

QUALITY ASSURANCE REPORT  
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM  
2005-2006

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, 2005-2006*, 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 remained within the quality control objectives for the networks in 2005 and 2006.

## 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. 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. As a reviewer, Christopher Lehmann, the NADP Quality Assurance Specialist, and now the CAL Director, helped in many aspects of this report. Without him, this report could not have been completed. The following reviewers contributed their time and input to the final report: Mark Rhodes, John Sherwell, and Greg Wetherbee. And a final thanks to the ISWS editor, Lisa Sheppard.

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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 Assurance Plan (QAP). The CAL was in compliance with the NADP QAP in 2005 and 2006.

Weekly QA procedures ensure that all materials coming into contact with the precipitation samples do not contaminate the samples. Any problems that arise must be investigated, documented, and eliminated if possible or practical. Blank analyses, matrix-spiked analyses, internal blind sample analyses for NTN and AIRMoN, and replicate analyses for 2005 and 2006 were in compliance with the NADP QAP.

Monthly evaluation of laboratory control charts, reanalysis samples, Ion Percent Differences, and Conductance Percent Differences showed the CAL to be in compliance with the NADP QAP for both 2005 and 2006.

Interlaboratory comparison studies are vital in determining CAL performance and that of other laboratories around the world doing similar work. In 2005 and again in 2006, the CAL participated in five different independent studies in addition to the U.S. Geological Survey (USGS), Branch of Quality Systems, laboratory intercomparison study program. The USGS operates the QA program for the NADP/NTN. The CAL performed well in this program. In 2005 and 2006, 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 National Water Research Institute (NWRI) of Canada conducted two intercomparison studies in 2005 and two in 2006. The CAL ranked "good" in both studies in 2005 and in 2006. The fifth intercomparison study each year was with the Norwegian Institute for Air Research (NILU) 23<sup>rd</sup> and the 24<sup>th</sup> European Monitoring and Evaluation Programme (EMEP) intercomparisons of analytical methods for atmospheric precipitation, for 2005 and 2006, respectively. All results were within the standard expected variation for the analyte.

Overall, the CAL has performed within the specifications of the NADP QA Plan, and has performed well in all intercomparison studies during 2005 and 2006. Based on these studies, the CAL continues to be one of the best atmospheric precipitation laboratories in the world.



## I. Introduction

This *Quality Assurance (QA) Report* describes and summarizes the results of the National Atmospheric Deposition Program (NADP) Central Analytical Laboratory (CAL) QA program for 2005 and 2006. 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 2005 and 2006, 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 2005 and 2006 are listed in Table I-1. Table I-1 includes the CAL method detection limits (MDLs) for 2005 and 2006. For more information about the MDL and how it is determined, see the CAL QAP and the CAL 2003 and 2004 QA Report.

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

### A. Summary of Methods

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 following pH and conductivity measurements. The AIRMoN samples are never filtered, but are kept at about 4°C in the 250-mL shipping bottles into which they were decanted at the site. The AIRMoN samples are analyzed in a specified order: pH and conductivity; ammonium and orthophosphate; chloride, nitrate, and sulfate; and calcium, magnesium, sodium, and potassium. This order of analysis was mandated in order to analyze the least stable parameters first. After the NTN samples are filtered, there is no specified order of analysis. For more details on NTN and AIRMoN sample handling and analyses, see the CAL QAP and the laboratory SOPs and the NADP Quality Management Plan (QMP), which provides general information about the CAL and NADP. These can be found at <http://nadp.sws.uiuc.edu/> and <http://nadp.isws.illinois.edu/cal/>.

**Table I-1. Analytes, Instrumentation, and MDLs for 2005 and 2006**

| <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 | 0.002 <sup>a</sup><br>0.002 <sup>b</sup> | 2004-2006                |
| Potassium (K <sup>+</sup> )                     | Inductively Coupled Plasma-Optical Emission Spectrometer | 0.001<br>0.002                           | 2004-2006                |
| Magnesium (Mg <sup>+</sup> )                    | Inductively Coupled Plasma-Optical Emission Spectrometer | 0.001<br>0.001                           | 2004-2006                |
| Sodium (Na <sup>+</sup> )                       | Inductively Coupled Plasma-Optical Emission Spectrometer | 0.003<br>0.002                           | 2004-2006                |
| Ammonium (NH <sub>4</sub> <sup>+</sup> )        | Phenate (Flow Injection Colorimetry)                     | 0.005<br>0.003                           | 1978-2006                |
| Orthophosphate (PO <sub>4</sub> <sup>3-</sup> ) | Ascorbic Acid (Flow Injection Colorimetry)               | 0.006<br>0.005                           | 1978-2006                |
| Chloride (Cl <sup>-</sup> )                     | Ion Chromatography                                       | 0.008<br>0.005                           | 1985-2006                |
| Nitrate (NO <sub>3</sub> <sup>-</sup> )         | Ion Chromatography                                       | 0.009<br>0.015                           | 1985-2006                |
| Sulfate (SO <sub>4</sub> <sup>2-</sup> )        | Ion Chromatography                                       | 0.013<br>0.015                           | 1985-2006                |
| pH  | Corning pH meter<br>Broadly-James Electrode              |  | 1997-2006<br>1989-2006   |
| Conductivity                                    | YSI Conductivity meter                                   |  | 2003-2006                |

**Notes:**

<sup>a</sup> The first number is the MDL for 2005.

<sup>b</sup> The second number is the MDL for 2006.

**Table I-2. NADP/NTN and NADP/AIRMoN Laboratory  
QA/QC Program Summary, 2005 and 2006**

- 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's deionized (DI) water.*
    - 2. *Use DI water and simulated rainwater for filter leaching.*
    - 3. *Use DI water and simulated rainwater for*
      - a. *Sample collection bucket.*
      - b. *Snap-on lids for sample collection bucket.*
      - c. *One-liter sample bottles.*
      - d. *Storage and shipping bags.*
  - B. *Analyze internal blind audit samples designated SWS1, SWS2, and SWS3.*
    - 1. *SWS1: Use simulated rainwater at two concentrations, unfiltered.*
    - 2. *SWS2: Use DI water and a simulated rainwater sample, unfiltered.*
    - 3. *SWS3: Use all four of the above solutions in rotation, filtered.*
  - C. *Split 2 percent of NTN samples for replicate analysis.*
  - D. *Split 2 percent of AIRMoN samples for replicate analysis.*
  - E. *Analyze internal blind audit sample for AIRMoN from site IL11.*
  
- III. *Monthly*
  - A. *Leach AIRMoN 250-mL HDPE bottles with simulated rainwater and analyze leachates with weekly blanks.*
  - B. *Evaluate internal blind audit and replicate data from printouts.*
  - C. *Select samples for reanalysis by computer-based ion percent and conductivity percent differences and random selection (1 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 Division, 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 that the instrumentation is working properly and to maintain the standardization of the instruments within strict control limits. These solutions are prepared in-house and are tested prior to use as QCS solutions (CAL QAP, 2006). 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. The two synthetic rain QCS solutions (or nutrient solutions for orthophosphate) are analyzed after standardization of the instrument and at the end of the analytical run. After every 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 determined at the beginning of the year, the instrument is considered to be out of control. The analyst must stop analysis as soon as this happens and determine why the measurement of the QCS was out of control. This might mean restandardizing the instrument, measuring another QCS, or getting a fresh solution of QCS to measure. Once it is determined that the instrument is in control, all samples measured since the last in-control QCS was analyzed are remeasured. Control charts and the measured concentrations of all QCS solutions are available upon request.

## **B. Significant Changes during 2005–2006**

- New Ion Chromatograph (Dionex ICS-2000), online, spring, 2005
- With the elimination of field chemistry at the NTN sites, the CAL stopped making check samples for NTN, but continues to make them for AIRMoN. The CAL still provides them on request.
- Shipping protocols changed to 4-in-1 from old black box shipping
- Scott Dossett retired, October 2005
- The CAL moved back into the upgraded sample processing laboratory, Room 209, 2006
- Updated CAL Quality Assurance Plan published, 2006
- Brigita Demir and Cathy Kohlen left the CAL, 2006
- Scott Smith and Erin Bristow hired as analysts for the CAL, 2006

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<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.





## 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 Specialist knows the identification number; 2) 2 percent of the network samples are split and analyzed in replicate; and 3) blanks and container leachates are prepared and analyzed. The AIRMoN internal blinds and replicates are also submitted weekly. AIRMoN bottle blanks and leachates are submitted monthly.

### A. Internal Blind Audit Samples

#### 1. NADP/NTN

Each week the QA Specialist submits three solutions of known concentrations with completed Field Observer Report Forms (FORFs) to the sample processing area where laboratory identification numbers are assigned. These samples are processed with the network samples, but two of the three samples are unfiltered to monitor for possible filter contamination. These samples are identified as sites SWS1, SWS2, and SWS3. In 2005 and 2006, the SWS1 samples were High-Purity Standards<sup>33</sup> Simulated Rainwater 1 (H-PS SR1) and an internally formulated and prepared simulated rainwater sample approximating the 95<sup>th</sup> percentile of the NTN sample concentrations (FR95), which were alternated weekly. The SWS2 samples were alternated weekly between DI water from the ion chromatography laboratory and an internally formulated and prepared synthetic rain sample that approximated the 10<sup>th</sup> percentile of NTN sample concentrations (FR10). The SWS1 and SWS2 samples were not filtered. The filtered SWS3 samples were H-PS SR1, FR95, DI water, and FR10 submitted in rotation. For 2006, only six or seven filtered samples were evaluated instead of the usual 13 due to the United States Geological Survey, Office of Water Quality, Branch of Quality Systems (USGS BQS) adding blind audit samples to the sample queue for the second half of the year.

Tables II-1 through Table II-8 summarize 2005 and 2006 data from the weekly internal blind audit samples for NTN. The blind samples are randomly dispersed throughout the sample queue, and, therefore, the derived bias and precision estimates are representative of Network precipitation sample measurements.

For 2005, the SWS1 and SWS2 samples overall show less bias and less variability than the filtered SWS3 samples, which have a smaller sample population for each solution. Sodium and potassium had higher standard deviations in the unfiltered sample than in the filtered sample for both SWS1 solutions. pH had higher variability in the FR10 solution, and the deionized water had several analytes with more variability in the unfiltered sample compared to the filtered sample. The biases for all but calcium and ammonium (FR95 and HPS-SR1, respectively) were lower in the filtered samples versus the unfiltered samples. The biases for all analytes for all but the HPS-SR1 samples for the unfiltered samples were less than the fifth percentile of NTN precipitation concentrations. The lower biases for the internally formulated samples could be a result of the initial concentration being determined by the laboratory, removing any potential initial bias in the measurement. The

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<sup>3</sup> High-Purity Standards, P.O. Box 41727, Charleston, SC 29423, catalog numbers SR-1 and SR-2.

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

**Table II-1. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, High Purity Standards Simulated Rainwater 1 (HPS-SR1), Unfiltered and Filtered, 2005**

| <i>Parameter</i>                   | <i>Target Concentration<sup>a</sup></i><br>(mg/L) | <i>Mean Concentration</i><br>(mg/L) | <i>Bias</i><br>(mg/L) | <i>Bias</i><br>(%) | <i>Standard Deviation</i><br>(mg/L) | <i>RSD<sup>d</sup></i><br>(%) | <i>MDL</i><br>(mg/L) | <i>5<sup>th</sup>%<sup>e</sup></i><br>(mg/L) |
|------------------------------------|---|-------------------------------------|-----------------------|--------------------|-------------------------------------|-------------------------------|----------------------|--|
| Calcium                            | 0.012   | 0.015 <sup>b</sup>                  | 0.003                 | 22.4               | 0.009                               | 59.0                          | 0.002                | 0.019  |
|                                    |   | 0.051 <sup>c</sup>                  | 0.039                 | 327.6              | 0.018                               | 33.2                          |                      |  |
| Magnesium                          | 0.019   | 0.019                               | 0.000                 | -2.0               | 0.002                               | 12.6                          | 0.001                | 0.003  |
|                                    |   | 0.014                               | -0.005                | -25.5              | 0.003                               | 19.2                          |                      |  |
| Sodium                             | 0.20  | 0.19                                | -0.01                 | -3.4               | 0.01                                | 3.1                           | 0.003                | 0.005  |
|                                    |   | 0.19                                | -0.01                 | -6.1               | 0.01                                | 3.1                           |                      |  |
| Potassium                          | 0.053   | 0.049                               | -0.004                | -7.1               | 0.003                               | 5.6                           | 0.001                | 0.003  |
|                                    |   | 0.046                               | -0.007                | -13.6              | 0.001                               | 2.7                           |                      |  |
| Ammonium                           | 0.100   | 0.062                               | -0.038                | -37.8              | 0.011                               | 17.0                          | 0.005                | 0.014  |
|                                    |   | 0.065                               | -0.035                | -34.7              | 0.013                               | 19.9                          |                      |  |
| Sulfate                            | 2.5   | 2.5                                 | 0.0                   | -0.1               | 0.0                                 | 1.9                           | 0.013                | 0.134  |
|                                    |   | 2.4                                 | -0.1                  | -3.2               | 0.0                                 | 2.1                           |                      |  |
| Nitrate                            | 0.50  | 0.50                                | 0.00                  | 0.1                | 0.01                                | 2.0                           | 0.009                | 0.168  |
|                                    |   | 0.49                                | -0.01                 | -2.3               | 0.01                                | 2.1                           |                      |  |
| Chloride                           | 0.25  | 0.22                                | -0.03                 | -13.4              | 0.01                                | 2.5                           | 0.008                | 0.020  |
|                                    |   | 0.22                                | -0.03                 | -13.0              | 0.01                                | 4.6                           |                      |  |
| pH<br>(units)                      | 4.23  | 4.30                                | 0.07                  | 1.7                | 0.02                                | 0.5                           |                      | 6.43   |
|                                    |   | 4.31                                | 0.08                  | 1.9                | 0.02                                | 0.4                           |                      |  |
| H<br>(µeq/L)                       | 58.9  | 49.9                                | -9.0                  | -15.2              | 2.4                                 | 5.0                           |                      | 0.4  |
|                                    |   | 49.0                                | -9.9                  | -16.8              | 2.0                                 | 4.0                           |                      |  |
| Specific<br>Conductance<br>(µS/cm) | 22.   | 25.4                                | 3.4                   | 15.6               | 0.5                                 | 1.9                           |                      | 3.3  |
|                                    |   | 25.6                                | 3.6                   | 16.5               | 0.5                                 | 2.0                           |                      |  |

**Notes:**

There were 26 unfiltered and 13 filtered HPR-SR1 (lot #410409) samples in 2005.

<sup>a</sup> Target Concentrations are those reported by High-Purity Standards.

<sup>b</sup> Concentration values for unfiltered H-PS SR1.

<sup>c</sup> Concentration values for filtered H-PS SR1.

<sup>d</sup> Relative Standard Deviation

<sup>e</sup> 5<sup>th</sup>% for NTN wet (W) samples for 2002-2006 with contaminated samples removed.

**Table II-2. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Internally Formulated Simulated Rain (05FR95), Unfiltered and Filtered, 2005**

| <i>Parameter</i>                   | <i>Target Concentration<sup>a</sup></i><br>(mg/L) | <i>Mean Concentration</i><br>(mg/L) | <i>Bias</i><br>(mg/L) | <i>Bias</i><br>(%) | <i>Standard Deviation</i><br>(mg/L) | <i>RSD<sup>d</sup></i><br>(%) | <i>MDL</i><br>(mg/L) | <i>5<sup>th</sup>%<sup>e</sup></i><br>(mg/L) |
|------------------------------------|---|-------------------------------------|-----------------------|--------------------|-------------------------------------|-------------------------------|----------------------|--|
| Calcium                            | 0.744   | 0.755 <sup>b</sup>                  | 0.011                 | 1.5                | 0.018                               | 2.4                           | 0.002                | 0.019  |
|                                    |   | 0.737 <sup>c</sup>                  | -0.007                | -1.0               | 0.023                               | 3.1                           |                      |  |
| Magnesium                          | 0.133   | 0.134                               | 0.001                 | 0.4                | 0.003                               | 2.2                           | 0.001                | 0.003  |
|                                    |   | 0.129                               | -0.004                | -3.1               | 0.004                               | 3.4                           |                      |  |
| Sodium                             | 0.647   | 0.650                               | 0.003                 | 0.5                | 0.019                               | 2.9                           | 0.003                | 0.005  |
|                                    |   | 0.624                               | -0.023                | -3.6               | 0.014                               | 2.2                           |                      |  |
| Potassium                          | 0.102   | 0.102                               | 0.000                 | -0.2               | 0.003                               | 2.7                           | 0.001                | 0.003  |
|                                    |   | 0.097                               | -0.005                | -5.3               | 0.002                               | 2.4                           |                      |  |
| Ammonium                           | 0.986   | 0.984                               | -0.002                | -0.2               | 0.012                               | 1.2                           | 0.005                | 0.014  |
|                                    |   | 0.957                               | -0.029                | -2.9               | 0.020                               | 2.1                           |                      |  |
| Sulfate                            | 3.812   | 3.802                               | -0.010                | -0.3               | 0.021                               | 0.6                           | 0.013                | 0.134  |
|                                    |   | 3.697                               | -0.115                | -3.0               | 0.047                               | 1.3                           |                      |  |
| Nitrate                            | 3.671   | 3.619                               | -0.052                | -1.4               | 0.032                               | 0.9                           | 0.009                | 0.168  |
|                                    |   | 3.527                               | -0.144                | -3.9               | 0.037                               | 1.1                           |                      |  |
| Chloride                           | 1.171   | 1.164                               | -0.007                | -0.6               | 0.011                               | 0.9                           | 0.008                | 0.020  |
|                                    |   | 1.137                               | -0.034                | -2.9               | 0.012                               | 1.1                           |                      |  |
| pH<br>(units)                      | 4.53  | 4.52                                | -0.01                 | -0.2               | 0.03                                | 0.8                           |                      | 6.43   |
|                                    |   | 4.52                                | -0.01                 | -0.3               | 0.02                                | 0.5                           |                      |  |
| H<br>(µeq/L)                       | 29.5  | 30.3                                | 0.8                   | 2.7                | 2.4                                 | 7.8                           |                      | 0.4  |
|                                    |   | 30.4                                | 0.9                   | 3.0                | 1.6                                 | 5.2                           |                      |  |
| Specific<br>Conductance<br>(µS/cm) | 32.6  | 33.1                                | 0.5                   | 1.5                | 0.4                                 | 1.3                           |                      | 3.3  |
|                                    |   | 32.9                                | 0.3                   | 1.0                | 0.5                                 | 1.6                           |                      |  |

**Notes:**

There were 26 unfiltered and 13 filtered samples in 2005.

<sup>a</sup> Target concentrations for the internally formulated simulated rainwater sample, 05FR95.

<sup>b</sup> Concentration values for unfiltered 05FR95.

<sup>c</sup> Concentration values for filtered 05FR95.

<sup>d</sup> Relative Standard Deviation

<sup>e</sup> 5<sup>th</sup>% for NTN wet (W) samples for 2002-2006 with contaminated samples removed.

**Table II-3. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Internally Formulated Simulated Rain (05FR10), Unfiltered and Filtered, 2005**

| <i>Parameter</i>                   | <i>Target Concentration<sup>a</sup></i><br>(mg/L) | <i>Mean Concentration</i><br>(mg/L) | <i>Bias</i><br>(mg/L) | <i>Bias</i><br>(%) | <i>Standard Deviation</i><br>(mg/L) | <i>RSD<sup>d</sup></i><br>(%) | <i>MDL</i><br>(mg/L) | <i>5<sup>th</sup>%<sup>e</sup></i><br>(mg/L) |
|------------------------------------|---|-------------------------------------|-----------------------|--------------------|-------------------------------------|-------------------------------|----------------------|--|
| Calcium                            | 0.025   | 0.025 <sup>b</sup>                  | 0.000                 | 1.4                | 0.001                               | 2.9                           | 0.002                | 0.019  |
|                                    |   | 0.027 <sup>c</sup>                  | 0.002                 | 6.8                | 0.002                               | 7.1                           |                      |  |
| Magnesium                          | 0.005   | 0.005                               | 0.000                 | -5.4               | 0.001                               | 12.5                          | 0.001                | 0.003  |
|                                    |   | 0.004                               | -0.001                | -24.6              | 0.001                               | 33.2                          |                      |  |
| Sodium                             | 0.009   | 0.009                               | 0.000                 | -4.3               | 0.001                               | 7.3                           | 0.003                | 0.005  |
|                                    |   | 0.009                               | 0.000                 | 0.9                | 0.001                               | 15.3                          |                      |  |
| Potassium                          | 0.003   | 0.003                               | 0.000                 | 7.7                | 0.001                               | 24.7                          | 0.001                | 0.003  |
|                                    |   | 0.003                               | 0.000                 | 12.8               | 0.001                               | 18.5                          |                      |  |
| Ammonium                           | 0.029   | 0.030                               | 0.001                 | 3.7                | 0.001                               | 3.6                           | 0.005                | 0.014  |
|                                    |   | 0.030                               | 0.001                 | 3.2                | 0.001                               | 4.8                           |                      |  |
| Sulfate                            | 0.228   | 0.220                               | -0.008                | -3.5               | 0.006                               | 2.8                           | 0.013                | 0.134  |
|                                    |   | 0.217                               | -0.011                | -4.9               | 0.005                               | 2.5                           |                      |  |
| Nitrate                            | 0.287   | 0.281                               | -0.006                | -2.1               | 0.006                               | 2.1                           | 0.009                | 0.168  |
|                                    |   | 0.275                               | -0.012                | -4.2               | 0.006                               | 2.2                           |                      |  |
| Chloride                           | 0.032   | 0.030                               | -0.002                | -7.5               | 0.002                               | 6.4                           | 0.008                | 0.020  |
|                                    |   | 0.030                               | -0.002                | -6.0               | 0.002                               | 5.8                           |                      |  |
| pH<br>(units)                      | 5.18  | 5.16                                | -0.02                 | -0.3               | 0.04                                | 0.8                           |                      | 6.43   |
|                                    |   | 5.17                                | -0.01                 | -0.2               | 0.03                                | 0.6                           |                      |  |
| H<br>(µeq/L)                       | 6.6   | 6.9                                 | 0.3                   | 4.6                | 0.6                                 | 8.9                           |                      | 0.4  |
|                                    |   | 6.8                                 | 0.2                   | 3.0                | 0.5                                 | 7.4                           |                      |  |
| Specific<br>Conductance<br>(µS/cm) | 3.7   | 3.9                                 | 0.2                   | 5.9                | 0.2                                 | 4.4                           |                      | 3.3  |
|                                    |   | 3.8                                 | 0.1                   | 3.3                | 0.2                                 | 4.8                           |                      |  |

**Notes:**

There were 26 unfiltered and 13 filtered internally formulated simulated rain samples (05FR10) in 2005.

<sup>a</sup> Target Concentrations for 05FR10.

<sup>b</sup> Concentration values for 05FR10.

<sup>c</sup> Concentration values for filtered 05FR10.

<sup>d</sup> Relative Standard Deviation

<sup>e</sup> 5<sup>th</sup>% for NTN wet (W) samples for 2002-2006 with contaminated samples removed.

**Table II-4. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Deionized Water (DI), Unfiltered and Filtered, 2005**

| <i>Parameter</i>                         | <i>MDL<br/>(mg/L)</i> | <i>Mean<br/>Concentration<br/>(mg/L)</i>   | <i>Bias<br/>(mg/L)</i> | <i>Bias<br/>(%)</i> | <i>Standard<br/>Deviation<br/>(mg/L)</i> | <i>RSD<sup>c</sup><br/>(%)</i> | <i>5<sup>th</sup>%<sup>d</sup><br/>(mg/L)</i> |
|--|-----------------------|--|------------------------|---------------------|--|--------------------------------|---|
| Calcium                                  | 0.002                 | <0.002 <sup>a</sup><br><0.002 <sup>b</sup> |                        |                     | 0.0005<br>0.0009                         |                                | 0.019   |
| Magnesium                                | 0.001                 | <0.001<br><0.001                           |                        |                     | 0.0002<br>0.000                          |                                | 0.003   |
| Sodium                                   | 0.003                 | <0.003<br><0.003                           |                        |                     | 0.002<br>0.001                           |                                | 0.005   |
| Potassium                                | 0.001                 | <0.001<br><0.001                           |                        |                     | 0.0006<br>0.0006                         |                                | 0.003   |
| Ammonium                                 | 0.005                 | <0.005<br><0.005                           |                        |                     | 0.001<br>0.002                           |                                | 0.014   |
| Sulfate                                  | 0.013                 | <0.013<br><0.013                           |                        |                     | 0.003<br>0.006                           |                                | 0.134   |
| Nitrate                                  | 0.009                 | <0.009<br><0.009                           |                        |                     | 0.003<br>0.000                           |                                | 0.168   |
| Chloride                                 | 0.008                 | <0.008<br><0.008                           |                        |                     | 0.004<br>0.003                           |                                | 0.020   |
| pH<br>(units)                            |                       | 5.69<br>5.66                               | 0.04<br>0.01           | 0.7<br>0.2          | 0.09<br>0.09                             | 1.7<br>1.7                     | 6.43  |
| Specific<br>Conductance<br>( $\mu$ S/cm) |                       | 1.2<br>1.2                                 | 0.3<br>0.3             | 30.2<br>33.3        | 0.2<br>0.2                               | 16.8<br>12.7                   | 3.3   |

**Notes:**

There were 26 unfiltered and 13 filtered DI samples in 2005.

<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>% for NTN wet (W) samples for 2002-2006 with contaminated samples removed

**Table II-5. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, High Purity Standards Simulated Rainwater 1 (HPS-SR1), Unfiltered and Filtered, 2006**

| <i>Parameter</i>                   | <i>Target Concentration<sup>a</sup></i><br>(mg/L) | <i>Mean Concentration</i><br>(mg/L) | <i>Bias</i><br>(mg/L) | <i>Bias</i><br>(%) | <i>Standard Deviation</i><br>(mg/L) | <i>RSD<sup>d</sup></i><br>(%) | <i>MDL</i><br>(mg/L) | <i>5<sup>th</sup>%<sup>e</sup></i><br>(mg/L) |
|------------------------------------|---|-------------------------------------|-----------------------|--------------------|-------------------------------------|-------------------------------|----------------------|--|
| Calcium                            | 0.012   | 0.015 <sup>b</sup>                  | 0.003                 | 25.7               | 0.001                               | 4.2                           | 0.002                | 0.019  |
|                                    |   | 0.047 <sup>c</sup>                  | 0.035                 | 287.5              | 0.008                               | 18.2                          |                      |  |
| Magnesium                          | 0.019   | 0.020                               | 0.001                 | 4.0                | 0.001                               | 2.6                           | 0.001                | 0.003  |
|                                    |   | 0.014                               | -0.006                | -28.9              | 0.002                               | 11.9                          |                      |  |
| Sodium                             | 0.20  | 0.19                                | -0.01                 | -3.8               | 0.004                               | 2.2                           | 0.002                | 0.005  |
|                                    |   | 0.19                                | -0.01                 | -5.8               | 0.004                               | 2.0                           |                      |  |
| Potassium                          | 0.049   | 0.049                               | 0.000                 | -0.2               | 0.001                               | 2.4                           | 0.002                | 0.003  |
|                                    |   | 0.047                               | -0.002                | -3.4               | 0.001                               | 2.3                           |                      |  |
| Ammonium                           | 0.10  | 0.10                                | 0.00                  | 4.4                | 0.002                               | 1.7                           | 0.003                | 0.014  |
|                                    |   | 0.10                                | 0.00                  | -1.5               | 0.002                               | 2.2                           |                      |  |
| Sulfate                            | 2.5   | 2.6                                 | 0.1                   | 2.1                | 0.025                               | 1.0                           | 0.015                | 0.134  |
|                                    |   | 2.5                                 | 0.0                   | -1.3               | 0.019                               | 0.8                           |                      |  |
| Nitrate                            | 0.52  | 0.51                                | -0.01                 | -1.3               | 0.007                               | 1.3                           | 0.015                | 0.168  |
|                                    |   | 0.49                                | -0.03                 | -5.0               | 0.007                               | 1.3                           |                      |  |
| Chloride                           | 0.25  | 0.22                                | -0.03                 | -11.1              | 0.003                               | 1.2                           | 0.005                | 0.020  |
|                                    |   | 0.22                                | -0.03                 | -13.1              | 0.004                               | 1.9                           |                      |  |
| pH<br>(units)                      | 4.35  | 4.30                                | -0.05                 | -1.0               | 0.01                                | 0.3                           |                      | 6.43   |
|                                    |   | 4.31                                | -0.04                 | -1.0               | 0.02                                | 0.5                           |                      |  |
| H<br>(µeq/L)                       | 44.7  | 49.6                                | 5.0                   | 11.1               | 1.5                                 | 3.0                           |                      | 0.4  |
|                                    |   | 49.2                                | 4.6                   | 10.2               | 2.6                                 | 5.2                           |                      |  |
| Specific<br>Conductance<br>(µS/cm) | 22.3  | 24.7                                | 2.4                   | 10.9               | 0.7                                 | 2.9                           |                      | 3.3  |
|                                    |   | 25.1                                | 2.8                   | 12.6               | 0.5                                 | 1.8                           |                      |  |

**Notes:**

There were 26 unfiltered and 6 filtered HPS-SR1 (lot # 530621) samples in 2006.

<sup>a</sup> Target Concentrations are those reported by High-Purity Standards.

<sup>b</sup> Concentration values for unfiltered H-PS SR1.

<sup>c</sup> Concentration values for filtered H-PS SR1.

<sup>d</sup> Relative Standard Deviation

<sup>e</sup> 5th% for NTN wet (W) samples for 2002-2006 with contaminated samples removed.

**Table II-6. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Internally Formulated Simulated Rain (06FR95), Unfiltered and Filtered, 2006**

| <i>Parameter</i>             | <i>Target Concentration (mg/L)</i> | <i>Mean Concentration (mg/L)</i> | <i>Bias (mg/L)</i> | <i>Bias (%)</i> | <i>Standard Deviation (mg/L)</i> | <i>RSD<sup>d</sup> (%)</i> | <i>MDL (mg/L)</i> | <i>5<sup>th</sup>%<sup>e</sup> (mg/L)</i> |
|------------------------------|------------------------------------|----------------------------------|--------------------|-----------------|----------------------------------|----------------------------|-------------------|---|
| Calcium                      | 0.748 <sup>a</sup>                 | 0.743 <sup>b</sup>               | -0.005             | -0.7            | 0.017                            | 2.3                        | 0.002             | 0.019                                     |
|                              |                                    | 0.755 <sup>c</sup>               | 0.007              | 1.0             | 0.020                            | 2.6                        |                   |   |
| Magnesium                    | 0.143                              | 0.141                            | -0.002             | -1.2            | 0.003                            | 1.9                        | 0.001             | 0.003                                     |
|                              |                                    | 0.138                            | -0.005             | -3.3            | 0.003                            | 2.0                        |                   |   |
| Sodium                       | 0.688                              | 0.692                            | 0.004              | 0.6             | 0.017                            | 2.5                        | 0.002             | 0.005                                     |
|                              |                                    | 0.661                            | -0.027             | -3.9            | 0.014                            | 2.1                        |                   |   |
| Potassium                    | 0.106                              | 0.108                            | 0.002              | 2.3             | 0.003                            | 2.5                        | 0.002             | 0.003                                     |
|                              |                                    | 0.105                            | -0.001             | -0.8            | 0.002                            | 2.1                        |                   |   |
| Ammonium                     | 1.058                              | 1.062                            | 0.004              | 0.3             | 0.017                            | 1.6                        | 0.003             | 0.014                                     |
|                              |                                    | 1.037                            | -0.021             | -2.0            | 0.011                            | 1.0                        |                   |   |
| Sulfate                      | 3.940                              | 3.921                            | -0.019             | -0.5            | 0.034                            | 0.9                        | 0.015             | 0.134                                     |
|                              |                                    | 3.827                            | -0.113             | -2.9            | 0.024                            | 0.6                        |                   |   |
| Nitrate                      | 3.818                              | 3.815                            | -0.003             | -0.1            | 0.030                            | 0.8                        | 0.015             | 0.168                                     |
|                              |                                    | 3.727                            | -0.091             | -2.4            | 0.012                            | 0.3                        |                   |   |
| Chloride                     | 1.234                              | 1.231                            | -0.003             | -0.3            | 0.009                            | 0.7                        | 0.005             | 0.020                                     |
|                              |                                    | 1.201                            | -0.033             | -2.7            | 0.007                            | 0.6                        |                   |   |
| pH (units)                   | 4.49                               | 4.47                             | -0.02              | -0.4            | 0.02                             | 0.4                        |                   | 6.43                                      |
|                              |                                    | 4.49                             | 0.00               | -0.1            | 0.02                             | 0.5                        |                   |   |
| H (µeq/L)                    | 32.4                               | 33.8                             | 1.4                | 4.3             | 1.3                              | 3.7                        |                   | 0.4                                       |
|                              |                                    | 32.7                             | 0.4                | 1.2             | 1.8                              | 5.6                        |                   |   |
| Specific Conductance (µS/cm) | 34.7                               | 34.3                             | -0.4               | -1.0            | 0.7                              | 2.0                        |                   | 3.3                                       |
|                              |                                    | 34.8                             | 0.1                | 0.2             | 0.4                              | 1.2                        |                   |   |

**Notes:**

There were 26 unfiltered and 7 filtered internally formulated simulated rainwater (06FR95) samples in 2006.

<sup>a</sup> Target concentrations for 06FR95.

<sup>b</sup> Unfiltered 06FR95.

<sup>c</sup> Filtered 06FR95.

<sup>d</sup> Relative Standard Deviation

<sup>e</sup> 5<sup>th</sup>% for NTN wet (W) samples for 2002-2006 with contaminated samples removed.

**Table II-7. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Internally Formulated Simulated Rain (06FR10), Unfiltered and Filtered, 2006**

| <i>Parameter</i>             | <i>Target Concentration (mg/L)</i> | <i>Mean Concentration (mg/L)</i> | <i>Bias (mg/L)</i> | <i>Bias (%)</i> | <i>Standard Deviation (mg/L)</i> | <i>RSD<sup>d</sup> (%)</i> | <i>MDL (mg/L)</i> | <i>5<sup>th</sup>%<sup>e</sup> (mg/L)</i> |
|------------------------------|------------------------------------|----------------------------------|--------------------|-----------------|----------------------------------|----------------------------|-------------------|---|
| Calcium                      | 0.026 <sup>a</sup>                 | 0.026 <sup>b</sup>               | 0.000              | -1.5            | 0.001                            | 3.3                        | 0.002             | 0.019                                     |
|                              |                                    | 0.028 <sup>c</sup>               | 0.002              | 8.3             | 0.002                            | 6.3                        |                   |   |
| Magnesium                    | 0.005                              | 0.005                            | 0.000              | 0.0             | 0.000                            | 0.0                        | 0.001             | 0.003                                     |
|                              |                                    | 0.004                            | -0.002             | -30.0           | 0.001                            | 14.3                       |                   |   |
| Sodium                       | 0.009                              | 0.009                            | 0.000              | -2.1            | 0.000                            | 4.5                        | 0.002             | 0.005                                     |
|                              |                                    | 0.010                            | 0.001              | 5.6             | 0.001                            | 5.3                        |                   |   |
| Potassium                    | 0.004                              | 0.004                            | 0.000              | -3.8            | 0.001                            | 13.9                       | 0.002             | 0.003                                     |
|                              |                                    | 0.004                            | 0.000              | 0.0             | 0.001                            | 14.4                       |                   |   |
| Ammonium                     | 0.031                              | 0.033                            | 0.002              | 4.8             | 0.002                            | 5.0                        | 0.003             | 0.014                                     |
|                              |                                    | 0.033                            | 0.002              | 5.4             | 0.003                            | 8.6                        |                   |   |
| Sulfate                      | 0.227                              | 0.220                            | -0.007             | -3.2            | 0.004                            | 1.8                        | 0.015             | 0.134                                     |
|                              |                                    | 0.214                            | -0.013             | -5.7            | 0.004                            | 1.9                        |                   |   |
| Nitrate                      | 0.284                              | 0.282                            | -0.002             | -0.7            | 0.007                            | 2.4                        | 0.015             | 0.168                                     |
|                              |                                    | 0.273                            | -0.011             | -3.8            | 0.004                            | 1.3                        |                   |   |
| Chloride                     | 0.030                              | 0.030                            | 0.000              | -1.5            | 0.001                            | 4.1                        | 0.005             | 0.020                                     |
|                              |                                    | 0.049                            | 0.019              | 62.8            | 0.042                            | 85.3                       |                   |   |
| pH (units)                   | 5.15                               | 5.16                             | 0.01               | 0.1             | 0.02                             | 0.4                        |                   | 6.43                                      |
|                              |                                    | 5.17                             | 0.02               | 0.5             | 0.05                             | 0.9                        |                   |   |
| H (µeq/L)                    | 7.1                                | 7.0                              | -0.1               | -1.3            | 0.4                              | 5.1                        |                   | 0.4                                       |
|                              |                                    | 6.7                              | -0.3               | -4.7            | 0.7                              | 10.4                       |                   |   |
| Specific Conductance (µS/cm) | 3.9                                | 3.9                              | 0.0                | -1.2            | 0.1                              | 3.9                        |                   | 3.3                                       |
|                              |                                    | 4.0                              | 0.1                | 3.0             | 0.4                              | 10.1                       |                   |   |

**Notes:**

There were 26 unfiltered and 6 filtered internally formulated simulated rainwater (06FR10) samples in 2006.

<sup>a</sup> Target concentrations for 06FR10.

<sup>b</sup> Unfiltered 06FR10.

<sup>c</sup> Filtered 06FR10.

<sup>d</sup> Relative Standard Deviation

<sup>e</sup> 5<sup>th</sup>% for NTN wet (W) samples for 2002-2006 with contaminated samples removed.



**Table II-8. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, Deionized Water (DI), Unfiltered and Filtered, 2006**

| <i>Parameter</i>                         | <i>MDL<br/>(mg/L)</i> | <i>Mean<br/>Concentration<br/>(mg/L)</i>  | <i>Bias<br/>(mg/L)</i> | <i>Bias<br/>(%)</i> | <i>Standard<br/>Deviation<br/>(mg/L)</i> | <i>RSD<sup>c</sup><br/>(%)</i> | <i>5<sup>th</sup>%<sup>d</sup><br/>(mg/L)</i> |
|--|-----------------------|---|------------------------|---------------------|--|--------------------------------|---|
| Calcium                                  | 0.002                 | <0.002 <sup>a</sup><br>0.004 <sup>b</sup> |                        |                     | 0.001<br>0.004                           |                                | 0.019   |
| Magnesium                                | 0.001                 | <0.001<br><0.001                          |                        |                     | 0.000<br>0.000                           |                                | 0.003   |
| Sodium                                   | 0.002                 | <0.002<br><0.002                          |                        |                     | 0.000<br>0.000                           |                                | 0.005   |
| Potassium                                | 0.002                 | <0.002<br><0.002                          |                        |                     | 0.001<br>0.001                           |                                | 0.003   |
| Ammonium                                 | 0.003                 | <0.003<br><0.003                          |                        |                     | 0.002<br>0.003                           |                                | 0.014   |
| Sulfate                                  | 0.015                 | <0.015<br><0.015                          |                        |                     | 0.003<br>0.000                           |                                | 0.134   |
| Nitrate                                  | 0.015                 | <0.015<br><0.015                          |                        |                     | 0.002<br>0.003                           |                                | 0.168   |
| Chloride                                 | 0.005                 | <0.005<br><0.005                          |                        |                     | 0.000<br>0.003                           |                                | 0.020   |
| pH<br>(units)                            | 5.65                  | 5.61<br>5.62                              | -0.04<br>-0.03         | -0.8<br>-0.5        | 0.1<br>0.1                               | 1.1<br>2.1                     | 6.43  |
| Specific<br>Conductance<br>( $\mu$ S/cm) | 0.9                   | 1.2<br>1.3                                | 0.3<br>0.4             | 38.7<br>49.2        | 0.2<br>0.3                               | 17.4<br>23.2                   | 3.3   |

**Notes:**

There were 26 unfiltered and 7 filtered DI samples in 2006.

<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>% for NTN wet (W) samples for 2002-2006 with contaminated samples removed.

biases for the filtered samples varied with the solution, with many being near or lower than the fifth percentile for the combined years of 2002-2006, minus contaminated samples and QC samples.

In 2006, the USGS BQS introduced a short-term study for double blinds at the CAL. For half of the year, the USGS BQS sent samples to specific sites which would send the unopened bottle to the CAL as if it were the sample for that week. Therefore, the sample was blind to the analysts and to the personnel receiving and processing samples. Also, the concentrations were unknown. The internal blinds originating within the CAL were blind to the analysts for Ca, Mg, Na, K, Cl, NO<sub>3</sub>, SO<sub>4</sub>, NH<sub>4</sub>, and PO<sub>4</sub>. Because the sample-prep personnel and the analyst for pH and conductivity received the internal blinds in 60-mL bottles rather than in the usual 1-L NTN bottles, the samples were evident to them but the concentrations were blind. The double-blind sample study was designed to determine whether a complete double-blind program would gain any additional information for the laboratory and its practices. For more information about this study, visit the USGS BQS Web page, [http://bqs.usgs.gov/precip/interlab\\_overview.htm](http://bqs.usgs.gov/precip/interlab_overview.htm). Because of the USGS BQS study, the CAL did not process any internal blind filtered samples for the second half of 2006. Therefore, instead of the usual 13 filtered samples for each type of solution, there are six or seven samples, depending on the type of sample and when it was introduced into the system.

For 2006, the SWS1 and SWS2 samples overall showed less bias and less variability than the filtered SWS3 samples. The FR95 solution had greater variability in the unfiltered samples. With only seven filtered samples, however, this variability could be an artifact of the number of filtered samples, not of the possible chemistry changes in the sample. Only potassium showed a higher bias in the unfiltered samples versus the filtered samples, and only for FR95. The biases for both the filtered and unfiltered solutions, though, were at or very near the detection limit and within the accepted noise of the instrument at the concentration of the solution. The biases for the filtered samples varied with the solution with most being near or lower than the fifth percentile of the NTN concentrations and within the noise of the instrument for that analyte at that concentration.

## 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 both 2005 and 2006, the solution used was an internally formulated and prepared simulated rain sample approximating the 95<sup>th</sup> percentile of the NTN concentrations. The concentrations are slightly different each year because of a different preparation batch, but are consistent for each year. The solutions are labeled 05FR95 for the solution used in 2005 and 06FR95 for the solution used in 2006.

Table II-9 and Table II-10 show the internal blind sample summary for 2005 and 2006, respectively. The difference seen in the target concentrations versus the concentrations measured at the CAL were less than or equal to the fifth percentile of the AIRMoN precipitation concentrations for the five-year period 2002-2006, and less than or equal to the method detection limit for 2005. Only sodium and chloride were greater than the fifth percentile concentration for 2006. Even though the biases were higher for sodium and chloride in 2006, they were still well within the noise of the instrument at the 95<sup>th</sup> percentile concentrations. This implies that the difference between the measured and the target amounts were within the noise of the instruments.

**Table II-9. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, AIRMoN, 2005**

| <i>Parameter</i>                   | <i>Target Concentration<sup>a</sup></i><br>(mg/L) | <i>Mean<sup>b</sup></i><br><i>Concentration</i><br>(mg/L) | <i>Bias</i><br>(mg/L) | <i>Bias</i><br>(%) | <i>Standard</i><br><i>Deviation</i><br>(mg/L) | <i>RSD<sup>c</sup></i><br>(%) | <i>MDL</i><br>(mg/L) | <i>5<sup>th</sup><sup>d</sup></i><br>(mg/L) |
|------------------------------------|---|---|-----------------------|--------------------|---|-------------------------------|----------------------|---|
| Calcium                            | 0.744   | 0.751   | 0.007                 | 1.0                | 0.022   | 2.9                           | 0.002                | 0.007                                       |
| Magnesium                          | 0.133   | 0.133   | 0.000                 | 0.6                | 0.004   | 2.6                           | 0.001                | 0.001                                       |
| Sodium                             | 0.647   | 0.649   | 0.002                 | 0.3                | 0.012   | 1.8                           | 0.003                | 0.003                                       |
| Potassium                          | 0.102   | 0.101   | -0.001                | -1.2               | 0.002   | 1.8                           | 0.001                | 0.003                                       |
| Ammonium                           | 0.986   | 0.994   | 0.008                 | 0.8                | 0.011   | 1.1                           | 0.005                | 0.037                                       |
| Sulfate                            | 3.812   | 3.804   | -0.008                | -0.2               | 0.031   | 0.8                           | 0.013                | 0.254                                       |
| Nitrate                            | 3.671   | 3.618   | -0.053                | -1.5               | 0.043   | 1.2                           | 0.009                | 0.238                                       |
| Chloride                           | 1.171   | 1.162   | -0.009                | -0.8               | 0.011   | 1.0                           | 0.008                | 0.017                                       |
| pH                                 | 4.53  | 4.51  | -0.02                 | -0.5               | 0.03  | 0.7                           |                      | 5.25  |
| H<br>(µeq/L)                       | 29.5  | 31.1  | 1.5                   | 5.2                | 2.1   | 6.9                           |                      | 5.6   |
| Specific<br>Conductance<br>(µS/cm) | 32.6  | 32.5  | -0.1                  | -0.4               | 1.3   | 4.1                           |                      | 5.6   |

**Notes:**

This tabulation included 48 internal blinds. Samples were simulated approximating the 95<sup>th</sup> percentile of NTN samples (05FR95).

<sup>a</sup> Target concentrations for 05FR95.

<sup>b</sup> Mean concentration obtained by the CAL from the AIRMoN internal blind samples for 2005.

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

<sup>d</sup> 5<sup>th</sup> percentile for AIRMoN samples for 2002-2006.

**Table IV-10. Analytical Bias and Precision Determined from Analysis of Internal Blind Audit Samples, AIRMoN, 2006**

| <i>Parameter</i>                   | <i>Target Concentration<sup>a</sup></i><br>(mg/L) | <i>Mean<sup>b</sup></i><br><i>Concentration</i><br>(mg/L) | <i>Bias</i><br>(mg/L) | <i>Bias</i><br>(%) | <i>Standard Deviation</i><br>(mg/L) | <i>RSD<sup>c</sup></i><br>(%) | <i>MDL</i><br>(mg/L) | <i>5<sup>th</sup><sub>0</sub><sup>d</sup></i><br>(mg/L) |
|------------------------------------|---|---|-----------------------|--------------------|-------------------------------------|-------------------------------|----------------------|---|
| Calcium                            | 0.748   | 0.749   | 0.001                 | 0.1                | 0.019                               | 2.6                           | 0.002                | 0.007   |
| Magnesium                          | 0.143   | 0.141   | -0.002                | -1.5               | 0.005                               | 3.4                           | 0.001                | 0.001   |
| Sodium                             | 0.688   | 0.678   | -0.010                | -1.5               | 0.024                               | 3.6                           | 0.002                | 0.003   |
| Potassium                          | 0.106   | 0.107   | 0.001                 | 0.8                | 0.004                               | 3.8                           | 0.002                | 0.003   |
| Ammonium                           | 1.058   | 1.045   | -0.013                | -1.2               | 0.030                               | 2.9                           | 0.003                | 0.037   |
| Sulfate                            | 3.940   | 3.883   | -0.057                | -1.4               | 0.054                               | 1.4                           | 0.015                | 0.254   |
| Nitrate                            | 3.818   | 3.762   | -0.056                | -1.5               | 0.093                               | 2.5                           | 0.015                | 0.238   |
| Chloride                           | 1.234   | 1.214   | -0.020                | -1.6               | 0.030                               | 2.4                           | 0.005                | 0.017   |
| pH<br>(units)                      | 4.49  | 4.50  | 0.01                  | 0.2                | 0.03                                | 0.6                           |                      | 5.25  |
| H<br>(µeq/L)                       | 32.4  | 31.8  | -0.5                  | -1.6               | 2.0                                 | 6.3                           |                      | 5.6   |
| Specific<br>Conductance<br>(µS/cm) | 34.7  | 32.7  | -2.0                  | -5.7               | 1.6                                 | 4.8                           |                      | 5.6   |

**Notes:**

This tabulation included 48 internal blinds. Samples were simulated approximating the 95<sup>th</sup> percentile of NTN samples (06FR95).

<sup>a</sup> Target concentrations for 06FR95.

<sup>b</sup> Mean concentration obtained by the CAL from the AIRMoN internal blind samples for 2006.

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

<sup>d</sup> 5<sup>th</sup> percentile for AIRMoN samples for 2002-2006.

## B. Replicate Samples

Replicate samples serve as another estimator of sample precision. Because these are blind, real precipitation samples, their concentration values should be representative of the large volume sample population. Two percent of the NTN and AIRMoN samples are split for blind replicate analysis. The replicates are separated in the analysis queue and are analyzed at different times from the original samples. In 2005 and half of 2006, the NTN samples were divided at the time of filtration into three 60-mL aliquots: one sample is put on the tray for transfer to the laboratory for initial analysis at its regular place in the queue, one sample is filtered for archival purposes, and one sample is sent back to sample processing where it is assigned a new and higher laboratory identification number and submitted for analysis later. In mid-2006 this protocol was changed. The sample chosen to be a split is marked on the back 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 and bag are 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 it 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 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-11 through II-15 summarize the analyses of replicate samples analyzed in 2005 and 2006 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 reanalysis. 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. For 2006, the summary was also split into before the split sample protocol change and after the change. Because these samples are actual precipitation samples, the concentration of the split samples can cover the entire range of concentrations found in precipitation. The standard deviation estimated from replicate measurements was used to calculate the standard deviations. The last column in Tables II-11 through II-14 show 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 blinds, filtered and unfiltered, for both 2005 and 2006 (Tables II-1 through II-8) to  $1.48 \times \text{MAD}$  shows similar cation and anion precision of the split samples. The percent differences for the network samples are greater for the more unstable species (e.g., orthophosphate, ammonium), showing that even a few days can make a difference in the concentration of certain analytes. The stable analytes have low percent differences and lower variability. The higher the concentrations of the analytes, the more variability there is between replicate measurements. For 2006, the percent differences for most of the analytes at most

**Table II-11. Replicate NADP/NTN Precipitation Samples, 2005**

| Analyte              | Level                 | Mean Percent Difference | Median Percent Difference | Standard Deviation of Paired Measurements | n   | MAD   | Estimate of Dispersion |
|----------------------|-----------------------|-------------------------|---------------------------|---|-----|-------|------------------------|
| pH                   | < 5                   | -0.2                    | -0.2                      | 0.03                                      | 133 | 0.02  | 0.03                   |
|                      | ≥ 5                   | -0.4                    | -0.3                      | 0.07                                      | 92  | 0.05  | 0.07                   |
| H                    | > 10 µeq/L            | 2.3                     | 2.3                       | 2.4                                       | 133 | 1.2   | 1.8                    |
|                      | ≤ 10 µeq/L            | 7.8                     | 3.5                       | 0.6                                       | 92  | 0.2   | 0.3                    |
| Specific Conductance | < 10 µS/cm            | 0.4                     | 0.0                       | 0.3                                       | 89  | 0.1   | 0.1                    |
|                      | ≥ 10 µS/cm            | 0.0                     | 0.0                       | 0.4                                       | 136 | 0.3   | 0.4                    |
| Calcium              | ≤ 0.02mg/L            | -29.1                   | -25.0                     | 0.004                                     | 16  | 0.004 | 0.006                  |
|                      | 0.02 < x ≤ 0.2 mg/L   | -11.7                   | -8.2                      | 0.005                                     | 154 | 0.006 | 0.009                  |
|                      | > 0.2 mg/L            | -0.3                    | 0.4                       | 0.019                                     | 55  | 0.010 | 0.015                  |
| Magnesium            | ≤ 0.01 mg/L           | 9.9                     | 0.0                       | 0.001                                     | 74  | 0.001 | 0.001                  |
|                      | 0.01 < x ≤ 0.1 mg/L   | 4.0                     | 3.8                       | 0.002                                     | 131 | 0.001 | 0.001                  |
|                      | > 0.1 mg/L            | 3.1                     | 2.9                       | 0.007                                     | 20  | 0.006 | 0.009                  |
| Sodium               | ≤ 0.03 mg/L           | 4.6                     | 0.0                       | 0.001                                     | 77  | 0.001 | 0.001                  |
|                      | 0.03 < x ≤ 0.3 mg/L   | 1.3                     | 1.3                       | 0.003                                     | 117 | 0.002 | 0.003                  |
|                      | > 0.3 mg/L            | 2.3                     | 2.2                       | 0.035                                     | 31  | 0.018 | 0.027                  |
| Potassium            | ≤ 0.01 mg/L           | 1.6                     | 0.0                       | 0.001                                     | 74  | 0.000 | 0.000                  |
|                      | 0.01 < x ≤ 0.1 mg/L   | 1.4                     | 0.0                       | 0.001                                     | 135 | 0.001 | 0.001                  |
| Chloride             | > 0.1 mg/L            | 0.7                     | 2.2                       | 0.005                                     | 16  | 0.005 | 0.007                  |
|                      | ≤ 0.08 mg/L           | -2.8                    | -1.7                      | 0.003                                     | 91  | 0.002 | 0.002                  |
|                      | 0.08 < x ≤ 0.8 mg/L   | 0.9                     | 1.0                       | 0.006                                     | 109 | 0.003 | 0.004                  |
|                      | > 0.8mg/L             | 2.4                     | 1.5                       | 0.104                                     | 22  | 0.030 | 0.044                  |
| Nitrate              | ≤ 0.09 mg/L           | -2.7                    | 0.9                       | 0.003                                     | 7   | 0.003 | 0.004                  |
|                      | 0.09 < x ≤ 0.9 mg/L   | 2.0                     | 1.5                       | 0.020                                     | 110 | 0.008 | 0.012                  |
|                      | > 0.9 mg/L            | 1.5                     | 1.5                       | 0.030                                     | 108 | 0.023 | 0.034                  |
| Sulfate              | ≤ 0.13 mg/L           | -1.4                    | 0.0                       | 0.004                                     | 13  | 0.005 | 0.007                  |
|                      | 0.13 < x ≤ 1.3 mg/L   | 1.8                     | 1.7                       | 0.016                                     | 122 | 0.012 | 0.017                  |
|                      | > 1.3 mg/L            | 1.8                     | 1.8                       | 0.039                                     | 90  | 0.033 | 0.048                  |
| Ammonium             | ≤ 0.05 mg/L           | -7.9                    | 0.0                       | 0.002                                     | 34  | 0.001 | 0.001                  |
|                      | 0.05 < x ≤ 0.5 mg/L   | 1.1                     | 1.4                       | 0.007                                     | 148 | 0.004 | 0.006                  |
|                      | > 0.5 mg/L            | 1.3                     | 1.5                       | 0.017                                     | 43  | 0.016 | 0.024                  |
| Orthophosphate       | 0.006 ≤ x ≤ 0.06 mg/L | -20.1                   | -14.7                     | 0.011                                     | 7   | 0.000 | 0.000                  |
|                      | 0.06 < x ≤ 0.6 mg/L   | 0.1                     | -1.5                      | 0.028                                     | 5   | 0.022 | 0.033                  |

**Table II-12. Replicate NADP/NTN Precipitation Samples, January through June, 2006**

| Analyte              | Level                 | Mean Percent Difference | Median Percent Difference | Standard Deviation of Paired Measurements | n  | MAD   | Estimate of Dispersion |
|----------------------|-----------------------|-------------------------|---------------------------|---|----|-------|------------------------|
| pH                   | < 5                   | 0.0                     | 0.0                       | 0.02                                      | 49 | 0.01  | 0.01                   |
|                      | ≥ 5                   | -0.2                    | -0.4                      | 0.05                                      | 56 | 0.04  | 0.06                   |
| H                    | > 10 µeq/L            | 0.4                     | 0.0                       | 1.1                                       | 49 | 0.9   | 1.3                    |
|                      | ≤ 10 µeq/L            | 4.3                     | 4.7                       | 0.4                                       | 56 | 0.2   | 0.4                    |
| Specific Conductance | < 10 µS/cm            | 2.4                     | 1.0                       | 0.3                                       | 43 | 0.2   | 0.3                    |
|                      | ≥ 10 µS/cm            | -1.1                    | -0.5                      | 0.5                                       | 62 | 0.4   | 0.7                    |
| Calcium              | ≤ 0.02 mg/L           | -23.6                   | -16.9                     | 0.003                                     | 6  | 0.003 | 0.004                  |
|                      | 0.02 < x ≤ 0.2 mg/L   | -8.3                    | -6.8                      | 0.005                                     | 58 | 0.005 | 0.007                  |
|                      | > 0.2 mg/L            | 0.2                     | 0.1                       | 0.007                                     | 41 | 0.004 | 0.006                  |
| Magnesium            | ≤ 0.01 mg/L           | 12.6                    | 0.0                       | 0.001                                     | 21 | 0.001 | 0.001                  |
|                      | 0.01 < x ≤ 0.1 mg/L   | 4.3                     | 3.7                       | 0.002                                     | 77 | 0.001 | 0.001                  |
|                      | ≥ 0.1 mg/L            | 4.0                     | 5.2                       | 0.007                                     | 7  | 0.007 | 0.010                  |
| Sodium               | ≤ 0.02 mg/L           | -0.3                    | 0.0                       | 0.001                                     | 19 | 0.000 | 0.000                  |
|                      | 0.02 < x ≤ 0.2 mg/L   | 0.2                     | 0.0                       | 0.003                                     | 59 | 0.001 | 0.001                  |
|                      | > 0.2 mg/L            | 1.2                     | 0.6                       | 0.015                                     | 27 | 0.006 | 0.009                  |
| Potassium            | ≤ 0.02 mg/L           | -1.3                    | 0.0                       | 0.001                                     | 46 | 0.001 | 0.001                  |
|                      | 0.02 < x ≤ 0.2 mg/L   | 1.0                     | 0.0                       | 0.001                                     | 54 | 0.001 | 0.001                  |
|                      | ≥ 0.2 mg/L            | -0.4                    | -0.8                      | 0.018                                     | 5  | 0.006 | 0.009                  |
| Chloride             | ≤ 0.05 mg/L           | 3.3                     | 0.0                       | 0.006                                     | 24 | 0.001 | 0.001                  |
|                      | 0.05 < x ≤ 0.5 mg/L   | 0.1                     | 0.8                       | 0.004                                     | 62 | 0.002 | 0.003                  |
|                      | > 0.5 mg/L            | 1.4                     | 1.7                       | 0.022                                     | 19 | 0.012 | 0.018                  |
| Nitrate              | ≤ 0.15 mg/L           | -1.8                    | 2.1                       | 0.006                                     | 8  | 0.004 | 0.005                  |
|                      | 0.15 < x ≤ 1.5 mg/L   | 1.5                     | 1.4                       | 0.012                                     | 72 | 0.010 | 0.015                  |
|                      | > 1.5 mg/L            | 1.6                     | 1.3                       | 0.029                                     | 25 | 0.033 | 0.049                  |
| Sulfate              | < 0.15 mg/L           | 1.2                     | 0.0                       | 0.002                                     | 12 | 0.002 | 0.002                  |
|                      | 0.15 < x ≤ 1.5 mg/L   | 1.5                     | 1.4                       | 0.011                                     | 59 | 0.011 | 0.016                  |
|                      | > 1.5 mg/L            | 1.5                     | 1.6                       | 0.031                                     | 34 | 0.033 | 0.049                  |
| Ammonium             | ≤ 0.03 mg/L           | 5.1                     | 0.0                       | 0.002                                     | 17 | 0.001 | 0.001                  |
|                      | 0.03 < x ≤ 0.3 mg/L   | 5.8                     | 1.9                       | 0.024                                     | 43 | 0.003 | 0.004                  |
|                      | > 0.3 mg/L            | 0.8                     | 1.4                       | 0.026                                     | 43 | 0.010 | 0.015                  |
| Orthophosphate       | 0.005 ≤ x ≤ 0.05 mg/L | -20.0                   | -20.0                     | 0.005                                     | 2  | 0.000 | 0.000                  |
|                      | 0.05 < x ≤ 0.5 mg/L   | -4.6                    | -3.7                      | 0.009                                     | 5  | 0.003 | 0.004                  |

**Table II-13. Replicate NADP/NTN Precipitation Samples, July through December, 2006**

| Analyte              | Level                 | Mean Percent Difference  | Median Percent Difference | Standard Deviation of Paired Measurements | n  | MAD   | Estimate of Dispersion |
|----------------------|-----------------------|--|---------------------------|---|----|-------|------------------------|
| pH                   | < 5                   | 0.04   | 0.0                       | 0.02                                      | 68 | 0.02  | 0.03                   |
|                      | ≥ 5                   | -0.04  | -0.3                      | 0.07                                      | 58 | 0.04  | 0.06                   |
| H                    | > 10 µeq/L            | -0.3   | 0.0                       | 1.3                                       | 68 | 0.9   | 1.4                    |
|                      | ≤ 10 µeq/L            | 3.3  | 3.5                       | 0.8                                       | 58 | 0.3   | 0.4                    |
| Specific Conductance | < 10 µS/cm            | 1.4  | 0.0                       | 0.2                                       | 60 | 0.1   | 0.1                    |
|                      | ≥ 10 µS/cm            | 0.7  | 0.3                       | 0.4                                       | 66 | 0.2   | 0.3                    |
| Calcium              | ≤ 0.02 mg/L           | -8.7   | 5.6                       | 0.002                                     | 7  | 0.002 | 0.003                  |
|                      | 0.02 < x ≤ 0.2 mg/L   | -0.6   | 0.0                       | 0.004                                     | 96 | 0.003 | 0.004                  |
|                      | > 0.2 mg/L            | -0.3   | -0.4                      | 0.009                                     | 23 | 0.006 | 0.009                  |
| Magnesium            | ≤ 0.01 mg/L           | 6.2  | 0.0                       | 0.001                                     | 45 | 0.000 | 0.000                  |
|                      | 0.01 < x ≤ 0.1 mg/L   | 1.2  | 0.0                       | 0.001                                     | 73 | 0.001 | 0.001                  |
|                      | ≥ 0.1 mg/L            | 0.0  | 0.8                       | 0.006                                     | 7  | 0.003 | 0.004                  |
| Sodium               | ≤ 0.02 mg/L           | -1.1   | 0.0                       | 0.002                                     | 50 | 0.001 | 0.001                  |
|                      | 0.02 < x ≤ 0.2 mg/L   | -0.7   | 0.0                       | 0.002                                     | 49 | 0.001 | 0.001                  |
|                      | > 0.2 mg/L            | 0.7  | 0.0                       | 0.015                                     | 27 | 0.006 | 0.009                  |
| Potassium            | ≤ 0.02 mg/L           | 1.4  | 0.0                       | 0.001                                     | 87 | 0.001 | 0.001                  |
|                      | 0.02 < x ≤ 0.2 mg/L   | 0.4  | 0.0                       | 0.002                                     | 39 | 0.001 | 0.001                  |
| Chloride             | ≤ 0.05 mg/L           | -0.6   | 0.0                       | 0.003                                     | 46 | 0.002 | 0.003                  |
|                      | 0.05 < x ≤ 0.5 mg/L   | 0.3  | 0.9                       | 0.003                                     | 58 | 0.003 | 0.004                  |
|                      | > 0.5 mg/L            | 0.1  | 0.5                       | 0.039                                     | 22 | 0.008 | 0.011                  |
| Nitrate              | ≤ 0.15 mg/L           | -1.3   | -0.4                      | 0.003                                     | 8  | 0.003 | 0.004                  |
|                      | 0.15 < x ≤ 1.5 mg/L   | 0.5  | 0.6                       | 0.007                                     | 96 | 0.006 | 0.009                  |
|                      | > 1.5 mg/L            | 0.3  | 0.2                       | 0.010                                     | 21 | 0.007 | 0.010                  |
| Sulfate              | < 0.15 mg/L           | 0.1  | -0.4                      | 0.001                                     | 6  | 0.001 | 0.001                  |
|                      | 0.15 < x ≤ 1.5 mg/L   | 0.7  | 0.7                       | 0.011                                     | 91 | 0.007 | 0.010                  |
|                      | > 1.5 mg/L            | 0.6  | 0.5                       | 0.016                                     | 28 | 0.014 | 0.020                  |
| Ammonium             | 0.003 ≤ x ≤ 0.03 mg/L | -9.4   | -7.4                      | 0.002                                     | 6  | 0.001 | 0.001                  |
|                      | 0.03 < x ≤ 0.3 mg/L   | -1.3   | -1.0                      | 0.007                                     | 84 | 0.003 | 0.004                  |
|                      | > 0.3 mg/L            | 1.2  | -0.1                      | 0.037                                     | 32 | 0.004 | 0.005                  |
| Orthophosphate       | 0.005 ≤ x ≤ 0.05 mg/L | no samples were greater than the detection limit for this time period. |                           |   |    |       |                        |



**Table II-14. Replicate NADP/AIRMoN Precipitation Samples, 2005**

| Analyte              | Level                                       | Mean Percent Difference                       | Median Percent Difference | Standard Deviation of Paired Measurements | n  | MAD   | Estimate of Dispersion |
|----------------------|---|---|---------------------------|---|----|-------|------------------------|
| pH                   | < 5   | 0.7   | 0.6                       | 0.04                                      | 24 | 0.04  | 0.06                   |
|                      | 1 sample greater than pH = 5, no statistics |   |                           |   |    |       |                        |
| H                    | > 10 µeq/L                                  | -6.2  | -5.6                      | 4.2                                       | 24 | 2.2   | 3.3                    |
| Specific Conductance | < 10 µS/cm                                  | -1.8  | -4.9                      | 0.4                                       | 6  | 0.4   | 0.5                    |
|                      | ≥ 10 µS/cm                                  | -5.6  | -4.7                      | 1.7                                       | 19 | 1.3   | 1.9                    |
| Calcium              | ≤ 0.02mg/L                                  | 2.8   | 0.0                       | 0.001                                     | 7  | 0.000 | 0.000                  |
|                      | 0.02 < x ≤ 0.2 mg/L                         | 0.1   | 0.0                       | 0.002                                     | 16 | 0.002 | 0.002                  |
|                      | > 0.2 mg/L                                  | -1.8  | -1.8                      | 0.005                                     | 2  | 0.006 | 0.008                  |
| Magnesium            | ≤ 0.01 mg/L                                 | 2.9   | 0.0                       | 0.000                                     | 12 | 0.000 | 0.000                  |
|                      | 0.01 < x ≤ 0.1 mg/L                         | -3.8  | -2.8                      | 0.001                                     | 10 | 0.001 | 0.001                  |
|                      | > 0.1 mg/L                                  | 1.0   | 1.0                       | 0.006                                     | 2  | 0.007 | 0.010                  |
| Sodium               | ≤ 0.03 mg/L                                 | 9.2   | 0.0                       | 0.001                                     | 12 | 0.001 | 0.001                  |
|                      | 0.03 < x ≤ 0.3 mg/L                         | -0.3  | 0.0                       | 0.002                                     | 10 | 0.001 | 0.001                  |
|                      | > 0.3 mg/L                                  | -0.3  | -0.4                      | 0.016                                     | 3  | 0.015 | 0.022                  |
| Potassium            | ≤ 0.01 mg/L                                 | 6.7   | -11.1                     | 0.005                                     | 9  | 0.001 | 0.001                  |
|                      | 0.01 < x ≤ 0.1 mg/L                         | -9.2  | -8.0                      | 0.001                                     | 15 | 0.002 | 0.003                  |
|                      | > 0.1 mg/L                                  | 1 sample greater than 0.1 mg/L, no statistics |                           |   |    |       |                        |
| Chloride             | ≤ 0.08 mg/L                                 | -11.6   | -1.7                      | 0.002                                     | 8  | 0.001 | 0.001                  |
|                      | 0.08 < x ≤ 0.8 mg/L                         | -1.1  | 0.0                       | 0.004                                     | 15 | 0.003 | 0.004                  |
|                      | > 0.8 mg/L                                  | 1.3   | 1.3                       | 0.025                                     | 2  | 0.034 | 0.051                  |
| Nitrate              | 0.09 < x ≤ 0.9 mg/L                         | 1.5   | 0.0                       | 0.020                                     | 14 | 0.004 | 0.005                  |
|                      | > 0.9 mg/L                                  | -1.2  | 0.3                       | 0.052                                     | 11 | 0.022 | 0.033                  |
| Sulfate              | 0.13 < x ≤ 1.3 mg/L                         | 1.8   | 0.4                       | 0.010                                     | 10 | 0.006 | 0.009                  |
|                      | > 1.3 mg/L                                  | -1.0  | -0.1                      | 0.035                                     | 15 | 0.010 | 0.015                  |
| Ammonium             | ≤ 0.05 mg/L                                 | -4.1  | -4.1                      | 0.001                                     | 2  | 0.002 | 0.002                  |
|                      | 0.05 < x ≤ 0.5 mg/L                         | -7.8  | -6.3                      | 0.021                                     | 19 | 0.010 | 0.015                  |
|                      | > 0.5 mg/L                                  | 0.9   | -1.5                      | 0.021                                     | 4  | 0.010 | 0.015                  |
| Orthophosphate       | 0.006 ≤ x ≤ 0.06 mg/L                       | -35.5   | -33.2                     | 0.006                                     | 12 | 0.004 | 0.006                  |

**Table II-15. Replicate NADP/AIRMoN Precipitation Samples, 2006**

| Analyte              | Level   | Mean Percent Difference   | Median Percent Difference | Standard Deviation of Paired Measurements | n  | MAD   | Estimate of Dispersion |  |
|----------------------|---|---|---------------------------|---|----|-------|------------------------|--|
| pH                   | < 5   | 1.3   | 1.1                       | 0.06                                      | 19 | 0.05  | 0.07                   |  |
|                      | ≥ 5   | 2.4   | 2.8                       | 0.11                                      | 5  | 0.14  | 0.21                   |  |
| H                    | > 10 µeq/L                                    | -12.2   | -10.9                     | 3.6                                       | 19 | 2.4   | 3.6                    |  |
|                      | ≤ 10 µeq/L                                    | -24.2   | -27.6                     | 1.1                                       | 5  | 0.8   | 1.2                    |  |
| Specific Conductance | ≤ 10 µS/cm                                    | -15.0   | -12.0                     | 0.9                                       | 7  | 0.6   | 0.9                    |  |
|                      | > 10 µS/cm                                    | -6.8  | -4.5                      | 1.8                                       | 17 | 1.6   | 2.4                    |  |
| Calcium              | ≤ 0.02 mg/L                                   | -0.6  | 0.0                       | 0.000                                     | 8  | 0.000 | 0.000                  |  |
|                      | 0.02 < x ≤ 0.2 mg/L                           | -0.1  | 0.0                       | 0.001                                     | 9  | 0.001 | 0.001                  |  |
|                      | > 0.2 mg/L                                    | -0.4  | -0.7                      | 0.011                                     | 7  | 0.005 | 0.007                  |  |
| Magnesium            | ≤ 0.01 mg/L                                   | -5.8  | 0.0                       | 0.000                                     | 11 | 0.000 | 0.000                  |  |
|                      | 0.01 < x ≤ 0.1 mg/L                           | -1.9  | 0.0                       | 0.001                                     | 9  | 0.000 | 0.000                  |  |
|                      | > 0.1 mg/L                                    | -0.5  | -0.8                      | 0.006                                     | 4  | 0.007 | 0.010                  |  |
| Sodium               | ≤ 0.02 mg/L                                   | 2.7   | 0.0                       | 0.000                                     | 10 | 0.000 | 0.000                  |  |
|                      | 0.02 < x ≤ 0.2 mg/L                           | -1.1  | -1.7                      | 0.001                                     | 9  | 0.001 | 0.001                  |  |
|                      | > 0.2 mg/L                                    | 2.1   | 2.0                       | 0.047                                     | 5  | 0.042 | 0.062                  |  |
| Potassium            | ≤ 0.02 mg/L                                   | -6.2  | -5.3                      | 0.001                                     | 15 | 0.001 | 0.001                  |  |
|                      | 0.02 < x ≤ 0.2 mg/L                           | -9.9  | -12.9                     | 0.004                                     | 8  | 0.004 | 0.006                  |  |
|                      | 1 sample greater than 0.2 mg/L, no statistics |   |                           |   |    |       |                        |  |
| Chloride             | ≤ 0.05 mg/L                                   | 7.1   | 4.2                       | 0.001                                     | 9  | 0.001 | 0.001                  |  |
|                      | 0.05 < x ≤ 0.5 mg/L                           | -1.1  | -0.3                      | 0.002                                     | 10 | 0.001 | 0.001                  |  |
|                      | > 0.5 mg/L                                    | 2.3   | 0.1                       | 0.214                                     | 5  | 0.006 | 0.00                   |  |
| Nitrate              | 0.15 < x ≤ 1.5 mg/L                           | 0.4   | 0.4                       | 0.006                                     | 16 | 0.004 | 0.007                  |  |
|                      | > 1.5 mg/L                                    | 0.04  | 0.3                       | 0.036                                     | 8  | 0.030 | 0.043                  |  |
| Sulfate              | ≤ 0.15 mg/L                                   | 1 sample less than 0.15 mg/L, no statistics                           |                           |   |    |       |                        |  |
|                      | 0.15 < x ≤ 1.5 mg/L                           | -0.8  | -0.6                      | 0.020                                     | 12 | 0.011 | 0.016                  |  |
|                      | > 1.5 mg/L                                    | -0.6  | -0.5                      | 0.027                                     | 11 | 0.022 | 0.033                  |  |
| Ammonium             | ≤ 0.03 mg/L                                   | 1 sample less than 0.03 mg/L, no statistics                           |                           |   |    |       |                        |  |
|                      | 0.03 < x ≤ 0.3 mg/L                           | -6.1  | -5.5                      | 0.006                                     | 12 | 0.008 | 0.011                  |  |
|                      | > 0.3 mg/L                                    | -4.6  | -4.4                      | 0.027                                     | 11 | 0.022 | 0.033                  |  |
| Orthophosphate       | 0.005 ≤ x ≤ 0.05 mg/L                         | -55.5   | -48.5                     | 0.006                                     | 14 | 0.001 | 0.001                  |  |
|                      | 0.05 < x ≤ 0.5 mg/L                           | 1 sample greater than 0.05 mg/L but less than 0.5 mg/L, no statistics |                           |   |    |       |                        |  |

of the concentrations were lower after the protocol change than before. There were a few exceptions, and those that were higher were not much higher. For the majority of the analytes, the percent difference before the protocol change was significantly higher than after the change. This implies that the filtration process is impacting the sample chemistry. Calcium mean and median percent differences dropped significantly with the new replicate protocol. The replicates after the protocol change see a filter the same way the original sample did, not after 200 mL of sample has been processed. This definitely indicates that the filtration process impacts the chemistry of the samples, primarily calcium.

AIRMoN replicates do not show the filtration impact because AIRMoN samples are not filtered. With smaller sample numbers, the percent differences show greater variability than do the NTN samples, but the standard deviation of paired differences and the estimate of dispersion are similar to NTN



### III. Blanks

Solutions referred to as “blanks” are either DI water solutions or in-house prepared simulated rainwater approximating the 25<sup>th</sup> percentile concentration of the NTN. These solutions are used to discern the cleanliness of supplies washed and used at the CAL and/or shipped to sites for field use. Aliquots of one of the two solutions are used to leach the cleaned supplies. The leachates are then analyzed for contamination. The term “blanks” traditionally has been used at the CAL to refer to both DI water leachates and simulated rainwater leachates. Blanks are known to the analysts and are identified as such by sample numbers that correspond to their various sources and weeks of collection. Blanks are collected and grouped by the sample processing staff. Both pH and conductivity are measured prior to the samples being analyzed by ion chromatography, inductively coupled plasma-optical emission, and flow injection analysis. These solutions are not filtered unless they are used to determine the cleanliness of the filters. Blanks are analyzed as a weekly set. The DI water blanks from the sample processing, 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.

The following tables contain a summary of the various blanks analyzed at the CAL. The fifth percentile of the NTN concentration for 2002-2006 is shown in appropriate tables to indicate whether potential “contamination” of the supplies is meaningful in the network. Although one or more analytes for each supply checked for each year show statistically significant biases, the bias is small and usually within the noise of the instrument for that analyte and much less than the fifth percentile concentration for NTN samples. The supplies with the largest number of biased analytes for both years are the filters with calcium, sulfate, chloride, and nitrate showing a statistical bias at the 95 percent confidence level. Even though these biases are significant and probably do mean that there is some slight adsorption of sulfate and nitrate and desorption of calcium in the filters, the amount is low (less than 5 percent for sulfate and nitrate and about 11 percent for calcium) compared to the fifth percentile of NTN concentrations.

**Table III-1. pH and Specific Conductance for Weekly DI Water Blanks, 2005**

|   | <i>Sample Processing<br/>Laboratory</i> | <i>Analytical<br/>Laboratory</i> | <i>Supply Preparatory<br/>Laboratory</i> |
|---|---|----------------------------------|--|
| <b>Median</b>                                       |   |                                  |  |
| pH (units)  | 5.72                                    | 5.74                             | 5.74                                     |
| Specific<br>Conductance ( $\mu\text{S}/\text{cm}$ ) | 1.0                                     | 0.9                              | 0.9                                      |
| <b>Maximum</b>                                      |   |                                  |  |
| pH (units)  | 5.84                                    | 5.99                             | 5.92                                     |
| Specific<br>Conductance ( $\mu\text{S}/\text{cm}$ ) | 1.5                                     | 1.4                              | 1.5                                      |
| <b>Minimum</b>                                      |   |                                  |  |
| pH (units)  | 5.53                                    | 5.52                             | 5.55                                     |
| Specific<br>Conductance ( $\mu\text{S}/\text{cm}$ ) | 0.7                                     | 0.7                              | 0.7                                      |
| <b>Target for DI</b>                                |   |                                  |  |
| pH (units)  | 5.65                                    |                                  |  |
| Specific<br>Conductance ( $\mu\text{S}/\text{cm}$ ) | 0.8                                     |                                  |  |

**Note:**

A total of 52 blank DI water samples was collected.

**Table III-2. pH and Specific Conductance for Weekly DI Water Blanks, 2006**

|                                 | <i>Sample Processing<br/>Laboratory</i> | <i>Analytical<br/>Laboratory</i> | <i>Supply Preparatory<br/>Laboratory</i> |
|---------------------------------|---|----------------------------------|--|
| Median                          |   |                                  |  |
| pH (units)                      | 5.61                                    | 5.62                             | 5.61                                     |
| Specific<br>Conductance (μS/cm) | 0.9                                     | 1.0                              | 1.0                                      |
| Maximum                         |   |                                  |  |
| pH (units)                      | 5.74                                    | 5.73                             | 5.72                                     |
| Specific<br>Conductance (μS/cm) | 1.4                                     | 1.4                              | 1.4                                      |
| Minimum                         |   |                                  |  |
| pH (units)                      | 5.48                                    | 5.49                             | 5.50                                     |
| Specific<br>Conductance (μS/cm) | 0.7                                     | 0.6                              | 0.7                                      |
| Target for DI                   |   |                                  |  |
| pH (units)                      | 5.65                                    |                                  |  |
| Specific<br>Conductance (μS/cm) | 0.8                                     |                                  |  |

**Note:**

A total of 52 blank DI water samples was collected.

**Table III-3. Analyte Concentrations Found in Filter Leachates, 2005**

| <i>Analyte</i>                     | <i>DI Water<br/>(mg/L)</i> | <i>5<sup>th</sup><br/>percentile<sup>a</sup><br/>(mg/L)</i> | <i>FR25<br/>Median<br/>(mg/L)</i> | <i>Target FR25<br/>Concentration<br/>(mg/L)</i> | <i>Bias<br/>(mg/L)</i> | <i>Critical<br/>Concentration (95%)<br/>(mg/L)</i> | <i>Statistically<br/>Biased?</i> |
|------------------------------------|----------------------------|---|-----------------------------------|---|------------------------|--|----------------------------------|
| Calcium                            | <0.002                     | 0.019   | 0.054                             | 0.052   | 0.006                  | 0.006  | yes                              |
| Magnesium                          | <0.001                     | 0.003   | 0.008                             | 0.010   | -0.002                 | 0.000  | no                               |
| Sodium                             | <0.003                     | 0.005   | 0.019                             | 0.019   | 0.000                  | 0.000  | no                               |
| Potassium                          | <0.001                     | 0.003   | 0.008                             | 0.008   | 0.000                  | 0.001  | no                               |
| Ammonium                           | <0.005                     | 0.014   | 0.089                             | 0.090   | - 0.002                | 0.002  | no                               |
| Orthophosphate                     | <0.006                     | 0.000   | 0.000                             | 0.000   | 0.000                  |  |                                  |
| Sulfate                            | <0.013                     | 0.134   | 0.495                             | 0.511   | -0.012                 | 0.007  | yes                              |
| Nitrate                            | <0.009                     | 0.168   | 0.564                             | 0.585   | -0.020                 | 0.006  | yes                              |
| Chloride                           | <0.008                     | 0.020   | 0.051                             | 0.053   | -0.002                 | 0.001  | yes                              |
| pH                                 | 5.67                       | 6.43  | 4.93                              | 4.94  | -0.01                  | 0.02   | no                               |
| Hydrogen ion<br>(µeq/L)            | 2.1                        | 0.4   | 11.7                              | 11.5  | 0.1                    |  |                                  |
| Specific<br>Conductance<br>(µS/cm) | 1.1                        | 3.3   | 6.8                               | 6.8   | 0.1                    | 0.21   | no                               |

**Note:**

A total of 52 blank samples was collected.

<sup>a</sup> 5<sup>th</sup> percentile for NTN wet (W) samples for 2002-2006 with contaminated samples removed.



**Table III-4. Analyte Concentrations Found in Filter Leachates, 2006**

| <i>Analyte</i>                           | <i>DI Water<br/>(mg/L)</i> | <i>5<sup>th</sup><br/>percentile<sup>a</sup><br/>(mg/L)</i> | <i>FR25<br/>Median<br/>(mg/L)</i> | <i>Target FR25<br/>Concentration<br/>(mg/L)</i> | <i>Bias<br/>(mg/L)</i> | <i>Critical<br/>Concentration (95%)<br/>(mg/L)</i> | <i>Statistically<br/>Biased?</i> |
|--|----------------------------|---|-----------------------------------|---|------------------------|--|----------------------------------|
| Calcium                                  | <0.002                     | 0.019   | 0.056                             | 0.053   | 0.004                  | 0.003  | yes                              |
| Magnesium                                | <0.001                     | 0.003   | 0.008                             | 0.010   | -0.002                 | 0.0005   | yes                              |
| Sodium                                   | <0.002                     | 0.005   | 0.019                             | 0.019   | 0.001                  | 0.001  | no                               |
| Potassium                                | <0.002                     | 0.003   | 0.009                             | 0.008   | 0.000                  | 0.0005   | no                               |
| Ammonium                                 | <0.003                     | 0.014   | 0.093                             | 0.093   | 0.000                  | 0.002  | no                               |
| Orthophosphate                           | <0.005                     | 0.000   | 0.000                             | 0.000   | 0.000                  |  |                                  |
| Sulfate                                  | <0.015                     | 0.134   | 0.499                             | 0.525   | -0.025                 | 0.006  | yes                              |
| Nitrate                                  | <0.015                     | 0.168   | 0.570                             | 0.590   | -0.019                 | 0.007  | yes                              |
| Chloride                                 | <0.005                     | 0.020   | 0.052                             | 0.053   | -0.001                 | 0.001  | no                               |
| pH                                       | 5.60                       | 6.43  | 4.94                              | 4.92  | 0.02                   | 0.01   | yes                              |
| Hydrogen ion<br>( $\mu$ eq/L)            | 2.5                        | 0.4   | 11.5                              | 12.0  | -0.4                   |  |                                  |
| Specific<br>Conductance<br>( $\mu$ S/cm) | 1.1                        | 3.3   | 6.8                               | 7.1   | -0.3                   | 0.1  | yes                              |

**Note:**

A total of 52 blank samples was collected.

<sup>a</sup> 5<sup>th</sup> percentile for NTN wet (W) samples for 2002-2006 with contaminated samples removed.

**Table III-5. Median Measured Mass as Micrograms ( $\mu\text{g}$ )/Bucket<sup>a</sup> Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in Upright Bucket Leachates, 2005**

| <i>Analyte</i>                                   | <i>DI Water<sup>a</sup></i> |                 | <i>FR25<sup>b</sup></i> |                                  |                         |                                  |
|--|-----------------------------|-----------------|-------------------------|----------------------------------|-------------------------|----------------------------------|
|  | <i>(50 mL)</i>              | <i>(150 mL)</i> | <i>(50 mL)</i>          | <i>Statistically Biased? 95%</i> | <i>(150 mL)</i>         | <i>Statistically Biased? 95%</i> |
| Calcium  | 0.250                       | 0.450           | 0.265                   | yes                              | 0.345                   | yes                              |
| Magnesium  | 0.050                       | 0.150           | <0.050                  | no                               | <0.150                  | no                               |
| Sodium   | <0.150                      | <0.450          | <0.150                  | no                               | <0.450                  | no                               |
| Potassium  | 0.100                       | 0.150           | 0.090                   | no                               | <0.150                  | no                               |
| Ammonium   | <0.250                      | <0.750          | <0.250                  | no                               | <0.750                  | no                               |
| Sulfate  | <0.650                      | <1.950          | <0.650                  | no                               | <1.950                  | no                               |
| Nitrate  | <0.450                      | <1.350          | -0.450                  | no                               | <1.350                  | no                               |
| Chloride   | <0.400                      | <1.200          | <0.400                  | no                               | <1.200                  | no                               |
| pH (units)                                       | 5.66                        | 5.67            | 5.02(4.94) <sup>c</sup> | yes                              | 4.96(4.94) <sup>c</sup> | no                               |
| Hydrogen ion ( $\mu\text{eq}/\text{bucket}$ )    | 0.1                         | 0.3             | 0.5                     |                                  | -0.1                    |                                  |
| Specific Conductance ( $\mu\text{S}/\text{cm}$ ) | 1.4                         | 1.2             | 6.4(6.8) <sup>c</sup>   | no                               | 6.7(6.8) <sup>c</sup>   | no                               |

**Notes:**

There were 52 blind sample weeks in 2005 with 104 50-mL DI water bucket blanks. MDLs are reported in Table I-3.

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

<sup>b</sup> The FR25 measured mass represents (median concentration measured in upright bucket leachates - target FR25 concentration)  $\times 50$  or 150 mL.

<sup>c</sup> Values in parentheses represent mean values for FR25 with no bucket contact.

**Table III-6. Median Measured Mass as Micrograms ( $\mu\text{g}$ )/Bucket<sup>a</sup> Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in Upright Bucket Leachates, 2006**

| <i>Analyte</i>                                   | <i>DI Water<sup>a</sup></i> |                 | <i>(50 mL)</i>          | <i>Statistically Biased? 95%</i> | <i>FR25<sup>b</sup></i> |                                  |
|--|-----------------------------|-----------------|-------------------------|----------------------------------|-------------------------|----------------------------------|
|  | <i>(50 mL)</i>              | <i>(150 mL)</i> |                         |                                  | <i>(150 mL)</i>         | <i>Statistically Biased? 95%</i> |
| Calcium  | 0.225                       | 0.450           | 0.150                   | no                               | 0.390                   | no                               |
| Magnesium  | 0.050                       | <0.150          | <0.050                  | no                               | <0.150                  | no                               |
| Sodium   | 0.100                       | <0.300          | 0.150                   | yes                              | <0.300                  | no                               |
| Potassium  | 0.100                       | <0.300          | <0.100                  | no                               | <0.100                  | no                               |
| Ammonium   | 0.250                       | 0.450           | <0.150                  | no                               | -0.525                  | no                               |
| Sulfate  | <0.750                      | <2.250          | <0.750                  | no                               | <2.250                  | yes                              |
| Nitrate  | <0.750                      | <2.250          | <0.750                  | no                               | <2.250                  | no                               |
| Chloride   | 0.400                       | 0.900           | <0.250                  | yes                              | <0.750                  | no                               |
| pH (units)                                       | 5.63                        | 5.62            | 5.00(4.92) <sup>c</sup> | yes                              | 4.96(4.92) <sup>c</sup> | yes                              |
| Hydrogen ion ( $\mu\text{eq}/\text{bucket}$ )    | -0.0                        | -0.0            | -0.1                    |                                  | -0.1                    |                                  |
| Specific Conductance ( $\mu\text{S}/\text{cm}$ ) | 1.4                         | 1.3             | 6.6(7.1) <sup>c</sup>   | yes                              | 6.8(7.1) <sup>c</sup>   | yes                              |

**Notes:**

There were 52 blind sample weeks in 2006 with 104 50-mL DI water bucket blanks.

MDLs are reported in Table I-3.

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

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

<sup>c</sup> Values in parentheses represent mean values for FR25 with no bucket contact.

**Table III-7. Median Measured Mass as Micrograms ( $\mu\text{g}$ )/Bottle<sup>a</sup> Found in Weekly Deionized (DI) Water and Simulated Rain (FR25) in HDPE 1-Liter Bottle Leachates, 2005**

| <i>Analyte</i>                                   | <i>DI Water</i> |                 | <i>(50 mL)</i>          | <i>Statistically Biased?</i> | <i>FR25<sup>b</sup></i> |                              |
|--|-----------------|-----------------|-------------------------|------------------------------|-------------------------|------------------------------|
|  | <i>(50 mL)</i>  | <i>(150 mL)</i> |                         |                              | <i>(150 mL)</i>         | <i>Statistically Biased?</i> |
| Calcium  | <0.100          | <0.300          | <0.100                  | no                           | <0.300                  | no                           |
| Magnesium  | <0.050          | <0.150          | <0.050                  | no                           | <0.150                  | no                           |
| Sodium   | <0.150          | <0.450          | <0.150                  | no                           | <0.450                  | no                           |
| Potassium  | 0.100           | <0.150          | 0.090                   | no                           | <0.150                  | no                           |
| Ammonium   | <0.250          | <0.750          | -0.575                  | no                           | -0.750                  | yes                          |
| Sulfate  | <0.650          | <1.950          | -0.650                  | no                           | <1.950                  | no                           |
| Nitrate  | <0.450          | <1.350          | -0.675                  | yes                          | <1.350                  | no                           |
| Chloride   | <0.400          | <1.200          | <0.400                  | no                           | <1.200                  | no                           |
| pH (units)                                       | 5.61            | 5.64            | 4.94(4.94) <sup>c</sup> | no                           | 4.94(4.94) <sup>c</sup> | no                           |
| Hydrogen ion ( $\mu\text{eq}/\text{bucket}$ )    | -0.2            | 0.0             | 0.0                     |                              | 0.0                     |                              |
| Specific Conductance ( $\mu\text{S}/\text{cm}$ ) | 1.3             | 1.2             | 6.9(6.8) <sup>c</sup>   | no                           | 6.9(6.8) <sup>c</sup>   | no                           |

**Notes:**

There were 52 blind sample weeks in 2005.

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

<sup>b</sup> The FR25 measured mass represents (median concentration measured in upright bucket leachates - target FR25 concentration)  $\times 50$  or  $150$  mL.

<sup>c</sup> Values in parentheses represent mean values for FR25 with no bucket contact.

**Table III-8. Median Measured Mass as Micrograms ( $\mu\text{g}$ )/Bottle<sup>a</sup> Found  
in Weekly Deionized (DI) Water and Simulated Rain (FR25)  
in HDPE 1-Liter Bottle Leachates, 2006**

| <i>Analyte</i>   | <i>DI Water</i> |                 | <i>(50 mL)</i>          | <i>Statistically Biased</i> | <i>FR25<sup>b</sup></i> |                             |
|--|-----------------|-----------------|-------------------------|-----------------------------|-------------------------|-----------------------------|
|  | <i>(50 mL)</i>  | <i>(150 mL)</i> |                         |                             | <i>(150 mL)</i>         | <i>Statistically Biased</i> |
| Calcium  | 0.100           | <0.300          | <0.100                  | no                          | <0.300                  | no                          |
| Magnesium  | <0.050          | <0.150          | <0.050                  | no                          | <0.150                  | no                          |
| Sodium   | <0.100          | <0.300          | <0.100                  | no                          | <0.300                  | no                          |
| Potassium  | 0.100           | <0.300          | <0.100                  | no                          | <0.300                  | no                          |
| Ammonium   | <0.150          | <0.450          | -0.400                  | no                          | -0.525                  | no                          |
| Sulfate  | <0.750          | <2.250          | -0.775                  | no                          | <2.250                  | yes                         |
| Nitrate  | <0.750          | <2.250          | <0.750                  | no                          | <2.250                  | no                          |
| Chloride   | <0.250          | <0.750          | <0.250                  | no                          | <0.750                  | no                          |
| pH (units)   | 5.58            | 5.58            | 4.92(4.92) <sup>c</sup> | no                          | 4.93(4.92) <sup>c</sup> | no                          |
| Hydrogen ion<br>( $\mu\text{eq}/\text{bucket}$ )       | 0.0             | 0.1             | 0.0                     |                             | -0.0                    |                             |
| Specific<br>Conductance<br>( $\mu\text{S}/\text{cm}$ ) | 1.4             | 1.3             | 7.0(7.1) <sup>c</sup>   | no                          | 7.1(7.1) <sup>c</sup>   | no                          |

**Notes:**

There were 52 blind sample weeks in 2006.

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

<sup>b</sup> The FR25 measured mass represents (median concentration measured in upright bucket leachates - target FR25 concentration)  $\times 50$  or  $150$  mL.

<sup>c</sup> Values in parentheses represent mean values for FR25 with no bucket contact.

**Table III-9. Analyte Concentration (mg/L) Found in 50 mL Deionized (DI) Water and 50 mL Simulated Rain (FR25) Used to Leach Snap-on Lids, 2005**

| <i>Analyte</i>             | <i>MDL<br/>(mg/L)</i> | <i>DI Water</i>        |                          | <i>FR25</i>            |                          | <i>Statistically<br/>significant bias?</i> | <i>FR25t<br/>Target<br/>Concentration<br/>(mg/L)</i> |
|----------------------------|-----------------------|------------------------|--------------------------|------------------------|--------------------------|--|--|
|                            |                       | <i>mean<br/>(mg/L)</i> | <i>median<br/>(mg/L)</i> | <i>mean<br/>(mg/L)</i> | <i>median<br/>(mg/L)</i> |  |  |
| Calcium                    | 0.002                 | 0.000                  | 0.002                    | 0.066                  | 0.055                    | no   | 0.052  |
| Magnesium                  | 0.001                 | 0.000                  | 0.000                    | 0.011                  | 0.010                    | no   | 0.010  |
| Sodium                     | 0.003                 | 0.000                  | 0.002                    | 0.023                  | 0.021                    | no   | 0.019  |
| Potassium                  | 0.001                 | 0.000                  | 0.001                    | 0.012                  | 0.010                    | no   | 0.008  |
| Ammonium                   | 0.005                 | 0.000                  | 0.014                    | 0.108                  | 0.105                    | yes  | 0.090  |
| Sulfate                    | 0.013                 | 0.000                  | 0.000                    | 0.531                  | 0.516                    | no   | 0.511  |
| Nitrate                    | 0.009                 | 0.000                  | 0.000                    | 0.579                  | 0.587                    | no   | 0.585  |
| Chloride                   | 0.008                 | 0.000                  | 0.000                    | 0.056                  | 0.054                    | no   | 0.053  |
| pH (units)<br>Hydrogen Ion |                       | 5.72                   | 5.72                     | 5.00                   | 5.00                     | yes  | 4.94   |
| (µeq/L)                    |                       | 1.9                    | 1.9                      | 10.2                   | 10.1                     |  | 11.5   |
| Specific<br>Conductance    |                       |                        |                          |                        |                          |  |  |
| (µS/cm)                    |                       | 1.2                    | 1.2                      | 6.8                    | 6.7                      | no   | 6.8  |

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

**Table III-10. Analyte Concentration (mg/L) Found in 50 mL Deionized (DI) Water and 50 mL Simulated Rain (FR25) Used to Leach Snap-on Lids, 2006**

| <i>Analyte</i>                     | <i>MDL</i><br>(mg/L) | <i>DI Water</i>       |                         | <i>FR25</i>           |                         | <i>Statistically significant bias?</i> | <i>FR25t Target Concentration</i><br>(mg/L) |
|------------------------------------|----------------------|-----------------------|-------------------------|-----------------------|-------------------------|--|---|
|                                    |                      | <i>mean</i><br>(mg/L) | <i>median</i><br>(mg/L) | <i>mean</i><br>(mg/L) | <i>median</i><br>(mg/L) |  |   |
| Calcium                            | 0.002                | 0.004                 | 0.003                   | 0.060                 | 0.056                   | no                                     | 0.053                                       |
| Magnesium                          | 0.001                | 0.001                 | 0.001                   | 0.011                 | 0.010                   | no                                     | 0.010                                       |
| Sodium                             | 0.002                | 0.006                 | 0.002                   | 0.024                 | 0.021                   | no                                     | 0.019                                       |
| Potassium                          | 0.002                | 0.007                 | 0.002                   | 0.014                 | 0.011                   | no                                     | 0.008                                       |
| Ammonium                           | 0.003                | 0.016                 | 0.013                   | 0.109                 | 0.107                   | yes                                    | 0.093                                       |
| Sulfate                            | 0.015                | 0.006                 | 0.000                   | 0.514                 | 0.518                   | no                                     | 0.525                                       |
| Nitrate                            | 0.015                | 0.004                 | 0.000                   | 0.584                 | 0.589                   | no                                     | 0.590                                       |
| Chloride                           | 0.009                | 0.009                 | 0.006                   | 0.058                 | 0.055                   | no                                     | 0.053                                       |
| pH (units)                         |                      | 5.66                  | 5.65                    | 4.98                  | 4.97                    | yes                                    | 4.92  |
| Hydrogen Ion<br>(µeq/L)            |                      | 2.2                   | 2.2                     | 10.5                  | 10.7                    |  | 12.0  |
| Specific<br>Conductance<br>(µS/cm) |                      | 1.3                   | 1.3                     | 6.7                   | 6.8                     | yes                                    | 7.1   |

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

**Table III-11. Analyte Concentration (mg/L) Found in Monthly Simulated Rain (FR25) AIRMoN 250-mL HDPE Bottle Leachates, 2005**

| <i>Analyte</i>                            | <i>FR 25 (50 mL)</i> |                      |  | <i>FR25 (150 mL)</i> |                      |  | <i>FR25 Target Concentration (mg/L)</i> |
|---|----------------------|----------------------|--|----------------------|----------------------|--|---|
|   | <i>mean (mg/L)</i>   | <i>median (mg/L)</i> | <i>Statistically significant bias?</i> | <i>mean (mg/L)</i>   | <i>median (mg/L)</i> | <i>Statistically significant bias?</i> |   |
| Calcium                                   | 0.053                | 0.053                | no                                     | 0.053                | 0.053                | no                                     | 0.052                                   |
| 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                                 | 0.008                | 0.009                | no                                     | 0.008                | 0.008                | no                                     | 0.008                                   |
| Ammonium                                  | 0.092                | 0.092                | no                                     | 0.092                | 0.092                | no                                     | 0.090                                   |
| Sulfate                                   | 0.511                | 0.509                | no                                     | 0.511                | 0.509                | no                                     | 0.511                                   |
| Nitrate                                   | 0.583                | 0.582                | no                                     | 0.582                | 0.582                | no                                     | 0.585                                   |
| Chloride                                  | 0.051                | 0.050                | no                                     | 0.051                | 0.051                | no                                     | 0.053                                   |
| pH (units)                                | 4.92                 | 4.93                 | no                                     | 4.93                 | 4.94                 | no                                     | 4.94                                    |
| Hydrogen Ion ( $\mu\text{eq/L}$ )         | 12.0                 | 11.7                 | no                                     | 11.7                 | 11.6                 | no                                     | 11.5                                    |
| Specific Conductance ( $\mu\text{S/cm}$ ) | 7.2                  | 7.2                  | yes                                    | 7.1                  | 7.1                  | yes                                    | 6.8                                     |
| n   | 12                   |                      |  | 12                   |                      |  |   |



**Table III-12. Analyte Concentration (mg/L) Found in Monthly Simulated Rain (FR25) AIRMoN 250-mL HDPE Bottle Leachates, 2006**

| <i>Analyte</i>                                  | <i>mean<br/>(mg/L)</i> | <i>FR 25 (50 mL)</i>     |  |                        | <i>FR25 (150 mL)</i>     |  |       | <i>FR25<br/>Target<br/>Concentration<br/>(mg/L)</i> |
|---|------------------------|--------------------------|--|------------------------|--------------------------|--|-------|---|
|   |                        | <i>median<br/>(mg/L)</i> | <i>Statistically<br/>significant bias?</i> | <i>mean<br/>(mg/L)</i> | <i>median<br/>(mg/L)</i> | <i>Statistically<br/>significant bias?</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   | 0.008 |   |
| Ammonium  | 0.096                  | 0.096                    | no   | 0.096                  | 0.096                    | no   | 0.093 |   |
| Sulfate   | 0.516                  | 0.518                    | no   | 0.519                  | 0.519                    | no   | 0.525 |   |
| Nitrate   | 0.586                  | 0.587                    | no   | 0.587                  | 0.586                    | no   | 0.590 |   |
| Chloride  | 0.052                  | 0.052                    | no   | 0.052                  | 0.052                    | no   | 0.053 |   |
| pH (units)                                      | 4.92                   | 4.92                     | no   | 4.92                   | 4.92                     | no   | 4.92  |   |
| Hydrogen Ion<br>( $\mu\text{eq/L}$ )            | 12.0                   | 12.0                     |  | 12.0                   | 11.9                     |  | 12.0  |   |
| Specific<br>Conductance<br>( $\mu\text{S/cm}$ ) | 7.0                    | 7.0                      | yes  | 7.0                    | 7.0                      | yes  | 7.1   |   |
| n   | 12                     |                          |  | 12                     |                          |  |       |   |

**Table III-13. Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Bags, 2005**

| <i>Analyte</i>                            | <i>DI Water (50 mL)</i> |                      | <i>FR25 (50 mL)</i> |                      | <i>Statistically significant bias?</i> | <i>FR25 Target Concentration (mg/L)</i> |
|---|-------------------------|----------------------|---------------------|----------------------|--|---|
|   | <i>mean (mg/L)</i>      | <i>median (mg/L)</i> | <i>mean (mg/L)</i>  | <i>median (mg/L)</i> |  |   |
| Calcium                                   | <0.002                  | <0.002               | 0.053               | 0.053                | no                                     | 0.052                                   |
| Magnesium                                 | <0.001                  | <0.001               | 0.010               | 0.010                | no                                     | 0.010                                   |
| Sodium                                    | <0.003                  | <0.003               | 0.020               | 0.019                | no                                     | 0.019                                   |
| Potassium                                 | <0.002                  | <0.002               | 0.009               | 0.009                | no                                     | 0.008                                   |
| Ammonium                                  | <0.005                  | <0.005               | 0.095               | 0.095                | yes                                    | 0.090                                   |
| Sulfate                                   | <0.013                  | <0.013               | 0.515               | 0.515                | no                                     | 0.511                                   |
| Nitrate                                   | <0.009                  | <0.009               | 0.586               | 0.586                | no                                     | 0.585                                   |
| Chloride                                  | <0.008                  | <0.008               | 0.053               | 0.052                | no                                     | 0.053                                   |
| pH (units)                                | 5.57                    | 5.60                 | 4.95                | 4.92                 | no                                     | 4.94                                    |
| Hydrogen Ion ( $\mu\text{eq/L}$ )         | 2.9                     | 2.5                  | 11.6                | 12.0                 | no                                     | 11.5                                    |
| Specific Conductance ( $\mu\text{S/cm}$ ) | 1.5                     | 1.4                  | 7.1                 | 7.2                  | no                                     | 6.8                                     |
| n   | 52                      |                      | 52                  |                      |  |   |

**Table III-14. Analyte Concentration (mg/L) Found in Deionized (DI) Water and Simulated Rain (FR25) Used to Leach Bags, 2006**

| <i>Analyte</i>               | <i>DI Water (50 mL)</i> |                      | <i>FR25 (50 mL)</i> |                      | <i>Statistically significant bias?</i> | <i>FR25 Target Concentration (mg/L)</i> |
|------------------------------|-------------------------|----------------------|---------------------|----------------------|--|---|
|                              | <i>mean (mg/L)</i>      | <i>median (mg/L)</i> | <i>mean (mg/L)</i>  | <i>median (mg/L)</i> |  |   |
| Calcium                      | <0.002                  | <0.002               | 0.054               | 0.054                | no                                     | 0.053                                   |
| Magnesium                    | <0.001                  | <0.001               | 0.010               | 0.010                | no                                     | 0.010                                   |
| Sodium                       | 0.006                   | 0.002                | 0.022               | 0.021                | no                                     | 0.019                                   |
| Potassium                    | 0.005                   | <0.002               | 0.009               | 0.009                | no                                     | 0.009                                   |
| Ammonium                     | 0.008                   | 0.008                | 0.101               | 0.101                | yes                                    | 0.093                                   |
| Sulfate                      | <0.015                  | <0.015               | 0.523               | 0.522                | no                                     | 0.525                                   |
| Nitrate                      | <0.015                  | <0.015               | 0.593               | 0.593                | no                                     | 0.590                                   |
| Chloride                     | <0.009                  | <0.098               | 0.054               | 0.053                | no                                     | 0.053                                   |
| pH (units)                   | 5.53                    | 5.56                 | 4.91                | 4.92                 | no                                     | 4.92                                    |
| Hydrogen Ion (µeq/L)         | 3.2                     | 2.8                  | 12.4                | 12.0                 | no                                     | 12.0                                    |
| Specific Conductance (µS/cm) | 1.6                     | 1.4                  | 7.3                 | 7.2                  | no                                     | 7.1                                     |
| n                            | 52                      |                      | 52                  |                      |  |   |



## IV. Monthly and Annual Quality Assurance Procedures

Monthly NADP/NTN and NADP/AIRMoN QA 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 samples are transmitted to the data-processing staff approximately twice a month. Data for AIRMoN samples are processed once a month. These analytical data are submitted for a reanalysis selection test that includes all samples with sufficient volume (internal blinds, field blanks, and collocated program samples included). 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 is measured prior to dilution. A sample is flagged if the ion percent difference (IPD) or conductivity percent difference (CPD) exceeds set limits as defined in the NADP 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 site. Additional information concerning the reanalysis of samples can be found there as well.

### B. Laboratory Round-Robin Programs

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

The 32<sup>nd</sup> and 33<sup>rd</sup> sets of the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) reference precipitation samples were shipped to participating laboratories in April and October, 2005, respectively. The 34<sup>th</sup> and 35<sup>th</sup> sets were shipped in April and November, 2006, 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 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 study's final report. For details on the results of the study, refer to <http://www.qasac-americas.org/>.

The CAL participated in four studies sponsored by the National Water Research Institute (NWRI) in Burlington, Ontario, Canada in 2005 and 2006. Begun in 1982 as the Long-Range Transport of Atmospheric Pollutants (LRTAP) program, the studies for 2005 were PT86 and PT87 (Alkema and Simser, 2005, and 2006a) and studies PT88 and PT89 for 2006 (Tinson,

2006, and Tinson, 2007). In 2005 and 2006, the CAL took part in the Trace Elements In Water PT studies as well as the Rain And Soft Waters studies.

NWRI samples included selected major ions, nutrients, and physical parameters in natural waters. The NWRI publishes a report that includes all the data and a summary of all laboratories participating in each study. For Study PT86, the CAL showed a low bias for nitrate + nitrite (the CAL only measures nitrate, but the results for Study PT86 needed a combination of nitrite + nitrate, resulting in a low bias for the CAL for this “analyte”). However, all other analytes in the Rain and Soft Waters study were “ideal” resulting in an overall rating of “good.” For Study PT87, no analytes were flagged and all were considered “ideal,” resulting in the CAL receiving a rating of “good.” In 2006, for study PT88, sodium was flagged high on one sample with all other analytes qualified as “ideal.” The performance of the CAL was rated as “good.” For PT89, no samples or ions were flagged, resulting in a rating of “good” for the CAL. For more information on these four studies, contact the National Laboratory for Environmental Testing, Water Science and Technology Directorate, Environment Canada, 867 Lakeshore Road, P.O. Box 5050, Burlington, ON, Canada, L7R 4A6.

The Norwegian Institute for Air Research (NILU) sponsored the 23<sup>rd</sup> and 24<sup>th</sup> European Monitoring and Evaluation Programme (EMEP) intercomparison of analytical methods for atmospheric precipitation in 2005 and 2006, respectively. There were four samples in each study. All results were within the standard expected variation for that analyte with the percent difference ranging from  $\pm 0.2$  percent to  $\pm 4.0$  percent with the minimum difference being sulfate at -0.2 percent and the largest difference being sodium at -4.0 percent for 2005. For 2006, the percent difference ranged from + 0.1 percent to + 5.5 percent with the largest difference being conductivity at -5.5 percent and the smallest difference being sulfate at 0.1 percent. For more information about the program or results, contact Hilde Thelle Uggerud ([htu@nilu.no](mailto:htu@nilu.no)) at the Norwegian Institute for Air Research.

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