



National Atmospheric Deposition Program

QUALITY ASSURANCE REPORT NATIONAL ATMOSPHERIC DEPOSITION PROGRAM 2007

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, 2007*, 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, presented in tables or brief written explanations. The CAL met the quality control objectives for the networks in 2007.

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. Christopher Lehmann and Van Bowersox, NADP Program Office, provided ongoing input and support throughout the year. Dedicated analytical staff analyze thousands of samples with the support of conscientious sample receiving and processing personnel. Pam Bedient helped compile and format the text, tables, and files. The following reviewers and editor contributed their time and input to the final report: Lisa Sheppard, Mark Rhodes, Greg Whetherbee, Mark Olson, and Christopher Lehmann, ISWS.

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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. The CAL must comply with all QA mandates in the NADP Quality Management Plan (QMP) and the CAL Quality Assurance Plan (QAP). The CAL was in compliance with the NADP QMP and the CAL QAP in 2007.

Weekly QA procedures ensure that 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 2007 were in compliance with the CAL 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 CAL QAP for 2007.

Interlaboratory comparison studies are vital in determining CAL performance and that of other laboratories around the world conducting similar work. In 2007, 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 in this program. In 2007, 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, its 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 Environment Canada Proficiency Testing Program conducted two intercomparison studies in 2007. The CAL received “good” ratings for both studies. The fifth intercomparison study was with the Norwegian Institute for Air Research (NILU) 25th European Monitoring and Evaluation Programme (EMEP) for intercomparisons of analytical methods for atmospheric precipitation. Results were within the standard expected variation for the analyte.

Overall, the CAL has performed within the specifications of the CAL QA Plan and has performed well in all intercomparison studies during 2007. Based on these studies, the CAL continues to be one of the most qualified 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 2007. 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 and tables, assesses the precision and bias, comparability, sensitivity, and quality 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 2007, the CAL analyzed samples from more than 250 NADP/National Trends Network (NTN) sites that collect weekly precipitation samples throughout the United States and one site in Canada. The Atmospheric Integrated Research Monitoring Network (AIRMoN) was implemented in 1992, and its QA program was initiated. Since then, NADP/NTN and NADP/AIRMoN have shared the same analytical staff and methodology. The AIRMoN sample protocol is different from those of the NTN, but both maintain the same high quality control (QC) and QA objectives.

The instrumentation and analytes measured during 2007 are listed in Table I-1. Table I-1 includes the CAL method detection limits (MDLs) for 2007. For more information about the MDL and how it is determined, see the CAL QAP or the CAL MDL Standard Operating Procedures.

The CAL data are assessed and improved through quality assurance programs. This report addresses QA data indicated in bold and italics 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.isws.illinois.edu/cal>.

A. Summary of Methods

The NTN samples are filtered into pre-rinsed 60-mL high-density polyethylene (HDPE) round bottles using 0.45 micrometer (μm) pore-size polyethersulfone filters. pH and conductivity are measured on an unfiltered aliquot. 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^a. In addition, view the NADP Quality Management Plan (QMP)^b, which provides general information about the CAL and NADP.

^a CAL SOPs are available electronically at <http://nadp.isws.illinois.edu/cal/>

^b The NADP QMP is available electronically at <http://nadp.isws.illinois.edu/>

Table I-1. Analytes, Instrumentation, and Method Detection Limits for 2007

<i>Analyte</i>	<i>Instrument</i>	<i>MDL (2007) (mg/L)</i>	<i>Instrumentation Method Used (years)</i>
Calcium (Ca ²⁺)	Inductively Coupled Plasma-Optical Emission Spectrometer	0.002	3
Potassium (K ⁺)	Inductively Coupled Plasma-Optical Emission Spectrometer	0.001	3
Magnesium (Mg ²⁺)	Inductively Coupled Plasma-Optical Emission Spectrometer	0.001	3
Sodium (Na ⁺)	Inductively Coupled Plasma-Optical Emission Spectrometer	0.001	3
Ammonium (NH ₄ ⁺)	Phenate (Flow Injection Colorimetry)	0.004	29
Orthophosphate (PO ₄ ³⁻)	Ascorbic Acid (Flow Injection Colorimetry)	0.004	29
Chloride (Cl ⁻)	Ion Chromatography	0.003	22
Nitrate (NO ₃ ⁻)	Ion Chromatography	0.017	22
Sulfate (SO ₄ ²⁻)	Ion Chromatography	0.010	22
pH	pH meter		29
	Combination Electrode		29
Conductivity	Conductivity meter		29

**Table I-2. NADP/NTN and NADP/AIRMoN Laboratory
Quality Assurance/Quality Control Program Summary, 2007**

- I. Daily (Quality Control)
 - A. Standardize instruments and verify standardization curves using Quality Control Check Samples (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 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; and*
 - 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.*
 - C. *Select samples for reanalysis by computer-based ion percent and conductivity percent differences and random selection (1 percent monthly for NTN and 2 percent 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 Discipline, Branch of Quality Systems in Denver every three months.*
 - E. *Validate QCS solution for field chemistry prior to shipment to sites as needed.*

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

Table I-2. (concluded)

V. Annually

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

Quality Control Check Samples (QCS) are used throughout the laboratory to confirm the instrumentation is working properly and to maintain the standardization of the instruments within control limits. These solutions are prepared in-house and are tested prior to use as QCS solutions (CAL QAP, 2008). 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. 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 12 samples, one of the QCS solutions and either a high or low calibration standard are 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 (± 3 standard deviations) determined shortly after preparation, 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.

B. Significant Changes during 2007

- Renovation for the new analytical lab for the Inductively Coupled Plasma completed
- Renovation and move for shipping and receiving and bucket washing room
- Lee Green hired as laboratory analyst
- Karen Harlin retired as CAL Director
- Christopher Lehmann hired as CAL Director
- Barbara Suever hired as data analyst
- Six-pack shipping protocol investigated
- New AIRMoN shipping protocol investigated
- Lid bags that are different from bucket bags (different size and manufacturer) introduced
- Quicker turn-around for evaluating and analyzing samples for reanalysis

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

II. Weekly Quality Assurance/Quality Control Procedures

Three QA activities occur on a weekly basis for NTN: 1) three solutions are submitted as internal blind samples for which only the QA chemist knows the identification number; 2) 2% of the NTN and AIRMoN 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 Samples

1. NADP/NTN

Each week the QA chemist 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 2007, the SWS1 samples were a certified reference material AES-02, lot 901, from the National Water Research Institute (NWRI) of Environment Canada and an internally formulated and prepared simulated rainwater sample approximating the 95th percentile of the NTN sample concentrations (FR95), which were alternated weekly. The SWS2 samples were alternated weekly between DI water from the flow injection analysis laboratory and an internally formulated and prepared synthetic rain sample that approximated the 10th percentile of NTN sample concentrations (FR10). The SWS1 and SWS2 samples were not filtered. The filtered SWS3 samples were AES-02, 07FR95, DI water, and 07FR10 submitted in rotation.

Tables II-1 through Table II-4 summarize 2007 data from the weekly internal blind audit samples for NTN. The QAP defines the bias goals for the CAL at different concentrations. For known concentrations at or near the detection limit, the maximum allowable bias is 100%. For concentrations at ten times the MDL, the allowable bias is $\pm 20\%$, and for concentrations at 100 times the MDL or greater, the allowable bias is $\pm 10\%$. All internal blind samples were within these limits. The blind samples are randomly dispersed throughout the sample queue, and, therefore, the derived bias and precision estimates are representative of precipitation sample measurements.

In 2007, with the introduction of the NWRI sample, concentrations of the solutions used were much more typical of rain samples from the NADP. Target concentrations for the NWRI sample were also closer to the concentrations found in the CAL (this was the main reason a new solution was found). The biggest difference was in the bias found for calcium. Previously, a high bias was always obtained for calcium in the order of 25% unfiltered and 300% filtered. Although in 2007 there was still a bias, it was about the same as the other ions, 3.9% unfiltered and 13.6% filtered. The bias found for ammonium using the NWRI sample is also considerably less than found previously. The 2007 bias for ammonium was -0.6% unfiltered and -1.7% filtered (negative values for bias for ammonium are expected since ammonium is not stable and will decrease over time). Previously, the biases were as high as -38% for filtered and unfiltered samples. The only other ion that showed improvement using the new solution was chloride, which went from -11 to -13% for filtered and unfiltered to 6.6% unfiltered and 10.1 % filtered. The physical parameter, specific conductance also decreased 11-16% over the past two

Table II-1. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, AES-02, Unfiltered and Filtered, 2007

<i>Parameter</i>	<i>Target Concentration^a</i> (mg/L)	<i>Mean Concentration</i> (mg/L)	<i>Bias</i> (mg/L)	<i>Bias</i> (%)	<i>Standard Deviation</i> (mg/L)	<i>RSD^d</i> (%)	<i>MDL</i> (mg/L)	<i>5th Percentile^e</i> (mg/L)
Calcium	0.164	0.170 ^b	0.006	3.9	0.006	3.7	0.002	0.023
		0.186 ^c	0.022	13.6	0.012	6.6		
Magnesium	0.030	0.031	0.001	2.1	0.002	5.2	0.001	0.003
		0.031	0.001	4.9	0.002	6.2		
Sodium	0.067	0.074	0.007	11.1	0.023	31.0	0.001	0.008
		0.077	0.010	14.9	0.028	37.0		
Potassium	0.030	0.030	0.000	1.1	0.002	5.2	0.001	0.004
		0.030	0.000	-1.5	0.002	6.6		
Ammonium	0.206	0.205	-0.001	-0.6	0.021	10.2	0.004	0.013
		0.206	-0.004	-1.7	0.027	13.0		
Sulfate	1.8	1.830	0.030	1.6	0.114	6.2	0.010	0.126
		1.771	-0.029	-1.6	0.147	8.3		
Nitrate	1.040	1.063	0.023	2.2	0.020	1.9	0.017	0.165
		1.046	0.006	0.6	0.028	2.6		
Chloride	0.12	0.128	0.008	6.6	0.023	17.7	0.003	0.022
		0.132	0.012	10.1	0.028	21.4		
pH (units)	4.53	4.52	-0.010	-0.3	0.08	1.7		6.43
		4.55	0.02	0.4	0.09	2.0		
H (µeq/L)	29.5	30.7	1.2	4.0	3.8	12.5		0.37
		28.8	-0.7	-2.4	4.4	15.4		
Specific Conductance (µS/cm)	16.5	17.1	0.6	3.5	1.2	7.1		3.2
		16.8	0.3	2.1	1.7	10.0		

Notes:

There were 25 unfiltered and 13 filtered AES-02 samples in 2007.

^a Target Concentrations are those reported by NWRI, Environment Canada.

^b Concentration values for unfiltered AES-02.

^c Concentration values for filtered AES-02.

^d Relative Standard Deviation

^e 5th percentile of NTN data for 2007 excluding contaminated samples.

Table II-2. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Internally Formulated Simulated Rain (07FR95), Unfiltered and Filtered, 2007

<i>Parameter</i>	<i>Target Concentration^a</i> (mg/L)	<i>Mean Concentration</i> (mg/L)	<i>Bias</i> (mg/L)	<i>Bias</i> (%)	<i>Standard Deviation</i> (mg/L)	<i>RSD^d</i> (%)	<i>MDL</i> (mg/L)	<i>5th Percentile^e</i> (mg/L)
Calcium	0.668	0.668 ^b	0.000	0.1	0.019	2.8	0.002	0.023
		0.664 ^c	-0.004	-0.6	0.022	3.3		
Magnesium	0.141	0.142	0.001	0.4	0.003	2.3	0.001	0.003
		0.136	-0.005	-3.5	0.003	1.9		
Sodium	0.678	0.682	0.004	0.6	0.024	3.5	0.001	0.008
		0.658	-0.020	-2.9	0.021	3.5		
Potassium	0.106	0.108	0.002	1.8	0.004	4.1	0.001	0.004
		0.104	-0.002	-2.0	0.004	3.4		
Ammonium	1.045	1.046	0.001	0.1	0.011	1.1	0.004	0.013
		1.024	-0.021	-2.0	0.013	1.3		
Sulfate	3.713	3.737	0.024	0.7	0.034	0.9	0.010	0.126
		3.642	-0.071	-1.9	0.035	1.0		
Nitrate	3.771	3.799	0.028	-0.7	0.040	1.0	0.017	0.165
		3.697	-0.074	-2.0	0.043	1.2		
Chloride	1.220	1.226	0.006	0.5	0.014	1.2	0.003	0.022
		1.200	-0.020	-1.6	0.015	1.3		
pH (units)	4.49	4.48	-0.01	-0.2	0.02	0.4		6.43
		4.49	0.00	0.0	0.01	0.3		
H (µeq/L)	32.4	33.1	0.7	2.2	1.3	4.0		0.37
		32.4	0.0	0.0	0.9	2.8		
Specific Conductance (µS/cm)	32.7	32.6	-0.1	-0.3	0.3	1.0		3.2
		32.7	0.0	0.1	0.3	0.9		

Notes:

There were 27 unfiltered and 13 filtered samples in 2007.

^a Target concentrations for the internally formulated simulated rainwater sample, 07FR95.

^b Concentration values for unfiltered 07FR95.

^c Concentration values for filtered 07FR95.

^d Relative Standard Deviation

^e 5th percentile of NTN data for 2007 excluding contaminated samples.

Table II-3. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Internally Formulated Simulated Rain (07FR10), Unfiltered and Filtered, 2007

<i>Parameter</i>	<i>Target Concentration^a</i> (mg/L)	<i>Mean Concentration</i> (mg/L)	<i>Bias</i> (mg/L)	<i>Bias</i> (%)	<i>Standard Deviation</i> (mg/L)	<i>RSD^d</i> (%)	<i>MDL</i> (mg/L)	<i>5th Percentile^e</i> (mg/L)
Calcium	0.026	0.026 ^b 0.027 ^c	0.000 0.001	0.9 3.0	0.003 0.002	9.6 8.2	0.002	0.023
Magnesium	0.005	0.005 0.004	0.000 -0.001	0.8 -26.2	0.000 0.000	6.7 12.5	0.001	0.003
Sodium	0.009	0.009 0.010	0.000 0.001	0.0 6.0	0.000 0.000	5.3 5.2	0.001	0.008
Potassium	0.004	0.004 0.004	0.000 0.000	5.8 0.0	0.001 0.001	11.9 13.9	0.001	0.004
Ammonium	0.032	0.034 0.034	0.002 0.002	5.8 7.7	0.002 0.005	7.3 15.0	0.004	0.013
Sulfate	0.220	0.220 0.214	0.000 -0.006	0.2 -2.6	0.003 0.002	1.2 1.0	0.010	0.126
Nitrate	0.281	0.282 0.275	0.001 -0.006	0.3 -2.2	0.004 0.003	1.3 1.1	0.017	0.165
Chloride	0.030	0.030 0.031	0.000 0.001	-0.5 4.9	0.002 0.002	5.7 6.7	0.003	0.022
pH (units)	5.15	5.14 5.14	-0.01 -0.01	-0.2 -0.2	0.04 0.04	0.8 0.7		6.43
H (µeq/L)	7.1	7.3 7.3	0.2 0.2	2.7 2.5	0.7 0.6		9.2 8.8	0.4
Specific Conductance (µS/cm)	3.7	3.8 3.9	0.1 0.2	2.7 4.4	-0.1 0.3	3.9 6.8		3.2

Notes:

There were 26 unfiltered and 13 filtered internally formulated simulated rain samples (07FR10) in 2007.

^a Target Concentrations for 07FR10.

^b Concentration values for 07FR10.

^c Concentration values for filtered 07FR10.

^d Relative Standard Deviation

^e 5th percentile of NTN data for 2007 excluding contaminated samples.

Table II-4. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Deionized Water (DI), Unfiltered and Filtered, 2007

<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^c (%)</i>	<i>5th Percentile^d (mg/L)</i>
Calcium	0.002	<0.002 ^a <0.002 ^b			0.0012 0.0009		0.023
Magnesium	0.001	<0.001 <0.001			0.0004 0.0004		0.003
Sodium	0.001	<0.001 0.001			0.0002 0.001		0.008
Potassium	0.001	<0.001 <0.001			0.0004 0.0007		0.004
Ammonium	0.004	0.004 0.005			0.002 0.003		0.013
Sulfate	0.010	<0.010 <0.010			0.000 0.000		0.126
Nitrate	0.017	<0.017 <0.017			0.002 0.000		0.165
Chloride	0.003	<0.003 0.003			0.000 0.003		0.022
pH (units)		5.55 5.56	-0.07 -0.07	-1.3 1.1	0.09 0.07	1.7 1.7	6.43
Specific Conductance (μ S/cm)		1.3 1.3	0.4 0.4	47.4 41.0	0.2 0.1	16.8 12.7	3.2

Notes: c

There were 26 unfiltered and 13 filtered DI samples in 2007.

^a Concentration values for unfiltered DI.

^b Concentration values for filtered DI.

^c Relative Standard Deviation

^d 5th percentile of NTN data for 2007 excluding contaminated samples.

pH of DI H₂O in equilibrium with CO₂ for 2007 = 5.62.

Specific conductance of DI H₂O in equilibrium with CO₂ for 2007 = 0.9 μ S/cm.

years to 3.5% unfiltered and 2.1% filtered. Although the filtered solution shows a higher bias (either more positive or more negative) than the unfiltered solution, the differences in 2007 were much less than previously.

The biases found for 07FR95 and 07FR0 solutions in 2007 agreed closely with the biases found for 2005 and 2006. There doesn't appear to be a significant difference over the past several years in these solutions.

The standard deviations and the relative standard deviations for all three solutions for 2007 were similar to the previous two years. The standard deviation and relative standard deviation for calcium were slightly higher for the FR10 and FR95 solutions, which are also shown in the higher MDL found for calcium for 2007.

The standard deviation for pH and specific conductivity and the bias for the specific conductance of deionized water used as a blind were unchanged. The bias for pH, however, was larger in 2007 with the mean pH dropping from the expected value of 5.62 to 5.55.

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 2007, the solution used was an internally formulated and prepared simulated rain sample approximating the 95th percentile of the NTN concentrations, 07FR95.

Table II-5 shows the internal blind sample summary for 2007. The bias between the target concentrations and the measured concentrations were less than the fifth percentile of the AIRMoN precipitation concentrations for 2007. For most of the analytes, the bias was less than or equal to the method detection limit. Only calcium, sodium, and ammonium biases were greater than the MDL. There was no bias for calcium for NTN, unfiltered (27 samples), but there was a 0.008 mg/L bias for AIRMoN (48 samples), which is greater than the MDL for calcium for the same solution (07FR95) measured on the same instrument and by the same analyst. Other than calcium, the difference between the measured and the target amounts was 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 large volume samples. 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 from the original samples. In 2007, the NTN samples chosen to be a split are marked on the bag as "split." When the sample processor receives it, pH and conductivity are measured and two 60-mL bottles are filled, one for immediate analysis and one archive. The bottle in the bag is then returned to the data technician. The 1-L bottle is set aside and about 100 samples later, the bag has a new identification number attached and is returned to the sample processing lab. There is no evidence on the bottle or bag that this sample has been through sample processing previously, therefore rendering the pH and conductivity results

Table II-5. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, AIRMoN, 2007

<i>Parameter</i>	<i>Target Concentration^a (mg/L)</i>	<i>Mean^b Concentration (mg/L)</i>	<i>Bias (mg/L)</i>	<i>Bias (%)</i>	<i>Standard Deviation (mg/L)</i>	<i>RSD^c (%)</i>	<i>MDL (mg/L)</i>	<i>5th Percentile^d (mg/L)</i>
Calcium	0.668	0.676	0.008	1.2	0.027	3.9	0.002	0.015
Magnesium	0.141	0.142	0.001	0.9	0.003	1.9	0.001	0.002
Sodium	0.678	0.681	0.003	0.4	0.016	2.3	0.001	0.005
Potassium	0.106	0.107	0.001	1.1	0.003	2.9	0.001	0.001
Ammonium	1.045	1.050	0.005	0.5	0.013	1.2	0.004	0.042
Sulfate	3.713	3.709	-0.004	-0.1	0.032	0.9	0.010	0.284
Nitrate	3.771	3.779	0.008	0.2	0.031	0.8	0.017	0.263
Chloride	1.220	1.222	0.002	0.1	0.012	1.0	0.003	0.016
pH	4.49	4.49	0.00	-0.1	0.02	0.6		5.24
H (µeq/L)	32.3	32.7	0.4	1.1	1.9	5.8		5.8
Specific Conductance (µS/cm)	32.7	33.0	0.3	1.0	0.8	2.3		5.5

Notes:

This tabulation included 48 internal blinds. Samples were simulated approximating the 95th percentile of NTN samples (07FR95).

^a Target concentrations for 07FR95.

^b Mean concentration obtained by the CAL from the AIRMoN internal blind samples for 2007.

^c RSD is Relative Standard Deviation.

^d 5th percentile of AIRMoN data for 2007 excluding contaminated samples.

blind to the analysts as well. The sample is then filtered into a 60-mL bottle for analysis and another 60-mL bottle for archival purposes. The NTN samples chosen for splits must have sufficient volume to fill four 60-mL bottles after filtration, original, replicate, and two archive bottles. The samples chosen generally have at least 500 mL of sample. The AIRMoN samples are split in a similar manner, although they are not filtered and no additional split is made for archival purposes. 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-6 and II-7 summarize the analyses of replicate samples analyzed in 2007 for NTN and AIRMoN. Differences are calculated by subtracting the original value from the reanalysis value so that the sign shows whether the concentrations went up or down between the original and replicate. The QAP requires the differences between original analysis and replicate analysis be no more than 10%. With the old way of filtering for split samples for NTN, this goal was hard if not impossible to achieve because of the impact that filtration has on the concentrations. With the system begun in 2007, the mean and the median for all levels of concentration are below 10%. Annual summaries of each ion were split into three sections, from the MDL up to 10 times the MDL, from 10 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 5 and above pH 5 for pH and below a conductivity of 10 microsiemens/centimeter ($\mu\text{S}/\text{cm}$) and above a conductivity of 10 $\mu\text{S}/\text{cm}$ for specific conductance. Because these samples are actual precipitation samples, the concentration of the split samples can cover the entire range of concentrations found in precipitation. By dividing the samples into concentrations that reflect the noise of the instrument, the user has a clearer understanding of what is happening with the real samples. The standard deviation estimated from paired measurements was used to calculate the standard deviations. The last column in Tables II-6 and II-7 shows a nonparametric estimator of variability from replicate determinations, where 1.48 times the Median Absolute Difference (MAD) is the estimator of dispersion (Helsel and Hirsch, 1992).

A comparison of the standard deviations for the internal blind samples (Table II -1 through II-4) for both NTN and AIRMoN to the estimate of dispersion for the split samples shows comparable cation and anion precision. The standard deviation for the paired samples is also comparable to the standard deviation of the internal blinds. The mean and median percent differences along with the standard deviation of paired measurements for the split samples are well within the bias and precision goals for the CAL as defined in the CAL QAP.

Table II-6. Replicate NADP/NTN Precipitation Samples, 2007

<i>Analyte</i>	<i>Level</i>	<i>Percent Difference</i>	<i>Median Percent Difference</i>	<i>Standard Deviation of Paired Measurements</i>	<i>n^a</i>	<i>MAD^b</i>	<i>Estimate of Dispersion</i>
Calcium	≤ 0.02mg/L	3.4	5.0	0.002	24	0.001	0.001
	0.02 < x ≤ 0.2 mg/L	-0.4	0.0	0.004	183	0.002	0.003
	> 0.2 mg/L	-0.1	0.0	0.013	53	0.008	0.018
Magnesium	≤ 0.01 mg/L	1.5	0.0	0.000	85	0.000	0.000
	0.01 < x ≤ 0.1 mg/L	1.4	0.0	0.001	163	0.001	0.001
	> 0.1 mg/L	-1.4	-2.1	0.003	12	0.003	0.004
Sodium	≤ 0.01 mg/L	-1.2	0.0	0.001	37	0.001	0.001
	0.01 < x ≤ 0.1 mg/L	0.1	0.0	0.002	148	0.001	0.001
	>0.1 mg/L	0.8	0.8	0.013	75	0.007	0.010
Potassium	≤ 0.01 mg/L	2.3	0.0	0.001	97	0.001	0.001
	0.01 < x ≤ 0.1 mg/L	-0.6	0.0	0.001	162	0.001	0.001
	> 0.1 mg/L	only one sample, no statistics					
Ammonium	≤ 0.04 mg/L	-3.6	-7.8	0.005	42	0.003	0.004
	0.04 < x ≤ 0.4	-2.5	-1.8	0.006	150	0.004	0.006
	> 0.4 mg/L	-0.3	-0.2	0.008	68	0.006	0.009
Sulfate	≤ 0.10 mg/L	1.1	1.3	0.002	10	0.002	0.002
	0.10 < x ≤ 1.0 mg/L	0.6	0.4	0.012	144	0.004	0.006
	> 1.0 mg/L	0.6	0.5	0.018	106	0.013	0.019
Nitrate	≤ 0.17 mg/L	-1.7	0.0	0.004	20	0.003	0.004
	0.17 < x ≤ 1.7 mg/L	0.2	0.2	0.007	215	0.005	0.009
	> 1.7 mg/L	0.4	0.3	0.016	25	0.009	0.013

Table II-6. Replicate NADP/NTN Precipitation Samples, 2007, concluded

<i>Analyte</i>	<i>Level</i>	<i>Mean Percent Difference</i>	<i>Median Percent Difference</i>	<i>Standard Deviation of Paired Measurements</i>	<i>n^a</i>	<i>MAD^b</i>	<i>Estimate of Dispersion</i>
Chloride	≤ 0.03 mg/L	3.2	1.9	0.002	46	0.002	0.003
	0.03 < x ≤ 0.3 mg/L	-0.4	0.0	0.004	161	0.002	0.003
	> 0.3mg/L	0.5	-0.2	0.020	53	0.005	0.007
Orthophosphate	≤ 0.04 mg/L	-45.9	-25.0	0.001	258	0.001	0.001
	0.04 < x ≤ 0.4 mg/L	0.2	-0.2	0.012	2	0.017	0.024
	> 0.4 mg/L	no samples at this concentration					
pH	< 5	-0.1	0.0	0.03	137	0.02	0.03
	≥ 5	-0.1	0.0	0.06	123	0.03	0.04
H	> 10 µeq/L	-0.1	0.0	1.8	137	1.0	1.5
	≤ 10 µeq/L	-0.1	0.0	0.5	113	0.2	0.3
Specific Conductance	< 10 µS/cm	0.2	0.0	0.2	138	0.1	0.1
	≥ 10 µS/cm	-0.2	0.0	0.6	122	0.3	0.4

Notes:

^a Number of samples

^b Median Absolute Difference

Table II-7. Replicate NADP/AIRMoN Precipitation Samples, 2007

<i>Analyte</i>	<i>Level</i>	<i>Mean Percent Difference</i>	<i>Median Percent Difference</i>	<i>Standard Deviation of Paired Measurements</i>	<i>n^a</i>	<i>MAD^b</i>	<i>Estimate of Dispersion</i>
Calcium	≤ 0.02 mg/L	-3.7	0.0	0.001	3	0.000	0.000
	0.02 < x ≤ 0.2 mg/L	-1.2	0.0	0.002	13	0.002	0.003
	> 0.2 mg/L	0.0	0.3	0.013	6	0.007	0.010
Magnesium	≤ 0.01 mg/L	-1.7	0.000	0.000	6	0.000	0.000
	0.01 < x ≤ 0.1 mg/L	0.1	0.000	0.001	16	0.001	0.001
	≥ 0.1 mg/L	no samples at this concentration					
Sodium	≤ 0.01 mg/L	7.5	7.1	0.001	6	0.001	0.001
	0.01 < x ≤ 0.1 mg/L	-1.0	-1.1	0.002	11	0.001	0.001
	> 0.1 mg/L	-0.7	-2.0	0.004	5	0.005	0.007
Potassium	≤ 0.01 mg/L	-1.5	0.0	0.001	6	0.000	0.001
	0.01 < x ≤ 0.1 mg/L	7.0	-8.4	0.002	16	0.002	0.004
	> 0.1 mg/L	no samples at this concentration					
Ammonium	≤ 0.04 mg/L	-1.0	-1.0	0.001	2	0.002	0.002
	0.04 < x ≤ 0.4 mg/L	-5.9	-5.1	0.013	11	0.009	0.013
	> 0.4 mg/L	-3.3	-2.9	0.021	9	0.019	0.028
Sulfate	< 0.10 mg/L	no samples at this concentration					
	0.10 < x ≤ 1.0 mg/L	-2.4	-1.4	0.018	8	0.011	0.016
	> 1.0 mg/L	-0.8	-0.7	0.025	14	0.020	0.030
Nitrate	≤ 0.17 mg/L	no samples at this concentration					
	0.17 < x ≤ 1.7 mg/L	-0.1	-0.2	0.007	17	0.006	0.009
	> 1.7 mg/L	0.1	0.0	0.015	5	0.024	0.036

Table II-7. Replicate NADP/AIRMoN Precipitation Samples, 2007, concluded

<i>Analyte</i>	<i>Level</i>	<i>Mean Percent Difference</i>	<i>Median Percent Difference</i>	<i>Standard Deviation of Paired Measurements</i>	<i>n^a</i>	<i>MAD^a</i>	<i>Estimate of Dispersion</i>
Chloride	≤ 0.03 mg/L	7.0	0.0	0.002	4	0.001	0.001
	0.03 < x ≤ 0.3 mg/L	2.3	0.0	0.004	14	0.001	0.001
	> 0.3 mg/L	0.2	0.4	0.007	4	0.006	0.008
Orthophosphate	≤ 0.04 mg/L no samples of higher concentration	-45.1	43.1	0.006	22	0.004	0.007
pH	< 5	1.6	1.7	0.07	19	0.08	0.12
	≥ 5	4.7	0.0	0.32	3	0.03	0.04
H	> 10 μeq/L	-14.3	-16.8	4.6	19	3.7	5.4
	≤ 10 μeq/L	-25.4	0.0	1.6	3	0.5	0.7
Specific Conductance	< 10 μS/cm	-2.5	-3.8	0.9	4	1.0	1.4
	≥ 10 μS/cm	-9.6	-8.5	1.9	18	1.5	2.2

Notes:

^a Number of samples

^b Median Absolute Difference

III. Blanks

Solutions referred to as “blanks” are either DI water solutions or in-house prepared 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. 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, analytical, 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. Supplies found to have large contamination of even one analyte are removed from inventory and discarded.

The following tables (Table III-1 through III-8) contain a summary of the various blanks analyzed at the CAL. The fifth percentile of the NTN concentration for 2007 is shown in appropriate tables to indicate whether potential contamination of the supplies is meaningful in the network. Calculations for the critical concentrations and for determining statistical bias can be found on the CAL Web site (<http://nadp.isws.illinois.edu/cal>).

The weekly deionized water blanks show the measured pH to be about 0.05 pH units lower than in previous years; the minimum pH was found to be about 0.26 pH units lower. For the sample processing laboratory the maximum is about the same as previously, but for the other two laboratories the maximum is also about 0.2 pH units higher.

In reviewing the filtrate concentrations, calcium has been statistically biased ($\alpha = 0.05$) for the past several years. In 2007, it was not biased. No changes were made to the solutions or filters. The previous bias might possibly have been based on erroneous target concentrations for calcium. Magnesium, sulfate, and nitrate continue to be statistically biased ($\alpha = 0.05$) in the filter blanks. Bucket blanks continue to have little contamination. Although the specific conductance for 2007 is statistically biased ($\alpha = 0.05$) for the higher volume, the value is the same as for the lower volume. Bottle blanks also continue to have little to no contamination. Again, the specific conductance shows a statistically biased ($\alpha = 0.05$) amount at the lower volume, but no other measurements or analytes are statistically biased. The snap-on lids, likewise, continue to have low contamination blanks with none showing a statistical bias ($\alpha = 0.05$). The AIRMoN bottles again only show specific conductance with a statistical bias ($\alpha = 0.05$).

Previously, bags used to store and ship buckets and lids have been a source of possible contamination. In 2007, separate lid bags were purchased to reduce plastic waste and to make packing lids in the 4-in-1 and then the 6-pack easier. The bucket bags continue to show some statistically biased ($\alpha = 0.05$) contamination for calcium, sodium, potassium, pH, and specific conductance. The impact is minimal and less than the noise of the instrument. The lid bags show no such contamination.

Table III-1. pH and Specific Conductance for Weekly DI Water Blanks, 2007

	<i>Sample Processing Laboratory</i>	<i>Analytical Laboratory</i>	<i>Supply Preparatory Laboratory</i>
Median			
pH (units)	5.56	5.55	5.57
Specific Conductance ($\mu\text{S}/\text{cm}$)	0.8	0.8	0.8
Maximum			
pH (units)	5.76	5.93	5.84
Specific Conductance ($\mu\text{S}/\text{cm}$)	2.1	1.9	2.0
Minimum			
pH (units)	5.22	5.27	5.26
Specific Conductance ($\mu\text{S}/\text{cm}$)	0.6	0.4	0.4
Target for DI			
pH (units)	5.62		
Specific Conductance ($\mu\text{S}/\text{cm}$)	0.9		
Number of samples	52	51	52

Table III-2. Median Analyte Concentrations Found in Filter Leachates, 2007

<i>Analyte</i>	<i>MDL (mg/L)</i>	<i>DI Water (mg/L)</i>	<i>FR25 Median (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	0.002	<0.002	0.054	0.053	0.001	0.003	no
Magnesium	0.001	<0.001	0.008	0.010	-0.002	0.001	yes
Sodium	0.001	<0.001	0.019	0.019	0.000	0.002	no
Potassium	0.001	<0.001	0.009	0.009	0.000	0.001	no
Ammonium	0.004	<0.004	0.094	0.096	- 0.002	0.005	no
Sulfate	0.010	<0.010	0.502	0.517	-0.015	0.006	yes
Nitrate	0.017	<0.017	0.570	0.585	-0.015	0.006	yes
Chloride	0.003	<0.003	0.053	0.052	0.001	0.004	no
pH		5.53	4.91	4.91	0.00	0.03	no
Hydrogen ion (µeq/L)		3.0	12.3	12.3	0.0		
Specific Conductance (µS/cm)		1.1	6.7	6.4	0.1	0.3	no

Note:

A total of 52 blank samples and 52 FR25 samples was collected.

Table III-3. Median Analyte Concentration Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in Upright Bucket Leachates, 2007

<i>Analyte</i>	<i>DI Water</i>			<i>Statistically Biased? 95%</i>	<i>FR25</i>	
	<i>(50 mL)</i>	<i>(150 mL)</i>	<i>(50 mL)</i>		<i>(150 mL)</i>	<i>Statistically Biased? 95%</i>
Calcium	0.004	0.003	0.057	no	0.056	no
Magnesium	0.001	<0.001	0.010	no	0.010	no
Sodium	0.002	0.001	0.022	no	0.021	no
Potassium	0.001	0.001	0.009	no	0.010	no
Ammonium	0.006	0.004	0.093	no	0.091	no
Sulfate	<0.010	<0.010	0.516	no	0.516	no
Nitrate	<0.017	<0.017	0.584	no	0.586	no
Chloride	0.008	<0.003	0.054	no	0.054	no
pH (units)	5.51	5.52	4.92	no	4.94	no
Hydrogen ion (µeq/bucket)	3.1	3.0	12.0		12.3	
Specific Conductance (µS/cm)	1.4	1.3	6.8	no	6.8	yes

Notes:

There were 52 “blank” sample weeks in 2007 with 104 50 mL DI water bucket blanks. MDLs and target concentrations for 07FR25 are reported in Table III-2.

Table III-4. Median Analyte Concentration Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in HDPE 1-Liter Bottle Leachates, 2007

<i>Analyte</i>	<i>DI Water</i>		<i>FR25</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	<0.002	<0.002	0.052	no	0.053	no
Magnesium	<0.001	<0.001	0.010	no	0.010	no
Sodium	<0.001	<0.001	0.019	no	0.019	no
Potassium	0.001	<0.001	0.009	no	0.009	no
Ammonium	<0.004	<0.004	0.091	no	0.093	no
Sulfate	<0.010	<0.010	0.515	no	0.518	no
Nitrate	<0.017	<0.017	0.583	no	0.584	no
Chloride	<0.003	<0.003	0.052	no	0.052	no
pH (units)	5.51	5.52	4.90	no	4.91	no
Hydrogen ion (µeq/bucket)	3.1	3.0	12.6		12.4	
Specific Conductance (µS/cm)	1.3	1.2	6.9	yes	6.8	no

Notes:

There were 52 blank sample weeks in 2007.
MDLs and target concentrations for 07FR25 are reported in Table III-2.

Table III-5. Analyte Concentration (mg/L) Found in 50 mL Deionized (DI) Water and 50 mL Simulated Rain (FR25) Used to Leach Snap-on Lids, 2007

<i>Analyte</i>	<i>MDL (mg/L)</i>	<i>DI Water</i>		<i>FR25</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>	<i>Statistically significant bias?</i>	
Calcium	0.002	0.003	<0.002	0.056	0.054	no	0.053
Magnesium	0.001	0.000	<0.001	0.010	0.010	no	0.010
Sodium	0.001	0.003	0.001	0.022	0.021	no	0.019
Potassium	0.001	0.007	0.001	0.010	0.010	no	0.009
Ammonium	0.004	0.012	0.012	0.104	0.103	no	0.096
Sulfate	0.010	0.004	<0.010	0.521	0.522	no	0.517
Nitrate	0.017	0.002	<0.017	0.590	0.590	no	0.585
Chloride	0.003	0.009	<0.003	0.054	0.053	no	0.052
pH (units)		5.53	5.54	4.93	4.92	no	4.91
Hydrogen Ion (µeq/L)		3.0	3.0	11.9	11.9		12.3
Specific Conductance (µS/cm)		1.4	1.4	6.8	6.7	no	6.6

Note: There were 52 weeks of snap-on lid blanks.

**Table III-6. Analyte Concentration (mg/L) Found in
Monthly Simulated Rain (FR25) AIRMoN 250-mL
HDPE Bottle Leachates, 2007**

<i>Analyte</i>	<i>FR 25 (50 mL)</i>			<i>FR25 (150 mL) FR25</i>			<i>Target Concentration (mg/L)</i>
	<i>mean (mg/L)</i>	<i>median (mg/L)</i>	<i>Statistically significant bias?@95%</i>	<i>mean (mg/L)</i>	<i>median (mg/L)</i>	<i>Statistically significant bias?@95%</i>	
Calcium	0.053	0.053	no	0.053	0.053	no	0.053
Magnesium	0.010	0.010	no	0.010	0.010	no	0.010
Sodium	0.019	0.019	no	0.019	0.019	no	0.019
Potassium	0.009	0.009	no	0.009	0.009	no	0.009
Ammonium	0.097	0.096	no	0.097	0.096	no	0.096
Sulfate	0.517	0.514	no	0.517	0.516	no	0.517
Nitrate	0.585	0.586	no	0.587	0.587	no	0.585
Chloride	0.052	0.052	no	0.051	0.051	no	0.052
pH (units)	4.90	4.91	no	4.90	4.91	no	4.91
Hydrogen Ion (µeq/L)	12.5	12.3	no	12.5	12.3	no	12.3
Specific Conductance (µS/cm)	6.9	6.8	yes	6.8	6.8	yes	6.6
n	11			11			

Note:

n is the number of blank samples for 2007.

Table III-7. Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Bucket Bags, 2007

<i>Analyte</i>	<i>DI Water (50 mL)</i>		<i>FR25 (50 mL)</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>	<i>Statistically significant bias?@95%</i>	
Calcium	0.005	0.002	0.056	0.056	yes	0.052
Magnesium	<0.001	<0.001	0.010	0.010	no	0.010
Sodium	0.012	0.009	0.031	0.030	yes	0.019
Potassium	0.007	0.003	0.012	0.012	yes	0.009
Ammonium	0.010	0.008	0.096	0.100	no	0.096
Sulfate	0.016	<0.010	0.521	0.521	no	0.517
Nitrate	<0.017	<0.017	0.588	0.588	no	0.585
Chloride	0.008	<0.003	0.053	0.053	no	0.052
pH (units)	5.28	5.28	4.84	4.84	yes	4.91
Hydrogen Ion (µeq/L)	5.7	5.2	14.6	14.6		12.3
Specific Conductance (µS/cm)	2.6	2.3	8.1	7.7	yes	6.6
n	40		40			

Note:

n is the number of blank samples for 2007.

**Table III-8. Analyte Concentration (mg/L) Found in
Deionized (DI) Water and Simulated Rain
(FR25) Used to Leach Lid Bags, 2007**

<i>Analyte</i>	<i>DI Water (50 mL)</i>		<i>FR25 (50 mL)</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>	<i>Statistically significant bias?</i>	
Calcium	<0.002	<0.002	0.053	0.053	no	0.053
Magnesium	<0.001	<0.001	0.010	0.010	no	0.010
Sodium	0.004	0.003	0.022	0.021	no	0.019
Potassium	0.003	<0.001	0.009	0.009	no	0.009
Ammonium	0.006	0.007	0.098	0.097	no	0.096
Sulfate	<0.010	<0.010	0.520	0.521	no	0.517
Nitrate	<0.017	<0.017	0.588	0.589	no	0.585
Chloride	<0.003	<0.003	0.052	0.052	no	0.052
pH (units)	5.51	5.51	4.91	4.91	no	4.91
Hydrogen Ion (µeq/L)	3.1	3.1	12.5	12.3	no	12.3
Specific Conductance (µS/cm)	1.3	1.3	6.9	6.8	no	6.6
n	33		32			

Note:

n is the number of blank samples for 2007.

IV. Monthly and Annual Quality Assurance Procedures

Monthly NADP/NTN and NADP/AIRMoN QA and QC activities at the CAL include: 1) review of internal blind sample data, and 2) 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 are summarized and reviewed prior to transmission to the USGS on a quarterly basis. The CAL also participates in several other laboratory round-robin studies.

A. Reanalysis Procedures

The analytical results of the NTN and AIRMoN samples are transmitted to the data processing staff approximately weekly. Previously NTN data were transmitted every other week and AIRMoN monthly, but this changed in 2007. The quicker turn-around for reanalysis, it was believed, would result in less time for any chemical changes in the sample, thereby improving the reanalysis to original comparison. All samples with sufficient volume (internal blinds, field blanks, and collocated program samples included) are included for possible reanalysis. Wet samples that need to be diluted to have sufficient volume for complete analysis for NTN are not reanalyzed because pH and relative conductivity are measured prior to dilution. A sample is flagged for reanalysis if the ion percent difference (IPD) or conductivity percent difference (CPD) exceeds set limits as defined in the reanalysis SOP. The computer algorithm for sample selection has been the same since 1987. The IPD and CPD for each year of the program can be found on the CAL Web site. Additional information concerning the reanalysis of samples can be found there as well.

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 chemist with suggested changes. After review by the QA chemist 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 the cause of the difference. 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.

In 2007 there were 777 samples pulled for mandatory or random reanalysis for NTN out of 13,958 samples. This included 598 samples with IPD outside the tolerance limits, 45 samples with CPD outside the tolerance limits (some samples are pulled for both IPD and CPD so there could be overlaps between these two sets of samples), and 149 random samples. Additional samples may be pulled by the analysts for additional checks. There were 145 edits made to the NTN database based on reanalysis findings. For AIRMoN in 2007 there were a total of 66 samples reanalyzed with 4 being pulled for CPD outside the tolerance limits, 25 being pulled for

IPD outside the tolerance limits, and 37 randomly pulled. There were 39 edits for AIRMoN based on reanalysis findings.

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 eight participating laboratories: a total of 104 samples per laboratory in 26 biweekly mailings. The protocol is designed to determine if the laboratories are producing comparable results. For details about this study and results, refer to the USGS Branch of Quality Systems at <http://bqs.usgs.gov/precip/index.htm>

The 36th and 37th sets of the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) reference precipitation samples were shipped to participating laboratories in April and October 2007, respectively. The CAL was 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. 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 studies' statistical evaluation. For details on the results of the study, refer to <http://www.qasac-americas.org>

The CAL participated in two studies sponsored by the National Water Research Institute (NWRI) in Burlington, Ontario, Canada in 2007. Begun in 1982 as the Long-Range Transport of Atmospheric Pollutants (LRTAP) program, the studies for 2007 were PT90 and PT91 (Tinson, 2007, and Tinson, 2008). The NWRI sponsors several different studies. In 2007, the CAL participated in the Rain and Soft Waters (RN) studies and in the Trace Elements in Water (TE) studies.

NWRI TE samples include selected trace elements in an acidic water matrix^c The NWRI publishes a report that includes all the data and summary of all the laboratories participating in each study. For Study PT90 TE, the CAL received a warning low flag for aluminum for one sample, an action high (outside control limits) for nickel for the same sample, and a second flag action high for zinc on a separate sample. Overall the performance of the CAL was rated as "good." For PT91, one sample for one ion (manganese) was flagged "warning high" resulting in a rating of "good" for the CAL. For the RN samples for Study PT90, the CAL analyzed ten parameters with none being biased and reported 100 results with no flags received resulting in a score of 0 percent or "good." For RN samples for Study PT91, the CAL reported ten parameters, no biases received, and 100 results with one chloride flag for action level low. This value though, was a decimal error. The number reported was 0.115, which should have been 1.15, which was well within limits. The CAL received a score of 0.5 percent or "good." For more information on

^c Trace elements are not normally analyzed in NADP samples. The CAL has the capability for analysis and participated in the external performance test. The results are included here for information only.

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 25th European Monitoring and Evaluation Programme (EMEP) intercomparison of analytical methods for atmospheric precipitation in 2007 (Uggerud and Hjellbrekke, 2008). There are four samples in each study. For a summary of the CAL results, see Tables IV-1 and IV-2. The target chloride value for G1 was 0.135 mg/L and the median was 0.136 mg/L. The CAL's reported value was 0.186 mg/L. For this same sample, the target concentration for sodium was 0.213 mg/L with a median of 0.208 mg/L. The CAL value was 0.245 mg/L. These would be outside the CALs acceptable limits for QCS or internal blinds. For more information about the program or results, see <http://tarantula.nilu.no/projects/ccc/reports.html>.

Table IV-1. Relative Random and Systematic Errors Obtained by the CAL in the Analysis of Precipitation Samples in the 25th Intercomparison of Analytical Methods within EMEP, NILU, 2007

Analyte	Random Error (%)	Systematic Error (%)
Calcium	no results reported ^a	
Magnesium	2	2
Sodium	5	1
Potassium	1	0
Ammonium	1	2
Sulfate	0	3
Nitrate	1	1
Chloride	10	1
H ⁺ calculated from pH	4	-7
Conductivity	2	0

Note:

^a Only three samples were analysed by NILU for calcium in this study. No statistics were available for calcium from NILU.

Table IV-2. Reported Results for Precipitation Samples Expressed as Percent Deviation from Expected Value, NILU, 25th Intercomparison Study, 2007

Analyte/Sample ID	G1 ^a	G2	G3	G4
Calcium	no Ca ²⁺ ^b	2	2	0
Magnesium	3	1	0	3
Sodium	15	1	2	-2
Potassium	1	0	-1	2
Ammonium	1	2	3	2
Sulfate	2	3	3	3
Nitrate	2	1	3	1
Chloride	38	-1	1	-2
pH (pH units)	0.05	0.03	0.04	0.03
Conductivity	-1	-2	2	2

Notes:

^a There are four samples in each NILU precipitation study set labeled G1, G2, G3, and G4.

^b Calcium was not analyzed by NILU for G1 for this study. Although the CAL measured calcium, it was near the detection limit. NILU did not do statistics for calcium for G1.

V. References

Central Analytical Laboratory Quality Assurance Plan. 2006. NADP QA Plan 2006-01, Version 2.0, Champaign, IL.

Central Analytical Laboratory Standard Operating Procedures, 2006 and 2007, Champaign, IL.

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

Ridder, T.B., T.A. Buisdhand, H.F.R. Reijnders, M.J. t'Hart, and J. Slanina. 1985. *Effects of Storage on the Composition of Main Components in Rainwater Samples*. *Atmospheric Environment* 19(5): 759-762.

Tinson, C. 2007. *Environment Canada Proficiency Testing Program - Rain and Soft Waters - Study 0090 –June to September 2007*, Report No. NLET-TN07-776. National Water Research Institute, National Laboratory for Environmental Testing, Burlington, Ontario, Canada.

Tinson, C. 2008. *Environment Canada Proficiency Testing Program - Rain and Soft Waters - Study 0091 –December 2007 to March 2008*, Report No. NLET-TN08-001. National Water Research Institute, National Laboratory for Environmental Testing, Burlington, Ontario, Canada.

Uggerud, H.Th. and A.-G. Hjellbrekke. 2008. *The Twenty-fifth Intercomparison of Analytical Methods within EMEP*. Norwegian Institute for Air Research, Kjeller, Norway.

APPENDIX A

Appendix A: CAL Staff

Christopher Lehmann, Karen Harlin

CAL Directors

Phyllis	Ballard
Pam	Bedient
Tom	Bergerhouse
Tracy	Dombek
Nina	Gartman
Lee	Green
Theresa	Ingersoll
Matt	Layden
Jeff	Pribble
Brenda	Riney
Jane	Rothert
Nichole	Samson
Scott	Smith
Barbara	Suever
Angela	Weddle