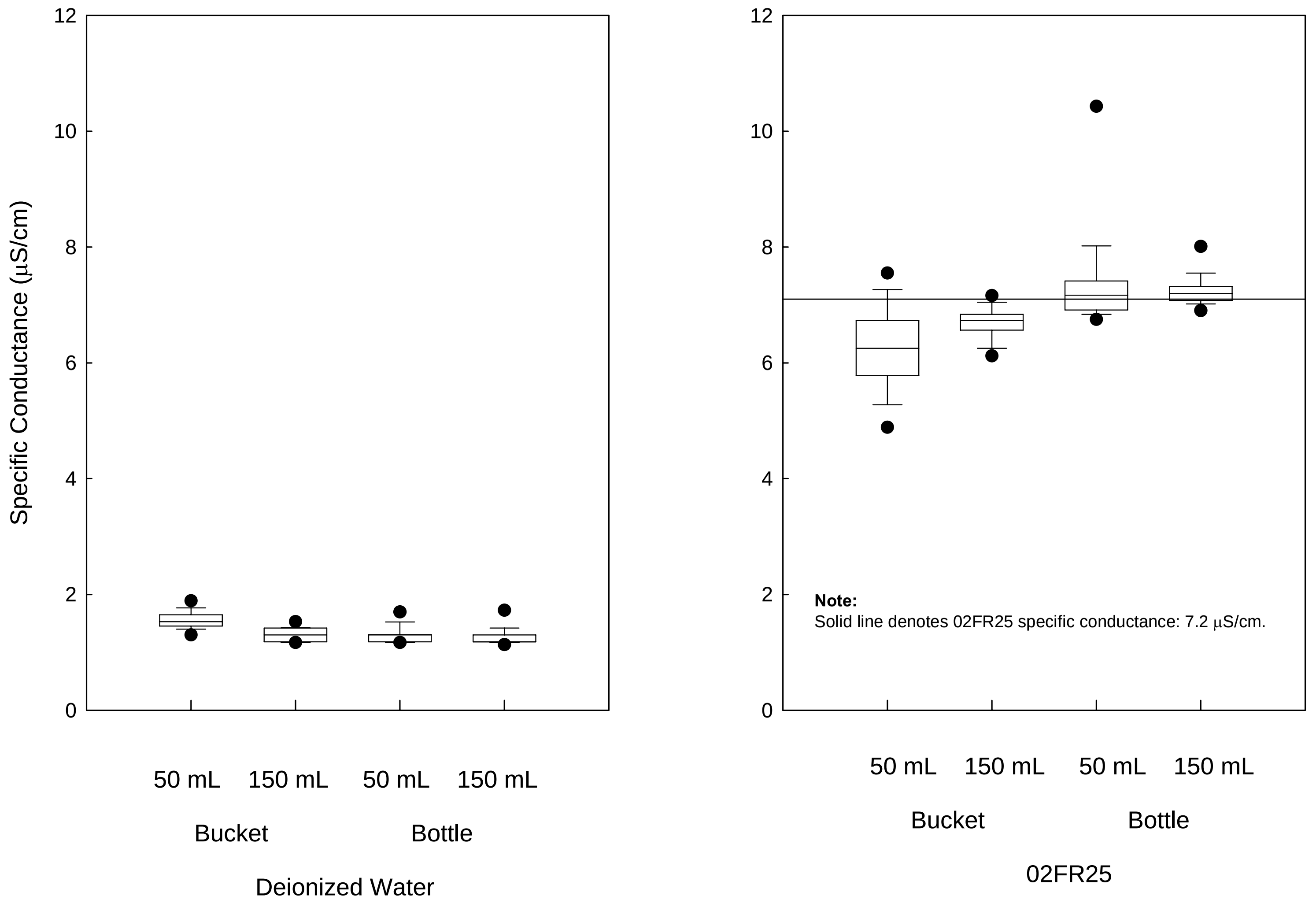


Figure B-87. pH found in upright bucket and 1-L NTN bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2002.



Note:
Solid line denotes 02FR25 specific conductance: 7.2 μS/cm.

Figure B-88. Specific conductance found in upright bucket and 1-L NTN bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2002.

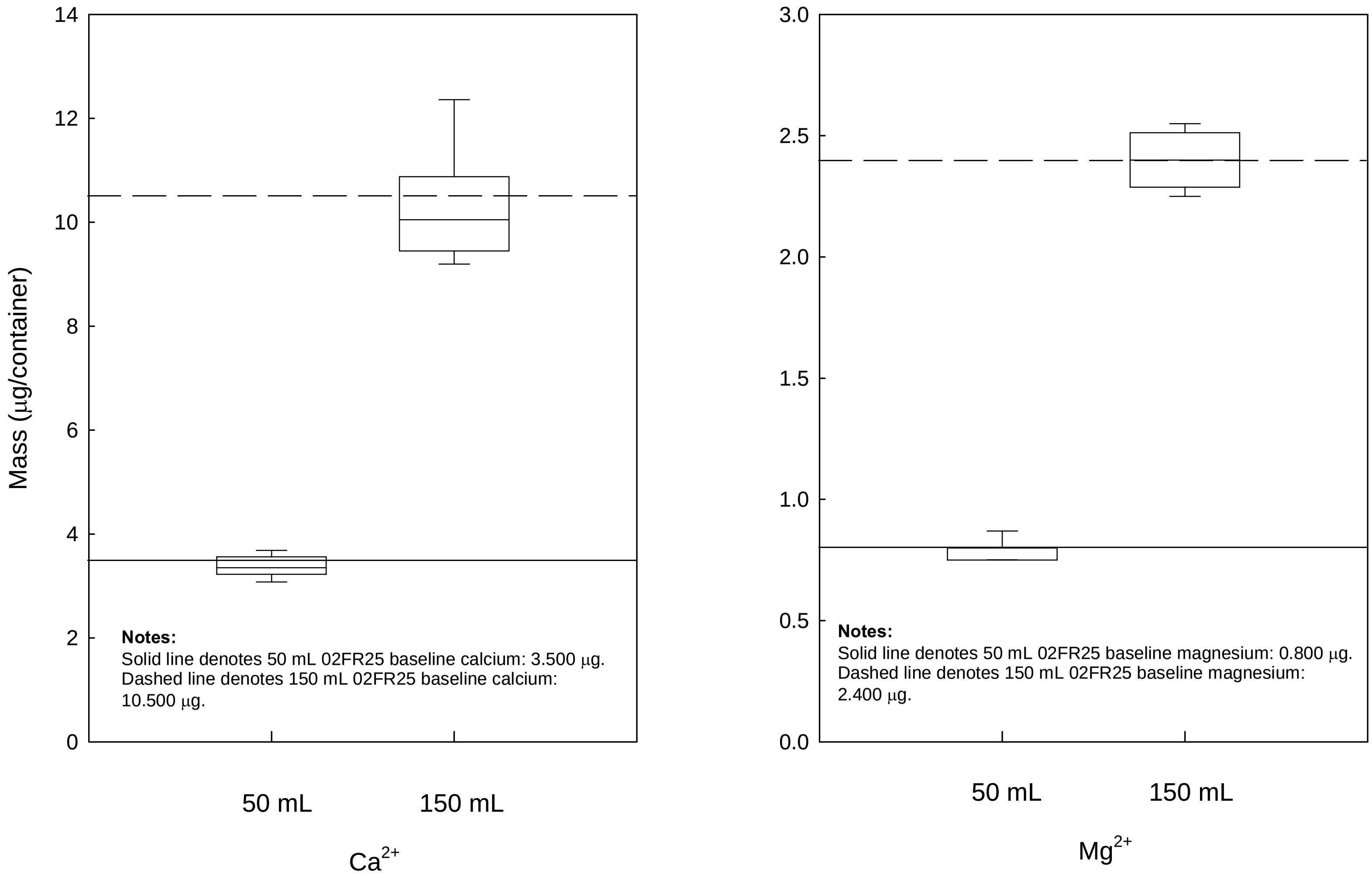


Figure B-89. Calcium and magnesium found in AIRMoN bottle synthetic rain solutions used as leaching agents, 2002.

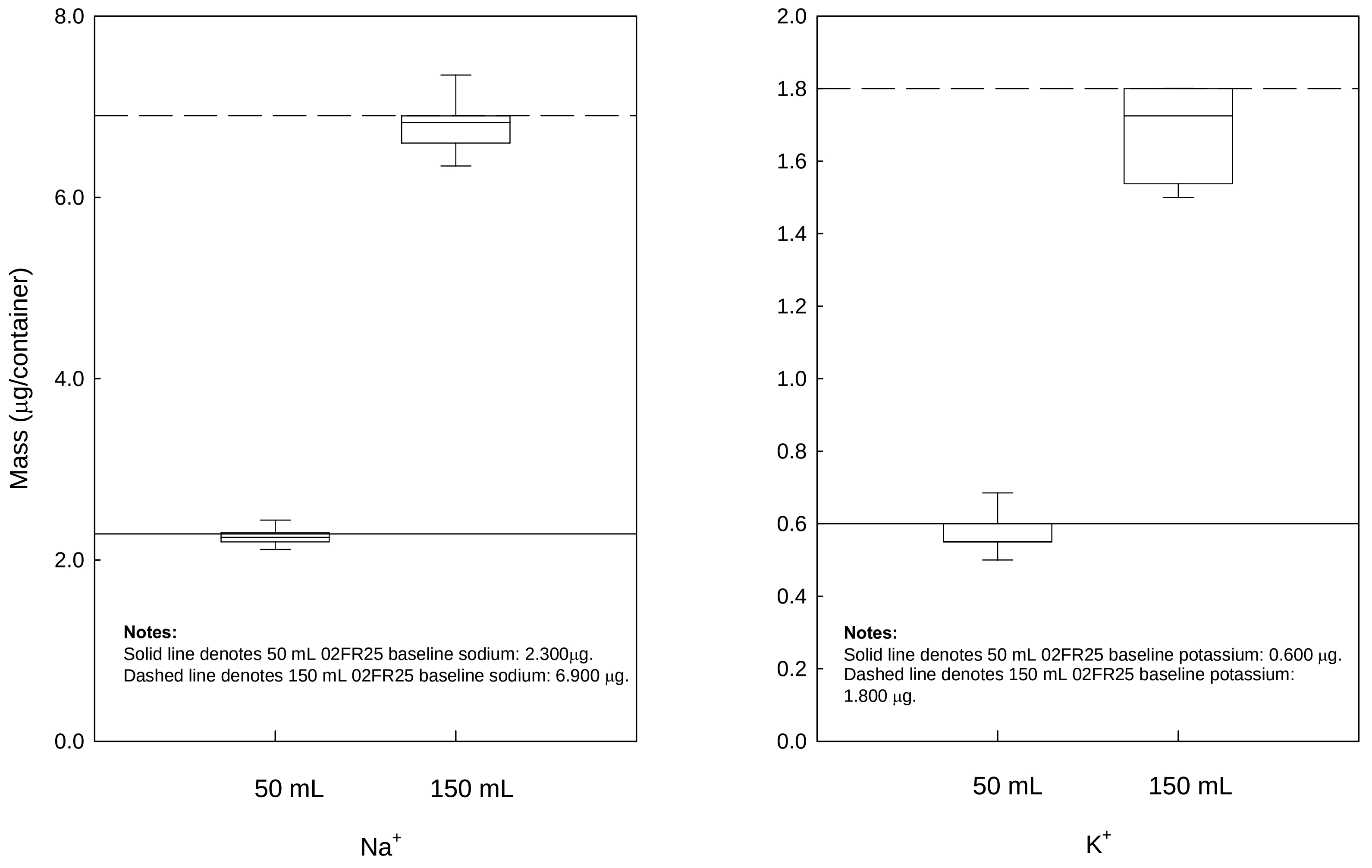


Figure B-90. Sodium and potassium found in AIRMoN bottle synthetic rain solutions used as leaching agents, 2002.

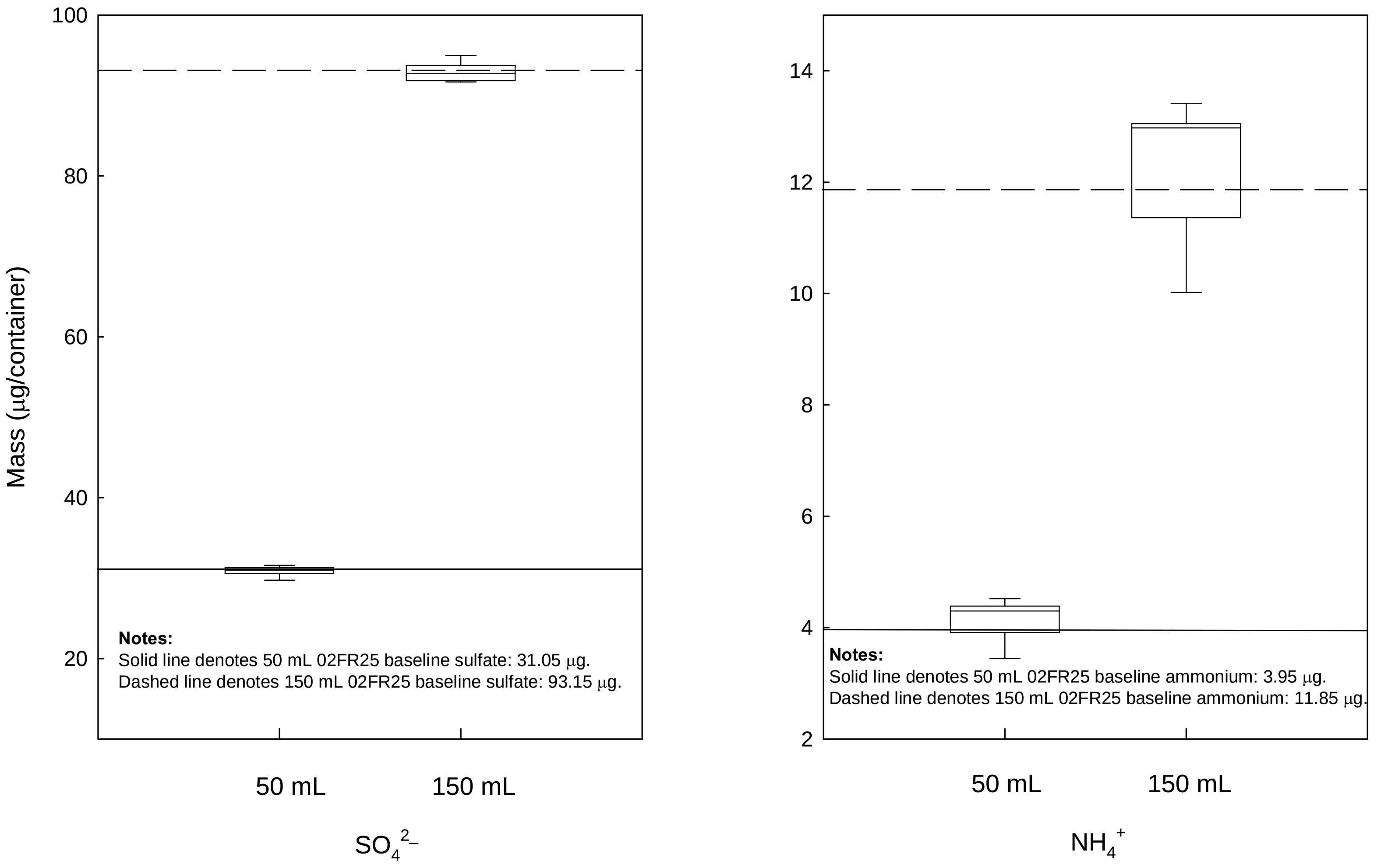
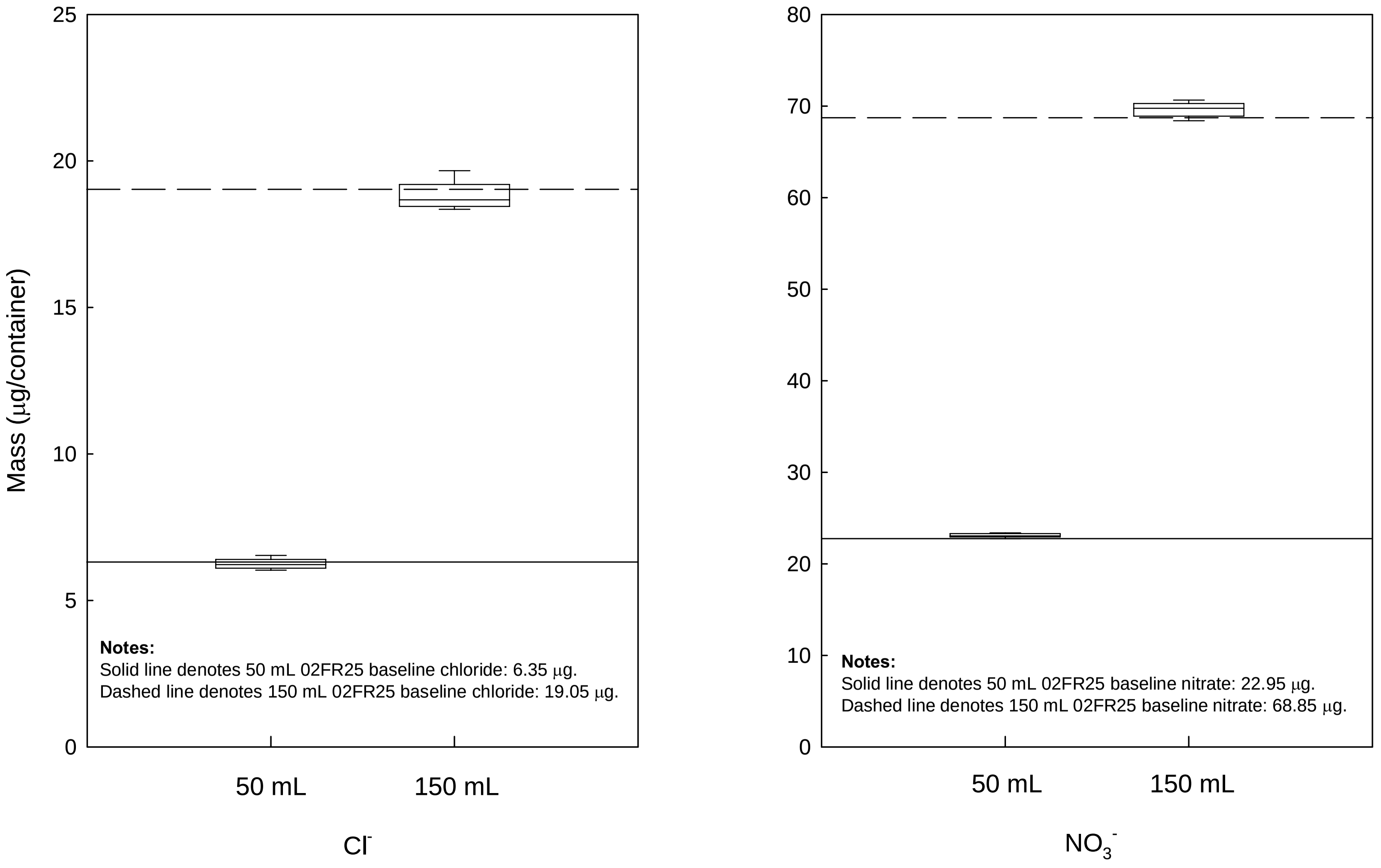


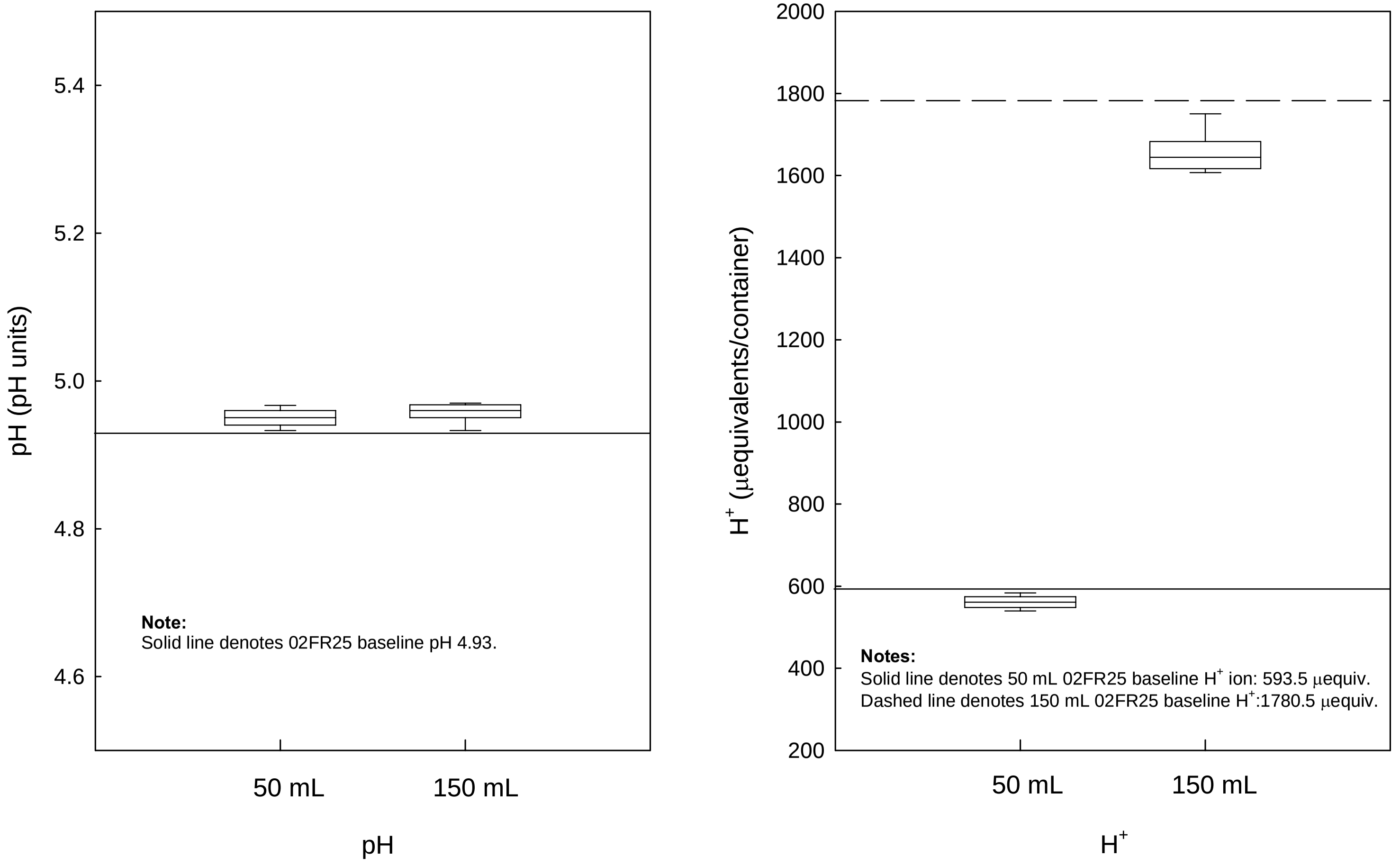
Figure B-91. Sulfate and ammonium found in AIRMoN bottle synthetic rain solutions used as leaching agents, 2002.



Notes:
Solid line denotes 50 mL 02FR25 baseline chloride: 6.35 µg.
Dashed line denotes 150 mL 02FR25 baseline chloride: 19.05 µg.

Notes:
Solid line denotes 50 mL 02FR25 baseline nitrate: 22.95 µg.
Dashed line denotes 150 mL 02FR25 baseline nitrate: 68.85 µg.

Figure B-92. Chloride and nitrate found in AIRMoN bottle synthetic rain solutions used as leaching agents, 2002.



Note:
Solid line denotes 02FR25 baseline pH 4.93.

Notes:
Solid line denotes 50 mL 02FR25 baseline H$^+$ ion: 593.5 μequiv.
Dashed line denotes 150 mL 02FR25 baseline H$^+$:1780.5 μequiv.

Figure B-93. pH and H$^+$ found in AIRMoN bottle synthetic rain solutions used as leaching agent, 2002.

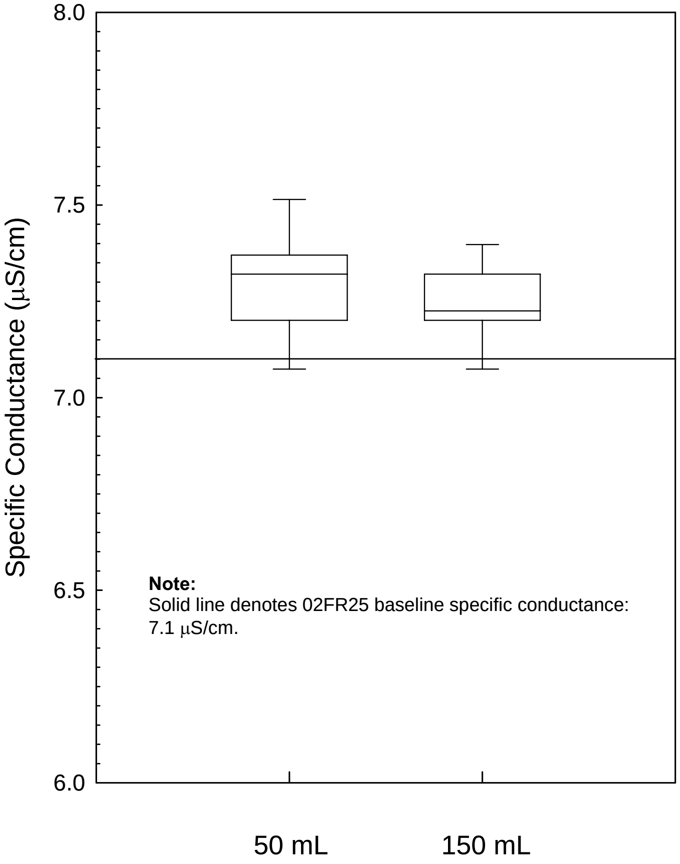


Figure B-94. Specific conductance of AIRMoN bottle synthetic rain solutions used as leaching agents, 2002.

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