NADP QA Report 2003-01

QUALITY ASSURANCE REPORT
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM, 2001

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 2003, scientists, students, educators, and others interested in the National Atmospheric Deposition Program (NADP) logged nearly 220,000 sessions and viewed more than 100,000 maps on the NADP Internet site. This site now annually receives more than 1.5 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 the leadership of State Agricultural Experiment Stations (SAES) 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. The NADP was initially 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, SAES reclassified IR-7 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, NADP agreed to coordinate operation of NAPAP's **National Trends Network (NTN)**. To benefit from shared siting criteria, identical operating procedures, and a shared analytical laboratory, NADP and NTN merged with the designation NADP/NTN. Many sampling sites are supported by the U.S. Geological Survey (USGS), 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 the 1990s, NADP expanded to include two additional networks. **The Atmospheric Integrated Research Monitoring Network (AIRMoN)**, which currently has nine sites, joined NADP in October 1992. The AIRMoN sites collect samples daily when precipitation occurs. Samples are refrigerated until analysis at the CAL for the same constituents measured in NTN samples. AIRMoN seeks to identify pollutant source/ receptor relationships and the effect of emissions changes on precipitation chemistry, combining measurements with atmospheric models. AIRMoN also evaluates new sample collection and preservation methods.

Another NADP network, the **Mercury Deposition Network (MDN)**, currently has nearly 80 sites and joined NADP in 1996. The MDN sites collect wet-only deposition samples that are sent to a laboratory specializing in mercury measurements. Frontier Geosciences, Inc. analyzes all samples for total mercury and some samples for methyl mercury. The MDN collects data on the wet deposition of mercury to surface waters, forested watersheds, and other receptors. Forty-three 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 importance of the atmospheric deposition of mercury as a cause of 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; Bureau of Land Management; Tennessee Valley Authority; 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.

For further information, contact:

NADP Program Office
Illinois State Water Survey
2204 Griffith Drive
Champaign, IL 61820

NADP Home Page: http://nadp.sws.uiuc.edu
E-mail: nadp@sws.uiuc.edu

The Illinois State Water Survey is an Affiliated Agency of the University of Illinois and a Division of the Illinois Department of Natural Resources

QUALITY ASSURANCE REPORT
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM
2001

Laboratory Operations
Central Analytical Laboratory

prepared by Jane Rothert
CAL Quality Assurance Specialist
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM
Illinois State Water Survey
2204 Griffith Drive
Champaign, IL 61820-7495
December 2003

Contents

Page

Figures

Tables

Abstract

The National Atmospheric Deposition Program (NADP) has been in operation since 1978. Since the beginning of the network, quality assurance has been of paramount importance. The *Quality Assurance Report, National Atmospheric Deposition Program, 2001*, describes the quality assurance/quality control measures used at the Central Analytical Laboratory (CAL) of the NADP/National Trends Network (NTN) and NADP/Atmospheric Integrated Research Monitoring Network (AIRMoN) and reports the results of these programs. The goal of the CAL quality assurance program is to provide reliable, consistent, high-quality data that 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 2001.

Acknowledgments

This *Quality Assurance Report*, a summary of the quality control/quality assurance measures in place at the Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) and the NADP/Atmospheric Integrated Research Monitoring Network (NADP/AIRMoN), is the product of many individuals. The U.S. Geological Survey (USGS) Branch of Quality Systems coordinates the external interlaboratory comparison program. Karen Harlin and Van Bowersox of the NADP Program Office provide ongoing input and support throughout the year. Dedicated analytical staff analyze thousands of samples with the support of conscientious sample receiving and processing personnel. Pam Bedient helped compile and format the text, tables, and files. The following reviewers and editors contributed their time and input to the final report: Greg Wetherbee, USGS; Karen Harlin, NADP/CAL; Eva Kingston, Illinois State Water Survey (ISWS); Mark Peden, NADP/CAL (retired); 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. 98-COOP-1-5925. 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). The precipitation samples collected by the National Trends Network (NTN) and the Atmospheric Integrated Research Monitoring Network (AIRMoN) of NADP are analyzed at the Central Analytical Laboratory (CAL) located at the Illinois State Water Survey in Champaign, Illinois. As the CAL for NADP, the laboratory must comply with all QA mandates in the NADP Quality Assurance Plan (QAP). The CAL was in compliance with the NADP QAP in 2001.

More samples were processed and analyzed in 2001 than in any other year in the history of NADP. Daily procedures include charting instrument standardization and maintenance and ensuring that the instruments are operating in statistical control. Following strict standard operating procedures from sample arrival at the CAL to data archival with the Program Office ensures sample integrity and quality data. 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 2001.

Weekly QA procedures include ensuring that all materials coming into contact with the precipitation samples do not contaminate the samples. Any problems that arise must be investigated and eliminated. All blank analyses, matrix-spiked analyses, internal blind sample analyses for NTN and AIRMoN, and replicate analyses for 2001 were in compliance with the NADP QAP.

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

Interlaboratory comparison studies are vital in determining how the CAL is performing compared with other laboratories around the world doing similar work. In 2001, the CAL participated in six different independent studies in addition to the U.S. Geological Survey (USGS) interlaboratory comparison study program. The USGS operates the external quality assurance program for the NADP/NTN. The CAL ranked third overall in the USGS intercomparison study although the differences between the seven laboratories participating were minor. In 2001, the CAL was under contract to prepare samples for the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) intercomparison studies. Although the CAL did participate in the studies, the CAL results were not included in the final study rankings because the samples were made and initially tested at the CAL. The CAL results, when unofficially compared with those from the other participating laboratories, were excellent. The National Water Research Institute (NWRI) of Canada conducted two intercomparison studies in 2001. The CAL continues to rank “satisfactory” or “good” in these intercomparisons. The CAL also participated in the Acid Deposition Monitoring Network in East Asia (EANET) sponsored by the Acid Deposition and Oxidant Research Center (ADORC), Japan. The CAL had no values outside ± 10 percent of the target concentrations. The sixth intercomparison study the CAL participated in was with the Norwegian Institute for Air Research (NILU), the 19th European Monitoring and Evaluation

Programme (EMEP) intercomparison of analytical methods for atmospheric precipitation. The CAL data showed a slight negative bias for ammonium, although whether it is statistically biased was not stated.

Overall the CAL has performed well in all intercomparison studies during 2001 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 2001. The procedures for supporting reliable data are demonstrated through a QA program that includes field and laboratory components. 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 spring 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 2001, the CAL analyzed samples from more than 200 NADP/National Trends Network (NTN) sites that collect weekly precipitation samples throughout the United States and parts of Canada. Samples were collected in buckets using a specified sampler. Buckets are removed each Tuesday morning and the samples are decanted into 1-liter, wide-mouthed, high-density polyethylene (HDPE) bottles and shipped with the sampling buckets to the CAL each week for processing. Figure I-1 illustrates a sample's journey after its arrival at the CAL.

The Atmospheric Integrated Research Monitoring Network (AIRMoN) protocol was implemented in 1992, and its QA program was established. Since then, NADP/NTN and NADP/AIRMoN have shared the same analytical staff and methodology. The AIRMoN sample protocol and analytical methodologies are different than those of the 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 ten years. Tracy Dombek was added to the CAL staff part time in 2001 to assist with atomic absorption spectrophotometry.

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 2001.

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 2001. Table I-3 lists the CAL Method Detection Limits (MDLs) for the analytes of interest and the methods used. This table also gives an historic perspective of how the analytical techniques and MDLs have changed over the course of the program and which samples these changes have affected. The MDLs are calculated annually or when there is a significant change in instrumentation or analyst using the method defined in Appendix A. Laboratory MDLs are maintained at or below the MDLs listed in the *NADP Quality Assurance Plan* (Simmons et al., 1991).

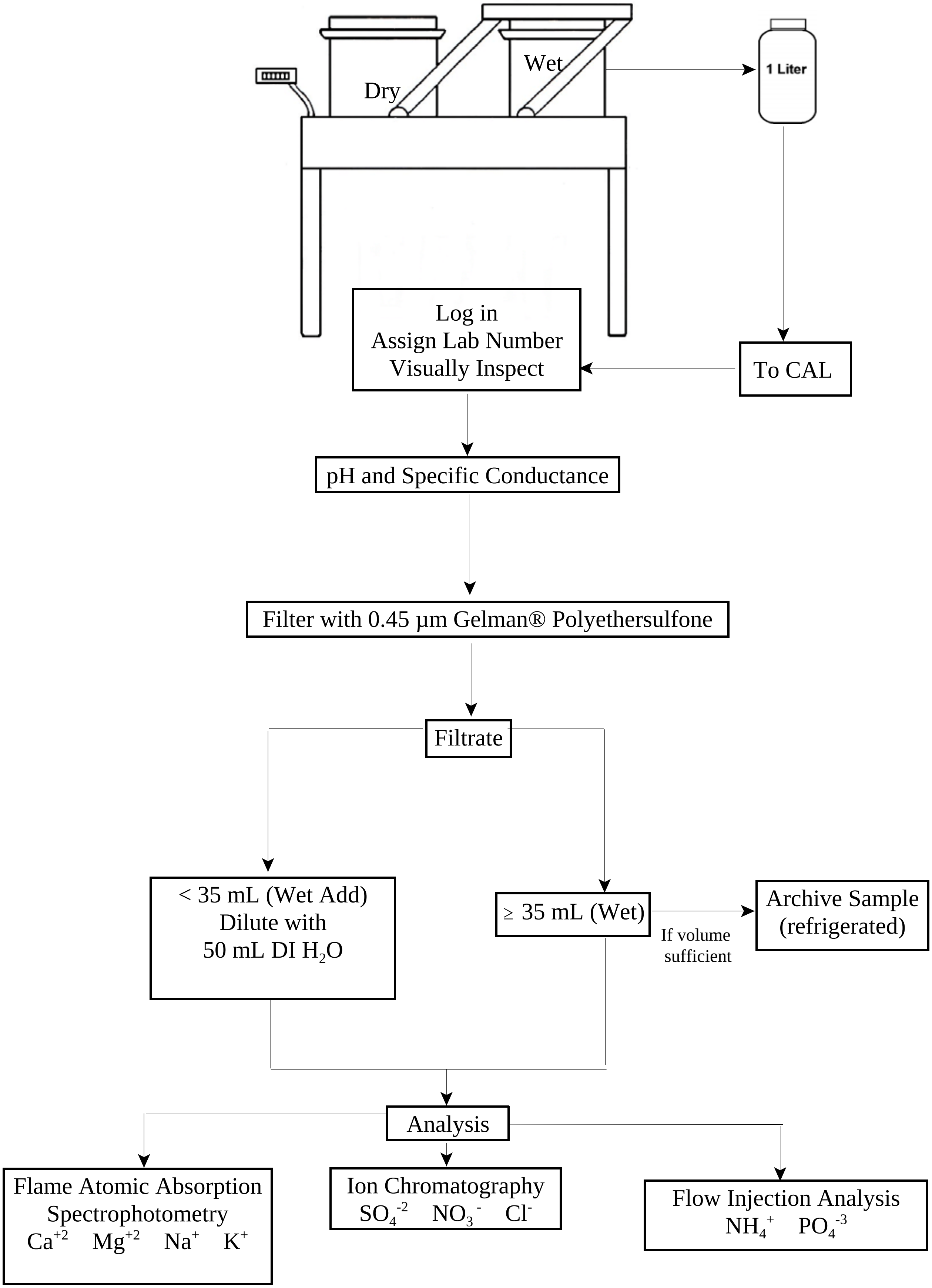


Figure I-1. NADP/NTN Sample Processing Flowchart, January 2001–December 2001.

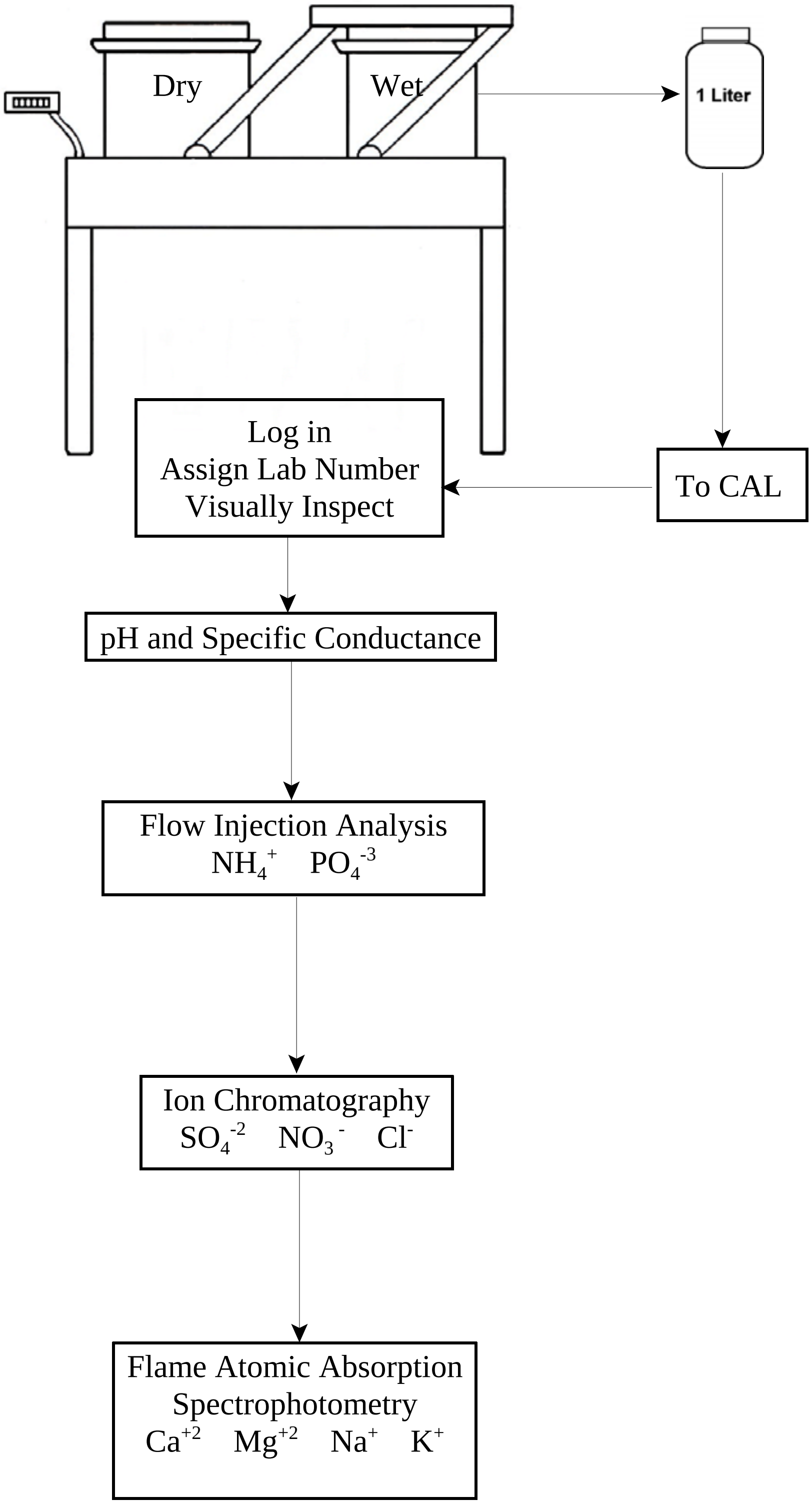


Figure I-2. NADP/AIRMoN Sample Processing Flowchart, January 2001–December 2001.

Table I-1. Central Analytical Laboratory Analytical Staff, 2001

Staff member	*Job function*	*Period of employment*
Sue Bachman	Analysis of ammonium	08/80 - 12/01
	Analysis of calcium, sodium, magnesium, and potassium	11/88 - 12/01
	Analysis of orthophosphate	01/94 - 12/01
	Sample processing coordinator	09/98 - 12/01
Phyllis Ballard	Bucket and bottle cleaning	09/97 - 04/01
	Sample receipt and processing	04/98 - 12/01
	AIRMoN sample receipt	06/99 - 12/01
Brigita Demir	Analysis of chloride, sulfate, and nitrate	09/81 - 12/01
Tracy Dombek	NTN analysis of calcium, sodium, magnesium, and potassium	08/01 - 12/01
Karen Harlin	Office of Atmospheric Chemistry Laboratory Supervisor	07/97 - 9/98
	NADP Assistant Coordinator	09/98 - 12/01
	NADP CAL Manager	09/98 - 9/00
	NADP CAL Director	09/00 - 12/01
Theresa Ingersoll	NTN sample receipt and processing	03/85 - 12/01
Tracie Patten	Analysis of pH and conductivity, and sample processing	09/98 - 12/01
Jeffrey Pribble	NTN sample receipt	07/87 - 12/01
	Supply procurement	07/87 - 12/01
	Backup NTN site liaison	01/01 - 12/01
Jane Rothert	AIRMoN Coordinator	05/92 - 12/01
	CAL Quality Assurance Specialist	07/97 - 12/01
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 - 12/01
	AIRMoN analysis of chloride, nitrate, and sulfate	06/99 - 12/01
	NTN analysis of ammonium and orthophosphate	12/00 - 12/01
Angela Weddle	NTN sample processing	06/95 - 12/97
	Analysis of pH and conductivity	10/89 - 12/01

Note:
The reporting period ended in December 2001. 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, 2001

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

Note:
The reporting period ended in December 2001.

Table I-3. Method Detection Limits (MDLs) for Precipitation Analysis, 1978–2001

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 01	NA6544 - NV9770	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 01	NA7300 - NV9770	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 01	NA7742 - NV9770	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 01	NA6001 - NV9770	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 01	NH6701 - NV9770	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 01	NS3701 - NV9770	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 01	NS3701 - NV9770	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 01	NS3701 - NV9770	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 01	NU7203 - NV9770	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 SO_4^{2-}/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 data were hand-entered using a double-entry system as a means of verification. Data from the atomic absorption spectrophotometer, the ion chromatograph, and the flow injection analyzer were electronically transferred to the database in 2001. The pH and conductivity measurements were double-entered manually through June 20, 2001 when the Laboratory Information Management System (LIMS) for the CAL went on line. These measurements now also are transferred electronically to the database. Once data have been verified and validated by CAL data management staff, they are sent to the Program Office for additional screening and coding before being made available for general usage on the Internet. Turnaround time for sample analysis and data processing is 120 days for NTN and 90 days for AIRMoN.

Table I-4 lists the percentile concentration values for all NADP/NTN samples of volume greater than 35 milliliters (mL) and with minimal contamination that were analyzed at the CAL in 2001. A sample is considered “contaminated” if it contains observable extraneous contamination that exhibits anomalous chemistry based on that particular site’s chemical history or if there are serious field or laboratory handling violations of that sample. There were 8,077 “wet” (W) samples in 2001 with a mean precipitation volume of 1454.4 mL and a median precipitation volume of 869.2 mL.

Table I-5 lists the percentile concentration values for AIRMoN samples having a sample volume large enough for a complete chemical analysis in 2001. There were 841 samples with a mean volume of 656.4 mL and a median volume of 407.4 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 1997 until the end of 2001. For NTN, 37,551 wet-only samples had no severe contamination, a mean sample volume of 1492.7 mL, and a median sample volume of 924.8 mL. For AIRMoN, 4,399 wet, non-Quality Assurance samples had no severe contamination, a mean sample volume of 686.4 mL and a median sample volume of 394.1 mL. Compared to the long-term averages, median NTN concentrations were about the same in 2001 and median AIRMoN concentrations were generally lower than previous years, although there was a new maximum for calcium.

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) summarizes the sample analysis methods. Various facets of the program have been modified and refined over the years. The CAL uses two types of QC procedures: intralaboratory and external laboratory intercomparison studies.

The CAL developed intralaboratory QA procedures to address the difficulties related to analyzing low ionic strength solutions. Internal QC standard (QCS) samples used in the laboratory are known to the analysts, who use them as guides to ensure the accuracy of their work. Other samples are unknown or blind to the analysts and are valuable ways of assessing sample bias and/or precision in the NADP/NTN and NADP/AIRMoN daily queue. Extensive

Table I-4. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/NTN Precipitation Samples, 2001

	Percentile concentration values (mg/L)									
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*99th*	*Maximum*
Calcium	-0.009	0.020	0.030	0.052	0.110	0.249	0.492	0.736	1.703	5.240
Magnesium	-0.003	0.003	0.005	0.009	0.020	0.043	0.082	0.126	0.257	1.690
Sodium	-0.003	0.006	0.009	0.019	0.048	0.132	0.387	0.711	1.980	13.760
Potassium	-0.003	-0.003	0.004	0.008	0.017	0.034	0.066	0.105	0.280	3.000
Ammonium	-0.02	-0.02	0.03	0.10	0.23	0.46	0.79	1.04	1.77	9.50
Sulfate	-0.010	0.145	0.245	0.533	1.060	1.827	2.873	3.716	5.965	27.334
Nitrate	-0.010	0.177	0.299	0.590	1.095	1.863	2.866	3.691	6.052	19.104
Chloride	-0.005	0.024	0.031	0.053	0.104	0.240	0.652	1.251	3.531	27.005
Orthophosphate	-0.009	-0.009	-0.009	-0.009	-0.009	-0.009	-0.009	-0.009	0.019	6.255
Lab pH (units)	3.42	4.17	4.28	4.52	4.88	5.36	5.95	6.32	6.74	7.30
Lab specific conductance (µS/cm)	1.6	3.5	4.5	7.6	12.9	21.0	32.4	40.9	65.9	238.6

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 = 8,077; mean sample volume = 1454.4 mL; and median sample volume = 869.2 mL. Negative numbers in this table represent the MDLs for each parameter.

Table I-5. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/AIRMoN Precipitation Wet-only Samples, 2001

	Percentile concentration values (mg/L)									
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*99th*	*Maximum*
Calcium	-0.015	0.007	0.013	0.034	0.078	0.177	0.370	0.604	1.246	5.252
Magnesium	-0.001	0.002	0.003	0.007	0.017	0.049	0.121	0.182	0.384	1.180
Sodium	-0.004	0.004	0.007	0.015	0.045	0.222	0.788	1.422	3.216	23.850
Potassium	-0.026	0.002	0.004	0.009	0.017	0.033	0.066	0.096	0.189	0.585
Ammonium	0.00	0.04	0.07	0.14	0.28	0.48	0.83	1.04	1.89	3.38
Sulfate	0.064	0.386	0.580	1.019	1.762	3.003	4.623	5.997	8.909	18.312
Nitrate	0.092	0.327	0.457	0.788	1.468	2.587	4.438	5.784	8.607	12.868
Chloride	0.000	0.027	0.040	0.075	0.168	0.521	1.493	2.501	5.102	18.836
Orthophosphate	-0.005	0.000	0.000	0.000	0.008	0.014	0.024	0.034	0.116	0.616
Lab pH (units)	3.50	3.90	3.99	4.17	4.40	4.62	4.89	5.03	5.47	7.00
Lab specific conductance (µS/cm)	3.0	7.7	10.2	16.2	25.5	40.7	61.0	74.6	110.5	169.9

Notes:
Only wet-only samples were used. Samples with a quality rating of C, signifying severe contamination, were not used to tabulate any of the values. All QC samples were removed. Total number of samples = 841; mean sample volume = 656.4 mL; and median sample volume = 407.4 mL. Negative numbers represent actual values measured, not MDLs, for each parameter.

Table I-6. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/NTN Precipitation Wet-only Samples, 1997–2001

	Percentile concentration values (mg/L)									
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*99th*	*Maximum*
Calcium	MDL	0.018	0.026	0.051	0.113	0.252	0.513	0.775	1.760	61.680
Magnesium	MDL	0.003	0.005	0.009	0.021	0.043	0.082	0.126	0.282	3.880
Sodium	MDL	0.007	0.010	0.022	0.049	0.128	0.342	0.637	2.190	16.880
Potassium	MDL	MDL	0.004	0.009	0.018	0.036	0.069	0.106	0.284	6.080
Ammonium	MDL	MDL	0.02	0.08	0.21	0.44	0.74	1.01	1.74	16.39
Sulfate	MDL	0.140	0.234	0.520	1.070	1.904	3.000	3.880	6.280	125.480
Nitrate	MDL	0.187	0.300	0.600	1.120	1.890	2.923	3.790	6.180	45.430
Chloride	MDL	0.024	0.030	0.057	0.109	0.230	0.581	1.110	3.572	35.000
Orthophosphate	MDL	MDL	MDL	MDL	MDL	MDL	MDL	MDL	0.027	1.580
Lab pH (units)	3.41	4.14	4.26	4.49	4.84	5.29	5.89	6.27	6.76	8.00
Lab specific conductance (µS/cm)	1.5	3.4	4.5	7.5	12.9	21.6	33.6	42.9	69.1	464.0

Notes:
Only wet-only samples were used. Samples with severe contamination were not used to tabulate any of the values. All QC samples were removed. Total number of samples = 37,551; mean sample volume = 1492.7 mL; and median sample volume = 924.8 mL. The MDLs 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, 1997–2001

	Percentile concentration values (mg/L)									
Parameter	*Minimum*	*5th*	*10th*	*25th*	*50th*	*75th*	*90th*	*95th*	*99th*	*Maximum*
Calcium	-0.015	0.011	0.019	0.042	0.095	0.213	0.451	0.726	1.493	5.252
Magnesium	-0.001	0.002	0.004	0.008	0.021	0.059	0.137	0.198	0.408	3.298
Sodium	-0.004	0.004	0.007	0.017	0.051	0.274	0.871	1.420	3.215	30.150
Potassium	-0.026	0.003	0.005	0.010	0.020	0.040	0.074	0.108	0.227	1.170
Ammonium	-0.02	0.03	0.06	0.13	0.27	0.51	0.86	1.12	1.94	4.48
Sulfate	0.040	0.370	0.558	1.060	1.810	3.164	4.895	6.040	9.777	19.420
Nitrate	0.050	0.300	0.440	0.811	1.500	2.680	4.426	5.795	9.322	20.590
Chloride	0.000	0.030	0.040	0.080	0.180	0.590	1.702	2.706	5.691	62.800
Orthophosphate	-0.006	0.000	0.000	0.000	0.005	0.013	0.025	0.041	0.125	1.516
Lab pH (units)	3.36	3.87	3.97	4.15	4.37	4.61	4.90	5.11	5.77	7.00
Lab specific conductance (µS/cm)	2.0	7.3	10.2	16.4	25.9	41.2	61.3	77.6	115.3	237.4

Notes:
Only wet-only samples were used. Samples with a quality rating of C, signifying severe contamination, were not used to tabulate any of the values. All QC samples were removed. Total number of samples = 4,399; mean sample volume = 686.4 mL; and median sample volume = 394.1 mL. Negative numbers represent actual values measured, not MDLs for each parameter.

analyses of blank and DI water-spiked solutions every week help identify and/or eliminate sources of contamination.

In addition to external QA studies performed by the USGS as an official part of network operations, the CAL participates in several international laboratory intercomparison studies. These studies allow the CAL to evaluate the quality of its work and 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 –2002). This report presents and discusses summaries of the results of existing QA programs in 2001.

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 where pH and specific conductance are measured following field protocols soon after sample collection and prior to shipping. Site operators use quality control standard (QCS) solutions as weekly check samples. These solutions are formulated and prepared at the CAL and then shipped to the sites. For NTN and AIRMoN, the QCS solution used in 2001 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 that are similar in ionic strength to that of the precipitation samples.

B. Laboratory QA Program

Precipitation samples are unpacked carefully upon arrival at the CAL. Information and requests written on the field forms are noted and logged into a database. Samples are transported to sample processing, assigned a sequential 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. When there is sufficient volume, a second sample aliquot is filtered into a square 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 one 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) are diluted after pH and conductivity are determined to ensure sufficient volume for a complete analysis of each sample.

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, 2001

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 every three months.
  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 in order to analyze the least stable parameters first. Samples are collected within 26 hours of precipitation start, refrigerated continuously after collection, and shipped within 7 days to the CAL (via next day air). Because low-volume AIRMoN samples are not diluted, there is not always sufficient sample volume for complete analysis; therefore, highest priority measurements are made first.

The pH meter is calibrated with commercially prepared buffer solutions of pH 7 and 4. The ability of the electrode to measure low ionic strength precipitation solutions is verified by measuring two solutions of simulated rainwater at ionic strengths simulating the 25th and 75th percentile concentrations of the NTN. These solutions are prepared in-house and are tested (Simmons et al., 1991) prior to use as QCS solutions. These solutions, referred to as FR25 and FR75, are used as QCS solutions for all measurements except for orthophosphate [orthophosphate is not stable, especially at the low concentrations found in NADP samples (Ridder et al., 1985)]. Instead, nutrient concentrates from Environmental Resource Association[1] are diluted and used for orthophosphate 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 instrument for a method defined in Appendix A. 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. 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.

[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.

Other weekly components of the program include submission of three samples as internal blinds and replicates. Two percent of the total NTN sample load are split and processed to separate the 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. The replicates, therefore, are analyzed at a different time than the original samples, usually on a separate day, with new calibration standards and check samples. The AIRMoN split sample protocol is similar to that for the NTN replicate program. The AIRMoN also has an internal blind program in which a sample of known concentration is submitted by the 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, which results in reanalysis of one percent of the NTN samples and 2.5 percent of the AIRMoN samples. This same program also calculates the ion percent and conductance percent difference for each 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.

Every two weeks, the USGS ships the CAL four interlaboratory comparison samples, which are analyzed as a group upon their arrival. The analysts know that the samples are intercomparison samples; however, they do not know the concentrations of the parameters in the samples. Every three months, the results from these analyses are submitted, reviewed, and sent to the USGS in Denver, Colorado. Other external agencies conducting interlaboratory comparisons operate on an annual or semiannual schedule. Those samples are analyzed with network samples but are identified as interlaboratory comparison samples. The results of these studies are used to evaluate performance of the CAL in relation to other laboratories in the United States, Canada, Norway, and Japan 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 the values are recorded and graphed on a daily control chart located near the instrument. These data are compiled and summarized at the end of the calendar year (Table III-1).

Data presented in Table III-1 represent bias and precision estimates under optimum conditions. The data were generated using QCS solutions known to the analysts, rather than precipitation or blind samples. The QCS solutions are stable, whereas the actual precipitation samples are susceptible to chemical change. The QCS solutions represent the optimum precision and bias to be expected from the analysis of samples and should be used in that context as data quality indicators. In 2001, they were comparable with previous years' data and fell within the QA specifications of the NADP QAP (Simmons et al., 1991). When the absolute bias exceeds the critical concentration at the 95th percentile, the bias (see Appendix A) is considered to be statistically significant. This bias could reflect instrument changes over the course of the year or could indicate that the original mean determined for that parameter was biased. Refer to the laboratory portion of the NADP QAP (Simmons et al., 1991) for more information.

Table III-1. Analytical Bias and Precision Determined from Analysis of Simulated Rain QCS, 2001

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?*
Calcium	0.076[a]	0.075	1416	-0.001	-1.1	0.004	4.8	0.003	no
	0.295[b]	0.293	478	-0.002	-0.5	0.011	3.8	0.007	no
Magnesium	0.017	0.017	1612	0.000	-0.3	0.001	6.4	0.0007	no
	0.066	0.066	478	0.000	-0.2	0.003	4.0	0.002	no
Sodium	0.049	0.048	1600	-0.0008	-1.5	0.002	4.6	0.001	no
	0.192	0.190	542	-0.002	-1.0	0.006	3.2	0.004	no
Potassium	0.013	0.013	1544	0.0004	2.7	0.001	8.5	0.0007	no
	0.050	0.051	514	0.001	2.4	0.002	3.8	0.001	no
Ammonium	0.08	0.08	1149	0.00	3.2	0.01	6.2	0.003	no
	0.35	0.35	861	-0.003	-0.9	0.01	2.1	0.005	no
Orthophosphate	0.035	0.033	1033	-0.002	-6.4	0.003	8.3	0.006	no
	0.089	0.085	840	-0.004	-4.1	0.006	7.1	0.0012	no
pH units (μeq/L)	4.92 (12.0)[c]	4.92 (12.0)	1035	0.003 (-0.07)	0.06 (-0.6)	0.02 (0.5)	0.4 (4.2)	0.01 (0.28)	no (no)
	4.35 (44.7)	4.35 (44.8)	959	-0.001 (0.16)	-0.03 (0.4)	0.02 (1.7)	0.4 (3.7)	0.01 (0.94)	no (no)
Specific Conductance (μS/cm)	7.16	7.18	1009	0.02	0.3	0.15	2.1	0.08	no
	27.0	27.0	878	0.0	0.0	0.2	0.7	0.11	no

Table III-1. (concluded)

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?*
Chloride (A side)	0.132	0.132	678	0.0002	0.1	0.002	1.8	0.001	no
	0.539	0.540	666	0.0008	0.1	0.007	1.2	0.004	no
Nitrate (A side)	0.481	0.479	683	-0.002	-0.5	0.007	1.5	0.004	no
	1.924	1.927	659	0.003	0.2	0.018	0.9	0.011	no
Sulfate (A side)	0.648	0.649	672	0.0009	0.1	0.007	1.1	0.004	no
	2.595	2.600	661	0.005	0.2	0.017	0.7	0.010	no
Chloride (B side)	0.132	0.133	614	0.0005	0.3	0.003	1.9	0.002	no
	0.539	0.541	596	0.002	0.4	0.005	0.9	0.004	no
Nitrate (B side)	0.481	0.478	611	-0.003	-0.7	0.005	1.1	0.004	no
	1.924	1.930	594	0.006	0.3	0.017	0.9	0.013	no
Sulfate (B side)	0.648	0.650	607	0.002	0.3	0.008	1.2	0.006	no
	2.595	2.604	588	0.009	0.3	0.019	0.7	0.014	no

Notes:

See Appendix A for definitions and formulas for Bias, Precision, RSD, and Critical concentrations.

Side A and Side B indicate the two separate ion chromatographic instruments used at the CAL.

[a]The first set of values for each parameter is for the 25th percentile solution (FR25).

[b]The second set of values for each parameter is for the 75th percentile solution (FR75).

[c]The pH data in parentheses are hydrogen ion concentrations expressed in microequivalents per liter (μeq/L).

IV. Weekly Quality Assurance/Quality Control Procedures

Three Quality Assurance (QA) activities 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, and AIRMoN bottle blanks and leachates are submitted monthly.

A. Internal Blind Audit

1. NADP/NTN

Each week the QA Specialist submits three solutions of known concentrations with completed Field Observer Report Forms (FORFs) to the sample processing area where laboratory identification numbers are assigned. These samples are processed with the network samples, but two of the three samples are unfiltered to monitor for possible filter contamination. These samples are identified as SWS1, SWS2, and SWS3. In 2001, the SWS1 samples were High-Purity Standards[2] 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 2001 data from the weekly internal blind audit samples for NTN. It is important to remember that the blind sample population is considerably smaller than that of the QCS solutions. Blind samples may occur at any point in the sample queue (for example, right after calibration or prior to the next QCS solution). The bias and precision estimates derived are, therefore, more representative of precipitation sample measurements than the measurement of the FR25 and FR75 solutions. The SWS1 and SWS2 samples overall show fewer contaminants and less variability than the filtered SWS3 samples (which have an even smaller sample population for each solution) with a few exceptions. The concentration for calcium in H-PS SR1 is very close to the detection limit, resulting in a higher standard deviation. This is true for other parameters too: the closer the measured concentration is to the detection limit of the instrument, the more noise in the measurement and the higher the Standard Deviation. 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.

Certified solutions of two different concentrations from High-Purity Standards were used for the SWS1 samples (Table IV-1) in 2001. These samples, H-PS SR1 (lot #023510), and H-PS SR2 (lot #033320), were of similar concentrations to those used in previous years

---

[2] 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 (HPS-SR1) and 2 (HPS-SR2), Unfiltered, 2001

Parameter	*Target Concentration* [a] *(mg/L)*	*Mean measured concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	0.015 [b]	0.022	0.007	45.4	0.036	165.8
	0.051 [c]	0.055	0.004	7.7	0.006	10.3
Magnesium	0.020	0.019	-0.001	-4.4	0.002	8.8
	0.051	0.048	-0.003	-6.7	0.003	5.7
Sodium	0.20	0.200	0.000	-0.1	0.008	3.8
	0.40	0.401	0.001	0.3	0.013	3.2
Potassium	0.054	0.052	-0.002	-4.4	0.004	7.3
	0.098	0.103	0.005	5.3	0.003	2.9
Ammonium [d]	0.100	0.03	-0.07	-73.2	0.02	68.8
	1.00	0.93	-0.07	-6.9	0.02	2.0
Sulfate	2.5	2.491	-0.009	-0.4	0.021	0.9
	10.1	10.125	0.025	0.3	0.079	0.8
Nitrate	0.50	0.504	0.004	0.7	0.007	1.3
	7.0	7.114	0.114	1.6	0.090	1.3
Chloride	0.25	0.218	-0.032	-12.6	0.003	1.3
	0.98	1.002	0.022	2.2	0.014	1.4
pH	4.15 (4.31)[e]	4.32	0.17 (0.01)	4.1 (0.2)	0.05	1.2
(units)	3.52 (3.57)	3.61	0.09 (0.04)	2.6 (1.2)	0.01	0.3
H	70.8 (49.0)	48.3	-22.5 (-0.7)	-31.8 (-1.4)	4.6	9.5
(µeq/L)	302.0 (269.2)	244.3	-57.8 (-24.9)	-19.1 (-9.3)	6.2	2.5
Conductivity	24	25.7	1.7	7.1	1.1	4.3
(µS/cm)	125	127.6	2.6	2.1	2.1	1.6

Notes:

There were 26 samples in each set.

[a] Target concentrations are those reported by High-Purity Standards. Numbers in parentheses are calculated pH and H concentrations.

[b] Concentration values for H-PS SR1 (lot # 023510).

[c] Concentration values for H-PS SR2 (lot # 033320).

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

[e] Numbers in parentheses are target values based on the ion balance of the solutions.

Table IV-2. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS2), Deionized (DI) Water and Internally Formulated Simulated Rain (01FR10), Unfiltered, 2001

Parameter	*Target concentration (mg/L)*	*Mean measured concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	<0.009 [a]	0.002			0.005	
	0.031 [b] [c]	0.032	0.001	4.0	0.009	26.6
Magnesium	<0.003	0.000			0.001	
	0.007	0.007	0.000	0.5	0.001	20.7
Sodium	<0.003	-0.001			0.002	
	0.020	0.018	-0.002	-8.1	0.002	11.8
Potassium	<0.003	-0.002			0.002	
	0.005	0.005	0.000	6.9	0.002	30.8
Ammonium	<0.02	-0.01			0.01	
	0.03	0.03	0.00	5.2	0.01	18.8
Sulfate	<0.010	0.001			0.003	
	0.260	0.257	-0.003	-1.0	0.007	2.5
Nitrate	<0.010	0.000			0.002	
	0.193	0.193	0.000	-0.2	0.004	2.0
Chloride	<0.006	0.000			0.002	
	0.053	0.054	0.001	1.1	0.002	2.8
pH	5.65	5.58	-0.07	-1.2	0.09	1.6
(units)	5.22	5.21	-0.01	-0.2	0.04	0.9
H	2.24	2.66	0.42	18.8	0.5	19.9
(µeq/L)	6.03	6.22	0.19	3.2	0.6	10.2
Conductivity	0.9	1.3	0.4	44.4	0.1	10.2
(µS/cm)	3.6	3.7	0.1	3.9	0.2	4.7

Notes:
There were 26 samples in each set.
[a] Concentration values for DI water.
[b] Concentration values for internally formulated simulated rain (01FR10).
[c] Concentration values for the 01FR10 are the mean of 7–11 analyses done immediately after sample preparation.

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, 2001

Parameter	*Target concentration* [a] *(mg/L)*	*Mean measured concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	0.015 [b]	0.058	0.043	286.7	0.017	28.8
	0.051 [c]	0.107	0.056	110.6	0.018	16.5
Magnesium	0.02	0.018	-0.002	-8.1	0.013	69.0
	0.051	0.047	-0.004	-8.1	0.002	4.9
Sodium	0.20	0.194	-0.006	-3.0	0.007	3.8
	0.40	0.392	-0.008	-1.9	0.014	3.6
Potassium	0.051	0.049	-0.002	-3.2	0.003	6.2
	0.098	0.098	0.000	-0.5	0.004	4.2
Ammonium [d]	0.100	0.03	-0.07	-67.2	0.02	64.4
	1.00	0.91	-0.09	-9.2	0.02	2.3
Sulfate	2.5	2.400	-0.100	-4.0	0.035	1.5
	10.1	9.758	-0.343	-3.4	0.065	0.7
Nitrate	0.50	0.489	-0.011	-2.3	0.011	2.2
	7.0	6.874	-0.126	-1.8	0.089	1.3
Chloride	0.25	0.216	-0.034	-13.6	0.004	1.6
	0.98	0.981	0.001	0.1	0.012	1.2
pH	4.15 (4.31)[e]	4.31	0.16 (0.00)	3.9 (0.0)	0.03	0.6
(units)	3.52 (3.57)	3.61	0.09 (0.04)	2.6 (1.1)	0.02	0.5
H	70.8 (49.0)	49.1	-21.7 (0.10)	-30.7 (0.2)	2.9	6.0
(μeq/L)	302.0 (269.2)	245.2	-56.8 (-23.9)	-18.8 (-8.9)	10.0	4.1
Conductivity	24	25.3	1.3	5.5	0.8	3.0
(μS/cm)	125	128.1	3.1	2.4	1.3	1.0

Notes:

There were 13 samples in each set.

[a] Target concentrations are those reported by High-Purity Standards. Numbers in parentheses are calculated pH and H concentrations.

[b] Concentration values for H-PS SR1 (lot # 023510).

[c] Concentration values for H-PS SR2 (lot # 033320).

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

[e] Numbers in parentheses are target values based on the ion balance of the solutions.

Table IV-4. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS3), Deionized (DI) Water and Internally Formulated Simulated Rain (01FR10), Filtered, 2001

Parameter	*Target concentration (mg/L)*	*Mean measured concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	<0.009[a]	0.003	0.003		0.013	
	0.031[b,c]	0.040	0.009	30.3	0.007	16.7
Magnesium	<0.003	0.000	0.000		0.001	
	0.007	0.005	-0.002	-26.4	0.001	23.6
Sodium	<0.003	0.001	0.001		0.002	
	0.020	0.019	-0.001	-4.2	0.002	12.6
Potassium	<0.003	0.000	0.000		0.003	
	0.005	0.005	0.000	4.6	0.002	42.1
Ammonium	<0.02	0.00	0.00		0.01	
	0.03	0.03	0.00	15.1	0.01	19.1
Sulfate	<0.010	0.002	0.002		0.005	
	0.260	0.253	-0.007	-2.7	0.006	2.3
Nitrate	<0.010	0.002	0.002		0.004	
	0.193	0.189	-0.005	-2.4	0.004	2.1
Chloride	<0.006	0.001	0.001		0.004	
	0.053	0.057	0.004	6.7	0.005	8.6
pH (units)	5.65	5.56	-0.10	-1.7	0.05	0.8
	5.22	5.22	0.00	0.0	0.06	1.1
H (μeq/L)	2.24	2.80	0.56	25.0	0.3	10.0
	6.03	6.10	0.07	1.2	0.8	12.9
Conductivity (μS/cm)	0.9	1.3	0.4	47.0	0.5	34.4
	3.6	3.9	0.3	9.2	0.7	18.0

Notes:
There were 13 samples in each set.
[a] Concentration values for DI water.
[b] Concentration values for internally formulated simulated rain (01FR10).
[c] Concentration values for the 01FR10 are the mean of 7–11 analyses done immediately after sample preparation.

and slightly higher than the internal QCS solutions made at the CAL. The H-PS SR1 sample is more similar in concentration to the higher concentration FR75 QCS solution for all analytes except calcium, magnesium, ammonium, chloride, and nitrate. The H-PS SR2 samples have even higher concentrations for all analytes except calcium and magnesium. The 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 percent 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 did the High-Purity Standards samples, which would be expected as the QCS solution concentrations were established by the CAL. High-Purity Standards does not certify the ammonium concentrations in their simulated rainwater samples. "Ammonium has been found not to be stable. These values are for information only" is stated on each simulated rainwater sample. A large positive bias between the laboratory measurements and the target concentration for calcium was determined for the filtered samples, and a smaller but still positive bias was determined for the unfiltered samples.

The SWS2 solutions are 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 are 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 the unfiltered and the filtered samples for all analytes in 2001, as tabulated in Tables IV-2 and IV-4. Sodium, sulfate, nitrate, and pH had a small negative bias in the SWS1 samples (Table IV-1). Magnesium, sodium, sulfate, nitrate and pH had a negative bias in the filtered solution. The percent bias for magnesium was large, but the actual difference was less than the MDL as the concentration for magnesium in the 01FR10 sample was less than two times the MDL. With the exception of magnesium, the bias for all components for both filtered and unfiltered solutions was less than the MDL. Biases at these levels may be most indicative of instrument noise. All biases in the 01FR10 samples, whether filtered or unfiltered, were less than the MDL and less than 10 percent.

The SWS3 H-PS samples (Table IV-3) had larger biases than most unfiltered SWS1 samples (Table IV-1). Some variation is normal and expected in the system and was observed in the differences between filtered and unfiltered samples in 2001. The RSD for H-PS SR1 solution for calcium and pH in 2001 was smaller than in 2000. The RSD for all the other parameters was higher for the H-PS SR1 solution. The difference for most constituents with higher RSDs was not much different than in 2000, except for ammonium and magnesium. The sodium bias from filtration, seen prior to 1998 and before the laboratory protocol change to the Gelman® filters, was not seen in 2001. There was a calcium bias in filtered samples compared with unfiltered samples for both H-PS SR1 and H-PS SR2, however. The RSD for the higher concentration H-PS SR2 varied between the ions measured, with most being very similar to the RSD found in 2000. Both the H-PS SR1 and H-PS SR2 had higher acidity than the solutions prepared at the CAL, the 01FR10, and DI water. The possibility that the calcium contamination from the filters is pH related is being researched.

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 01FR10 simulated rainwater solution and DI water, filtered and unfiltered, statistics. 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 AIRMoN. Sample receiving staff at the CAL have no indication that this is not a real precipitation sample. Every effort is made to ensure that the sample is “blind” to the analytical and receiving staff. After submitting the sample to the AIRMoN receiving staff, the site operator submits a copy of the FOF to the AIRMoN liaison so that the database can reflect the true identity of the sample, and the date and time “on” can be corrected for the real sample submitted immediately after the QA sample. These samples are processed in the laboratory as AIRMoN precipitation samples.

Internal blind samples used in 2001 were simulated rainwater prepared for the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) intercomparison study for 2000 (Coleman et al., 2000). 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-seven laboratories worldwide participated in the 2001 WMO/GAW intercomparison study.

The percent bias of samples in the AIRMoN internal blind program was similar to the percent bias for 2000. Some parameters were slightly higher, and some were slightly lower. The bias for all parameters was at or below the MDL for each parameter. The percent RSD

Table IV-5. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, AIRMoN, 2001

Parameter	*Target WMO/GAW concentration*[a] *(mg/L)*	*CAL mean concentration*[b] *(mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*	*Critical concentration (mg/L)*	*Statistically significant bias?*
Calcium	0.114	0.112	-0.002	-2.2	0.007	6.6	0.007	no
Magnesium	0.033	0.031	-0.002	-5.8	0.002	4.8	0.002	no
Sodium	0.148	0.148	0.000	0.2	0.005	3.3	0.008	no
Potassium	0.030	0.029	-0.001	-3.7	0.002	7.3	0.002	no
Ammonium	0.22	0.20	-0.02	-8.6	0.01	2.9	0.01	yes
Sulfate	1.339	1.341	0.002	0.1	0.013	1.0	0.013	no
Nitrate	1.059	1.057	-0.002	-0.2	0.009	0.9	0.010	no
Chloride	0.280	0.277	-0.003	-1.1	0.004	1.5	0.005	no
pH units	4.56	4.56	0.00	-0.1	0.02	0.4	0.02	no
Hydrogen ion (µeq/L)	27.5	27.8	0.2	0.9	1.2	4.5	1.1	no
Specific Conductance (µS/cm)	15.5	17.1	1.6	10.0	0.6	3.7	0.57	yes

Notes:

This tabulation included 48 internal blinds. Samples were simulated rainwater prepared for the 2000 World Meteorological Organization intercomparison study.

[a] Target concentration used by the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) in their analysis of the data in the 2000 WMO/GAW intercomparison study.

[b] Mean concentration obtained by the CAL from the AIRMoN internal blind samples for 2001.

for the AIRMoN blind samples was higher for more parameters in 2001 than in 2000. Specific conductance was the only parameter that showed a statistical bias in 2000. Both specific conductance and ammonium showed a statistical bias in 2001, with ammonium being biased low and specific conductance being biased high.

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 where it is 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 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, their 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 2001 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 (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). The median values used to split the 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

Table IV-6. Variance Estimated from Analysis of Replicate NADP/NTN Precipitation Samples, 2001

	Standard Deviation Estimated from Paired Measurements[a] *(mg/L)*			
Parameter	*Low*	*High*	*Total*	*(1.48) × MAD*[b]
Calcium	0.010	0.028	0.021	0.010
Magnesium	0.002	0.024	0.017	0.003
Sodium	0.005	0.029	0.021	0.003
Potassium	0.002	0.004	0.003	0.003
Ammonium	0.01	0.02	0.01	0.01
Sulfate	0.010	0.052	0.038	0.015
Nitrate	0.019	0.038	0.030	0.012
Chloride	0.003	0.054	0.038	0.004
Orthophosphate	0.000	0.000	0.000	0.000
pH (units)	0.03	0.06	0.05	0.03
Hydrogen ion (µeq/L)	2.05	0.89	1.58	0.97
Specific conductance (µS/cm)	0.65	0.78	0.72	0.30
Number of pairs	121	121	242	242

Notes:

[a] "Standard Deviation Estimated from Paired Measurements" is defined in Appendix A.

[b] MAD is Median Absolute Difference.

Table IV-7. Variance Estimated from Analysis of Replicate NADP/AIRMoN Precipitation Samples, 2001

Parameter	*Standard Deviation Estimated from Paired Measurements* [a] *(mg/L)* *Low*	*High*	*Total*	*(1.48) × MAD* [b]
Calcium	0.007	0.012	0.010	0.008
Magnesium	0.0007	0.009	0.006	0.001
Sodium	0.001	0.044	0.031	0.003
Potassium	0.002	0.005	0.003	0.003
Ammonium	0.01	0.03	0.02	0.02
Sulfate	0.015	0.048	0.035	0.020
Nitrate	0.014	0.062	0.045	0.012
Chloride	0.006	0.097	0.069	0.007
Orthophosphate	0.004	0.011	0.008	0.004
pH (units)	0.06	0.07	0.06	0.03
Hydrogen ion (µeq/L)	7.62	2.60	5.69	2.89
Specific conductance (µS/cm)	1.2	3.6	2.7	1.8
Number of pairs	15	15	30	30

Notes:

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

[b] MAD is Median Absolute Difference.

calculate the 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, where 1.48 times the Median Absolute Difference (MAD) is the estimator of dispersion (Helsel and Hirsch, 1992). A comparison of the Standard Deviations for the QCS solutions (Table III-1), SWS1 (Table IV-1), and SWS3 (Table IV-3) to 1.48 × MAD shows comparable cation and anion precision of the split samples.

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 formulation below 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.

Figures B-55–B-72 in Appendix B show graphically where the replicate samples fall in this formulation for NTN and AIRMoN for 2001. There was one NTN calcium value outside this limit; five NTN magnesium values outside the limit; and two NTN sodium values, no potassium values, one NTN ammonium value, one NTN sulfate value, two NTN nitrate values, and one AIRMoN chloride value outside the limits. There were 242 NTN replicates and 30 AIRMoN replicates.

C. Blanks

Solutions referred to as “blanks” are either DI water solutions or a solution of 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 are then 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” are known to the analysts and 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 the samples being analyzed by ion chromatography, atomic absorption, and flow injection analysis. These solutions are not filtered unless they are used to determine the 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 are then 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. Calcium shows a slight but statistically relevant positive bias in the FR25 leachate. Magnesium, sulfate, and nitrate show a slight but statistically relevant negative bias in the FR25 leachate. No biases are seen in the DI water leachates. Gelman polyethersulfone filters first were used in January 1998. Prior to this, Millipore™ HAWP filters were used, and sodium contamination from the filters was a recurring problem. There is no sodium contamination with the Gelman filters. The biases found for calcium, magnesium, sulfate, and nitrate agree with the results of the filtered vs. unfiltered internal blind samples: the filtered samples show a higher concentration of calcium and a positive bias and a lower concentration for magnesium, sulfate, and nitrate with a negative bias. As was stated in Section IV.A.1, there is some evidence that the degree of bias for calcium and the 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.

Table IV-8. pH and Specific Conductance for Weekly DI Water Blanks, 2001

Parameter	*Sample Processing Laboratory*	*Atomic Absorption Laboratory*	*Service Laboratory*
Median			
pH (units)	5.63	5.63	5.65
Specific conductance (µS/cm)	0.9	0.9	0.9
Maximum			
pH (units)	5.79	6.67	5.82
Specific conductance (µS/cm)	1.8	3.0	1.5
Minimum			
pH (units)	5.39	5.40	5.42
Specific conductance (µS/cm)	0.7	0.7	0.7

Note:
A total of 52 blank samples were collected.

Table IV-9. Median Analyte Concentrations Found in Filter Leachates, 2001

Parameter	*DI water (mg/L)*	*FR25 (mg/L)*	*FR25 target concentration (mg/L)*	*Statistically significant bias?*
Calcium	<0.009	0.082	0.075	yes
Magnesium	<0.003	0.014	0.017	yes
Sodium	<0.003	0.047	0.048	no
Potassium	<0.003	0.012	0.013	no
Ammonium	<0.02	0.08	0.08	no
Orthophosphate	<0.009	0.000	0.000	no
Sulfate	<0.010	0.621	0.639	yes
Nitrate	<0.010	0.459	0.474	yes
Chloride	<0.005	0.130	0.132	no
pH	5.61	4.92	4.93	no
Hydrogen ion (µeq/L)	2.48	12.0	11.7	no
Specific conductance (µS/cm)	1.2	7.3	7.5	no

Note:
A total of 52 blank samples were collected.

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 150-mL portions; and two FR25 solutions 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, sodium, ammonium, nitrate, and chloride in the 50-mL samples above the MDL. None of the analytes were above the MDL for the 150-mL DI samples. The FR25 leachates had sodium, ammonium, nitrate, and chloride in the 50-mL aliquot. Sodium, nitrate, and chloride were present in the 150-mL aliquot. The presence of these constituents is believed to be related to bag contamination. Continued research is being conducted to find a clean bag in which to store cleaned buckets and lids. This also indicates that low-volume samples are at greater risk of contamination by the buckets. Precipitation samples with low volumes generally have higher concentrations of analytes and, therefore, should not have been affected adversely by contamination. The median contamination in 50-mL aliquots for calcium was equivalent to 0.001 mg/L, which would not adversely affect the concentration of calcium in a sample.

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 either the DI water leachates or the FR25 leachates. Loss of sulfate, nitrate, and chloride was evident in the 50-mL aliquots, and loss of ammonium was evident in the 150-mL aliquots for FR25, however. For sulfate, chloride, nitrate, and ammonium, the loss was essentially the detection limit for that analyte, which for low-volume samples is less than the amount of analyte present.

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, 2001

	DI Water[a]			*FR25*[b]	
Parameter	*(50 mL)*	*(150 mL)*	*(50 mL)*	*(50 mL)*	*(150 mL)*
Calcium	0.300	<0.675	<0.225	<0.250	<0.675
Magnesium	<0.075	<0.225	<0.075	<0.075	<0.225
Sodium	0.100	<0.225	0.100	0.125	0.225
Potassium	<0.075	<0.225	<0.075	<0.075	<0.225
Ammonium	1.33	<1.50	1.10	0.85	<1.50
Sulfate	<0.250	<0.750	<0.250	<0.250	<0.750
Nitrate	0.650	<0.750	0.475	0.950	0.825
Chloride	0.850	<0.375	0.900	0.650	1.200
pH (units)	5.61	5.59	5.62	5.04 (4.93)[c]	4.95 (4.93)[c]
Hydrogen ion (µeq/bucket)	0.124	0.386	0.121	-0.126	-0.080
Specific conductance (µS/cm)	1.5	1.3	1.6	6.8(7.3)[c]	7.3 (7.3)[c]

Notes:

There were 52 blind sample weeks in 2001. Table I-3 reports MDLs.

[a] Mass/bucket represents the concentration in µg/mL × 50 or 150 mL. Values reported as less than the detection limit (<) 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.

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, 2001

	DI Water		*FR25*[b]	
Parameter	*(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	<0.075	<0.225
Potassium	<0.075	<0.225	<0.075	<0.225
Ammonium	<0.50	<1.5	<0.50	-1.8
Sulfate	<0.250	<0.750	-0.400	<0.750
Nitrate	<0.250	<0.750	-0.450	<0.750
Chloride	<0.125	<0.375	-0.150	<0.375
pH (units)	5.54	5.57	4.94 (4.93)[c]	4.92 (4.93)[c]
Hydrogen ion (μeq/bucket)	0.14	0.40	-0.01	0.04
Specific conductance (μS/cm)	1.3	1.2	7.3 (7.3)[c]	7.4 (7.3)[c]

Notes:

There were 52 blind sample weeks in 2001.

[a] Mass/bucket represents the concentration in μg/mL × 50 or 150 mL. Values reported as less than the 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 bottle leachates - target FR25 concentration) × 50 or 150 mL.

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

5. Snap-on Lid Blanks

Snap-on lids are used to contain the sample in the bucket between the collector and the site field laboratory. At the CAL two lids are inverted on the laboratory bench, and 50 mL of DI water are measured onto one lid and 50 mL of FR25 onto the other lid. They are covered with large plastic domes for 24 hours to prevent dry deposition contamination. Table IV-12 shows the median concentrations found on the snap-on lid “blanks.” No parameters were found to be above the MDL.

6. AIRMoN Bottles

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

Once a month, two AIRMoN 250-mL bottles are used for AIRMoN bottle blanks. Although only two bottles are tested each month, 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 bottle was FR25 solution. One bottle had a 50-mL aliquot; the other had a 150-mL aliquot. Table IV-13 shows no significant difference between the leachate values of FR25 in AIRMoN bottle blanks and the target FR25 concentrations used for either the 50-mL aliquot or the 150-mL aliquot.

7. Bag Blanks

Bag blanks were added to the blanks regime in January 2001. The presence of sodium, chloride, magnesium, and occasionally other ions in bucket blanks resulted in the QA Specialist and Laboratory Director once again reviewing the bags used to store the buckets and lids before and after shipping and at the sites. The company furnishing the CAL with bags changed their supplier, resulting in a change in the bags used at the CAL. The bag chosen was not 100 percent clean, necessitating the use of bag blanks. Continued effort is being made to monitor the bags and to obtain bags that are as free from contamination as possible.

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 calcium, magnesium, sodium, and ammonium in the FR25 leachates. Although both the DI water leachates and the FR25 leachates contained approximately the same amount of excess chloride, there was sufficient variation in the concentration found in the FR25 leachate to deem the bias to be insignificant at the 99

Table IV-12. Median Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Snap-on Lids, 2001

Parameter	*DI water (50 mL)*	*FR25 (50 mL)*	*FR25 target concentration (mg/L)*
Calcium	<0.009	0.076	0.075
Magnesium	<0.003	0.017	0.017
Sodium	<0.003	0.049	0.048
Potassium	<0.003	0.013	0.013
Ammonium	<0.02	0.09	0.08
Sulfate	<0.010	0.640	0.639
Nitrate	<0.010	0.474	0.474
Chloride	<0.005	0.134	0.132
pH (units)	5.62	4.94	4.93
Hydrogen ion (µeq/L)	2.40	11.5	11.8
Specific conductance (µS/cm)	1.3	7.3	7.5

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, 2001

Analyte	*FR25 (50 mL)*	*FR25 (150 mL)*	*FR25 target concentration (mg/L)*
Calcium	0.071	0.073	0.075
Magnesium	0.017	0.017	0.017
Sodium	0.048	0.048	0.048
Potassium	0.012	0.012	0.013
Ammonium	0.08	0.08	0.08
Sulfate	0.639	0.643	0.639
Nitrate	0.472	0.473	0.474
Chloride	0.130	0.131	0.132
pH (units)	4.91	4.92	4.93
Hydrogen ion (μeq/L)	12.3	12.0	11.8
Specific conductance (μS/cm)	7.4	7.4	7.5

Notes:
There were 11 months of AIRMoN bottle blanks and spikes except for chloride, nitrate, and sulfate. There were only 9 months of data for the 150-mL spike.

Table IV-14. Median Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Bags, 2001

Analyte	*DI water (50 mL)*	*FR25 (50 mL)*	*FR25 target concentration (mg/L)*	*Statistically significant bias?*
Calcium	0.012	0.084	0.075	yes
Magnesium	<0.003	0.019	0.017	yes
Sodium	0.006	0.053	0.048	yes
Potassium	<0.003	0.013	0.013	no
Ammonium	<0.02	0.10	0.08	yes
Sulfate	<0.010	0.632	0.639	no
Nitrate	<0.010	0.479	0.474	no
Chloride	0.032	0.159	0.132	no
pH (units)	5.57	4.97	4.93	no
Hydrogen ion (µeq/L)	2.72	10.7	11.8	no
Specific conductance (µS/cm)	1.7	7.4	7.5	no

Note:
There were 49 weeks of bag blanks and bag spikes.

percent confidence level. Sodium and calcium were also present above the MDL in the DI water leachate samples. The median bias was about equal to the MDL for all statistically biased analytes, resulting in a very small amount in low-volume solutions with high concentrations, or resulting in amounts within the noise level for low-volume samples.

V. Monthly Quality Assurance Procedures

Monthly NADP/NTN and NADP/AIRMoN-wet QA activities by the QA Specialist include: 1) evaluation of control charts summarizing the daily QCS analyses to determine if any change occurred 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-wet samples also are processed once a month for 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). 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:

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

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

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

Samples are flagged for reanalysis if:

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

Table V-1. Conversion Factors for Reanalysis Calculations

Analyte	*Milligrams/Liter (mg/L) to Microequivalents/L (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-wet. 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:

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

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 2001, approximately 12,479 NTN samples were logged in, and 9,265 samples were classified as “W” (wet) with 133 field blanks. A total of 9,398 samples were eligible for reanalysis. These samples had volumes of 35 mL or more, by definition of “W” samples. The 485 samples flagged for reanalysis included one percent of the total number of samples chosen randomly. A total of 206 individual measurement changes were made to 114 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 1,518 samples logged in for AIRMoN with 1,001 “W” samples (samples with enough liquid for a complete analysis) and 194 field blanks, a total of 1,195 samples were eligible for reanalysis. Of this total 57 samples were flagged for reanalysis, including three percent of the total number selected randomly. There were 10 edits on 8 of the 57 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 1998–2001 median IPDs were positive for NTN, but negative for AIRMoN. A negative value indicates a measured cation excess, a positive value indicates an excess of 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 that are not measured at the CAL. Organic acids are commonly seen with the ion chromatograph but not quantified. Because the median IPD is very close to zero, anions measured very nearly equal cations measured in AIRMoN samples.

The CPD consistently has exhibited a negative skew since 1979, with 2001 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 for AIRMoN, that contribute to measured conductivity but are not measured or present in calculated conductivity.

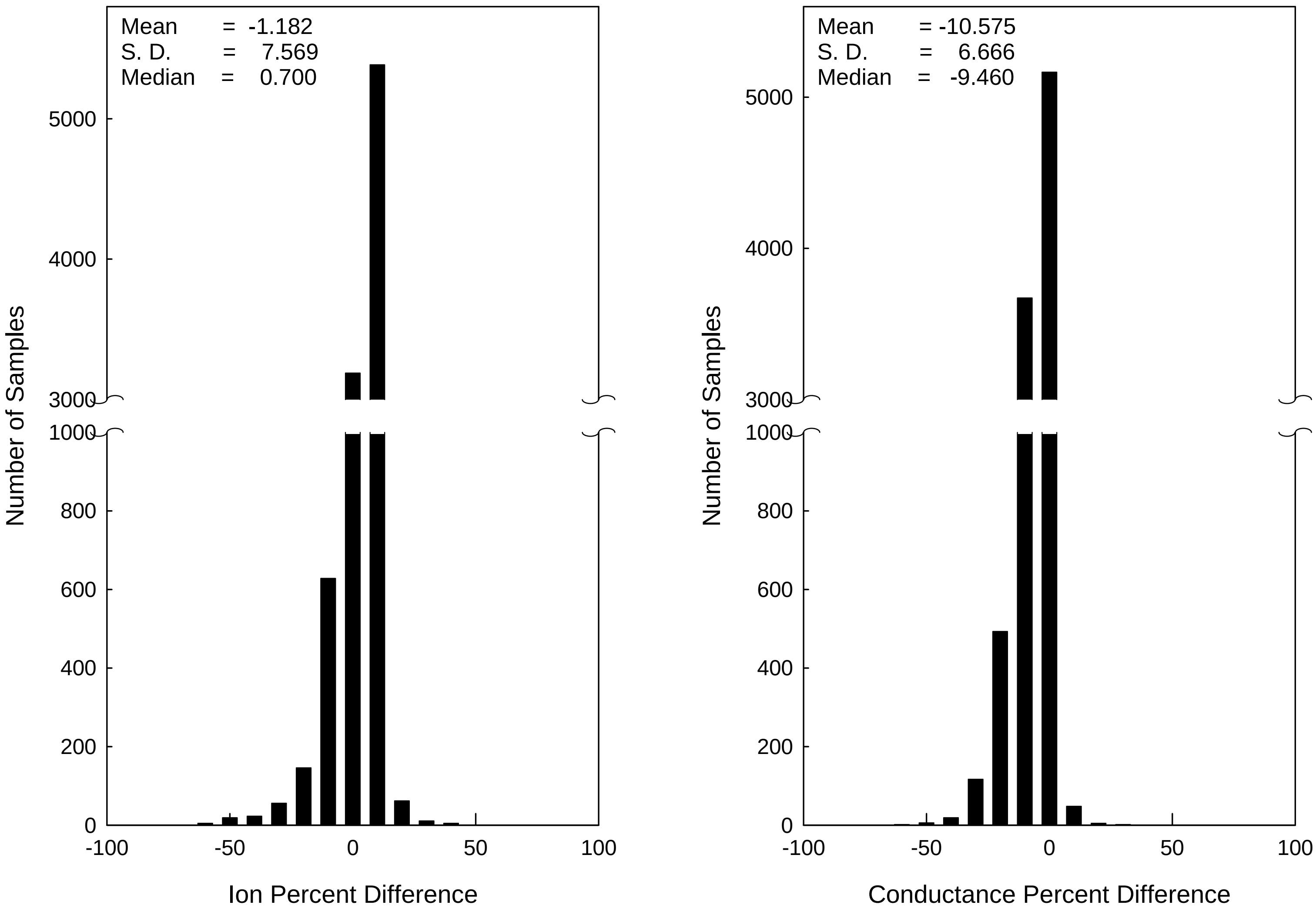


Figure V-1. Ion Percent Difference and Conductance Percent Difference for 9,398 NADP/NTN wet samples, 2001.

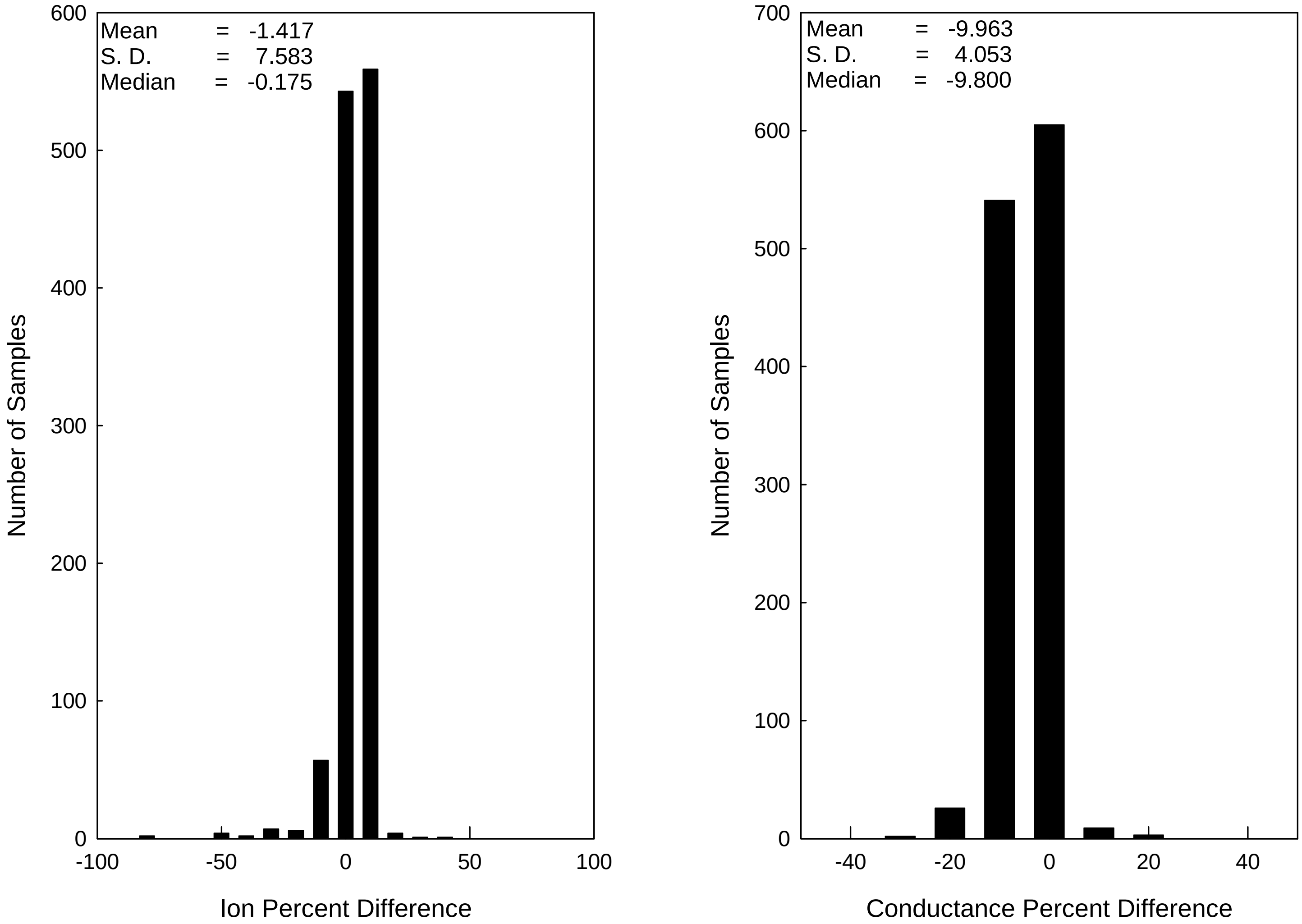


Figure V-2. Ion Percent Difference and Conductance Percent Difference for 1,195 NADP/AIRMoN wet samples, 2001.

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 was designed to determine if the laboratories are producing comparable results.

The Interlaboratory Comparison Program included seven laboratories in 2001:

- Illinois State Water Survey NADP Central Analytical Laboratory (CAL), Champaign, Illinois
- Meteorological Service of Canada (MSC), Ontario, Canada
- Environmental Science and Engineering, Inc. (ESE), Gainesville, Florida
- Ontario Ministry of the Environment, Water Quality Section (MOE), Ontario, Canada
- Shepard Analytical (SA), Simi Valley, California
- Acid Deposition and Oxidant Research Center (ADORC), Niigata-shi, Japan
- Norwegian Institute of Air Research (NILU), Kjeller, Norway

All laboratories participated for the entire year in 2001.

Samples used in 2001 were comprised of three types: (1) National Institute of Standards and Technology (NIST) traceable solutions prepared by High-Purity Standards and diluted by the USGS, (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 50th and 90th percentile absolute differences of replicate samples obtained by the seven laboratories participating in 2001. Figures V-3 and V-4 are graphs showing these same results.

For comparison, laboratory rankings were determined by summing the 50th and 90th percentile absolute differences (Table V-3). The CAL was ranked first for hydrogen ion, ranked second for calcium, tied for second for magnesium and ammonium, ranked third for sulfate and specific conductance, ranked fourth for potassium, ranked fifth for nitrate, and ranked sixth for chloride. The CAL was ranked third overall among the seven laboratories participating in the Interlaboratory Comparison Program in 2001. The CAL's summed 50th and 90th percentile absolute differences of replicate samples were slightly higher during 2001 than in 2000. The summed 50th and 90th percentile absolute differences for the ADORC and MSC laboratories were lower during 2001 than during 2000. The USGS will publish complete results of the 2001 study minus the laboratory rankings.

Rankings given in this report are relative numbers comparing the seven laboratories and do not define the quality of the laboratories. Further inspection of the numbers shows little difference among the seven laboratories. When looking at the percentile sum relative to the detection limit, the CAL sum was less than the MDL for calcium, magnesium, and ammonium. The CAL sum was greater than the MDL for other analytes. For no analyte was the sum greater than ten times the MDL, with chloride being the highest, about three times the MDL. Concentration ranges for analytes and the acceptable variance for the CAL for that analyte at that concentration are found in Table V-4. A comparison of the percentile differences for the CAL and the allowable values for bias shows that the CAL was within specifications for these samples. For most analytes, the CAL was within three times the f-pseudosigma (control limits) as defined by the USGS and within the accepted bias of the NADP. A distinct negative bias was found in ammonium concentrations even though the concentrations reported were, for the most part, within the control limits. There was a very slight positive bias for sulfate although most results were within the control limits.

Table V-2. The 50th and 90th Percentile Absolute Differences for Analysis of Replicate Samples, Interlaboratory Comparison Program, 2001

	CAL[a]		*MSC*[b]		*ESE*[c]		*MOE*[d]		*SA*[e]		*ADORC*[f]		*NILU*[g]	
Analyte	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*	*50th*	*90th*
Calcium	0.002	0.006	0.002	0.008	0.003	0.012	0.00	0.020	0.001	0.004	0.001	0.004	0.010	0.030
Magnesium	0.00	0.001	0.00	0.002	0.001	0.001	0.00	0.005	0.00	0.001	0.00	0.001	0.00	0.00
Sodium	0.002	0.008	0.001	0.005	0.001	0.005	0.002	0.015	0.001	0.006	0.000	0.003	0.00	0.010
Potassium	0.001	0.004	0.001	0.003	0.001	0.004	0.00	0.010	0.00	0.002	0.00	0.001	0.00	0.010
Ammonium	0.00	0.010	0.001	0.007	0.003	0.007	0.010	0.020	0.00	0.010	0.00	0.010	0.00	0.020
Sulfate	0.005	0.018	0.002	0.012	0.010	0.020	0.00	0.050	0.010	0.020	0.00	0.020	0.020	0.040
Nitrate	0.003	0.029	0.003	0.014	0.005	0.022	0.015	0.050	0.00	0.01	0.00	0.01	0.005	0.040
Chloride	0.002	0.012	0.002	0.007	0.003	0.008	0.00	0.03	0.00	0.010	0.00	0.010	0.00	0.010
Hydrogen ion (µeq/L)	0.020	0.920	0.420	1.18	0.100	0.920	0.170	3.58	0.210	0.990	0.410	1.70	0.520	1.65
Specific conductance (µS/cm)	0.10	0.60	–	–	0.20	0.80	0.40	1.6	0.10	0.20	0.20	0.60	0.10	0.30

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

Notes:

All measurements are in mg/L unless otherwise indicated.

[a] Illinois State Water Survey NADP Central Analytical Laboratory, USA.

[b] Meteorological Service of Canada, Canada.

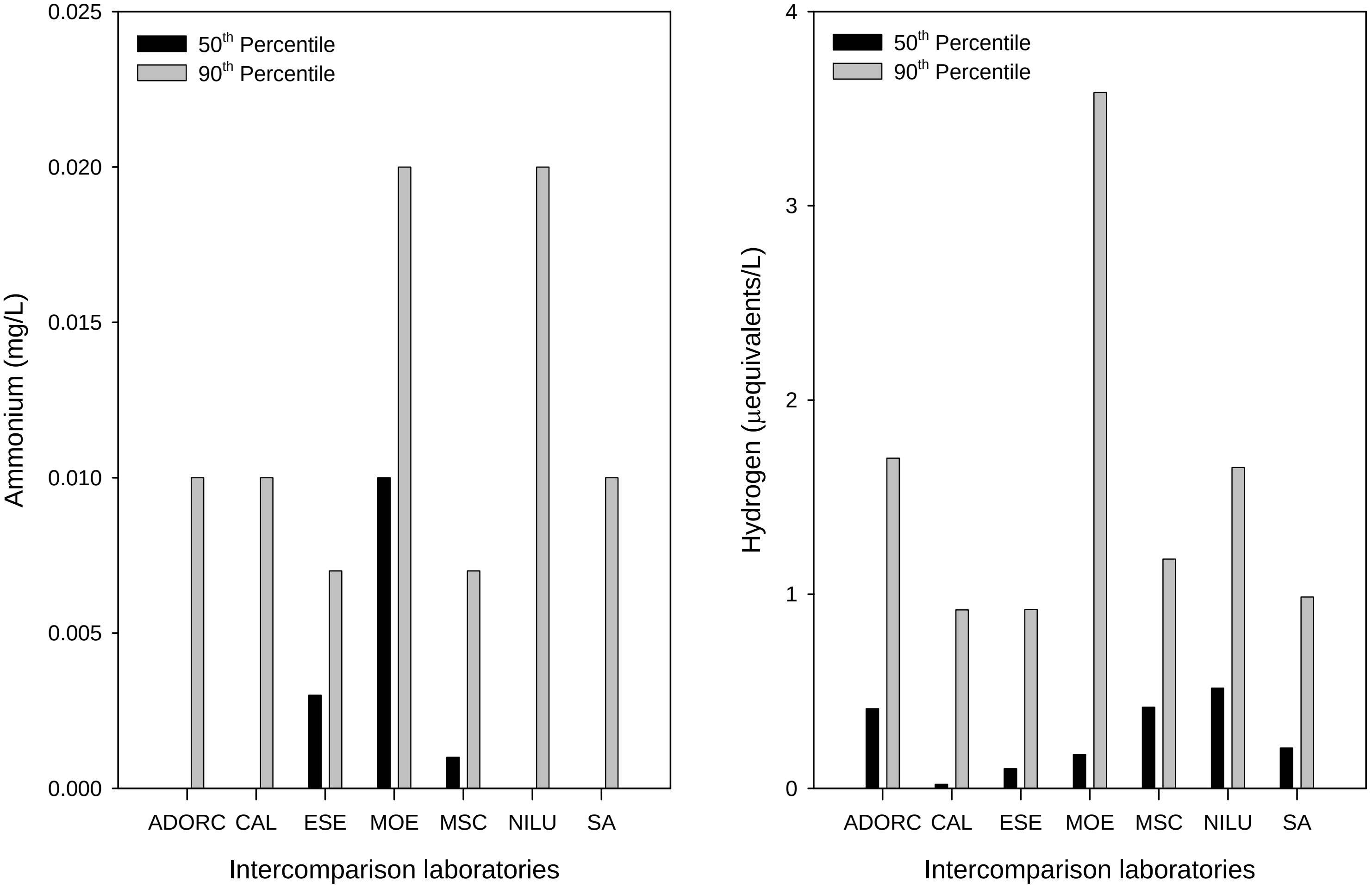
[c] Environmental Science and Engineering, Inc., USA

[d] Ontario Ministry of the Environment, Canada.

[e] Shepard Analytical, USA.

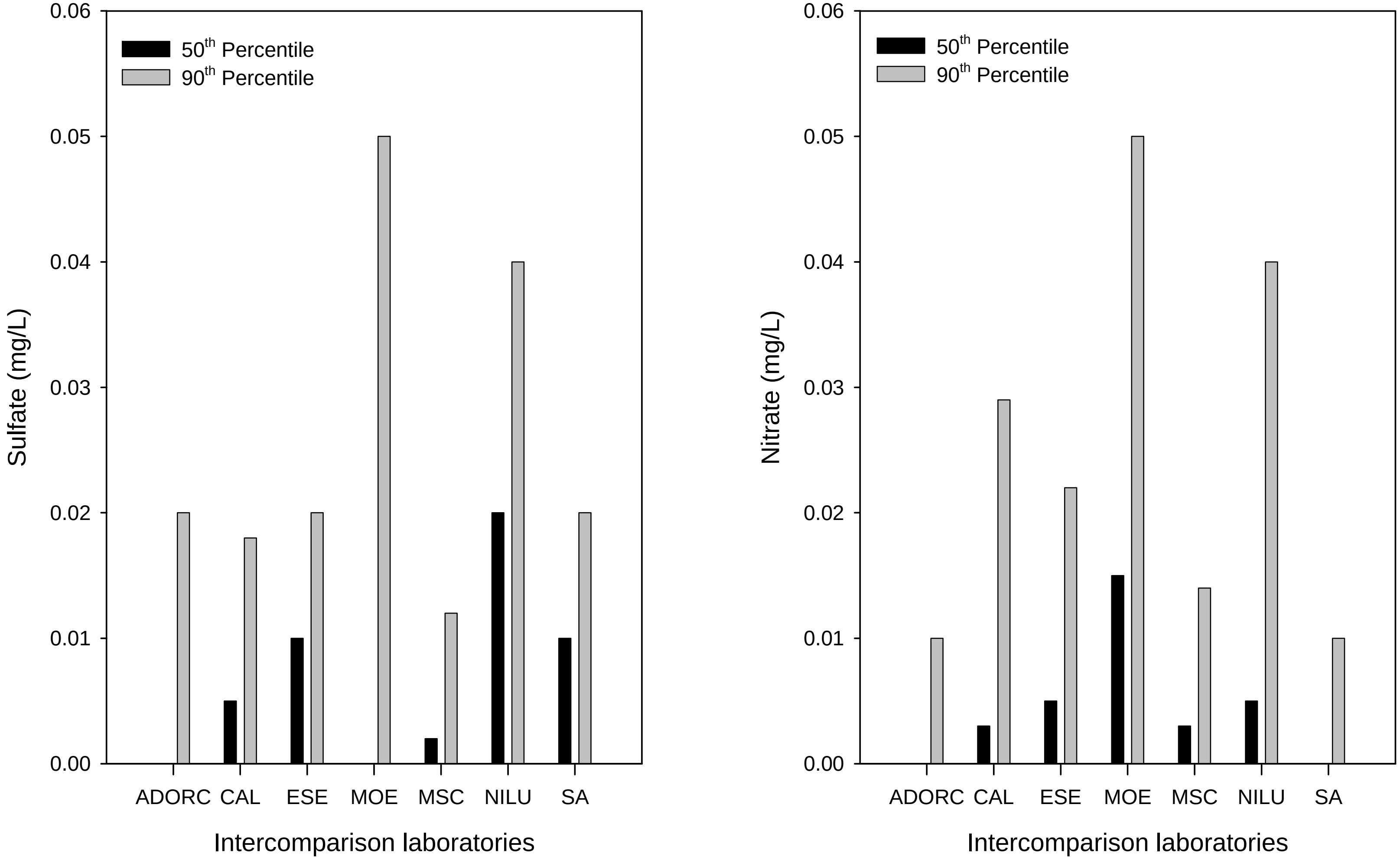
[f] Acid Deposition and Oxidant Research Center, Japan.

[g] Norwegian Institute for Air Research, Norway.



Notes: The laboratories involved in the intercomparison study were the NADP Central Analytical Laboratory (CAL), the Meteorological Service of Canada (MSC), Environmental Science and Engineering (ESE), the Ontario Ministry of the Environment (MOE), Shepard Analytical (SA), the Acid Deposition and Oxidant Research Center of Japan (ADORC), and the Norwegian Institute for Air Research (NILU). Data were provided by USGS Water Resources Division Branch of Quality Systems.

Figure V-3. Ammonium and hydrogen 50th and 90th percentile absolute differences for the seven laboratories, USGS Interlaboratory Comparison Study, 2001.



Notes: The laboratories involved in the intercomparison study were the NADP Central Analytical Laboratory (CAL), the Meteorological Service of Canada (MSC), Environmental Science and Engineering (ESE), the Ontario Ministry of the Environment (MOE), Shepard Analytical (SA), the Acid Deposition and Oxidant Research Center of Japan (ADORC), and the Norwegian Institute for Air Research (NILU). Data were provided by USGS Water Resources Division Branch of Quality Systems.

Figure V-4. Sulfate and nitrate 50th and 90th percentile absolute differences for the seven laboratories, USGS Interlaboratory Comparison Study, 2001.

Table V-3. USGS Interlaboratory Comparison Program Ranking Summary, 2001

Analyte	*CAL*[a]		*MSC*[b]		*ESE*[c]		*MOE*[d]		*SA*[e]		*ADORC*[f]		*NILU*[g]	
	Sum	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*	*Sum*	*Rank*
Calcium	0.008	3	0.010	4	0.015	5	0.02	6	0.005	1 tie	0.005	1 tie	0.040	7
Magnesium	0.001	2 tie	0.002	5 tie	0.002	5 tie	0.005	7	0.001	2 tie	0.001	2 tie	0.0	1
Sodium	0.017	5 tie	0.006	2 tie	0.006	2 tie	0.017	7	0.007	4	0.003	1	0.010	5 tie
Potassium	0.005	4 tie	0.004	3	0.005	4 tie	0.010	6 tie	0.002	2	0.001	1	0.010	6 tie
Ammonium	0.010	2 tie	0.008	1	0.010	2 tie	0.030	7	0.010	2 tie	0.010	2 tie	0.020	6
Sulfate	0.023	3	0.014	1	0.030	4 tie	0.050	6	0.030	4 tie	0.020	2	0.060	7
Nitrate	0.032	5	0.017	3	0.027	4	0.065	7	0.010	1 tie	0.010	1 tie	0.045	6
Chloride	0.014	6	0.009	1	0.011	5	0.030	7	0.010	2 tie	0.010	2 tie	0.010	2 tie
Hydrogen ion (µeq/L)	0.94	1	1.60	4	1.02	2	3.76	7	1.23	3	2.11	5	2.17	6
Specific conductance (µS.cm)	0.7	3	not available	1.0	5	2	6	0.3	1	0.8	4	0.35	2	
Ranking without specific conductance		4		3		5		7		2		1		6
Overall ranking		3	incomplete			4		6		2		1		5

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

Notes:
All values 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, USA.
[b] Meteorological Service of Canada, Canada.
[c] Environmental Science and Engineering, USA.
[d] Ontario Ministry of the Environment, Canada.
[e] Shepard Analytical, USA.
[f] Acid Deposition and Oxidant Research Center, Japan.
[g] Norwegian Institute for Air Research, Norway.

Table V-4. Target Values and Allowable Biases, USGS Interlaboratory Comparison Program, 2001

Analyte	*SP1*		*SP2*		*SP5*		*SP97*		*SP98c*	
(mg/L)	*Target*	*Bias**	*Target*	*Bias*	*Target*	*Bias*	*Target*	*Bias*	*Target*	*Bias*
Calcium	0.443	0.088	0.444	0.089	0.554	0.111	0.122	0.024	0.017	0.017
Magnesium	0.095	0.019	0.072	0.014	0.176	0.035	0.017	0.017	0.035	0.007
Sodium	0.415	0.083	0.350	0.070	0.442	0.088	0.025	0.025	0.208	0.042
Potassium	0.076	0.015	0.060	0.012	0.081	0.016	0.023	0.023	0.056	0.011
Ammonium	0.68	0.14	0.55	0.11	0.70	0.14	0.28	0.06	0.11	0.11
Chloride	0.581	0.058	0.442	0.088	0.708	0.071	0.054	0.011	0.229	0.046
Nitrate	2.065	0.207	2.938	0.294	2.511	0.251	1.173	0.117	0.560	0.112
Sulfate	3.812	0.381	2.310	0.231	4.460	0.446	1.130	0.226	2.399	0.240
pH (pH units)	4.43		4.52		4.34		4.77		4.40	
Hydrogen ion (µequiv/L)	37.2		30.2		45.7		17.0		39.8	
Specific conductance (µS/cm)	29.5		23.0		34.3		11.2		20.4	

Notes:
All values are in mg/L unless otherwise indicated.
*The bias in this table represents the NADP stated bias allowed for each analyte at the concentration of that specific analyte for that sample (Rothert, 2002).

VI. Semiannual and Annual Quality Assurance Procedures

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

Each year the CAL participates in interlaboratory comparison studies not sponsored by the NADP. There were six studies in 2001: two studies conducted by the World Meteorological/Global Atmospheric Watch, Geneva, Switzerland; two studies conducted by the National Water Research Institute, Burlington, Ontario, Canada; one study conducted by Acid Deposition and Oxidant Research Center, Niigata-shi, Japan; and one study conducted by the the Norwegian Institute for Air Research, Kjeller, Norway.

A. World Meteorological Organization/Global Atmospheric Watch

The 24th and 25th sets of WMO/GAW reference precipitation samples were shipped to participating laboratories in April and October 2001, respectively. The CAL had a contract to prepare the simulated precipitation samples used in these studies. Samples were shipped to 96 laboratories, and 67 laboratories reported results to the WMO Quality Assurance/Science Activity Center for the Americas located at the Atmospheric Science Research Center in Albany, New York (Coleman et al., 2001). 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 with the study laboratories, the CAL results were not ranked; however, CAL results agreed well with the study means and target values.

Without benefit of the statistical input of the other laboratories, the CAL data consistently appear to be low for ammonium concentrations and high for specific conductance. All other parameters vary and have no obvious trend. Whether these biases for ammonium and specific conductance are statistically significant is not known. 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 2001 were FP78 and FP79 (Blum and Alkema, 2001a, 2001b). The NWRI samples included selected major ions, nutrients, and physical parameters in natural waters. Median concentrations from all reporting

Table VI-1. 24th World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) Acid Rain Performance Survey, 2001

Analyte	*Sample 1*			*Sample 2*			*Sample 3*		
	Target	*Mean*	*CAL*	*Target*	*Mean*	*CAL*	*Target*	*Mean*	*CAL*
Calcium	0.340	0.335	0.333	0.154	0.153	0.152	0.790	0.789	0.754
Magnesium	0.100	0.099	0.094	0.054	0.050	0.051	0.250	0.247	0.234
Sodium	0.421	0.408	0.423	0.152	0.143	0.153	1.320	1.301	1.328
Potassium	0.129	0.127	0.126	0.087	0.082	0.084	0.288	0.288	0.278
Ammonium (as N)	0.474	0.477	0.44	0.223	0.223	0.21	1.030	1.045	0.96
Sulfate (as S)	0.840	0.818	0.837	0.377	0.369	0.369	1.765	1.736	1.784
Nitrate (as N)	0.429	0.419	0.424	0.166	0.166	0.167	0.907	0.911	0.939
Chloride	0.781	0.764	0.783	0.300	0.299	0.290	2.081	2.056	2.070
pH (pH units)	4.61	4.63	4.64	5.12	5.07	5.04	4.45	4.44	4.47
Hydrogen ion µeq/L	24.5	23.4	22.9	7.6	8.5	9.1	35.5	36.3	33.9
Specific conductance (µS/cm)	21.8	21.2	22.6	8.4	9.2	9.8	42.6	42.2	44.3

Notes:
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. All values are in mg/L unless otherwise indicated.

Table VI-2. 25th World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) Acid Rain Performance Survey, 2001

Analyte	*Sample 1*			*Sample 2*			*Sample 3*		
	Target	*Mean*	*CAL*	*Target*	*Mean*	*CAL*	*Target*	*Mean*	*CAL*
Calcium	0.262	0.257	0.236	0.050	0.055	0.043	0.110	0.126	0.111
Magnesium	0.053	0.051	0.049	0.015	0.016	0.013	0.043	0.042	0.039
Sodium	0.191	0.180	0.181	0.038	0.033	0.036	0.083	0.079	0.080
Potassium	0.043	0.044	0.041	0.019	0.025	0.017	0.031	0.034	0.030
Ammonium (as N)	0.340	0.349	0.32	0.080	0.081	0.07	0.160	0.160	0.15
Sulfate (as S)	0.709	0.695	0.710	0.177	0.170	0.173	0.343	0.334	0.338
Nitrate (as N)	0.451	0.450	0.462	0.126	0.128	0.125	0.250	0.257	0.260
Chloride	0.281	0.273	0.277	0.070	0.072	0.067	0.119	0.114	0.116
pH (pH units)	4.48	4.46	4.46	4.98	4.98	4.95	4.75	4.75	4.74
Hydrogen ion µeq/L	33.1	34.7	34.7	10.5	10.5	11.2	17.8	17.8	18.2
Specific conductance (µS/cm)	21.3	22.3	23.9	6.1	6.5	7.1	11.1	11.4	12.4

Notes:
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. All values are in mg/L unless otherwise indicated.

laboratories were used as target values. Most samples were surface waters or precipitation samples for which calculated or certified values were not known. High, very high, low, or very low results were noted. These flags were based on the biases observed from the median values found in the study and the biases of the other laboratories. A score was computed from these flagged samples. Zero, therefore, denoted the optimum score indicating that all parameters were within the expected range of the target values. For a complete explanation of the flagging system used in these studies, refer to the original reports (Blum and Alkema, 2001a and 2001b).

Tables VI-3 and VI-4 show the median results and the CAL results for both studies. For Study FP78, the CAL had two high specific conductance values. Although the ammonium concentrations received no flags, the values were consistently lower than the median, resulting in a second flagged analyte. The resultant overall ranking for the CAL was tenth out of the 36 laboratories reporting numbers and a rating of “satisfactory” (four of the laboratories ranked above the CAL analyzed less than 10 parameters). For Study FP79, the CAL received 12 low or very low flags: two low flags (calcium), two low flags and five very low flags (magnesium), and three low flags (sodium). This resulted in three parameters biased low, giving the CAL an overall median of 21.1 percent, resulting in a rating of “moderate”. For a description of how “flags” are assigned to the NWRI interlaboratory comparison samples, see their summary reports (Blum and Alkema, 2001a and 2001b).

The NWRI summarizes performance results for the past ten studies (Studies 0070–0079). The CAL received a median score of 4.6 based on the percentage of biased parameters and flagged results on the studies. This was the sixth lowest score (the lower the score, the better the laboratory and the ranking) of the 32 ranked laboratories and was rated “good”.

C. The Acid Deposition Monitoring Network in East Asia

In 2001, the CAL participated in the Acid Deposition Monitoring Network in East Asia’s (EANET) intercomparison study sponsored by ADORC, Japan. Twenty-four laboratories are mandated through their participation in EANET to participate in this study. Four cooperative laboratories also participated, including the CAL. As a cooperative laboratory, CAL data results were not used to evaluate the participating laboratories' results. Table V-5 shows target values, mean values, and CAL values found in the study.

The CAL results for pH, specific conductance, chloride, nitrate, sulfate, and sodium match fairly well with target and/or mean concentrations in the study. One potassium value was in excellent agreement, and one potassium value was low. Calcium, magnesium, and ammonium were all lower than the target or mean values. Data Quality Objectives (DQOs) for the study were ± 15 percent of the target value for every constituent. Table VI-5 includes the percentile difference for each constituent for the CAL mean values versus the target values. The CAL had no values outside ± 10 percent of the target concentrations.

Table VI-3. National Water Research Institute (NWRI) Soft Water Interlaboratory Study FP78, Spring 2001

	Sample 1		*Sample 2*		*Sample 3*		*Sample 4*		*Sample 5*	
Analyte	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	0.710	0.716	0.167	0.167	1.820	1.783	2.017	2.039	2.170	2.207
Magnesium	0.162	0.155	0.030	0.029	0.460	0.447	0.329	0.316	0.551	0.550
Sodium	0.050	0.052	0.065	0.067	0.060	0.062	0.626	0.610	0.784	0.773
Potassium	0.018	0.018	0.028	0.028	0.101	0.105	0.422	0.423	0.195	0.195
Ammonium (as N)	0.171	0.163	0.162	0.152	0.185	0.177	0.012	<0.02	0.005	<0.02
Sulfate	2.190	2.203	1.850	1.828	3.140	3.151	5.631	5.625	7.036	6.984
Nitrate (as N)	0.267	0.267	0.235	0.235	1.165	1.181	0.420	0.427	0.053	0.056
Chloride	0.119	0.116	0.121	0.118	0.313	0.317	0.460	0.482	0.748	0.770
pH (pH units)	5.28	5.25	4.52	4.52	4.93	4.97	5.39	5.40	5.41	5.42
Specific conductance µS/cm	11.0	12.1	16.5	18.1	24.1	25.3	23.7	24.6	25.6	26.8

	Sample 6		*Sample 7*		*Sample 8*		*Sample 9*		*Sample 10*	
Analyte	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	0.810	0.798	2.999	2.984	2.729	2.675	3.054	3.045	2.077	1.994
Magnesium	0.393	0.385	0.684	0.662	0.967	0.953	0.446	0.425	0.509	0.508
Sodium	2.910	2.851	4.000	4.052	0.286	0.299	1.500	1.421	0.640	0.629
Potassium	0.290	0.277	0.391	0.402	0.157	0.159	0.360	0.359	0.236	0.232
Ammonium (as N)	0.005	<0.02	0.009	<0.02	0.176	0.164	0.005	<0.02	0.040	0.033
Sulfate	2.250	2.282	2.040	2.076	5.418	5.418	3.210	3.271	6.350	6.371
Nitrate (as N)	0.046	0.049	0.178	0.191	2.112	2.127	0.230	0.237	0.004	0.006
Chloride	4.615	4.693	6.154	6.173	0.549	0.559	0.960	0.985	0.531	0.558
pH pH units	5.57	5.57	6.87	6.83	4.49	4.52	6.69	6.87	6.29	6.38
Specific conductance µS/cm	26.1	27.6	41.8	44.4	44.4	47.2	28.0	29.1	23.0	23.7

Table VI-4. National Water Research Institute (NWRI) Soft Water Interlaboratory Study FP79, Fall 2001

	Sample 1		*Sample 2*		*Sample 3*		*Sample 4*		*Sample 5*	
Analyte	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	0.617	0.567	0.125	0.118	2.902	2.745	2.782	2.615	2.545	2.375
Magnesium	0.170	0.151	0.038	0.033	0.655	0.591	1.060	0.930	0.610	0.548
Sodium	0.074	0.071	0.169	0.160	0.152	0.144	0.297	0.283	2.203	2.061
Potassium	0.018	0.017	0.029	0.029	0.281	0.288	0.168	0.162	0.511	0.491
Ammonium (as N)	0.061	0.057	0.116	0.108	0.228	0.221	0.384	0.365	0.031	0.026
Sulfate	1.324	1.315	1.305	1.310	5.008	5.051	4.005	4.055	4.737	4.766
Nitrate (as N)	0.375	0.376	0.253	0.251	1.927	1.910	0.610	0.612	0.071	0.071
Chloride	0.156	0.155	0.293	0.298	0.531	0.533	0.534	0.545	1.713	1.701
pH pH units	5.20	5.20	4.60	4.61	4.59	4.62	6.95	7.09	6.82	6.97
Specific conductance µS/cm	9.9	10.8	14.6	15.7	40.9	42.0	31.2	31.5	32.0	32.4

	Sample 6		*Sample 7*		*Sample 8*		*Sample 9*		*Sample 10*	
Analyte	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*	*Median*	*CAL*
Calcium	2.870	2.672	3.000	2.714	0.280	0.260	2.267	2.077	2.319	2.196
Magnesium	0.840	0.752	0.550	0.480	0.067	0.060	0.600	0.523	0.660	0.578
Sodium	0.340	0.319	2.058	1.930	0.070	0.067	1.241	1.151	0.128	0.119
Potassium	0.200	0.205	0.360	0.345	0.030	0.028	0.280	0.280	0.105	0.106
Ammonium (as N)	0.023	0.024	0.002	<0.02	0.220	0.207	0.003	<0.02	0.081	0.081
Sulfate	6.852	6.844	3.860	3.877	1.619	1.617	2.795	2.795	5.105	5.141
Nitrate (as N)	0.030	0.635	0.171	0.171	0.243	0.241	0.000	0.000	1.535	1.526
Chloride	0.486	0.491	2.130	2.146	0.140	0.137	1.920	1.940	0.309	0.309
pH pH units	6.36	6.51	6.82	7.01	4.82	4.86	6.86	7.00	4.47	4.50
Specific conductance µS/cm	29.7	30.1	32.5	33.0	11.7	23.3	25.4	25.7	39.0	39.5

Table VI-5. The Acid Deposition Monitoring Network in East Asia (EANET) Interlaboratory Comparison Study, 2001

Analyte	*Sample 1*				*Sample 2*			
	Target	*Mean*	*CAL*	*Difference (%)*	*Target*	*Mean*	*CAL*	*Difference (%)*
Calcium	1.178	1.170	1.112	-5.6	0.441	0.437	0.415	-5.9
Magnesium	0.284	0.282	0.259	-8.9	0.190	0.182	0.171	-9.8
Sodium	1.179	1.149	1.156	-2.0	0.200	0.205	0.198	-1.0
Potassium	0.387	0.383	0.357	-7.8	0.192	0.188	0.188	-1.9
Ammonium	1.091	1.138	1.04	-4.3	0.328	0.346	0.31	-6.2
Sulfate	5.735	5.735	5.75	0.4	1.931	1.960	1.929	-0.1
Nitrate	3.924	3.962	3.94	0.7	1.705	1.723	1.696	-0.5
Chloride	3.591	3.552	3.61	0.6	0.549	0.549	0.551	0.3
pH pH units	4.10	4.12	4.11	0.2	4.85	4.90	4.85	0.0
Specific conductance µS/cm	62.3	60.5	62.6	0.5	15.5	15.6	16.2	4.5

Notes:
Target and mean values were taken from the Acid Deposition Monitoring Network in East Asia (EANET) report of 2002. The CAL values were the mean values obtained at the laboratory and reported to the EANET as a cooperative laboratory.

D. Norwegian Institute for Air Research

The Norwegian Institute for Air Research (NILU) sponsored the 19th European Monitoring and Evaluation Programme (EMEP) intercomparison of analytical methods for atmospheric precipitation in late summer 2001. There were four samples in the study. Table VI-6 presents study results. The CAL results show no apparent bias other than ammonium values that were less than 10 percent of the target concentrations and, therefore, biased low. All other results were within the standard expected variation for that analyte.

Table VI-6. Norwegian Institute for Air Research (NILU) European Monitoring and Evaluation Programme 19th Intercomparison of Analytical Methods, 2001

	Sample 1		*Sample 2*		*Sample 3*		*Sample 4*	
Analyte	*Target*	*CAL*	*Target*	*CAL*	*Target*	*CAL*	*Target*	CAL
Calcium	0.230	0.230	0.335	0.334	0.383	0.381	0.268	0.265
Magnesium	0.093	0.088	0.155	0.148	0.186	0.176	0.108	0.102
Sodium	0.427	0.422	0.384	0.376	0.649	0.636	0.682	0.657
Potassium	0.102	0.097	0.127	0.122	0.280	0.268	0.331	0.304
Ammonium	0.481	0.45	0.321	0.30	0.561	0.52	0.281	0.26
Sulfate	1.509	1.501	0.953	0.950	1.113	1.108	1.400	1.384
Nitrate	0.698	0.702	0.497	0.498	0.760	0.761	0.563	0.557
Chloride	0.203	0.198	0.261	0.255	0.753	0.752	0.637	0.630
pH pH units	4.125	4.18	4.523	4.56	4.456	4.49	4.187	4.24
Specific conductance µS/cm	42.40	42.6	22.7	23.3	30.1	31.0	38.8	38.7

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 2001. 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 once again 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.

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 2001 compared to that estimated in 2000. Potassium, ammonium, and chloride were improved, nitrate stayed the same, but 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 01FR25 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 coordinator. Analytical results for these internal blind samples showed that the precision calculated for the solution used in 2001, the WMO/GAW 2000, 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 2001. 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 2001. 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 seven laboratories in 2001. Four different sample matrices were used and shipped to the laboratories every two weeks. Half of all samples sent to the laboratories in this study were natural precipitation samples prepared (without verification of the target values) by the CAL. The 50th and 90th percentile absolute differences for these samples indicated that the CAL had good results, ranking third. 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 acceptable limits.

In 2001, the CAL participated in six additional interlaboratory comparisons: two with the WMO/GAW, two studies from the NWRI, one study with the NILU, and one with the ADORC. 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-seven laboratories participated in the WMO/GAW 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, comparison of the data from the CAL with theoretical and median values from the other 67 laboratories, indicated that the CAL results were acceptable. The NWRI results over the last ten studies indicate that the CAL is ranked sixth overall of 32 ranked laboratories. The CAL received two high specific conductance flags, and ammonium was biased low even though it received no flags in Study FP78. The CAL received three low sodium flags, seven low or very low magnesium flags, and two low flags for calcium in Study FP79. These results gave the CAL a “satisfactory” rating for the first study and a “moderate” rating for the second study. A comparison of the last ten studies resulted in a median score for the CAL of 4.6 percent or a “good” rating (5 percent or less is required for a “good” rating). The CAL results for the ADORC study were within expected limits for all parameters. 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.

REFERENCES

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

Blum, J., and H. Alkema. 2001a. *Ecosystem Performance Evaluation QA Program - Rain and Soft Waters - Study FP 78 –Spring 2001, Report No. NLET-TN01-006*. National Water Research Institute National Laboratory for Environmental Testing, Burlington, Ontario, Canada.

Blum, J., and H. Alkema. 2001b. *Ecosystem Performance Evaluation QA Program - Rain and Soft Waters - Study FP 79 –Fall 2001, Report No. NLET-TN01-011*. National Water Research Institute National Laboratory for Environmental Testing, Burlington, Ontario, Canada.

Coleman, T.L., P.J. Galvin, and V.A. Mohnen. 2001. *Report of the 24th Intercomparison of WMO/GAW Precipitation Chemistry*. World Meteorological Organization/Global Atmosphere Watch, Atmospheric Sciences Research Center, University of Albany, State University of New York, Albany, NY (http://marble.asrc.cestm.albany.edu/qasac/lab_ic.html#results, accessed December 12, 2003).

Coleman, T.L., P.J. Galvin, and V.A. Mohnen. 2002. *Report of the 25th Intercomparison of WMO/GAW Precipitation Chemistry*. World Meteorological Organization/Global Atmosphere Watch, Atmospheric Sciences Research Center, University of Albany, State University of New York, Albany, NY (http://marble.asrc.cestm.albany.edu/qasac/lab_ic.html#results, accessed December 12, 2003).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Rothert, J.E. 2001. *Quality Assurance Report, National Atmospheric Deposition Program, 1999, Laboratory Operations, Central Analytical Laboratory*. NADP Program Office, Illinois State Water Survey, Champaign, IL.

Rothert, J.E. 2002. *Quality Assurance Report, National Atmospheric Deposition Program, 2000, Laboratory Operations, Central Analytical Laboratory*. NADP Program Office, Illinois State Water Survey, Champaign, IL.

Simmons, C.L., S.R. Dossett, W.C. Eaton, B.A. Malo, M.E. Peden, and D.S. Bigelow. 1991. *Quality Assurance Plan NADP/NTN Deposition Monitoring*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO.

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

Stensland, G.J, R.G. Semonin, M.E. Peden, V.C. Bowersox, F.F. McGurk, L.M. Skowron, M.J. Slater, and R.K. Stahlhut. 1980. *NADP Quality Assurance Report - Central Analytical Laboratory, January 1979 through December 1979*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO.

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

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 percent 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. Sample identity 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. Sample identity is known to the processing staff only. Analyte concentrations are unknown to the analysts. These data are valuable in assessing bias and precision for network samples.

Term	Abbreviation	Definition
Mean	$\bar{\mathbf{x}}$	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. Percent 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 the 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 Standard	**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 Deviation		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): $s = \sqrt{\frac{\Sigma d^2}{2k}}$ where: d = difference of duplicate measurements k = number of sets of duplicate measurements

Term	Abbreviation	Definition
Variance	s^2	The best measure of the dispersion of repeated results or precision (Anderson, 1987). $$s^2 = \frac{\sum d^2}{2n}$$ where: d = $X_i - X'_i$, the difference between value 1 and 2 of pair i n = the number of pairs of data

Appendix B:

Weekly QA/QC Procedures: Tables and Figures

2001

Table B-1. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, High-Purity Standards Simulated Rainwater 1 (H-PS SR1), 2001

Parameter	*Target concentration[a] (mg/L)*	*Mean measured concentrations (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	0.015	0.022[b]	0.007	45.4	0.036	165.8
		0.058[c]	0.043	286.7	0.017	28.8
Magnesium	0.020	0.019	-0.001	-4.4	0.002	8.8
		0.018	-0.002	-8.1	0.013	69.0
Sodium	0.20	0.200	-0.001	-0.1	0.008	3.8
		0.194	-0.006	-3.0	0.007	3.8
Potassium	0.054	0.052	-0.002	-4.4	0.004	7.3
		0.049	-0.002	-3.2	0.003	6.2
Ammonium	0.100	0.03	-0.07	-73.2	0.02	68.8
		0.03	-0.07	-67.2	0.02	64.4
Sulfate	2.5	2.490	-0.009	-0.4	0.021	0.9
		2.400	-0.100	1.5	0.035	1.5
Nitrate	0.50	0.504	0.004	0.7	0.007	1.3
		0.489	-0.011	-2.3	0.011	2.2
Chloride	0.25	0.218	-0.032	-12.6	0.003	1.3
		0.216	-0.034	-13.6	0.004	1.6
pH[d]	4.15 (4.31)	4.32	0.17 (0.01)	4.1 (0.2)	0.05	1.2
		4.31	0.16 (0.00)	3.9 (0.00)	0.03	0.6
Hydrogen ion (µeq/L)	70.8 (49.0)	48.3	-22.8 (-1.0)	-32.2 (-1.9)	4.6	9.5
		49.1	-21.7 (0.09)	-30.7 (0.2)	2.9	6.0
Specific conductance[d] (µS/cm)	24	25.7	1.7	7.1	1.1	4.3
		25.3	1.3	5.5	0.8	3.0

Notes:
There were 26 unfiltered samples and 13 filtered samples in each set. Numbers in parentheses are the calculated pH and H values based on the ion balance of the solution.

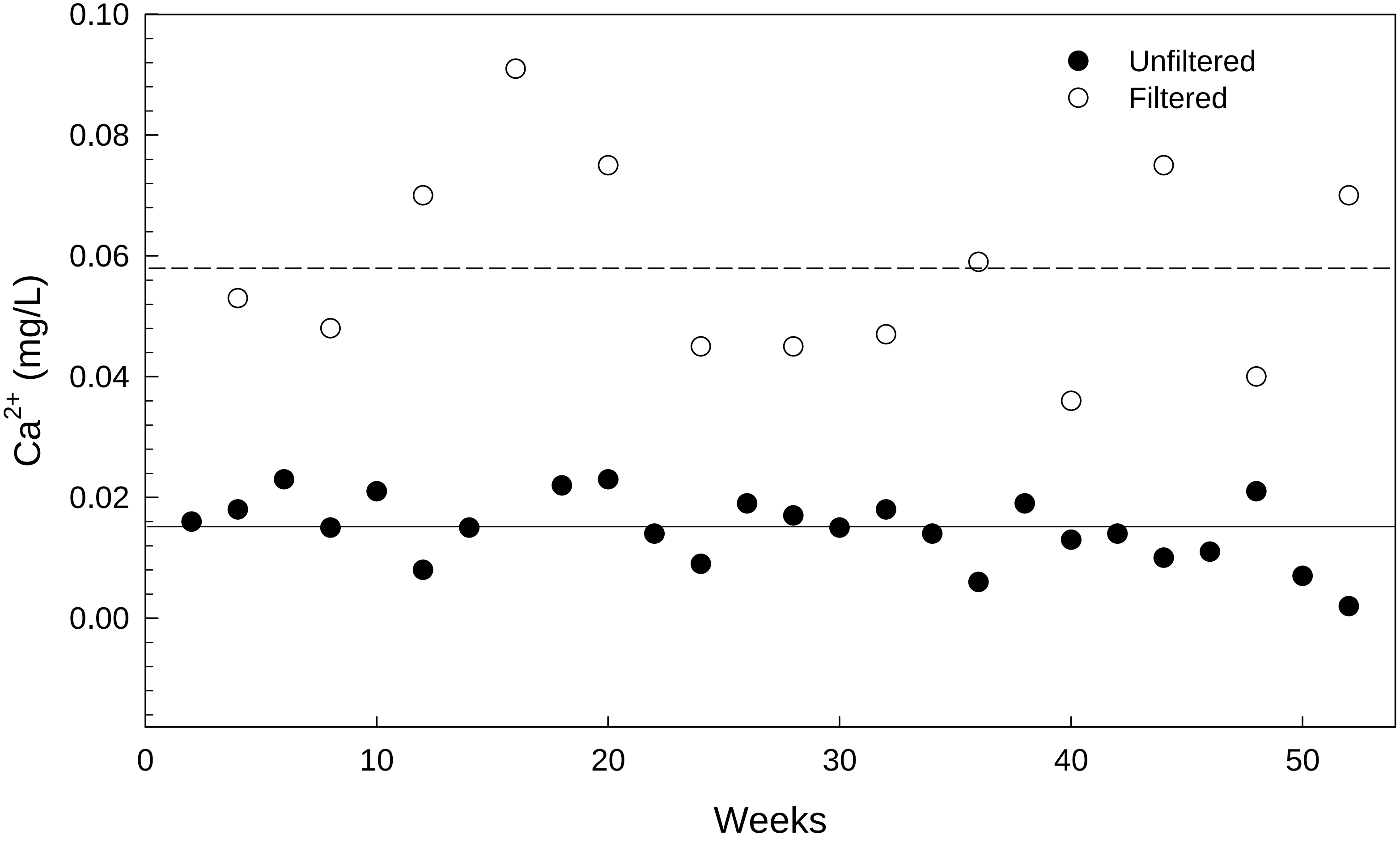
[a] Target values provided by High-Purity Standards for Simulated Rainwater 1.
[b] The first set of values for each parameter is for unfiltered samples.
[c] The second set of values for each parameter is for filtered samples.
[d] Both pH and specific conductance are measured on unfiltered samples prior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

Table B-2. Unfiltered Internal Blind Concentrations for High-Purity Standards Simulated Rainwater 1 (H-PS SR1), 2001

Weeks	*pH (units)*	*H (µeq/L)*	*Specific conductance (µS/cm)*	*Cl^- (mg/L)*	*NO_3^- (mg/L)*	*SO_4^{-2} (mg/L)*	*NH_4^- (mg/L)*	*Ca^{+2} (mg/L)*	*Mg^{+2} (mg/L)*	*Na^+ (mg/L)*	*K^+ (mg/L)*
2	4.31	48.98	29.6	0.217	0.502	2.510	0.013	0.016	0.019	0.208	0.049
4	4.29	51.29	26.5	0.218	0.498	2.514	0.006	0.018	0.024	0.205	0.054
6	4.33	46.77	26.0	0.219	0.509	2.518	0.014	0.023	0.019	0.200	0.051
8	4.31	48.98	26.4	0.220	0.514	2.508	0.000	0.015	0.021	0.201	0.050
10	4.55	28.18	27.6	0.218	0.505	2.486	0.030	0.021	0.020	0.196	0.052
12	4.33	46.77	25.6	0.215	0.501	2.481	0.030	0.008	0.021	0.210	0.052
14	4.34	45.71	25.5	0.220	0.500	2.472	0.031	0.015	0.021	0.207	0.049
16	4.27	53.70	26.0	0.214	0.514	2.484	0.009		0.018	0.206	0.051
18	4.34	45.71	24.8	0.213	0.507	2.491	0.017	0.022	0.019	0.216	0.067
20	4.33	46.77	24.7	0.220	0.509	2.494	0.035	0.023	0.022	0.207	0.052
22	4.32	47.86	25.2	0.222	0.495	2.495	0.018	0.014	0.018	0.193	0.050
24	4.30	50.12	24.6	0.214	0.495	2.492	0.030	0.009	0.018	0.197	0.050
26	4.30	50.12	25.2	0.220	0.502	2.484	0.031	0.019	0.019	0.197	0.049
28	4.31	48.98	24.0	0.218	0.500	2.435	0.035	0.017	0.019	0.195	0.051
30	4.28	52.48	26.1	0.220	0.507	2.493	0.018	0.015	0.017	0.190	0.048
32	4.30	50.12	26.5	0.213	0.504	2.501	0.026	0.018	0.019	0.195	0.052
34	4.30	50.12	25.7	0.219	0.492	2.502	0.042	0.014	0.017	0.192	0.051
36	4.31	48.98	25.2	0.220	0.508	2.460	0.031	0.006	0.016	0.186	0.049
38	4.31	48.98	25.5	0.216	0.520	2.465	0.038	0.019	0.019	0.198	0.053
40	4.28	52.48	26.2	0.222	0.498	2.544	0.017	0.013	0.018	0.189	0.052
42	4.30	50.12	25.9	0.218	0.496	2.501	0.027	0.014	0.018	0.189	0.049
44	4.32	47.86	25.1	0.220	0.494	2.488	0.029	0.010	0.019	0.198	0.054
46	4.31	48.98	24.7	0.219	0.507	2.467	0.026	0.011	0.018	0.208	0.057
48	4.32	47.86	25.1	0.220	0.504	2.488	0.025	0.021	0.020	0.202	0.053
50	4.30	50.12	25.5	0.225	0.507	2.505	0.017	0.007	0.019	0.207	0.049
52	4.32	47.86	24.9	0.218	0.504	2.488	0.102	0.002	0.019	0.202	0.048
Mean	4.32	48.30	25.7	0.218	0.504	2.491	0.027	0.015	0.019	0.200	0.052
Median	4.31	48.98	25.5	0.219	0.504	2.492	0.027	0.015	0.019	0.199	0.051
Target	4.15		24	0.25	0.50	2.5	0.100	0.015	0.020	0.20	0.054

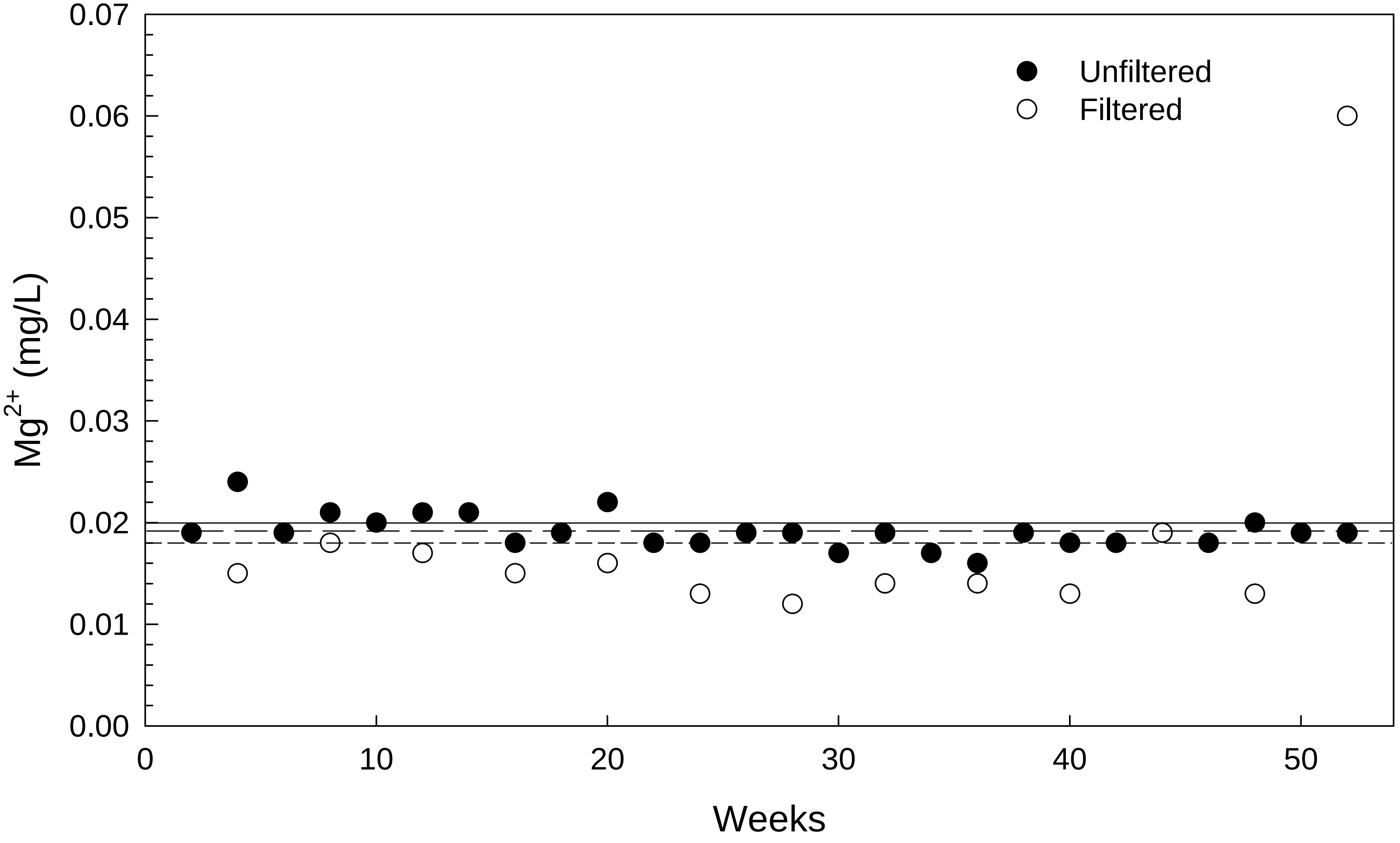
Table B-3. Filtered Internal Blind Concentrations for High-Purity Standards Simulated Rainwater 1 (H-PS SR1), 2001

Weeks	*pH (units)*	*H (μeq/L)*	*Specific conductance (μS/cm)*	*Cl^- (mg/L)*	*NO_3^- (mg/L)*	*SO_4^{-2} (mg/L)*	*NH_4^- (mg/L)*	*Ca^{+2} (mg/L)*	*Mg^{+2} (mg/L)*	*Na^+ (mg/L)*	*K^+ (mg/L)*
4	4.31	48.98	26.1	0.218	0.491	2.416	0.033	0.053	0.015	0.203	0.048
8	4.35	44.67	25.5	0.218	0.499	2.429	0.018	0.048	0.018	0.201	0.051
12	4.30	50.12	25.3	0.215	0.491	2.376	0.038	0.070	0.017	0.203	0.049
16	4.30	50.12	26.1	0.218	0.491	2.413	0.021	0.091	0.015	0.201	0.048
20	4.30	50.12	26.2	0.215	0.489	2.417	0.028	0.075	0.016	0.190	0.051
24	4.30	50.12	23.3	0.221	0.502	2.404	0.035	0.045	0.013	0.190	0.047
28	4.29	51.29	25.4	0.219	0.499	2.432	0.033	0.045	0.012	0.185	0.047
32	4.29	51.29	25.3	0.211	0.490	2.425	0.021	0.047	0.014	0.192	0.051
36	4.29	51.29	25.9	0.211	0.467	2.306	0.031	0.059	0.014	0.180	0.047
40	4.30	50.12	24.7	0.211	0.467	2.357	0.028	0.036	0.013	0.188	0.047
44	4.33	46.77	25.2	0.220	0.485	2.405	0.027	0.075	0.019	0.195	0.058
48	4.29	51.29	25.5	0.214	0.489	2.408	0.014	0.040	0.013	0.192	0.048
52	4.38	41.69	24.8	0.217	0.491	2.415	0.099	0.070	0.060	0.201	0.050
Mean	4.31	49.06	25.3	0.216	0.489	2.400	0.033	0.058	0.018	0.194	0.049
Median	4.30	50.12	25.4	0.217	0.491	2.413	0.028	0.053	0.015	0.192	0.048
Target	4.15		24	0.25	0.50	2.5	0.100	0.015	0.020	0.20	0.054



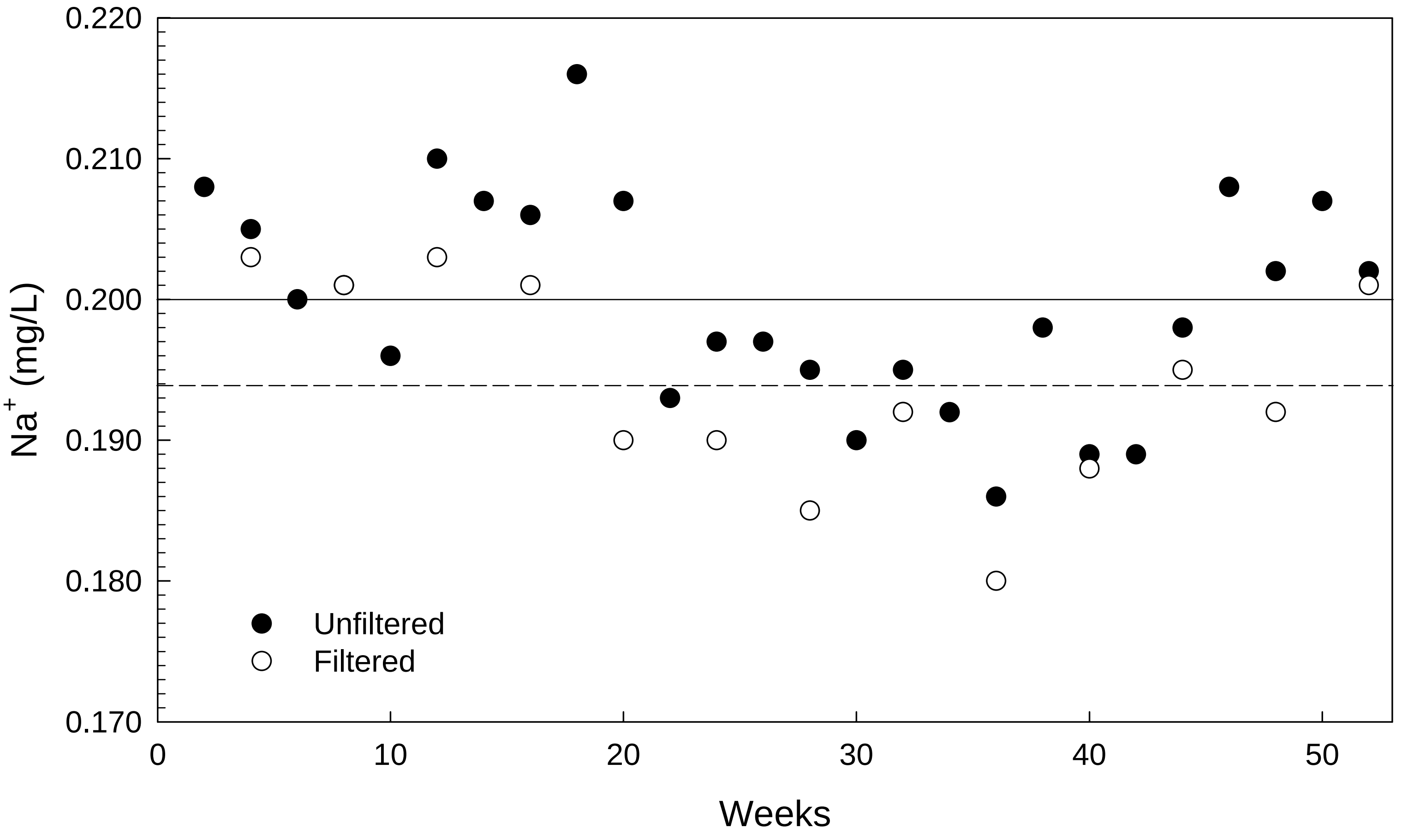
Note:
Solid line denotes target and mean unfiltered Ca^{2+} concentration: 0.015 mg/L; and short dashed line denotes mean filtered Ca^{2+} concentration: 0.058 mg/L.

Figure B-1. Comparison of NTN filtered and unfiltered internal blind samples, (calcium), High-Purity Standards, SR1, 2001.



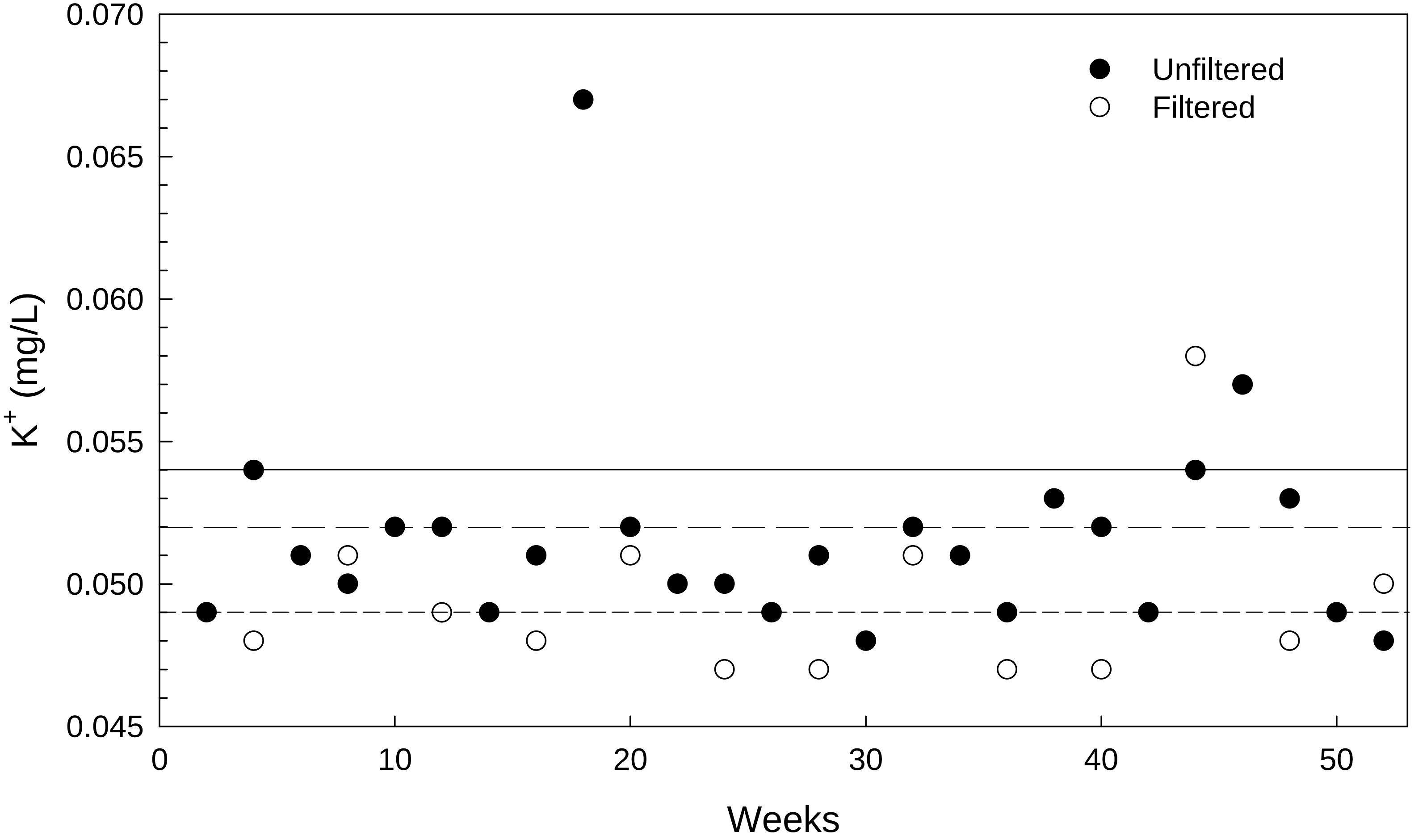
Note:
Solid line denotes target Mg^{2+} concentration: 0.020 mg/L; long dashed line denotes mean unfiltered Mg^{2+} concentration: 0.019 mg/L; and short dashed line denotes mean filtered Mg^{2+} concentration: 0.018 mg/L.

Figure B-2. Comparison of NTN filtered and unfiltered internal blind samples, (magnesium), High-Purity Standards, SR1, 2001.



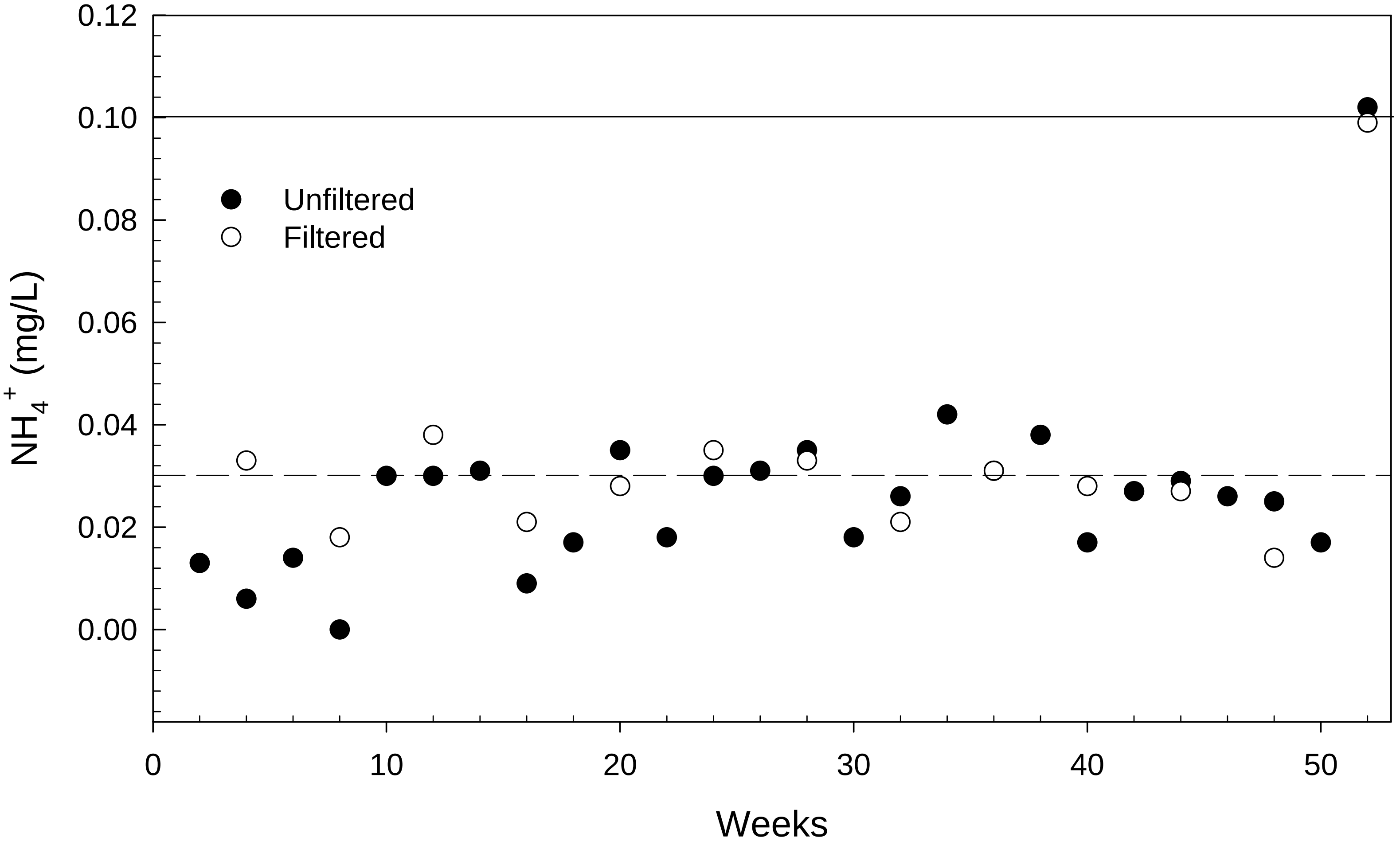
Note:
Solid line denotes the target and the mean unfiltered Na^+ concentration: 0.200 mg/L; and short dashed line denotes the mean filtered Na^+ concentration: 0.194 mg/L.

Figure B-3. Comparison of NTN filtered and unfiltered internal blind samples, (sodium), High-Purity Standards, SR1, 2001.



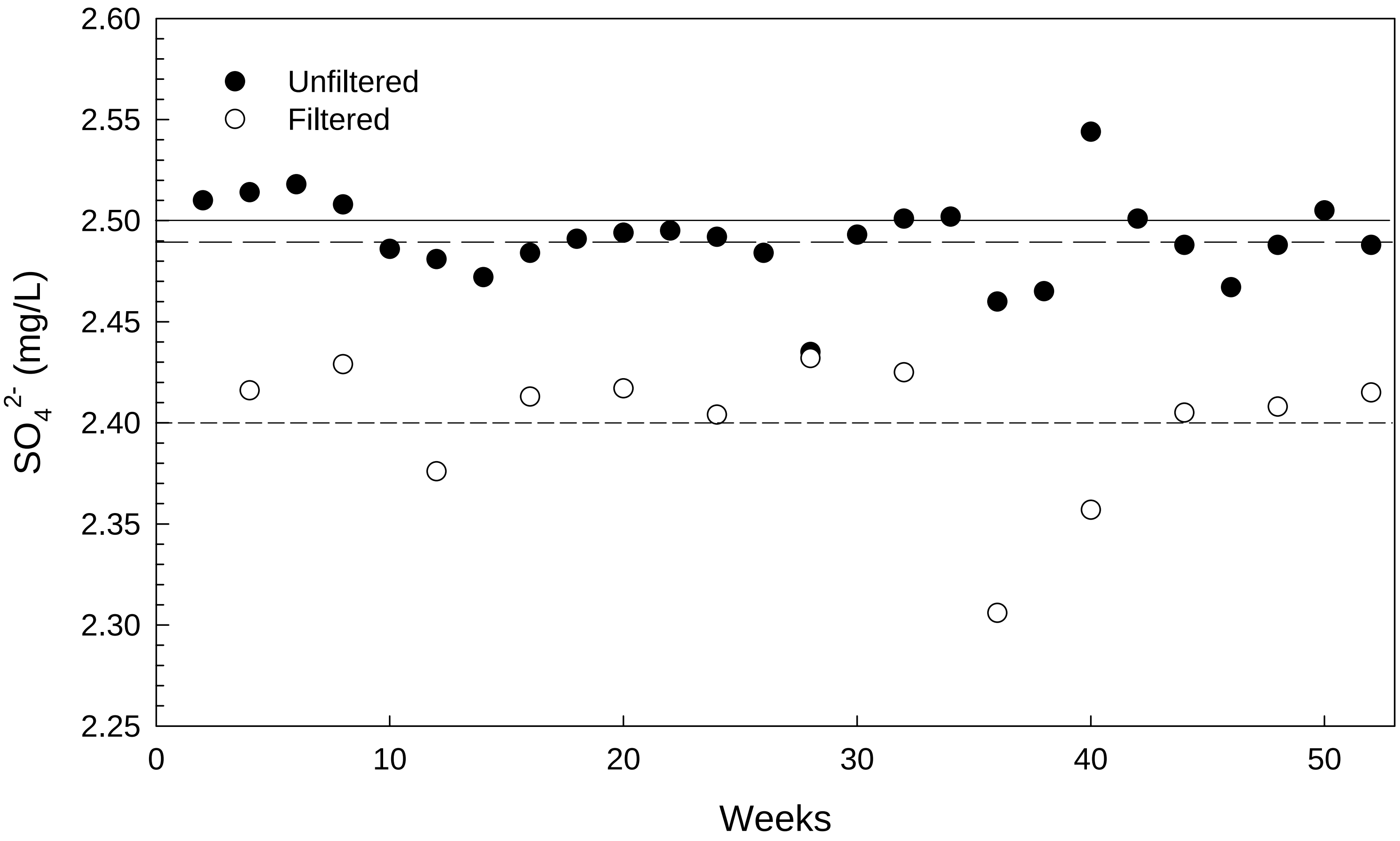
Note:
Solid line denotes target K^+ concentration: 0.054 mg/L; long dashed line denotes mean unfiltered K^+ concentration: 0.052 mg/L; and short dashed line denotes mean filtered K^+ concentration: 0.049 mg/L.

Figure B-4. Comparison of NTN filtered and unfiltered internal blind samples, (potassium), High-Purity Standards, SR1, 2001.



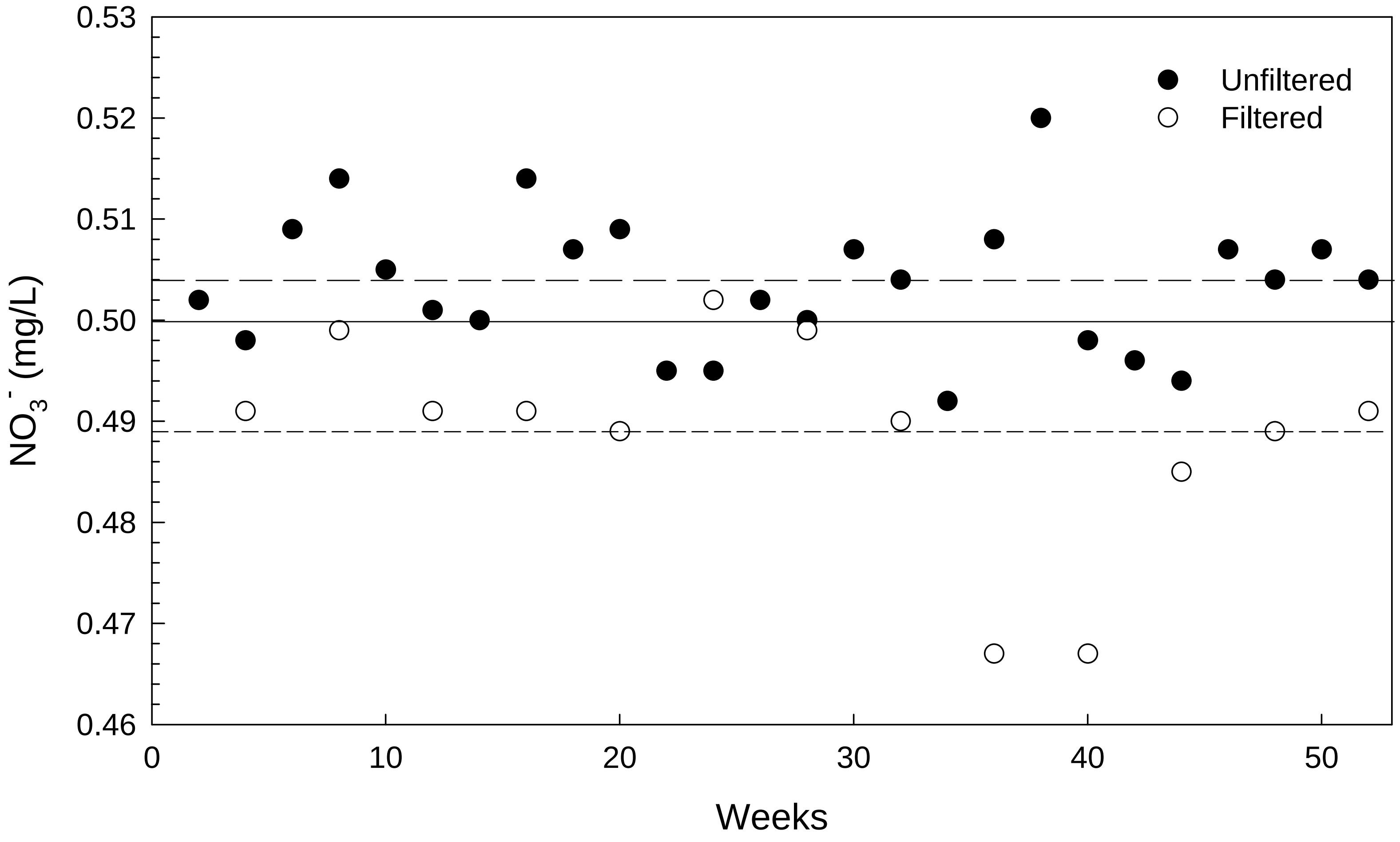
Note:
Solid line denotes target NH_4^+ concentration: 0.1 mg/L; and dashed line denotes mean filtered and unfiltered NH_4^+ concentration: 0.03 mg/L. Because NH_4^+ is unstable, according to High-Purity Standards, these data should be used for information purposes only.

Figure B-5. Comparison of NTN filtered and unfiltered internal blind samples, (ammonium), High-Purity Standards, SR1, 2001.



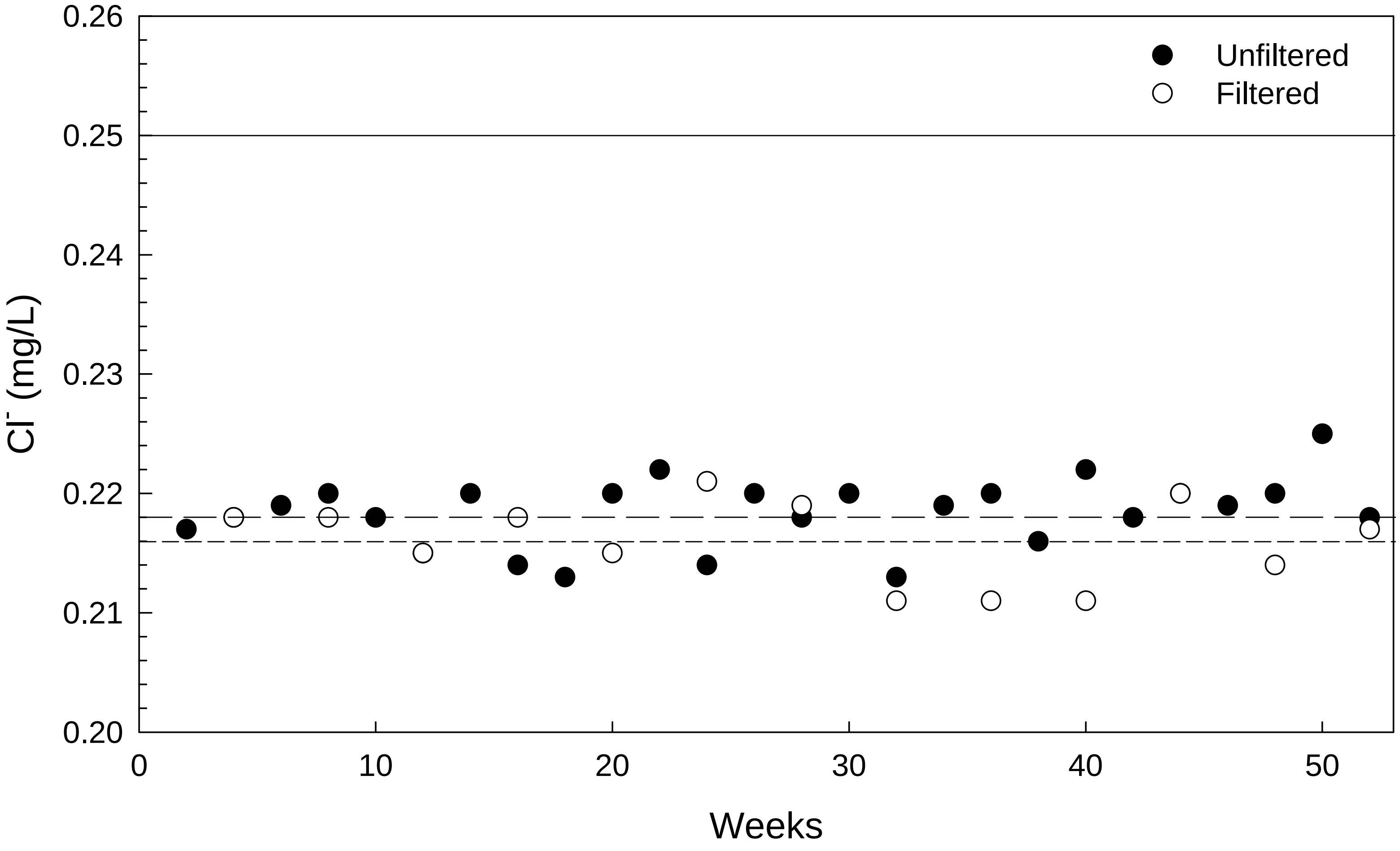
Note:
Solid line denotes target SO_4^{2-} concentration: 2.5 mg/L; long dashed line denotes mean unfiltered SO_4^{2-} concentration: 2.490 mg/L; and short dashed line denotes mean filtered SO_4^{2-} concentration: 2.400 mg/L.

Figure B-6. Comparison of NTN filtered and unfiltered internal blind samples, (sulfate), High-Purity Standards, SR1, 2001.



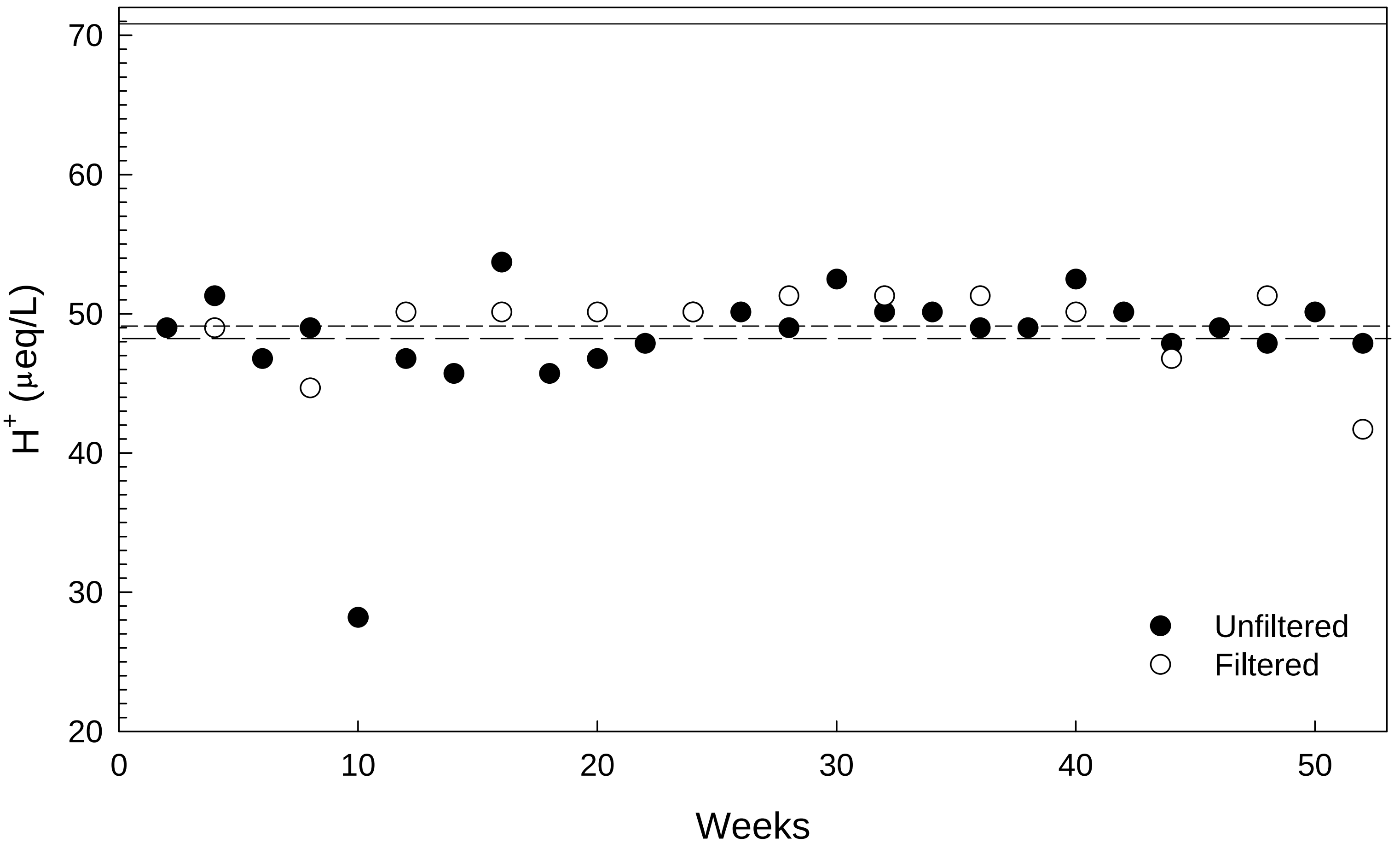
Note:
Solid line denotes target NO_3^- concentration: 0.50 mg/L; long dashed line denotes mean unfiltered NO_3^- concentration: 0.504 mg/L; and short dashed line denotes mean filtered NO_3^- concentration: 0.489 mg/L.

Figure B-7. Comparison of NTN filtered and unfiltered internal blind samples, (nitrate), High-Purity Standards, SR1, 2001.



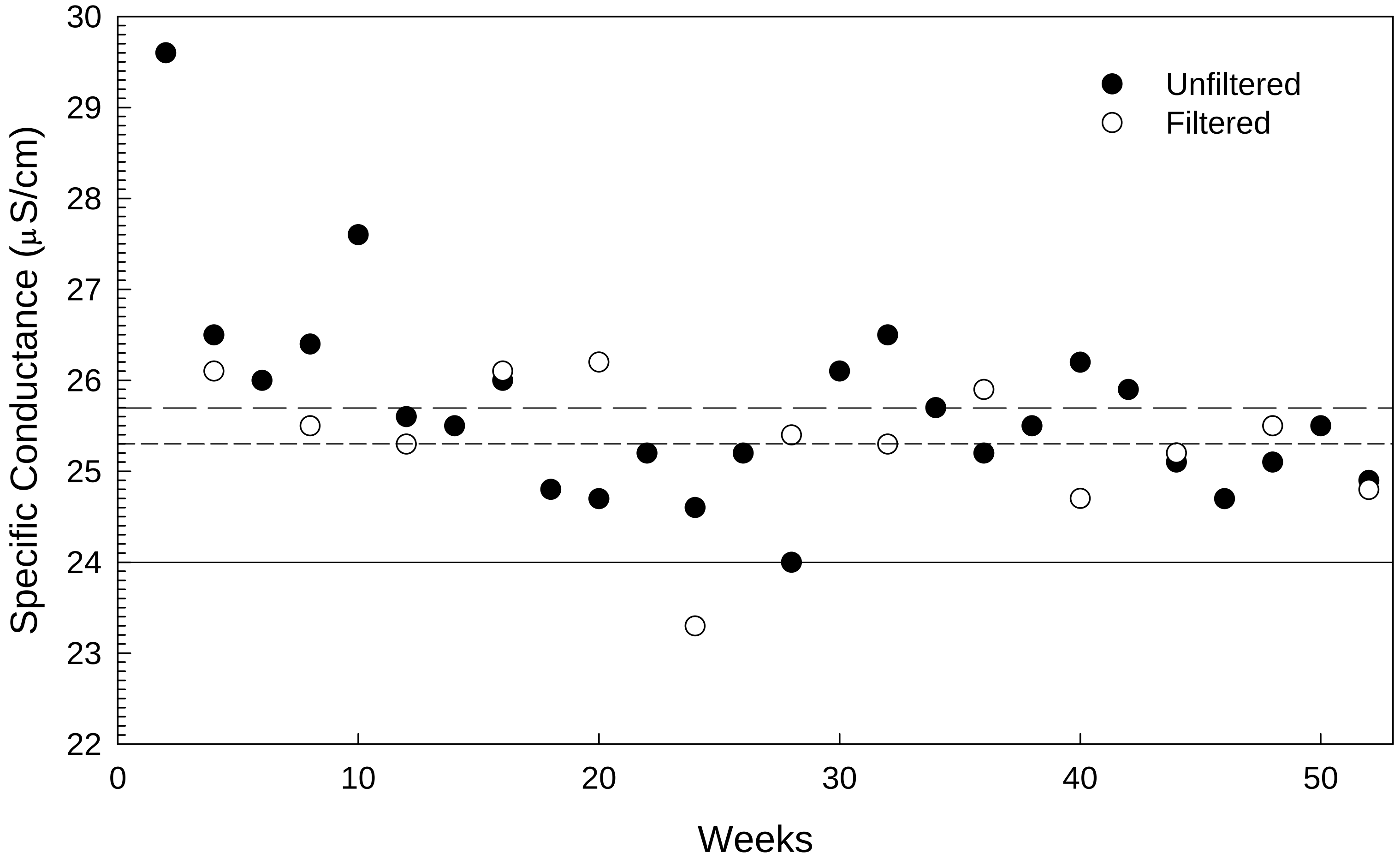
Note:
Solid line denotes target Cl$^-$ concentration: 0.25 mg/L; long dashed line denotes mean unfiltered Cl$^-$ concentration: 0.218 mg/L; and short dashed line denotes mean filtered Cl$^-$ concentration: 0.216 mg/L.

Figure B-8. Comparison of NTN filtered and unfiltered internal blind samples, (chloride), High-Purity Standards, SR1, 2001.



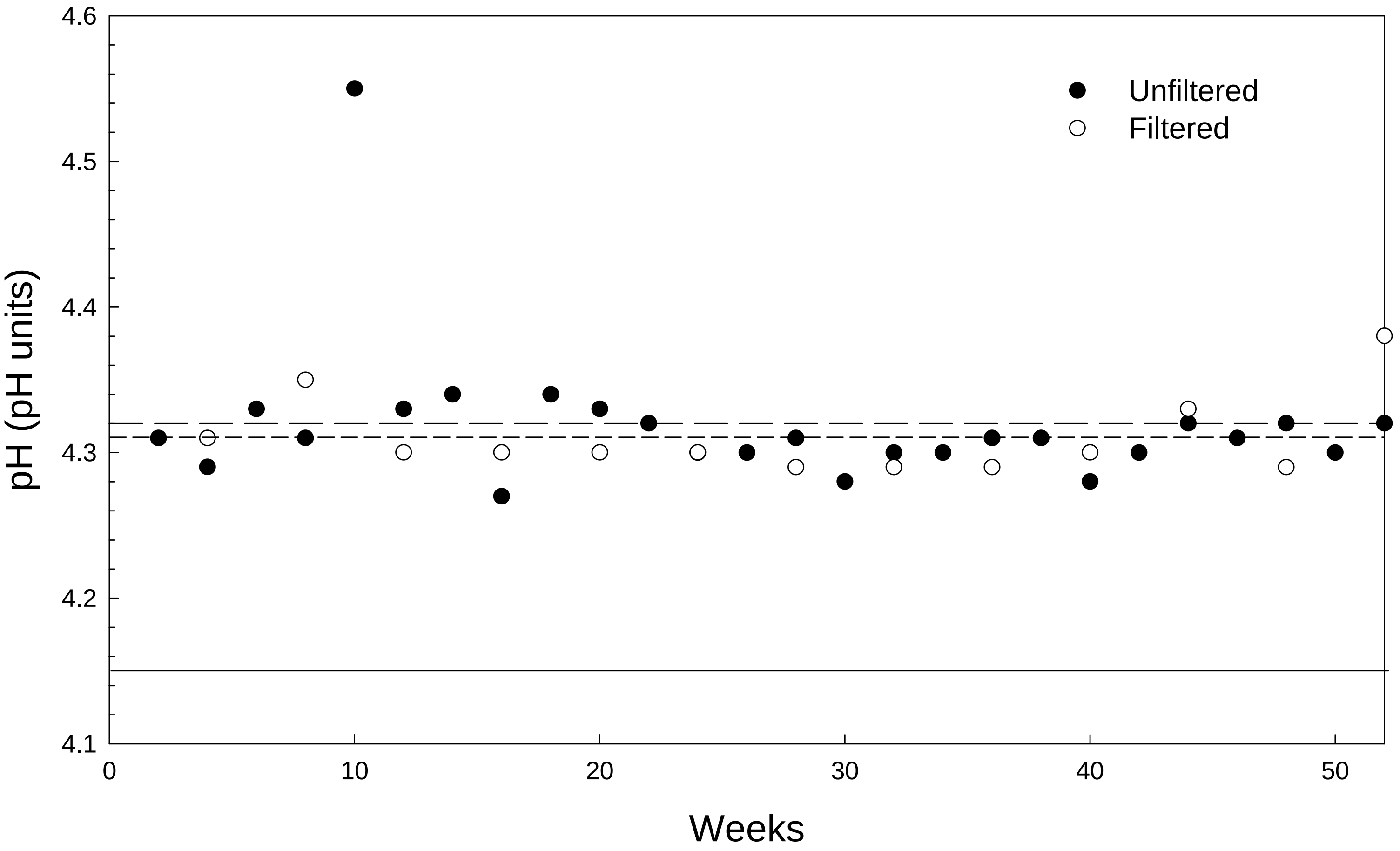
Note:
Solid line denotes target H^+ concentration: 70.8 µeq/L; long dashed line denotes mean unfiltered H^+ concentration: 48.3 µeq/L; and short dashed line denotes mean filtered H^+ concentration: 49.1 µeq/L.

Figure B-9. Comparison of NTN filtered and unfiltered internal blind samples, (hydrogen), High-Purity Standards, SR1, 2001.



Note:
Solid line denotes target specific conductance: 24 µS/cm; long dashed line denotes mean unfiltered specific conductance: 25.7 µS/cm; and short dashed line denotes mean filtered specific conductance: 25.3 µS/cm.

Figure B-10. Comparison of NTN filtered and unfiltered internal blind samples, (specific conductance), High-Purity Standards, SR1, 2001.



Note:
Solid line denotes target pH: 4.15; long dashed line denotes mean unfiltered pH: 4.32; and short dashed line denotes mean filtered and ion balance target pH: 4.31.

Figure B-11. Comparison of NTN filtered and unfiltered internal blind samples (pH), High-Purity Standards, SR1, 2001.

Table B-4. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, High-Purity Standards Simulated Rainwater 2 (H-PS SR2), 2001

Parameter	*Target concentration*[a] *(mg/L)*	*Mean measured concentrations (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	0.051	0.055[b]	0.004	7.7	0.006	10.3
		0.107[c]	0.056	110.6	0.018	16.5
Magnesium	0.051	0.048	-0.003	-6.7	0.003	5.7
		0.047	-0.004	-8.1	0.002	4.9
Sodium	0.40	0.401	0.001	0.3	0.013	3.2
		0.392	-0.008	-1.9	0.014	3.6
Potassium	0.098	0.103	0.005	5.3	0.003	2.9
		0.098	0.000	-0.5	0.004	4.2
Ammonium	1.00	0.93	-0.07	-6.9	0.02	2.0
		0.91	-0.09	-9.1	0.02	2.3
Sulfate	10.1	10.125	0.025	0.3	0.079	0.8
		9.758	-0.343	-3.4	0.065	0.7
Nitrate	7.0	7.114	0.114	1.6	0.090	1.3
		6.874	-0.126	-1.8	0.089	1.3
Chloride	0.98	1.002	0.022	2.2	0.014	1.4
		0.981	0.001	0.1	0.012	1.2
pH[d]	3.52 (3.57)[e]	3.61	0.09 (0.04)	2.6 (1.2)	0.01	0.3
		3.61	0.09 (0.04)	2.6 (1.1)	0.02	0.5
Hydrogen ion (µeq/L)	302.0 (269.2)	244.3	-57.8 (-24.9)	-19.1 (-9.3)	6.2	2.5
		245.2	-56.8 (-23.9)	-18.8 (-8.9)	10.0	4.1
Specific conductance[d] (µS/cm)	125	127.6	2.6	2.1	2.1	1.6
		128.1	3.1	2.4	1.3	1.0

Notes:

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

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

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

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

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

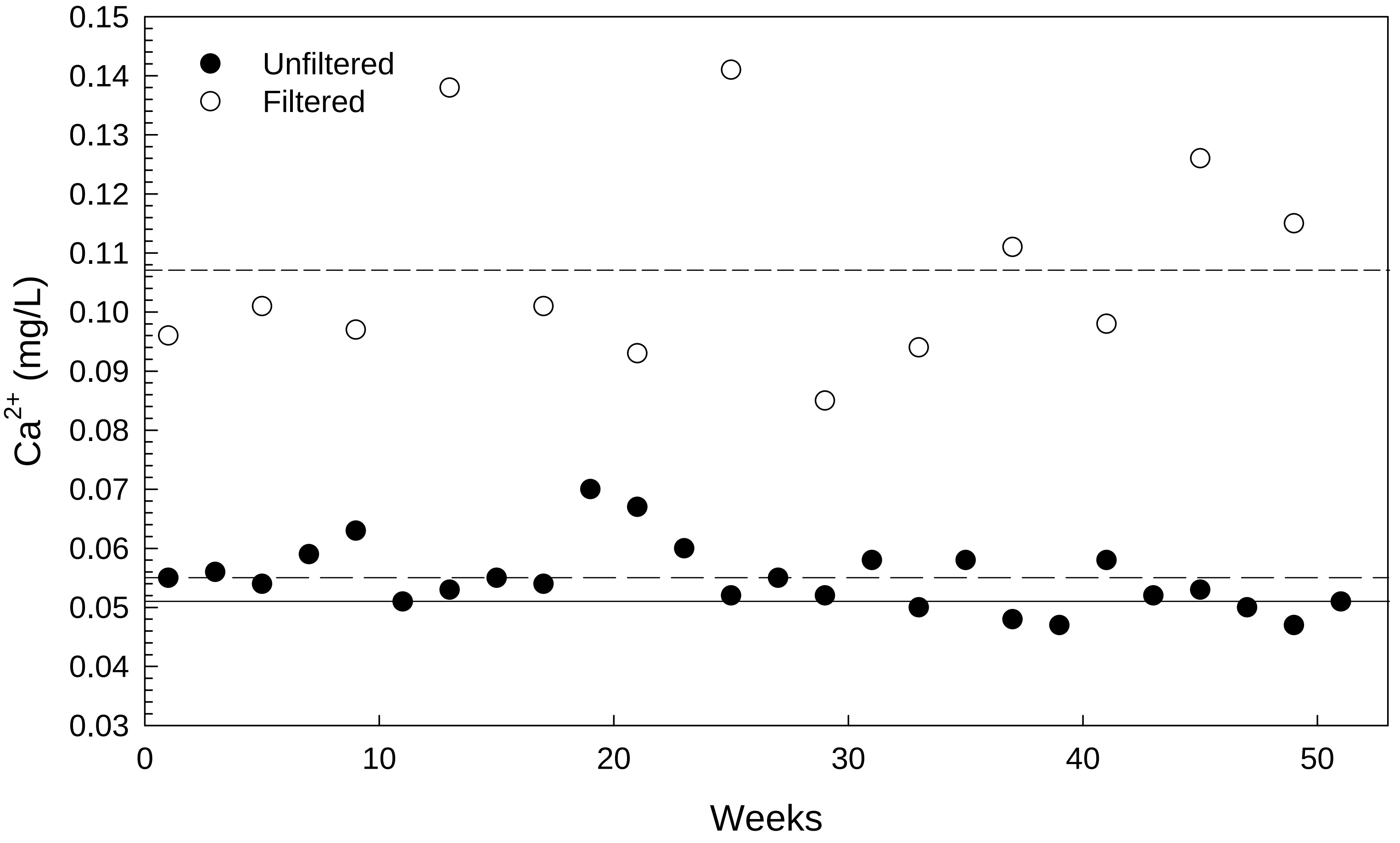
[e] Numbers in parentheses are calculated pH and H^+ based on the ion balance for the sample.

Table B-5. Unfiltered Internal Blind Concentrations for High-Purity Standards Simulated Rainwater 2 (H-PS SR2), 2001

Weeks	*pH (units)*	*H (μeq/L)*	*Specific conductance (μS/cm)*	*Cl^- (mg/L)*	*NO_3^- (mg/L)*	*SO_4^{-2} (mg/L)*	*NH_4^- (mg/L)*	*Ca^{+2} (mg/L)*	*Mg^{+2} (mg/L)*	*Na^+ (mg/L)*	*K^+ (mg/L)*
1	3.61	245.5	129.7	1.012	6.947	10.237	0.956	0.055	0.045	0.408	0.100
3	3.59	257.0	130.2	0.990	7.028	10.100	0.992	0.056	0.046	0.405	0.101
5	3.62	239.9	129.7	1.004	7.113	10.096	0.920	0.054	0.049	0.415	0.100
7	3.61	245.5	129.0	1.017	7.092	10.080	0.938	0.059	0.054	0.398	0.106
9	3.64	229.1	129.7	1.003	7.055	10.162	0.944	0.063	0.050	0.413	0.108
11	3.60	251.2	129.8	0.998	7.040	10.140	0.919	0.051	0.046	0.390	0.102
13	3.60	251.2	127.9	0.987	7.120	10.120	0.916	0.053	0.051	0.418	0.105
15	3.61	245.5	128.7	0.980	7.160	10.080	0.926	0.055	0.050	0.421	0.106
17	3.62	239.9	127.3	0.984	7.095	10.158	0.929	0.054	0.048	0.425	0.104
19	3.61	245.5	126.6	1.001	6.940	10.110	0.911	0.070	0.050	0.411	0.103
21	3.61	245.5	125.4	1.016	7.044	10.048	0.920	0.067	0.047	0.402	0.100
23	3.62	239.9	125.7	1.019	7.168	10.112	0.926	0.060	0.045	0.406	0.106
25	3.60	251.2	125.6	1.005	7.106	10.028	0.957	0.052	0.046	0.399	0.102
27	3.63	234.4	121.1	1.000	7.088	10.037	0.909	0.055	0.044	0.385	0.098
29	3.60	251.2	129.1	0.994	7.258	10.295	0.904	0.052	0.046	0.388	0.104
31	3.63	234.4	131.1	0.999	7.222	10.172	0.952	0.058	0.044	0.388	0.099
33	3.61	245.5	127.6	1.001	7.010	10.101	0.934	0.050	0.046	0.385	0.104
35	3.62	239.9	127.5	0.994	7.101	10.025	0.934	0.058	0.046	0.387	0.101
37	3.61	245.5	126.5	1.012	7.084	10.108	0.924	0.048	0.052	0.396	0.099
39	3.60	251.2	127.9	0.986	7.068	9.984	0.929	0.047	0.049	0.387	0.103
41	3.61	245.5	126.4	0.991	7.121	10.146	0.928	0.058	0.048	0.403	0.104
43	3.62	239.9	127.4	0.986	7.156	10.232	0.936	0.052	0.048	0.387	0.104
45	3.62	239.9	126.8	1.010	7.204	10.028	0.929	0.053	0.047	0.387	0.108
47	3.61	245.5	126.2	0.998	7.200	10.216	0.916	0.050	0.051	0.422	0.105
49	3.61	245.5	126.2	1.023	7.224	10.206	0.922	0.047	0.046	0.394	0.103
51	3.61	245.5	128.0	1.041	7.318	10.238	0.928	0.051	0.043	0.412	0.109
Mean	3.61	244.3	127.6	1.00	7.110	10.130	0.930	0.050	0.050	0.400	0.100
Median	3.61	245.5	127.6	1.00	7.100	10.110	0.930	0.050	0.050	0.400	0.100
Target	3.52		125	0.98	7.0	10.1	1.00	0.051	0.051	0.40	0.098

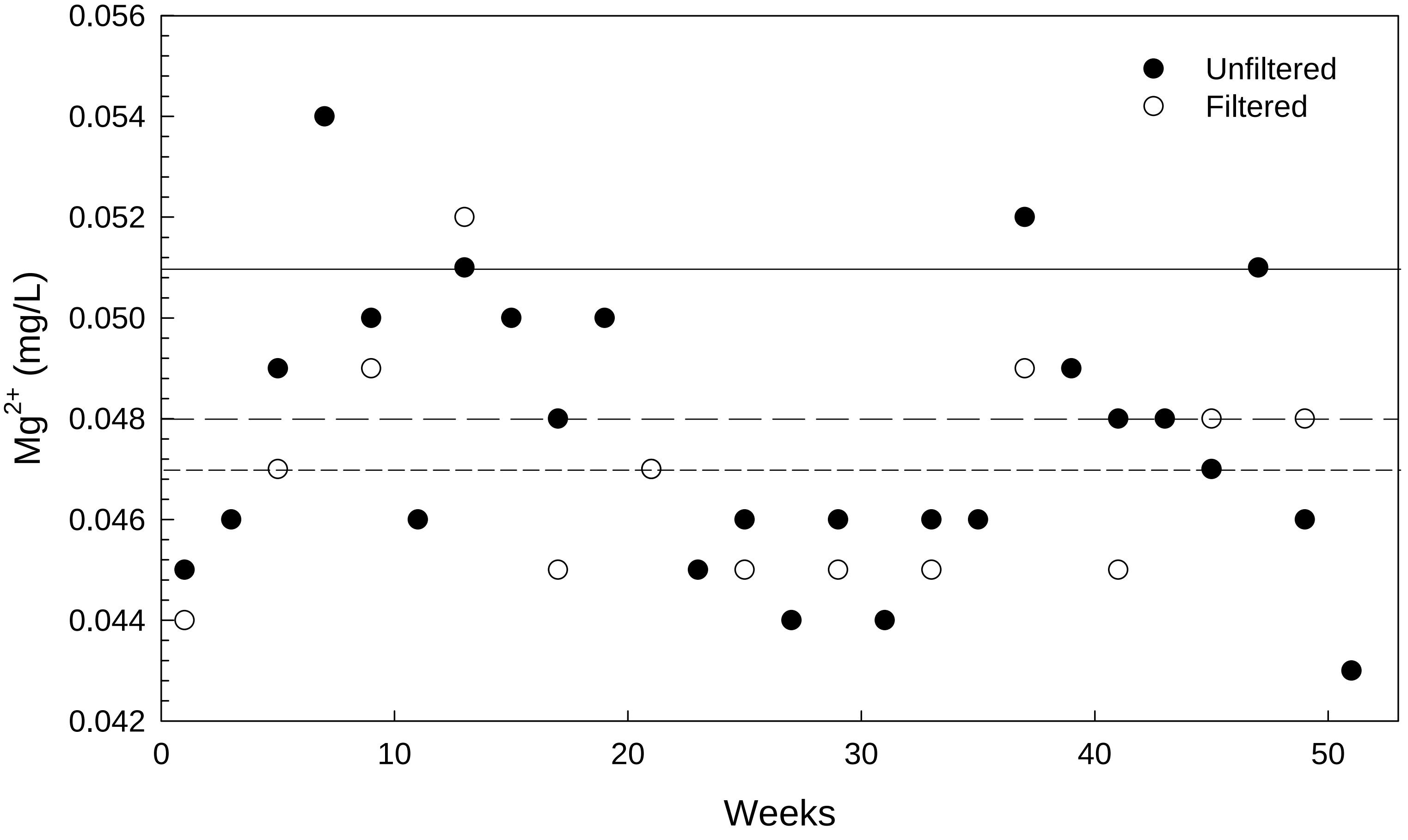
Table B-6. Filtered Internal Blind Concentrations for High-Purity Standards Simulated Rainwater 2 (H-PS SR2), 2001

Weeks	*pH (units)*	*H (μeq/L)*	*Specific conductance (μS/cm)*	*Cl^- (mg/L)*	*NO_3^- (mg/L)*	*SO_4^- (mg/L)*	*NH_4 (mg/L)*	*Ca^{+2} (mg/L)*	*Mg^{+2} (mg/L)*	*Na^+ (mg/L)*	*K^+ (mg/L)*
1	3.59	257.0	129.9	0.985	6.678	9.780	0.968	0.096	0.044	0.392	0.096
5	3.63	234.4	129.2	0.986	6.871	9.761	0.886	0.101	0.047	0.408	0.093
9	3.59	257.0	129.7	0.985	6.904	9.724	0.915	0.097	0.049	0.400	0.093
13	3.59	257.0	128.1	0.970	6.932	9.740	0.902	0.138	0.052	0.394	0.097
17	3.65	223.9	127.4	0.970	6.816	9.682	0.899	0.101	0.045	0.422	0.104
21	3.61	245.5	126.6	0.982	6.940	9.740	0.895	0.093	0.047	0.374	0.097
25	3.60	251.2	126.6	0.981	6.902	9.660	0.927	0.141	0.045	0.383	0.100
29	3.60	251.2	128.1	0.983	6.804	9.788	0.902	0.085	0.045	0.392	0.094
33	3.61	245.5	129.4	0.971	6.780	9.748	0.890	0.094	0.045	0.382	0.096
37	3.61	245.5	126.4	1.001	6.841	9.829	0.904	0.111	0.049	0.377	0.099
41	3.61	245.5	126.9	0.959	6.928	9.904	0.907	0.098	0.045	0.406	0.099
45	3.62	239.9	129.0	0.981	7.012	9.696	0.896	0.126	0.048	0.375	0.106
49	3.63	234.4	127.4	1.002	6.954	9.795	0.908	0.115	0.048	0.396	0.093
Mean	3.61	245.2	128.1	0.980	6.870	9.760	0.910	0.110	0.050	0.390	0.100
Median	3.61	245.5	128.1	0.980	6.900	9.750	0.900	0.100	0.050	0.390	0.100
Target	3.52		125	0.98	7.0	10.1	1.00	0.051	0.051	0.40	0.098



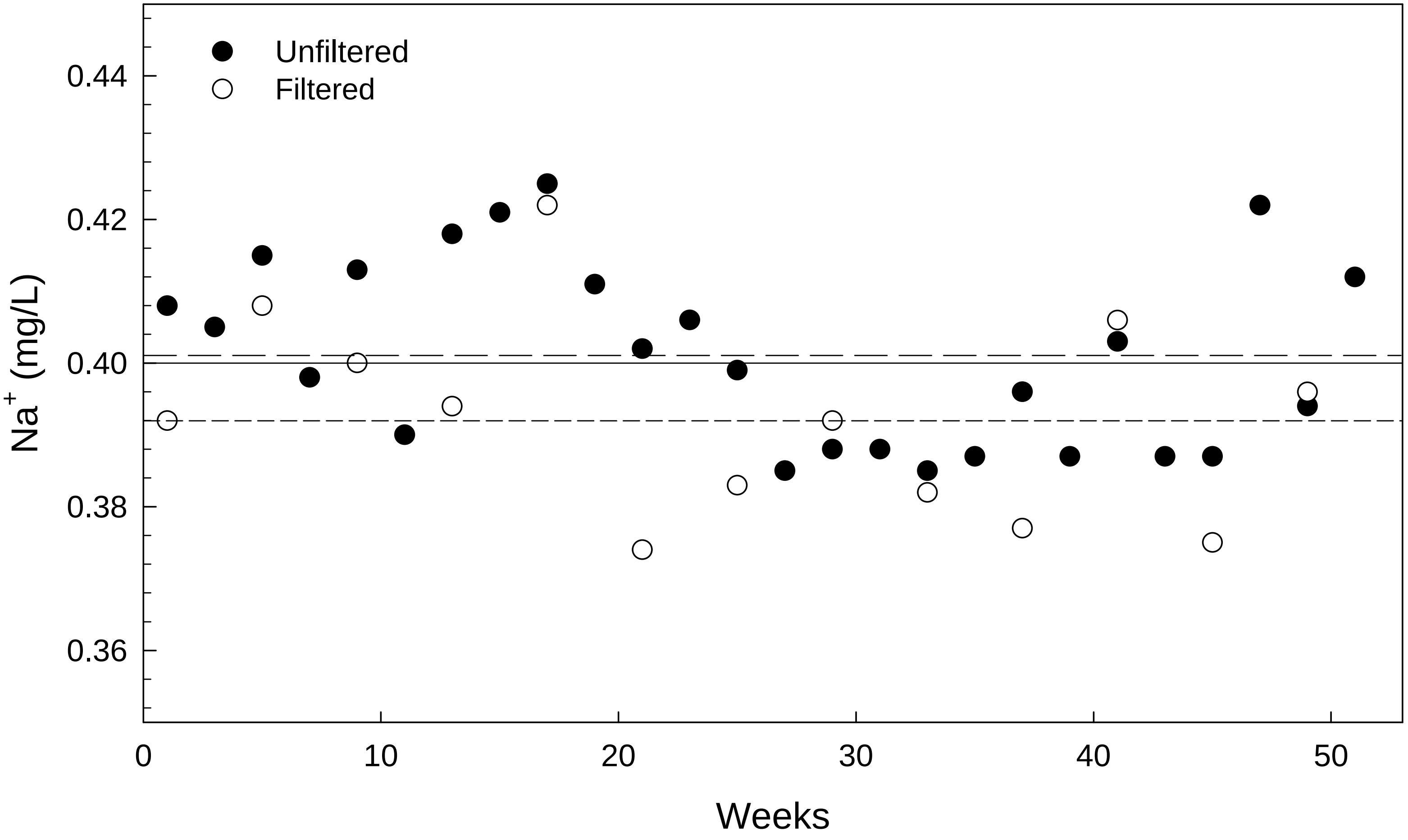
Note:
Solid line denotes target Ca^{2+} concentration: 0.051 mg/L; long dashed line denotes mean unfiltered Ca^{2+} concentration: 0.055 mg/L; and short dashed line denotes mean filtered Ca^{2+} concentration: 0.107 mg/L.

Figure B-12. Comparison of NTN filtered and unfiltered internal blind samples, (calcium), High-Purity Standards, SR2, 2001.



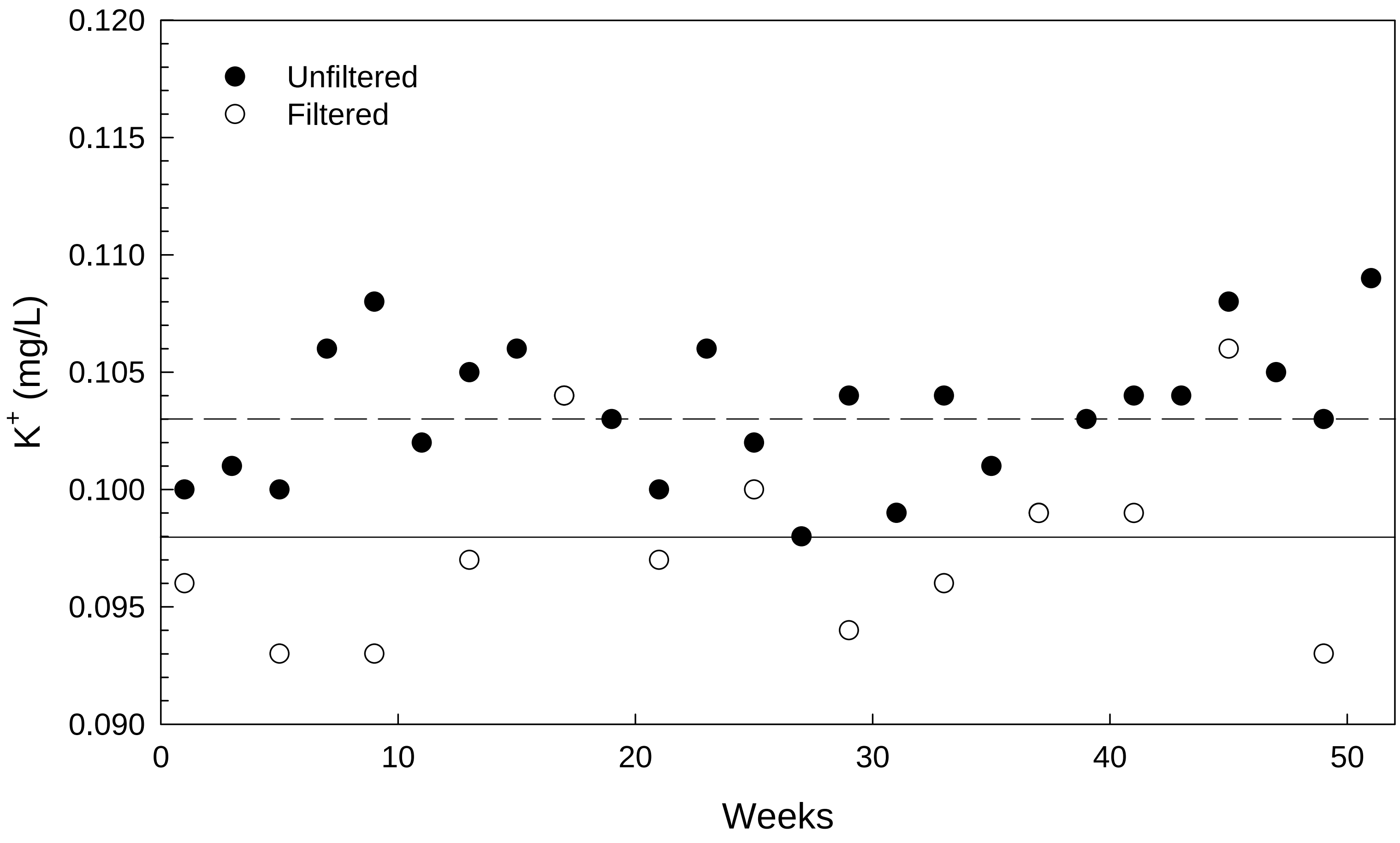
Note:
Solid line denotes target Mg^{2+} concentration: 0.051 mg/L; long dashed line denotes mean unfiltered Mg^{2+} concentration: 0.048 mg/L; and short dashed line denotes mean filtered Mg^{2+} concentration: 0.047 mg/L.

Figure B-13. Comparison of NTN filtered and unfiltered internal blind samples, (magnesium), High-Purity Standards, SR2, 2001.



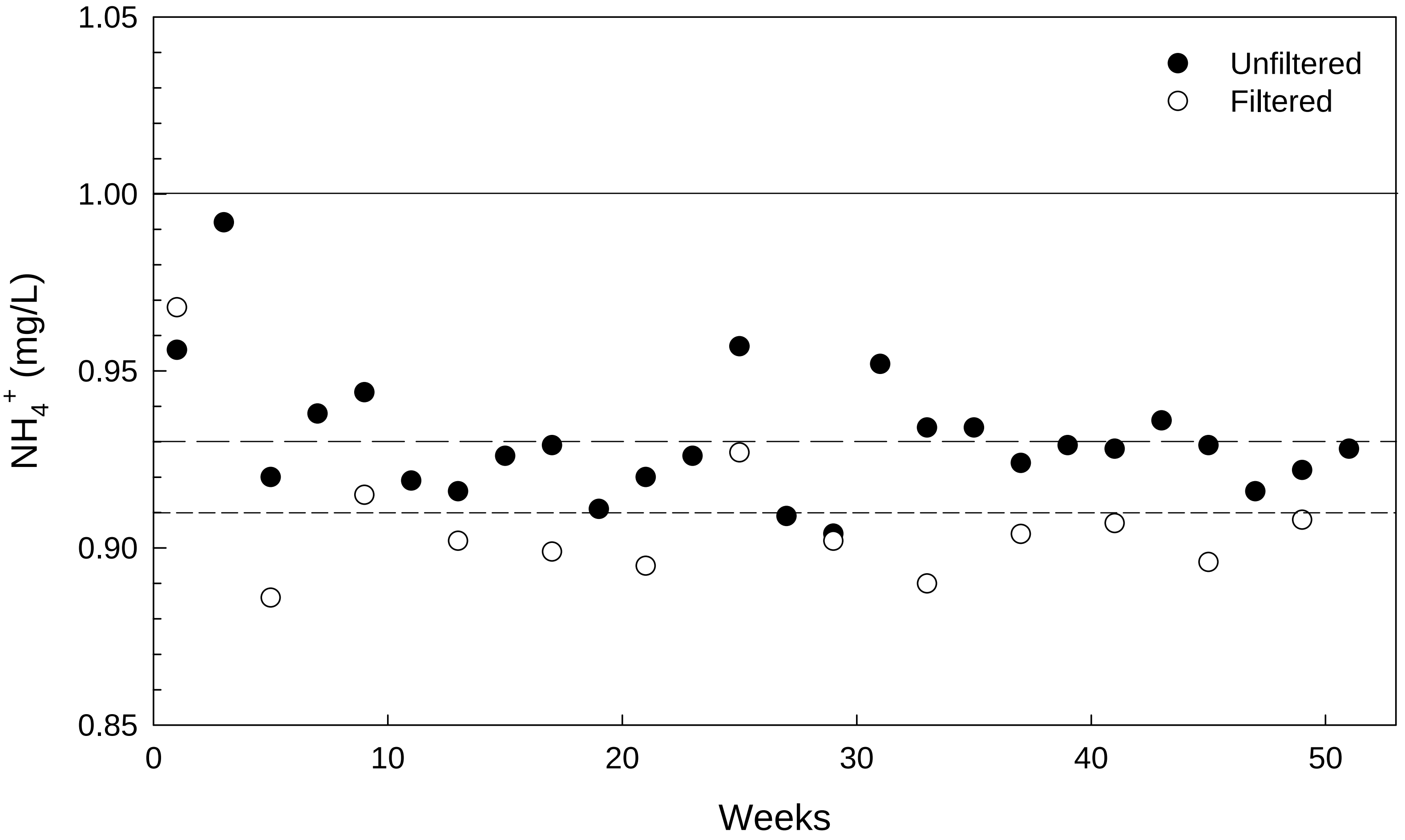
Note:
Solid line denotes target Na$^+$ concentration: 0.40 mg/L; long dashed line denotes mean unfiltered Na$^+$ concentration: 0.401 mg/L; and short dashed line denotes mean filtered Na$^+$ concentration: 0.392 mg/L.

Figure B-14. Comparison of NTN filtered and unfiltered internal blind samples, (sodium), High-Purity Standards, SR2, 2001.



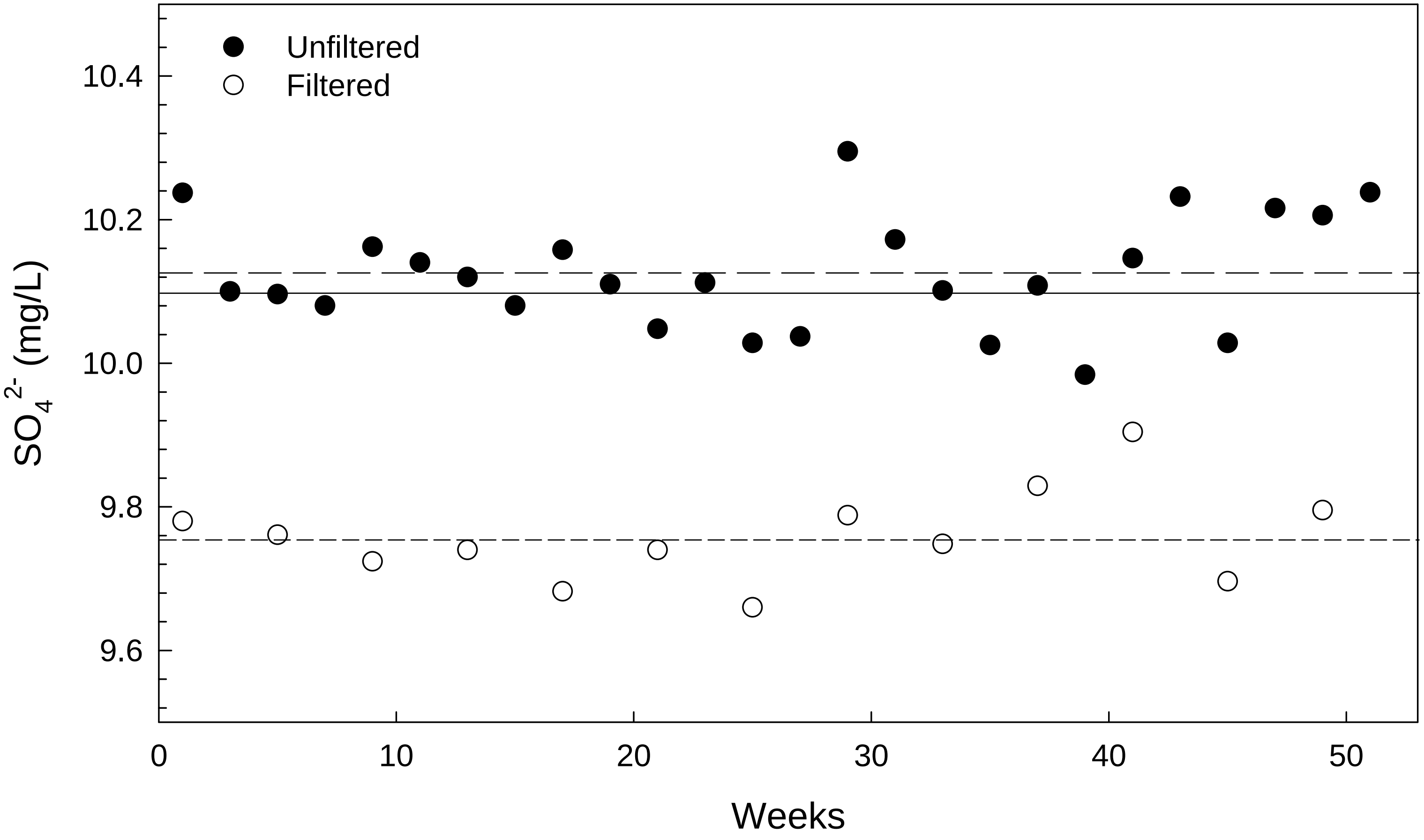
Note:
Solid line denotes target and mean filtered K$^+$ concentration: 0.098 mg/L; and long dashed line denotes mean unfiltered K$^+$ concentration: 0.103 mg/L.

Figure B-15. Comparison of NTN filtered and unfiltered internal blind samples, (potassium), High-Purity Standards, SR2, 2001.



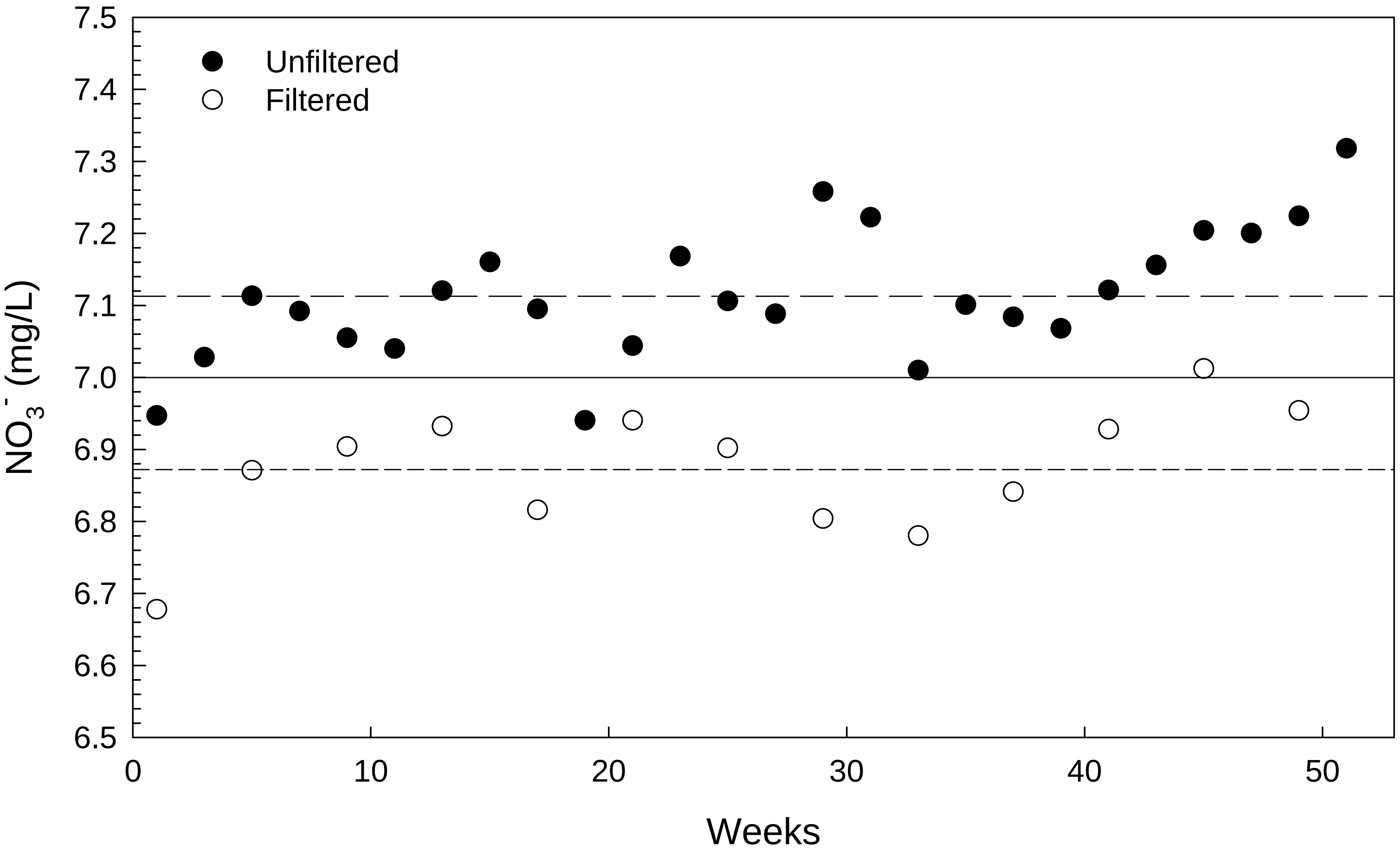
Note:
Solid line denotes target NH_4^+ concentration: 1.00 mg/L; long dashed line denotes mean unfiltered NH_4^+ concentration: 0.93 mg/L; and short dashed line denotes mean filtered NH_4^+ concentration: 0.91 mg/L.
Because NH_4^+ is unstable, according to High-Purity Standards, this data should be used for information purposes only.

Figure B-16. Comparison of NTN filtered and unfiltered internal blind samples, (ammonium), High-Purity Standards, SR2, 2001.



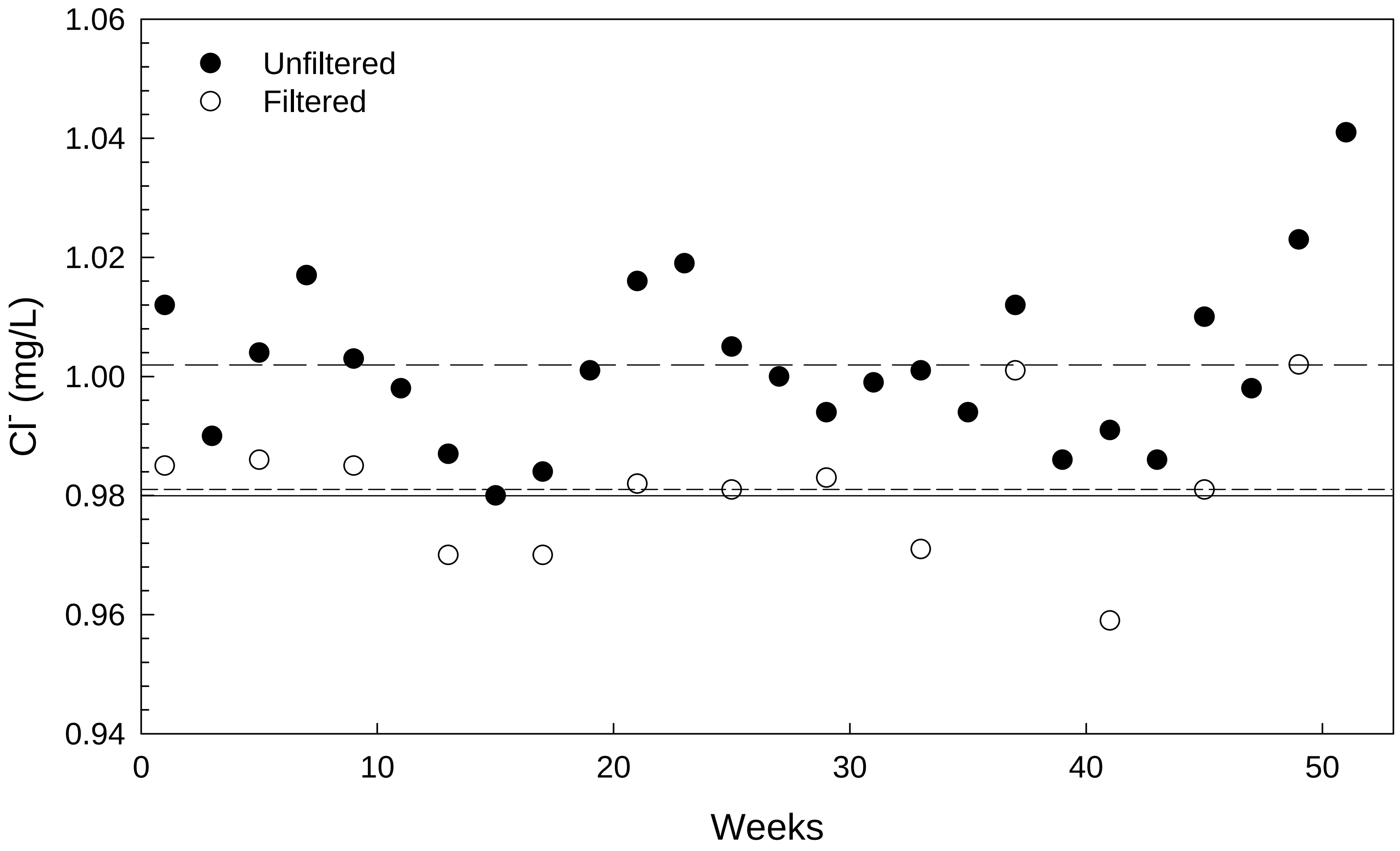
Note:
Solid line denotes target SO_4^{2-} concentration: 10.100 mg/L; long dashed line denotes mean unfiltered SO_4^{2-} concentration: 10.125 mg/L; and short dashed line denotes mean filtered SO_4^{2-} concentration: 9.758 mg/L.

Figure B-17. Comparison of NTN filtered and unfiltered internal blind samples, (sulfate), High-Purity Standards, SR2, 2001.



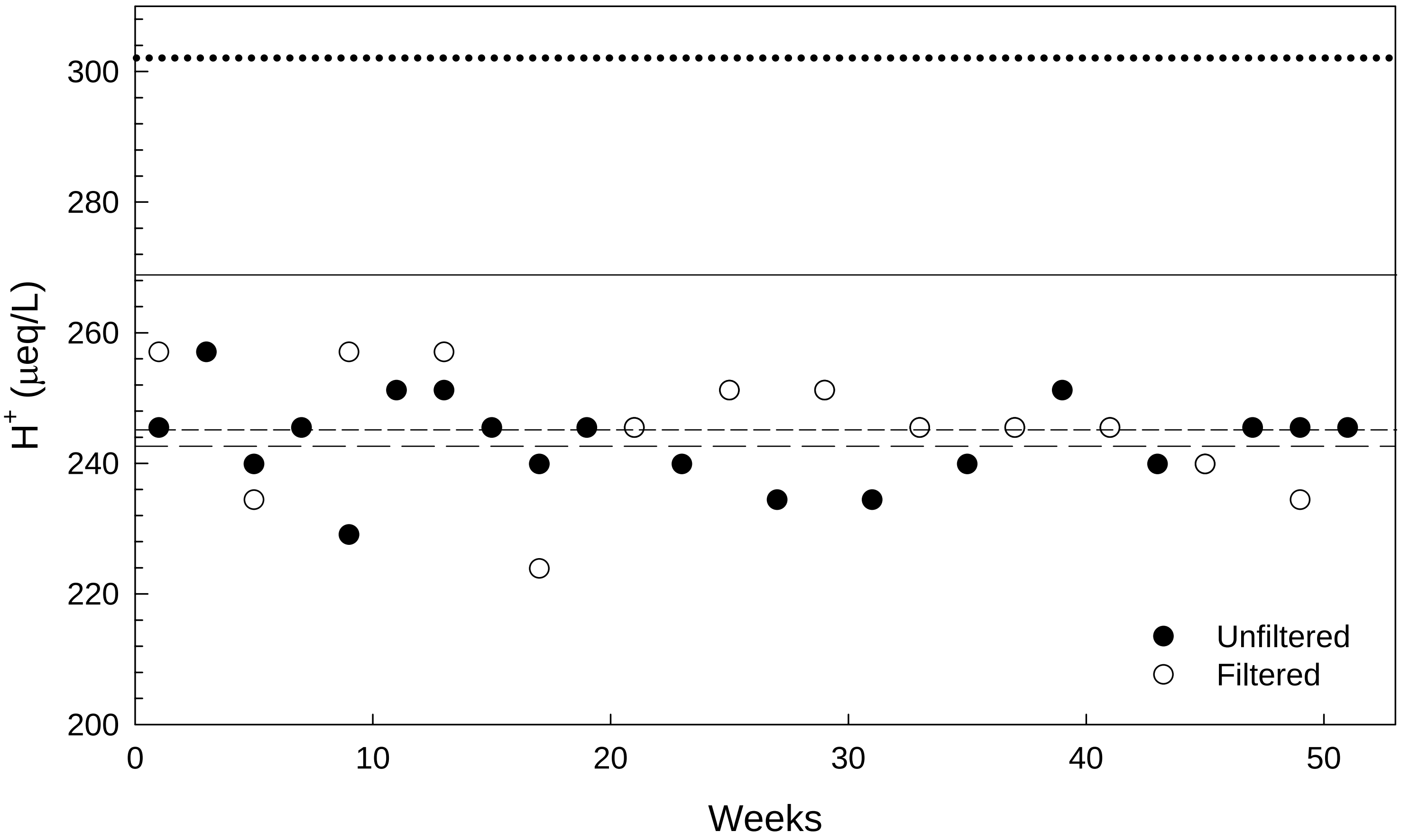
Note:
Solid line denotes target NO_3^- concentration: 7.000 mg/L; long dashed line denotes mean unfiltered NO_3^- concentration: 7.114 mg/L; and short dashed line denotes mean filtered NO_3^- concentration: 6.874 mg/L.

Figure B-18. Comparison of NTN filtered and unfiltered internal blind samples, (nitrate), High-Purity Standards, SR2, 2001.



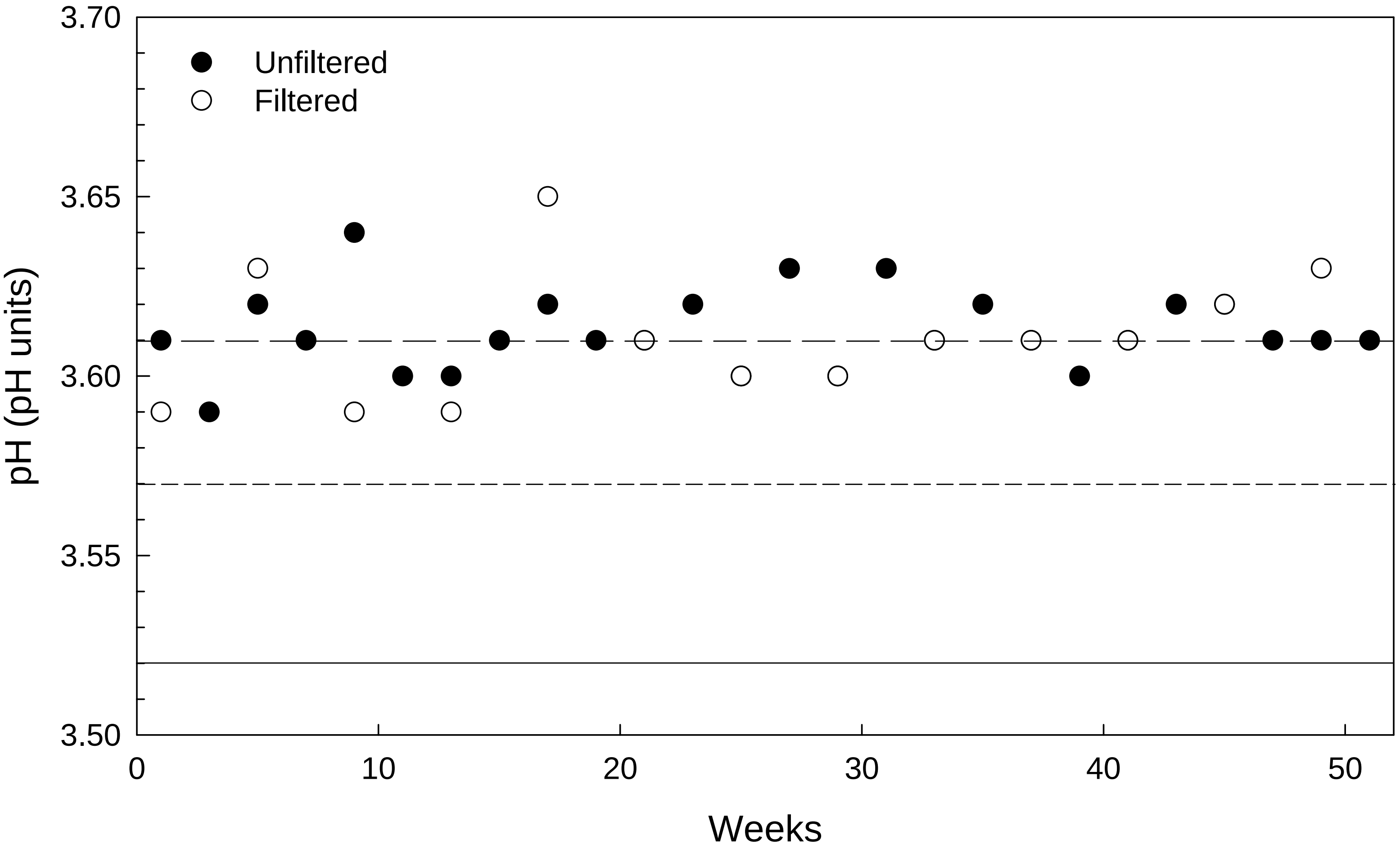
Note:
Solid line denotes target Cl^- concentration: 0.980 mg/L; long dashed line denotes mean unfiltered Cl^- concentration: 1.002 mg/L; and short dashed line denotes mean filtered Cl^- concentration: 0.981 mg/L.

Figure B-19. Comparison of NTN filtered and unfiltered internal blind samples, (chloride), High-Purity Standards, SR2, 2001.



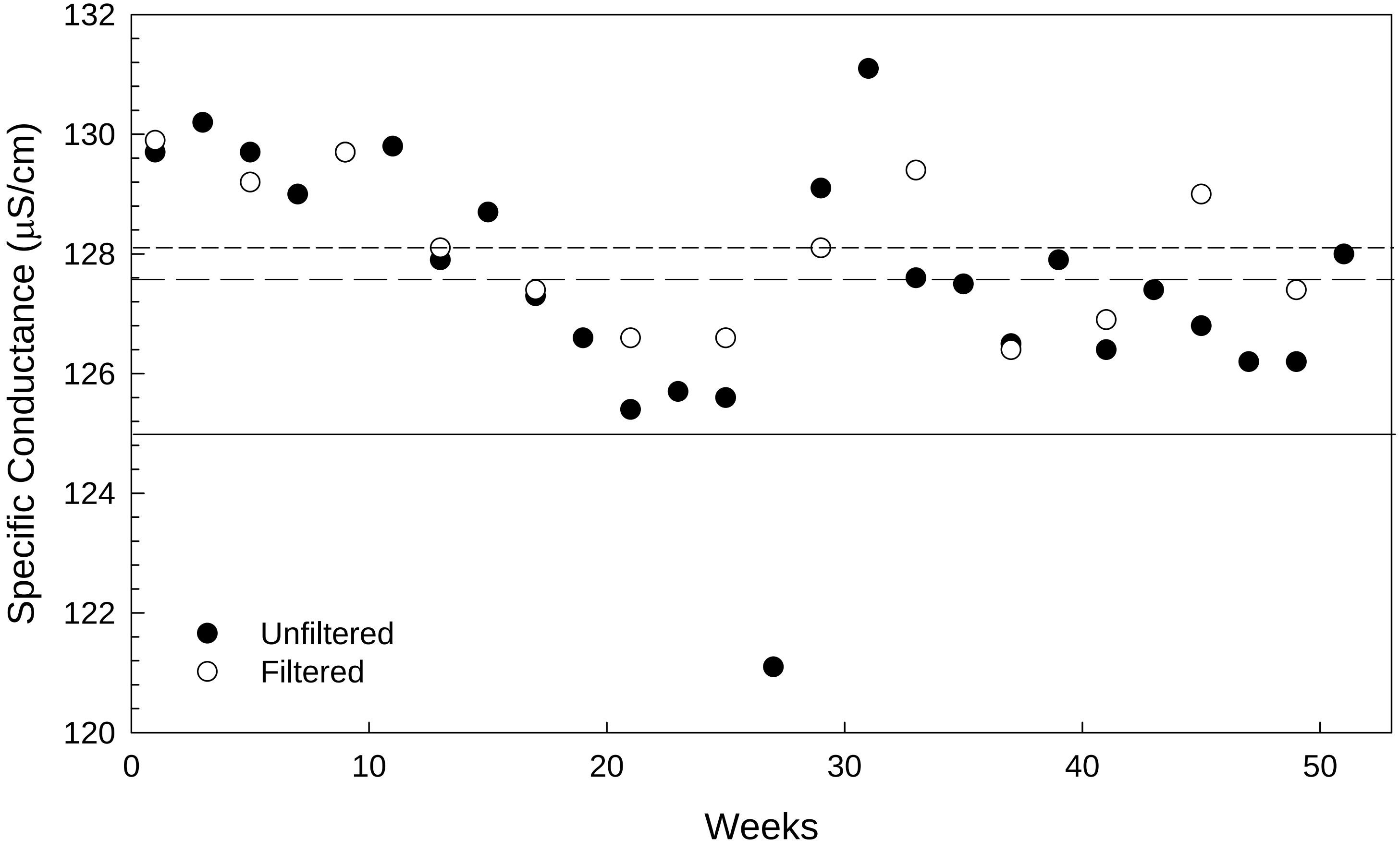
Note:
Dotted line denotes H-PS target H^+ concentration: 302.0 µeq/L; solid line denotes ion balance target H^+ concentration: 269.2 µeq/L; long dashed line denotes mean unfiltered H^+ concentration: 244.3 µeq/L; and short dashed line denotes mean filtered H^+ concentration: 245.2 µeq/L.

Figure B-20. Comparison of NTN filtered and unfiltered internal blind samples, (hydrogen), High-Purity Standards, SR2, 2001.



Note:
Solid line denotes target pH: 3.52; long dashed line denotes mean filtered and unfilted pH: 3.61; and short dashed line denotes ion balance target pH: 3.57.

Figure B-21. Comparison of NTN filtered and unfiltered internal blind samples, (pH), High-Purity Standards, SR2, 2001.



Note:
Solid line denotes target specific conductance: 125 μS/cm; long dashed line denotes mean unfiltered specific conductance: 127.6 μS/cm; and short dashed line denotes mean filtered specific conductance: 128.1 μS/cm.

Figure B-22. Comparison of NTN filtered and unfiltered internal blind samples, (specific conductance), High-Purity Standards, SR2, 2001.

Table B-7. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, Internally Formulated Simulated Rain (01FR10), 2001

Parameter	*Target concentration (mg/L)*	*Mean measured concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	0.031*	0.032	0.001	4.0	0.009	26.6
		0.040	0.009	30.3	0.007	16.7
Magnesium	0.007	0.007	0.000	0.5	0.001	20.7
		0.005	-0.002	-26.4	0.001	23.6
Sodium	0.020	0.018	-0.002	-8.1	0.002	11.8
		0.019	-0.001	-4.2	0.002	12.6
Potassium	0.005	0.005	0.000	6.9	0.002	30.8
		0.005	0.000	4.6	0.002	42.1
Ammonium	0.03	0.03	0.00	5.2	0.01	18.8
		0.03	0.00	15.1	0.01	19.1
Sulfate	0.260	0.257	-0.003	-1.0	0.007	2.5
		0.253	-0.007	-2.7	0.006	2.3
Nitrate	0.193	0.193	0.000	-0.2	0.004	2.0
		0.189	-0.005	-2.4	0.004	2.1
Chloride	0.053	0.054	0.001	1.1	0.002	2.8
		0.057	0.004	6.7	0.005	8.6
pH (units)	5.22	5.21	-0.01	-0.2	0.04	0.9
		5.22	0.00	0.0	0.06	1.1
Hydrogen ion (µeq/L)	6.03	6.22	0.19	3.2	0.6	10.2
		6.10	0.07	1.2	0.8	12.9
Specific conductance (µS/cm)	3.6	3.7	0.1	3.9	0.2	4.7
		3.9	0.3	9.2	0.7	18.0

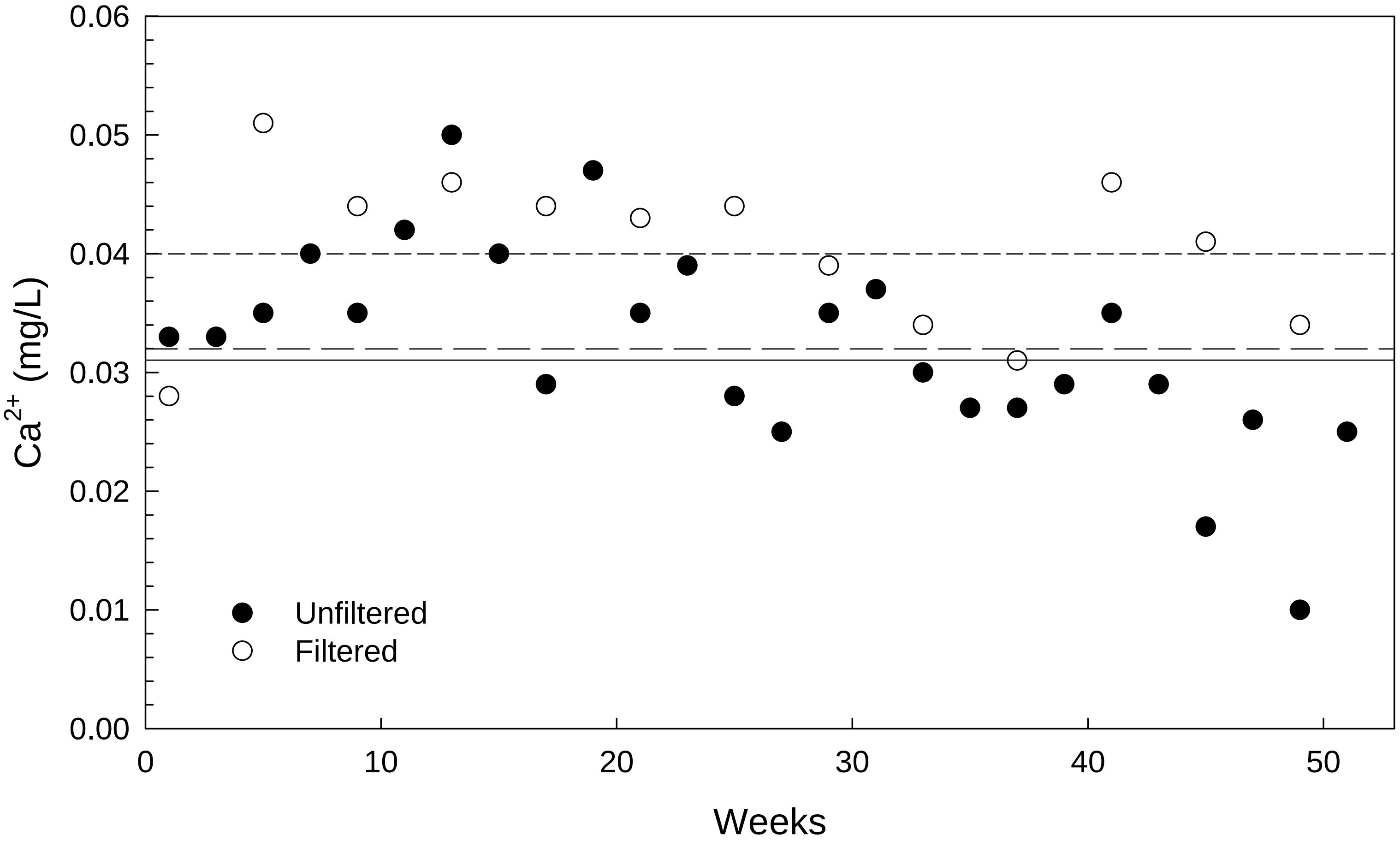
Notes:
There were 26 unfiltered samples and 13 filtered samples in each set.
*The concentration values for the 01FR10 are the mean of 7–11 analyses done immediately after sample preparation.

Table B-8. Unfiltered Internal Blind Concentrations for Internally Formulated Simulated Rainwater (01FR10), 2001

Weeks	*pH (units)*	*H (μeq/L)*	*Specific conductance (μS/cm)*	*Cl^- (mg/L)*	*NO_3^- (mg/L)*	*SO_4^{-2} (mg/L)*	*NH_4^- (mg/L)*	*Ca^{+2} (mg/L)*	*Mg^{+2} (mg/L)*	*Na^+ (mg/L)*	*K^+ (mg/L)*
1	5.19	6.46	3.7	0.054	0.192	0.258	0.022	0.033	0.007	0.019	0.005
3	5.13	7.41	3.8	0.055	0.201	0.262	0.018	0.033	0.008	0.023	0.007
5	5.25	5.62	3.7	0.054	0.193	0.259	0.024	0.035	0.007	0.012	0.003
7	5.19	6.46	3.9	0.052	0.192	0.256	0.022	0.040	0.009	0.019	0.006
9	5.21	6.17	3.8	0.053	0.189	0.266	0.028	0.035	0.008	0.019	0.005
11	5.25	5.62	4.1	0.055	0.189	0.252	0.024	0.042	0.008	0.018	0.008
13	5.19	6.46	3.5	0.052	0.191	0.248	0.021	0.050	0.010	0.021	0.002
15	5.22	6.03	3.9	0.056	0.194	0.273	0.030	0.040	0.006	0.020	0.004
17	5.17	6.76	3.9	0.054	0.193	0.259	0.027	0.029	0.006	0.021	0.004
19	5.22	6.03	3.8	0.056	0.197	0.252	0.024	0.047	0.008	0.020	0.006
21	5.21	6.17	3.9	0.053	0.190	0.264	0.029	0.035	0.007	0.019	0.005
23	5.16	6.92	3.7	0.052	0.190	0.261	0.013	0.039	0.008	0.019	0.006
25	5.18	6.61	3.7	0.054	0.205	0.258	0.036	0.028	0.007	0.018	0.007
27	5.18	6.61	3.6	0.053	0.196	0.256	0.029	0.025	0.008	0.018	0.006
29	5.21	6.17	3.7	0.053	0.193	0.261	0.031	0.035	0.007	0.017	0.004
31	5.21	6.17	3.8	0.052	0.191	0.255	0.027	0.037	0.008	0.019	0.007
33	5.21	6.17	3.9	0.054	0.194	0.267	0.024	0.030	0.006	0.018	0.006
35	5.28	5.25	3.7	0.053	0.189	0.266	0.034	0.027	0.006	0.018	0.004
37	5.24	5.75	3.5	0.053	0.191	0.253	0.029	0.027	0.008	0.017	0.005
39	5.12	7.59	3.5	0.053	0.189	0.244	0.021	0.029	0.006	0.018	0.004
41	5.24	5.75	3.7	0.053	0.189	0.257	0.029	0.035	0.006	0.017	0.007
43	5.21	6.17	4.0	0.053	0.194	0.253	0.030	0.029	0.006	0.017	0.005
45	5.30	5.01	3.5	0.056	0.189	0.253	0.028	0.017	0.007	0.020	0.008
47	5.14	7.24	3.6	0.057	0.193	0.248	0.029	0.026	0.007	0.014	0.007
49	5.26	5.50	3.4	0.052	0.194	0.255	0.028	0.010	0.002	0.017	0.006
51	5.25	5.62	3.9	0.051	0.192	0.258	0.027	0.025	0.007	0.020	0.002
Mean	5.21	6.22	3.7	0.054	0.193	0.257	0.026	0.032	0.007	0.018	0.005
Median	5.21	6.17	3.7	0.053	0.192	0.257	0.028	0.033	0.007	0.018	0.005
Target	5.22		3.6	0.053	0.193	0.260	0.025	0.031	0.007	0.020	0.005

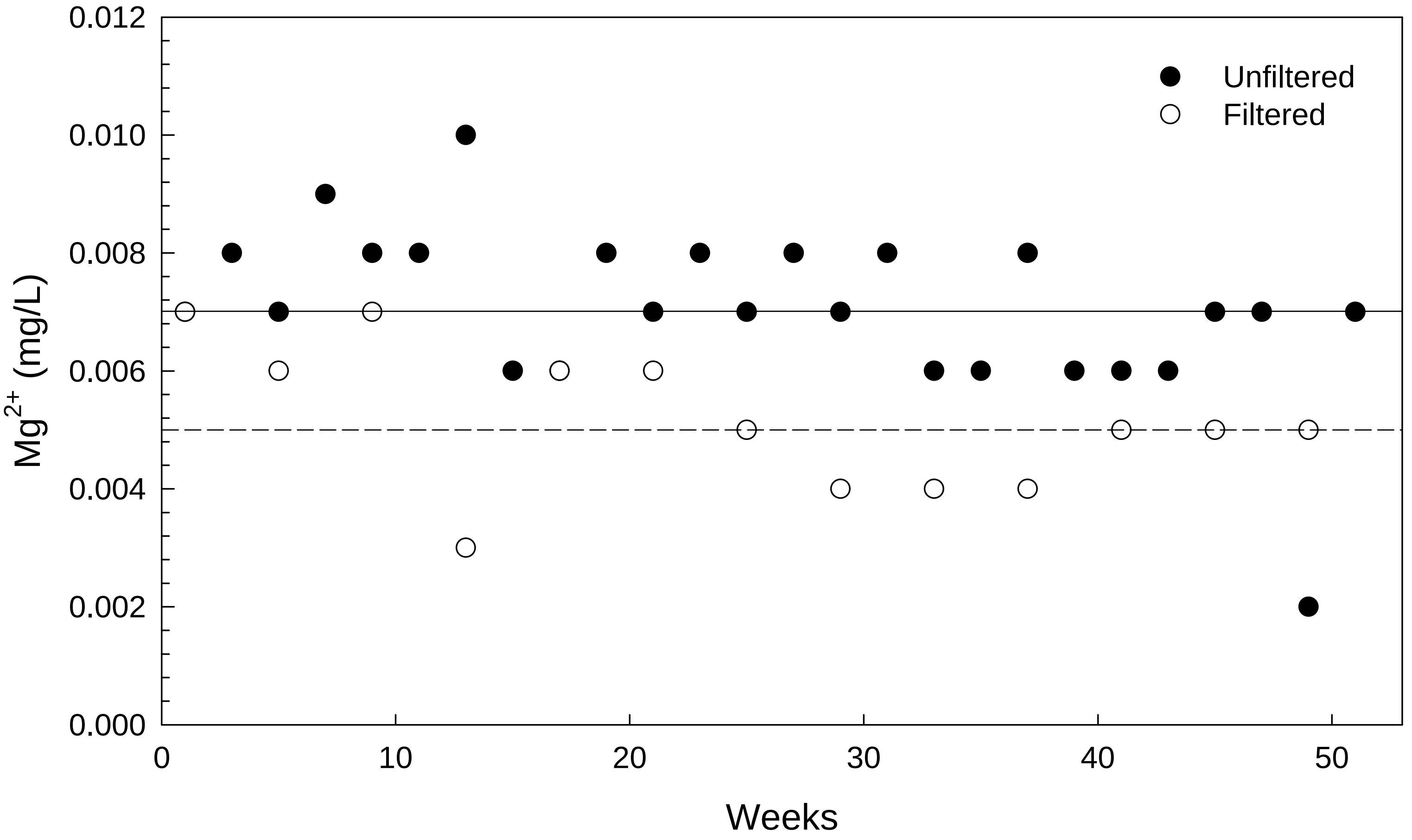
Table B-9. Filtered Internal Blind Concentrations for Internally Formulated Simulated Rainwater (01FR10), 2001

Weeks	*pH (units)*	*H (μeq/L)*	*Specific conductance (μS/cm)*	*Cl^- (mg/L)*	*NO_3^- (mg/L)*	*SO_4^{-2} (mg/L)*	*NH_4^- (mg/L)*	*Ca^{+2} (mg/L)*	*Mg^{+2} (mg/L)*	*Na^+ (mg/L)*	*K^+ (mg/L)*
1	5.18	6.61	4.1	0.058	0.189	0.254	0.027	0.028	0.007	0.019	0.007
5	5.22	6.03	3.5	0.050	0.185	0.239	0.027	0.051	0.006	0.020	0.001
9	5.31	4.90	6.1	0.064	0.189	0.247	0.027	0.044	0.007	0.022	0.010
13	5.21	6.17	3.5	0.061	0.196	0.261	0.027	0.046	0.003	0.023	0.005
17	5.13	7.41	3.9	0.060	0.192	0.253	0.027	0.044	0.006	0.023	0.005
21	5.20	6.31	3.8	0.056	0.186	0.256	0.016	0.043	0.006	0.019	0.005
25	5.32	4.79	3.5	0.060	0.188	0.261	0.039	0.044	0.005	0.020	0.004
29	5.16	6.92	3.9	0.051	0.188	0.257	0.031	0.039	0.004	0.018	0.006
33	5.29	5.13	3.5	0.051	0.180	0.254	0.036	0.034	0.004	0.018	0.004
37	5.18	6.61	3.6	0.057	0.186	0.255	0.027	0.031	0.004	0.017	0.004
41	5.23	5.89	3.6	0.055	0.189	0.251	0.032	0.046	0.005	0.017	0.005
45	5.23	5.89	3.7	0.062	0.191	0.251	0.031	0.041	0.005	0.015	0.008
49	5.18	6.61	4.4	0.050	0.191	0.251	0.027	0.034	0.005	0.018	0.004
Mean	5.22	6.10	3.9	0.057	0.188	0.253	0.029	0.040	0.005	0.019	0.005
Median	5.21	6.17	3.7	0.057	0.189	0.254	0.027	0.043	0.005	0.019	0.005
Target	5.22		3.6	0.053	0.193	0.260	0.025	0.031	0.007	0.020	0.005



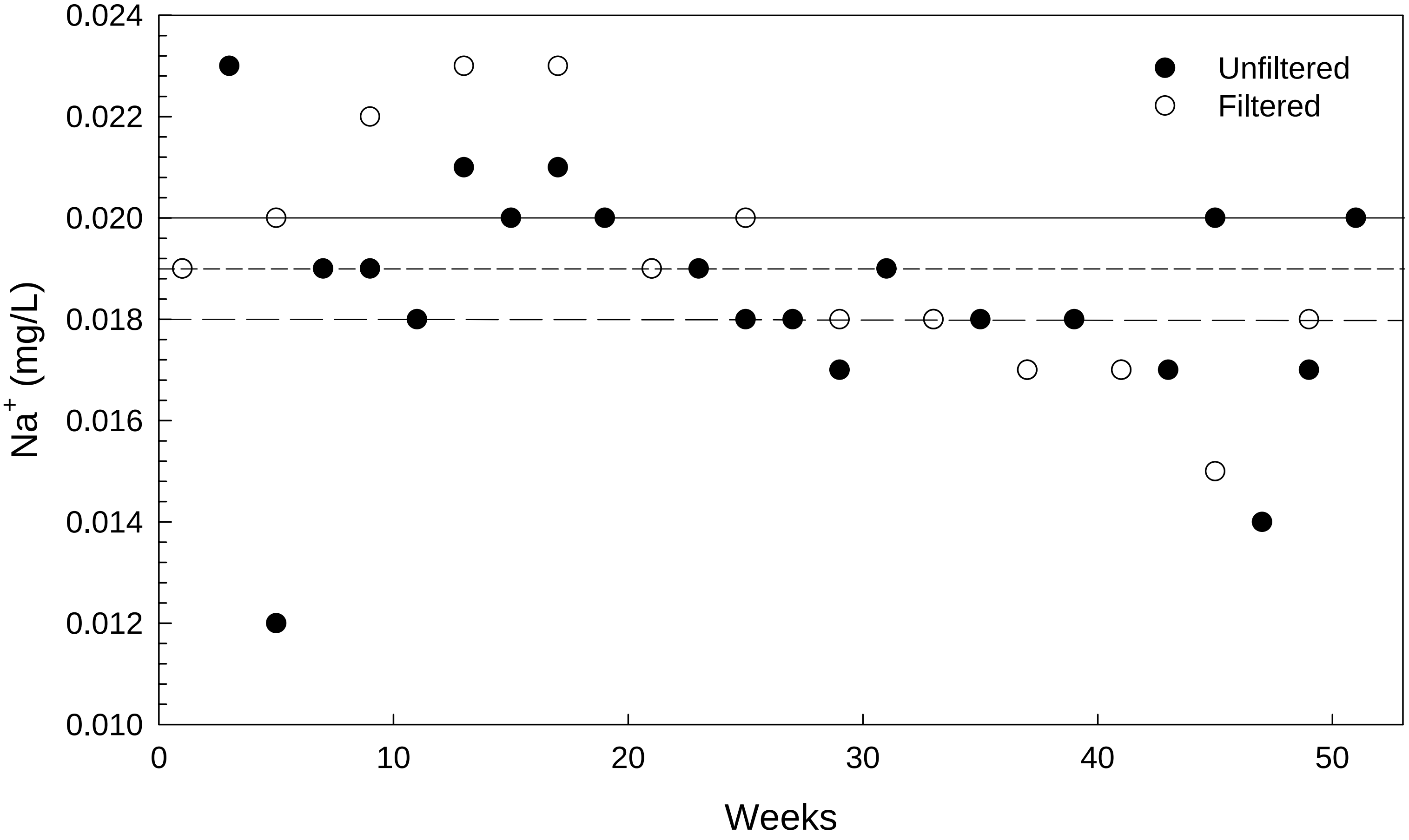
Note:
Solid line denotes target Ca^{2+} concentration: 0.031 mg/L; long dashed line denotes mean unfiltered Ca^{2+} concentration: 0.032 mg/L; and short dashed line denotes mean filtered Ca^{2+} concentration: 0.040 mg/L.

Figure B-23. Comparison of NTN filtered and unfiltered internal blind samples, (calcium), internally formulated simulated rain (01FR10), 2001.



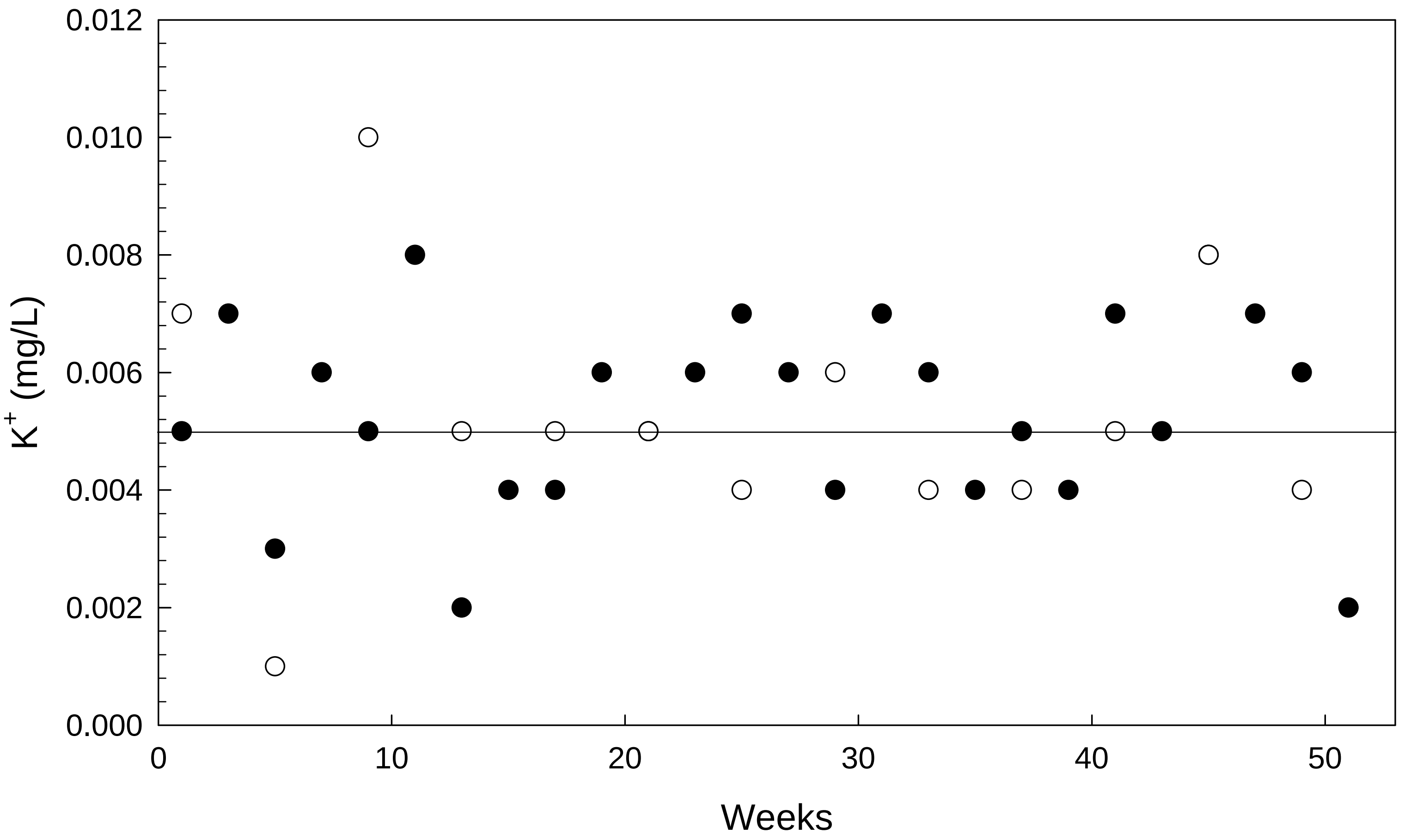
Note:
Solid line denotes target and mean unfiltered Mg^{2+} concentration: 0.007 mg/L; and short dashed line denotes mean filtered Mg^{2+} concentration: 0.005 mg/L.

Figure B-24. Comparison of NTN filtered and unfiltered internal blind samples, (magnesium), internally formulated simulated rain (01FR10), 2001.



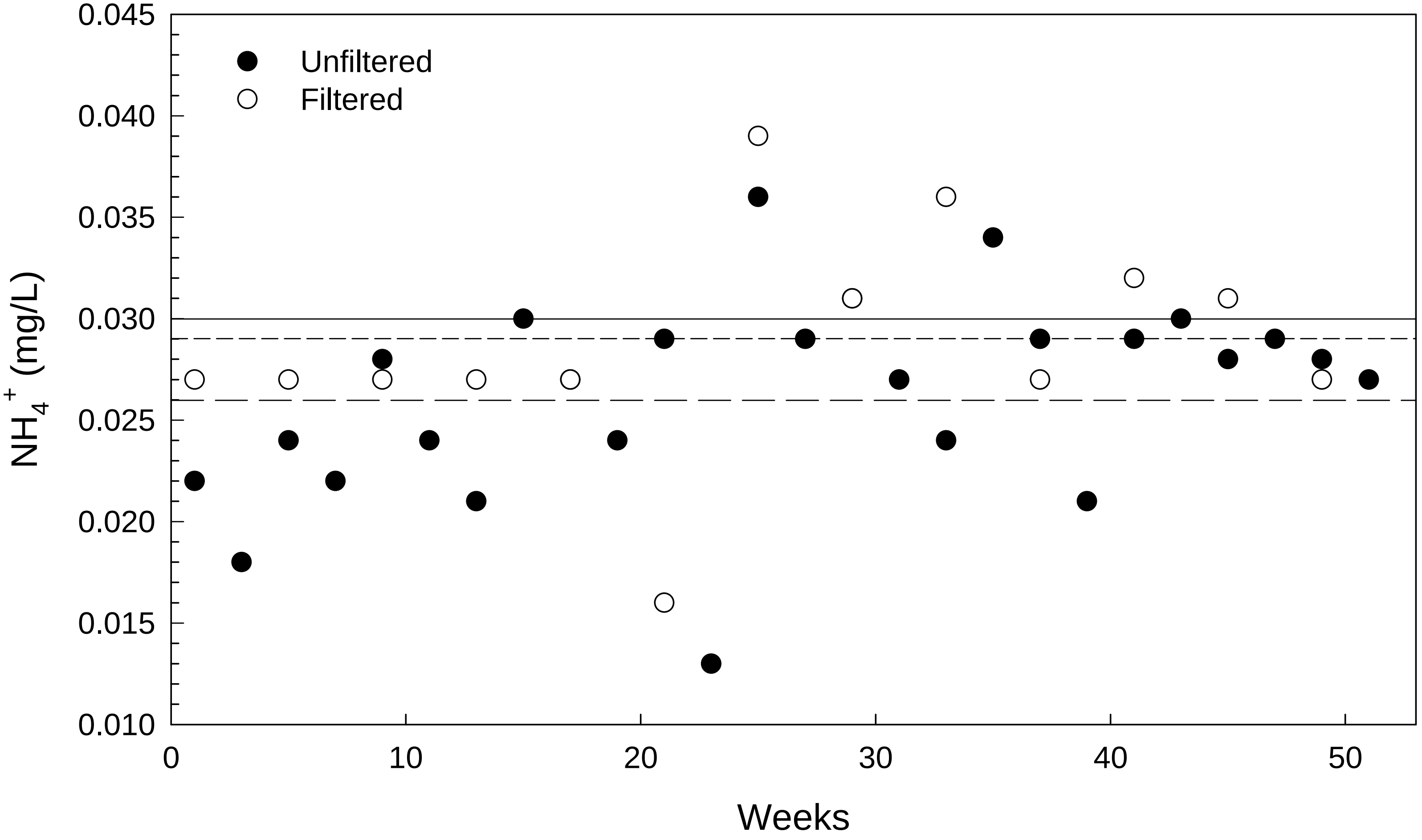
Note:
Solid line denotes target Na^+ concentration: 0.020 mg/L; long dashed line denotes mean unfiltered Na^+ concentration: 0.018 mg/L; and short dashed line denotes mean filtered Na^+ concentration: 0.019 mg/L.

Figure B-25. Comparison of NTN filtered and unfiltered internal blind samples, (sodium), internally formulated simulated rain (01FR10), 2001.



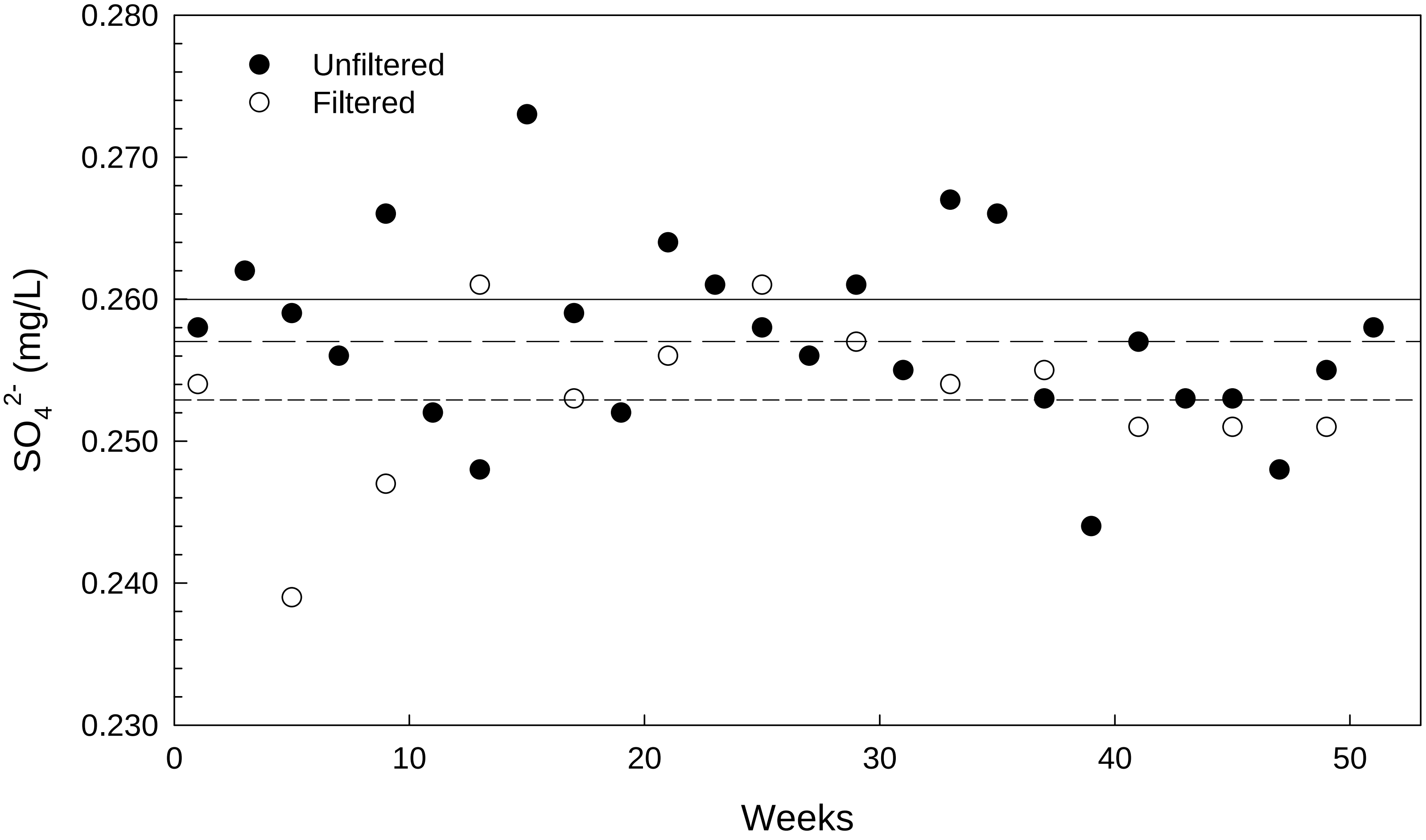
Note:
Line denotes target, mean unfiltered, and mean filtered K^+ concentration: 0.005 mg/L.

Figure B-26. Comparison of NTN filtered and unfiltered internal blind samples, (potassium), internally formulated simulated rain (01FR10), 2001.



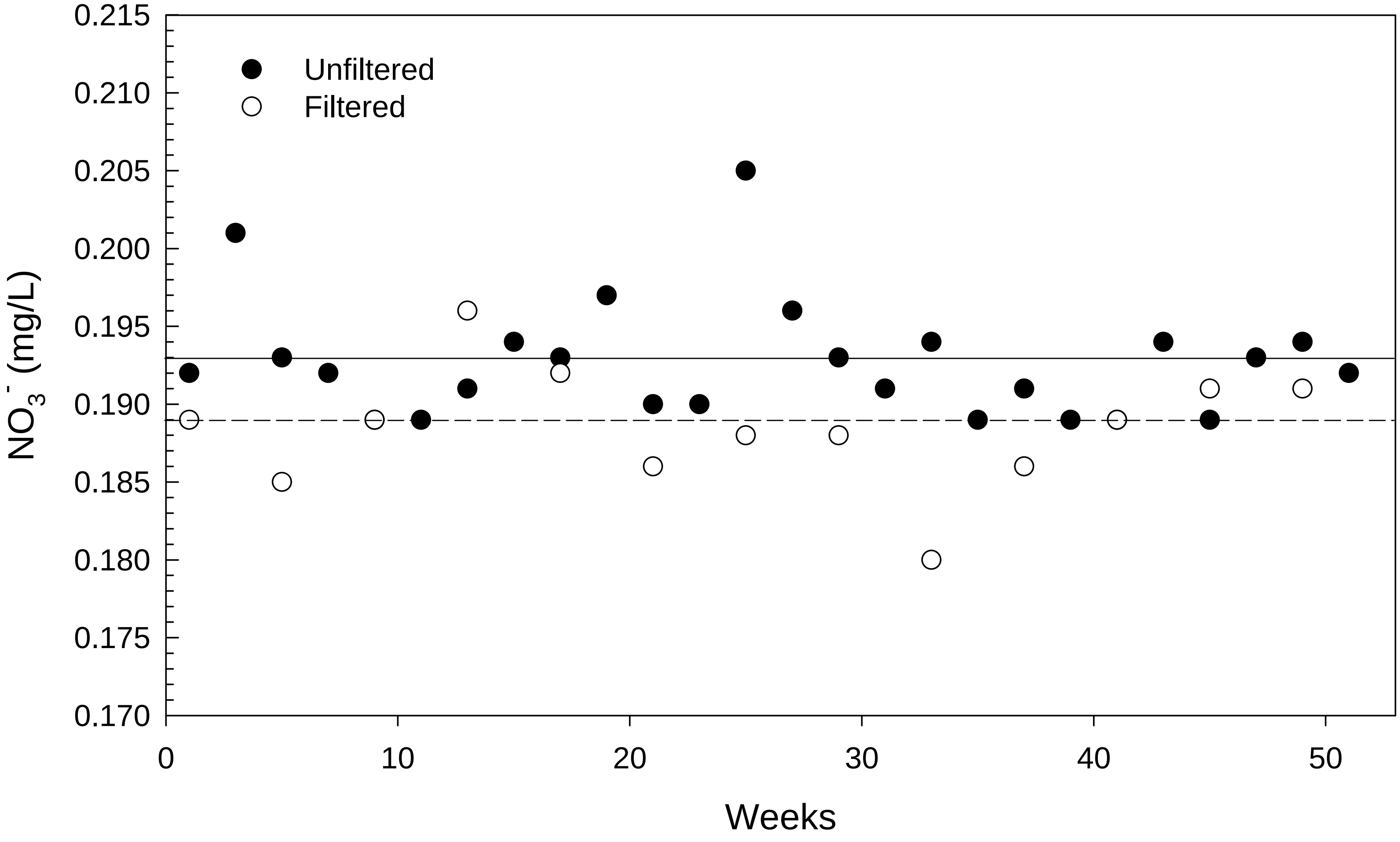
Note:
Solid line denotes target NH_4^+ concentration: 0.03 mg/L; long dashed line denotes mean unfiltered NH_4^+ concentration: 0.026 mg/L; and short dashed line denotes mean filtered NH_4^+ concentration: 0.029 mg/L.

Figure B-27. Comparison of NTN filtered and unfiltered internal blind samples, (ammonium), internally formulated simulated rain (01FR10), 2001.



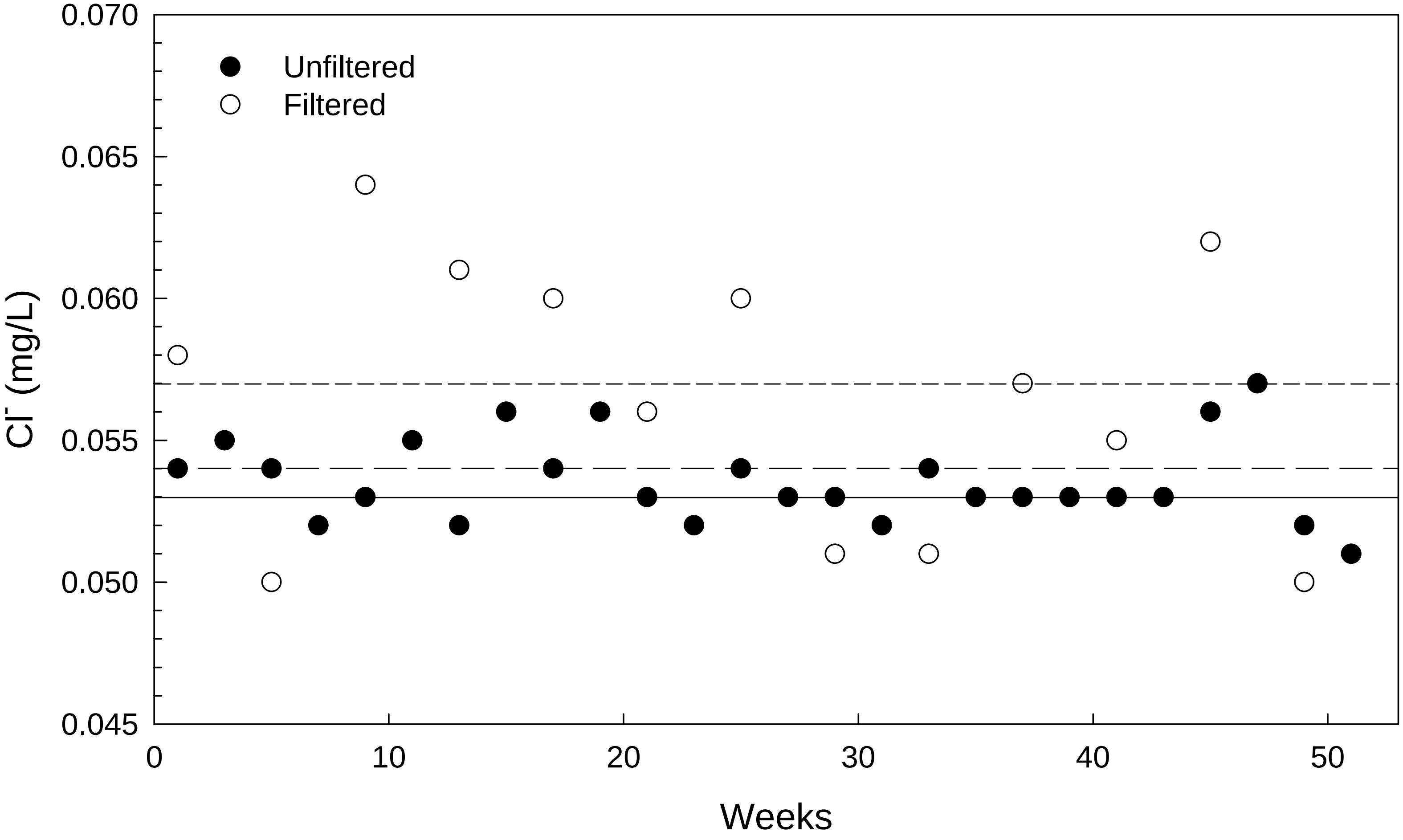
Note:
Solid line denotes target SO_4^{2-} concentration: 0.260 mg/L; long dashed line denotes mean unfiltered SO_4^{2-} concentration: 0.257 mg/L; and short dashed line denotes mean filtered SO_4^{2-} concentration: 0.253 mg/L.

Figure B-28. Comparison of NTN filtered and unfiltered internal blind samples, (sulfate), internally formulated simulated rain (01FR10), 2001.



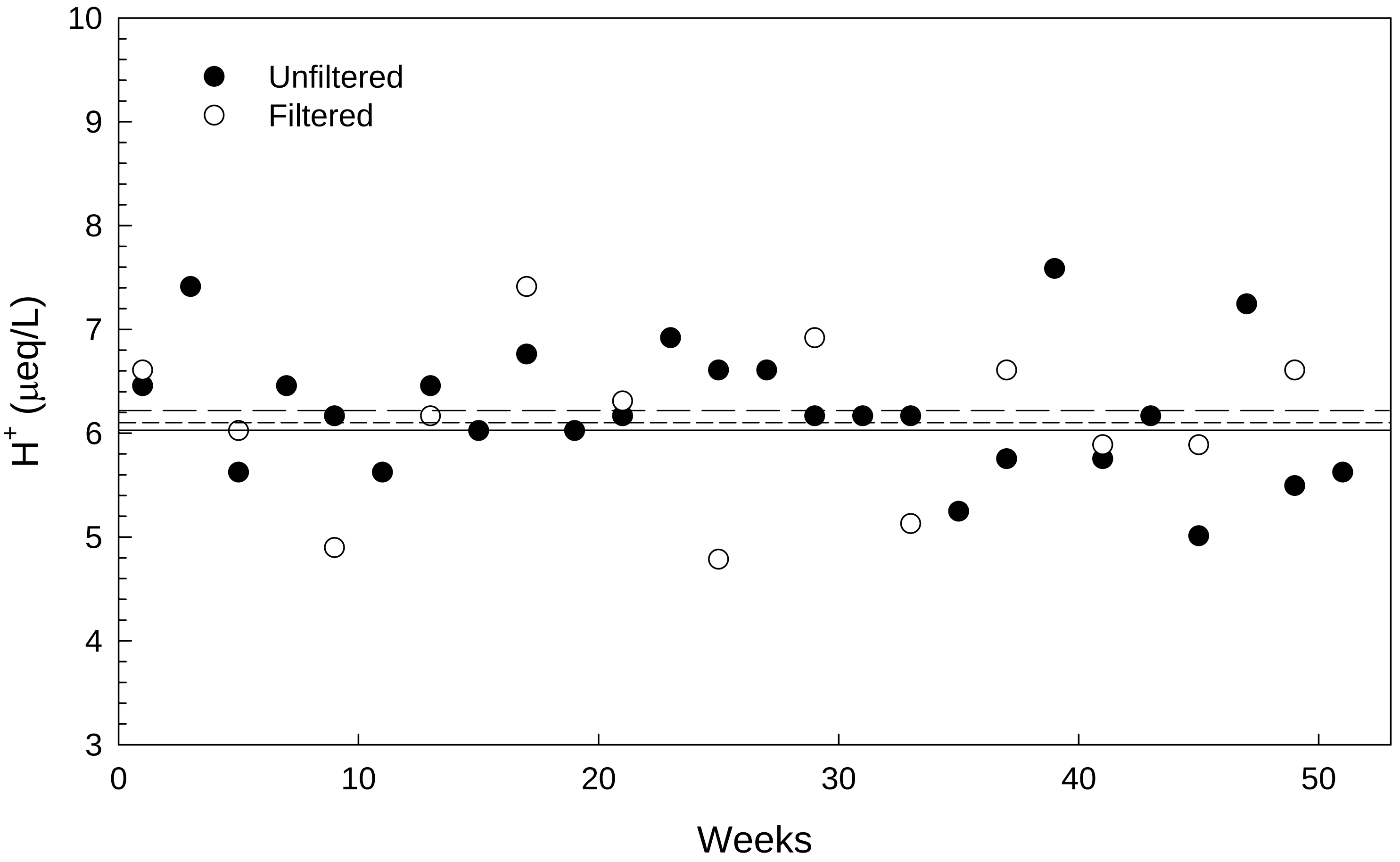
Note:
Solid line denotes target and mean unfiltered NO_3^- concentration: 0.193 mg/L; and short dashed line denotes mean filtered NO_3^- concentration: 0.189 mg/L.

Figure B-29. Comparison of NTN filtered and unfiltered internal blind samples, (nitrate), internally formulated simulated rain (01FR10), 2001.



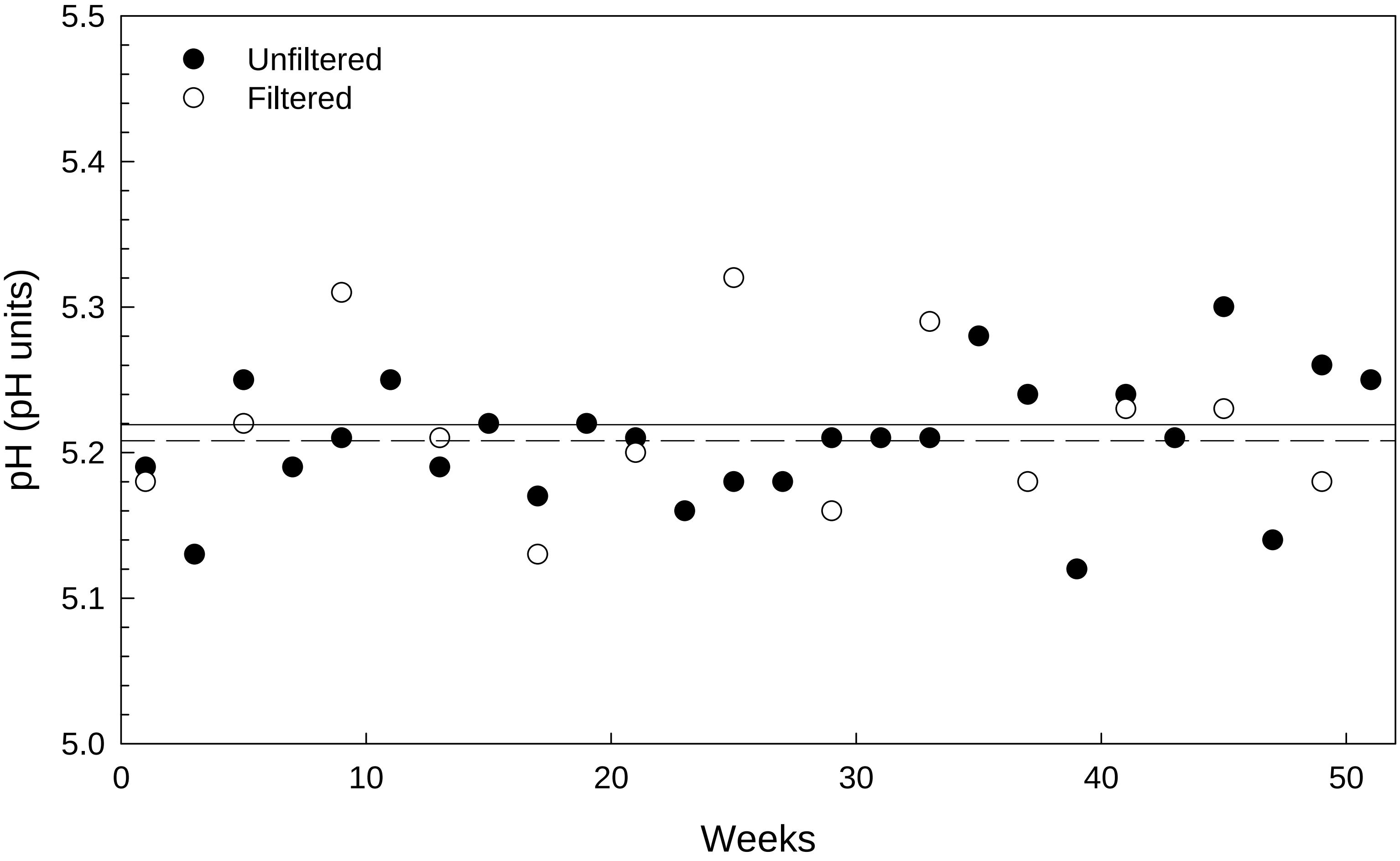
Note:
Solid line denotes target Cl$^-$ concentration: 0.053 mg/L; long dashed line denotes mean unfiltered
Cl$^-$ concentration: 0.054 mg/L; and short dashed line denotes mean filtered Cl$^-$ concentration: 0.057 mg/L.

Figure B-30. Comparison of NTN filtered and unfiltered internal blind samples, (chloride), internally formulated simulated rain (01FR10), 2001.



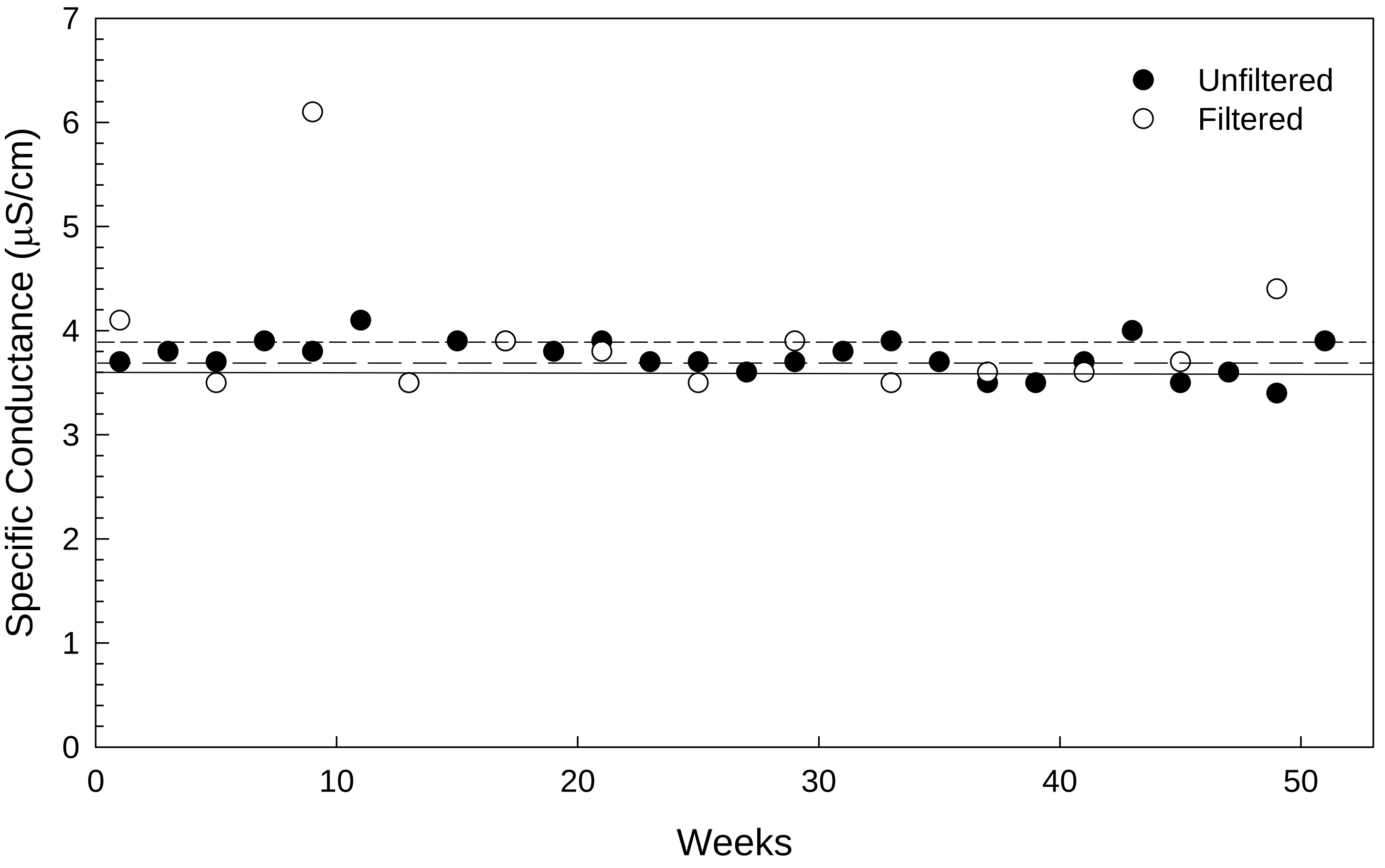
Note:
Solid line denotes target H^+ concentration: 6.03 µeq/L; long dashed line denotes mean unfiltered H^+ concentration: 6.22 µeq/L; and short dashed line denotes mean filtered H^+ concentration: 6.10 µeq/L.

Figure B-31. Comparison of NTN filtered and unfiltered internal blind samples, (hydrogen), internally formulated simulated rain (01FR10), 2001.



Note:
Solid line denotes target and mean filtered pH: 5.22; and dashed line denotes mean unfiltered pH: 5.21.

Figure B-32. Comparison of NTN filtered and unfiltered internal blind samples, (pH), internally formulated simulated rain (01FR10), 2001.



Note:
Solid line denotes target specific conductance: 3.6 µS/cm; long dashed line denotes mean unfiltered specific conductance: 3.7 µS/cm; and short dashed line denotes mean filtered specific conductance: 3.9 µS/cm.

Figure B-33. Comparison of NTN filtered and unfiltered internal blind samples, (specific conductance), internally formulated simulated rain (01FR10), 2001.

Table B-10. Comparison of Filtered and Unfiltered Internal Blind Audit Samples, Deionized (DI) Water, 2001

Parameter	*Target concentration (mg/L)*	*Mean measured concentration (mg/L)*	*Bias (mg/L)*	*Bias (%)*	*Standard Deviation (mg/L)*	*RSD (%)*
Calcium	<0.009	0.002	0.002		0.005	
		0.003	0.003		0.013	
Magnesium	<0.003	0.000	0.000		0.001	
		0.000	0.000		0.001	
Sodium	<0.003	-0.001	-0.001		0.002	
		0.001	0.001		0.002	
Potassium	<0.003	-0.002	-0.002		0.002	
		0.000	0.000		0.003	
Ammonium	<0.02	-0.01	-0.01		0.01	
		0.00	0.00		0.01	
Sulfate	<0.010	0.001	0.001		0.003	
		0.002	0.002		0.005	
Nitrate	<0.010	0.000	0.000		0.002	
		0.002	0.002		0.004	
Chloride	<0.006	0.000	0.000		0.002	
		0.001	0.001		0.004	
pH (units)	5.65	5.58	-0.07	-1.2	0.09	1.6
		5.56	-0.10	-1.7	0.05	0.8
H (μeq/L)	2.24	2.66	0.42	18.8	0.5	19.9
		2.80	0.56	25.0	0.3	10.0
Conductivity (μS/cm)	0.9	1.3	0.4	44.4	0.1	10.2
		1.3	0.4	47.0	0.5	34.4

Note:

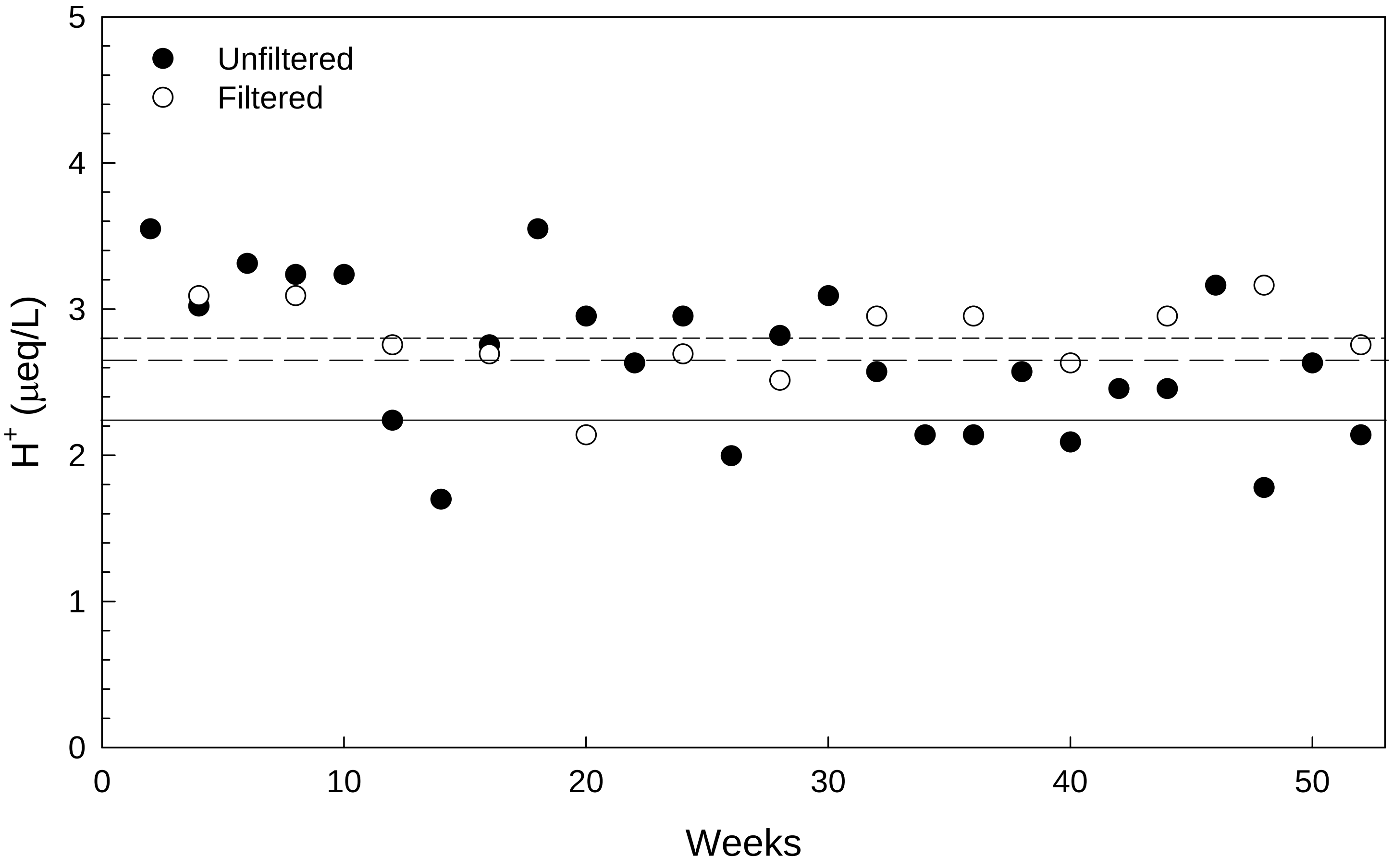
There were 26 unfiltered samples and 13 filtered samples in each set.

Table B-11. Unfiltered Internal Blind Concentrations for Deionized Water (DI), 2001

Weeks	*pH (units)*	*H (μeq/L)*	*Specific conductance (μS/cm)*	*Cl^- (mg/L)*	*NO_3^- (mg/L)*	*SO_4^{-2} (mg/L)*	*NH_4^- (mg/L)*	*Ca^{+2} (mg/L)*	*Mg^{+2} (mg/L)*	*Na^+ (mg/L)*	*K^+ (mg/L)*
2	5.45	3.55	1.4	0.000	0.000	0.000	-0.008	-0.002	0.000	0.000	0.000
4	5.52	3.02	1.1	0.000	0.000	0.000	-0.007	0.009	0.003	0.001	-0.002
6	5.48	3.31	1.3	0.000	0.000	0.000	-0.003	0.002	-0.001	0.000	-0.003
8	5.49	3.24	1.5	0.000	0.000	0.006	0.000	0.011	0.003	-0.001	0.000
10	5.49	3.24	1.2	0.000	0.000	0.000	-0.009	0.000	0.000	0.002	-0.003
12	5.65	2.24	1.1	0.000	0.010	0.005	0.003	-0.001	0.001	0.001	-0.001
14	5.77	1.70	1.3	0.011	0.000	0.000	-0.003	-0.010	0.000	0.000	-0.002
16	5.56	2.75	1.2	0.000	0.000	0.009	-0.008	0.008	-0.001	0.000	-0.001
18	5.45	3.55	1.4	0.000	0.000	0.000	-0.012	0.007	-0.001	0.001	-0.002
20	5.53	2.95	1.4	0.000	0.000	0.000	-0.005	0.001	0.002	0.002	0.000
22	5.58	2.63	1.3	0.000	0.000	0.000	0.000	0.010	0.002	0.001	0.001
24	5.53	2.95	1.5	0.000	0.000	0.000	0.003	0.001	-0.001	-0.001	-0.005
26	5.70	2.00	1.4	0.000	0.000	0.000	-0.010	0.000	0.000	-0.001	-0.003
28	5.55	2.82	1.3	0.000	0.000	0.000	0.000	0.004	0.001	-0.002	0.001
30	5.51	3.09	1.4	0.000	0.000	0.000	-0.003	0.007	0.001	-0.002	-0.004
32	5.59	2.57	1.1	0.000	0.000	0.014	-0.003	0.003	0.003	-0.001	0.000
34	5.67	2.14	1.2	0.000	0.000	0.000	0.000	0.002	0.000	-0.001	-0.002
36	5.67	2.14	1.5	0.000	0.000	0.000	-0.007	0.007	0.000	0.000	0.000
38	5.59	2.57	1.2	0.000	0.000	0.000	-0.012	0.004	-0.001	-0.002	-0.002
40	5.68	2.09	1.1	0.000	0.000	0.000	-0.010	0.002	-0.001	-0.002	-0.002
42	5.61	2.45	1.2	0.000	0.000	0.000	-0.011	-0.007	-0.001	-0.001	-0.003
44	5.61	2.45	1.5	0.000	0.000	0.000	-0.007	-0.005	0.000	-0.001	0.000
46	5.50	3.16	1.3	0.000	0.000	0.000	-0.010	-0.004	-0.001	-0.004	-0.002
48	5.75	1.78	1.3	0.000	0.000	0.000	-0.011	0.006	0.000	-0.001	0.003
50	5.58	2.63	1.4	0.000	0.000	0.000	-0.011	-0.005	-0.001	-0.002	-0.002
52	5.67	2.14	1.2	0.000	0.000	0.000	-0.006	-0.001	0.000	-0.005	-0.005
Mean	5.58	2.66	1.3	0.000	0.000	0.001	-0.006	0.002	0.000	-0.001	-0.002
Median	5.58	2.63	1.3	0.000	0.000	0.000	-0.007	0.002	0.000	-0.001	-0.002
Target	5.65	2.24	1.3	<0.006	<0.010	<0.010	<0.02	<0.009	<0.003	<0.003	<0.003

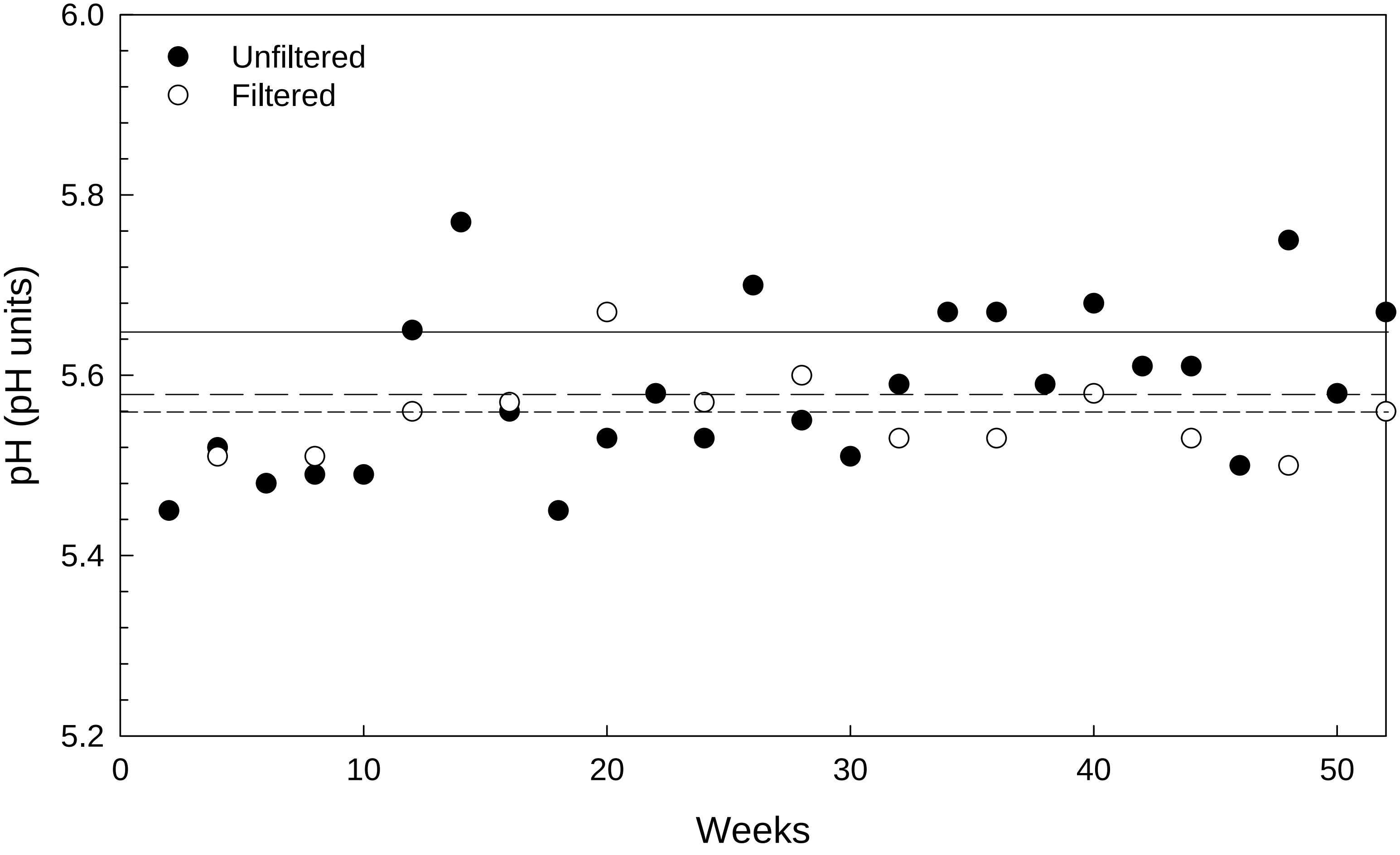
Table B-12. Filtered Internal Blind Concentrations for Deionized (DI) Water, 2001

Weeks	*pH (units)*	*H (μeq/L)*	*Specific conductance (μS/cm)*	*Cl^- (mg/L)*	*NO_3^- (mg/L)*	*SO_4^{-2} (mg/L)*	*NH_4^- (mg/L)*	*Ca^{+2} (mg/L)*	*Mg^{+2} (mg/L)*	*Na^+ (mg/L)*	*K^+ (mg/L)*
4	5.51	3.09	1.1	0.000	0.000	0.000	-0.004	0.002	0.002	0.001	-0.001
8	5.51	3.09	1.3	0.000	0.000	0.000	-0.005	0.031	0.002	0.001	-0.001
12	5.56	2.75	1.2	0.000	0.000	0.000	-0.009	0.003	0.001	0.001	0.005
16	5.57	2.69	1.1	0.000	0.000	0.000	-0.003	0.005	-0.001	0.002	-0.001
20	5.67	2.14	1.3	0.000	0.000	0.000	-0.002	0.026	0.002	0.000	0.005
24	5.57	2.69	1.3	0.000	0.010	0.000	-0.009	-0.004	0.001	0.003	0.001
28	5.60	2.51	1.3	0.000	0.010	0.019	-0.003	0.010	0.000	0.001	-0.001
32	5.53	2.95	1.2	0.016	0.000	0.000	0.017	-0.010	-0.001	-0.001	-0.001
36	5.53	2.95	1.1	0.000	0.000	0.000	0.012	-0.008	0.000	0.000	0.000
40	5.58	2.63	2.8	0.000	0.000	0.000	-0.014	-0.007	0.000	-0.001	-0.002
44	5.53	2.95	1.2	0.000	0.000	0.000	-0.011	-0.002	0.000	-0.001	-0.002
48	5.50	3.16	1.0	0.000	0.000	0.000	-0.006	0.000	-0.001	0.002	-0.001
52	5.56	2.75	1.3	0.000	0.000	0.000	-0.011	-0.002	0.000	-0.002	-0.003
Mean	5.56	2.80	1.3	0.001	0.002	0.001	-0.004	0.003	0.000	0.000	-0.000
Median	5.56	2.75	1.2	0.000	0.000	0.000	-0.005	0.000	0.000	0.001	-0.001
Target	5.65	2.24	1.3	<0.006	<0.010	<0.010	<0.02	<0.009	<0.003	<0.003	<0.003



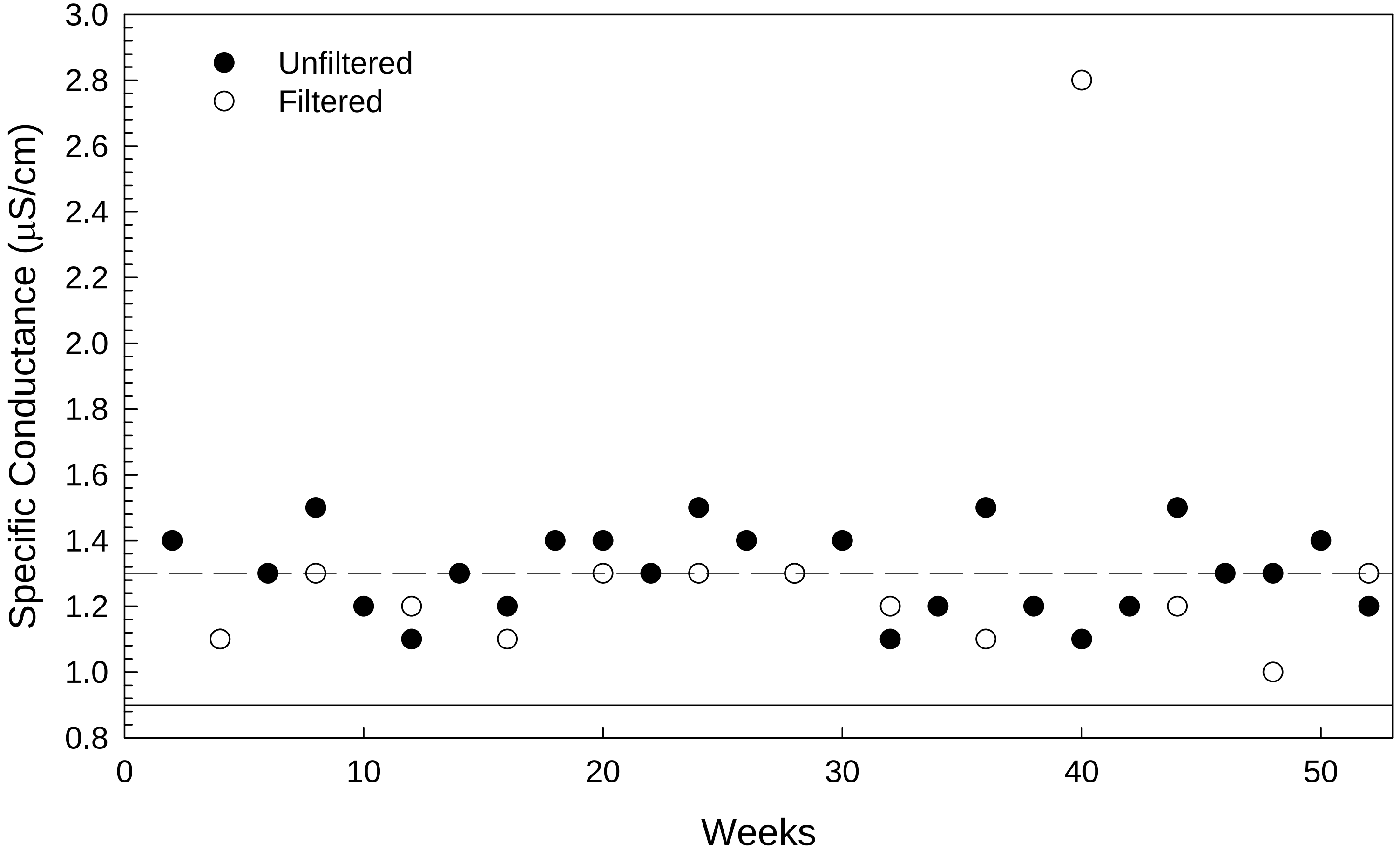
Note:
Solid line denotes target H^+ concentration: 2.24 μeq/L; long dashed line denotes mean unfiltered H^+ concentration: 2.66 μeq/L; and short dashed line denotes mean filtered H^+ concentration: 2.80 μeq/L.

Figure B-34. Comparison of NTN filtered and unfiltered internal blind samples, (hydrogen), deionized (DI) water, 2001.



Note:
Solid line denotes target pH: 5.65; long dashed line denotes mean unfiltered pH: 5.58; and short dashed line denotes mean filtered pH: 5.56.

Figure B-35. Comparison of NTN filtered and unfiltered internal blind samples, (pH), deionized (DI) water, 2001.

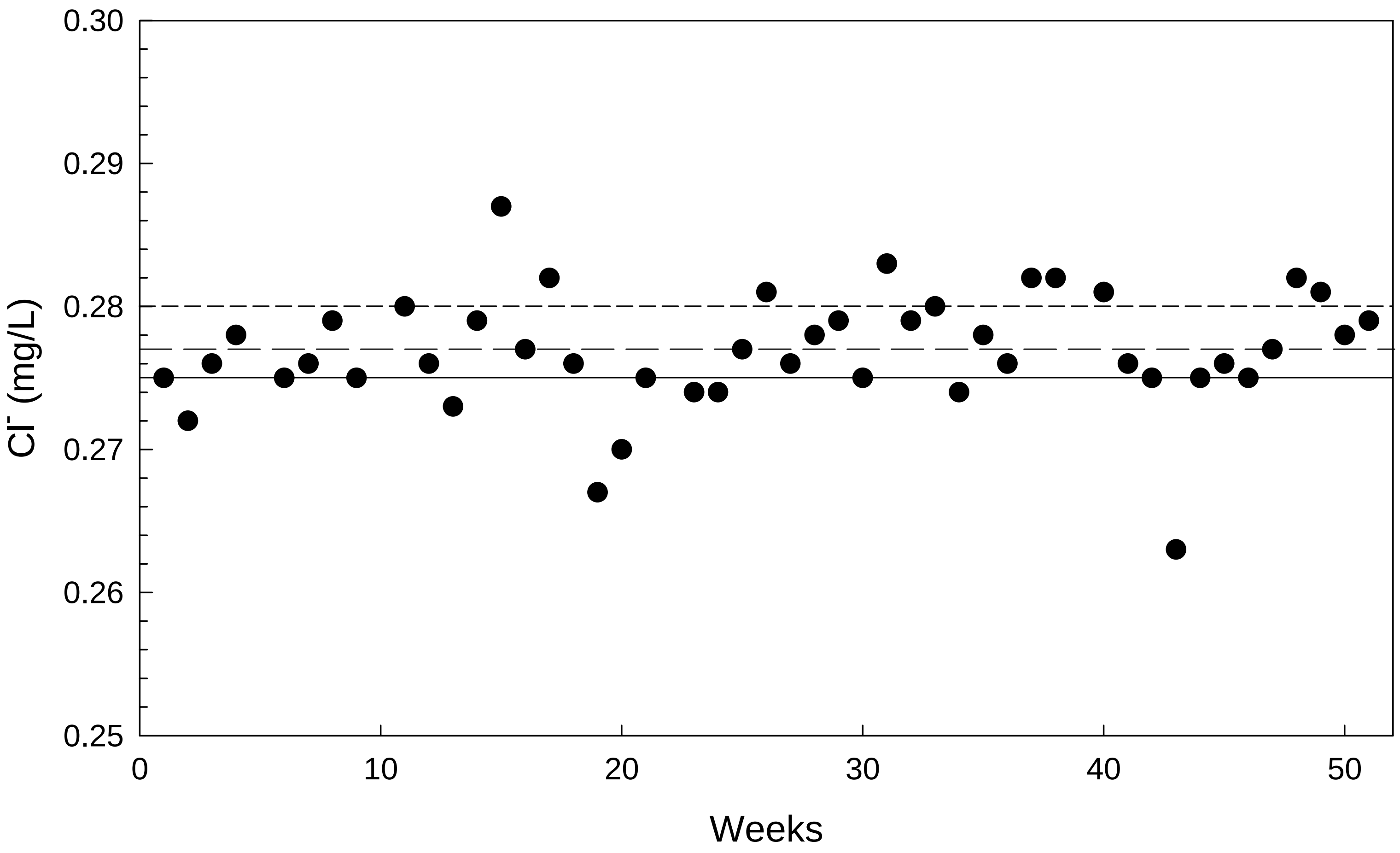


Note:
Solid line denotes target specific conductance: 0.9 µS/cm; and long dashed line denotes mean filtered and unfiltered specific conductance: 1.3 µS/cm.

Figure B-36. Comparison of NTN filtered and unfiltered internal blind samples, (specific conductance), deionized (DI) water, 2001.

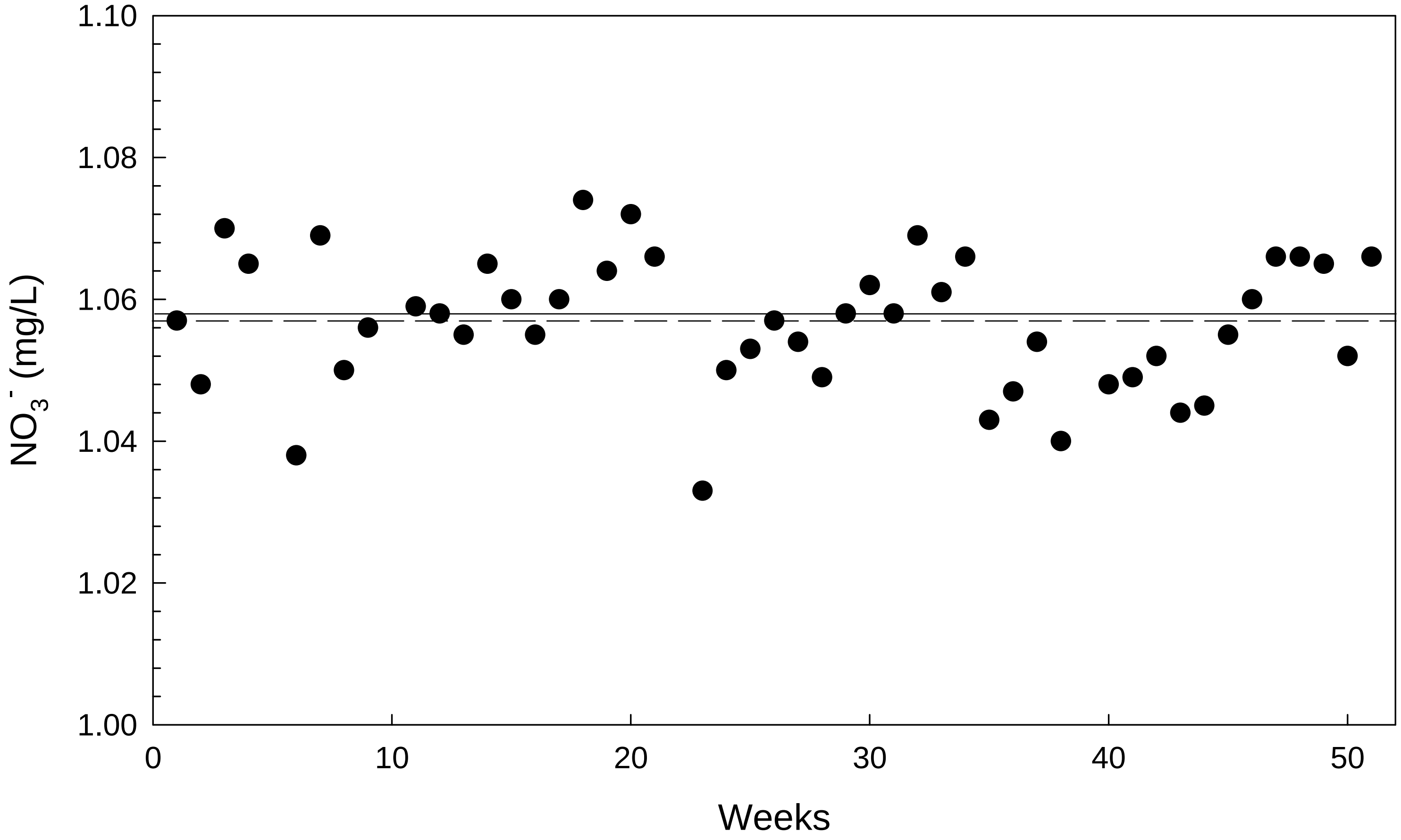
Table B-13. AIRMoN Internal Blind Concentrations for WMO/GAW 2000 Sample #2, 2001

Weeks	*Cl^-* *(mg/L)*	*NO_3^-* *(mg/L)*	*SO_4^{2-}* *(mg/L)*	*NH_4^+* *(mg/L)*	*Ca^{2+}* *(mg/L)*	*Mg^{2+}* *(mg/L)*	*Na^+* *(mg/L)*	*K^+* *(mg/L)*	*Specific conductance* *(µS/cm)*	*pH* *(units)*	*H^+* *(µeq/L)*
1	0.275	1.057	1.331	0.204	0.115	0.030	0.147	0.031	16.9	4.55	28.18
2	0.272	1.048	1.334	0.219	0.102	0.029	0.141	0.027	17.1	4.54	28.84
3	0.276	1.070	1.336	0.213	0.114	0.030	0.152	0.028	17.0	4.55	28.18
4	0.278	1.065	1.353	0.208	0.112	0.031	0.143	0.028	16.8	4.54	28.84
6	0.275	1.038	1.337	0.193	0.114	0.032	0.148	0.029	17.8	4.52	30.20
7	0.276	1.069	1.349	0.200	0.121	0.032	0.148	0.028	17.8	4.54	28.84
8	0.279	1.050	1.371	0.194	0.117	0.031	0.148	0.029	17.9	4.53	29.51
9	0.275	1.056	1.359	0.195	0.121	0.032	0.146	0.029	18.0	4.54	28.84
11	0.280	1.059	1.356	0.198	0.120	0.034	0.152	0.029	17.4	4.54	28.84
12	0.276	1.058	1.347	0.190	0.118	0.031	0.152	0.026	17.5	4.56	27.54
13	0.273	1.055	1.360	0.190	0.114	0.031	0.149	0.026	17.6	4.56	27.54
14	0.279	1.065	1.341	0.193	0.110	0.033	0.151	0.026	17.9	4.53	29.51
15	0.287	1.060	1.300	0.201	0.127	0.032	0.152	0.033	17.4	4.54	28.84
16	0.277	1.055	1.317	0.189	0.127	0.032	0.152	0.033	17.4	4.53	29.51
17	0.282	1.060	1.342	0.196	0.119	0.033	0.155	0.030	17.5	4.58	26.30
18	0.276	1.074	1.326	0.196	0.119	0.033	0.154	0.030	17.2	4.57	26.92
19	0.267	1.064	1.346	0.193	0.121	0.030	0.159	0.029	17.2	4.54	28.84
20	0.270	1.072	1.345	0.193	0.117	0.029	0.160	0.028	17.2	4.53	29.51
21	0.275	1.066	1.348	0.188	0.124	0.032	0.153	0.031	17.5	4.54	28.84
23	0.274	1.033	1.347	0.191	0.115	0.032	0.158	0.028	15.7	4.59	25.70
24	0.274	1.050	1.339	0.192	0.114	0.031	0.155	0.028	16.6	4.58	26.30
25	0.277	1.053	1.340	0.198	0.103	0.031	0.152	0.026	16.7	4.58	26.30
26	0.281	1.057	1.340	0.198	0.105	0.031	0.152	0.027	16.7	4.58	26.30
27	0.276	1.054	1.332	0.195	0.110	0.029	0.148	0.029	16.7	4.58	26.30
28	0.278	1.049	1.331	0.197	0.109	0.028	0.145	0.028	16.4	4.55	28.18
29	0.279	1.058	1.341	0.194	0.116	0.032	0.149	0.029	15.9	4.58	26.30
30	0.275	1.062	1.320	0.196	0.115	0.032	0.147	0.030	17.1	4.55	28.18
31	0.283	1.058	1.343	0.196	0.108	0.032	0.143	0.030	16.3	4.54	28.84
32	0.279	1.069	1.351	0.199	0.102	0.026	0.144	0.032	16.7	4.56	27.54
33	0.280	1.061	1.344	0.195	0.107	0.032	0.144	0.030	17.5	4.55	28.18
34	0.274	1.066	1.347	0.194	0.105	0.030	0.144	0.031	16.8	4.56	27.54
35	0.278	1.043	1.353	0.199	0.100	0.031	0.144	0.031	17.5	4.54	28.84
36	0.276	1.047	1.353	0.200	0.109	0.030	0.147	0.030	17.3	4.56	27.54
37	0.282	1.054	1.354	0.198	0.103	0.030	0.144	0.030	17.1	4.54	28.84
38	0.282	1.040	1.349	0.198	0.109	0.031	0.144	0.029	17.4	4.54	28.84
40	0.281	1.048	1.335	0.191	0.116	0.028	0.141	0.030	16.5	4.58	26.30
41	0.276	1.049	1.329	0.197	0.109	0.032	0.147	0.029	16.7	4.56	27.54
42	0.275	1.052	1.342	0.195	0.101	0.031	0.148	0.026	16.7	4.56	27.54
43	0.263	1.044	1.347	0.195	0.103	0.031	0.147	0.027	16.9	4.57	26.92
44	0.275	1.045	1.310	0.195	0.105	0.031	0.142	0.029	16.5	4.58	26.30
45	0.276	1.055	1.330	0.190	0.096	0.033	0.138	0.025	19.3	4.60	25.12
46	0.275	1.060	1.344	0.195	0.109	0.031	0.149	0.034	16.8	4.56	27.54
47	0.277	1.066	1.342	0.195	0.110	0.031	0.155	0.029	16.7	4.55	28.18
48	0.282	1.066	1.331	0.200	0.107	0.032	0.145	0.025	16.7	4.56	27.54
49	0.281	1.065	1.342	0.203	0.108	0.032	0.145	0.025	16.0	4.56	27.54
50	0.278	1.052	1.338	0.198	0.112	0.033	0.147	0.030	16.7	4.57	26.92
51	0.279	1.066	1.332	0.194	0.103	0.031	0.146	0.031	16.4	4.60	25.12



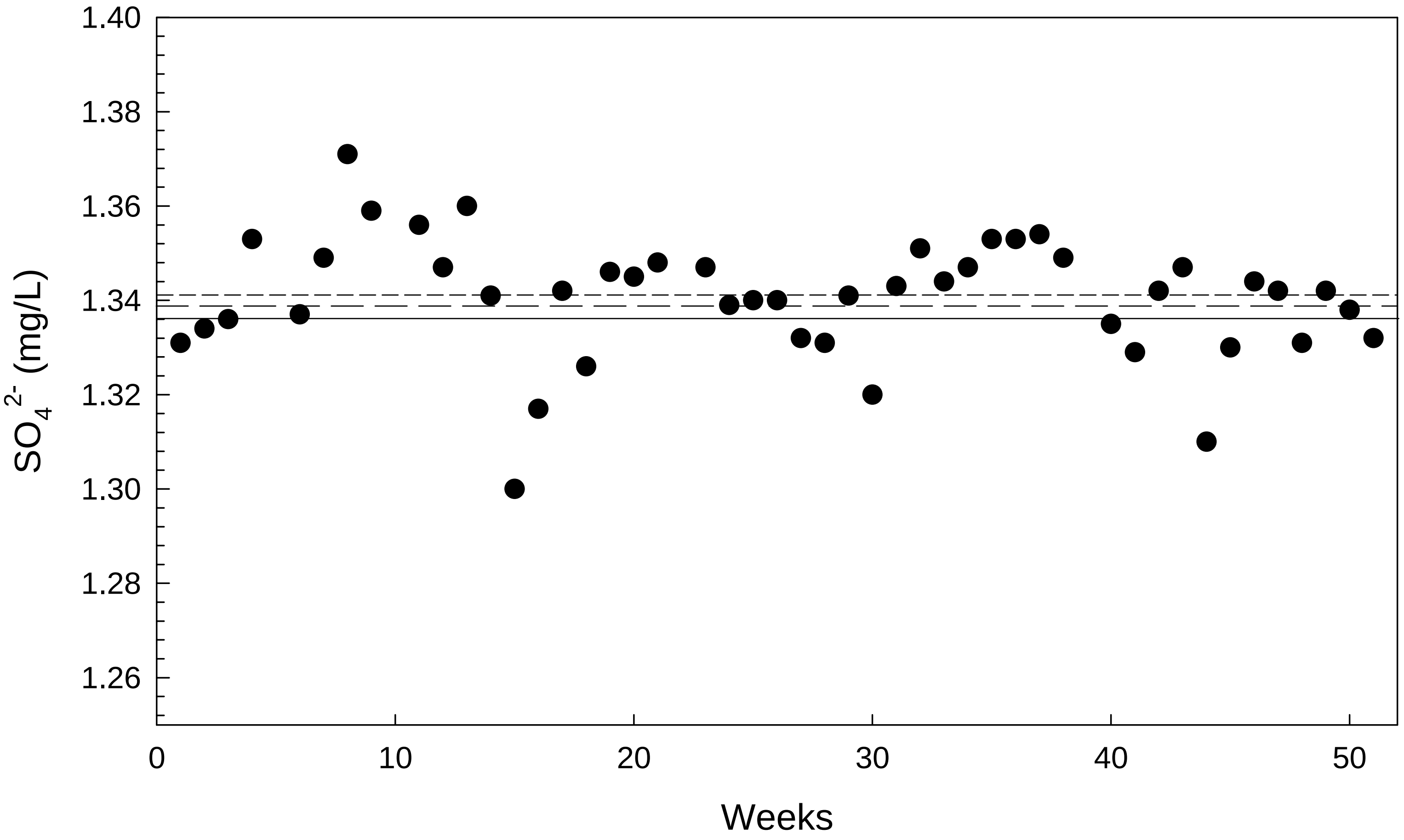
Note:
Solid line is mean Cl^- WMO/GAW 2000 sample #2 concentration: 0.275 mg/L; short dashed line is target Cl^- WMO/GAW 2000 sample #2 concentration: 0.280 mg/L; and long dashed line is mean Cl^- internal blind concentration: 0.277 mg/L.

Figure B-37. AIRMoN internal blind samples (chloride),
WMO/GAW 2000 sample #2, 2001.



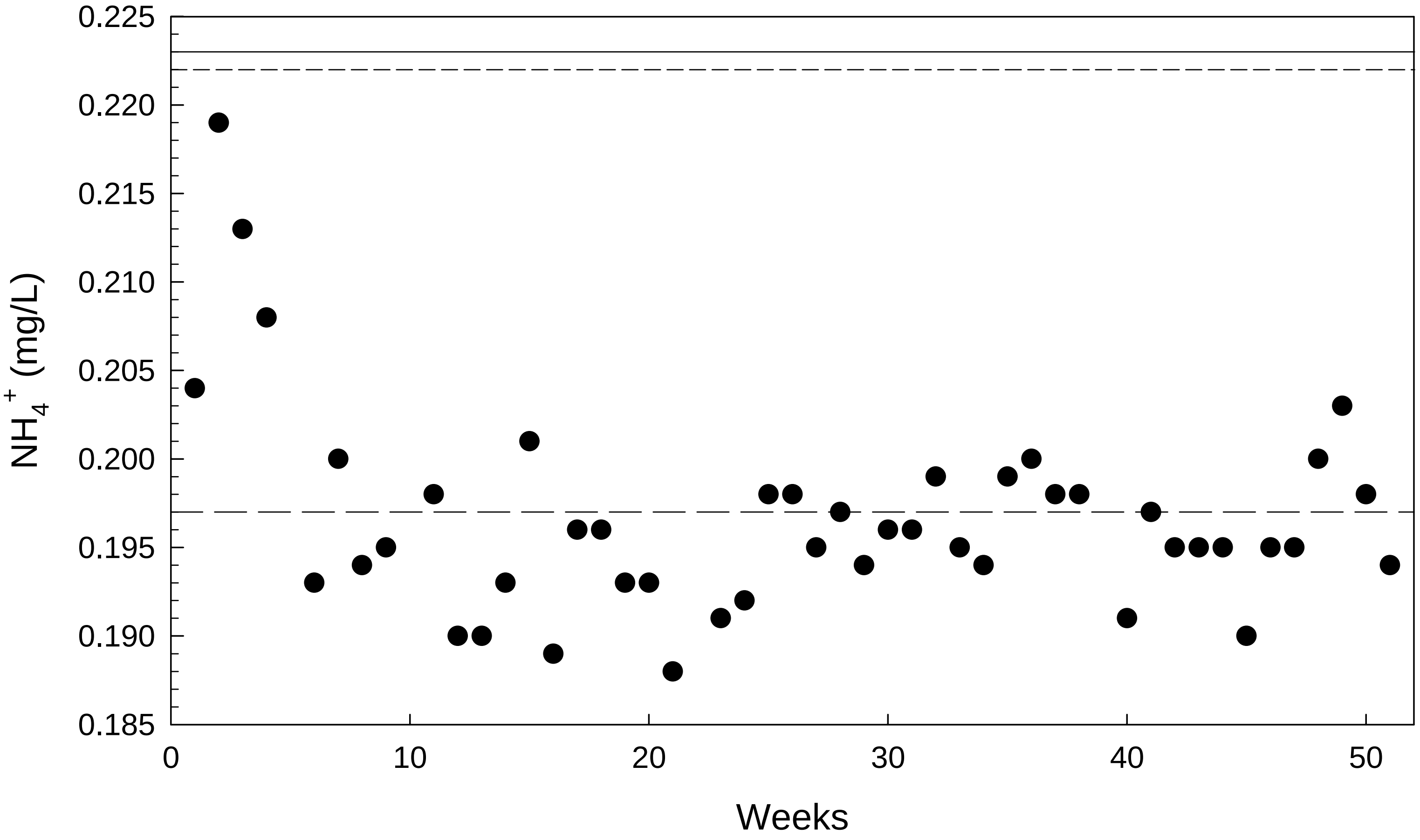
Note:
Solid line is mean and target NO_3^- WMO/GAW 2000 sample #2 concentration: 1.058 mg/L; and dashed line is mean NO_3^- internal blind concentration: 1.057 mg/L.

Figure B-38. AIRMoN internal blind samples, (nitrate),
WMO/GAW 2000 sample #2, 2001.



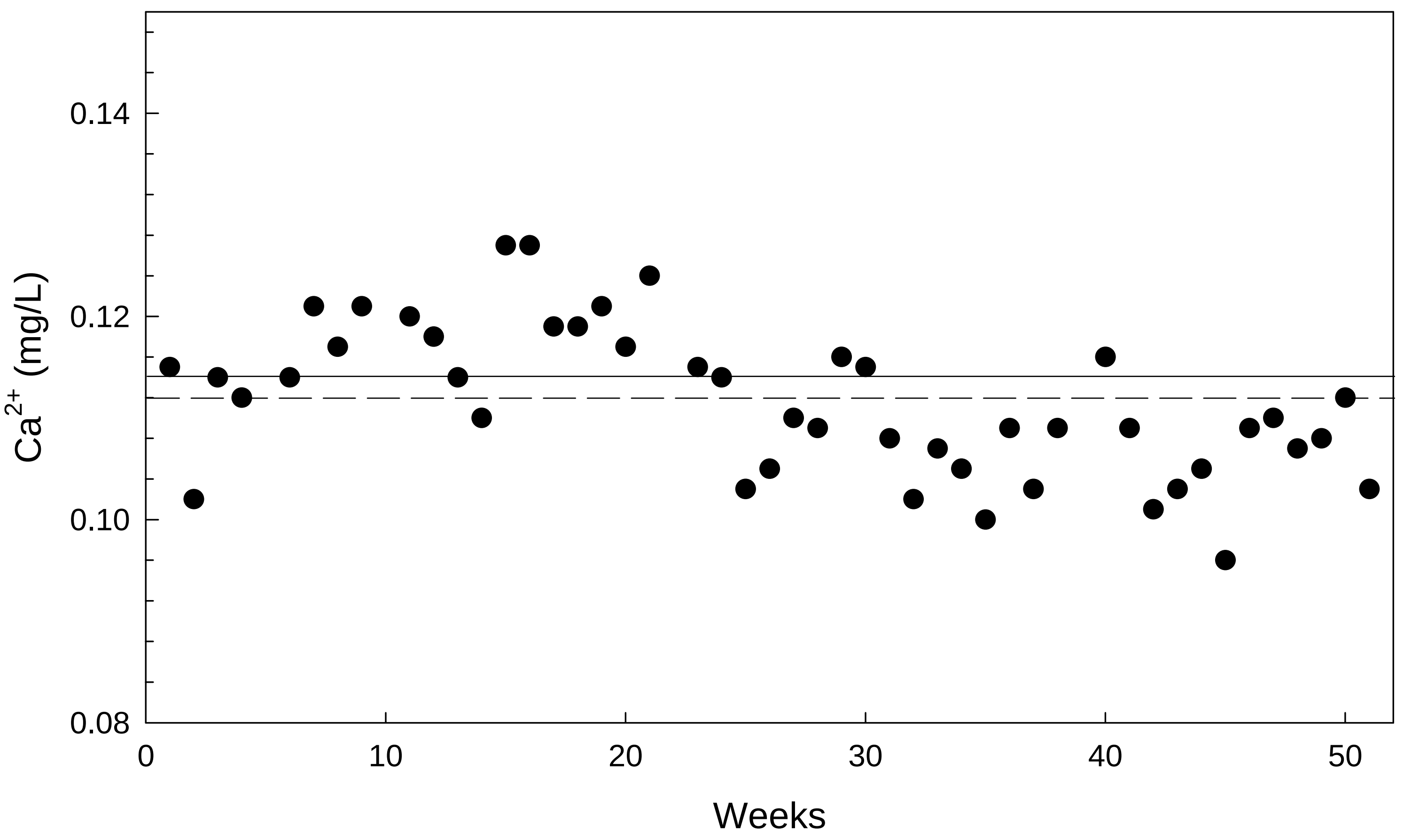
Note:
Solid line is mean SO_4^{2-} WMO/GAW 2000 sample #2 concentration: 1.336 mg/L; short dashed line is target SO_4^{2-} WMO/GAW 2000 sample #2 concentration: 1.339 mg/L; and long dashed line is mean SO_4^{2-} internal blind concentration: 1.341 mg/L.

Figure B-39. AIRMoN internal blind samples (sulfate), WMO/GAW 2000 sample #2, 2001.



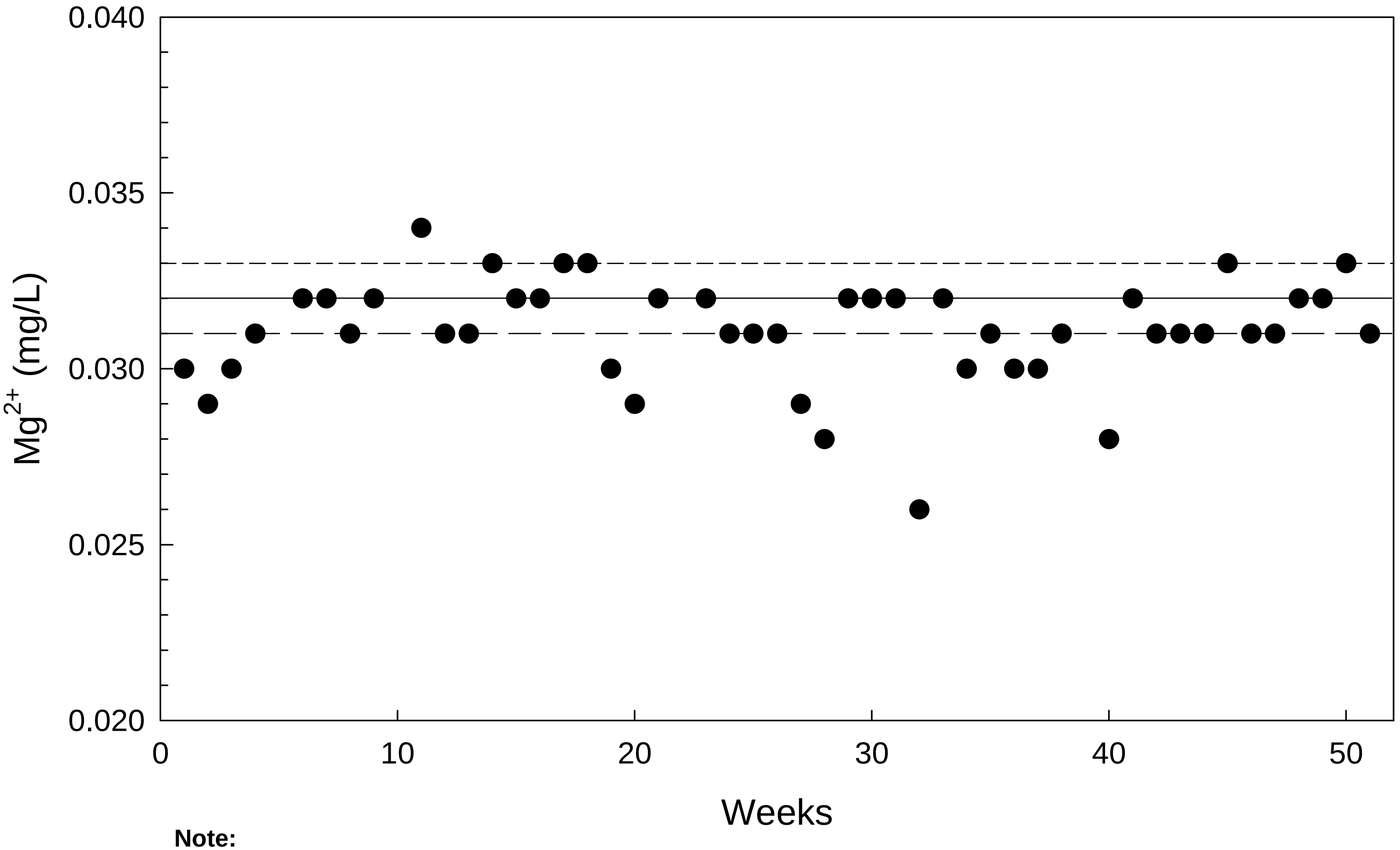
Note:
Solid line is mean NH_4^+ WMO/GAW 2000 sample #2 concentration: 0.223 mg/L; short dashed line is target NH_4^+ WMO/GAW 2000 sample #2 concentration: 0.222 mg/L; and long dashed line is mean NH_4^+ internal blind concentration: 0.197 mg/L.

Figure B-40. AIRMoN internal blind samples (ammonium), WMO/GAW 2000 sample #2, 2001.



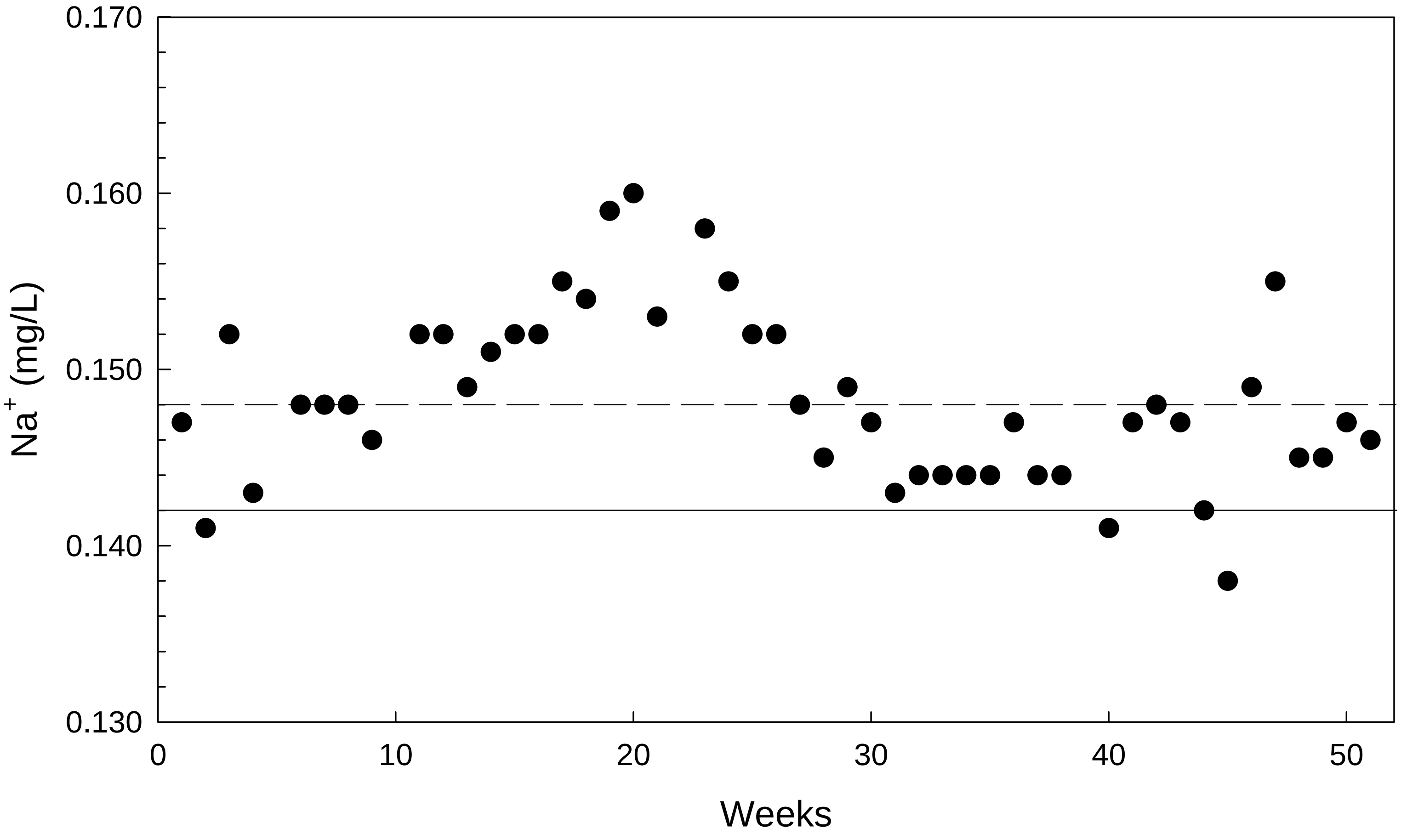
Note:
Solid line is mean and target Ca^{2+} WMO/GAW 2000 sample #2 concentration: 0.114 mg/L; and dashed line is mean Ca^{2+} internal blind concentration: 0.112 mg/L.

Figure B-41. AIRMoN internal blind samples (calcium), WMO/GAW 2000 sample #2, 2001.



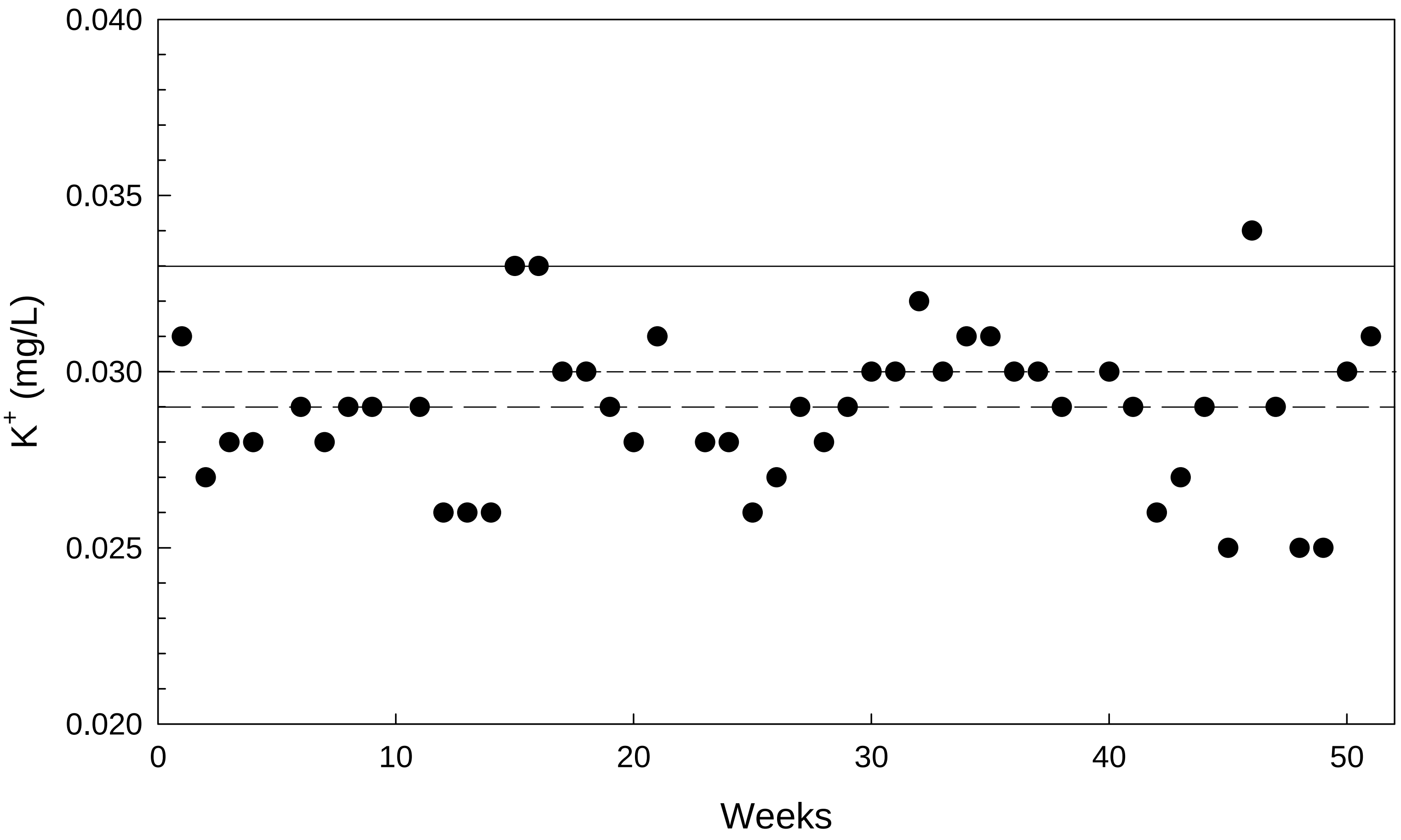
Note:
Solid line is mean Mg^{2+} WMO/GAW 2000 sample #2 concentration: 0.032 mg/L; short dashed line is target Mg^{2+} WMO/GAW 2000 sample #2 concentration: 0.033 mg/L; and long dashed line is mean Mg^{2+} internal blind concentration: 0.031 mg/L.

Figure B-42. AIRMoN internal blind samples (magnesium), WMO/GAW 2000 sample #2, 2001.



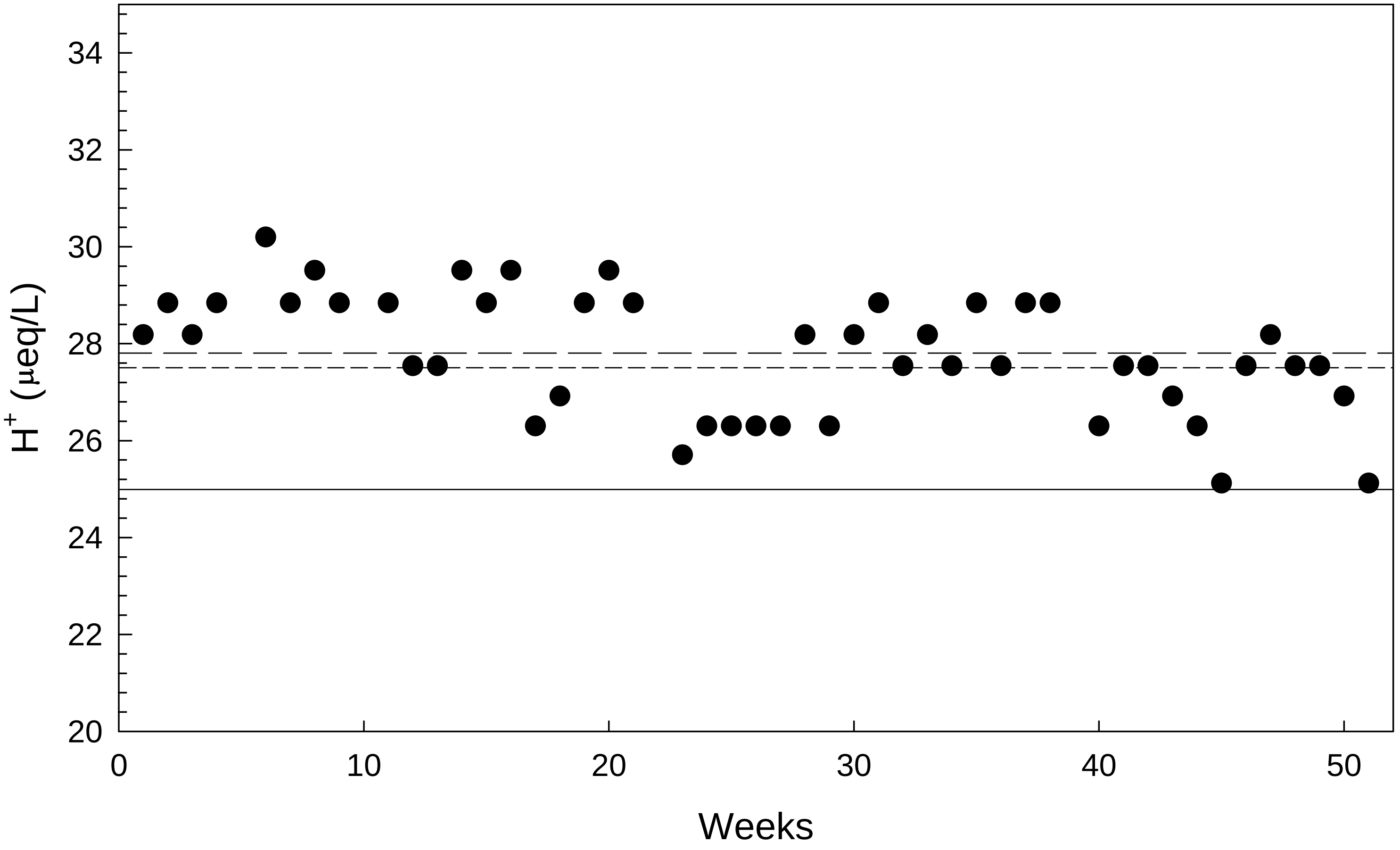
Note:
Solid line is mean Na$^+$ WMO/GAW 2000 sample #2 concentration: 0.142 mg/L; dashed line is mean Na$^+$ internal blind and target Na$^+$ WMO/GAW 2000 sample #2 concentration: 0.148 mg/L.

Figure B-43. AIRMoN internal blind samples (sodium), WMO/GAW 2000 sample #2, 2001.



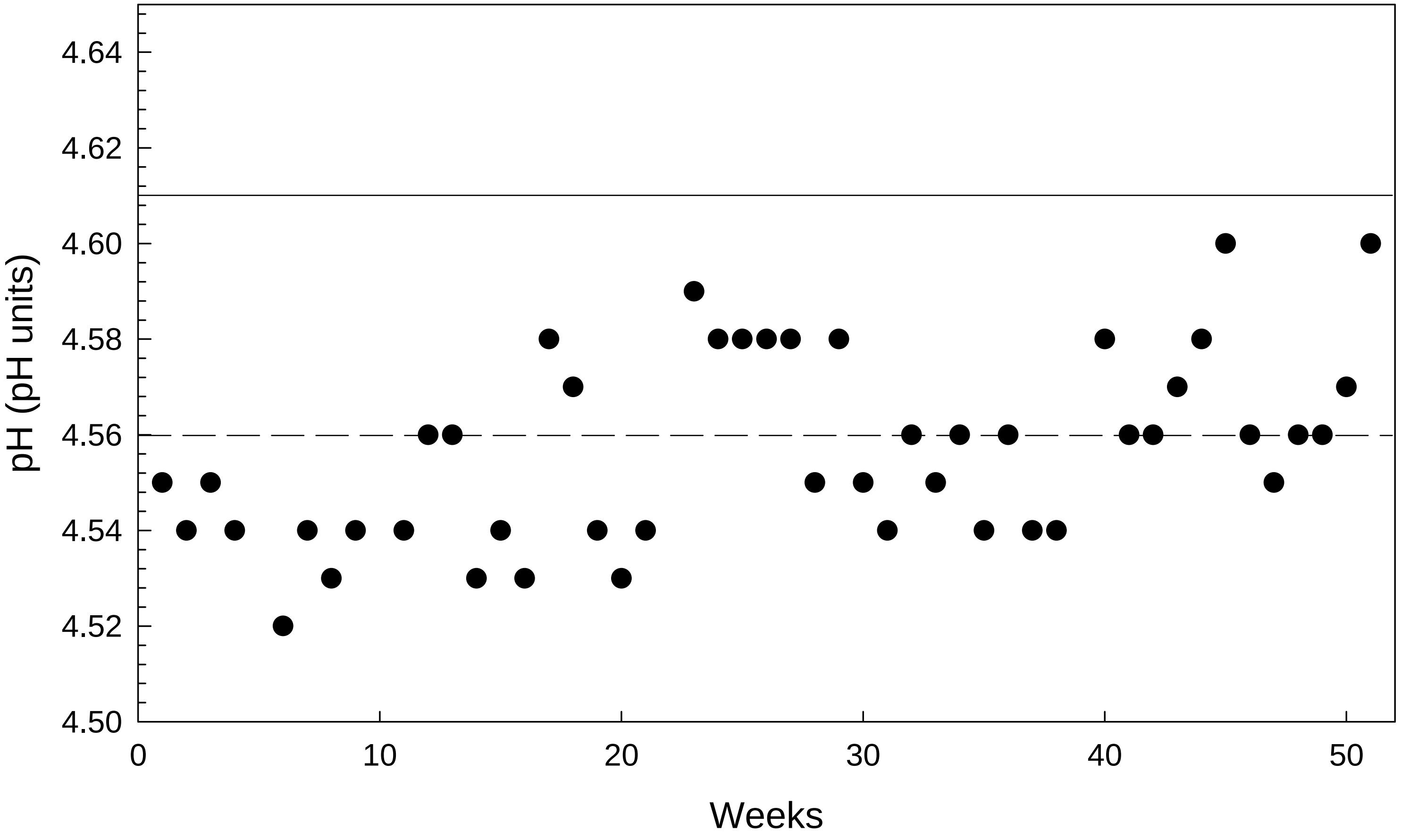
Note:
Solid line is mean K^+ WMO/GAW 2000 sample #2 concentration: 0.033 mg/L; short dashed line is target K^+ WMO/GAW 2000 sample #2 concentration: 0.030 mg/L; and long dashed line is mean K^+ internal blind concentration: 0.029 mg/L.

Figure B-44. AIRMoN internal blind samples (potassium), WMO/GAW 2000 sample #2, 2001.



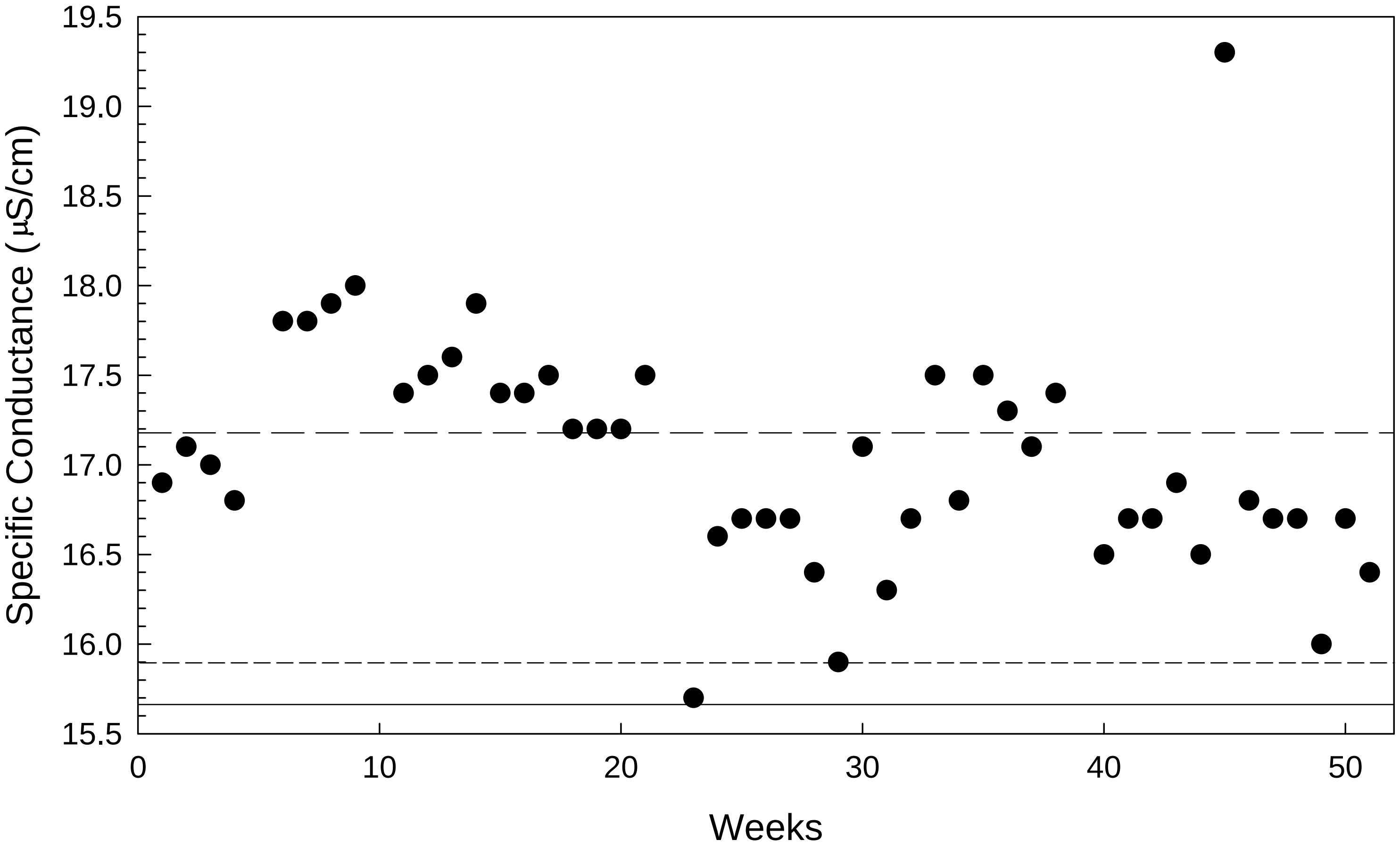
Note:
Solid line is mean H^+ WMO/GAW 2000 sample #2 concentration: 24.5 μeq/L; short dashed line is target H^+ WMO/GAW 2000 sample #2 concentration: 27.5 μeq/L; and long dashed line is mean H^+ internal blind concentration: 27.8 μeq/L.

Figure B-45. AIRMoN internal blind samples (hydrogen ion), WMO/GAW 2000 sample #2, 2001.



Note:
Solid line is mean pH for WMO/GAW 2000 sample #2: 4.61; dashed line is mean pH for internal blind samples and target pH for WMO/GAW 2000 sample #2 concentration: 4.56.

Figure B-46. AIRMoN internal blind samples (pH),
WMO/GAW 2000 sample #2, 2001.



Note:
Solid line is mean specific conductance for WMO/GAW 2000 sample #2: 15.2 µS/cm; short dashed line is target specific conductance for WMO/GAW 2000 sample #2: 15.5 µS/cm; and long dashed line is mean specific conductance for internal blinds: 17.1µS/cm.

Figure B-47. AIRMoN internal blind samples (specific conductance), WMO/GAW 2000 sample #2, 2001.

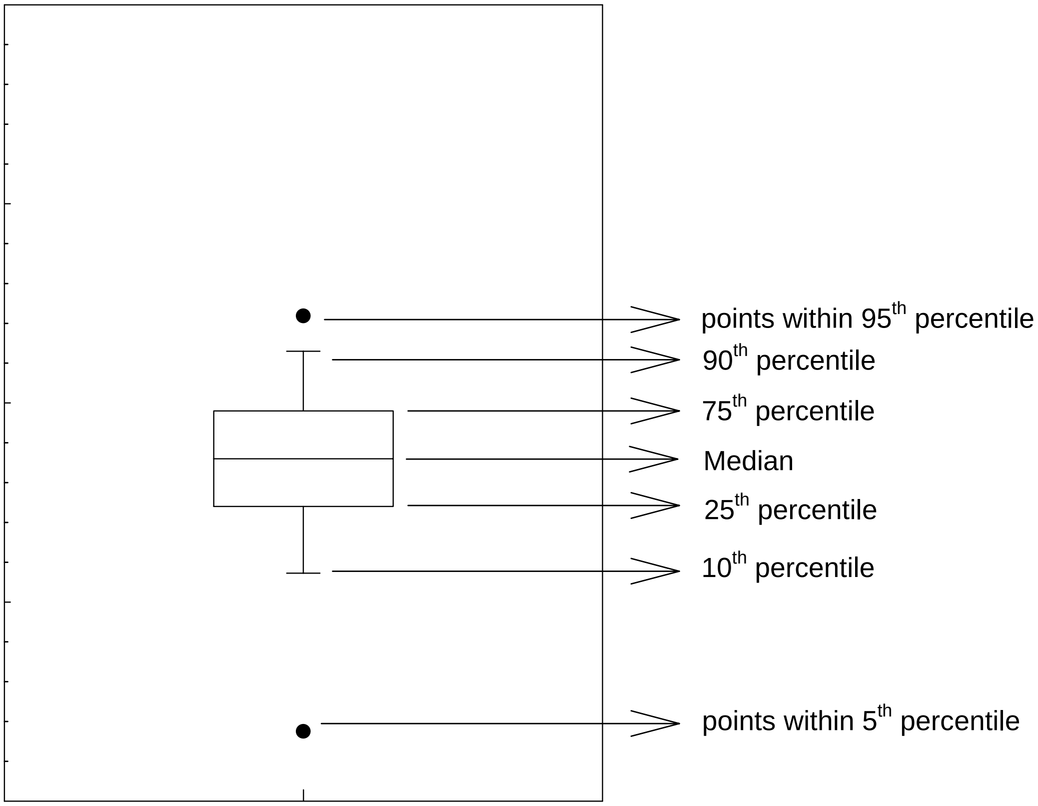


Figure B-48. An explanation of the box and whisker plots used in this report, 2001.

Table B-14. 5th, 50th, and 95th Percentile Concentration Values of Parameters Measured in Replicate Samples, NTN, 2001

	Percentile concentration values (mg/L)		
Parameter	*5th*	*50th*	*95th*
Calcium	0.018	0.097	0.555
Magnesium	0.004	0.023	0.171
Sodium	0.008	0.064	1.402
Potassium	0.003	0.018	0.096
Ammonium	<0.02	0.16	0.84
Sulfate	0.234	1.016	3.176
Nitrate	0.120	0.861	2.735
Chloride	0.027	0.126	2.427
pH (units)	4.24	4.90	6.08
Hydrogen ion (μeq/L)	0.83	12.7	57.4
Specific conductance (μS/cm)	4.4	11.8	37.0

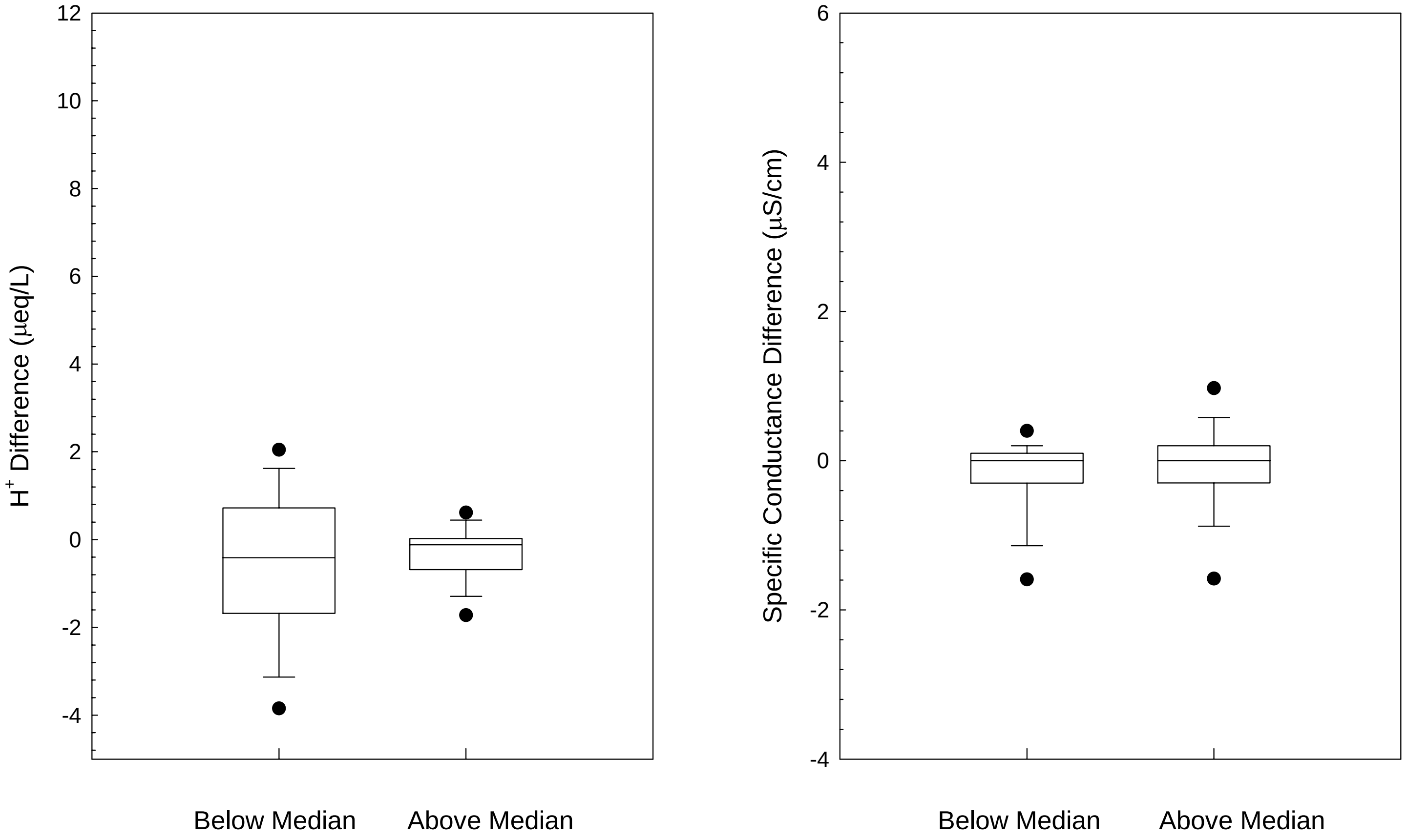


Figure B-49. Results of NTN replicate analysis, hydrogen ion (H^+) and specific conductance, 2001.

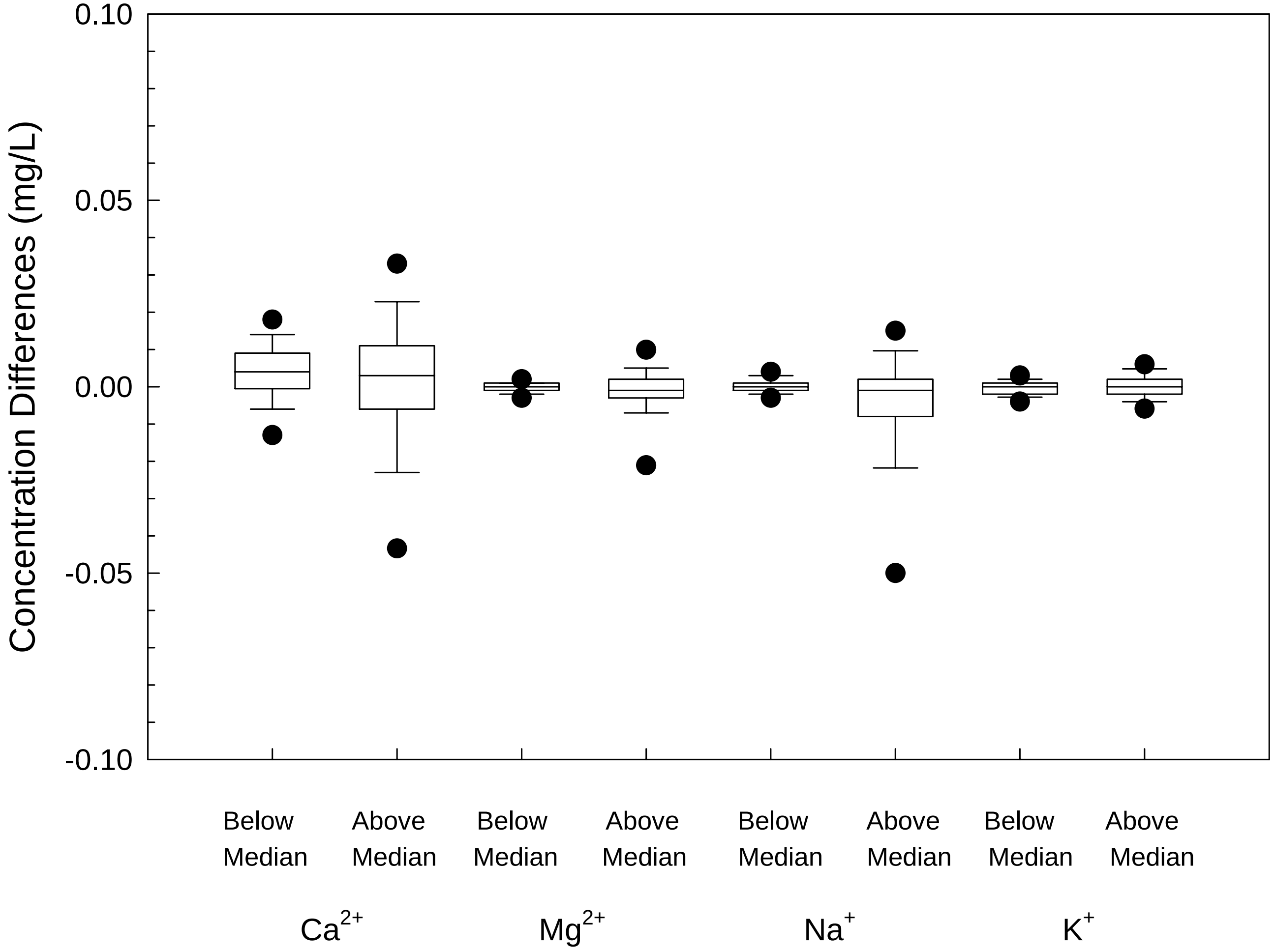


Figure B-50. Results of NTN replicate analysis, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}), 2001.

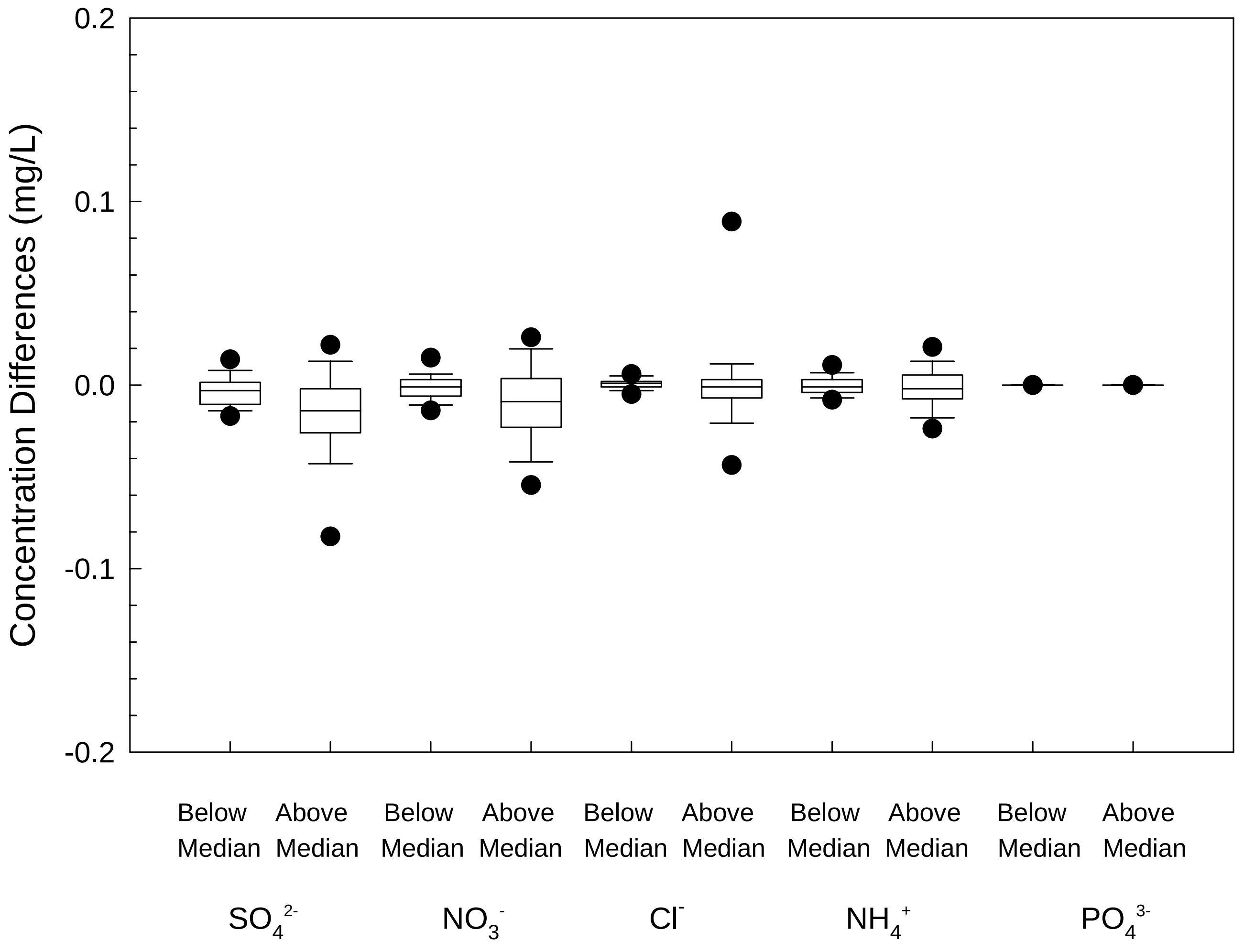


Figure B-51. Results of NTN replicate analysis, sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), and orthophosphate (PO_4^{3-}), 2001.

Table B-15. 5th, 50th, and 95th Percentile Concentration Values of Parameters Measured in Replicate Samples, AIRMoN, 2001

	Percentile concentration values (mg/L)		
Parameter	*5th*	*50th*	*95th*
Calcium	0.008	0.081	0.430
Magnesium	0.002	0.019	0.240
Sodium	0.005	0.045	1.725
Potassium	0.003	0.017	0.110
Ammonium	0.04	0.28	1.09
Orthophosphate	0.000	0.010	0.051
Sulfate	0.339	2.057	4.217
Nitrate	0.320	1.642	6.544
Chloride	0.020	0.171	3.249
pH (units)	4.04	4.28	4.93
Hydrogen ion (μeq/L)	11.75	53.09	91.20
Specific conductance (μS/cm)	8.0	31.6	64.3

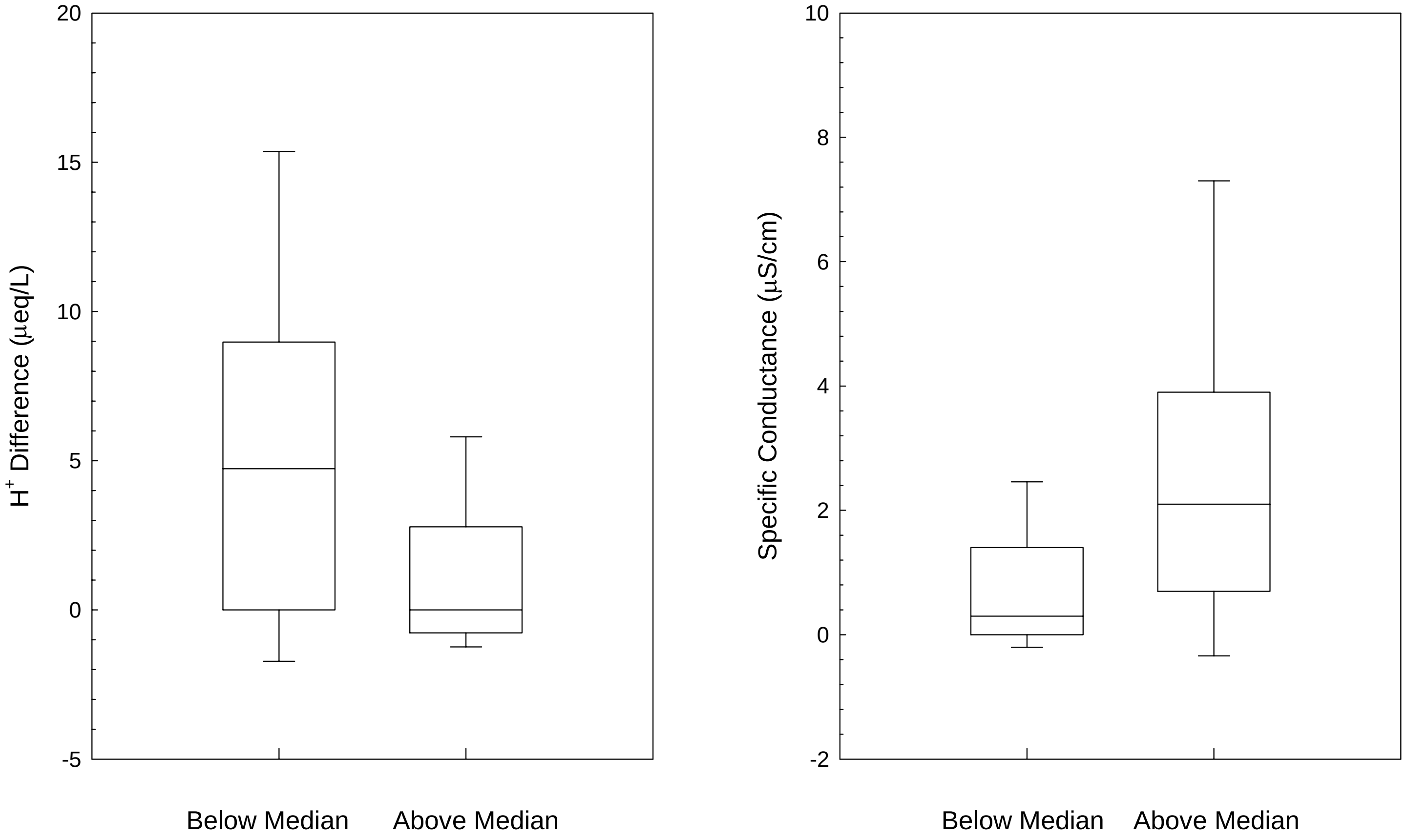


Figure B-52. Results of AIRMoN replicate analysis, hydrogen ion (H^+) and specific conductance, 2001.

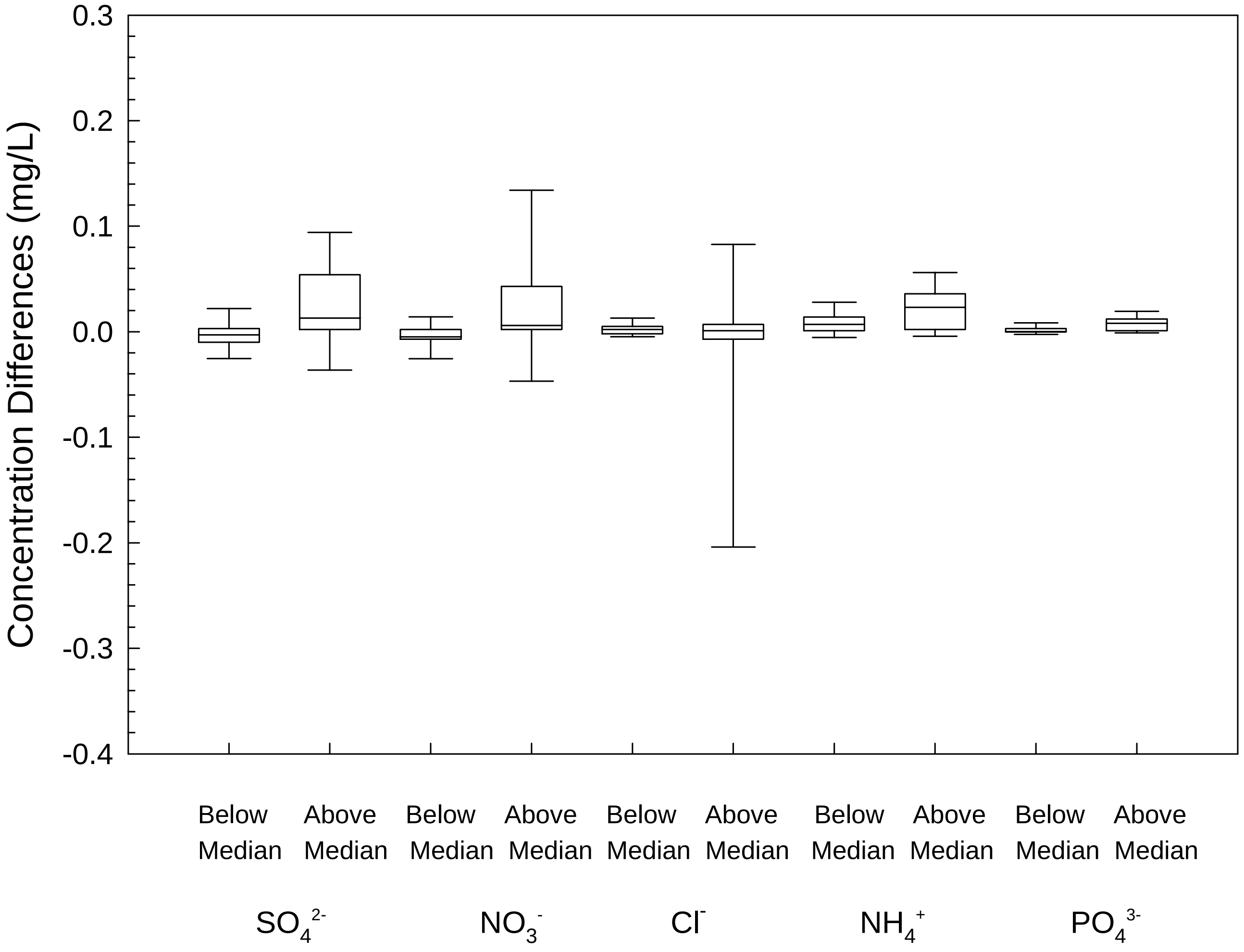


Figure B-53. Results of AIRMoN replicate analysis, sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), and orthophosphate (PO_4^{3-}), 2001.

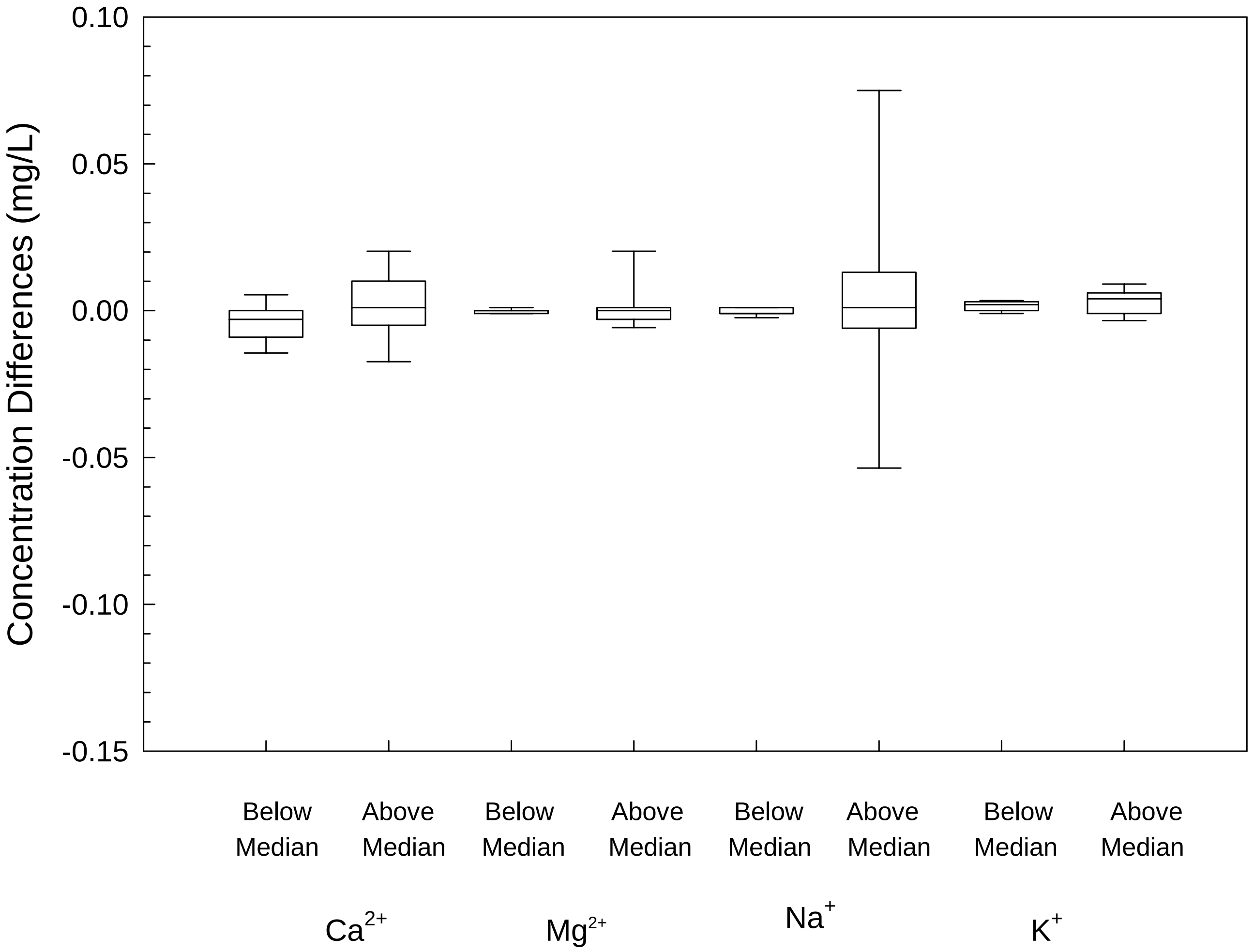


Figure B-54. Results of AIRMoN replicate analysis, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}), 2001.

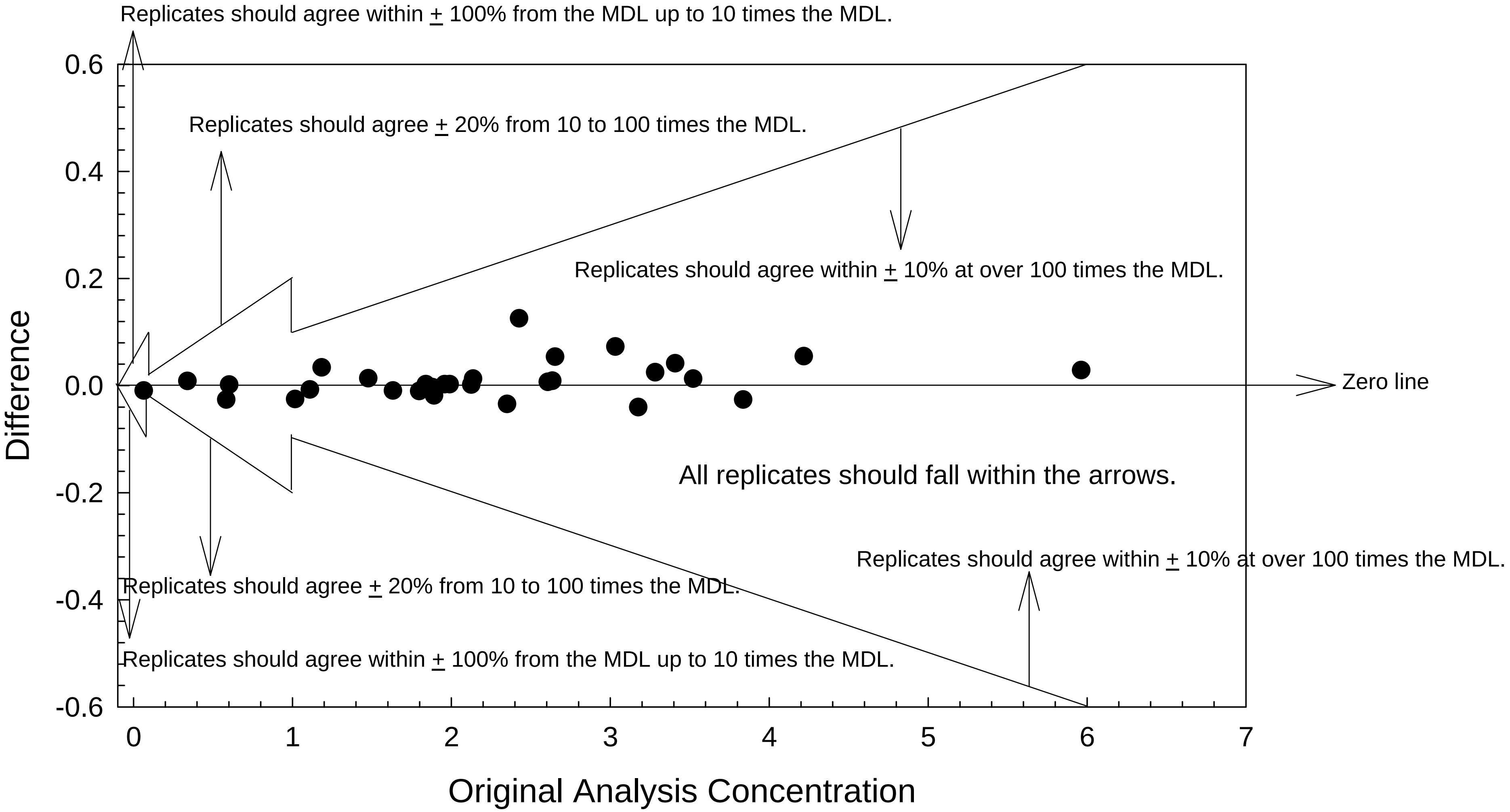


Figure B-55. An explanation of percentage graphs used in this report, 2001.

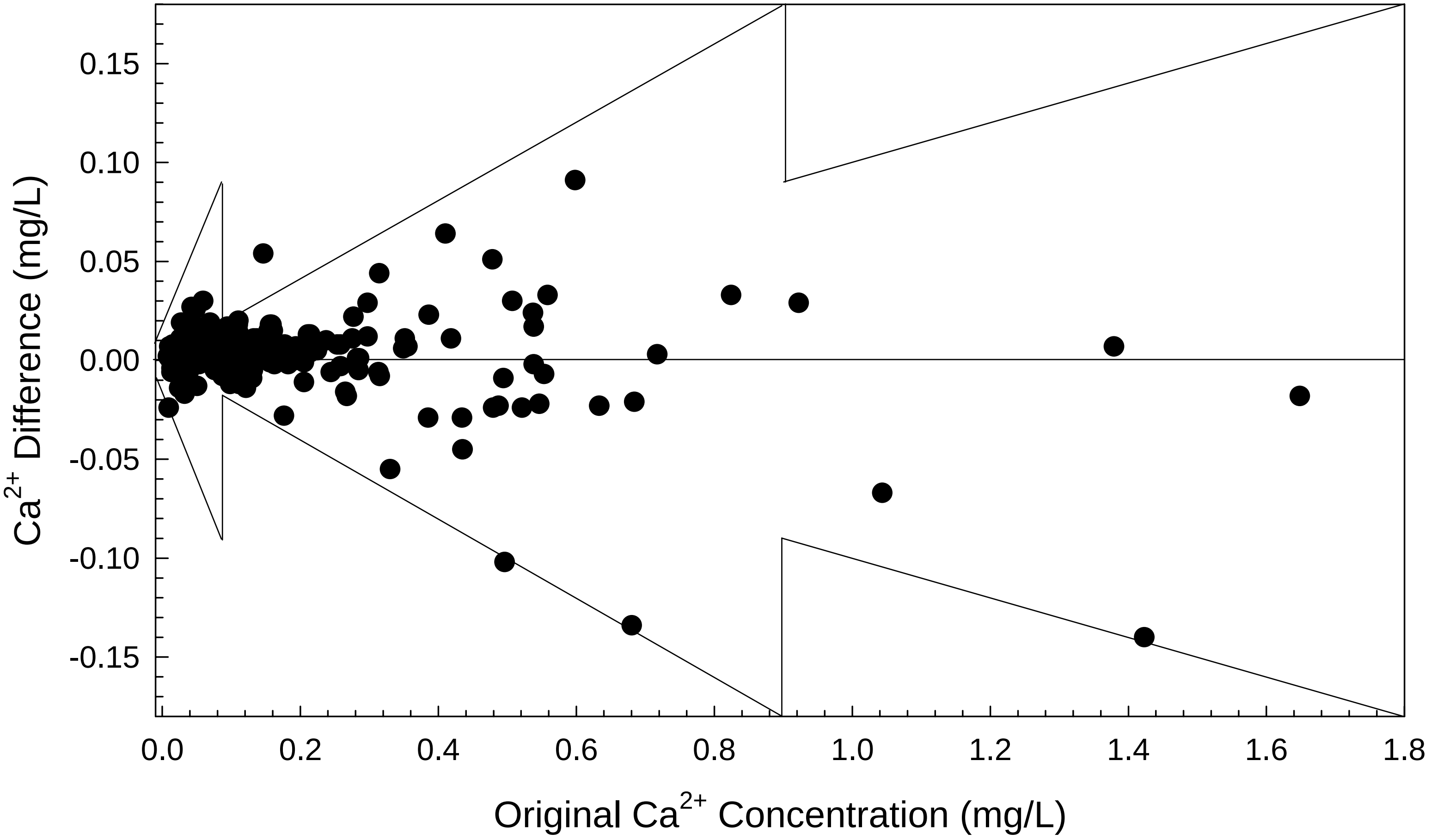


Figure B-56. NTN replicate sample differences (original - replicate) for Ca^{2+}, 2001.

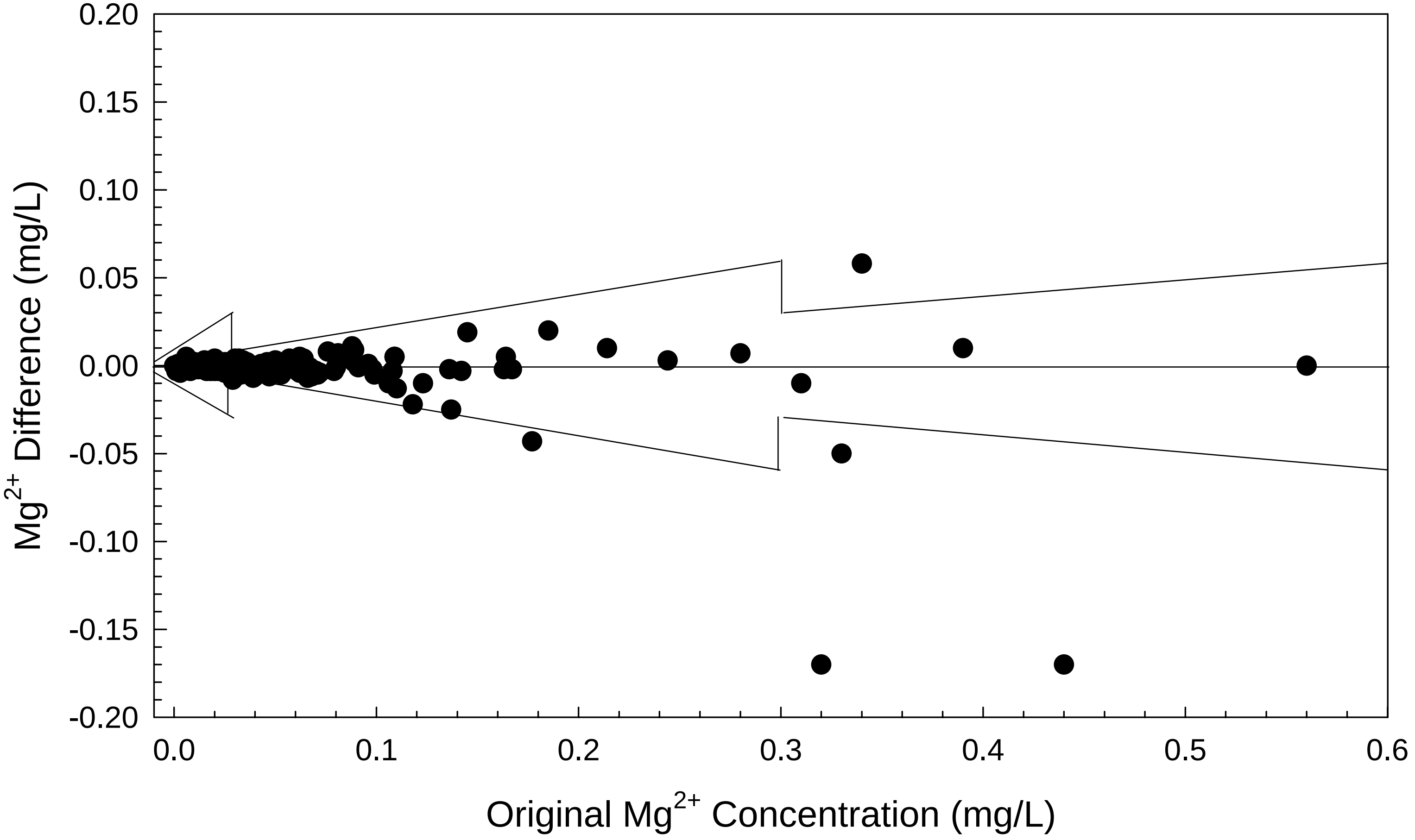


Figure B-57. NTN replicate sample differences (original - replicate) for Mg^{2+}, 2001.

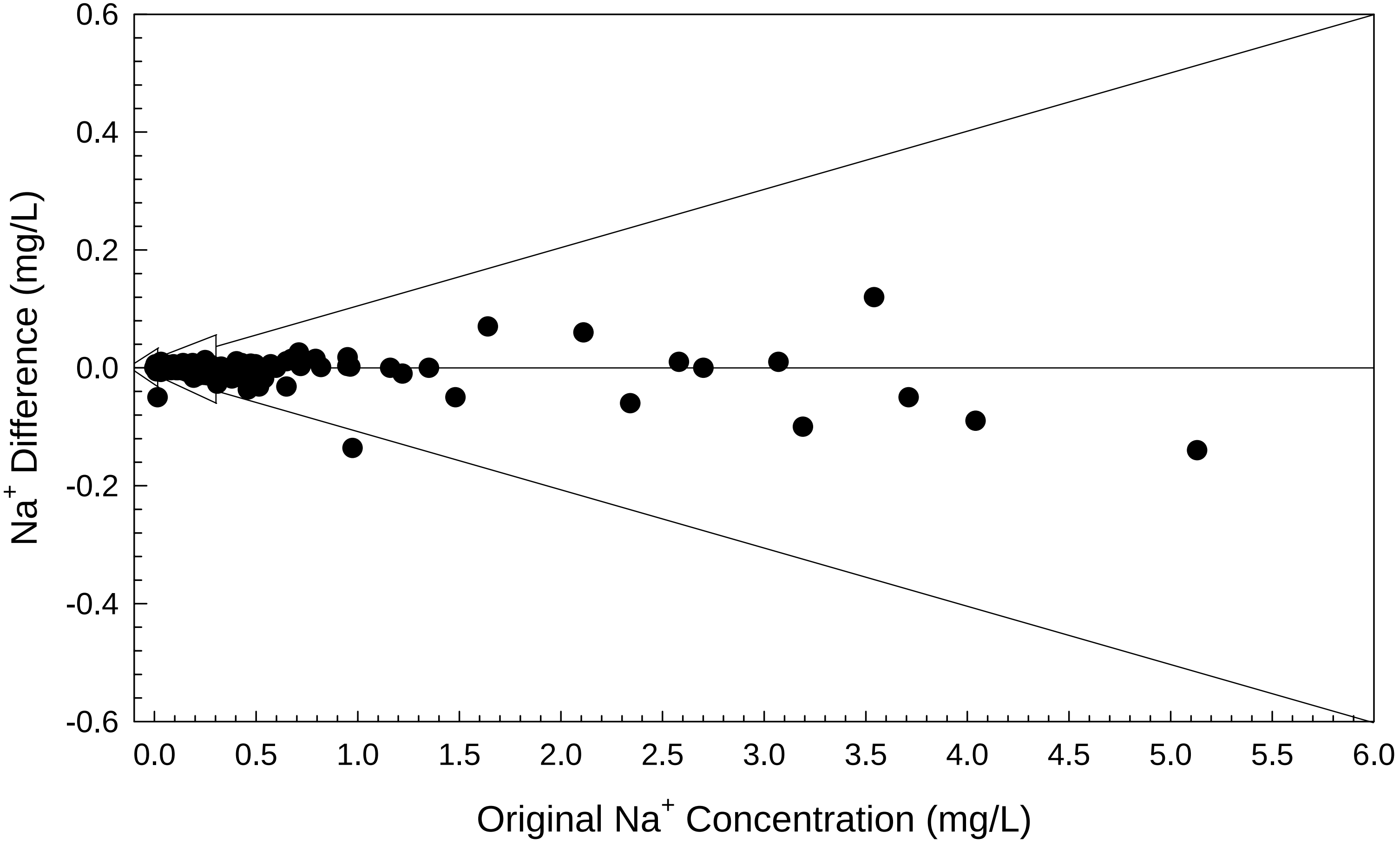


Figure B-58. NTN replicate sample differences (original - replicate) for Na$^+$, 2001.

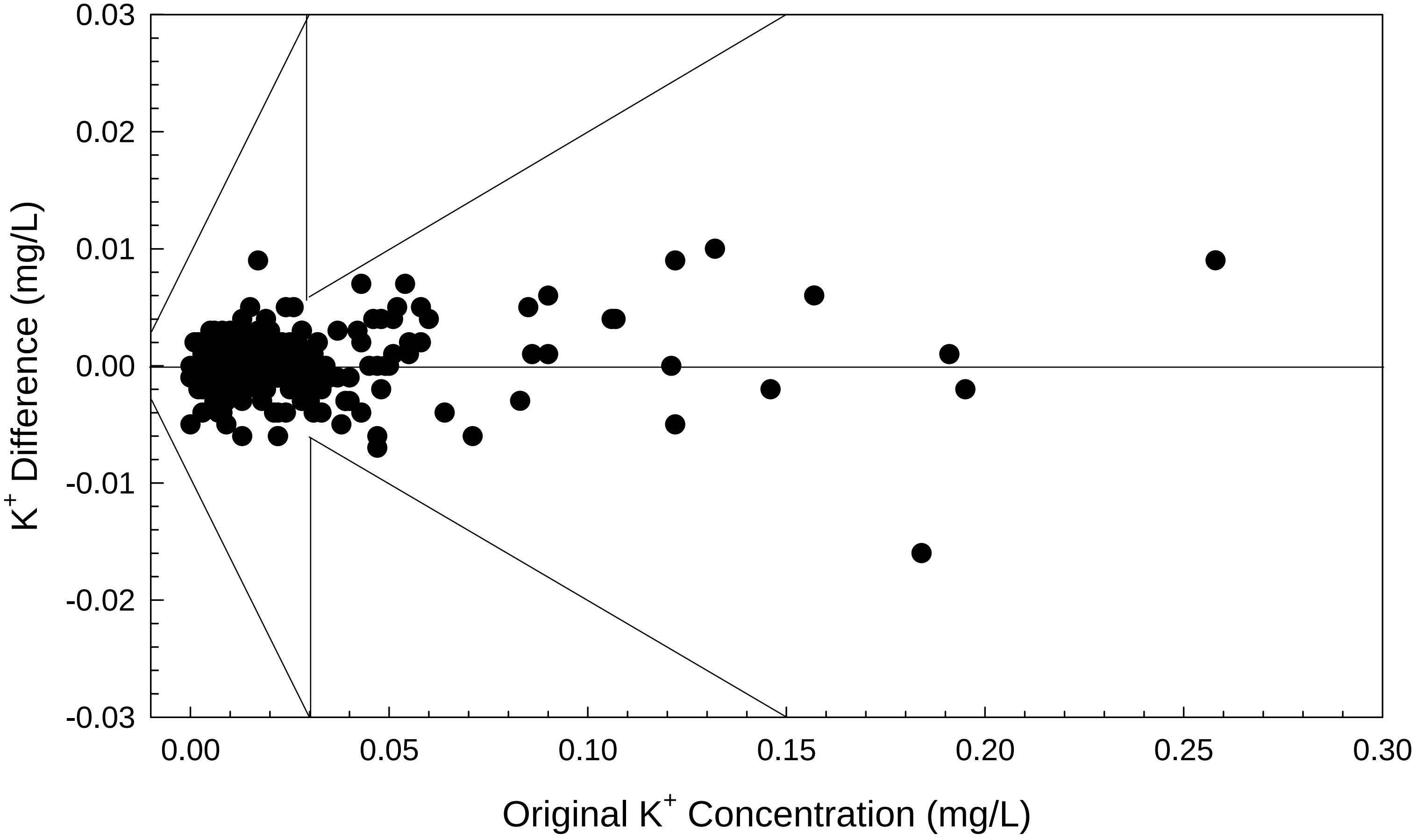


Figure B-59. NTN replicate sample differences (original - replicate) for K^+, 2001.

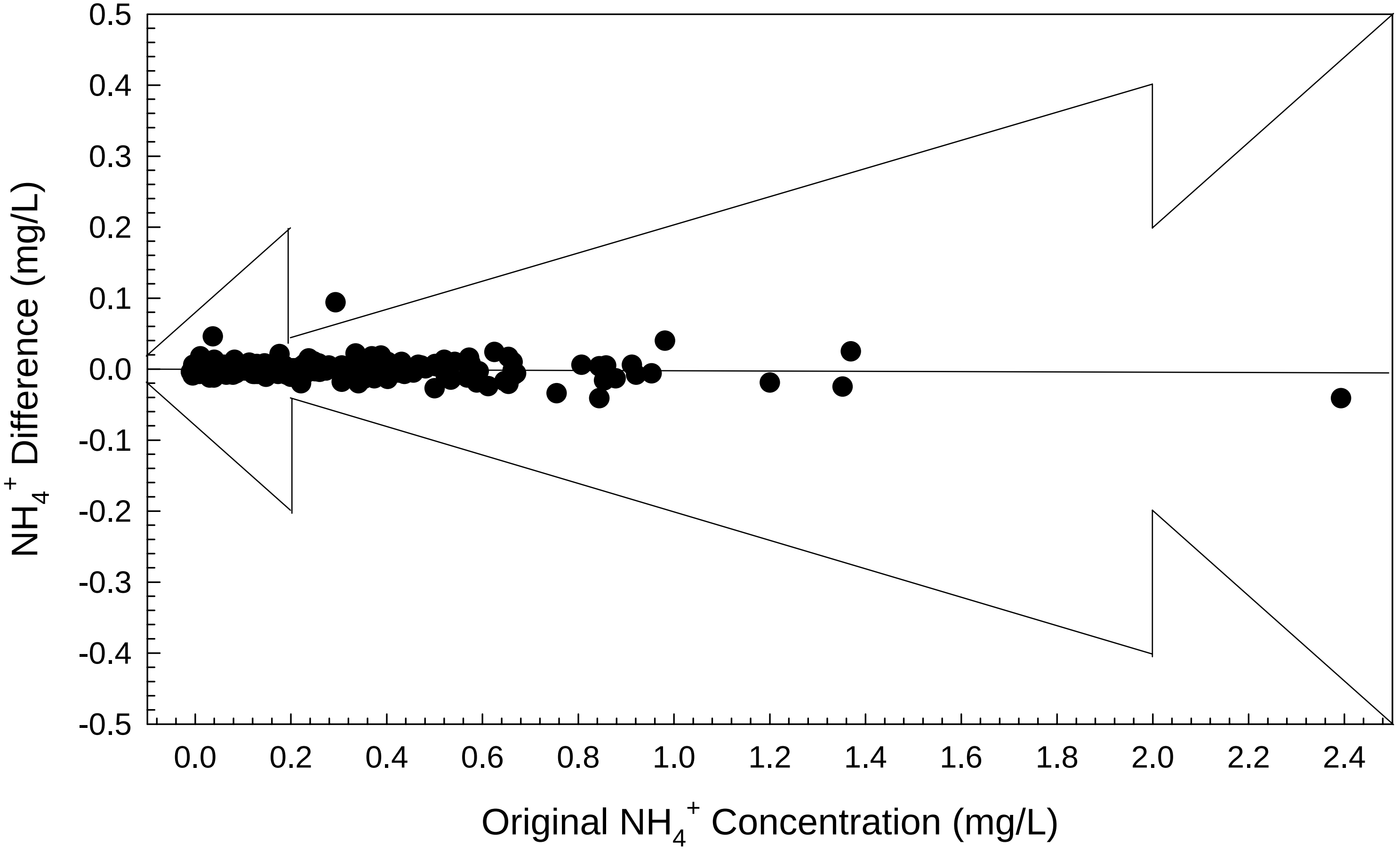


Figure B-60. NTN replicate sample differences (original - replicate) for NH$_4^+$, 2001.

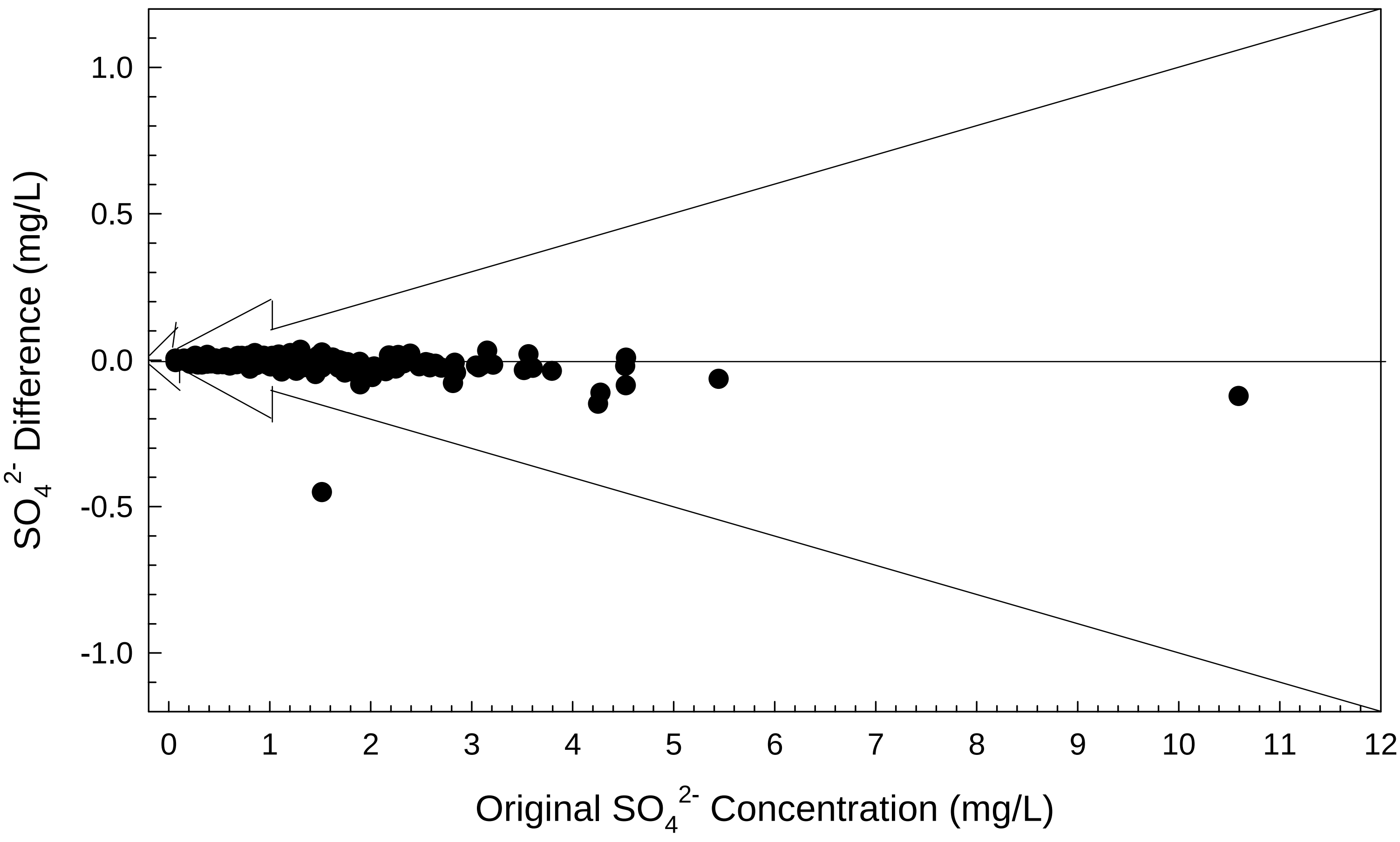


Figure B-61. NTN replicate sample differences (orginal-replicate) for SO_4^{2-}, 2001.

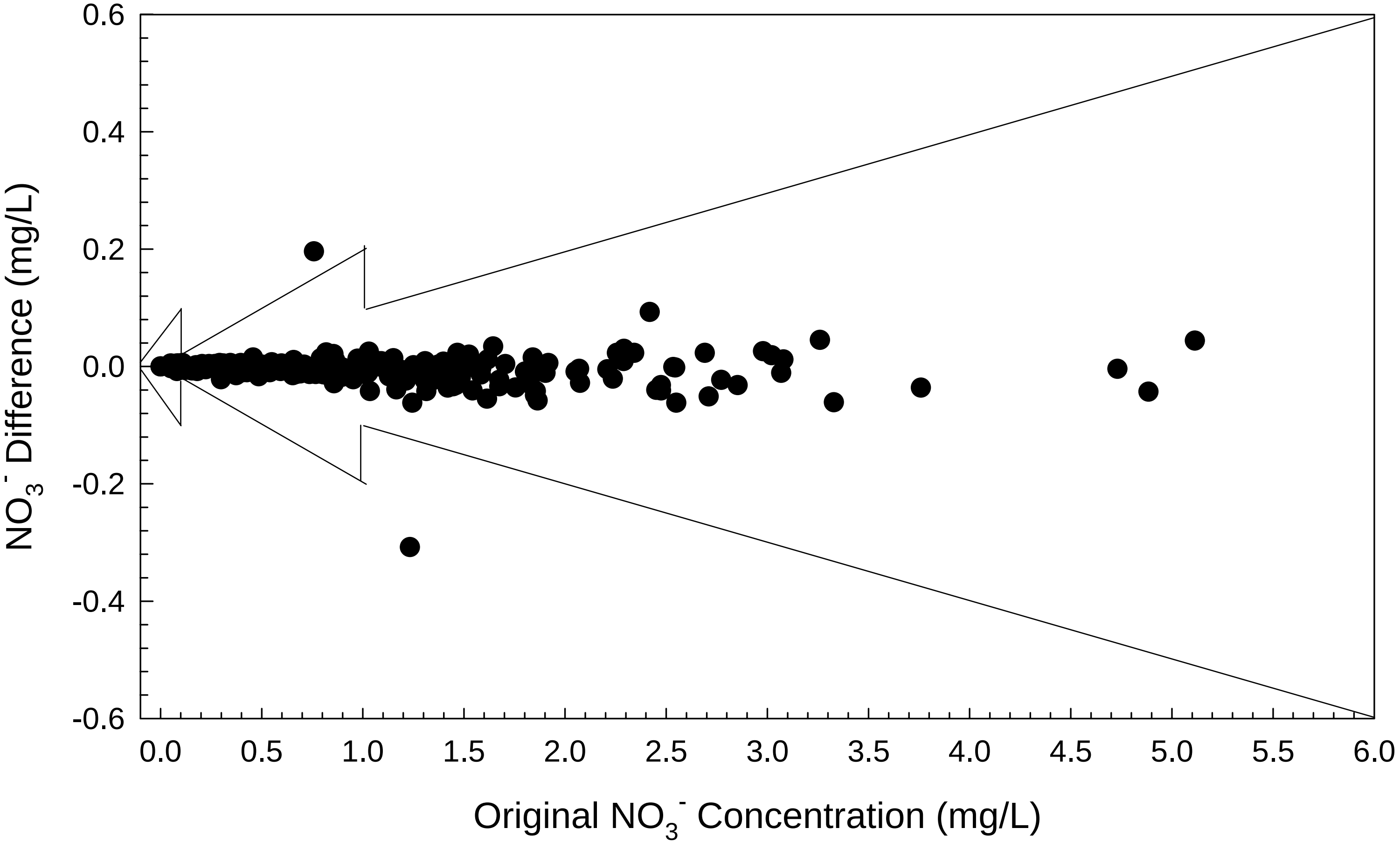


Figure B-62. NTN replicate sample differences (original - replicate) for NO_3^-, 2001.

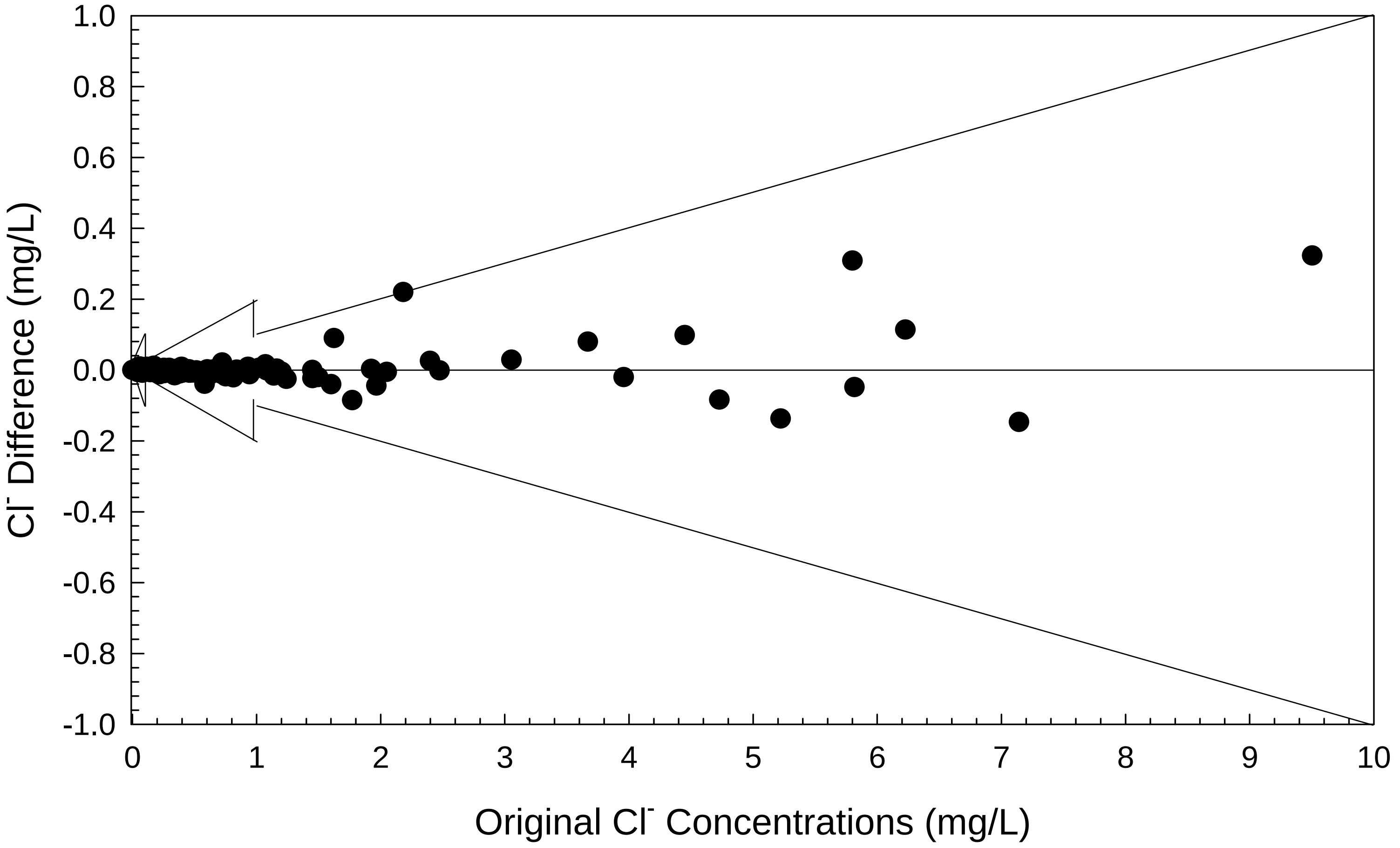


Figure B-63. NTN replicate sample differences (original - replicate) for Cl^-, 2001.

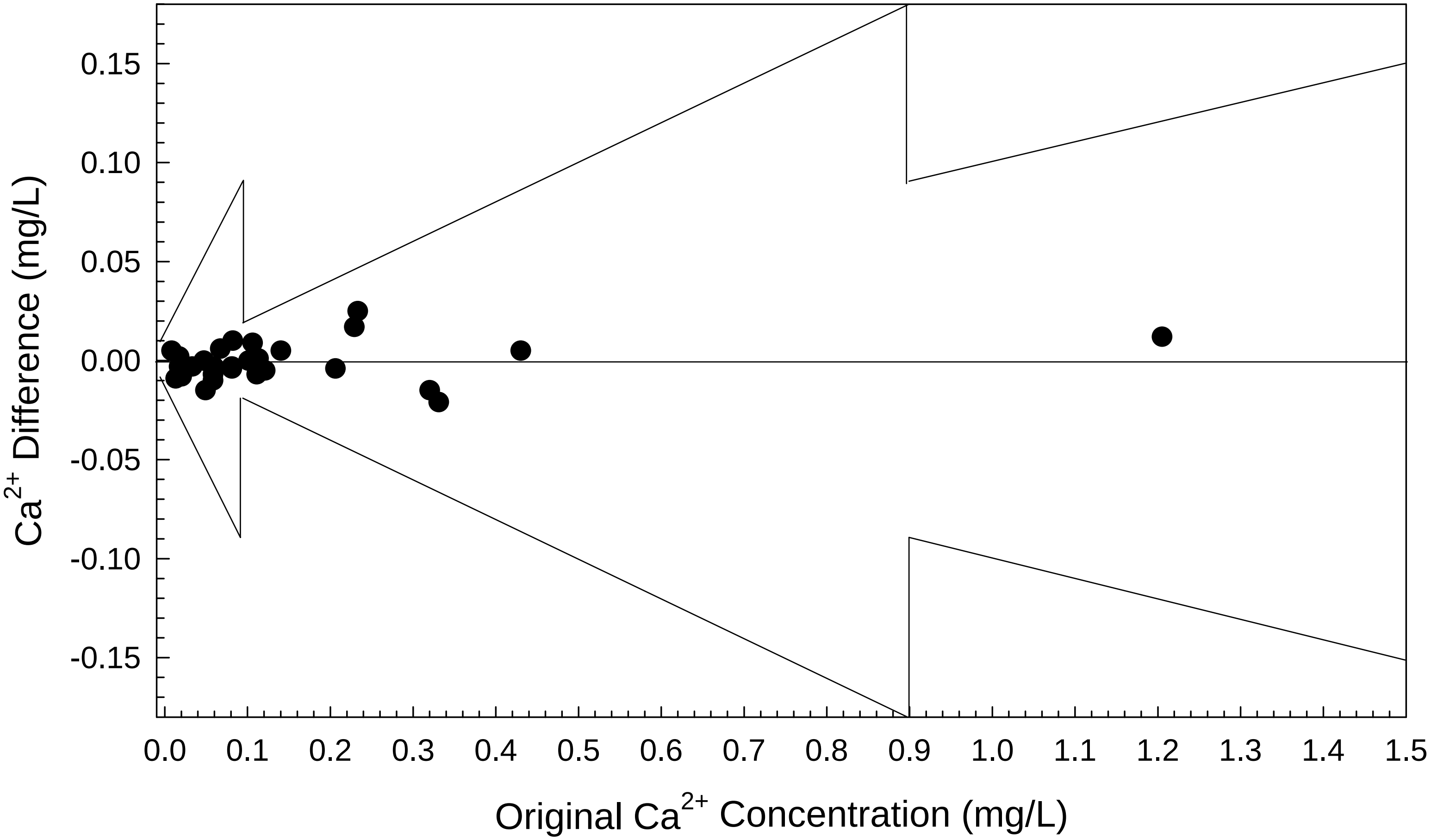


Figure B-64. AIRMoN replicate sample differences (original-replicate) for Ca^{2+}, 2001.

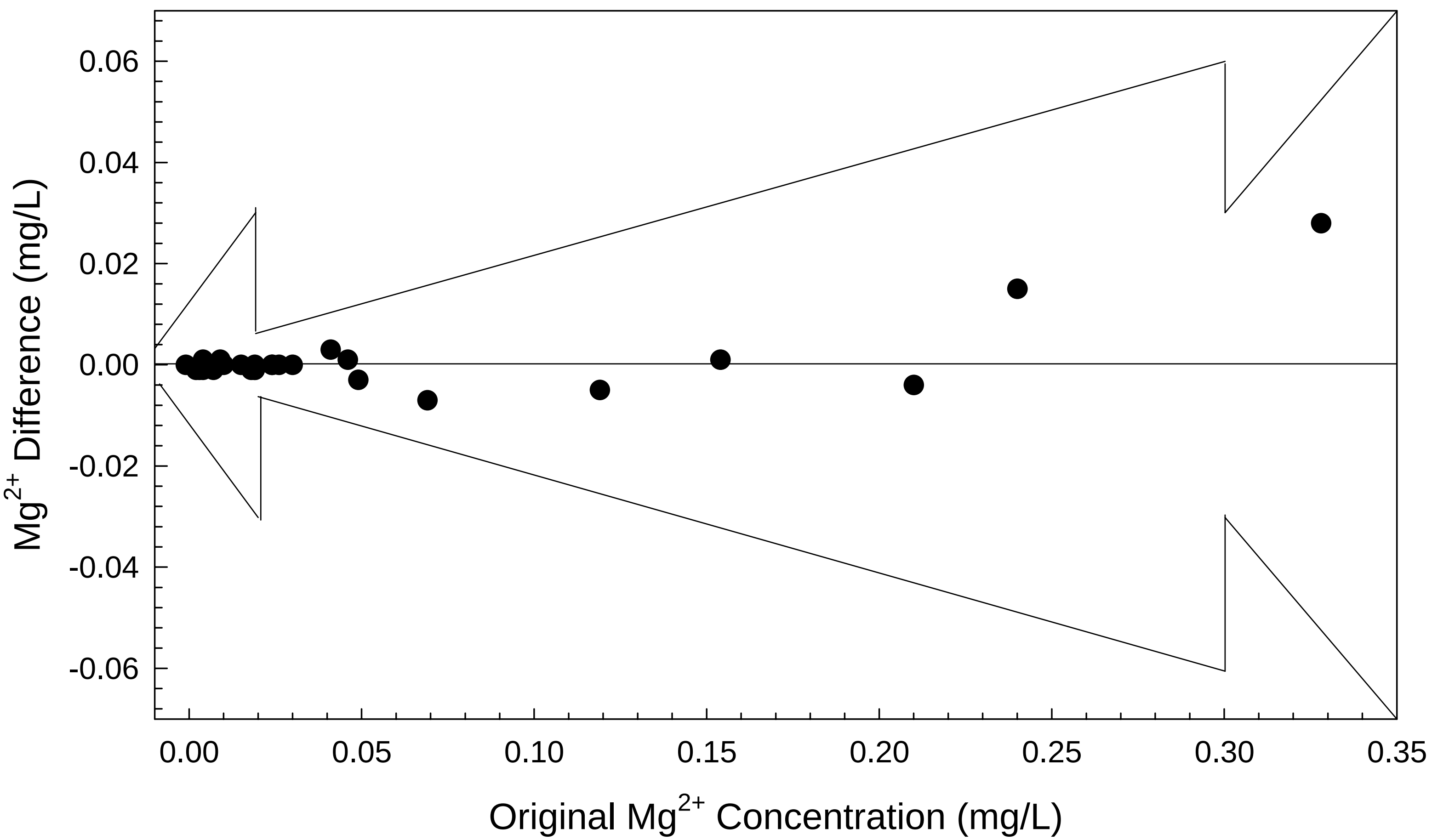


Figure B-65. AIRMoN replicate sample differences (original - replicate) for Mg^{2+}, 2001.

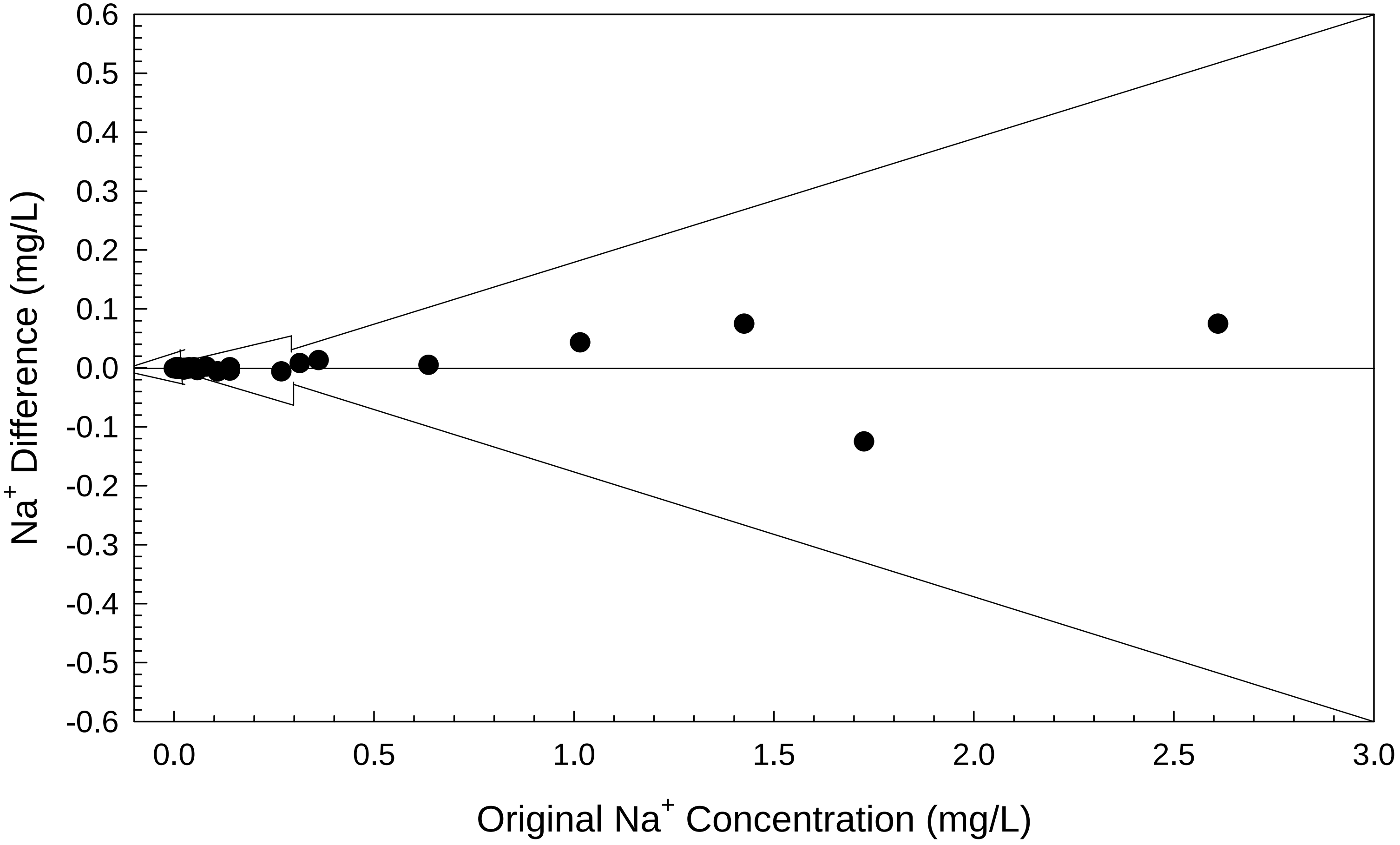


Figure B-66. AIRMoN replicate sample differences (original-replicate) for Na$^+$, 2001.

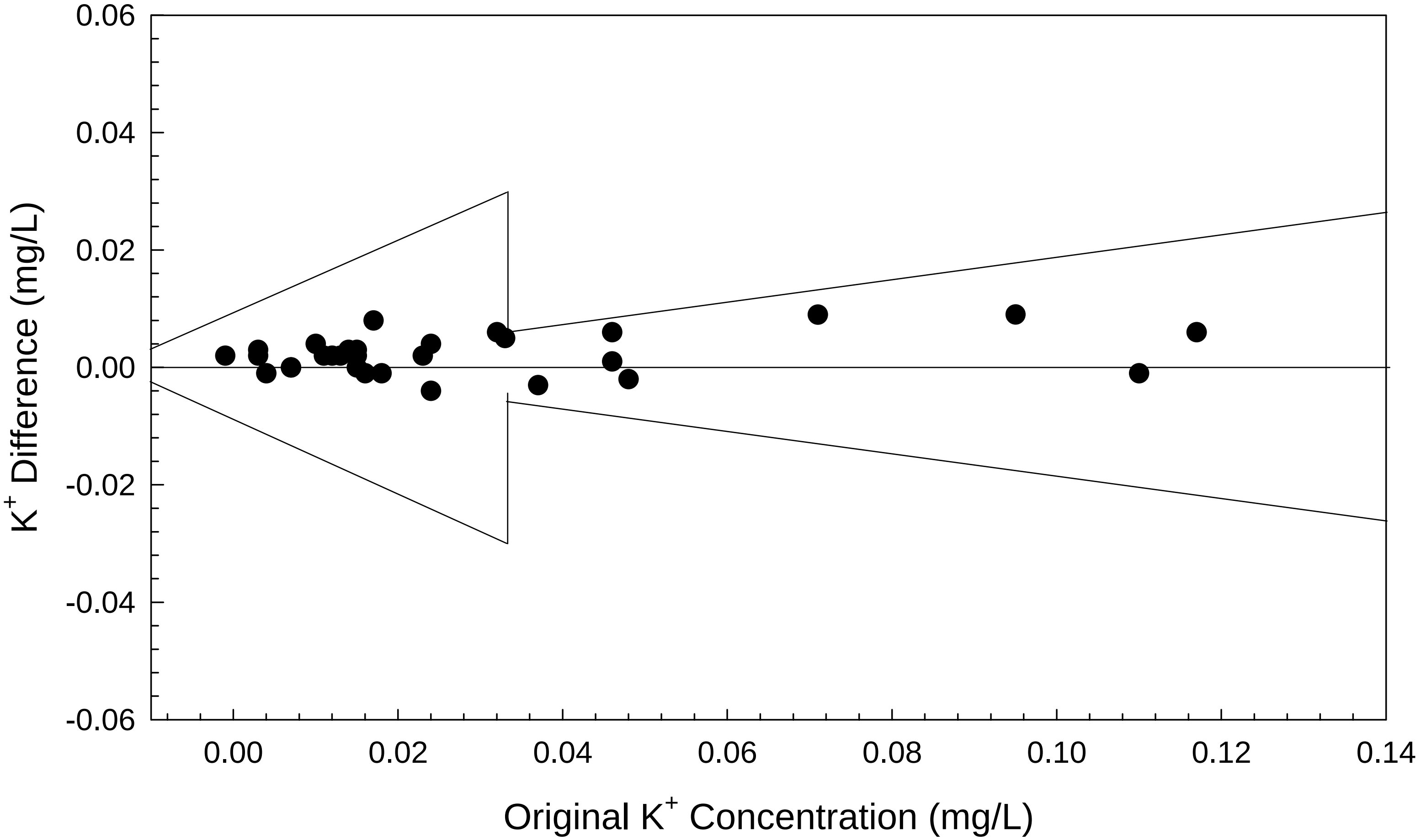


Figure B-67. AIRMoN replicate sample differences (original - replicate) for K$^+$, 2001.

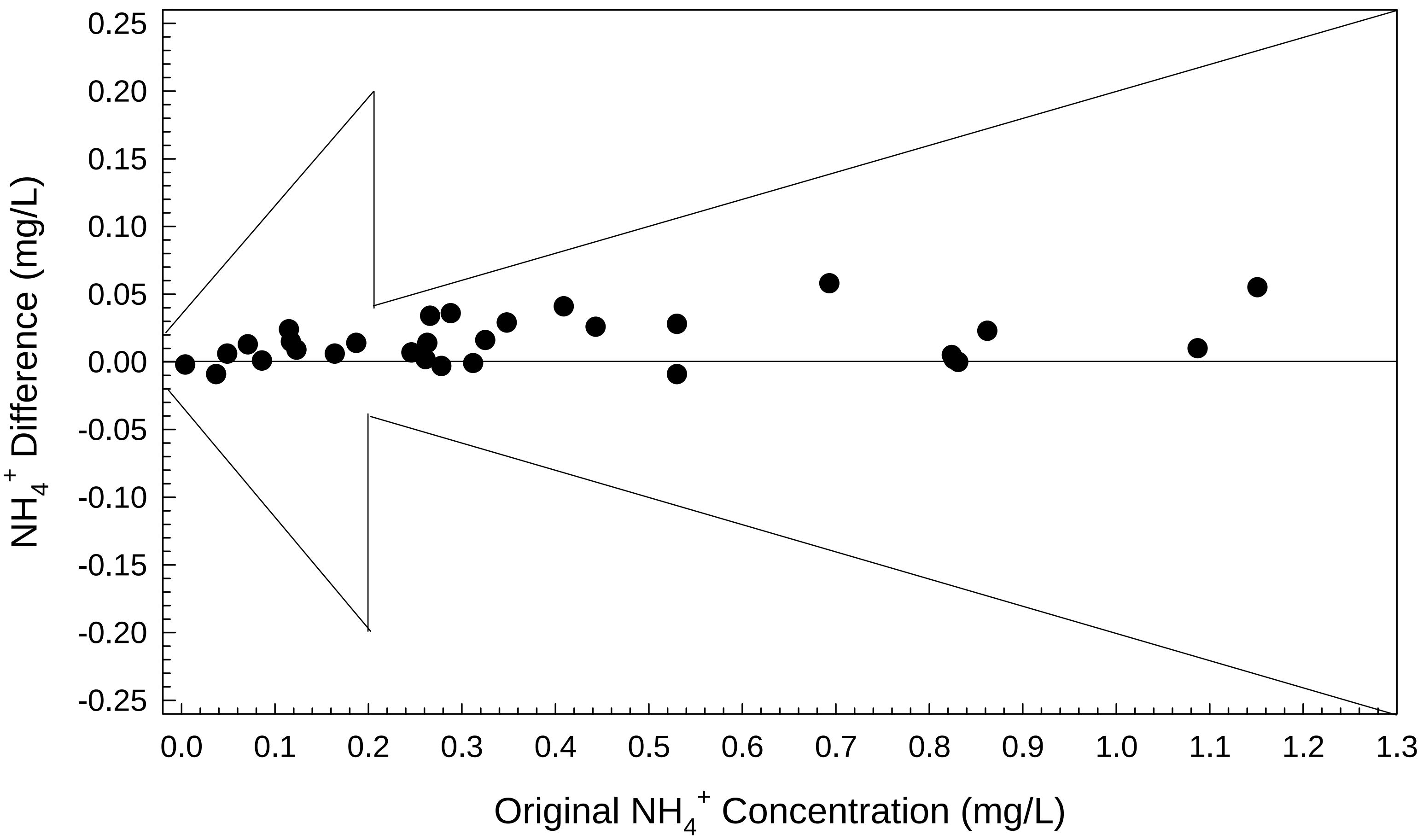


Figure B-68. AIRMoN replicate sample differences (original - replicate) for NH_4^+, 2001.

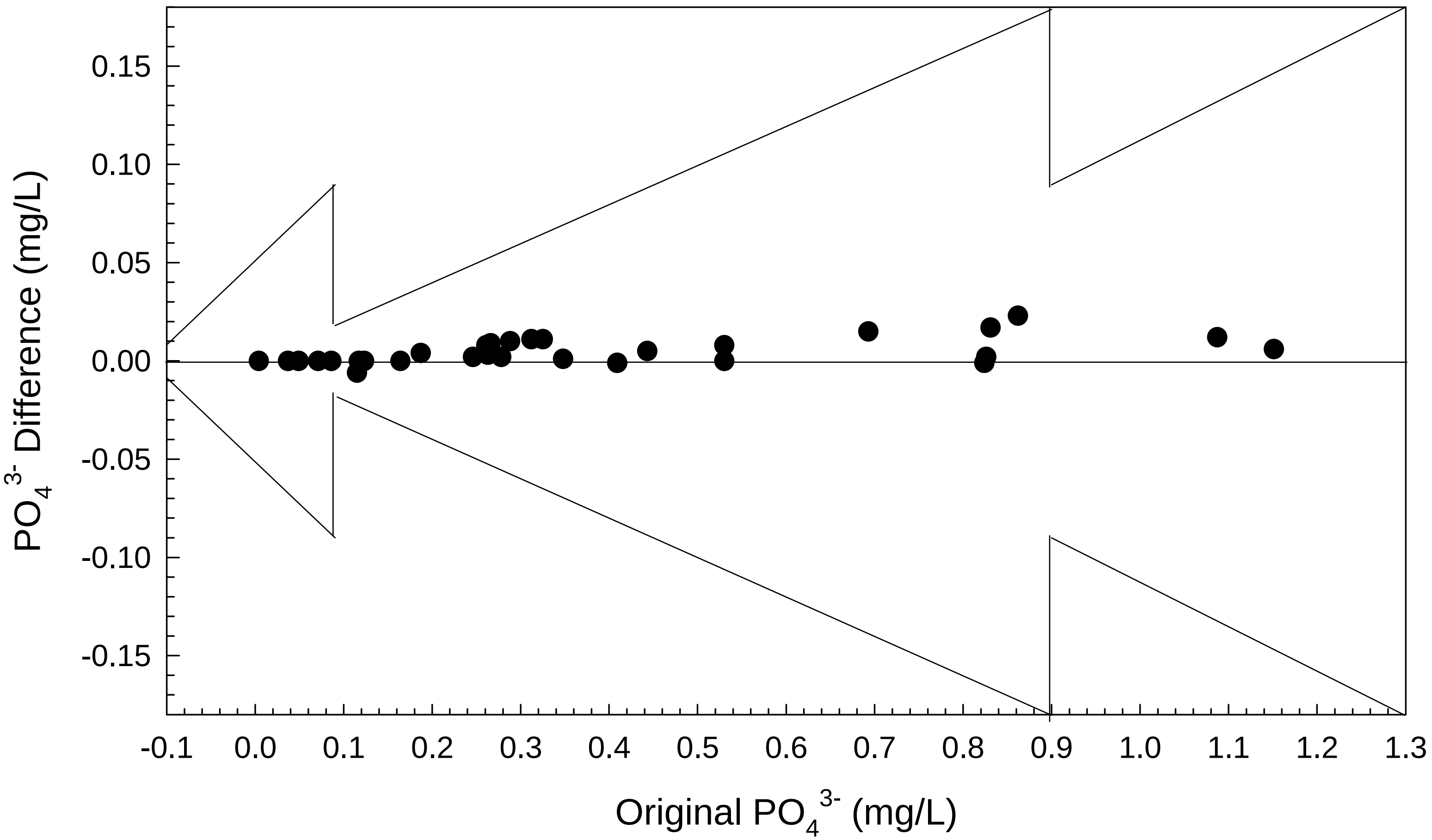


Figure B-69. AIRMoN replicate sample differences (original - replicate) for PO_4^{3-}, 2001.

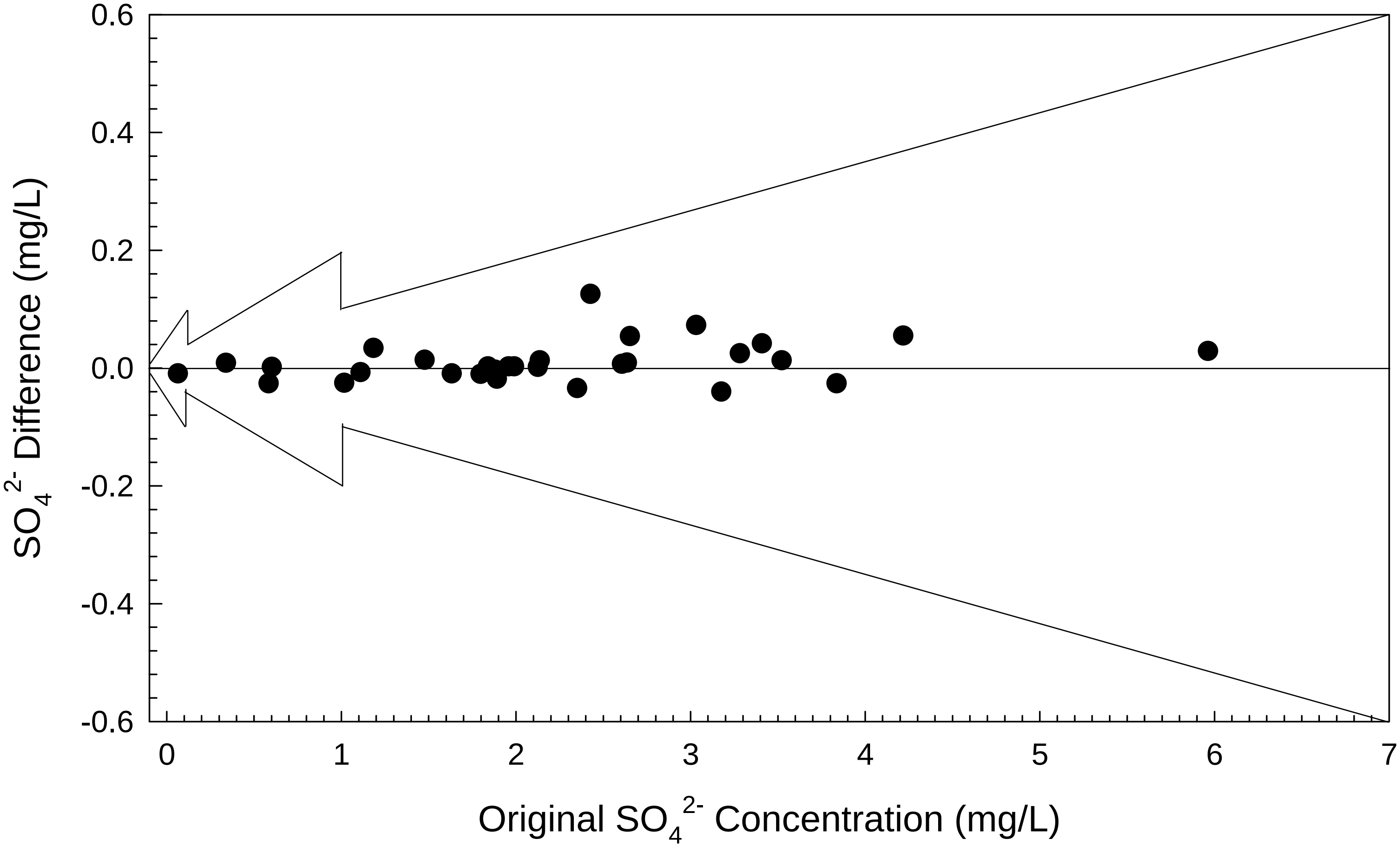


Figure B-70. AIRMoN replicate sample differences (original - replicate) for SO_4^{2-}, 2001.

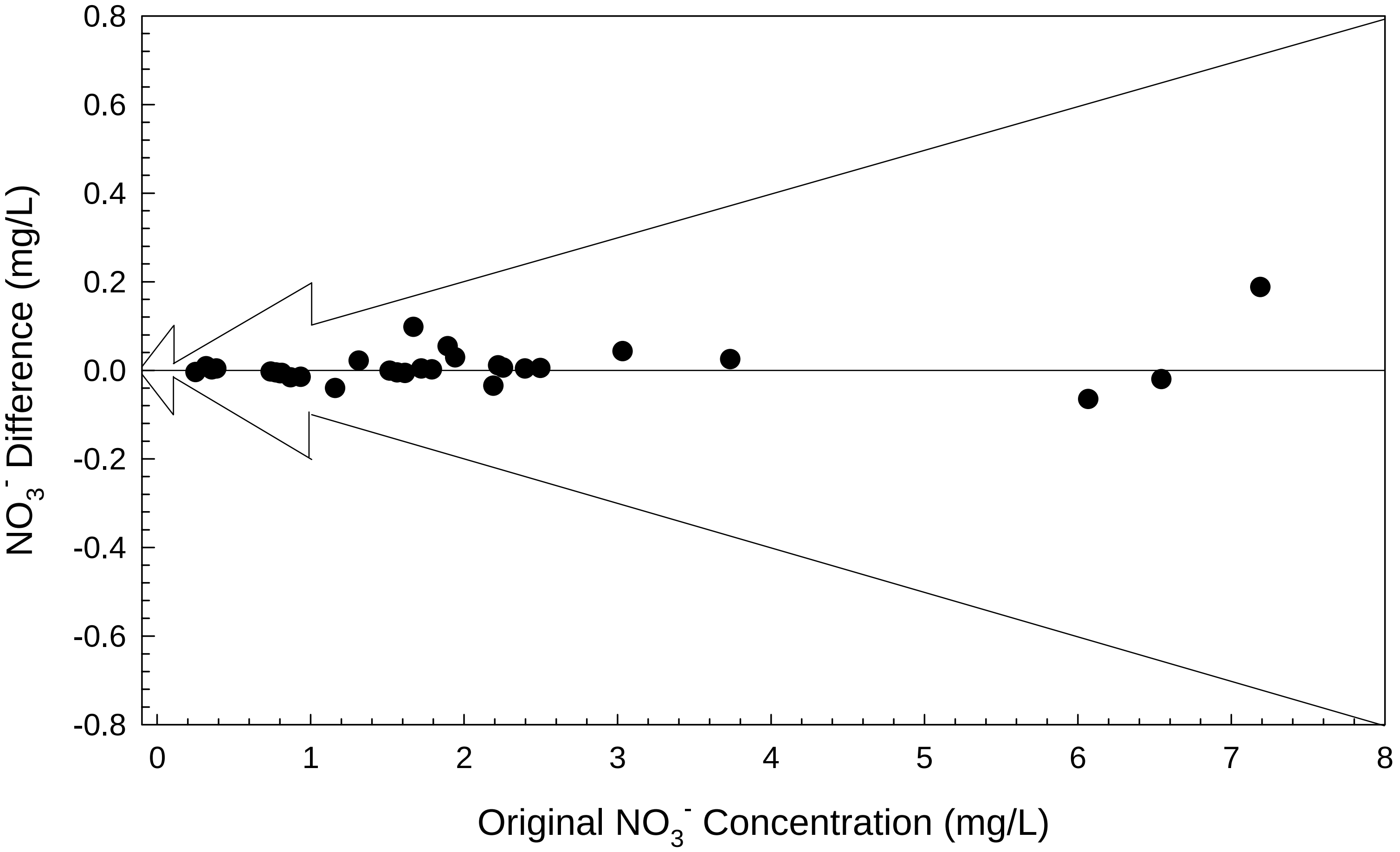


Figure B-71. AIRMoN replicate sample differences (original - replicate) for NO_3^-, 2001.

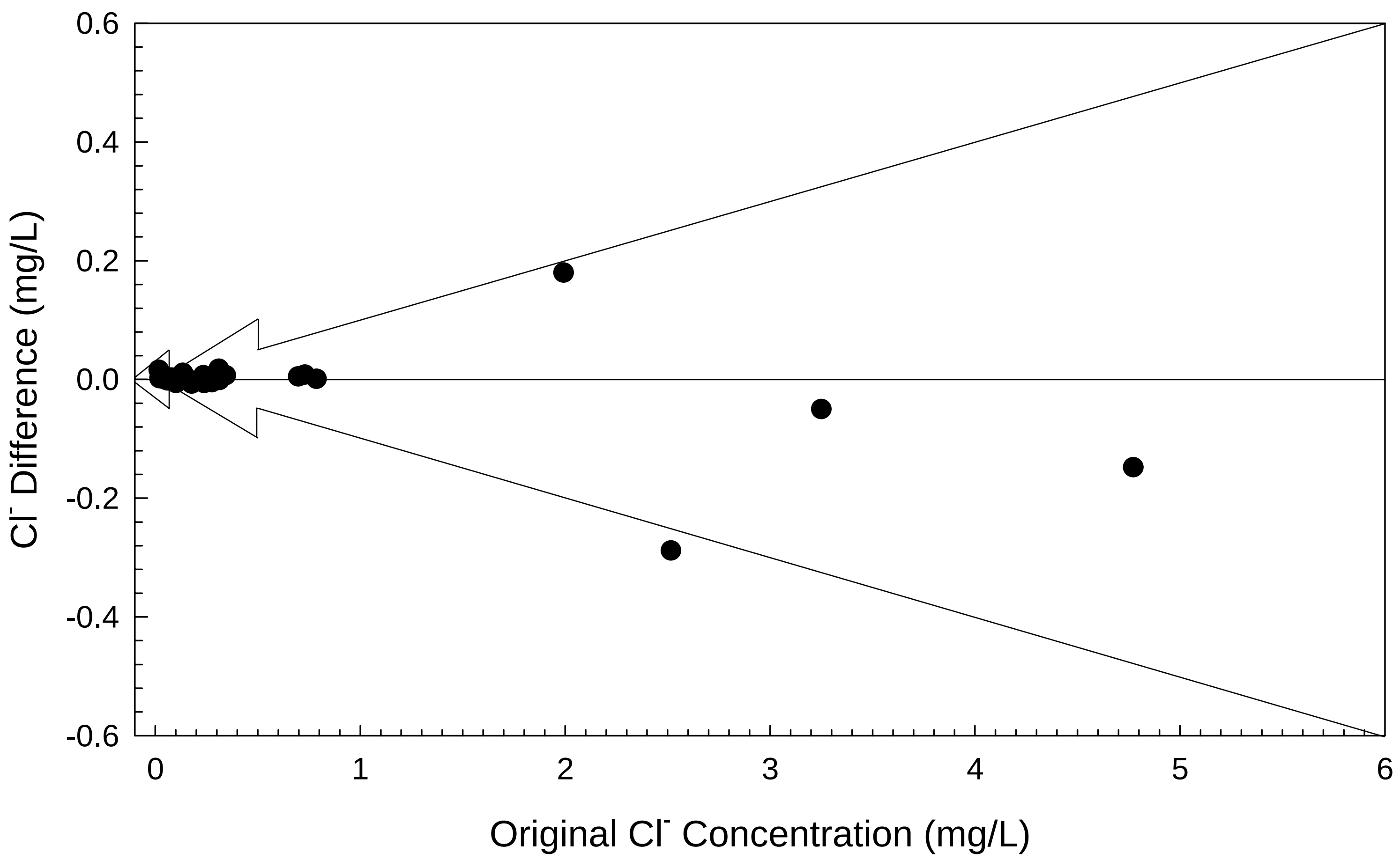


Figure B-72. AIRMoN replicate sample differences (original - replicate) for Cl^-, 2001.

Table B-16. Percent of Ion Concentrations above MDL Found in Weekly Deionized (DI) Water Blanks and Leachates, 2001

Blank	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Ammonium*	*Phosphate*	*Chloride*	*Nitrate*	*Sulfate*
DI (Rm 209)	3.8	3.8	0.0	3.8	0.0	0.0	0.0	1.9	3.8
DI (Rm 304)	1.9	1.9	3.8	7.7	0.0	0.0	7.7	0.0	0.0
DI (Rm 323)	1.9	1.9	0.0	1.9	0.0	0.0	0.0	1.9	0.0
Filter	11.5	3.8	11.5	5.8	0.0	0.0	17.3	1.9	1.9
Bucket - 50 mL	26.9	7.7	28.8	15.4	59.6	0.0	84.6	57.7	1.9
Bucket - 150 mL	15.4	3.8	11.5	13.5	13.5	0.0	40.4	13.5	1.9
Bucket - 50 mL	25.0	9.6	30.8	9.6	51.9	0.0	84.6	50.0	1.9
Bottle - 50 mL	11.5	1.9	1.9	5.8	0.0	0.0	1.9	0.0	0.0
Bottle - 150 mL	3.8	3.8	0.0	3.8	0.0	0.0	1.9	3.8	0.0
Lid - 50 mL	5.8	1.9	7.7	11.5	7.7	0.0	15.4	5.8	0.0
Bag - 50 mL	53.8	36.5	55.8	19.2	40.4	46.2	94.2	1.9	11.5

Note:
There were 52 weeks of blank samples.

Table B-17. Percent of Ion Concentrations Above and Below Control Limits Found in Weekly Simulated Rain (FR25) Leachates, 2001

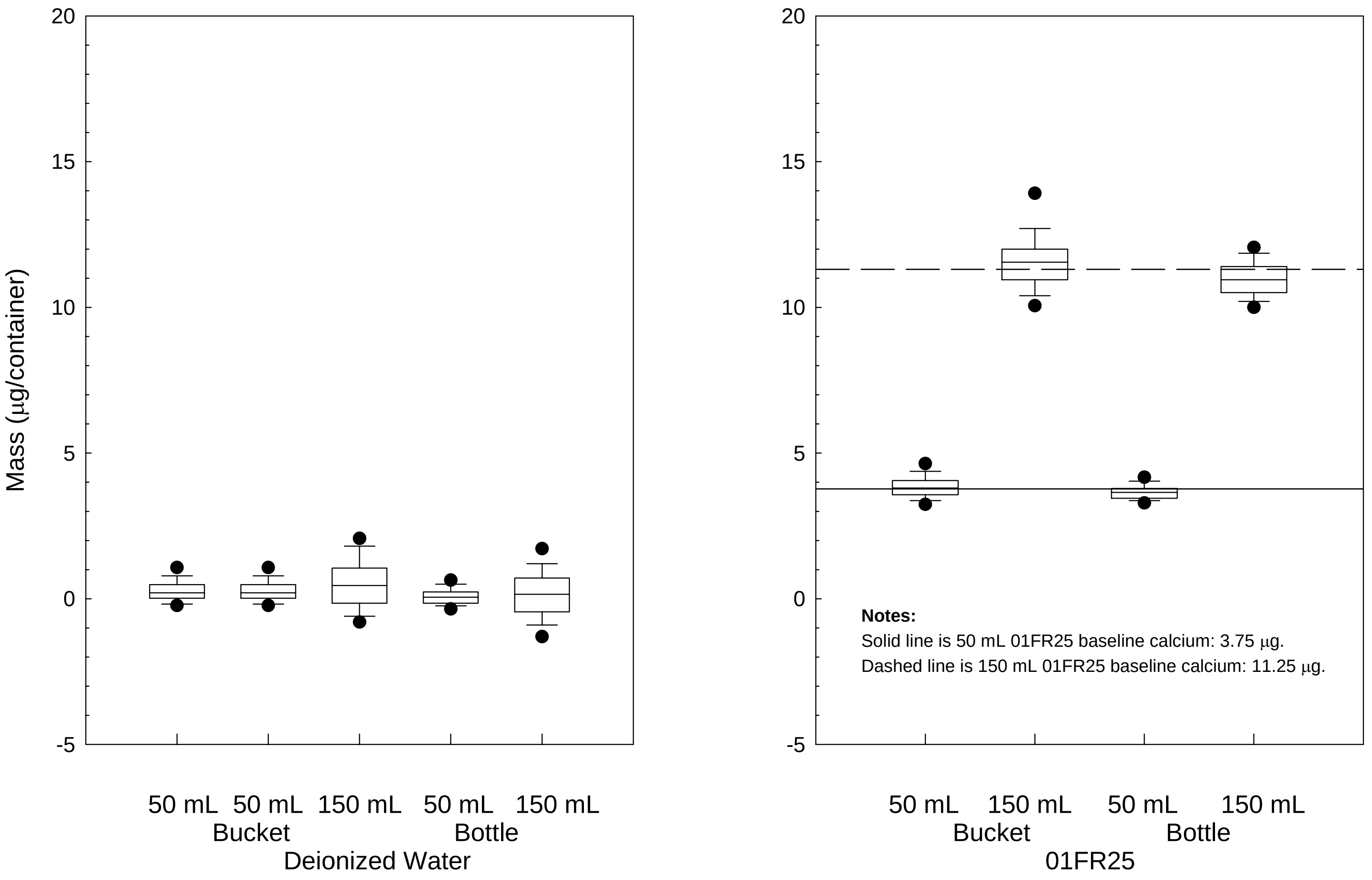
Blank	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Ammonium*	*Chloride*	*Nitrate*	*Sulfate*
Filter	0.0[a]	28.8	1.9	9.6	15.4	0.0	48.0	26.9
	30.8[b]	0.0	0.0	1.9	1.9	1.9	0.0	0.0
Bucket - 50 mL	5.8	0.0	0.0	17.3	5.8	0.0	9.6	36.5
	15.4	5.8	7.7	15.4	57.7	63.5	21.2	5.8
Bucket - 150 mL	1.9	0.0	0.0	11.5	26.9	0.0	1.9	1.9
	9.6	3.8	9.6	9.6	30.8	38.5	23.1	1.9
Bottle - 50 mL	3.8	0.0	0.0	5.8	48.1	0.0	19.2	0.0
	0.0	0.0	0.0	7.7	0.0	0.0	0.0	0.0
Bottle - 150 mL	1.9	1.9	0.0	1.9	19.2	0.0	3.8	0.0
	0.0	0.0	0.0	3.8	0.0	0.0	0.0	0.0
Lid - 50 mL	0.0	0.0	0.0	1.9	1.9	0.0	1.9	3.8
	0.0	0.0	1.9	7.7	34.6	3.8	0.0	0.0
AIRMoN Bottle - 50 mL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
AIRMoN Bottle - 150 mL	0.0	0.0	0.0	0.0	0.0	0.0	11.1	0.0
	0.0	0.0	0.0	0.0	0.0	11.1	0.0	0.0

Note:

Fifty-two NTN matrix spikes were analyzed. Eleven monthly AIRMoN matrix spikes were analyzed, and 9 AIRMoN matrix spikes were analyzed for Cl^-, NO_3^-, and SO_4^{2-}.

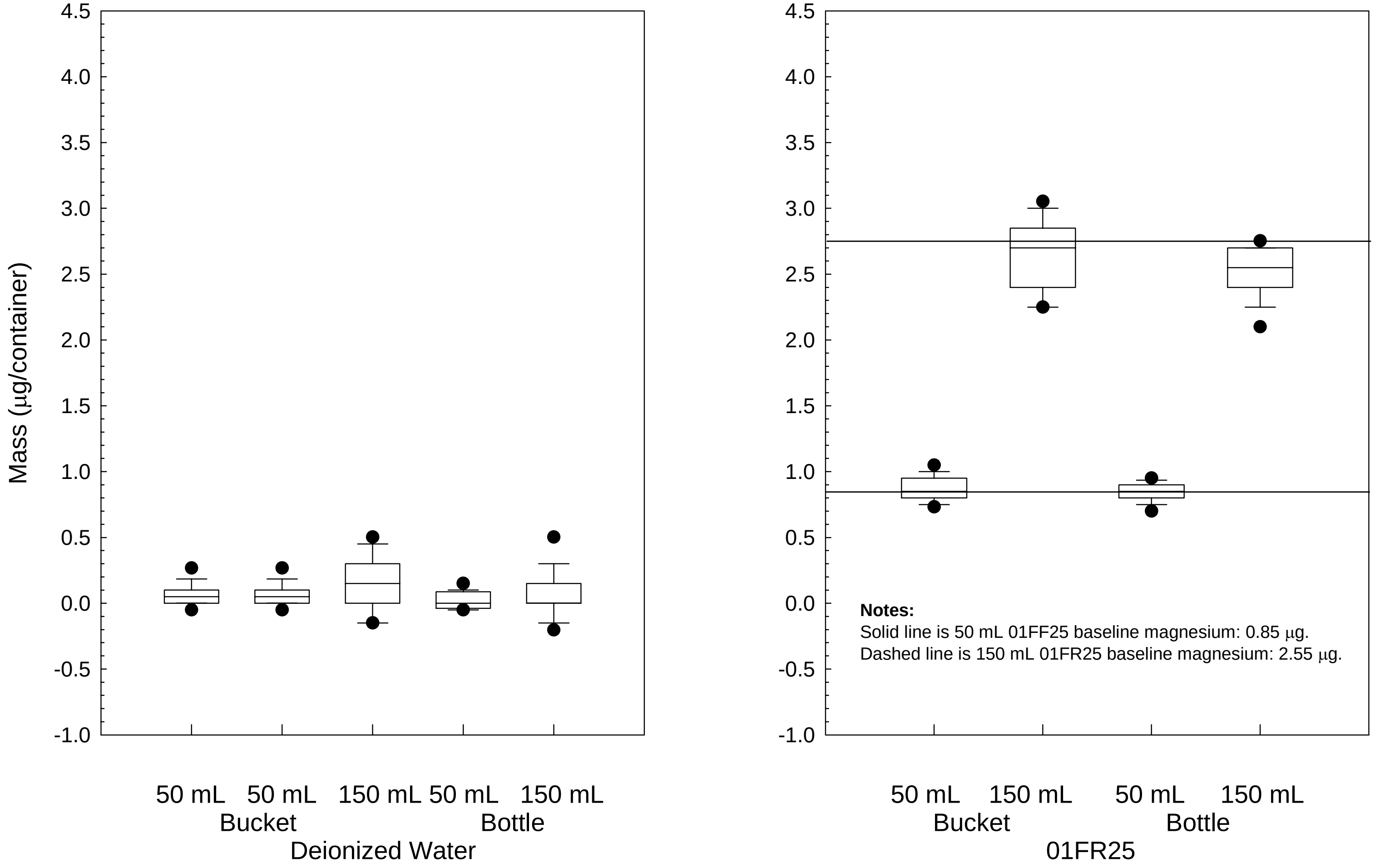
[a] Top numbers are the percent of samples above the upper control limit.

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



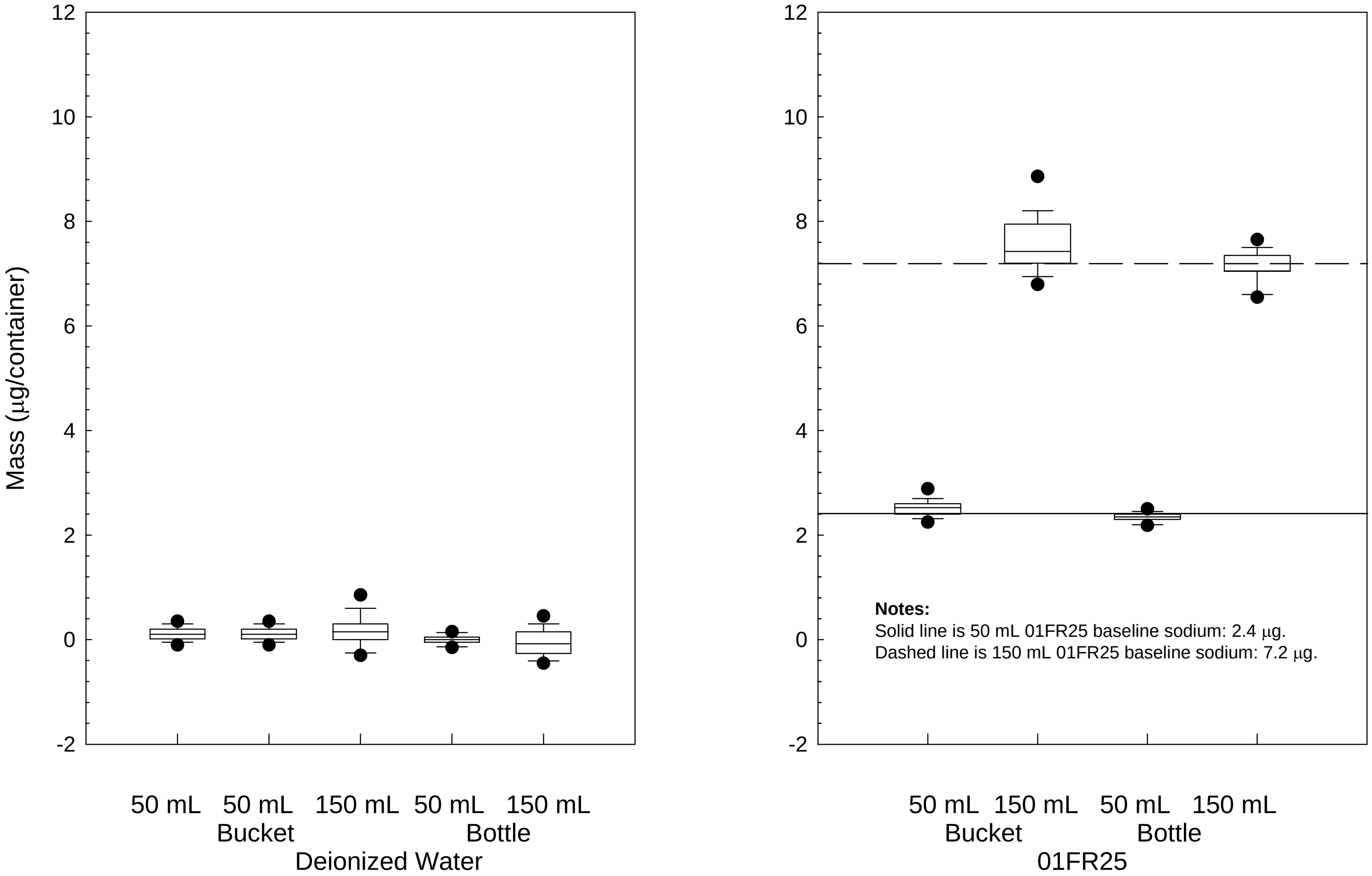
Notes:
Solid line is 50 mL 01FR25 baseline calcium: 3.75 µg.
Dashed line is 150 mL 01FR25 baseline calcium: 11.25 µg.

Figure B-73. Calcium found in upright bucket and 1-L bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2001.



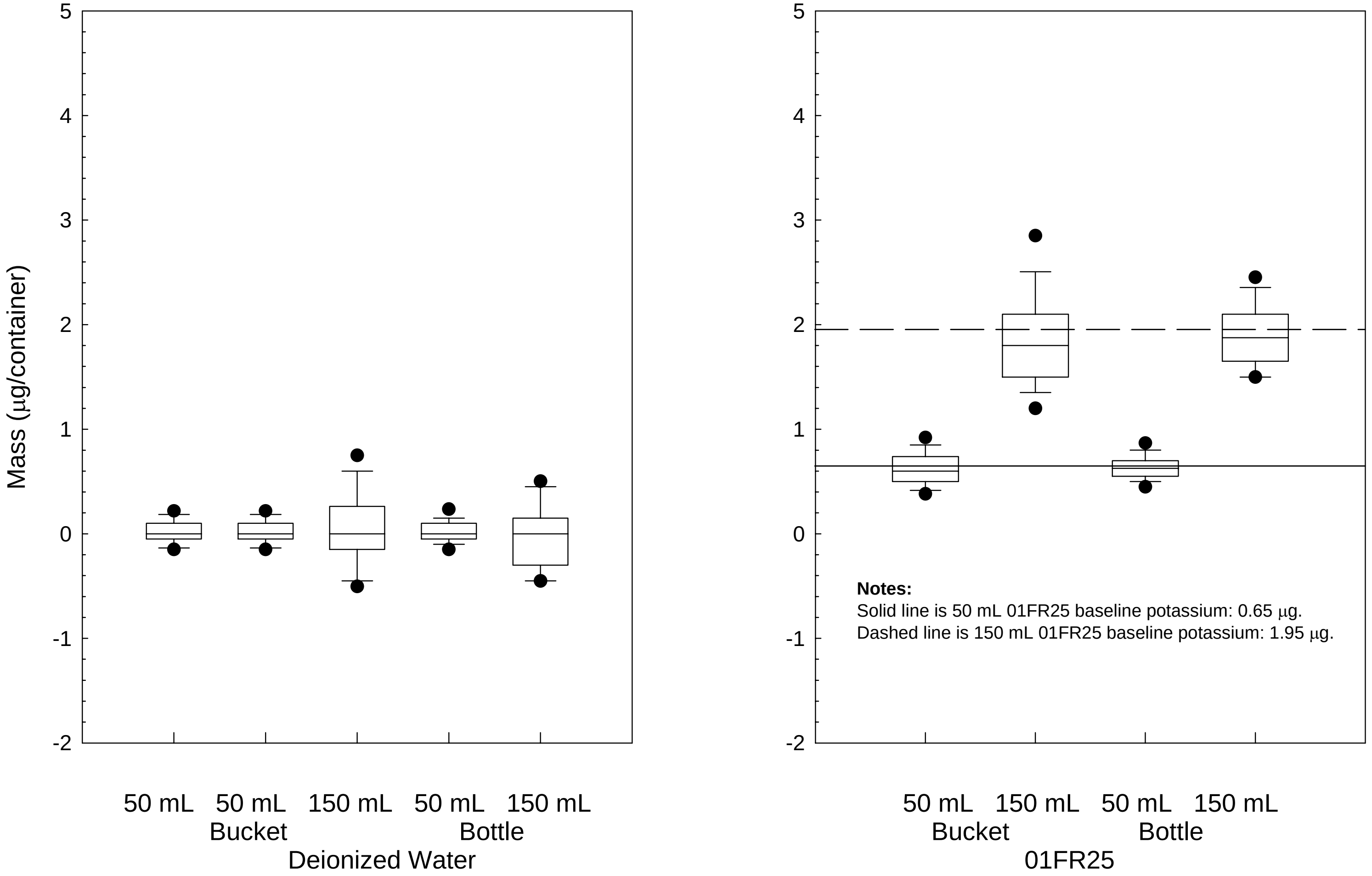
Notes:
Solid line is 50 mL 01FF25 baseline magnesium: 0.85 µg.
Dashed line is 150 mL 01FR25 baseline magnesium: 2.55 µg.

Figure B-74. Magnesium found in upright bucket and 1-L bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2001.



Notes:
Solid line is 50 mL 01FR25 baseline sodium: 2.4 µg.
Dashed line is 150 mL 01FR25 baseline sodium: 7.2 µg.

Figure B-75. Sodium found in upright bucket and 1-L bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2001.



Notes:
Solid line is 50 mL 01FR25 baseline potassium: 0.65 µg.
Dashed line is 150 mL 01FR25 baseline potassium: 1.95 µg.

Figure B-76. Potassium found in upright bucket and 1-L bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2001.

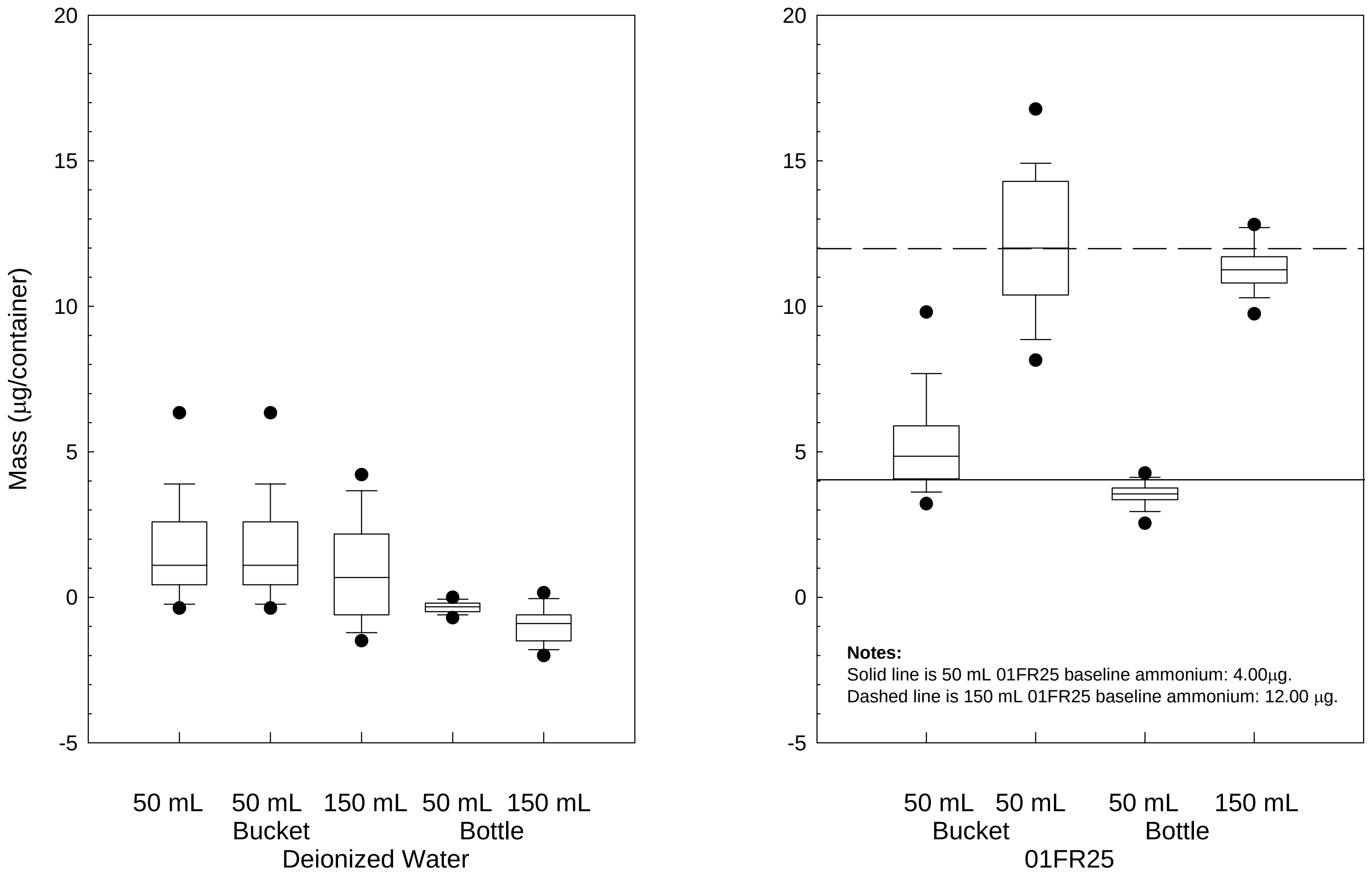


Figure B-77. Ammonium found in upright bucket and 1-L bottle deionized water blanks and synthetic rain solutins used as leaching agents, 2001.

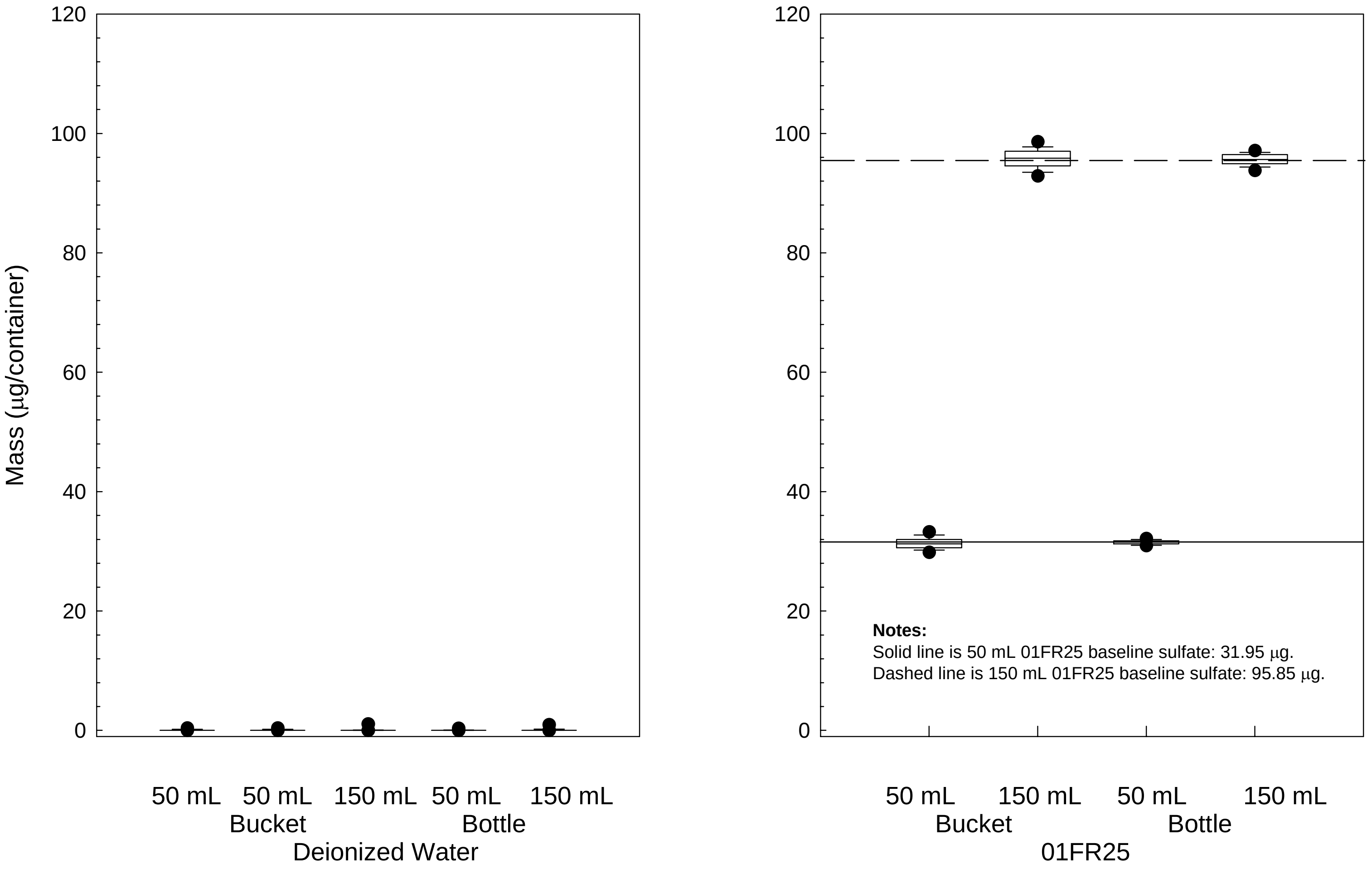
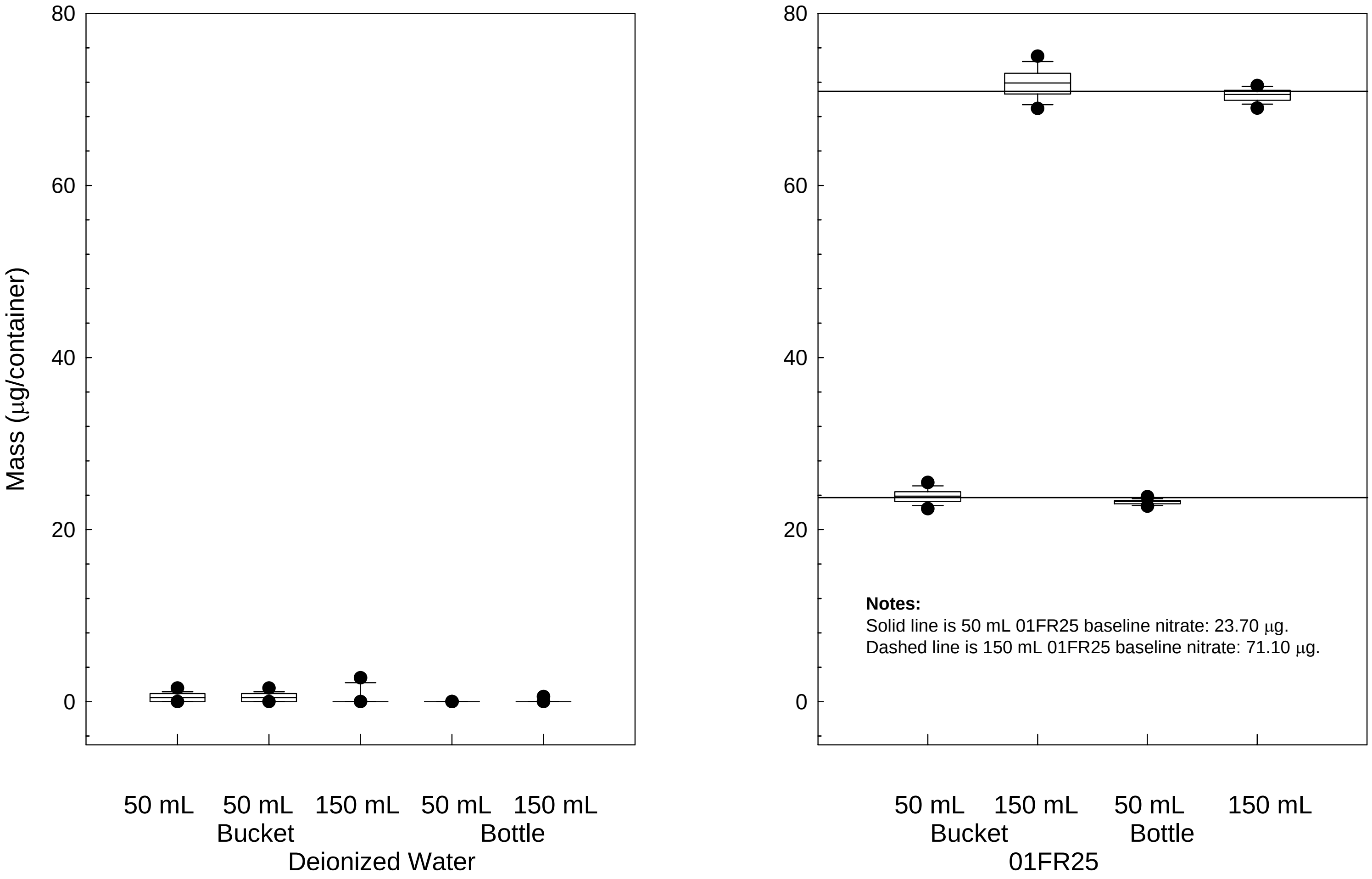


Figure B-78. Sulfate found in upright bucket and 1-L bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2001.



Notes:
Solid line is 50 mL 01FR25 baseline nitrate: 23.70 µg.
Dashed line is 150 mL 01FR25 baseline nitrate: 71.10 µg.

Figure B-79. Nitrate found in upright bucket and 1-L bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2001.

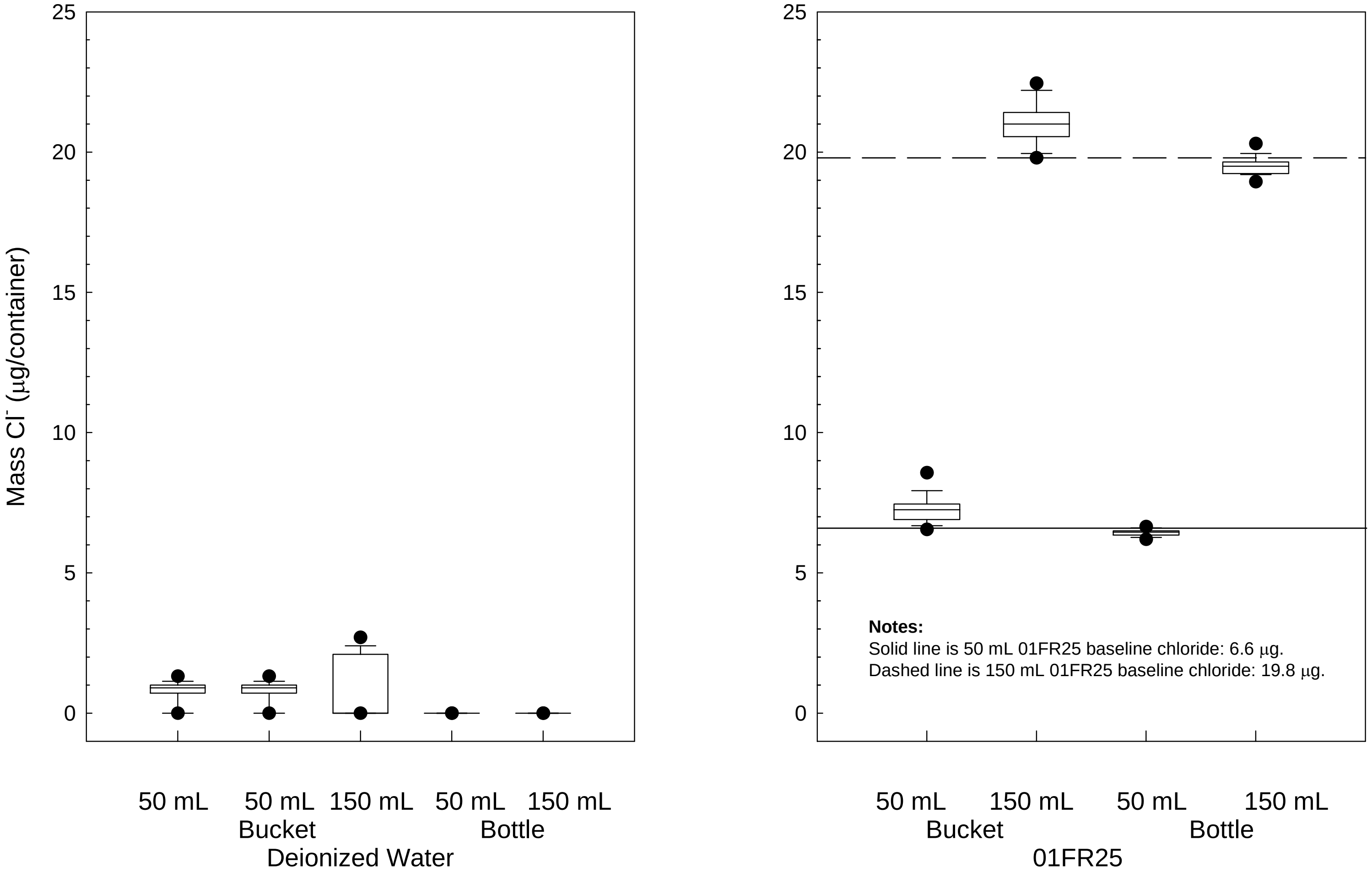
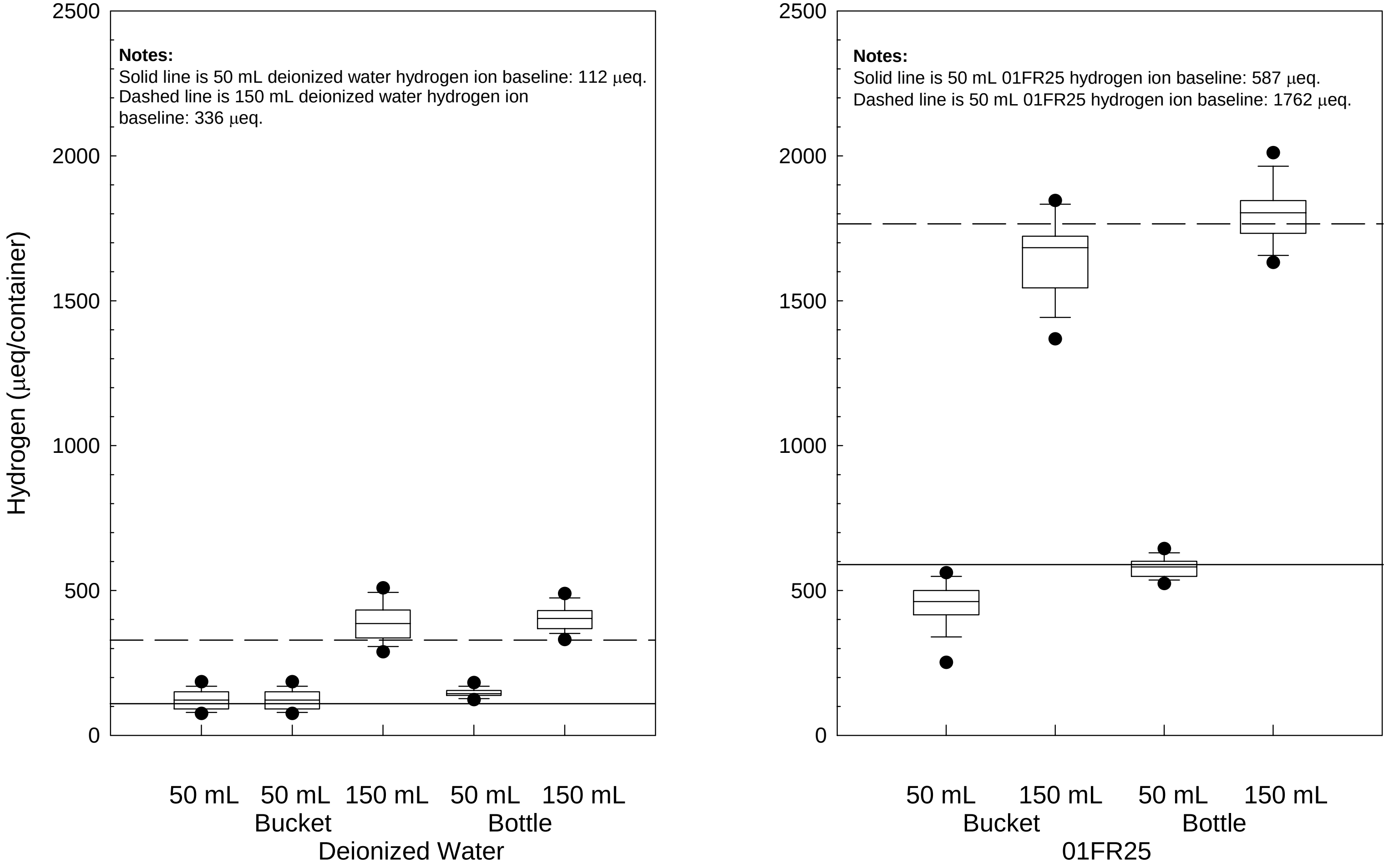


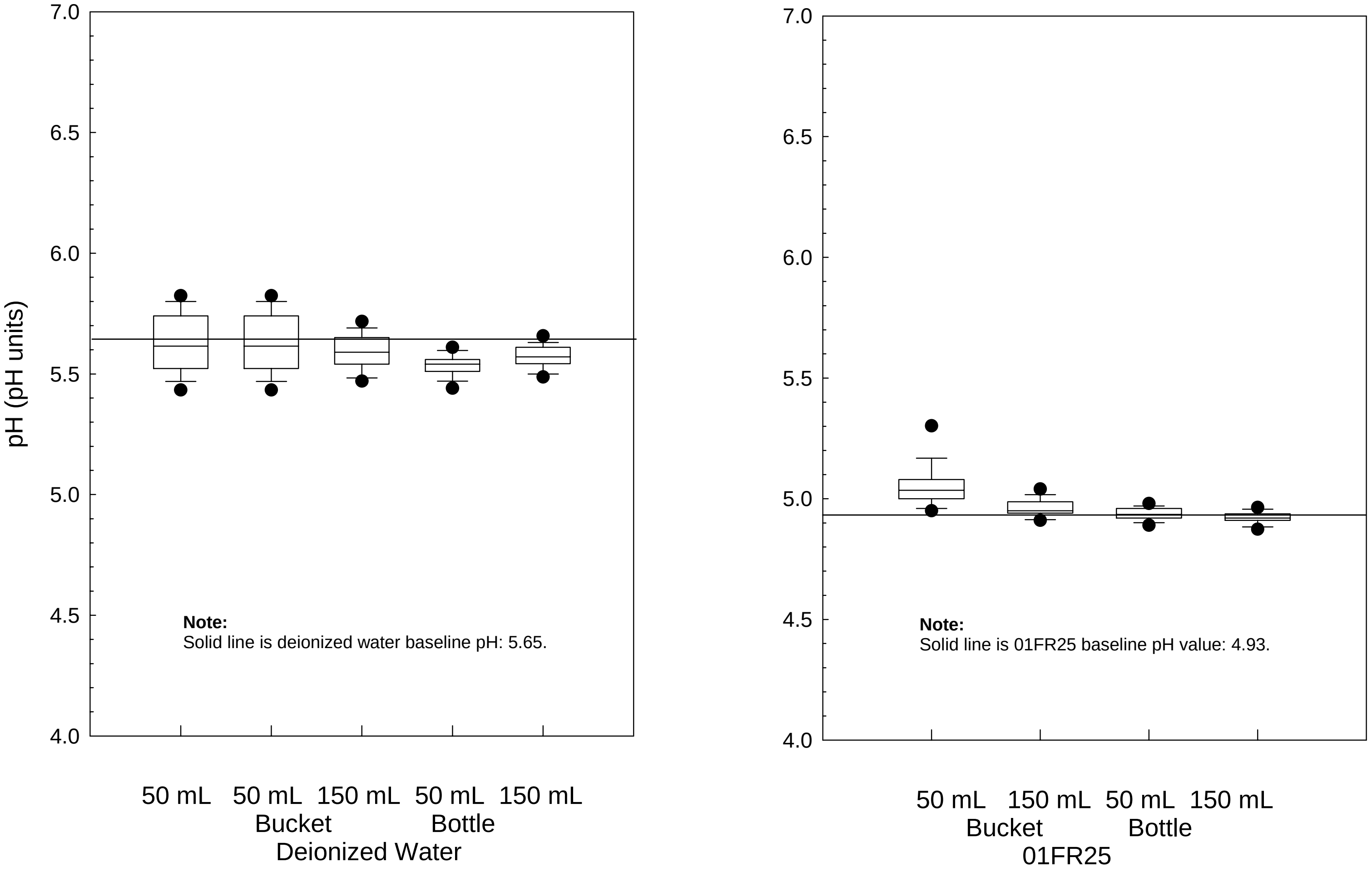
Figure B-80. Chloride found in upright bucket and 1-L bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2001.



Notes:
Solid line is 50 mL deionized water hydrogen ion baseline: 112 μeq.
Dashed line is 150 mL deionized water hydrogen ion baseline: 336 μeq.

Notes:
Solid line is 50 mL 01FR25 hydrogen ion baseline: 587 μeq.
Dashed line is 50 mL 01FR25 hydrogen ion baseline: 1762 μeq.

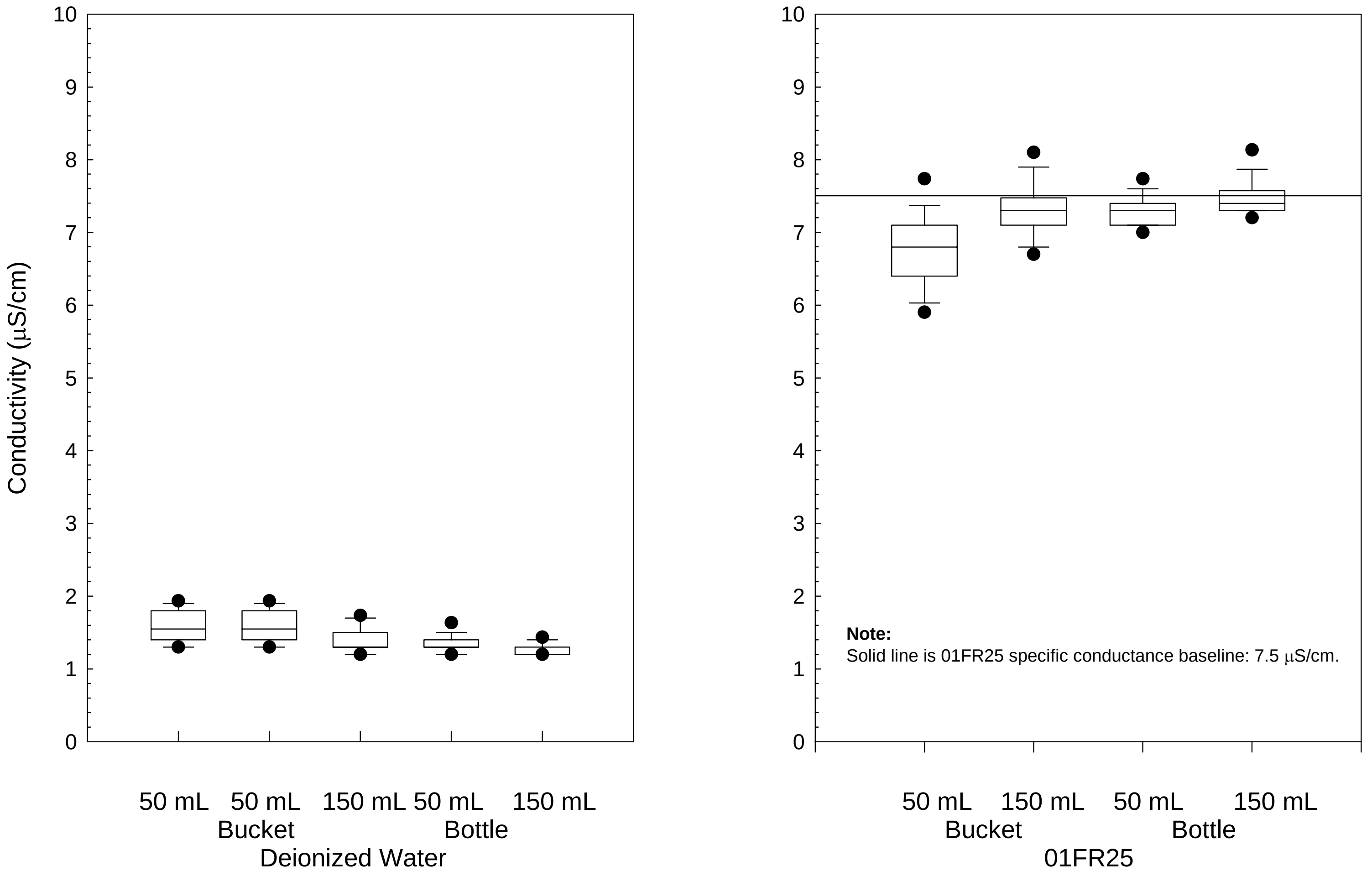
Figure B-81. Hydrogen ion found in upright bucket and 1-L bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2001.



Note:
Solid line is deionized water baseline pH: 5.65.

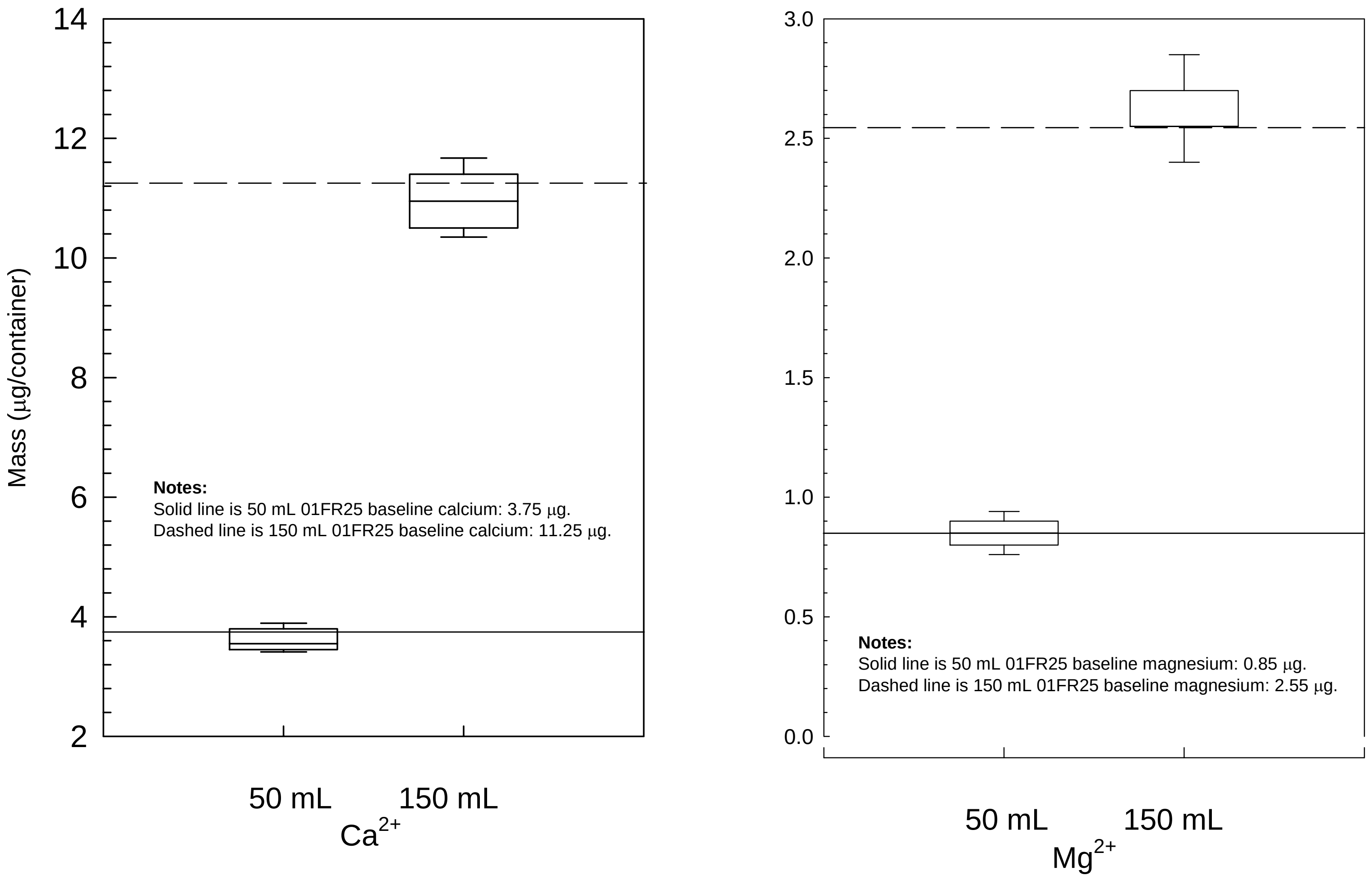
Note:
Solid line is 01FR25 baseline pH value: 4.93.

Figure B-82. pH found in upright bucket and 1-L bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2001.



Note:
Solid line is 01FR25 specific conductance baseline: 7.5 µS/cm.

Figure B-83. Conductivity found in upright bucket and 1-L bottle deionized water blanks and synthetic rain solutions used as leaching agents, 2001.



Notes:
Solid line is 50 mL 01FR25 baseline calcium: 3.75 µg.
Dashed line is 150 mL 01FR25 baseline calcium: 11.25 µg.

Notes:
Solid line is 50 mL 01FR25 baseline magnesium: 0.85 µg.
Dashed line is 150 mL 01FR25 baseline magnesium: 2.55 µg.

Figure B-84. Calcium and magnesium found in AIRMoN bottle synthetic rain solutions used as leaching agents, 2001.

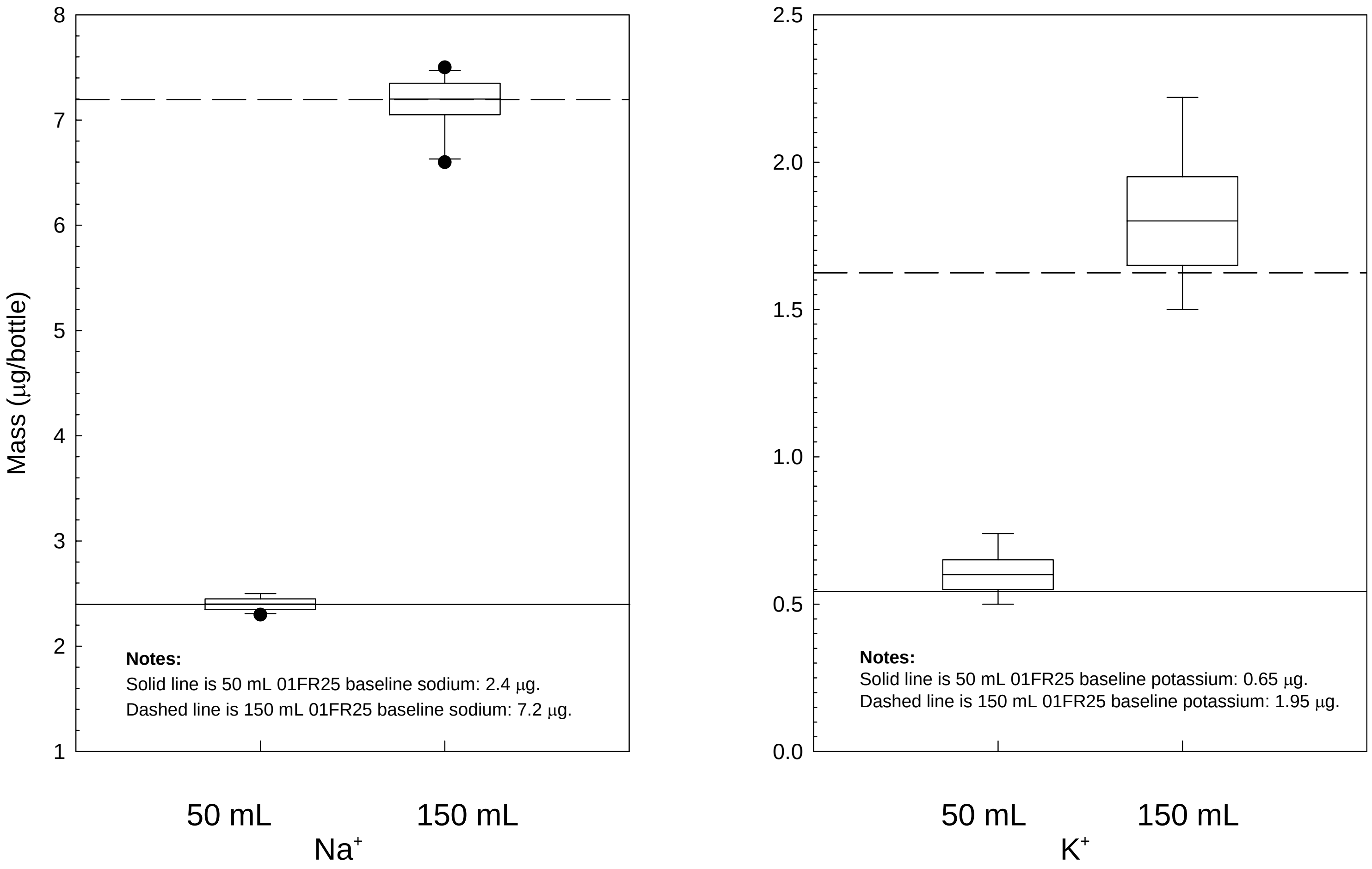
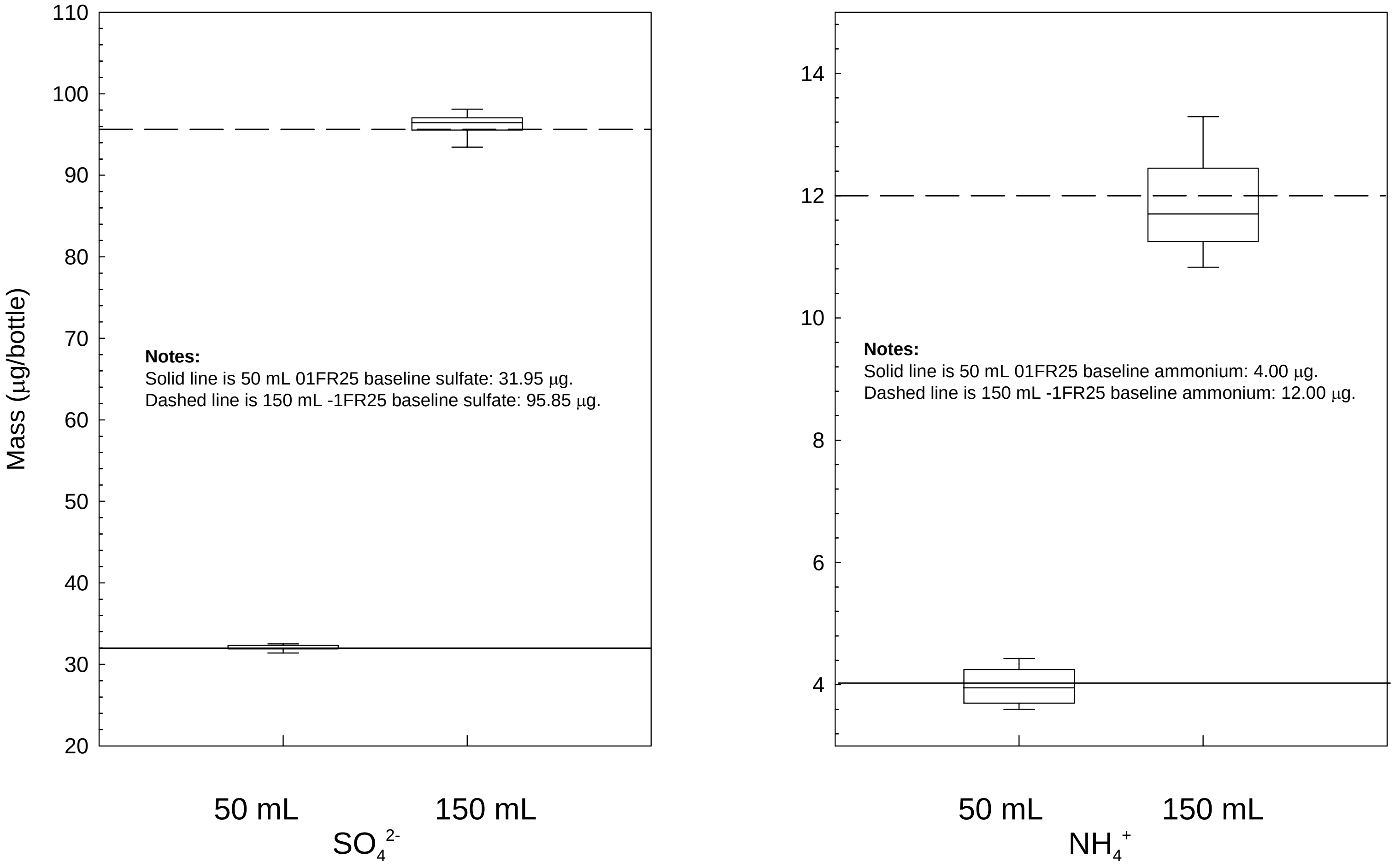


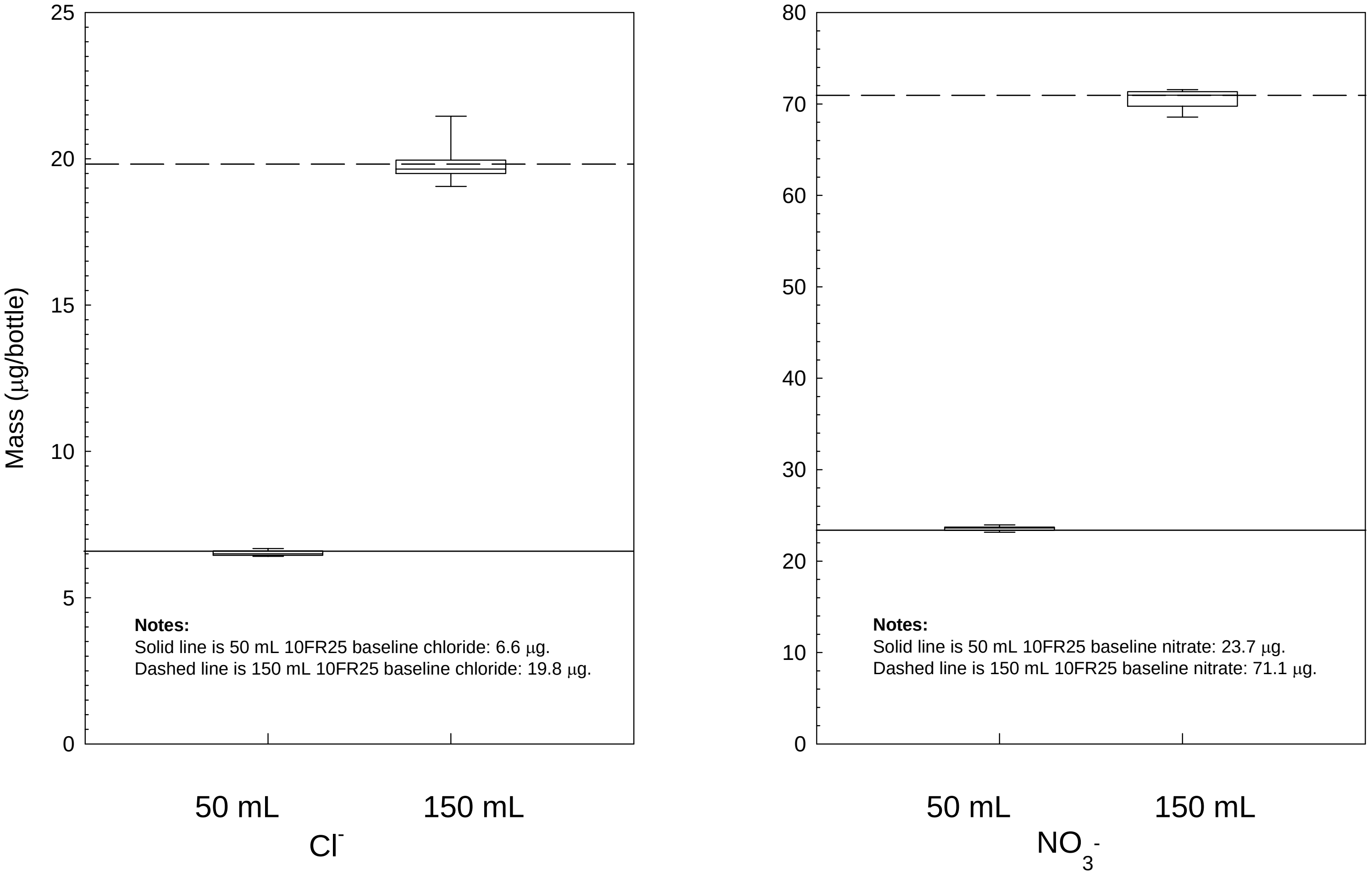
Figure B-85. Sodium and potassium found in AIRMoN bottle synthetic rain solutions used as leaching agents, 2001.



Notes:
Solid line is 50 mL 01FR25 baseline sulfate: 31.95 µg.
Dashed line is 150 mL -1FR25 baseline sulfate: 95.85 µg.

Notes:
Solid line is 50 mL 01FR25 baseline ammonium: 4.00 µg.
Dashed line is 150 mL -1FR25 baseline ammonium: 12.00 µg.

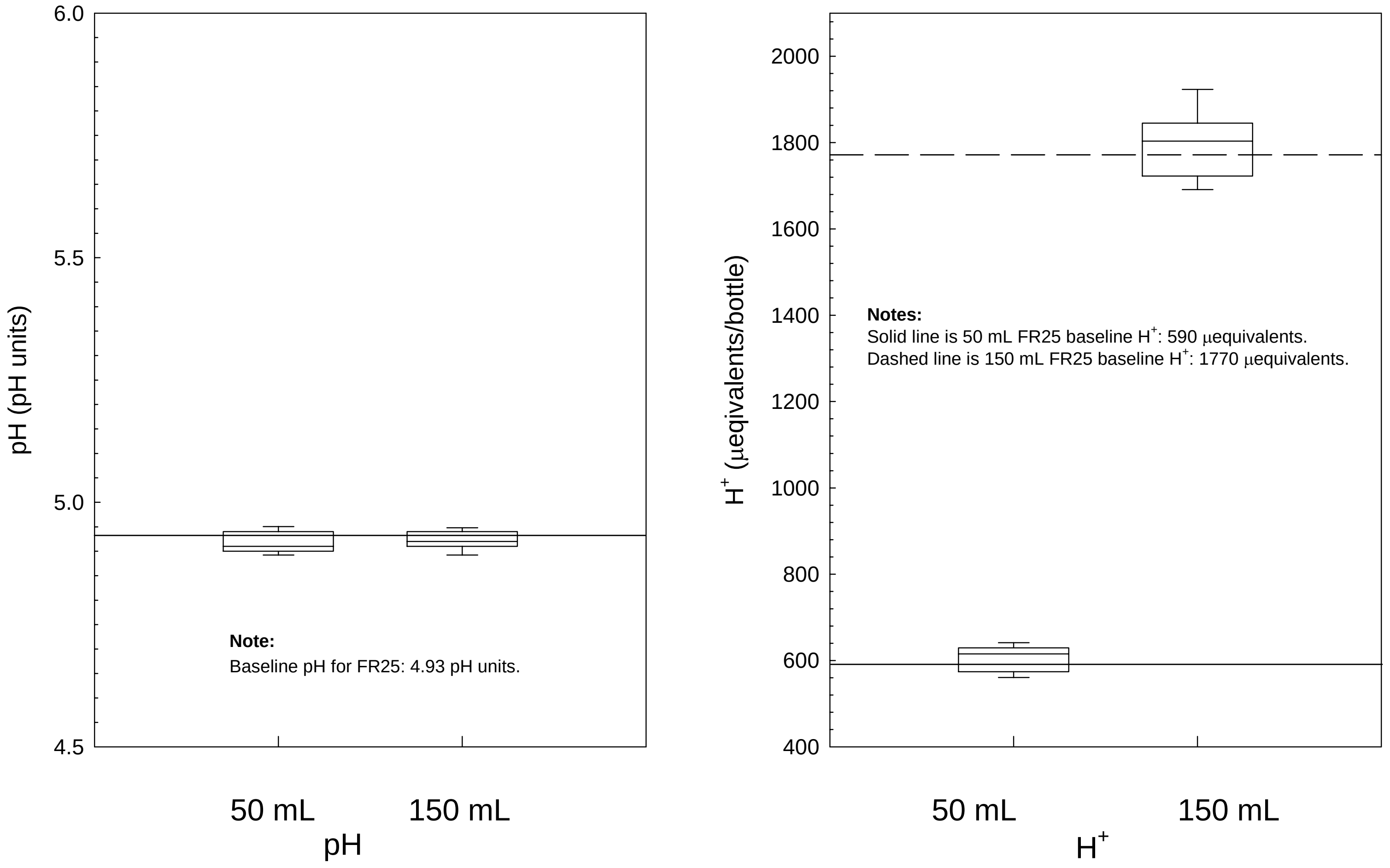
Figure B-86. Sulfate and ammonium found in AIRMoN bottle synthetic rain solutions used as leaching agents, 2001.



Notes:
Solid line is 50 mL 10FR25 baseline chloride: 6.6 µg.
Dashed line is 150 mL 10FR25 baseline chloride: 19.8 µg.

Notes:
Solid line is 50 mL 10FR25 baseline nitrate: 23.7 µg.
Dashed line is 150 mL 10FR25 baseline nitrate: 71.1 µg.

Figure B-87. Chloride and nitrate found in AIRMoN bottle synthetic rain solutions as leaching agents, 2001.



Note:
Baseline pH for FR25: 4.93 pH units.

Notes:
Solid line is 50 mL FR25 baseline H^+: 590 μequivalents.
Dashed line is 150 mL FR25 baseline H^+: 1770 μequivalents.

Figure B-88. pH and H^+ found in AIRMoN bottle synthetic rain solutions (01FR25) used as leaching agents, 2001.

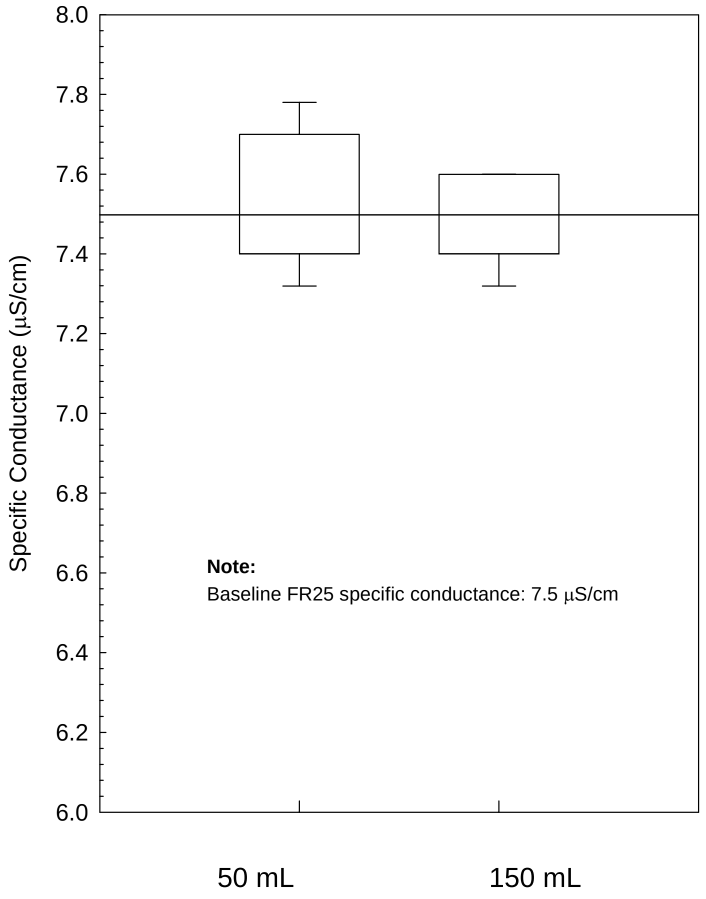


Figure B-89. Specific conductance found in AIRMoN bottle synthetic rain solutions (01FR25) used as leaching agents, 2001.

Illinois State
WATER
SURVEY

ILLINOIS
DEPARTMENT OF
NATURAL
RESOURCES

ILLINOIS