QUALITY ASSURANCE REPORT
NADP/NTN DEPOSITION MONITORING

Laboratory Operations
Central Analytical Laboratory
1991

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

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

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

Illinois State Water Survey
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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 NADFs precipitation chemistry network were established to provide information about geographical patterns and temporal trends in the deposition of acidic chemicals and nutrients. Initially organized as Regional Project NC-141 by the North Central Region of the SAES, the NADP was endorsed by all four regions in 1982, at which time it became Interregional Project IR-7. A decade later, the SAES reclassified IR-7 as a National Research Support Project, NRSP-3.

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

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

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1991 QUALITY ASSURANCE REPORT
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Laboratory Operations
Central Analytical Laboratory
January 1991 through December 1991

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ACKNOWLEDGEMENTS

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I. INTRODUCTION

In August 1991, the Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) received and analyzed its 100,000th wet deposition sample. Analysis of precipitation samples began in the summer 1978 and has continued to the present time making the NADP/NTN "... the longest-running, national-scale, atmospheric wet deposition monitoring network in the world."(1).

From the beginning, the laboratory has operated with a strict system of quality control (QC), which has enabled its analysts to produce well documented and dependable data. A Quality Assurance Plan (2) prescribes the methods used to conduct and document the chemical and physical analyses of each sample. These analyses are then verified mathematically using ion balance and specific conductance calculations. Voluntary participation in national and international interlaboratory comparison studies ensures the comparability of CAL results with those of its peers throughout the world and finally the U.S. Geological Survey (USGS) acts as the official external auditing agency of the NADP/NTN laboratory program.

Annual reports (3-10) describe the development of the quality assurance program and document the daily, weekly, monthly, semi-annual, and annual procedures followed at the CAL. The format of this report is the same as that of the 1989 and 1990 reports.

Quality Assurance Reports of Laboratory Operations for the previous years (1978-1990) are available from the Illinois State Water Survey or the Program Coordinator's Office at Colorado State University. The quality assurance data summarized in these reports are additionally available in tabular form upon request from the CAL.

II. LABORATORY QUALITY ASSURANCE - A GENERAL DESCRIPTION

The information presented in this report summarizes the laboratory QA/QC data collected throughout 1991. The report classifies the components of the QA program according to the frequency of their occurrence: daily, weekly, monthly, semiannually, and annually. These activities are summarized in Table II-l and are described in subsequent sections.

Internal QA/QC procedures, developed over the past 13 years provide the data required to evaluate the analytical equipment, personnel performance, and analytical procedures of the CAL. From this information the accuracy and precision of the reported values can be assured. Results of the USGS external audits are also summarized as are data from CAL participation in national and international interlaboratory comparisons.

Few modifications of the established program occurred in 1991. The processing of samples has not changed since mid-1987 (Figure II-l). There were no personnel or analytical methods changes. Internally prepared simulated rain at concentration levels near the 25th and 75th percentile concentration values of the network continued to serve as the quality control solutions (QCS) used following instrument calibration and during sample runs. Samples obtained from the Canadian National Water Research Institute were used in the internal blind sample submission program. The replicate and reanalysis protocols in place since 1989 were not altered. Deionized water, filter leachates, and sample collection and shipping bucket leachates were analyzed weekly to assess their contributions to the sample chemistry. The USGS external audit evaluated the contribution of the sample container and sample handling to sample chemistry in the blind-audit program and the performance of the CAL compared to its peers in the interlaboratory comparison program.

TABLE II-l NADP/NTN Laboratory QC/QA Program Summary

- I. Daily
  - A. Instruments calibrated, calibration curves verified using low- and high-level control standards.
    - 1. Internally formulated solutions of simulated rain representing 25th and 75th percentile concentrations of network samples used for all physical and chemical parameters.
    - 2. Values of control standards recorded.
  - B. Records of standard preparation and instrument maintenance updated by analysts.
- II. Weekly
  - A. Blanks analyzed.
    - 1. Deionized water collected from sample processing, atomic absorption, and bucket washing laboratories.
    - 2. Filter leachates "A" and "B" collected after 300 mL deionized water (DI) rinse.
      - a. DI
      - b. pH 4.3 nitric acid
    - 3. Bucket leachates of 50 and 150 mL collected from upright and inverted buckets.
      - a. DI
      - b. pH 4.3 nitric acid
    - 4. Procedures expanded when contamination indicated.
  - B. Internal blind samples submitted to sample processing as sites SWS1, SWS2, and SWS3.
    - 1. SWS1 alternated NWRI EA-22 and EB-17, unfiltered.
    - 2. SWS2 alternated DI and pH 4.3 nitric acid, unfiltered.
    - 3. SWS3 rotated all of the above, filtered.
  - C. Newly prepared check samples validated and approved for shipment to the field.
  - D. Replicate data collected and evaluated.
- III. Monthly
  - A. Control charts generated from daily control standards data inspected.
  - B. Chemistry of internal blind samples evaluated from field printouts.
  - C. Reanalysis list based on verification of chemical analysis using ion balance and specific conductance calculations sent to laboratory.
    - 1. Reanalyses of selected samples evaluated.
    - 2. Suggestions for data corrections made and sent to data management.
  - D. Analyses of USGS interlab comparison samples verified.
- IV. Annually and semi-annually
  - A. Summary of annual quality assurance in report form submitted for publication.
  - B. Reports for Subcommittee on Network Operations presented at spring and fall meetings.
  - C. Interlaboratory comparison samples from external agencies analyzed and data reported when requested.

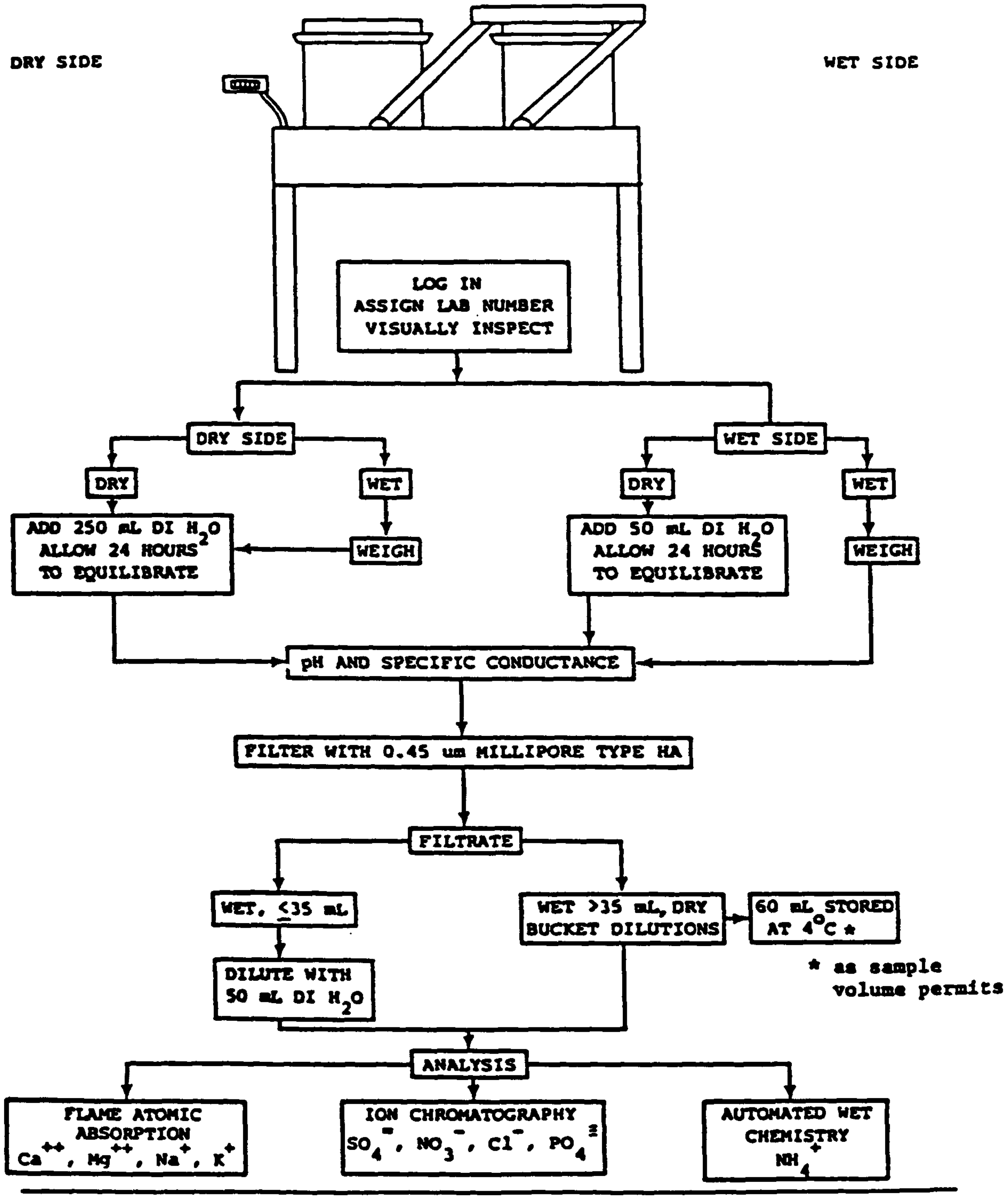


FIGURE II-1. Sample processing flowchart, January 1991-December 1991.

III. DAILY QUALITY CONTROL PROCEDURES

In 1991 200 NADP/NTN sites collected weekly precipitation samples throughout the United States. The operators at each site remove only enough sample for field measurements of pH and conductivity; the remaining sample is shipped to the CAL in the collection bucket with a sealed lid. Upon receipt at the CAL, samples are unpacked and routed to sample processing where the various procedures illustrated in the flow chart (Figure II-l) go into effect. Samples with volumes > 35 milliliters (mL) are designated "wet" samples and undergo the entire suite of analyses. Initially several milliliters are poured into small vials for laboratory pH and conductivity measurements. A portion of the remaining sample is then filtered using Millipore™ type HAWP, 0.45µm filters into a 60 mL high-density polyethylene bottle for transport to the laboratories where the major ions are measured. If sample volume permits, an additional 60 mL of sample is filtered, labeled, and stored at 4°C for archival purposes.

The analytical staff (Table III-l) and methods of analysis (Table III-2) have remained the same since 1989.

TABLE III-1
Central Analytical Laboratory
Analytical Staff, 1991

Staff Member/Job Function	Period of Employment
Sue Bachman	
NH_4+	August 1980 - December 1991
Ca^{++}, Mg^{++}, Na^+, K^+	November 1988 - December 1991
Jackie Damara Sample processing, pH, conductivity	September 1983 - May 1986 January 1988 - December 1991
Brigita Demir $SO_4=$, NO_3^-, CI^-, $PO4^{3-}$	September 1981 - December 1991
Pat Dodson Sample processing	September 1980 • December 1991
Angela Haley Sample receipt and processing	October 1989 • December 1991
Theresa Ingersoll Sample receipt and processing	March 1985 - December 1991
Kenni James Quality assurance	October 1987 - December 1991
Mark Peden Laboratory manager	July 1978 - December 1991
Jeffrey Pribble Sample receipt	July 1987 - December 1991

TABLE III-2
Method Detection limits (MDLs) for the Analysis
of Precipitation Samples, 1978-1991

Analyte	Method*	MDL (mg/L)	Dates
Calcium	Flame Atomic Absorption	0.02 0.009	7/78-10/80 10/80-12/91
Magnesium	Flame Atomic Absorption	0.002 0.003	7/78-10/80 10/80-12/91
Sodium	Flame Atomic Absorption	0.004 0.003	7/78-10/80 10/80-12/91
Potassium	Flame Atomic Absorption	0.004 0.003	7/78-10/80 10/80-12/91
Ammonium	Automated Phenate, Colorimetric	0.02	7/78-12/91**
Sulfate	Automated Methyl Thymol Blue, Colorimetric	0.10	7/78-5/85
	Ion Chromatography	0.03	5/85-12/91
Nitrate/Nitrite	Automated Cadmium Reduction, Colorimetric	0.02	7/78-5/85
Nitrate	Ion Chromatography	0.03	5/85-12/91
Chloride	Automated Ferricyanide Colorimetric	0.05 0.02	7/78-3/81 3/81-5/85
	Ion Chromatography	0.03	5/85-12/91
Orthophosphate	Automated Ascorbic Acid Colorimetric	0.003 0.01	7/78-2/86 2/86-7/87
	Ion Chromatography	0.02	7/87-12/91

Notes:
*For a complete description of the most recent methods, see *Methods for Collection and Analysis of Precipitation (11).*
**Equipment upgrade in 1989 did not alter the MDL.

Each of the methods employed for the various parameters requires calibration of instrumentation using known standards, which are in turn verified with certified quality control solutions (QCS) or solutions traceable to certified standards. Beginning in 1990, the CAL has used two concentrations of in-house simulated rain traceable to the National Institute of Standards and Technology (NIST). The two concentrations approximate the 25th and 75th percentile values for network precipitation (Table III-3). The original stock solution was prepared at the CAL as part of a separate Illinois State Water Survey U.S. Department of Energy (DOE) contract.(12) Results from the U.S. Environmental Protection Agency (USEPA) diluted nutrient concentrate, which has always been used as a QCS for phosphate, are compiled for the first time in 1991 and are included. The inclusion of these results is in partial response to a Network Operations Subcommittee recommendation to the Data Management Subcommittee to release orthophosphate data only by special request and include with each request documentation stating the limitations of the PO_4 data.

Samples are not analyzed until the instruments are calibrated to the analyst's satisfaction and the QCS results are within the control limits specified. The values of the QCS are recorded each time they are analyzed and then entered into a computer program to generate an historical record in the form of monthly control charts. The QCS data as shown in Table III-4 indicate that the percent bias for the cations is lower than in 1990 and the precision expressed as the relative standard deviation (RSD) is better for all but the 75th percentile magnesium and 25th percentile ammonium. The anion percent bias is better for the 75th percentile concentrations of all three simulated rain parameters. The precision improved for all but the 75th percentile chloride. The phosphate data indicates high percent bias and RSD for the low concentration and acceptable results for the 0.30 mg/L solution. The pH and conductance bias and precision summaries are similar to those for 1990.

The bias and precision data for all parameters (Table III-4) fall well within the goals for laboratory measurements outlined in the network QA Plan (2). The percent biases are less than 5 percent for all of the parameters. The RSD exceeds 5 percent for only the 25th percentile magnesium, potassium, ammonium, and chloride solutions.

TABLE III-3 Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/NTN Precipitation, 1991

	Percentile Concentration Value (mg/L)									
Parameter	Min.	5th	10th	25th	50th	75th	90th	95th	99th	Max.
Calcium	<0.009	0.013	0.021	0.047	0.113	0.262	0.550	0.886	2.153	17.40
Magnesium	<0.003	0.003	0.005	0.010	0.022	0.048	0.093	0.148	0.372	3.00
Potassium	<0.003	<0.003	0.003	0.009	0.020	0.042	0.086	0.134	0.353	8.30
Sodium	<0.003	0.014	0.020	0.035	0.070	0.162	0.372	0.650	2.120	20.00
Ammonium	<0.02	<0.02	<0.02	0.07	0.19	0.40	0.66	0.92	1.52	20.20
Nitrate	<0.03	0.17	0.29	0.57	1.05	1.80	2.87	3.69	6.18	21.93
Chloride	<0.03	0.04	0.05	0.08	0.13	0.26	0.56	1.01	3.52	39.00
Sulfate	<0.03	0.19	0.30	0.62	1.19	2.23	3.54	4.74	8.11	37.57
Phosphate	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.03	0.09	5.95
pH (units)	3.08	4.06	4.19	4.44	4.90	5.48	6.11	6.39	6.84	7.87
Cond. (µS/cm)	1.4	3.3	4.4	7.2	12.5	23.2	36.5	48.3	80.7	408

Notes:
Number of samples = 6,915
Mean sample volume = 1,482 ml; median sample volume = 917.2 mL

Source: National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) 1991 wet-side samples.

TABLE III-4 Analytical Bias and precision Determined from Analysis of Simulted Rain QCS 1991

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)	Critical Conc. (mg/L)	Statist. Significant Bias?
Calcium	0.077[a]	0.077	518	0.000	0.0	0.002	2.9	0.001	NO
	0.307[b]	0.307	497	0.000	0.0	0.003	1.0	0.002	NO
Magnesium	0.018	0.018	509	0.000	0.0	0.001	5.6	0.000	NO
	0.070	0.070	500	0.000	0.0	0.002	2.3	0.001	NO
Potassium	0.014	0.014	507	0.000	0.0	0.001	10	0.001	NO
	0.055	0.055	503	0.000	0.0	0.002	3.4	0.001	NO
Sodium	0.048	0.047	592	-0.001	-2.1	0.002	3.3	0.001	YES
	0.190	0.189	585	-0.001	-0.5	0.003	1.7	0.001	NO
Ammonium	0.09	0.09	551	0.00	0.0	0.01	12.3	0.00(5)[c]	NO
	0.37	0.37	445	0.00	0.0	0.02	4.5	0.00(8)	NO
Nitrate	0.48	0.48	1077	0.00	0.7	0.01	1.9	0.00(3)	YES
	1.94	1.95	1141	0.01	0.6	0.03	1.7	0.01(2)	NO
Chloride	0.14	0.13	1175	-0.01	-4.6	0.01	6.8	0.00(3)	YES
	0.54	0.53	1218	-0.01	-1.7	0.01	2.7	0.00(5)	YES
Sulfate	0.64	0.64	1088	0.00	-0.6	0.01	1.4	0.00(4)	YES
	2.58	2.59	1148	0.01	0.4	0.03	1.2	0.01(2)	NO
Phosphate	0.06	0.05	132	-0.01	-16	0.01	20.0	0.00(2)	YES
	0.30	0.30	90	0.00	0.0	0.01	3.3	0.00(3)	NO
pH units (µeq/L)	4.90(12.6)[d]	4.89(12.8)	1721	(0.19)	(1.5)	0.03	6.9	(0.351)	NO
	4.31(49.0)	4.33(46.8)	1718	(-1.97)	(-4.0)	0.02	4.0	(0.731)	YES
Conductivity (µS/cm)	7.20	7.33	1020	0.13	1.8	0.12	1.7	0.053	YES
	28.1	27.9	1020	-0.17	-0.6	0.35	1.3	0.148	YES

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. Critical concentration values in parentheses are provided for information, d. The pH data in parentheses are in microequivalents.

See Glossary for definitions of and formulas for Bias, Standard Deviation, Precision, and Critical Concentration.

IV. WEEKLY QUALITY CONTROL/QUALITY ASSURANCE PROCEDURES

Quality assurance procedures that are conducted on a weekly basis include the analysis of internal blind audit samples, replicate samples, and laboratory blank solutions.

A. INTERNAL BLIND AUDIT

The internal blind audit was instituted in the summer of 1984 to provide another means of evaluating the quality of the laboratory data. Since 1987, three blind samples have been submitted each week, each bearing special NADP/NTN site designations, SWS1, SWS2, or SWS3. SWS1 and SWS2 samples are not filtered but the SWS3 sample is. In 1991 the samples used from SWS1 are two concentrations of rainwater provided by the Canadian National Water Research Institute (CNWRI). These solutions had previously been used in the CNWRI's Eulerian Model evaluation studies. Average laboratory median values and their standard deviations were provided as target values. These target values do not represent certified values, but are just median values from the laboratories participating in the Eulerian Model Evaluation study over a period of two years. The SWS2 samples are the same as they have been, DI water from the ion chromatography/flow injection analysis (IC/FIA) laboratory and internally formulated pH 4.3 nitric acid used as a network quality control solution (QCS). SWS3 samples are the four solutions used as SWS1 and SWS2 samples. The SWS3 analyses provides a method of assessing the effect of filtration on network samples. The data from the analyses of these samples are summarized in Tables IV-l-IV-4.

Comparison of the SWS1 and QCS analyses yields widely differing results for bias and precision of the cations, better agreement with the anions, higher percent bias and poorer precision for conductivity and pH. All of the ions are within the goals set in the QA Plan except for the precision of the 0.039 mg/L sodium, which is high. The low-level potassium is only twice the stated method detection limit (MDL) and within the stated goals. The precision values for sodium analyses are variable, presumably due to contamination from handling. The precision of the lower level chloride sample is similar to the sodium. The near-detection levels of ammonium make the statistics inappropriate while the nitrate and sulfate bias and precision are quite acceptable and nearly comparable to the QCS. Predictably, the filtered samples from SWS3 contain higher concentrations of sodium and chloride and slightly higher conductances. The potassium results are variable and the RSD higher than desirable. The filters obviously do not contribute ammonium nor alter the pH. A comparison of the results returned with these solutions illustrates the wider variability in random sample analysis over those obtained immediately after calibration. Near-detection level cation analyses results especially have a higher degree of uncertainty but this is predictable and therefore accounted for in the QA Plan by larger allowable bias and precision percentages at the lower concentrations.

The SWS2 samples also provide a way to look at either false positives or sample contamination, other than the filtering process. With the exception of sodium, the DI water analysis is acceptable. The sodium content and lower pH must account for the increased conductivity. The pH 4.3 solution has a larger amount of sodium and a higher standard deviation (s) for nitrate, chloride and sulfate, indicating the values are not always below detection levels. The pH and conductances are near the target values. The filtered samples show more variability in calcium, magnesium, sodium, and conductivity. The filtered DI and pH 4.3 nitric acid results are similar to previous years' data. Tables B-l and B-2 and the control chart figures in Appendix B (Figures B-l - B-20) are tabular and graphic representations of the filtered and unfiltered ion concentrations for the Canada National Water Research Institute Eulerian Study samples.

TABLE IV-1 Analytical Bias and Precision Determined from
Analysis of Internal Blind Audit Samples (SWS1), Canada National Water research Institute
Eulerian Study Samples EB-17 EA-22, Unfiltered, 1991

Parameter	Target Conc. (mg/L)	Measured Cone. (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD
Calcium	0.139[a] 0.335[b]	0.149 0.338	25 25	0.010 0.003	7.2 0.9	0.006 0.008	4.0 2.4
Magnesium	0.029 0.070	0.027 0.068	25 25	-0.002 -0.002	-6.9 -2.9	0.002 0.003	7.4 4.4
Potassium	0.007 0.058	0.004 0.056	24 25	-0.003 -0.002	-42.9 -3.6	0.003 0.005	75.0 8.9
Sodium	0.039 0.044	0.041 0.043	25 25	0.002 -0.001	5.1 -2.3	0.014 0.005	34.2 11.6
Ammonium	0.03(9)[c] 0.023	0.02 <0.02	25 25	-0.02	-50.0	0.02	100
Nitrate	0.13(3) 2.15(2)	0.13 2.23	25 25	0.00 0.08	0.0 3.7	0.00 0.04	0.0 1.8
Chloride	0.05(4) 0.09(2)	0.06 0.09	25 25	0.01 0.00	11.1 0.0	0.02 0.01	33.3 11.1
Sulfate	1.22 1.55	1.23 1.59	25 25	0.01 0.04	0.8 2.6	0.02 0.03	1.6 1.9
pH (units) µeq/L	(4.85)[d] 14.19 (4.42) 38.46	(4.78) 16.46 (4.38) 41.58	25 25	2.27 3.12	16 8.1	1.05 1.95	6.4 4.7
Conductivity (µS/cm)	8.82 21.58	9.2 22.0	25 25	0.4 0.4	4.3 1.9	0.4 0.6	4.4 2.7

Notes:
a. The first set of values for each parameter is for EB-17. b. The second set of values for each parameter is for EA-22.
c. In excess of significant figure values in parentheses are provided for information, d. The pH data in parentheses are pH units. These have been converted to microequivalents for calculations.

TABLE IV-2 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples (SWS2), Deionized (DI) Water and pH 4.3 QCS, Unfiltered, 1991

Parameter	Target Conc. (mg/L)	Measured Cone. (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)
Calcium	< 0.009[a]	<0.009	26				
	<0.009[b]	< 0.009	24				
Magnesium	< 0.003	< 0.003	26				
	< 0.003	< 0.003	24				
Potassium	< 0.003	< 0.003	26				
	< 0.003	0.003	24				
Sodium	< 0.003	0.004	26	0.002[c]	100	0.007	175
	< 0.003	0.007	24	0.006	367	0.018	257
Ammonium	<0.02	<0.02	26				
	<0.02	<0.02	24				
Nitrate	<0.03	<0.03	26				
	3.12	3.17	24	0.05	1.6	0.08	2.5
Chloride	<0.03	<0.03	26				
	<0.03	<0.03	24				
Sulfate	<0.03	<0.03	26				
	<0.03	<0.03	24				
pH (units)	(5.62)[d]2.34	(5.55) 2.83	26	0.49	20.7	0.54	19.1
/teq/L	(4.30)50.12	(4.31)49.22	24	-0.90	-1.8	2.48	5.0
Conductivity	0.9	1.3	26	0.4	44.4	0.6	46.2
(/iS/cm)	21.8	21.3	24	-0.5	-2.3	0.9	4.23

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 calculation purposes MDLs are given the value of 0.5(MDL). d. The pH data in parenthses are pH units. These have been converted to microequivalents for calculations.

TABLE IV-3 Analytical Bias and Precision Determined from Analysis
of Internal Blind Audit Samples (SWS3), Canada National Water Research Institute Eulerian Study
Samples EB-17 and EA-22, Filtered, 1991

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)
Calcium	0.139[a] 0.335[b]	0.142 0.331	13 11	0.003 -0.004	2.2 -1.2	0.008 0.008	5.6 2.4
Magnesium	0.029 0.070	0.026 0.067	13 11	-0.003 -0.003	-10.3 -4.3	0.002 0.003	7.7 4.5
Potassium	0.007 0.058	0.004 0.051	13 11	-0.003 -0.007	-42.9 -12.1	0.003 0.009	75.0 17.6
Sodium	0.039 0.044	0.071 0.066	13 11	0.032 0.022	82.0 50.3	0.017 0.018	23.9 27.3
Ammonium	0.03(9)[c] 0.02(3)	0.02 <0.02	13 11	-0.02	-50.0	0.01	50.0
Nitrate	0.13(3) 2.15(2)	0.17 2.20	13 11	0.04 0.05	27.8 2.3	0.02 0.04	11.8 1.8
Chloride	0.05(4) 0.09(2)	0.11 0.12	13 11	0.06 0.03	104 30.5	0.05 0.02	45.4 16.7
Sulfate	1.21(7) 1.55(4)	1.19 1.53	13 11	-0.03 -0.02	-2.2 -0.5	0.03 0.03	2.5 2.0
pH (units) *μSq/L*	(4.85)[d] 14.19 (4.42) 38.46	(4.79) 16.40 (4.37) 42.80	13 11	2.21 4.34	15.6 11.3	1.24 2.36	7.6 5.5
Conductivity (μS/cm)	8.82 21.58	9.4 22.1	13 11	0.6 0.5	6.6 2.4	0.4 0.3	4.3 1.4

Notes:
a. The first set of values for each parameter is for EB-17. b. The second set of values for each parameter is for EA-22.
c. In excess of significant figure values in parenthses are provided for information d. The pH data in parenthses are pH units. These have been converted to microequivalents for calculations.

TABLE IV-4 Analytical Bias and Precision Determined from Analysis
of Internal Blind Audit Samples (SWS3), Deionized (DI) Water and pH 4.3 QCS, Filtered, 1991

Parameter	Target Conc. (mg/L)	Measured Conc. (mg/L)	Number of Replicates	Bias (mg/L)	Bias (%)	Precision s (mg/L)	Precision RSD (%)
Calcium	<0.009[a] <0.009[b]	<0.009 <0.009	13 13				
Magnesium	<0.003 <0.003	<0.003 <0.003	13 13				
Potassium	<0.003 <0.003	<0.003 <0.003	13 13				
Sodium	<0.003 <0.003	0.030 0.018	13 13	0.028[c] 0.016	1400 800	0.020 0.012	66.7 66.7
Ammonium	<0.02 <0.02	<0.02 <0.02	13 13				
Nitrate	<0.03 3.12	0.04 3.03	13 13	0.02 -0.09	100 -2.9	0.02 0.07	50.0 2.3
Chloride	<0.03 <0.03	0.05 0.03	13 13	0.03	150	0.02	40.0
Sulfate	<0.03 <0.03	<0.03 <0.03	13 13				
pH (units) µeq/L	(5.63)[d]2.34 (4.30)50.12	(5.61) 2.48 (4.31)49.39	13 13	0.14 -0.73	5.8 -1.4	0.45 2.55	18.2 5.2
Conductivity (µS/cm)	0.9 21.8	1.7 21.9	13 13	0.8 0.1	88.9 0.5	1.2 1.1	70.6 5.0

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 calculation purposes MDLs are given the value of 0.5 (MDL). d. The pH data in parenthses are pH units. These have been covnerted to microequivalents for calculations.

B. REPLICATE SAMPLES

Two percent of all weekly network samples are split into three 60-mL portions. Two samples are given the same number: one is analyzed immediately, the second is refrigerated for archival purposes. The third sample is returned to the sample processing group, given another sequential number, and then resubmitted to the laboratory. The first and third samples may be analyzed on the same day or on different days after as long as one week. When both samples have been analyzed and the data submitted, data management recodes the second sample back to its original "0" designation but with an additional "Q" (quality assurance) modifier. These 0/Q splits, as they are called, then appear consecutively twice a month on ion balance printouts. The quality assurance specialist inspects these two analyses each time a printout is issued and estimates the precision of network samples. The results of these analyses are presented as replicate sample differences and displayed as box plots in Appendix B. Box plots as used in this report are defined in the glossary (Appendix A).

The information presented in Table IV-5 is a brief summary of the replicates analyzed in 1991. The low range contains values from the method detection limit (MDL) to the replicate population median value; the high range contains values with concentrations from the median to the highest value (Table B-3). The differences are calculated by subtracting the reanalysis value from the original. The mean difference is a simple mean of all of these differences. The standard deviation estimated from duplicate measurements, defined in the glossary, has been used to calculate the standard deviations.

The standard deviations for the higher concentrations of the cations are higher than those of the SWS 3 samples. The standard deviations estimated from replicate analysis of the anions and pH and conductivity are similar to or lower than the standard deviations calculated from the analysis of the filtered blind samples. With the exception of the higher concentrations of calcium and magnesium, the results of the standard deviations calculated from the replicate samples in 1991 are lower than the comparable measurements in 1990. The variation in the replicate samples compared to blind samples and the QCS indicate random handling contamination or greater inherent variability between standard solutions and actual random samples.

TABLE IV-5 Mean Differences and Standard Deviations Estimated from Replicate Analyses of Network Precipitation Samples, 1991

Parameter	Mean Difference[a]	Standard Deviation (low conc.)	Standard Deviation (high conc.)
Calcium (mg/L)	0.002	0.010	0.028
Magnesium (mg/L)	-0.002	0.002	0.031
Sodium (mg/L)	0.003	0.003	0.024
Potassium (mg/L)	0.000	0.003	0.011
Ammonium (mg/L)	0.00	0.01	0.05
Sulfate (mg/L)	0.00	0.02	0.02
Nitrate (mg/L)	0.01	0.06	0.02
Chloride (mg/L)	0.00	0.01	0.06
pH(µeq/L)	-0.17	0.55	1.23
Conductivity (µS/cm)	-0.19	0.57	0.44
Number of Pairs	155	78	77

Note:
a. The difference is calculated by subtracting the reanalysis value from the original value.

C. BLANKS

Blank data have been summarized from three sources: the laboratory deionized water, the sample filtering process, and the buckets and lids used for sample collection and shipping. These data are used to estimate the contributions from these sources to the chemistry of the sample. Deionized water is randomly collected each week from three work areas. Leachates from the filters are collected using both DI water and pH 4.3 nitric acid. Upright and inverted buckets are leached overnight with 50 and 150 mL of the same two solutions. All of these "blanks" are subjected to the entire sample analysis procedure.

1. Deionized Water Blanks

Deionized water is collected in the atomic absorption laboratory, the sample processing work area, and the bucket washing work area. The median values of the cation and anion analyses of the samples from each source are all below the method detection limits (MDLs). Table IV-6 shows the median values for pH and conductivity for the DI water in 1991.

TABLE IV-*6* Median Values for pH and Conductivity
for Weekly Deionized (DI) Water Blanks, 1991

	Sample Processing Laboratory	Atomic Absorption Laboratory	Service Laboratory
pH (units)	5.63	5.63	5.63
Conductivity (µS/cm)	0.9	0.9	0.9
Number of weeks	46	40	41

2. Filter Blanks

If the sample volume exceeds 35 mL, it is designated as "wet", aliquots are removed for pH and conductivity, and the remaining sample is filtered into a 60-mL high density polyethylene (HDPE) bottle for transfer to the laboratory for cation and anion analyses. To evaluate the contribution of this procedure to the ion sample chemistry, the sample filtering process is repeated each week using DI collected randomly and pH 4.3 nitric acid. The DI water source is the sample processing work area. The filters are leached first with 300 mL of DI water, as are all filters used for network samples. Two sequential 50-mL portions of DI water or pH 4.3 nitric acid are then filtered, collected, and labeled "A" and "B". The results of the laboratory analyses of these blank samples are presented in Table IV-7. Sodium at five times the detection limit was found in the "A" portion of both solutions. The levels of sodium contamination correspond to approximately the 5th percentile of sodium values found in natural network samples. The other ions are absent. The pH of the DI water is not significantly different from the sample processing DI water and the pH 4.3 nitric acid pH was well within acceptable limits. The conductivities are not significantly different from the target values. (note that the pH and conductivity are measured on unfiltered network samples.) From these summaries, with the exception of sodium, it is assumed that the filtration process has a negligible effect on the sample chemistry .

TABLE IV-7 Median Analyte Concentrations Found
in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Filter Leacnates, 1991

Analyte	DI Water A[a]	DI Water B[b]	pH 4.3 Nitric Acid A[a]	pH 4.3 Nitric Acid B[b]
Calcium	<0.009	<0.009	<0.009	<0.009
Magnesium	<0.003	<0.003	<0.003	<0.003
Potassium	<0.003	<0.003	<0.003	<0.003
Sodium	0.015	<0.003	0.014	<0.003
Ammonium	<0.02	<0.02	<0.02	<0.02
Nitrate	<0.03	<0.03	3.12[c]	3.19°
Chloride	<0.03	<0.03	<0.03	<0.03
Sulfate	<0.03	<0.03	<0.03	<0.03
pH (units)	5.59	5.58	4.33[d]	4.32[d]
H^+(μeq/L)	2.57	2.63	46.8	47.9
Conductivity (μS/cm)	1.2	1.1	20.8[e]	21.4[e]
Number of weeks	47	47	47	47

Notes:
a. First 50-mL filtrate after 300 mL DI water filter rinse.
b. Second consecutive 50 mL filtrate after 300 mL DI water filter rinse.
c. Theoretical value equals 3.12 mg/L.
d. Theoretical value equals 4.30 pH units.
e. Theoretical value equals 21.8 /μS/cm.

3. Bucket Blanks

The bucket leachate procedure followed in 1991 has not changed since its inception at the end of 1989. Aliguots of 50- and 150-mL of DI water and pH 4.3 nitric acid are poured into each of four sample collection buckets, which are covered with snap-on lids and left overnight. The leachates are poured into 60 mL bottles for analysis. This procedure is repeated and the buckets are covered and sealed with a standard water-tight lid, inverted, and left overnight. The leachates are then collected for analysis.

Analyses of the eight bucket-blank leachates are presented in Tables IV-8 and IV-9. The concentrations of the major ions are expressed as median-measured mass in micrograms (μg) /bucket. The pH and conductivity values are the median measurements of the solutions collected from the buckets. The upright solutions indicate a near-detection level value for calcium in the pH 4.3 nitric acid and slight sodium contamination in both 50-mL solutions. The anion concentrations are at detection level with an acceptable deviation from the theoretical nitrate concentration of the nitric acid. The pH and conductivities are also within the acceptable range.

The inverted bucket leachates clearly implicate the lid or its o-ring portion. Calcium and sodium are present in all four solutions, but magnesium and potassium are not present in the 150-mL DI water leachates. Chloride and sulfate have been leached in both 50-mL solutions, and sulfate is still detectable in the 150-mL nitric acid. All four blanks are neutralized, the 50-mL portion more than the 150-mL portion. The conductivities of the nitric acid are lower, corresponding to the higher pH, lower H^+ concentration.

Box plots of the bucket blank leachates (Appendix B, Figures B-24 - B-33) illustrate the median analyte values as well as the variance of the 1991 analyses. These plots emphasize the variability of the contribution of the bucket lid to the sample chemistry. For calculation purposes, detection limit values are expressed as one-half the MDL (in µg/mL) times 50 or 150 mL; thus there are no zero values. A median line at the detection limit value with no corresponding "box" indicates no variance from the 10th to the 90th percentile.

TABLE IV-8 Median Measured Mass as Micrograms (µg)/Bucket[a] Found in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Upright Bucket Leachates, 1991

Analyte	DI Water (50 mL)	DI Water (150 mL)	pH 4.3 Nitric Acid (50 mL)	pH 4.3 Nitric Acid (150 mL)
Calcium	<0.225	<0.675	0.500	<0.675
Magnesium	<0.075	<0.225	<0.075	<0.225
Potassium	<0.075	<0.225	<0.075	<0.225
Sodium	0.400	<0.225	0.400	<0.225
Ammonium	<0.50	<1.50	<0.50	<1.50
Nitrate	<0.75	<2.25	151 (156)[b]	465 (468)[b]
Chloride	<0.75	<2.25	<0.75	<2.25
Sulfate	<0.75	<2.25	<0.75	<2.25
pH (units)	5.55 (5.63)[b]	5.56 (5.63)[b]	4.38 (4.30)[b]	4.34 (4.30)[b]
$[H^+]$ (µeq/bucket)	0.14 (0.12)[b]	0.41 (0.37)[b]	2.08 (2.50)[b]	6.86 (7.52)[b]
Conductivity (µS/cm)	1.4 (0.9)[b]	1.3 (0.9)[b]	19.4 (21.8)[b]	20.6 (21.8)[b]
Number of weeks	45	45	45	45

Notes:

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

b. Values in parentheses represent those of DI water or pH 4.3 nitric acid analyzed with no bucket contact.

TABLE IV-9 Median Measured Mass as Micrograms (µg)/Bucket[a] Found in Weekly Deionized (DI) Water and pH 4.3 Nitric Acid Inverted Bucket Leachates, 1991

Analyte	DI Water (50 mL)	DI Water (150 mL)	pH 4.3 Nitric Acid (50 mL)	pH 4.3 Nitric Acid (150 mL)
Calcium	1.50	2.40	2.35	3.0
Magnesium	0.20	<0.225	0.25	0.45
Potassium	0.20	<0.225	0.25	0.45
Sodium	0.95	1.35	1.20	1.50
Ammonium	<0.50	<1.50	<0.50	<1.50
Nitrate	<0.75	<2.25	146 (156)[b]	460 (468)[b]
Chloride	1.50	<2.25	2.00	<2.25
Sulfate	2.50	<2.25	3.50	6.00
pH (units)	6.06 (5.63)[b]	5.83 (5.63)[b]	4.51 (4.30)[b]	4.39 (4.30)[b]
[H^+] (µeq/L/bucket)	0.04 (0.12)[b]	0.22 (0.34)[b]	1.55 (2.50)[b]	6.10 (7.52)[b]
Conductivity (µS/cm)	1.8 (0.9)[b]	1.3 (0.9)[b]	15.7 (21.8)[b]	19.0 (21.8)[b]
Number of weeks	45	45	45	45

Notes:

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

b. Values in parentheses represent those of DI water or pH 4.3 nitric acid analyzed with no bucket contact.

V. MONTHLY QUALITY ASSURANCE PROCEDURES

Quality assurance procedures that occur on a monthly basis include the evaluation of the control charts generated from the daily analysis of QCS, the review of site printouts of the internal blind samples, and the reanalysis of samples that did not meet the ion balance and conductance criteria. Additionally, the analyses of samples submitted to the laboratory as part of the USGS interlaboratory comparison are reviewed prior to being sent to the USGS.

A. REANALYSIS PROCEDURES

Twice a month the 400-500 samples analyzed during the previous two weeks are subjected to a reanalysis selection test. Samples are flagged for either an anion/cation imbalance or difference between the calculated and measured specific conductance. The algorithm used in 1991 was the same as for the four previous years.

1. Ion Percent Difference

Ion concentrations measured in milligrams per liter (mg/L) are converted to microequivalents per liter (µeg/L) using the factors listed in Table V-l (13). The measured ion values and pH, in addition to the 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:

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

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

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

Samples are flagged for reanalysis if:

$IS < 50$ µeq/L	and IPD> ± 60%
$50 \le IS < 100$ µeq/L	and IPD> ± 30%
$IS \ge 100$ µeq/L	and IPD> ± 15%

TABLE V-1
Factors Used to Convert Milligrams per Liter (mg/L) to Microequivalents per Liter (µeq/L) for Ion Precent Difference (IPD) Calculations

Analyte	Conversion Factor
Calcium	49.90
Magnesium	82.26
Sodium	43.50
Potassium	25.57
Ammonium	55.44
Sulfate	20.83
Nitrate	16.13
Chloride	28.21
Orthophosphate	31.59
Hydrogen	992.2
Bicarbonate	16.39
Hydroxide	58.8

TABLE V-2
Factors Used to Convert Microequivalents per Liter (µeq/L) to Equivalent Conductance for Conductance Precent Difference (CPD) Calculations

Analyte	Conversion Factor
Hydrogen	350
Calcium	59.5
Magnesium	53.0
Sodium	50.1
Potassium	73.5
Ammonium	73.5
Bicarbonate	44.5
Hydroxide	198
Sulfate	80.0
Nitrate	71.4
Chloride	76.3
Orthophosphate	69.0

2. Conductance Percent Difference

Conductance percent difference (CPD) compares the calculated and measured conductivity. The ion concentrations, expressed as µeq/L, are multiplied by the conductance conversion factors listed in Table V-2 (14), summed, and then divided by 1000 in order to calculate the theoretical conductivity. This value is then compared to the measured conductivity. The CPD is calculated as follows:

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

Samples are flagged for reanalysis if:

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

All samples selected are reanalyzed, providing sufficient volume remains and the sample has not been flagged as contaminated. When the reanalysis is completed, the QA specialist, with documentation from the analysts, determines which values, if any, should be corrected. 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 1991, 529 of the 10,300 (-5%) samples analyzed were flagged for reanalysis. One hundred seventy four data changes were made to 113 of the 529 samples selected. Figures V-1 and V-2 are histograms of the IPD and CPD values for samples whose volume exceeded 35 mL. The mean, standard deviation, median, and number of wet samples are presented on each figure.

The IPD histogram exhibits a positive skew as it always has, the mean (3.70%) and median (3.39%) are higher than in 1990 (2.60% and 2.18%) but lower than in 1986, 1988, and 1989. In 1987 these values were 3.2% and 3.1%, respectively. These positive skews indicate a slight anion excess. The CPD continues to exhibit a negative skew with a mean value(-8.64%) comparable to 1989 and a median value (-6.13%) similar to the 1990 and 1989 median values. A negative skew is indicative of a measured conductance higher than the calculated conductance, as expected since the basic analysis does not account for all parameters contained in precipitation.

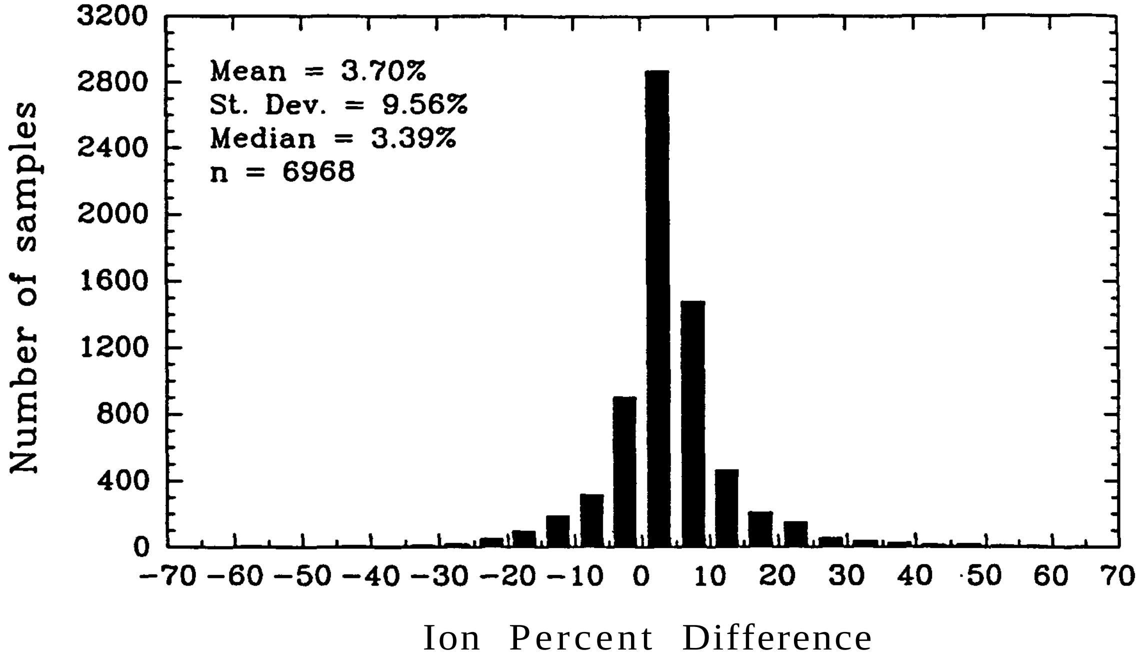


FIGURE V-1. Ion Percent Difference (IPD) histogram for NADP/NTN wet-side samples, 1991.

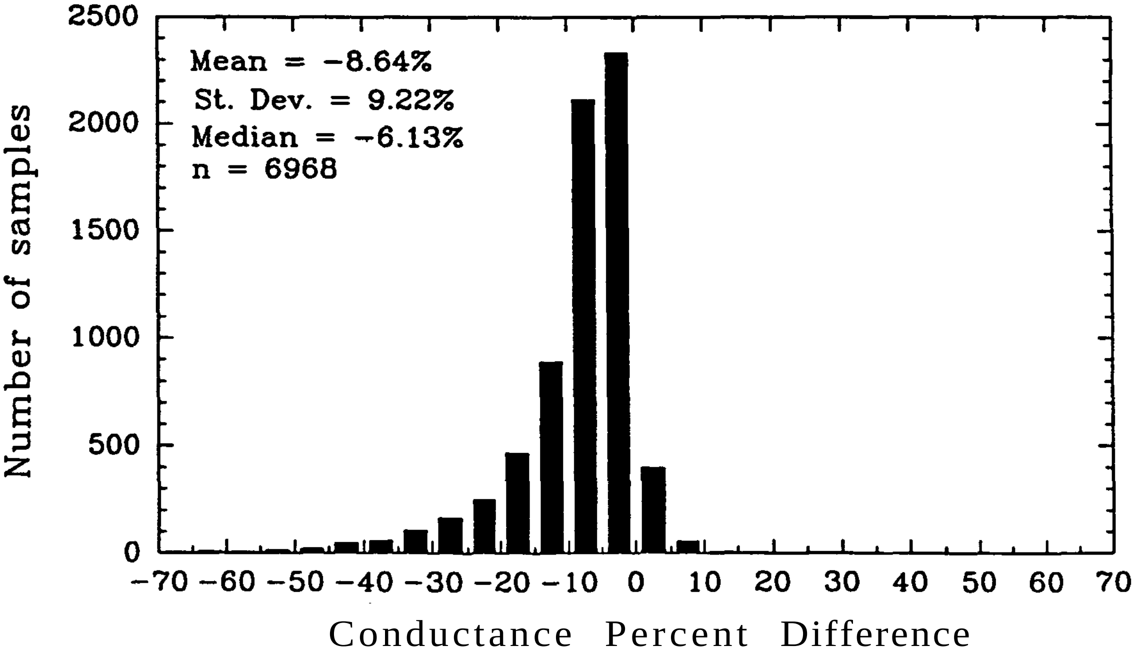


FIGURE V-2. Conductance Percent Difference (CPD) histogram for NADP/NTN vet-side samples, 1991.

B. USGS INTERLABORATORY COMPARISON

The U.S. Geological Survey (USGS) serves as the primary external auditor of the CAL. There are several components of the external audit of which the interlaboratory comparison, which began in fall 1982, is one. It is designed to determine whether participating laboratories are producing comparable results. Each month several sets of blind samples of differing matrices are mailed to the participating laboratories for analysis.

In 1991 the interlaboratory comparison program included four laboratories: (1) Illinois State Water Survey, Central Analytical Laboratory (CAL); (2) Inland Waters Directorate, National Water Quality Laboratory (IWD); (3) Environmental Science and Engineering, Inc. (ESE); and (4) Ontario Ministry of the Environment, Water Quality Section (MOE). Samples from four sources were used in the 1991 study: (1) synthetic wet-deposition samples and deionized water samples prepared by the USGS, (2) synthetic wet-deposition stock solutions supplied by the U.S. Environmental Protection Agency (USEPA) in concentrate and diluted by the USGS, (3) standard reference samples prepared and certified by the National Institute of Standards and Technology (NIST), and (4) natural-deposition samples collected at NADP/NTN sites and bottled by the CAL.

Samples used for the 1991 program were shipped as blind samples to the participating laboratories approximately every 2 weeks. Final data compilations were submitted quarterly to the USGS.

Analyte bias for the participating laboratories was evaluated using NIST standard reference materials with certified analyte concentrations + the estimated uncertainty. Each laboratory received 18 NIST samples in 1991. The median analysis of each matrix was compared to the NIST values. The CAL reported 12 median analyses out of 22 that were outside the range of uncertainty for the NIST samples. The other laboratories reported as follows: MOE and ESE 8 and 7 out of 22 out of range and IWD had 8 out of 19 out of range. These CAL results indicated low calcium, low sodium, low potassium, high sulfate, low pH, and high specific conductance biases. Of these biases only two were beyond the bias limits set by the QA Plan: the high concentration (0.419 + 0.015 mg/L) sodium was too low at 0.384 mg/L and the high specific conductance (130+ 2 µS/cm) was too high at 135.3 µS/cm. It is interesting to note that all four laboratories were higher than the NIST confidence interval for the sulfate concentration of SRM 2694-1, the CAL being the lowest of the four.

Results of the Kruskal-Wallis test run by the USGS to examine bias between the laboratories indicate no significant difference in analyte measurements for calcium, magnesium, sodium, potassium, ammonium, chloride, nitrate, sulfate, hydrogen ion, or specific conductance from any of the four laboratories.

Six ultrapure DI water samples were submitted to the laboratories. The CAL had only one sodium determination greater than the minimum reporting limit. Values in excess of the minimum reporting limits indicate possible contamination.

The final report containing the entire external NADP/NTN audit is available from the USGS.(15)

VI. SEMI-ANNUAL AND ANNUAL QUALITY ASSURANCE PROCEDURES

Annually, when all of the data for the samples analyzed during the January 1-December 31 period have been verified and entered, the daily, weekly, and monthly QA data are summarized for the annual report and scientific presentations. The results of the USGS external audit are summarized for the same period of time. The CAL portion of this audit includes a blind audit sample procedure as well as the interlaboratory comparison previously described (Section V.,B.). In addition, throughout the year the CAL participates, on a voluntary basis, in several interlaboratory comparison studies. In 1991 there were seven studies in which the CAL was a participant: two conducted by the USEPA, three conducted by the Canada National Water Research Institute (NWRI), one by the European Monitoring and Evaluation Programme (EMEP)-Intercomparison XII, and one by the World Meteorological Organization (WMO)-Fourteenth Analysis on Reference Precipitation Samples.

A. USGS EXTERNAL AUDIT PROGRAM

The USGS's NADP/NTN blind audit program and interlaboratory comparison study are used to evaluate the effects of sample handling and shipping on the bias and precision of analyte determinations and to determine the bias and precision of the analytical results. In 1991, as in 1990, 32 blind audit samples were sent to selected NADP/NTN site operators each quarter. Nearly two-thirds of all sites were asked to participate. Detailed sample processing instructions accompany each blind audit sample. The median analyte concentrations of the solutions used are between the 25th and 75th percentiles of actual precipitation collected at NADP/NTN sites. The six solutions used in 1991 were pH 4.3 nitric acid prepared by the CAL, Ultrapure deionized water from the USGS, two solutions prepared by the USGS (one from dissolved salts and deionized water and the other a precipitation quality assurance sample prepared by the USGS standard water reference sample project), and two USEPA concentrates diluted by the USGS Acid Rain Project.

Samples containing either 250, 500, or 1,000 mL of the solutions described are sent to assess any volume-related biases. Operators are asked to pour 70 percent of the blind audit sample into a clean NADP/NTN sample bucket and treat it as if it were the weekly sample. The remaining solution is sent to the CAL in the bottle. Both samples are given sequential network sample numbers and submitted to the laboratory as weekly samples. Complete bucket and bottle analyses are available for 123 of 128 blind audit samples. The procedure tests for bias in overall sample handling procedures from the point of sample collection in the field through laboratory analysis.

The median bucket sample concentrations are larger than the median bottle concentrations for calcium, magnesium, sodium, potassium, ammonium, chloride, nitrate, and sulfate. The median determinations for bucket samples are smaller than the median bottle determinations for hydrogen ion and conductance. At a significance level of $\alpha = 0.01$, only ammonium shows no differences between bucket and bottle concentrations.

The sample volume study shows that as volume increases, slight decreases in the median difference between the bucket and bottle analyses are measured for magnesium, sodium, sulfate, hydrogen ion, and specific conductance. Calcium, potassium, ammonium, chloride, and nitrate do not have a consistent change in concentration as volume increases. (15)

B. INTERLABORATORY COMPARISON STUDIES

In 1991, the CAL participated in seven national and international interlaboratory performance studies, which are briefly described in this section. The analytical data for the samples analyzed are presented in the tables in Appendix C.

1. U.S. Environmental Protection Agency (Two Studies)

The USEPA in Research Triangle Park (EPA/RTP), North Carolina contracted Management Technology for a series of acid rain audits. The CAL participated in the studies in June and December of 1991. The results are compared to USEPA-determined values and the percent difference calculated. The number of participating laboratories is not provided. The CAL mean percent difference for all ten parameters is 4.81 percent in June and 4.04 percent in December. These results are consistent with past performances in this audit and have been tabulated in Tables C-l and C-2.

2. Canada National Water Research Institute (Three Studies)

The Canadian program for Long-Range Transport of Atmospheric Pollutants (LRTAP) was begun in 1982. The CAL has participated since the fourth study in fall 1983. In 1991 the CAL participated in Studies L-26 (16), L-27 (17) , and L-28 (18). The LRTAP studies consist of selected major ions, nutrients, and physical measurements in water. Median concentrations are used as target values for flagging results, since most of the samples are surface waters or precipitation, and calculated or certified values are unknown. The laboratory results are ranked and flagged. A score for the study is computed as the sum of the percent bias and percent flags; therefore a zero score indicates the optimum performance.

The CAL scores for 1991 are variable. In study L-26, the score is 12.06 due to a high pH bias and two flags; one high pH and a one magnesium. The overall laboratory ranking was twelfth out of 60 laboratories. Study L-27 cites a low bias for calcium, a flag for an extremely low chloride, two high pHs, and one very high pH. (A review of the flagged pH results in both studies shows them to be in the pH range of 6.29 to 7.30.) The resulting score is 20.9 and the ranking is fifteenth out of 61 laboratories. The final study for 1991 shows a big improvement. There are two flags for erratic chloride results leading to a final score of 2.15 and a rank of third out of 65 laboratories, first out of those performing nine or more parameters. LRTAP data are presented in Tables C-3, C-4, and C-5.

3. Norwegian Institute for Air Research (One Study)

The twelfth intercomparison of analytical methods within the European Monitoring and Evaluation Programme (EMEP) was conducted in 1991. The samples, consisting of four synthetic precipitation preparations, arrived and were analyzed in March. EMEP sent the expected results later in the spring. Sodium and potassium exhibit a noticeably low bias, a negative ammonium bias is more variable. Table C-6 shows the data from this study.

4. World Meteorological Organization (One study)

The Fourteenth Analysis on Reference Precipitation Samples was conducted in 1991 and the samples requiring dilution appeared without prior notification in late July with a September 1 deadline. This study was done with the collaboration of the Atmospheric Research and Exposure Assessment Laboratory of the USEPA. The prescribed procedure is similar to that of the EPA/RTP studies. The true values are provided along with the results from the participating laboratories. The CAL mean percent difference is 4.91%, similar to the aforementioned studies. The true values and CAL analyses are tabulated in Table C-7.

VII. SUMMARY

The chapters of this QA report summarize the results of the NADP/NTN laboratory QA program for 1991. The procedures have been briefly described, and the analytical results presented and discussed.

The data indicate that daily QCS solutions exhibit the best accuracy and precision and that both the bias and precision of these samples are within the goals set by the network. The solutions used for the internal blind audit in 1991 are natural samples obtained from the Canadian National Water Research Institute and the target values are average measured median values obtained from several studies. The analyses of these samples have produced estimates of uncertainty, which are not as accurate or precise as the QCS. There is better agreement for the anions than the cations. The pH and conductivity exhibit a higher bias and poorer precision. The parameters are within the QA goals except for the precision of the 0.039 mg/L sodium solution. The effects of filtration are most evident in the sodium and chloride biases. The precision calculated from replicate sample analyses again indicates poor precision for sodium and chloride and greater variability for the higher concentrations of calcium and magnesium.

The DI water from three laboratory sources continues to be of excellent quality. The leachates from the filtering process contain sodium at five times the detection limit in both "A" solutions, but no other ions are present and the pH and conductivities are not altered. The upright bucket blank leachates show small amounts of sodium in the 50-mL portion, but the other ions are absent. The inverted blank leachates contain calcium and sodium in both volumes, but magnesium and potassium are not detectable in the 150 mL samples. Chloride and sulfate are detected, the pHs are raised, and the conductivities of the nitric acid solutions are lower.

The reanalysis program has not changed since 1987. Approximately 5.1 percent of the samples analyzed were flagged for reanalysis and 0.15 percent of the total number of measured analytes required changes to their initial chemical analysis. The IPD histogram has a positive skew, slightly higher than in 1990. The CPD histogram exhibits a negative skew with a median value similar to 1989 and 1990.

The USGS external audit of the CAL consists of a blind audit sample procedure and an interlaboratory comparison study. Reference samples that were subjected to the network's sample handling procedures and laboratory analysis are biased for all analytes except ammonium. The median concentrations are higher for all of the ions and less for hydrogen and conductivity compared to aliquots that were not subjected to sample handling procedures. The sample volume study shows that as volume increases, slight decreases in the median difference between the bucket and bottle analyses are measured for magnesium, sodium, sulfate, hydrogen ion, and specific conductance. The interlaboratory comparison shows the median values from the participating laboratories to be comparable. The CAL has the highest number of significantly different values for the NIST-certified simulated rain and reported 1 sodium value above detection in the ultrapure deionized water.

Participation in seven interlaboratory studies conducted by national and international agencies indicates that the CAL results compare favorably to those of its peers throughout the world.

APPENDIX A

GLOSSARY OF TERMS

GLOSSARY OF TERMS

Term	Abbreviation	Definition
Accuracy		The degree of agreement between an observed value and an accepted reference value. The concept of accuracy includes both bias (systematic error) and precision (random error).
Bias		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 homogenous sample and the accepted true value. Bias = measured value - true value
Box Plot		A graphical summary representation of the distribution of a set of data, the top and bottom of the box representing the 25th and 75th percentile. The horizontal line represents the median concentration, and the lower and upper Ts extend to the 10th and 90th percentile concentrations.
Control Chart		A graphical plot of test results with respect to time or sequence of measurement, together with limits within which they are expected to lie when the system is in a state of statistical control (19).
Critical Concentration		A calculated concentration used to determine if the measured bias is or is not statistically significant (20). $\mathit{Critical\ Concentration} = t * s_{sp} * \sqrt{1/n_1 + 1/n_2}$

Term	**Abbreviation**	**Definition**
		where: $s_{sp} = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}$ s_{sp} = pooled standard deviation S_1 = standard deviation of reference solution measurements s_2 = standard deviation of daily QCS measurements n = number of values t = t statistic at the 95% confidence level and $(n_1 + n_2) - 2$ degrees of freedom
External Blind Sample		A 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 all. These data are valuable in assessing bias and precision for network samples.
Mean	$\bar{x}$	The average obtained by dividing a sum by the number of its addends. $\bar{x} = \sum_{i=1}^{n} x_i/n$

Term	Abbreviation	Definition
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 homogenous 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 homogenous sample by a specific procedure, expressed in terms of dispersion of the values obtained about the mean value. It is often reported as the sample standard deviation (s).
Quality Assessment		The system of procedures that ensures that QC practices are achieving the desired goal in terms of data quality. Included is a continuous evaluation of analytical performance data.
Quality Assurance	**QA**	An integrated system of activities involving planning, QC, reporting, and remedial action to ensure that a product or service meets defined standards of quality.

Term	Abbreviation	Definition
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
Replicates (Splits)		Two aliguots 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. $s = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{n-1}}$

Term	Abbreviation	Definition
		where: x_i = each individual value $\bar{x}$ = the mean of all the 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 (19): $s = \sqrt{\frac{\sum d^2}{2k}}$ where: d = difference of duplicate measurements k = number of sets of duplicate measurements

APPENDIX B

Weekly Procedures: Tables and Figures

1991

TABLE B-l Comparison of Filtered and Unfiltered Internal Blind Samples
Using Canada National Water Research Institute (CNWRI)
Eulerian Study Samples EB-17, 1991

Parameter	Target Conc.[a]	Measured Conc.	Number of Values (n)	Bias	% Bias	Standard Deviation (s)	% RSD
Calcium	0.139	0.149[b]	25	0.010	7.2	0.006	4.0
		0.142[c]	13	0.003	2.2	0.008	5.6
Magnesium	0.029	0.027	25	-0.002	-6.9	0.002	7.4
		0.026	13	-0.003	-10.3	0.002	7.7
Potassium	0.007	0.004	24	-0.003	-42.9	0.003	75.0
		0.004	13	-0.003	-42.9	0.003	75.0
Sodium	0.039	0.041	24	0.002	5.1	0.014	34.2
		0.071	13	0.032	82.0	0.017	23.9
Ammonium	0.04	0.02	25	-0.02	-50.0	0.02	100
		0.02	13	-0.02	-50.0	0.01	50.0
Nitrate	0.13	0.13	25	0.00	0.0	0.00	0.0
		0.17	13	0.04	27.8	0.02	11.8
Chloride	0.05	0.06	25	0.01	11.1	0.02	33.3
		0.11	13	0.06	104	0.05	45.4
Sulfate	1.22	1.23	25	0.01	0.8	0.02	1.6
		1.19	13	-0.03	-2.2	0.03	2.5
H^+ (µeq/L)	14.19	16.46	25	2.27	16.0	1.05	6.4
		16.40	13	2.21	15.6	1.24	7.6
Conductivity (µS/cm)	8.82	9.2	25	0.4	4.3	0.4	4.4
		9.4	13	0.6	6.6	0.4	4.3

Notes:
a. Target values provided by CNWRI are measured median values from the several Eulerian studies.
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.

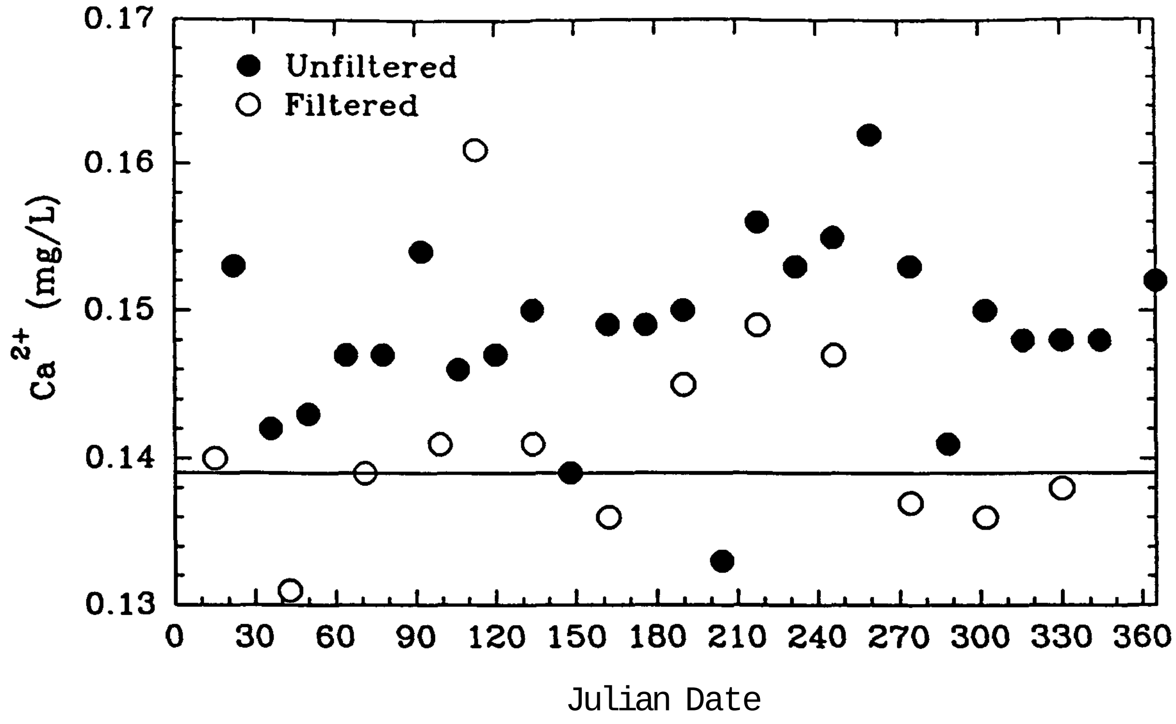


FIGURE B-1. Comparison of filtered and unfiltered internal blind samples (calcium EB-17), 1991.

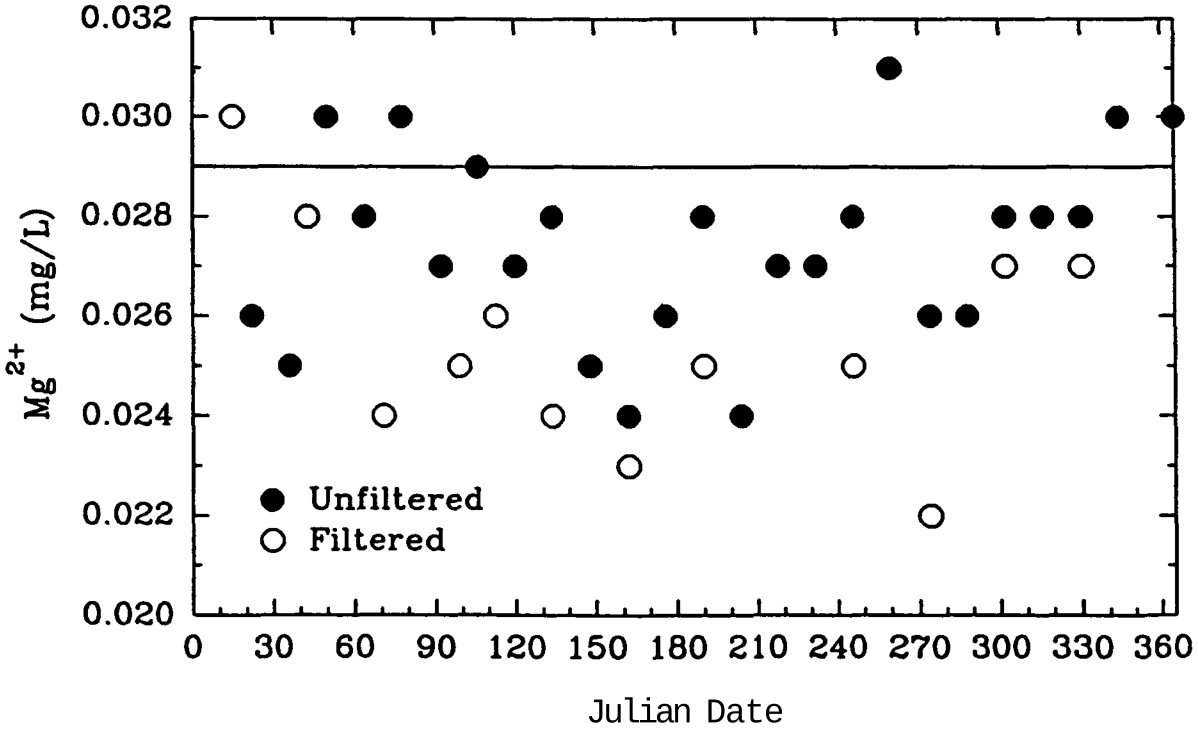


FIGURE B-2. Comparison of filtered and unfiltered internal blind samples (magnesium EB-17), 1991.

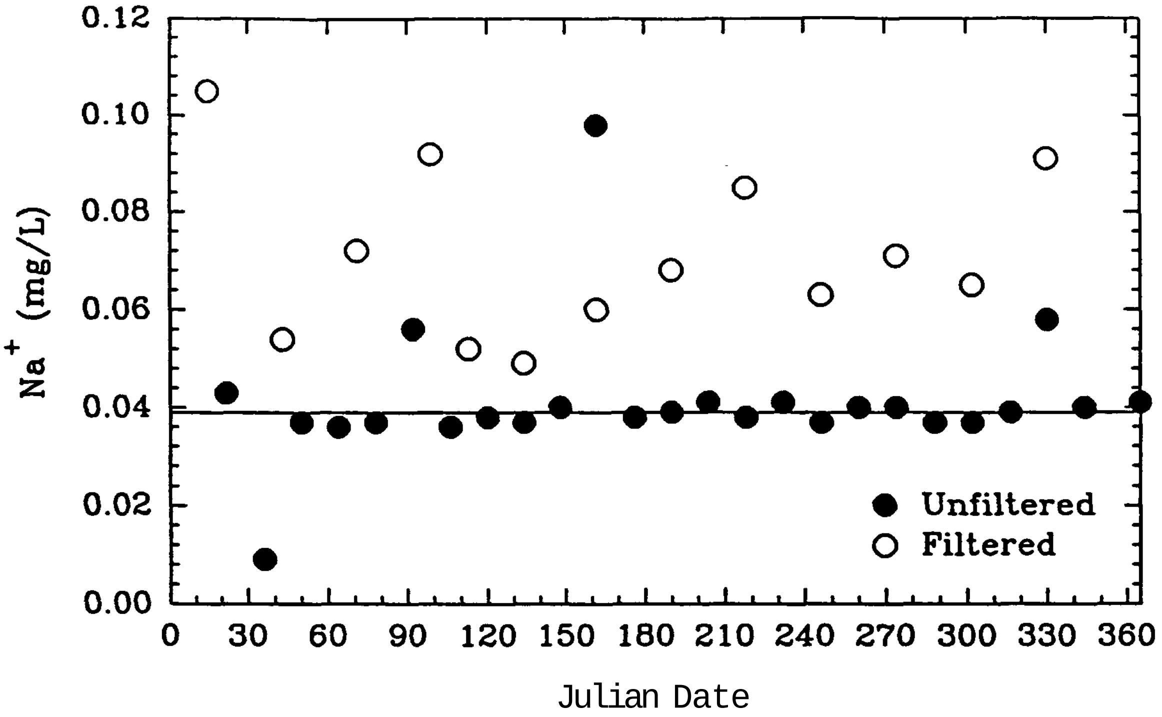


FIGURE B-3. Comparison of filtered and unfiltered internal blind samples (sodium EB-17), 1991.

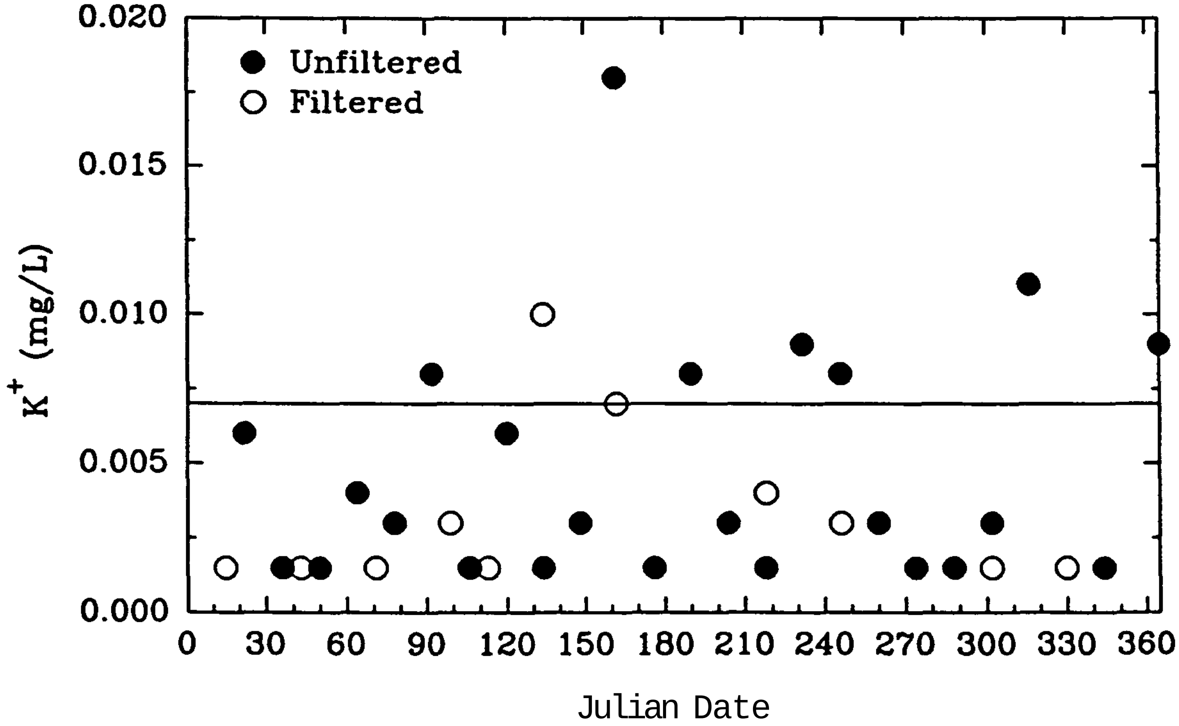


FIGURE B-4. Comparison of filtered and unfiltered internal blind samples (potassium EB-17), 1990.

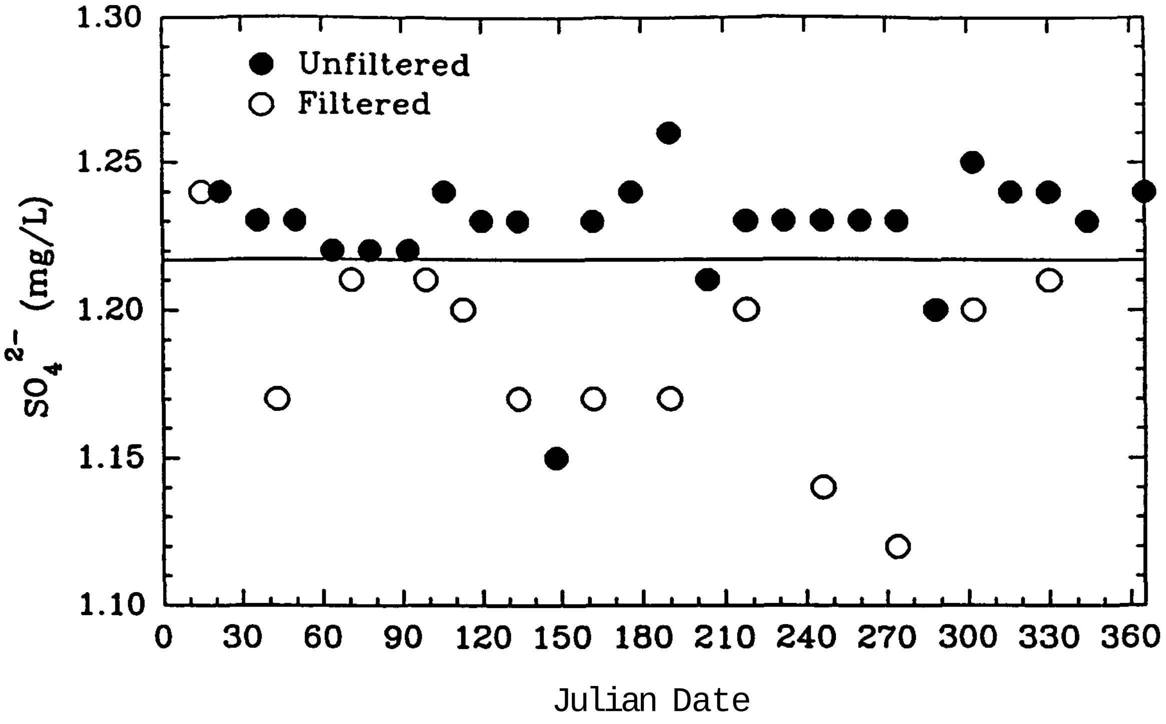


FIGURE B-5. Comparison of filtered and unfiltered internal blind samples (sulfate EB-17), 1991.

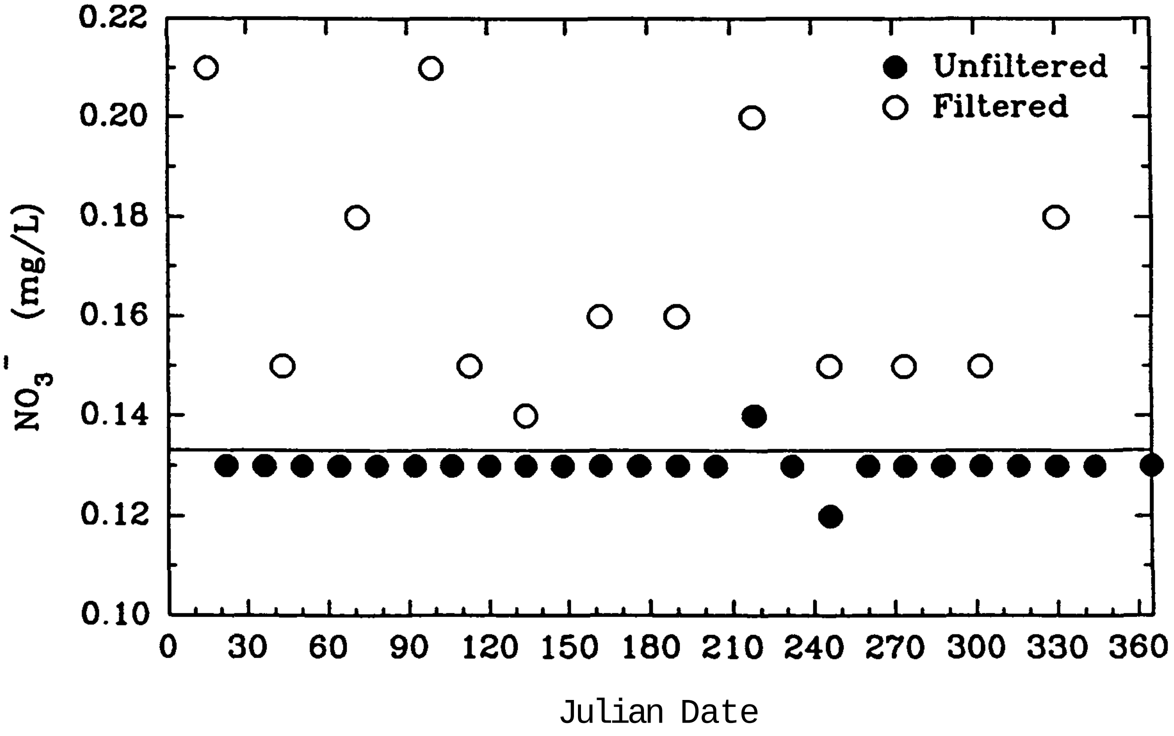


FIGURE B-6. Comparison of filtered and unfiltered internal blind samples (nitrate EB-17), 1991.

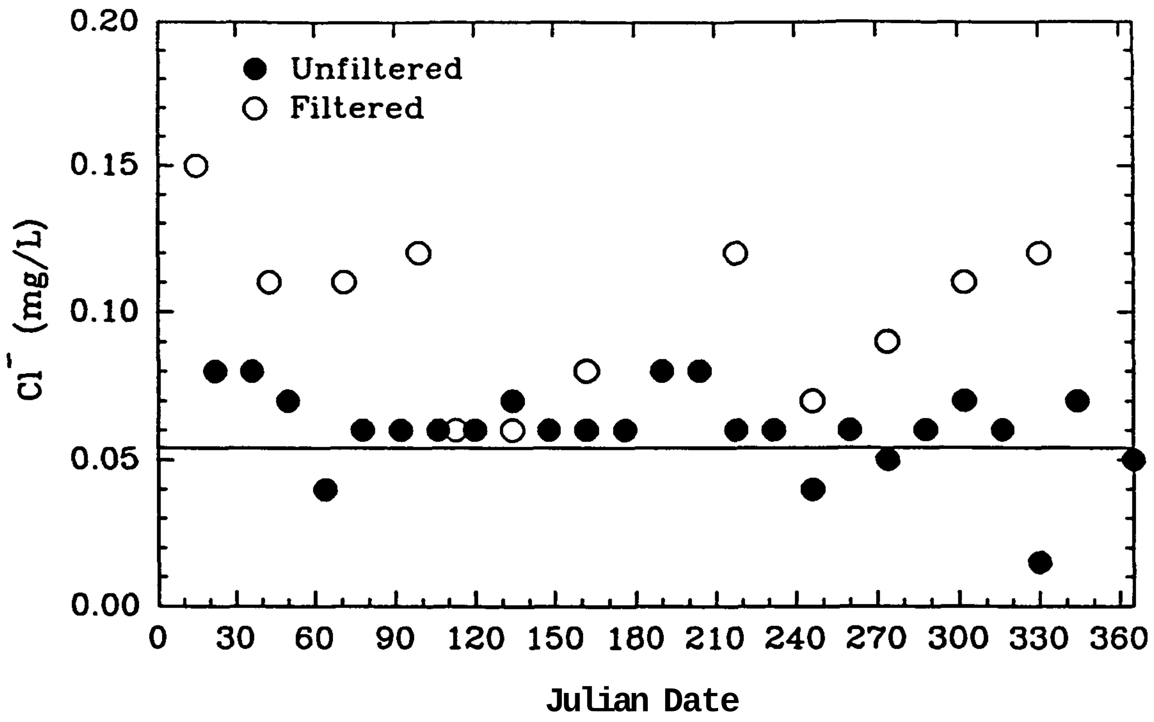


FIGURE B-7. Comparison of filtered and unfiltered internal blind samples (chloride EB-17), 1991.

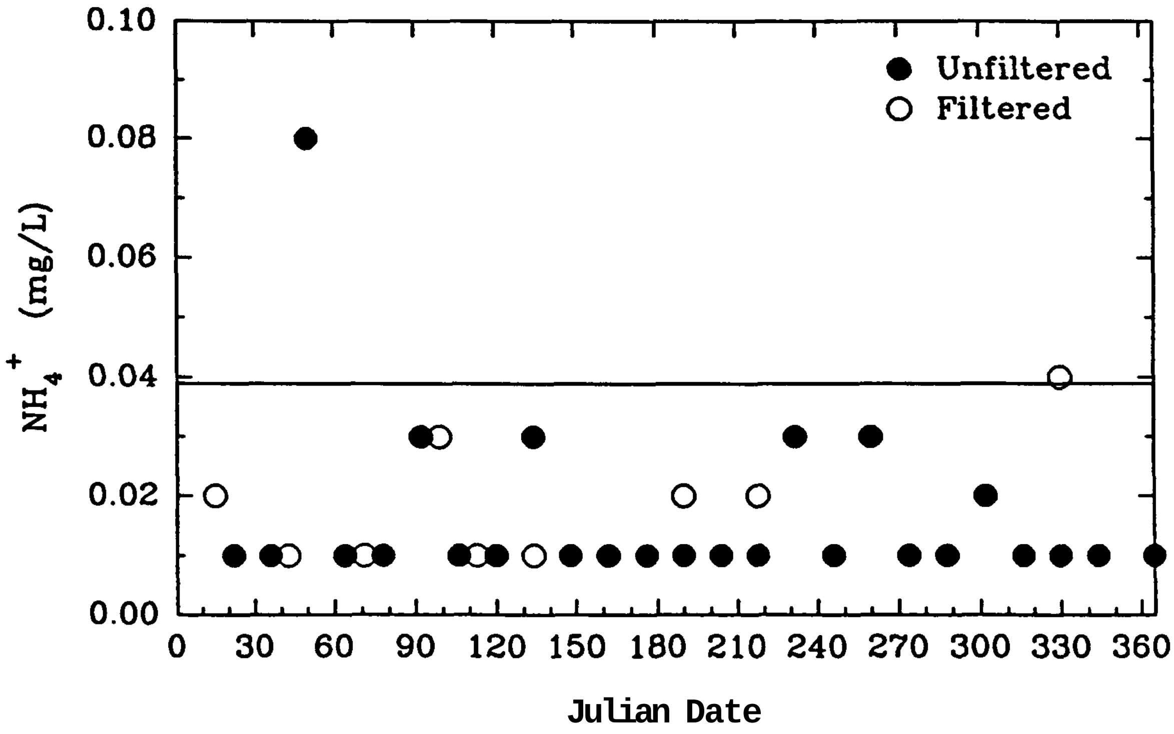


FIGURE B-8. Comparison of filtered and unfiltered internal blind samples (ammonium EB-17), 1991.

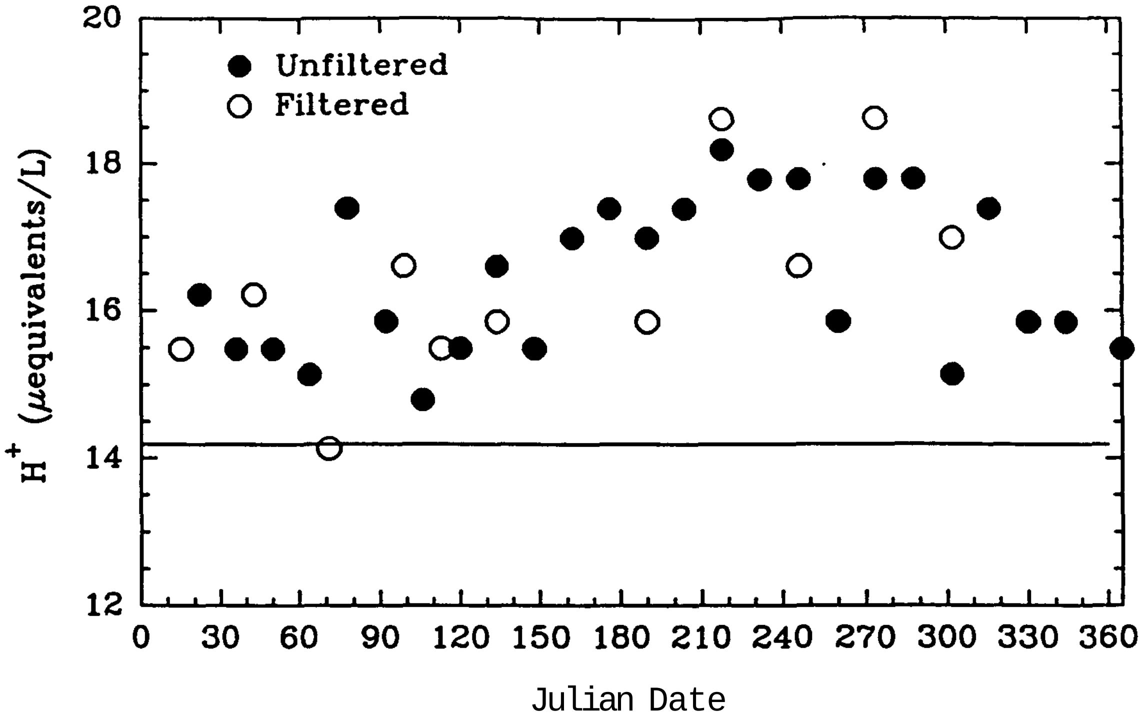


FIGURE B-9. Comparison of filtered and unfiltered internal blind samples (H^+ EB-17), 1991.

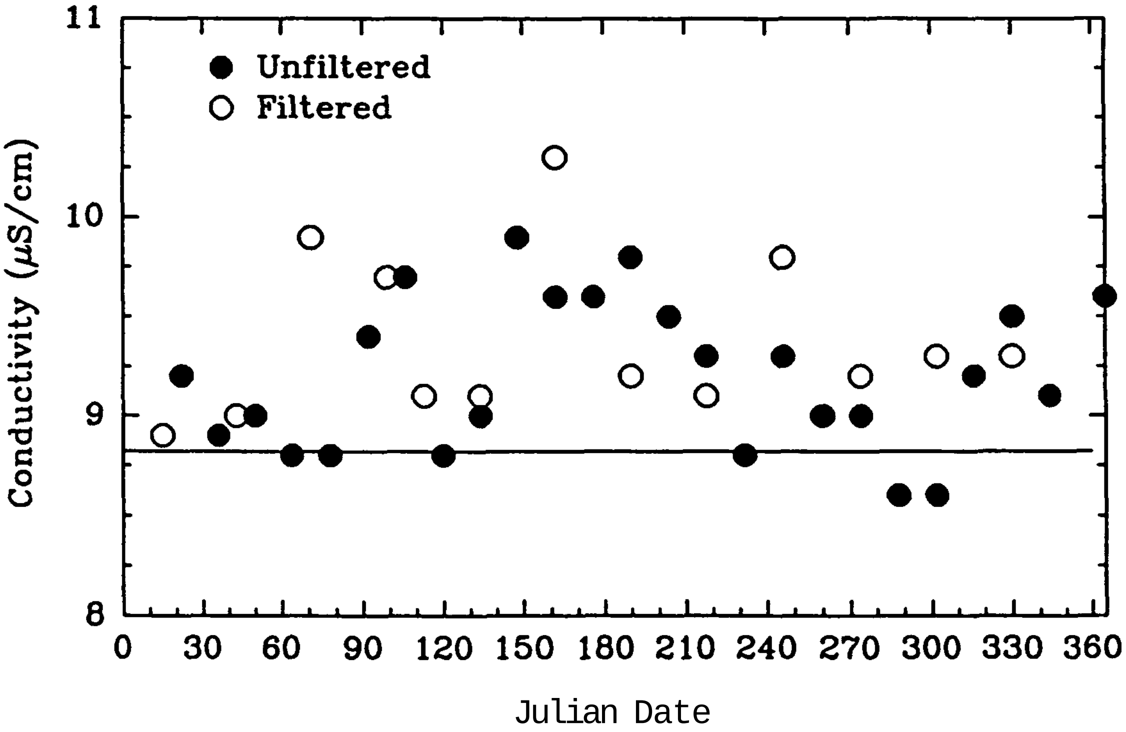


FIGURE B-10. Comparison of filtered and unfiltered internal blind samples (conductivity EB-17), 1991.

TABLE B-2 Comparison of Filtered and Unfiltered Internal Blind Samples
Using Canada National Water Research Institute (CNRWI)
Eulerian Study Samples EA-22,1991

Parameter	Target Conc.[a]	Measured Conc.	Number of Values (n)	Bias	% Bias	Standard Deviation (s)	% RSD
Calcium	0.335	0.338[b] 0.331[c]	25 11	0.003 -0.004	0.9 -1.2	0.008 0.008	2.4 2.4
Magnesium	0.070	0.068 0.067	25 11	-0.002 -0.003	-2.9 -4.3	0.003 0.003	4.4 4.5
Potassium	0.058	0.056 0.051	25 11	-0.002 -0.007	-3.4 -12.1	0.005 0.009	8.9 17.6
Sodium	0.044	0.043 0.066	25 11	-0.001 0.022	-2.3 50.3	0.005 0.018	11.6 27.3
Ammonium	0.023	<0.02 <0.02	25 11			0.00 0.00	0.0 0.0
Nitrate	2.15	2.23 2.20	25 11	0.08 0.05	3.7 2.2	0.04 0.04	1.8 1.8
Chloride	0.09	0.09 0.12	25 11	0.00 0.03	0.0 30.4	0.01 0.02	11.1 16.7
Sulfate	1.55	1.59 1.53	25 11	0.04 -0.02	2.6 -1.5	0.03 0.03	1.9 2.0
H^+ (µeq/L)	38.46	41.58 42.80	25 11	3.12 4.34	8.1 11.3	1.95 2.36	4.7 5.5
Conductivity (µS/cm)	21.58	22.0 22.1	25 11	0.4 0.5	1.9 2.4	0.6 0.3	2.7 1.4

Notes:
a. Target values provided by CNWRI are measured median values from the several Eulerian studies.
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.

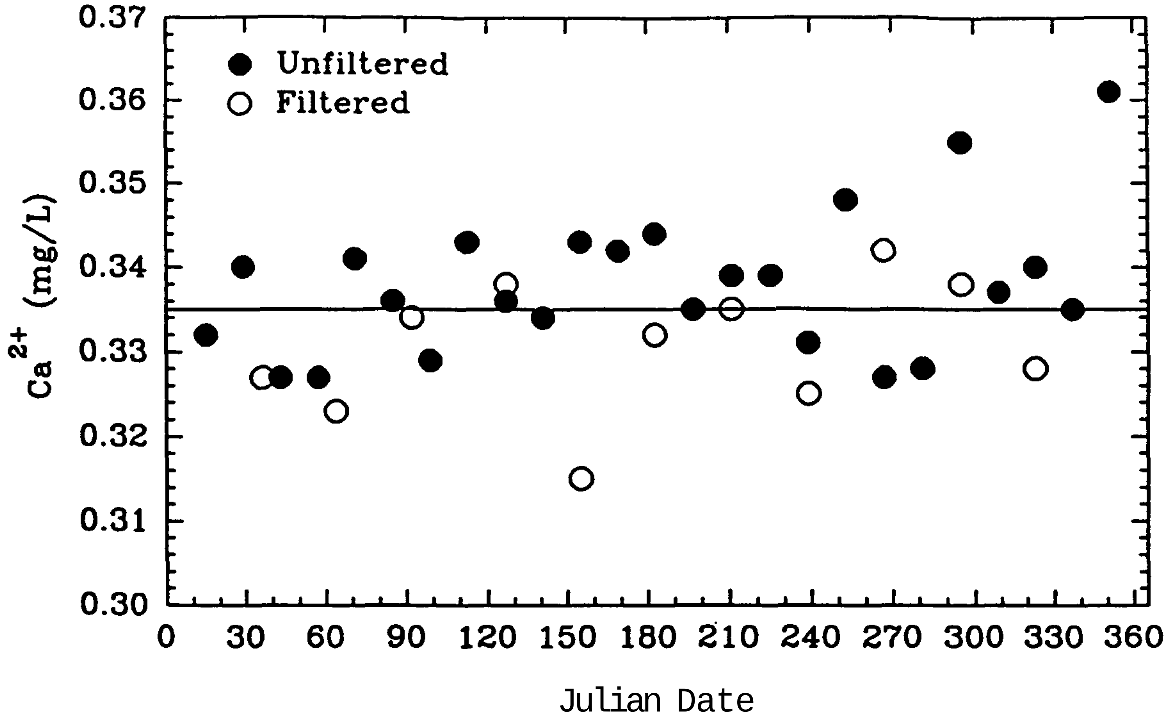


FIGURE B-11. Comparison of filtered and unfiltered internal blind samples (calcium EA-22), 1991.

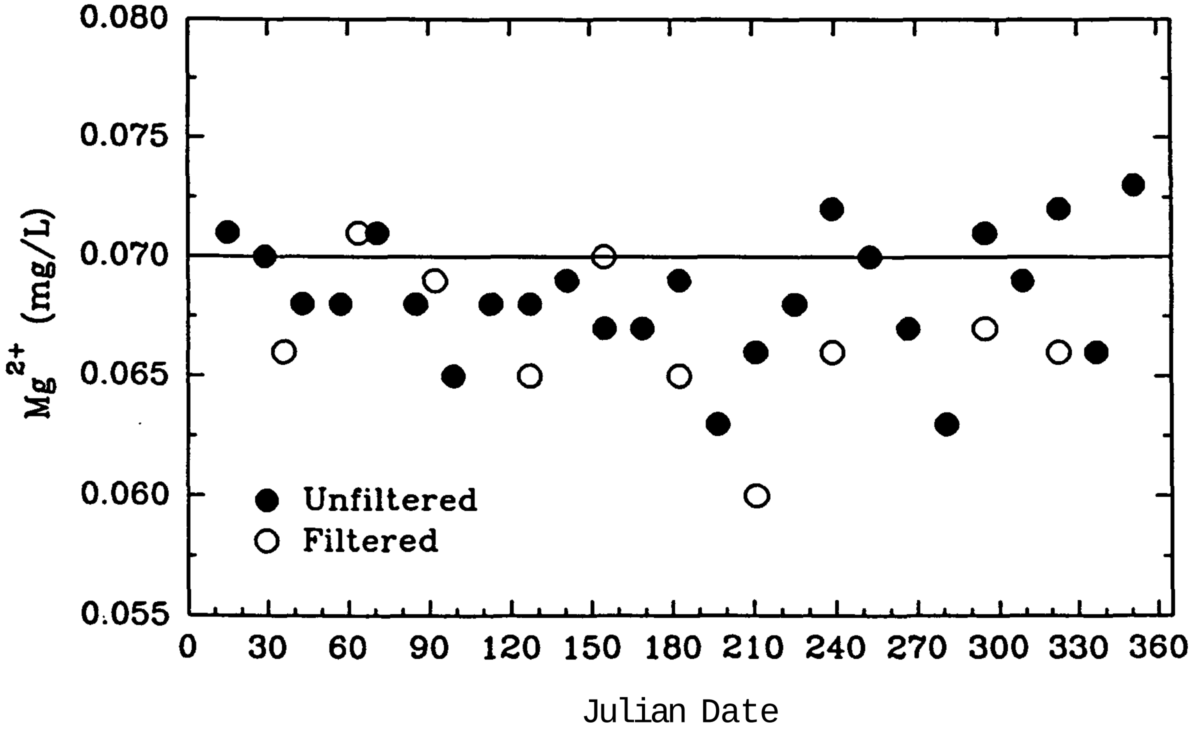


FIGURE B-12. Comparison of filtered and unfiltered internal blind samples (magnesium EA-22), 1991.

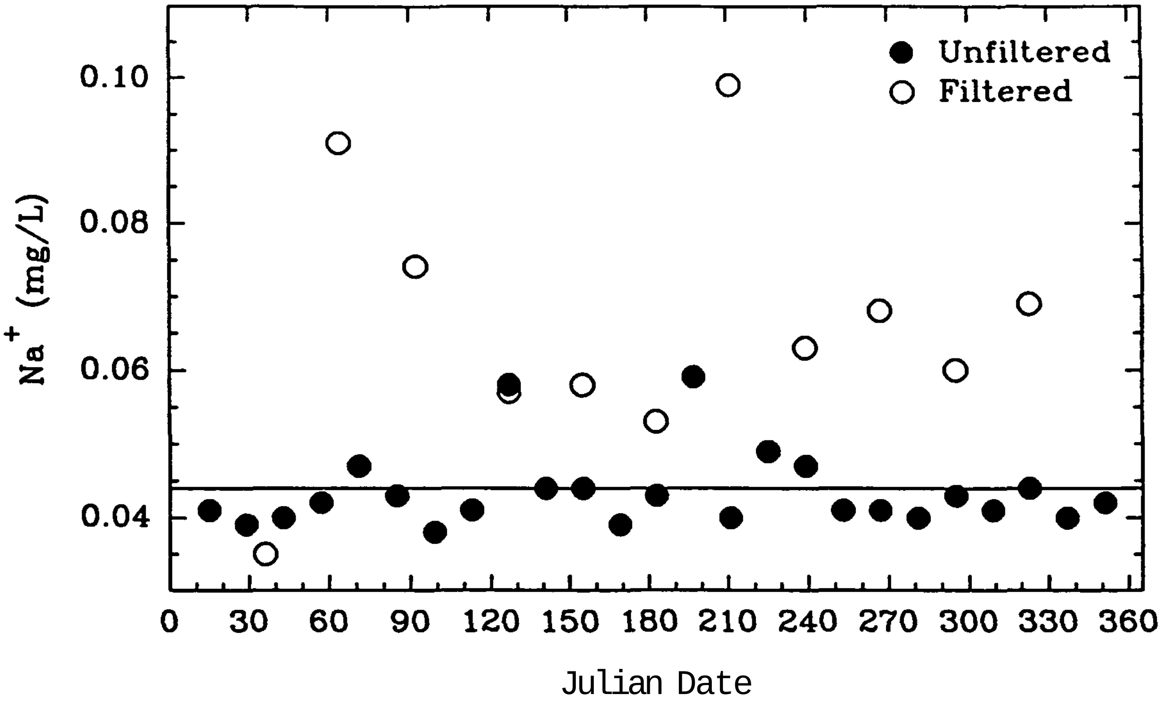


FIGURE B-13. **Comparison of filtered and unfiltered internal blind samples (sodium EA-22), 1991.**

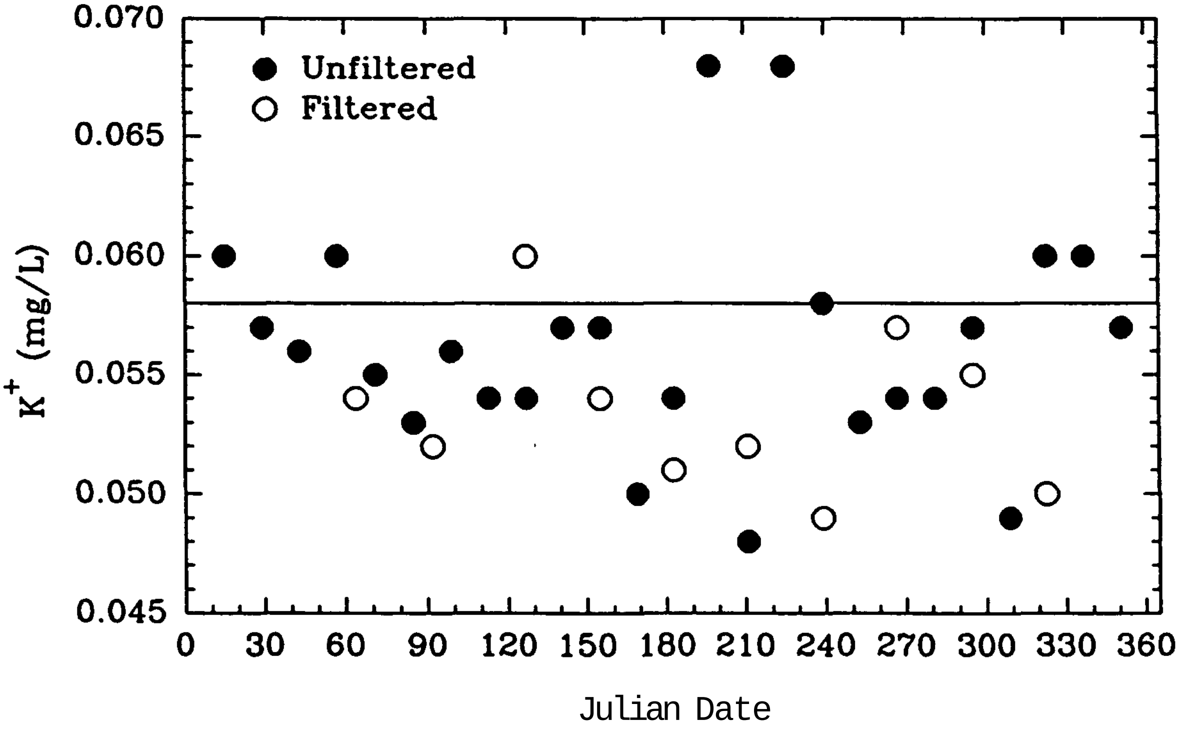


FIGURE B-14. **Comparison of filtered and unfiltered internal blind samples (potassium EA-22), 1991.**

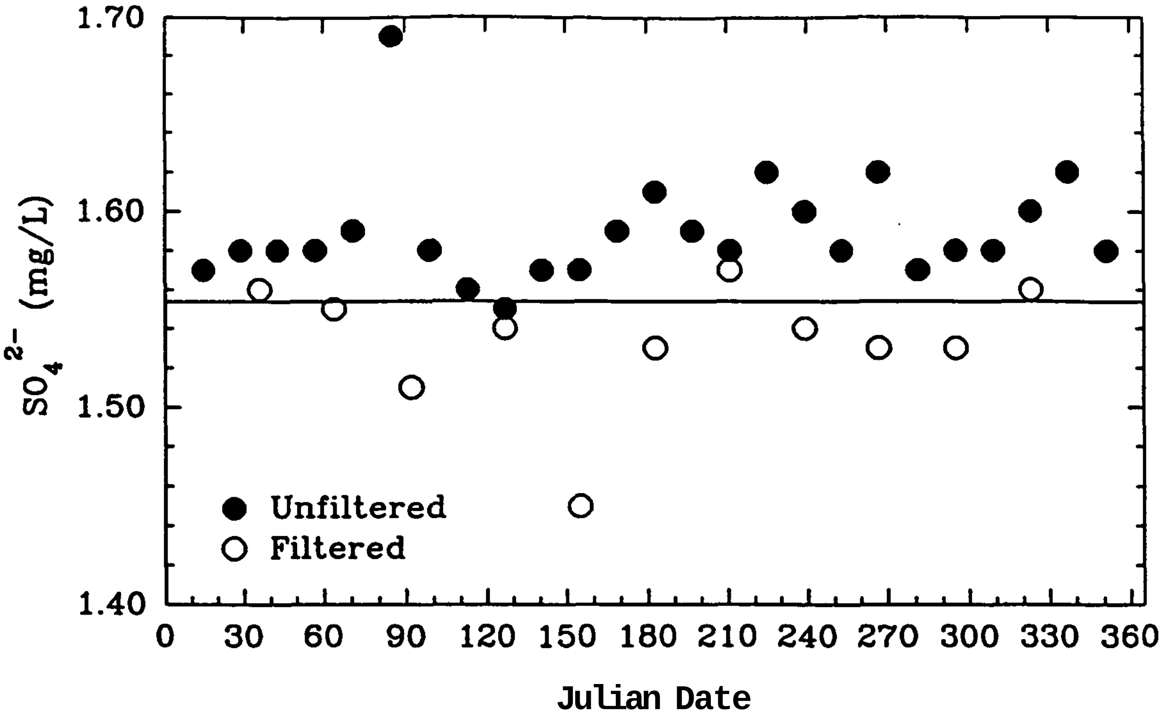


FIGURE B-15. Comparison of filtered and unfiltered internal blind samples (sulfate EA-22), 1991.

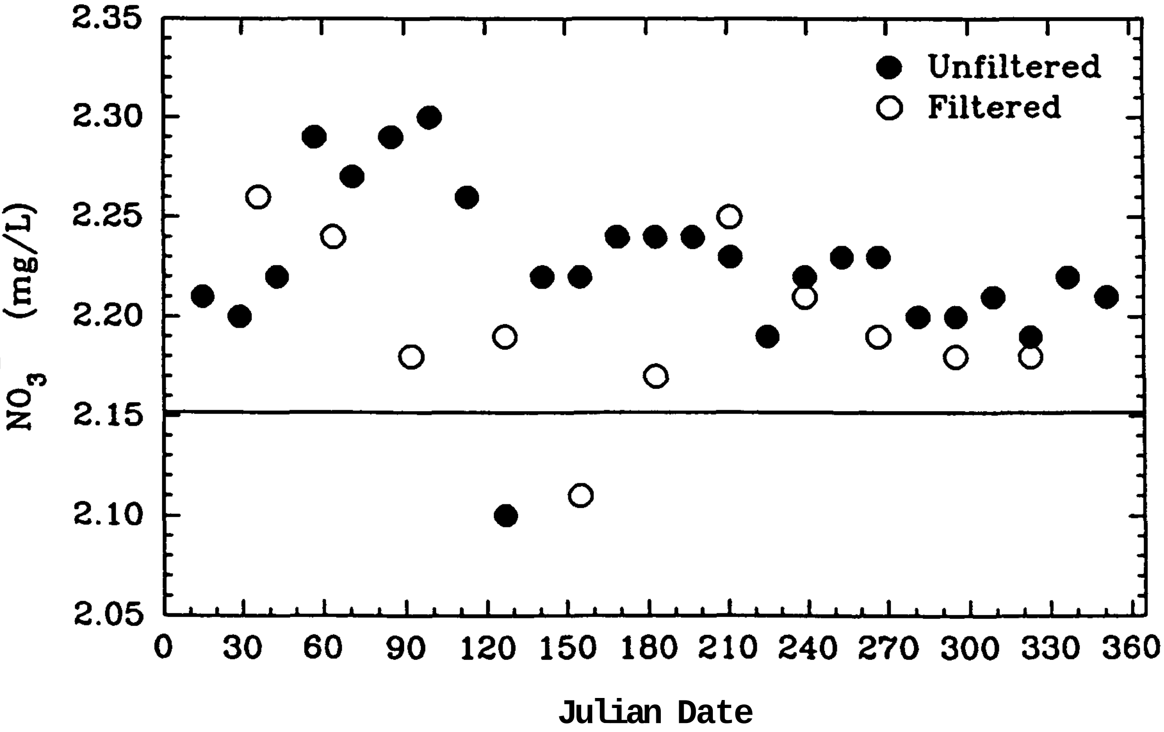


FIGURE B-16. Comparison of filtered and unfiltered internal blind samples (nitrate EA-22), 1991.

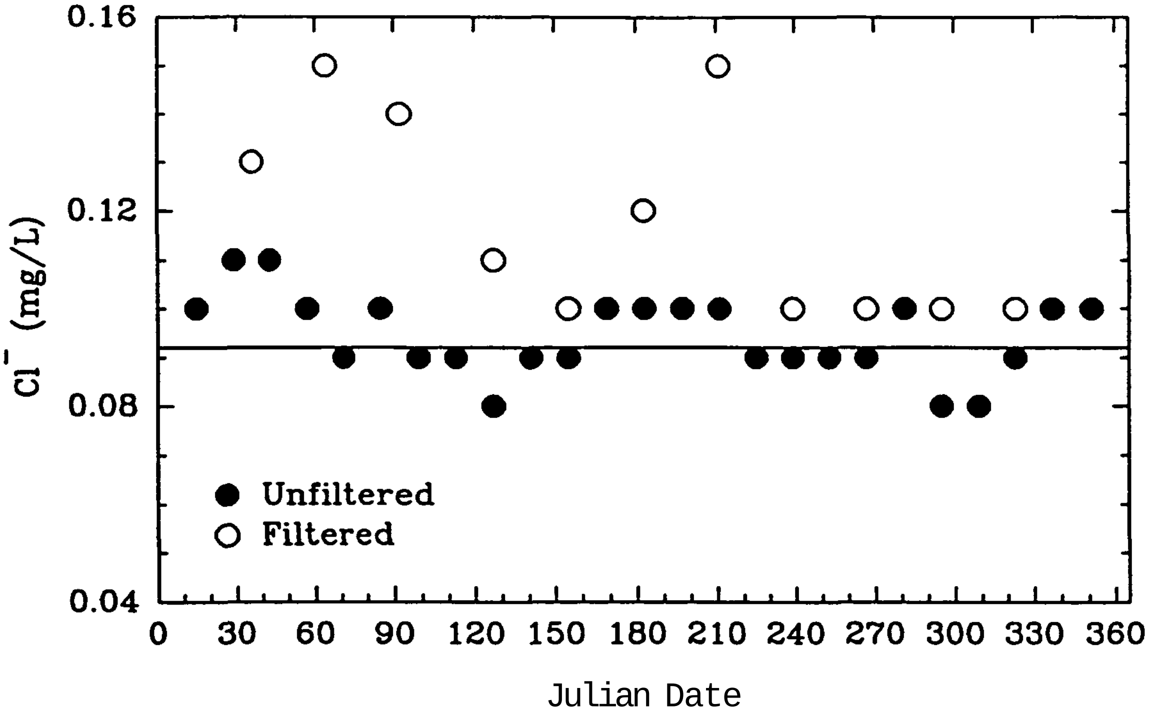


FIGURE B-17. Comparison of filtered and unfiltered internal blind samples (chloride EA-22), 1991.

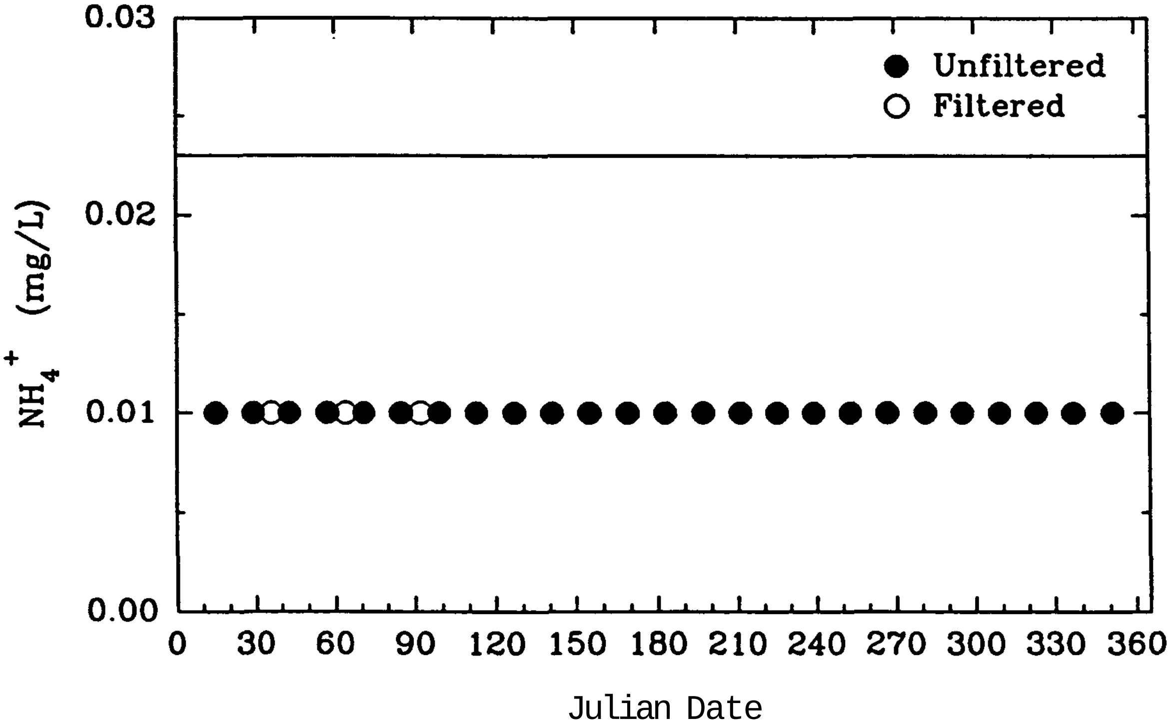


FIGURE B-18. Comparison of filtered and unfiltered internal blind samples (ammonium EA-22), 1991.

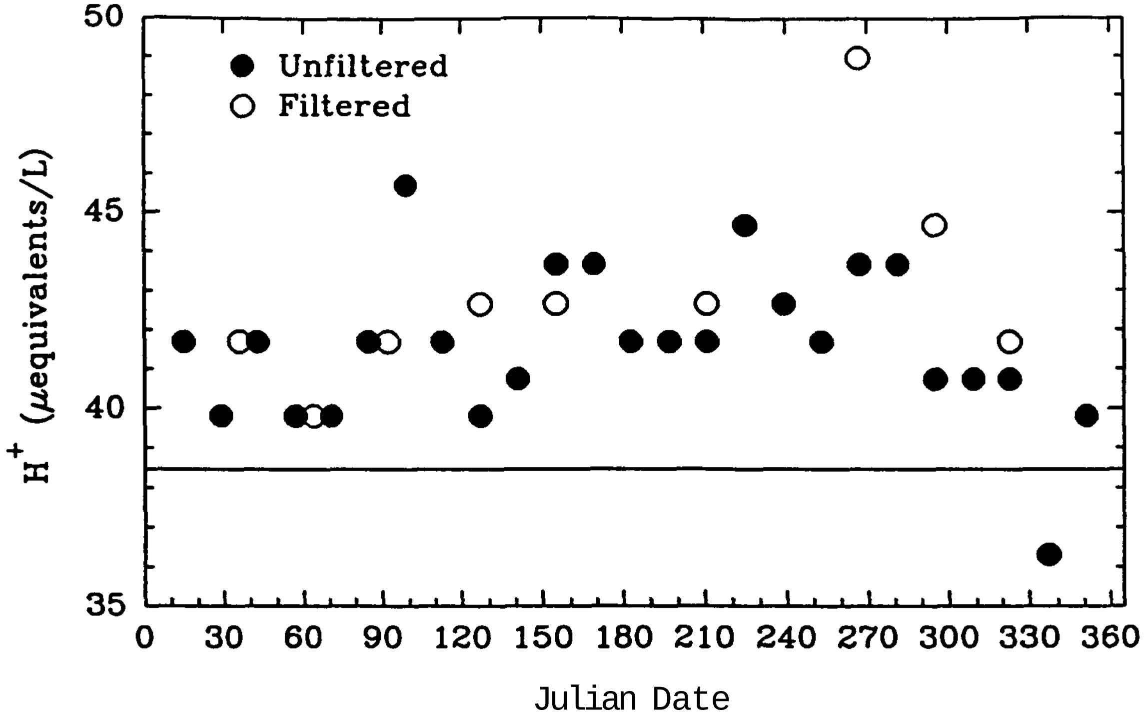


FIGURE B-19. Comparison of filtered and unfiltered internal blind samples (H^+ EA-22), 1991.

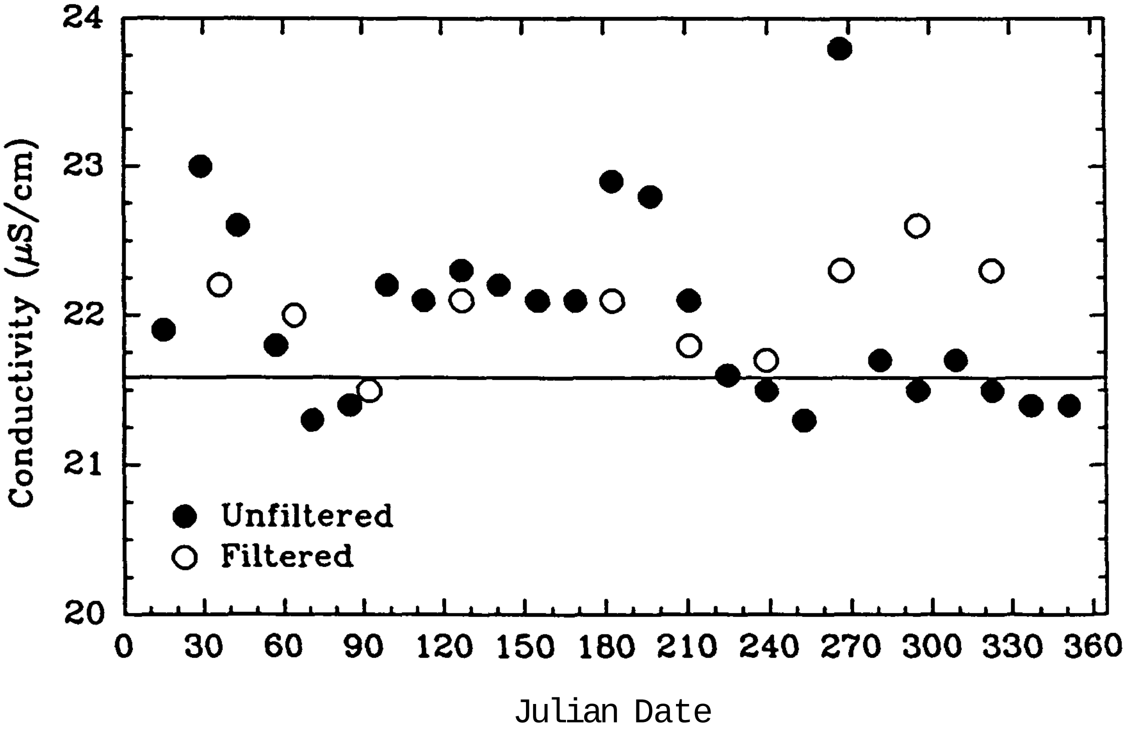
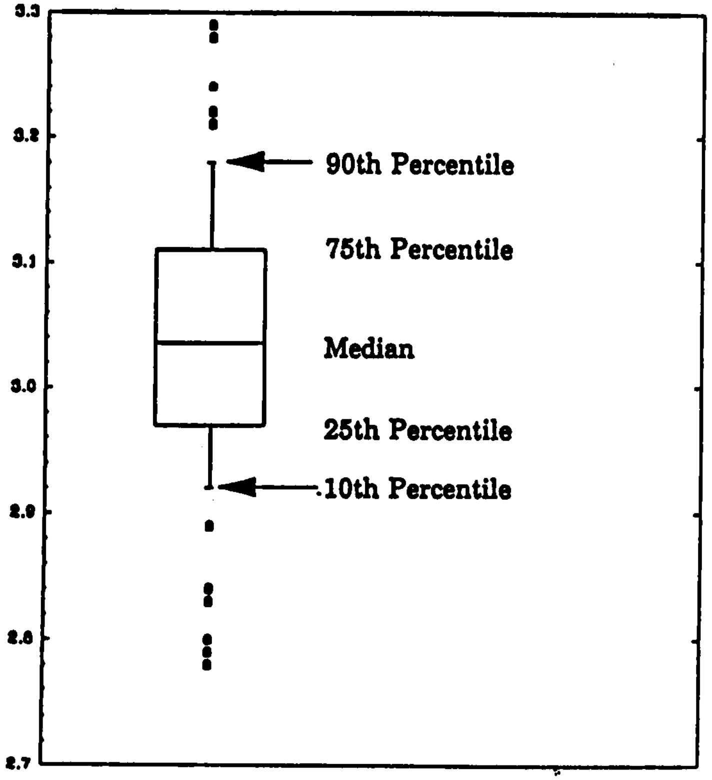


FIGURE B-20. Comparison of filtered and unfiltered internal blind samples (conductivity EA-22), 1991.

TABLE B-3 50th and 95th Percentile Concentration Values of Chemical and Physical Parameters Measured in Replicate (O/Q) Samples, 1991

Parameter	Percentile Concentration Values (mg/L) 50th	95th
Calcium	0.107	0.698
Magnesium	0.024	0.117
Potassium	0.020	0.139
Sodium	0.064	0.707
Ammonium	0.17	0.60
Nitrate	0.93	2.41
Chloride	0.12	1.25
Sulfate	1.08	2.82
pH (units) H^+(μeq/L)	4.99 10.23	4.22 59.92
Conductivity (μS/cm)	11.20	33.10

DIAGRAM OF BOXPLOTS USED OM THE FOLLOWING PAGES



All values beyond the 10th and 90th percentiles are graphed individually, as on a point graph.

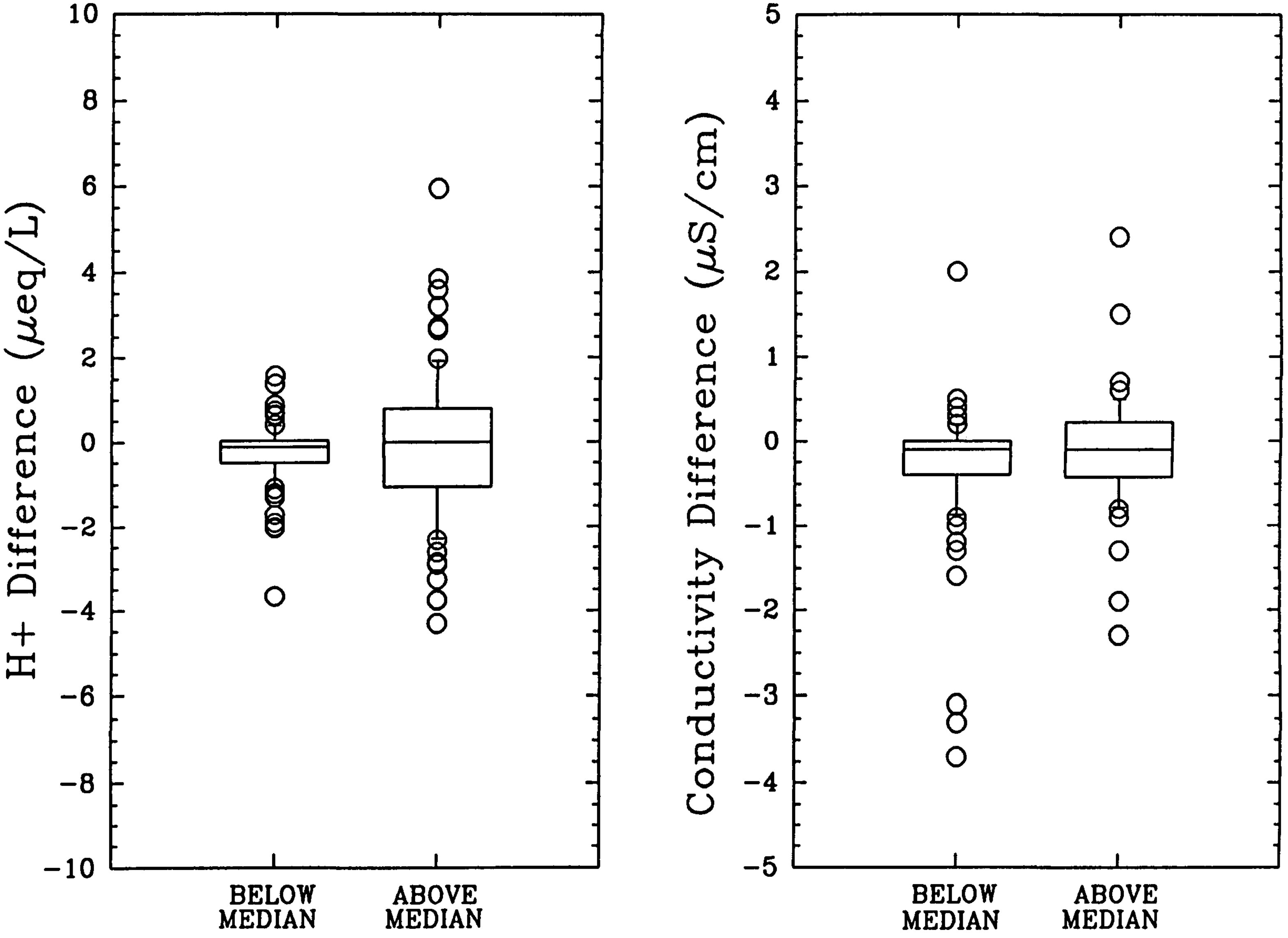


FIGURE B-21. Results of O/Q replicate analysis, pH and conductivity, 1991.

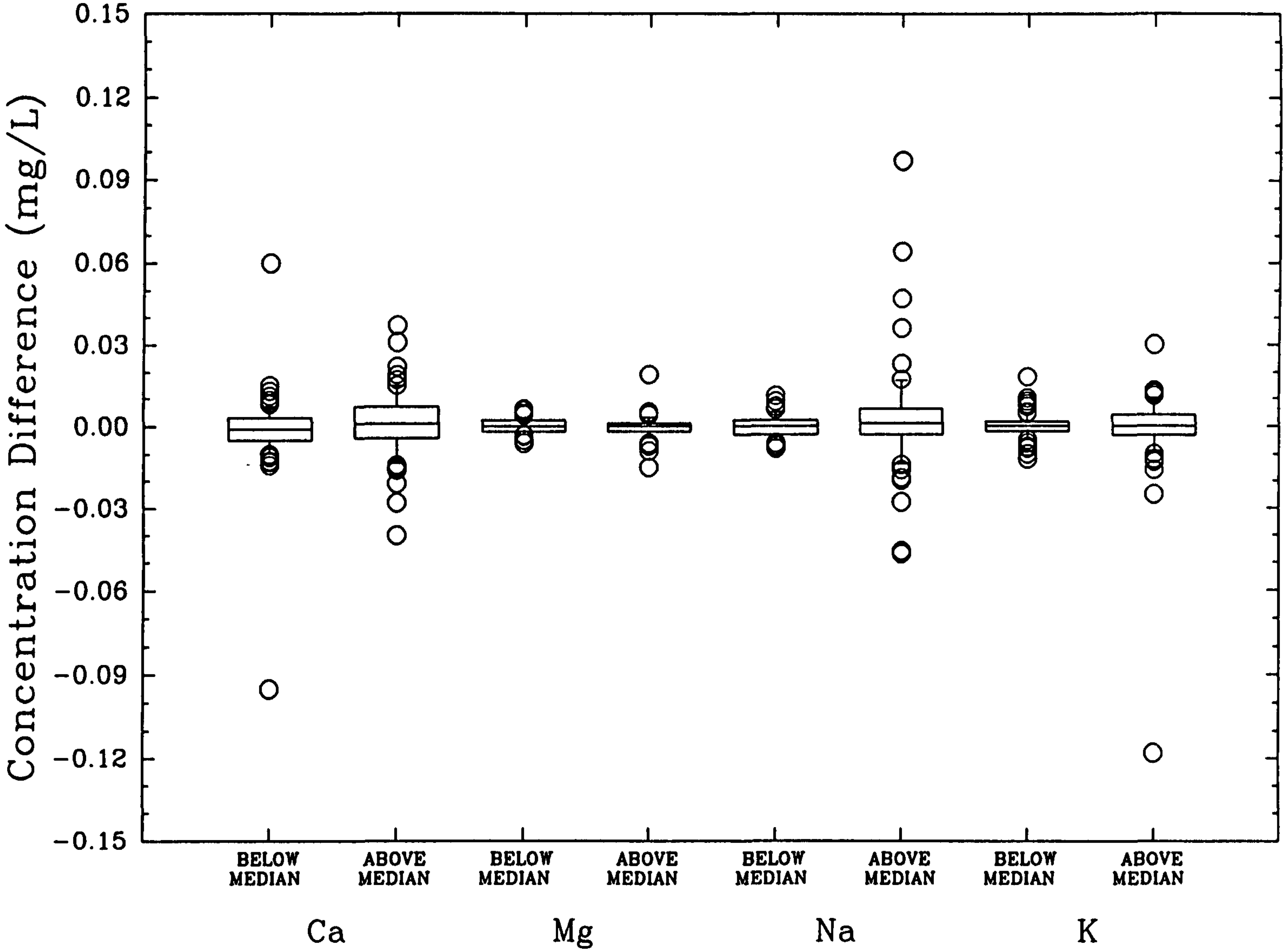


FIGURE B-22. Results of O/Q replicate analysis for calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K), 1991.

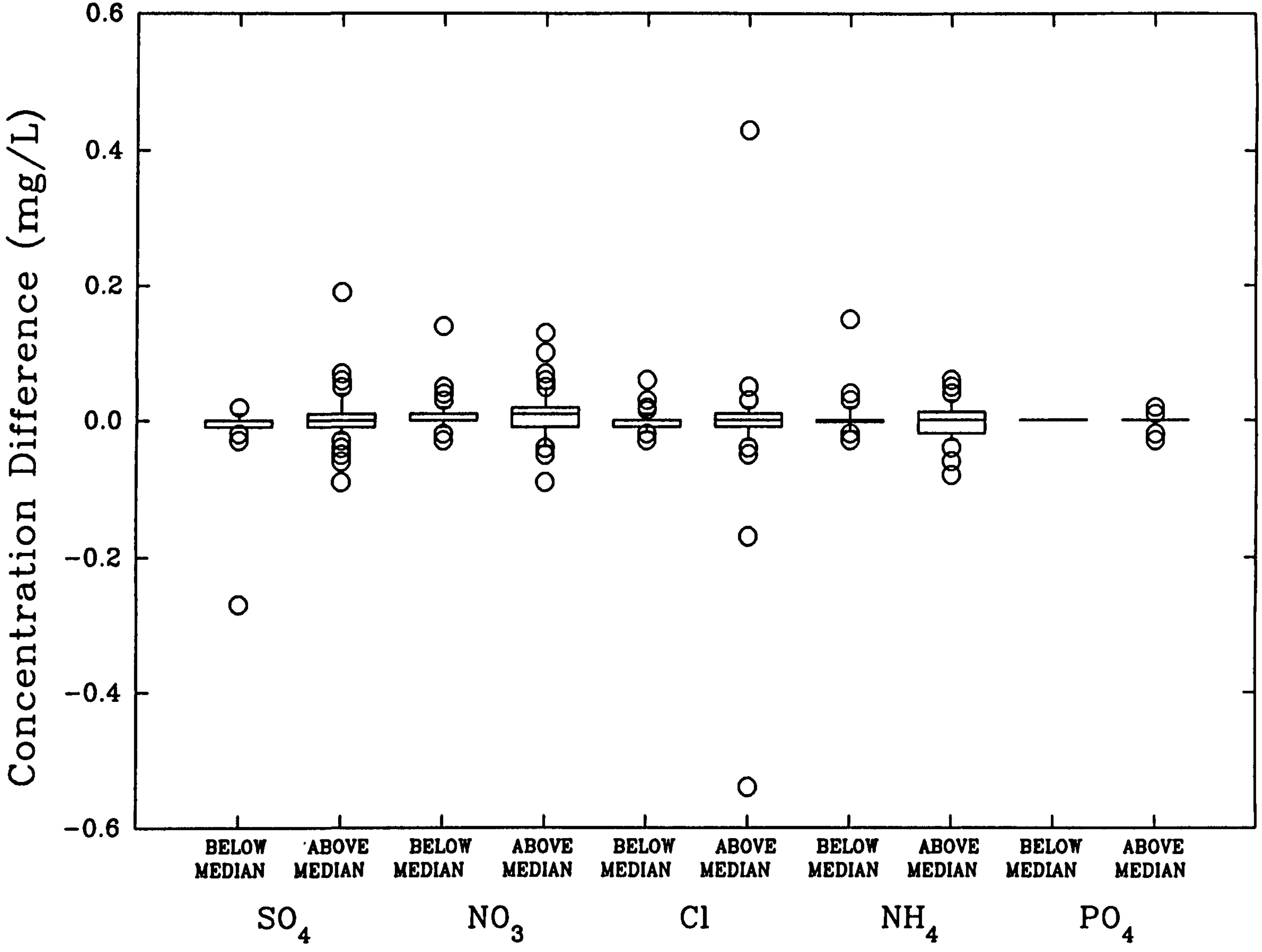


FIGURE B-23. Results of O/Q replicate analysis for sulfate (SO_4), nitrate (NO,), chloride (C1), ammonium (NH_4), and phosphate (PO_4), 1991.

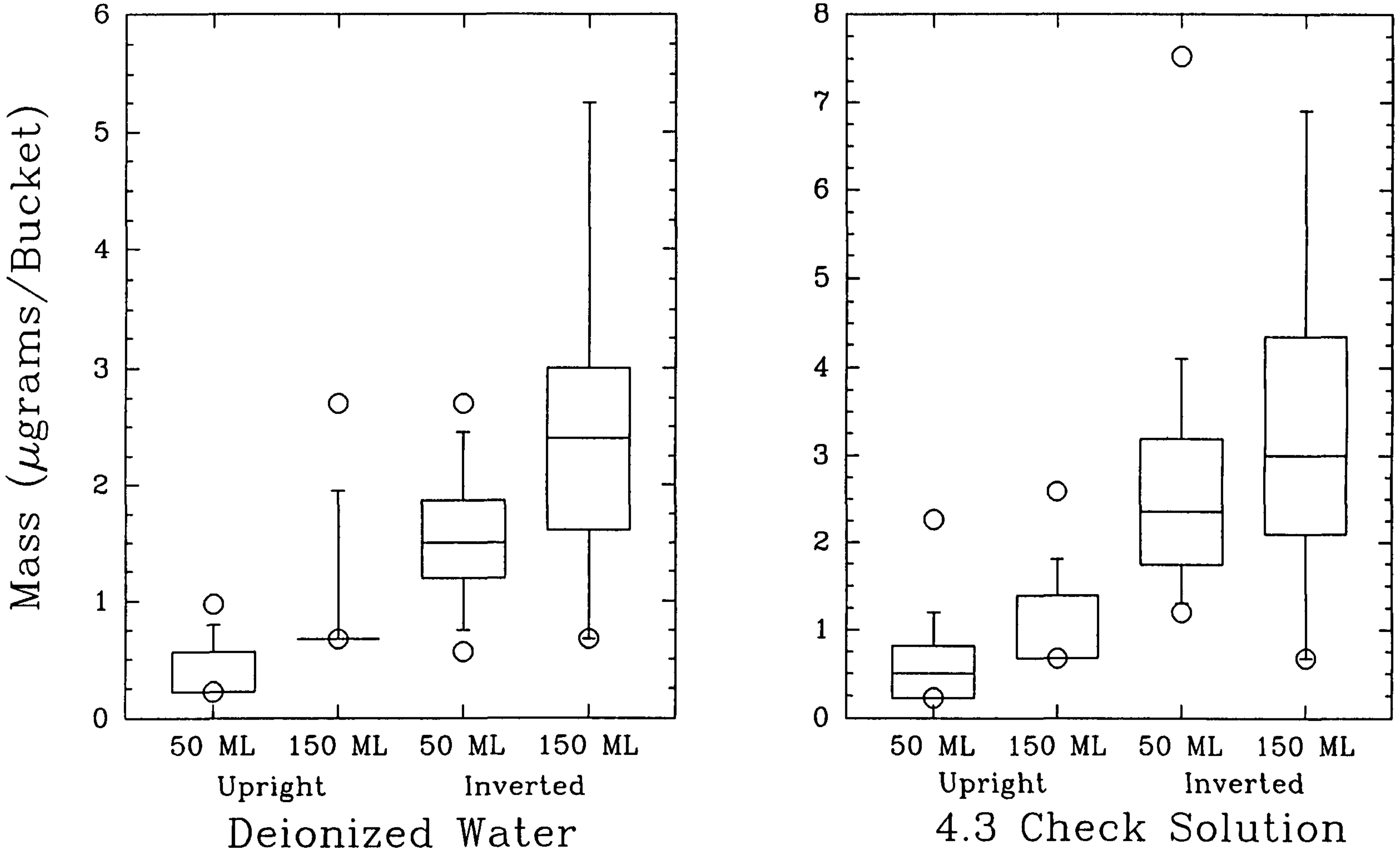


FIGURE B-24. Calcium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1991.

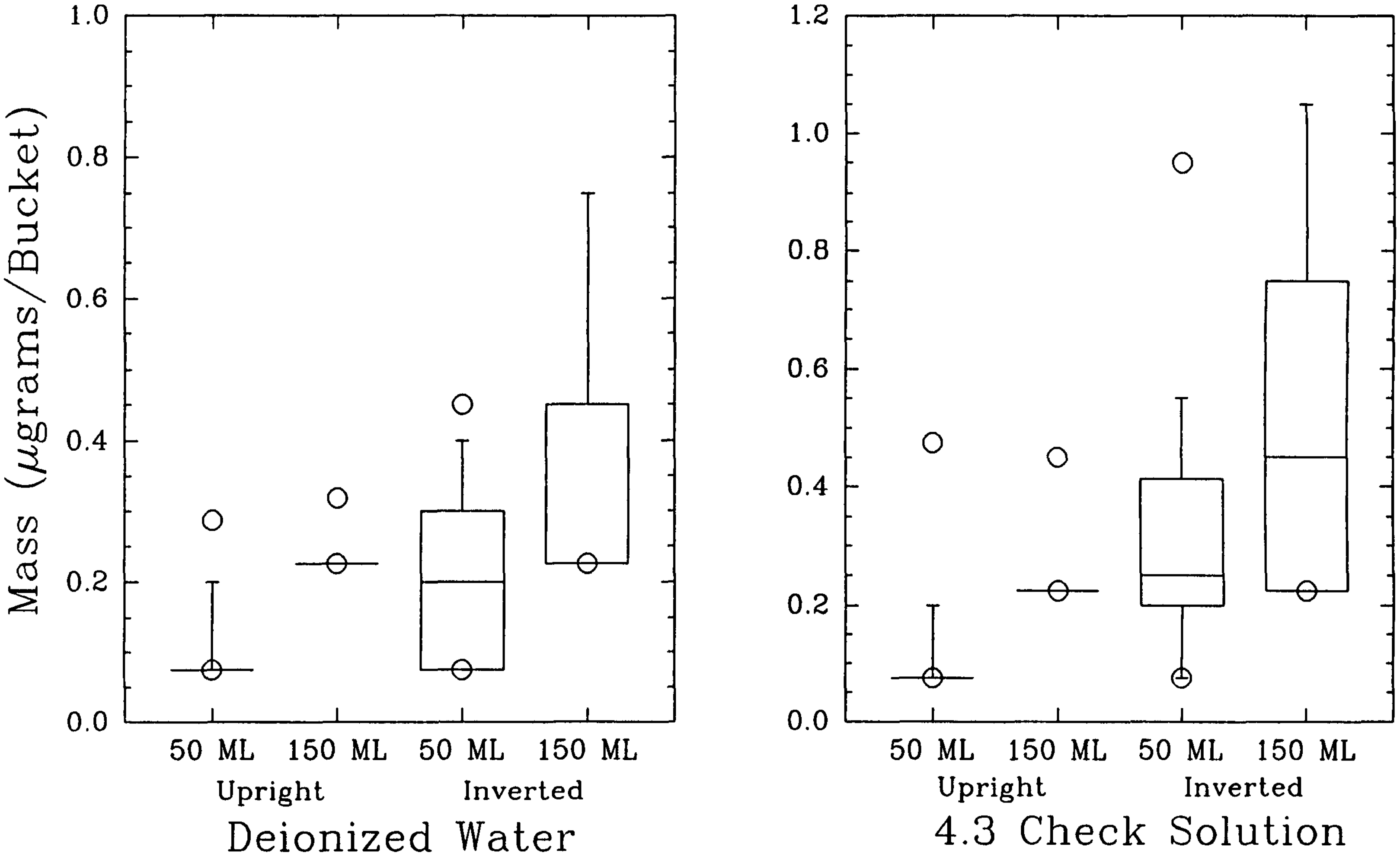


FIGURE B-25. Magnesium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1991.

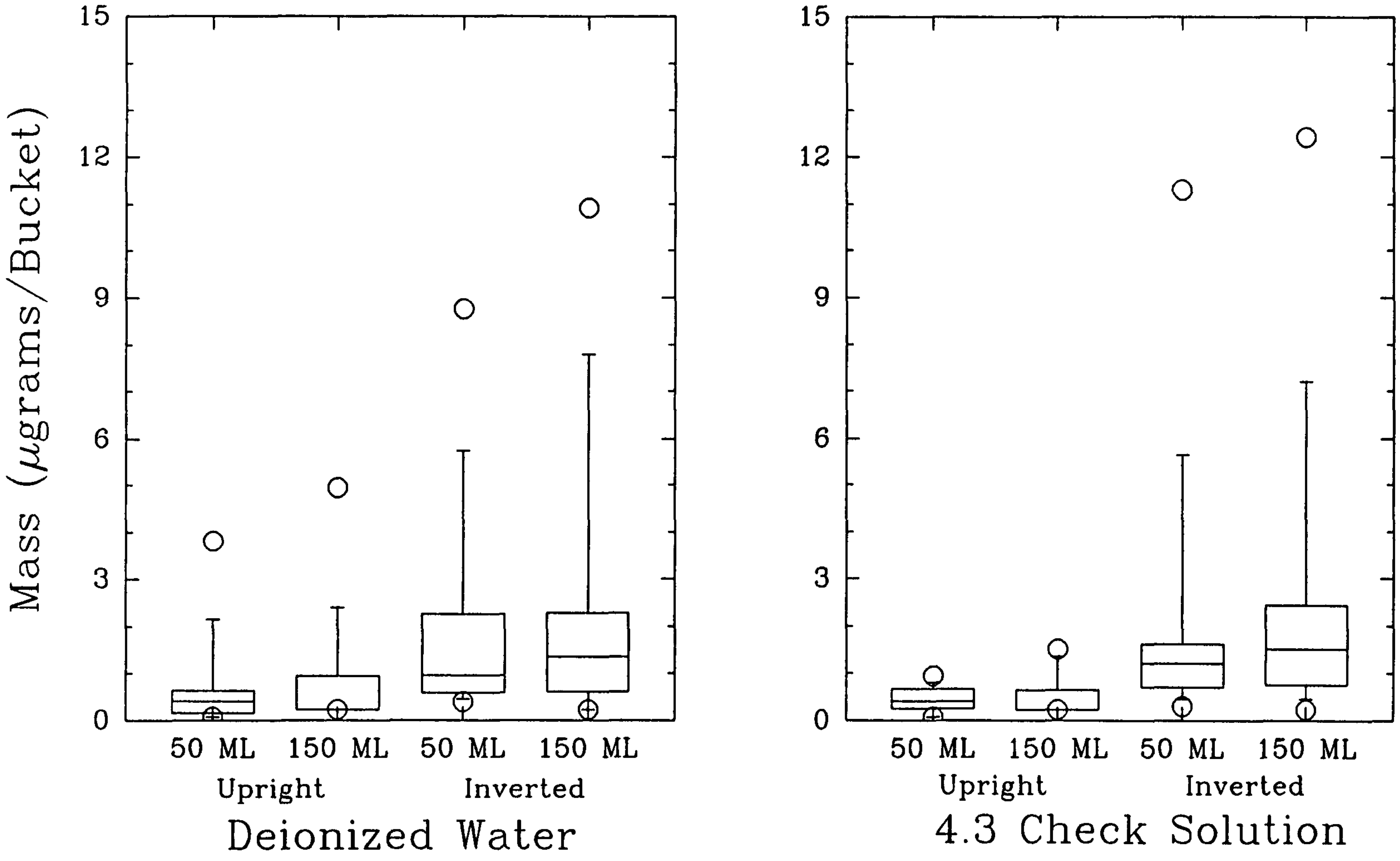


FIGURE B-26. Sodium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1991.

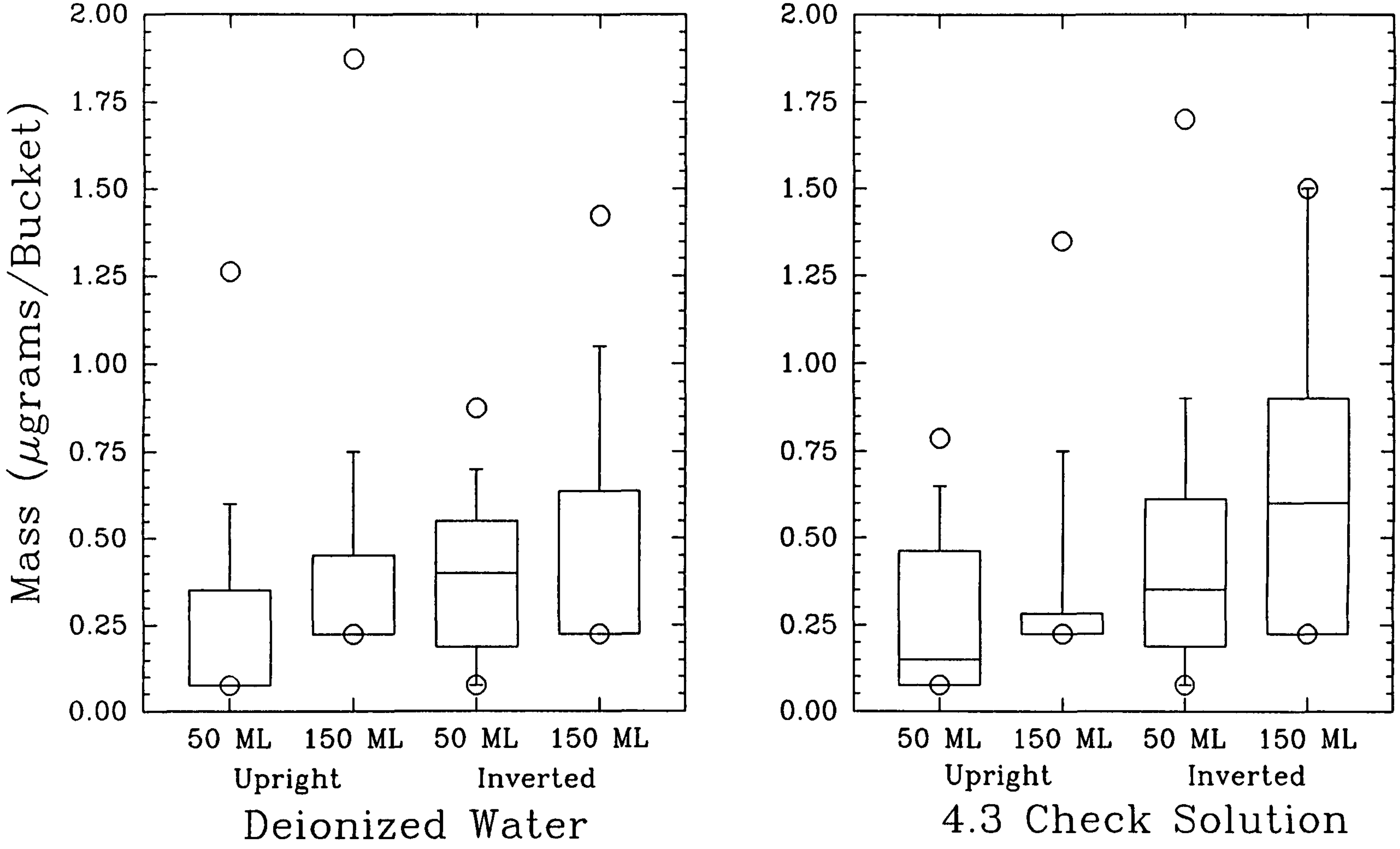


FIGURE B-27. Potassium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1991.

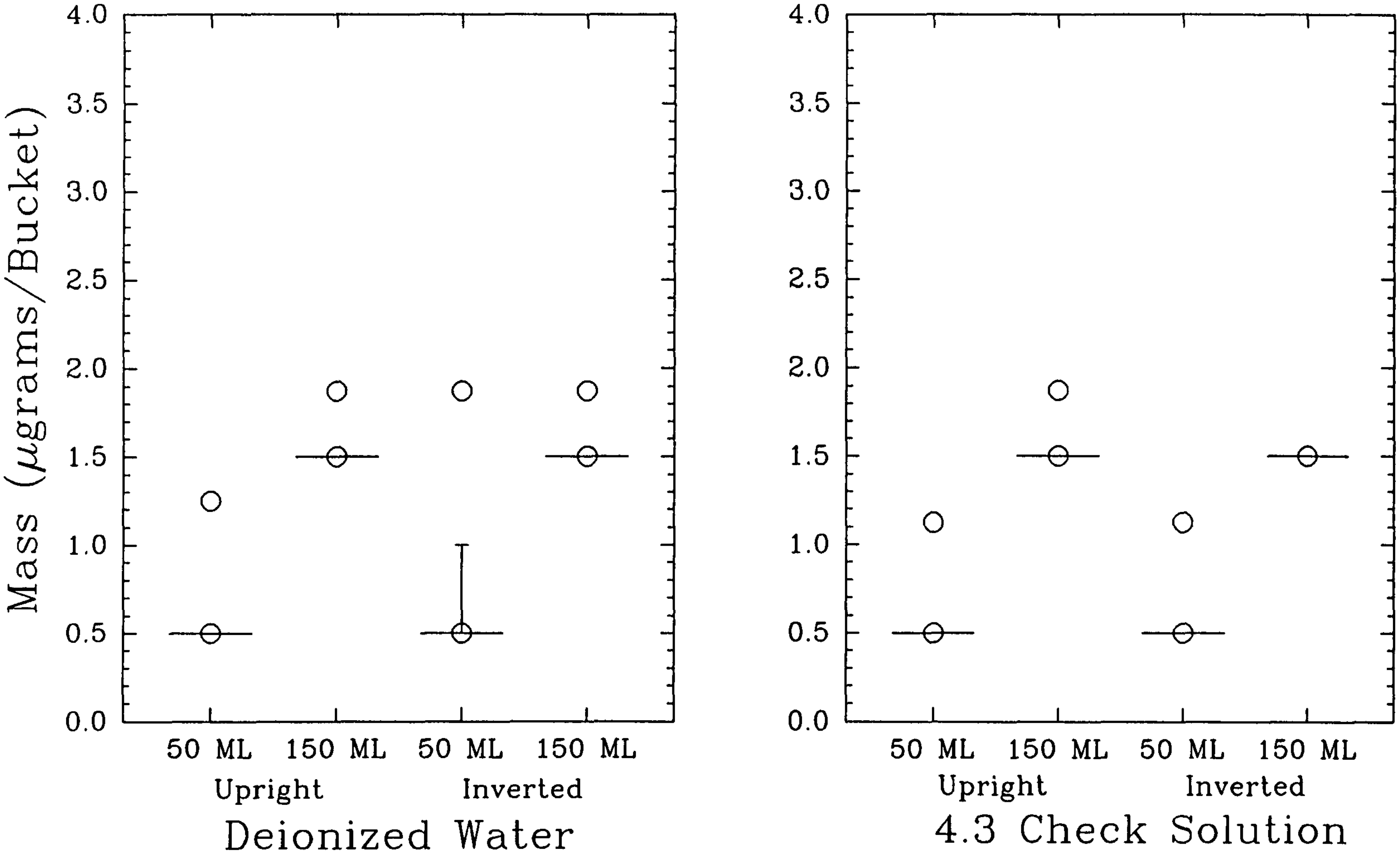


FIGURE B-28. Ammonium found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1991.

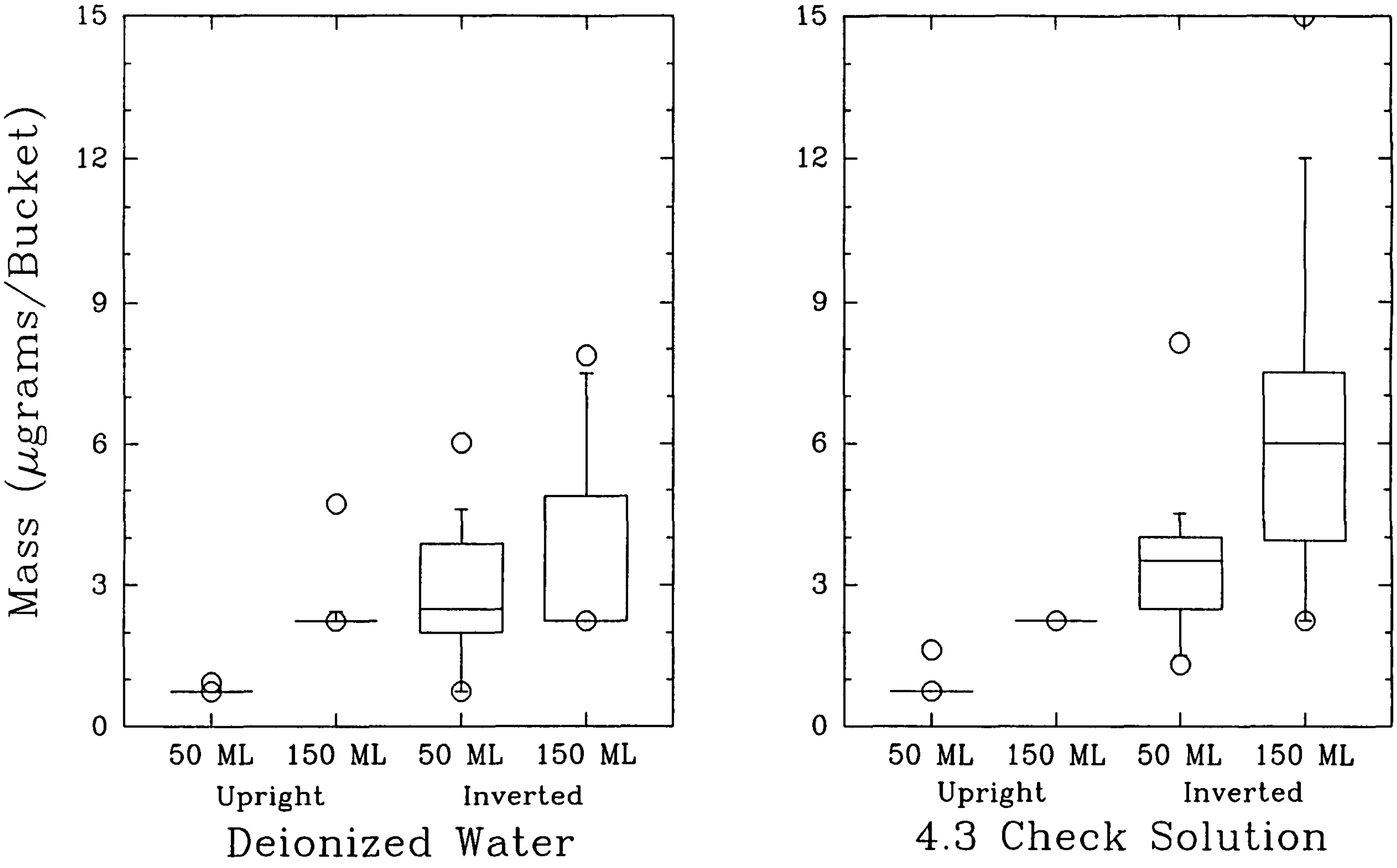


FIGURE B-29. Sulfate found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1991.

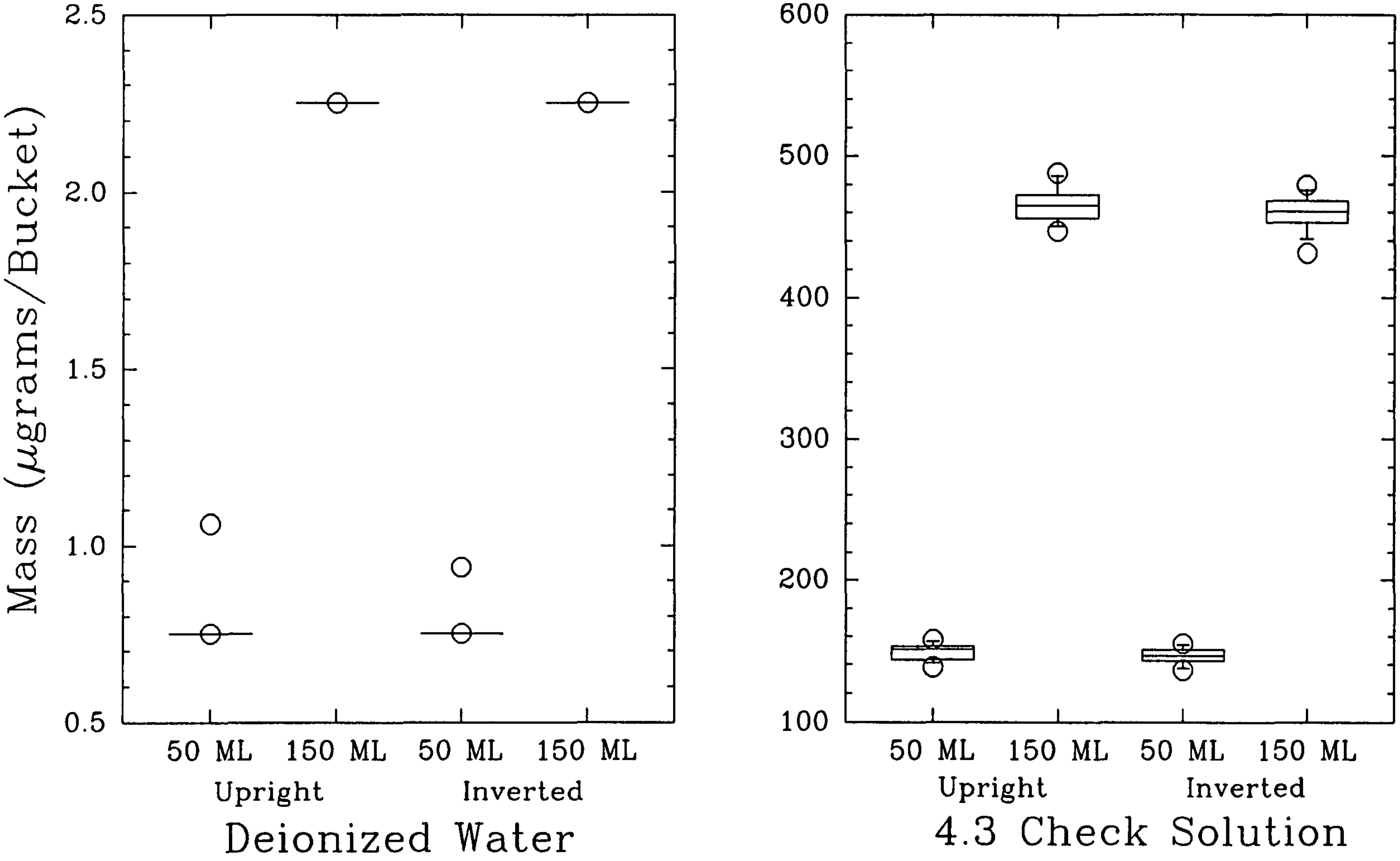


FIGURE B-30. Nitrate found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1991.

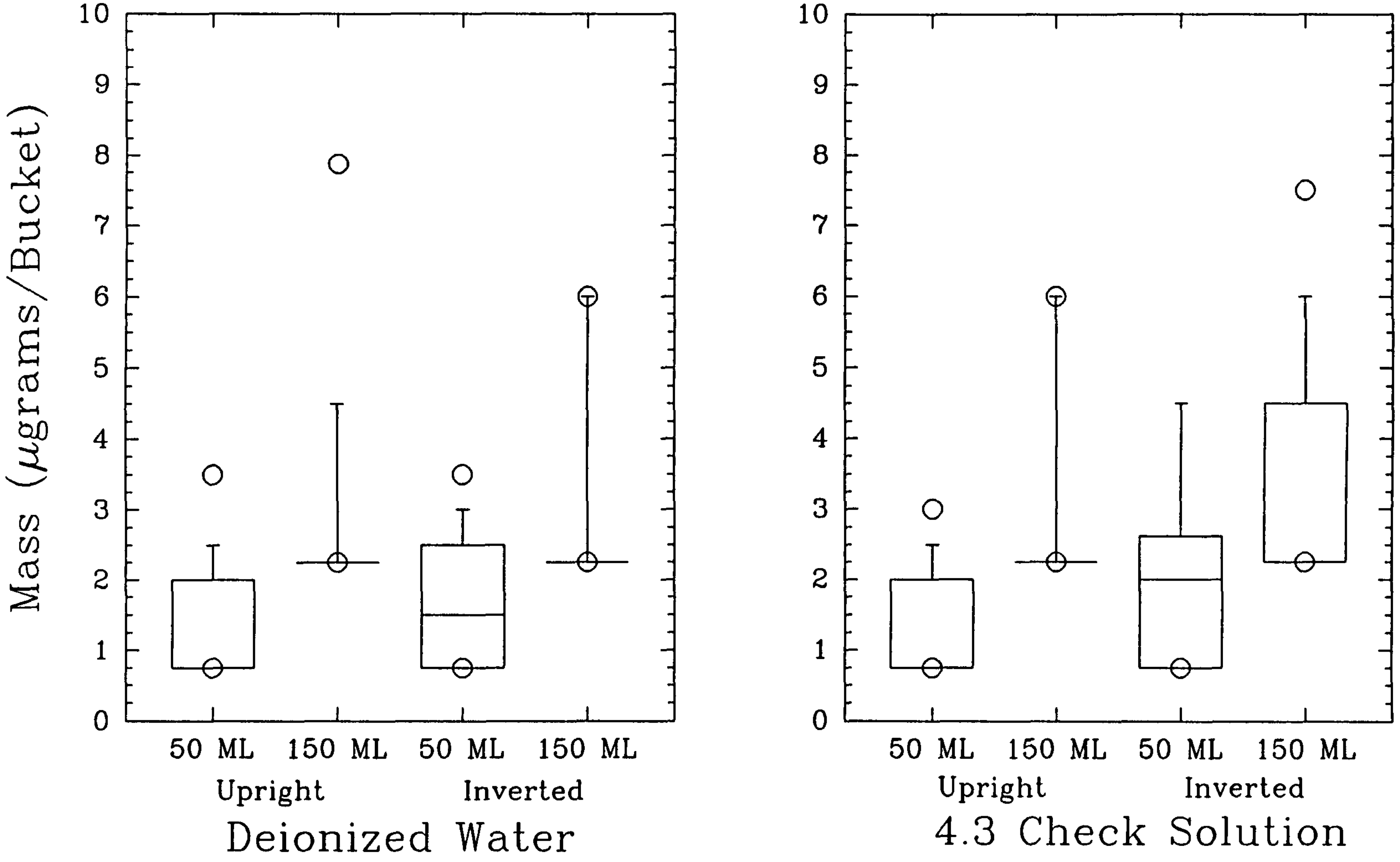


FIGURE B-31. Chloride found in upright and inverted bucket blanks, using DI water and pH 4.3 QCS as leaching agents, 1991.

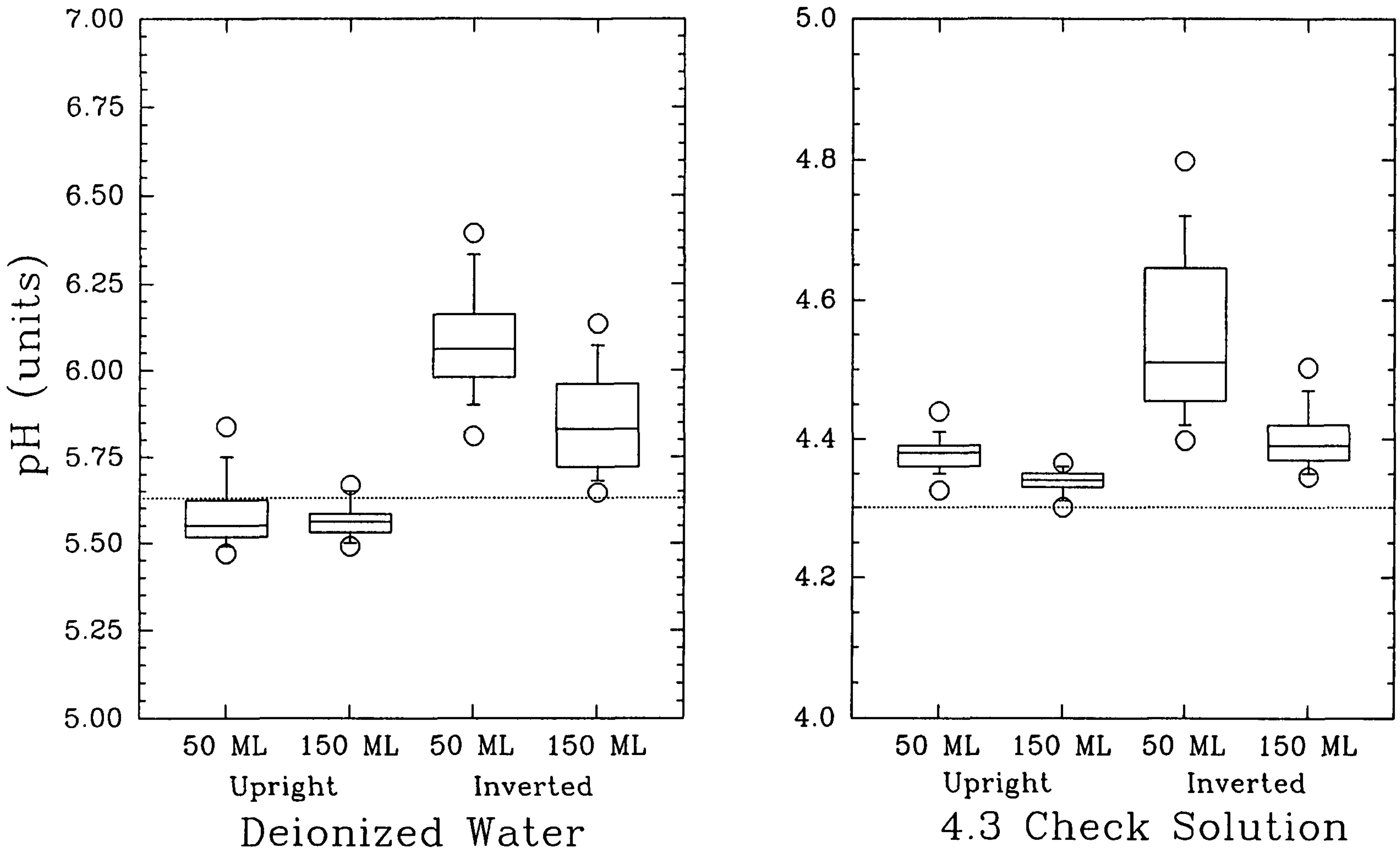


FIGURE B-32. pH of upright and inverted bucket blanks leached with DI water and pH 4.3 QCS, 1991.

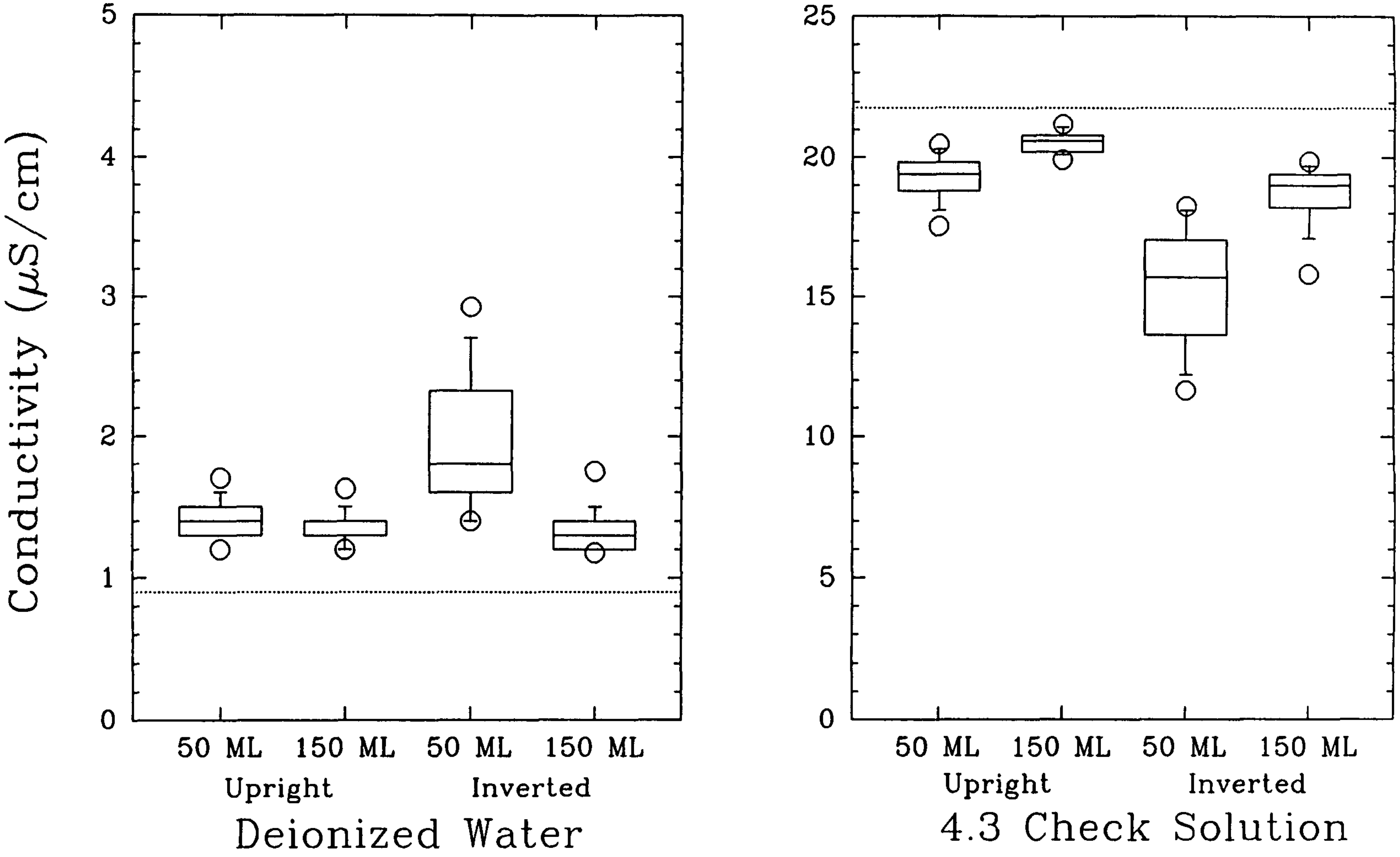


FIGURE B-33. **Conductivity of upright and inverted bucket blanks leacbed with DI water and pH 4.3 QCS, 1991.**

APPENDIX C

Interlaboratory Comparison Data:

USEPA, LRTAP, EMEP, WMO

1991

TABLE C-l
USEPA RTP Acid Rain Performance Survey, June 1991

Parameter (mg/L)	Sample Number 1026 CAL	1026 USEPA	2362 CAL	2362 USEPA	3605 CAL	3605 USEPA
Calcium	0.057	0.057	0.133	0.136	0.402	0.391
Magnesium	0.024	0.023	0.020	0.020	0.121	0.117
Sodium	0.243	0.245	0.307	0.285	1.780	1.870
Potassium	0.075	0.078	0.078	0.086	0.757	0.775
Ammonium	0.14	0.15	0.85	0.81	1.15	1.10
Nitrate	0.62	0.64	0.62	0.66	4.74	4.53
Chloride	0.39	0.39	0.65	0.65	2.89	2.84
Sulfate	1.68	1.55	8.18	7.52	12.55	11.32
pH (units)	4.49	4.50	3.91	3.88	3.66	3.62
Conductivity (µS/cm)	17.7	15.6	65.5	62.8	126.9	123.1

TABLE C-2
USEPA RTP Acid Rain Performance Survey, December 1991

Parameter (mg/L)	Sample Numbe 1325 CAL	1325 USEPA	2038 CAL	2038 USEPA	3729 CAL	3729 USEPA
Calcium	0.052	0.048	0.109	0.101	0.153	0.135
Magnesium	0.036	0.036	0.020	0.020	0.094	0.087
Sodium	0.183	0.177	0.231	0.235	1.360	1.256
Potassium	0.082	0.080	0.073	0.075	0.536	0.514
Ammonium	0.09	0.10	0.71	0.71	0.42	0.44
Nitrate	0.49	0.49	0.49	0.51	3.85	3.86
Chloride	0.29	0.291	0.33	0.323	1.12	1.134
Sulfate	2.10	1.93	12.46	11.64	6.47	6.08
pH (units)	4.41	4.40	3.70	3.70	3.92	3.90
Conductivity (µS/cm)	20.6	19.3	100.8	96.7	67.7	65.6

TABLE C-3
LRTAP Interlaboratory Comparability Study L-26, March 1991,
CAL, Values Compared to NWRI Median Values for all Participating Laboratories

Sample Number

Parameter (mg/L)	1		2		3		4		5	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	4.004	4.070	6.464	6.480	1.714	1.770	3.987	4.100	0.568	0.572
Magnesium	0.473	0.480	0.611	0.620	0.666	0.670	0.477	0.480	0.060	0.060
Sodium	0.520	0.562	0.767	0.814	4.025	4.065	0.513	0.565	5.483	5.590
Potassium	0.198	0.209	0.260	0.280	0.263	0.288	0.198	0.212	0.205	0.220
Ammonium	0.04	0.04	0.06	0.07	<0.02	0.01	0.03	0.03	<0.02	0.01
Nitrate	3.19	3.15	0.44	0.45	0.22	0.22	3.19	3.16	1.06	1.07
Chloride	0.17	0.18	0.39	0.39	5.26	5.14	0.18	0.19	1.29	1.27
Sulfate	5.71	5.60	5.88	5.73	2.83	2.78	5.71	5.60	2.68	2.63
pH (units)	6.73	6.60	7.26	7.15	6.54	6.36	6.81	6.65	7.15	6.98
Conductivity (µS/cm)	31.8	32.2	45.0	45.5	35.7	36.1	31.8	32.2	30.4	30.6

TABLE C-3 (continued)
LRTAP Interlaboratory Comparability Study L-26, March 1991, CAL Values Compared to NWRI Median Values for all Participating Laboratories

Parameter (mg/L)	Sample Number 6		7		8		9		10	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	0.942	0.985	3.974	3.905	2.355	2.400	0.746	0.756	3.138	3.255
Magnesium	0.199	0.200	0.744	0.760	0.679	0.670	0.454	0.450	0.977	1.070
Sodium	0.090	0.100	0.201	0.220	1.209	1.190	3.015	3.110	0.202	0.204
Potassium	0.035	0.040	0.194	0.208	0.379	0.410	0.280	0.297	0.180	0.190
Ammonium	<0.02	0.01	0.22	0.21	0.05	0.05	0.05	0.05	1.53	1.46
Nitrate	0.09	0.10	4.47	4.42	<0.03	0.04	0.18	0.18	7.08	7.13
Chloride	0.10	0.11	3.43	3.36	0.24	0.24	4.38	4.27	0.53	0.52
Sulfate	6.02	6.01	7.36	7.22	3.78	3.69	1.95	1.94	6.76	6.65
pH (units)	4.26	4.25	4.49	4.48	6.99	6.88	5.41	5.34	6.66	6.36
Conductivity (µS/cm)	33.1	33.2	51.0	51.1	25.9	26.1	27.2	27.7	42.8	43.3

TABLE2C-4
LRTAP Interlaboratory Comparability Study L-26, July 1991
CAL, Values Compared to NWRI Median Values for all Participating Laboratories

Parameter (mg/L)	Sample Number 1		2		3		4		5	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	0.926	0.987	4.090	4.095	2.063	2.210	2.897	3.110	1.693	1.800
Magnesium	0.197	0.200	0.477	0.472	0.454	0.452	0.738	0.740	0.672	0.671
Sodium	0.091	0.100	0.529	0.550	0.815	0.835	0.987	1.010	4.060	4.030
Potassium	0.034	0.040	0.201	0.215	0.127	0.140	0.511	0.540	0.269	0.290
Ammonium	<0.02	<0.01	<0.02	0.04	0.10	0.10	<0.02	0.03	<0.02	0.01
Nitrate	0.09	0.10	3.19	3.16	<0.03	0.04	0.53	0.53	0.22	0.21
Chloride	0.10	0.11	0.19	0.18	0.53	0.56	1.21	1.21	5.26	5.16
Sulfate	6.01	6.02	5.60	5.56	0.75	0.76	7.87	7.74	2.80	2.78
pH (units)	4.25	4.26	6.84	6.75	4.91	4.92	6.68	6.58	6.53	6.38
Conductivity (/tS/cm)	34.0	33.5	31.8	31.9	21.9	21.7	33.7	33.7	36.5	35.9

TABLE C-4 (continued)
LRTAP Interlaboratory Comparability Study L-26-July 1991
CAL Values Compared to NWRI Median Values for all Participating Laboratories

Parameter (mg/L)	Sample Number									
	6		7		8		9		10	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	2.303	2.475	1.469	1.550	3.062	3.287	12.81	13.30	6.430	6.530
Magnesium	0.668	0.670	0.578	0.570	0.978	1.060	2.860	2.760	0.635	0.620
Sodium	1.330	1.340	0.524	0.540	0.189	0.200	1.280	1.299	0.796	0.808
Potassium	0.204	0.220	0.458	0.480	0.176	0.190	0.476	0.500	0.273	0.287
Ammonium	<0.02	<0.01	<0.02	<0.01	1.46	1.48	<0.02	<0.01	0.05	0.06
Nitrate	3.01	3.05	0.97	0.98	7.13	7.17	1.55	1.55	0.49	0.49
Chloride	2.47	2.48	0.19	0.20	0.49	0.51	1.07	1.32	0.35	0.38
Sulfate	6.21	6.24	3.26	3.24	6.70	6.66	3.32	3.27	5.77	5.76
pH (units)	5.04	5.06	6.48	6.28	6.82	6.46	7.90	7.71	7.51	7.30
Conductivity (µS/cm)	35.9	35.1	18.6	18.6	43.5	43.5	95.0	95.5	45.4	45.8

TABLE C-5
LRTAP Interlaboratory Comparability Study L-26, December 1991, CAL, Values Compared to NWRI Median Values for all Participating Laboratories

Parameter (mg/L)	Sample Number 1		2		3		4		5	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	1.290	1.300	0.321	0.320	0.765	0.766	1.330	1.330	12.92	13.35
Magnesium	0.272	0.270	0.067	0.070	0.244	0.240	0.386	0.380	2.740	2.750
Sodium	0.130	0.140	1.003	1.000	0.053	0.060	0.085	0.090	1.337	1.310
Potassium	0.056	0.060	2.657	2.600	0.046	0.050	0.073	0.071	0.497	0.500
Ammonium	<0.02	<0.01	<0.02	<0.01	<0.02	<0.01	<0.02	<0.01	<0.02	<0.01
Nitrate	0.13	0.13	12.04	12.04	0.84	0.84	1.24	1.18	1.59	1.62
Chloride	0.14	0.14	4.00	4.00	0.15	0.15	0.23	0.24	1.69	1.33
Sulfate	7.07	7.16	1.81	1.79	3.68	3.68	3.58	3.54	3.36	3.30
pH (units)	4.23	4.23	3.72	3.72	4.55	4.53	5.72	5.58	7.79	7.74
Conductivity (µS/cm)	39.3	37.6	104.1	101.6	21.4	21.4	14.6	15.0	95.2	94.3

TABLE C-5 (continued)
LRTAP Interlaboratory Comparability Study L-26, December 1991,
CAL Values Compared to NWRI Median Values for all Participating Laboratories

Parameter (mg/L)	Sample Number 6		7		8		9		10	
	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI	CAL	NWRI
Calcium	8.49	8.65	7.01	7.07	6.91	6.98	2.405	2.440	6.820	6.880
Magnesium	2.65	2.65	0.744	0.760	0.736	0.745	0.690	0.690	0.733	0.740
Sodium	0.196	0.200	0.898	0.896	0.872	0.860	1.206	1.180	0.873	0.859
Potassium	0.320	0.322	0.250	0.250	0.249	0.240	0.419	0.414	0.238	0.240
Ammonium	2.06	2.14	.03	.04	<0.02	0.01	<0.02	<0.01	0.03	0.03
Nitrate	13.1	13.0	0.40	0.40	0.35	0.35	0.22	0.22	0.27	0.26
Chloride	0.69	0.84	0.35	0.34	0.30	0.29	0.24	0.24	0.29	0.28
Sulfate	23.12	22.80	6.40	6.45	6.28	6.27	3.74	3.70	6.31	6.30
pH (units)	6.57	6.48	7.37	7.28	7.39	7.23	7.06	7.03	7.37	7.22
Conductivity (µS/cm)	98.2	97.4	49.4	49.2	48.1	48.1	26.1	26.2	47.5	47.6

TABLE C-6
EMEP Intercomparison #12
April 1991

Parameter (mg/L)	Sample Number G1 CAL	G1 EMEP	G2 CAL	G2 EMEP	G3 CAL	G3 EMEP	G4 CAL	G4 EMEP
Calcium	0.303	0.307	0.788	0.814	0.705	0.728	0.339	0.345
Magnesium	0.181	0.186	0.148	0.155	0.309	0.310	0.284	0.279
Sodium	0.784	0.864	0.650	0.709	0.565	0.617	1.018	1.100
Potassium	0.371	0.407	0.281	0.306	0.422	0.458	0.245	0.255
Ammonium	0.27	0.31	0.39	0.41	0.63	0.67	0.73	0.78
Nitrate	2.79	2.73	3.28	3.21	4.34	4.19	4.65	4.52
Chloride	0.76	0.75	0.35	0.35	0.29	0.29	0.87	0.87
Sulfate	5.87	5.79	6.50	6.40	5.45	5.37	4.64	4.57
pH (units)	4.06	4.05	4.11	4.10	4.29	4.30	4.30	4.26
Conductivity (µS/cm)	50.4	51.4	48.6	49.9	39.5	40.3	39.5	42.1

TABLE C-7
WMO Fourteenth Analysis on Reference Precipitation Samples
August 1991

	Sample Number					
	1187		2427		3764	
Parameter	CAL	WMO	CAL	WMO	CAL	WMO
Calcium	0.060	0.057	0.138	0.136	0.414	0.391
Magnesium	0.021	0.023	0.018	0.020	0.117	0.117
Sodium	0.239	0.245	0.282	0.285	1.835	1.870
Potassium	0.062	0.078	0.080	0.086	0.736	0.775
Ammonium	0.13	0.15	0.80	0.81	1.08	1.10
Nitrate	0.62	0.64	0.62	0.66	4.60	4.53
Chloride	0.390	0.398	0.650	0.650	2.89	2.843
Sulfate	1.68	1.55	8.15	7.52	12.6	11.3
pH (units)	4.48	4.50	3.89	3.886	3.65	3.621
Conductivity (µS/cm)	17.4	15.64	65.7	62.818	125.7	123.19

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