

QUALITY ASSURANCE REPORT NADP/NTN DEPOSITION MONITORING

Laboratory Operations
Central Analytical Laboratory
1995

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

A Cooperative Research Program of the
State Agricultural Experiment Stations
and other Federal, State, and Private
Research Organizations • IR-7



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.

A number of federal agencies support NADP/NTN research and monitoring including: U.S. Geological Survey (USGS) - Water Resources Division; U.S. Geological Survey (USGS) - Biological Resources Division; Cooperative State Research, Education, and Extension Service (CSREES); U.S. Forest Service (USFS); National Park Service (NPS); Bureau of Land Management (BLM); National Oceanic and Atmospheric Administration (NOAA); Environmental Protection Agency; and U.S. Fish and Wildlife Service (USFWS). 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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**1995 QUALITY ASSURANCE REPORT
NADP/NTN DEPOSITION MONITORING**

**Laboratory Operations
Central Analytical Laboratory
January 1995 - December 1995**

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ACKNOWLEDGMENTS

This Laboratory Operations Quality Assurance Report, a summary of the quality control/quality assurance measures in place at the Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program/ National Trends Network (NADP/NTN) and NADP/Atmospheric Integrated Research Monitoring Network (NADP/AIRMoN), is the product of many individuals. Mark Peden, the laboratory manager, and Van Bowersox, CAL Director, provide ongoing input and support throughout the laboratory year. The analyses of the thousands of samples are performed by a dedicated staff of analysts with the support of conscientious sample receiving and processing personnel. Leon Olszewski provided computer support for part of the year. Andrea Morden-Moore contributed additional computer products for the completion of the report. Lacie Jeffers provided input for the text and tables. Thanks to the following editors for their time and input to the final report: Mark Peden, Eva Kingston, Cary Eaton, John Sherwell and Jeff Litteral.

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. Thirty-five sites were in operation by December 1979. In 1995, the NADP CAL is still at the ISWS, and there are 200 NADP/National Trends Network (NTN) sites collecting precipitation throughout the United States. The samples are collected in buckets using a specified wet/dry sampler. The buckets are removed each Tuesday. Beginning in January 1994, the sample is decanted from the collection bucket into a 1-liter wide-mouth high-density polyethylene (HDPE) bottle and shipped, with the dirty bucket, to the CAL each week. Figure I-1 illustrates the sample's journey after its arrival at the CAL.

In 1994 The Atmospheric Integrated Research Monitoring Network (AIRMoN) protocol was defined and its QA program put into place. Since that time NADP/AIRMoN and NADP/NTN have shared the same analytical staff and methodology. AIRMoN sample protocol differs in that samples are collected daily if a precipitation event occurs, chilled, and shipped in an insulated container. pH and conductivity are measured on receipt, the sample remains in its original 250 mL HDPE bottle and is refrigerated at all times except when aliquots are poured for ion analysis. The ions are analyzed in a specified order; ammonium, anions, and the atomic absorption cations.

Table I-1 lists the staff who are responsible for samples from the time they reach the ISWS until the analytical data have been verified and transmitted to the Coordination Office at Colorado State University. The majority of the staff have been employed at the Illinois State Water Survey for more than ten years, and all are committed to the project. Jackie Damara, an employee since 1983, left in 1995 and was not replaced. Her tasks were reassigned to her staff and others working in the CAL. The employees performing the sample analyses are responsible for implementing quality control (QC) procedures within their analytical scheme. Analytical methods are revised as technology improves and new instruments are purchased. Each time an instrument update occurs, a comprehensive study is performed to assure comparability of the data. Detection limits are verified and reported. Table I-2 lists the CAL method detection limits (MDL) for the ions of interest as well as the method.

From the beginning of the network, the analytical data have been entered into a large central database. In the early years, these data were hand entered using a double-entry system as a means of verification. Currently, the data from the atomic absorption, ion chromatography, and flow injection instruments are electronically transferred to the database. The pH and conductivity results are still double-entered manually. At the end of the calendar year, the data are compiled and made available for annual reports and individual site chemistries. Table I-3 lists the percentile concentration values for all of the samples of volume greater than 35 milliliters (mL) analyzed by the CAL in 1995. It also includes the

number of "wet" (W) samples and the mean and median sample volumes for the year. The concentration values have been consistent since the network was expanded to include the entire United States in 1982 and 1983.

The ion concentrations displayed on Tables I-3 and I-4 indicate the dilute nature of the precipitation samples analyzed in the laboratory. In order for the data to be meaningful, it is necessary to incorporate an extensive quality assurance (QA) program in the laboratory. Several components of the QA program have evolved from the time the very first sample was analyzed. The Network Quality Assurance Plan (1) summarizes the methods used to document the analysis of each sample. The various facets of the program have been modified and refined over the years. The quality control (QC) samples are known to the analysts, who use them as guides to ensure the accuracy of their work. Other samples are unknown or blind to the analysts and are valuable ways of assessing the actual bias and/or precision of samples in the NADP/NTN/AIRMoN daily queue. Extensive analyses of blank solutions are performed every week in order to identify and/or eliminate sources of contamination. Participation in several international laboratory intercomparison studies in addition to the mandated study performed by the U.S. Geological Survey (USGS) enables the CAL to evaluate the quality of its work as compared to peer laboratories throughout the United States, Canada, and Europe. The history of the CAL program can be found in the Laboratory QA reports published annually since 1986 and available from the CAL or the Coordination Office (2-13). This report presents and discusses summaries of the results of QA programs in place in 1995.

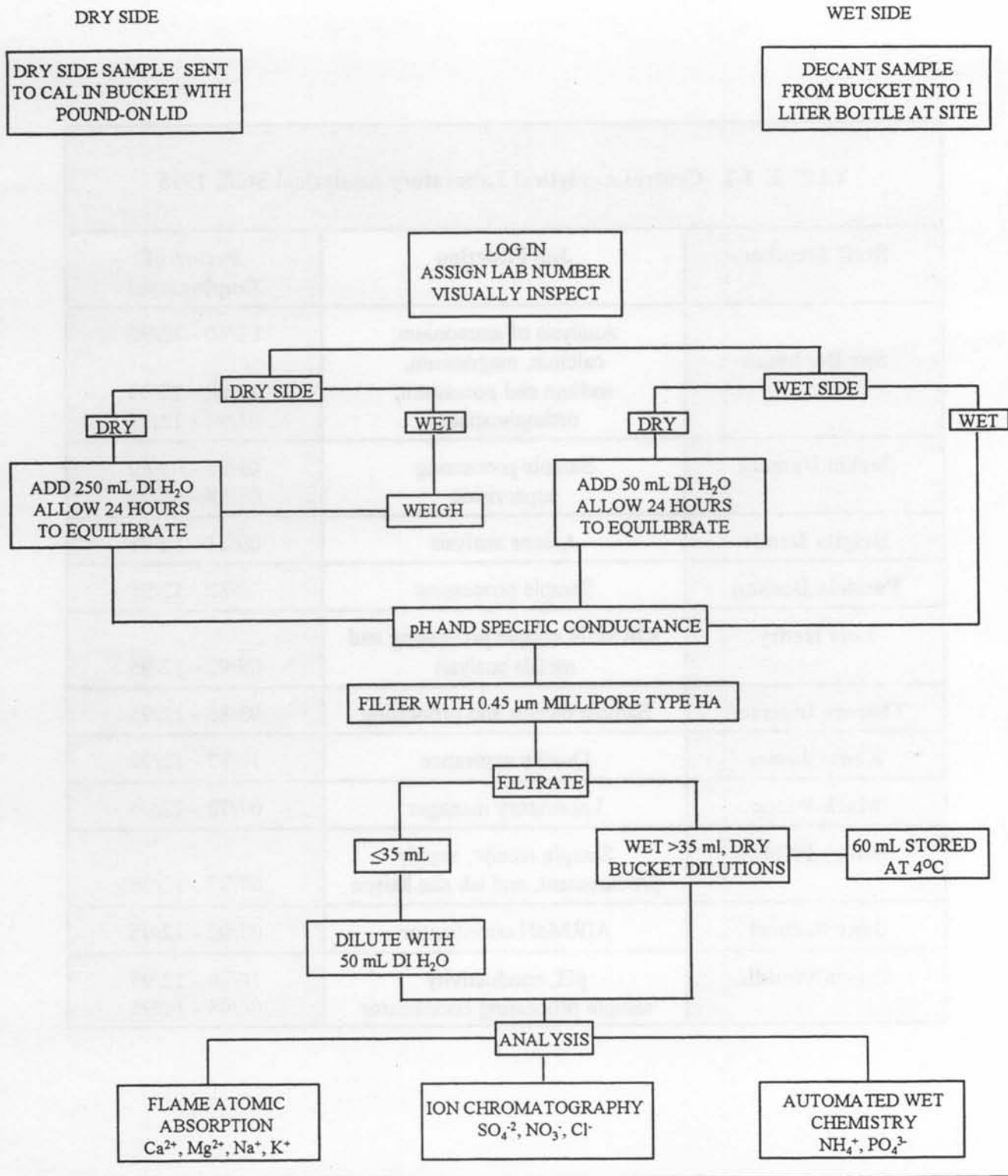


FIGURE I-1 Sample processing flowchart, January 1995-December 1995

TABLE I-1 Central Analytical Laboratory Analytical Staff, 1995

Staff Member	Job Function	Period of Employment
Sue Bachman	Analysis of ammonium; calcium, magnesium, sodium and potassium; orthophosphate	08/80 - 12/95 11/88 - 12/95 01/94 - 12/95
Jackie Damara	Sample processing supervision	09/83 - 05/86 01/88 - 06/95
Brigita Demir	Anions analysis	09/81 - 12/95
Patricia Dodson	Sample processing	09/80 - 12/95
Lori Henry	AIRMoN sample processing and metals analysis	08/92 - 12/95
Theresa Ingersoll	Sample receipt and processing	03/85 - 12/95
Kenni James	Quality assurance	10/87 - 12/95
Mark Peden	Laboratory manager	07/78 - 12/95
Jeffrey Pribble	Sample receipt, supply procurement, and lab site liaison	07/87 - 12/95
Jane Rothert	AIRMoN coordinator	05/92 - 12/95
Angela Weddle	pH, conductivity sample processing coordinator	10/89 - 12/95 06/95 - 12/95

TABLE I-2 Method Detection Limits (MDLs) for Precipitation Analysis, 1995

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

TABLE I-3 Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/NTN Precipitation, 1995

Parameter	Percentile Concentration Value (mg/L)											Max.
	Min.	5th	10th	25th	50th	75th	90th	95th	99th			
Calcium	-0.009	0.012	0.020	0.046	0.106	0.242	0.492	0.763	1.926	11.4		
Magnesium	-0.003	0.003	0.005	0.010	0.021	0.043	0.082	0.125	0.283	1.79		
Sodium	-0.003	0.020	0.026	0.041	0.072	0.148	0.356	0.631	1.822	7.74		
Potassium	-0.003	-0.003	0.003	0.008	0.018	0.037	0.072	0.108	0.278	3.14		
Ammonium	-0.02	0.02	0.04	0.09	0.22	0.44	0.73	1.00	1.72	4.32		
Sulfate	-0.03	0.12	0.22	0.49	0.99	1.82	3.03	4.01	6.77	17.96		
Nitrate	-0.03	0.15	0.26	0.56	1.03	1.81	2.88	3.83	6.47	22.40		
Chloride	-0.03	0.03	0.04	0.06	0.12	0.23	0.57	1.09	2.83	13.6		
o-Phosphate	-0.003	-0.003	-0.003	-0.003	-0.003	-0.003	0.003	0.004	0.012	0.600		
pH(units)	3.49	4.11	4.25	4.49	4.84	5.26	5.77	6.16	6.71	7.80		
Cond. (µS/cm)	1.5	3.1	4.3	7.1	11.9	21.0	33.3	44.5	73.1	201		

Notes: Number of samples = 6875; mean sample volume = 1578 mL; median sample volume = 999 mL.

**TABLE I-4 Percentile Concentration Values of Chemical and Physical Parameters
Measured in NADP/AIRMoN Precipitation, 1995**

Percentile Concentration Values (mg/L)

Parameter	Min.	5th	10th	25th	50th	75th	90th	95th	Max.
Calcium	-0.006	0.006	0.015	0.037	0.093	0.199	0.401	0.610	2.54
Magnesium	-0.001	0.002	0.003	0.007	0.018	0.038	0.083	0.151	1.010
Sodium	-0.001	0.004	0.008	0.016	0.036	0.099	0.313	0.778	9.70
Potassium	-0.003	0.001	0.003	0.009	0.018	0.035	0.069	0.097	0.568
Ammonium	0.00	0.03	0.05	0.15	0.33	0.57	0.92	1.24	3.06
Sulfate	0.05	0.27	0.52	0.99	1.82	3.08	4.86	6.05	19.26
Nitrate	0.05	0.29	0.43	0.94	1.74	2.99	4.49	6.14	12.12
Chloride	0.00	0.03	0.04	0.07	0.14	0.27	0.73	1.44	16.66
o-Phosphate	0.00	0.00	0.00	0.00	0.00	0.007	0.014	0.020	0.135
pH(units)	3.43	3.85	3.96	4.14	4.35	4.61	4.87	5.09	6.65
Cond. (μ S/cm)	2.1	7.1	9.9	15.8	26.0	40.4	59.2	79.5	201.3

Notes: Number of samples = 678; mean sample volume = 662.4 mL; median sample volume = 351.1 mL

II. LABORATORY QUALITY ASSURANCE - A GENERAL DESCRIPTION

This report summarizes the results of the quality assurance (QA) program in effect at the CAL in 1995. Table II-1 summarizes the various QA/QC components and their frequency of occurrence. The QA of chemical measurements begins in the field where pH and conductivity are measured soon after sample collection and prior to shipping. Quality control standards (QCS) solutions are formulated and prepared at the CAL and shipped to the sites. In 1995, the two QCS solutions were a potassium chloride solution with a specific conductance of 75 microsiemens per centimeter ($\mu\text{S}/\text{cm}$) and a dilute nitric acid solution with a pH of 4.3 and specific conductance of 21.8 $\mu\text{S}/\text{cm}$. The first solution is used to obtain the correction factor for the conductivity cell; the second solution is used as the QCS for the pH calibration. Since calibration buffer solutions are of high ionic strength, it is necessary to verify that the probe will measure solutions that are similar to precipitation in ionic strength. The second solution is also used as a conductivity check sample.

When the field samples reach the CAL, they are unpacked with care, and the information and requests written on the field forms are noted. They are then transported to sample processing where they are visually inspected and assigned a sequential number. Samples are then taken to the laboratory where pH and conductivity are measured and aliquots of each sample are filtered from the 1-liter shipping bottle into a 60-milliliter (mL) round bottle. When there is sufficient volume, two samples are filtered into the smaller bottles: one in the round bottle for immediate ion analysis, the other in a square bottle for archival purposes. Samples from the Atmospheric Integrated Research and Monitoring Network (AIRMoN) are never filtered, but rather are shipped and stored at 4 degrees Celsius in the 250-mL bottles into which they were decanted at the site.

The pH meter is calibrated with commercially prepared buffer solutions of pH 7 and 4. The ability of the electrode to measure low ionic strength precipitation solutions is verified by measuring two solutions of simulated rainwater at ionic strengths emulating the 25th and 75th percentile concentrations of the network. These solutions are made in-house and tested extensively prior to being made available for use as QCS solutions and referred to as Faux Rain 25 (FR25) and Faux Rain 75 (FR75) by the analytical staff. They are used as QCS solutions for the entire suite of ions except for phosphate, which is too unstable, especially at the low concentrations found in NADP samples. U.S. Environmental Protection Agency (USEPA) nutrient concentrates are diluted and used for phosphate QCS.

After filtration, the samples in the round 60-mL bottles are placed on a tray which contains 9 rows of 12 bottles each. The tray is taken to the main laboratory building and placed with other sample trays containing samples awaiting analysis for the major ions. (AIRMoN samples are stored on trays in the walk-in cooler in the sample processing area and are analyzed in a specified order: ammonium and phosphate; sulfate, nitrate, and chloride; and finally calcium, magnesium, sodium, and potassium.) The analysts select the trays containing the samples with numbers in the next sequence and analyze them either by atomic absorption,

ion chromatography, or flow injection automated colorimetric analyses. These instruments are calibrated using standards which bracket the concentration range of the samples. The calibration curve is then verified with the two QCS solutions, FR25 and FR75. The values of these two solutions are recorded and summarized monthly for control charts, and monthly means and standard deviations are calculated. The annual summary is presented in Table III-1. The statistics presented in this table represent optimum analytical conditions. These standards are analyzed immediately after calibration solutions or blanks have been analyzed and regularly throughout the sample run. The operator is fully aware of their concentration values and uses them to ascertain whether or not the instrument is maintaining calibration.

Each week blank solutions are collected from various sources and submitted as a batch to the laboratory for analysis as blank samples. These samples are used to indicate possible sources of contamination both from the sample collection and shipping activity and the materials used in the laboratory. The deionized (DI) water used for standards preparation, bucket and bottle washing, rinse water, and filter leaching is monitored regularly, and samples are collected each week from DI water outlets in the atomic absorption laboratory, the sample preparation laboratory, and the bucket washing laboratory. DI water and FR25 are allowed to remain in sample collection buckets and lids, shipping bottles, and AIRMoN bottles for 24 hours prior to being decanted into 60 mL bottles. These leachates and filtrates from two filters complete the sources of the blanks solutions.

Other weekly components of the program are three samples submitted as internal blinds and four or five samples that are split so that the duplicates are submitted with new sample numbers unknown to the analysts.

Events that occur on a monthly rotation are the submission of reanalysis lists to the laboratory so that samples with an ion or conductance imbalance can be reanalyzed and archival samples, if available, can be used to support either the original or reanalysis values if there is a large discrepancy in the analytical results. Every three months USGS Laboratory Intercomparison results are submitted, reviewed, and sent on to the USGS in Denver. These samples are analyzed as a group and their source is known to the analysts.

Other external agencies that conduct interlaboratory comparisons operate on an annual or semiannual schedule. These samples are analyzed with network samples but are identified as interlaboratory comparison samples. The results of these studies are used to evaluate the performance of the CAL in relation to peer laboratories in North America and Europe.

**TABLE II-1 NADP/NTN Laboratory QC/QA Program Summary,
1995**

- 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 and plotted on daily control charts.
 - 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, and 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.**

III. DAILY QUALITY CONTROL PROCEDURES

Each morning prior to analysis, the analysts prepare reagents and standards and evaluate the performance of the analytical instrumentation. Standards preparation and instrument maintenance information are recorded in notebooks that are kept in the individual laboratories. Calibration standards are analyzed according to the standard operating procedure of the method and are followed by the measurement of quality control solutions (QCS) in order to ensure the validity of the calibration curve. FR25 and FR75 are used to test the standards at two levels that are relevant to the precipitation samples being measured. Each time QCS are measured throughout the sample run, the values are recorded and graphed on a daily control chart located near the instrument. These daily data are combined monthly for the monthly control charts kept on file in the Quality Assurance (QA) Specialist's office. The same data are compiled and summarized at the end of each calendar year and are presented in Table III-1.

The data presented on this table represent optimum figures for bias and precision. They are comparable to previous years and fall within the specifications the laboratory is expected to meet. Refer to the laboratory portion of the Network QA Plan (1) for more information.

TABLE III-1 Analytical Bias and Precision Determined from Analysis of Simulated Rain QCS, 1995

Parameter	Target Concentration (mg/L)	Measured Concentration (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision _s (mg/L)	Precision RSD (%)	Critical Concentration (mg/L)	Statistically Significant Bias?
Calcium	0.093 ^a	0.093	2106	0.0	0.0	0.002	2.2	0.002	NO
	0.388 ^b	0.378	782	-0.010	-2.6	0.010	2.6	0.006	YES
Magnesium	0.016	0.016	1264	0.0	0.0	0.000	0.0	0.000	NO
	0.068	0.068	494	0.0	0.0	0.002	2.9	0.001	NO
Sodium	0.046	0.046	1644	0.0	0.0	0.001	2.2	0.001	NO
	0.187	0.189	537	0.002	1.1	0.006	3.2	0.004	NO
Potassium	0.014	0.013	303	-0.001	-7.1	0.001	7.7	0.001	NO
	0.052	0.054	482	0.002	3.8	0.002	3.7	0.002	NO
Ammonium	0.09	0.09	519	0.00	0.0	0.01	13.5	0.01	NO
	0.38	0.38	385	0.00	0.0	0.01	3.4	0.01	NO
Sulfate	0.59	0.59	1095	0.0	0.0	0.01	1.5	0.01	NO
	2.43	2.44	1060	0.01	0.2	0.02	0.7	0.01	NO
Nitrate	0.48	0.47	1101	-0.01	-2.1	0.01	2.1	0.01	NO
	1.96	1.96	1057	0.0	-0.2	0.02	1.0	0.01	NO
Chloride	0.16	0.16	1096	0.0	1.9	0.01	3.7	0.00	NO
	0.69	0.68	1051	-0.01	-1.4	0.03	4.4	0.02	NO
o-Phosphate	0.024	0.021	360	-0.003	-12.5	0.003	14.3	0.001	YES
	0.059	0.056	310	-0.003	5.4	0.003	5.4	0.001	YES
pH units (µeq/L) ^c	4.92(12.0)	4.94(11.5)	2279	0.02(-0.6)	0.41(-4.7)	0.02(0.49)	0.4(4.3)	0.01(0.31)	YES
	4.36(43.6)	4.36(43.2)	2109	0.0(-0.4)	0.0(-1.0)	0.01(1.1)	0.2(2.7)	0.01(0.71)	NO
Conductivity (µS/cm)	7.16	7.02	1050	-0.14	-1.9	0.11	1.6	0.07	YES
	27.5	27.4	1050	-0.06	-0.2	0.12	0.4	0.08	NO

Notes: ^a The first set of values for each parameter is for the 25th percentile solution. ^b The second set of values for each parameter is for the 75th percentile solution. ^c The pH data in parentheses are hydrogen ion concentrations expressed in microequivalents per liter. See Appendix A for definitions and formulas for Bias, Standard Deviation, Precision, and Critical Concentration.

IV. WEEKLY QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES

Three QA activities occur on a weekly basis: three solutions, for which only the QA specialist knows the concentrations, are submitted as internal blind samples; two percent of the network samples are split and analyzed in duplicate; and 17-19 blanks and container leachates are bottled and analyzed. AIRMoN field blanks and internal blinds are also submitted on a weekly schedule.

A. Internal Blind Audit

Each week the QA Specialist submits three solutions of known concentrations and accompanying field forms to the sample processing area where sample numbers are assigned. These samples are taken into the laboratory with the network samples and treated as such except that two of the three samples bypass the filtering process. The sites for these samples are coded as SWS1, SWS2, and SWS3. In 1995, SWS1 samples were High Purity Standards Simulated Rainwater I (HPS-SRI) and II (HPS-SRII) which were alternated weekly. SWS2 samples were DI water from the ion chromatography laboratory and pH 4.3 nitric acid QCS solution which were also alternated weekly. SWS1 and SWS2 samples were not filtered. SWS3 samples were all of the former mentioned samples submitted in rotation and filtered.

Tables IV-1 through IV-4 summarize the data from these weekly samples. It is important to remember that the blind sample population is considerably smaller than that of the QCS and that these samples may fall anywhere in the sample queue, for example, right after calibration or prior to the next QCS. The bias and precision estimates derived are therefore more like those of real samples sent in from the sites. Samples from SWS1 and SWS2 show fewer contaminants and less variability than the filtered counterparts from SWS3 (which has an even smaller sample population for each solution). Also note the differences in concentrations of each parameter, remembering that the QCS concentrations mimic those of the network. The bias percentages for most parameters are higher, the exceptions being the lower magnesium concentration, both potassium concentrations, and the low specific conductance. The ammonium bias for the lower concentration is explained by the measurements being close to the detection limit, a situation where a small difference in concentration results in a large percent difference. Percent relative standard deviation (RSD) is more variable than percent bias when the two groups of solutions are compared. The percent RSD is generally higher for the metallic elements analyzed by atomic absorption, lower for ammonium, and similar for the anions analyzed by ion chromatography.

The SWS2 solutions are for the most part blanks, one is DI water, the other is acidified DI water. These solutions are placed randomly among the network samples so that their analytical results can indicate if there is a problem with sample carryover or false positives. A cursory look at Table IV-2 shows that these results are very reasonable. The ubiquitous sodium is only faintly present and the other ions are absent. In both filtered SWS3 solutions, sodium is present; its concentration is higher in the acidified solution.

The SWS3 values using HPS solutions (Table IV-3) are incredibly variable and show a high percent bias for both calcium (lower concentration not significant) and sodium. Ammonium at the lower concentration exhibits a large percent bias because each 0.01 mg/L difference from the target concentrations results in a 10 percent bias fluctuation. A negative sulfate bias has been observed in the filtered samples since the beginning of the internal blind program. Filtered blank solutions (Table IV-4) contain varying amounts of sodium but never as much as seen in the HPS filtered solutions. The acidified solution (pH 4.3 nitric acid) contains higher concentrations of sodium than the DI water. Tables B-1 and B-2 in Appendix B are tabular comparisons of the filtered and unfiltered solutions from HPS submitted as internal blind samples. They are followed by figures displaying the data for each parameter.

B. Replicate Samples

Two percent of the weekly samples are split for duplicate analysis. They are divided at the time of filtration into three 60 mL portions: one is put on the tray for transfer to the lab, one is filtered into a square bottle for archival purposes, and the third is sent back to sample processing to be assigned a higher number and resubmitted for analysis. The original and duplicate sample may be analyzed on the same day or several days apart, depending on their location on the tray. After analysis, the data management staff recodes the duplicate with the original sample number followed by a "Q"(quality control) so that the original "S"(sample) and "Q" portions appear consecutively on the bimonthly printout.

Replicate samples serve as another estimator of sample precision. Since these samples are also blind to the analysts, their concentration values should produce valid precision data. The analyses of replicate samples performed in 1995 are summarized in Table IV-5. Differences are calculated by subtracting the reanalysis value from the original. The annual summaries of each ion have been split into two sections. The median concentration for the year is determined for each analyte (Appendix B, Table B-3). The box plots (Figures B-21 through 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 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 1995 duplicate data set. A comparison of the standard deviation values for the QCS, SWS1, and SWS3 samples to the variance for the replicate samples shows the cation and anion precisions to be comparable. The precision of the duplicate pH and conductance samples is better than that of the QCS and internal blind samples.

TABLE IV-1 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS1), High Purity Standards Simulated Rainwater I (HPS-SRI) and II (HPS-SRII), Unfiltered, 1995									
Parameter	Target Concentration (mg/L)	Measured Concentration (mg/L)	Number of Samples n	Bias (mg/L)	Bias %	Precision s (mg/L)	Precision RSD (%)		
Calcium	0.015 ^a	0.016	25	0.001	6.7	0.003	18.8		
	0.052 ^b	0.056	25	0.004	7.7	0.005	8.9		
Magnesium	0.026	0.026	25	0.0	0.0	0.001	3.8		
	0.049	0.045	25	-0.004	-8.2	0.003	6.7		
Sodium	0.200	0.208	25	0.008	4.0	0.019	9.1		
	0.380	0.400	25	0.020	5.3	0.012	3.0		
Potassium	0.050	0.050	25	0.0	0.0	0.003	6.0		
	0.100	0.100	25	0.0	0.0	0.004	4.0		
Ammonium	0.10 ^c	0.12	25	0.02	20.0	0.01	8.3		
	1.00	1.02	25	0.02	2.00	0.02	2.0		
Sulfate	2.50	2.58	25	0.08	3.2	0.02	0.8		
	10.10	10.30	25	0.20	2.0	0.06	0.6		
Nitrate	0.50	0.52	24	0.02	4.0	0.01	1.9		
	7.10	7.19	25	0.09	1.3	0.06	0.8		
Chloride	0.25	0.24	25	-0.01	-4.0	0.01	4.2		
	0.98	1.00	25	0.02	2.0	0.05	5.0		
pH units (µeq/L)	4.30(50.1) ^d	4.32(47.9)	25	0.02(-4.2)	0.5(-8.7)	0.02(2.42)	0.5(2.1)		
	3.60(252)	3.60(251)	25	0.0(-1)	0(-0.4)	0.02(8.69)	0.6(3.5)		
Conductivity µS/cm	25.0	24.8	25	-0.2	-0.8	0.61	2.5		
	128	127.3	25	-0.7	-0.8	2.28	1.8		

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 is these standards has been found to be unstable. ^d Values in parentheses represent hydrogen ion concentrations expressed as microequivalents per liter.

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, 1995

Parameter	Target Concentration (mg/L)	Measured Concentration (mg/L)	Number of Samples n	Bias (mg/L)	Bias %	Precision s (mg/L)	Precision RSD (%)
Calcium	<0.009 ^a	<0.009	25			0.003	
	<0.009 ^b	<0.009	25			0.002	
Magnesium	<0.003	<0.003	25			0.000	
	<0.003	<0.003	25			0.000	
Sodium	<0.003	0.003	25			0.002	66.7
	<0.003	0.005	25			0.012	240
Potassium	<0.003	<0.003	25			0.001	
	<0.003	<0.003	25			0.000	
Ammonium	<0.02	<0.02	25			0.00	
	<0.02	<0.02	25			0.01	
Sulfate	<0.03	<0.03	25			0.00	
	<0.03	<0.03	25			0.00	
Nitrate	<0.03	<0.03	25			0.00	
	3.12	3.20	25	0.08	2.6	0.07	2.2
Chloride	<0.03	<0.03	25			0.00	
	<0.03	<0.03	25			0.01	
pH units (µeq/L)	5.71(1.95) ^c	5.53(2.93)	25	-0.18(0.98)	-3.2(50.2)	0.20(1.07)	3.6(36.5)
	4.30(50.1)	4.32(48.1)	25	0.02(-2.0)	0.46(-4)	0.02(2.07)	0.5(4.3)
Conductivity µS/cm	0.8	1.0	25	0.2	25	0.2	20
	21.8	21.7	25	-0.1	-0.5	0.6	2.8

Notes: ^a 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. ^c The pH data in parentheses are hydrogen ion concentrations in microequivalents per liter.

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, 1995

Parameter	Target Concentration (mg/L)	Measured Concentration (mg/L)	Number of Samples n	Bias (mg/L)	Bias %	Precision s (mg/L)	Precision RSD (%)
Calcium	0.015 ^a	0.025	13	0.010	66.7	0.007	28
	0.052 ^b	0.085	12	0.033	63.5	0.036	42
Magnesium	0.026	0.027	13	0.001	3.8	0.003	11
	0.049	0.051	12	0.002	4.1	0.006	11.8
Sodium	0.200	0.280	13	0.080	40	0.035	12.5
	0.380	0.459	11	0.079	21	0.034	0.9
Potassium	0.050	0.049	13	-0.001	-2.0	0.003	6.1
	0.100	0.101	13	0.001	1.0	0.006	5.9
Ammonium	0.10 ^c	0.16	13	0.06	60	0.04	25
	1.00	1.07	13	0.07	7.0	0.10	9.3
Sulfate	2.50	2.48	13	-0.02	-0.8	0.04	1.6
	10.10	9.87	13	-0.23	-2.3	0.09	0.9
Nitrate	0.50	0.60	13	0.10	20	0.06	10
	7.10	7.01	13	-0.09	-1.3	0.13	1.8
Chloride	0.25	0.29	13	0.04	16	0.03	10
	0.98	1.00	13	0.02	2.0	0.06	6
pH units (µeq/L)	4.30(52.5) ^d	4.31(49.4)	13	0.01(-3.1)	0.2(-5.9)	0.02(2.3)	0.5(4.7)
	3.60(252)	3.60(252)	13	0.0(0)	0(0)	0.01(7.24)	0.3(2.9)
Conductivity µS/cm	25.0	25.1	13	0.1	0.4	0.5	2.0
	128	129	13	1	0.8	1.9	1.5

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 Values in parentheses represent hydrogen ion concentrations expressed as microequivalents per liter.

TABLE IV-4 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS3), Delionized (DI) Water and pH 4.3 QCS, Filtered, 1995									
Parameter	Target Concentration (mg/L)	Measured Concentration (mg/L)	Number of Samples n	Bias (mg/L)	Bias %	Precision s (mg/L)	Precision RSD (%)		
Calcium	<0.009 ^a	<0.009	12			0.0			
	<0.009 ^b	<0.009	12			0.007			
Magnesium	<0.003	<0.003	12			0.0			
	<0.003	0.004	12	0.002 ^c		0.005			
Sodium	<0.003	0.050	12	0.048		0.030	60		
	<0.003	0.070	9	0.068		0.009	12.8		
Potassium	<0.003	<0.003	12			0.0			
	<0.003	0.003	12			0.006			
Ammonium	<0.02	0.03	12	0.02		0.03			
	<0.02	0.09	12	0.08		0.05	55.6		
Sulfate	<0.03	<0.03	12			0.0			
	<0.03	<0.03	12			0.0			
Nitrate	<0.03	0.07	11	0.05		0.03	14.3		
	3.12	3.28	12	0.16	5.1	0.11	3.4		
Chloride	<0.03	0.07	12	0.05		0.03	42.8		
	<0.03	0.05	12	0.03		0.01	20		
pH units (µeq/L)	5.71(1.95) ^d	5.56(2.8)	12	-0.15(0.85)	-2.6(43.6)	0.07(0.40)	1.2(14.3)		
	4.30(50.1)	4.31(48.6)	12	0.01(-1.5)	0.10(-3.0)	0.02(1.53)	0.5(3.1)		
Conductivity µS/cm	0.8	1.1	12	0.3	37.8	0.3	27.3		
	21.8	21.7	12	-0.1	-0.5	0.6	2.8		

Notes: ^a 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. ^c For calculations, MDLs are given the value of 0.5(MDL). ^d The pH data in parentheses are hydrogen ion concentrations in microequivalents per liter.

**TABLE IV-5 Variance Estimated from Analysis of Replicate Network
Precipitation Samples, 1995**

Parameter	Standard Deviation Estimated from Paired Measurements ^a			(1.048328) x MAD ^b
	(Low Conc.)	(High Conc.)	(Total)	
Calcium	0.005	0.011	0.009	0.004
Magnesium	0.001	0.001	0.001	0.001
Sodium	0.003	0.010	0.007	0.002
Potassium	0.002	0.003	0.003	0.002
Ammonium	0.01	0.03	0.02	0.01
Sulfate	0.01	0.02	0.01	0.01
Nitrate	0.01	0.02	0.02	0.01
Chloride	0.03	0.02	0.03	0
Phosphate	0.001	0.006	0.004	0
H ⁺ (µeq/L)	1.53	0.63	1.17	0.52
Conductivity (µS/cm)	0.36	0.54	0.46	0.31
Number of pairs	92	92	184	184

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

C. Blanks

Solutions referred to as "blanks" are known to the analysts and identified by numbers that correspond to their various sources. The solutions are collected and grouped by the sample processing staff. pH and conductivity are measured prior to the samples being transported to the IC and AA laboratories, as a set of blanks, for inclusion in the weekly analytical scheme. In 1995, two solutions were used to leach filters, bottles, buckets, and lids: DI water from the sample processing laboratory and the lower concentration QCS (FR25).

1. Deionized Water Blanks

The conductivity or resistance of deionized (DI) water, used for rinsing, leaching, and making reagents and standards, is monitored constantly at several places. There is an in-line resistivity meter at the source of all DI water in the laboratory building and in all of the laboratories on the wall-mounted polishing units. Once a week, 60-mL samples are collected from three sources; the AA laboratory, the bucket-washing service laboratory, and the sample processing laboratory. These samples undergo a complete analysis in addition to specific conductance. The DI water showed no median ion values above the MDLs. Table IV-6 shows the median pH and conductivity for the DI from the three laboratories. These values are similar to those of past years.

	Sample Processing Laboratory	Atomic Absorption Laboratory	Service Laboratory
pH (units)	5.64	5.71	5.69
Conductivity (μS/cm)	0.6	0.8	0.6
Number of weeks	50	50	50

2. Filter Leachates

Prior to filtering a weekly sample, the Millipore™ type HAWP, 0.45 micrometer (μm) filter is rinsed with 250-300 mL of DI water. Following the DI rinse, all samples with a volume greater than 35 mL are poured from the 1-liter shipping bottle through the filter into a 60-mL wide-mouth HDPE bottle. In order to estimate any contribution from the filter to the sample chemistry, two sets of filter leachates are collected and analyzed each week. The filter is rinsed, 50 mL of DI water are filtered into a sample bottle and labeled "A", then a another 50 mL of DI water is filtered through the same filter and labeled "B". This procedure is repeated with another DI-rinsed filter using FR25 for the "A" and "B" filtrates.

Table IV-7 shows median analyte concentrations for these filtrates. The DI water samples show a sodium contribution to the "A" portion and a resulting higher conductivity. The FR25 filtrates show a high sodium in the "A" filtrate that has been considerably diminished in the "B" portion. The reduction in sulfate, found for years in the filtered blind samples, is not apparent in the filter leachates of FR25.

Analyte	DI Water A ^a	DI Water B ^b	FR 25 ^c A ^a	FR 25 B ^b
Calcium	<0.009	<0.003	0.092	0.096
Magnesium	<0.003	<0.003	0.017	0.017
Sodium	0.030	0.007	0.093	0.057
Potassium	<0.003	<0.003	0.013	0.013
Ammonium	<0.02	<0.03	0.10	0.10
Sulfate	<0.03	<0.03	0.58	0.60
Nitrate	<0.03	<0.03	0.51	0.48
Chloride	<0.03	<0.03	0.19	0.17
pH	5.64	5.63	4.98	4.96
Conductivity	1.2	0.8	7.0	7.0
Number of weeks	50	50	50	50

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=0.095, Mg = 0.017, Na = 0.048, K = 0.015, NH₄ = 0.09, SO₄ = 0.61, NO₃ = 0.49, Cl = 0.17, pH(units) = 4.92, Conductivity ($\mu\text{S}/\text{cm}$) = 7.3

3. Bucket Blanks

Sample collection buckets are made of HDPE and have a 13-liter capacity. These buckets are washed at the CAL, bagged prior to removal from the washing machine, and shipped to sites for weekly placement on the samplers. Buckets on the "wet" side remain on the collector for one week and collect whatever precipitation falls from Tuesday to Tuesday. The sample is transported from the collector to the site laboratory in this bucket. The effect of buckets on sample chemistry has been a subject of interest for many years. The USGS performs a blind audit annually where a portion of samples of known concentrations is poured from a bottle into the bucket at the site and submitted as a network sample while the bottle portion is returned to the CAL and analyzed for comparison. The CAL has performed bucket studies since the beginning of the network.

The weekly procedure for "bucket blanks" includes leaching four buckets for five days with two solutions of two different volumes: DI water and FR25 in 50- and 150-mL portions. They are measured into the buckets and left covered with snap-on lids in the sample processing laboratory. At the end of five days, the four solutions are poured in appropriately labeled 60-mL bottles for inclusion in the blanks set.

Table IV-8 shows median mass per bucket found in these weekly leachates. Note that these values are the leachate concentrations in $\mu\text{g/mL}$ times the number of milliliters of leachate for the DI and the concentrations minus the FR25 target value times the number of milliliters for the FR25. Calcium, sodium, and potassium lead the list of possible bucket contaminants. There are higher concentrations in the 50-mL portion and more dilute solutions when 150-mL portions are used. This information would be of greater value if small deposition samples were clean; however, that is usually not the case. Smaller volume weekly samples contain high concentrations of the predominating ions that overwhelm the bucket input. The smaller volume sample is slightly neutralized by longer contact with the bucket, and the corresponding conductance is lower.

**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, 1995**

Analyte	DI Water (50 mL)	DI Water (150 mL)	FR25 (50 mL) ^b	FR25 (150 mL) ^b
Calcium	<0.225	<0.675	0.25	0.900
Magnesium	<0.075	<0.225	0.05	<0.225
Sodium	0.65	<0.225	0.65	0.900
Potassium	0.35	<0.225	0.65	0.600
Ammonium	<0.50	<1.5	<0.50	<1.5
Sulfate	<0.75	<2.25	<2.25	<2.25
Nitrate	<0.75	<2.25	<2.25	<2.25
Chloride	<0.75	<2.25	0.5	<2.25
pH (units) [H ⁺]($\mu\text{eq}/\text{bucket}$)	5.59 0.128	5.57 0.404	5.07(4.92) ^c 0.426(0.601) ^c	4.98(4.92) ^c 0.534(0.601) ^c
Conductivity ($\mu\text{S}/\text{cm}$)	1.5	1.2	6.5(7.26) ^c	7.3(7.26) ^c
Number of weeks	50	50	50	50

Notes: ^a Mass/bucket 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. ^b FR25 measured mass = (median concentration measured in upright bucket leachates - target FR25 concentration) \times 50 or 150 mL. ^c Values in parentheses () represent target values for FR25 with no bucket contact.

4. Bottle Blanks

One-liter HDPE wide-mouth bottles have been used as shipping containers for the NADP/NTN samples since January 1994. The sample collected in the bucket is transported back to the field laboratory and then poured into the bottle. (If it is frozen, it is necessary to wait until the entire sample volume thaws and can be poured.) Aliquots from the bottle are then poured into small tubes for determinations of pH and specific conductance. The remaining bottle sample, the Field Observer Report Form (FORF), and the empty bucket are returned to the CAL in the black mailer as soon as possible. The pH and conductivity samples are poured from the bottle and then the smaller filtered portions are collected and the remaining sample is discarded. Bottles are washed and reused.

Table IV-9 shows the median measured mass found in bottle leachates and shows them to be clean. Only a small percentage of these blanks contain any analytes above the MDL or beyond the limits for the FR25.

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, 1995				
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	<0.225
Sodium	<0.075	<0.225	<0.075	<0.225
Potassium	0.150	<0.225	<0.075	<0.225
Ammonium	<0.50	<1.5	<0.50	<0.50
Sulfate	<0.75	<2.25	<0.75	<2.25
Nitrate	<0.75	<2.25	<0.75	<2.25
Chloride	<0.75	<2.25	<0.75	<2.25
pH (units)	5.54	5.57	4.94(4.92) ^c	4.92(4.92) ^c
[H ⁺]($\mu\text{eq}/\text{bottle}$)	0.14	0.40	0.57,(0.60) ^c	0.60,(0.60) ^c
Conductivity ($\mu\text{S}/\text{cm}$)	1.3	1.2	7.0 (7.26)	7.3(7.26)
Number of weeks	50	50	50	50

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. ^b FR25 leachate measured mass = (median concentration measured in bottle leachates - target FR25 concentration) \times 50 or 150 mL. Detection values are assigned to negative differences. ^c Values in parentheses represent target values for FR25 with no bottle contact.

5. Snap-on Lid Blanks

Snap-on lids are used to contain the sample in the bucket between the collector and the site laboratory. At the CAL two lids are inverted on the laboratory bench, and 50 mL of DI water are measured into one and 50 mL of FR25 into the other. They are covered with large plastic domes and left for 24 hours. Table IV-10 showing the median concentrations from the lid leachates indicates that sodium persists in small amounts. Potassium and sodium exceed the MDL for DI water and the FR25 control limits. Excess calcium is also in more than 50 percent of the FR25 leachates. This weekly lid experiment represents an extreme case for a field sample. Small volume samples would rarely come into contact with the lid and larger volumes of precipitation would sufficiently dilute the ions so that they would not be a contamination factor in the actual samples.

**TABLE IV-10 Median Analyte Concentrations (mg/L)
Found in Deionized (DI) Water and Simulated Rain 25
(FR25) used to Leach Snap-on Lids, 1995.**

Analyte	DI Water (50 mL)	FR25 ^a (50 mL)
Calcium	<0.009	0.101 (0.095)
Magnesium	<0.003	0.018 (0.017)
Sodium	0.007	0.052 (0.048)
Potassium	0.003	0.017 (0.015)
Ammonium	<0.02	0.10 (0.09)
Sulfate	<0.02	0.60 (0.61)
Nitrate	<0.02	0.49 (0.49)
Chloride	<0.02	0.17 (0.17)
pH (units)	5.61	4.96 (4.92)
Conductivity (μ S/cm)	1.2	7.0 (7.3)
Number of lids	50	50
Notes: ^a Target concentrations given in parentheses		

6. AIRMoN Bottles

AIRMoN bottles are 250-mL wide-mouth HDPE bottles into which are poured the event samples collected in the same type of 13-liter buckets used for NADP/NTN weekly samples. These bottles are rinsed with DI water prior to shipment and are used only once. Table IV-11 shows that the bottles are clean and the control limits are rarely exceeded.

TABLE IV-11 Median Analyte Concentrations Found in Monthly Simulated Rain (FR25) AIRMoN 250-mL HDPE Bottle Leachates, 1995		
Analyte (mg/L)	FR25 (50 mL)	FR25 (150 mL)
Calcium	0.096	0.095
Magnesium	0.017	0.017
Sodium	0.048	0.049
Potassium	0.014	0.014
Ammonium	0.09	0.09
Sulfate	0.60	0.60
Nitrate	0.47	0.47
Chloride	0.16	0.16
pH (units)	4.94	4.94
Conductivity ($\mu\text{S}/\text{cm}$)	7.0	7.0
Number of bottles	12	12
Notes: FR25 target concentrations (mg/L): Ca = 0.095, Mg = 0.017, Na = 0.048, K = 0.015, $\text{NH}_4 = 0.09$, $\text{SO}_4 = 0.61$, $\text{NO}_3 = 0.49$, Cl = 0.17, pH = 4.92 units, and Conductivity = 7.26 $\mu\text{S}/\text{cm}$		

7. AIRMoN Internal Blind Samples

Four times per month, the Illinois 11 (Bondville) site operator submits a laboratory QA sample for inclusion in the AIRMoN analysis queue. These samples are one of three types: the pH 4.3 nitric acid QCS, the FR75 solution, or the FR25 solution. The site operator receives these samples from the AIRMoN laboratory coordinator. Each sample is sealed in a bottle and enclosed in a plastic bag. The weight of the bottle and type of solution are written on the bag. Quality assurance samples are submitted only on days when no wet deposition was collected. A FOF (Field Observers Form) accompanies each sample. The sealed QA sample is weighed and the sample volume and a corresponding precipitation amount are recorded on the form. In addition, target pH and conductivity values are reported on the field chemistry section of the FOF. Throughout these steps, the operator never opens the bottle before delivering it to the sample receiving person at the CAL. "On" and "off" dates and times are recorded on the FOF and bottle as if the sample were a real wet deposition sample. Every effort is made to ensure that the sample is "blind" to the analytical staff. When the sample is submitted, a copy of the FOF is sent to the AIRMoN laboratory coordinator so that the database can be edited to show the true identity of the sample. These samples travel through the laboratory as AIRMoN network precipitation samples.

Table IV-12 summarizes the results of the AIRMoN internal blind samples. Although there are listed detection limits for AIRMoN analytical data, all values are reported as measured, even negative values. As a consequence, the pH 4.3 nitric acid QCS parameters have large relative standard deviations (RSD) for those values at or below detection, and these have not been included on the table.

The RSD reported in this table for the FR25 and FR75 are within the data quality objectives of the AIRMoN Quality Assurance Plan. There was, however, one analyte in each of the simulated rain samples that had an excessive value. These values, 0.107 mg/L ammonium for the FR25 and 0.39 mg/L potassium for the FR75, were not included in the calculations but were eliminated using a statistical outlier test. The number of replicates for ammonium and potassium in this table reflects these deletions.

A comparison of the values obtained for the pH 4.3 QCS in the AIRMoN internal blind program with those of the unfiltered NADP/NTN internal blind samples shows the RSDs to be very similar. This is a good indication that the values for NADP/AIRMoN samples are comparable to the NADP/NTN analytical results.

TABLE IV-12 AIRMoN INTERNAL BLIND SAMPLES, 1995

pH 4.3 Nitric Acid QCS							
Parameter	Target (mg/L)	Measured (mg/L)	Number	Bias (mg/L)	Bias %	Std. Dev. s (mg/L)	RSD %
Calcium	0	-0.0014	19			0.005	
Magnesium	0	-0.0004	19			0.0007	
Sodium	0	0.003	19			0.006	
Potassium	0	-0.0006	19			0.005	
Ammonium	0	0.011	19			0.026	
Sulfate	0	0.0005	19			0.002	
Nitrate	3.12	3.22	19	0.095	3.05	0.054	1.69
Chloride	0	0	19			0.005	
pH(units)	4.3	4.32	19	0.024	0.551	0.015	0.34
H ⁺ (µeq/L)	50.1	47.5	19	-2.61	-5.21	1.57	3.3
Conductivity (µS/cm)	21.8	21.7	19	-0.12	-0.53	0.44	2.01
Internally Formulated Simulated Rain, 75th Percentile Solution (FR75)							
Calcium	0.292	0.307	18	0.015	5.19	0.038	1.2
Magnesium	0.068	0.068	18	0.000	0.08	0.002	3.1
Sodium	0.188	0.188	18	0.000	0.06	0.006	3.3
Potassium	0.056	0.055	17	-0.001	-1.58	0.002	3.2
Ammonium	0.36	0.38	18	0.02	5.56	0.017	4.6
Sulfate	2.43	2.44	18	0.008	0.34	0.008	0.3
Nitrate	1.9	1.92	18	0.018	0.94	0.03	1.6
Chloride	0.49	0.55	18	0.059	12	0.07	13.8
pH (units)	4.35	4.36	18	0.01	0.31	0.012	0.26
H ⁺ (µeq/L)	44.7	43.4	18	-1.33	-2.98	1.15	2.7
Conductivity (µS/cm)	26.9	26.8	18	-0.05	-0.19	0.4	1.5

TABLE IV-12 AIRMoN INTERNAL BLIND SAMPLES, 1995							
Internally Formulated Simulated Rain, 25th Percentile Solution (FR25)							
Parameter	Target (mg/L)	Measured (mg/L)	Number	Bias (mg/L)	Bias %	Std. Dev. s (mg/L)	RSD %
Calcium	0.072	0.078	14	0.006	8.04	0.007	9.32
Magnesium	0.016	0.017	14	0.001	5.8	0.001	4.72
Sodium	0.047	0.051	14	0.004	7.9	0.004	8.28
Potassium	0.013	0.014	14	0.001	4.4	0.001	10.7
Ammonium	0.09	0.098	13	0.008	9.4	0.01	10.4
Sulfate	0.61	0.606	14	-0.004	-0.59	0.01	1.34
Nitrate	0.48	0.48	14	-0.002	-0.15	0.01	2.4
Chloride	0.13	0.14	14	0.013	9.89	0.02	12.8
pH(units)	4.92	4.92	14	-0.002	-0.44	0.02	0.38
H+(μ eq/L)	12.09	12	14	0.086	0.714	0.53	4.41
Conductivity (μ S/cm)	7.25	7.41	14	0.16	2.27	0.3	4.04

V. MONTHLY QUALITY ASSURANCE ACTIVITIES

Monthly NADP/NTN and AIRMoN QA activities include the evaluation of the control charts summarizing the daily QCS analyses, review of the printouts containing internal blind samples data, reanalysis of samples flagged for either an ion or conductivity imbalance or both, and AIRMoN field blanks. Data for samples analyzed in the USGS laboratory intercomparison study are summarized and reviewed prior to transmission to the USGS on a quarterly basis.

A. Reanalysis Procedures

The analytical results of network samples are transmitted to the data processing staff approximately twice a month in sets of 400, 500, or 600. These analytical data are submitted to a reanalysis selection test. A sample is flagged if the ion balance or conductivity percent difference exceeds set limits. The computer algorithm for selection has been the same since 1987.

1. Ion Percent Difference (IPD)

Ion concentrations are measured in milligrams per liter (mg/L). These concentrations are converted to microequivalents per liter ($\mu\text{eq/L}$) using factors listed in Table V-1 (14). The measured ion values as well as pH and calculated values for bicarbonate and hydroxide are used to calculate the ion percent difference IPD. The ion sum (IS) is equal to the sum of the measured cations, measured anions, and calculated anions. The IPD is calculated as follows:

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

$$\text{Cation sum} = [\text{H}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+]$$

$$\text{Anion sum} = [\text{HCO}_3^-] + [\text{OH}^-] + [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{PO}_4^{3-}]$$

Samples are flagged for reanalysis if:

$\text{IS} < 50 \mu\text{eq/L}$	and	$\text{IPD} > \pm 60\%$
$50 \leq \text{IS} < 100 \mu\text{eq/L}$	and	$\text{IPD} > \pm 30\%$
$\text{IS} \geq 100 \mu\text{eq/L}$	and	$\text{IPD} > \pm 15\%$

2. Conductance Percent Difference (CPD)

Conductance percent difference (CPD) compares the calculated and measured conductivity. Ion concentrations as $\mu\text{eq/L}$ are multiplied by conductance conversion factors listed on Table V-1 (15), summed, and then divided by 1000 in order to calculate the theoretical conductivity. This value is compared to the measured conductivity, and the CPD is calculated as follows:

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

Samples are flagged for reanalysis if:

$$10\% < \text{CPD} < -40\%$$

The samples selected are reanalyzed unless they are flagged for contamination and exhibit excessive ion concentrations, or the volume is insufficient. The final list of samples is compiled and sent to the laboratory and the samples are analyzed again. The analysts then submit the results to the QA Specialist with suggestions for changes to the database. The final decision is then made and sent to data management. When no explanation can be found for differences between the original and reanalysis values, the original data are reported. All reanalysis values are maintained in the laboratory's computerized database along with the original analyses.

3. IPD and CPD Histograms

In 1995, 10,800 samples were logged, and of these 6875 were classified "W" which would make them eligible for the reanalysis program. A total of 357 samples were flagged for reanalysis, and changes were made to 91 samples and 117 individual measurements. Figures V-1 and V-2 are histograms of the IPD and CPD values, respectively, for samples whose volume exceeded 35 mL. The mean, standard deviation, median, and number of wet samples are presented on each figure.

The IPD mean and median values fluctuated between zero and 5.6 from 1979 through 1993. Both values fell below zero in 1994 and 1995. A negative value indicates a cation excess, which was not observed while the samples were being shipped to the laboratory in buckets with pound-on lids containing butadiene rubber o-rings to ensure a watertight seal. Studies throughout the life of the program implicated the o-ring as a source of sample contamination and alteration. It was noted that the pH of solutions in contact with the o-ring rose and that an ion exchange reaction seemed to have taken place. Since the beginning of 1994, samples have been shipped to the laboratory in 1-liter wide-mouth bottles with screw-on lids and no gaskets. The laboratory pHs are more similar to the field pHs, the hydrogen ion concentrations are more stable and probably account for a cation excess not seen since 1978 when there were 239 samples for the year. The IPD histogram should retain the

negative skew in the near future if the shipping container change is the reason and the sampling sites are similarly distributed.

The CPD has exhibited a negative skew consistently since 1979. The 1995 mean (-6.25) and median (-5.39) values are very similar to their counterparts in 1994: mean (-6.27) and median (-5.52). Negative CPD indicates that the measured conductivity exceeds the calculated conductivity. This is expected due to the nature of the NADP analyses. There are undoubtedly parameters, such as trace metals and organic species, that are not being quantified that contribute to the measured conductivity.

TABLE V-1 Conversion Factors for Reanalysis Calculations

Analyte	Milligrams/Liter (mg/L) to Microequivalents/L ($\mu\text{e/L}$)^a for Ion Percent Difference. Multiply by:	Microequivalents/L ($\mu\text{e/L}$) to Equivalent Conductance^b for Conductance Percent Difference Multiply by:
Calcium	49.90	59.5
Magnesium	82.26	53.0
Sodium	43.50	50.1
Potassium	25.57	73.5
Ammonium	55.44	73.5
Sulfate	20.83	80.0
Nitrate	16.13	71.4
Chloride	28.21	76.3
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)*

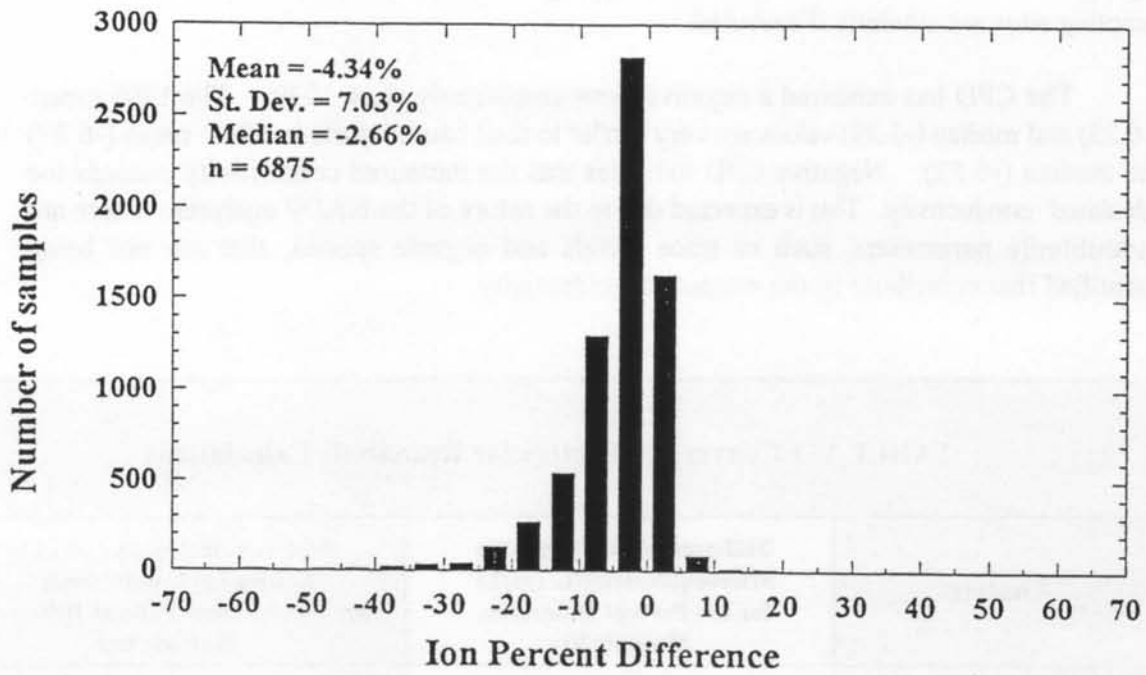


FIGURE V-1 Ion Percent Difference (IPD) histogram for NADP/NTN wet-side samples, 1995

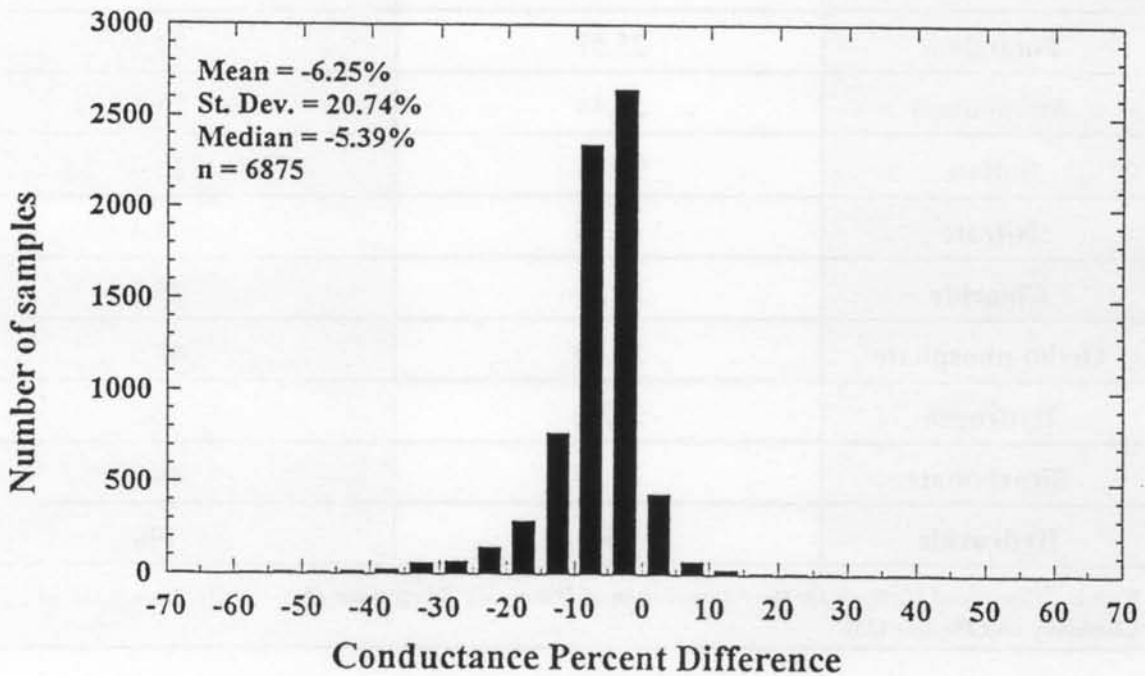


FIGURE V-2 Conductance Percent Difference (CPD) histogram for NADP/NTN wet-side samples, 1995

B. AIRMoN Field Blanks

AIRMoN field blanks are collected monthly, as are AIRMoN bottle blanks. On the first Tuesday of each 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 from the CAL are poured in and the bucket is covered with the snap-on lid. The bottle is recapped and taken back to the laboratory with the covered bucket and the sample remaining inside is given a "DK" designation. The bucket containing the CAL solution is agitated and allowed to stand overnight or at least two hours. pH and conductivity measurements of the bucket solution are made, and the solution is poured into the 250-mL sample bottle and shipped to the CAL along with the "DK" sample. Both samples undergo a complete chemical analysis at the CAL.

Four different solutions were used in the AIRMoN field blank program in 1995: pH 4.3 nitric acid (the network pH check sample), DI water, and two concentrations of simulated rain emulating the 25th (FR25) and 75th (FR75) percentile concentrations of the NADP/NTN network. These solutions are used because their pH and conductivity are similar to precipitation samples. Both the site personnel and the analysts know that the solutions were field blanks for evaluating effects of the collection bucket, shipping bottle, and handling.

The results summarized in Table V-2 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 V-2
AIRMoN Field Blanks Mean Differences of Bucket Minus Bottle (DF-DK) and Standard Deviations, 1995

Solution	SO ₄	NO ₃	Cl	NH ₄	PO ₄	Ca	Mg	Na	K	Cond.	pH	n
DI Water	-0.014 ^a	0.004	-0.004	0.01	0	0.008	0.001	0.003	0.002	0.46	-0.09	7
	0.056 ^b	0.035	0.016	0.021	0	0.004	0	0.004	0.001	0.6	0.13	
pH 4.3 HNO ₃	0.036	0.024	0.016	0.009	-0.001	0.018	0.003	0.006	0.003	-0.08	0.01	14
	0.094	0.054	0.013	0.016	0.004	0.016	0.003	0.007	0.002	1.66	0.03	
FR25	0.014	0.021	0.012	0.019	0.001	0.005	0.001	0.005	0.002	0.36	-0.01	14
	0.013	0.012	0.021	0.023	0.003	0.009	0.001	0.003	0.003	0.47	0.04	
FR75	0.04	0.041	0.025	0.019	0.001	0.012	0.003	0.007	0.006	-0.13	0.01	17
	0.035	0.04	0.02	0.012	0.003	0.017	0.004	0.003	0.004	0.68	0.01	

Notes: ^a The first set of values for each parameter for each solution is the mean difference. ^b The second set of values for each parameter for each solution is the standard deviation. 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 analyses.

C. USGS Interlaboratory Comparison

The interlaboratory comparison conducted by the USGS, primary external auditor of the NADP/NTN, began in the fall of 1982 as a portion of the external audit of the CAL. The USGS mails several sets of blind samples of differing matrices to participating laboratories each month. The audit has been designed to determine if the laboratories are producing comparable results.

In 1995 the interlaboratory comparison program included five laboratories: (1) the Illinois State Water Survey (CAL); (2) Atmospheric Environment Service (AES); (3) Environmental Science and Engineering (ESE); (4) Ontario Ministry of the Environment (MOE); and (5) Global Geochemistry Corporation (GGC).

The samples are shipped to the laboratories approximately every two weeks throughout the year. Samples used in 1995 included (1) certified samples (samples prepared and certified by NIST), (2) uncertified synthetic precipitation 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 participated for the entire year and received a total of 18 NIST samples. The median laboratory analysis of each analyte for each certified matrix was compared to the NIST certified values. The CAL reported 8 median analyses out of 15 that were outside the range of uncertainty for these samples. The other participating laboratories results ranged from 4 to 7 median analyses out of 13 to 15 that were outside the range of uncertainty for the NIST samples. Results of a Friedman test for interlaboratory bias indicate significant ($\alpha = 0.01$) differences in analyte measurements between the five laboratories for calcium, magnesium, sodium, potassium, chloride, sulfate, nitrate, pH and specific conductance. 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-3). Differences were calculated from 13 natural and 13 synthetic sample pairs for each laboratory.

Six ultrapure DI water samples were also submitted to each of the laboratories. Values in excess of the minimum reporting limits indicate possible contamination. The CAL and one other lab did not report any analyte determinations above reporting limits for DI samples in 1995.

The results of the 1995 study will be published as *External Quality-Assurance for the National Atmospheric Deposition Program and National Trends Network During 1995*, written by John Gordon and Jeff Litteral.

TABLE V-3 50th and 90th Percentile Absolute Differences for Analysis of Replicate Samples Determined by Five Laboratories Participating in the 1995 Interlaboratory Comparison Program											
Analyte	CAL		AES		ESE		MOE		GGC		
	50th	90th	50th	90th	50th	90th	50th	90th	50th	90th	
Calcium	0.000	0.010	0.003	0.020	0.001	0.005	0.002	0.011	0.001	0.004	
Magnesium	0.001	0.002	0.000	0.002	0.000	0.001	0.001	0.004	0.001	0.002	
Sodium	0.002	0.006	0.002	0.009	0.001	0.006	0.003	0.016	0.002	0.004	
Potassium	0.001	0.003	0.001	0.008	0.000	0.001	0.001	0.005	0.001	0.003	
Ammonium	0.000	0.020	0.002	0.010	0.004	0.017	0.000	0.006	0.002	0.009	
Sulfate	0.000	0.020	0.008	0.029	0.006	0.030	0.010	0.050	0.010	0.035	
Nitrate	0.010	0.020	0.012	0.048	0.004	0.013	0.000	0.031	0.010	0.028	
Chloride	0.000	0.020	0.006	0.025	0.002	0.010	0.000	0.010	0.002	0.006	
Hydrogen ion	0.100	0.500	---	---	0.200	0.900	0.100	1.000	0.100	0.370	
Specific Conductance	0.361	2.590	0.357	1.993	0.534	3.051	0.000	1.167	0.720	2.590	

VI. SEMIANNUAL AND ANNUAL QUALITY ASSURANCE PROCEDURES

The annual report is written each year as the information from the previous year is summarized and interpreted. The network database contains the analyses of the replicate samples and the internal blind samples, and the summaries of this information are usually the final computer product needed for the completion of the report. Blanks and QCS information are stored on Personal Computer (PC) files and are available in mid-January. These reports are edited both internally at the Illinois State Water Survey and externally by scientists associated with NADP/NTN and AIRMoN. QA information and other NADP information are summarized regularly for reports and the semiannual network meetings.

Each year the CAL participates in several interlaboratory comparisons. In 1995, there were four studies: one from the World Meteorological Organization (WMO) in Geneva, Switzerland; one from the Norwegian Institute for Air Research in Lillestrom, Norway; and two from the National Water Research Institute, Burlington, Ontario, Canada. The data from these studies are presented in Appendix C.

A. World Meteorological Organization

The 18th analysis of reference precipitation samples was shipped to participating laboratories in August 1995. The deadline for mailing the analyses was October 31, 1995. Sixteen laboratories participated in the analysis of samples 1-3 and the data were sent to the USEPA in Research Triangle Park (RTP), North Carolina. Target values were sent to participating laboratories after the results were received. In 1995 the CAL mean percent absolute difference was 5.08, about what it has been in the past, but not as good as in 1994. There was one result exceeding the data quality objective, the conductivity of sample 2306. Thirty-six laboratories participated, and there was no ranking, just a chart listing each laboratory for each sample with cartoon faces when limits were exceeded. The target values and the CAL results are included in Table C-1 in Appendix C.

B. Norwegian Institute for Air Research

Samples for the 15th intercomparison of analytical methods within the European Monitoring and Evaluation Programme (EMEP) arrived from Norway in July. The analytical data were due September 15. The study consists of four samples that arrive ready for analysis. The CAL results compared to the calculated results are presented in Table C-2. The mean absolute percent difference for ten parameters for four samples is 1.66, an excellent result, better than results last year and previous years.

C. Canada National Water Research Institute

The Canadian program for Long-Range Transport of Atmospheric Pollutants (LRTAP) has been in effect since 1982. In 1995, the CAL participated in two studies, L-38 in March and L-39 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.

The CAL scores for 1995 were 0 for L-38 and 10.20 for L-39 due to three high pH values, four high sodium values, one high chloride value, and two low calcium values. The CAL ranked number one out of 51 labs in L-38 and 15th out of 35 laboratories in L-39 (17 and 18). The data for these studies are presented in Tables C-3 and C-4.

VII. SUMMARY

This report summarizes the results from the quality assurance program in place at the Central Analytical Laboratory of the NADP/NTN/AIRMoN Network in 1995. The information presented is in the form of tables, figures, and brief written explanations. The appendices provide supplemental information.

Those quality assurance activities that occur on a daily basis are the operation, calibration, and maintenance of the scientific instruments that are used to analyze the samples and provide the data. Daily records are kept documenting reagent and standards preparation and instrument performance and maintenance. Calibration curves are verified using CAL laboratory internally formulated simulated rain solutions emulating the 25th and 75th concentration levels of the network as QCS. The analytical values of the QCS are recorded and used to construct daily control charts and summarized at the end of the month as monthly control charts. QCS data indicate that potassium at the low level is slightly (0.001 mg/L) negatively biased and at the higher level shows a slight positive bias. The precision values are excellent and for the most part compare well to the corresponding values from 1994. All of the bias and precision values are well within the specifications of the Network Quality Assurance Plan (1).

The internal blinds program provides bias and precision values that should more closely mimic those of real samples and evaluates the contribution of the filtration process to the sample chemistry. Bias and precision numbers are higher than for the QCS, which has been explained by the random location of the samples in the sample queue and the ion concentrations. The SWS2 blanks solutions indicate that there are little or no sample carry-over or false positives. Filtration lends variability to all samples as well as a positive bias for calcium and sodium and a negative bias for sulfate.

Replicate network samples serve to verify the precision of real sample analyses. Comparison of variance to that of the QCS and internal blinds shows the replicate samples to be comparable for the cations and anions and better for the pH and conductivity measurements, which is interesting, considering the 'Q' sample is filtered. The pH and conductivity are measured on the 'S' sample prior to filtration.

Deionized (DI) water and filter and container leachates are analyzed weekly to determine if there is contamination present or if the sample chemistry is altered by either the filter or any of the containers that the sample contacts. DI water from three sources throughout the laboratory is perennially ion-free with pHs in the mid-5s and conductivity less than one. Filters leached with DI water and FR25 show both initial filtrates to contain measurable sodium and raised conductivity. The second or "B" portion contains considerably less sodium. Filter leachates do not exhibit the sulfate reduction seen in the internal blind program, but the concentrations are different. Bucket leachates show slight elevations in

calcium, sodium, and potassium concentrations. A dilution effect is seen when larger leachate volumes are used. The lower volume samples have higher pHs and reduced conductivity. One-liter bottle leachates are virtually clean. Snap-on lids, when leached, appear to contribute sodium and some calcium. Most weeks at most sites, there is little or no contact of the sample with the lid used to cap the bucket for transport to the laboratory. AIRMoN bottles, used only once, are clean.

The AIRMoN internal blind program is a cooperative project with the Bondville site operator and the AIRMoN Coordinator. The results for the analyses of these samples show that the relative standard deviations for the FR25 and FR75 are within the data quality objectives of the Network QA Plan. The RSD of the pH 4.3 nitric acid solution is comparable to that of the same solution, unfiltered, in the NADP/NTN internal blind program.

When the weekly NADP samples have been analyzed, the data are transferred in batches to the data management section. Data management compiles semimonthly printouts containing the data for 400 to 500 samples. Those samples with volume of greater than 35 milliliters and designated as "Wet" or "W" undergo complete laboratory analysis, and the results are submitted for an ion balance and a calculated versus measured conductance test. Samples not meeting the acceptance criteria are flagged and reanalyzed. In 1995, of the 6875 samples of "W" designation, 357 were flagged and 117 individual values in 91 samples were changed. The Ion Percent Difference (IPD) mean and median for the year are negative, indicating a cation excess. This phenomenon was observed in 1994 for the first time and has been attributed to the change in shipping protocol. The Conductance Percent Difference (CPD) has been skewed negatively since 1979, indicating that measured conductivity exceeds the calculated conductivity.

AIRMoN field blanks, begun in 1994, continued in 1995. The differences in concentrations of the solution sent to the site in a bottle and the solution poured into a sample bucket and then submitted as a sample are not statistically different but are highly variable.

The USGS Interlaboratory Comparison included five laboratories in 1994. Four different sample matrices were used as samples that were shipped to these laboratories every two weeks. Analyte bias is evaluated using NIST standard reference samples. The CAL reported 8 median analyses out of 15 that were outside the range of uncertainty for these samples, the other laboratories results varied from 4 to 7 median analyses out of 13 to 15 out of the range. A Friedman test for interlaboratory bias indicates significant differences in analyte measurements between the five laboratories for calcium, magnesium, sodium, potassium, chloride, sulfate, nitrate, pH and specific conductance. 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.

In 1995, the CAL participated in four interlaboratory comparisons: World Meteorological Organization (WMO), Norwegian Institute for Air Research (EMEP), and two studies from the Canada National Water Research Institute (LRTAPs). The results were good to excellent: the WMO analyses were comparable to previous performances, the EMEP mean absolute percent difference of 1.66 is the best performance in this study since the CAL has participated, and the LRTAPs were mixed, with the L-38 score being perfect and the L-39 an average score due to several flags. The scores from these studies indicate that the CAL results compare favorably to those of its peers throughout North America and Europe.

REFERENCES

1. Simmons, C.L., S.R. Dossett, W.C. Eaton, B.A. Malo, M.E. Peden, and D.S. Bigelow: *Quality Assurance Plan NADP/NTN Deposition Monitoring*; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Fort Collins, CO 80523; October 1990.
2. Stensland, G.J., R.G. Semonin, M.E. Peden, V.C. Bowersox, F.F. McGurk, L.M. Skowron, M.J. Slater, and R. K. Stahlhut: *NADP Quality Assurance Report - Central Analytical Laboratory, January 1979 through December 1979*; Champaign, IL 61820; 1980.
3. Lockard, J.M.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, July 1978 through December 1983*; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Fort Collins, CO 80523; May 1987.
4. Peden, J.M.L.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1984 through December 1985*; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Fort Collins, CO 80523; May 1988.
5. James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1986 through December 1986*; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Fort Collins, CO 80523; October 1988.
6. James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1987 through December 1987*; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Fort Collins, CO 80523; October 1989.
7. James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1988 through December 1988*; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Fort Collins, CO 80523; March 1990.

8. James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1989 through December 1989*; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Fort Collins, CO 80523; April 1991.
9. James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1990 through December 1990*; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Fort Collins, CO 80523; April 1992.
10. James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1991 through December 1991*; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Fort Collins, CO 80523; June 1993.
11. James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1992 through December 1992*; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University, Fort Collins, CO 80523, June 1994.
12. James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1993 through December 1993*; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University, Fort Collins, CO 80523, June 1995.
13. James, K.O.W.: *Quality Assurance Report, NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, January 1994 through December 1994*; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University, Fort Collins, CO 80523, June 1996.
14. *Standard Methods for the Examination of Water and Wastewater*; 14th edition; American Public Health Association; Washington, D.C.; p. 35; 1976.
15. *CRC Handbook of Chemistry and Physics*; 67th edition; 1986-1987; CRC Press, Inc.; Boca Raton, FL; pp. D-167 and D-168; 1987.

16. Gordon, J. D. and J. Litteral: *External Quality Assurance Results for the National Atmospheric Deposition Program and the National Trends Network During 1995*; U.S. Geological Survey-Water Resources Investigation Report; Arvada, CO; in review.
17. Aspila, K. and N. Arafat: *LRTAP Interlaboratory Study L-38 for Major Ions and Nutrients*; National Water Research Institute-Canada; Burlington, Ontario; July 1995.
18. Aspila, K. and N. Arafat: *LRTAP Interlaboratory Study L-39 for Major Ions and Nutrients*; National Water Research Institute-Canada; Burlington, Ontario; February 1996.
19. Taylor, J.K.: *Quality Assurance of Chemical Measurements*; Lewis Publishers, Inc.; Chelsea, MI; pp. 22, 123, and 247; 1987.
20. Anderson, R.L.: *Practical Statistics for Analytical Chemists*; Van Nostrand Reinhold Company; New York, NY; pp. 74, 75, 79, and 303; 1987.
21. Glaser, J.A., D.L. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde: "Trace Analyses for Wastewaters", *Environmental Science and Technology*; Vol. 15, No. 12, pp. 1426-1435; 1981.

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 <u>I</u> s 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 (19).
Critical Concentration		A calculated concentration used to determine whether the measured bias is statistically significant (20).

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

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. $\bar{x} = \sum_{I=1}^n x_i / n$
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 (21).
Percent Bias		The difference between the mean value obtained by repeated analysis of a homogeneous sample and the accepted true value expressed as a percentage of the true value. $\%Bias = 100 * [(V_m - V_t)/V_t]$ where: V_m = measured value V_t = true value
Precision		The degree of agreement of repeated measurements of a homogeneous sample by a specific procedure, expressed in terms of dispersion of the values obtained about the mean value. It is often reported as the sample standard deviation (s).

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

Term	Abbreviation	Definition
Replicates (Splits)		Two aliquots of the same sample treated identically throughout the laboratory analytical procedure. Analyses of laboratory replicates are beneficial when assessing precision associated with laboratory procedures but not with collection and handling. 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,

1995

TABLE B-1 Comparison of Filtered and Unfiltered Internal Blind Samples High Purity Standards Simulated Rainwater I (HPS-SRI), 1995									
Parameter	Target Concentration ^a (mg/L)	Measured Concentration (mg/L)	Number of Samples n	Bias (mg/L)	Bias %	Precision s (mg/L)	Precision RSD (%)		
Calcium	0.015	0.016 ^b	25	0.001	6.7	0.003	18.8		
		0.025 ^c	13	0.010	66.7	0.007	28.0		
Magnesium	0.026	0.026	25	0.0	0.0	0.001	3.8		
		0.027	13	0.001	3.8	0.003	11.0		
Sodium	0.200	0.208	25	0.008	4.0	0.019	9.1		
		0.280	13	0.080	40.0	0.035	12.5		
Potassium	0.050	0.050	25	0.0	0.0	0.003	6.0		
		0.049	13	-0.001	2.0	0.003	6.1		
Ammonium	0.10	0.12	25	0.02	20.0	0.01	8.3		
		0.15	12	0.05	50.0	0.03	20.0		
Sulfate	2.50	2.58	25	0.08	3.2	0.02	0.8		
		2.48	13	-0.02	-0.8	0.04	1.6		
Nitrate	0.50	0.52	24	0.02	4.0	0.01	1.9		
		0.60	13	0.10	20.0	0.06	10.0		
Chloride	0.25	0.24	25	-0.01	-4.0	0.01	4.2		
		0.29	13	0.04	16.0	0.03	10.0		
pH (units) µeq/L	4.30(52.5)	4.32(48.3)	25	0.02(-4.2)	0.5(-8.7)	0.02(2.42)	0.5(2.1)		
		4.31(49.4) ^d	13	0.01(-3.1)	0.2(-5.9)	0.02(2.3)	0.5(4.7)		
Conductivity µS/cm	25.0	24.8	25	-0.2	-0.8	0.61	2.5		
		25.1 ^d	13	0.1	0.4	0.5	2.0		

Notes: ^a Target values provided by HPS for Simulated Rainwater I. ^b The first set of values for each parameter is for unfiltered samples. ^c The second set of values for each parameter is for filtered samples. ^d pH and conductivity are measured on unfiltered sample prior to filtering.

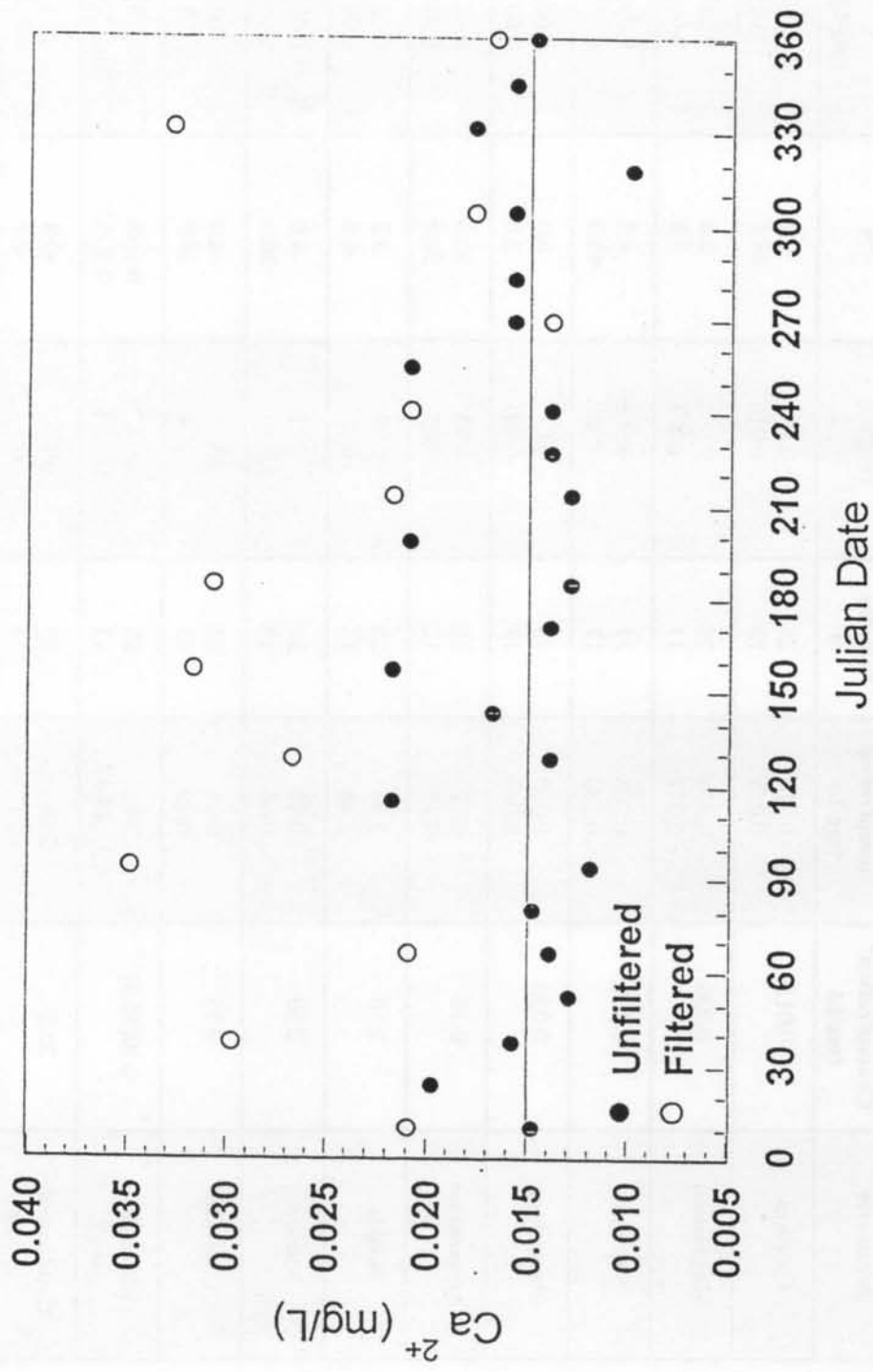


FIGURE B-1 Comparison of filtered and unfiltered internal blind samples (calcium HPS-SRD), 1995.

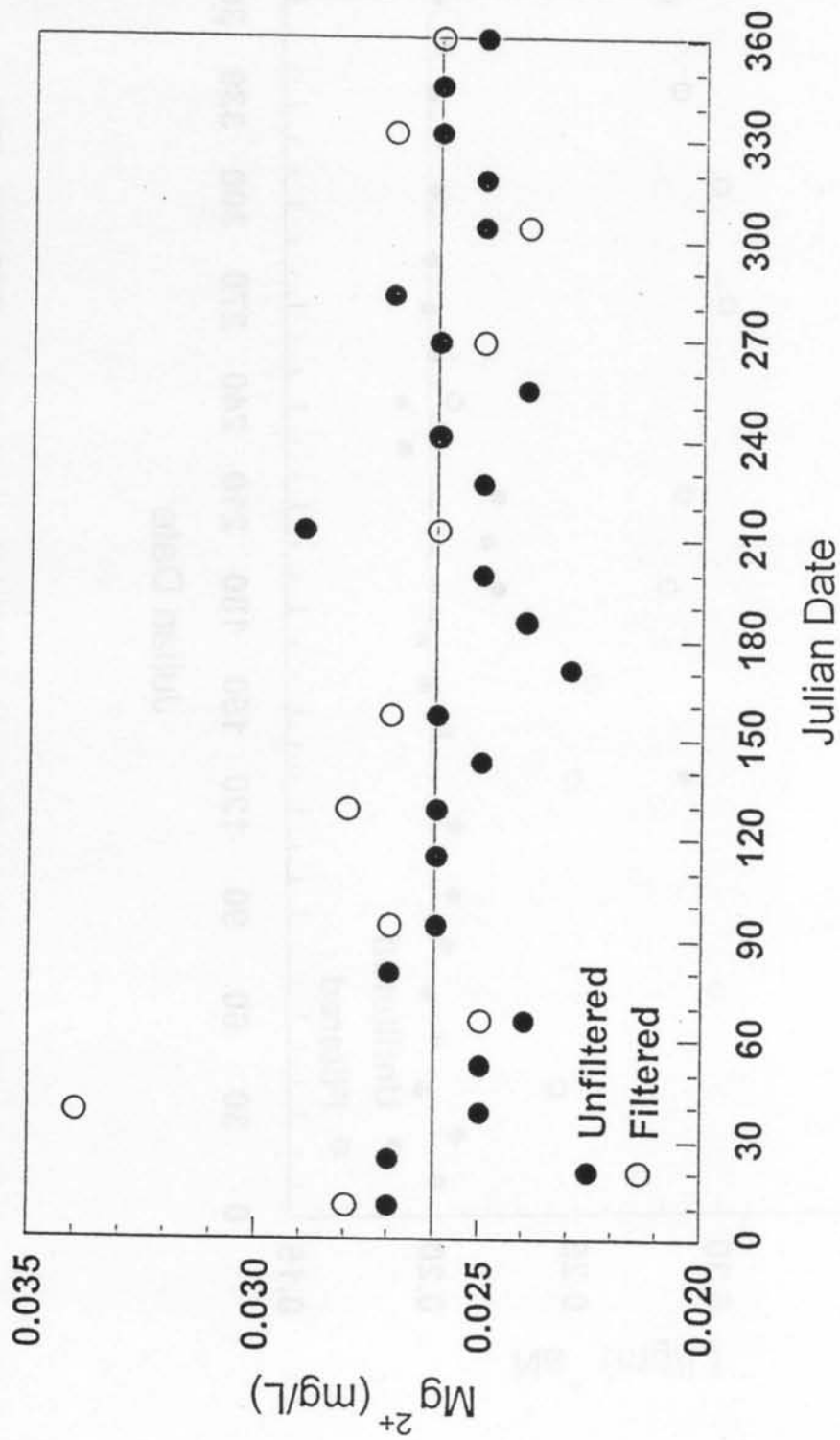


FIGURE B-2 Comparison of filtered and unfiltered internal blind samples (magnesium HPS-SRI), 1995.

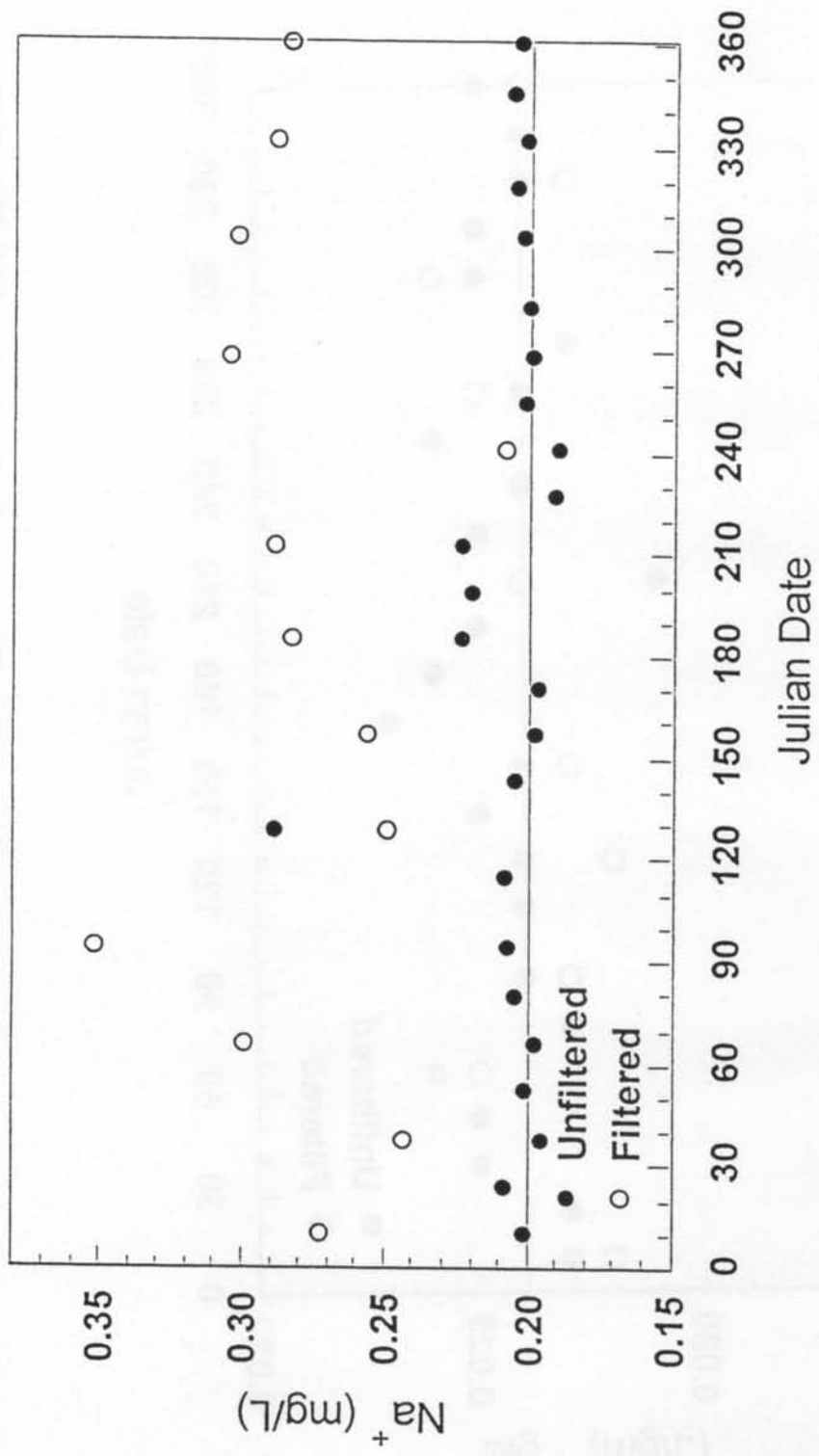


FIGURE B-3 Comparison of filtered and unfiltered internal blind samples (sodium HPS-SRD), 1995.

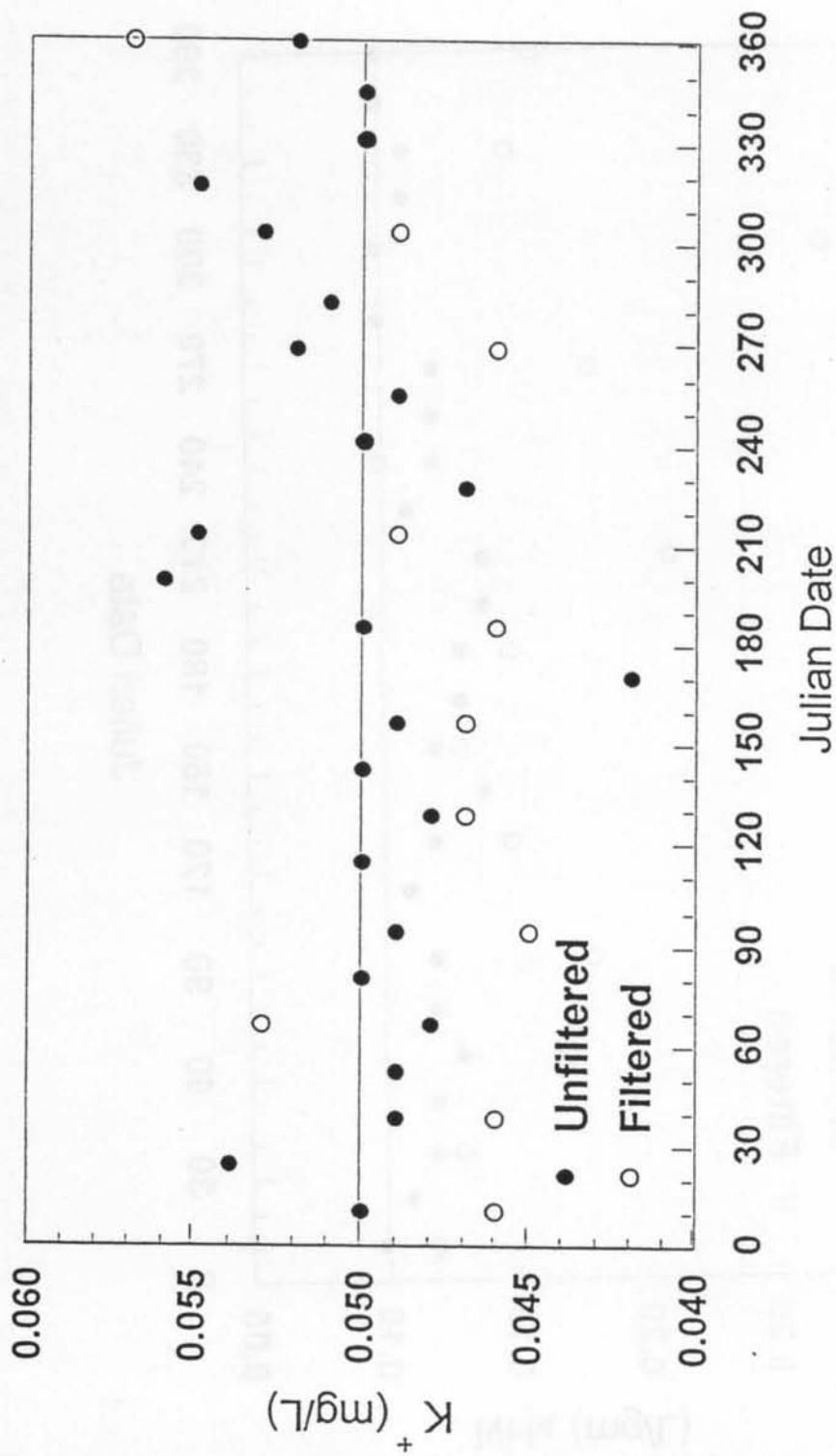


FIGURE B-4 Comparison of filtered and unfiltered internal blind samples (potassium HPS-SRD), 1995.

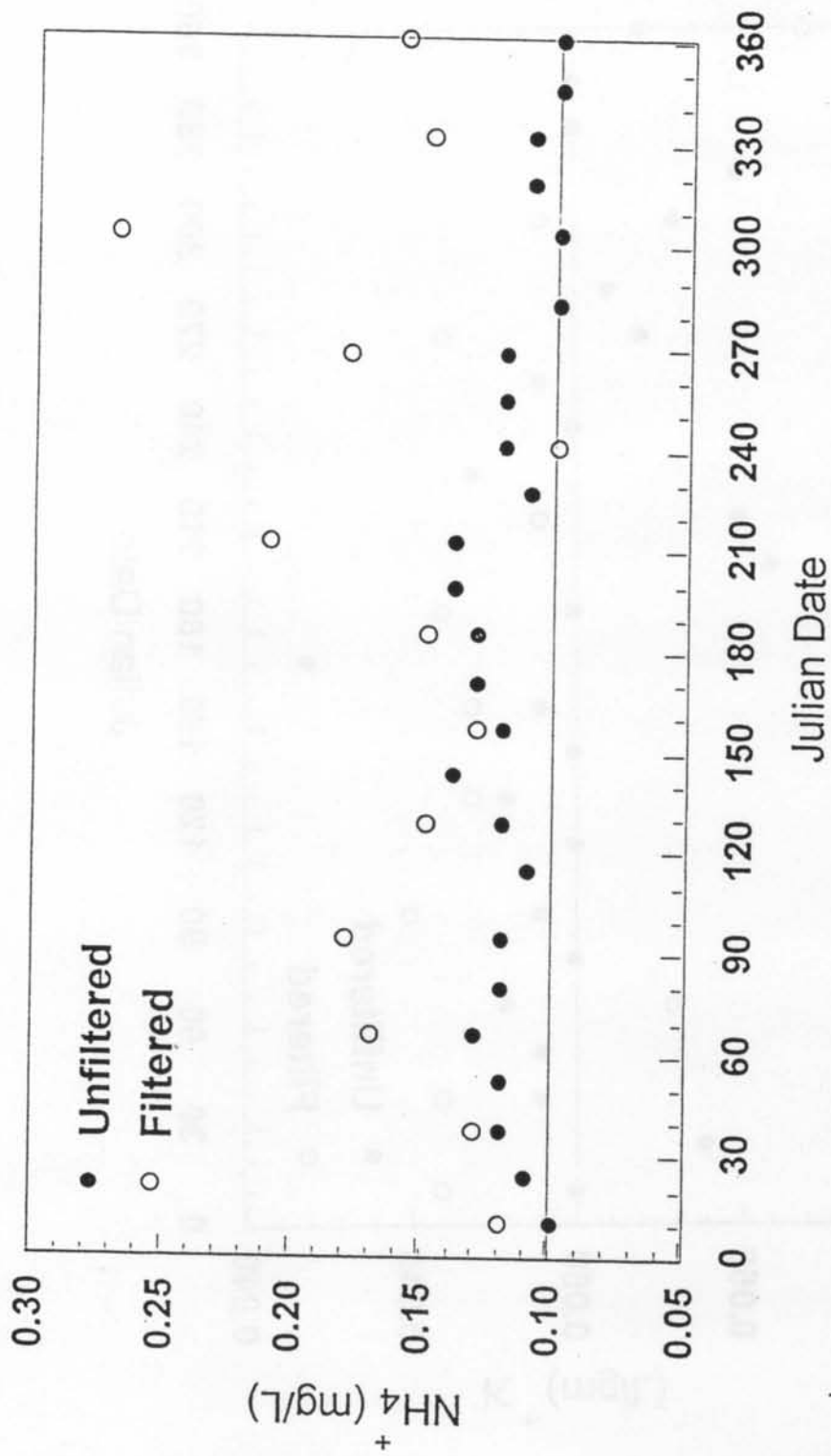


FIGURE B-5 Comparison of filtered and unfiltered internal blind samples (ammonium HPS-SRI), 1995.

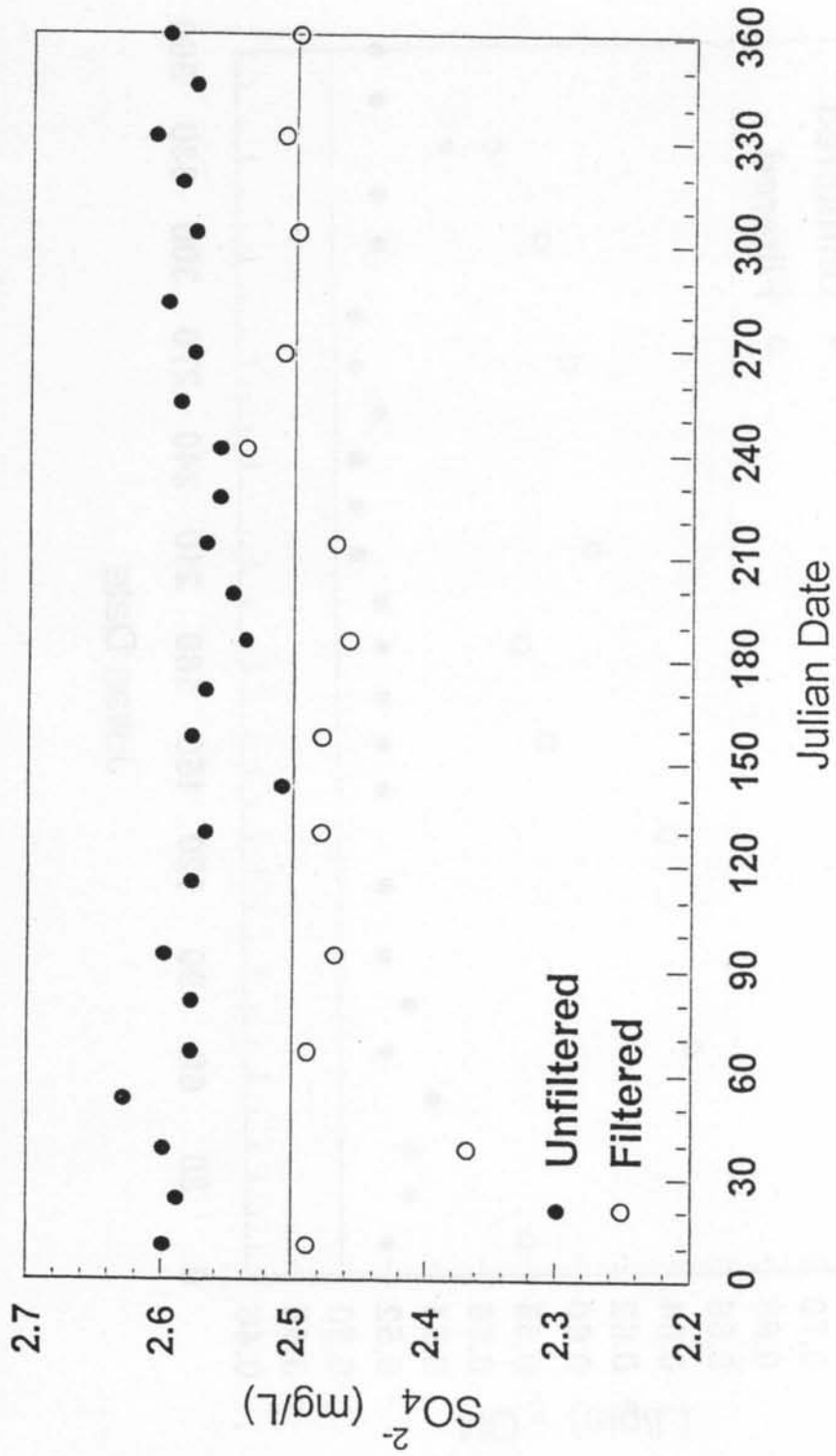


FIGURE B-6 Comparison of filtered and unfiltered internal blind samples (sulfate HPS-SRI), 1995.

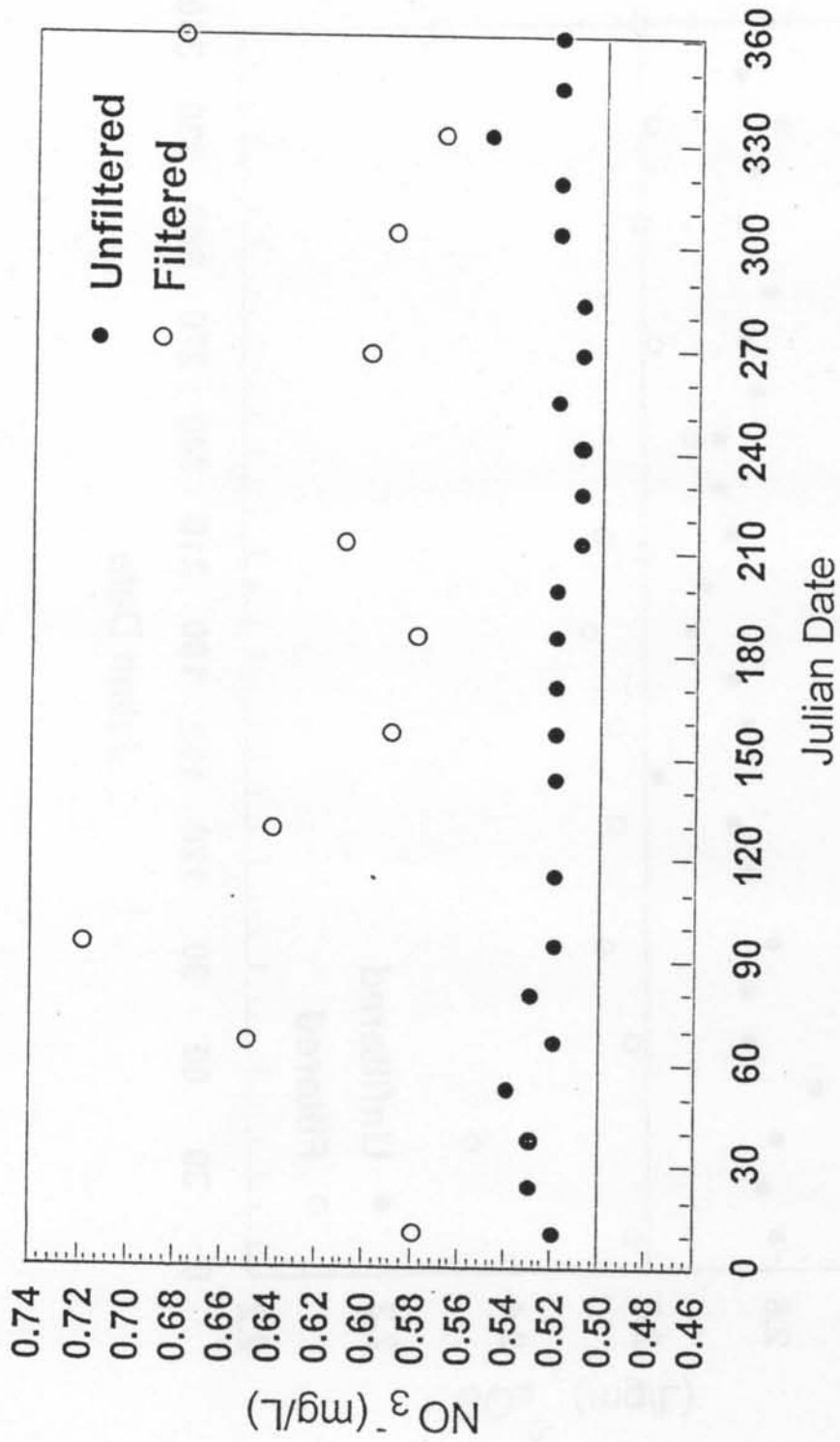


FIGURE B-7 Comparison of filtered and unfiltered internal blind samples (nitrate HPS-SRI), 1995.

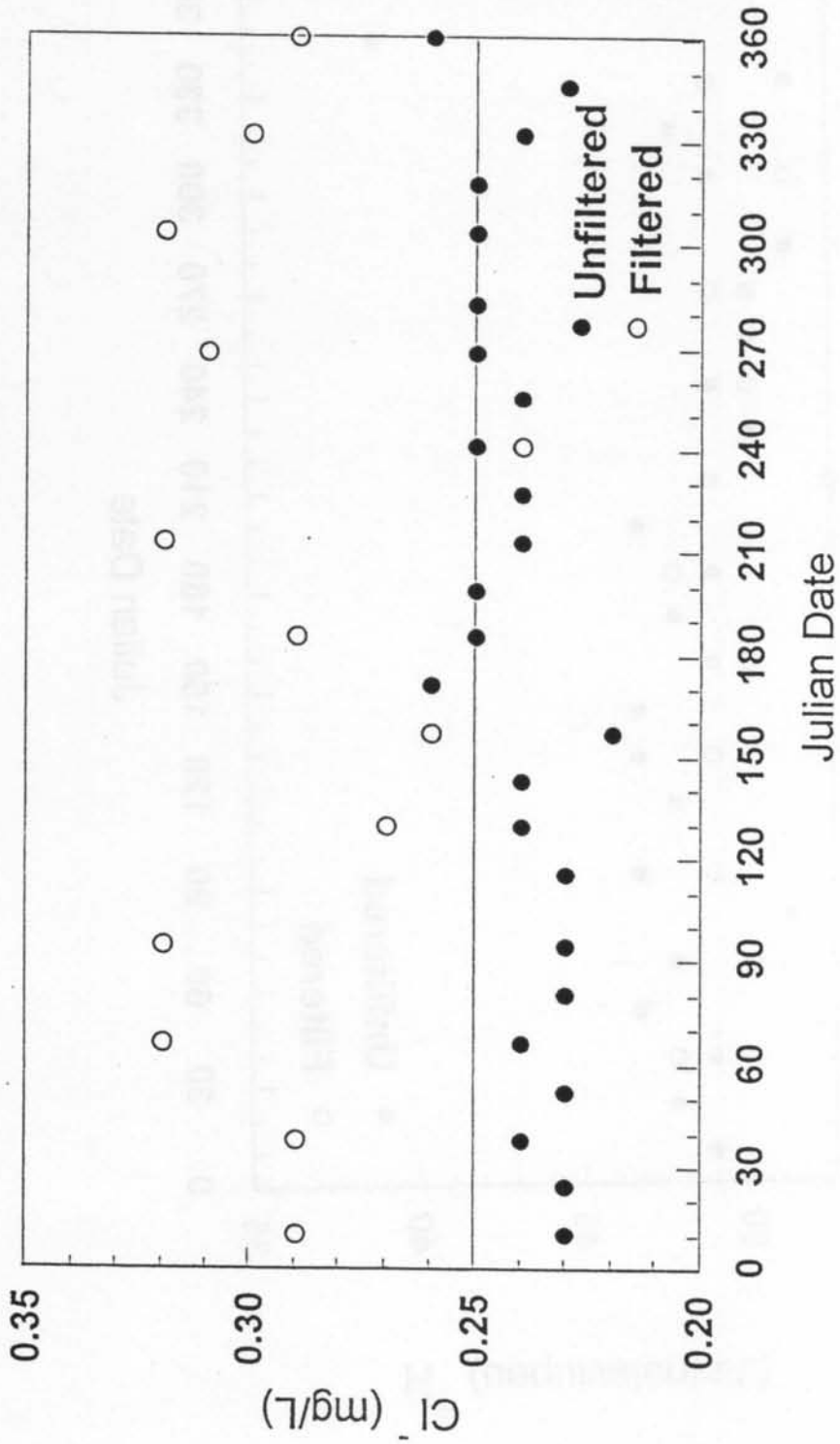


FIGURE B-8 Comparison of filtered and unfiltered internal blind samples (chloride HPS-SRI), 1995.

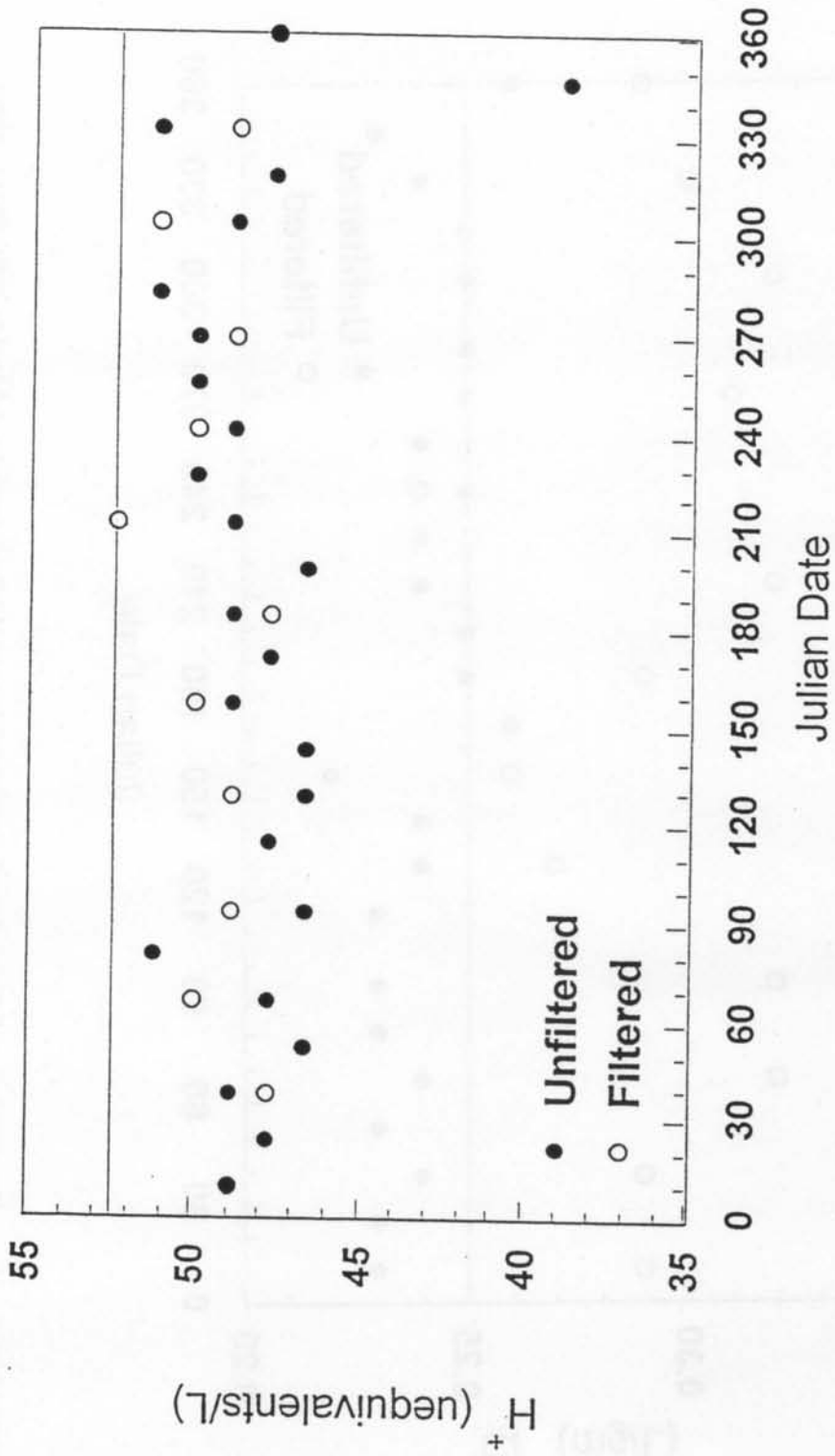


FIGURE B-9 Comparison of filtered and unfiltered internal blind samples (H^+ HPS-SRD), 1995.

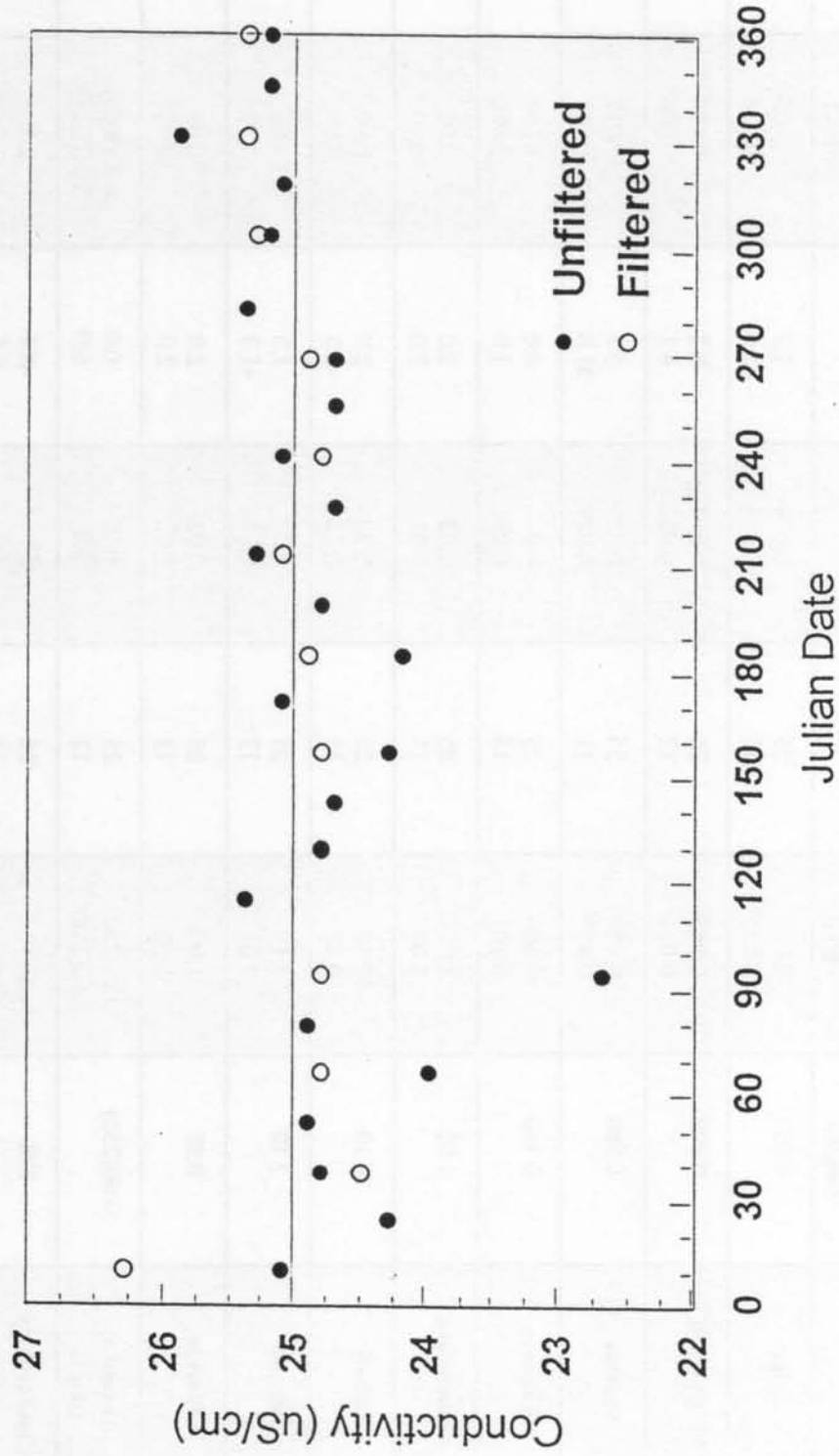


FIGURE B-10 Comparison of filtered and unfiltered internal blind samples (Conductivity HPS-SRD), 1995.

TABLE B-2 Comparison of Filtered and Unfiltered Internal Blind Samples, High Purity Standards Simulated Rainwater II (HPS-SRID), 1995

Parameter	Target Concentration* (mg/L)	Measured Concentration (mg/L)	Number of Samples n	Bias (mg/L)	Bias %	Precision s (mg/L)	Precision RSD (%)
Calcium	0.052	0.056 ^b	25	0.004	7.7	0.005	8.9
		0.085 ^c	12	0.033	63.5	0.038	42.0
Magnesium	0.049	0.045	25	-0.004	-8.2	0.003	6.7
		0.051	12	0.002	4.1	0.006	11.8
Sodium	0.380	0.400	25	0.020	5.3	0.012	3.0
		0.459	11	0.079	21.0	0.034	9.9
Potassium	0.100	0.100	25	0.0	0.0	0.004	4.0
		0.101	13	0.001	1.0	0.006	5.9
Ammonium	1.00	1.02	25	0.02	2.0	0.02	2.0
		1.07	13	0.07	7.0	0.10	9.3
Sulfate	10.10	10.30	25	0.20	2.0	0.06	0.6
		9.87	13	-0.23	-2.3	0.09	0.9
Nitrate	7.10	7.19	25	0.09	1.3	0.06	0.8
		7.01	13	-0.09	-1.3	0.13	1.8
Chloride	0.98	1.00	25	0.02	2.0	0.05	5.0
		1.00	13	0.02	2.0	0.06	6.0
pH (units) µeq/L	3.60(252)	3.60(252)	25	0.0	0.0	0.02(8.69)	0.6(3.5)
		3.60(252) ^d	13	0.0	0.0	0.01(7.24)	0.3(2.9)
Conductivity µS/cm	128	127.3	25	-0.7	-0.8	2.28	1.8
		129 ^d	13	1.0	0.8	1.9	1.5

Notes: * Target values provided by HPS for Simulated Rainwater II. ^b The first set of values for each parameter is for unfiltered samples. ^c The second set of values for each parameter is for filtered samples. ^d pH and conductivity are measured on unfiltered sample prior to filtering.

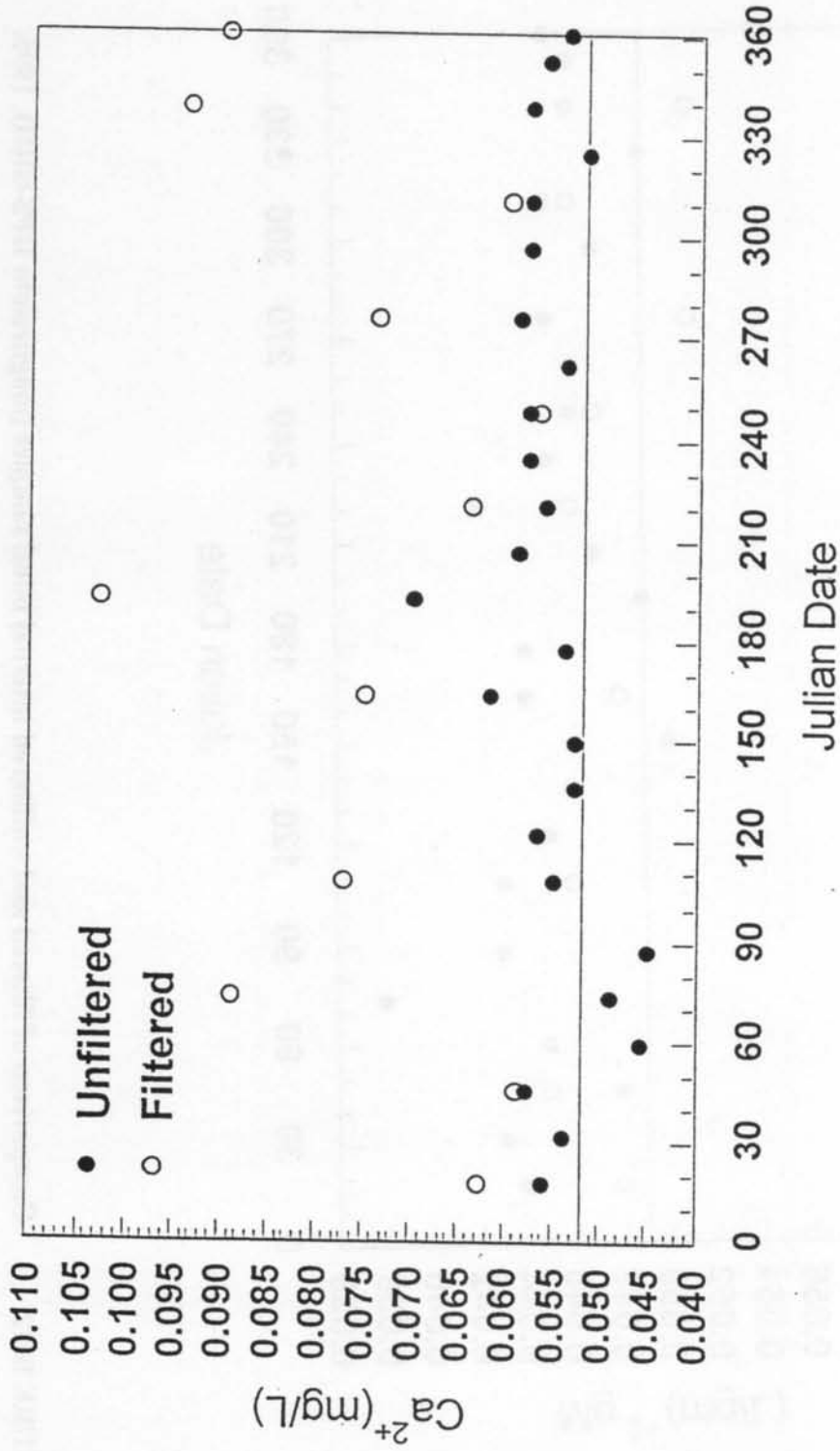


FIGURE B-11 Comparison of filtered and unfiltered internal blind samples (calcium HPS-SRID), 1995.

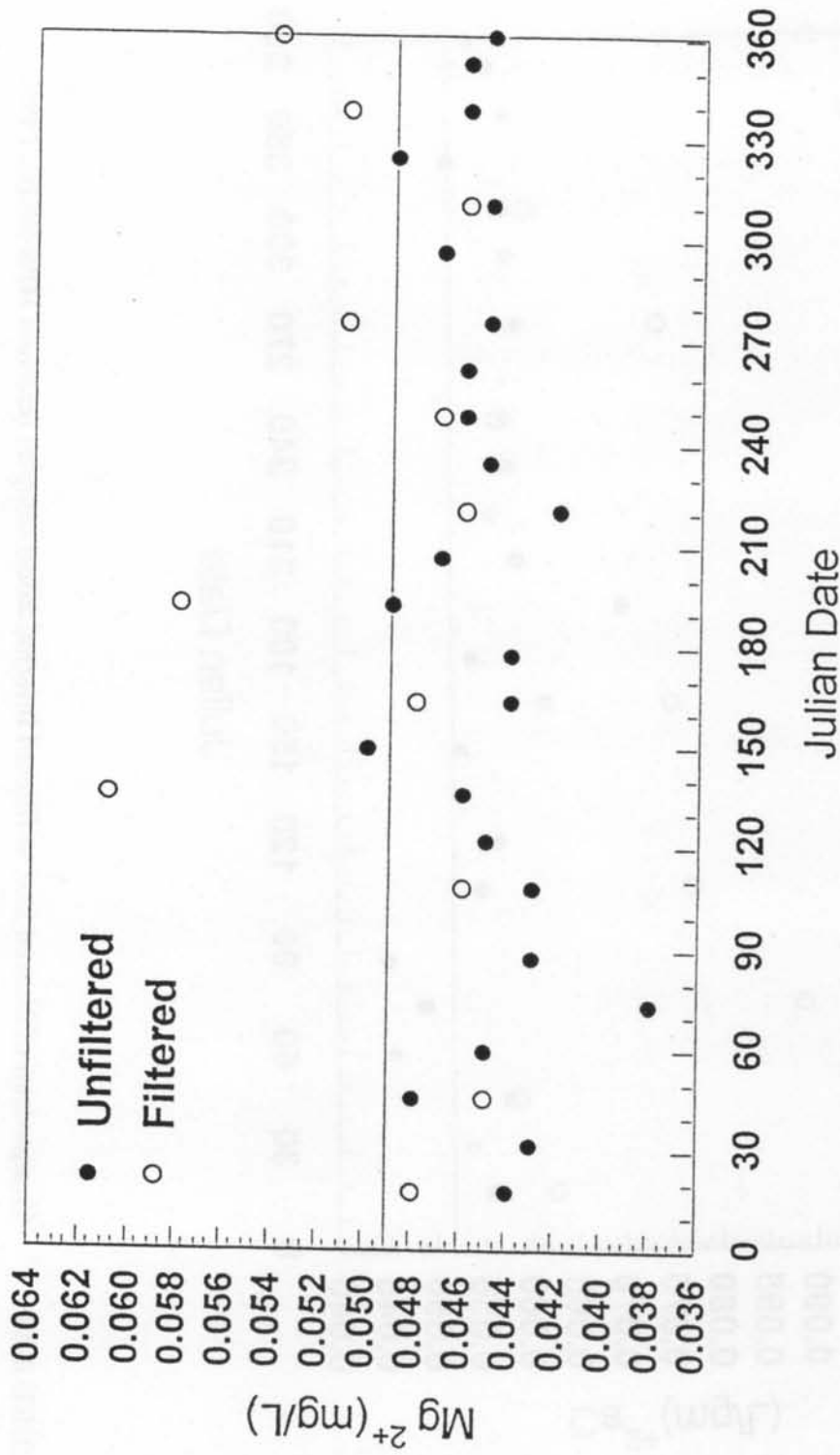


FIGURE B-12 Comparison of filtered and unfiltered internal blind samples (magnesium HPS-SRII), 1995.

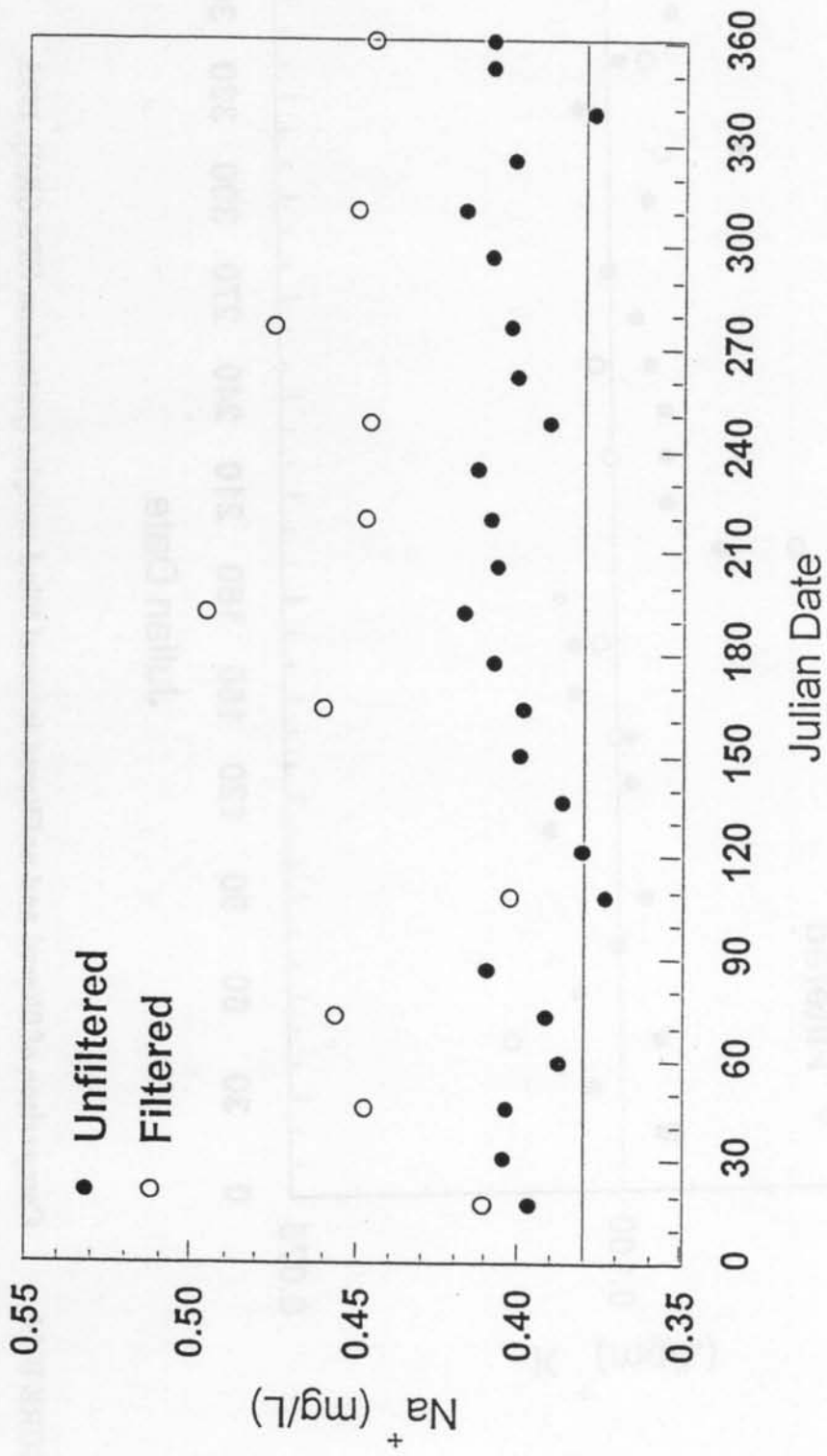


FIGURE B-13 Comparison of filtered and unfiltered internal blind samples (sodium HPS-SRID), 1995.

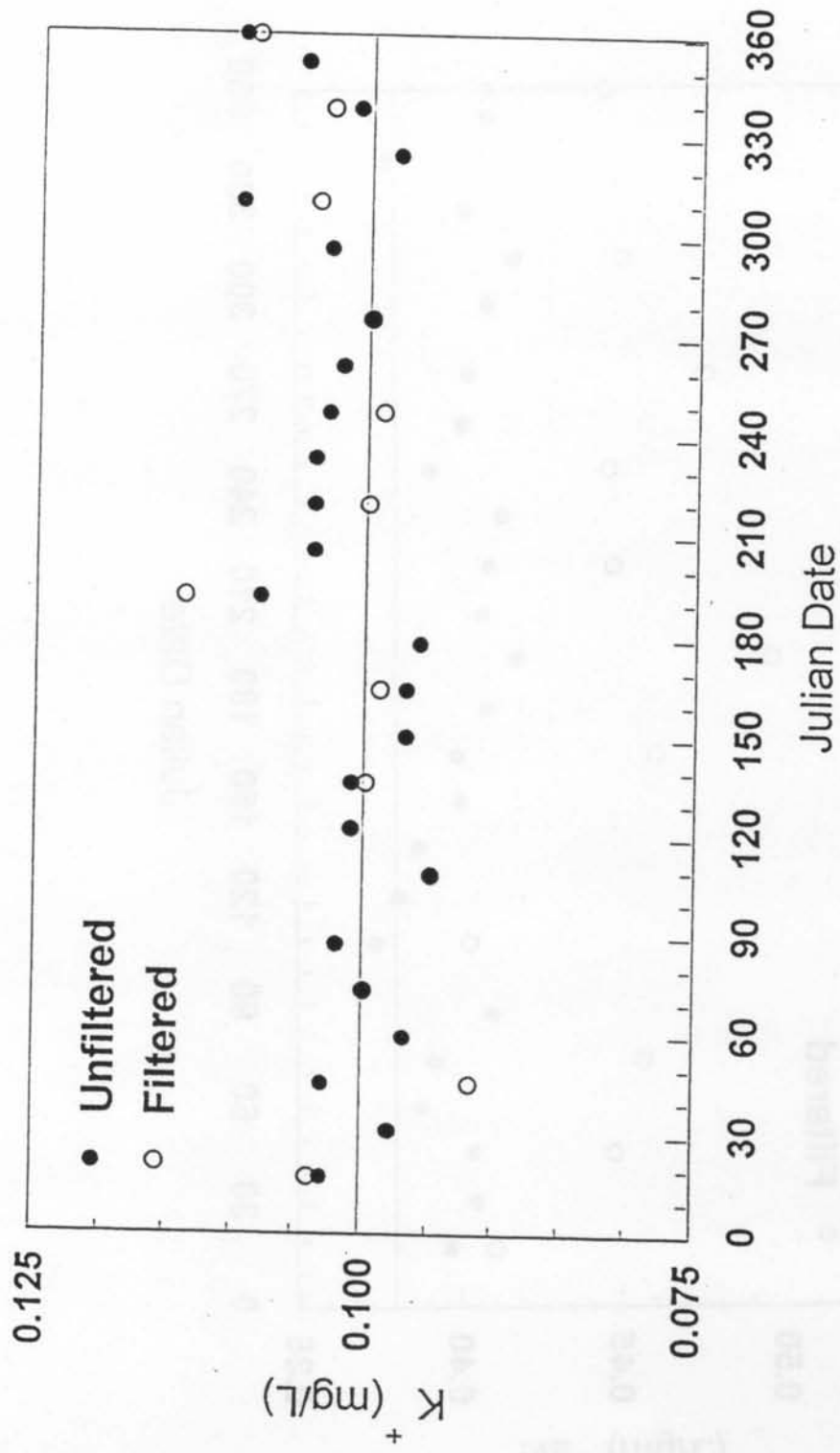


FIGURE B-14 Comparison of filtered and unfiltered internal blind samples (potassium HPS-SRII), 1995.

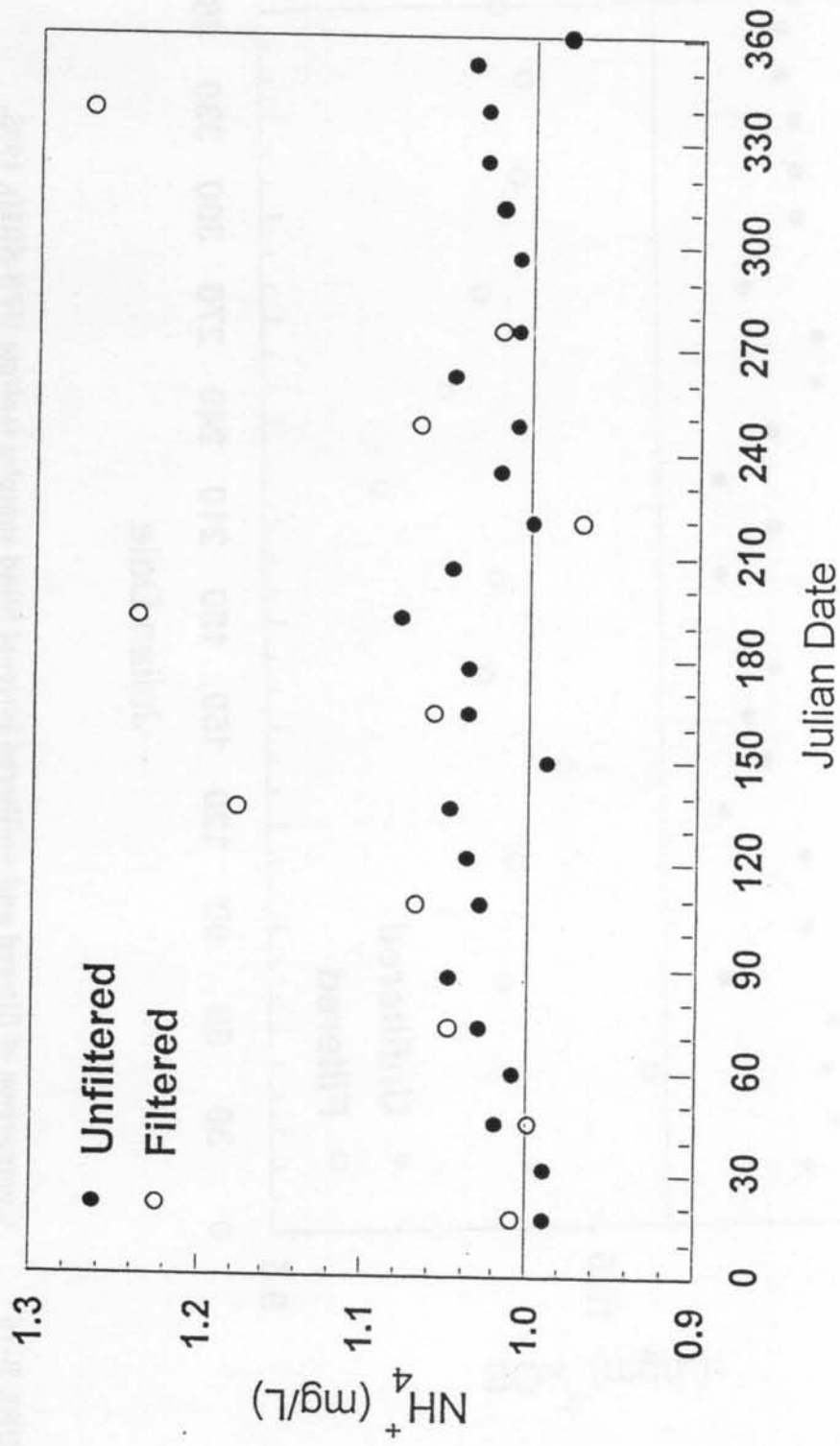


FIGURE B-15 Comparison of filtered and unfiltered internal blind samples (ammonium HPS-SRID), 1995.

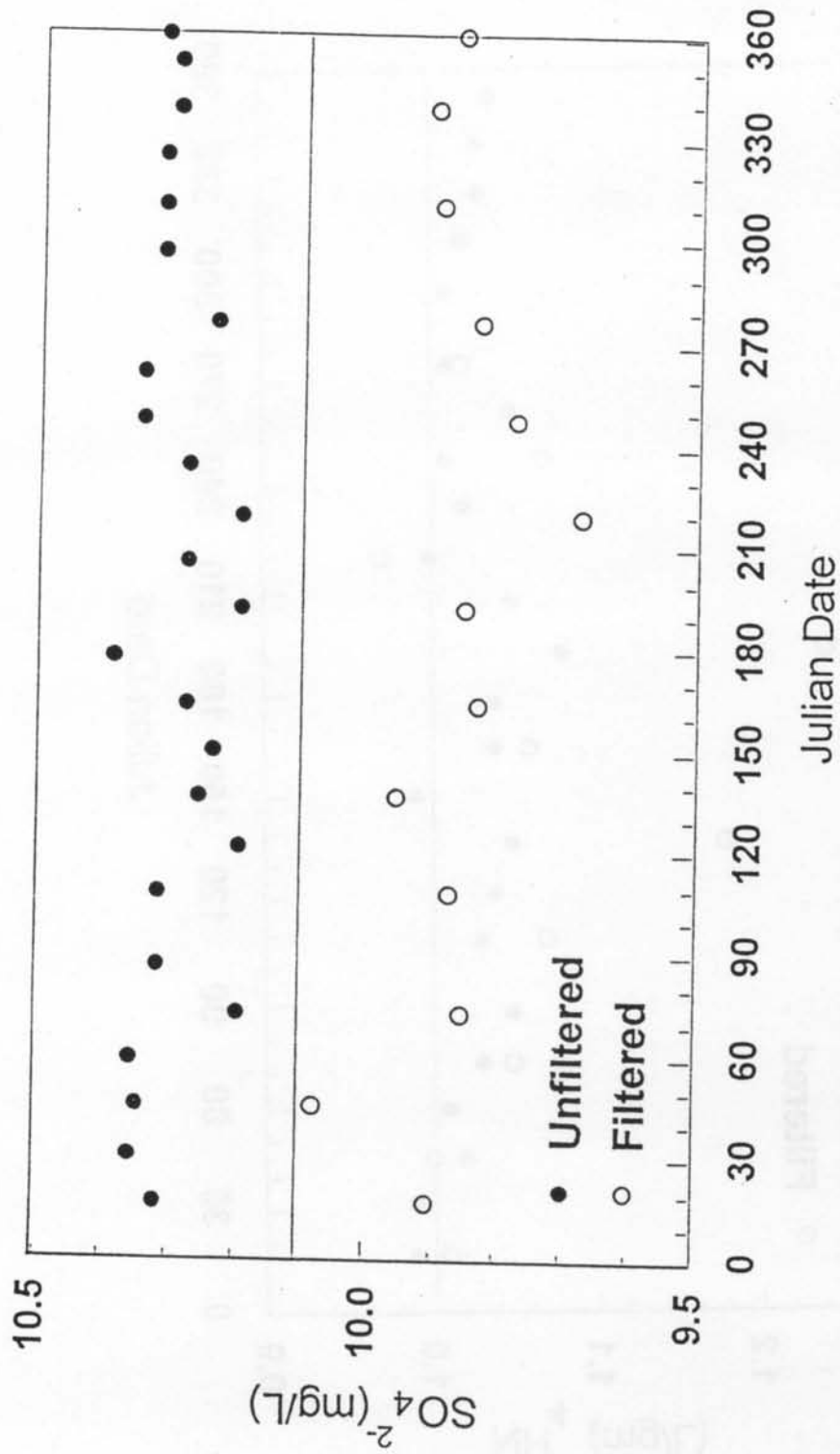


FIGURE B-16 Comparison of filtered and unfiltered internal blind samples (sulfate HPS-SRID), 1995.

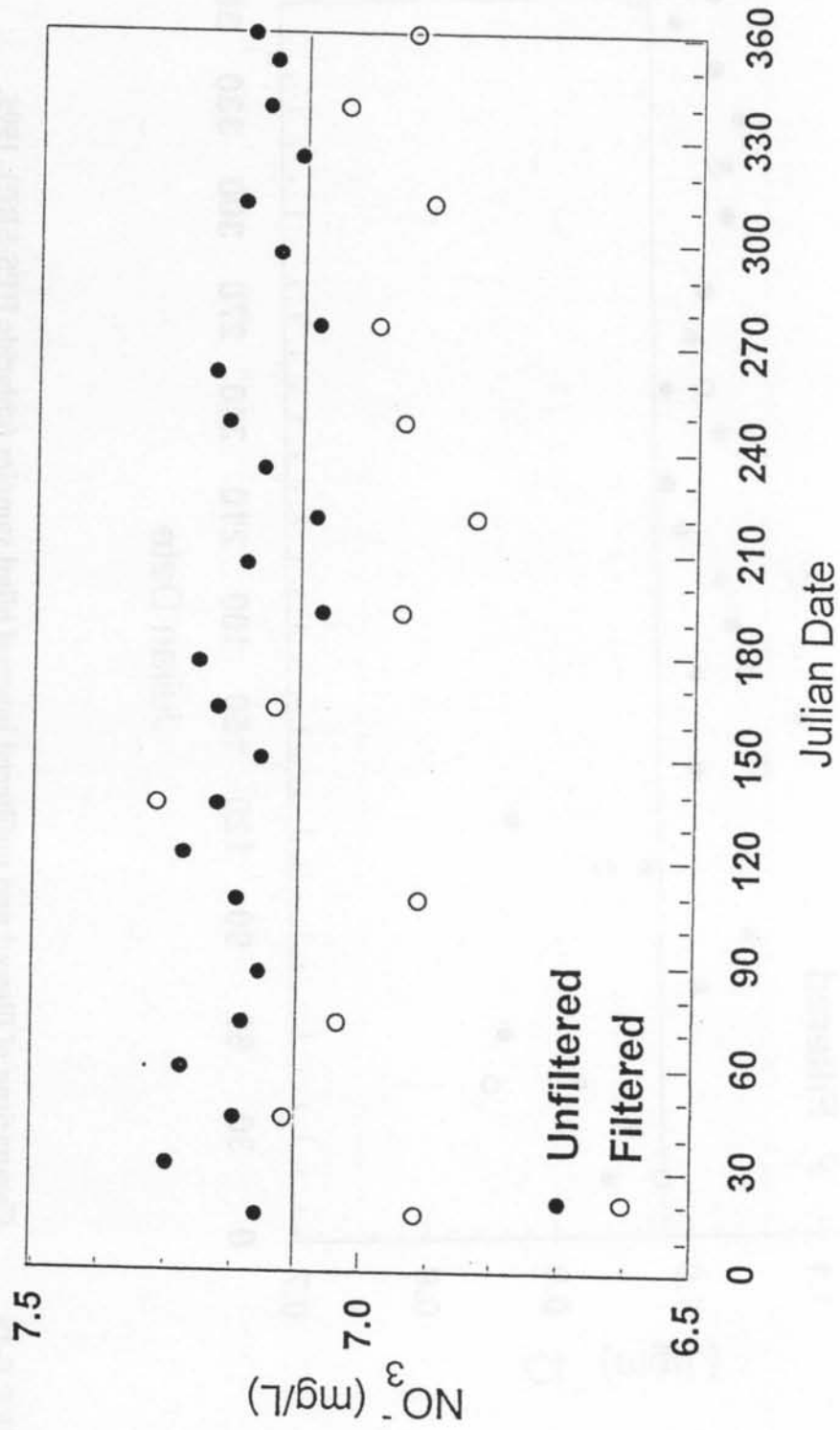


FIGURE B-17 Comparison of filtered and unfiltered internal blind samples (nitrate HPS-SRID), 1995.

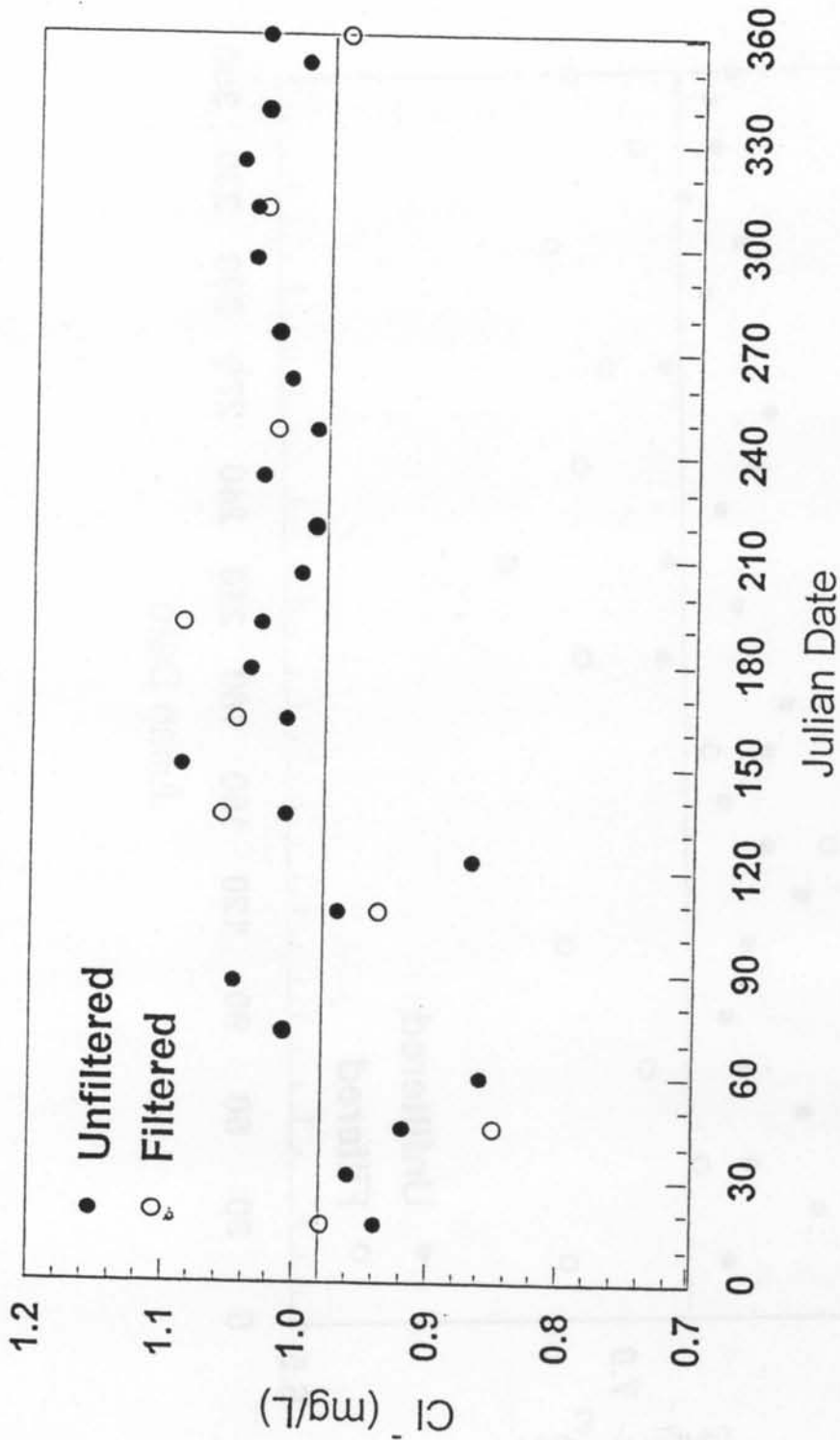


FIGURE B-18 Comparison of filtered and unfiltered internal blind samples (chloride HPS-SRID), 1995.

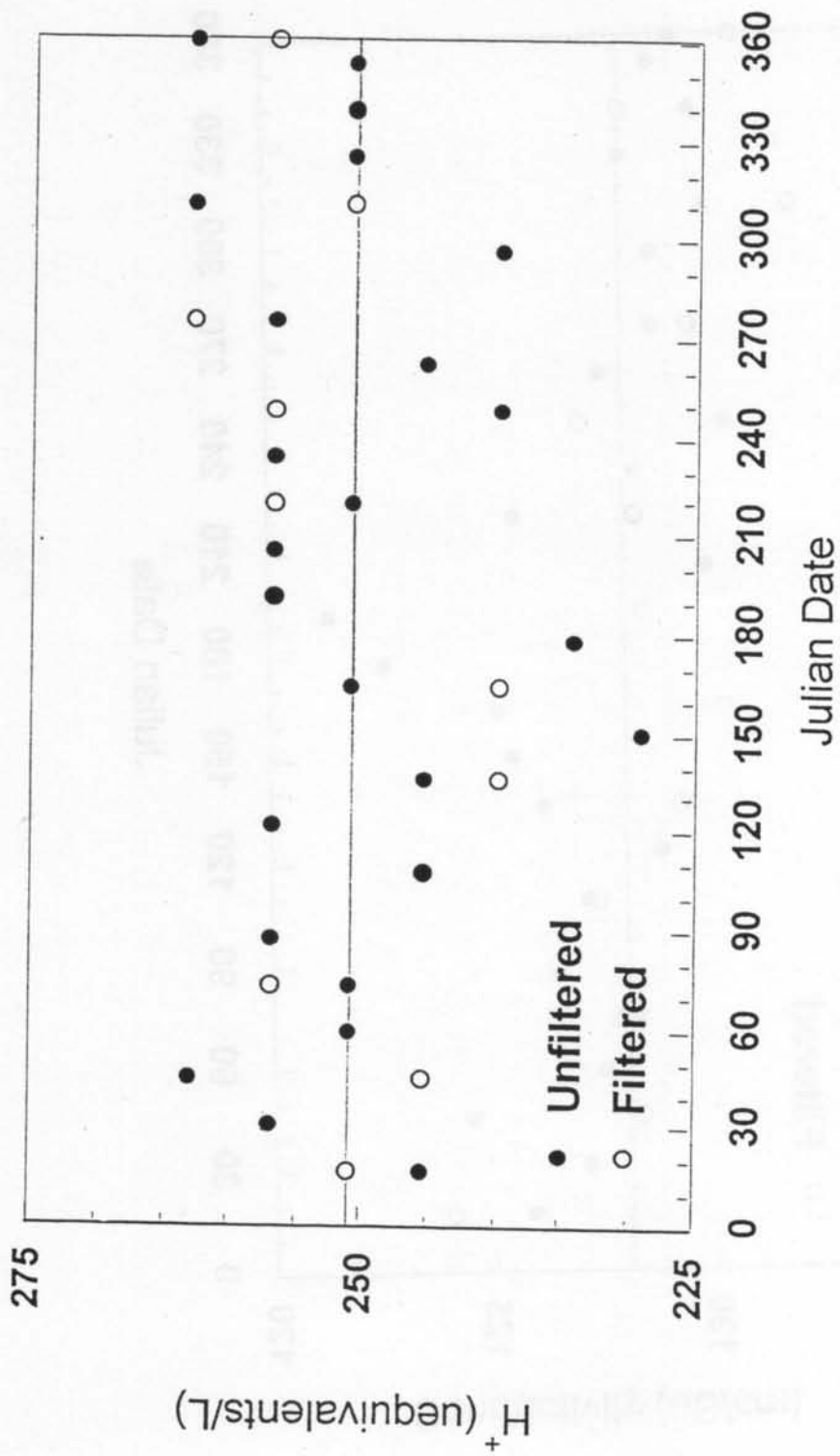


FIGURE B-19 Comparison of filtered and unfiltered internal blind samples (H⁺ HPS-SRID), 1995.

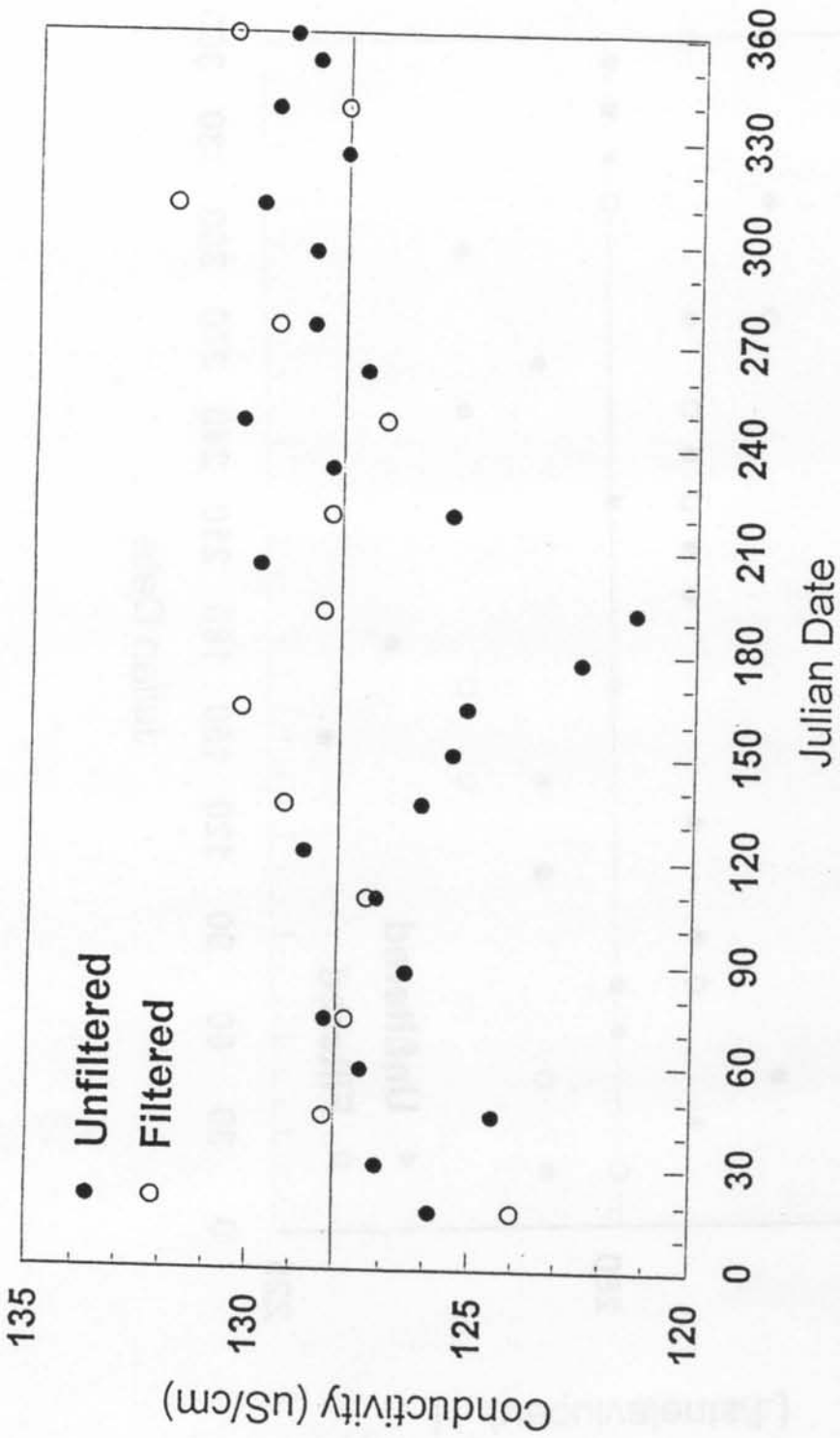


FIGURE B-20 Comparison of filtered and unfiltered internal blind samples (Conductivity HPS-SRID), 1995.

TABLE B-3 50th and 95th Percentile Concentration Values of Parameters Measured in Replicate (S/Q) Samples, 1995

Parameter	Percentile Concentration Values (mg/L)	
	50th	95th
Calcium	0.083	0.688
Magnesium	0.019	0.091
Sodium	0.054	0.400
Potassium	0.016	0.074
Ammonium	0.16	1.11
Sulfate	0.88	3.71
Nitrate	0.92	3.38
Chloride	0.10	0.56
pH (units)	4.84	6.11
H ⁺ (µeq/L)	14.3	57.5
Conductivity (µS/cm)	11.5	33.5

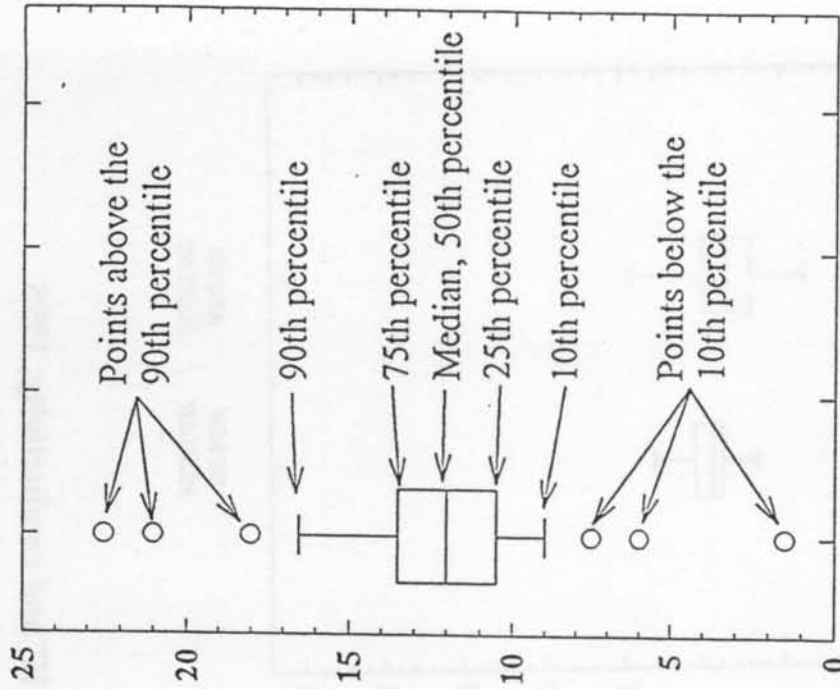


DIAGRAM OF BOXPLOTS USED ON FOLLOWING PAGES

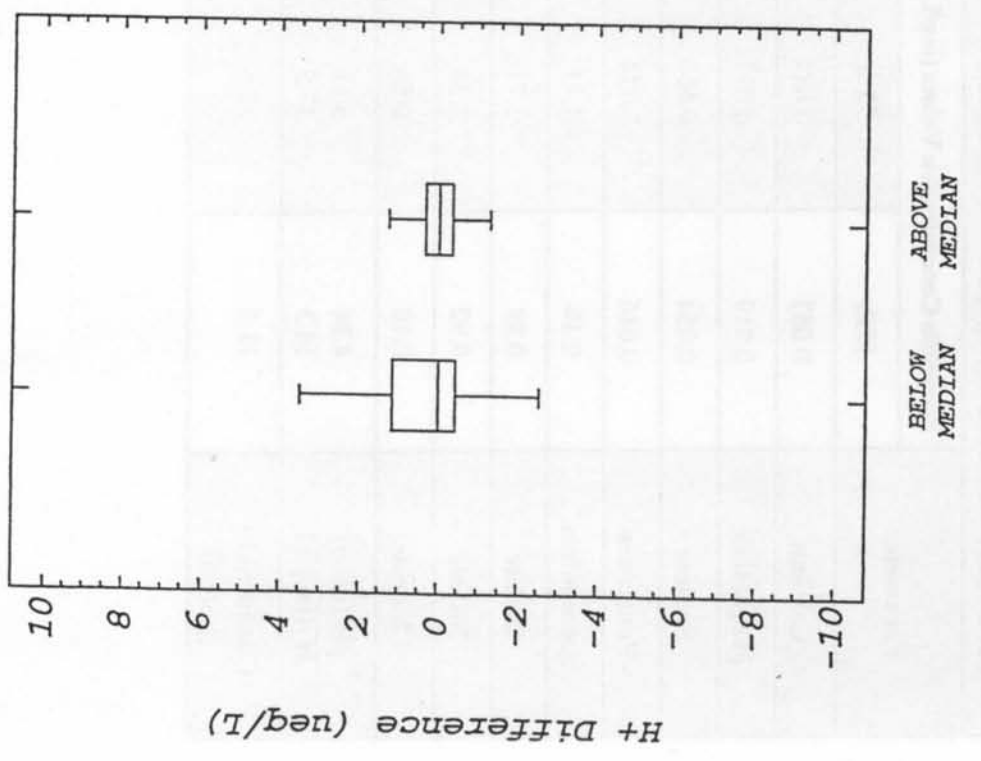
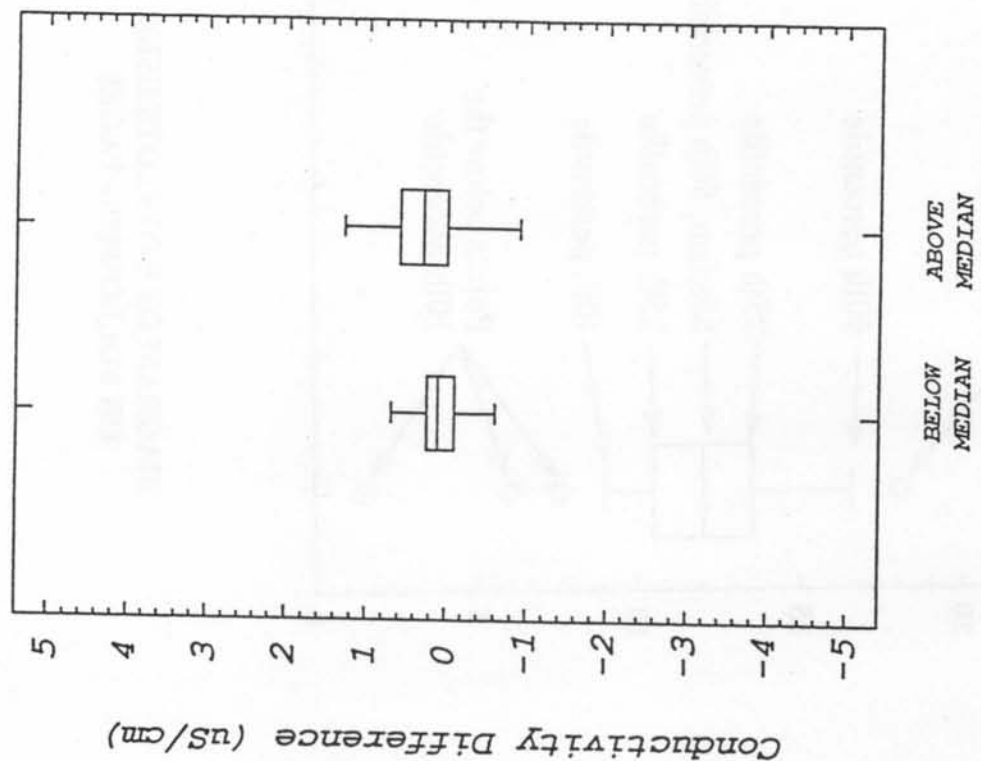


FIGURE B-21 Results of S/Q replicate analysis, H⁺ and conductivity, 1995

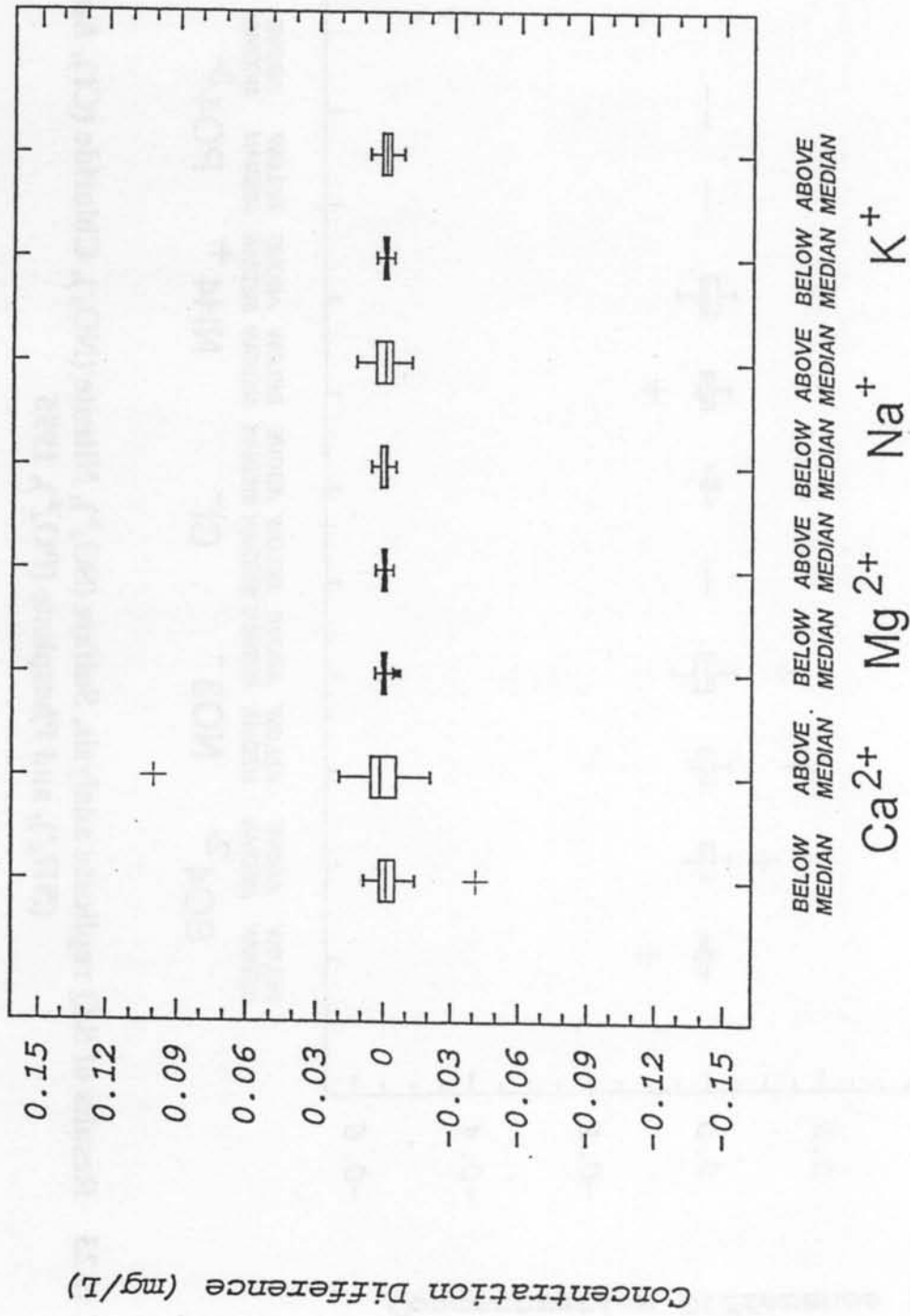


FIGURE B-22 Results of S/Q replicate analysis, Calcium (Ca²⁺), Magnesium (Mg²⁺), Sodium (Na⁺), and Potassium (K⁺), 1995

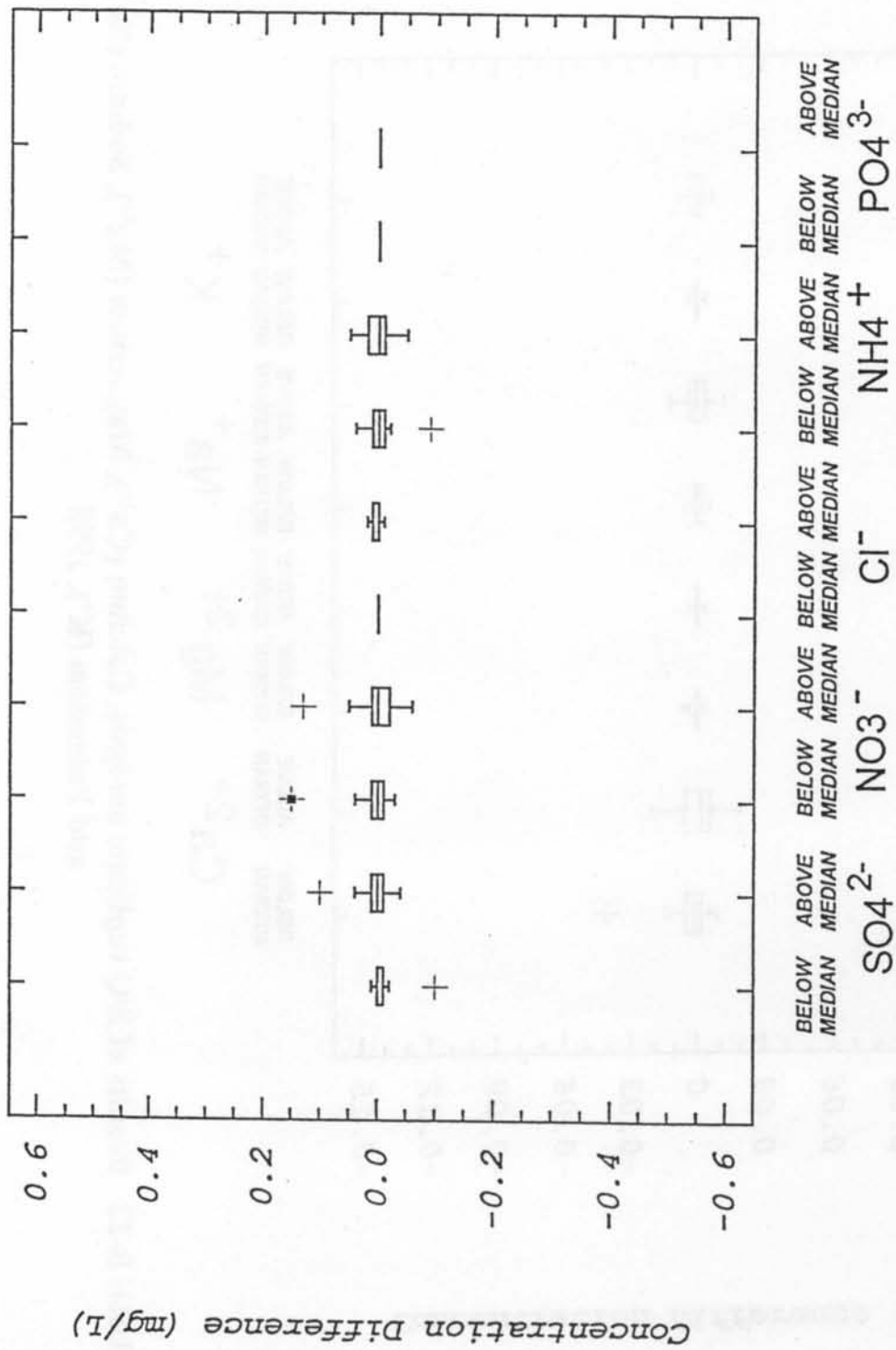


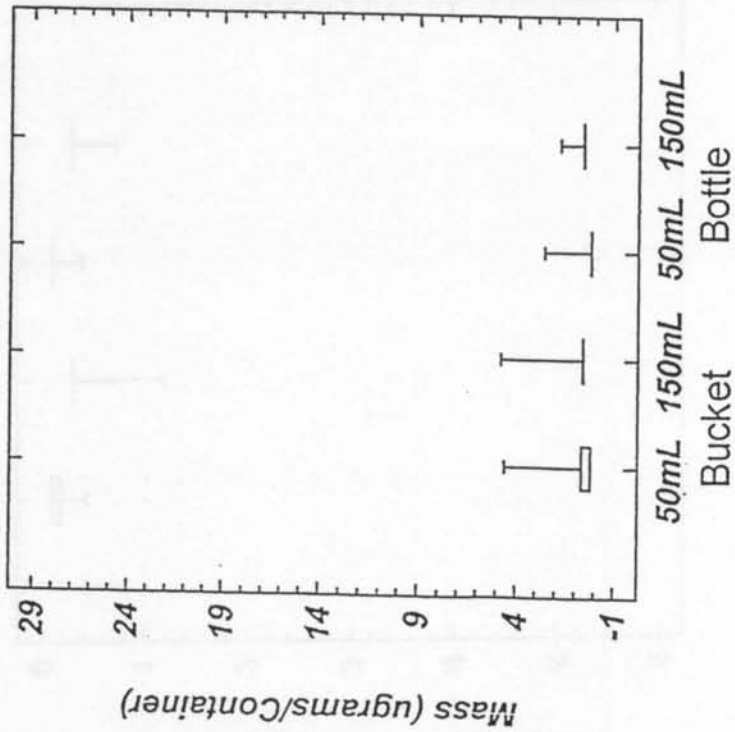
FIGURE B-23 Results of S/Q replicate analysis, Sulfate (SO₄²⁻), Nitrate (NO₃⁻), Chloride (Cl⁻), Ammonium (NH₄⁺), and Phosphate (PO₄³⁻), 1995

**TABLE B-4 Percent of Ion Concentrations Above MDLs Found
in Weekly Deionized (DI) Water Blanks and Leachates, 1995**

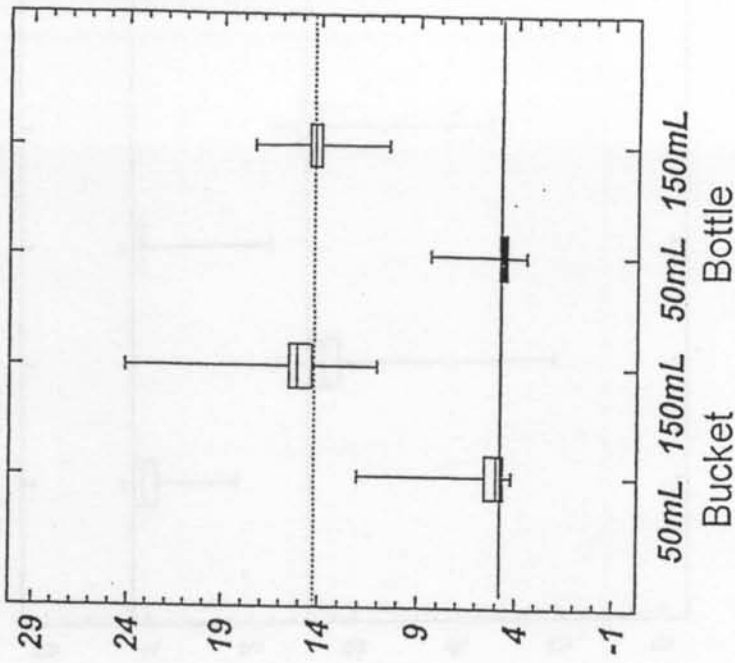
Blank	Calcium	Magnesium	Sodium	Potassium	Ammonium	Sulfate	Nitrate	Chloride	Phosphate	Number
DI-(209)	2	2	28	6	8	0	0	0	0	50
DI-(304)	6	4	46	8	8	0	0	0	6	50
DI-(323)	4	6	42	6	6	2	0	4	6	50
Filter A	6	4	100	10	48	0	86	62	4	50
Filter B	2	4	94	8	20	2	4	2	6	50
Bucket 50	42	42	100	80	22	0	12	56	10	50
Bucket 150	22	18	92	50	14	0	0	8	10	50
Bottle 50	6	12	42	54	10	0	0	0	14	50
Bottle 150	6	6	32	36	8	0	0	0	6	50
Lid 50	26	22	84	58	42	0	2	12	4	50

**TABLE B-5 Percent of Ion Concentrations Above Control Limits Found
in Weekly Simulated Rain (FR25) Blanks and Leachates, 1995**

Blank	Calcium	Magnesium	Sodium	Potassium	Ammonium	Sulfate	Nitrate	Chloride	Phosphate	Number
Filter A	22	14	98	4	26	0	60	52	8	50
Filter B	36	8	68	0	6	8	2	2	2	50
Bucket 50	60	48	80	74	10	2	2	42	14	50
Bucket 150	58	22	58	44	0	0	8	12	6	50
Bottle 50	18	22	22	28	0	0	0	0	22	50
Bottle 150	12	8	22	4	2	2	0	0	10	50
Lid 50	62	28	48	34	10	8	4	20	6	50
AIRMoN 50	8.3	0	33.3	0	0	8.33	0	0	8.3	12
AIRMoN 150	8.3	8.3	16.7	0	0	8.3	0	0	0	12

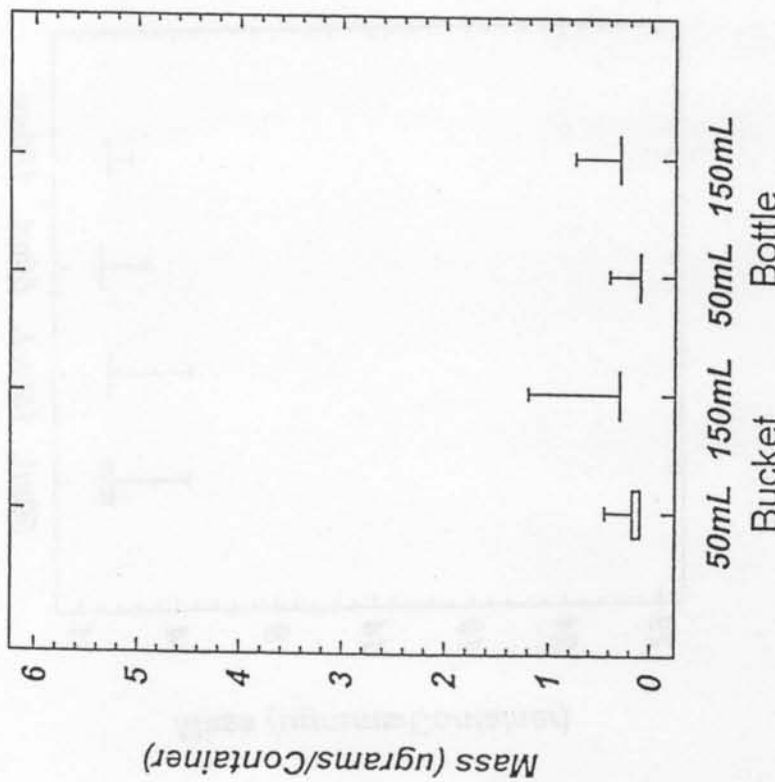
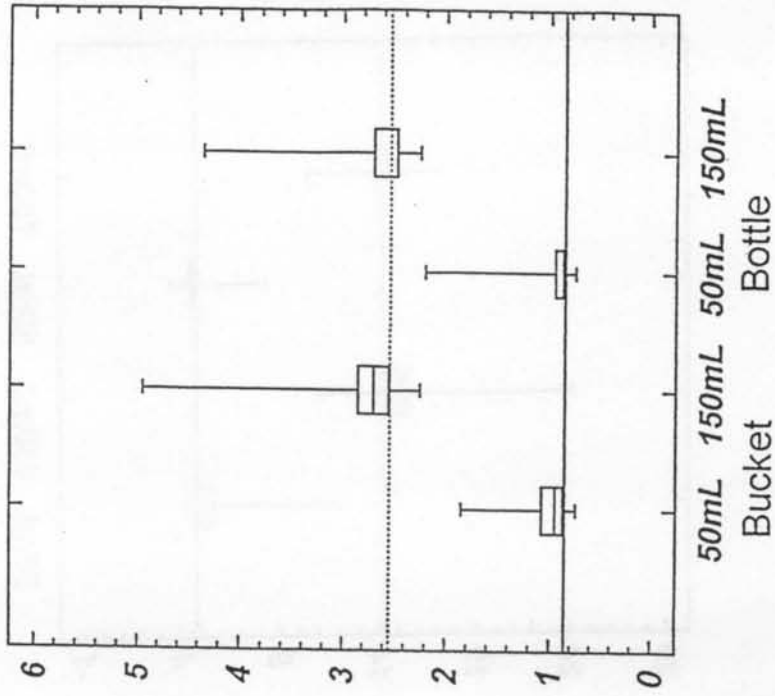


Deionized Water



FR25

FIGURE B-24. Calcium found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1995. FR25 baseline values shown as solid line (50 mL) and dashed line (150 mL).



Deionized Water

FR25

FIGURE B-25. Magnesium found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1995. FR25 baseline values shown as solid line (50 mL) and dashed line (150 mL).

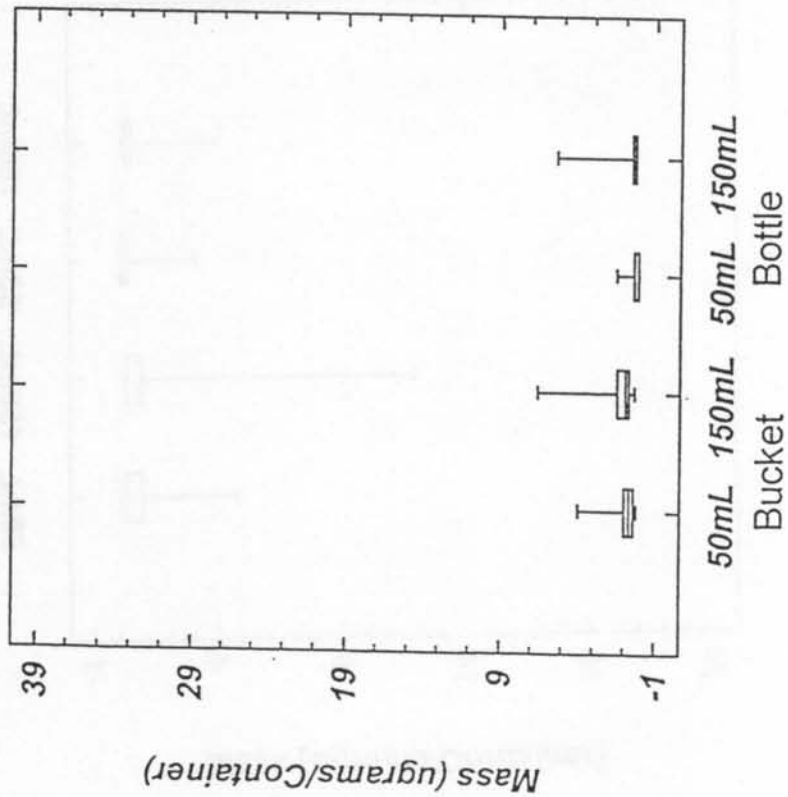
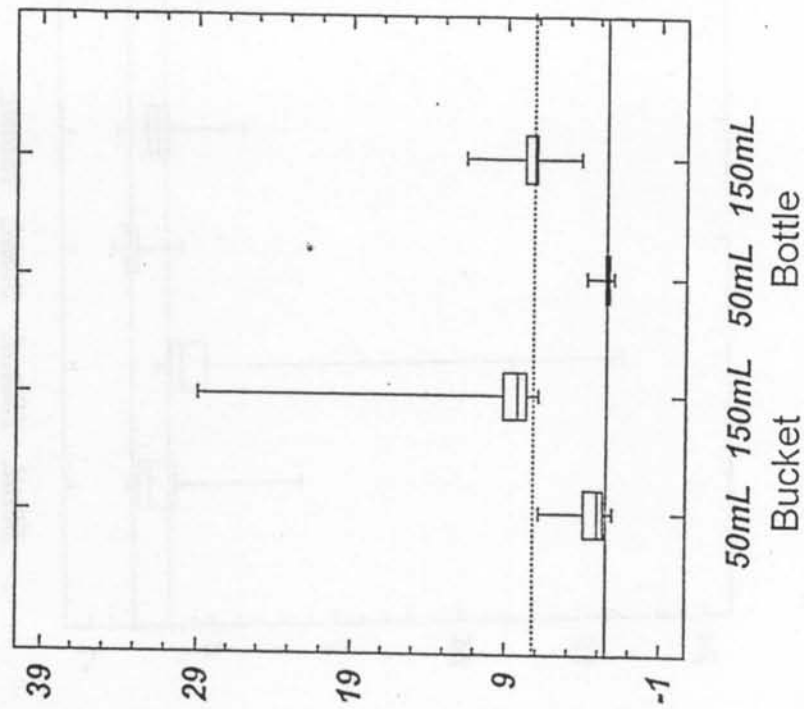
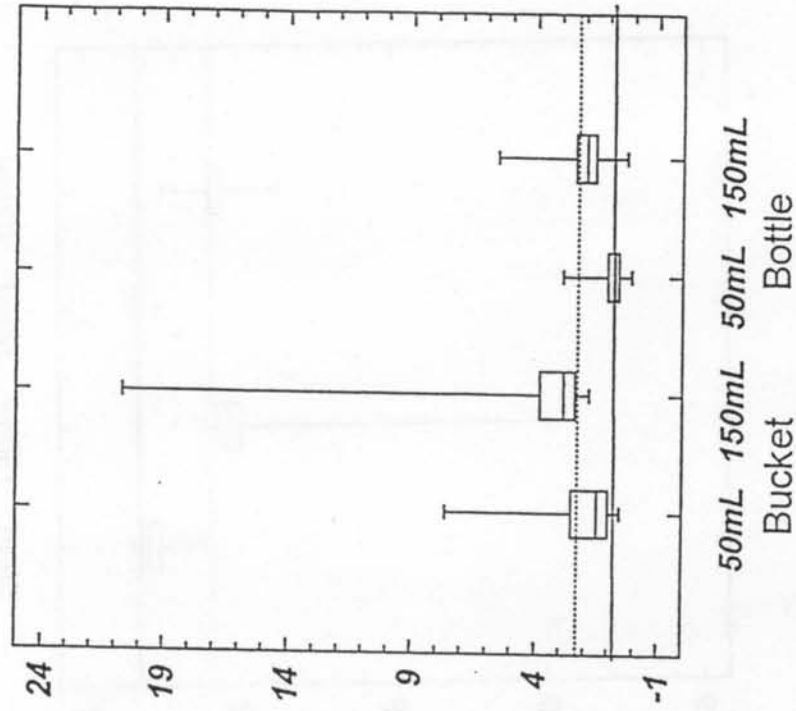
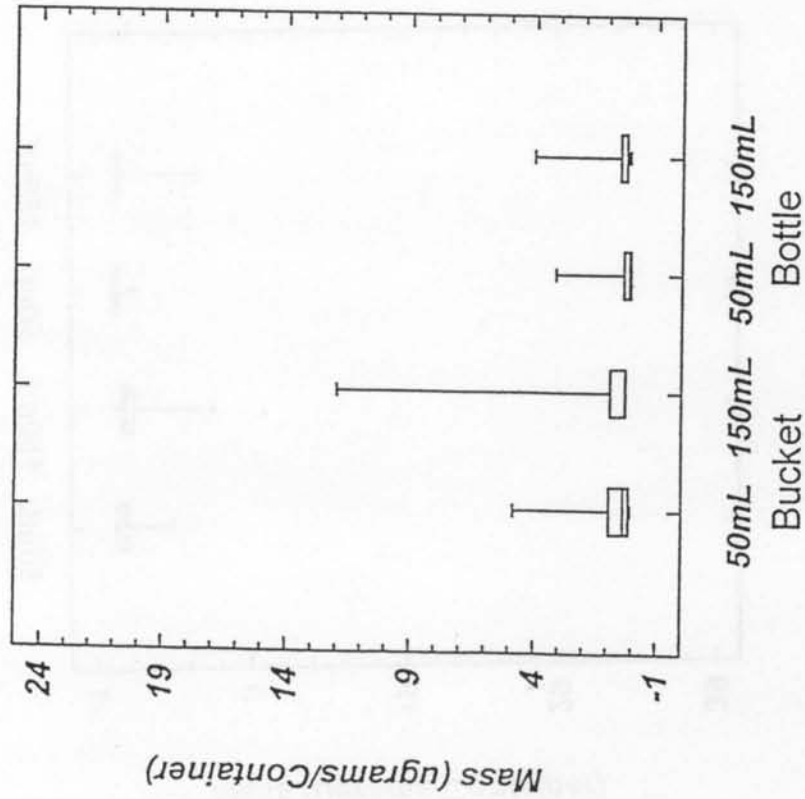


FIGURE B-26. Sodium found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1995. FR25 baseline values shown as solid line (50 mL) and dashed line (150 mL).



Deionized Water

FR25

FIGURE B-27. Potassium found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1995. FR25 baseline values shown as solid line (50 mL) and dashed line (150 mL).

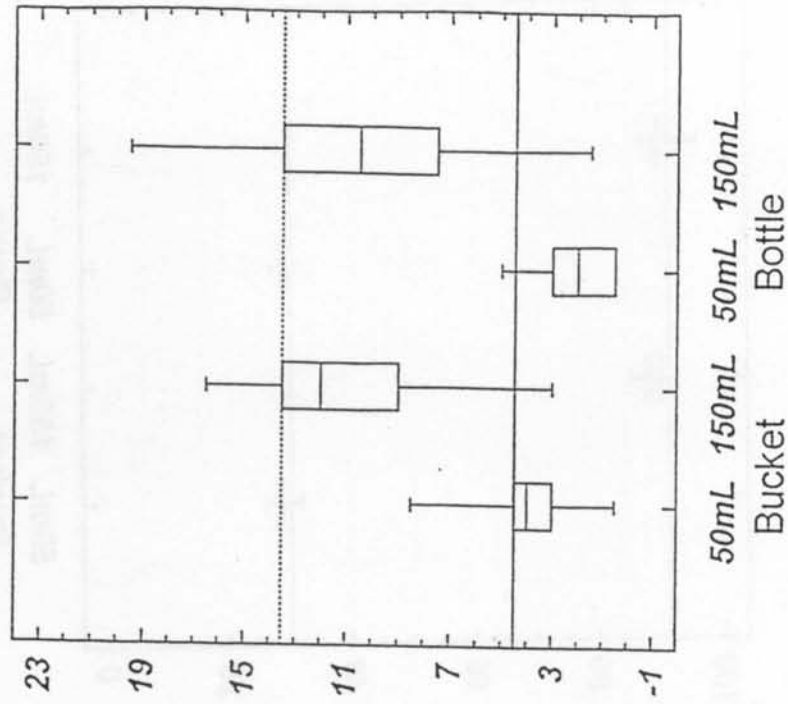
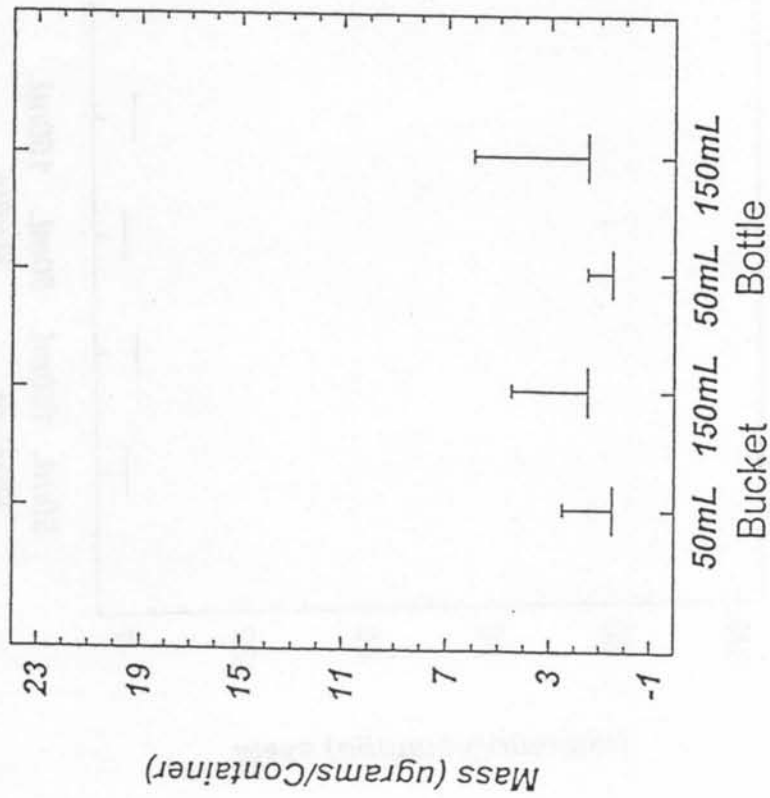
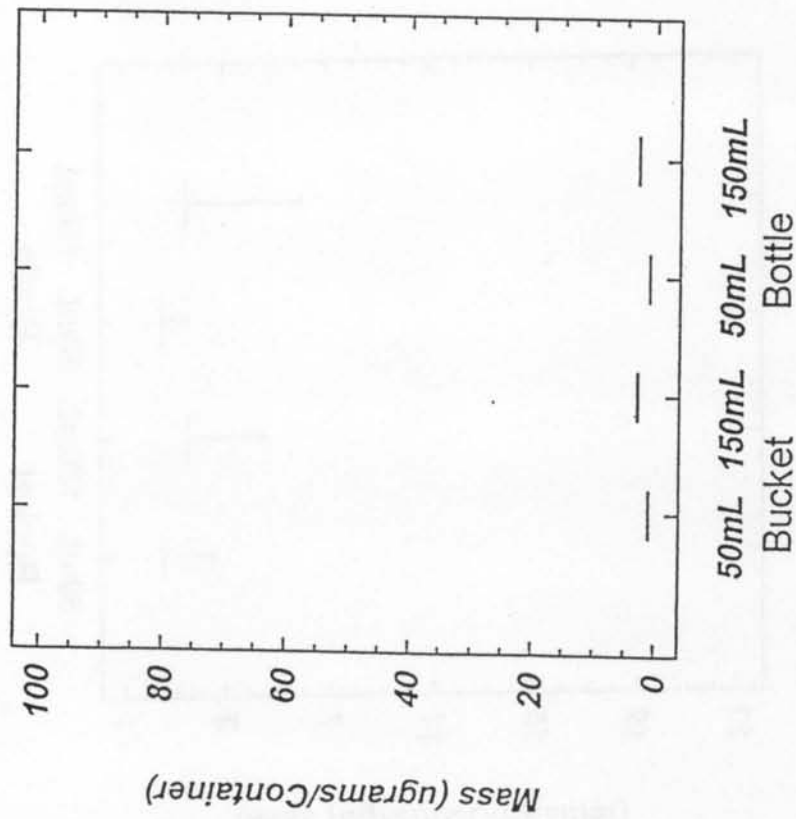
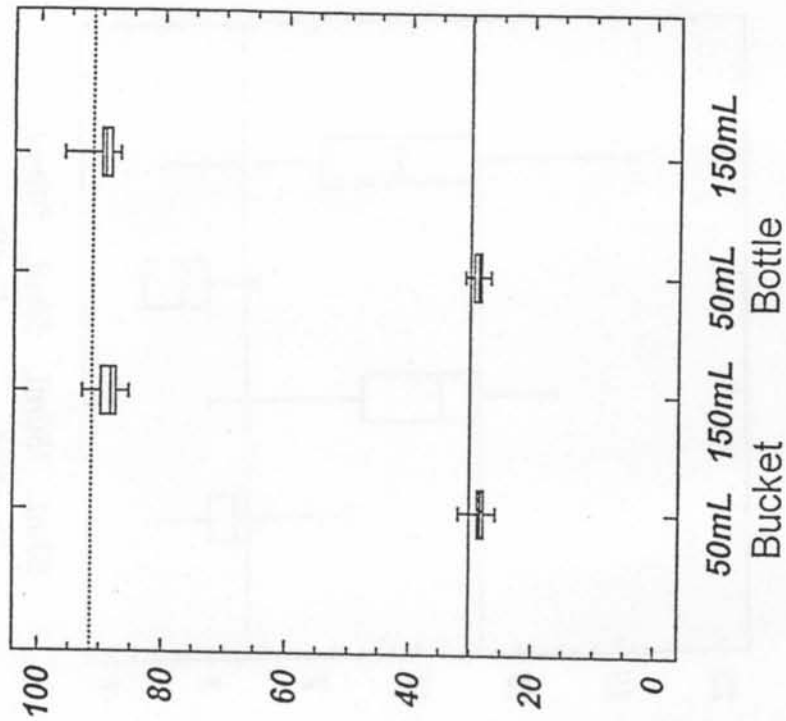


FIGURE B-28. Ammonium found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1995. FR25 baseline values shown as solid line (50 mL) and dashed line (150 mL).

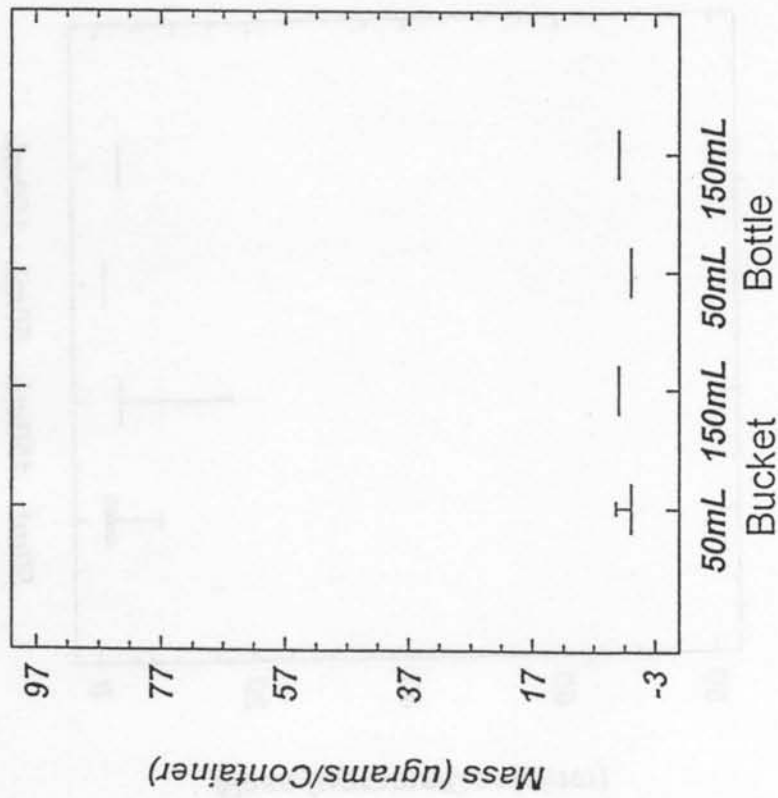


Deionized Water



FR25

FIGURE B-29. Sulfate found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1995. FR25 baseline values shown as solid line (50 mL) and dashed line (150 mL).



Deionized Water

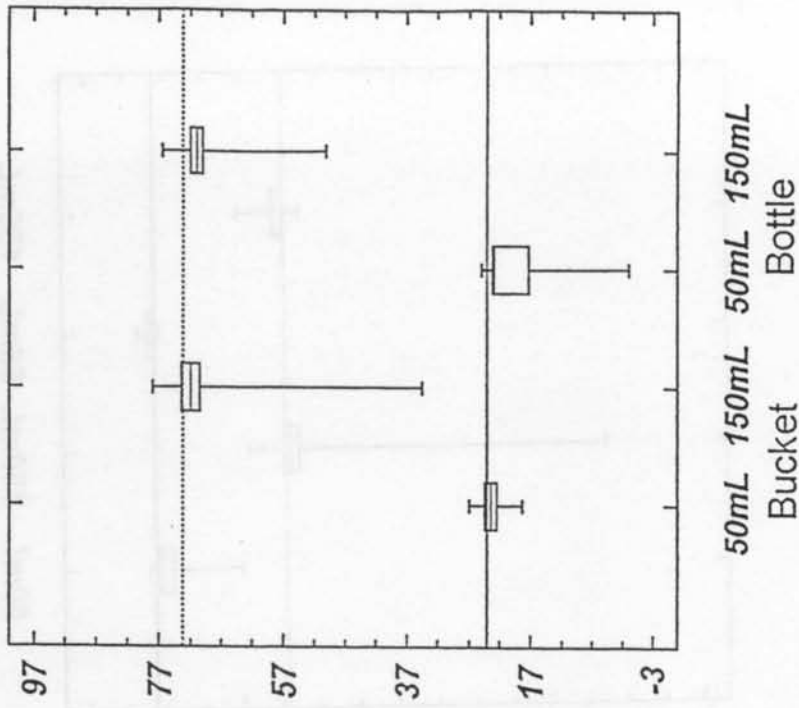


FIGURE B-30. Nitrate found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1995. FR25 baseline values shown as solid line (50 mL) and dashed line (150 mL).

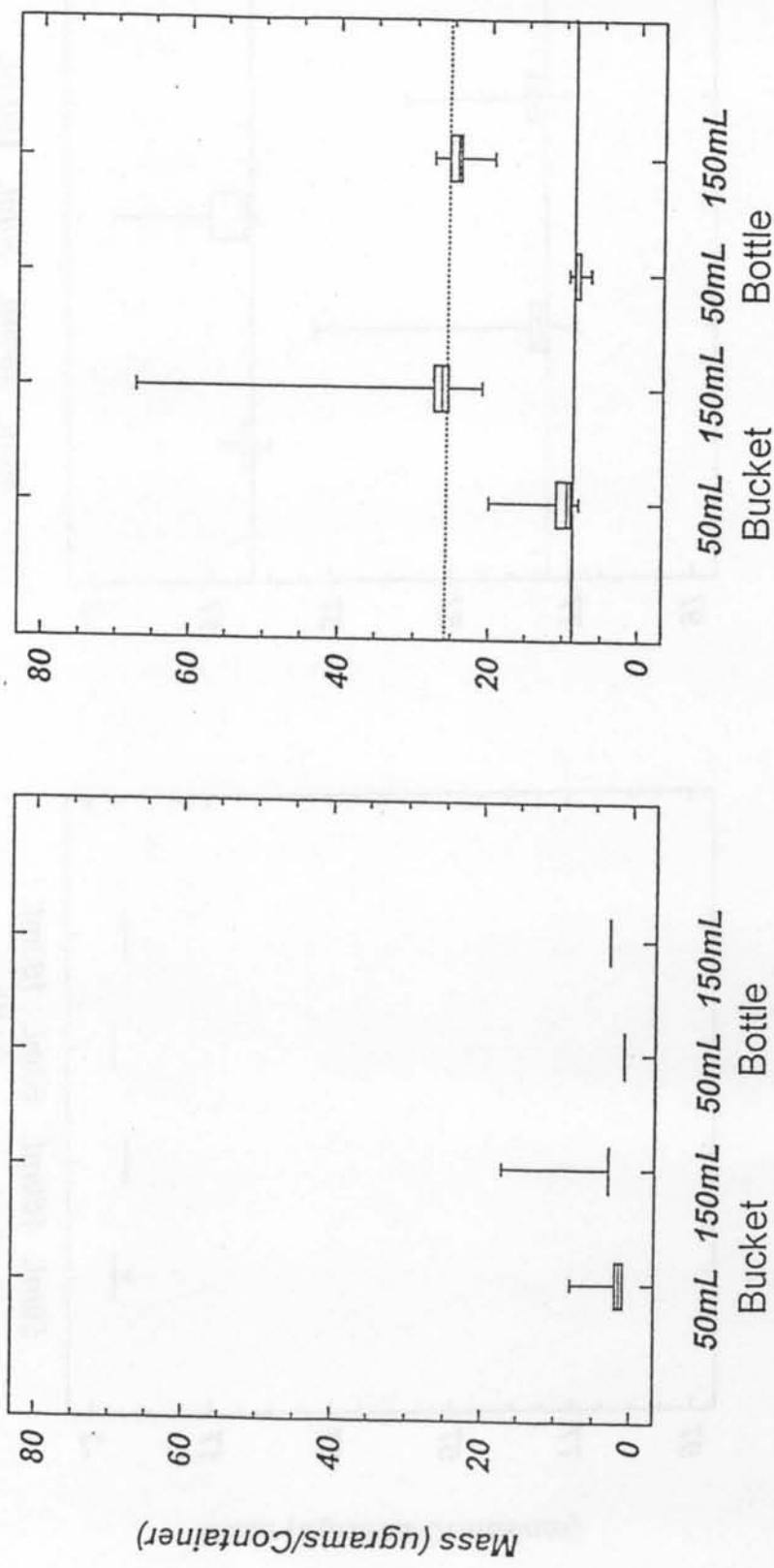
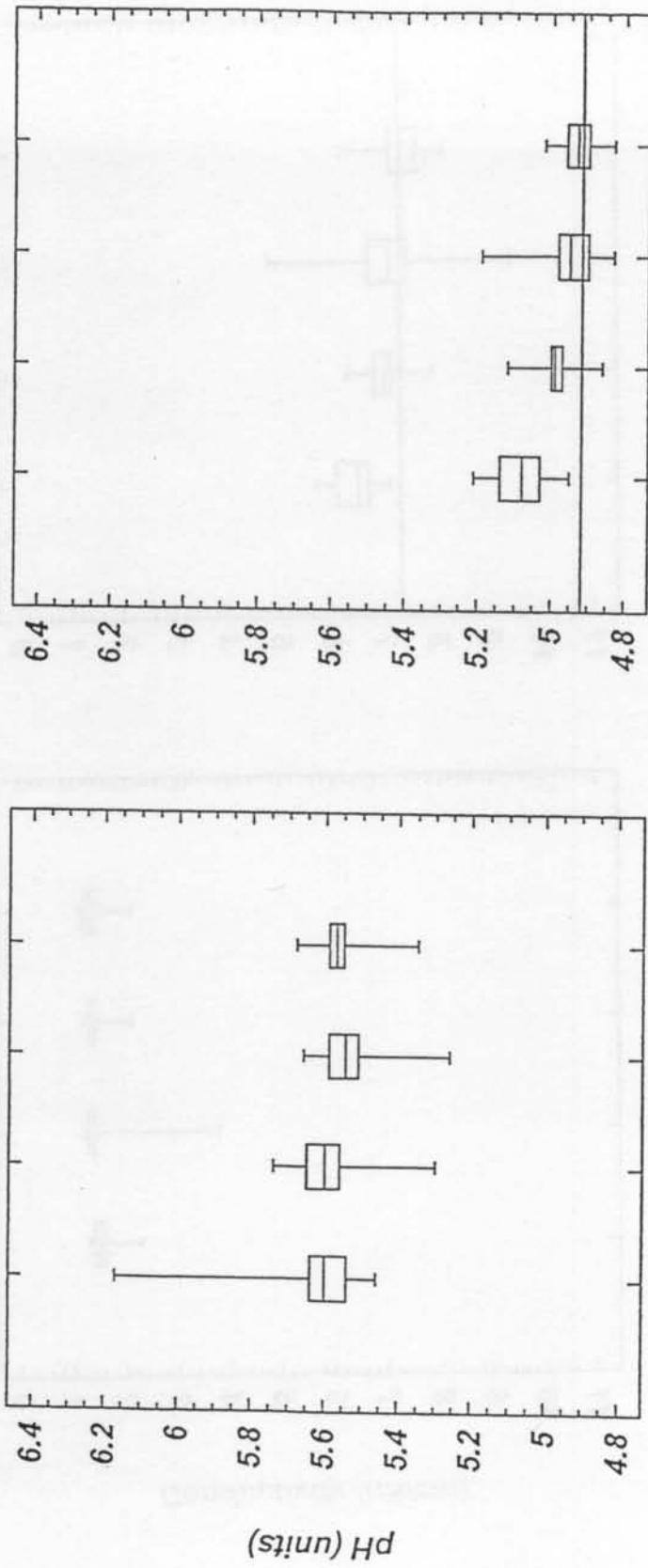


FIGURE B-31. Chloride found in upright bucket blanks and 1-liter bottles, using DI water and FR25 QCS as leaching agents, 1995. FR25 baseline values shown as solid line (50 mL) and dashed line (150 mL).



Deionized Water

FR25

FIGURE B-32. pH of upright bucket blanks and 1-liter bottles leached with DI water and FR25 QCS, 1995. Baseline value for FR25 shown as solid line.

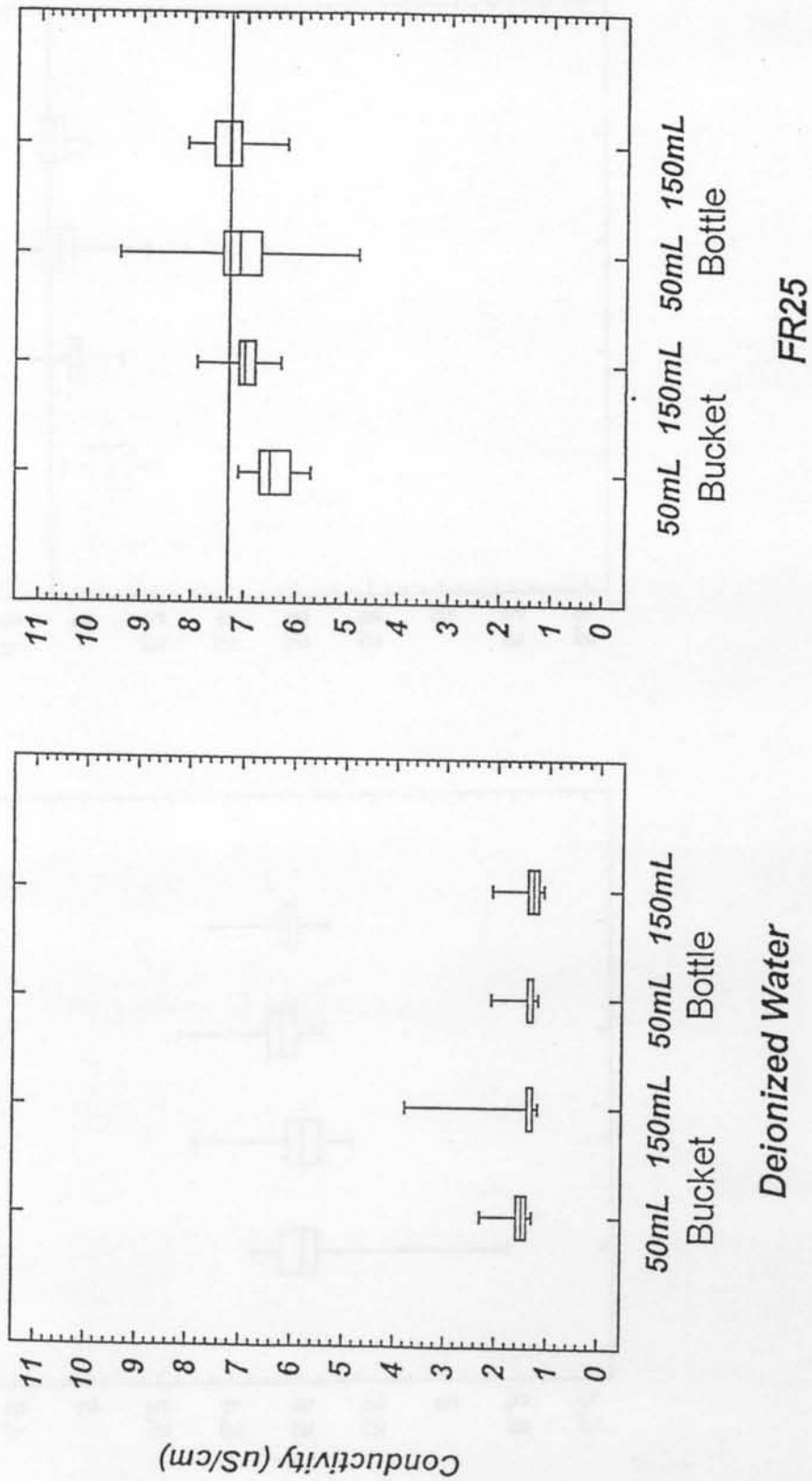


FIGURE B-33. Conductivity of upright bucket blanks and 1-liter bottles leached with DI water and FR25 QCS, 1995. Target values for FR25 shown as solid line.

APPENDIX C

INTERLABORATORY COMPARISON DATA:

WMO, EMEP, LRTAP,

1995

TABLE C-1 WMO Acid Rain Performance Survey, 1995

Analyte	Units	Sample 1136		Sample 2306		Sample 3502	
		Expected	CAL	Expected	CAL	Expected	CAL
Calcium	mg/L	0.053	0.053	0.373	0.376	0.051	0.052
Magnesium	mg/L	0.021	0.024	0.111	0.116	0.075	0.077
Sodium	mg/L	0.237	0.261	1.776	1.809	0.393	0.414
Potassium	mg/L	0.076	0.077	0.771	0.760	0.078	0.078
Ammonium	mgN/L	0.117	0.13	0.831	0.86	0.472	0.49
Sulfate	mgS/L	0.519	0.67	3.689	4.14	2.713	3.06
Nitrate	mgN/L	0.14	0.14	2.118	2.18	1.789	1.83
Chloride	mg/L	0.397	0.41	2.845	2.99	1.291	1.35
pH	pH units	4.49	4.44	3.51	3.53	3.53	3.54
Conductivity	µS/cm	16.4	17.7	155	140	134	134

TABLE C-2 EMEP - Fifteenth Intercomparison of Methods, 1995

Analyte	Units	Sample G-1		Sample G-2		Sample G-3		Sample G-4	
		Expected	CAL	Expected	CAL	Expected	CAL	Expected	CAL
Calcium	mg/L	0.211	0.212	0.402	0.397	0.326	0.318	0.249	0.246
Magnesium	mg/L	0.093	0.095	0.108	0.109	0.248	0.245	0.217	0.217
Sodium	mg/L	0.526	0.527	0.601	0.602	0.300	0.308	0.338	0.341
Potassium	mg/L	0.178	0.180	0.229	0.230	0.280	0.275	0.127	0.128
Ammonium	mgN/L	0.25	0.26	0.18	0.18	0.44	0.41	0.56	0.53
Sulfate	mgS/L	1.51	1.52	1.88	1.88	0.97	0.97	0.97	0.97
Nitrate	mgN/L	0.35	0.35	0.28	0.29	0.54	0.56	0.61	0.62
Chloride	mg/L	0.81	0.83	0.93	0.93	0.46	0.46	0.52	0.53
pH	units	4.12	4.14	4.06	4.08	4.62	4.57	4.52	4.50
Conductivity	µS/cm	41.6	41.9	48.0	48.3	22.5	24.2	25.1	26.3

TABLE C-3 NWRI Soft Waters Interlaboratory Study L-38, MARCH 1995

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	1.95	1.95	4.60	4.48	0.120	0.121	2.60	2.62	2.90	2.88
Magnesium	mg/L	0.470	0.472	0.824	0.823	0.040	0.037	0.997	0.988	0.692	0.688
Sodium	mg/L	0.604	0.601	0.557	0.549	0.168	0.168	0.280	0.281	0.960	0.947
Potassium	mg/L	0.230	0.229	0.195	0.198	0.030	0.029	0.160	0.158	0.472	0.476
Ammonium	mgN/L	0.016	0.02	0.287	0.29	0.138	0.15	0.290	0.30	0.018	0.03
Sulfate	mg/L	6.04	6.13	5.85	5.85	1.30	1.29	3.80	3.85	6.90	6.73
Nitrate	mgN/L	0.006	0.005T	0.867	0.87	0.254	0.25	0.54	0.54	0.05	0.05
Chloride	mg/L	0.500	0.49	0.49	0.47	0.29	0.29	0.46	0.45	1.04	1.05
pH	units	6.20	6.28	7.00	7.11	4.61	4.65	6.93	7.04	6.72	6.82
Conductivity	µS/cm	21.8	21.7	39.8	39.7	14.8	14.2	29.0	28.7	30.95	30.8
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	3.990	3.885	0.280	0.275	1.95	1.90	2.10	1.997	1.436	1.429
Magnesium	mg/L	1.40	1.393	0.070	0.067	0.310	0.307	0.570	0.564	0.296	0.290
Sodium	mg/L	0.418	0.417	0.070	0.071	0.600	0.592	1.16	1.206	0.144	0.147
Potassium	mg/L	0.230	0.235	0.030	0.028	0.410	0.408	0.260	0.264	0.054	0.051
Ammonium	mgN/L	0.157	0.16	0.232	0.23	0.017	0.03	0.005	0.02t	0.003	0.02w
Sulfate	mg/L	4.40	4.49	1.60	1.58	5.44	5.46	2.60	2.61	0.144	0.147
Nitrate	mgN/L	0.35	0.35	0.24	0.24	0.41	0.41	0.0075	0.005t	0.036	0.04
Chloride	mg/L	0.78	0.79	0.14	0.13	0.43	0.43	1.78	1.78	0.15	0.15
pH	units	7.2	7.31	4.85	4.83	5.27	5.29	6.83	6.87	4.36	4.46
Conductivity	µS/cm	38.4	38.6	12.1	12.0	23.8	23.8	23.9	24.0	33.2	33.3

0.00 score # 1 of all labs = 51

TABLE C-4 NWRI Soft Water Interlaboratory Study L-39, October 1995

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	0.276	0.277	0.120	0.129	2.810	2.855	1.424	1.427	2.600	2.62
Magnesium	mg/L	0.070	0.068	0.040	0.039	0.580	0.573	0.297	0.291	0.653	0.679
Sodium	mg/L	0.070	0.067	0.163	0.170	0.110	0.111	0.143	0.143	1.76	1.99
Potassium	mg/L	0.030	0.028	0.030	0.028	0.180	0.180	0.054	0.054	0.368	0.360
Ammonium	mgN/L	0.23	0.25	0.13	0.14	0.002	0.02w	0.003	0.02t	0.11	0.12
Sulfate	mg/L	1.62	1.61	1.31	1.30	1.87	1.88	6.87	6.84	5.84	5.81
Nitrate	mgN/L	0.24	0.24	0.26	0.25	0.46	0.46	0.03	0.04	0.006	0.01
Chloride	mg/L	0.14	0.13	0.30	0.29	0.20	0.20	0.15	0.15	3.06	2.99
pH	units	4.81	4.79	4.58	4.58	6.88	7.09	4.35	4.36	6.40	6.51
Conductivity	µS/cm	12.4	13.2	15.4	15.6	22.0	21.7	33.0	32.9	33.4	33.4
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	1.49	1.52	4.56	4.39	10.10	9.62	13.60	13.3	14.15	13.5
Magnesium	mg/L	0.490	0.490	0.787	0.812	2.59	2.62	2.82	2.82	3.83	3.83
Sodium	mg/L	0.230	0.234	2.56	2.77	4.72	5.14	1.38	1.45	2.60	2.82
Potassium	mg/L	0.056	0.056	0.570	0.551	0.920	0.886	0.510	0.499	0.807	0.784
Ammonium	mgN/L	0.50	0.50	0.005	0.02t	0.009	0.02t	0.003	0.02t	0.007	0.02t
Sulfate	mg/L	4.23	4.23	4.56	4.55	9.09	9.12	3.49	3.48	4.94	4.96
Nitrate	mgN/L	0.64	0.64	0.25	0.25	0.41	0.40	0.31	0.31	0.11	0.11
Chloride	mg/L	0.55	0.55	1.88	2.07	5.60	5.61	1.46	1.46	2.26	2.25
pH	units	6.11	6.18	7.06	7.31	7.44	7.67	7.82	7.97	7.86	7.98
Conductivity	µS/cm	21.6	22.0	44.2	45.0	97.3	97.3	97.7	97.8	111	112

10.20 = 15 of 35 pH flagged high 3, 7, 8; sodium flagged very high on sample 7, 10, extremely high on 5 & 8, chloride high 7, calcium low 8, 10

