

NADP QA Report 2010-01  
ISWS Contract Report 2010-02

# QUALITY ASSURANCE REPORT

## NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

### 2008

Laboratory Operations  
Central Analytical Laboratory

prepared by Jane Rothert  
CAL Quality Assurance Chemist

University of Illinois  
Institute of Natural Resource Sustainability  
National Atmospheric Deposition Program  
Illinois State Water Survey  
2204 Griffith Drive  
Champaign, IL 61820-7495

February 2010



National Atmospheric  
Deposition Program



## 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, 2008*, 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 its quality control objectives for the networks in 2008.

## 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. Drs. Christopher Lehmann, CAL Director, and David Gay, Program Coordinator, provide ongoing input and support throughout the year. Dedicated 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: Mark Rhodes (NADP Program Office), Greg Wetherbee (USGS), Melissa Rury (EPA), Lisa Sheppard (ISWS editor), and Christopher Lehmann (ISWS).

The NADP is a cooperative research support program entitled National Research Support Project - 3: A Long-Term Monitoring Program in Support of Atmospheric Chemical Deposition. State Agricultural Experiment Stations, federal, state, and local government agencies, universities, and nongovernmental organizations support the NADP, as does the Cooperative State Research, Education, and Extension Service, U.S. Department of Agriculture, under Agreement No. 2008-39134-19508. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the author and do not necessarily reflect the views of the U.S. Department of Agriculture or any other sponsor.

## Executive Summary

The *NADP Network Quality Assurance Plan* 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 Assurance Plan (QAP), and was in full compliance in 2008.

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. Although some contamination problems were encountered with the sampling buckets during 2008, no samples were compromised. Blank analyses, matrix-spiked analyses, internal blind sample analyses for NTN and AIRMoN, and replicate analyses for 2008 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 2008.

Interlaboratory comparison studies are vital in determining CAL performance and that of other laboratories around the world conducting similar analyses. In 2008, the CAL participated in five different independent studies in addition to the U.S. Geological Survey (USGS) interlaboratory comparison program. The USGS operates the QA program for the NADP/NTN. The CAL performed well in this program. In 2008, 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. However, the CAL results were favorable when compared with those from other participating laboratories. The National Water Research Institute (NWRI) of Canada conducted two intercomparison studies in 2008. The CAL received a “good” rating for both studies. The fifth intercomparison study was with the Norwegian Institute for Air Research (NILU) 26<sup>th</sup> European Monitoring and Evaluation Programme (EMEP) for intercomparisons of analytical methods for atmospheric precipitation. Results from this study were unavailable at the time this report was prepared.

Overall, the CAL has performed within the specifications of the NADP QA Plan, and has performed well in all intercomparison studies during 2008. Based on these studies, the CAL continues to be one of the leading atmospheric precipitation laboratories in the world.



## Table of Contents

	<i>Page</i>
Abstract.....	iii
Acknowledgements.....	iv
Executive Summary.....	v
Table of Contents.....	vii
List of Tables.....	ix
Acronyms, Symbols, and Abbreviations.....	x
I. Introduction.....	1
A. Summary of Methods.....	1
B. Significant Changes during 2008.....	5
C. Significant QA Activities during 2008.....	5
II. Weekly Quality Assurance/Quality Control Procedures.....	7
A. Internal Blind Audit Samples.....	7
1. NADP/NTN.....	7
2. NADP/AIRMoN.....	17
B. Replicate Samples.....	20
III. Blanks.....	27
IV. Monthly and Annual Quality Assurance Procedures.....	37
A. Reanalysis Procedures.....	37
B. Laboratory Round-Robin Programs.....	38
V. References.....	39
Appendix A: Web Pages.....	41
Appendix B CAL Staff.....	45





## List of Tables

*Page*

<b>Table I-1</b>	Analytes, Instrumentation, and Method Detection Limits for 2008 .....	2
<b>Table I-2</b>	NADP/NTN and NADP/AIRMoN Laboratory Quality Assurance/ Quality Control Program Summary, 2008 .....	3
<b>Table II-1</b>	Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, AES-05, Unfiltered and Filtered, 2008 .....	8
<b>Table II-2</b>	Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Internally Formulated Simulated Rain (08FR95), Unfiltered and Filtered, 2008 .....	9
<b>Table II-3</b>	Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Internally Formulated Simulated Rain (08FR10), Unfiltered and Filtered, 2008 .....	10
<b>Table II-4</b>	Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Deionized Water (DI), Unfiltered and Filtered, 2008 .....	11
<b>Table II-5</b>	Filtered vs. Unfiltered NTN Blinds, AES-05, 2008 .....	13
<b>Table II-6</b>	Filtered vs. Unfiltered NTN Blinds, 08FR95, 2008 .....	14
<b>Table II-7</b>	Filtered vs. Unfiltered NTN Blinds, 08FR10, 2008 .....	15
<b>Table II-8</b>	Filtered vs. Unfiltered NTN Blinds, DI Water, 2008 .....	16
<b>Table II-9</b>	Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, AIRMoN, 2008 .....	18
<b>Table II-10</b>	AIRMoN vs NTN 08FR95 $n_{\text{AIRMoN}} = 48$ , $n_{\text{NTN}} = 26$ , $t_{95,72}$ , 2008 .....	19
<b>Table II-11</b>	Replicate NADP/NTN Precipitation Samples, 2008 .....	21
<b>Table II-12</b>	Replicate NADP/AIRMoN Precipitation Samples, 2008 .....	23
<b>Table III-1</b>	pH and Specific Conductance for Weekly DI Water Blanks, 2008 .....	28
<b>Table III-2</b>	Median Analyte Concentration Found in Filter Leachates, 2008 .....	29
<b>Table III-3</b>	Median Analyte Concentration Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in Upright Bucket Leachates, 2008	
<b>Table III-4</b>	Median Analyte Concentration Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in HDPE 1-Liter Bottle Leachates, 2008 .....	31
<b>Table III-5</b>	Analyte Concentration (mg/L) Found in 50 mL Deionized (DI) Water and 50 mL Simulated Rain (FR25) Used to Leach Snap-on Lids, 2008 .....	32
<b>Table III-6</b>	Analyte Concentration (mg/L) Found in Monthly Simulated Rain (FR25) AIRMoN 250-mL HDPE Bottle Leachates, 2008 .....	33
<b>Table III-7</b>	Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Bucket Bags, 2008 .....	34
<b>Table III-8</b>	Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Lid Bags, 2008 .....	35

## Acronyms, Symbols, and Abbreviations

°	Degree
µeq	Microequivalent
µS	MicroSiemen
AES	Identification of precipitation sample purchased from NWRI
AIRMoN	Atmospheric Integrated Research Monitoring Network
C	Centigrade
Ca <sup>+2</sup>	Calcium ion
CAL	Central Analytical Laboratory
Cl <sup>-</sup>	Chloride ion
cm	Centimeter
DI	Deionized (water)
EMEP	European Monitoring and Evaluation Programme
FIA	Flow-Injection Analysis
FOF	Field Observer Form (AIRMoN)
FORF	Field Observer Report Form (NTN)
FR	Synthetic rain sample identification
HDPE	High Density Polyethylene
H <sub>3</sub> O <sup>+</sup>	Hydronium ion
IC	Ion Chromatograph
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometer
IL11	AIRMoN and NTN precipitation collection site at Bondville, IL
ISWS	Illinois State Water Survey
K <sup>+</sup>	Potassium ion
L	Liter
LIMS	Laboratory Information Management System
MAD	Median Absolute Difference
MDL	Method Detection Limit
Mg <sup>+2</sup>	Magnesium ion
mg	Milligrams
mL	Milliliter
n	Number of samples
Na <sup>+</sup>	Sodium ion
NADP	National Atmospheric Deposition Program
NH <sub>4</sub> <sup>+</sup>	Ammonium ion
NILU	Norwegian Institute for Air Research
NO <sub>3</sub> <sup>-</sup>	Nitrate ion
NTN	National Trends Network
NWRI	National Water Research Institute, Environment Canada
pH	Negative logarithm to the base 10 of the molar concentration of H <sub>3</sub> O <sup>+</sup>

## Acronyms and Symbols, concluded

PO <sub>4</sub> <sup>-3</sup>	Orthophosphate ion
PT	Proficiency Testing
QA	Quality Assurance
QAP	Quality Assurance Plan
QC	Quality Control
QCS	Quality Control Sample
QMP	Quality Management Plan
RN	Rain and Soft Waters for NWRI PT studies
RSD	Relative Standard Deviation
SO <sub>4</sub> <sup>-2</sup>	Sulfate ion
SOP	Standard Operating Procedure
SQL	Structured Query Language
SWS	Internal blind sample site identification
UI	University of Illinois
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WMO/GAW	World Meteorological Organization/Global Atmospheric Watch



## I. Introduction

This Quality Assurance (QA) Report describes and summarizes the results of the National Atmospheric Deposition Program (NADP) Central Analytical Laboratory's (CAL) QA program for 2008. The procedures for supporting reliable data are initiated 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. (See Appendix A for a listing of Web pages appropriate to this report.)

The Atmospheric Chemistry Laboratory at the Illinois State Water Survey (ISWS) was selected in 1978 to be the CAL for the NADP—a role it has held ever since. In 2008, the CAL analyzed samples from more than 250 NADP/National Trends Network (NTN) sites that collect weekly precipitation samples across the United States and at one site in Canada. The Atmospheric Integrated Research Monitoring Network (AIRMoN) and its QA program were implemented in 1992. 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 2008 are listed in Table I-1. Also included in Table I-1 are the CAL method detection limits (MDLs) for 2008 and the instrument length of service as of 2008. For more information about the MDL and how it is determined, see the CAL QAP or the CAL MDL standard operating procedure.

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 through the CAL Web page (Appendix A).

### A. Summary of Methods

NTN and AIRMoN samples are continuously received at the CAL for analysis. Upon receipt, the NTN samples are filtered into pre-washed 60-mL high-density polyethylene (HDPE) round bottles using 0.45 micrometer ( $\mu\text{m}$ ) pore-size polyethersulfone filters. Conductivity and pH 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. In addition, the NADP Quality Management Plan (QMP) provides general information about the CAL and NADP.

**Table I-1. Analytes, Instrumentation, and Method Detection Limits for 2008**

<i>Analyte</i>	<i>Instrument</i>	<i>MDL</i>	<i>Length of service</i>
Calcium (Ca <sup>2+</sup> )	Inductively Coupled Plasma-Optical Emission Spectrometer	0.006	2004-2008
Potassium (K <sup>+</sup> )	Inductively Coupled Plasma-Optical Emission Spectrometer	0.001	2004-2008
Magnesium (Mg <sup>+</sup> )	Inductively Coupled Plasma-Optical Emission Spectrometer	0.001	2004-2008
Sodium (Na <sup>+</sup> )	Inductively Coupled Plasma-Optical Emission Spectrometer	0.001	2004-2008
Ammonium (NH <sub>4</sub> <sup>+</sup> )	Phenate (Flow Injection Colorimetry)	0.006	1978-2008
Orthophosphate (PO <sub>4</sub> <sup>3-</sup> )	Ascorbic Acid (Flow Injection Colorimetry)	0.004	1978-2008
Chloride (Cl <sup>-</sup> )	Ion Chromatography, Dionex	0.004	1985-2008
Nitrate (NO <sub>3</sub> <sup>-</sup> )	Ion Chromatography, Dionex	0.009	1985-2008
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	Ion Chromatography, Dionex	0.007	1985-2008
pH	pH meter		2008
	Combination Electrode		1989-2008
Conductivity	Conductivity meter		2003-2008

**Table I-2. NADP/NTN and NADP/AIRMoN Laboratory  
Quality Assurance/Quality Control Program Summary, 2008**

**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 25<sup>th</sup> and 75<sup>th</sup> 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.*
    - 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.***

Note: Italicized QA/QC programs are addressed in this QA report.



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 25<sup>th</sup> and 75<sup>th</sup> 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 the Environmental Resource Association<sup>1</sup> 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 ( $\pm 3$  standard deviations) 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 analyzed since the last in-control QCS was analyzed are reanalyzed. Control charts and the measured concentrations of all QCS solutions are available upon request.

#### **B. Significant Changes during 2008**

- Kim Attig hired as analyst
- Barbara Suever departed as data specialist
- New buckets found which do not need risers to fit the NTN and AIRMoN collectors
- New suppliers for lid and bucket bags
- New Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) room renovation completed and ICP-OES moved
- Corning pH meters replaced with Mettler pH meters

(For a complete listing of CAL staff for 2008, see Appendix B.)

#### **C. Significant QA Activities during 2008**

The NADP's Quality Management Plan mandates that external reviews occur once every three years. On July 29–31, 2008, the CAL was reviewed by the following team:

Michael Kolian, U.S. Environmental Protection Agency  
Mike McHale, U.S. Geological Survey (USGS)  
Chris Rogers, MACTEC Engineering and Consulting, Inc  
Denise Schmidt, Cary Institute of Ecosystem Studies

---

<sup>1</sup> Environmental 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.

Gregory Wetherbee, USGS (team leader)  
Mark Rhodes, ISWS, NADP Program Office (observer)

A summary of review findings is listed below. All issues are fully resolved.

- Apply reagent labels to Flow Injection Analysis (FIA) pump tubing and refresh glassware labeling in the labs as labels fade/deteriorate.
- Complete an offsite data backup every week. Daily Laboratory Information Management System backups should be sent to the Program Office's server daily to provide an out-of-building daily backup.
- Run a check between the Program Office Web site database and the CAL LIMS just before the annual values are computed and the maps are produced. (This is a Program Office function, not a CAL function.)
- Remove the ammonium hydroxide stored in the hood where ammonium is analyzed by FIA.
- Put waste containers on the floor in the FIA room in secondary containment per University of Illinois policy.
- Add the "user ID" to the Structured Query Language (SQL) Server databases to identify who made changes and when.

## II. Weekly 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 chemist knows the identification number; 2) 2 percent 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 blind samples are identified as sites SWS1, SWS2, and SWS3. In 2008, the SWS1 samples were 1) a certified reference material, AES-05, lot 1107, from the National Water Research Institute (NWRI) of Environment Canada and 2) an internally formulated and prepared simulated rainwater sample approximating the 95<sup>th</sup> percentile of the NTN sample concentrations (08FR95). These were alternated weekly. The SWS2 samples were alternated weekly between deionized (DI) water from the flow injection analysis laboratory and an internally formulated and prepared synthetic rain sample that approximated the 10<sup>th</sup> percentile of NTN sample concentrations (08FR10). The SWS1 and SWS2 samples were not filtered. The filtered SWS3 samples were AES-02, 08FR95, DI water, and 08FR10 submitted in rotation.

Table II-1 through Table II-4 show the 2008 laboratory data derived from the weekly internal blind samples for NTN. Blind samples are randomly dispersed throughout the sample queue; therefore, the derived bias and precision estimates are representative of precipitation sample measurements. The Quality Assurance Plan (QAP) defines the bias goals for the CAL at different concentrations as follows:

- 1) for known concentrations at or near the detection limit, the maximum allowable bias is 100 percent,
- 2) for concentrations at 10 times the method detection limit (MDL), the allowable bias is  $\pm 20$  percent, and
- 3) for concentrations at 100 times the MDL or greater, the allowable bias is  $\pm 10$  percent.

All calculated biases from the internal blind samples were within these limits. Only five analyte concentrations show a percent bias over 10 percent (see Table II-3). The analytes are calcium for the filtered AES-05 with a concentration less than 100 times the MDL, and calcium, magnesium, sodium, and chloride in filtered 08FR10 with concentrations less than 10 times the MDL for all four analytes. The concentrations for all five of these analyte concentrations are such that the noise of the instrument is greater than the bias shown.

In 2008 for the AES-05 blind sample, the largest difference was in the percent bias found for calcium for filtered samples (Table II-1). Previously, a high bias was always obtained for calcium in the order of 25 percent unfiltered and 300 percent filtered from the purchased

**Table II-1. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, AES-05, Unfiltered and Filtered, 2008**

<i>Parameter</i>	<i>Target Concentration<sup>a</sup></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<sup>d</sup></i> (%)(mg/L)	<i>MDL</i> (mg/L)	<i>5<sup>th</sup> Percentile<sup>e</sup></i> (mg/L)
Calcium	0.186	0.194 <sup>b</sup>	0.008	4.3	0.003	1.5	0.006	0.022
		0.205 <sup>c</sup>	0.019	10.2	0.006	2.9		
Magnesium	0.038	0.038	0.000	0.0	0.001	2.6	0.001	0.003
		0.037	-0.001	-2.6	0.001	2.7		
Sodium	0.181	0.185	0.004	2.2	0.003	1.6	0.001	0.006
		0.180	-0.001	-0.6	0.005	2.8		
Potassium	0.027	0.027	0.000	0.0	0.001	3.7	0.001	0.004
		0.026	-0.001	-3.7	0.001	3.8		
Ammonium	0.310	0.300	-0.010	-3.4	0.004	1.3	0.006	0.007
		0.295	-0.015	-5.0	0.006	2.0		
Sulfate	1.28	1.288	0.008	0.6	0.013	1.0	0.007	0.125
		1.265	-0.015	-1.2	0.013	1.0		
Nitrate	1.146	1.164	0.018	1.5	0.016	1.4	0.009	0.149
		1.138	-0.008	-0.7	0.015	1.3		
Chloride	0.223	0.230	0.007	3.1	0.003	1.3	0.004	0.020
		0.227	0.004	1.8	0.002	0.8		
pH (units)	4.89	4.88	-0.01	-0.2	0.03	0.6		6.52
		4.89	0.00	0.0	0.04	0.8		
H (µeq/L)	12.9	13.1	0.2	1.7	0.9	6.9		0.30
		13.0	0.1	0.9	1.1	8.5		
Specific Conductance (µS/cm)	10.8	11.1	0.3	2.8	0.2	1.8		3.1
		11.1	0.3	2.8	0.3	2.7		

**Notes:**

There were 27 unfiltered and 14 filtered AES-05 samples in 2008.

<sup>a</sup> Target Concentrations are those reported by NWRI, Environment Canada

<sup>b</sup> Concentration values for unfiltered AES-05

<sup>c</sup> Concentration values for filtered AES-05

<sup>d</sup> Relative Standard Deviation

<sup>e</sup> 5th percentile of NTN data for 2008 excluding contaminated samples

**Table II-2. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Internally Formulated Simulated Rain (08FR95), Unfiltered and Filtered, 2008**

<i>Parameter</i>	<i>Target Concentration<sup>a</sup></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<sup>d</sup></i> (%)	<i>MDL</i> (mg/L)	<i>5<sup>th</sup> Percentile<sup>e</sup></i> (mg/L)
Calcium	0.664	0.669 <sup>b</sup>	0.005	0.7	0.016	2.5	0.006	0.022
		0.666 <sup>c</sup>	0.002	0.2	0.022	3.4		
Magnesium	0.144	0.144	-0.000	-0.2	0.003	2.3	0.001	0.003
		0.140	-0.005	-3.3	0.003	2.5		
Sodium	0.693	0.687	-0.006	-0.9	0.019	2.8	0.001	0.006
		0.671	-0.022	-3.2	0.011	1.7		
Potassium	0.109	0.110	0.001	-0.9	0.004	3.2	0.001	0.004
		0.107	-0.002	-2.0	0.003	3.0		
Ammonium	1.060	1.048	-0.013	-1.2	0.008	0.8	0.006	0.007
		1.025	-0.035	-3.3	0.009	0.9		
Sulfate	3.778	3.782	0.004	0.1	0.046	1.2	0.007	0.125
		3.677	-0.101	-2.7	0.066	1.8		
Nitrate	3.878	3.860	0.017	-0.4	0.035	0.9	0.009	0.149
		3.758	-0.120	-3.1	0.060	1.6		
Chloride	1.257	1.243	-0.014	-1.1	0.010	0.8	0.004	0.020
		1.214	-0.043	-3.4	0.012	1.0		
pH (units)	4.51	4.48	-0.03	-0.6	0.02	0.5		6.52
		4.48	-0.04	-0.8	0.02	0.5		
H (µeq/L) Specific	30.8	33.0	2.2	7.1	1.8	5.3		0.30
		33.5	2.7	8.6	1.9	5.6		
Conductance (µS/cm)	33.4	32.9	-0.5	-1.5	0.4	1.3		3.1
		32.9	-0.5	-1.5	0.6	1.9		

**Notes:**

There were 26 unfiltered and 13 filtered samples in 2008.

<sup>a</sup> Target concentrations for the internally formulated simulated rainwater sample, 08FR95

<sup>b</sup> Concentration values for unfiltered 08FR95

<sup>c</sup> Concentration values for filtered 08FR95

<sup>d</sup> Relative Standard Deviation

<sup>e</sup> 5<sup>th</sup> percentile of NTN data for 2008 excluding contaminated samples

**Table II-3. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Internally Formulated Simulated Rain (08FR10), Unfiltered and Filtered, 2008**

<i>Parameter</i>	<i>Target Concentration<sup>a</sup></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<sup>d</sup></i> (%)	<i>MDL</i> (mg/L)	<i>5<sup>th</sup> Percentile<sup>e</sup></i> (mg/L)
Calcium	0.025	0.026 <sup>b</sup> 0.031 <sup>c</sup>	0.001 0.006	4.9 25.7	0.002 0.005	9.0 15.8	0.006	0.022
Magnesium	0.005	0.005 0.004	0.000 -0.001	1.2 -24.2	0.000 0.001	5.9 15.5	0.001	0.003
Sodium	0.009	0.009 0.011	0.000 0.002	2.1 21.0	0.000 0.003	3.7 25.5	0.001	0.006
Potassium	0.004	0.004 0.004	0.000 0.000	0.6 -3.2	0.000 0.000	10.4 11.5	0.001	0.004
Ammonium	0.030	0.030 0.031	0.000 0.001	1.4 4.6	0.001 0.001	3.2 4.4	0.006	0.007
Sulfate	0.221	0.217 0.212	-0.004 -0.009	-1.9 -4.1	0.005 0.004	2.1 2.0	0.007	0.125
Nitrate	0.285	0.282 0.277	-0.003 -0.008	-1.1 -3.0	0.005 0.005	1.6 1.7	0.009	0.149
Chloride	0.030	0.030 0.033	0.000 0.003	0.0 10.1	0.002 0.004	5.2 13.5	0.004	0.020
pH (units)	5.16	5.16 5.14	-0.06 -0.01	-0.0 -0.2	0.05 0.05	0.9 1.0		6.52
H (µeq/L)	7.0	7.0 7.2	0.1 0.3	1.0 3.6		0.8 11.2	10.9	0.3
Specific Conductance (µS/cm)	3.8	3.9 3.8	0.1 0.0	2.8 0.5	0.3 0.2	7.2 5.3		3.1

**Notes:**

There were 26 unfiltered and 13 filtered internally formulated simulated rain samples (08FR10) in 2008.

<sup>a</sup> Target Concentrations for 08FR10

<sup>b</sup> Concentration values for unfiltered 08FR10

<sup>c</sup> Concentration values for filtered 08FR10

<sup>d</sup> Relative Standard Deviation

<sup>e</sup> 5<sup>th</sup> percentile of NTN data for 2008 excluding contaminated samples

**Table II-4. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Deionized Water (DI), Unfiltered and Filtered, 2008**

<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<sup>c</sup> (%)</i>	<i>5<sup>th</sup>Percentile<sup>d</sup> (mg/L)</i>
Calcium	0.006	<0.006 <sup>a</sup> <0.006 <sup>b</sup>			0.001 0.001		0.022
Magnesium	0.001	<0.001 <0.001			0.000 0.000		0.003
Sodium	0.001	<0.001 0.001			0.000 0.001		0.006
Potassium	0.001	<0.001 <0.001			0.000 0.000		0.004
Ammonium	0.006	<0.006 <0.006			0.002 0.001		0.007
Sulfate	0.007	<0.007 <0.007			0.000 0.000		0.125
Nitrate	0.009	<0.009 <0.009			0.000 0.002		0.149
Chloride	0.004	<0.004 <0.004			0.001 0.003		0.020
pH (units)		5.61 5.59	-0.01 -0.03	-0.2 -0.5	0.1 0.1	1.8 1.8	6.52
Specific Conductance ( $\mu$ S/cm)		1.3 1.3	0.4 0.4	44.4 44.4	0.3 0.1	23.1 7.7	3.1

**Notes:**

There were 27 unfiltered and 13 filtered DI samples in 2008.

<sup>a</sup> Concentration values for unfiltered DI

<sup>b</sup> Concentration values for filtered DI

<sup>c</sup> Relative Standard Deviation

<sup>d</sup> 5<sup>th</sup> percentile of NTN data for 2008 excluding contaminated samples

pH of DI H<sub>2</sub>O in equilibrium with CO<sub>2</sub> for 2008 = 5.62

Specific conductance of DI H<sub>2</sub>O in equilibrium with CO<sub>2</sub> for 2008 = 0.9  $\mu$ S/cm

standard used as a blind sample. Although in 2008 there was still a bias, it was similar to 2007 and to the other ions: 4.3 percent unfiltered and 10.2 percent filtered. The percent bias found for ammonium using the NWRI sample, AES-05, is less than found in 2007 using the NWRI sample, AES-02, and less than was seen using the previously purchased samples. The 2008 percent bias for ammonium was -3.4 percent unfiltered and -5.0 percent filtered. In 2007, the percent bias for ammonium was -0.6 percent unfiltered and -1.7 percent filtered (negative values for bias for ammonium are expected since ammonium is not stable and the concentration will decrease over time). Previously the percent biases were as high as -38 percent for filtered and unfiltered. Chloride continued to show improvement using the Canadian samples with even lower biases in 2008 than was seen in 2007 (3.1 percent unfiltered and 1.8 percent filtered in 2008 versus 6.6 percent unfiltered and 10.1 percent filtered in 2007). The bias in specific conductance also decreased from 11 percent and 16 percent in 2005 and 2006, respectively, to 3.5 percent (unfiltered) and 2.1 percent (filtered) in 2007 to 2.8 percent (filtered and unfiltered) in 2008. All other analytes showed smaller percent biases in 2008 for the purchased AES-05 than were found in 2007 on AES-02 except for filtered potassium and filtered nitrate. Both were slightly more negative (bias increased slightly) (-1.5 in 2007 vs. -3.7 in 2008 for potassium and 0.6 in 2007 vs. -0.7 in 2008 for nitrate) but were well within the expected noise of the instruments.

The percent biases found for 08FR95 (Table II-2) and 08FR10 (Table II-3) solutions in 2008 agreed closely with the percent biases found for 2007. For 08FR95, seven biases went down slightly, one remained the same, and 14 increased slightly. All biases for both years were less than 10 percent and may be more indicative of the initial concentration measured by the laboratory in determining the concentrations of these solutions than in any changes in the instrumentation or measurement during the year. Three analytes (sulfate, nitrate, and chloride) had a lower bias in the unfiltered solution than was obtained in 2007, but showed an increased bias in the filtered solutions. These are probably legitimate biases due to changes occurring in the instrument over the course of the year. Again, no analyte had a percent bias greater than 10 percent for 08FR95 in 2008, implying that most of the bias may be random noise due to the instrument. For 08FR10, 14 biases in 2008 were greater than was seen for those same analytes for 2007. The percent biases again are small except for the filtered percent biases for calcium (25.7 percent), magnesium (-24.2 percent), and sodium (21.0 percent). Although these percent biases seem high, the actual concentrations for each of these analytes are 0.025 milligrams/Liter (mg/L), 0.005 mg/L, and 0.009 mg/L, which are four, five, and nine times the MDL, respectively. Two analytes (potassium and chloride) showed a decrease in the percent bias for the unfiltered samples and an increase in the percent bias in the filtered sample. Since these ions are measured on different instruments, the change may be due to filtration or to just an artifact of the system noise since the bias is actually very low. There does not appear to be a significant difference over the past several years with these solutions.

Measurements of deionized water (DI) blanks indicated no significant bias in 2008 (Table II-4). The standard deviation for pH and specific conductivity and the bias for the specific conductance of DI used as a blind were unchanged between 2007 and 2008.

Tables II-5 through II-8 compare the filtered with the unfiltered samples for statistical differences. Although most of the noise is presumed to be background noise associated with the handling and analysis of the samples, some of the differences between the filtered and unfiltered samples may be due to the filtration process itself. Although any statistical difference can not be



**Table II-5. Filtered vs. Unfiltered NTN Blinds, AES-05, 2008**

<i>Parameter</i>	<i>Pooled Standard Deviation</i>	<i>Filtered Mean-Unfiltered Mean</i>	<i>Critical Concentration<sub>95%</sub><sup>a</sup></i>	<i>Statistically Biased?</i>
Calcium <sup>b</sup>	0.004	0.010	0.003	yes
Magnesium	0.001	-0.001	0.000	yes
Sodium	0.004	-0.004	0.003	yes
Potassium	0.001	-0.001	0.001	no
Ammonium	0.005	-0.005	0.003	yes
Sulfate	0.013	-0.024	0.009	yes
Nitrate	0.016	-0.027	0.011	yes
Chloride	0.002	-0.003	0.002	yes
pH (pH units)	0.03	0.01	0.02	no
H (µeq/L)	1.0	-0.2	0.6	no
Specific Conductance (µS/cm)	0.2	0.0	0.1	no

**Notes:**

<sup>a</sup> Critical concentration at the 95 percent confidence level

<sup>b</sup> All concentrations are given as mg/L unless otherwise specified.

**Table II-6. Filtered vs. Unfiltered NTN Blinds, 08FR95, 2008**

<i>Parameter</i>	<i>Pooled Standard Deviation</i>	<i>Filtered Mean-Unfiltered Mean</i>	<i>Critical Concentration<sub>95%</sub><sup>a</sup></i>	<i>Statistically Biased?</i>
Calcium <sup>b</sup>	0.019	0.003	0.013	no
Magnesium	0.003	-0.004	0.002	yes
Sodium	0.017	-0.016	0.012	yes
Potassium	0.003	-0.003	0.002	yes
Ammonium	0.009	-0.022	0.006	yes
Sulfate	0.053	-0.104	0.037	yes
Nitrate	0.045	-0.102	0.031	yes
Chloride	0.010	-0.029	0.007	yes
pH (pH units)	0.02	-0.01	0.02	no
H (µeq/L)	1.8	0.5	1.2	no
Specific Conductance (µS/cm)	0.5	0.0	0.3	no

**Notes:**

<sup>a</sup> Critical concentration at the 95 percent confidence level

<sup>b</sup> All concentrations are given as mg/L unless otherwise specified.

**Table II-7. Filtered vs. Unfiltered NTN Blinds, 08FR10, 2008**

<i>Parameter</i>	<i>Pooled Standard Deviation</i>	<i>Filtered Mean-Unfiltered Mean</i>	<i>Critical Concentration<sub>95%</sub></i>	<i><sup>a</sup>Statistically Biased?</i>
Calcium <sup>b</sup>	0.003	0.005	0.002	yes
Magnesium	0.000	-0.001	0.000	yes
Sodium	0.002	0.002	0.001	yes
Potassium	0.000	0.000	0.000	no
Ammonium	0.001	0.001	0.001	no
Sulfate	0.005	-0.005	0.003	yes
Nitrate	0.005	-0.005	0.003	yes
Chloride	0.008	0.001	0.006	no
pH (pH units)	0.05	-0.01	0.03	no
H (µeq/L)	0.8	0.2	0.5	no
Specific Conductance (µS/cm)	0.3	-0.1	0.2	no

**Notes:**

<sup>a</sup> Critical concentration at the 95 percent confidence level

<sup>b</sup> All concentrations are given as mg/L unless otherwise specified.

**Table II-8. Filtered vs. Unfiltered NTN Blinds, DI Water, 2008**

<i>Parameter</i>	<i>Pooled Standard Deviation</i>	<i>Filtered Mean-Unfiltered Mean</i>	<i>Critical Concentration<sub>95%</sub></i>	<i><sup>a</sup>Statistically Biased?</i>
Calcium <sup>b</sup>	0.001	0.001	0.001	no
Magnesium	0.000	0.000	0.000	no
Sodium	0.001	0.001	0.000	yes
Potassium	0.000	0.000	0.000	no
Ammonium	0.002	0.001	0.001	no
Sulfate	0.000	0.000	0.000	no
Nitrate	0.001	0.001	0.001	no
Chloride	0.002	0.002	0.001	yes
pH (pH units)	0.12	-0.02	0.08	no
H (µeq/L)	0.6	0.1	0.4	no
Specific Conductance (µS/cm)	0.2	0.0	0.2	no

**Notes:**

<sup>a</sup> Critical concentration at the 95 percent confidence level

<sup>b</sup> All concentrations are given as mg/L unless otherwise specified.

guaranteed to be caused by the filtration process, looking at the statistical differences between the filtered and unfiltered samples should give an indication of how the filtration process is affecting the samples. A pooled standard deviation is generated for this comparison. This assumes that filtered and unfiltered samples are statistically different. A critical concentration is determined at the 95<sup>th</sup> percentile confidence interval, meaning that only 5 percent of the samples fall outside this value naturally. If the difference between the means of the filtered and unfiltered samples is greater than the critical concentration, the difference falls outside the statistical expectation more than 5 percent of the time. For AES-05, only potassium, pH, and specific conductance were not statistically biased (Table II-5). However, the difference between the filtered and unfiltered samples for all but sulfate, nitrate, and possibly sodium were less than or equal to the minimum detection limit, implying the difference could still be within the noise of the instrument. For 08FR95 (Table II-6), calcium, pH, and specific conductance did not show a statistical bias between the filtered and unfiltered samples. Calcium was not biased because of the large pooled standard deviation and the large critical concentration resulting from more noise in the analysis. The other analytes all showed large differences between the mean of the filtered solutions and the mean of the unfiltered solutions. For the lower synthetic rain solution (Table II-7), potassium and ammonium are not statistically different along with pH and conductivity. The critical concentration for these low analyte concentrations is very low, even though the difference is less than the method detection limit for all of the analytes. At these concentrations, the bias is probably not relevant, although it is statistically different. For DI (Table II-8), sodium and chloride show a statistical bias. Although the numbers are at or below the MDL, this could be caused by handling the filtered sample and could be a true artifact of the filtration process, or simply could be an artifact of the measurements being at or below the detection limit.

## **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 2008, the solution used was an internally formulated and prepared simulated rain sample approximating the 95<sup>th</sup> percentile of the NTN concentrations, 08FR95.

Table II-9 shows the internal blind sample summary for 2008. The bias between the target concentrations and the measured concentrations were less than the 5th percentile of the AIRMoN precipitation concentrations for 2008. For most of the analytes, the bias was less than or equal to the method detection limit. Calcium, sodium, and ammonium biases were greater than the MDL. Half of the analytes had higher biases in 2008 than in 2007 (calcium, ammonium, sulfate, nitrate, and chloride). Since all three analytes measured by the ion chromatograph had higher biases, this could be a result of the instrument calibration or other instrument-related bias. However, even for these five analytes, the differences between 2007 and 2008 were small and the percent bias for all analytes was less than 10 percent, or within the expected noise of the analysis. The standard deviation for 2008 either went down (0.027 in 2007 vs. 0.014 in 2008 for calcium), or was very similar to that for 2007. Again, the IC analytes, specifically sulfate and nitrate, had higher standard deviations in 2008 than in 2007, staying consistent with the bias results, although chloride actually had a slightly lower standard deviation.

Since 08FR95 is used by both AIRMoN and NTN, Table II-10 is a comparison of the two blind programs. Although the instrumentation and the analyst were the same for both networks,

**Table II-9. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, AIRMoN, 2008**

<i>Parameter</i>	<i>Target Concentration<sup>a</sup></i> (mg/L)	<i>Mean<sup>b</sup></i> <i>Concentration</i> (mg/L)	<i>Bias</i> (mg/L)	<i>Bias</i> (%)	<i>Standard Deviation</i> (mg/L)	<i>RSD<sup>c</sup></i> (%)	<i>MDL</i> (mg/L)	<i>5<sup>th</sup> Percentile<sup>d</sup></i> (mg/L)
Calcium	0.664	0.671	0.007	1.0	0.014	2.0	0.006	0.006
Magnesium	0.144	0.144	0.000	0.2	0.003	2.1	0.001	0.001
Sodium	0.693	0.687	-0.006	-0.8	0.014	2.0	0.001	0.002
Potassium	0.109	0.110	0.001	0.7	0.002	2.2	0.001	0.003
Ammonium	1.060	1.046	-0.014	-1.3	0.011	1.1	0.006	0.036
Sulfate	3.778	3.771	-0.007	-0.2	0.055	1.5	0.007	0.213
Nitrate	3.878	3.859	-0.019	-0.5	0.042	1.1	0.009	0.218
Chloride	1.257	1.240	-0.017	-1.4	0.011	0.9	0.004	0.016
pH	4.51	4.49	-0.02	-0.4	0.03	0.6		5.25
H (µeq/L)	30.9	32.3	1.4	4.6	2.0	6.3		5.6
Specific Conductance (µS/cm)	33.4	33.1	-0.3	-0.8	0.6	1.8		5.1

**Notes:**

This tabulation included 48 internal blinds. Samples were simulated approximating the 95<sup>th</sup> percentile of NTN samples (08FR95).

<sup>a</sup> Target concentrations for 08FR95

<sup>b</sup> Mean concentration obtained by the CAL from the AIRMoN internal blind samples for 2008

<sup>c</sup> RSD is Relative Standard Deviation

<sup>d</sup> 5<sup>th</sup> percentile of AIRMoN data for 2008 excluding contaminated samples

**Table II.10 AIRMoN vs NTN 08FR95  $n_{\text{AIRMoN}} = 48$ ,  $n_{\text{NTN}} = 26$ ,  $t_{95,72}$ , 2008**

<i>Parameter</i>	<i>mean NTN</i>	<i>mean AIRMoN</i>	<i>Std Dev NTN</i>	<i>Std Dev AIRMoN</i>	<i>Difference<sub>N-A</sub><sup>a</sup></i>	<i>Std Dev<sub>pooled</sub></i>	<i>Critical<sup>b</sup> Concentration</i>	<i>Statistically Biased?</i>
Calcium <sup>c</sup>	0.669	0.671	0.016	0.014	-0.002	0.015	0.007	no
Magnesium	0.144	0.144	0.003	0.003	0.000	0.003	0.002	no
Sodium	0.687	0.687	0.019	0.014	0.000	0.016	0.001	no
Potassium	0.110	0.110	0.004	0.002	0.000	0.003	0.001	no
Ammonium	1.048	1.046	0.008	0.011	0.002	0.010	0.005	no
Sulfate	3.782	3.771	0.046	0.055	0.011	0.052	0.025	no
Nitrate	3.860	3.859	0.035	0.042	0.001	0.040	0.019	no
Chloride	1.243	1.240	0.010	0.011	0.003	0.011	0.005	no
pH (pH units)	4.48	4.49	0.02	0.03	-0.01	0.03	0.01	no
H (µeq/L)	33.0	32.3	1.8	2.0	0.7	2.0	0.95	no
Specific Conductance (µS/cm)	32.9	33.1	0.4	0.6	-0.2	0.5	0.3	no

**Notes:**

<sup>a</sup> N = NTN, A = AIRMoN

<sup>b</sup> Critical concentration at the 95 percent confidence level

<sup>c</sup> All concentrations are given as mg/L unless otherwise specified.

when looking at the bias and standard deviation for each program, there appears to be a difference. However, when reviewed statistically at the 95 percent confidence level, no analyte concentrations from AIRMoN were statistically different from the unfiltered NTN concentrations.

## **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 separately from the original samples. In 2008, the NTN samples chosen to be split were marked on the bag as “split.” When the sample processor receives the marked bag, pH and conductivity are measured and two 60 mL bottles are filled, one for immediate analysis and one to 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, thereby rendering the pH and conductivity results 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: one original, one 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-11 and II-12 summarize the analyses of replicate samples analyzed in 2008 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 percent. For NTN, the way of filtering for split samples prior to 2007 made achieving small differences between the original and the replicate sample hard, if not impossible, to achieve because of the impact that filtration has on concentration. With the new method of filtering replicates begun in 2007 (i.e., filtering the split separate from the original so it is treated exactly like the original sample), the mean and the median percent differences for all levels of concentration are below 10 percent. 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 per 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.



**Table II-11. Replicate NADP/NTN Precipitation Samples, 2008**

<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<sup>a</sup></i>	<i>MAD<sup>b</sup></i>	<i>Estimate of Dispersion</i>
Calcium	≤ 0.06mg/L	3.1	1.3	0.002	90	0.002	0.003
	0.06 < x ≤ 0.6 mg/L	0.2	0.1	0.006	165	0.004	0.006
	> 0.6 mg/L	1.5	1.2	0.019	5	0.023	0.033
Magnesium	≤ 0.01 mg/L	-0.9	0.0	0.001	74	0.000	0.000
	0.01 < x ≤ 0.1 mg/L	1.1	0.3	0.001	167	0.001	0.001
	> 0.1 mg/L	0.8	-0.1	0.005	19	0.004	0.006
Sodium	≤ 0.01 mg/L	6.5	1.0	0.001	32	0.000	0.001
	0.01 < x ≤ 0.1 mg/L	0.3	-0.6	0.001	136	0.001	0.001
	>0.1 mg/L	0.4	0.7	0.022	92	0.006	0.009
Potassium	≤ 0.01 mg/L	2.9	0.2	0.000	78	0.000	0.001
	0.01 < x ≤ 0.1 mg/L	-0.2	0.3	0.001	173	0.001	0.001
	> 0.1 mg/L	-1.2	0.6	0.006	9	0.005	0.007
Ammonium	≤ 0.06 mg/L	-7.0	-5.6	0.004	42	0.003	0.004
	0.06 < x ≤ 0.6	-2.1	-1.7	0.007	190	0.004	0.006
	> 0.6 mg/L	-0.8	-0.5	0.015	28	0.007	0.011
Sulfate	≤ 0.07 mg/L	-0.1	-0.1	0.001	2	0.001	0.001
	0.07 < x ≤ 0.7 mg/L	0.3	0.2	0.006	99	0.003	0.005
	> 0.7 mg/L	0.9	0.5	0.031	159	0.013	0.020
Nitrate	≤ 0.09 mg/L	-5.6	-3.4	0.007	6	0.005	0.007
	0.09 < x ≤ 0.9 mg/L	0.09	0.1	0.008	163	0.005	0.007
	> 0.9 mg/L	0.3	0.3	0.019	91	0.015	0.022

**Table II-11. Replicate NADP/NTN Precipitation Samples, 2008, 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<sup>a</sup></i>	<i>MAD<sup>b</sup></i>	<i>Estimate of Dispersion</i>
Chloride	≤ 0.04 mg/L	4.2	1.3	0.002	58	0.001	0.001
	0.04 < x ≤ 0.4 mg/L	0.2	0.4	0.003	149	0.002	0.002
	> 0.4mg/L	0.0	-0.2	0.054	53	0.008	0.012
Orthophosphate	≤ 0.04 mg/L	-102.7	-58.9	0.001	258	0.001	0.001
	0.04 < x ≤ 0.4 mg/L	-6.0	-6.0	0.003	2	0.004	0.006
	> 0.4 mg/L	no samples at this concentration					
pH	< 5	0.2	0.2	0.04	134	0.03	0.04
	≥ 5	0.2	0.2	0.06	126	0.05	0.07
H	> 10 µeq/L	-1.4	-2.3	2.5	134	1.6	2.3
	≤ 10 µeq/L	-0.6	-2.3	0.7	126	0.4	0.5
Specific Conductance	< 10 µS/cm	0.5	0.0	0.2	135	0.1	0.2
	≥ 10 µS/cm	-0.3	0.0	0.4	125	0.2	0.3

**Notes:**

<sup>a</sup> Number of samples

<sup>b</sup> Median Absolute Difference

**Table II-12. Replicate NADP/AIRMoN Precipitation Samples, 2008**

<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<sup>a</sup></i>	<i>MAD<sup>b</sup></i>	<i>Estimate of Dispersion</i>
Calcium	≤ 0.06 mg/L	-0.1	0.0	0.003	14	0.001	0.001
	0.06 < x ≤ 0.6 mg/L	-0.4	-0.8	0.001	18	0.002	0.003
	> 0.6 mg/L	1 sample, no statistics, % difference = 1.7		1			
Magnesium	≤ 0.01 mg/L	5.0	0.0	0.001	8	0.001	0.001
	0.01 < x ≤ 0.1 mg/L	-0.7	0.0	0.001	21	0.001	0.001
	≥ 0.1 mg/L	-1.0	-2.4	0.005	4	0.005	0.007
Sodium	≤ 0.01 mg/L	2.4	11.1	0.001	7	0.001	0.001
	0.01 < x ≤ 0.1 mg/L	3.9	3.2	0.002	15	0.001	0.001
	> 0.1 mg/L	-0.7	-1.5	0.038	11	0.002	0.003
Potassium	≤ 0.01 mg/L	-4.0	0.0	0.001	9	0.000	0.000
	0.01 < x ≤ 0.1 mg/L	2.4	-4.9	0.008	23	0.002	0.003
	> 0.1 mg/L	1 sample, no statistics, % difference = -3.5		1			
Ammonium	≤ 0.06 mg/L	1.8	-2.3	0.001	4	0.001	0.001
	0.06 < x ≤ 0.6 mg/L	-2.8	-2.1	0.011	26	0.004	0.006
	> 0.6 mg/L	-5.7	-7.3	0.016	3	0.049	0.073
Sulfate	< 0.07 mg/L	no samples at this concentration					
	0.07 < x ≤ 0.7 mg/L	1.3	0.9	0.018	8	0.007	0.010
	> 0.7 mg/L	-0.6	-0.4	0.025	25	0.010	0.015
Nitrate	≤ 0.09 mg/L	no samples at this concentration					
	0.09 < x ≤ 0.9 mg/L	0.1	0.1	0.011	19	0.005	0.007
	> 0.9 mg/L	0.3	0.0	0.021	14	0.018	0.027

**Table II-12. Replicate NADP/AIRMoN Precipitation Samples, 2008, 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<sup>a</sup></i>	<i>MAD<sup>b</sup></i>	<i>Estimate of Dispersion</i>
Chloride	≤ 0.04 mg/L	4.9	3.6	0.002	7	0.003	0.004
	0.04 < x ≤ 0.4 mg/L	0.7	-0.2	0.006	22	0.004	0.006
	> 0.4 mg/L	1.8	1.0	0.096	4	0.035	0.050
Orthophosphate	≤ 0.04 mg/L	-5.5	-35.0	0.005	33	0.002	0.003
	no samples of higher concentration						
pH	< 5	0.7	0.6	0.06	25	0.04	0.06
	≥ 5	1.3	0.5	0.09	8	0.03	0.04
H	> 10 µeq/L	-6.2	-6.7	3.4	25	2.4	3.6
	≤ 10 µeq/L	-2.7	-5.4	1.3	8	0.6	0.9
Specific Conductance	< 10 µS/cm	-6.0	-7.7	0.6	9	0.4	0.6
	≥ 10 µS/cm	-5.8	-3.6	1.3	24	0.8	1.2

**Notes:**

<sup>a</sup> Number of samples

<sup>b</sup> Median Absolute Difference

The standard deviation estimated from paired measurements was used to calculate the standard deviations. The last column in Tables II-11 and II-12 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 for both NTN (Tables II-1 through II-4) and AIRMoN (Table II-9) with the estimate of dispersion or with the paired standard deviations for the replicate samples shows comparable cation and anion precision. Some estimates of dispersion are greater than the internal blind standard deviations and some are less. One would expect greater variability in real precipitation samples as these are not going to be as stable as synthetically prepared solutions. The standard deviations of comparable concentrations with the internal blinds and replicates are similar, reinforcing the fact that the higher the concentration of the sample, the more noise will be found. 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.

A comparison between NTN and AIRMoN standard deviations and estimates of dispersion for replicate samples shows that there is little difference between the two networks. For most analytes and at most concentrations, the estimate of dispersion is very similar. The overall number of replicate samples for AIRMoN is much smaller than for NTN, which could be the reason for the minor differences that do exist. As expected, the highest variability is calculated from the smallest sample sets. The differences between the networks might be less if the sample sizes were equivalent. AIRMoN should, because of refrigeration from sample collection through analysis, have a smaller variability, but that is not obvious from this data. This does show up in the orthophosphate numbers. For NTN the amount of orthophosphate measured is generally at or below the detection limit for both the original and the replicate sample. For AIRMoN, although the values are low, orthophosphate concentration is above the detection limit. The mean percent difference between the two networks is an indication of this difference in concentration of orthophosphate.



### III. Blanks

Solutions referred to as “blanks” are either deionized (DI) water solutions or in-house prepared simulated rainwater approximating the 25<sup>th</sup> percentile concentration of the NTN (FR25). 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. 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. DI water blanks from the sample processing, the two analytical, and the bucket-washing service laboratories are also included in this set of samples. Specifics on how the blanks are prepared can be found in the CAL Quality Assurance Plan (QAP) and laboratory Standard Operating Procedures (SOP). Supplies found to have large contamination of even one analyte are removed from the inventory and discarded.

Tables III-1 through III-8 contain a summary of the various blanks analyzed at the CAL. The calculations for the critical concentrations and for determining statistical bias can be found on the CAL Web site (see App. A).

In general, looking at all the ammonium blank concentrations (Tables III-2 to III-8), ammonium appears to be statistically biased low for all higher volume blanks (150 mL). This would not be expected if the bias was blank dependent or random, implying the initial concentration of the solution used for blanks may have had the wrong ammonium concentration. Most of the blanks measured had a mean concentration of ammonium of about 0.090 milligrams/Liter (mg/L), whereas the target concentration was 0.095 mg/L. The noise was greater in the lower volume (50 milliliters (mL)) blanks resulting in some showing a bias and others not, although the mean concentration is still lower than the target concentration. No additional comments about the statistical bias of ammonium will be made during the discussion of blanks. pH appears to be biased low in a majority of the blanks (Tables III-1 to III-8). Again, this should not happen across all blanks without a systematic error, which is probably the target value used for the check sample.

The weekly deionized water blanks (Table III-1) show the measured pH to be about the same as in 2007, which was about 0.05 pH units lower than in previous years. The spread for pH in 2008 was narrower than in 2007, from a high of about 5.8 to a low of about 5.4 compared to a high of about 5.9 and a low of about 5.2 found in 2007.

Calcium has been statistically biased ( $\alpha = 0.05$ ) in the filter blanks for the past several years. In 2008 as in 2007, it was not biased (Table III-2). No changes were made to the solutions or the filters. In 2008 only magnesium was statistically biased ( $\alpha = 0.05$ ) in the filter blanks. Statistically biased does not necessarily mean that the bias impacts typical sample concentrations, or that the bias is relevant to the sample concentrations. It does mean that the noise of the measurement of the target concentration does not overlap with the noise of the measurement of the blank, in this case the filter blank. If the bias is near the method detection limit (MDL), its impact on the samples, even if statistically valid, will not be seen above the expected noise of the measurement. It has been previously proven by U.S. Geological Survey (USGS) (<http://bqs.usgs.gov/precip/>) and others that filtration does impact the sample

**Table III-1. pH and Specific Conductance for Weekly DI Water Blanks, 2008**

		<i>Sample Processing Laboratory</i>	<i>Analytical Lab-1</i>	<i>Supply Preparatory Laboratory</i>	<i>Analytical Lab-2</i>
Median					
pH (units)		5.56	5.58	5.59	5.56
Specific Conductance	( $\mu\text{S}/\text{cm}$ )	0.9	0.8	0.8	0.9
Maximum					
pH (units)		5.84	5.88	5.85	5.77
Specific Conductance	( $\mu\text{S}/\text{cm}$ )	1.6	1.5	1.4	1.6
Minimum					
pH (units)		5.44	5.42	5.45	5.42
Specific Conductance	( $\mu\text{S}/\text{cm}$ )	0.4	0.4	0.4	0.6
Target for DI					
pH (units)		5.62			
Specific Conductance	( $\mu\text{S}/\text{cm}$ )	0.9			
Number of samples		52	52	52	52



**Table III-2. Median Analyte Concentration Found in Filter Leachates, 2008**

<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>Uncertainty (95%) (mg/L)</i>	<i>Statistically Biased? (<math>\alpha = 0.05</math>)</i>
Calcium	0.006	<0.006	0.055	0.054	0.001	0.004	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	0.005	no
Potassium	0.001	<0.001	0.009	0.009	0.000	0.001	no
Ammonium	0.006	<0.006	0.090	0.095	-0.007	0.005	yes <sup>a</sup>
Sulfate	0.007	<0.007	0.497	0.525	-0.035	0.050	no
Nitrate	0.009	<0.009	0.574	0.593	-0.030	0.057	no
Chloride	0.004	<0.004	0.052	0.053	0.002	0.005	no
pH		5.54	4.91	4.95	0.03	0.04	no
Hydrogen ion ( $\mu\text{eq/L}$ )		2.9	12.3	11.2	0.9		
Specific Conductance ( $\mu\text{S/cm}$ )		1.1	6.8	6.9	-0.2	0.4	no

**Note:**

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

<sup>a</sup> See text for an explanation of the statistical bias for ammonium.

**Table III-3. Median Analyte Concentration Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in Upright Bucket Leachates, 2008**

<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? (<math>\alpha=0.05</math>)</i>	<i>(150 mL)</i>	<i>Statistically Biased? (<math>\alpha=0.05</math>)</i>
Calcium	0.002	<0.006	0.054	no	0.054	no
Magnesium	0.001	<0.001	0.011	no	0.010	no
Sodium	0.001	<0.001	0.020	no	0.020	no
Potassium	<0.001	<0.001	0.009	no	0.010	no
Ammonium	<0.006	<0.006	0.092	no	0.090	yes <sup>a</sup>
Sulfate	<0.007	<0.007	0.519	no	0.512	no
Nitrate	<0.009	<0.009	0.593	no	0.588	no
Chloride	0.006	<0.004	0.055	no	0.054	no
pH (units)	5.52	5.52	4.90	yes <sup>b</sup>	4.90	yes <sup>b</sup>
Hydrogen ion ( $\mu\text{eq}/\text{bucket}$ )	3.0	3.0	12.6		12.6	
Specific Conductance ( $\mu\text{S}/\text{cm}$ )	1.4	1.3	7.1	yes	7.0	no
n <sup>c</sup>	103	103	53		52	

**Notes:**

MDLs and target concentrations for 07FR25 are reported in Table III-2.

<sup>a</sup> See text for an explanation of the statistical bias for ammonium.

<sup>b</sup> See text for an explanation of the statistical bias for pH.

<sup>c</sup> n is the number of blanks or leachate sample weeks in 2008.

**Table III-4. Median Analyte Concentration Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in HDPE 1-Liter Bottle Leachates, 2008**

<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 (<math>\alpha=0.05</math>)</i>	<i>(150 mL)</i>	<i>Statistically Biased (<math>\alpha=0.05</math>)</i>
Calcium	<0.006	<0.006	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	<0.006	<0.006	0.090	yes <sup>a</sup>	0.091	yes <sup>a</sup>
Sulfate	<0.007	<0.007	0.509	no	0.510	yes
Nitrate	<0.009	<0.009	0.584	no	0.585	yes
Chloride	<0.004	<0.004	0.052	no	0.052	no
pH (units)	5.53	5.55	4.91	no	4.90	yes <sup>b</sup>
Hydrogen ion ( $\mu\text{eq}/\text{bucket}$ )	3.0	2.8	12.3		12.6	
Specific Conductance ( $\mu\text{S}/\text{cm}$ )	1.2	1.1	6.9	no	6.9	no

**Notes:**

There were 52 blank sample weeks in 2008 with 104 DI water bottle blanks.

MDLs and target concentrations for 08FR25 are reported in Table III-2.

<sup>a</sup> See text for an explanation of the statistical bias for ammonium.

<sup>b</sup> See text for an explanation of the statistical bias for pH.

**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, 2008**

<i>Analyte</i>	<i>MDL</i> (mg/L)	<i>DI Water</i>		<i>FR25</i>			<i>FR25</i> <i>Target</i> <i>Concentration</i> (mg/L)
		<i>mean</i> (mg/L)	<i>median</i> (mg/L)	<i>mean</i> (mg/L)	<i>median</i> (mg/L)	<i>Statistically</i> <i>significant bias?</i>	
Calcium	0.006	<0.006	<0.006	0.056	0.053	no	0.053
Magnesium	0.001	<0.001	<0.001	0.011	0.010	no	0.010
Sodium	0.001	<0.001	<0.001	0.021	0.020	no	0.019
Potassium	0.001	0.003	<0.001	0.010	0.010	no	0.009
Ammonium	0.006	0.008	<0.006	0.103	0.093	no	0.095
Sulfate	0.007	<0.007	<0.007	0.5323	0.511	no	0.525
Nitrate	0.009	<0.009	<0.009	0.607	0.589	no	0.593
Chloride	0.004	<0.004	<0.004	0.055	0.053	no	0.053
pH (units)		5.53	5.54	4.90	4.91	yes <sup>a</sup>	4.95
Hydrogen Ion ( $\mu$ eq/L)		3.0	2.9	12.6	12.3		11.2
Specific Conductance ( $\mu$ S/cm)		1.1	1.1	7.2	6.9	no	6.9

**Notes:**

There were 52 weeks of snap-on lid blanks.

<sup>a</sup> See text for an explanation of the statistical bias for pH.

**Table III-6. Analyte Concentration (mg/L) Found in  
Monthly Simulated Rain (FR25) AIRMoN 250-mL  
HDPE Bottle Leachates, 2008**

<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?@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	0.052	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	0.091	0.092	yes <sup>a</sup>	0.092	0.092	yes <sup>a</sup>	0.095
Sulfate	0.517	0.514	no	0.514	0.508	yes	0.525
Nitrate	0.587	0.586	no	0.588	0.586	no	0.593
Chloride	0.052	0.052	no	0.051	0.052	yes	0.053
pH (units)	4.91	4.91	yes <sup>b</sup>	4.90	4.89	yes <sup>b</sup>	4.95
Hydrogen Ion ( $\mu$ eq/L)	12.5	12.4		12.7	12.9		11.2
Specific Conductance ( $\mu$ S/cm)	6.9	6.9	no	7.0	6.9	no	6.9
N <sup>c</sup>	16			13			

**Notes:**

<sup>a</sup> See text for an explanation of the statistical bias for ammonium.

<sup>b</sup> See text for an explanation of the statistical bias for pH.

<sup>c</sup> n is the number of blanks or leachate sample weeks in 2008.

**Table III-7. Analyte Concentration (mg/L) Found in  
Deionized (DI) Water and Simulated Rain  
(FR25) Used to Leach Bucket Bags, 2008**

<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	<0.006	<0.006	0.053	0.053	no	0.053
Magnesium	0.001	0.001	0.011	0.010	no	0.010
Sodium	<0.001	<0.001	0.020	0.019	no	0.019
Potassium	<0.001	<0.001	0.010	0.009	no	0.009
Ammonium	<0.006	<0.006	0.092	0.092	no	0.095
Sulfate	<0.007	<0.007	0.511	0.510	no	0.525
Nitrate	<0.009	<0.009	0.586	0.585	no	0.593
Chloride	0.004	0.004	0.055	0.053	no	0.053
pH (units)	5.53	5.53	4.91	4.91	no	4.95
Hydrogen Ion ( $\mu$ eq/L)	3.0	3.0	12.5	12.3		11.2
Specific Conductance ( $\mu$ S/cm)	1.2	1.2	7.1	6.9	no	6.9
n <sup>a</sup>	80			40		

**Notes:**

<sup>a</sup> n is the number of blanks or leachate sample weeks in 2008.

**Table III-8. Analyte Concentration (mg/L) Found in  
Deionized (DI) Water and Simulated Rain  
(FR25) Used to Leach Lid Bags, 2008**

<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	<0.0062	<0.006	0.053	0.053	no	0.053
Magnesium	<0.001	<0.001	0.010	0.010	no	0.010
Sodium	0.001	<0.001	0.020	0.019	no	0.019
Potassium	<0.001	<0.001	0.010	0.009	no	0.009
Ammonium	<0.006	<0.006	0.094	0.093	no	0.095
Sulfate	<0.007	<0.007	0.514	0.512	no	0.525
Nitrate	<0.009	<0.009	0.588	0.588	no	0.593
Chloride	<0.004	<0.004	0.053	0.052	no	0.053
pH (units)	5.53	5.53	4.91	4.91	no	4.95
Hydrogen Ion (µeq/L)	3.0	3.0	12.4	12.3	no	11.2
Specific Conductance (µS/cm)	1.1	1.1	7.0	6.9	no	6.9
n <sup>a</sup>	114		53			

**Notes:**

<sup>a</sup>n is the number of blanks or leachate sample weeks in 2008.

concentration for certain analytes. The CAL continually monitors the filters in an effort to keep this impact low. In 2008, the bias of magnesium, -0.002 mg/L, was within the noise of the instrument (Table III-2).

Although the routine weekly bucket blanks (Table III-3) showed no statistical biases or other problems in 2008, new bucket cleanliness was a problem. The source for purchasing new buckets could not provide the CAL with buckets as clean as previously. As such, no new buckets were introduced to the system from April 2008 through the end of the year. The new buckets mainly had ammonium contamination, but they also had calcium. New washing and leaching procedures were tried for the new buckets to determine what was needed to clean the buckets. Additional bucket blanks were run to determine the source of the ammonium contamination. The dishwasher water was checked and the dishwashers were cleaned. Most bucket blanks, after being rewashed several times, were no longer contaminated, so increased wash time for new buckets became the normal procedure for bucket washing. For a description of the bucket washing procedures for both new and used buckets, see SOP PR-0009.

Bottle blanks (Table III-4) appeared to have more contamination than in previous years with nitrate and sulfate having a statistically significant low bias in the larger volume (150 mL) blanks, implying the bottles are adsorbing sulfate and nitrate. There is, in fact, little difference between the low volume blank and the high volume blank means. Looking at the mean sulfate and nitrate concentrations in all of the blanks, it appears that the original target concentrations were also off for these ions, but only in a few blanks were they statistically relevant. If this is truly the case, then there is no contamination or adsorption into the bottles. Thus, sample concentrations would not be affected.

The snap-on lids (Table III-5), bucket bags (Table III-7), and lid bags (Table III-8) continue to have little or no statistically significant bias. This could be either because all of these use only the low volume (50 mL) blank solutions or because the solutions do not stay in them as long as the solutions in the other blanks. The samples either do not come into contact or are in contact a very short time; therefore, with the current bags and lid washing procedures, there should be little to no contamination of the sample.

The AIRMoN bottles (Table III-6) show some potentially statistical bias for ammonium, pH, sulfate, and chloride. For the reasons mentioned above, the bias is not considered relevant.



## **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 U.S. Geological Survey (USGS) interlaboratory comparison study are summarized and reviewed prior to the data being transmitted 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. All samples with sufficient volume (internal blinds, field blanks, and collocated program samples) 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 the 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 CAL QAP (Simmons et al., 1991). 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 page. 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 percent 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 reason. If the discrepancy is related to the instrument or anything other than the sample chemistry changing between the original sample and reanalysis, the analysts must remeasure all samples surrounding the reanalysis sample to ensure 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 2008 there were 692 samples targeted for reanalysis for NTN out of a total of 13,725 samples. This included 459 samples pulled for IPD, 103 samples pulled for CPD (some samples with bad IPD may also have bad CPD, so there could be overlaps between these two sets of samples), and 135 random samples pulled. Additional samples may be pulled by the analysts for additional checks. There were 187 edits made to the NTN database based on reanalysis findings. For AIRMoN in 2008 there were a total of 88 samples targeted for reanalysis out of 1352 samples. Twenty-one samples were pulled for CPD, 53 were pulled for IPD, and 27 were randomly pulled. There were 12 edits for AIRMoN based on reanalysis findings.

## **B. Laboratory Round-Robin Programs**

The interlaboratory comparison program conducted by the USGS began in 1982 as a portion of the external QA oversight of the CAL for the NADP/NTN. Every four weeks, the USGS mails one set of four blind samples of different matrices to eight participating laboratories, totaling 48 samples per laboratory in 12 monthly 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 Web page (see App. A).

The 38<sup>th</sup> and 39<sup>th</sup> sets of the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) reference precipitation samples were shipped to participating laboratories in April and October 2008, respectively. 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 Centre 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 the WMO/GAW Quality Assurance Science Activity Centre-Americas Web page (see App. A).

The CAL participated in two studies sponsored by the National Water Research Institute (NWRI) in Burlington, Ontario, Canada in 2008. Begun in 1982 as the Long-Range Transport of Atmospheric Pollutants (LRTAP) program, the studies for 2008 were PT92 and PT93 (Tinson, 2008, and Tinson, 2009). Although the NWRI sponsors several different types of sample sets with each study, in 2008 the CAL participated only in the Rain and Soft Waters (RN) studies.

The NWRI publishes a report that includes all the data and a summary of all the laboratories participating in each study. For the RN samples for Study PT 92, the CAL analyzed 10 parameters with final results showing no biases, and no flags were received, which resulted in a score of 0 percent or a "good" rating. For Study PT91, the CAL reported the routine 10 parameters contracted for NADP as well as total nitrogen (TN). For the eleven parameters measured, no biases were detected, and for the 110 results, no flags were received. The CAL received a score of 0 percent or a rating of "good." For more information on these 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 26th European Monitoring and Evaluation Programme (EMEP) intercomparison of analytical methods for atmospheric precipitation in 2008. As of this time, the results of this study are not available. For more information about the NILU, refer to their Web page (see App. A).

## V. REFERENCES

- Central Analytical Laboratory. 2008. *Quality Assurance Plan*, Version 2.0. CAL, Champaign, IL.
- Central Analytical Laboratory. 2008. *Standard Operating Procedures*. CAL, Champaign, IL.
- Helsel, D. R. and R. M. Hirsch. 1992. *Statistical Methods in Water Resources*. Amsterdam, The Netherlands: Elsevier Science Publishers.
- National Atmospheric Deposition Program. 2008. QA Plan 2008-01. NADP, Champaign, IL.
- 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.
- Simmons, C. L., S. R. Dossett, W. C. Eaton, B. A. Malo, M. E. Peden, and D. S. Bigelow. 1991. *Quality Assurance Plan, NADP/NTN Deposition Monitoring*. NADP/NTN Coordinator's Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO.
- Tinson, C. 2008. *Environment Canada Proficiency Testing Program - Rain and Soft Waters - Study 0092 –June to September 2008, Report No. NLET-TN08-004*. 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 0093 –December 2008 to March 2009, Report No. WSTD #09-001*. National Water Research Institute National Laboratory for Environmental Testing, Burlington, Ontario, Canada.



## APPENDIX A



## Appendix A: Web Sites

NADP CAL Quality Assurance Plan:

<http://nadpweb2.sws.uiuc.edu/ops/cal/Shared%20Documents/Forms/NADP%20Documents.aspx>

NADP CAL Standard Operating Procedures:

<http://nadpweb2.sws.uiuc.edu/ops/cal/SOPs%20Final/Forms/ANSOPs.aspx>

NADP/CAL:

<http://nadp.isws.illinois.edu/cal/>

USGS Branch of Quality Systems:

<http://bqs.usgs.gov/precip/>

World Meteorological Organization/Global Atmospheric Watch Quality Assurance Science Activity Centre-Americas:

<http://www.qasac-americas.org/>

Norwegian Institute for Air Research:

<http://tarantula.nilu.no/projects/ccc/reports.html>





## APPENDIX B



## Appendix B: CAL Staff

Christopher Lehmann                      CAL Director

Kim	Attig
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