

QUALITY ASSURANCE REPORT
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM
2003-2004

Laboratory Operations
Central Analytical Laboratory

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Abstract

The National Atmospheric Deposition Program (NADP) and the Central Analytical Laboratory (CAL) have been in operation since 1978. Since the beginning of the network, quality assurance has been of paramount importance. The *Quality Assurance Report, National Atmospheric Deposition Program, 2003-2004*, describes the quality assurance measures used at the CAL for the NADP/National Trends Network (NTN) and NADP/Atmospheric Integrated Research Monitoring Network (AIRMoN), and reports the results of these programs. The goal of the CAL quality assurance program is to provide reliable, consistent, high-quality data that fulfill the needs of researchers and other data users. This is achieved by incorporating quality control and quality assurance checks throughout the sample flow process. System blanks and control checks are included at strategic sample and data flow points. Results are compiled to generate information about the quality of the data, which are presented in tables, figures, or brief written explanations. The CAL was within the quality control objectives for the networks in 2003 and 2004.

Acknowledgments

This *Quality Assurance Report*, a product of many individuals, summarizes the quality assurance measures at the Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) and the NADP/Atmospheric Integrated Research Monitoring Network (NADP/AIRMoN). The U.S. Geological Survey (USGS) Branch of Quality Systems coordinates the external interlaboratory comparison program. Karen Harlin and Van Bowersox, NADP Program Office, provide ongoing input and support throughout the year. Dedicated analytical staff analyze thousands of samples with the support of conscientious sample receiving and processing personnel. Pam Bedient helped compile and format the text, tables, and files. Christopher Lehmann reviewed this document and provided valuable input.

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Executive Summary

The *Quality Assurance Plan NADP/NTN Deposition Monitoring* defines the quality assurance (QA) goals of the National Atmospheric Deposition Program (NADP). Precipitation samples collected by the National Trends Network (NTN) and the Atmospheric Integrated Research Monitoring Network (AIRMoN) of NADP are analyzed at the Central Analytical Laboratory (CAL) located at the Illinois State Water Survey in Champaign, Illinois. As the CAL for NADP, the laboratory must comply with all QA mandates in the NADP Quality Assurance Plan (QAP). The CAL was in compliance with the NADP QAP in 2003 and 2004.

Weekly QA procedures ensure that all materials coming into contact with the precipitation samples do not contaminate the samples. Any problems that arise must be investigated, documented, and eliminated if possible or practical. Blank analyses, matrix-spiked analyses, internal blind sample analyses for NTN and AIRMoN, and replicate analyses for 2003 and 2004 were in compliance with the NADP QAP.

Monthly evaluation of laboratory control charts, reanalysis samples, Ion Percent Differences, and Conductance Percent Differences showed the CAL to be in compliance with the NADP QAP for both 2003 and 2004.

Interlaboratory comparison studies are vital in determining CAL performance and that of other laboratories around the world doing similar work. In 2003 and again in 2004, the CAL participated in five different independent studies in addition to the U.S. Geological Survey (USGS) laboratory intercomparison study program. The USGS operates the QA program for the NADP/NTN. The CAL performed well with the USGS program. In 2003 and 2004, the CAL was under contract to prepare samples for the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) intercomparison studies. Although the CAL participated in the studies, the CAL results were not included in the final study statistics because samples were made and initially tested at the CAL. The CAL results were favorable, when unofficially compared with those from other participating laboratories. The National Water Research Institute (NWRI) of Canada conducted two intercomparison studies in 2003 and two in 2004. The CAL ranked "satisfactory" in 2003 and "good" in 2004. The fifth intercomparison study each year was with the Norwegian Institute for Air Research (NILU) 21st and 22nd European Monitoring and Evaluation Programme (EMEP) intercomparisons of analytical methods for atmospheric precipitation. All results were within the standard expected variation for the analyte.

Overall, the CAL has performed within the specifications of the NADP QA Plan as well as performing well in all intercomparison studies during 2003 and 2004. Based on these intercomparison studies, the CAL continues to be one of the best atmospheric precipitation laboratories in the world.

I. Introduction

This *Quality Assurance (QA) Report* describes and summarizes the results of the National Atmospheric Deposition Program (NADP) Central Analytical Laboratory (CAL) QA program for 2003 and 2004. The procedures for supporting reliable data are demonstrated through a QA program, which is defined in the CAL Quality Assurance Plan (QAP) and laboratory Standard Operating Procedures (SOPs). This report, through text, figures, and tables, assesses the precision and bias of the data generated and reported through the NADP.

The Atmospheric Chemistry Laboratory at the Illinois State Water Survey (ISWS) was selected in the spring of 1978 to be the CAL for the NADP – a role it has held ever since. In 2003 and 2004, the CAL analyzed samples from more than 250 NADP/National Trends Network (NTN) sites that collect weekly precipitation samples throughout the United States and parts of Canada. The Atmospheric Integrated Research Monitoring Network (AIRMoN) protocol was implemented in 1992, and its QA program was put into place. Since then, NADP/NTN and NADP/AIRMoN have shared the same analytical staff and methodology. The AIRMoN sample protocol and analytical methodologies are different from those of NTN, but both maintain the same high quality control (QC) objectives. For specific details about both NADP/NTN and NADP/AIRMoN analysis protocols refer to the CAL QAP and SOPs for the laboratory and data operations.

The policy at the CAL has always been to take the lead role in improving analytical techniques for atmospheric deposition. As laboratory techniques improve and as better instrumentation becomes available, the CAL has always changed to improve the quality of the data. In addition, new staff are hired as the need arises. One new employee was hired for the laboratory in 2004, Catherine Kohonen. John Ingram was hired in May, 2003, to replace the departing Angela Rakow in the data review team. There were two retirees in 2003. Sue Bachman retired beginning January, 2003, and Greg Dzursin retired in May, 2003. In January 2004, the Ion Coupled Plasma-Optical Emission Spectrometer came online replacing the Flame Atomic Absorption Spectrometer for calcium, sodium, magnesium, and potassium.

The instrumentation and analytes measured during 2003 and 2004 are listed in Table I-1. In 2004, a new method was developed to determine Method Detection Limits (MDLs), using one of the internal blind solutions. The sample used approximates the tenth percentile of NADP/NTN precipitation samples. Using this low concentration sample and having it pass through the laboratory as a blind, the MDLs could more accurately reflect the conditions seen by the precipitation samples themselves. Table I-1 includes the MDLs for 2003 and 2004. For more information about the MDL, see the CAL QAP. Laboratory MDLs are maintained at or below the MDLs listed in the *NADP Quality Assurance Plan* (Simmons et al., 1990, revised 1993).

The CAL data is assessed and improved through quality assurance programs. This report addresses QA data indicated in bold in Table I-2, which summarizes the various QA/QC components and their frequency of occurrence. Supporting information, including a glossary of terms and calculations used in this document, is available at <http://nadp.sws.uiuc.edu/cal..>

Table I-1. Analytes, Instrumentation, and MDLs for 2003 and 2004.

<i>Analyte</i>	<i>Instrument</i>	<i>MDL</i>	<i>Length of service</i>
Calcium (Ca ²⁺)	Flame Atomic Absorption Spectrometer	0.009 ^a	1978-2003
	Ion Coupled Plasma-Optical Emission Spectrometer	0.002 ^b	2004
Potassium (K ⁺)	Flame Atomic Absorption Spectrometer	0.003	1978-2003
	Ion Coupled Plasma-Optical Emission Spectrometer	0.001	2004
Magnesium (Mg ⁺)	Flame Atomic Absorption Spectrometer	0.003	1978-2003
	Ion Coupled Plasma-Optical Emission Spectrometer	0.001	2004
Sodium (Na ⁺)	Flame Atomic Absorption Spectrometer	0.003	1978-2003
	Ion Coupled Plasma-Optical Emission Spectrometer	0.003	2004
Ammonium (NH ₄ ⁺)	Phenate (Flow Injection Colorimetry)	0.02	1978-2004
Orthophosphate (PO ₄ ³⁻)	Phenate (Flow Injection Colorimetry)	0.009	1978-2004
Chloride (Cl ⁻)	Ion Chromatography	0.005	1985-2004
Nitrate (NO ₃ ⁻)	Ion Chromatography	0.010	1985-2004
Sulfate (SO ₄ ²⁻)	Ion Chromatography	0.010	1985-2004
pH	Corning pH meter		1997-2004
	Broadly-James Electrode		1989-2004
Conductivity	YSI Conductivity meter		2003-2004

Notes:

^a The first number is the MDL for 2003.

^b The second number is the MDL for 2004

**Table I-2. NADP/NTN and NADP/AIRMoN Laboratory
QA/QC Program Summary, 2003 and 2004**

- I. Daily (Quality Control)
 - A. Standardize instruments and verify standardization curves using QCS.
 - 1. Use CAL-formulated solutions of simulated rainwater, QCS solutions that represent the 25th and 75th percentile concentrations of network samples.
 - 2. Measure QCS solutions every 12 samples.
 - 3. Record and plot QCS solution values on daily control charts.
 - 4. Repeat standardization as indicated by QCS solution measurements.
 - B. Prepare records of standards preparation and update instrument maintenance records.
 - C. Inspect control charts generated from QCS solution measurements.

- II. Weekly
 - A. Evaluate laboratory water and supplies for cleanliness.
 - 1. Analyze the laboratory's deionized (DI) water.
 - 2. Use DI water and simulated rainwater for filter leaching.
 - 3. Use DI water and simulated rainwater for
 - a. Sample collection bucket.
 - b. Snap-on lids for sample collection bucket.
 - c. One-liter sample bottles.
 - d. Storage and shipping bags.
 - B. Analyze internal blind audit samples designated SWS1, SWS2, and SWS3.
 - 1. SWS1: Use simulated rainwater at two concentrations, unfiltered.
 - 2. SWS2: Use DI water and a simulated rainwater sample, unfiltered.
 - 3. SWS3: Use all four of the above solutions in rotation, filtered.
 - C. Split 2 percent of NTN samples for replicate analysis.
 - D. Split 2 percent of AIRMoN samples for replicate analysis.
 - E. Analyze internal blind audit sample for AIRMoN from site IL11.

- III. Monthly
 - A. Leach AIRMoN 250-mL HDPE bottles with simulated rainwater and analyze leachates with weekly blanks.
 - B. Evaluate internal blind audit and replicate data from printouts.
 - C. Select samples for reanalysis by computer-based ion percent and conductivity percent differences and random selection (1% monthly for NTN and 2% monthly for AIRMoN).
 - 1. Evaluate reanalysis data.
 - 2. Edit data record as needed.
 - D. Measure USGS interlaboratory comparison samples every two weeks and send to the USGS, Water Resources Division, Branch of Quality Systems in Denver every three months.
 - E. Validate QCS solution for field chemistry prior to shipment to sites as needed.

Table I-2 (concluded)

IV. Semiannually

- A. Prepare reports for spring and fall NADP subcommittee meetings.
- B. Participate in additional interlaboratory comparisons.

V. Annually

- A. Submit QA report for publication.
- B. Participate in interlaboratory comparisons.
- C. Compute laboratory MDLs.

The NTN samples are filtered into pre-washed 60-mL high-density polyethylene (HDPE) round bottles using 0.45 micrometer (μm) pore-size polyethersulfone filters following pH and conductivity measurements. The AIRMoN samples are never filtered, but are kept at about 4°C in the 250-mL shipping bottles into which they were decanted at the site. The AIRMoN samples are analyzed in a specified order: pH and conductivity; ammonium and orthophosphate; chloride, nitrate, and sulfate; and calcium, magnesium, sodium, and potassium. This order of analysis was mandated in order to analyze the least stable parameters first. After the NTN samples are filtered, there is no specified order of analysis. For more details on NTN and AIRMoN sample handling and analyses, see the CAL QAP and the laboratory SOPs.

Quality Control Check Samples (QCS) are used throughout the laboratory to confirm that the instrumentation is working properly and to maintain them within strict control limits. These solutions are prepared in-house and are tested (Simmons et al., 1991) prior to use as QCS solutions. These solutions, referred to as FR25 and FR75, approximate the 25th and 75th percentile of the NTN precipitation samples and are used as QCS solutions for all measurements except for orthophosphate [orthophosphate is not stable, especially at the low concentrations found in NADP samples (Ridder et al., 1985)]. Instead, nutrient concentrates from Environmental Resource Association¹ are diluted and used for orthophosphate QCS solutions. The two synthetic rain QCS solutions (or nutrient solutions for orthophosphate) are analyzed after standardization of the instrument and at the end of the analytical run. After every twelve samples, one of the QCS solutions and either a high or low calibration standard is analyzed to monitor the instrument during the course of the analytical run. If the high QCS is analyzed, then a low standard is analyzed with it and vice versa. If any of the QCS solutions analyzed at any time during the run are outside the tolerance levels determined at the beginning of the year, the instrument is considered to be out of control. The analyst must stop analysis as soon as this happens and determine why the measurement of the QCS was out of control. This might mean restandardizing the instrument, measuring another QCS, or getting a fresh solution of QCS to measure. Once it is determined that the instrument is in control, all samples measured since the last in control QCS was analyzed are remeasured. Control charts and the measured concentrations of all QCS solutions are available upon request.

Significant Changes during 2003 - 2004

- New Varian ICP-OES for cations (Na, K, Ca, Mg) purchased and put into service for samples analyzed after January 1, 2004.
- Equipment and software for Flow Injection Analysis of ammonia and orthophosphate was updated in 2004.
- Sample handling protocols for “Wet Add” (WA) samples changed to “Wet Dilute” (WD) for samples received after January 1, 2004.

¹Environmental Resource Association, 5540 Marshall Street, Arvada, CO 80002, Simple Nutrients, catalog number 584.
Disclaimer: The use of trade or manufacturer’s names does not constitute an endorsement by the Illinois State Water Survey, the NADP, or the CAL

II. Quality Assurance/Quality Control Procedures

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

A. Internal Blind Audit

1. NADP/NTN

Each week the QA Specialist submits three solutions of known concentrations with completed Field Observer Report Forms (FORFs) to the sample processing area where laboratory identification numbers are assigned. These samples are processed with the network samples, but two of the three samples are unfiltered to monitor for possible filter contamination. These samples are identified as sites SWS1, SWS2, and SWS3. In 2003 and 2004, the SWS1 samples were High-Purity Standards² Simulated Rainwater 1 (H-PS SR1) and 2 (H-PS SR2), which were alternated weekly. The SWS2 samples were alternated weekly between DI water from the ion chromatography laboratory and a synthetic rain sample made in house that approximated the 10th percentile of NTN sample concentrations (FR10). The SWS1 and SWS2 samples were not filtered. The filtered SWS3 samples were H-PS SR1, H-PS SR2, DI water, and FR10 submitted in rotation.

Tables II-1 through Table II-8 summarize the 2003 and 2004 data from the weekly internal blind audit samples for NTN. The blind samples are randomly dispersed throughout the sample queue, and, therefore, the derived bias and precision estimates are representative of precipitation sample measurements. The SWS1 and SWS2 samples overall show less bias and less variability than the filtered SWS3 samples which have a smaller sample population for each solution. For parameters with concentrations near the detection limits, there is a higher standard deviation due to the noise of the instrument and, therefore, the measurement. The filtered internally formulated synthetic precipitation samples (FR10) and the filtered DI water also show less bias than the filtered High-Purity Standards samples except for parameters close to the detection limits. The lower biases for parameters in the internally formulated solution, both filtered and unfiltered, may be due to the initial concentrations for this solution as determined in the laboratory, eliminating biases caused by the instrument or instrument standardization calibration. The High-Purity Standards solutions have lower pH than either DI water or the FR10 solution. The lower pH may cause leaching from the filters and, therefore, producing a bias in those solutions. This possible explanation of what is occurring with the QCS solutions and possibly the samples is being investigated.

²High-Purity Standards, P.O. Box 41727, Charleston, SC 29423, catalog numbers SR-1 and SR-2.

Disclaimer: The use of trade or manufacturer's names does not constitute an endorsement by the Illinois State Water Survey, the NADP, or the CAL.

Table II-1. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, High Purity Standards Simulated Rainwater 1 (HPS-SR1) Unfiltered and Filtered, 2003

<i>Parameter</i>	<i>Target Concentration^a</i> <i>(mg/L)</i>	<i>Mean Concentration</i> <i>(mg/L)</i>	<i>Bias</i> <i>(mg/L)</i>	<i>Bias</i> <i>(%)</i>	<i>Standard Deviation</i> <i>(mg/L)</i>	<i>RSD</i> <i>(%)(mg/L)</i>	<i>MDL</i> <i>(mg/L)</i>	<i>5th%</i>
Calcium	0.012	0.011 ^b	-0.001	-10.3	0.004	36.1	0.009	0.017
		0.048 ^c	0.036	299.4	0.018	38.5		
Magnesium	0.019	0.020	0.001	5.3	0.002	8.4	0.003	0.003
		0.014	-0.005	-25.9	0.002	16.1		
Sodium	0.20	0.196	-0.004	-2.0	0.005	2.4	0.003	0.004
		0.188	-0.012	-6.0	0.003	1.7		
Potassium	0.053	0.050	-0.003	-6.3	0.002	3.1	0.003	0.002
		0.048	-0.005	-9.0	0.002	3.8		
Ammonium	0.100	0.150	0.050	50.0	0.014	9.0	0.02	0.022
		0.139	0.039	39.0	0.012	8.4		
Sulfate	2.47	2.512	0.042	1.7	0.020	0.8	0.010	0.130
		2.416	-0.054	-2.2	0.018	0.8		
Nitrate	0.50	0.501	0.001	0.3	0.006	1.3	0.010	0.269
		0.486	-0.014	-2.8	0.005	1.1		
Chloride	0.25	0.219	-0.031	-12.4	0.004	1.8	0.005	0.026
		0.213	-0.037	-6.0	0.004	1.7		
pH (units)	4.36	4.35	-0.01	-0.2	0.02	0.5		6.43
		4.35	-0.01	-0.3	0.02	0.4		
H (µeq/L)	43.7	44.7	1.1	2.5	2.3	5.1		0.4
		45.1	1.4	3.3	1.7	3.7		
Specific Conductance (µS/cm)	21	23.7	2.7	12.7	1.1	4.8		3.4
		23.7	2.7	12.8	1.0	4.1		

Notes:

There were 26 unfiltered and 13 filtered HPS-SR1 (lot #232505) samples in 2003.

^a Target Concentrations are those reported by High-Purity Standards.

^b Concentration values for unfiltered H-PS SR1.

^c Concentration values for filtered H-PS SR1

Table II-2. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, High Purity Standards Simulated Rainwater 1 (HPS-SR1), Unfiltered and Filtered, 2004

<i>Parameter</i>	<i>Target Concentration^a</i> <i>(mg/L)</i>	<i>Mean Concentration</i> <i>(mg/L)</i>	<i>Bias</i> <i>(mg/L)</i>	<i>Bias</i> <i>(%)</i>	<i>Standard Deviation</i> <i>(mg/L)</i>	<i>RSD</i> <i>(%)</i>	<i>MDL</i> <i>(mg/L)</i>	<i>5th%</i> <i>(mg/L)</i>
Calcium	0.012	0.013 ^b	0.001	9.6	0.007	49.7	0.002	0.020
		0.041 ^c	0.029	239.1	0.006	14.6		
Magnesium	0.019	0.019	0.000	0.6	0.002	7.9	0.001	0.003
		0.012	-0.007	-35.6	0.001	5.7		
Sodium	0.20	0.190	-0.010	-4.8	0.006	3.2	0.003	0.006
		0.185	-0.015	-7.3	0.009	4.7		
Potassium	0.053	0.049	-0.005	-8.5	0.002	3.1	0.001	0.003
		0.047	-0.006	-11.5	0.002	5.0		
Ammonium	0.100	0.101	0.001	0.7	0.006	5.7	0.005	0.013
		0.102	0.002	1.5	0.004	3.9		
Sulfate	2.47	2.491	0.021	0.8	0.022	0.9	0.013	0.135
		2.390	-0.080	-3.2	0.035	1.5		
Nitrate	0.50	0.497	-0.003	-0.7	0.006	1.1	0.009	0.169
		0.479	-0.021	-4.1	0.009	1.8		
Chloride	0.25	0.214	-0.036	-14.5	0.005	2.2	0.008	0.019
		0.210	-0.040	-16.0	0.006	3.0		
pH (units)	4.32	4.34	0.02	0.4	0.03	0.7		6.53
		4.33	0.01	0.3	0.03	0.6		
H (µeq/L)	47.9	46.0	-1.9	-3.9	3.1	6.7		0.3
		46.5	-1.3	-2.8	2.6	5.7		
Specific Conductance (µS/cm)	22	23.9	1.9	8.4	0.8	3.2		3.4
		24.1	2.1	9.4	1.1	4.6		

Notes:

There were 26 unfiltered and 13 filtered HPR-SR1 (lot # 334413) samples in 2004.

^a Target Concentrations are those reported by High-Purity Standards.

^b Concentration values for unfiltered H-PS SR1.

^c Concentration values for filtered H-PS SR1.

Table II-3. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, High Purity Standards Simulated Rainwater 2 (HPS-SR2) Unfiltered and Filtered, 2003

<i>Parameter</i>	<i>Target Concentration^a</i> <i>(mg/L)</i>	<i>Mean Concentration</i> <i>(mg/L)</i>	<i>Bias</i> <i>(mg/L)</i>	<i>Bias</i> <i>(%)</i>	<i>Standard Deviation</i> <i>(mg/L)</i>	<i>RSD</i> <i>(%)(mg/L)</i>	<i>MDL</i> <i>(mg/L)</i>	<i>5th%</i>
Calcium	0.055	0.054 ^b 0.103 ^c	-0.001 0.048	-1.0 88.0	0.013 0.039	23.3 37.7	0.009	0.017
Magnesium	0.051	0.050 0.049	-0.001 -0.002	-2.5 -3.4	0.001 0.002	2.9 5.0	0.003	0.003
Sodium	0.40	0.389 0.384	-0.011 -0.019	-2.7 -4.8	0.012 0.008	3.0 2.1	0.003	0.004
Potassium	0.093	0.102 0.099	0.009 0.006	10.0 6.7	0.003 0.003	3.0 2.9	0.003	0.002
Ammonium	1.00	0.987 0.955	-0.013 -0.045	-1.3 -4.5	0.025 0.032	2.5 3.4	0.02	0.022
Sulfate	10.1	10.208 9.893	0.108 -0.207	1.1 -2.9	0.104 0.097	1.0 1.0	0.010	0.130
Nitrate	7.00	7.126 6.924	0.126 -0.076	1.8 -1.4	0.071 0.083	1.0 1.2	0.010	0.269
Chloride	0.98	0.985 0.958	0.005 -0.022	0.5 -2.9	0.014 0.019	1.4 2.0	0.005	0.026
pH (units)	3.57	3.61 3.61	0.04 0.04	1.2 5.7	0.02 0.02	0.6 0.5		6.43
H (µeq/L)	269.2	243.1 244.8	-26.0 -24.4	-9.7 -36.1	11.4 10.5	4.7 4.3		0.4
Specific Conductance (µS/cm)	113.3	125.9 126.4	12.6 13.1	11.2 7.0	1.7 1.9	1.4 1.5		4.83.4

Notes:

There were 26 unfiltered and 13 filtered HPS-SR2 (lot #232503) samples in 2003.

^a Target Concentrations are those reported by High-Purity Standards.

^b Concentration values for unfiltered H-PS SR2.

^c Concentration values for filtered H-PS SR2.

Table II-4. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, High Purity Standards Simulated Rainwater 1 (HPS-SR1), Unfiltered and Filtered, 2004

<i>Parameter</i>	<i>Target Concentration^a</i> <i>(mg/L)</i>	<i>Mean Concentration</i> <i>(mg/L)</i>	<i>Bias</i> <i>(mg/L)</i>	<i>Bias</i> <i>(%)</i>	<i>Standard Deviation</i> <i>(mg/L)</i>	<i>RSD</i> <i>(%)</i>	<i>MDL</i> <i>(mg/L)</i>	<i>5th%</i> <i>(mg/L)</i>
Calcium	0.055	0.057 ^b	0.002	4.4	0.018	31.3	0.002	0.020
		0.094 ^c	0.039	71.5	0.012	12.4		
Magnesium	0.050	0.049	-0.001	-2.1	0.001	2.7	0.001	0.003
		0.048	-0.002	-3.2	0.003	6.1		
Sodium	0.40	0.385	-0.015	-3.7	0.012	3.2	0.003	0.006
		0.379	-0.021	-5.2	0.009	2.4		
Potassium	0.093	0.102	0.009	9.7	0.003	3.2	0.001	0.003
		0.100	0.007	7.9	0.004	4.0		
Ammonium	1.00	0.985	-0.015	-1.5	0.013	1.3	0.005	0.013
		0.959	-0.041	-4.1	0.014	1.5		
Sulfate	10.1	10.126	0.026	0.3	0.140	1.4	0.013	0.135
		9.804	-0.296	-2.9	0.173	1.8		
Nitrate	7.0	7.093	0.093	1.3	0.099	1.4	0.009	0.169
		6.901	-0.099	-1.4	0.100	1.4		
Chloride	0.98	0.980	0.000	0.0	0.019	2.0	0.008	0.019
		0.952	-0.028	-2.9	0.034	3.6		
pH (units)	3.43	3.60	0.17	5.1	0.03	0.7		6.53
		3.63	0.20	5.7	0.03	0.7		
H (µeq/L)	371.5	249.4	-122.1	-32.9	15.0	6.0	0.3	
		237.4	-134.1	-36.1	14.7	6.2		
Specific Conductance (µS/cm)	118	126.8	8.8	7.4	1.8	1.4		3.4
		126.3	8.3	7.0	3.0	2.4		

Notes:

There were 26 unfiltered and 13 filtered HPR-SR2 (lot # 334508) samples in 2004.

^a Target Concentrations are those reported by High-Purity Standards.

^b Concentration values for unfiltered H-PS SR2.

^c Concentration values for filtered H-PS SR2.

Table II-5. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Internally Formulated Simulated Rain (03FR10), Unfiltered and Filtered, 2003

<i>Parameter</i>	<i>Target Concentration (mg/L)</i>	<i>Mean Concentration (mg/L)</i>	<i>Bias (mg/L)</i>	<i>Bias (%)</i>	<i>Standard Deviation (mg/L)</i>	<i>RSD (%)</i>	<i>MDL (mg/L)</i>	<i>5th% (mg/L)</i>
Calcium	0.026 ^a	0.027 ^b	0.0009	3.4	0.005	18.7	0.009	0.017
		0.032 ^c	0.006	23.4	0.008	24.6		
Magnesium	0.006	0.007	0.001	16.0	0.0006	9.3	0.003	0.003
		0.005	-0.001	-17.9	0.001	25.8		
Sodium	0.018	0.017	-0.0006	-3.2	0.001	8.6	0.003	0.004
		0.019	0.0006	3.4	0.003	16.8		
Potassium	0.005	0.006	0.0007	15.4	0.001	18.8	0.003	0.002
		0.006	0.0008	16.9	0.003	48.3		
Ammonium	0.037	0.038	0.0007	1.8	0.003	6.7	0.02	0.022
		0.041	0.004	10.4	0.005	11.1		
Sulfate	0.245	0.245	0.0002	0.8	0.008	3.4	0.010	0.130
		0.241	-0.004	-1.5	0.003	1.8		
Nitrate	0.187	0.187	0.0003	0.2	0.003	1.9	0.010	0.269
		0.184	-0.003	-1.5	0.003	1.8		
Chloride	0.050	0.054	0.004	7.8	0.003	5.6	0.005	0.026
		0.055	0.005	10.6	0.002	11.5		
pH (units)	5.22	5.25	0.03	0.5	0.03	0.7		6.43
		5.24	-0.25	-4.2	0.6	9.7		
H (µeq/L)	6.0	5.70	-0.3	-5.6	0.4	7.7		0.4
		5.77	-0.25	-4.2	0.6	9.7		
Specific Conductance (µS/cm)	3.4	3.5	0.1	4.2	0.3	8.9		3.4
		3.7	0.3	8.8	0.6	15.9		

Notes:

There were 26 unfiltered and 13 filtered 03FR10 samples in 2003.

^a Target concentrations for 03FR10.

^b Unfiltered 03FR10.

^c Filtered 03FR10.

Table II-6 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Internally Formulated Simulated Rain (04FR10), Unfiltered and Filtered, 2004

<i>Parameter</i>	<i>Target Concentration (mg/L)</i>	<i>Mean Concentration (mg/L)</i>	<i>Bias (mg/L)</i>	<i>Bias (%)</i>	<i>Standard Deviation (mg/L)</i>	<i>RSD (%)</i>	<i>MDL (mg/L)</i>	<i>5th% (mg/L)</i>
Calcium	0.030 ^a	0.033 ^b 0.030 ^c	0.003 0.000	11.5 -0.4	0.005 0.0007	16.3 2.3	0.009	0.017
Magnesium	0.007	0.005 0.007	-0.002 0.000	-28.6 -3.3	0.001 0.0004	26.0 6.2	0.003	0.003
Sodium	0.019	0.019 0.019	0.000 0.000	0.4 -0.8	0.001 0.001	4.3 7.0	0.003	0.004
Potassium	0.005	0.004 0.004	-0.001 -0.001	-15.4 -15.4	0.0004 0.0004	10.0 10.0	0.003	0.002
Ammonium	0.038	0.037 0.037	-0.001 -0.001	-3.6 -3.8	0.002 0.002	9.6 5.1	0.02	0.022
Sulfate	0.251	0.248 0.255	-0.003 0.004	-1.1 1.5	0.005 0.005	2.0 2.0	0.010	0.130
Nitrate	0.189	0.187 0.192	-0.002 0.003	-0.9 1.4	0.005 0.003	2.6 1.8	0.010	0.269
Chloride	0.053	0.053 0.053	0.000 0.000	0.7 0.3	0.002 0.003	3.6 5.8	0.005	0.026
pH (units)	5.23	5.22 5.24	-0.01 0.01	-0.16 0.3	0.06 0.06	1.1 1.1		6.43
H (µeq/L)	5.9	6.06 5.8	0.017 -0.1	2.9 -2.5	0.8 0.7	13.6 13.0		0.4
Specific Conductance (µS/cm)	3.3	3.9 3.9	0.6 0.6	18.9 17.2	0.5 0.4	13.6 9.6		3.4

Notes:

There were 26 unfiltered and 13 filtered 04FR10 samples in 2004.

^a Target concentrations for 04FR10.

^b Unfiltered 04FR10.

^c Filtered 04FR10.

Table II-7. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Deionized Water (DI), Unfiltered and Filtered, 2003

<i>Parameter</i>	<i>MDL (mg/L)</i>	<i>Mean Concentration (mg/L)</i>	<i>Bias (mg/L)</i>	<i>Bias (%)</i>	<i>Standard Deviation (mg/L)</i>	<i>RSD (%)</i>	<i>5th% (mg/L)</i>
Calcium	0.009	<0.009 ^a <0.009 ^b	0.000 0.000		0.005 0.005		0.017
Magnesium	0.003	<0.003 <0.003	0.000 0.000		0.0007 0.0006		0.003
Sodium	0.003	<0.003 <0.003	0.000 0.000		0.001 0.001		0.004
Potassium	0.003	<0.003 <0.003	0.000 0.000		0.003 0.0009		0.002
Ammonium	0.02	<0.02 <0.02	0.000 0.000		0.000 0.004		0.022
Sulfate	0.010	<0.010 <0.010	0.000 0.000		0.002 0.004		0.130
Nitrate	0.010	<0.010 <0.010	0.000 0.000		0.000 0.002		0.269
Chloride	0.005	<0.005 <0.005	0.000 0.000		0.003 0.004		0.026
pH (units)		5.62 5.62	-0.03 -0.03	-0.5 -0.6	0.07 0.03	1.3 0.6	6.43
H (µeq/L)		2.4 2.4	0.2 0.2	8.1 8.1	0.4 0.2	16.4 7.4	0.4
Specific Conductance (µS/cm)		1.3 1.3	0.4 0.4	39.1 39.8	0.2 0.5	17.5 39.3	3.4

Notes:

There were 26 unfiltered and 13 filtered DI samples in 2003.

^a Concentration values for unfiltered DI.

^b Concentration values for filtered DI.

Table II-8. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Deionized Water (DI), Unfiltered and Filtered, 2004

<i>Parameter</i>	<i>MDL (mg/L)</i>	<i>Mean Concentration (mg/L)</i>	<i>Bias (mg/L)</i>	<i>Bias (%)</i>	<i>Standard Deviation (mg/L)</i>	<i>RSD (%)</i>	<i>5th% (mg/L)</i>
Calcium	0.002	<0.002 ^a <0.002 ^b	0.000 0.000		0.0006 0.002		0.017
Magnesium	0.001	<0.001 <0.001	0.000 0.000		0.000 0.000		0.003
Sodium	0.003	<0.003 <0.003	0.000 0.000		0.0004 0.001		0.004
Potassium	0.001	<0.001 <0.001	0.000 0.000		0.0008 0.000		0.002
Ammonium	0.005	<0.005 <0.005	0.000 0.000		0.003 0.003		0.022
Sulfate	0.013	<0.013 <0.013	0.000 0.000		0.000 0.005		0.130
Nitrate	0.009	<0.009 <0.009	0.000 0.000		0.000 0.000		0.269
Chloride	0.008	<0.008 <0.008	0.000 0.000		0.002 0.005		0.026
pH (units)	5.65	5.75 5.71	0.10 0.06	1.7 1.1	0.18 0.12	3.2 2.1	6.43
H (µeq/L)	2.2	1.9 2.0	-0.3 -0.2	-12.0 -10.6	0.7 0.5	37.0 26.8	0.4
Specific Conductance (µS/cm)	0.9	1.3 1.2	0.4 0.3	45.7 34.2	0.3 0.2	24.7 16.7	3.4

Notes:

There were 26 unfiltered and 13 filtered DI samples in 2004.

^a Concentration values for unfiltered DI.

^b Concentration values for filtered DI.

2. NADP/AIRMoN

Four times per month, the IL11 (Bondville, Illinois) site operator submits an internal blind sample for inclusion in the AIRMoN analysis queue. In 2003, the solution used was World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) 2002O sample #2 prepared at the CAL for the WMO/GAW second interlaboratory study for 2002. In 2004, two WMO/GAW solutions were used, WMO/GAW 2003O sample #2 and WMO/GAW 2004A sample #2, both prepared at the CAL for the WMO/GAW studies for 2003 and 2004. The “target” concentrations used for statistical comparison were the median found by all participating laboratories in the intercomparison studies. (Coleman et al, 2003 and 2004). Approximately 70 laboratories worldwide participate in these studies.

Table II-9 and Table II-10 are the internal blind sample summary for 2003 and 2004 respectively. The difference seen in the target concentrations versus the concentrations measured at the CAL were less than or equal to the fifth percentile of precipitation concentration and less than or equal to the method detection limit for both 2003 and 2004. This implies that the difference between the measured and the target amounts were within the noise of the instruments.

B. Replicate Samples

Replicate samples serve as another estimator of sample precision. Because these are blind, real precipitation samples, their concentration values should be representative of the large volume sample population. Two percent of the NTN and AIRMoN samples are split for blind replicate analysis. The replicates are separated in the analysis queue and are analyzed at different times than the original samples. The NTN samples are divided at the time of filtration into three 60-mL aliquots: one sample is put on the tray for transfer to the laboratory for initial analysis at its regular place in the queue, one sample is filtered for archival purposes, and one sample is sent back to sample processing where it is assigned a new and higher laboratory identification number and submitted for analysis later. The NTN samples chosen for splits must have sufficient volume to fill three 60-mL bottles after filtration, original, replicate, and archive bottles. The AIRMoN samples are split in a similar manner, although they are not filtered. For more details about how samples are split and how the laboratory identification number is used to track the replicate, refer to the CAL QAP.

Tables II-11 through II-14 summarize the analyses of replicate samples analyzed in 2003 and 2004 for NTN and AIRMoN. Differences are calculated by subtracting the reanalysis value from the original value. Annual summaries of each ion were split into three sections, from the MDL up to ten times the MDL, from ten times the MDL to 100 times the MDL, and samples with concentrations greater than 100 times the MDL. For pH and conductivity two levels were used, below pH of 5 and above pH of 5 for pH and below conductivity of 10 $\mu\text{S}/\text{cm}$ and above a conductivity of 10 $\mu\text{S}/\text{cm}$ for conductance. Because these samples are actual precipitation samples, the concentration of the split samples can cover the entire range of concentrations found in precipitation. The standard deviation estimated from replicate measurements was used to calculate the standard deviations. The last column in Tables II-11 through 14 shows a nonparametric estimator of variability from replicate determinations, where 1.48 times the Median Absolute Difference (MAD) is the estimator of dispersion (Helsel and Hirsch, 1992). A comparison of the Standard Deviations for the SWS1 (Table IV-1) and SWS3 (Table IV-3) to $1.48 \times \text{MAD}$ shows comparable cation and anion precision of the split samples.

Table II-9 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, AIRMoN, 2003

<i>Parameter</i>	<i>Target Concentration^a</i> (mg/L)	<i>Mean^c</i> <i>Concentration</i> (mg/L)	<i>Bias</i> (mg/L)	<i>Bias</i> (%)	<i>Standard</i> <i>Deviation</i> (mg/L)	<i>RSD^d</i> (%)	<i>MDL</i> (mg/L)	<i>5th%</i> (mg/L)
Calcium	0.110 ^b	0.107	-0.003	-2.6	0.005	4.8	0.009	0.004
Magnesium	0.043	0.041	-0.002	-3.7	0.001	3.4	0.003	0.002
Sodium	0.078	0.081	0.003	4.0	0.002	2.9	0.003	0.003
Potassium	0.030	0.030	0.0004	1.5	0.002	5.3	0.003	0.003
Ammonium	0.209	0.206	-0.003	-1.6	0.010	4.8	0.02	0.035
Sulfate	1.028	1.032	0.004	0.4	0.009	0.9	0.010	0.227
Nitrate	1.120	1.116	-0.004	-0.4	0.010	0.9	0.010	0.214
Chloride	0.117	0.117	-0.0002	-0.2	0.003	3.0	0.005	0.018
pH	4.76	4.59	-0.17	-3.6	0.02	0.5		5.20
H (µeq/L)	17.4	25.8	8.4	48.3	1.3	4.9		6.3
Specific Conductance (µS/cm)	11.4	14.9	3.5	30.7	0.3	2.2		5.5

Notes:

This tabulation included 48 internal blinds. Samples were simulated rainwater prepared for the 2002 World Meteorological Organization intercomparison study.

^a Median concentrations used by the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) in their analysis of the data in the 2002 WMO/GAW intercomparison study.

^b The WMO/GAW 2002 O sample number 2.

^c Mean concentration obtained by the CAL from the AIRMoN internal blind samples for 2003.

^d RSD is Relative Standard Deviation.

Table IV-10 Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, AIRMoN, 2004

<i>Parameter</i>	<i>Target Concentration^a</i> (mg/L)	<i>Mean^d</i> <i>Concentration</i> (mg/L)	<i>Bias</i> (mg/L)	<i>Bias</i> (%)	<i>Standard</i> <i>Deviation</i> (mg/L)	<i>RSD^e</i> (%)	<i>MDL</i> (mg/L)	<i>5th%</i> (mg/L)
Calcium	0.051 ^b	0.049	-0.002	-4.0	0.001	2.2	0.002	0.008
	0.260 ^c	0.259	-0.001	-0.5	0.004	1.4		
Magnesium	0.016	0.014	-0.002	-9.6	0.000	3.4	0.001	0.001
	0.052	0.052	0.000	0.8	0.001	1.5		
Sodium	0.038	0.039	0.001	1.8	0.002	4.2	0.003	0.004
	0.190	0.189	-0.001	-0.4	0.004	1.9		
Potassium	0.019	0.018	-0.001	-3.3	0.001	4.1	0.001	0.003
	0.042	0.042	0.000	-0.1	0.001	2.2		
Ammonium	0.106	0.098	-0.008	-7.2	0.002	2.5	0.005	0.036
	0.443	0.442	-0.001	-0.2	0.006	1.3		
Sulfate	0.536	0.544	0.008	1.5	0.007	1.2	0.013	0.286
	2.112	2.129	0.017	0.8	0.012	0.6		
Nitrate	0.567	0.563	-0.004	-0.7	0.006	1.1	0.009	0.268
	1.970	2.007	0.037	1.9	0.017	0.9		
Chloride	0.069	0.068	-0.001	-2.1	0.002	2.6	0.008	0.014
	0.270	0.271	0.001	0.3	0.009	3.2		
pH (units)	4.96	4.64	-0.32	-6.5	0.02	0.4		5.18
	4.46	4.35	-0.11	-2.5	0.03	0.6		
H (µeq/L)	11.0	23.1	12.1	100.6	1.0	4.5		6.6
	34.7	45.0	10.3	29.7	2.6	5.8		
Specific Conductance (µS/cm)	6.8	11.6	4.8	70.8	0.3	2.2		5.9
	22.5	27.4	4.9	21.7	0.7	2.4		

Notes:

This tabulation included 48 internal blinds. Samples were simulated rainwater prepared for the 2003 and 2004 World Meteorological Organization intercomparison study.

^a Median concentrations used by the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) in their analysis of the data in the 2003 and 2004 WMO/GAW intercomparison study.

^b The WMO/GAW 2003 O sample number 2.

^c The WMO/GAW 2004 A sample number 2.

^d Mean concentration obtained by the CAL from the AIRMoN internal blind samples for 2004.

^e RSD is Relative Standard Deviation.

Table II-11. Replicate NADP/NTN Precipitation Samples, 2003

<i>Analyte</i>	<i>Level</i>	<i>Mean Percent Difference</i>	<i>Median Percent Difference</i>	<i>Standard Deviation</i>	<i>n</i>	<i>MAD</i>	<i>MAD* 1.48</i>
pH	< 5	0.5	0.4	0.02	131	0.02	0.03
	>=5	0.9	0.6	0.08	113	0.03	0.04
H	>10 µeq/L	1.3	1.1	1.3	131	1.10	1.64
	<=10 µeq/L	0.5	0.3	0.8	113	0.30	0.49
Specific Conductance	< 10 µS/cm	7.1	3.8	0.5	107	0.2	0.3
	>= 10 µS/cm	2.4	1.4	0.5	137	0.2	0.3
Calcium	<=0.09ppm	32.3	16.3	0.007	142	0.006	0.009
	0.09<x<=0.9 ppm	4.7	3.7	0.009	94	0.008	0.012
	>0.9 ppm	3.7	3.7	0.063	8	0.044	0.066
Magnesium	<=0.03 ppm	18.4	10.0	0.002	155	0.001	0.001
	0.03<x<=0.3 ppm	5.9	5.3	0.004	86	0.003	0.004
	>0.3 ppm	3.9	5.7	0.028	3	0.035	0.052
Sodium	<=0.03 ppm	21.2	7.3	0.001	82	0.001	0.001
	0.03<x<=0.3 ppm	3.4	2.5	0.003	112	0.002	0.003
	>0.3 ppm	3.2	2.4	0.041	50	0.014	0.021
Potassium	=<0.03 ppm	17.5	8.3	0.001	178	0.001	0.001
	0.03<x<=0.3 ppm	4.0	2.9	0.003	63	0.002	0.003
	>0.3 ppm	4.4	2.9	0.021	3	0.015	0.
Chloride	<0.06 ppm	9.8	6.7	0.003	67	0.002	0.003
	0.06<x<0.6 ppm	4.0	2.6	0.006	136	0.004	0.006
	>0.6 ppm	1.7	1.4	0.070	41	0.017	0.025
Nitrate	<0.1 ppm	23.2	10.0	0.010	6	0.008	0.012
	0.1<x<1.0 ppm	2.2	1.9	0.009	149	0.008	0.012
	> 1.0 ppm	1.3	1.3	0.022	89	0.021	0.031
Sulfate	<0.1 ppm	11.4	8.9	0.005	8	0.006	0.010
	0.1<x<1.0 ppm	2.6	1.9	0.011	123	0.010	0.015
	>1.0 ppm	1.5	1.4	0.026	113	0.025	0.037
Ammonium	<0.2 ppm	6.2	1.9	0.003	134	0.002	0.003
	0.2<x<2.0	2.4	1.5	0.019	109	0.006	0.009
	>2.0 ppm	1 sample > 2.0 ppm, no statistics					
Orthophosphate	<0.09 ppm	0.6	0.0	0.0006	241	0.000	0.000
	0.09<x<0.9 ppm	22.5	22.5	0.019	2	0.023	0.034
	>0.9 ppm	1 sample > 0.9 ppm, no statistics					

Table II-12. Replicate NADP/NTN Precipitation Samples, 2004

<i>Analyte</i>	<i>Level</i>	<i>Mean Percent Difference</i>	<i>Median Percent Difference</i>	<i>Standard Deviation of Differences</i>	<i>n</i>	<i>MAD</i>	<i>MAD* 1.48</i>
pH	< 5	0.7	0.5	0.07	19	0.02	0.03
	>5	1.3	1.0	0.14	112	0.05	0.07
H	>10 µeq/L	7.9	5.7	5.6	119	1.36	2.01
	<10 µeq/L	16.6	12.2	1.0	112	0.41	0.60
Specific Conductance	< 10 µS/cm	4.1	2.4	0.5	114	0.1	0.1
	> 10 µS/cm	2.4	1.1	0.9	117	0.2	0.3
Calcium	<0.03 ppm	28.3	24.0	0.010	44	0.006	0.009
	0.03<x<0.3 ppm	10.1	6.6	0.015	168	0.006	0.009
	>0.3 ppm	2.6	1.9	0.033	19	0.012	0.018
Magnesium	<0.01 ppm	14.7	0.0	0.002	77	0.000	0.000
	0.01<x<0.1 ppm	7.7	6.3	0.004	141	0.002	0.003
	>0.1 ppm	4.7	4.8	0.019	13	0.009	0.013
Sodium	<0.02 ppm	8.4	5.3	0.001	71	0.001	0.001
	0.02<x<0.2 ppm	3.6	2.8	0.007	110	0.002	0.003
	>0.2 ppm	4.1	3.3	0.097	50	0.014	0.021
Potassium	<0.01 ppm	10.3	0.0	0.001	76	0.000	0.000
	0.01<x>0.1 ppm	4.3	3.7	0.003	140	0.001	0.001
	>0.1 ppm	4.2	3.9	0.022	15	0.006	0.
Chloride	<0.08 ppm	14.9	8.3	0.011	96	0.003	0.004
	0.08<x<0.8 ppm	3.0	2.1	0.015	112	0.005	0.007
	>0.8 ppm	3.3	1.7	0.415	23	0.031	0.046
Nitrate	<0.09 ppm	4.6	3.7	0.003	6	0.002	0.004
	0.09<x<0.9 ppm	2.2	1.6	0.017	146	0.007	0.010
	> 0.9 ppm	1.9	1.7	0.062	79	0.025	0.037
Sulfate	<0.13 ppm	4.6	2.7	0.004	11	0.003	0.004
	0.13<x<1.3 ppm	2.2	1.6	0.029	152	0.009	0.013
	>1.3 ppm	1.9	1.8	0.072	68	0.040	0.059
Ammonium	<0.05 ppm	17.2	3.6	0.002	43	0.001	0.001
	0.05<x<0.5 ppm	3.4	2.2	0.017	159	0.004	0.006
	>0.5 ppm	2.3	1.5	0.048	29	0.015	0.022
Orthophosphate	<0.06 ppm	104.8	70.8	0.006	223	0.002	0.003
	0.06<x<0.6 ppm	16.1	3.3	0.090	6	0.008	0.011
	>0.6 ppm	3.7	3.7	0.044	2	0.028	0.041

Table II-13. Replicate NADP/AIRMoN Precipitation Samples, 2003

<i>Analyte</i>	<i>Level</i>	<i>Mean Percent Difference</i>	<i>Median Percent Difference</i>	<i>Standard Deviation of Differences</i>	<i>n</i>	<i>MAD</i>	<i>MAD* 1.48</i>
pH	< 5	1.0	0.7	0.04	30	0.03	0.04
	>5	1.0	0.4	0.06	5	0.06	0.09
H	< 10 µeq/L	11.2	4.7	0.7	30	0.45	0.67
	> 10 µeq/L	9.4	7.2	6.7	5	2.80	4.13
Specific Conductance	< 10 µS/cm	5.6	3.0	0.8	7	0.4	0.6
	> 10 µS/cm	6.7	4.8	1.4	28	1.0	1.4
Calcium	<0.09ppm	57.5	13.3	0.005	25	0.006	0.009
	0.09<x<0.9 ppm	3.1	2.9	0.005	10	0.004	0.007
Magnesium	<0.03 ppm	28.9	0.0	0.0006	24	0.000	0.000
	0.03<x<0.3 ppm	6.1	5.4	0.003	11	0.002	0.003
Sodium	<0.03 ppm	40.4	23.2	0.001	16	0.001	0.001
	0.03<x<0.3 ppm	3.7	3.8	0.003	15	0.002	0.003
	>0.3 ppm	0.4	0.4	0.007	4	0.008	0.011
Potassium	<0.03 ppm	19.1	12.7	0.002	29	0.001	0.001
	0.03<x>0.3 ppm	9.7	7.7	0.005	6	0.004	0.006
Chloride	<0.06 ppm	7.6	4.8	0.005	13	0.001	0.001
	0.06<x<0.6 ppm	4.5	2.6	0.006	18	0.006	0.010
	>0.6 ppm	0.4	0.4	0.007	4	0.006	0.010
Nitrate	0.1<x<1.0 ppm	1.1	0.9	0.005	15	0.006	0.009
	> 1.0 ppm	0.9	0.8	0.014	19	0.10	0.015
Sulfate	0.1<x<1.0 ppm	2.4	2.2	0.011	14	0.012	0.017
	>1.0 ppm	1.1	1.1	0.025	21	0.018	0.027
Ammonium	<0.2 ppm	7.9	5.2	0.005	18	0.004	0.006
	0.2<x<2.0	4.8	4.2	0.019	17	0.020	0.030
Orthophosphate	<0.09 ppm	51.7	47.4	0.006	35	0.003	0.004

Table II-14. Replicate NADP/AIRMoN Precipitation Samples, 2004

<i>Analyte</i>	<i>Level</i>	<i>Mean Percent Difference</i>	<i>Median Percent Difference</i>	<i>Standard Deviation of Differences</i>	<i>n</i>	<i>MAD</i>	<i>MAD* 1.48</i>
pH	< 5	0.8	0.6	0.03	28	0.02	0.04
H	> 10 µeq/L	8.3	5.7	3.6	28	1.80	2.66
Specific Conductance	< 10 µS/cm	4.8	5.0	0.3	4	0.4	0.6
	> 10 µS/cm	4.4	2.2	1.1	24	0.6	1.0
Calcium	<0.03 ppm	4.1	4.1	0.0008	11	0.001	0.001
	0.03<x<0.3 ppm	1.4	2.8	0.011	13	0.001	0.001
	>0.3 ppm	4.0	2.8	0.016	4	0.010	0.014
Magnesium	<0.01 ppm	9.0	0.0	0.0004	13	0.000	0.000
	0.01<x<0.1 ppm	3.0	2.5	0.001	13	0.001	0.001
	> 0.1 ppm	2.5	2.5	0.008	2	0.008	0.012
Sodium	<0.02 ppm	28.1	15.3	0.0008	10	0.001	0.001
	0.02<x<0.2 ppm	3.3	2.9	0.002	11	0.002	0.003
	>0.2 ppm	3.2	2.0	0.066	7	0.009	0.013
Potassium	<0.01 ppm	6.8	0.0	0.0004	10	0.000	0.000
	0.01<x>0.1 ppm	9.8	4.1	0.004	16	0.001	0.001
	> 0.1 ppm	5.1	5.1	0.005	2	0.006	0.009
Chloride	<0.08 ppm	12.5	4.9	0.006	10	0.002	0.003
	0.08<x<0.8 ppm	3.3	1.7	0.007	16	0.003	0.004
	> 0.8 ppm	1.8	1.8	0.061	2	0.081	0.120
Nitrate	0.09<x<0.9 ppm	2.4	1.3	0.009	10	0.006	0.009
	> 0.9 ppm	1.7	0.6	0.0005	18	0.006	0.010
Sulfate	0.13<x<1.3 ppm	3.3	1.1	0.031	12	0.010	0.015
	>1.3 ppm	0.9	0.9	0.050	16	0.018	0.027
Ammonium	<0.05 ppm	10.4	9.9	0.004	4	0.004	0.005
	0.05<x<0.5 ppm	6.6	5.7	0.012	18	0.008	0.012
	> 0.5 ppm	5.4	3.7	0.036	6	0.034	0.051
Orthophosphate	<0.06 ppm	79.7	54.5	0.006	27	0.004	0.006

III. Blanks

Solutions referred to as “blanks” are either DI water solutions or a solution of simulated rainwater approximating the 25th percentile concentration of the NTN. These solutions are used to discern the cleanliness of supplies washed and used at the CAL and/or shipped to sites for field use. Aliquots of one of the two solutions are used to leach the cleaned supplies. The leachates are then analyzed for contamination. The term “blanks” traditionally has been used at the CAL to refer to both DI water leachates and simulated rainwater leachates. “Blanks” are known to the analysts and are identified as such by sample numbers that correspond to their various sources and weeks of collection. “Blanks” are collected and grouped by the sample processing staff. Both pH and conductivity are measured prior to the samples being analyzed by ion chromatography, atomic absorption, and flow injection analysis. These solutions are not filtered unless they are used to determine the cleanliness of the filters. “Blanks” are analyzed as a weekly set. The DI water blanks from the sample processing, atomic absorption, and bucket-washing service laboratories also are included in this set of samples. Specifics on how the “blanks” are prepared can be found in the CAL QAP and laboratory SOPs. The following tables contain a summary of the various “blanks” analyzed at the CAL. The fifth percentile of the NTN concentration is shown in appropriate tables to show whether potential “contamination” of the supplies is meaningful in the network.

Table III-1. pH and Specific Conductance for Weekly DI Water Blanks, 2003

	<i>Sample Processing Laboratory</i>	<i>Atomic Absorption Laboratory</i>	<i>Service Laboratory</i>
Median			
pH (units)	5.66	5.67	5.67
Specific Conductance ($\mu\text{S}/\text{cm}$)	0.9	0.9	0.9
Maximum			
pH (units)	5.82	5.91	5.87
Specific Conductance ($\mu\text{S}/\text{cm}$)	1.3	1.5	1.2
Minimum			
pH (units)	5.55	5.57	5.57
Specific Conductance ($\mu\text{S}/\text{cm}$)	0.7	0.7	0.7
Target for DI			
pH (units)	5.65		
Specific Conductance ($\mu\text{S}/\text{cm}$)	0.8		

Note:

A total of 52 blank DI water samples were collected.

Table III-2. pH and Specific Conductance for Weekly DI Water Blanks, 2004

	<i>Sample Processing Laboratory</i>	<i>Atomic Absorption Laboratory</i>	<i>Service Laboratory</i>
Median			
pH (units)	5.67	5.66	5.67
Specific Conductance ($\mu\text{S}/\text{cm}$)	1.0	1.0	0.9
Maximum			
pH (units)	6.00	5.97	6.00
Specific Conductance ($\mu\text{S}/\text{cm}$)	1.4	1.5	1.5
Minimum			
pH (units)	5.47	5.50	5.51
Specific Conductance ($\mu\text{S}/\text{cm}$)	0.7	0.6	0.6
Target for DI			
pH (units)	5.65		
Specific Conductance ($\mu\text{S}/\text{cm}$)	0.8		

Note:

A total of 52 blank DI water samples were collected.

Table III-3. Median Analyte Concentrations Found in Filter Leachates, 2003

<i>Analyte</i>	<i>DI Water (mg/L)</i>	<i>5th percentile (mg/L)</i>	<i>FR25 (mg/L)</i>	<i>Target FR25 Concentration (mg/L)</i>	<i>Bias (mg/L)</i>	<i>Critical Concentration (95%) (mg/L)</i>	<i>Statistically Biased?</i>
Calcium	<0.009	0.017	0.074	0.070	0.004	0.002	yes
Magnesium	<0.003	0.003	0.014	0.015	-0.001	0.001	no
Sodium	<0.003	0.004	0.045	0.047	-0.002	0.001	yes
Potassium	<0.003	0.002	0.013	0.013	0.000	0.001	no
Ammonium	<0.02	0.022	0.089	0.094	-0.005	0.003	yes
Orthophosphate	<0.009	0.000	0.000	0.000	0.000		
Sulfate	<0.010	0.130	0.591	0.614	-0.023	0.005	yes
Nitrate	<0.010	0.269	0.448	0.465	-0.017	0.005	yes
Chloride	<0.006	0.026	0.129	0.128	0.001	0.002	no
pH	5.63	6.43	4.96	4.93	0.03	0.02	yes
Hydrogen ion (µeq/L)	2.37	0.4	11.2	11.7	-0.5		yes
Specific Conductance (µS/cm)	1.0	3.4	6.8	7.0	-0.2	0.13	yes

Note:

A total of 52 blank samples were collected.

Table III-4. Median Analyte Concentrations Found in Filter Leachates, 2004

<i>Analyte</i>	<i>DI Water (mg/L)</i>	<i>5th percentile FR25 (mg/L)</i>	<i>Target FR25 (mg/L)</i>	<i>Bias (mg/L)</i>	<i>Critical Concentration (95%) (mg/L)</i>	<i>Statistically Biased?</i>	
Calcium	<0.002	0.020	0.075	0.074	0.001	0.003	no
Magnesium	<0.001	0.003	0.014	0.017	-0.003	0.001	yes
Sodium	<0.003	0.006	0.044	0.045	-0.001	0.001	no
Potassium	<0.001	0.003	0.011	0.012	-0.001	0.001	no
Ammonium	<0.005	0.013	0.089	0.091	-0.002	0.002	no
Orthophosphate	<0.007	0.000	0.000	0.000	0.000	0.000	no
Sulfate	<0.013	0.135	0.604	0.628	-0.023	0.005	yes
Nitrate	<0.009	0.169	0.449	0.465	-0.015	0.003	yes
Chloride	<0.008	0.019	0.126	0.131	-0.004	0.002	yes
pH	5.63	6.53	4.93	4.93	0.01	0.03	no
Hydrogen ion (µeq/L)	2.37	0.3	11.7	11.9	-0.2		no
Specific Conductance (µS/cm)	1.2	3.4	7.1	7.1	0.03	0.14	no

Note:

A total of 52 blank samples were collected.

**Table III-5. Median Measured Mass as Micrograms (µg)/Bucket^a Found
in Weekly Deionized (DI) Water and Simulated Rain (FR25)
in Upright Bucket Leachates, 2003**

<i>Analyte</i>	<i>DI Water^a</i>		<i>FR25^b</i>			
	<i>(50 mL)</i>	<i>(150 mL)</i>	<i>(50 mL)</i>	<i>Statistically Biased? 95%</i>	<i>(150 mL)</i>	<i>Statistically Biased? 95%</i>
Calcium	<0.225	<0.675	<0.225	no	<0.675	no
Magnesium	<0.075	<0.225	0.100	no	0.300	no
Sodium	<0.075	<0.225	<0.075	no	<0.225	no
Potassium	0.100	<0.225	<0.075	no	<0.225	no
Ammonium	3.200	4.05	1.60	no	1.95	yes
Sulfate	<0.250	<0.750	-1.000	no	-2.250	yes
Nitrate	<0.250	<0.750	-0.250	no	<0.750	no
Chloride	<0.150	<0.450	0.400	no	0.825	no
pH (units)	5.69	5.66	5.07(4.93) ^c	no	5.02(4.93) ^c	yes
Hydrogen ion (µeq/bucket)	0.102	0.328	-0.162	no	-0.296	yes
Specific Conductance (µS/cm)	1.5	1.3	6.4(7.0) ^c	no	6.6(7.0) ^c	yes

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Notes:

There were 52 blind sample weeks in 2003 with 104 50 mL DI water bucket blanks.

MDLs are reported in Table I-3.

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

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

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

**Table III-6. Median Measured Mass as Micrograms (µg)/Bucket^a Found
in Weekly Deionized (DI) Water and Simulated Rain (FR25)
in Upright Bucket Leachates, 2004**

<i>Analyte</i>	<i>DI Water^a</i>		<i>FR25^b</i>			
	<i>(50 mL)</i>	<i>(150 mL)</i>	<i>(50 mL)</i>	<i>Statistically Biased? 95%</i>	<i>(150 mL)</i>	<i>Statistically Biased? 95%</i>
Calcium	0.250	0.450	<0.050	no	<0.675	no
Magnesium	<0.025	<0.075	<0.025	no	<0.075	no
Sodium	<0.075	<0.225	0.100	no	<0.225	no
Potassium	<0.025	0.150	<0.025	no	<0.075	no
Ammonium	0.675	0.900	0.025	no	<0.375	no
Sulfate	<0.325	<0.975	-1.200	no	-1.200	yes
Nitrate	<0.200	<0.675	-0.250	no	<0.675	no
Chloride	<0.200	<0.600	<0.200	no	<0.600	no
pH (units)	5.65	5.68	5.06(4.93) ^c	no	4.99(4.93) ^c	yes
Hydrogen ion (µeq/bucket)	0.112	0.313	-0.152		-0.227	
Specific Conductance (µS/cm)	1.4	1.3	6.6(7.1) ^c	no	6.8(7.1) ^c	yes

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Notes:

There were 52 blind sample weeks in 2004 with 104 50 mL DI water bucket blanks.

MDLs are reported in Table I-3.

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

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

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

Table III-7. Median Measured Mass as Micrograms (μg)/Bottle^a Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in HDPE 1-Liter Bottle Leachates, 2003

<i>Analyte</i>	<i>DI Water</i>		<i>FR25^b</i>			
	<i>(50 mL)</i>	<i>(150 mL)</i>	<i>(50 mL)</i>	<i>Statistically Biased?</i>	<i>(150 mL)</i>	<i>Statistically Biased?</i>
Calcium	<0.225	<0.675	<0.225	no	<0.675	no
Magnesium	<0.075	<0.225	0.100	no	0.300	no
Sodium	<0.075	<0.225	-0.100	no	-0.300	no
Potassium	0.100	<0.225	<0.075	no	<0.225	no
Ammonium	<0.50	<1.50	-0.95	no	<1.50	no
Sulfate	<0.250	<0.750	-0.650	no	<0.750	no
Nitrate	<0.250	<0.750	-0.450	no	<0.750	no
Chloride	<0.150	<0.450	<0.150	no	<0.450	no
pH (units)	5.59	5.59	4.96(4.93) ^c	no	4.96(4.93) ^c	no
Hydrogen ion ($\mu\text{eq}/\text{bucket}$)	0.13	0.39	0.01	no	0.01	no
Specific Conductance ($\mu\text{S}/\text{cm}$)	1.3	1.2	6.9(7.0) ^c	no	6.9(7.0) ^c	no

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Notes:

There were 52 blind sample weeks in 2003.

^a Mass/bucket represents the concentration in $\mu\text{g}/\text{mL} \times 50$ or 150 mL. Detection limit values are expressed as the $(\text{MDL in } \mu\text{g}/\text{mL})/2 \times 50$ or 150 mL.

^b The FR25 measured mass represents $(\text{median concentration measured in upright bucket leachates} - \text{target FR25 concentration}) \times 50$ or 150 mL.

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

Table III-8. Median Measured Mass as Micrograms (μg)/Bottle^a Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in HDPE 1-Liter Bottle Leachates, 2004

<i>Analyte</i>	<i>DI Water</i>		<i>FR25^b</i>			
	<i>(50 mL)</i>	<i>(150 mL)</i>	<i>(50 mL)</i>	<i>Statistically Biased?</i>	<i>(150 mL)</i>	<i>Statistically Biased?</i>
Calcium	0.050	<0.150	<0.050	no	<0.150	no
Magnesium	<0.025	<0.075	<0.025	no	<0.075	no
Sodium	<0.075	<0.225	<0.075	no	<0.225	no
Potassium	0.050	<0.075	0.070	no	<0.075	no
Ammonium	<0.125	<0.375	-0.639	yes	<0.375	yes
Sulfate	<0.325	<0.975	<0.325	yes	<0.975	no
Nitrate	<0.225	<0.675	-0.242	yes	<0.675	no
Chloride	<0.200	<0.600	<0.200	yes	<0.600	yes
pH (units)	5.61	5.61	4.95(4.93) ^c	no	4.94(4.93) ^c	no
Hydrogen ion ($\mu\text{eq}/\text{bucket}$)	0.12	0.37	-0.03	no	-0.04	no
Specific Conductance ($\mu\text{S}/\text{cm}$)	1.3	1.2	7.1(7.1) ^c	no	7.2(7.1) ^c	no

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Notes:

There were 52 blind sample weeks in 2004.

^a Mass/bucket represents the concentration in $\mu\text{g}/\text{mL} \times 50$ or 150 mL. Detection limit values are expressed as the $(\text{MDL in } \mu\text{g}/\text{mL})/2 \times 50$ or 150 mL.

^b The FR25 measured mass represents $(\text{median concentration measured in upright bucket leachates} - \text{target FR25 concentration}) \times 50$ or 150 mL.

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

Table III-9. Analyte Concentration (mg/L) Found in 50 mL Deionized (DI) Water and 50 mL Simulated Rain (FR25) Used to Leach Snap-on Lids, 2003

<i>Analyte</i>	<i>MDL (mg/L)</i>	<i>DI Water</i>		<i>FR25</i>		<i>Statistically significant bias?</i>	<i>FR25t Target Concentration (mg/L)</i>
		<i>mean (mg/L)</i>	<i>median (mg/L)</i>	<i>mean (mg/L)</i>	<i>median (mg/L)</i>		
Calcium	0.009	0.000	-0.001	0.073	0.074	no	0.070
Magnesium	0.003	0.001	0.000	0.017	0.017	yes	0.015
Sodium	0.003	0.002	0.001	0.048	0.047	no	0.047
Potassium	0.003	0.002	0.002	0.016	0.015	no	0.013
Ammonium	0.02	0.019	0.017	0.106	0.106	yes	0.094
Sulfate	0.010	0.001	0.000	0.602	0.615	no	0.614
Nitrate	0.010	0.001	0.000	0.459	0.467	no	0.465
Chloride	0.006	0.002	0.000	0.136	0.134	yes	0.128
pH (units)		5.68	5.68	5.02	5.00	no	4.93
Hydrogen Ion (μ eq/L)		2.09	2.09	9.9	10.0	no	11.7
Specific Conductance (μ S/cm)		1.3	1.2	6.6	6.8	no	7.0

Note:

There were 52 weeks of snap-on lid blanks.

Table III-10. Analyte Concentration (mg/L) Found in 50 mL Deionized (DI) Water and 50 mL Simulated Rain (FR25) Used to Leach Snap-on Lids, 2004

<i>Analyte</i>	<i>MDL (mg/L)</i>	<i>DI Water</i>		<i>FR25</i>		<i>Statistically significant bias?</i>	<i>FR25t Target Concentration (mg/L)</i>
		<i>mean (mg/L)</i>	<i>median (mg/L)</i>	<i>mean (mg/L)</i>	<i>median (mg/L)</i>		
Calcium	0.002	0.003	0.001	0.077	0.076	yes	0.074
Magnesium	0.001	0.001	0.000	0.017	0.017	no	0.017
Sodium	0.003	0.004	0.002	0.047	0.047	no	0.045
Potassium	0.001	0.001	0.001	0.013	0.013	yes	0.012
Ammonium	0.005	0.011	0.012	0.103	0.103	yes	0.091
Sulfate	0.013	0.003	0.000	0.638	0.637	yes	0.628
Nitrate	0.009	0.000	0.000	0.473	0.473	yes	0.465
Chloride	0.008	0.002	0.000	0.132	0.132	no	0.131
pH (units)		5.70	5.69	4.97	4.97	yes	4.93
Hydrogen Ion (μ eq/L)		2.05	2.07	10.8	10.7	yes	11.7
Specific Conductance (μ S/cm)		1.2	1.3	7.1	7.1	no	7.1

Note:

There were 52 weeks of snap-on lid blanks.

Table III-11. Analyte Concentration (mg/L) Found in Monthly Simulated Rain (FR25) AIRMoN 250-mL HDPE Bottle Leachates, 2003

<i>Analyte</i>	<i>FR 25 (50 mL)</i>			<i>FR25 (150 mL)</i>			<i>FR25 Target Concentration (mg/L)</i>
	<i>mean (mg/L)</i>	<i>median (mg/L)</i>	<i>Statistically significant bias?</i>	<i>mean (mg/L)</i>	<i>median (mg/L)</i>	<i>Statistically significant bias?</i>	
Calcium	0.070	0.072	no	0.069	0.072	no	0.070
Magnesium	0.016	0.017	no	0.016	0.017	yes	0.015
Sodium	0.046	0.045	yes	0.046	0.045	yes	0.047
Potassium	0.014	0.014	yes	0.013	0.014	no	0.013
Ammonium	0.092	0.094	no	0.092	0.093	no	0.094
Sulfate	0.615	0.615	no	0.615	0.618	no	0.614
Nitrate	0.465	0.466	no	0.466	0.466	no	0.465
Chloride	0.133	0.133	yes	0.132	0.132	yes	0.128
pH (units)	4.93	4.94	no	4.94	4.94	no	4.93
Hydrogen Ion (µeq/L)	11.6	11.6	no	11.4	11.5	no	11.7
Specific Conductance (µS/cm)	7.2	7.2	no	7.0	7.1	no	7.0
n	12			12			

Table III-12. Analyte Concentration (mg/L) Found in Monthly Simulated Rain (FR25) AIRMoN 250-mL HDPE Bottle Leachates, 2004

<i>Analyte</i>	<i>mean (mg/L)</i>	<i>FR 25 (50 mL)</i>			<i>FR25 (150 mL)</i>			<i>FR25 Target Concentration (mg/L)</i>
		<i>median (mg/L)</i>	<i>Statistically significant bias?</i>	<i>mean (mg/L)</i>	<i>median (mg/L)</i>	<i>Statistically significant bias?</i>		
Calcium	0.075	0.075	no	0.074	0.075	no	0.074	
Magnesium	0.017	0.017	no	0.017	0.017	no	0.017	
Sodium	0.046	0.046	no	0.045	0.045	no	0.045	
Potassium	0.012	0.012	no	0.012	0.012	no	0.012	
Ammonium	0.093	0.093	yes	0.094	0.094	yes	0.091	
Sulfate	0.631	0.631	no	0.630	0.631	no	0.628	
Nitrate	0.468	0.468	no	0.465	0.464	no	0.465	
Chloride	0.130	0.129	no	0.128	0.129	yes	0.131	
pH (units)	4.92	4.92	no	4.93	4.94	yes	4.93	
Hydrogen Ion (μ eq/L)	12.0	12.0		11.8	11.6		11.7	
Specific Conductance (μ S/cm)	7.4	7.4	yes	7.3	7.3	yes	7.1	
n	12			12				

Table III-13. Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Bags, 2003

<i>Analyte</i>	<i>DI Water (50 mL)</i>		<i>FR25 (50 mL)</i>		<i>Statistically significant bias?</i>	<i>FR25 Target Concentration (mg/L)</i>
	<i>mean (mg/L)</i>	<i>median (mg/L)</i>	<i>mean (mg/L)</i>	<i>median (mg/L)</i>		
Calcium	<0.009	<0.009	0.074	0.076	no	0.070
Magnesium	<0.003	<0.003	0.017	0.017	yes	0.015
Sodium	0.006	0.004	0.051	0.050	no	0.047
Potassium	<0.003	<0.003	0.014	0.014	no	0.013
Ammonium	0.03	<0.02	0.111	0.100	no	0.094
Sulfate	0.013	<0.010	0.604	0.618	no	0.614
Nitrate	<0.010	<0.010	0.463	0.472	no	0.465
Chloride	0.007	<0.006	0.133	0.134	no	0.128
pH (units)	5.48	5.55	4.94	4.95	no	4.93
Hydrogen Ion (µeq/L)	3.94	2.82	12.1	11.2	no	11.7
Specific Conductance (µS/cm)	2.1	1.5	7.2	7.4	no	7.1
n	59		58			

Table III-14. Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Bags, 2004

<i>Analyte</i>	<i>DI Water (50 mL)</i>		<i>FR25 (50 mL)</i>		<i>Statistically significant bias?</i>	<i>FR25 Target Concentration (mg/L)</i>
	<i>mean (mg/L)</i>	<i>median (mg/L)</i>	<i>mean (mg/L)</i>	<i>median (mg/L)</i>		
Calcium	<0.002	<0.002	0.075	0.075	yes	0.074
Magnesium	<0.001	<0.001	0.017	0.017	no	0.017
Sodium	0.005	<0.003	0.051	0.047	no	0.045
Potassium	0.002	<0.001	0.013	0.012	no	0.012
Ammonium	<0.005	<0.005	0.093	0.095	yes	0.091
Sulfate	<0.013	<0.013	0.631	0.635	no	0.628
Nitrate	<0.009	<0.009	0.472	0.473	yes	0.465
Chloride	<0.008	<0.008	0.132	0.133	no	0.131
pH (units)	5.56	5.55	4.93	4.94	no	4.93
Hydrogen Ion (µeq/L)	2.82	2.82	11.7	11.5	no	11.7
Specific Conductance (µS/cm)	1.5	1.4	7.5	7.5	yes	7.1
n	52		53			

IV. Monthly and Annual Quality Assurance Procedures

Monthly NADP/NTN and NADP/AIRMoN QA activities by the QA Specialist include: 1) evaluation of control charts summarizing the daily QCS analyses to determine if any change occurred in CAL analytical instrument performance, 2) review of computer printouts containing internal blind sample data, and 3) review of reanalyses of samples flagged either for an ion or conductivity imbalance or both. Data for samples analyzed in the USGS laboratory intercomparison study also are summarized and reviewed prior to transmission to the USGS on a quarterly basis. The CAL also participates in several other laboratory intercomparison studies.

A. Reanalysis Procedures

The analytical results of the NTN samples are transmitted to the data processing staff approximately twice a month in sets of 500 – 600 samples. Data for AIRMoN samples also are processed once a month for sets of about 120 samples. These analytical data are submitted for a reanalysis selection test that includes all samples with sufficient volume (internal blinds, field blanks, and collocated program samples). WA samples for NTN are not reanalyzed because the pH and relative conductivity is measured prior to dilution. A sample is flagged if the ion percent difference (IPD) or conductivity percent difference (CPD) exceeds set limits as defined the NADP QAP (Simmons et al., 1991). The computer algorithm for sample selection has been the same since 1987.

Selected samples are reanalyzed unless they are flagged for contamination and exhibit excessive ion concentrations as defined in the NADP work statement or the volume is insufficient. The final list of samples is compiled and sent for reanalysis. After reanalyzing the samples and reviewing the results, analysts submit the results to the QA Specialist with suggested changes. After review by the QA Specialist and the CAL data specialist, a final decision is made and the data are edited as needed. When no explanation can be found for differences greater than 10% per the QAP between the original and reanalysis values, the original sample is reanalyzed a second time. For NTN, analysis of the refrigerated archive sample also may be required. When the reanalysis results do not agree with the original results, the analysts must determine why. If the reason for the discrepancy is related to the instrument, or anything other than sample chemistry changing between original and reanalysis, the analysts must remeasure all samples surrounding the reanalysis sample to make sure no other sample was affected and that all sample results were in control and are correct. Reanalysis values are maintained in the CAL computerized database along with the original analysis values.

B. Laboratory Round-robin Programs

The Interlaboratory Comparison Program conducted by the USGS began in the fall of 1982 as a portion of the external QA oversight of the CAL for the NADP/NTN. Every two weeks, the USGS mails one set of four blind samples of different matrices to participating laboratories: a total of 104 samples in 26 biweekly mailings. The protocol is designed to determine if the laboratories are producing comparable results. For details about this study and results, see the USGS Branch of Quality Systems at http://bqs.usgs.gov/precip/new/frontpage_home.htm.

The 28th and 29th sets of the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) reference precipitation samples were shipped to participating laboratories in April and October, 2003, respectively. The 30th and 31st sets were shipped in April and October, 2004. The CAL has contracted to prepare the simulated precipitation samples used in these studies. Samples were shipped to about 100 laboratories with about 60-70 laboratories reporting results to the WMO Quality Assurance/Science Activity Center for the Americas located at the Atmospheric Science Research Center in Albany, New York (Coleman et al., 2003). Because the samples were prepared at the CAL and CAL analysts confirmed the target concentrations, the analytical results obtained by the CAL during the actual studies were not included in the study's final report. For details on the results of the study, refer to <http://www.qasac-americas.org/>

The CAL participated in four studies sponsored by the National Water Research Institute (NWRI) in Burlington, Ontario, Canada in 2003 and 2004. Begun in 1982 as the Long-Range Transport of Atmospheric Pollutants (LRTAP) program, the studies for 2003 were FP82 and FP83 (Blum and Alkema, 2003a, 2003b) and studies FP84 and FP85 for 2004 (Alkema and Bloom, 2004, and Alkema and Simser, 2005).

NWRI samples included selected major ions, nutrients, and physical parameters in natural waters. The NWRI publishes a report which includes all the data and summary of all the laboratories participating in each study. For Study FP82, the CAL showed a low bias for magnesium, one low value for sodium, and one high value for pH resulting in an overall rating of "satisfactory". For Study FP83, the CAL had four bias "flags" assigned again resulting in a rating of "satisfactory". In 2004, Studies FP84 and FP85, no samples or ions were flagged resulting in a rating of "good" for the CAL. For more information on these four studies, contact the National Laboratory for Environmental Testing, Water Science and Technology Directorate, Environment Canada, 867 Lakeshore Road, P.O. Box 5050, Burlington, ON, Canada, L7R 4A6.

The Norwegian Institute for Air Research (NILU) sponsored the 21st and 22nd European Monitoring and Evaluation Programme (EMEP) intercomparison of analytical methods for atmospheric precipitation in 2003 and 2004, respectively. There were four samples in each study. All results were within the standard expected variation for that analyte. For more information about the program or results, contact Hilde Th. Uggerud (htu@nilu.no) at the Norwegian Institute for Air Research.