

MP177

QUALITY ASSURANCE REPORT NADP/NTN DEPOSITION MONITORING

Laboratory Operations
Central Analytical Laboratory
1994

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

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



A contribution to the
Task Group on Deposition Monitoring
Lead Agency: U.S. Geological Survey

The National Atmospheric Deposition Program (NADP) was initiated in 1977 under the leadership of the 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, the first sites of the NADP's precipitation chemistry network were established to provide information about geographical patterns and temporal trends in the deposition of acidic chemicals and nutrients. Initially organized as Regional Project NC-141 by the North Central Region of the SAES, the NADP was endorsed by all four regions in 1982, at which time it became Interregional Project IR-7. A decade later, the SAES reclassified IR-7 as a National Research Support Project, NRSP-3.

In 1982, the federally-supported National Acid Precipitation Assessment Program (NAPAP) was established to provide broadened support for research into the causes and effects of acid deposition. This program includes research, monitoring and assessment activities that emphasize the timely development of a firm scientific basis for decision making. Because of its experience in designing, organizing and operating a national-scale monitoring network, the NADP was asked to assume responsibility for coordinating the operation of the National Trends Network (NTN) of NAPAP. As the NADP and NTN had common siting criteria and operational procedures, and shared a common analytical laboratory, the networks were merged with the designation NADP/NTN. Many of the NTN sites are supported by the U.S. Geological Survey (USGS), which serves as the lead federal agency for deposition monitoring under NAPAP.

Seven federal agencies support NADP/NTN research and monitoring under NAPAP: the USGS, U.S. Department of Agriculture (USDA) Cooperative State Research, Education, and Extension Service (CSREES) and U.S. Forest Service (USFS), National Park Service (NPS), Bureau of Land Management (BLM), National Oceanic and Atmospheric Administration (NOAA), and the Environmental Protection Agency (EPA). Additional support is provided by various other federal agencies, state agencies, universities, public utilities and industry, as well as the SAES. The current network consists of approximately 200 sites.

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**1994 QUALITY ASSURANCE REPORT
NADP/NTN DEPOSITION MONITORING**

**Laboratory Operations
Central Analytical Laboratory
January 1994 through December 1994**

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I. INTRODUCTION

The Atmospheric Chemistry Laboratory at the Illinois State Water Survey (ISWS) was selected in the summer of 1978 to be the Central Analytical Laboratory (CAL) for the National Atmospheric Deposition Program (NADP). CAL operations began on October 1, 1978, with 14 NADP sites. In 1982 NADP merged with the National Trends Network (NTN), and the designation changed to NADP/NTN. The number of sites has increased over the years to 200, and the CAL has remained at the ISWS. In 1994 several procedural changes were introduced in order to better quantify the constituents of weekly precipitation samples. With these modifications, the laboratory Quality Control (QC)/Quality Assurance (QA) Program continued to evolve during 1994.

Beginning on January 11, 1994, samples collected at the sites were decanted from the collection bucket into 1-liter wide-mouth high density polyethylene (HDPE) bottles for shipping to the CAL. This altered field procedure requires close observations on the part of the site operators so that the appearance of the sample at the time the bucket is removed from the collector is accurately reported on the Field Form for contamination coding. Since great care is taken to see that a representative sample is sent from sites, the laboratory is charged with observing stringent QC protocols.

The NADP/NTN Quality Assurance Plan (1) summarizes the methods used to analyze and document each sample. This report describes the procedures used at the CAL and presents summaries of these activities to better enable the data user to evaluate the analytical results. Modifications made in 1994 are described in some detail, while ongoing procedures are described in more detail in previous annual reports. All of these reports are available from the Coordinator's Office at Colorado State University (2-12).

II. LABORATORY QUALITY ASSURANCE - A GENERAL DESCRIPTION

This report summarizes the data gathered from the laboratory internal and external QA/QC programs in 1994, the year during which the Atmospheric Integrated Research Monitoring Network (AIRMoN) protocol was defined and its QA program was put into place. Summaries of these QA data are included in this report along with those from the weekly network. Data are summarized and presented in order of the frequency of the activity from which they are generated: daily, weekly, monthly, and annually.

There were no changes to the GAL staff in 1994. The analytical staff members, their job functions, and length of employment are listed in Table II-1.

Samples collected on January 11, 1994 and thereafter are decanted into 1-liter bottles for shipment to the laboratory. The change in shipping protocol resulted from consideration of years of data that show that the lids, pounded onto the collection buckets for shipment, contributed to the chemistry of the sample. In order to better assess the contribution from the buckets and bottles used as sample collectors and containers, the laboratory blank program has been modified. Buckets, snap-on lids, bottles, and filters were all leached with both deionized (DI) water and a solution of laboratory-prepared simulated rain with an ion matrix similar to the 25th percentile concentration values of the network. This solution is referred to as FR25 by the CAL staff.

Buckets are leached for a longer period of time, Monday through Friday, instead of overnight. Simulated rain solutions corresponding to both the 25th (FR25) and 75th (FR75) percentile concentrations of the network are used as Quality Control Standards (QCS) and have been monitored throughout the year to ensure they have remained stable.

The methodology for determining orthophosphate was changed from ion chromatography (IC) to flow injection analysis (FIA), an automated wet chemical procedure that is more sensitive and efficient. Phosphate and ammonium are analyzed simultaneously by this method. The cations calcium, magnesium, sodium, and potassium have been determined by atomic absorption (AA) since the beginning of the network. A new AA instrument was purchased in 1993 and brought on line in November 1994. The new instrument enables real-time electronic data capture, which was recommended during the past two laboratory audits. The method detection limits (MDLs) are the same as for the previous instrument that had been in service since 1980. The MDLs for the ions of interest are provided in Table II-2.

The laboratory QC/QA program is summarized in Table II-3, and the flowchart in Figure II-1 illustrates the fate of a sample after it reaches the CAL. Instrument calibration is verified using FR25 and FR75, and the results of these analyses are presented graphically on monthly control charts. Simulated rainwater purchased from High Purity Standards (HPS) in Charleston, South Carolina, is used as blind samples in the laboratory's internal QA program. Replicate

samples and reanalysis sample identification follow the same protocol as they have since 1989. Intercomparison programs conducted by the US Geological Survey (USGS) and international sources have remained a significant method of evaluating CAL performance in relation to that of its peers analyzing precipitation throughout the world.

TABLE II-1 Central Analytical Laboratory Analytical Staff, 1994

Staff Member	Job Function	Period of Employment
Sue Bachman	Ammonium Calcium, magnesium, sodium and potassium Orthophosphate	08/80 - 12/94 11/88 - 12/94 01/94 - 12/94
Jackie Damara	Sample processing supervision	09/83 - 05/86 01/88 - 12/94
Brigita Demir	Anions analysis	09/81 - 12/94
Patricia Dodson	Sample processing	09/80 - 12/94
Lori Henry	AIRMoN sample processing and metals analysis	08/92 - 12/94
Theresa Ingersoll	Sample receipt and processing	03/85 - 12/94
Kenni James	Quality assurance	10/87 - 12/94
Mark Peden	Laboratory manager	07/78 - 12/94
Jeffrey Pribble	Sample receipt, supply procurement, and lab site liaison	07/87 - 12/94
Jane Rothert	AIRMoN coordinator	05/92 - 12/94
Angela Weddle	pH, conductivity IC data reduction	10/89 - 12/94 08/92 - 12/94

TABLE II-2 Method Detection Limits (MDLs) for Precipitation Analysis, 1994

Ion	MDL (mg/L)	Dates	Method
Calcium	0.02	07/78 - 10/80	Flame Atomic Absorption
	0.009	10/80 - 12/94	
Magnesium	0.002	07/78 - 10/80	Flame Atomic Absorption
	0.003	10/80 - 12/94	
Sodium	0.004	07/78 - 10/80	Flame Atomic Absorption
	0.003	10/80 - 12/94	
Potassium	0.004	07/78 - 10/80	Flame Atomic Absorption
	0.003	10/80 - 12/95	
Ammonium	0.02	07/78 - 12/94	Automated Phenate, Colorimetric
Sulfate	0.10	07/78 - 05/85	Automated Methyl Thymol Blue, Colorimetric
	0.03	05/85 - 12/94	Ion Chromatography
Nitrate/Nitrite	0.02	07/78 - 05/85	Automated Cadmium Reduction, Colorimetric
Nitrate	0.03	05/85 - 12/94	Ion Chromatography
Chloride	0.05	07/78 - 03/81	Automated Ferricyanide, Colorimetric
	0.02	03/81 - 05/85	Ion Chromatography
	0.03	05/85 - 12/94	
Orthophosphate	0.003	07/78 - 02/86	Automated Ascorbic Acid, Colorimetric
	0.01	02/86 - 07/87	Ion Chromatography
	0.02	07/87 - 12/93	
	0.003	01/94 - 12/94	Automated Ascorbic Acid, Colorimetric

Notes: *Methods for Collection and Analysis of Precipitation* (13) describes methods as they were in 1986. Instrument and software upgrades and method modifications are contained in laboratory procedures manuals, which are continually revised and are located in the laboratory where the analyses are performed.

**TABLE II-3 NADP/NTN Laboratory QC/QA Program Summary,
1994**

- I. Daily**
 - A. Instruments calibrated, calibration curves verified using QCS.**
 - 1. CAL-formulated solutions of simulated rain represent the 25th and 75th percentile concentrations of network samples.**
 - 2. QCS values recorded.**
 - B. Records of standards preparation and instrument maintenance updated.**

- II. Weekly**
 - A. Blanks analyzed.**
 - 1. Deionized (DI) water.**
 - 2. Filter leachates using DI water and simulated rainwater.**
 - 3. Upright bucket leachates using DI water and simulated rainwater.**
 - 4. Liter bottle leachates using DI water and simulated rainwater.**
 - 5. Snap-on lid leachates using DI water and simulated rainwater.**
 - B. Internal blind audit samples from sites SWS1, SWS2, SWS3.**
 - 1. SWS1: High Purity Standards (HPS) simulated rainwater I and II, unfiltered.**
 - 2. SWS2: DI water and pH 4.3 nitric acid, unfiltered.**
 - 3. SWS3: all four of the above solutions in rotation, filtered.**
 - C. Two percent of samples split for duplicate analysis.**
 - D. Quality control solutions validated prior to shipment to sites.**

- III. Monthly**
 - A. AIRMoN 250-mL HDPE bottles leached with simulated rainwater; leachates analyzed with weekly blanks.**
 - B. AIRMoN field blanks collected and analyzed with weekly blanks.**
 - C. Inspection of control charts (generated from QCS responses).**
 - D. Internal blind and replicate data evaluated from printouts.**
 - E. Samples for reanalysis selected by computer based on ion balance and conductance calculations.**
 - 1. Reanalysis data evaluated.**
 - 2. Suggestions for data changes made to data management**
 - F. USGS interlaboratory comparison analyses evaluated prior to transmission.**

- IV. Annually and semiannually**
 - A. Quality assurance report submitted for publication.**
 - B. Subcommittee reports prepared for spring and fall NADP/NTN meetings.**
 - C. Laboratory participates in external interlaboratory comparisons.**

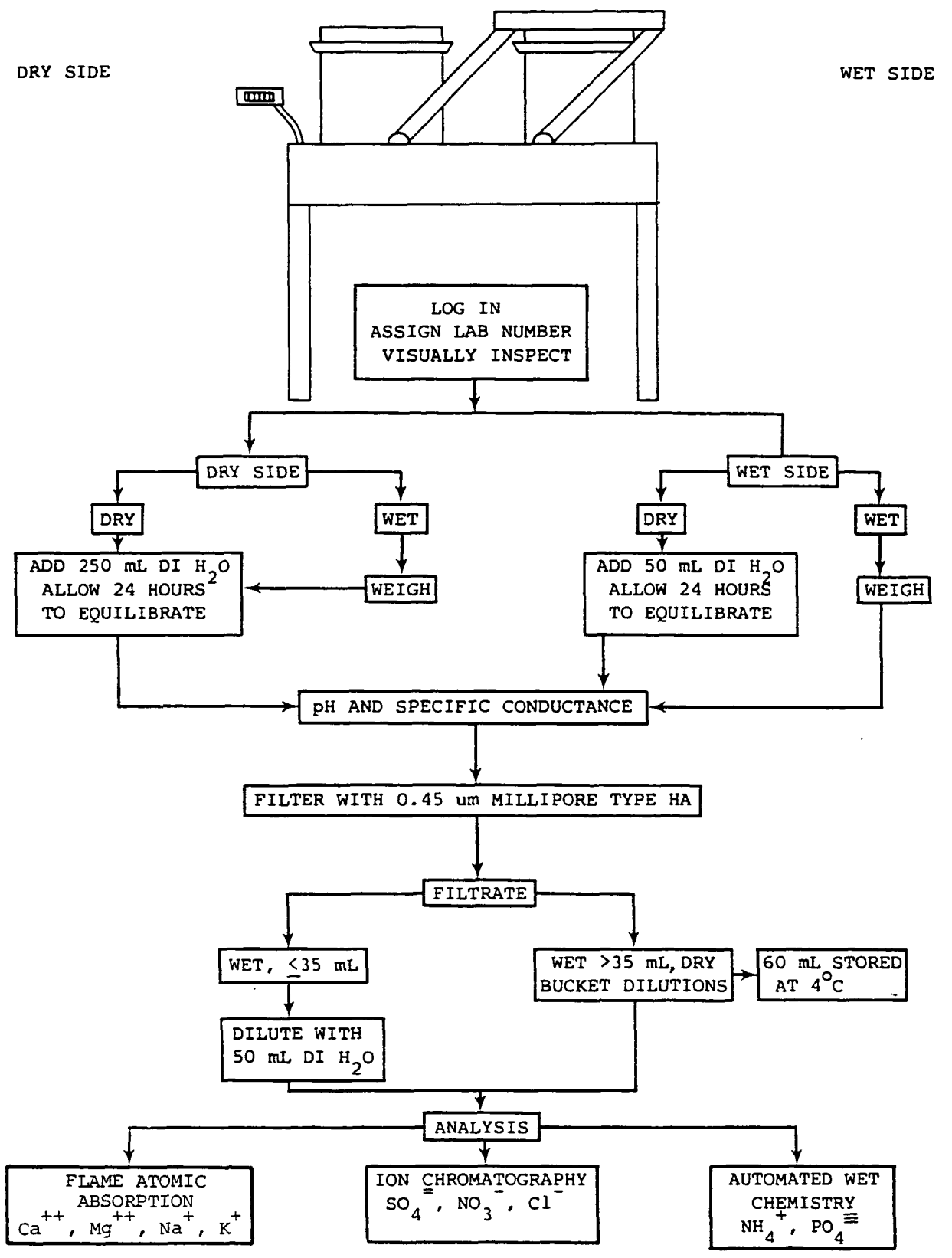


FIGURE II-1 Sample processing flowchart, January 1994-December 1994

III. DAILY QUALITY CONTROL PROCEDURES

The change in shipping protocol resulted in a change in CAL shipping and receiving operating procedures. After January 11, the daily samples began arriving at the laboratory in bottles, instead of the collection buckets. The empty buckets, with snap-on lids rather than the lids with o-rings used previously, accompany the sample bottle in the black shipping box. Site operators have been charged with careful observation of the appearance of the bucket sample, and the Field Observer Report Form (FORF) has been modified to include a Sample Condition category with check boxes. The bottle and its accompanying bucket are sent to data processing with the field form for the assignment of a consecutive sample number. The bucket and bottle then go on to the laboratory. There, sample processing staff examine the bucket a final time prior to washing, record any further observations on the lab sheet, and assign a contamination code to the sample. A sample aliquot is then poured from the shipping bottle for pH and conductance measurements. Filtration through a Millipore™ type HAWP, 0.45-um filter into a 60-mL round HDPE bottle, which is labeled with the consecutive sample number, occurs prior to the sample's placement on a tray of 108 samples for transport to the laboratory for cation and anion analyses. If there is sufficient volume, an additional 60-mL aliquot is filtered into a square HDPE bottle, labeled with the same number, and stored at 4° C for archival purposes. Traditionally these samples have been used to verify reanalysis results and for limited research.

The instruments used for ion analyses are all calibrated prior to analysis each day and again as often as the method demands. The calibration curves are verified throughout the day using quality control standards (QCS) which are simulated rain emulating the 25th (FR25) and 75th (FR75) percentile concentrations of the network samples (Table III-1). These solutions are formulated and tested in the fall prior to their use in the laboratory the next calendar year. These QCS, traceable to National Institute of Standards and Technology (NIST) certified standards have been in use since January 1990. United States Environmental Protection Agency (USEPA) diluted nutrient concentrate is used as the phosphate QCS (Table III-2).

NADP/NTN sample concentrations have proven to be consistent since the network reached its current nationwide distribution of sites. Therefore, the FR25 and FR75 contain approximately the same ion concentrations each year. Daily QCS data are summarized each month on control charts and the annual data are summarized in tabular form in this report. Table III-2 shows a comparison of target concentrations with a mean value for the QCS measurements for the entire year. The standard deviation is also calculated for the life of the solution. The data from these analyses illustrate the optimum bias and precision values for the measurement process.

The cation bias is negligible, and the precision expressed as percent relative standard deviation (%RSD) is statistically the same as it was in 1993. The anion values show bias similar to the previous year, with chloride being slightly higher. Precision (RSD) is similar

to 1993 for all anions. Phosphate, with its lower detection limit, had concentrations quantified in a few more samples. The bias is lower than last year, and the precision is similar.

There are fewer pH QCS measurements made in 1994 due to observations made in the 1993 laboratory audit that the frequency of measurement was excessive and should be reduced. Bias and precision measurements for pH are not appreciably different from 1993 values. The conductivity bias is similar to the previous year, and the precision is better. All bias and precision measurements results fell within the goals for laboratory measurements outlined in the network QA plan (1).

**TABLE III-1 Percentile Concentration Values of Chemical and Physical Parameters
Measured in NADP/NTN Precipitation, 1994**

Percentile Concentration Value (mg/L)										
Parameter	Min.	5th	10th	25th	50th	75th	90th	95th	99th	Max.
Calcium	-0.009	0.013	0.021	0.044	0.104	0.244	0.512	0.787	1.846	10.54
Magnesium	-0.003	-0.003	0.004	0.009	0.021	0.044	0.086	0.130	0.297	2.53
Sodium	-0.003	0.016	0.020	0.033	0.063	0.136	0.318	0.598	1.847	21.0
Potassium	-0.003	-0.003	0.004	0.009	0.018	0.036	0.072	0.111	0.256	1.93
Ammonium	-0.02	0.02	0.04	0.09	0.21	0.43	0.73	0.97	1.73	83
Sulfate	-0.03	0.15	0.25	0.56	1.12	1.96	3.17	4.18	6.80	16
Nitrate	-0.03	0.18	0.32	0.60	1.09	1.81	2.80	3.71	5.90	26
Chloride	-0.03	0.03	0.04	0.07	0.11	0.22	0.54	1.00	3.1	38
o-Phosphate	-0.003	-0.003	-0.003	-0.003	-0.003	-0.003	0.005	0.006	0.015	1.25
pH(units)	3.46	4.10	4.21	4.45	4.78	5.22	5.74	6.16	6.65	7.66
Cond.(μ S/cm)	1.5	3.6	4.8	7.8	13.2	22.0	34.9	45.2	72.1	179
Notes: Number of Samples = 6908 Mean sample volume = 1470 mL; median sample volume = 906 mL										

Source: National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) 1994 wet-side samples.

**TABLE III-2 Analytical Bias and Precision Determined from Analysis
of Simulated Rain QCS, 1994**

Parameter	Target Concentration (mg/L)	Measured Concentration (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision (mg/L)	Precision RSD (%)	Critical Concentration (mg/L)	Statist. Signif. Bias?
Calcium	0.072 ^a	0.072	446	0.000	0.0	0.001	1.8	0.001	NO
	0.075	0.074	310	-0.001	-1.3	0.002	2.6	0.001	NO
	0.292 ^b	0.293	591	0.001	0.3	0.002	0.9	0.002	NO
Magnesium	0.016	0.016	446	0.000	0.0	0.001	6.5	0.001	NO
	0.016	0.016	312	0.000	0.0	0.001	7.5	0.001	NO
	0.068	0.068	585	0.000	0.0	0.001	1.8	0.001	NO
Sodium	0.047	0.046	452	-0.001	-2.1	0.001	2.4	0.001	YES
	0.033	0.052	305	-0.001	-1.9	0.001	2.7	0.001	YES
	0.188	0.188	602	0.000	0.0	0.002	1.0	0.001	NO
Potassium	0.013	0.013	445	0.000	0.0	0.001	8.4	0.001	NO
	0.016	0.016	292	0.000	0.0	0.001	8.0	0.001	NO
	0.056	0.056	598	0.000	0.0	0.001	2.3	0.001	NO
Ammonium	0.09	0.09	326	0.00	0.0	0.01	11.4	0.00(7) ^c	NO
	0.10	0.08	208	-0.02	-16.0	0.01	11.1	0.00(6)	YES
	0.36	0.36	367	0.00	0.0	0.01	3.5	0.00(8)	NO
Sulfate	0.61	0.60	690	-0.01	-1.0	0.01	2.0	0.00(8)	NO
	0.62	0.62	467	0.00	0.0	0.01	1.9	0.00(7)	NO
	2.43	2.44	1109	0.01	0.6	0.03	1.1	0.01(6)	NO
Nitrate	0.48	0.47	694	-0.01	-1.5	0.01	1.9	0.00(6)	YES
	0.49	0.49	465	0.00	0.0	0.01	2.1	0.00(6)	NO
	1.90	1.92	1114	0.02	1.0	0.02	1.2	0.01(4)	YES
Chloride	0.13	0.13	693	0.00	0.0	0.01	3.4	0.00(4)	NO
	0.13	0.14	469	0.01	3.8	0.01	4.1	0.00(3)	YES
	0.49	0.51	1139	0.02	3.3	0.01	2.5	0.00(8)	YES
o-Phosphate	0.024	0.022	376	-0.002	-8.3	0.003	12.8	0.001	YES
	0.060	0.060	339	0.000	0.0	0.004	6.41	0.002	NO
pH units	4.92(12.0)	4.93(11.8)	975	(-0.2)	(-1.7)	(0.78)	(6.6)	(0.35)	NO
	4.91(12.3)	4.93(11.8)	691	(-0.5)	(-4.1)	(0.68)	(5.7)	(0.41)	YES
	4.35(44.7)	4.36(43.7)	1664	(-1.0)	(-2.2)	(1.85)	(4.2)	(0.82)	YES
Conductivity (µS/cm)	7.25	6.97	500	-0.28	-3.9	0.12	1.7	0.06	YES
	7.11	7.15	385	0.04	0.6	0.11	1.5	0.07	NO
	26.9	26.8	885	-0.10	-0.4	0.17	0.6	0.08	YES

Notes:^a The first two sets of values for each parameter are for the 25th percentile solutions. ^b The second set of values for each parameter is for the 75th percentile solution.
^c Critical concentration values in parentheses are provided for information as the method is accurate to 0.01. ^d The pH data in parentheses are in microequivalents.
 See Appendix A for definitions of and formulas for Bias, Standard Deviation, Precision, and Critical Concentration.

IV. WEEKLY QUALITY CONTROL/QUALITY ASSURANCE PROCEDURES

There are three key quality assurance activities that occur on a weekly basis: a set of three internal blind solutions is submitted to the laboratory; two percent of all samples are split for duplicate analysis; and 17 blanks and container leachates are collected and analyzed to assess the contributions from the DI water, sample collection buckets, shipping bottles, filters, and smaller storage bottles to the sample chemistry.

A. Internal Blind Audit

Each week the QA specialist submits three samples to the sample processing staff for inclusion in the set of sequentially numbered samples for analysis. These three samples are given the site designations SWS1, SWS2, and SWS3. The samples corresponding to SWS1 are two different concentrations of simulated rainwater formulated by High Purity Standards in Charleston, South Carolina. SWS2 samples may be either DI water from the ion chromatography laboratory or the pH 4.3 check solution (pH 4.3 nitric acid). While samples from these two sources are not filtered at any time, the samples from SWS3 are filtered after pH and conductance, as are network samples. SWS3 samples are the four solutions used for SWS1 and SWS2, submitted in rotation. The internal blind audit provides an estimate of the effects of filtration as well as an additional way to assess bias and precision.

Tables IV1-IV4 summarize the results of the internal blind audit. Table IV-1 shows that the percent biases for several parameters in the commercially prepared simulated rainwater are larger than for the QCS and that the precision is not as good. However, the values for both statistics are within the specifications of the QA Plan. The reader should recall that QCS are known to the analyst, are measured immediately after calibration and repeatedly throughout the sample run, and that there are usually 50 times more of those measurements made than internal blind measurements

The summary of data from the analysis of DI water and pH 4.3 nitric acid indicates that blank solutions give results that are at or near detection levels of analytes when analyzed at random. These results indicate that the measurements are not contaminated by carryover from previous samples and that measurements near the blank standard are consistent. The excessively high values of percent bias and precision for detected ions are due to the method of calculation, which sets numbers less than the MDL equal to one half of the MDL.

SWS3 sample results indicate that contamination and variability are introduced when samples are filtered. They also show that calcium and sodium concentrations increase while sulfate and nitrate concentrations decrease. The standard deviations indicate that variability increases with filtration and the filtered blank solutions (Table IV-4) confirm the persistence of sodium. Tables B-1 and B-2 and the control chart figures in Appendix B are tabular and graphic representations, respectively, of the filtered and unfiltered ion concentrations in the High Purity Standards simulated rainwater I and II.

TABLE IV-1 Analytical Bias and Precision Determined from Analysts of Internal Blind Audit Samples (SVYSI), High Purity Standards Simulated Rainwater I (HPS-SRI) and II (HPS-SRII), Unfiltered, 1994

Parameter	Target Concentration (mg/L)	Measured Concentration (mg/L)	No. Replicates	Bias (mg/L)	Bias (%)	Precisions (mg/L)	Precision RSD (%)
Calcium	0.015 ^a	0.017	26	0.002	13.3	0.003	17.6
	0.052 ^b	0.056	26	0.004	7.7	0.006	10.7
Magnesium	0.028	0.029	26	0.001	3.6	0.001	3.4
	0.063	0.060	26	-0.003	-4.8	0.002	3.3
Sodium	0.200	0.205	26	0.005	2.5	0.005	2.4
	0.430	0.446	26	0.016	5.3	0.012	2.7
Potassium	0.050	0.052	26	0.002	4.0	0.003	5.8
	0.100	0.110	26	0.010	10.0	0.003	2.7
Ammonium	0.10 ^c	0.11	26	0.01	10.0	0.01	9.1
	1.00	0.96	26	-0.04	-4.0	0.03	3.1
Sulfate	2.70	2.60	26	-0.10	-3.7	0.06	2.3
	10.10	10.34	26	0.24	2.4	0.31	3.0
Nitrate	0.50	0.54	26	0.04	8.0	0.02	3.7
	7.30	7.39	26	0.09	1.2	0.24	3.2
Chloride	0.25	0.23	26	-0.02	-8.0	0.01	4.3
	0.98	0.97	26	-0.01	-1.0	0.04	4.1
pH (units) µeq/L	(4.28) ^d 52.48	(4.30)50.14	26	-2.34	-4.5	1.35	2.7
	(3.57) 269.2	(3.60)251.1	26	-18.1	-6.7	7.8	3.1
Conductivity µS/cm	25.0	25.3	26	0.3	1.2	0.6	2.4
	127.0	128.1	26	1.1	0.9	1.6	1.2

Notes: ^aThe first set of values for each parameter is for HPS-SR-I . ^b The second set of values for each parameter is for HPS-SR-II. ^cAmmonium values are for information only, since ammonium in these standards has been found to be unstable. ^d The pH data in parentheses are pH units, which have been converted to microequivalents per liter for calculations.

**TABLE IV-2 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS2),
Deionized (DI) Water and pH 4.3 QCS, Unfiltered, 1994**

Parameter	Target Concentration (mg/L)	Measured Concentration (mg/L)	No. Repli- cates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)
Calcium	<0.009 ^a <0.009 ^b	<0.009 <0.009	26 26				
Magnesium	<0.003 <0.003	<0.003 <0.003	26 26				
Sodium	<0.003 <0.003	<0.003 0.006	26 26	0.004 ^c	200	0.006	100
Potassium	<0.003 <0.003	<0.003 <0.003	26 26				
Ammonium	<0.02 <0.02	<0.02 0.02	26 26	0.01	100	0.04	200
Sulfate	<0.03 <0.03	<0.03 0.03	26 26	0.01	50.0	0.07	233
Nitrate	<0.03 3.12	<0.03 3.30	26 26	0.18	5.8	0.07	2.1
Chloride	<0.03 <0.03	<0.03 <0.03	26 26				
pH (units) µeq/L	(5.72) ^d 1.91 (4.30)50.12	(5.56) 2.76 (4.30) 49.6	26 26	0.85 -0.52	44.5 -1.0	0.52 2.03	18.8 4.1
Conductivity (µS/cm)	0.7 21.8	1.2 22.3	26 26	0.5 0.5	71.4 2.3	0.4 0.8	33.3 3.6
<p align="center">Notes: ^a The first set of values for each parameter is for DI water ^b The second set of values for each parameter if for pH 4.3 QCS, ^c For calculations, MDLs are given the value of 0.5(MDL). ^dThe pH data in parentheses are pH units, which have been converted to microequivalents per liter for calculations.</p>							

**TABLE IV-3 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS3),
High Purity Standards Simulated Rainwater I (HPS-SRI) and II (HPS-SRII), Filtered, 1994**

Parameter	Target Concentration (mg/L)	Measured Concentration (mg/L)	No. Repli- cates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)
Calcium	0.015 ^a	0.024	12	0.009	60.0	0.006	25.0
	0.052 ^b	0.066	11	0.014	26.9	0.007	10.6
Magnesium	0.028	0.030	12	0.002	7.1	0.003	10.0
	0.063	0.063	11	0.000	0.0	0.003	4.8
Sodium	0.200	0.254	12	0.054	27.0	0.022	8.7
	0.430	0.492	11	0.062	14.4	0.030	6.1
Potassium	0.050	0.050	12	0.000	0.0	0.007	14.0
	0.100	0.101	11	0.001	1.0	0.005	5.0
Ammonium	0.10 ^c	0.15	12	0.05	50.0	0.05	33.3
	1.00	0.96	11	-0.04	-4.0	0.03	3.1
Sulfate	2.70	2.49	12	-0.21	-7.8	0.09	3.6
	10.10	9.86	11	-0.24	-2.4	0.33	3.3
Nitrate	0.50	0.59	12	0.09	18.0	0.04	6.8
	7.30	7.13	11	-0.17	-2.3	0.27	3.8
Chloride	0.25	0.28	12	0.03	12.0	0.04	14.3
	0.98	0.99	11	0.01	1.0	0.04	4.0
pH (units) µeq/L	(4.28) ^d 52.5	(4.30) 49.6	12	-2.9	-5.5	3.17	6.4
	(3.57) 269.2	(3.60) 253.4	11	-15.8	-5.8	7.14	2.8
Conductivity µS/cm	25.0	25.3	12	0.3	1.2	0.4	1.6
	127.0	128.0	11	1.0	0.8	1.0	0.8

Notes:^a The first set of values for each parameter is for HPS-SRI.^b The second set of values for each parameter is for HPS-SRII.
^c Ammonium values are for information only, since ammonium in these standards has been found *to be unstable*.^d The pH data in parentheses are pH units, which have been converted to microequivalents per liter for calculations.

TABLE IV-4 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS3), Delonized (DI) Water and PH 4.3 QCS, Filtered, 1994							
Parameter	Target Concentration (mg/L)	Measured Concentration (mg/L)	No. Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)
Calcium	<0.009 ^a	<0.009	13	0.005 ^c	100	0.011	110
	<0.009 ^b	0.010	12				
Magnesium	<0.003	<0.003	13				
	<0.003	<0.003	12				
Sodium	<0.003	0.060	13	0.058	2900	0.050	83.3
	<0.003	0.043	12	0.041	2050	0.027	62.8
Potassium	<0.003	<0.003	13				
	<0.003	<0.003	12				
Ammonium	<0.02	0.04	13	0.03	300	0.04	100
	<0.03	0.05	12	0.04	400	0.03	60.0
Sulfate	<0.03	<0.03	13				
	<0.03	<0.03	12				
Nitrate	<0.03	0.03	13	0.12	3.8	0.04	12
	3.12	3.24	12				
Chloride	<0.03	0.06	13	0.04	200	0.05	83.3
	<0.03	0.04	12	0.02	100	0.03	75.0
pH (units) µeq/L	(5.72) ^d 1.91	(5.51)3.11	13	1.20	63.2	0.42	13.5
	(4.30)50.12	(4.31)48.8	12	-1.29	-2.6	1.95	4.0
Conductivity (µS/cm)	0.7	1.1	13	0.4	57.1	0.2	18.2
	21.8	22.0	12	0.2	0.9	0.4	1.8

Notes: * The first set of values for each parameter is for DI water. ^b The second set of values for each parameter is for pH 4.3 QCS.
* For calculations, MDLs are given the value of 0.5(MDL). ^dThe pH data in parentheses are pH units, which have been converted to microequivalents per liter for calculations.

B. Replicate Samples

Two percent of all weekly samples, designated by the sample processing technician, are split for duplicate analysis. These samples are then divided into three 60-mL portions at the time of filtration. The first portion is analyzed in the weekly scheme, the second is stored for archival purposes, and the third is sent back to sample processing, given a later number, and resubmitted for analysis. The first and third portions may be analyzed on the same day or on different days, depending on the location of the duplicate in the sample queue. After analysis, the data management staff recodes the third portion with the original number (S) followed by a "Q"(quality control) modifier. The samples then appear consecutively on the bimonthly printout.

The analyses of replicate samples performed in 1994 are summarized in Table IV-5. Differences are obtained by subtracting the reanalysis value from the original. The annual summaries for each ion have been split into two sections. The median concentration for the year is determined for each analyte (Table B-3). The box plots (Figures B-21-B-23) are constructed to show differences for the lower concentrations, from zero to the median, and the higher concentrations, from the median to the highest concentrations. The standard deviation estimated from duplicate measurements, defined in the glossary (Appendix A), has been used to calculate the standard deviations for three categories: concentrations below the ion median concentration, concentrations above the median concentration, and the entire population. The fourth column of Table IV-5 shows a nonparametric estimator of variance from duplicate determinations, where 1.048328 times the Median Absolute Difference (MAD) is the estimator of the standard deviation of the 1994 duplicate data set.

With the exception of the above median concentrations of calcium, potassium, and ammonium, the standard deviations are similar to those of the QCS and SWS1 samples. Box plots are used to graphically represent the replicate sample differences in Appendix B.

Table IV-5 Variance Estimated from Analysis of Replicate Network Precipitation Samples, 1994				
Parameter	Standard Deviation Estimated from Paired Measurements^a			(1.048328) x MAD^b (Total)
	(Low Conc.)	(High Conc.)	(Total)	
Calcium	0.003	0.017	0.013	0.003
Magnesium	0.001	0.001	0.001	0.001
Sodium	0.001	0.006	0.004	0.002
Potassium	0.001	0.014	0.010	0.002
Ammonium	0.01	0.10	0.07	0.01
Sulfate	0.01	0.04	0.03	0.01
Nitrate	0.02	0.02	0.03	0.01
Chloride	0.00(5)	0.05	0.03	0.01
Phosphate	0.0	0.007	0.005	0.0
H+(µeq/mL)	0.51	2.07	1.55	0.58
Conductivity (µS/cm)	0.35	0.60	0.55	0.31
Number of Pairs	73	73	146	146

Notes:^a Defined in glossary with equation ^b MAD=Median Absolute Difference

C. Blanks

Each week a set of blanks is prepared and analyzed. In 1994 DI water was collected from the Sample Processing Laboratory, the Atomic Absorption Laboratory, and the Service Laboratory where collection buckets and shipping bottles are washed. Filters were rinsed with 300 mL of DI water and then two consecutive 50-mL portions of DI water or simulated rain QCS were filtered and collected. Collection buckets were leached with 50 and 150 mL of the same two solutions for five to seven days, instead of overnight as was done in the past. Bottles used for shipping samples back to the laboratory and snap-on bucket fids were leached with the same size aliquots of the same solutions. Smaller bottles used for AIRMoN sample shipping were leached for a week once a month with 50 and 150 mL of the simulated rain. AIRMoN field blanks are also included in this section in spite of their monthly occurrence.

1. Deionized Water Blanks

DI water is monitored daily for resistance at its centralized source in the laboratory building. Once a week 50 to 60 mL of DI water are collected in 60-mL HDPE bottles from three laboratories for complete analysis. In 1994, as in recent years, there were no median ion concentrations exceeding the detection limit. Table IV-6 summarizes the pH and conductance of DI water from the three laboratories. The median pH values are lower than those from the same sources in 1993. The conductivities are statistically the same.

	Sample Processing Laboratory (209)	Atomic Absorption Laboratory (304)	Service Laboratory (323)
pH (units)	5.66	5.72	5.68
Conductivity ($\mu\text{S}/\text{cm}$)	0.8	0.7	0.7
Number of weeks	50	50	50

2. Filter Blanks

After pH and conductivity have been measured, Millipore™ type HAWP, 0.45-micrometer (μm) filters are used to filter all samples with volumes greater than 35 mL. Samples are poured from the shipping bottles into the filtering apparatus, and the filtrate is collected in smaller 60-mL HDPE bottles. To quantify the contribution of the filters to the sample chemistry, a series of filtrates is collected weekly and analyzed. After the initial 300-mL DI water rinse of the filter, 50 mL of DI water are filtered and collected as sample "A". Then a second 50-mL portion of DI water is passed through the same filter and designated as sample "B". The procedure is repeated with another filter and simulated rain (FR25), which is filtered in two 50-mL portions that are also collected as samples "A" and "B". Table IV-7 shows the median concentration values for the filtered solutions. The individual ion concentrations are of particular interest since pH and conductance measurements are performed on unfiltered samples, except when samples have to be reanalyzed.

TABLE IV-7 Median Analyte Concentrations Found in Weekly Deionized (DI) Water and Simulated Rain 25 (FR25) Filter Leachates, 1994				
Analyte	DI Water A^a	DI Water B^b	FR25^c A^a	FR25^c B^b
Calcium	<0.009	<0.009	0.073	0.075
Magnesium	<0.003	<0.003	0.017	0.017
Sodium	0.024	0.005	0.077	0.053
Potassium	<0.003	<0.003	0.014	0.015
Ammonium	<0.02	<0.02	0.10	0.09
Sulfate	<0.03	<0.03	0.60	0.61
Nitrate	0.04	<0.03	0.50	0.49
Chloride	<0.03	<0.03	0.15	0.14
pH	5.62	5.63	4.96	4.94
Conductivity	1.2	1.0	6.9	7.0
Number of weeks	49	49	49	49
<p>Notes: ^a First 50-mL filtrate after 300-mL DI water rinse. ^b Second consecutive 50-mL filtrate after 300-mL DI water filter rinse. ^c FR25 concentrations (mg/L): Ca =0.075, Mg =0.016, Na =0.053, K=0.016, NH₄=0.10, SO₄ = 0.62, NO₃= 0.49, Cl =0.13, pH (units)=4.91, Conductivity (μS/cm) = 7.11.</p>				

While increased sodium concentrations noted in the filtered blind solutions are apparent in the filter blanks, the filter contribution is not as consistent nor as high. Table B-4 in Appendix B shows that there are detectable/excess sodium concentrations in 98 percent of both of the A portions of filtrate. The B portions exhibit lower concentrations and fewer samples with sodium in excess of the control limits of the simulated rain solution. A corresponding chloride concentration difference is not noted, possibly due to the difference in sensitivities of the instrumentation measuring cations and anions. A small increase in nitrate is indicated in the DI water sample, and this amount is present in 69 percent of the A samples. Twenty-four percent of the FR25 A samples exceed the control limits for nitrate for the solution. The reduction in sulfate, noted for years in the filtered blind solutions (Tables IV-1 and IV-3), is not apparent in these filtered FR25 samples.

3. Bucket Blanks

HDPE buckets with a capacity of 13 liters have been used in the wet/dry sampler as collection vessels since the network began. In order to evaluate the bucket contribution to sample chemistry, a series of internal special studies and the USGS blind audit have continued for most of the project. On the basis of the data accumulated in the past and an intense special study conducted in 1993 and 1994, it was decided that while buckets would continue to serve as the sample collection containers, a portion of the sample would be decanted into a 1-liter wide mouth HDPE bottle for shipping. Analytical data demonstrated that the lids used to seal the sample in the buckets contributed noticeably to the chemistry of low-volume samples. The 1994 blanks protocol was modified so that only upright buckets are leached with DI water and FR25, and the time period for the evaluation was changed from overnight to five to seven days to better simulate the time a sample can be in the bucket on the sampler. Both 50 and 150 mL portions of the two solutions are used.

The data summarized in Table IV-8 show that there is a slight contribution of sodium and potassium from the bucket, as well as a slight increase in pH with a corresponding slight decrease in conductivity. Tables B-4 and B-5 show that concentrations greater than detection are present in a significant percentage of the bucket blanks for calcium in the 50- mL leachate, sodium in both DI water portions and the 50-mL FR25 portion, potassium in the DI water portions and 50 mL-FR25 portion and chloride in the 50-mL DI water portion.

4. Bottle Blanks

Since January 11, 1994, site operators have been instructed to pour the samples from the collection bucket into a 1-liter wide-mouth HDPE bottle at the site laboratory. The site chemistry is then performed on aliquots poured from the bottle, and the remaining sample is shipped to the CAL in the bottle. Precipitation remaining in the bucket is discarded, and the bucket, snap-on lid, and bottled sample are shipped to the CAL in the black shipping box. The FORF has been modified so that the site operator is charged with making more careful observations of the contents of the collection bucket prior to decanting the sample. This information becomes vital to the laboratory for assigning contamination codes since the entire bucket sample is no longer available. In an effort to evaluate the contribution, if any, of the 1-liter bottles to the sample chemistry, these containers were added to the blanks scheme in 1994.

DI water and simulated rain were poured in 50- and 150-mL portions into bottles that were selected randomly from among bottles that had been washed and rinsed with DI water. The solutions remained in the bottles for one to four days, were poured into 60-mL bottles that have been rinsed with DI water, and sent to the laboratory for analysis. These data are

summarized in Table IV-9 and indicate that the bottles do not contribute to the sample chemistry. Tables B-4 and B-5 in Appendix B show that very few of the bottles' leachates had concentrations in excess of the detection limit.

TABLE IV-8 Median Measured Mass as Micrograms (µg)/Bucket^a Found in Weekly Deionized (DI) Water and Simulated Rain 25 (FR25) Upright Bucket Leachates, 1994				
Analyte	DI Water (50 mL)	DI Water (150 mL)	FR25 (50 mL)^b	FR25 (150 mL)^b
Calcium	0.500	<0.675	0.450	0.900
Magnesium	<0.075	<0.225	0.150	0.300
Sodium	0.650	0.600	0.500	0.300
Potassium	0.450	0.600	0.500	0.750
Ammonium	<0.50	<1.50	<0.50	<1.50
Sulfate	<0.75	<2.25	<0.75	<2.25
Nitrate	<0.75	<2.25	<0.75	<2.25
Chloride	1.50	<2.25	1.50	1.50
pH (units)	5.61	5.60	5.07(4.91) ^c	4.99(4.91) ^c
[H⁺](µeq/bucket)	0.122	0.375	0.425(0.615) ^c	1.53(1.84) ^c
Conductivity (µS/cm)	1.5	1.4	6.4(7.1) ^c	6.7(7.1) ^c
Number of weeks	50	50	50	50
<p>Notes: a Mass/bucket represents the concentration in µg/mL x 50 or 150 mL. Detection limit values are expressed as the MDL(in µg/mL)/2 x 50 or 150 mL b FR25 leachate measured mass = (median concentration measuredJ in upright bucket leachates - target FR25 concentration) x 50 or 150 mL c Values in parentheses () represent target values for FR25 with no bucket contact</p>				

**TABLE IV—9 Median Measured Mass as Micrograms (μg)/ Bottle^a Found
in Weekly Deionized (DI) Water and Simulated Rain 25 (FR25)
HDPE 1-Liter Bottle Leachates, 1994**

Analyte	DI Water (50 mL)	DI Water (150 mL)	FR25 (50 mL) ^b	FR25 (150 mL) ^b
Calcium	<0.225	<0.675	<0.225	<0.675
Magnesium	<0.075	<0.225	<0.075	0.150
Sodium	<0.075	<0.225	<0.075	<0.225
Potassium	<0.075	<0.225	<0.075	<0.225
Ammonium	<0.50	<1.5	<0.50	<1.5
Sulfate	<0.75	<2.25	<0.75	<2.25
Nitrate	<0.75	<2.25	<0.75	<2.25
Chloride	<0.75	<2.25	<0.75	<2.25
pH (units) [H ⁺]($\mu\text{eq}/\text{bottle}$)	5.53 0.148	5.55 0.423	4.93 (4.91) ^c 0.585 (0.615) ^c	4.93 (4.91) ^c 1.76(1.84) ^c
Conductivity ($\mu\text{S}/\text{cm}$)	13	13	7.0(7.11) ^c	7.1 (7.11) ^c
Number of weeks	50	50	50	50
<p>Notes:^a Mass/bottle represents the concentration in $\mu\text{g}/\text{mL} \times 50$ or 150 mL. Detection limit values are expressed as the MDL(in $\mu\text{g}/\text{mL}$)/2 $\times 50$ or 150 mL</p> <p>^b FR25 leachate measured mass = (median concentration measured in bottle leachates -target FR25 concentration) $\times 50$ or 150 m. Detection values are assigned to negative differences</p> <p>^c Values in parentheses () represent target values for FR25 with no bottle contact</p>				

5. Snap-on Lid Blanks

Site operators have been instructed to use snap-on lids for the sample collection buckets when transporting the sample from the collector to the site laboratory. In order to obtain lid leachates at the CAL, the lids are placed with the top surface on the laboratory

counter, 50-mL aliquots of DI water or FR25 are measured into them, and large plastic covers are placed over them for 24 hours. These solutions are then poured into the 60-mL bottles and included with the blanks for analysis. The DI water solution results show slight sodium contamination and increased ammonium. The FR25 results show elevated calcium and ammonium (the same amount as in the DI water) and reduced nitrate amounts. Tables B-4 and B-5 show that the ammonium concentrations exceed the MDLs in more than 80 percent of both solutions' samples and sodium exceeds the MDL in greater than half of the DI water samples. The FR25 solutions contain altered concentrations of calcium, sulfate, and nitrate in more than 50 percent of the samples. Table IV-10 summarizes these data. It is important to note that these results represent an extreme case in which very small amounts of these solutions are in constant contact with the lid surface for an extended period of time. One assumes that the actual sample traveling from the collector to the laboratory has little contact with the lid, and if it does, its volume is large enough to be unaffected.

TABLE IV-10 Median Analyte Concentrations (in mg/L) Found in Deionized (DI) Water and Simulated Rain 25 (FR25) Snap-on Lid Leachates, 1994		
Analyte	50 mL DI water	50 mL FR25^a
Calcium	<0.009	0.086 (0.075)*
Magnesium	<0.003	0.019 (0.016)
Sodium	0.004	0.057 (0.053)
Potassium	<0.003	0.019 (0.016)
Ammonium	0.09	0.20(0.10)*
Sulfate	<0.03	0.69 (0.62)
Nitrate	<0.03	0.55 (0.49)*
Chloride	<0.03	0.15(0.13)
pH (units)	5.61	4.97 (4.91)
Conductivity (μS/cm)	1.9	7.7(7.11)
Number of lids	49	49
<p>Notes: a Target concentrations given in parentheses (). * indicates that leachate concentration is beyond QCS control limits.</p>		

6. AIRMoN Bottles

The AIRMoN site operators collect samples in 13 liter buckets and pour them into 250-mL wide-mouth HDPE bottles for shipment to the CAL. Randomly selected 250-mL bottles are leached once a month with 50- and 150-mL aliquots of FR25. The summarized data displayed in Table IV-11 indicate that the bottles do not contribute to the chemistry of the sample.

TABLE IV-11 Median Analyte Concentrations Found in Monthly Simulated Rain (FR25) AIRMoN 250-mL HDPE Bottle Leachates, 1994		
Analyte (mg/L)	50 mL FR25^a	150 mL FR25^a
Calcium	0.074	0.074
Magnesium	0.016	0.016
Sodium	0.051	0.050
Potassium	0.015	0.015
Ammonium	0.08	0.09
Sulfate	0.61	0.61
Nitrate	0.49	0.48
Chloride	0.13	0.13
pH (units)	4.94	4.94
Conductivity (µS/cm)	7.1	7.0
Number of bottles	7	7
<p>Notes: FR25 Target Concentrations (mg /L):Ca=0.075, Mg = 0.016, Na = 0.053, K = 0.016, NH₄=0.10, SO₄=0.62, N O₃ = 0.49. Cl=0.13, pH = 4.91 units, Conductivity = 7.11 µS/ cm</p>		

7. AIRMoN Field Blanks

AIRMoN field blanks are collected monthly, as are AIRMoN bottle blanks. They are obtained on the first Tuesday of the month when there has been no precipitation and fewer than six lid openings since the last bucket change. The bucket is removed from the collector and approximately 125 mL of solution from a bottle sent by the CAL are poured into the bucket which is then covered with a snap-on lid. The bottle is recapped and taken, with the bucket, back to the field laboratory. The sample remaining in the bottle is given a "DK" designation. The bucket containing the CAL solution is agitated and then allowed to stand overnight or at least two hours. pH and conductivity measurements of the bucket solution are made, the solution is poured into a 250 mL bottle and it is shipped to the CAL along with the "DK" sample.. The sample from the bucket is given a "DF" designation and treated as a valid precipitation sample. Both samples undergo a complete chemical analysis at the CAL.

Five different solutions were used in the AIRMoN field blank program in 1994: pH 4.3 nitric acid (the same solution used as a check sample for NADP/NTN field sites), pH 4.9 nitric acid solution containing sodium chloride so that the conductance is approximately 14 $\mu\text{S}/\text{cm}$, deionized water, and simulated rain whose concentrations approximate the 25th (FR25) and 75th (FR75) percentile concentrations of precipitation samples of the NADP/NTN network. These solutions and concentrations were chosen because their pH and conductance are similar to those of precipitation samples. Both the site personnel and the analysts knew that these solutions were field blanks for evaluating effects of the collection bucket, shipping bottle, and handling on the sample's integrity.

The results summarized in Table IV-12 show that when the concentrations of analytes in the bottled solution are subtracted from those found in the bucket, the differences are not chemically significant and are highly variable. There are small positive differences for most analytes, but the standard deviations are so high that it is impossible to conclude that AIRMoN samples are affected by the collection bucket or by packaging/shipment after their removal from the wet-dry collector.

TABLE IV-12 AIRMoN Field Blanks Mean Differences of Bucket Minus Bottle (DF-DK) and Standard Deviations, 1994

Solution	SO₄	NO₃	Cl	NH₄	PO₄	Ca	Mg	Na	K	Cond.	pH	n
DI Water	0.012 ^a 0.012 ^b	0.016 0.010	0.002 0.011	0.004 0.008	0.001 0.003	0.010 0.011	0.002 0.003	0.003 0.002	0.002 0.001	0.46 0.63	-0.05 0.14	10
pH 4.3 HNO₃	0.038 0.114	0.046 0.073	0.014 0.020	0.009 0.021	0.000 0.005	0.016 0.020	0.002 0.002	0.006 0.009	0.005 0.007	0.06 0.97	0.010 .02	68
pH 4.9 QCS	0.105 0.210	0.065 0.048	0.008 0.049	0.010 0.014	-0.001 0.002	0.024 0.040	0.004 0.006	0.094 0.171	0.005 0.003	0.88 1.28	-0.01 0.06	4
FR25	0.024 0.011	0.042 0.043	0.011 0.016	0.025 0.038	0.002 0.003	0.014 0.038	0.002 0.005	0.006 0.004	0.004 0.005	0.48 0.90	0.01 0.10	17
FR75	0.036 0.032	0.048 0.042	0.017 0.012	0.016 0.016	-0.001 0.003	0.019 0.038	0.002 0.002	0.006 0.006	0.002 0.002	-0.23 0.88	0.01 0.01	10

Notes; ^a The first set of values for each parameter for each solution are the mean differences. ^b The second set of values for each parameter for each solution are standard deviations. Solutions are shipped to AIRMoN sites in Bottles from the CAL, 125 mL are poured into the collection bucket (DF) and the remaining aliquot is returned in the original bottle (DK). "DF"s follow sample protocol. Returned samples undergo complete chemical analysis.

V. MONTHLY QUALITY ASSURANCE PROCEDURES

Several QA activities occur at monthly or bimonthly intervals. Each time a QCS is measured during the analysis of precipitation samples, the value is recorded, entered and stored in a computer file. At the end of each month the values are used to plot control charts for each analyte. These charts, which present a graphical representation of the QCS analyses as well as the monthly mean and standard deviation values, are evaluated and then stored in a notebook in the QA Specialist's office as an historical record of daily analytical results.

Sample collection sites receive monthly printouts from the CAL's data management group that contain information about the samples submitted as well as draft results of their chemical analysis. The QA Specialist receives three of these printouts, one for each of the internal blind sites (SWS1, SWS2, and SWS3). These summaries present the analyses of the internal blind samples in an immediate format so that questionable analytical results may be addressed in a timely manner. Additionally bimonthly computer printouts summarize the results of all the samples analyzed in a two-week period, roughly 400 to 500 samples. From these chemical data, a list of samples to be reanalyzed is generated based on analyses that were flagged according to the reanalysis criteria described below. Additionally, results of analyses of the samples sent to the CAL from the USGS as part of the official External Audit Interlaboratory Comparison are evaluated by the QA Specialist prior to the data being released.

A. Reanalysis Procedures

Each month the CAL data management staff generate two computer printouts that contain the analytical results from the most recently analyzed 900 to 1000 samples. The computer program contains an algorithm that identifies samples for reanalysis. Samples are flagged for either an anion/cation imbalance or for differences between the measured and calculated specific conductance. The algorithm used in 1994 has been in use since 1987.

All samples selected are completely reanalyzed, provided that sufficient volume remains and the sample is not physically or chemically contaminated. A list of random numbers is also compiled by the computer and samples corresponding to one percent of the total are chosen for reanalysis from this list. The flagged samples are retrieved from storage, and assembled on a separate tray. A list of samples is sent to the laboratory with a due date for the reanalysis. The analysts return the analysis data with their observations and/or explanations when there is a large discrepancy between the original and reanalysis value. If there is an archival sample, it is also analyzed to settle differences. If no justification can be found to change analytical values, the original data are maintained. For all samples reanalyzed, the original, the reanalysis, and the corrected final data are all maintained in the computerized data base.

1. Ion Percent Difference (IPD)

Ion concentrations measured in milligrams per liter (mg/L) are converted to microequivalents per liter ($\mu\text{eq/L}$) by multiplying them by the factors listed in Table V-1. Measured ion values, pH, and calculated values for bicarbonate and hydroxide are all used in the ion percent difference calculation. The ion sum (IS) is equal to the sum of the measured cations, measured anions, and calculated anions. The IPD is calculated as follows:

$$\text{IPD} = \frac{\text{Anion sum} - \text{Cation sum}}{\text{Anion sum} + \text{Cation sum}} \times 100$$

Cation sum = $[\text{IT}] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+]$ expressed as $\mu\text{eq/L}$

Anion sum = $[\text{HCO}_3^-] + [\text{Off}] + [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{PO}_4^{3-}]$ expressed as $\mu\text{eq/L}$

Samples are flagged for IPD reanalysis if:

$$\begin{array}{lll} \text{IS} < 50 \text{ ueq/L} & \text{and} & \text{IPD} > \pm 60\% \\ 50 \leq \text{IS} < 100 \text{ } \mu\text{eq/L} & \text{and} & \text{IPD} > \pm 30\% \\ \text{IS} \geq 100 \text{ } \mu\text{eq/L} & \text{and} & \text{IPD} > \pm 15\% \end{array}$$

2. Conductance Percent Difference (CPD)

Conductance percent difference (CPD) is an operation performed to compare the calculated and measured conductivities. The ion concentrations, expressed as $\mu\text{eq/L}$ (as they are for the ion balance calculations), are multiplied again by the conductance conversion factors listed in the third column of Table V-1. These values are then added and the total divided by 1000. This quotient is then compared to the conductance measured in the laboratory.

Calculated conductance = $(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+ + \text{NH}_4^+ + \text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^- + \text{PO}_4^{3-} + \text{H}^+ \text{HCO}_3^- + \text{OH}^-) 1000$ expressed as equivalent conductance. The CPD is calculated as

$$\text{CPD} = \frac{\text{Calculated conductance} - \text{measured conductance}}{\text{Measured conductance}} \times 100$$

Samples are flagged for CPD reanalysis if $10\% < \text{CPD} < -40\%$.

3. IPD and CPD Histograms

In 1994, 447 samples were selected from the 11,204 samples analyzed. Of those, 6908 contained sufficient volume to be classified as wet (W) and therefore be eligible for the reanalysis program. The samples selected represent 3.99 percent of the total and 6.47 percent

of the W samples. There were 133 data changes to 79 of the 447 samples reanalyzed. Figures V-1 and V-2 are histograms of the IPD and CPD values, respectively, for samples whose volume exceeds 35 mL. The mean, standard deviation, median, and number of wet samples are presented on each figure.

The IPD histogram exhibits a negative skew for the first time since 1983 when it was only slightly skewed in that direction. There was a -2.8 percent mean value for the network in 1978. The mean (-2.96 percent) and median (-1.44 percent) differ from every previous year since the network expanded to include the entire continental United States. Negative skews indicate a cation excess. The CPD histogram continues to exhibit a negative skew as it has since 1979. The mean CPD value for 1994 is -6.27 percent and the median -5.52 percent. The mean is higher than 14 previous years and the median is similar to 1993. One expects these values to be negative as a negative skew is indicative of a measured conductance higher than the calculated conductance. The ions included in the calculated conductance do not always represent all species present.

TABLE V-1 Conversion Factors for Reanalysis Calculations		
Analyte	Milligrams/Liter (mg/L) to Microequivalents/L (µeq/L)^a for IPD Multiply by:	Microequivalents/L (µeq/L) to Equivalent Conductance^b for CPD 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
Ortho-phosphate	31.59	69.0
Hydrogen	992.2	350
Bicarbonate	16.39	44.5
Hydroxide	58.8	198
Notes: ^a Standard Methods for the Examination of Water and Wastewater (14)		
^b CRC Handbook of Chemistry and Physics (15)		

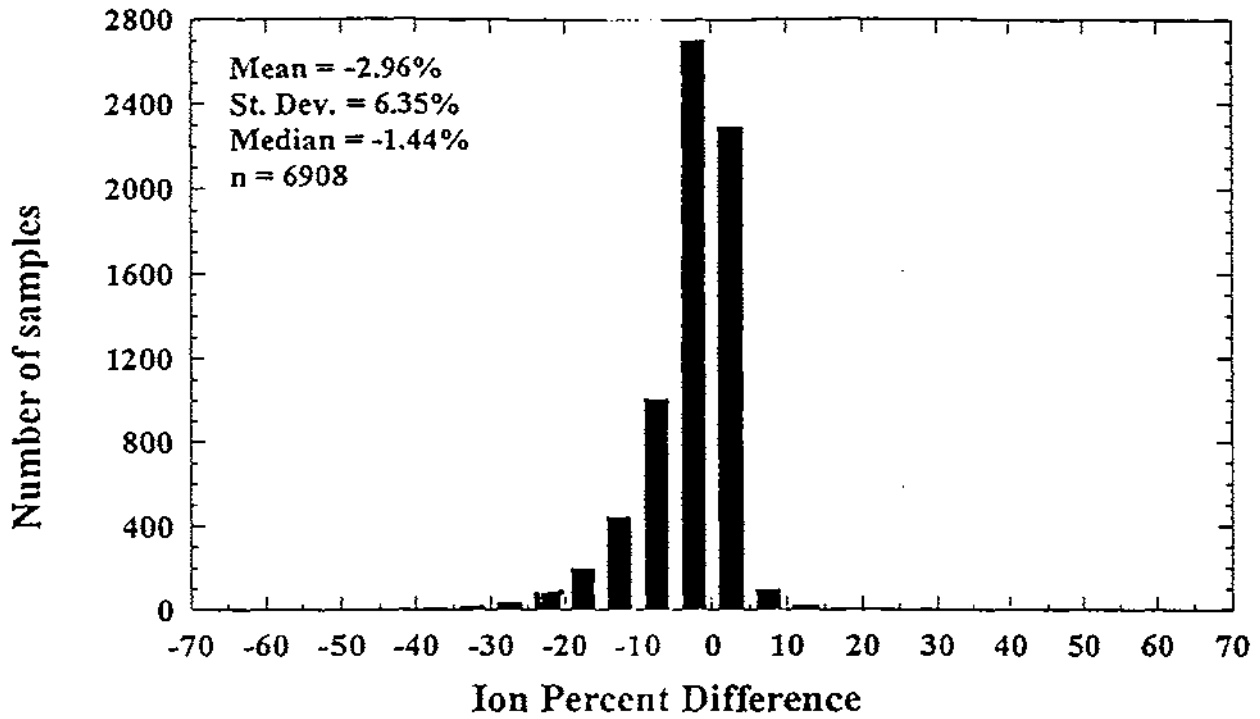


FIGURE V-1. Ion Percent Difference (IPD) histogram for NADP/NTN wet-side samples, 1994.

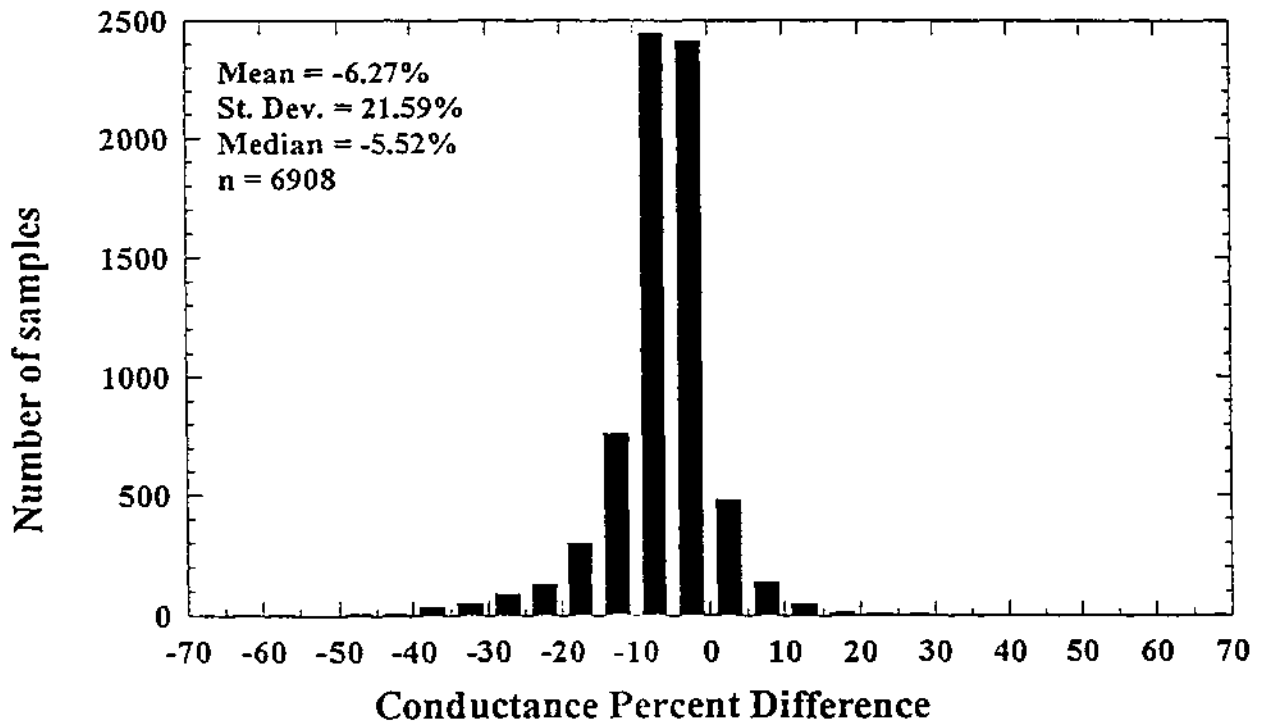


FIGURE V-2 Conductance Percent Difference (CPD) histogram for NADP/NTN wet-side samples, 1994.

B. USGS INTERLABORATORY COMPARISON

The USGS serves as the primary external auditor of the NADP/NTN and the CAL. The interlaboratory comparison, which began in fall 1982, is one of several components of the external audit. The audit is designed to determine whether participating laboratories are producing comparable results. Each month several sets of blind samples of differing matrices are mailed to the participating laboratories for analysis.

In 1994 the interlaboratory comparison program included five laboratories: (1) Illinois State Water Survey (CAL); (2) Environmental Science and Engineering, Gainesville, Florida (ESE); (3) Atmospheric Environment Service, Downsview, Ontario (AES); (4) Ontario Ministry of the Environment, Rexdale Ontario (MOE) and (5) Global Geochemistry Corporation, Canoga Park, California (GGC).

The samples are shipped to the laboratories approximately every two weeks throughout the year; Samples used in 1994 included (1) certified samples (samples prepared and certified by NIST); (2) uncertified synthetic reference samples prepared and bottled by the USGS; (3) natural deposition samples collected at NADP/NTN sites and bottled by the CAL; and (4) ultrapure DI water samples prepared by the USGS. Data reports from the participating laboratories are submitted quarterly to the USGS.

Analyte bias for the participating laboratories is evaluated using NIST standard reference samples with certified analyte concentrations +/- the estimated uncertainty. Each laboratory that participated for the entire year received 18 NIST samples. The median laboratory analysis of each analyte for each certified matrix was compared to the NIST certified values. The CAL reported the six median analyses out of 15 that were outside the range of uncertainty for the NIST samples. The other participating laboratories results ranged from 3 to 7 median analyses out of 15 that were outside the range of uncertainty for the NIST samples. Results of a Friedman test for interlaboratory bias indicate statistically significant ($\alpha = 0.01$) differences in analyte measurements for calcium, magnesium, sodium, ammonium, chloride, nitrate, sulfate, hydrogen ion, and specific conductance between the five laboratories. Laboratory precision was estimated for each analyte by calculating the 50th and 90th percentile of the absolute differences for the results reported for the replicate natural and synthetic wet-deposition samples (Table V-2). Differences were calculated from 90 sample pairs for each laboratory.

Six ultrapure DI water samples were submitted to the laboratories. Values in excess of the minimum reporting limits indicate possible contamination. The CAL reported no analytes above reporting limits for all the DI samples analyzed. The CAL was the only participating laboratory in 1994 that did not report at least one analyte determination above reporting limits for the DI samples.

The final report containing the entire external NADP/NTN results will be available from the USGS in late 1996 and is titled *External Quality-Assurance Results for the National Atmospheric Deposition Program and National Trends Network During 1994 (16)*.

TABLE V-2 50th and 90th Percentile Absolute Differences for Analysis of Replicate Samples Determined by Five Laboratories Participating in the 1994 Interlaboratory Comparison Program

Analyte	CAL		AES		ESE		MOE		GGC	
	50th	90th	50th	90th	50th	90th	50th	90th	50th	90th
Calcium	0.000	0.000	0.000	0.010	0.001	0.004	0.002	0.010	0.002	0.011
Magnesium	0.001	0.001	0.000	0.000	0.000	0.001	0.001	0.005	0.001	0.002
Sodium	0.001	0.004	0.000	0.010	0.003	0.009	0.003	0.007	0.002	0.005
Potassium	0.001	0.009	0.000	0.010	0.001	0.004	0.001	0.022	0.001	0.016
Ammonium	0.000	0.010	0.003	0.015	0.004	0.017	0.001	0.008	0.003	0.010
Sulfate	0.000	0.030	0.010	0.110	0.006	0.020	0.010	0.150	0.014	0.038
Nitrate	0.010	0.020	0.010	0.040	0.004	0.022	0.000	0.027	0.013	0.029
Chloride	0.000	0.010	0.010	0.020	0.003	0.009	0.000	0.030	0.003	0.023
Hydrogen ion	0.23	4.16	0.72	1.76	1.80	8.71	.39	3.58	1.02	5.45
Specific Cond.	0.15	1.20	—	—	0.20	0.80	0.30	1.30	0.12	0.80

VI. SEMIANNUAL AND ANNUAL QUALITY ASSURANCE PROCEDURES

Each year after all of the samples have been entered in the data base, the information from the QA samples is retrieved and summarized for the annual report. The internal blind sample data and the split samples data are retrieved following data verification of all samples analyzed from January through December. The summaries are published in the annual report and are available for users of the NADP/NTN sample data. In addition to the USGS laboratory intercomparison study, the CAL participates in international intercomparison studies throughout the year, which included five studies in 1994: one from the World Meteorological Organization in Geneva, Switzerland, one from the Norwegian Institute for Air Research in Lillestrom, Norway, and three from the National Water Research Institute, Burlington, Ontario, Canada. The data from these studies are presented in Appendix C.

A. World Meteorological Organization (One Study)

The seventeenth analysis of reference precipitation samples was sponsored by the World Meteorological Organization (WMO). For this study, three samples are mailed from the USEPA Atmospheric Research and Exposure Assessment Laboratory in Research Triangle Park (RTP), North Carolina, in July. The samples arrive as concentrates and are diluted according to directions and bottled for submission to the laboratory. The analytical results are mailed back to RTP prior to the due date. WMO sends target values some time after the analytical results have reached RTP. In 1994 the CAL mean percent difference for all ten parameters for the three samples is 2.26 percent, an improvement over results from recent years. The data are presented in Table C-1. The final report for this study was received in September 1995 and contained a graphic overview of the participating laboratories identified by code numbers. All of the CAL results were within the data quality objectives (DQO), many of the other participants exceeded the DQOs for one or more components. The participants were not ranked in this report.

B. Norwegian Institute for Air Research (One Study)

The fourteenth intercomparison of methods within the European Monitoring and Evaluation Programme (EMEP) was conducted by the Norwegian Institute for Air Research in July. Samples for this study are prepared using distilled water and inorganic salts at concentrations similar to precipitation and arrive ready for analysis. The data, presented in Table C-2, show that 90 percent of the CAL values are within five percent of expected concentrations, and the mean absolute percent difference for four samples often parameters each is 2.38 percent.

C. CANADA NATIONAL WATER RESEARCH INSTITUTE (Three Studies)

The Canadian program for Long-Range Transport of Atmospheric Pollutants (LRTAP) began in 1982, and the CAL has been a participant since the fourth study in fall 1983. In 1994 there were three studies: L-35 in March, L-36 in June, and L-37 in October. LRTAP studies include selected major ions, nutrients, and physical parameters in water. Median concentrations are used as target values for flagging results. Most of the samples are surface waters or precipitation, so calculated or certified values are not known. The final score is computed as the sum of the percent biases and the percent of flags assigned; therefore zero denotes the optimum score.

CAL scores for 1994 were 2.13 for L-35 due to high pH in samples 2 and 6; 3.06 for L-36 due again to high pH in samples 1, 7, and 5; and 2.02 for study L-37 due to high and very high pH for samples 5 and 2. The data for these studies are presented in Tables C-3, C-4, and C-5. The rankings are fifth of 48 laboratories (first of those analyzing more than seven parameters) for L-35, second of 50 laboratories (first of those analyzing more than one parameter) for L-36, and fourth of 45 laboratories (first of those analyzing more than nine parameters) for L-37 (17, 18, and 19).

VII. SUMMARY

This report presents the results of the NADP/NTN and AIRMoN QC/QA programs in 1994. These programs are summarized in the order in which they are addressed in the laboratory, using tables, figures, and short verbal explanations. The appendices provide additional information and explanations.

The CAL staff remained unchanged in 1994. There was one analytical method change. Orthophosphate is now determined by the automated colorimetric ascorbic acid reduction method using a flow injection instrument rather than the segmented flow method used prior to ion chromatography. The MDL was lowered from 0.02 to 0.003 mg/L, so there are a few more samples with detectable levels of phosphate.

The CAL formulated simulated rain solutions with concentration values near the 25th and 75th percentile concentration levels of the network wet samples were used again as QCS. The concentrations and identity of these QCS are known to the analysts. They are analyzed immediately after standardization of the instrumentation and thus the bias and precision estimates derived from their analysis are similar from year to year. All of the bias and precision measurements fall within the specifications of the Network QA Plan.

Simulated rainwaters at the concentrations purchased from High Purity Standards of Charleston, South Carolina, serve as two of the internal blind audit solutions, while DI water and pH 4.3 nitric acid are the other two. Data from these solutions provide another estimate of bias and precision. The samples are included in the analysis stream as real precipitation samples and are truly blind to the analysts. The blind audit summaries show that bias and precision estimates although not as good as those from QCS data, are acceptable and within the goals set in the QA Plan. Filtered SWS3 samples show that filtration does slightly alter the chemistries of samples by introducing small increases in calcium and sodium concentrations and causing small decreases in nitrate and sulfate concentrations.

Replicate samples are another method used to assess the precision of the analytical process. Results from the 1994 replicates indicate that the precision of all but the greater than median concentrations of calcium, potassium, and ammonium are as good as those of the QCS and SWS1 blind samples.

In order to quantify the effect of external sources on the concentrations of the ions in the samples, a system of blank solutions is analyzed weekly. The DI water, collected from three of the main laboratories, shows water of excellent quality. The effect of filtration is evaluated by filtering DI water and FR25 QCS in two portions each week. Results show detectable sodium concentrations in 98 percent of the first 50 mL filtered after the initial 300-mL rinse. The sodium contribution noted in the blind program is not as pronounced in the blanks. Twenty-four percent of the FR25 "A" filter samples exceed nitrate concentration

limits. The bucket blank leachates show small amounts of sodium and potassium, raised pH, and lower conductivity. There are small amounts of calcium in the 50-mL leachates. Bottle blanks, which now replace inverted bucket blanks, show that the leachates from the 1-liter bottles used to ship samples back to the CAL are clean and do not contribute to the chemistry of the samples. The snap-on lids used for transporting the sample from the site to the field laboratory show elevated calcium and ammonium concentrations after a week of contact with the leaching solutions. AIRMoN 250-mL bottles are also clean and AIRMoN field blanks show variable and insignificant differences between the samples poured into the collection buckets and those that remained in the shipping bottle.

The sample reanalysis protocol remained as it has been since 1987. In 1994, 447 samples were selected for reanalysis; this represents 6.47 percent of the W samples for which there was enough volume for a total analysis. Although the Ion Percent Difference histogram exhibited a negative skew for the first time since 1983, the Conductance Percent Difference histogram continues to be negative and similar to 1993.

The USGS Interlaboratory Comparison showed that the CAL reported 6 out of 15 median analyses that were outside the range of the NIST samples submitted blind to the laboratory in an effort to evaluate analyte bias. Results of a Friedman test for interlaboratory bias indicate statistically significant differences in analyte measurements for calcium, magnesium, sodium, ammonium, chloride, nitrate, sulfate, hydrogen ion, and specific conductance between the five laboratories. The CAL was the only laboratory reporting no measurable analyte concentrations for the Ultrapure DI water samples.

Five interlaboratory studies conducted by Canada, Norway, and the World Meteorological Organization indicate that CAL results compare favorably to those of its peer laboratories throughout the world.

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		<p>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.</p> <p>Bias = measured value - true value</p>
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 (20).
Critical Concentration		A calculated concentration used to determine whether the measured bias is statistically significant (21).

$$\text{Critical Concentration} = t * s_{sp} * \sqrt{1/n_1 + 1/n_2}$$

Term	Abbreviation	Definition
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where:

$$s_{sp} = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}$$

S_{sp} = pooled standard deviation

S_1 = standard deviation of reference solution measurements

S_2 = standard deviation of daily QCS measurements

n = number of values

t = t statistic at the 95% confidence level and $(n_1 + n_2) - 2$ degrees of freedom

External Blind Sample

A QA sample of known analyte concentrations submitted to the laboratory by an external agency. These samples arrive at the CAL as normal weekly rain samples and undergo routine processing and analysis. The identity of the sample is unknown to the CAL until all analyses are complete. Data are used to assess contamination potential from handling and shipping.

Internal Blind Sample

A QA sample of known analyte concentrations submitted to the laboratory by the QA specialist. The identity of the sample is known to the processing staff only. The analyte concentrations are unknown to the analysts. These data are valuable in assessing bias and precision for network samples.

Term	Abbreviation	Definition
Mean	\bar{x}	The average obtained by dividing a sum by the number of its addends. $x = \sum_{I=1}^n x_i / n$
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 (22).
Percent Bias		The difference between the mean value obtained by repeated analysis of a homogeneous sample and the accepted true value expressed as a percentage of the true value. $\%Bias = 100 * [(V_m - V_t)/V_t]$ <i>where: V_m = measured value V_t = true value</i>
Precision		The degree of agreement of repeated measurements of a homogeneous sample by a specific procedure, expressed in terms of dispersion of the values obtained about the mean value. It is often reported as the sample standard deviation (s).

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

Term	Abbreviation	Definition
Replicates (Splits)		Two aliquots of the same sample treated identically throughout the laboratory analytical procedure. Analyses of laboratory replicates are beneficial when assessing precision associated with laboratory procedures but not with collection and handling. Also referred to as splits.
Sensitivity		The method signal response per unit of analyte.
Standard Deviation	s	The number representing the dispersion of values around their mean.
		$s = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n-1}}$
		where: x_i = each individual value \bar{x} = the mean of all values n = number of values
Standard Deviation Estimated from Paired Measurements		The standard deviation may be estimated from the differences of several sets of paired measurements using the equation (20):
		$s = \sqrt{\frac{\sum d^2}{2k}}$
		where: d = difference of duplicate measurements k = number of sets of duplicate measurements

APPENDIX B

WEEKLY QC/QA PROCEDURES: TABLES AND FIGURES

1994

**TABLE B-1 Comparison of Filtered and Unfiltered Internal Blind Samples
High Purity Standards Simulated Rainwater I (HPS-SRI), 1994**

Parameter	Target Conc.^a (mg/L)	Measured Conc. (mg/L)	No. Repli- cates	Bias (mg/L)	% Bias	Precision (s) (mg/L)	% RSD
Calcium	0.015	0.017^b	26	0.002	13.3	0.003	17.6
		0.024^c	12	0.009	60.0	0.006	25.0
Magnesium	0.028	0.029	26	0.001	3.6	0.001	3.4
		0.030	12	0.002	7.1	0.003	10.0
Sodium	0.200	0.205	26	0.005	2.5	0.005	2.4
		0.254	12	0.054	27.0	0.022	8.7
Potassium	0.050	0.052	26	0.002	4.0	0.003	5.8
		0.050	12	0.000	0.0	0.007	14.0
Ammonium	0.10	0.11	26	0.01	10.0	0.01	9.1
		0.15	12	0.05	50.0	0.05	33.3
Sulfate	2.70	2.60	26	-0.10	-3.7	0.06	2.3
		2.49	12	-0.21	-7.8	0.09	3.6
Nitrate	0.50	0.54	26	0.04	8.0	0.02	3.7
		0.59	12	0.09	18.0	0.04	6.8
Chloride	0.25	0.23	26	-0.02	-8.0	0.01	4.3
		0.28	12	0.03	12.0	0.04	14.3
H+ (µeq/L)	52.48	50.14	26	-2.3	-4.5	1.35	2.7
		49.6^d	12	-2.9	-5.5	3.17	6.4
Conductivity (µS/cm)	25.0	25.3	26	0.3	1.2	0.6	2.4
		25.3^d	12	0.3	1.2	0.4	1.6

Notes:^a Target values provided by HPS for Simulated Rainwater I.

^bThe first set of values for each parameter is for unfiltered samples, ^c The second set of values for each parameter is for filtered samples. ^d pH and conductivity are measured on unfiltered sample prior to filtering.

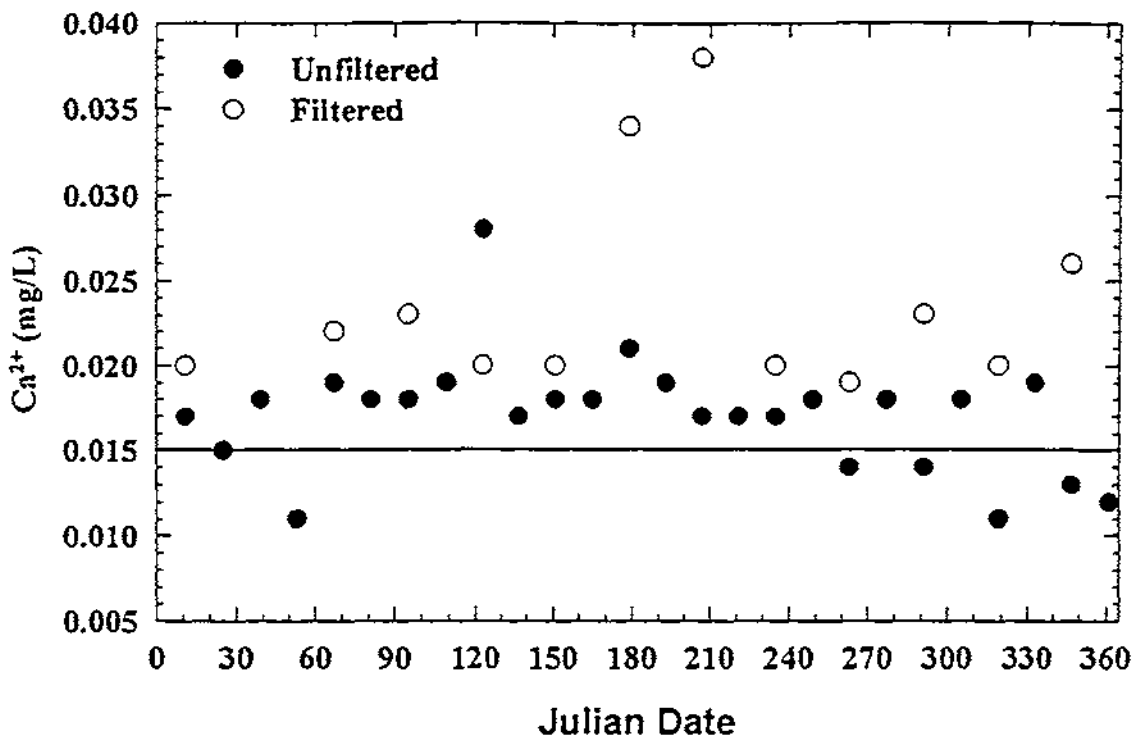


FIGURE B-1. Comparison of filtered and unfiltered internal blind samples (calcium HPS-SRI), 1994.

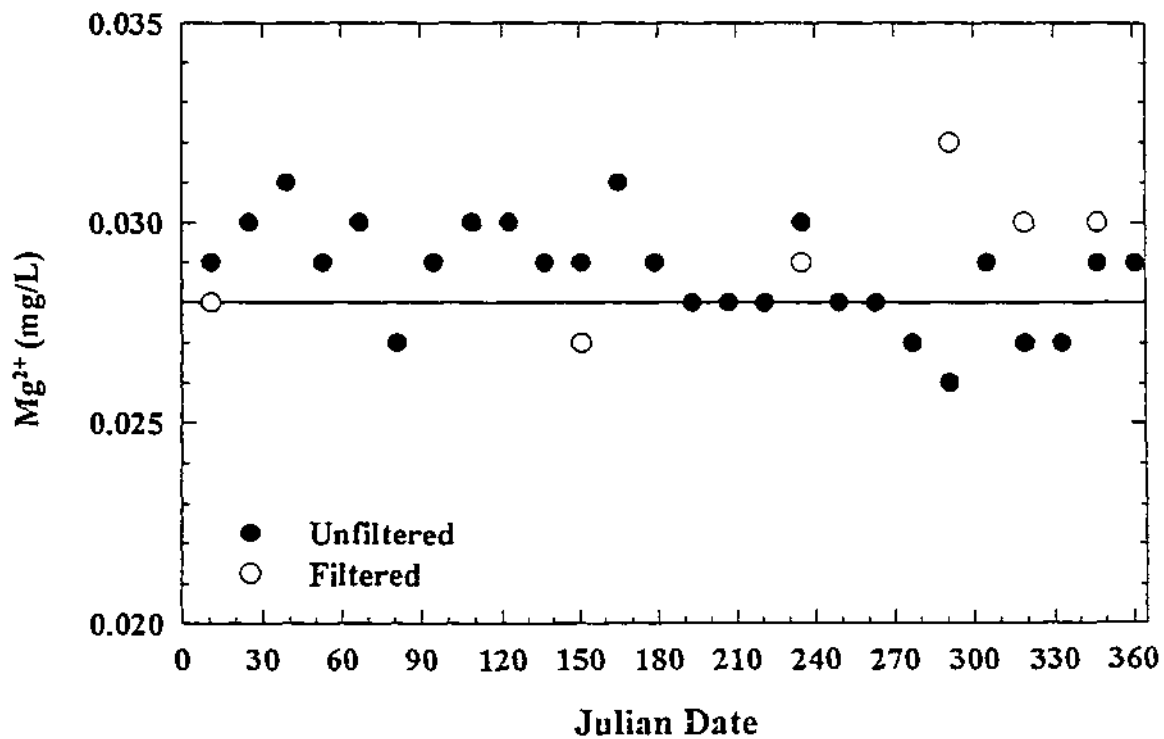


FIGURE B-2. Comparison of filtered and unfiltered internal blind samples (magnesium HPS-SRI), 1994.

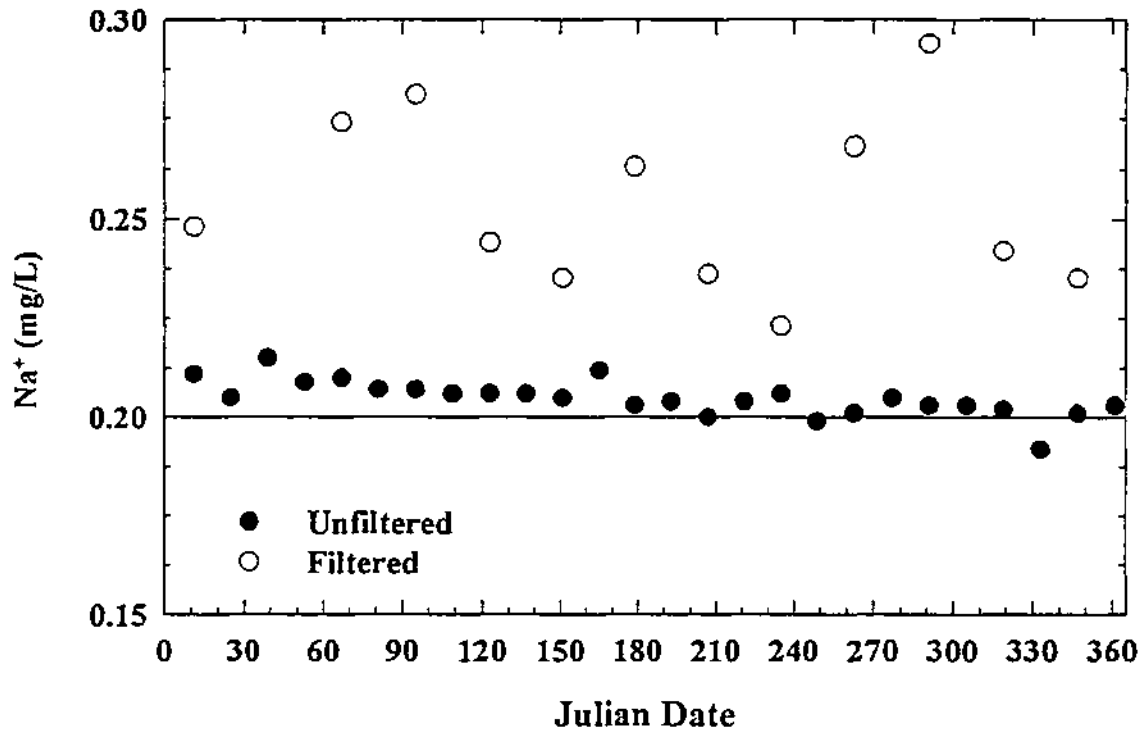


FIGURE B-3. Comparison of filtered and unfiltered internal blind samples (sodium HPS-SRI), 1994.

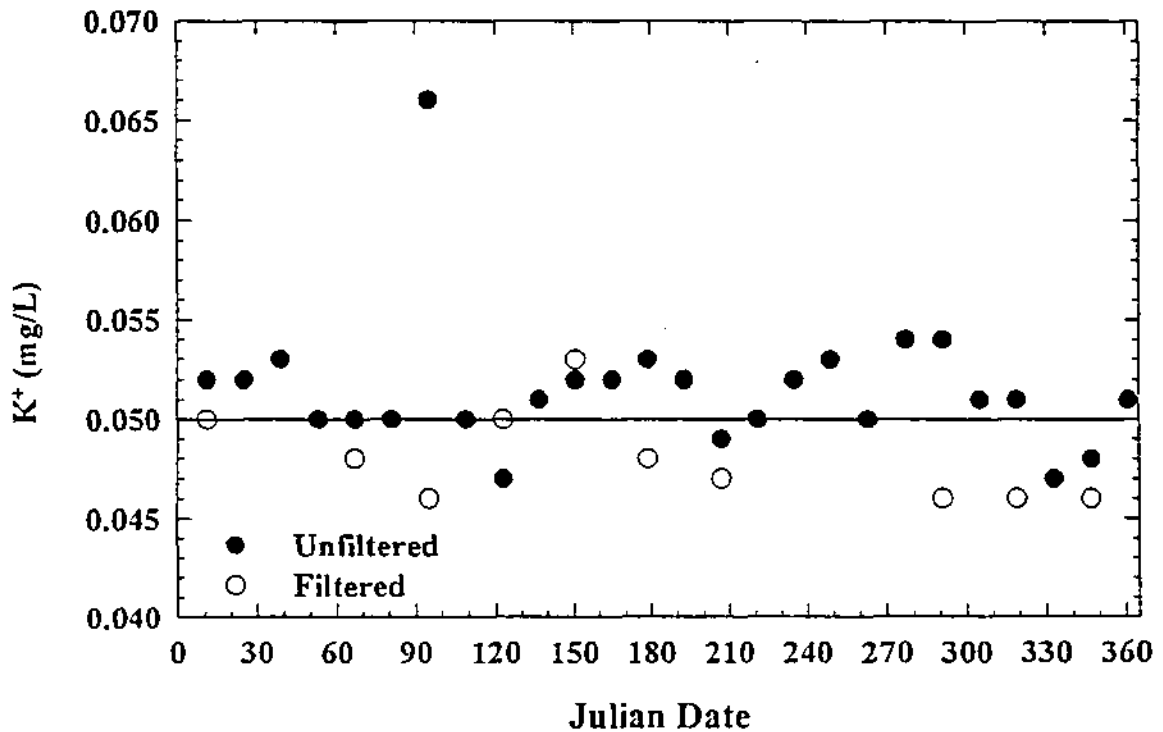


FIGURE B-4. Comparison of filtered and unfiltered internal blind samples (potassium HPS-SRI), 1994.

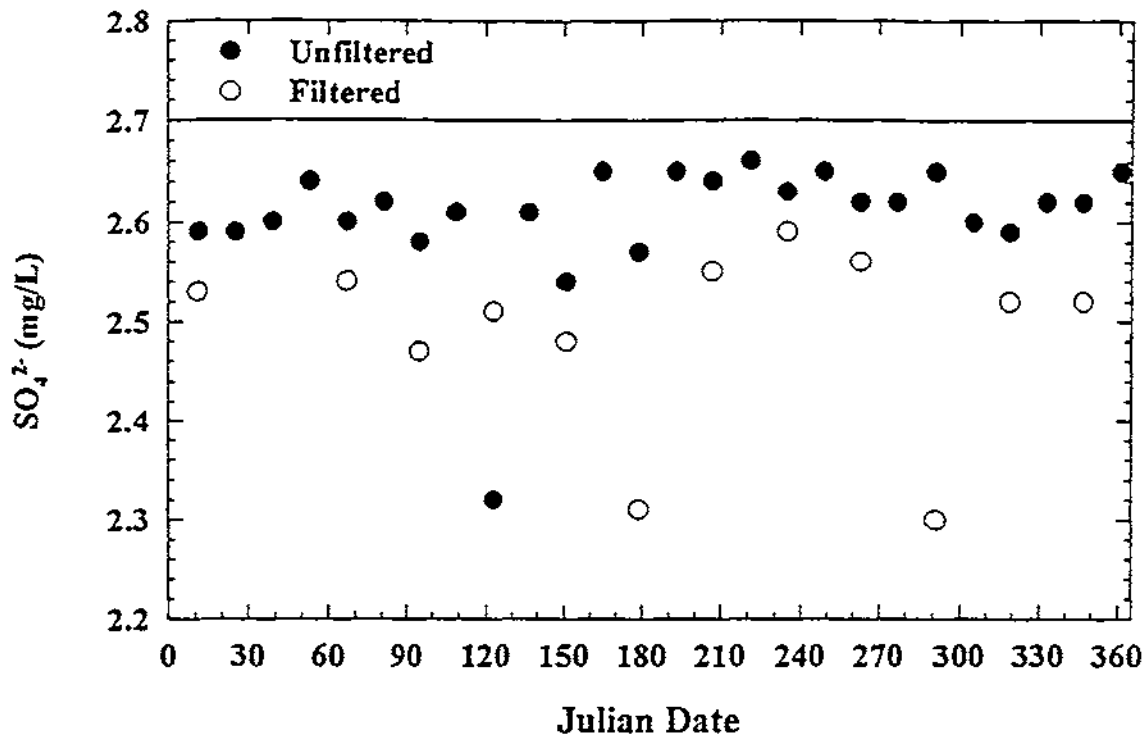


FIGURE B-5. Comparison of filtered and unfiltered internal blind samples (sulfate HPS-SRI), 1994.

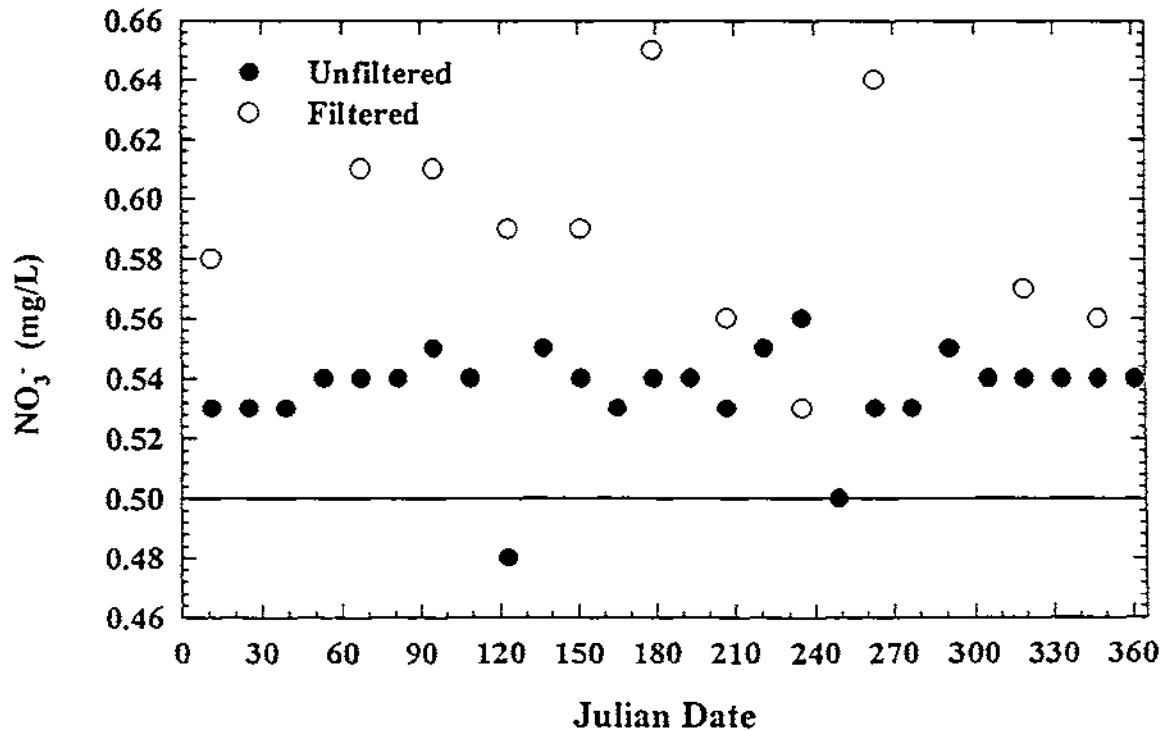


FIGURE B-6. Comparison of filtered and unfiltered internal blind samples (nitrate HPS-SRI), 1994.

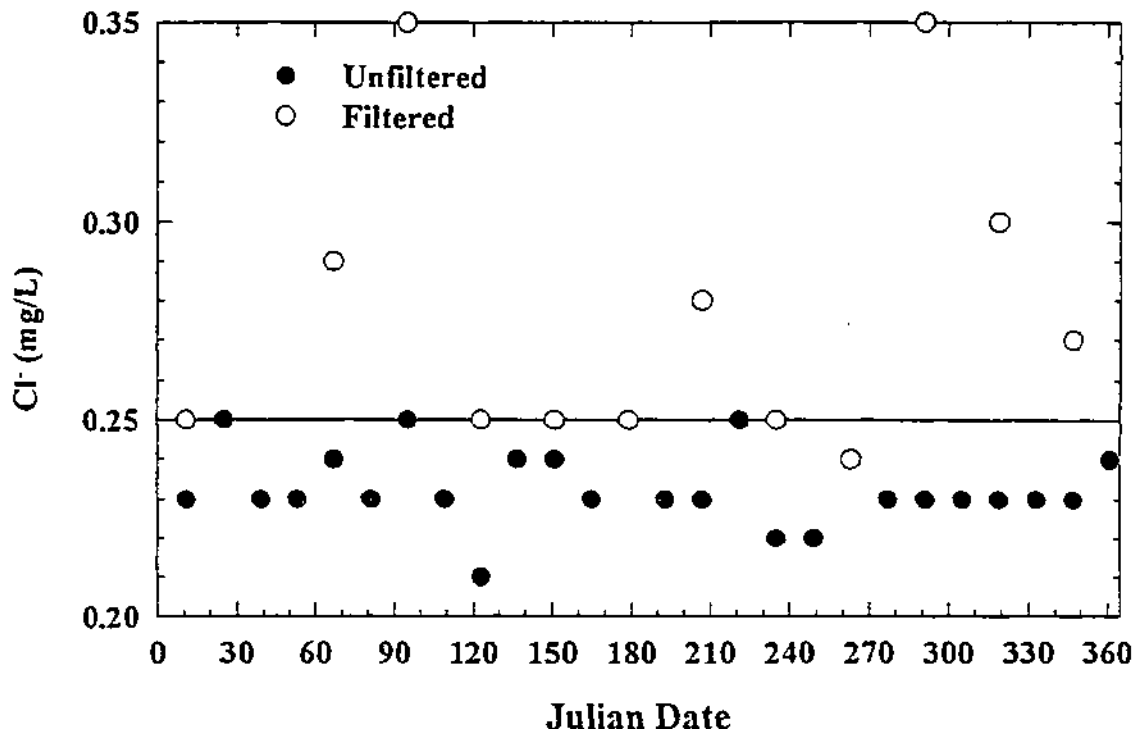


FIGURE B-7. Comparison of filtered and unfiltered internal blind samples (chloride HPS-SRI), 1994.

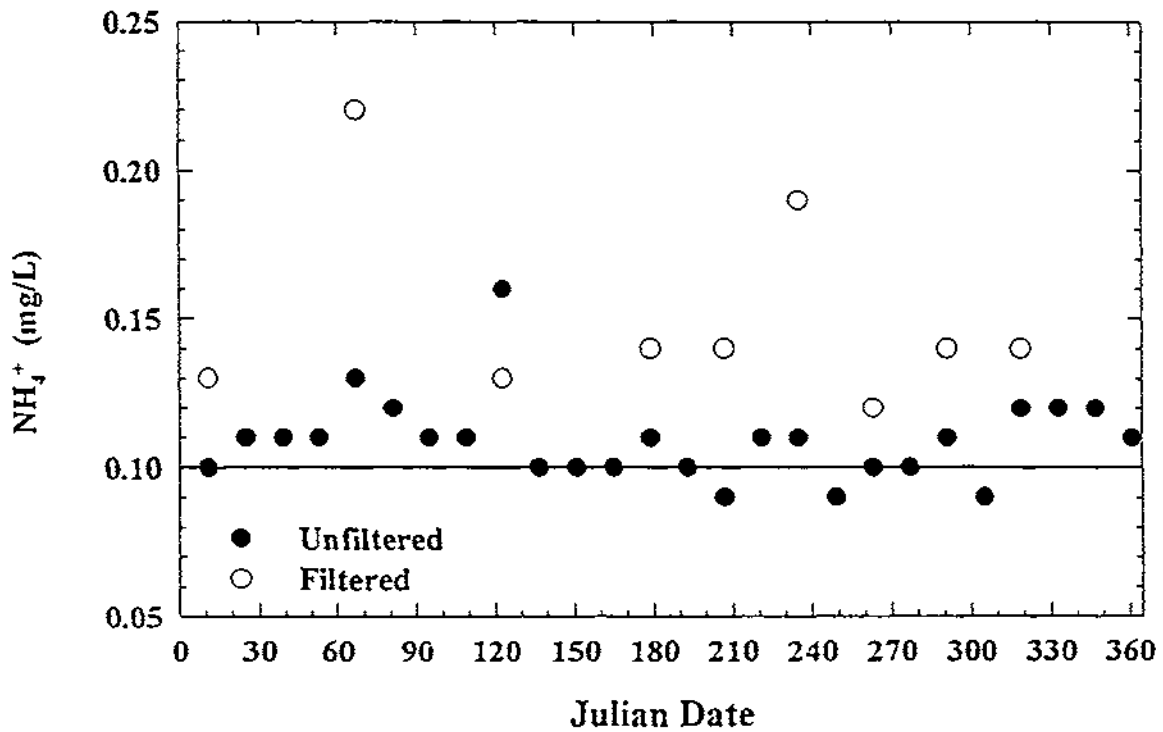


FIGURE B-8. Comparison of filtered and unfiltered internal blind samples (ammonium HPS-SRI), 1994.

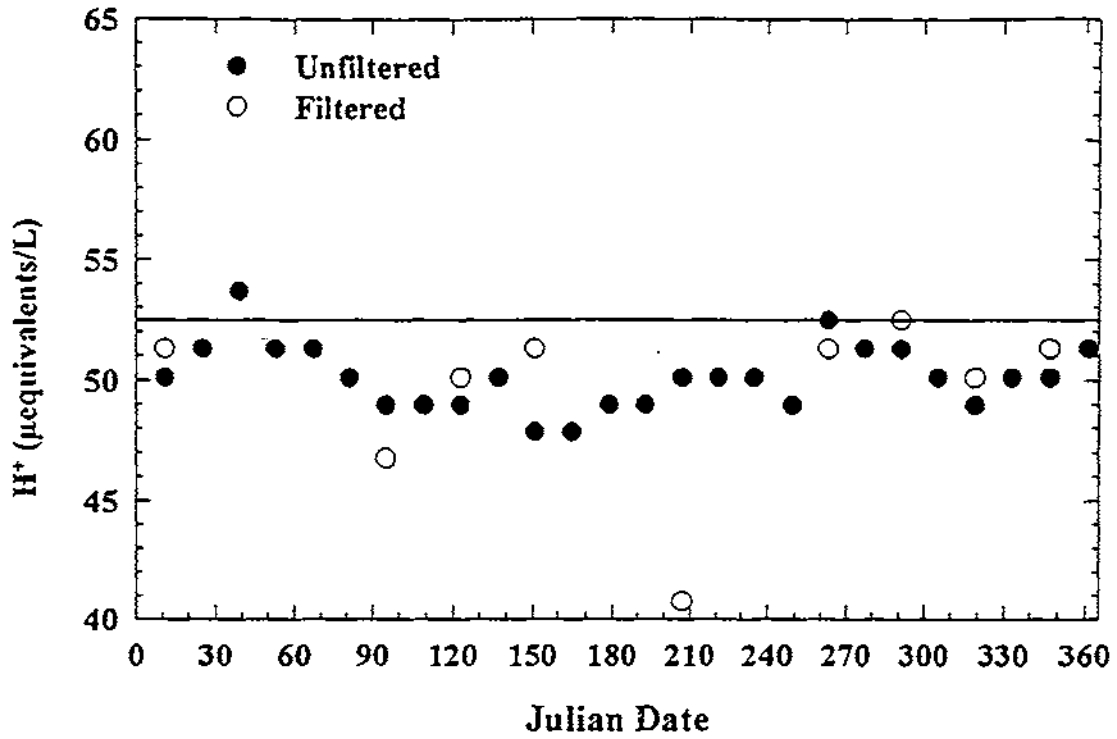


FIGURE B-9. Comparison of filtered and unfiltered internal blind samples (H^+ HPS-SRI), 1994.

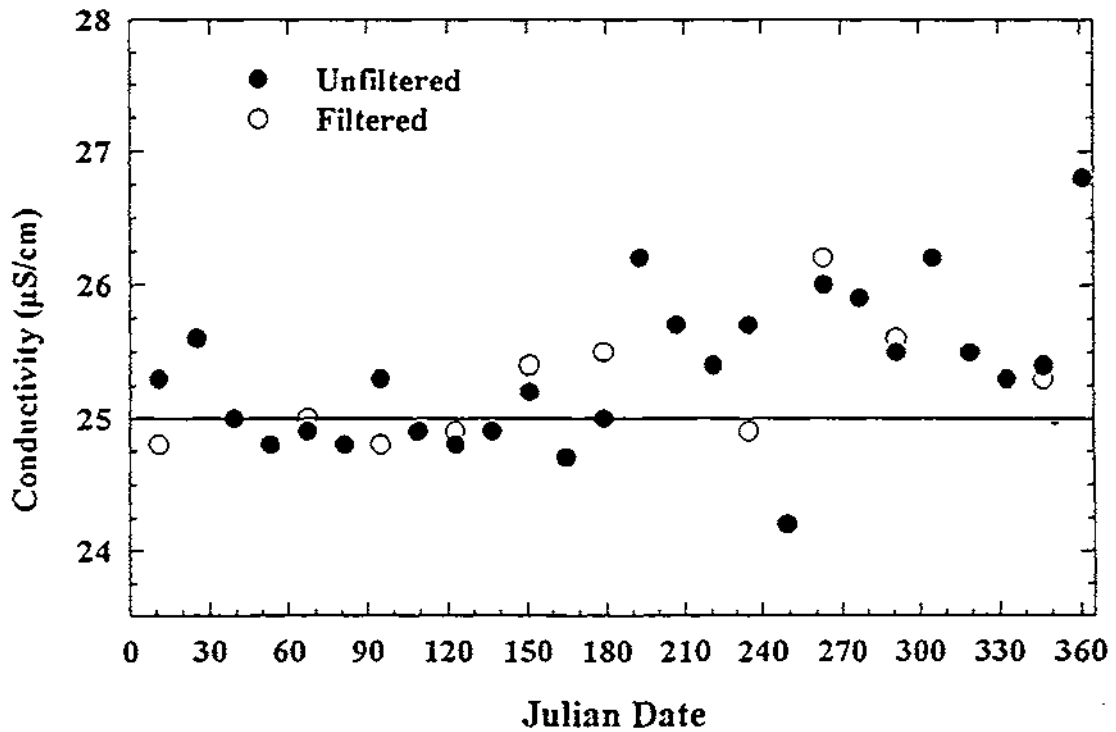


FIGURE B-10. Comparison of filtered and unfiltered internal blind samples (conductivity HPS-SRI), 1994.

**TABLE B-2 Comparison of Filtered and Unfiltered Internal Blind Samples
High Purity Standard's Simulated Rainwater II (HPS-SRII), 1994**

Parameter	Target Conc.^a (mg/L)	Measured Conc. (mg/L)	No. Repli- cates	Bias (mg/L)	% Bias	Precision (s) (mg/L)	% RSD
Calcium	0.052	0.056^b	26	0.004	7.7	0.006	10.7
		0.066^c	11	0.014	26.9	0.007	10.6
Magnesium	0.063	0.060	26	-0.003	-4.8	0.002	3.3
		0.063	11	0.000	0.000	0.003	4.8
Sodium	0.430	0.446	26	0.016	5.3	0.012	2.7
		0.492	11	0.062	14.4	0.030	6.1
Potassium	0.100	0.110	26	0.010	10.0	0.003	2.7
		0.101	11	0.001	1.0	0.005	5.0
Ammonium	1.00	0.96	26	-0.04	-4.0	0.03	3.1
		0.96	11	-0.04	-4.0	0.03	3.1
Sulfate	10.10	10.34	26	0.24	2.4	0.31	3.0
		9.86	11	-0.24	-2.4	0.33	3.3
Nitrate	7.30	7.39	26	0.09	1.2	.24	3.2
		7.13	11	-0.17	-2.3	.27	3.8
Chloride	0.98	0.97	26	-0.01	-1.0	0.04	4.1
		0.99	11	0.01	1.0	0.04	4.0
H+ (µeq/L)	269.2	251.1	26	-18.1	-6.7	7.8	3.1
		253.4^d	11	-15.8	-5.8	7.14	2.8
Conductivity (µS/cm)	127	128.1	26	1.1	0.9	1.6	1.2
		128.0^d	11	1.0	0.8	1.0	0.8

Notes: ^a Target values provided by HPS for Simulated Rainwater H.

^bThe first set of values for each parameter is for unfiltered samples. ^c The second set of values for each parameter is for filtered samples. ^d pH and Conductivity are measured on unfiltered sample prior to filtering.

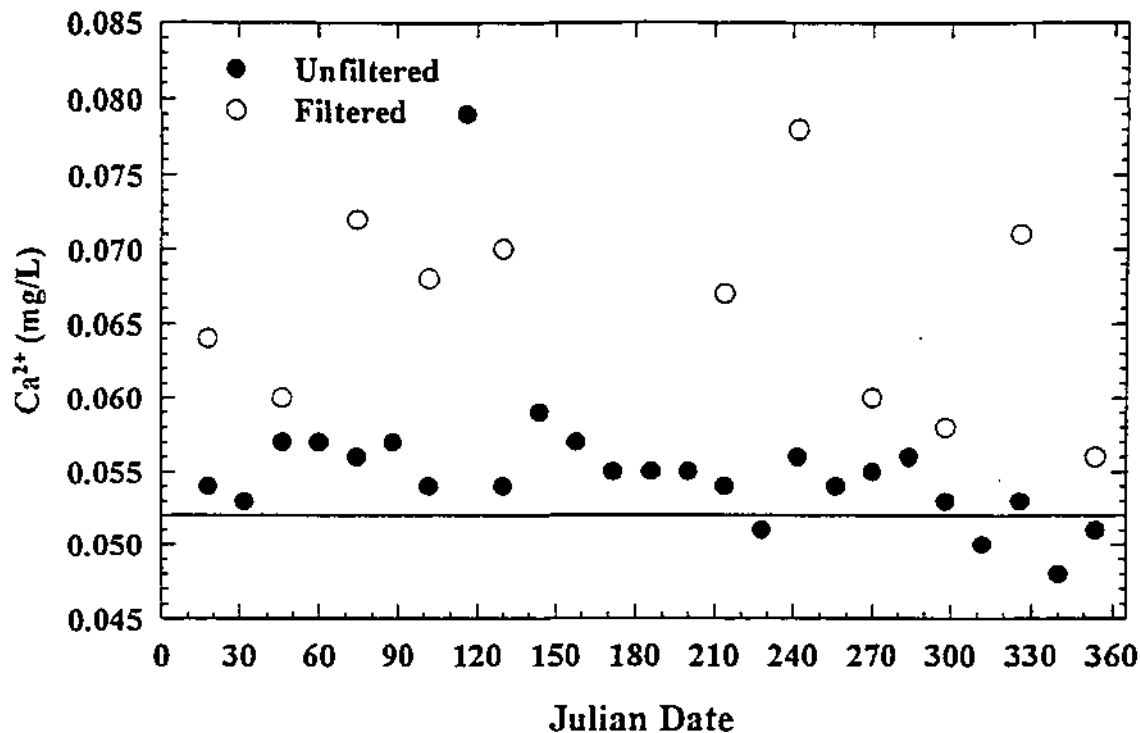


FIGURE B-11. Comparison of filtered and unfiltered internal blind sample (calcium HPS-SRII), 1994.

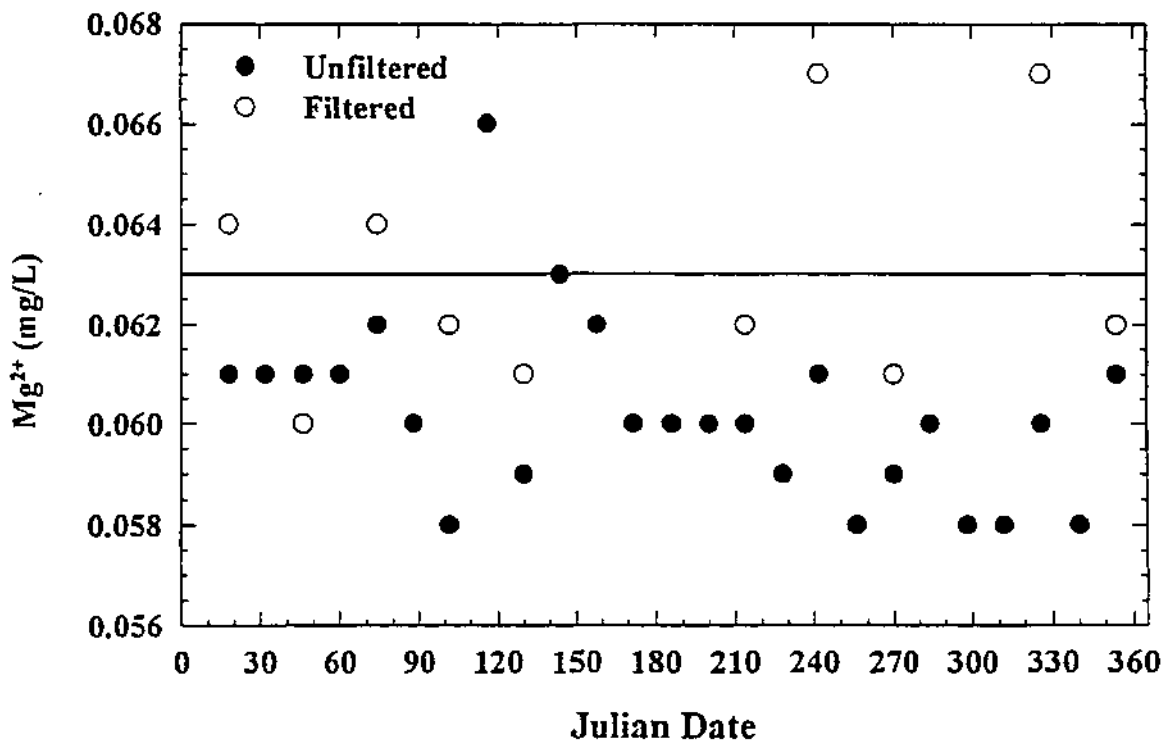


FIGURE B-12. Comparison of filtered and unfiltered internal blind samples (magnesium HPS-SRII), 1994.

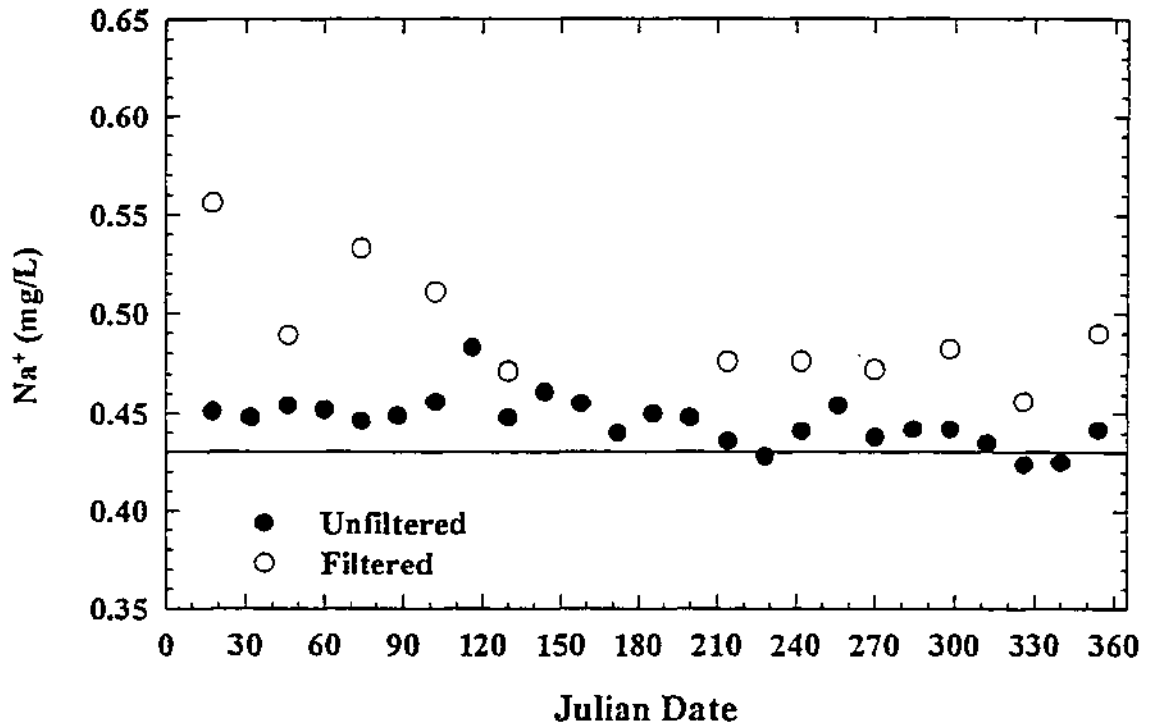


FIGURE B-13. Comparison of filtered and unfiltered internal blind samples (sodium HPS-SRII), 1994.

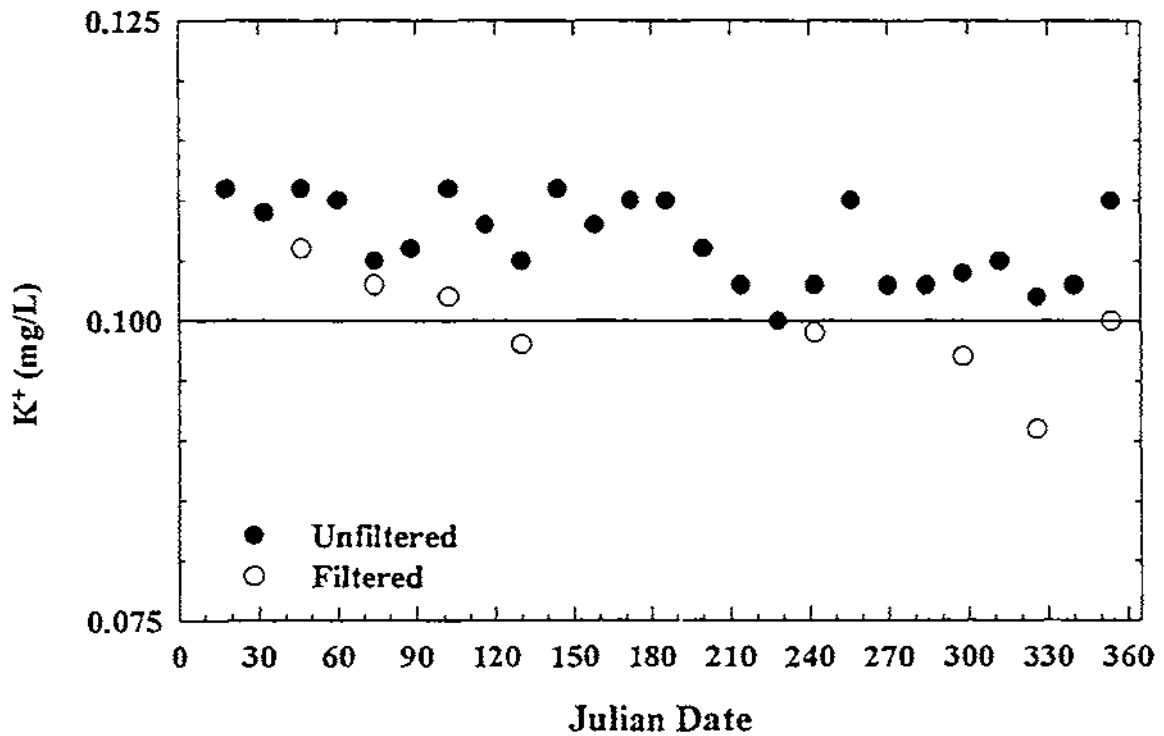


FIGURE B-14. Comparison of filtered and unfiltered internal blind samples (potassium HPS-SRII), 1994.

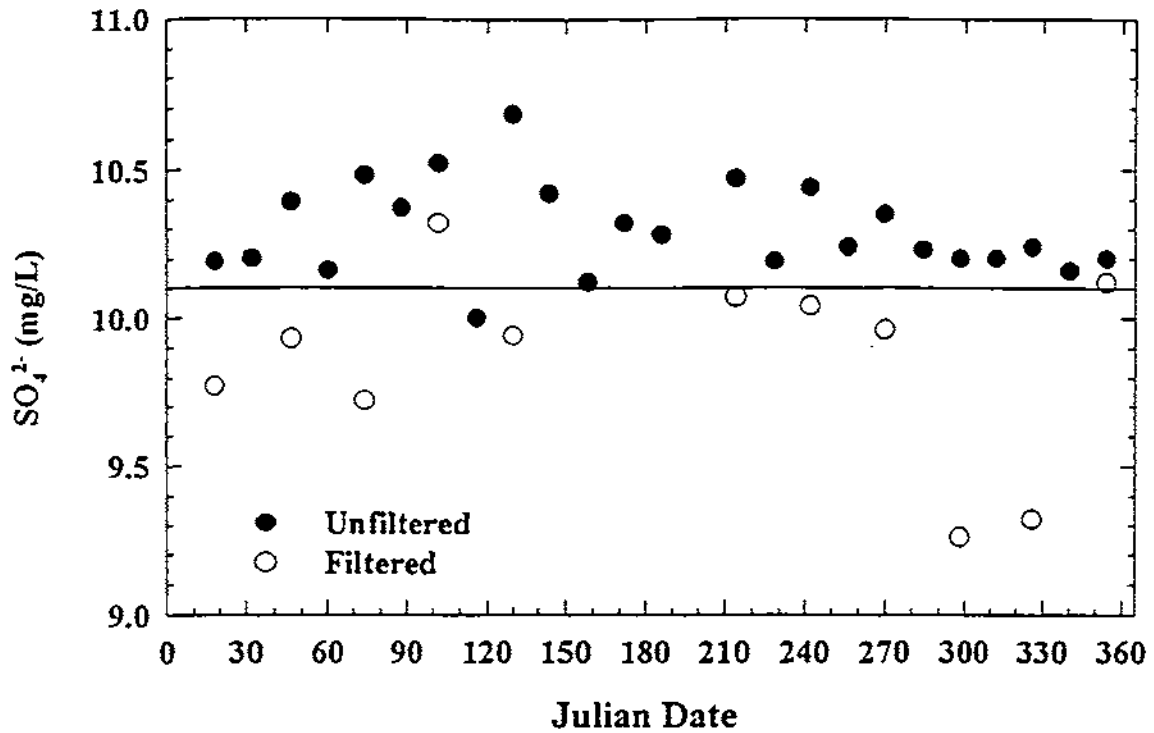


FIGURE B-15. Comparison of filtered and unfiltered internal blind samples (sulfate HPS-SRII), 1994.

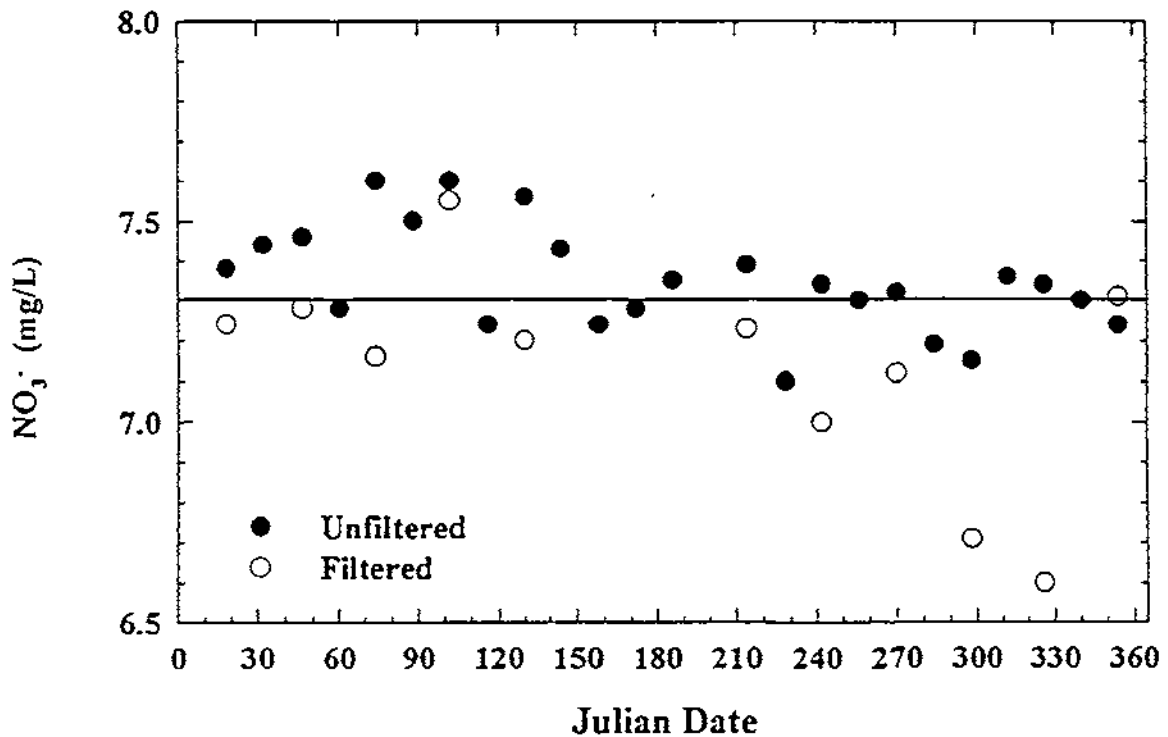


FIGURE B-16. Comparison of filtered and unfiltered internal blind samples (nitrate HPS-SRII), 1994.

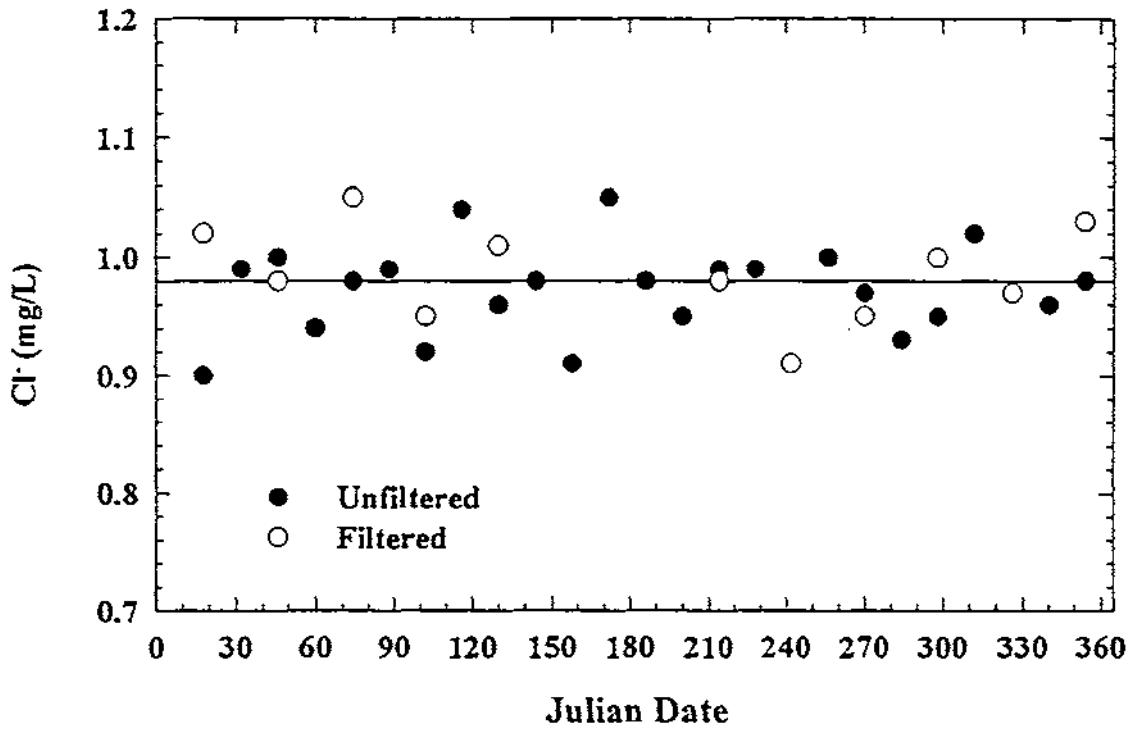


FIGURE B-17. Comparison of filtered and unfiltered internal blind samples (chloride HPS-SRII), 1994.

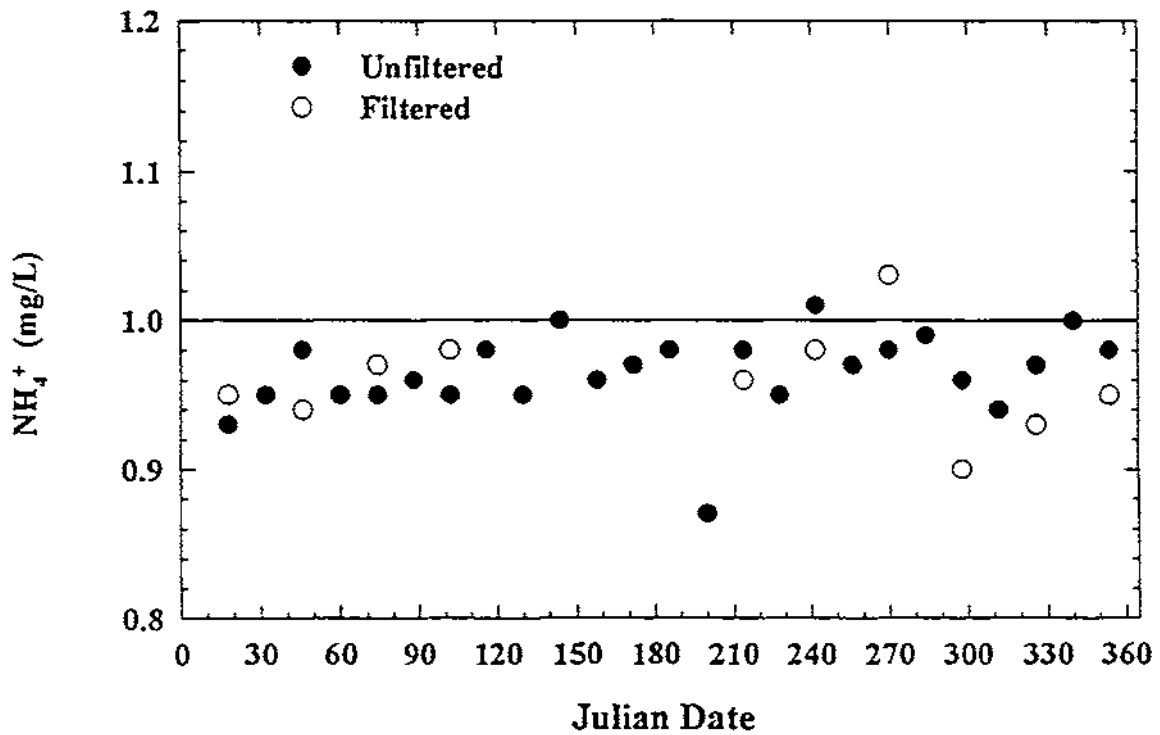


FIGURE B-18. Comparison of filtered and unfiltered internal blind samples (ammonium HPS-SRII), 1994.

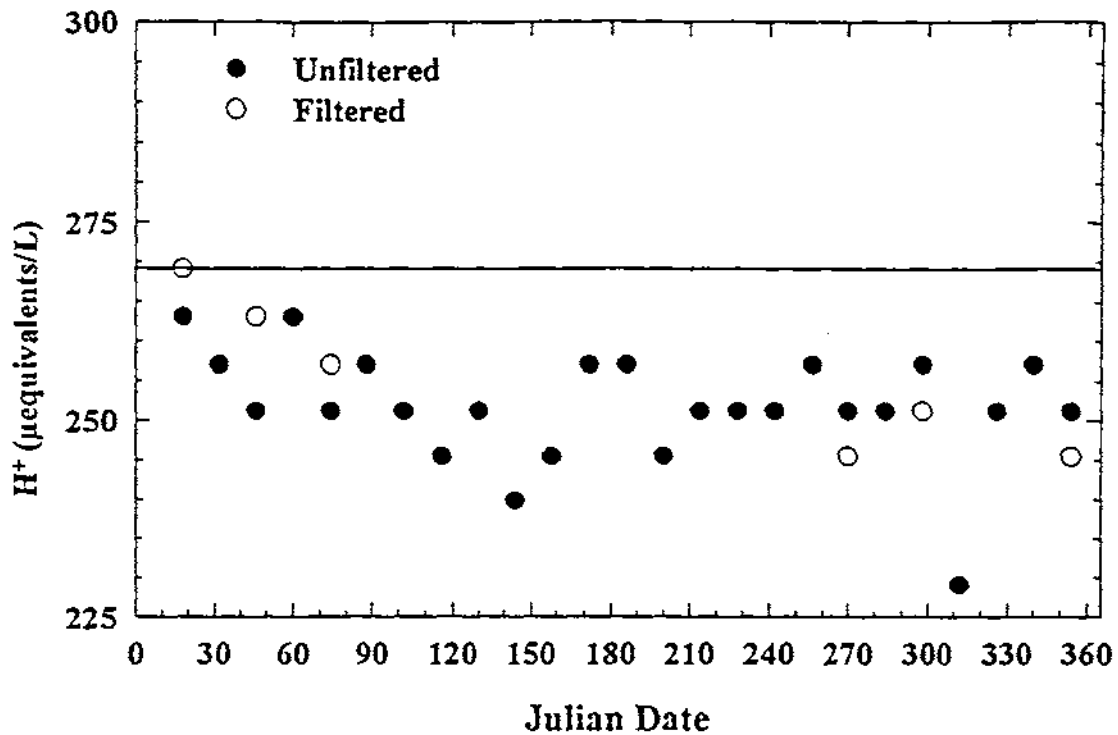


FIGURE B-19. Comparison of filtered and unfiltered internal blind samples (H⁺ HPS-SRII), 1994.

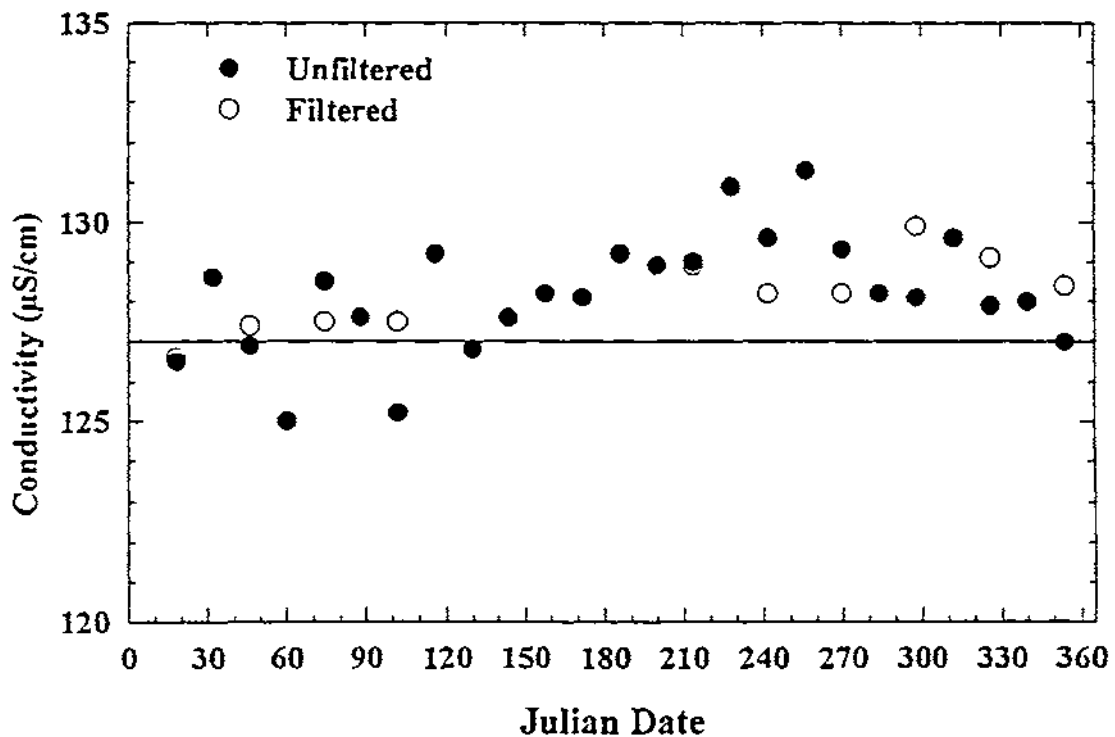
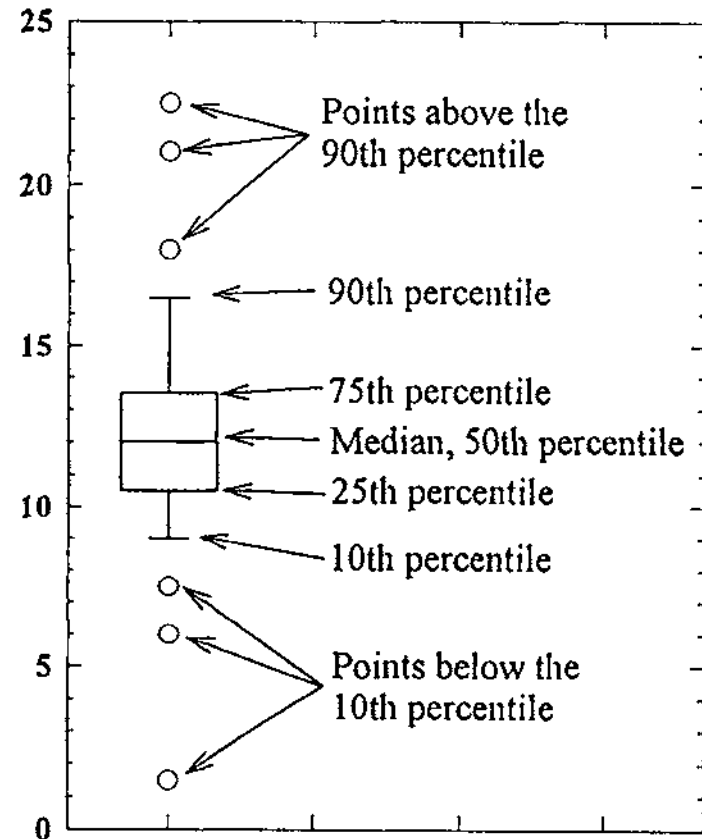


FIGURE B-20. Comparison of filtered and unfiltered internal blind samples (conductivity HPS-SRII), 1994.

TABLE B-3 50th and 95th Percentile Concentration Values of Parameters Measured in Replicate (S/Q) Samples, 1994		
Parameter	Percentile Concentration Values (mg/L)	
	50th	95th
Calcium	0.080	0.640
Magnesium	0.020	0.080
Sodium	0.050	0.430
Potassium	0.020	0.11
Ammonium	0.22	0.93
Sulfate	1.09	4.10
Nitrate	0.92	3.13
Chloride	0.12	0.71
pH (units)	4.80	4.05
H+ ($\mu\text{eq/L}$)	15.95	89.2
Conductivity ($\mu\text{S/cm}$)	13.0	48.8



**DIAGRAM OF BOXPLOTS USED
ON FOLLOWING PAGES**

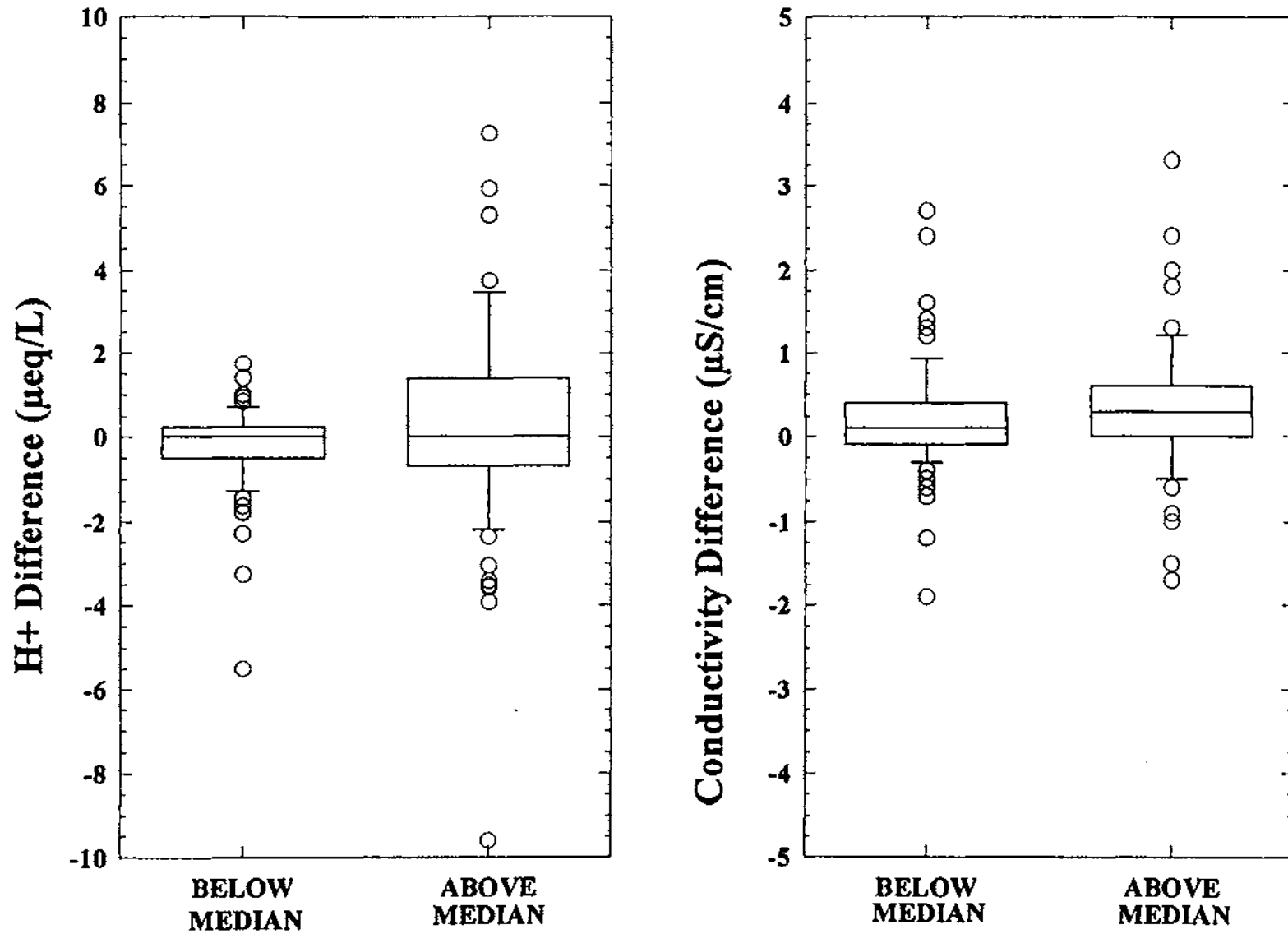


FIGURE B-21. Results of S/Q replicate analysis, H⁺ and conductivity, 1994.

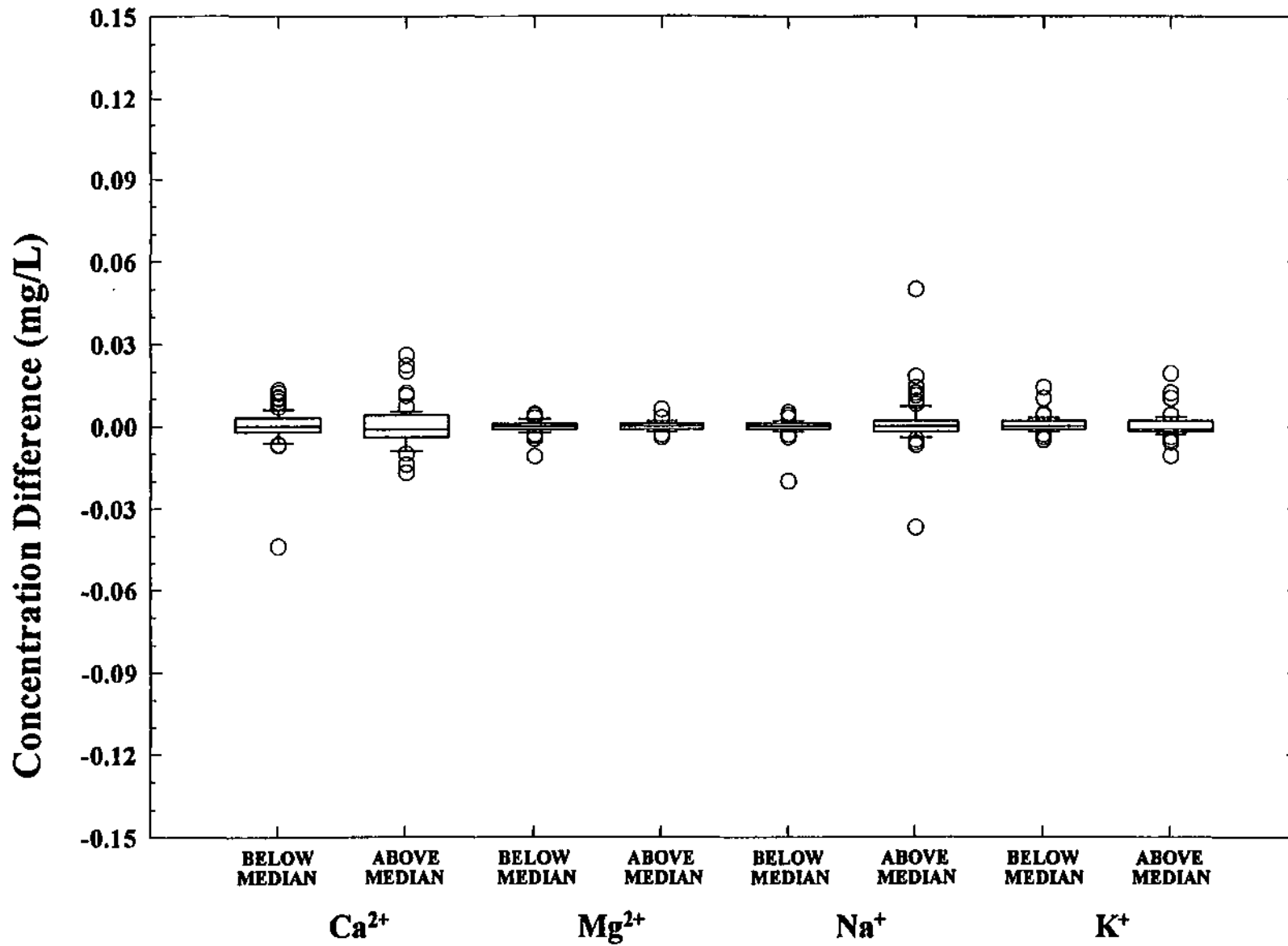


FIGURE B-22. Results of S/Q replicate analysis for calcium (Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺), and potassium (K⁺), 1994.

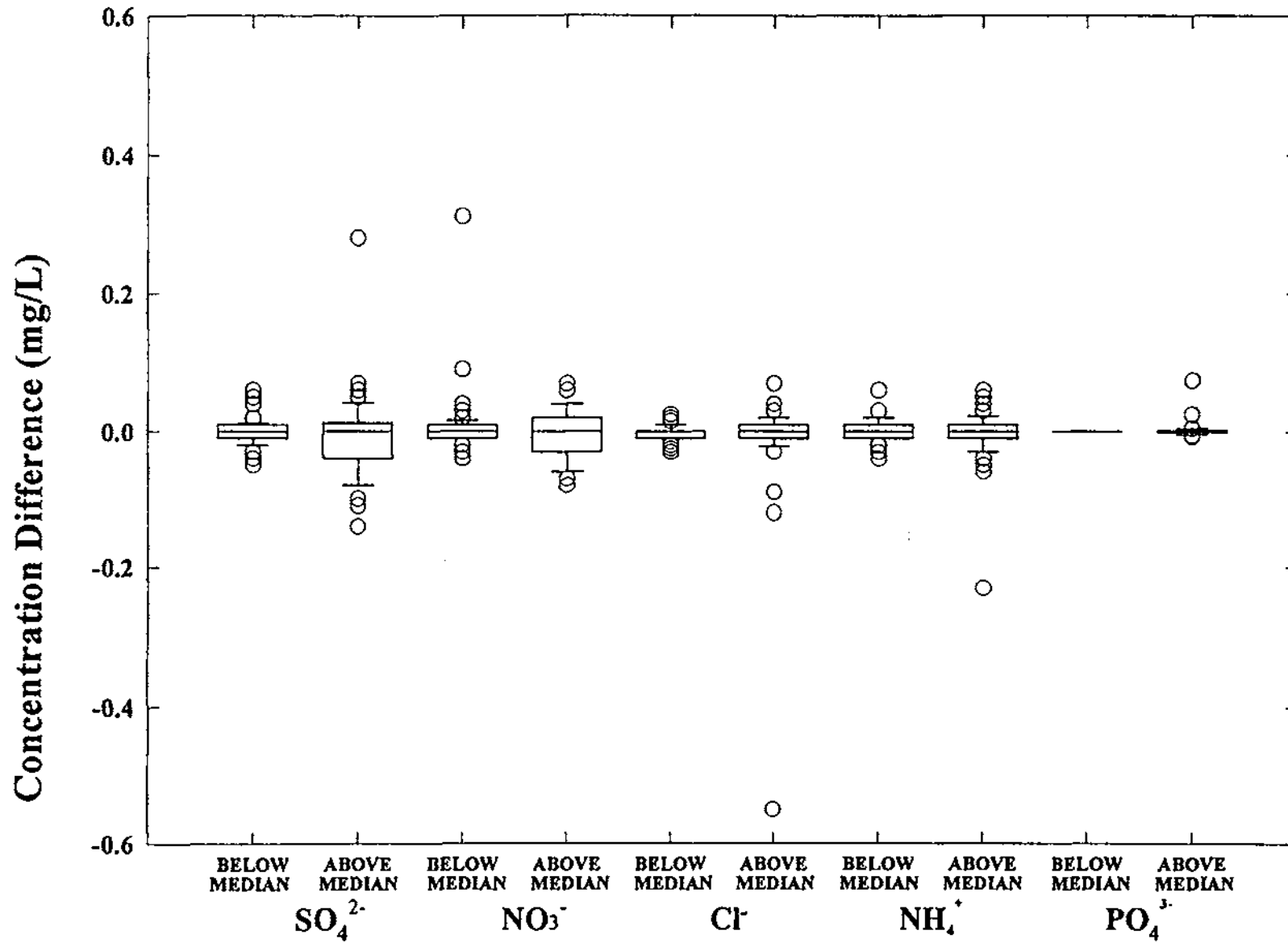


FIGURE B-23 Results of S/Q replicate analysis for sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), and phosphate (PO_4^{3-}), 1994.

**TABLE B-4 Percent of Ion Concentrations above MDLs Found in
Weekly Deionized (DI)Water Blanks and Leachates, 1994**

Blank	Calcium	Magnesium	Sodium	Potassium	Ammonium	Sulfate	Nitrate	Chloride	Phosphate	Number
DI-(209)	0.0	0.0	6.0	0.0	10.0	0.0	0.0	2.0	2.0	50
DI-(304)	0.0	0.0	10.0	2.0	14.0	0.0	0.0	2.0	10.0	50
DI-(323)	0.0	4.0	6.0	2.0	14.0	0.0	2.0	2.0	14.0	50
Fitter A	4.1	2.0	98.0	4.1	28.6	0.0	69.4	44.9	12.2	49
Filter B	0.0	0.0	85.7	4.1	16.3	2.0	2.0	6.1	12.2	49
Bucket 50	60.0	12.0	96.0	90.0	28.0	12.0	22.0	58.0	32.0	50
Bucket 150	12.0	4.0	70.0	62.0	32.0	6.0	4.0	12.0	26.0	50
Bottle 50	6.0	8.0	22.0	38.0	12.0	6.0	0.0	4.0	24.0	50
Bottle 150	2.0	2.0	14.0	14.0	10.0	0.0	0.0	4.0	14.0	50
Lid 50	14.3	10.2	53.1	42.9	81.6	6.1	4.1	20.4	26.5	49

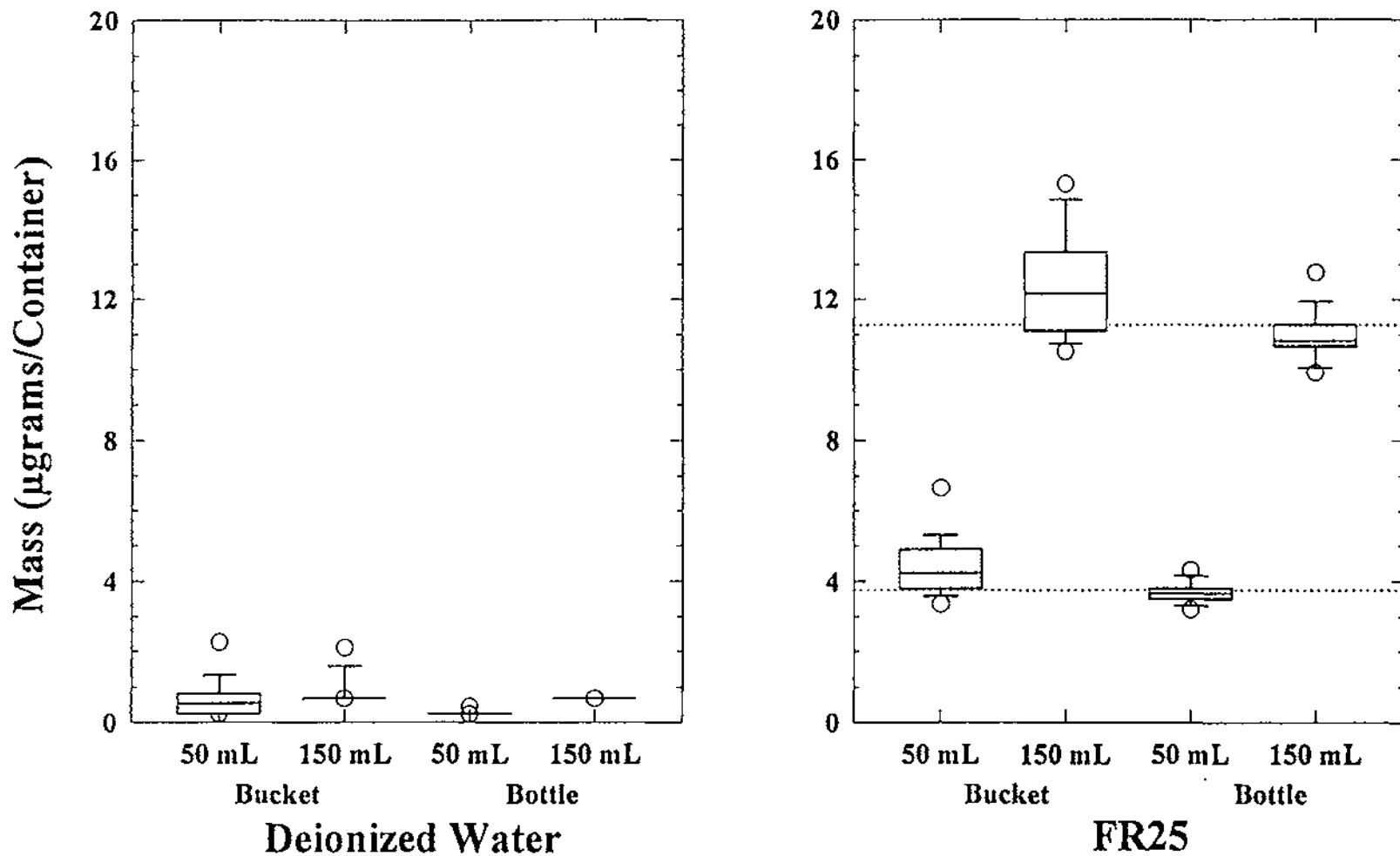


FIGURE B-24. Calcium found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1994. FR25 baseline values shown as dotted lines.

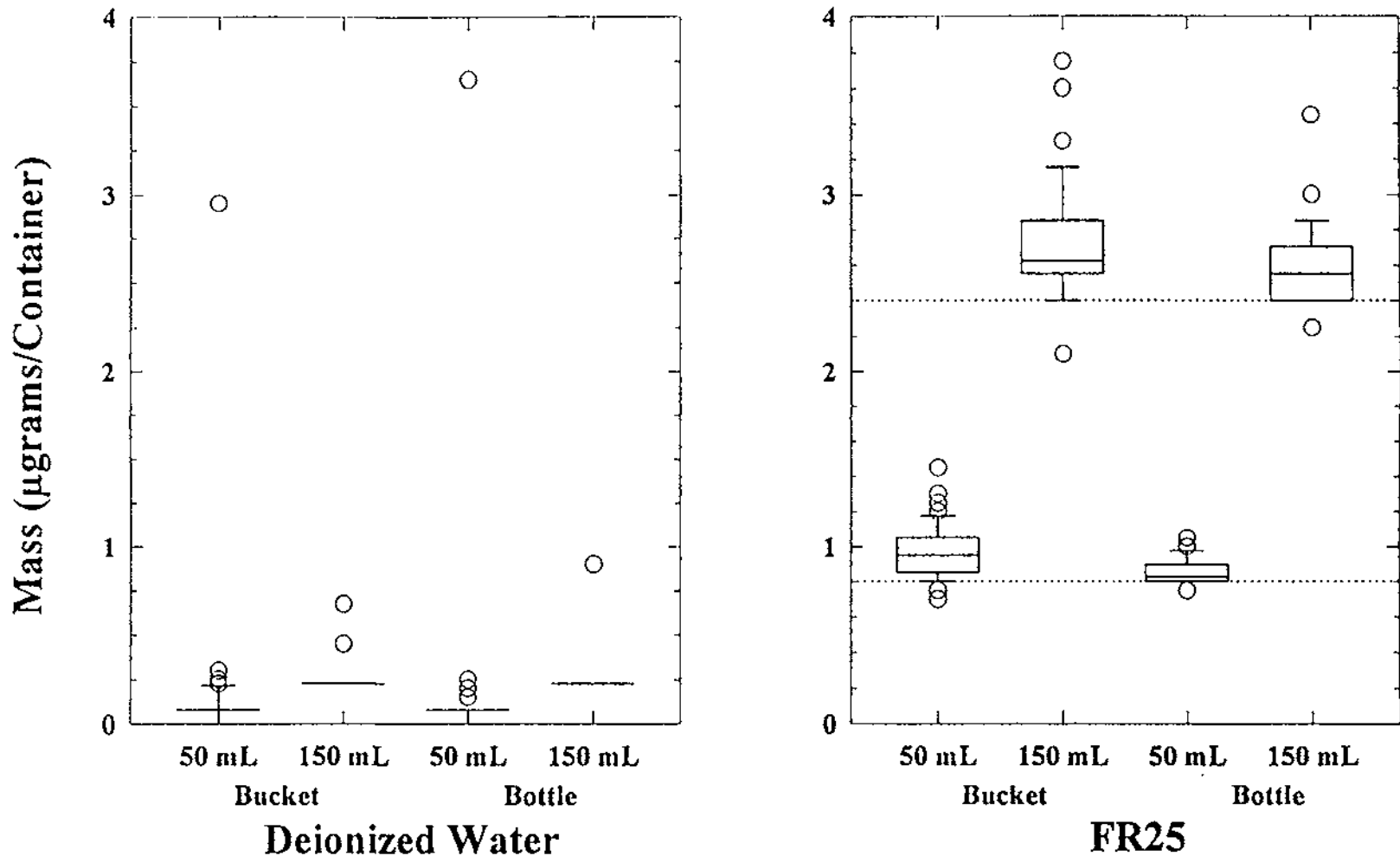


FIGURE B-25. Magnesium found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1994. FR25 baseline values shown as dotted lines.

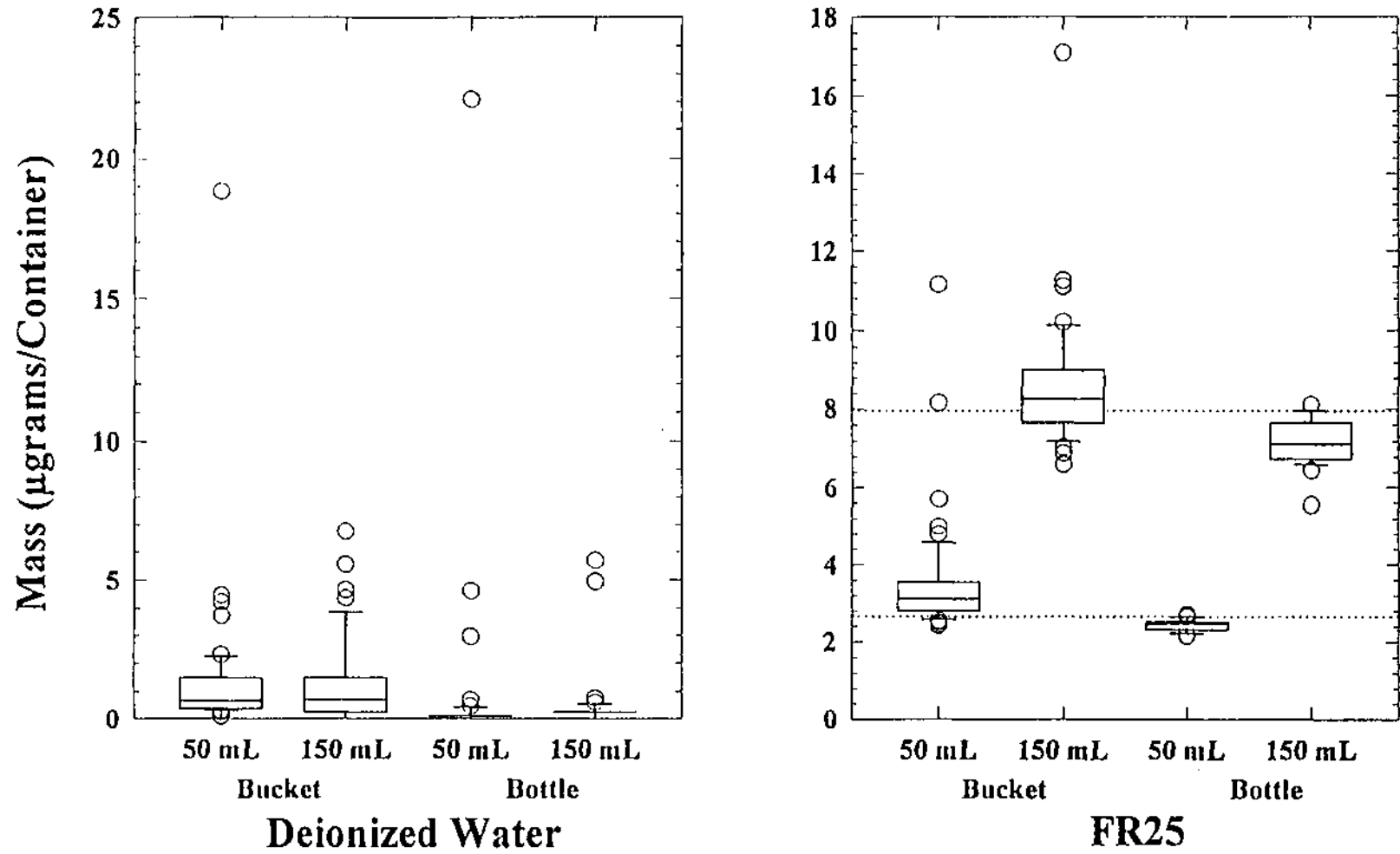


FIGURE B-26. Sodium found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1994. FR25 baseline values shown as dotted lines.

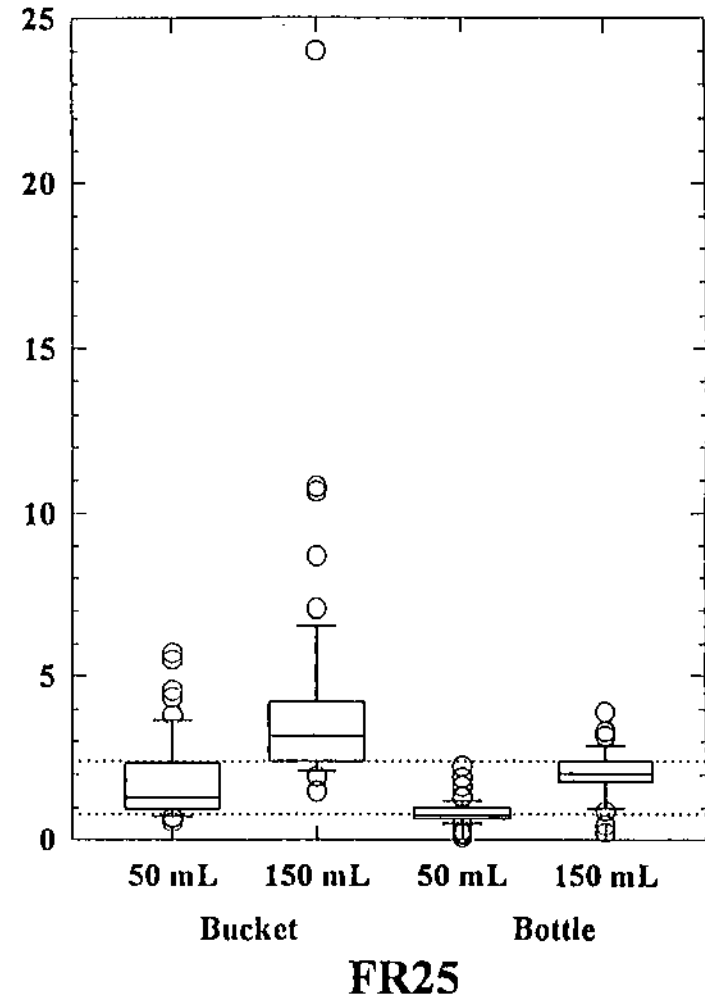
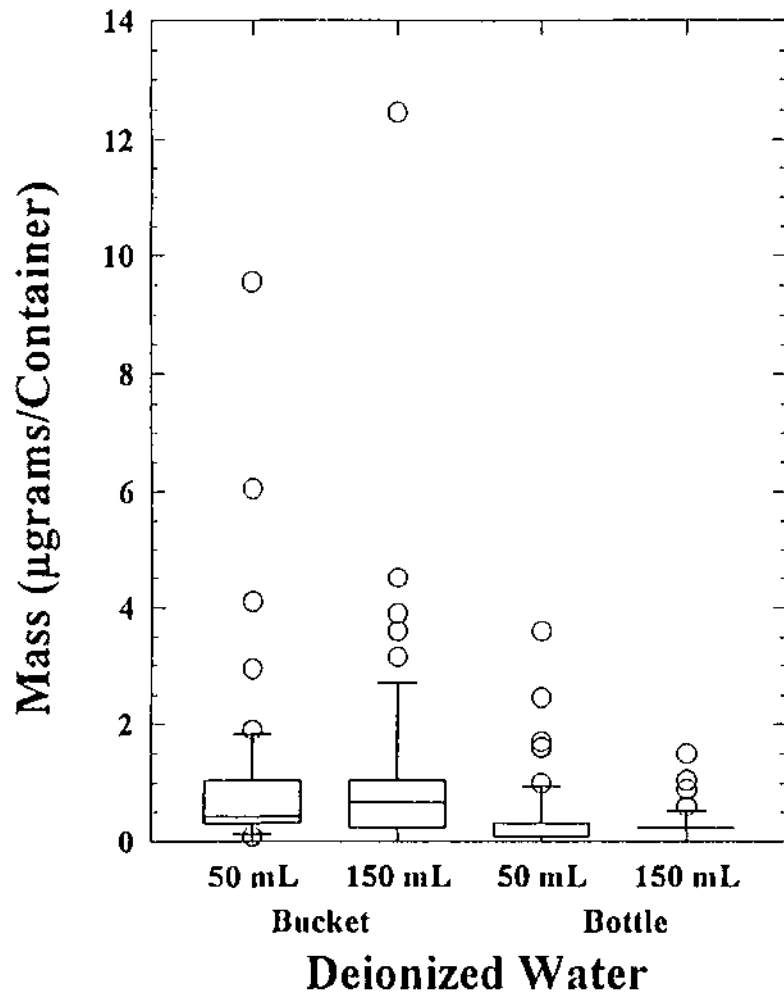


FIGURE B-27. Potassium found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1994. FR25 baseline values shown as dotted lines.

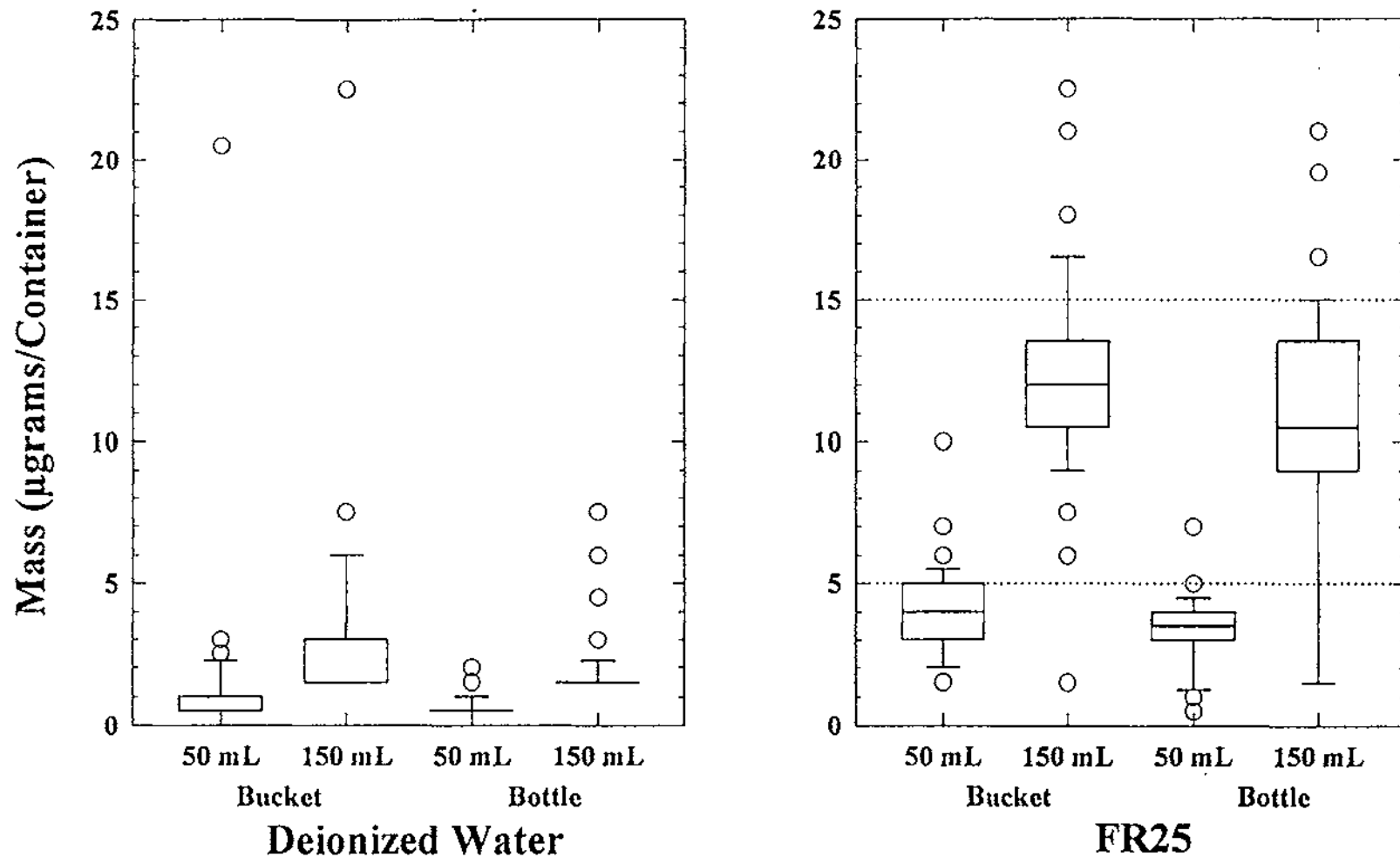


FIGURE B-28. Ammonium found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1994. FR25 baseline values shown as dotted lines.

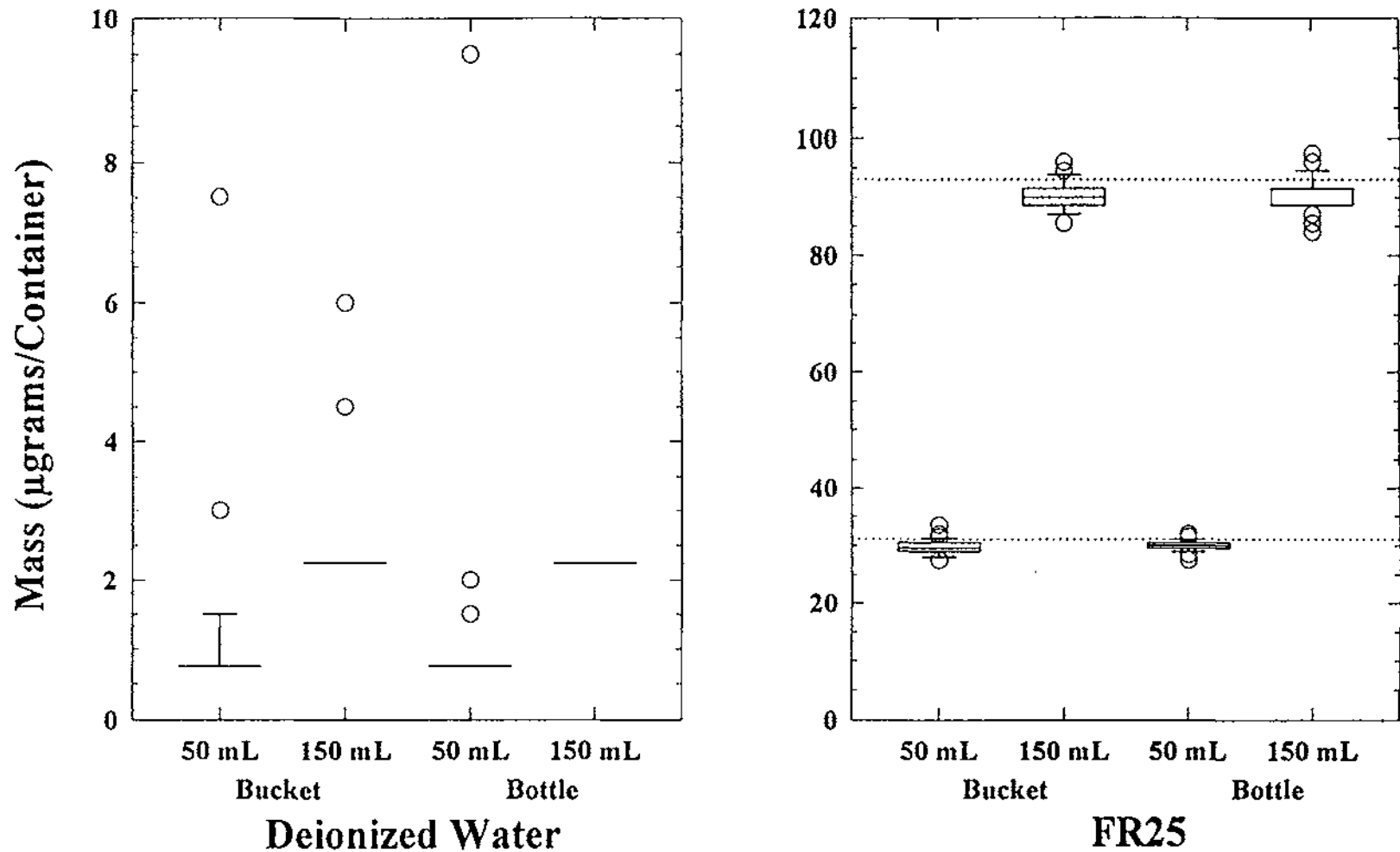


FIGURE B-29. Sulfate found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1994. FR25 baseline values shown as dotted lines.

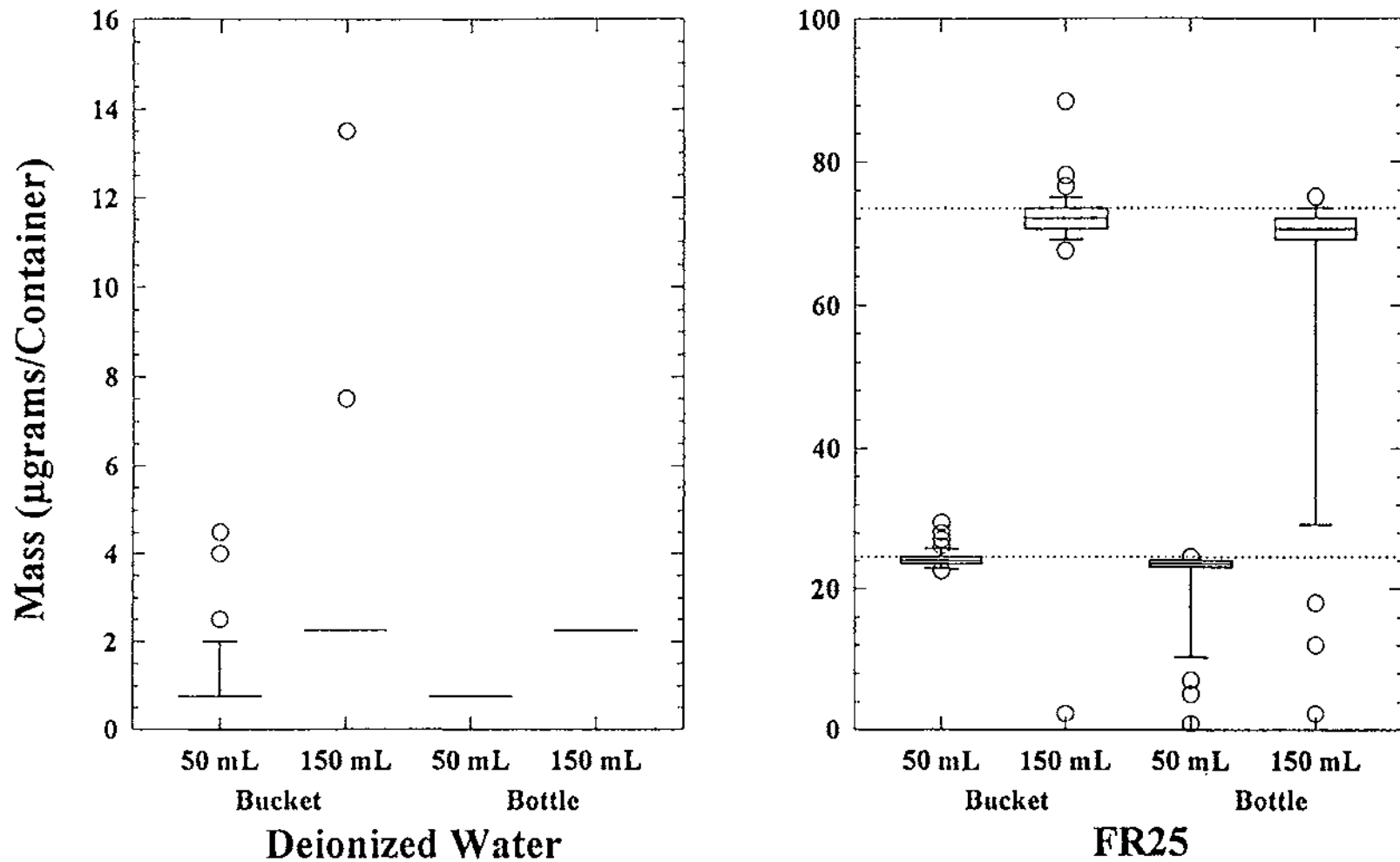


FIGURE B-30. Nitrate found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1993. FR25 baseline values shown as dotted lines.

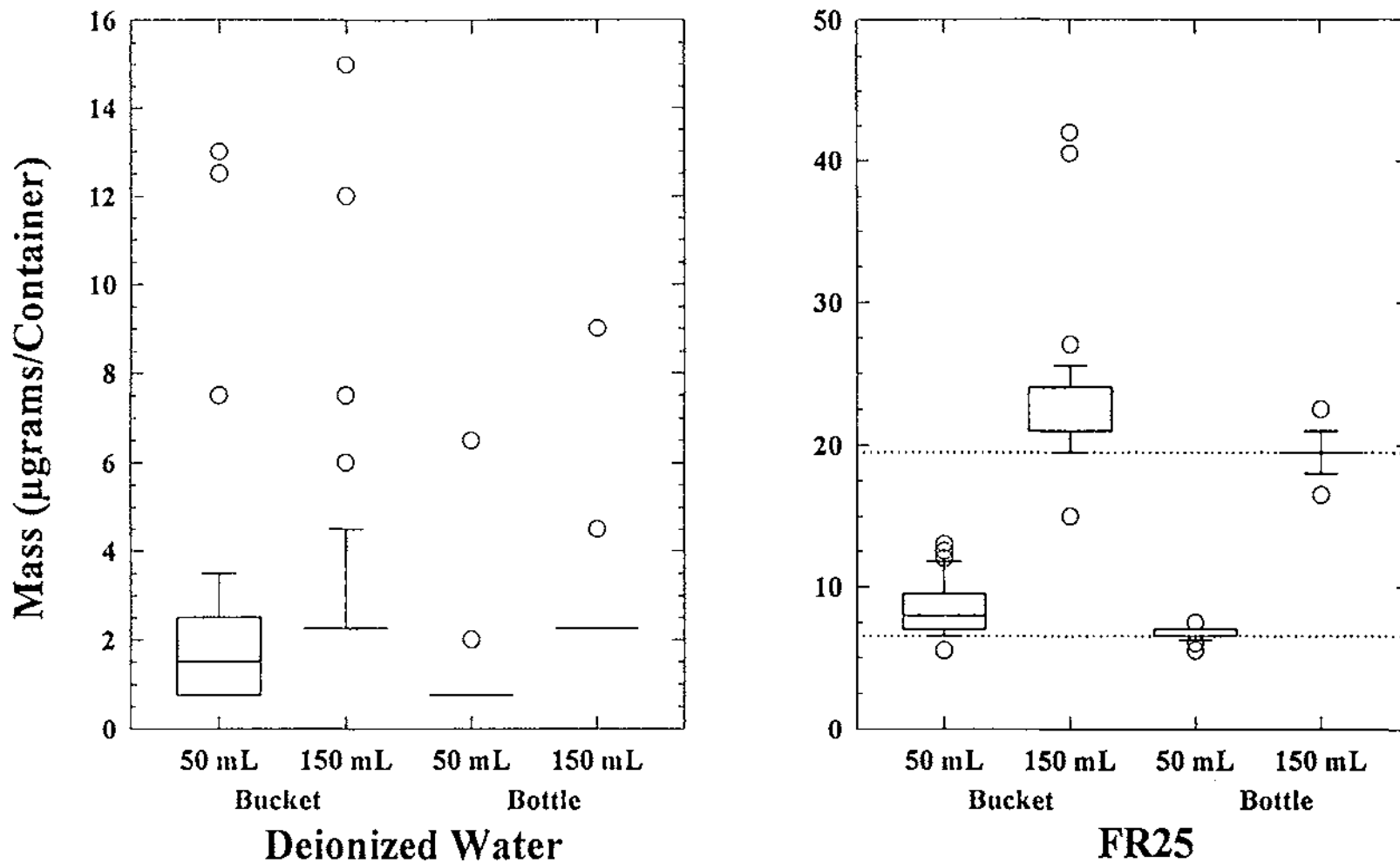


FIGURE B-31. Chloride found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1994. FR25 baseline values shown as dotted lines.

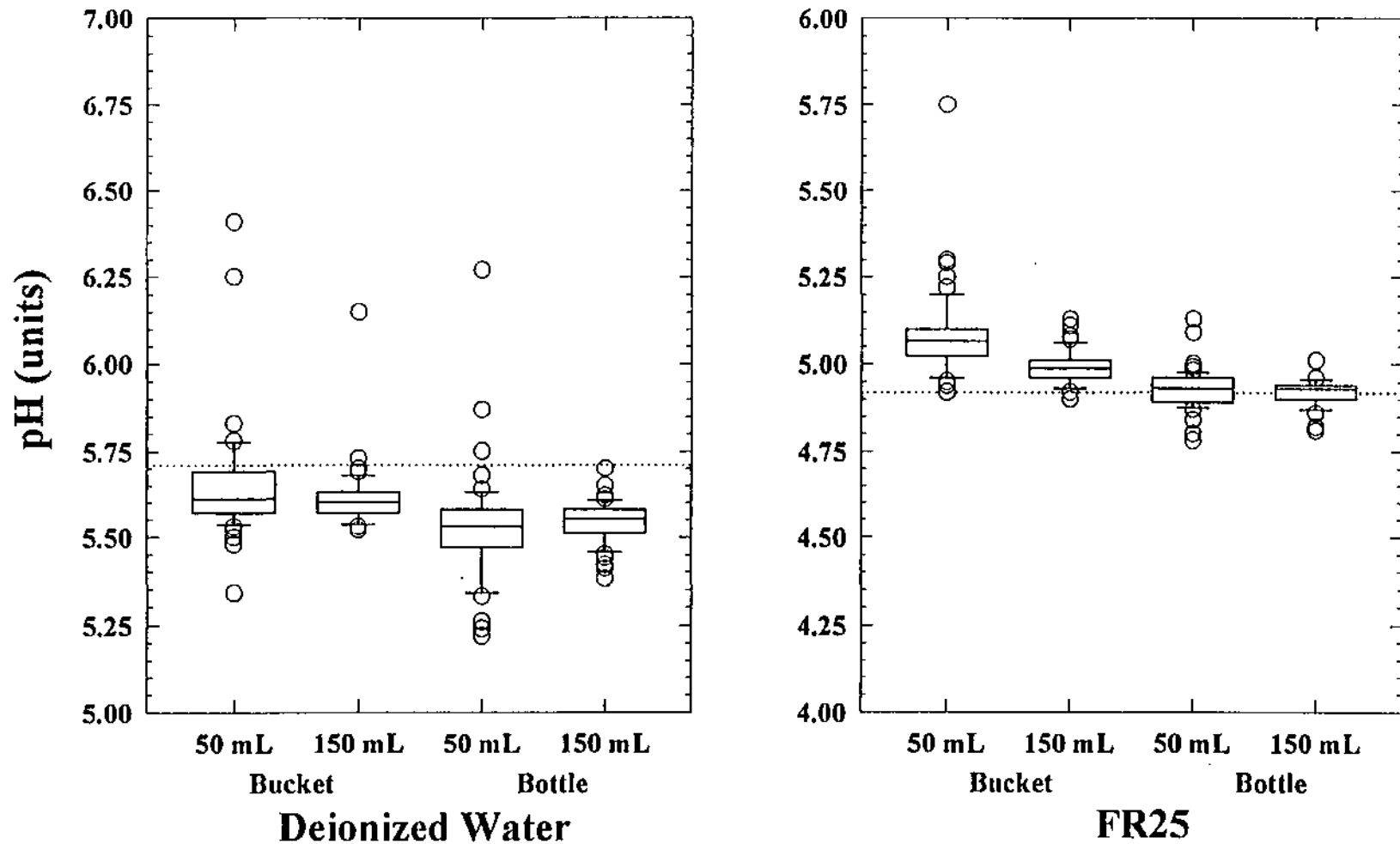


FIGURE B-32. pH of upright bucket blanks and 1-liter bottles leached with DI water and FR25 QCS, 1994. Target values for DI water and FR25 shown as dotted lines.

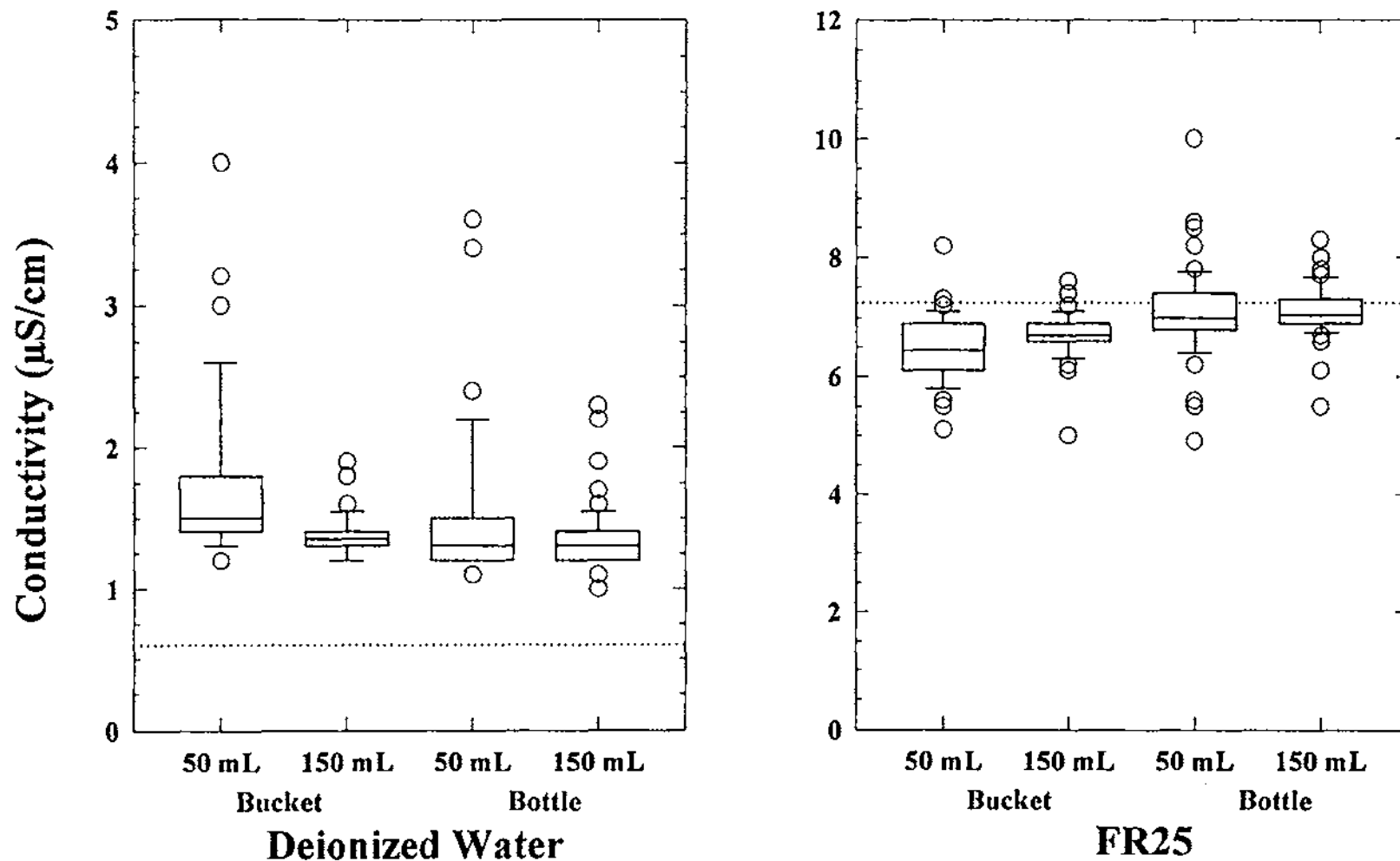


FIGURE B-33. Conductivity of upright bucket blanks and 1-liter bottles leached with DI water and FR25 QCS, 1994. Target values for DI water and FR25 shown as dotted lines.

APPENDIX C

INTERLABORATORY COMPARISON DATA:

WMO, EMEP, LRTAP

1994

TABLE C-1
WMO SEVENTEENTH ANALYSIS ON REFERENCE PRECIPITATION SAMPLES (1994)

Analyte	Units	Sample 1521		Sample 2542		Sample 3541	
		Target	CAL	Target	CAL	Target	CAL
Calcium	mg/L	0.059	0.064	0.135	0.142	0.006	<0.009
Magnesium	mg/L	0.024	0.023	0.019	0.019	0.079	0.079
Sodium	mg/L	0.243	0.248	0.249	0.252	0.49	0.491
Potassium	mg/L	0.075	0.078	0.084	0.086	0.095	0.099
Ammonium	mgN/L	0.112	0.11	0.621	0.63	0.774	0.79
Sulfate	mgS/L	0.526	0.53	2.686	2.63	0.659	3.89
Nitrate	mgN/L	0.14	0.14	0.117	0.12	1.383	1.32
Chloride	mg/L	0.394	0.39	0.638	0.66	0.937	0.97
pH	pH units	4.499	4.54	3.894	3.93	3.55	3.59
Conductivity	$\mu\text{S/cm}$	16.41	16.5	64.07	64.4	130.99	131.2

**TABLE C-2
EMEP - FOURTEENTH INTERCOMPARISON OF METHODS (1994)**

Analyte	Units	Sample G-1		Sample G-2		Sample G-3		Sample G-4	
		Target	CAL	Target	CAL	Target	CAL	Target	CAL
Calcium	mg/L	0.192	0.196	0.383	0.388	0.345	0.347	0.23	0.233
Magnesium	mg/L	0.124	0.124	0.155	0.157	0.232	0.233	0.201	0.204
Sodium	mg/L	0.37	0.374	0.386	0.393	0.558	0.575	0.537	0.541
Potassium	mg/L	0.255	0.264	0.153	0.16	0.204	0.209	0.102	0.106
Ammonium	mgN/L	0.401	0.39	0.481	0.47	0.602	0.58	0.682	0.62
Sulfate	mgS/L	1.439	1.45	1.793	1.81	0.871	0.87	0.802	0.80
Nitrate	mgN/L	0.558	0.57	0.634	0.65	0.74	0.75	0.816	0.84
Chloride	mg/L	0.405	0.41	0.347	0.36	0.695	0.70	0.579	0.62
pH	units	4.16	4.17	4.097	4.11	4.74	4.67	4.66	4.52
Conductivity	µS/cm	39.83	40.0	46.32	46.8	22.68	24.0	23.58	26.4

TABLE C-3
LRTA PINTERLAB ORATORY STUDY NO. 35 MARCH 1994
COMPARISON OF CALVAL UESTOINTI RLABORATORY MEDIAN VALUES

Analyte	Units	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
		Median	CAL	Median	CAL	Median	CAL	Median	CAL	Median	CAL
Calcium	mg/L	1.93	1.937	6.135	6.117	6.135	0.647	0.81	0.817	2.05	2.06
Magnesium	mg/L	0.31	0.32	1.515	1.569	0.39	0.399	0.39	0.4	0.487	0.497
Sodium	mg/L	0.6	0.6	1.15	1.171	2.76	2.767	2.93	2.945	0.497	0.504
Potassium	mg/L	0.41	0.424	0.275	2.8	0.26	0.266	0.29	0.3	0.212	0.222
Ammonium	mgN/L	0.02	0.02	0.75	0.75	0.03	0.03	0.02	0.02	0	-0.02
Sulfate	mg/L	5.4	5.43	8.85	8.94	2.19	2.17	2.16	2.23	6.33	6.31
Nitrate	mgN/L	0.41	0.41	1.19	1.2	0.01	0.01	0	-0.02	0	-0.02
Chloride	mg/L	0.44	0.44	2.15	2.15	4.46	4.26	4.68	4.6	0.4	0.36
pH	units	5.33	5.34	6.99	7.23	5.22	5.27	5.39	5.51	6.09	6.22
Conductivity	µS/cm	23.3	23.6	62.3	63.2	26	26.5	26.9	26.8	26.9	21.9
Analyte	Units	Sample 6		Sample 7		Sample 8		Sample 9		Sample 10	
		Median	CAL	Median	CAL	Median	CAL	Median	CAL	Median	CAL
Calcium	mg/L	3.03	3.079	13.4	13.57	0.97	0.991	1.55	1.576	8.583	8.583
Magnesium	mg/L	0.933	0.95	2.792	2.881	0.202	0.21	0.576	0.594	1.14	1.185
Sodium	mg/L	1.23	1.259	1.376	1.38	0.094	0.098	0.542	0.558	1.459	1.494
Potassium	mg/L	0.55	0.568	0.505	5.25	0.4	0.04	0.498	0.51	0.312	0.331
Ammonium	mgN/L	0.003	0.002	0.002	0.02	0.002	0.02	0.03	0.02	0.03	0.03
Sulfate	mg/L	7.47	7.42	3.5	3.54	0.25	0.25	3.3	3.35	7.42	7.43
Nitrate	mgN/L	0.001	0.002	0.313	0.31	0.02	0.03	0.24	0.23	0.07	0.07
Chloride	mg/L	1.26	1.26	1.42	1.47	0.11	0.11	0.22	0.2	1.55	1.53
pH	units	6.55	6.8	7.77	7.89	6.81	6.81	6.42	6.57	7.41	7.53
Conductivity	µS/cm	34.4	34.9	95.95	97.1	7.79	7.6	19	18.8	63	63.6

**TABLE C-4 LRTAP INTERLABORATORY STUDY NO. 36 JUNE 1994
COMPARISON OF CALVALUES TO INTERLABORATORY MEDIAN VALUES**

Analyte	Units	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
		Median	CAL	Median	CAL	Median	CAL	Median	CAL	Median	CAL
Calcium	mg/L	2.853	2.856	3.986	3.988	0.165	0.167	0.155	0.158	2.655	2.667
Magnesium	mg/L	0.592	0.588	1.411	1.413	0.03	0.028	0.03	0.029	0.66	0.65
Sodium	mg/L	0.11	0.112	0.416	0.416	0.065	0.065	0.096	0.097	1.76	1.783
potassium	mg/L	0.179	0.184	0.227	0.234	0.03	0.027	0.03	0.027	0.369	0.377
Ammonium	mgN/L	0.06	0.07	0.16	0.16	0.18	0.18	0.21	0.21	0.12	0.12
Sulfate	mg/L	1.87	1.92	4.36	4.33	1.8	1.85	1.55	1.58	5.76	5.79
Nitrate	mgN/L	0.4	0.4	0.35	0.34	0.24	0.24	0.21	0.21	0.01	-0.01
Chloride	mg/L	0.2	0.2	0.78	0.77	0.12	0.12	0.19	0.17	3.02	2.99
pH	units	6.86	7.12	7.42	7.41	4.55	4.52	4.65	4.64	6.12	6.38
Conductivity	µS/cm	22.7	22.7	38	38	16.4	17	14.4	14.4	33.5	33.5
Analyte	Units	Sample 6		Sample 7		Sample 8		Sample 9		Sample 10	
		Median	CAL	Median	CAL	Median	CAL	Median	CAL	Median	CAL
Calcium	mg/L	2.8	2.786	6.515	6.498	6.941	6.849	7.04	6.944	5.84	5.798
Magnesium	mg/L	0.59	0.581	0.63	0.618	0.74	0.73	0.756	0.738	1.63	1.63
Sodium	mg/L	0.925	0.91	0.821	0.821	0.847	0.847	0.88	0.854	1	0.959
Potassium	mg/L	0.42	0.419	0.312	0.319	0.24	0.246	0.243	0.248	0.736	0.758
Ammonium	mgN/L	0.09	0.11	0.01	-0.02	0.01	0.02	0.01	-0.02	0.05	0.05
Sulfate	mg/L	0.99	1.02	5.86	5.87	6.33	6.38	6.28	6.37	8.34	8.48
Nitrate	mgN/L	0.01	0	0.2	0.2	0.07	0.07	0.11	0.11	0.09	0.09
Chloride	mg/L	0.93	0.92	0.46	0.44	0.07	0.29	0.11	0.29	0.09	0.96
pH	units	4.17	4.17	7.23	7.44	7.29	7.49	7.34	7.51	7.34	7.41
Conductivity	µS/cm	47	47.4	45	45.2	47.3	47.5	48	48	53.1	53.2

**TABLE C-5 LRTAP INTERLABORATORY STUDY NO. 37 OCTOBER 1994
COMPARISON OF CAL VALUES TO INTERLABORATORY MEDIAN VALUES**

Analyte	Units	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
		Median	CAL	Median	CAL	Median	CAL	Median	CAL	Median	CAL
Calcium	mg/L	13.5	13.49	2.55	2.568	2.801	2.822	6.76	6.798	2.87	2.87
Magnesium	mg/L	2.804	2.807	0.604	0.616	0.592	0.586	0.632	0.628	0.584	0.582
Sodium	mg/L	1.37	1.367	2.194	2.19	0.93	0.915	0.824	0.812	0.112	0.112
Potassium	mg/L	0.5	0.505	0.5	0.507	0.41	0.411	0.285	0.289	0.173	0.18
Ammonium	mgN/L	0.01	-0.02	0.03	0.03	0.08	0.08	0.1	0.1	0.06	0.06
Sulfate	mg/L	3.45	3.53	4.59	4.7	1.03	1.04	5.85	5.96	1.87	1.9
Nitrate	mgN/L	0.29	0.29	0.07	0.07	0	0	0.14	0.14	0.4	0.4
Chloride	mg/L	1.43	1.39	1.67	1.68	0.9	0.88	0.39	0.37	0.2	0.2
pH	units	7.8	7.93	6.6	6.88	4.17	4.2	7.28	7.36	6.9	7.13
Conductivity	$\mu\text{S/cm}$	97	96.2	32.2	31.9	46.6	46.3	46.5	22.7	22.8	118.2
Analyte	Units	Sample 6		Sample 7		Sample 8		Sample 9		Sample 10	
		Median	CAL	Median	CAL	Median	CAL	Median	CAL	Median	CAL
Calcium	mg/L	8.8	8.81	4.6	4.681	2.92	2.942	2.62	2.643	1.95	1.997
Magnesium	mg/L	2.688	2.68	0.824	0.828	0.688	0.69	1	1.007	0.476	0.478
Sodium	mg/L	0.2	0.2	0.551	0.549	0.95	0.939	0.277	0.28	0.6	0.608
Potassium	mg/L	0.322	0.326	0.19	0.196	0.464	0.471	0.15	0.161	0.23	0.235
Ammonium	mgN/L	0.9	0.9	0.29	0.3	0.02	0.02	0.29	0.31	0.02	-0.02
Sulfate	mg/L	23.15	23.6	5.78	5.87	6.82	6.93	3.75	3.8	5.99	6.19
Nitrate	mgN/L	4.28	4.44	0.85	0.86	0.05	0.05	0.54	0.54	0	0
Chloride	mg/L	0.92	0.85	0.48	0.48	1.03	1.02	0.46	0.46	0.5	0.5
pH	units	4.25	4.26	7	7.13	6.71	6.76	7	7.05	6.26	6.26
Conductivity	$\mu\text{S/cm}$	118	118.2	40	39.5	30.8	30.6	29.2	28.9	21.8	22

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