Quality Assurance Report
National Atmospheric Deposition Program
2013

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 (UIUC), has analyzed and processed data on wet deposition samples for the National Atmospheric Deposition Program (NADP) since 1978. The CAL is within the Illinois State Water Survey of the Prairie Research Institute at UIUC. 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). The other two NADP networks with samples not analyzed at CAL include the Mercury Deposition Network (MDN) and the Atmospheric Mercury Network (AMNet). More information on the NADP is available at http://nadp.isws.illinois.edu.

Wet deposition samples, collected as part of the NTN and AIRMoN , 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 2 (2013) and Table 3 (2014).

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 2013

- Tracy Dombek left the position of Quality Assurance Chemist in January 2013;
- Kim Attig left the position of Assistant Chemist (ICP) in January 2013:
- Angela Weddle was approved to work on FIA (as a backup) in January 2013;
- Brian Kerschner started working as an Assistant Data Manager in March 2013;
- Brenda Riney was approved to work on ICP (as a backup) in April 2013;
- Nina Gartman started working as a Quality Assurance Lab Project Specialist in May 2013;
- Lee Green started working as an Analytical Lab Supervisor in May 2013;
- Katie Blades started working as an Assistant Chemist (ICP) in June 2013;
- Annette Wells started working as an Assistant Chemist (FIA) in June 2013;
- Sybil Anderson was hired as the Special Projects Coordinator in June 2013;
- Marcelo Vieira joined CAL as a visiting scholar in September 2013 working on ammonia flux studies in collaboration with the Department of Civil & Environmental Engineering at UIUC.
- Gustava Hoskinks started working as a Technical Assistant (pH/conductivity and filtering) in September 2013;
- Britta Langsjoen started working as a Technical Assistant (supplies preparation lab) in October 2013;
- Research was completed to assess the uncertainty that is introduced as a result of sample dilution, using NTN samples (in 2012 the same research was conducted using QC samples).
- Research continued to minimize NH_3 background during the processing AMoN passive Radiello samplers. In 2013 efforts focused on checking containers used for transportation of samplers to sites and back to the CAL.

Quality Assurance/Quality Control

Objectives

Quality Assurance (QA)/Quality Control (QC) within the CAL is an "all-hands" effort. This is a multitiered program that includes bench-level QC, laboratory management-level QA and participation in external QA monitoring efforts. 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.

CAL Quality Control activities are defined as those processes which continually verify the quality of data during analytical runs. This includes daily analytical verification (measuring quality control standards, split and replicate samples during the analytical run) and control chart monitoring.

CAL Quality Assurance activities are defined as those processes which ensure data quality after analysis. This includes weekly blank checks; supply checks; internal and external blind sample checks; reanalysis checks; special studies designated to improve quality; and participation in external Quality Assurance Programs.

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 split, replicate and reanalysis samples. A maximum difference between replicate, split and reanalysis samples shall not exceed ±10% if the value is ≥ 100 times the MDL, and ± 20% if the value is between 10 and 100 times MDL. When the differences are out of control, corrective actions are determined by the analysts (with the help of QA Chemist and the CAL Director as needed). For example, if a split or replicate sample is out of control, a second sample may be measured immediately following the out-of control sample to confirm or negate that the instrument was out of control. If this second sample is also out of control, the instrument is stopped and restandardized, and all affected samples must be reanalyzed. If the reanalysis sample is out of control, the analyst analyzes the archive bottle of the sample and sends comments to the QA Chemist explaining why the reanalysis value is out of control (e.g., chemistry changed, a technical mistake took place when running the original sample, etc.) with recommendations to edit the original value. Control charts are used to evaluate long-term instrument precision and any drifts in the data.

- **Accuracy** is a measure of correctness. It shows how closely the data represent the true value. Accuracy is evaluated through the use of blind (i.e., samples not readily identifiable to the analysts) samples and through 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, the use of reanalysis samples, internal blind data and external laboratory comparison studies.

Summary of QA/QC procedure

Instrument Detection Limit. Blank samples without analytes (e.g., DI water samples) are analyzed to evaluate false positive result for each instrument. The results are used to calculate the *Instrument Detection Limit* (**IDL**).

Method Detection Limit (MDL) is 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 low concentration standards (Cation MDL and Anion MDL standards), that are approximately three to five times the projected MDL for each analyte, are used to determine MDLs for Na^+, Ca^{2+}, Mg^{2+}, K^+, NH_4^+, NO_3^-, Cl^-, SO_4^{2-}, Br^- and PO_4^{3-}. Conductivity and pH do not have defined MDLs; instead, those values are 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 MDLs for the upcoming year. Thus, solutions measured during 2012 are used to calculate MDLs for 2013. The calculated MDLs are provided to the NADP Program Office for data released to the public.

In 2012 methods for calculating the MDLs were based on results of analysis of blind low concentration samples which passed through all steps of processing NTN and AIRMoN samples. As such, the MDLs for NTN and AIRMoN for 2013 were reported separately. Also the IDL values for 2013, based on the results of analysis of DI samples through 2012, are reported (Table 2).

Table 2. IDLs and NTN/AIRMoN MDLs for 2013

Ion	IDL (mg/L)	NTN MDLs* (mg/L)	AIRMoN MDL** (mg/L)
Calcium	**0.0005**	**0.027**	**0.004**
Potassium	**0.0005**	**0.001**	**0.001**
Magnesium	**0.0006**	**0.009**	**0.001**
Sodium	**0.0004**	**0.002**	**0.001**
Chloride	**0.0004**	**0.003**	**0.009**
Nitrate	**0.0004**	**0.025**	**0.007**
Sulfate	**0.0004**	**0.005**	**0.015**
Bromide	**0.0004**	**0.005**	**0.010**
Ammonium	**0.006**	**0.016**	**0.009**
Orthophosphate	**0.004**	**0.0013**	**0.005**

*for NTN sample range TK8784SW – TM2704SW **for AIRMoN sample range AC7604L – AC8683L

The MDL study continued in 2013. A number of blind low concentration MDL standards were analyzed during the year. Half of them passed through all steps of processing NTN and AIRMoN samples before the analysis, the other half did not. DI water blind samples were also analyzed. The results were used to calculate IDLs and MDLs (laboratory MDL, NTN and AIRMoN MDLs) for 2014 (Table 3).

A method to determine MDLs for AMoN is in development.

Table 3. 2014 MDLs and IDLs

Ion	IDL for 2014 mg/L	Laboratory MDL for 2014 mg/L	AIRMoN MDL* for 2014 mg/L	NTN MDL** for 2014 mg/L
Calcium	0.0005	0.001	0.009	0.019
Potassium	0.0007	0.001	0.001	0.001
Magnesium	0.0002	0.001	0.001	0.005
Sodium	0.0007	0.001	0.001	0.005
Chloride	0.0000	0.004	0.005	0.008
Nitrate	0.0000	0.004	0.004	0.007
Sulfate	0.0004	0.002	0.004	0.005
Bromide	0.0000	0.004	0.005	0.005
Ammonium	0.006	0.008	0.016	0.017
Orthophosphate	0.004	0.004	0.005	0.009

*For AIRMoN sample range starting with AC8684L

**For NTN sample range starting with TM2705SW

Analytical verification. Each analyst uses two or three check samples, prepared from standards or reagents purchased from a different source than chemicals used to prepare calibration standards to verify calibration. 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.

Replicate samples. Each analyst selects a minimum of two to three samples at random per week as replicate samples. 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 (±10% if the value is ≥ 100 times the MDL, and ± 20% if the value is between 10 and 100 times MDL). If any of the results fall out of control, evaluation and corrective actions are determined by the analyst. All replicate results are evaluated monthly by the QA chemist.

Split samples. 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% if the value is ≥ 100 times the MDL, and ± 20% if the value is between 10 and 100 times MDL). The QA chemist verifies results for all duplicate samples monthly.

Control charts. Data variability and deviation from target specifications are monitored using control charts. Control chart limits are monitored daily using an internal verification standard termed "faux rain" (**FR**), low and high concentration control solutions (**FL** and **FH**), prepared by analysts, and DI water (**FB**). When results of analysis for daily control internal standards fall outside of control limits, analysis of the affected samples is repeated.

The CAL prepares an internal verification standard termed "faux rain" (**FR50**) as a dedicated matrix spike solution with target concentrations that represent the 50th percentile level of analytes measured in NTN rain water samples. This solution contains all CAL analytes except for PO_4^{3-} , as PO_4^{3-} affects the NH_4^+ concentration. FR50 solution is made in small batches 3-4 times a year, and labeled FR501301, FR501302, etc.

Orthophosphate internal verification standards (**FLN** and **FHN**) are prepared separately using standards purchased from VHG Labs (http://www.vhglabs.com/) (Table 4).

To set annual control chart limits, all internal standards are analyzed a minimum of seven times at the end of the previous year. The average of these results is the target value for the control chart for the current year. Limits are established at twice the standard deviation (2σ) for the warning limits, and 3σ for the control limits. The control limits for 2013 were based on control charts at the end of 2012.

Table 4. Orthophosphate control solution target concentrations

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

Internal blind samples. Internal blind samples are evaluated monthly. Five different solutions (see their target concentrations in Table 5) are used for the internal blind study: deionized water (DI), Anion MDL standard, Cation MDL standard, FR50, and AES-05 (an external certified reference standard is purchased from Environment Canada (https://www.ec.gc.ca/)). The QA Chemist uses blind sample control limits to evaluate instrument and analyst performance. In 2013, blind samples were submitted weekly for both NTN and AIRMoN networks. The procedures included the full sampling procedure (and supplies) used for each of the networks. For example, before sending a blind solution to the laboratory for analysis, it 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 before the analysis, and the AIRMoN sample was not.

Table 5. Control internal and external blind solutions target concentrations

	DI Water Target Concentration	FR50 Target Concentration	Cation MDL Target Concentration	Anion MDL Target Concentration	AES-05 Target Concentration
pH	5.62	4.80	5.55	5.55	4.90
Specific Conductance (µS/cm)	0.7*	10.6	1.7	1.6	10.8
Calcium (mg/L)	<0.003*	0.123	0.010	0	0.187
Magnesium (mg/L)	<0.001*	0.023	0.005	0	0.037
Sodium (mg/L)	<0.002*	0.049	0.005	0.013	0.181
Potassium (mg/L)	<0.001*	0.021	0.006	0.032	0.028
Chloride (mg/L)	<0.005*	0.098	0.064	0.021	0.225
Sulfate (mg/L)	<0.005*	0.828	0.019	0.015	1.28
Nitrate (mg/L)	<0.006*	0.958	0.043	0.023	1.15
Bromide (mg/L)	<0.004*	0.020	NA	0.015	NA
Ammonium (mg/L)	<0.007*	0.227	0.027	0.005	0.312
Orthophosphate(mg/L)	<0.005*	NA	NA	0.023	NA

* The average historic MDL value

Reanalysis Samples. Chemistry results are reviewed by the analysts on a weekly basis for data completeness before they are released to the data manager. Ion Percent Difference (IPD) and Conductivity Percent Difference (CPD) are calculated to identify samples for reanalysis (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.

The flow of data from the CAL to the NADP Program Office is shown in Figure 1.

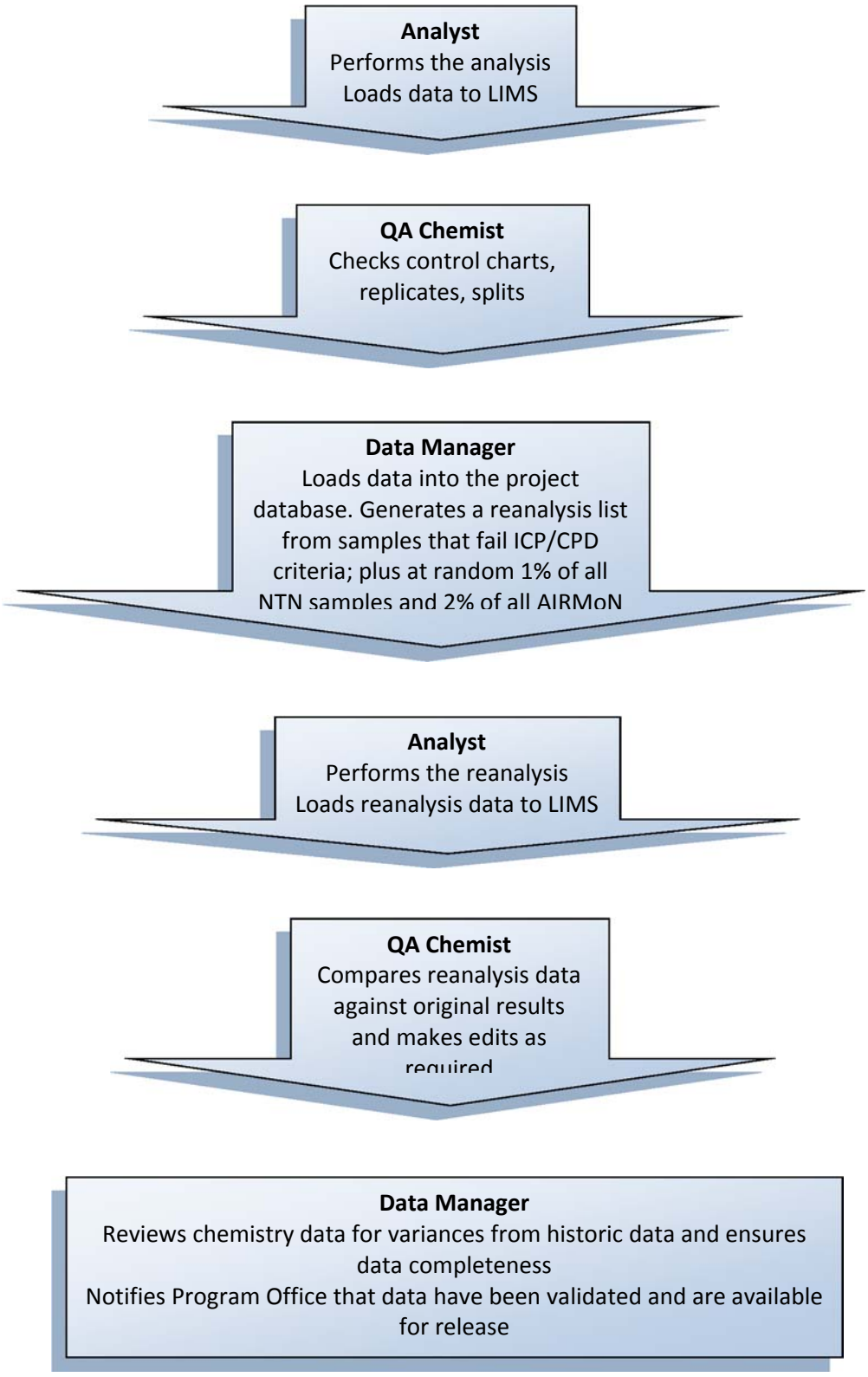

Figure 1. Flow of data from the CAL to the Program Office

Quality Control Discussion

Control Charts

In 2013, all analytical values for FR50, low (FL) and high (FH) concentration check solutions and DI water (FB) were within control for NTN, AIRMoN and AMoN data submitted to NADP. The acceptable ranges for FR50, FL, FH and FB check solutions for all analytes are shown in Table 6. The Data Quality objectives (DQOs) as defined in the CAL QAP were met.

Table 6. Acceptable ranges for QC check solutions in 2013

	FR50	FL	FH	FB
pH	4.83 ± 0.10	4.33 ± 0.09	6.95 ± 0.09	5.62 ± 0.30
Specific Conductance (µS/cm)	10.1 ± 0.9	5.2 ± 0.3	20.0 ± 1.5	1.1 ± 0.5
Calcium (mg/L)	0.125 ± 0.009	0.040 ± 0.003	0.505 ± 0.039	0.000 ± 0.001
Magnesium (mg/L)	0.023 ± 0.002	0.010 ± 0.001	0.102 ± 0.006	0.000 ± 0.001
Sodium (mg/L)	0.055 ± 0.006	0.040 ± 0.003	0.505 ± 0.033	0.000 ± 0.001
Potassium (mg/L)	0.020 ± 0.004	0.010 ± 0.002	0.103 ± 0.007	0.000 ± 0.001
Chloride (mg/L)	0.101 ± 0.009	0.025 ± 0.003	3.050 ± 0.120	0.000 ± 0.001
Sulfate (mg/L)	0.837 ± 0.042	0.500 ±0.024	5.000 ± 0.165	0.000 ± 0.001
Nitrate (mg/L)	0.958 ± 0.048	0.495 ± 0.027	4.975 ± 0.150	0.000 ± 0.001
Bromide (mg/L)	0.021 ± 0.004	0.025 ± 0.004	3.050 ± 0.120	0.000 ± 0.001
Ammonium (mg/L)	0.227 ± 0.009	0.090 ± 0.011	1.300 ± 0.075	0.000 ± 0.006
Orthophosphate(mg/L)	N/A	0.010 ± 0.006	0.100 ± 0.012	0.000 ± 0.006

An example of control chart is shown in Figure 2.

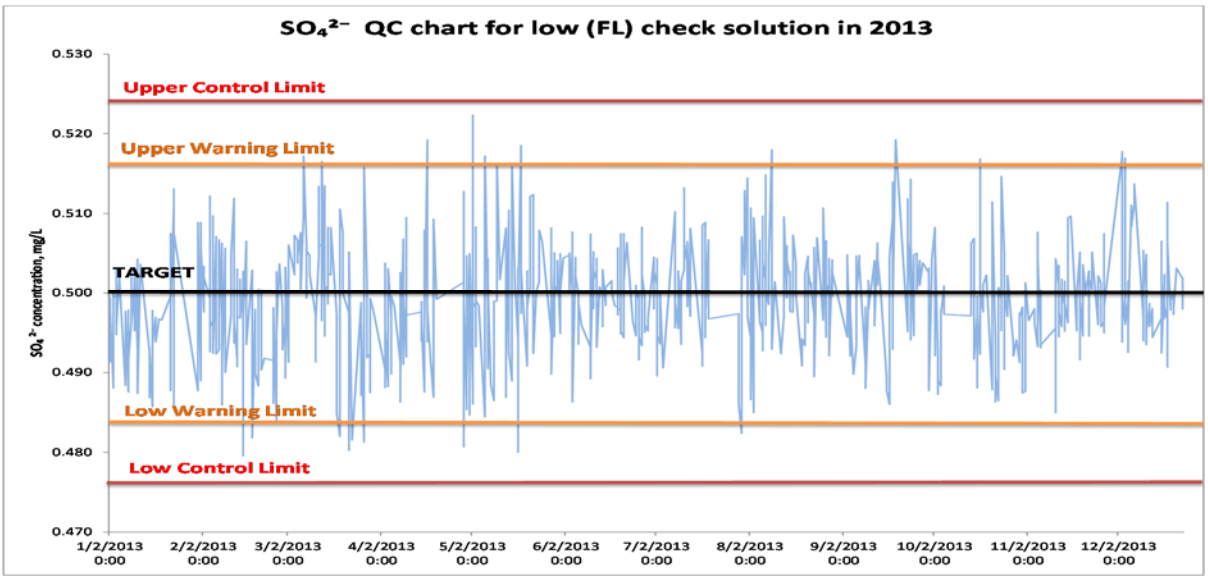

Figure 2. Example of control chart

Split Samples

For split samples, the allowable bias for analytes with concentrations at 10 to 100 times the MDL is ± 20 percent. The allowable bias for analytes with concentrations at ≥ 100 times the MDL is ± 10 percent.

150 pairs of split samples for NTN and AIRMoN were processed in 2013. The minimum, average, maximum and median percent differences are shown in Table 7.

Since 95% of all NTN samples for 5 year period (2008 -2012) have PO_4^{3-} and Br^- concentrations lower than 100 times the MDL, the replicate results for orthophosphate and bromide replicates are not shown. Only internal QC solutions are used to evaluate precision and accuracy for PO_4^{3-} and Br^- analysis.

There is no practical MDL for pH; hence the results for pH replicates are also shown. In practice, the allowable bias for pH less than 5.0 is 0.1 pH unit. The allowable bias for pH greater than 5.0 is 0.3 pH unit.

The allowable bias for conductivity between 10 and 100 µS/cm is 10%. The allowable bias for conductivity greater than 100 µS/cm is 6%.

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 7. Minimum, average, maximum and median absolute percent differences for split samples in 2013

Parameter	n	Minimum percent difference (%)	Average percent difference (%)	Maximum percent difference (%)	Median percent difference (%)
pH	150	0	0.6	3.3	0.4
Specific Conductance	150	0	1.4	8.3	1.1
Calcium	149	0	1.9	15.8	1.1
Potassium	150	0	2.0	16.2	1.4
Magnesium	146	0	1.3	8.7	0.8
Sodium	148	0	1.3	7.3	0.9
Chloride	150	0	1.2	11.0	0.5
Sulfate	150	0	0.6	9.9	0.3
Nitrate	150	0	0.5	4.8	0.3
Ammonium	143	0	1.3	9.5	0.7

The results of split samples met the requirements in 2013 as specified in the 2011 CAL Quality Assurance Plan.

Replicate Samples

For replicate samples (as for split samples), the allowable bias for analytes with concentrations at 10 to 100 times the MDL is ± 20 percent (Table 8). The allowable bias for analytes with concentrations at ≥ 100 times the MDL is ± 10 percent (Table 9).The allowable bias for conductivity between 10 and 100 µS/cm is 10%. The allowable bias for conductivity greater than 100 µS/cm is 6%. Since 99.5% of all NTN samples for 5 year (2008 -2012) period have conductivity values lower than 100 µS/cm, only the results for conductivity replicates with the allowable bias of 10% are shown (Table 8).

Table 8. Replicate samples, concentrations 10 to 100 times the MDL (maximum allowable bias 20%)

Parameter	Concentration Range: 10 to 100 x MDL	n	Average RPD %	Maximum RPD %	Minimum RPD %
pH	pH > 5.00	164	1.3	7.8	0
Specific Conductance*	10 to 100 µS/cm*	260	2.5	9.8	0
Calcium	0.010 – 0.100 mg/L	91	1.7	10.3	0.3
Potassium	0.010 – 0.100 mg/L	144	3.6	12.0	0.1
Magnesium	0.010 – 0.100 mg/L	136	2.2	9.2	0.1
Sodium	0.010 – 0.100 mg/L	121	3.2	11.5	0.3
Chloride	0.040 – 0.400 mg/L	170	1.3	7.1	0
Sulfate	0.040 – 0.400 mg/L	79	1.4	7.6	0
Nitrate	0.040 – 0.400 mg/L	55	1.2	5.6	0
Ammonium	0.080 – 0.800 mg/L	139	1.9	12.8	0

*Allowable bias for this range of conductivity value is 10%

Table 9. Replicate samples, concentrations greater than 100 times the MDL (maximum allowable bias 10%)

Parameter	Concentration Range: > 100 x MDL	n	Average RPD %	Maximum RPD %	Minimum RPD %
pH	pH < 5.00	96	0.7	1.9	0
Calcium	> 0.100 mg/L	112	1.3	8.4	0.1
Potassium	> 0.100 mg/L	21	2.7	8.1	0.4
Magnesium	> 0.100 mg/L	23	1.9	4.4	0.7
Sodium	> 0.100 mg/L	65	2.5	8.9	0.2
Chloride	> 0.400 mg/L	38	0.9	7.7	0.1
Sulfate	> 0.400 mg/L	191	0.7	5.5	0
Nitrate	> 0.400 mg/L	218	0.7	7.5	0
Ammonium	> 0.800 mg/L	10	1.3	3.6	0.6

The results of replicate samples met the requirements in 2013.

Quality Assurance Discussion

Polisher and Reverse Osmosis Deionized (RO DI) Water Blanks

RO DI water is monitored weekly. Polisher DI water is monitored once a month.

The polisher and RO DI water blanks met acceptance criteria (all analytes concentrations were less than the MDLs for each analalyte) for 2013 (Table 10).

Table 10. Number of results outside the target limits for polisher and RO blanks in 2013

Parameter	Polisher DI N=60	RO Water N=49
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
Bromide	0	0
Ammonium	0	0
Orthophosphate	0	0

Supply Checks

New supplies are evaluated before they are introduced for site or laboratory use according to the frequency in Table 11. In addition, washed/reused supply cleanliness is monitored daily (Table 12). Buckets and bottles are tested for a 24-hour period. Lids are tested for a 2-hour period. New supplies are tested using DI water. Rewashed and reused supplies are tested using FR50 solution. All results are monitored weekly by the QA Chemist.

Table 11. Summary of NTN and AIRMoN new supply checks

Supply Type	Test Frequency	Test Solution	Test Volume	Contact Time
buckets	1 per 16	DI	150 mL	24 hours
bucket lids	1 per 15	DI	50 mL	2 hours
1 L bottles	1 per 24	DI	150 mL	24 hours
250 mL AIRMoN bottles	1 per 24	DI	50 mL	24 hours
bucket bags	1 per box (50)	DI	150 mL	24 hours
lid bags	1 per box (100)	DI	150 mL	24 hours
filters	2 per lot and weekly	DI/FR50	50 mL	N/A

Table 12. Summary of NTN and AIRMoN washed/reused supply checks

Supply	Test frequency	Test Solution	Volume	Contact Time
1 Bucket	Daily	FR50	150 mL	24 hours
1 NTN Bottle	Daily	FR50	150 mL	24 hours
1 Lid	Daily	FR50	50 mL	2 hours

For DI water supply blanks, target levels are based on historic and current MDLs. They are also compared to the 1st percentile of analyte concentrations in NTN samples for the five - year period from 2008 to 2012. This method is under evaluation and may change in 2015.

For FR50 supply check samples, target levels are based on historic precision measured in check samples prepared with FR50 solution. Box and whisker plots 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.

NTN Sample Filters: DI Water and FR50 Solution Checks

In 2013, most concentrations of analytes in DI water eluents from NTN sample filters were less than the 1st percentile of NTN sample concentrations for the five-year period. A few outliers were detected in DI water eluents for Na^+ and Cl^- (Table 13). The median concentrations of these ions found on filters were 0.001 mg/L for Na^+ (MDL level) and < 0.001 mg/L for CL^- (< MDL level). Box and whisker plots for Na^+ and Cl^- concentrations in eluents from filters leached with DI water are shown in Figure 3.

The concentrations for all analytes found when leaching filters with FR50 were low in 2013, with a bias of the same magnitude as the MDL. A few outliers were detected in FR50 eluents for K^+ and Cl^- (Table 13).

When sample volume allows, filters are rinsed with some sample volume before collecting a filtered sample for analysis (see SOP PR-1055 for details). For samples of volume greater than 200 mL, filters are rinsed with 50 mL of sample. For samples of volume between 100 mL and 200 mL, 20 mL of sample is used as the rinse. For the samples of volume less than 100 mL filters are not rinsed. In many cases low-volume samples have higher concentrations of analytes; the relative bias from any filter contamination is lower for such samples.

Table 13. Number of results outside of target limits in 2013 for filter blanks

Parameter	DI N=51	FR50 N=51
pH	0	0
Specific Conductance	0	0
Calcium	0	0
Potassium	0	2
Magnesium	0	0
Sodium	2	0
Chloride	1	3
Sulfate	0	0
Nitrate	0	0
Ammonium	0	0
Bromide	0	0
Orthophosphate	0	NA

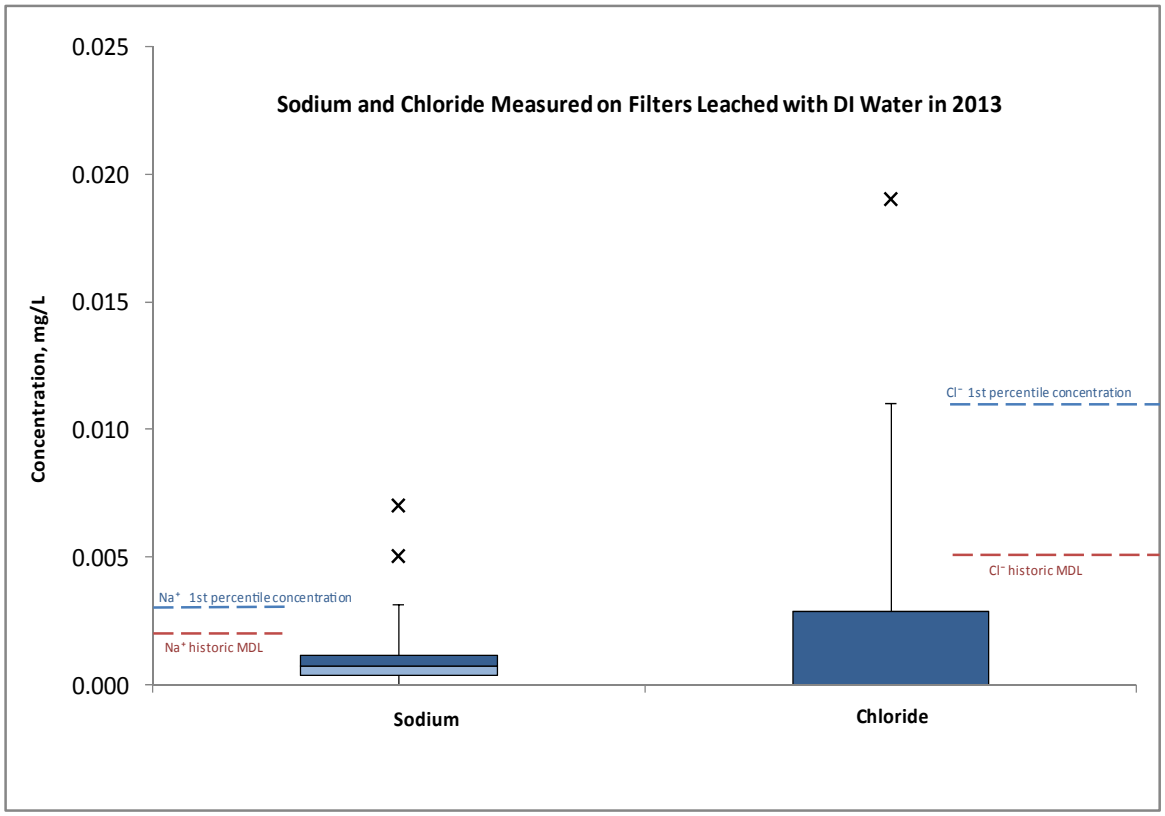

Figure 3. Box and whisker plot showing Na^+ and Cl^- concentrations measured in DI used to leach filters for weekly blanks in 2013. The historic Na^+ and Cl^- MDLs and the 1st percentile Na^+ and CL^- concentrations for NTN samples in 2008 – 2012 are shown for comparison

Buckets, Bottles and Lids Checks

New buckets, bottles (NTN and AIRMoN) and bucket lids for site and laboratory use are tested with DI water (see Table 11).

Washed and reused buckets, bucket lids and NTN 1L bottles are tested with FR50 solution (see Table 12).

When analyte concentrations exceed target levels for supplies that are washed and reused, 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.

New Buckets. Calcium is used in the manufacture of plastic buckets and has been detected in new buckets used to collect NTN and AIRMoN wet deposition samples. In the CAL, new buckets are leached with hydrochloric acid to remove Ca^{2+}, and then washed and tested. In 2013, the concentration of Ca^{2+} in new leached and washed buckets is lower than the 1st percentile Ca^{2+} concentration for NTN samples (Figure 4). The median concentration of Ca^{2+} found in new buckets was 0.004 mg/L.

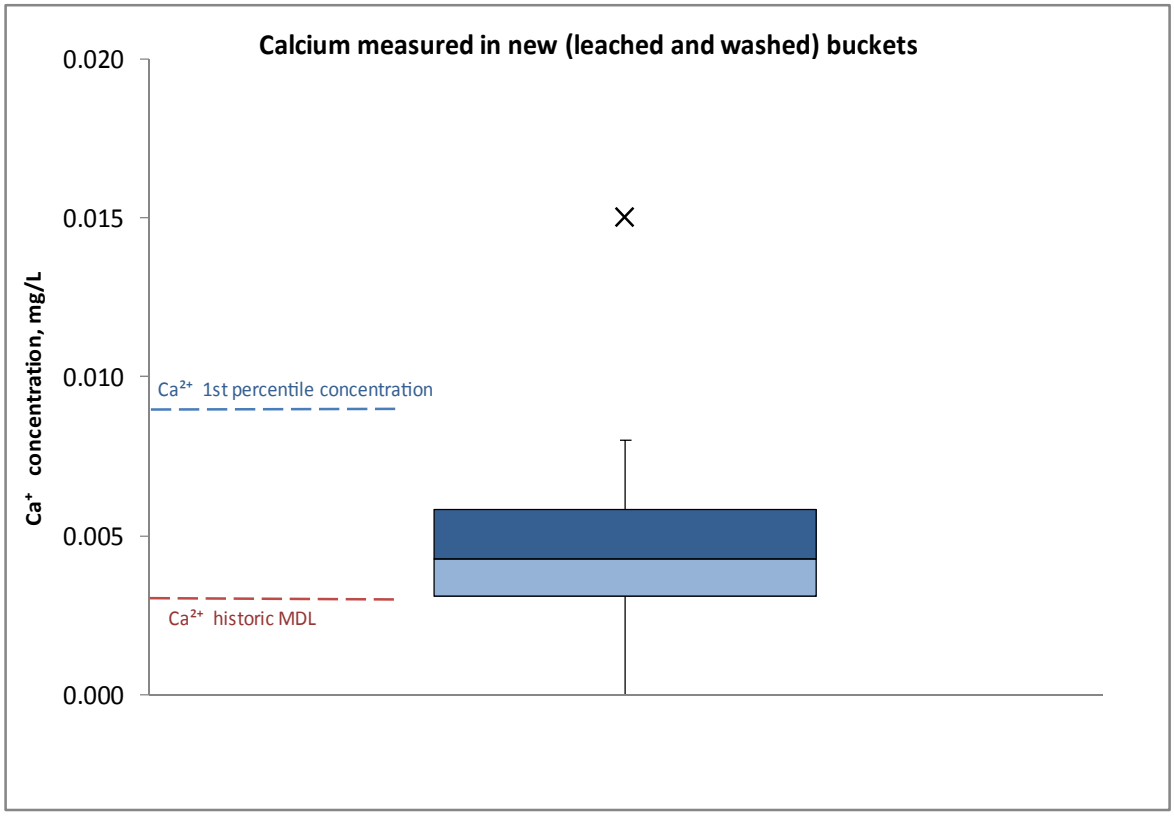

Figure 4. Box and whisker plot showing Ca^{2+} concentrations measured in new buckets blanks in 2013. The historical Ca^{2+} MDL and the 1st percentile Ca^{2+} concentration for NTN samples in 2008 – 2012 are shown for comparison

Washed and Reused Buckets. During 2013, one bucket was selected from the buckets washed each day and tested for a period of 24 hours using 150 mL of FR50 solution. Results outside of target limits are shown in Table 14. Eight buckets were responsible for the thirteen exceedances. All buckets were rewashed and retested, and five of them were found to be within control limits. Three buckets did not pass the second check and were discarded.

Table 14. Number of results outside of target limits in 2013 for washed and reused buckets tested with FR50 solution

Parameter	FR50 24 Hours N=251
pH	2
Specific Conductance	0
Calcium	3
Potassium	0
Magnesium	2
Sodium	3
Chloride	2
Sulfate	0
Nitrate	0
Ammonium	1
Bromide	0
Orthophosphate	NA

The levels of Ca^{2+}, detected routinely in washed and reused buckets, were low in 2013 and mostly were within historic allowable control limits for FR50 solution. Only three outliers for calcium were detected in 2013. Results for each batch of FR50 solution are shown in Figure 5. Target Ca^{2+} concentrations are slightly different in each batch.

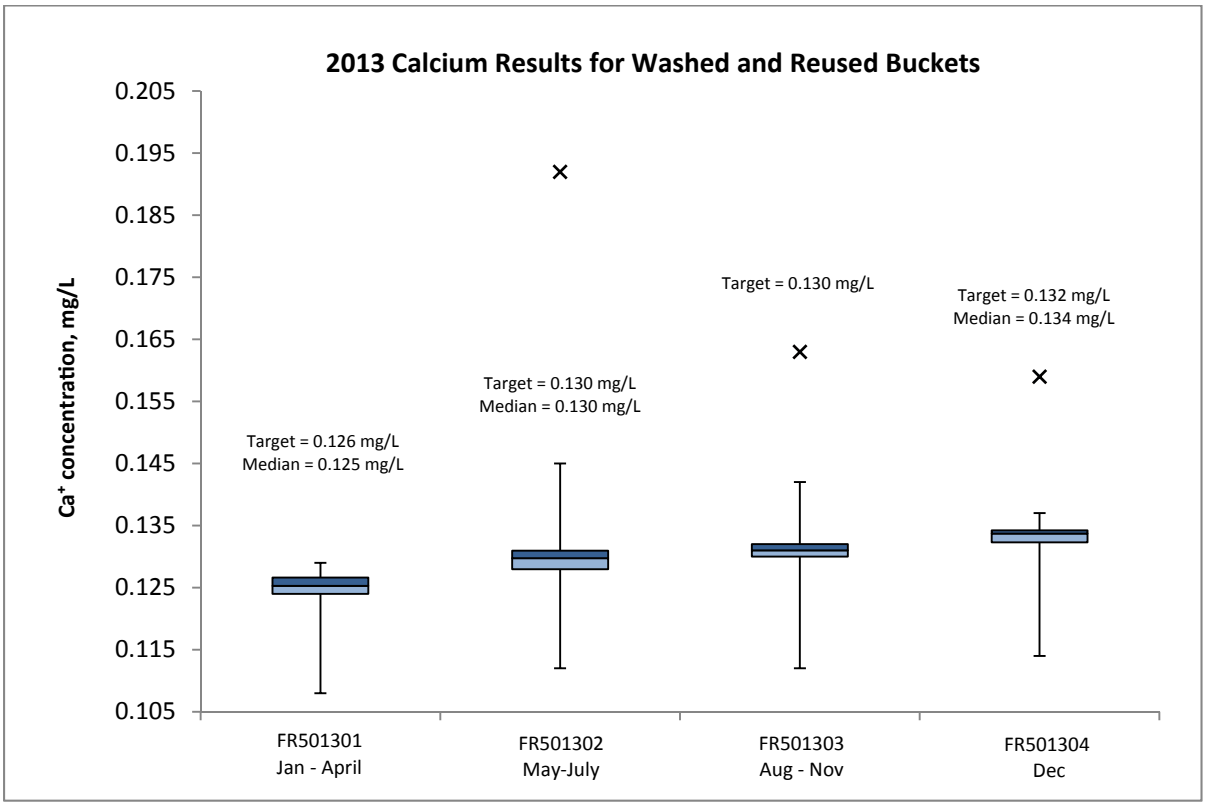

Figure 5. Box and whisker plot showing Ca^{2+} concentrations for washed and reused buckets tested with FR50 solution in 2013

In 2010 – 2013 a few NH_4^+ values out of control limits were detected in washed and reused bucket tests. 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 6 shows NH_4^+ results measured in FR50 bucket tests in 2013. Only one NH_4^+ outlier was detected during the second quarter.

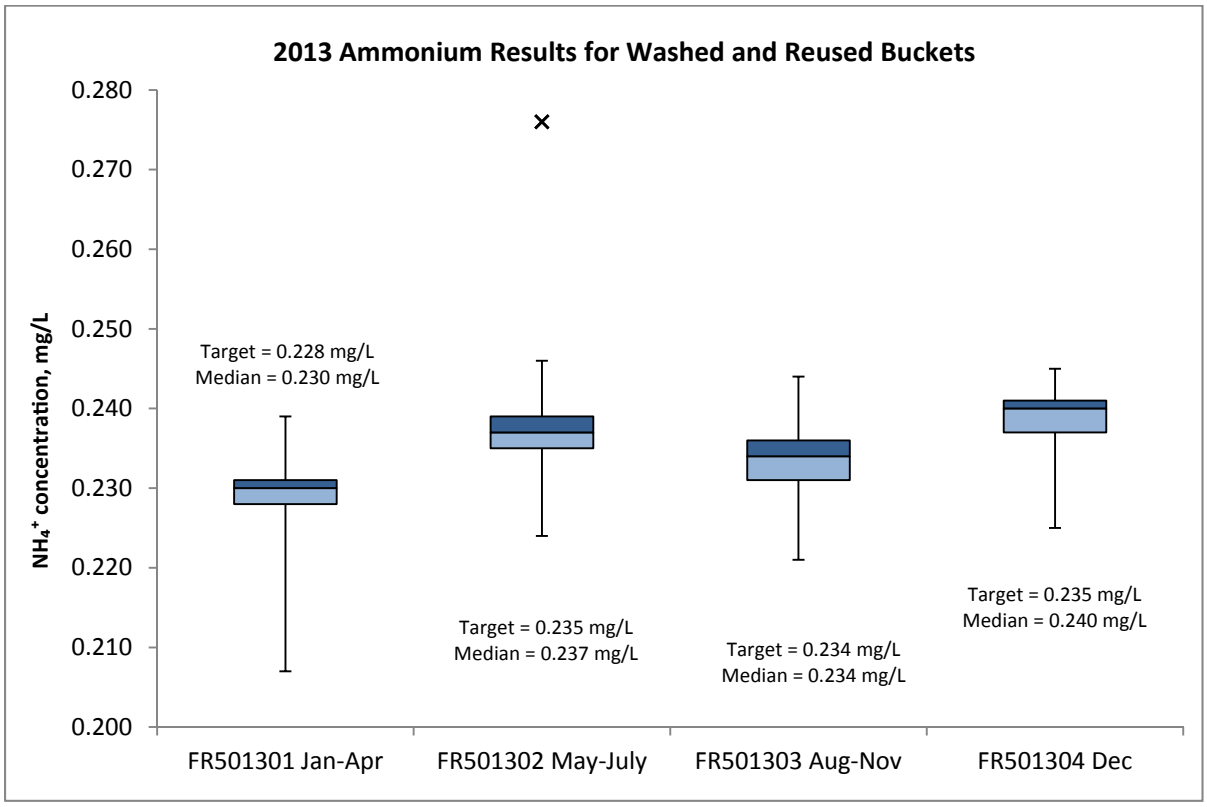

Figure 6. Box and whisker plot showing NH_4^+ concentrations for washed and reused buckets tested with FR50 solution in 2013

AIRMoN bottles are single-use Thermo-Fisher 250-mL Nalgene ™ bottles that are not rewashed or reused. NTN 1-L bottles are Nalgene ™ bottles that are rewashed and reused.

New NTN 1-L and AIRMoN 250-mL bottles. New NTN and AIRMoN bottle blank results were within the acceptable limits for all analytes throughout 2013, and there were no outliers.

Washed and Reused NTN 1-L Bottles. During 2013, one NTN bottle was selected from the bottles washed each day and tested for a period of 24 hours using 150 mL of FR50 solution. Results outside of target limits are shown in Table 15. The outliers for Na^+ (1) and NH_4^+ (4) occurred in five bottles. All of these bottles were rewashed and retested, and all of them were subsequently found to be within control limits.
The single Na^+ outlier was 0.069 mg/L versus a target of 0.055 mg/L and a median of 0.055 mg/L.

Figure 7 shows NH_4^+ results measured in FR50 bottle tests in 2013.

Table 15. Number of results outside of target limits in 2013 for washed and reused NTN 1-L bottles tested with FR50 solution

Parameter	FR50 24 Hours N=147
pH	0
Specific Conductance	0
Calcium	0
Potassium	0
Magnesium	0
Sodium	1
Chloride	0
Sulfate	0
Nitrate	0
Ammonium	4
Bromide	0
Orthophosphate	NA

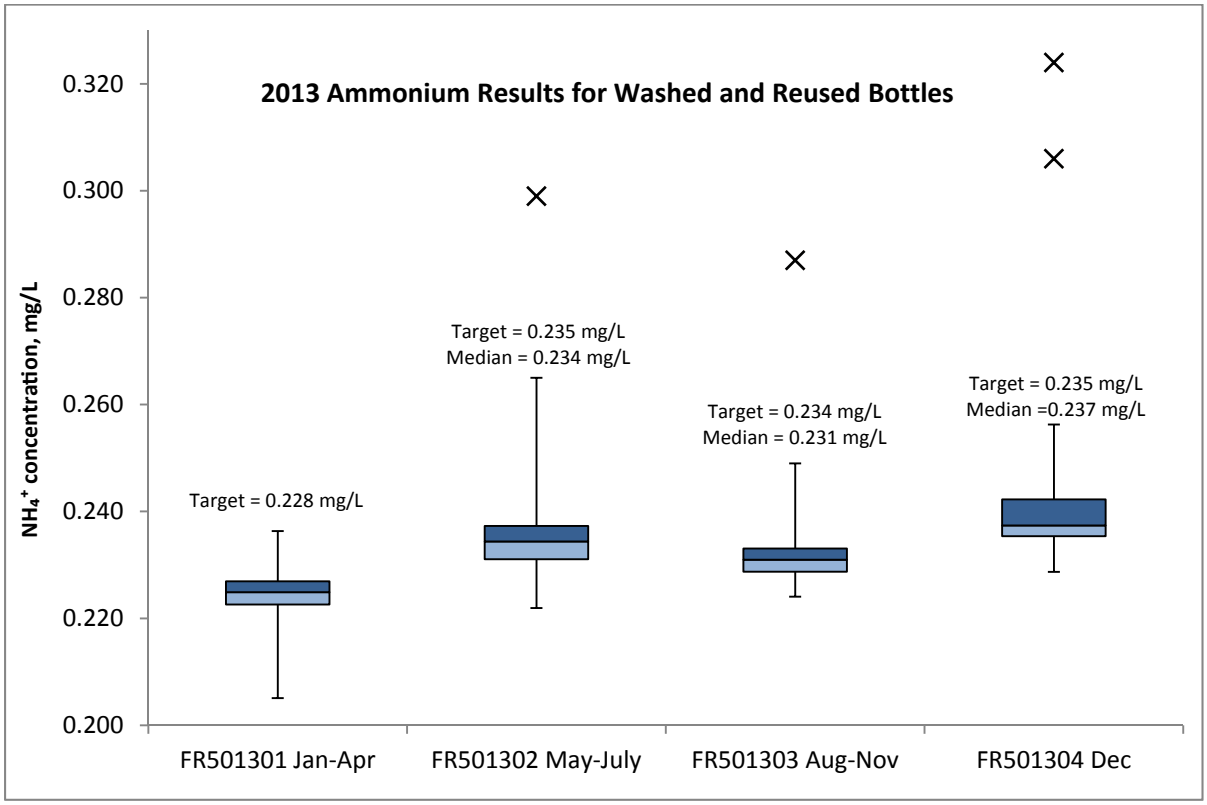

Figure 7. Box and whisker plot showing NH_4^+ concentrations for washed and reused NTN 1-L bottle tested with FR50 solution in 2013

New Lids. One lid from every 15 new lids is tested with DI water. Four new lid blanks representing sixty new lids were tested in 2013. Two of them had elevated NH_4^+ concentration 0.012 mg/L, versus the historic MDL 0.007 mg/L. After being rewashed, those lids passed the second check.

Washed and Reused Lids. Lid blanks tested with FR50 in 2013 indicated ten outliers for Na^+ (Table 16, Figure 8). Those lids were rewashed and retested. They passed the second check. Na^+ is episodically detected in lid bag blanks too, indicating that the lid bags are the likely origin of sodium found on lids (see Figure 9). The single Ca^{2+} outlier was 0.195 mg/L versus a target concentration of 0.130 mg/L and a median concentration of 0.132 mg/L. Three K^+ outliers were 0.038, 0.040 and 0.034 mg/L versus a target concentration of 0.021 mg/L and a median concentration of 0.022 mg/L. Two CL^- outliers were 0.117 and 0.119 mg/L versus a target concentration of 0.103 mg/L and a median concentration of 0.105 mg/L. The single NH_4^+ outlier was 0.298 mg/L versus a target concentration of 0.235 mg/L and a median concentration of 0.241 mg/L.

Table 16. Number of results outside of target limits in 2013 for washed and reused bucket lids tested with FR50 solution

Parameter	FR50 N=246
pH	0
Specific Conductance	0
Calcium	1
Potassium	3
Magnesium	0
Sodium	10
Chloride	2
Sulfate	0
Nitrate	0
Ammonium	1
Bromide	0
Orthophosphate	NA

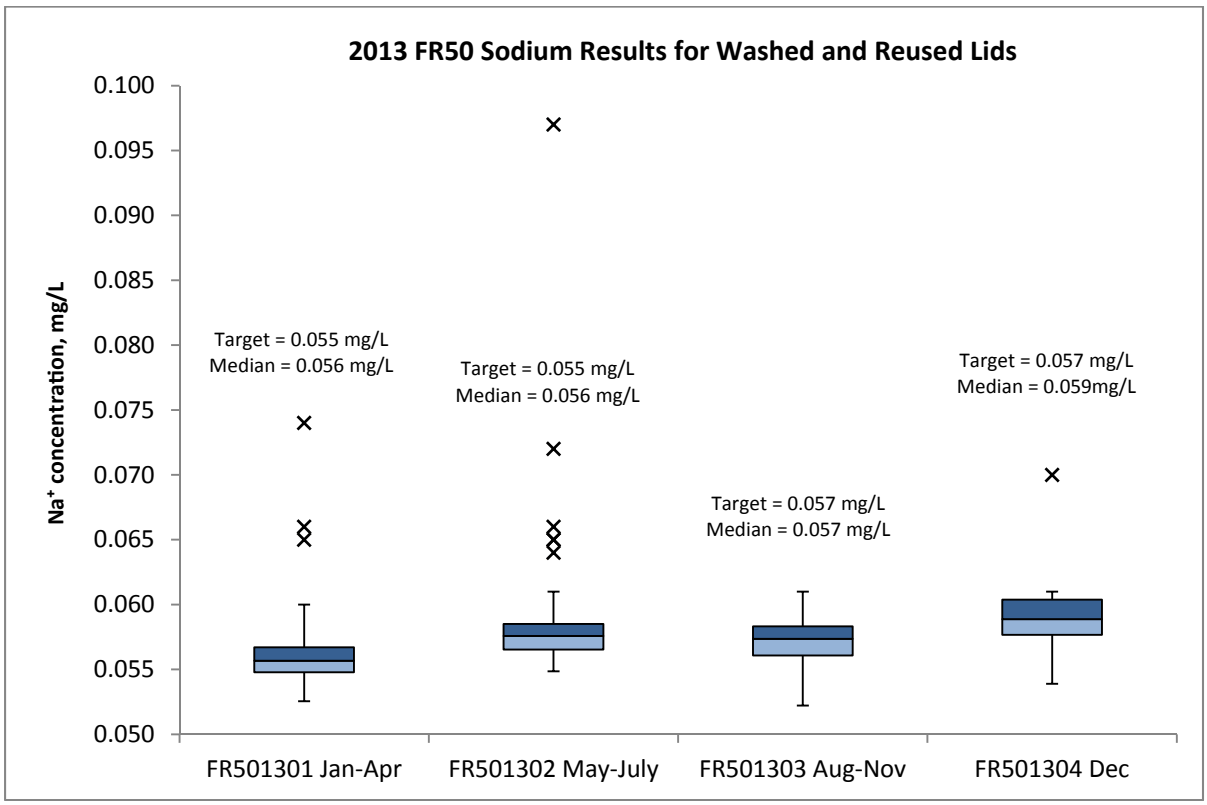

Figure 8. Box and whisker plot showing Na^+ concentrations for washed and reused lids tested with FR50 solution in 2013

Bags Checks

Lid and bucket bags are tested with DI water whenever a new shipment of bags is received. Additionally, one bag from each carton (box) is tested before releasing for use. On average, one lid bag and one bucket bag are checked weekly. If a bag fails the acceptance test, one to two additional bags from the lot (carton, box) are tested. If those bags fail the second check, the entire box is rejected.

Lid Bags. If analytes (especially Na^+) exceed target limits in both original and additional checks, 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 released for use. If they fail, the bags are rejected. Slightly elevated levels of Na^+ and NH_4^+ were detected in lid bag blanks in 2013. Nine outliers were detected for Na+, and seven outliers were detected for NH_4^+ (Figure 9). All bags passed additional checks, and no bags were rejected. The median concentration of Na^+ found in lid bags was 0.001 mg/L. The median concentration of NH_4^+ found in lid bags was 0.004 mg/L (which is lower than the MDL level).

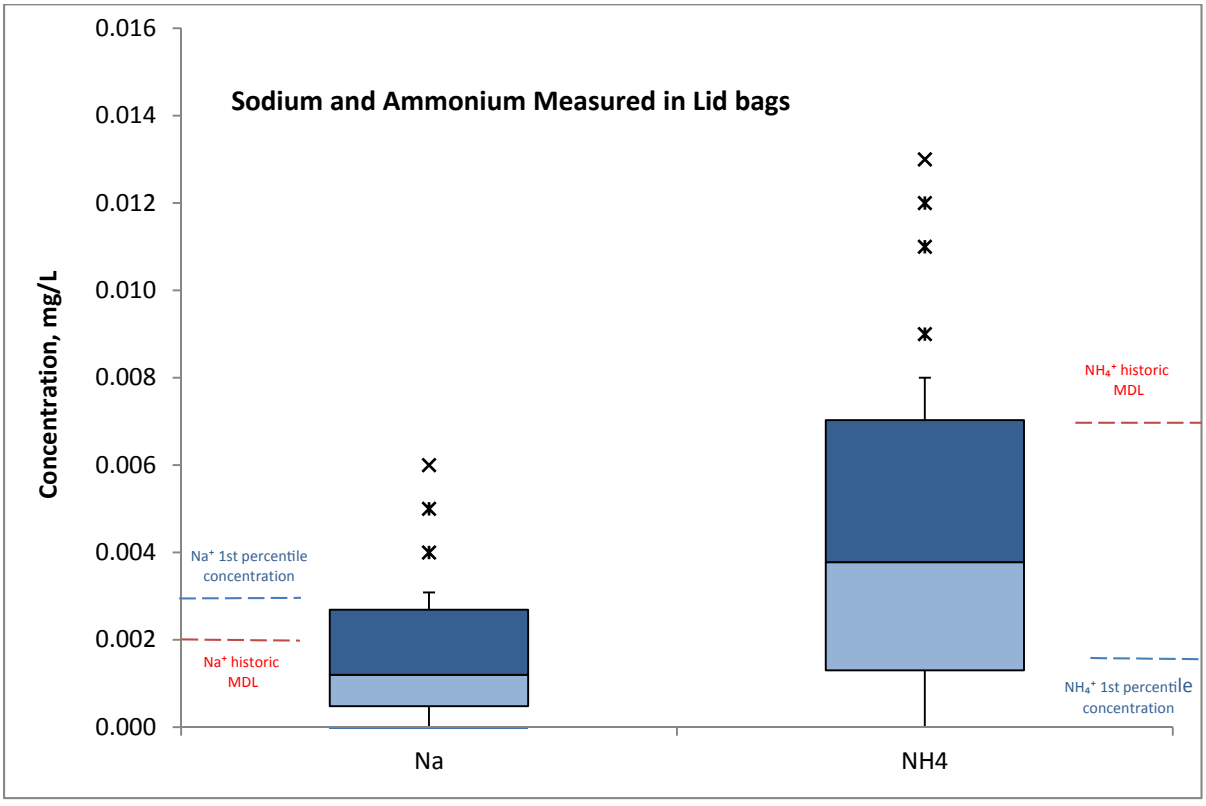

Figure 9. Box and whisker plot showing Na^+ and NH_4^+ concentrations for lid bags tested with DI water in 2013. The historic Na^+ and NH_4^+ MDLs and the 1st percentiles Na^+ and NH_4^+ concentrations for NTN samples in 2008 – 2012 are shown for comparison.

Bucket Bags. All bucket bag blank results were within the acceptable target limits for all analytes throughout 2013.

Internal Blind AES-05 and FR50 Results

Results for internal AES-05 and FR50 blind samples were used to assess post-analysis accuracy and precision of the laboratory throughout the year. The relative standard deviation (RSD) and percent recovery were calculated to evaluate precision and accuracy. The recovery and relative standard deviation (RSD) of AES-05 and FR50 met acceptance criteria in 2013. The results are presented in Tables 17 and 18.

Table 17. Relative Standard Deviations (RSDs) and percent mean recoveries for internal blind AES-05 solution

Parameter	Target	RSD Unfiltered N = 7 (%)	RSD Filtered N = 7 (%)	Recovery Unfiltered N = 7 (%)	Recovery Filtered N = 7 (%)
pH	4.90	0.3	NA	99.4	NA
Specific Conductance	10.8 µS/cm	1.2	2.0	107.0	103.8
Calcium	0.187 mg/L	3.5	3.9	105.3	109.6
Potassium	0.028 mg/L	3.3	4.9	93.7	93.6
Magnesium	0.037 mg/L	3.4	2.5	104.6	101.5
Sodium	0.181 mg/L	1.4	2.6	99.3	99.7
Chloride	0.225 mg/L	2.6	1.5	106.3	104.1
Sulfate	1.28 mg/L	1.0	1.1	101.3	99.1
Nitrate	1.15 mg/L	1.5	1.2	101.5	99.5
Ammonium	0.312 mg/L	3.9	3.8	99.9	97.7

Table 18. Relative Standard Deviations (RSDs) and percent mean 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	0.5	NA	99.8	NA
Specific Conductance	10.6 µS/cm	1.4	NA	101.8	NA
Calcium	0.123 mg/L	3.1	3.0	100.9	100.9
Potassium	0.023 mg/L	2.0	5.1	101.1	100.5
Magnesium	0.049 mg/L	2.4	8.9	99.0	101.0
Sodium	0.021 mg/L	1.9	1.6	99.5	99.7
Chloride	0.098 mg/L	2.9	2.9	100.5	100.2
Sulfate	0.828 mg/L	1.7	1.9	99.2	98.3
Nitrate	0.958 mg/L	1.5	1.8	100.1	98.9
Ammonium	0.227 mg/L	3.1	5.0	104.1	103.2
Bromide	0.020 mg/L	16.7	6.4	98.2	95.0

Reanalysis Samples

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, (SOP DA-0067.1). An additional 2 percent of samples are selected at random for reanalysis. The results of reanalysis are reviewed by the QA Chemist, and required edits are made (see the flow of data from the CAL to the NADP Program Office in Figure 1).

After reviewing the results of reanalysis, a total of 194 edits were made for NTN samples and 2 edits were made for AIRMoN samples. The edits, with explanations are stored in the NTN and AIRMoN databases.

The number of NTN, AIRMoN, AMoN and supplies check samples analyzed in 2013, including counts of reanalysis, split, blind and control chart samples, is shown in Table 19.

Table 19. Number of real and Quality Control/Quality Assurance (QC/QA) samples analyzed during 2013

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	**11092**	**1209**	**133**	**94**	pH/conductivity = 8555 (37%) ICP/OES = 3865 (21%) FIA = 6480 (27%) IC = 4508 (24%)
AIRMoN	**819**	**113**	**16**	**94**	
Supplies Check Samples	**1023**	**NA**	**NA**	**NA**	
AMoN	**3208**	**NA**	**NA**	**NA**	

AMoN

Upon receipt at the CAL, Sigma-Aldrich Radiello ® passive-type air samples for the AMoN network are stored in a freezer (at -17.5 °C). Samples are extracted and analyzed in batches once a week.

Extracts are analyzed by FIA using the similar method determination of NH_4^+ as for NTN and AIRMoN samples (SOP AN-4022). FR50, FH, FL and DI standards are analyzed during the run for quality control. The analyst also chooses 1-2 samples per batch as replicate samples. All NH_4^+ values for QC standards were within allowable limits in 2013.

During the extraction process, five QA samples are generated to evaluate the background NH_3 levels. This set includes:

- Lab Air Blank (1 passive air sampler device with core located in the lab throughout two week period);
- Hood Air Blank (1 passive air sampler device with core located in the working hood throughout two week period);
- Hood Extraction Blank (passive air sampler device with core located in the working hood throughout the extraction period (1-3 hours), 1 per extraction batch);
- Lab DI Blank (DI water used for extractions, 1 per extraction batch);
- New Core Blank (unused cartridge core as received from supplier, 1 per extraction batch. Additionally, 2 new core blanks are run when a new lot is received).

The results of the lab AMoN QA samples for 2013 are shown in Figure 10.

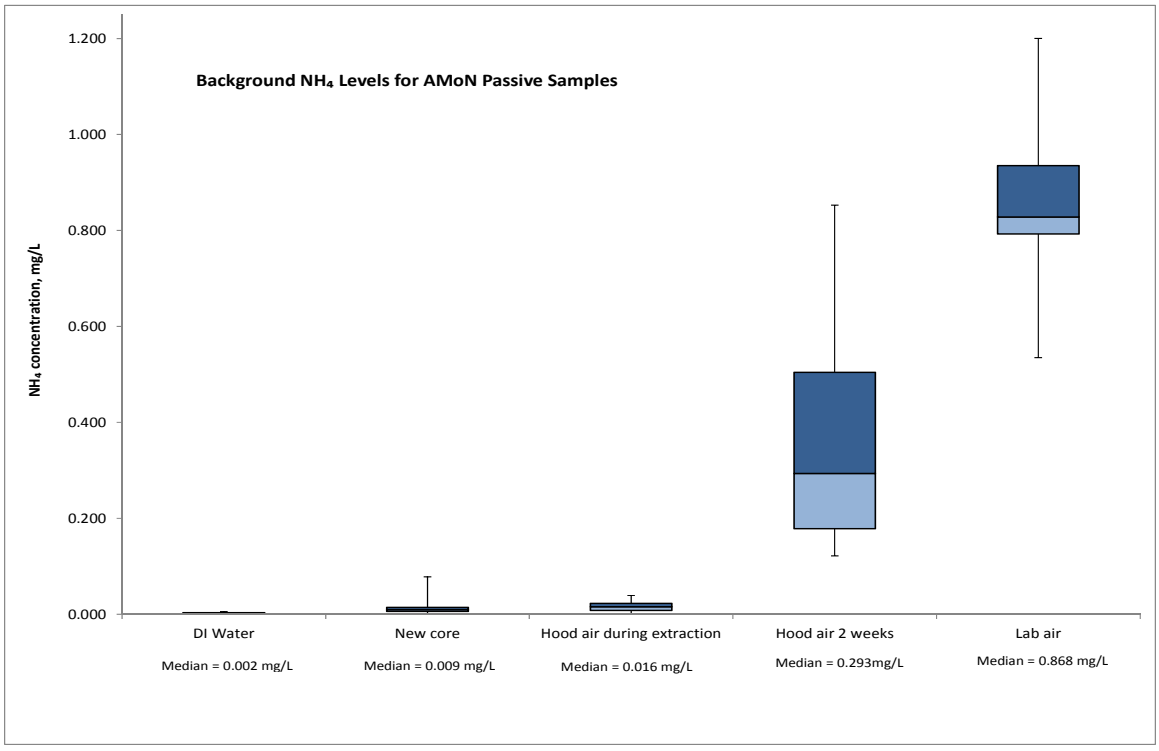

Figure 10. Box and whisker plot showing NH_4^+ concentrations measured in 2013 in AMoN QA samples: laboratory DI water; 10 mL extracts of new cores blanks, hood air blanks and laboratory air blanks

The precision of AMoN triplicate results were calculated as the median absolute relative percent difference (ARPD) of valid deployed samplers measurements, and as the relative standard deviation (RSD) (see Table 20).

Table 20. Median absolute relative percent difference (ARPD) and mean relative standard deviation (RSD) for triplicate AMoN samples

Year	Count	Median ARPD (%)	Mean RSD (%)
2007	59	8.3	12.1
2008	370	7.3	11.5
2009	528	6.8	9.7
2010	521	6.0	10.1
2011*	82	10.5	20.8
2012	90	6.4	12.5
2013	91	4.1	5.1

* Triplicate measurement frequency was decreased from one in every deployment to one in every forth deployment in 2011

The CAL compares measurements between Radiello ® passive-type air samplers and URG (University Research Glass) denuders, exposed side by side at IL11 during a year. The average and median RPDs of NH_3 results at IL11 measured using Radiello samplers and URG denuders are shown in Table 21.

Table 21. Average and median RPDs* for NH_3 measured at IL 11 using Radiello ® passive-type air samplers and URG denuders in 2013

Year	Median RPD (%)	Average RPD (%)	Count
2013	3.0	4.1	27

* $\text{RPD (\%)} = \frac{\text{Radiello value} - \text{URG denuder value}}{\text{URG denuder value}} \ 100$

AMoN Travel Blanks Study

The results of the travel sampler blanks for 2013 are shown in Figure 11. Travel blanks are sent to field sites along with regular samplers but are not opened or deployed.

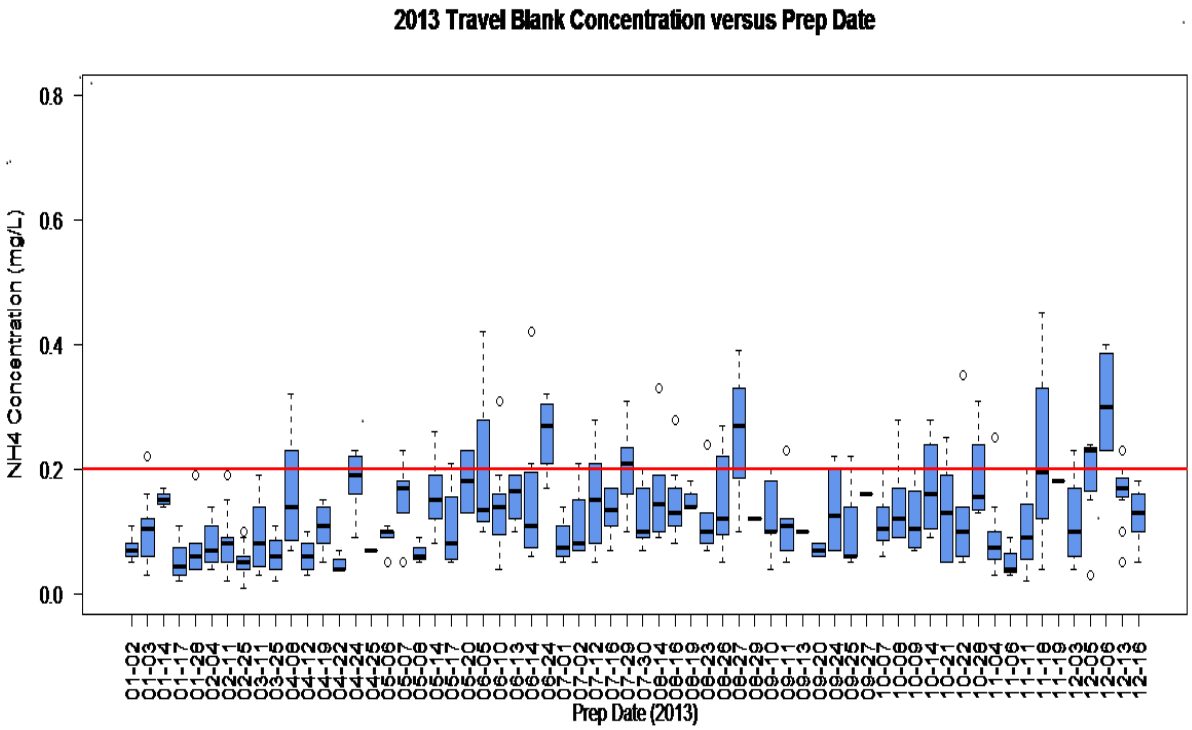

Figure 11. Box and whisker plot showing NH_4^+ concentrations in 10 mL extracts of AMoN passive travel blanks in 2013, grouped by preparation date

The AMoN travel blanks acceptance limit is 0.200 mg/L of NH_4^+ in the 10 mL sampler extract. The median NH_4^+ concentration is 0.106 mg/L in 2013, but like in previous years, numerous travel blanks exceeded the limits throughout the year (Figure 11), and the amount of exceedances is persistently increasing (14.9% in 2013 vs. 8.4 % in 2012).

The reason for the numerous travel blank exceedances continues to be investigated. In 2011-2012; efforts were focused on alternate methods for cleaning the reused passive sampler bodies. The current procedure of cleaning, started November 2012 (SOP PR 4044), includes:

1. sonicating the bodies in ~ 2% heated (60 °C) KOH (DECON 90) laboratory detergent solution during 2 hours;
2. an overnight soak in this solution;
3. followed by a sonication rinse in DI water;
4. the final sonication rinse of sampler bodies is analyzed for NH_4^+ and PO_4^{3-} .

Additional cleanings are added if necessary. The cleaning procedure is complete when the concentration of NH_4^+ and PO_4^{3-} in DI after the final sonication rinse is lower than the MDL. These changes did not reduce the background levels detected in travel blanks, and thus the investigation continued.

In November 2013, the CAL began testing the glass jars that are used for transportation of samplers to sites and back to CAL. The research will continue in 2014.

Special Studies

NTN Samples Dilution Study

A study was conducted in 2012-2013 to assess the uncertainty that is introduced when a sample is diluted.

The following conclusions were made:

- Historic WD samples with dilution factors between 1.8 and 6.6 are valid;
- Non-diluted samples provide better measurements for many analytes, particularly for Ca^{2+}, Mg^{2+}, Br^{-} and PO_4^{3-}.

Details of that study are presented in a poster at the Fall 2013 NADP Scientific Symposium. The title of the poster is "Sample Dilution Study", and it is available on the NADP website (http://nadp.isws.illinois.edu/nadp2013).

External Quality Assurance

The CAL participated in four external proficiency testing studies throughout 2013. The study identifier and websites with study details and results are shown in Table 22. The CAL's performance was consistent with that of other top-performing laboratories participating in each of the studies.

Table 22. 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 48 and 49	World Meteorological Organization/Global Atmospheric Watch (WMO/GAW)	http://www.qasac-americas.org/
Study 102 and 103	Environment Canada Proficiency Testing Program	Available upon request
Study 31	Norwegian Institute for Air Research (NILU)	Available upon request

Conclusions

The CAL performed consistently throughout 2013 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.isws.illinois.edu/lib/qaplans/qapCal2011.pdf

NADP Network Quality Assurance Plan 2011
05http://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.

Sample Dilution Study. N. Gartman, M. Rhodes, C. Lehmann and T. Dombek. Poster, presented at the Annual Meeting and Scientific Symposium of the National Atmospheric Deposition Program, Park City, UT October 8 - 11, 2013.