Quality Assurance Report
National Atmospheric Deposition Program
2012

Laboratory Operations
Central Analytical Laboratory

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Introduction

The Central Analytical Laboratory (CAL), located in Champaign, Illinois, on the campus of the University of Illinois, has analyzed and processed data on wet deposition samples for the National Atmospheric Deposition Program (NADP) since 1978. NADP is composed of five research monitoring networks, and the CAL analyzes samples for three of the networks: the National Trends Network (NTN), the Atmospheric Integrated Research Monitoring Network (AIRMoN), and the Ammonia Monitoring Network (AMoN).

Wet deposition samples collected for the NTN and AIRMoN networks are measured for acidity (as pH), specific conductance, sulfate (SO_4^{-2}), nitrate (NO_3^-), chloride (Cl^-), bromide (Br^-), ammonium (NH_4^+), orthophosphate (PO_4^{-3}), calcium (Ca^{+2}), magnesium (Mg^{+2}), potassium (K^+), and sodium (Na^+) ions. The collection of precipitation samples for the two networks differ in that AIRMoN samples are collected daily and NTN samples are collected weekly. For consistency in this report, acidity is reported in pH units, conductivity is reported as µS/cm (micro-Siemens per centimeter), and ions are reported as mg/L (milligrams per liter, where 1 mg/L = 1 ppm (part per million)).

AMoN passive-type air sampler extracts are analyzed for ammonium ion (NH_4^+) concentration, which is used to calculate ambient gaseous ammonia (NH_3) concentrations.

The CAL follows guidelines specified in the NADP Network Quality Assurance Plan (QAP), which is available on the NADP website (http://nadp.isws.illinois.edu/lib). The CAL uses specific Data Quality Indicators (DQIs) detailed in the CAL's QAP. This document is available from the CAL's website (http://nadp.isws.illinois.edu/CAL). The analytical methods used for each ion are shown in Table 1. Instrument and method detection limits are provided in Table 6 (2012) and Table 12 (2013).

Table 1. CAL analytical methods

	Instument/Vendor/Method
pH	Ion-Specific Electrode / Broadley-James Corporation
Specific Conductance	Electrical Conductivity Cell / YSI Inc / 3253 CELL K=1.0/cm
Bromide	Ion Chromatography (IC) / Thermo / Dionex ICS 2000 and Dionex ICS 5000
Chloride	Ion Chromatography (IC) / Thermo / Dionex ICS 2000 and Dionex ICS 5000
Nitrate	Ion Chromatography (IC) / Thermo / Dionex ICS 2000 and Dionex ICS 5000
Sulfate	Ion Chromatography (IC) / Thermo / Dionex ICS 2000 and Dionex ICS 5000
Ammonium	Flow Injection Analysis (FIA) Colorimetry/Lachat Instruments/QuikChem 8000 and QuikChem 8500
Orthophosphate	Flow Injection Analysis (FIA) Colorimetry/Lachat Instruments/QuikChem 8000 and QuikChem 8500
Calcium	Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)/Agilent Technologies/VISTA-PRO
Magnesium	Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)/Agilent Technologies/VISTA-PRO
Sodium	Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)/Agilent Technologies/VISTA-PRO
Potassium	Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)/Agilent Technologies/VISTA-PRO

Significant Changes in 2012

- Research continued on methods for measuring elemental carbon, organic carbon (Torres, Bond, and Lehmann, 2011), and total phosphorus (Green and Lehmann, 2011) in wet deposition samples.
- Instrument Detection Limits (IDL) were determined for 2012 by measurement of monthly polisher water system checks (January 2012).
- Methods for calculating the Method Detection Limits (MDL) were modified to include sample collection buckets and 1-L sample bottles for NTN samples, and sample collection buckets and 250-mL sample bottles for AIRMoN samples (January 2012 – December 2012).
- New Dionex ICS-5000 was placed into operation beginning with sample LABNO TJ6382SW for NTN and AC6578L for AIRMoN (January 24, 2012).
- New ICP Expert II software was used starting with NTN sample TK1874SW and AIRMoN sample AC7066L (June 22, 2012).
- NTN samples were refrigerated following filtration, starting with sample TJ8425SW (March 19, 2012).
- The procedures for checking washed buckets, bottles, and lids were modified. One sample of each supply type selected from the supplies was washed each day and tested for a period of 24 hours using the in-house FR50 quality control (QC) solution (June 2012).
- The numbering sequence for supply checks was changed to a Laboratory Information Management System (LIMS) project format and a sequential number scheme (August 2012).

- AMoN passive sampler bodies were placed in the oven overnight to dry following sonication and before being placed into the vacuum desiccator (January 2012 – April 2012).
- AMoN passive air sampler body cleaning procedure was modified to include an overnight soak in the sonicator. Sampler bodies are no longer placed in the oven and the vacuum desiccator. They are placed into the clean air bench for drying and covered with a laboratory wipe (May 2012).
- AMoN passive samplers were prepared by placing the cores into the sampler bodies using a polyethylene gloved hand, instead of inverting them into test tubes (June 2012).
- The cleaning procedure for passive AMoN sampler bodies has been modified to add laboratory detergent (DECON 90) to the sonication water with heating, and to an overnight soak (July 2012).
- The final sonicator bath solution for AMoN passive air sampler body cleaning was analyzed for NH_4^+ and PO_4^{3-} (November 2012).

Quality Assurance/Quality Control

Objectives

Quality Assurance (QA)/Quality Control (QC) within the CAL is an "all-hands" effort. CAL team members work together to maintain compliance with project Data Quality Objective (DQO) requirements and strive to improve upon current methods. Standard Operating Procedures (SOPs) are followed to ensure that data products from the CAL are of documented high quality and reproducibility.

The overall quality of NADP data is assessed through DQIs, including precision, accuracy, and comparability.

- **Precision** is a measure of data reproducibility and random error. The CAL's analytical precision is assessed by the use of control charts and blind, split, and replicate samples. Control charts are used to evaluate long-term instrument precision and any drifts in the data. Blind samples are masked from the analytical staff, and are used to evaluate the detection limits. Sample analytical precision is evaluated by split samples. Replicate samples are used to evaluate instrument precision throughout the duration of the analytical run.
- **Accuracy** is a measure of correctness and how closely the data represent the true value. Accuracy is evaluated through the use of blind samples and participation in external laboratory comparison studies.
- **Comparability** is measured by comparing the variability of one set of data with respect to another. Comparability is evaluated through daily control charts, internal blind data, and external laboratory comparison studies.

Summary of Procedures

Method Detection Limits (MDLs). Two solutions are prepared and used to evaluate MDLs for each analyte. These solutions, labeled Cation MDL and Anion MDL, are prepared at concentrations that are approximately three to five times the projected MDL for each analyte.

Control Charts. Data variability and deviation from target specifications are monitored daily using control charts. The CAL prepares an internal verification standard termed "faux rain" (FR) as a dedicated matrix spike solution with target concentrations that represent the 50^{th} percentile level of analytes measured in NTN rain water samples (designated as FR50). This solution contains all CAL analytes except for PO_4^{3-}, and is used for quality control. Orthophosphate standards are purchased from the Environmental Resource Associates[1] , and are diluted as necessary. To set annual control chart limits, internal blind samples are measured a minimum of seven times. The average of these

[1] Environmental Resource Associates, 5540 Marshall Street, Arvada, CO 80002, Simple Nutrients, catalog number 584.

results is the target value for the control chart. Control limits are established at twice the standard deviation (2σ) for the warning limits, and 3σ for the control limits. The control limits for 2012 were based on viewing control charts at the end of 2011 and adjusting them when limits were too wide. Control chart limits are monitored daily using FR50, low and high concentration control solutions, and DI water. When results for daily control solutions fall outside of control limits, analysis of the affected samples is repeated.

Analytical Verification. Each analyst purchases second-source standards to prepare two or three check standards. The number of check standards depends upon the calibration range. The target concentrations for the check standards are determined by each analyst and confirmed by the QA chemist.

Internal blind samples (i.e., samples not readily identifiable to the analyst) are evaluated monthly. Five different solutions are used for the internal blind study: deionized water (DI), Anion MDL, Cation MDL, FR50, and AES-05 (an external certified reference standard is purchased from RTC[2]). The QA Chemist uses blind sample control limits to evaluate instrument and analyst performance.

In 2012, blind samples were submitted weekly for both NTN and AIRMoN networks; the procedures were modified to include the full sampling procedure (and supplies) used for each of the networks. For example, a FR50 solution was placed in a sample collection bucket and allowed to sit overnight; part of that solution was poured into a 1-L NTN bottle, and the remainder was poured into a 250 mL AIRMoN bottle. The NTN sample was filtered, and the AIRMoN sample was not.

The NTN wet-dilution study for low-volume samples started in November 2012 to assess the uncertainty that is introduced as a result of sample dilution. This study will continue in 2013.

Each analyst selects a minimum of two to three samples at random per week as a replicate sample. These samples are analyzed once sequentially and an additional one to two times later in the sample sequence. The analyst calculates a relative percentage difference to determine if the sample results are within control limits. If any of the results fall out of control, evaluation and corrective actions should be determined by the analyst. All replicate results are evaluated monthly by the QA chemist. There were no results out of control in 2012.

Approximately 1 out of every 100 samples is selected for duplicate submission during the filtration process. The sample is split, filtered through two different filters, and placed sequentially in the analytical queue. The percentage difference is evaluated between the duplicate samples by the analyst. Corrective actions are determined by the analysts when the differences are out of control (> 10%). The QA chemist verifies results for all duplicate samples monthly.

[2] RTC, 2931 Soldier Springs Road, Post Office Box 1346, Laramie, WY 82070.
Disclaimer: The use of trade or manufacturer's names does not constitute an endorsement by the University of Illinois, NADP, or project sponsors.

Supply Checks. New supplies are evaluated before they are introduced for site or laboratory use according to the frequency in Table 4. In addition, washed/reused supply cleanliness was monitored weekly up through June 2012, after which a daily check of supplies was implemented (Table 5). For washed/reused supplies, 1 bucket, 1 bottle, and 1 lid (if washed) was taken and tested for a 24-hour period (bottles and buckets) or for a 2-hour period (lids). All results are monitored weekly by the QA Chemist.

Table 2. Control and internal blind solution target concentrations for NTN and AIRMoN

	50th percentile Target concentration	Cation MDL Target concentration	Anion MDL Target concentration	AES-05 Target concentration
CAL Designation	**FR50**	**LV120001**	**LU120001**	**AES-05**
pH	4.80	5.56	5.60	4.90
Specific Conductance (µS/cm)	10.6	1.5	1.1	10.8
Calcium (mg/L)	0.123	0.007	0.001	0.187
Magnesium (mg/L)	0.023	0.004	0	0.037
Sodium (mg/L)	0.049	0.005	0.008	0.181
Potassium (mg/L)	0.021	0.005	0.034	0.028
Chloride (mg/L)	0.098	0.061	0.021	0.225
Sulfate (mg/L)	0.828	0.019	0.018	1.28
Nitrate (mg/L)	0.958	0.042	0.024	1.15
Ammonium (mg/L)	0.227	0.031	0.005	0.312
Orthophosphate(mg/L)	NA	NA	0.030	NA

Table 3. Orthophosphate control solution concentrations
RTC, 2931 Soldier Springs Road, Post Office Box 1346, Laramie, WY 82070

	Low standard	High standard
Orthophosphate (mg/L)	0.030	0.150

Table 4. NTN and AIRMoN new supply checks

Supply Type	Test Frequency	Test Solution	Test Volume	Contact Time	Label (through July 2012)*
buckets	1 per 16	DI	150 mL	24 hours	CB
bucket lids	1 per 15	DI	50 mL	4 hours	CC
1 L bottles	1 per 24	DI	150 mL	24 hours	CN
250 mL AIRMoN bottles	1 per 24	FR50	50 mL	24 hours	CN
bucket bags	1 per box (50)	DI	150 mL	24 hours	CF
lid bags	1 per box (100)	DI	150 mL	24 hours	CF
filters	2 per lot and weekly	DI/FR50	50 mL	N/A	CD/BB/BC
polisher water (all labs)	Monthly	N/A	50 mL	N/A	CA

*Beginning August 2012, the numbering sequence for supply checks was changed into a LIMS project format using a sequential number scheme

Table 5. Summary of NTN and AIRMoN weekly washed/reused supply checks

Supply	Test Solution	Volume	Contact Time	Label *
RO water	NA	50 mL	NA	A
Filter	DI		NA	B
Filter	FR50		NA	C
Bucket **		150 mL	1 day	D
Bucket **			1 day	E
Bucket **			1 day	F
Bucket **			1 week	G
Bucket **			1 week	H
Bucket **			1 week	I
Bottle **			1 day	J
Bottle **			1 day	K
Bottle **			1 day	L
Bottle **			1 week	M
Bottle **			1 week	N
Bottle **			1 week	O
Lid ***		50 mL	4 hours	P
Lid ***			4 hours	Q
Lid ***	DI		4 hours	R
Lid ***			4 hours	S

*Beginning August 2012 the numbering sequence for supply checks was changed into Laboratory Information Management System (LIMS) project format using a sequential number scheme.

**Beginning June 2012 the procedures for checking washed buckets and bottles were modified. One of each bucket or bottle was selected from the supplies washed each day and tested for a period of 24 hours using the in-house FR50 solution.

***Beginning June 2012 the procedure for checking washed lids was modified. One of each lid was selected from the supplies washed each day and tested for a period of 2 hours using in-house FR50 solution.

Quality Control Discussion

Method Detection Limits

Method Detection Limits (MDLs) are defined by the U.S. Environmental Protection Agency (EPA) 40 CFR 136.2 document as the "minimum concentration of analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero." The EPA provides guidelines for calculating MDLs. Two standards are used to determine MDLs for Na^+, Ca^{2+}, Mg^{2+}, K^+, $NH4^+$, NO_3^-, Cl^-, SO_4^{2-}, Br^- and PO_4^{3-}. Conductivity and pH do not have defined MDLs; instead, the value is calculated based on a measure of long-term variability. Samples used to determine MDLs are blind to the analysts.

MDL study results are compiled at the end of each calendar year and are used to compute the MDL for the upcoming year. The calculated MDLs are provided to the NADP Program Office for data released to the public. Thus, solutions measured during 2011 are used to calculate MDLs for 2012 (Table 6). See Table 1 for methods.

Table 6. NTN/AIRMoN MDLs for 2012

Ion	MDL (mg/L)
Calcium	0.005
Potassium	0.003
Magnesium	0.002
Sodium	0.002
Chloride	0.009
Nitrate	0.010
Sulfate	0.010
Ammonium	0.009
Orthophosphate	0.005

Control Charts

In 2012, all analytical values for FR50, low and high concentration check solutions, AES-05, and DI water were within control. The Data Quality Objectives (DQOs) as defined in the CAL QAP were met. Further details are provided in Table 15.

Weekly Blank Results

Weekly blank target levels are based on historic and current MDLs for deionized water blanks and the historic precision measured in blanks using the FR50 solution. Box and whisker plots, as shown in Figure 1, are used to identify outliers. Throughout this report, a standard boxplot format is used; the boxes indicate the 1st, median, and 3rd quartiles of the data. The whiskers illustrate 1.5 times the interquartile range (1st to 3rd quartiles, indicated by the box length). "X" designates points that are outside 1.5 times the interquartile range; such values are considered statistical outliers.

Polisher and Reverse Osmosis Deionized (RO DI) Water Blanks

The polisher and RO DI water blanks met all acceptance criteria for 2012 (Table 7). No measurements were observed to be outside the MDL target limits shown in Table 6.

Table 7. Number of samples outside the target limits for polisher and RO blanks in 2012

Parameter	Polisher DI N=60	RO Water N=48
pH	0	0
Specific Conductance	0	0
Calcium	0	0
Potassium	0	0
Magnesium	0	0
Sodium	0	0
Chloride	0	0
Sulfate	0	0
Nitrate	0	0
Ammonium	0	0
Orthophosphate	0	0

NTN Sample Filters: DI Water and FR50 Solution

The concentrations of all analytes in DI water blanks in 2012 were typically less than the 5th percentile of NTN sample concentrations for the five-year period from 2008 to 2012. Low levels of Na^+ and Cl^- were detected in DI water eluent from NTN sample filter supply tests (Table 8). The median concentration of Na^+ found on filters was 0.001 mg/L, and the median concentration of Cl^- found on filters was 0.003 mg/L. One outlier was noted for SO_4^{2-}. Box and whisker plots for Na^+ and Cl^- from filters leached with DI water are shown in Figure 1. Box and whisker plots for Ca^{2+} from filters leached with FR50 are shown in Figure 2.

The levels of Na^+, Cl^-, and c Ca^{2+} found when leaching filters with both DI and FR50 were low in 2012, with a bias of the same magnitude as the MDL. When sample volume allows, filters are rinsed with sample prior to sample collection (see SOP PR-1055 for details). Filters are rinsed with 50 mL for samples of volume greater than 200 mL. For samples of volume between 100 mL and 200 mL, 20 mL of sample is used as the rinse. In many cases low-volume samples have higher concentrations of analytes; the relative bias from any filter contamination is lower for such samples.

Table 8. Number of results outside of target limits in 2012 for filter blanks

Parameter	DI N=51	FR50 N=51
pH	0	0
Specific Conductance	0	1
Calcium	0	0
Potassium	0	0
Magnesium	0	0
Sodium	2	0
Chloride	1	0
Sulfate	1	0
Nitrate	0	0
Ammonium	0	0
Bromide	0*	0*
Orthophosphate	0	NA

*N=22

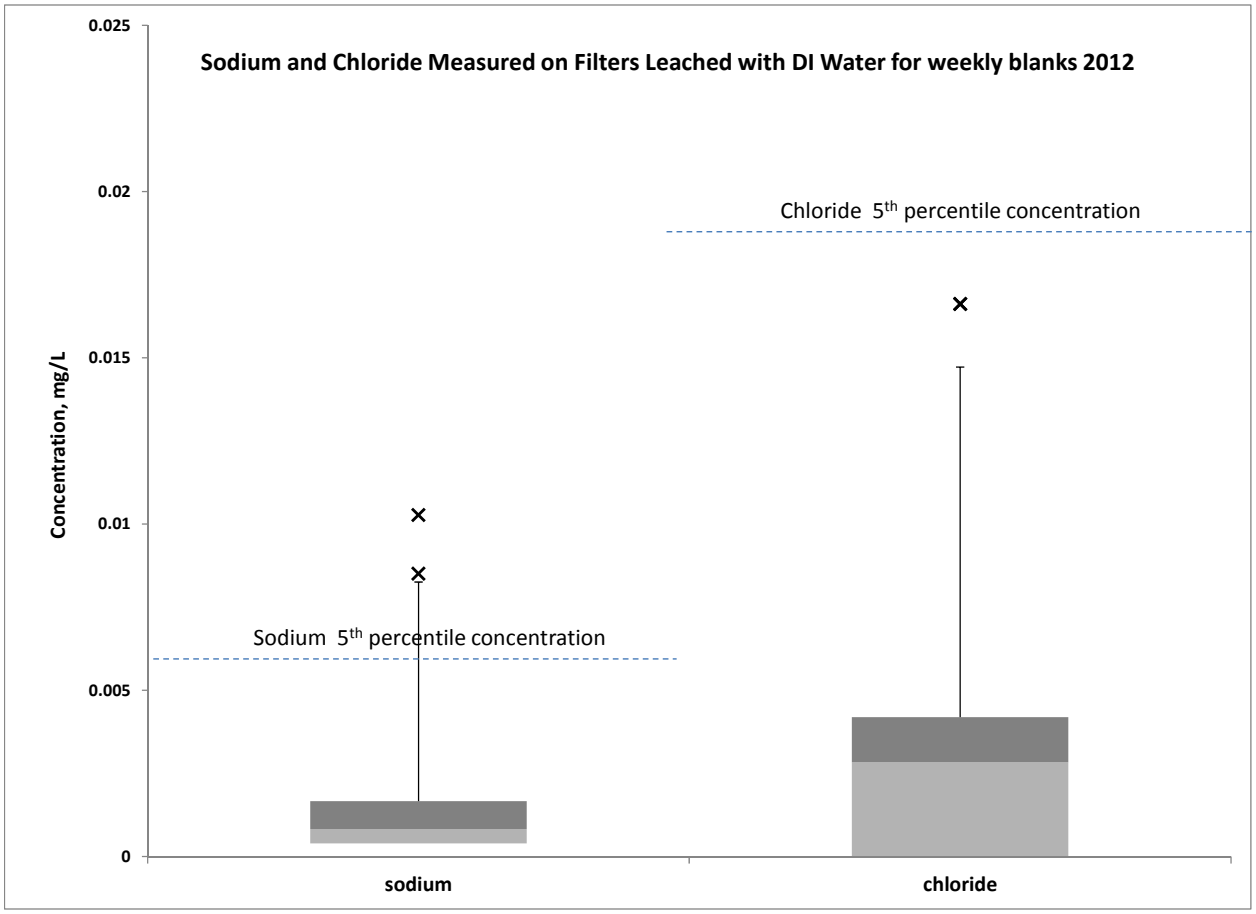

Figure 1. Box and whisker plot of sodium and chloride measured in DI used to leach filters for weekly blanks in 2012. The 5th percentile concentration for NTN samples from 2008 – 2012 is shown for comparison.

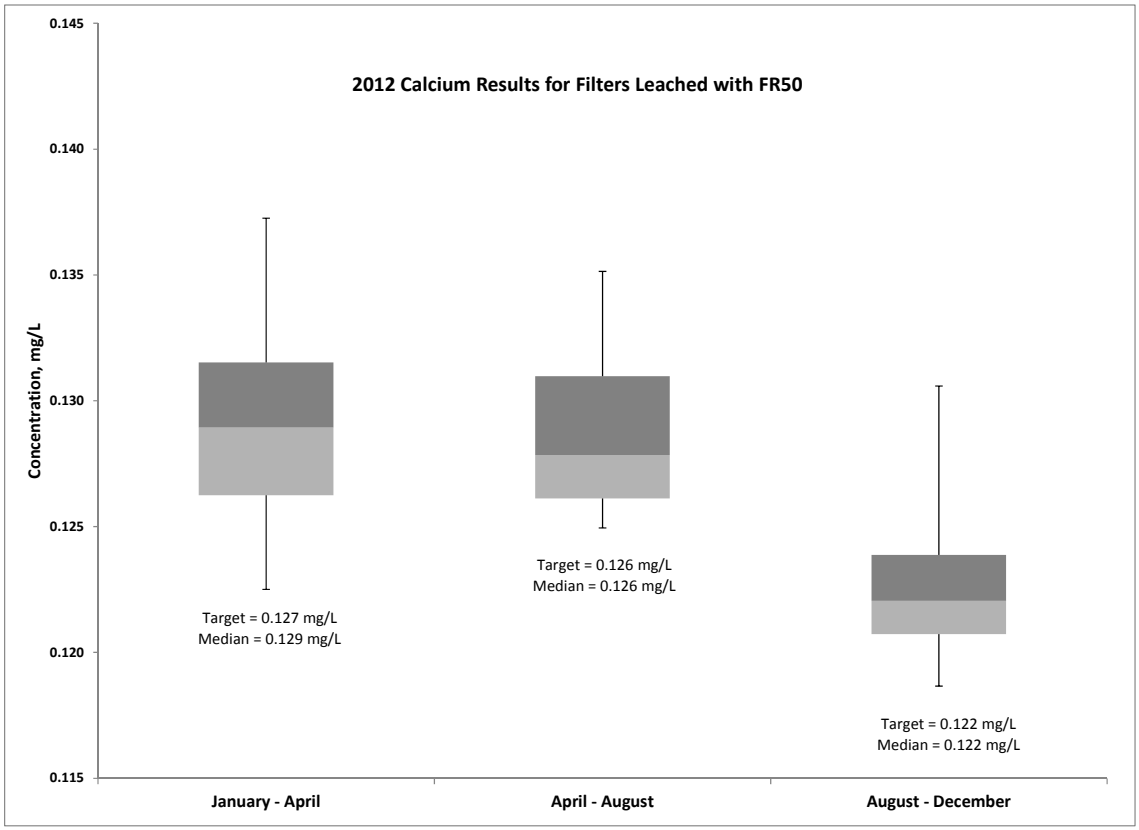

Figure 2. Box and whisker plot of calcium measured in FR50 used to leach filters for weekly blanks in 2012

Supply Checks: Buckets, Bottles, and Lids

The same buckets are used for both NTN and AIRMoN sample collection. Buckets are tested by storing 150 mL of FR50 solution in them. The duration of solution contact with the supply was modified in 2012. Through June 2012, the FR50 solution was allowed to remain in contact with the supply for one full week. This mimics the maximum contact with precipitation that may occur in the field. It is likely that contamination will dissolve readily in the test solution if it is present. To test this theory, the 24-hour exposed blank results (211 buckets) were compared to week-long results (66 buckets). The data were found to be comparable. Starting in June 2012, the procedure was modified from 1 week to 24 hours; one bucket was selected from the buckets washed each day and tested for a period of 24 hours using the FR50 solution.

Results outside of target limits for 150 mL FR50 samples stored in buckets for 24 hours and 1 week during 2012 are shown in Table 9. The outliers for Ca^{2+}, Cl^{-}, and NH_4^{+} occurred in the buckets tested for 24 hours. Three buckets were rewashed and tested, and each was found to be within control limits. The two buckets with NH_4^{+} below the control limits were discarded. The outliers for pH, specific conductance, NO_3^{-}, and NH_4^{+} occurred in the buckets tested for 1 week. Those buckets were rewashed and retested. Six of them passed the second check. Four buckets with NH_4^{+} out of the control limits were discarded.

When analyte concentrations exceed target levels for supplies that are washed and reused (e.g., sample collection buckets, lids, and NTN 1-L sample bottles), the supply is rewashed and rechecked. If the supply does not pass the second check, it is discarded. Supplies are also discarded in cases in which NH_4^{+} concentrations are below the control limits.

Table 9. Number of results outside of target limits in 2012 for sampler buckets in contact with 150 mL FR50 solution

Parameter	FR50 24 Hours N=211	FR50 1 Week N=66
pH	0	1
Specific Conductance	0	1
Calcium	1	0
Potassium	0	0
Magnesium	0	0
Sodium	0	0
Chloride	1	0
Sulfate	0	0
Nitrate	0	2
Ammonium	2	6
Bromide	0*	NA
Orthophosphate	NA	NA

*N = 95

Calcium is used during bucket manufacturing for plastic extrusion and as a filler. Ca^{2+} has been detected in new buckets, and as a result, new buckets are leached with nitric acid to remove Ca^{2+}. The levels detected routinely are low and are within the allowable control limits. Outliers for calcium were not detected in 2012. Results for 2012 are shown in Figure 3.

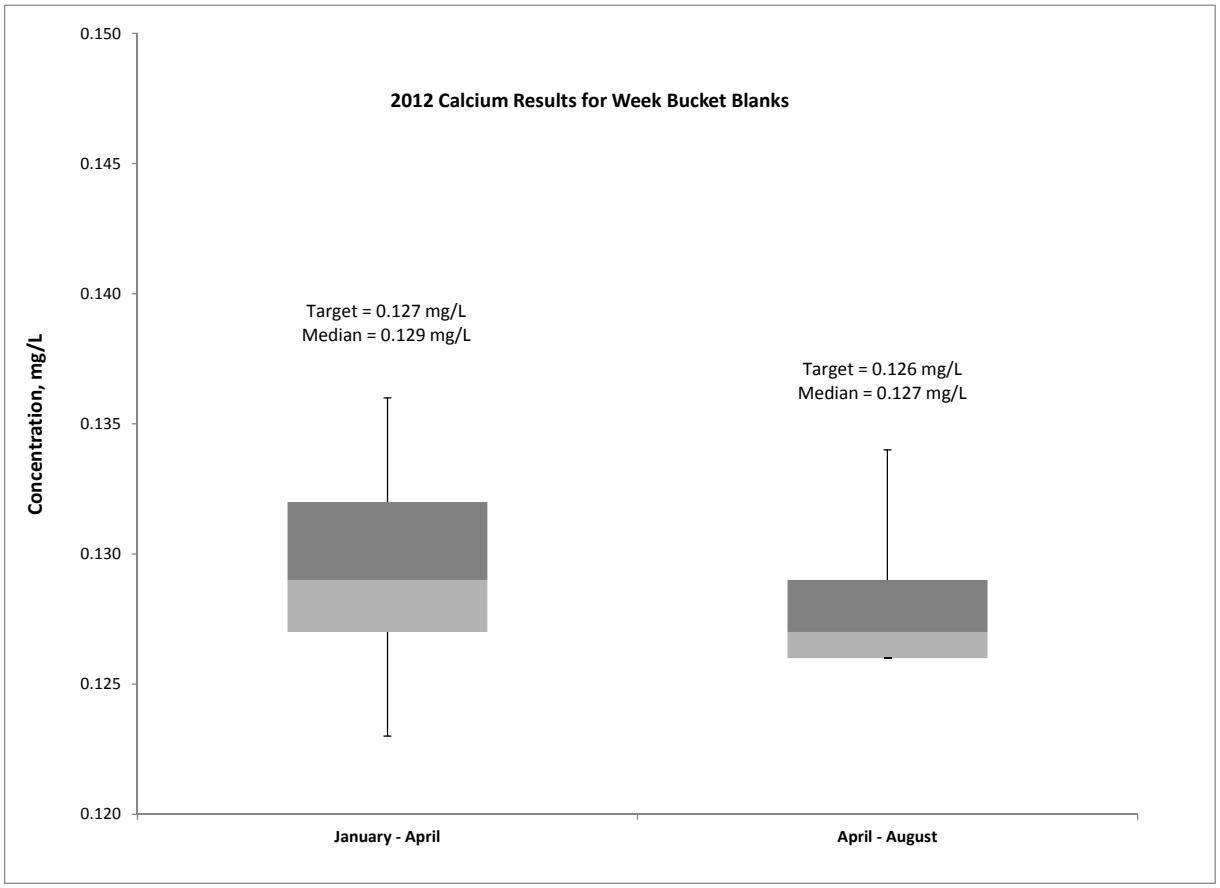

Figure 3. Box and whisker plot showing calcium concentrations for sampler buckets in contact with FR50 solution for a one-week duration in 2012

NH_4^+ exceeded control limits 10 times throughout the year in FR50 bucket blank tests. Figure 4 shows NH_4^+ results measured in both 24-hour and weekly blanks. The variability in NH_4^+ results may be due to a number of factors, including absorption of NH_3 from the ambient air, an excess of rinse water in supplies, or losses due to biological processes.

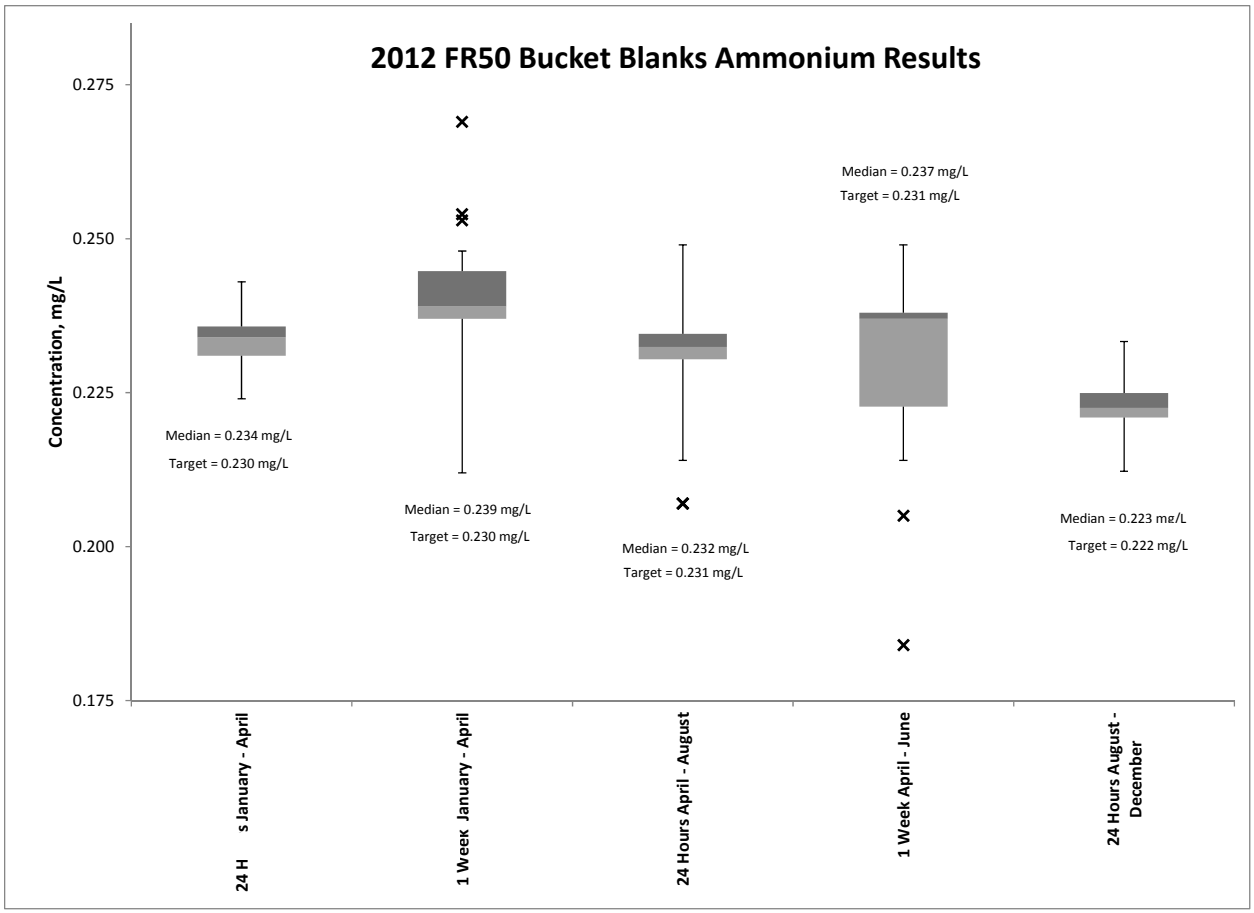

Figure 4. Box and whisker plot showing ammonium concentrations for sampler buckets in contact with FR50 solution for 24 hour and one-week durations in 2012

The 1-L sample bottles are washed and reused. The number of NTN 1-L sample bottle blank results outside of control limits during 2012 is shown in Table 10. Figure 5 compares the FR50 blank data for both 24-hour and week-long samples. There appears to be a consistent negative bias in NH_4^+values. This could be due to a biological process. However the bias is less than the MDL for NH_4^+.

Table 10. Number of results outside of target limits in 2012 for NTN 1-L sample bottle blanks tested with FR50 solution

Parameter	FR50 24 Hours N=142	FR50 1 Week N=66
pH	0	0
Specific Conductance	0	0
Calcium	0	0
Potassium	0	0
Magnesium	0	0
Sodium	0	0
Chloride	0	0
Sulfate	0	0
Nitrate	0	0
Ammonium	5	6
Bromide	0*	NA
Orthophosphate	NA	NA

* N = 51

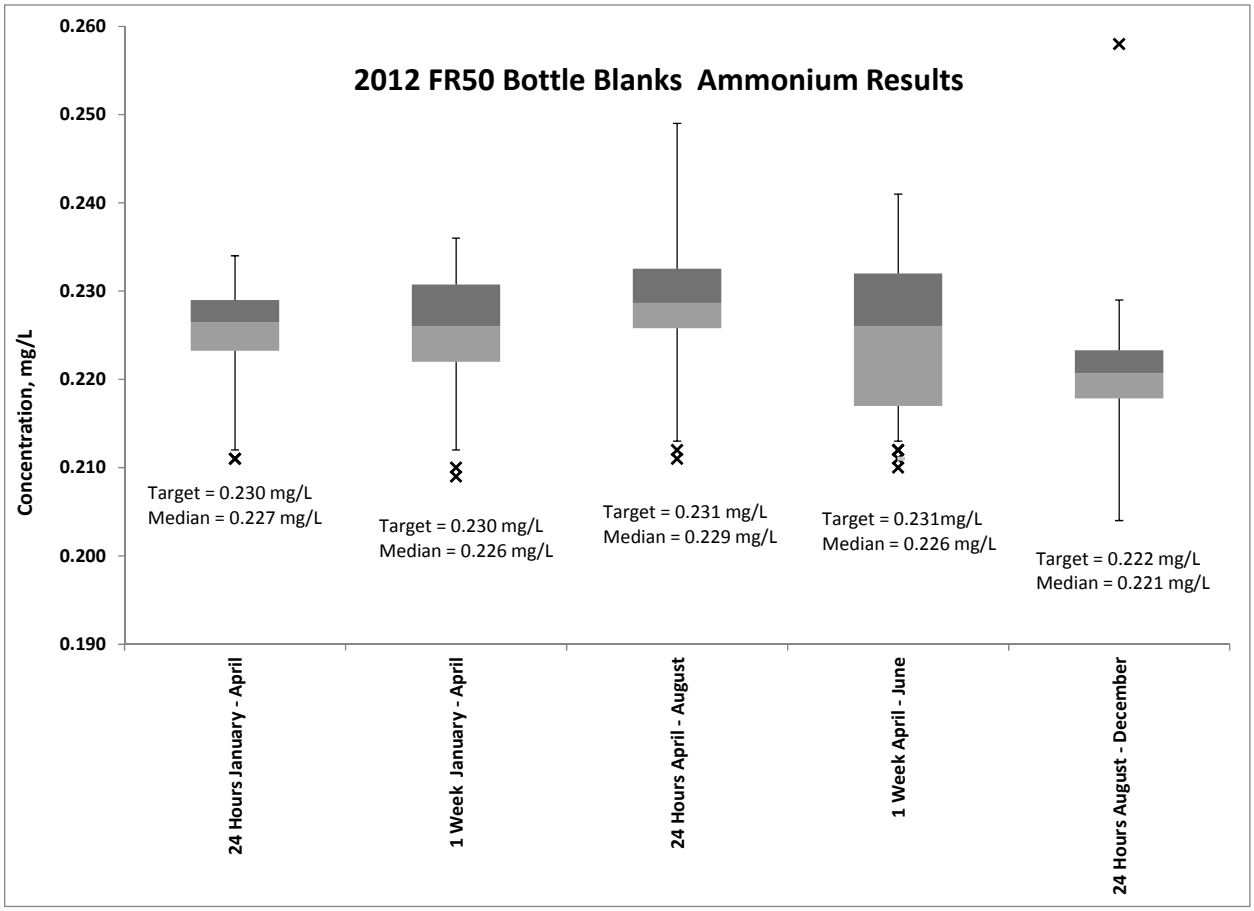

Figure 5. Box and whisker plot of ammonium concentrations measured in NTN 1-L sample bottle blanks tested with FR50 solution in 2012

Lid blanks tested with FR50 in 2012 indicated Na^+ and Cl^- bias (Table 11). Na^+ was also detected in lid bag blanks, indicating that the bags are the likely origin of sodium found on lids.

Sodium in lid bags was also reported in 2010 - 2011. Alternate bags were investigated, but they showed higher levels of contamination than bags currently used. The 2012 median was slightly above the target concentration for sodium in January – April, but decreased in May – December (Figure 6). The elevated Na^+ concentration varies between individual packages.

Chloride bias was low (< MDL) for the same supplies.

Table 11. Number of results outside of target limits for sample bucket lids tested with FR50 solution in 2012

Parameter	FR50 N=183
pH	0
Specific Conductance	0
Calcium	0
Potassium	0
Magnesium	0
Sodium	2
Chloride	2
Sulfate	0
Nitrate	0
Ammonium	0
Bromide	0*
Orthophosphate	NA

*N=95

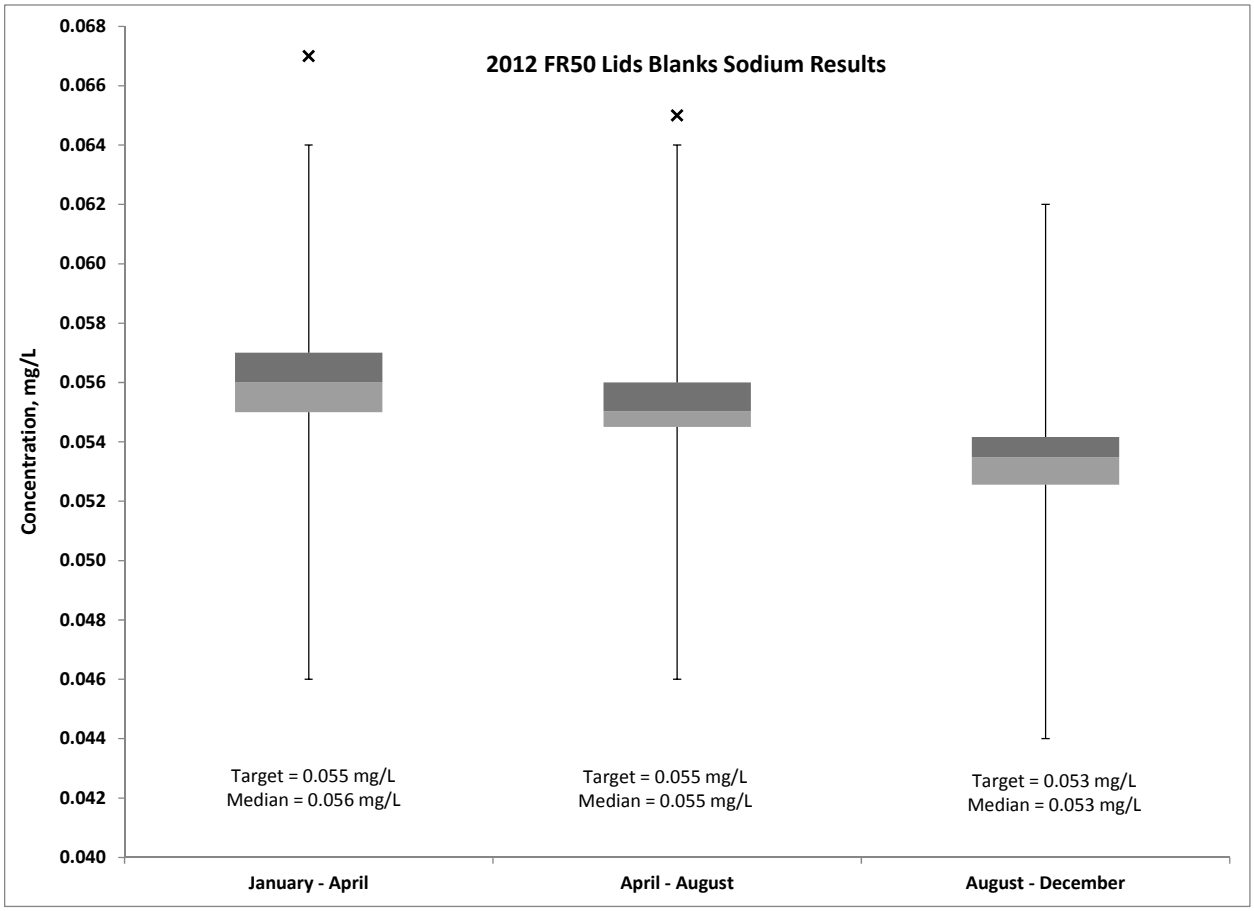

Figure 6. Box and whisker plot showing sodium measured in lid blanks tested with FR50 solution in 2012

The median concentration of NH_4^+ in lid blanks tested with DI water (Figure 7) is slightly higher than the lids tested with FR50 solution (Figure 8). It is speculated that ambient concentrations of NH_3 in the laboratory air are the cause of the elevated concentrations in the DI water.

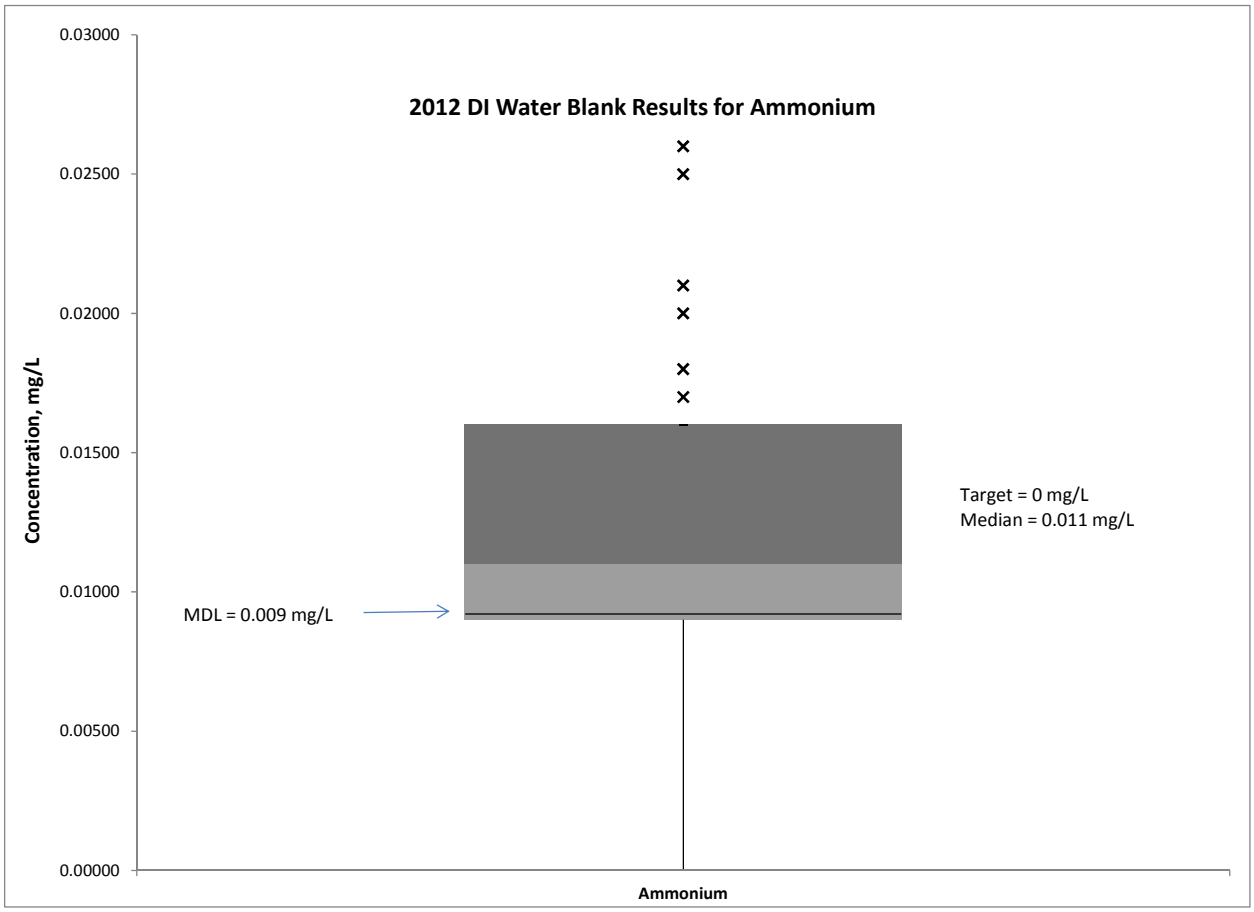

Figure 7. Box and whisker plot showing ammonium measured in lid blanks tested with DI water in January – June 2012. The MDL is indicated for comparison

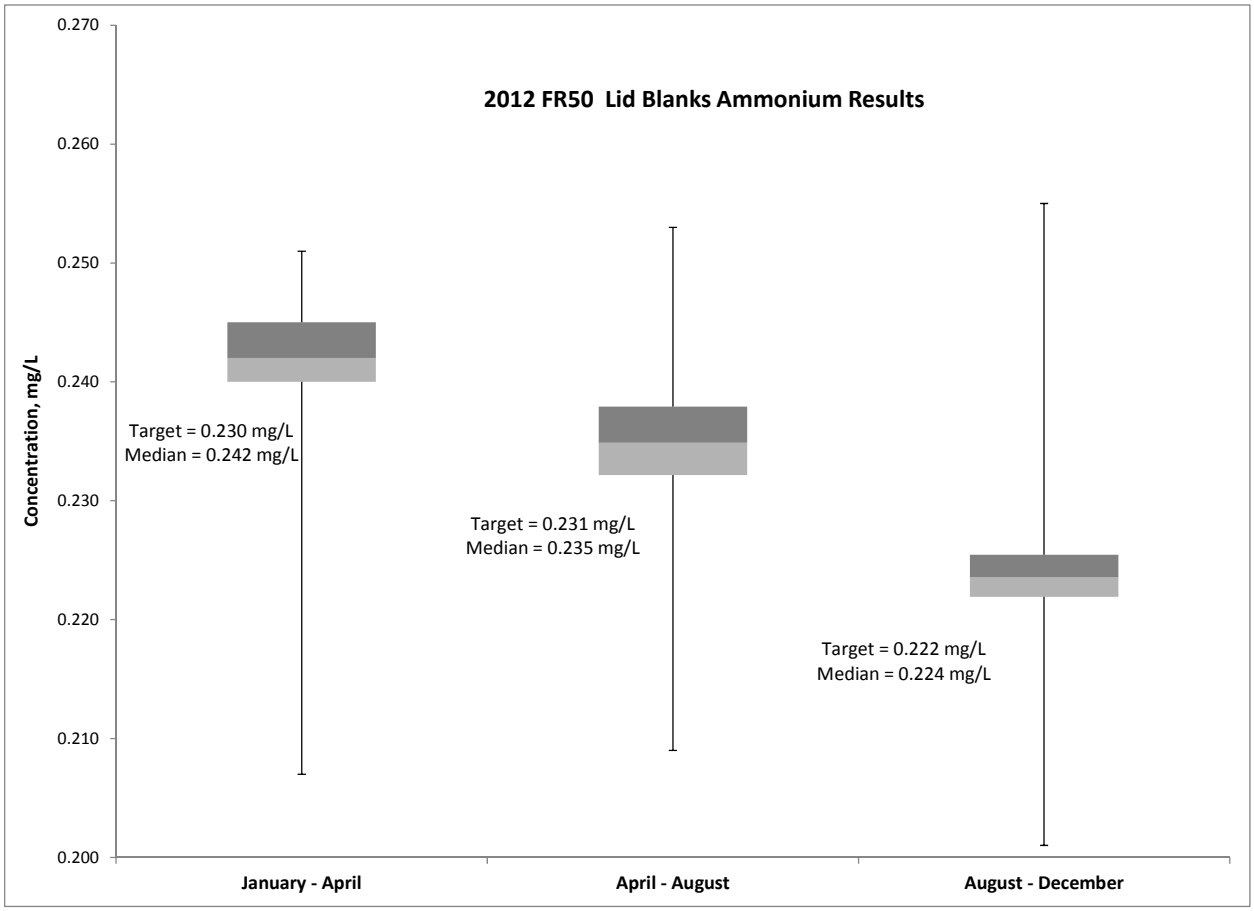

Figure 8. Box and whisker plot showing ammonium measured in lid blanks tested with FR50 solution in 2012

AIRMoN bottles are single-use 250-mL Nalgene bottles that are not rewashed or reused. AIRMoN bottle-blank analyses were within the acceptable limits for all analytes throughout 2012 and there were no outliers.

Lid Bags

Lid bags are acceptance tested whenever a new shipment of bags is received. If a bag fails the acceptance test, one to two additional bags from the lot are tested. If analytes (especially Na^+) exceed target limits, the lid bags are evaluated by placing clean lids into the bags. The lids remain in

contact with the bags for at least 24 hours. If the lid blank results do not exceed limits, the bags are used; if they fail, the bags are rejected.

Lid bags from a different manufacturer were evaluated. These bags were found to contain even higher levels of Na^+ and were rejected from further consideration.

Bucket Bags

New bucket bags are tested whenever a new shipment of bags is received. All bucket bag results were within the acceptable target limits for all analytes throughout 2012.

Quality Assurance Discussion

Internal Blind Results

Results for internal blind samples were used to assess post-analysis accuracy and precision of the laboratory throughout the year. The IDLs and MDLs were calculated using analytical results for DI water and MDL solutions. These samples were blind to the analysts. The relative standard deviation (RSD) and percent recovery were calculated to evaluate precision and accuracy for FR50 and AES-05 solutions.

IDL and MDL Results

The MDL study continued during 2012. Analyses of filtered blind samples were used to calculate MDLs for NTN for 2013. Analyses of unfiltered samples were used to calculate MDLs for AIRMoN. DI water samples were used to calculate IDLs. Results from the 2012 MDL and IDL studies are shown in Table 12.

Table 12. 2013 MDLs and IDLs

Ion	MDL for 2013		IDL for 2013 NTN & AIRMoN (mg/L)
	NTN (mg/L)	AIRMoN (mg/L)	
Calcium	0.027	0.004	0.0005
Potassium	0.001	0.001	0.0005
Magnesium	0.009	0.001	0.0006
Sodium	0.002	0.001	0.0004
Chloride	0.003	0.009	0.0004
Nitrate	0.025	0.007	0.0004
Sulfate	0.005	0.015	0.0004
Ammonium	0.016	0.009	0.006
Orthophosphate	0.013	0.005	0.004
Bromide	0.005	0.010	0.0004

AES-05 and FR50 Solution Results

The recovery and relative standard deviation (RSD) of AES-05 and FR50 met acceptance criteria in 2012. The results are presented in Tables 13 and 14. To evaluate the effect of sample wet dilution (WD) procedures in the NTN, FR50 and AES-05 were submitted to the laboratory following NTN protocols. The results of this study were reported at the 2013 NADP Annual Meeting.

Table 13. Relative Standard Deviations (RSDs) and percent recoveries for internal blind AES-05 solution

Parameter	Target	RSD Unfiltered N = 8 (%)	RSD Filtered N = 8 (%)	Recovery Unfiltered N = 8 (%)	Recovery Filtered N = 8 (%)
pH	4.90	0.9	NA	99.1	NA
Specific Conductance	10.8 µS/cm	3.1	NA	107.9	NA
Calcium	0.187 mg/L	2.1	4.5	109.6	111.4
Potassium	0.037 mg/L	3.0	6.1	97.7	88.6
Magnesium	0.181 mg/L	1.5	3.0	106.4	95.0
Sodium	0.028 mg/L	1.6	4.3	100.6	94.6
Chloride	0.225 mg/L	1.8	5.3	105.0	97.6
Sulfate	1.28 mg/L	1.4	3.2	100.6	93.7
Nitrate	1.15 mg/L	1.5	3.7	101.8	94.8
Ammonium	0.312 mg/L	2.2	11.5	98.5	98.2

Table 14. Relative Standard Deviations (RSDs) and percent recoveries for internal blind FR50 solution

Parameter	Target	RSD Unfiltered N = 24 (%)	RSD Filtered N = 11 (%)	Recovery Unfiltered N = 24 (%)	Recovery Filtered N = 11 (%)
pH	4.80	0.4	NA	99.3	NA
Specific Conductance	10.6 µS/cm	1.8	NA	102.3	NA
Calcium	0.123 mg/L	2.1	6.3	99.7	103.6
Potassium	0.023 mg/L	3.4	8.8	98.7	89.4
Magnesium	0.049 mg/L	2.1	13.1	98.4	82.8
Sodium	0.021 mg/L	2.3	6.7	101.1	98.6
Chloride	0.098 mg/L	4.8	7.5	102.3	92.2
Sulfate	0.828 mg/L	1.3	4.6	99.4	90.8
Nitrate	0.958 mg/L	1.6	4.7	99.6	91.8
Ammonium	0.227 mg/L	1.8	9.5	102.0	98.3
Bromide	0.020 mg/L	17.7	25.0	111.3	120.7

Reanalysis, Split, and Replicate Samples

The number of samples analyzed in the NTN and AIRMoN, including counts of reanalysis, split, blind, and control chart samples, is shown in Table 15. The flow of data from the CAL to the NADP Program Office is shown in Figure 9. Chemistry results are reviewed by the analysts on a weekly basis for data completeness before they are released to the data manager. The data manager calculates the Ion Percent Difference (IPD) and Conductivity Percent Difference (CPD) to identify samples for reanalysis, following SOP DA-0067.1. An additional 2 percent of samples are selected at random for reanalysis. The results are reviewed by the QA Chemist and required edits are made. A total of 132 edits were made for NTN samples and 17 edits were made for AIRMoN samples.

The CAL processed 153 pairs of split samples for NTN and AIRMoN in 2012. The median percent difference was less than 1 percent for each analyte.

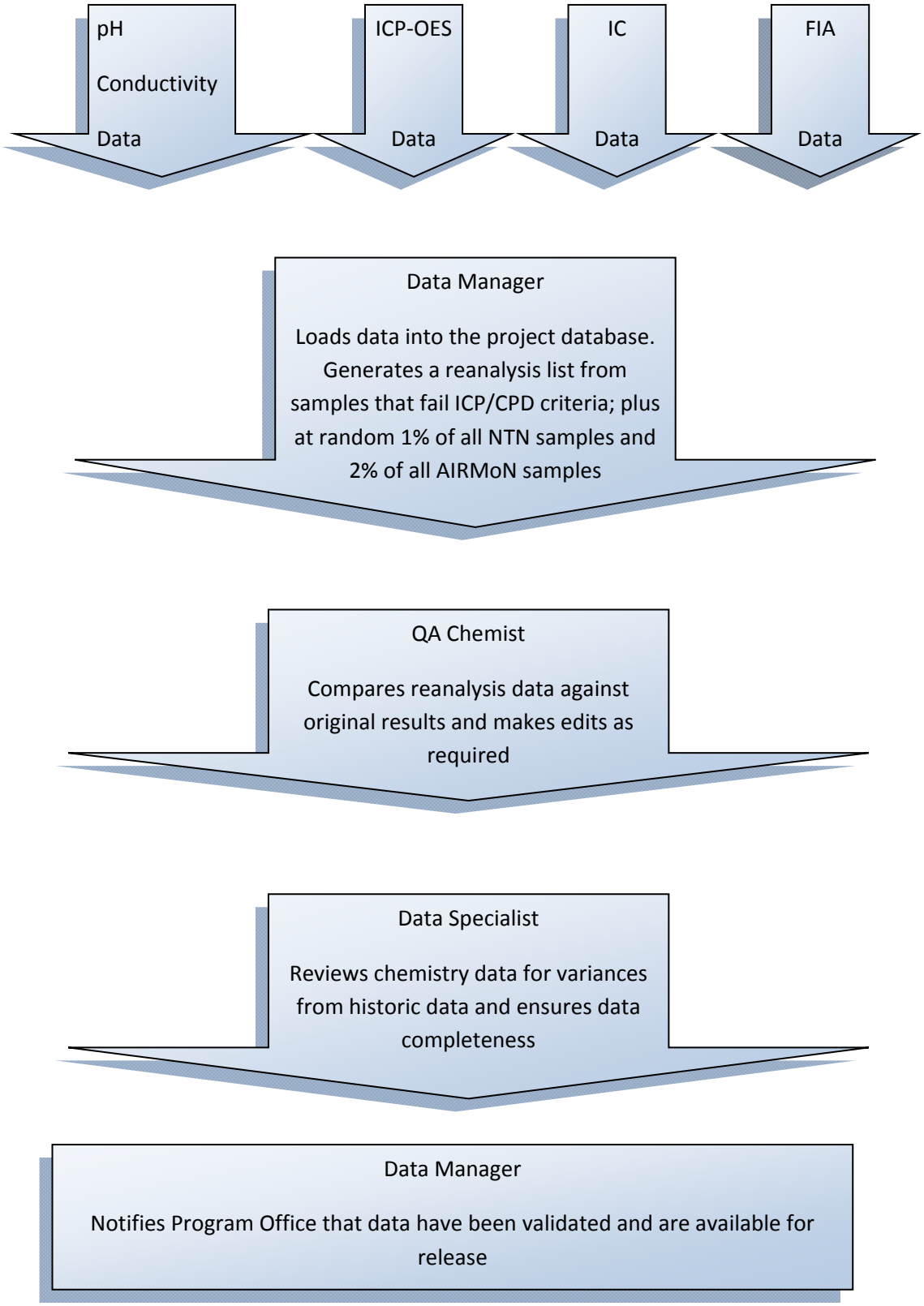

Figure 9. Flow of data from the CAL to the Program Office

Table 15. Number of real and Quality Control (QC) samples analyzed during 2012

Network	Number of Real Samples Analyzed	Number of QC Samples			Number of Control Chart Checks (percentage of samples analyzed)
		Reanalysis Samples	Split Samples	Blind Samples	
NTN	10155	1396	133	82	pH/conductivity = 5696 (34%) ICP/OES = 3917 (26%) FIA = 5957 (35%) IC = 5125 (31%)
AIRMoN	1022	185	20	30	

CAL met requirements for analytical precision for all analytes in 2012. For replicates, the allowable bias for analytes with concentrations at 10 to 100 times the MDL is ± 20 percent (Table 16). The allowable bias for analytes with concentrations at ≥ 100 times the MDL is ± 10 percent (Table 17). There is no practical MDL for pH; hence the results for all of the pH replicates are also shown in Table 16. If samples fall outside the allowable bias for the Relative Percent Difference (RPD), analysts investigate the cause and analyze additional samples within the run.

Table 16. Replicate samples, concentrations 10 to 100 times the MDL (max allowable bias 20%)

Parameter	Concentration Range: 10 to 100 x MDL	n	Average RPD %	Maximum RPD %	Minimum RPD %
pH	NA	301	1.3	5.5	0
Specific Conductance	>3 µS/cm	266	4.2	11.6	0
Calcium	0.050 – 0.500 mg/L	119	2.5	10.0	0
Potassium	0.030 – 0.300 mg/L	95	3.5	12.4	0.2
Magnesium	0.020 – 0.200 mg/L	126	2.4	8.3	0.1
Sodium	0.020 – 0.200 mg/L	99	2.6	3.9	0.2
Chloride	0.090 – 0.900 mg/L	148	1.0	4.7	0
Sulfate	0.100 – 1.000 mg/L	190	1.0	4.8	0
Nitrate	0.100 – 1.000 mg/L	158	1.0	2.3	0
Ammonium	0.090 – 0.900 mg/L	124	1.5	3.0	0.1

Table 17. Replicate samples, concentrations greater than 100 times the MDL (max allowable bias 10%)

Parameter	Concentration Range: > 100 x MDL	n	Average RPD %	Maximum RPD %	Minimum RPD %
Specific Conductance	> 15 µS/cm	73	2.6	6.1	0.1
Calcium	> 0.500 mg/L	32	2.4	4.5	0.1
Potassium	> 0.300 mg/L	5	3.1	3.3	0.8
Magnesium	> 0.200 mg/L	13	1.8	2.2	0.2
Sodium	> 0.200 mg/L	50	2.3	3.3	0.2
Chloride	> 0.900 mg/L	23	1.3	3.7	0.1
Sulfate	> 1.000 mg/L	107	0.7	4.4	0
Nitrate	> 1.000 mg/L	142	0.7	4.8	0
Ammonium	> 0.900 mg/L	26	0.8	1.2	0.1

AMoN

Passive-type air samples for the AMoN network are stored in a freezer (-17.5 °C) upon receipt at the CAL. Samples are extracted and analyzed in batches once a week. During the extraction process, four additional QC samples are generated to evaluate the background levels. These samples include:

- Lab DI Blank (water used for extractions, 1 per extraction batch)
- Hood Blank (passive air sampler device with core located in the hood throughout the extraction period, 1 per extraction batch)
- New Core Blank (unused cartridge as received from supplier, 2 per extraction batch).

The results of the sampler blanks for 2012 are shown in Figure 10. The AMoN's blank acceptance limit is 0.200 mg/L of NH_4^+ in the 10-mL sampler extract. All DI water, new core blanks, and hood blanks were below the acceptable limits. Numerous travel blanks (8.4%) sent with deployed samples to field sites exceeded the limits throughout the year (Figure 10).

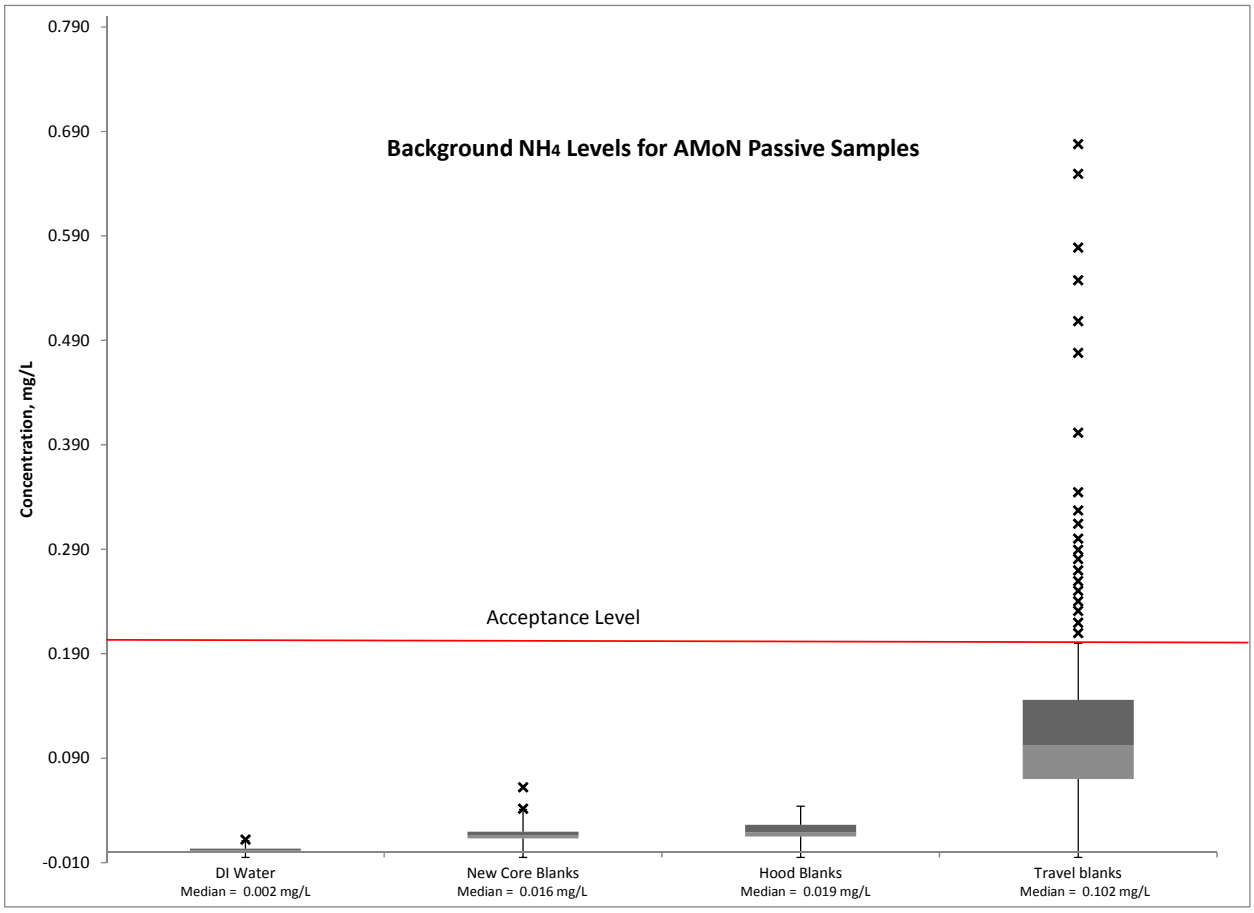

Figure 10. Box and whisker plot for ammonium ion concentrations in AMoN laboratory DI water blanks, new core blanks, hood blanks and deployed travel blanks in sampler extracts in 2012

The reason for the numerous travel blank exceedances continues to be investigated. In 2012 efforts focused on alternate methods for cleaning the passive sampler bodies. As of the end of 2012, these changes did not reduce the background levels detected in travel blanks (Figure 11), and thus the investigation of alternate cleaning methods will continue.

A timeline of cleaning procedures tested in 2012 is as follow:

- **January 2012** – Passive sampler bodies where cleaned by sonication in DI water, dried overnight in an incubator oven at 40°C, and placed in a vacuum desiccator.
- **May 2012** – Modified sampler body cleaning procedures to include an overnight soak in the sonicator. Sampler bodies were no longer placed in the oven and the desiccator; instead they were dried in the clean air bench covered with a laboratory wipe.
- **June 2012** – Passive samplers were assembled by placing the cores into the sample bodies using a polyethylene gloved hand, instead of inverting them into test tubes.
- **July 2012** – Modified sampler body cleaning procedures by adding laboratory detergent with KOH (DECON 90) to the sonication bath with heating to 60 °C and during the overnight soak.
- **November 2012** – The final sonication rinse of sampler bodies was analyzed for NH_4^+ and PO_4^{3-}, and additional cleanings were added as necessary.

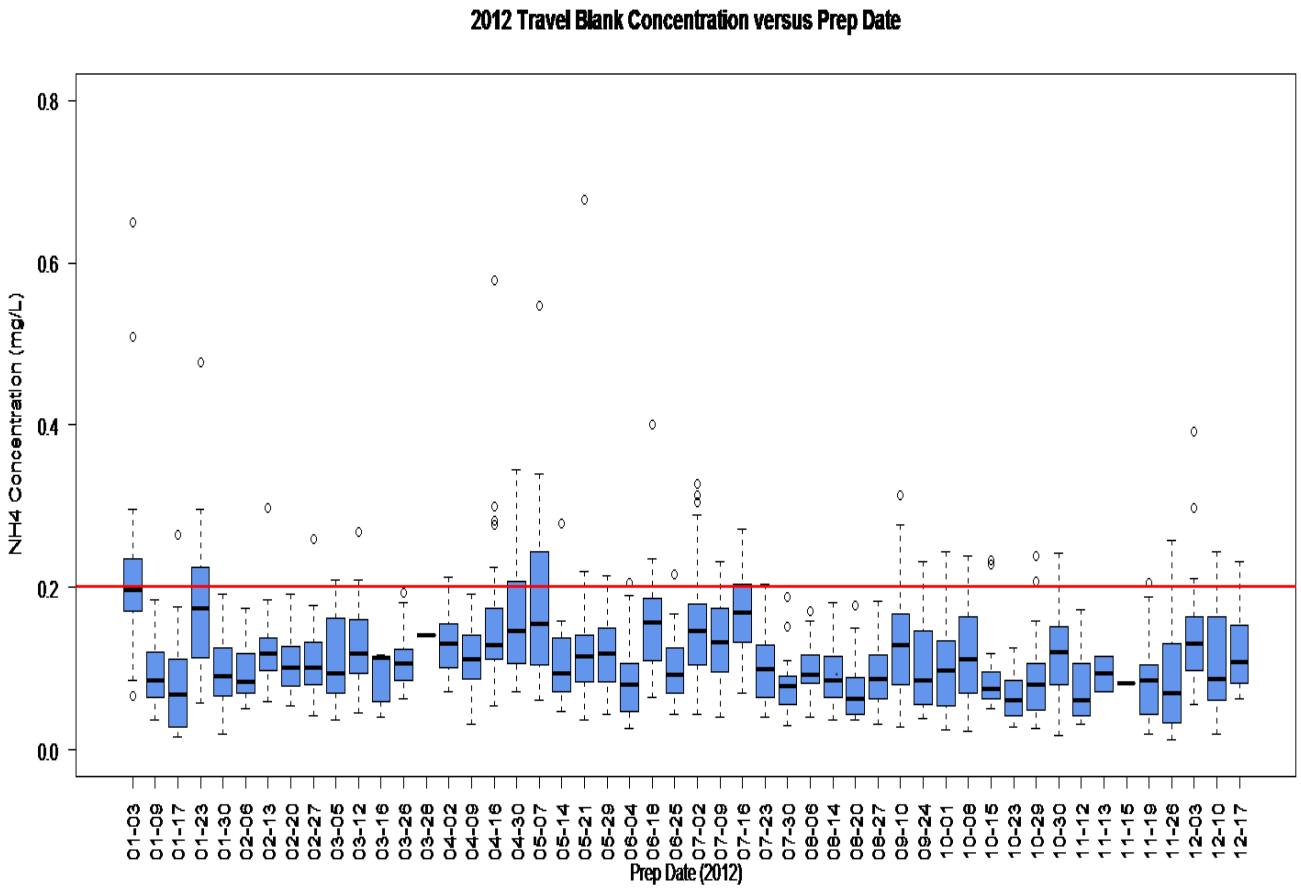

Figure 11. Box and whisker plot for ammonium ion concentrations in 10 mL extracts of AMoN passive sampler travel blanks, grouped by preparation date

The RPD of AMoN triplicate results improved in 2012 as compared to 2009 –2011. The RPDs were calculated as the range of valid measurements by the three deployed samplers divided by the average of the triplicate results. The average and median RPDs are shown in Table 18.

Table 18. Average and median RPDs for triplicate AMoN samples

Year	Median RPD (%)	Average RPD (%)	Count
2009	12.3	17.1	400
2010	10.6	19.7	464
2011	19.1	37.5	96
2012	4.3	10.5	87

External Quality Assurance

The CAL participated in four external proficiency testing studies throughout 2012. The study identifier and websites with study details and results are shown in Table 19. The CAL's performance was consistent with that of other top-performing laboratories participating in each of the studies.

Table 19. Interlaboratory comparison studies

Study Identifier	Managing Agency	Details and Results
Interlaboratory Comparison Program	U.S. Geological Survey	http://bqs.usgs.gov/precip/interlab_overview.php
Study 46 and 47	World Meteorological Organization/Global Atmospheric Watch (WMO/GAW)	http://www.qasac-americas.org/
Study 100 and 101	Environment Canada Proficiency Testing Program	Available upon request
Study 30	Norwegian Institute for Air Research (NILU)	Available upon request

Conclusions

The CAL performed consistently throughout 2012 and met the guidelines as specified in the NADP Network Quality Assurance Plan (QAP).

References

Central Analytical Laboratory SOPs can be found at
http://nadp.isws.illinois.edu/cal/summary_of_procedures.html

National Atmospheric Deposition Program/Central Analytical Laboratory Quality Assurance Plan, Version 6.0 July 2011. http://nadp.sws.uiuc.edu/lib/qaplans/qapCal2011.pdf

NADP Network Quality Assurance Plan 2011-05
http://nadp.isws.illinois.edu/lib/qaplans/NADP_Network_Quality_Assurance_Plan.pdf

Title 40 Code of Federal Regulations Part 136. Vol. 49 No 209, "Federal Register," Rules and Regulations, Appendix B, pp. 198-199, October, 1984, revised Nov 13, 2009.

Evaluation of Methods for Measuring Particulate Carbon in Precipitation. Alexander Torres, Tami Bond & Christopher Lehmann. Presented at the 2011 Annual Meeting and Scientific Symposium of the National Atmospheric Deposition Program, October 25-28, 2011, Providence, RI.

Measurement of Total Phosphorus in AIRMoN Samples by the NADP/CAL. Lee Green & Christopher Lehmann. Presented at the 2011 Annual Meeting and Scientific Symposium of the National Atmospheric Deposition Program, October 25-28, 2011, Providence, RI.