

Quality Assurance Report
National Atmospheric Deposition Program
2014

Laboratory Operations
Central Analytical Laboratory

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List of Abbreviations

AIRMoN	Atmospheric Integrated Research Monitoring Network
AMoN	Ammonia Monitoring Network
CAL	Central Analytical Laboratory
DI	Deionized Water
FB	Deionized Water Quality Control Internal Blank
FH	High Concentration Quality Control Internal Blank
FIA	Flow Injection Analysis
FL	Low Concentration Quality Control Internal Blank
FR50	A synthetic rainwater solution formulated to approximate the 50 th percentile concentrations of NADP/NTN
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
MDL	Method Detection Limit
NADP	National Atmospheric Deposition Program
NTN	National Trends Network
QA	Quality Assurance
QC	Quality Control
PO	Program Office
SOP	Standard Operating Procedure

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. 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). 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 differs in that AIRMoN samples are collected daily and NTN samples are collected weekly. Also, NTN does not report PO_4^{3-} . For consistency in this report, acidity is reported in pH units, conductivity is reported as $\mu\text{S}/\text{cm}$ (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 (see Reference 1). A summary of CAL standard operating procedures (SOPs) is available on the CAL website (see Reference 2). The analytical methods used for each ion are shown in Table 1. Instrument and method detection limits are provided in Table 2 (2014) and Table 3 (2015).

Table 1. CAL Analytical Methods

	Analytical Method/Instrument/Vendor	Method / CAL SOP #
pH	Electrometric Method of pH Measurement with a Glass Electrode / Ion-Selective Glass Electrode / <i>Broadley-James Corporation</i> / Seven Multi pH-Meter / <i>Mettler Toledo</i>	EPA Method 150.1 USGS Method I-1586 CAL SOP AN-0023
Specific Conductance	Conductance by Conductivity Meter / Electrical Conductivity Cell YSI 3253 K=1.0/cm; YSI 3200 Conductivity Instrument / <i>YSI Inc</i>	EPA Method 120.1 CAL SOP AN-0019
Bromide (Br⁻) Chloride (Cl⁻) Nitrate (NO₃⁻) Sulfate (SO₄²⁻)	Ion Chromatography (IC) / Dionex ICS 2000 and Dionex ICS 5000 / <i>Thermo</i>	EPA Method 300.1 ASTM Method D-5085-95 CAL SOP AN-0018
Ammonium (NH₄⁺)	Flow Injection Analysis (FIA) Colorimetry / QuikChem 8500/ <i>HACH/Lachat Instruments</i>	EPA Method 350.1 Lachat Method 10-107-06-1B CAL SOP AN-0014 CAL SOP AN-4022
Orthophosphate (PO₄³⁻)	Flow Injection Analysis (FIA) Colorimetry / QuikChem 8500/ <i>HACH/Lachat Instruments</i>	EPA Method 365.1 Lachat Method 10-115-01-1B CAL SOP AN-0021
Calcium (Ca²⁺) Magnesium (Mg²⁺) Sodium (Na⁺) Potassium (K⁺)	Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) / VISTA-PRO / <i>Agilent Technology</i>	EPA Method 200.7 ASTM Method D1976-12 CAL SOP AN-0016

Figure 1 shows the CAL’s organization. It is important to note that QA chemist works independently, and reports to CAL director.

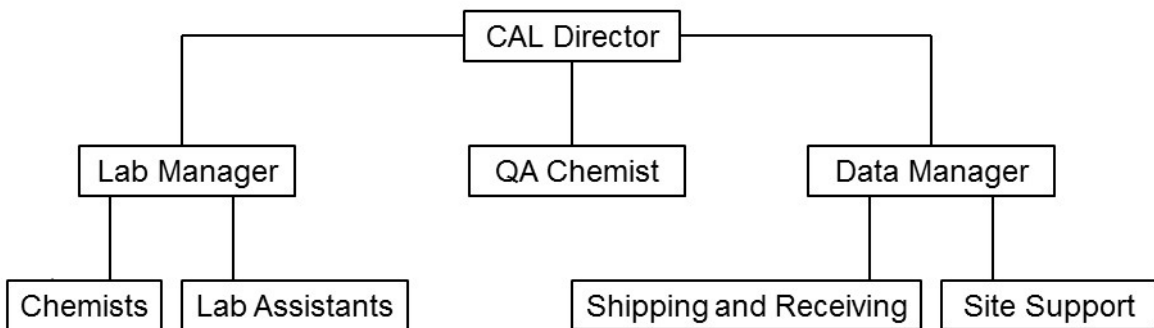


Figure 1. CAL’s organization

Significant Changes in 2014

- The 2014 QA Plan (Version 7) was approved and posted on the NADP website in May 2014.
- The new Ion Chromatography instrument Thermo/Dionex ICS-5000 was installed in March 2014. The instrument was approved by 8/20/2014.
- The new Flow Injection Analysis instrument QuickChem 8500 for AMoN network was installed in March 2014. The instrument was approved 6/23/2014.
- DI water polishers were upgraded. Five new polishers (Milli-Q Advantage) from Evoqua Water Technologies were installed in May 2014.
- The external review of the CAL was conducted in June 3-5, 2014.
- Following a recommendation from subcommittees, the AIRMoN changed to bag sampling on 10/1/2014.
- Staff changes:
 - Gustava Hoskins left the position of technical assistant in May 2014.
 - Molly Romine began working as a sample processing assistant as a temporary employee (May – November 2014).
 - Ruth Parish was hired as a sample data processing assistant from May 2014 to December 2014 (temporary employee).
 - Theresa Ingersoll left the position of samples receiving clerk in June 2014.
 - Lydia Douglas began sample data processing in January 2014, and began working as a supplies processing assistant in June 2014.
 - Katie Blaydes was approved to measure pH and conductivity in August 2014.
 - Annette Wells was approved for working on IC on 9/5/2014 and for sample processing on 12/15/14.

Quality Assurance/Quality Control

Objectives

Quality Assurance (QA)/Quality Control (QC) within the CAL is an “all-hands” effort. This is a multi-tiered 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 $\pm 10\%$ if the value is ≥ 100 times the MDL, or $\pm 20\%$ if the value is between 10 and 100 times MDL. If the value is less than 10 times MDL, a maximum allowable bias shall not exceed \pm MDL [2014 QAP Section B-4.2.2]. 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 (i.e. samples, analyzed after the last check that was in control) must be reanalyzed. If the reanalysis sample is out of control, the analyst analyzes the archive bottle of the sample and sends comments to 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 procedures

Instrument Detection Limit. Blank samples without analytes (e.g., deionized water [2014 CAL QAP: Section B-6.1.3]) are analyzed to evaluate false positive results for each instrument. The results are used to calculate the *Instrument Detection Limit (IDL)*.

Method Detection Limit (MDL) [2014 QAP Section B-4.2] 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 measured throughout the year on all instruments. Cation MDL standard is used to determine MDL for cations (Ca^{2+} , K^+ , Mg^{2+} , Na^+ and NH_4^+), and Anion MDL standard is used to determine MDL for anions (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 2013 are used to calculate MDLs for 2014 (Table 2), and solutions measured during 2014 are used to calculate MDLs for 2015 (Table 3). The calculated MDLs are provided to the NADP Program Office for data released to the public.

Approximately once a month QA specialists sent six blind samples to the laboratory for analysis:

- one Anion MDL and one Cation MDL samples;
- one Anion MDL and one Cation MDL samples processed as an NTN sample;
- one Anion MDL and one Cation MDL samples processed as an AIRMoN sample.

Deionized (DI) water blind samples were also analyzed. The results were used to calculate IDLs and MDLs (laboratory MDL; NTN and AIRMoN MDLs).

Table 2. 2014 MDLs and IDLs

Ion	IDL (mg/L)	Laboratory MD (mg/L)	AIRMoN MDL* (mg/L)	NTN MDL** (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	0.000	0.004	0.005	0.008
Nitrate	0.000	0.004	0.004	0.007
Sulfate	0.000	0.002	0.004	0.005
Bromide	0.000	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 AC8684L – AC9681L

**For NTN sample range TM2705SW – TN6516SW

Table 3. 2015 MDLs and IDLs

Ion	IDL (mg/L)	Laboratory MDL (mg/L)	AIRMoN MDL* (mg/L)	NTN MDL** (mg/L)
Calcium	0.0005	0.002	0.002	0.009
Potassium	0.0010	0.001	0.001	0.002
Magnesium	0.0004	0.001	0.001	0.002
Sodium	0.0007	0.001	0.001	0.006
Chloride	0.002	0.004	0.004	0.005
Nitrate	0.000	0.004	0.004	0.005
Sulfate	0.002	0.004	0.004	0.005
Bromide	0.000	0.004	0.004	0.005
Ammonium	0.007	0.008	0.009	0.016
Orthophosphate	0.002	0.004	0.004	0.005

*For AIRMoN sample range starting with AC9682L

**For NTN sample range starting with TN6516SW

A method to determine MDLs for AMoN is in development.

Daily quality control is assured through the use of QC check samples, replicate samples, split samples. Details are presented in the Quality Assurance Plan (QAP). 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) (Table 4). “Faux rain” FR50 is 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 PO₄³⁻, as PO₄³⁻ affects the NH₄⁺ concentration.

Table 4. Target mean concentrations and acceptable ranges ($\pm 3 \times \text{stdev}$) for QC check solutions in 2014

Parameter	FR50	FL	FH	FB
pH	4.88 \pm 0.12	4.35 \pm 0.10	6.97 \pm 0.10	5.63 \pm 0.30
Specific Conductance ($\mu\text{S}/\text{cm}$)	9.7 \pm 1.0	5.3 \pm 0.5	20.3 \pm 2.0	1.0 \pm 0.6
Calcium (mg/L)	0.132 \pm 0.009	0.040 \pm 0.004	0.500 \pm 0.039	0.000 \pm 0.001
Magnesium (mg/L)	0.024 \pm 0.003	0.010 \pm 0.001	0.102 \pm 0.010	0.000 \pm 0.001
Sodium (mg/L)	0.057 \pm 0.006	0.040 \pm 0.004	0.500 \pm 0.039	0.000 \pm 0.001
Potassium (mg/L)	0.021 \pm 0.003	0.010 \pm 0.002	0.102 \pm 0.010	0.000 \pm 0.001
Chloride (mg/L)	0.106 \pm 0.009	0.025 \pm 0.006	3.025 \pm 0.120	0.000 \pm 0.004
Sulfate (mg/L)	0.861 \pm 0.036	0.501 \pm 0.030	5.000 \pm 0.165	0.000 \pm 0.002
Nitrate (mg/L)	0.986 \pm 0.036	0.493 \pm 0.030	5.000 \pm 0.165	0.000 \pm 0.004
Bromide (mg/L)	0.019 \pm 0.003	0.024 \pm 0.005	3.025 \pm 0.120	0.000 \pm 0.004
Ammonium (mg/L)	0.235 \pm 0.015	0.050 \pm 0.009	1.500 \pm 0.075	0.000 \pm 0.008
Orthophosphate(mg/L)	N/A	0.015 \pm 0.003	0.100 \pm 0.009	0.000 \pm 0.004

Orthophosphate internal verification standards (**FLN** and **FHN**) are prepared separately using standards purchased from VHGLabs (<http://www.vhglabs.com/>) (Table 5).

Table 5. Target concentrations and acceptable ranges for orthophosphate QC solutions in 2014

Parameter	Low standard (FLN)	High standard (FHN)
Orthophosphate (mg/L)	0.031 \pm 0.006	0.155 \pm 0.015

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.

Internal blind samples [2014 QAP Section B-9.2]. Internal blind samples are evaluated monthly. Five different solutions (see their target concentrations in Table 6) are used for the internal blind study: deionized water (DI), Anion MDL standard, Cation MDL standard, FR50 and BIGMOOSE-02. BIGMOOSE-02 is an external soft lake water certified reference standard purchased from Environment Canada (<https://www.ec.gc.ca/>). No external rain water certified reference standards were available for purchase in 2014.

In 2014, blind samples were submitted weekly for both NTN and AIRMoN networks. Blind samples are processed in the same way as field samples, including exposure to sampling buckets and lids used for each of the networks.

Table 6. Control internal and external blind solutions target concentrations

Parameter	DI Water Target Concentration	FR50 Target Concentration	Cation MDL Target Concentration	Anion MDL Target Concentration	BIGMOOSE-02 Target Concentration
pH	5.63	4.88	5.55	5.55	6.02
Specific Conductance (µS/cm)	1.0	9.7	1.7	1.6	21.2
Calcium (mg/L)	<0.004*	0.132	0.010	0.000	2.010
Magnesium (mg/L)	<0.002*	0.024	0.005	0.000	0.327
Sodium (mg/L)	<0.002*	0.057	0.005	0.013	0.731
Potassium (mg/L)	<0.002*	0.021	0.006	0.032	0.326
Chloride (mg/L)	<0.005*	0.106	0.064	0.021	0.462
Sulfate (mg/L)	<0.005*	0.861	0.019	0.015	5.080
Nitrate (mg/L)	<0.005*	0.986	0.043	0.023	0.792
Bromide (mg/L)	<0.005*	0.019	NA	0.015	NA
Ammonium (mg/L)	<0.008*	0.235	0.027	0.005	0.034
Orthophosphate(mg/L)	<0.005*	NA	NA	0.023	NA

* The average historic (2009 – 2014) MDL value

Reanalysis Samples [2014 QAP Section C-2.0]. 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 Figure 2 illustrates the flow of data from the CAL to the NADP Program Office.

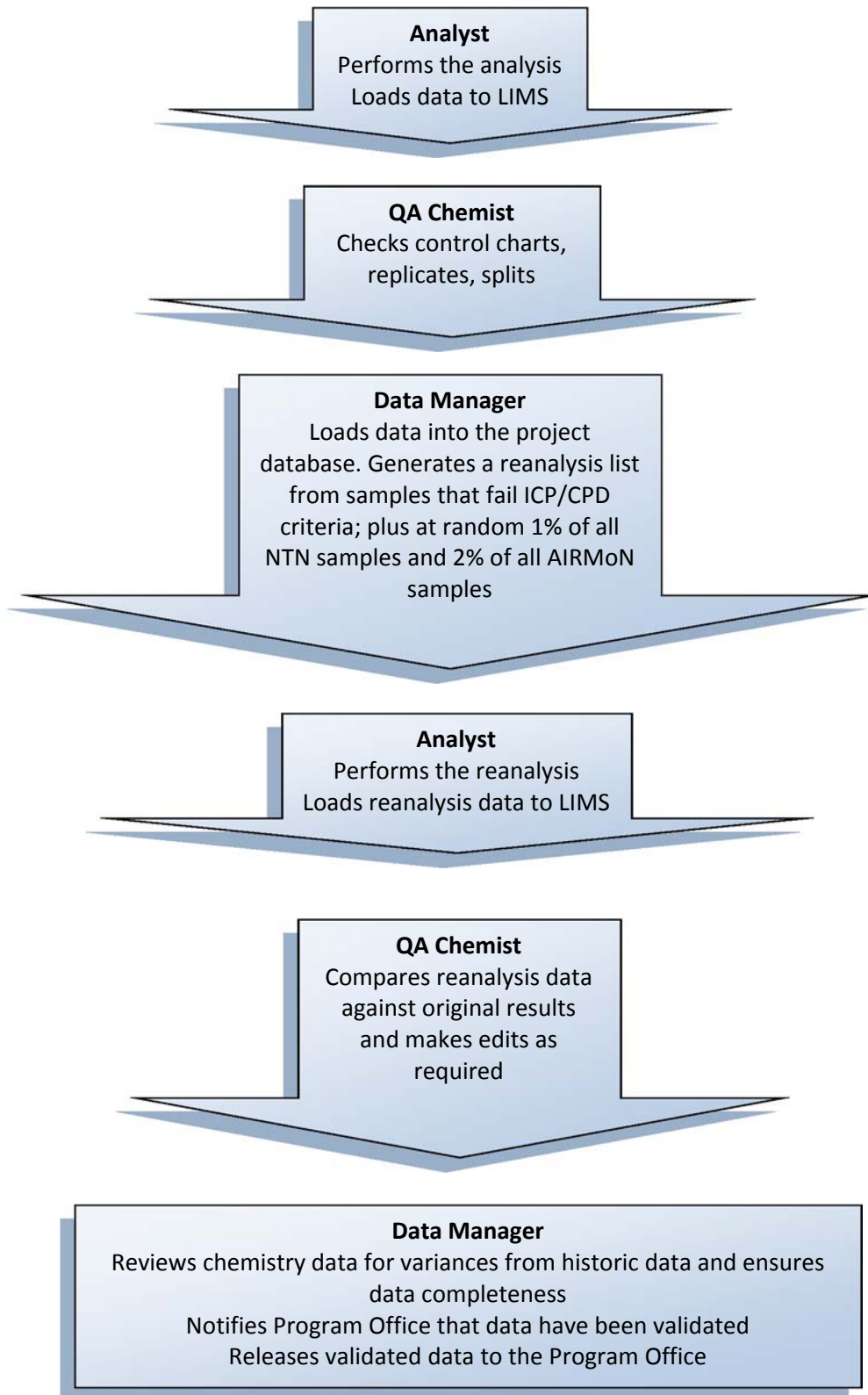


Figure 2. Flow of data from the CAL to the Program Office

Quality Control Discussion

Control Charts

In 2014, all analytical values for FR50, FL, FH and FB check solutions were within control for NTN, AIRMoN and AMoN data submitted to the Program Office [2014 QAP Section C-5.6.3]. Number of analyzed QC samples (FR50, FL, FH and FB) for each analyte and number and percentage of measurements within the warning ranges are presented in Table 7. The Data Quality Objectives (DQOs) as defined in the CAL QAP were met.

A maintenance schedule is established for each instrument. If QC measurements exceed warning limits over two times in a row, the instrument is restandardized. If that does not resolve the problem, further corrective actions are taken as described in [2014 QAP Sections 5.6.3.2 – 5.6.3.4].

An example control chart is shown in Figure 3.

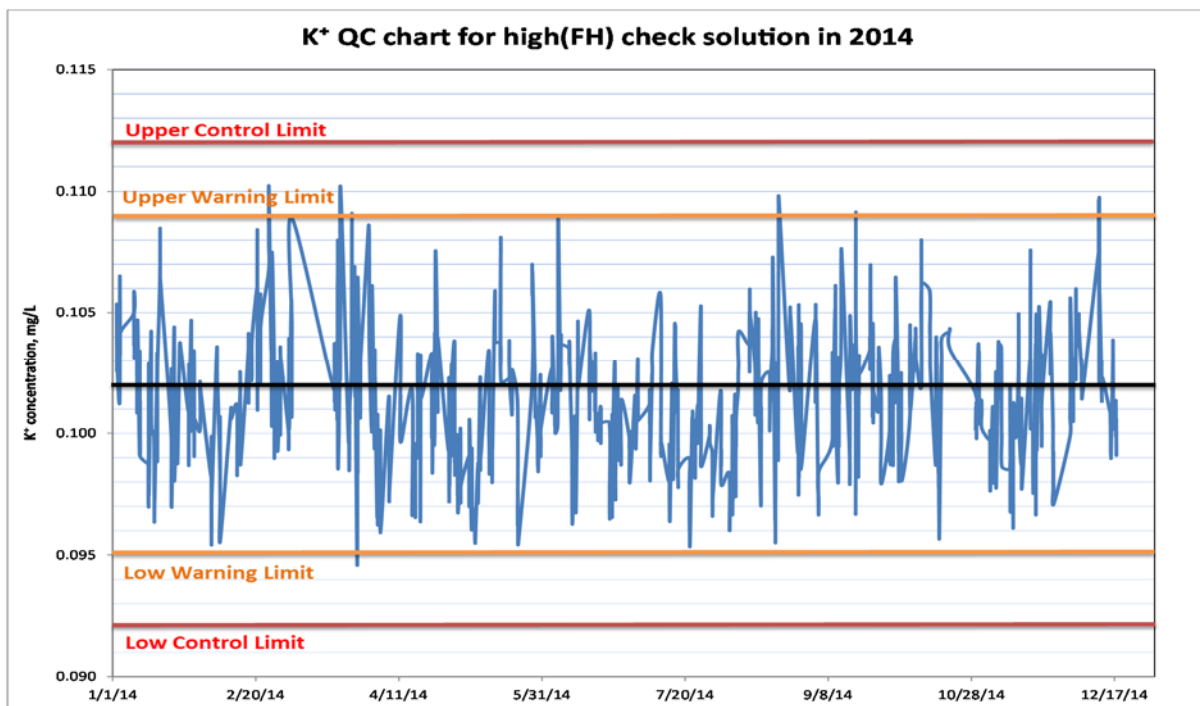


Figure 3. Example control chart in 2014

Table 7. Number of analyzed QC samples (FR50, FL, FH and FB) and number and percentage of QC values exceeding the warning limits in 2014

Parameter	FR50			FL			FH			FB		
	N	Number of values exceeding warning	% of values exceeding warning limits	N	Number of values exceeding warning	% of values exceeding warning limits	N	Number of values exceeding warning	% of values exceeding warning limits	N	Number of values exceeding warning	% of values exceeding warning limits
pH	1038	50	4.82	1571	11	0.70	1591	4	0.25	1197	17	1.42
Specific Conductance (µS/cm)	753	12	1.59	1362	10	0.73	1378	0	0.00	826	32	3.87
Calcium (mg/L)	1008	40	3.97	877	0	0.00	1109	27	2.43	361	0	0.00
Magnesium (mg/L)	1039	8	0.77	897	0	0.00	1107	2	0.18	364	0	0.00
Sodium (mg/L)	1033	1	0.10	888	0	0.00	1096	33	3.01	353	0	0.00
Potassium (mg/L)	1027	11	1.07	896	0	0.00	1097	15	1.37	342	3	0.88
Chloride (mg/L)	1007	15	1.49	1117	9	0.81	1002	7	0.70	664	0	0.00
Sulfate (mg/L)	997	11	1.10	1124	19	1.69	1000	19	1.90	668	0	0.00
Nitrate (mg/L)	994	11	1.11	1124	20	1.78	999	3	0.30	669	0	0.00
Bromide (mg/L)	999	8	0.80	1124	3	0.27	999	14	1.40	669	0	0.00
Ammonium (mg/L)	983	15	1.53	1249	17	1.36	1153	46	3.99	944	0	0.00
Orthophosphate(mg/L)	NA	NA	NA	1003	8	0.80	915	19	2.08	661	26	3.93

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. The results of split samples met the requirements in 2014 as specified in the 2014 CAL Quality Assurance Plan.

133 pairs of split samples for NTN and AIRMoN were processed. The minimum, average, maximum and median Absolute Percent Differences (APD) * are shown in Table 8. Only pairs with concentrations of analytes higher than 10 times the MDL were evaluated.

Since 95% of all NTN samples for the 5 year period (2009 -2013) 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.

If samples fall outside the allowable variability for the Absolute Percent Difference (APD), analysts investigate the cause and analyze additional samples within the run.

* APD =abs (value1-value2) / average (value1+value2) x 100%

Table 8. Minimum, mean, maximum and median absolute percent differences (APDs) for split samples in 2014

Parameter	Minimum percent difference (%)	Mean percent difference (%)	Median percent difference (%)	Maximum percent difference (%)
pH	0.0	0.6	0.4	5.1
Specific Conductance	0.0	1.6	0.9	13.3
Calcium	0.0	2.8	1.6	19.4
Potassium	0.0	2.8	1.3	53.7*
Magnesium	0.0	2.5	1.7	19.8
Sodium	0.0	0.8	1.0	18.4
Chloride	0.0	1.4	0.5	16.6
Sulfate	0.0	0.7	0.3	6.6
Nitrate	0.0	0.6	0.2	12.0
Ammonium	0.0	1.7	0.9	20.0

* The high APD value (53.7%) was detected for the pair of split AIRMoN samples AC9191L. Upon reanalysis the same results were obtained. AIRMoN samples are not filtered, and the presence of particles in the original sample and the fact that potassium concentrations in precipitation are typically very low caused the large maximum percent difference in the concentration of potassium.

Replicate Samples

Tables 9 and 10 show the absolute percent difference (APD) values for replicate NTN and AIRMoN samples. Table 9 includes samples whose concentrations were 10 to 100 times the MDL, and conductivity values were 10 to 100 $\mu\text{S}/\text{cm}$ (allowable bias for analytes is $\pm 20\%$; for conductivity $\pm 10\%$). Table 10 includes samples whose concentrations were ≥ 100 times the MDL (allowable bias $\pm 10\%$). Only 0.5% of all NTN samples have conductivity values higher than 100 $\mu\text{S}/\text{cm}$, so conductivity results are not presented for this range.

Table 9. Replicate samples, concentrations 10 to 100 times the MDL

Parameter	Concentration Range: 10 to 100 x MDL	N	Minimum APD %	Average APD %	Maximum APD %
pH	pH > 5.00	146	0.0	1.0	3.6
Specific Conductance	10 to 100 µS/cm	38	0.0	2.6	6.9
Calcium	0.010 – 0.100 mg/L	77	0.3	4.7	17.3
Potassium	0.010 – 0.100 mg/L	121	0.0	4.4	16.1
Magnesium	0.010 – 0.100 mg/L	121	0.3	3.6	14.1
Sodium	0.010 – 0.100 mg/L	90	0.5	3.6	21.3
Chloride	0.040 – 0.400 mg/L	172	0.0	1.2	17.3
Sulfate	0.020 – 0.200 mg/L	27	0.2	1.6	6.1
Nitrate	0.040 – 0.400 mg/L	54	0.1	1.0	3.5
Ammonium	0.080 – 0.800 mg/L	96	0.2	2.8	20.1

Table 10. Replicate samples, concentrations greater than 100 times the MDL

Parameter	Concentration Range: > 100 x MDL	N	Minimum APD %	Average APD %	Maximum APD %
pH	pH < 5.00	52	0.2	0.8	2.1
Calcium	> 0.100 mg/L	92	0.1	2.7	8.9
Potassium	> 0.100 mg/L	14	0.4	2.8	6.9
Magnesium	> 0.100 mg/L	12	1.0	2.8	5.4
Sodium	> 0.100 mg/L	60	0.1	3.1	9.0
Chloride	> 0.400 mg/L	39	0.0	0.4	2.3
Sulfate	> 0.200 mg/L	234	0.0	0.6	5.5
Nitrate	> 0.400 mg/L	207	0.0	0.4	5.4
Ammonium	> 0.800 mg/L	10	0.3	1.0	1.8

The results of replicate samples met the requirements as specified in the 2014 CAL Quality Assurance Plan Sections B-4.2 – B-4.4.

Quality Assurance Discussion

Reverse Osmosis Deionized (RO DI) and Polisher Deionized (DI) Water Blanks

Deionized water generated through CAL's Reverse Osmosis System is used in the bucket room for washing supplies (buckets, lids, bottles, AMoN glass jars). The RO deionized water, passed through additional polishers, is used for analysis, standards preparation, etc.

RO DI water is tested weekly. Conductivity of RO DI is monitored multiple times during the day when operations are taking place. Polisher DI water is tested once a month.

Table 11 shows the number of exceedances for the RO and polisher DI water blanks.

Table 11. Number of results outside control limits for RO and polishers DI water blanks in 2014

Parameter	RO Water N=50	Polisher DI N=60
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

The polisher and RO DI water blanks met the 2014 acceptance criteria.

Supply Checks

New supplies are evaluated before they are introduced for site or laboratory use at the frequencies specified in Table 12. New supplies are tested using DI water. Polyethersulfone filters are tested using both DI water and FR50 solution.

New brushes for cleaning buckets and bottles are soaked in 6L jars with DI water (changed daily) until no contaminants are detected in DI water.

Table 12. Summary of NTN and AIRMoN new supply checks

Supply Type	Test Frequency	Test Solution	Test Volume	Contact Time
buckets	1 per 8	DI	150 mL	24 hours
bucket lids	1 per 15	DI	50 mL	2 hours
NTN 1-L bottles	1 per 24	DI	150 mL	24 hours
250 mL AIRMoN bottles	1 per 24	DI	50 mL	24 hours
60 mL bottles	1 per batch rinsed	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
bucket and bottle brushes	each	DI	6L	Until DI water is clean
Radiello® cores	2 per lot	DI	10 mL	24 hours

Typically 250 used buckets, lids and 1L bottles are washed weekly. Washed and reused supply cleanliness is monitored daily (Table 13).

Washed and reused supplies are tested using FR50 solution.

Table 13. Summary of NTN and AIRMoN washed/reused supply check

Supply Type	Test Frequency	Test Solution	Test Volume	Contact Time
1 bucket	Daily	FR50	150 mL	24 hours
1 NTN 1-L bottle	Daily	FR50	150 mL	24 hours
1 bucket lid	Daily	FR50	50 mL	24 hours

For new supplies, target levels are based on average historic and current lab MDLs. Values are also compared to the 5th percentile of analyte concentrations in NTN and AIRMoN samples for the five-year period from 2009 to 2013. This method is under evaluation and may change in 2015.

For used supplies, 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 the quartiles plus or minus 1.5 times the interquartile range (1st to 3rd quartiles, indicated by the box length). Values plotted as "X" designate points that are outside the quartiles plus or minus 1.5 times the interquartile range. Such values are considered outside values.

NTN Sample Filters: DI Water and FR50 Solution Checks

Polyethersulfone filters are used to separate the dissolved and suspended fractions found in NTN precipitation samples [2014 QAP Section 6.2]. 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 2014, concentrations of analytes in **DI water** eluents from NTN sample filters were less than average historic MDL concentrations presented in Table 6. No outliers were detected.

The concentrations for all analytes found when leaching filters with **FR50** were within a bias of the same magnitude as the bias established for FR50 QC standard. No outliers were detected.

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 12). Washed and reused buckets, bucket lids and NTN 1L bottles are tested with FR50 solution (see Table 13). More details are in SOPs PR-0009 and PR-0041.

New Buckets. Calcium is used in the manufacture of plastic buckets and sometimes has been detected in new buckets used to collect NTN and AIRMoN wet deposition samples. New buckets are leached with hydrochloric acid to remove Ca²⁺, and then washed and tested.

One bucket per each set of 8 new leached buckets is tested. Seventeen new leached buckets, representing 136 new buckets were tested during 2014. The elevated concentration of calcium was detected in one new bucket DI test solution. All 8 buckets from this set were releached, rewashed and tested again. After the second leaching, the concentration of calcium in DI test solution was 0.001 mg/L.

In 2014, the concentration of Ca^{2+} in new leached and washed buckets was less than the 5th percentile Ca^{2+} concentration for NTN and AIRMoN samples (Figure 4). The median concentration of Ca^{2+} found in new buckets was ~ 0.002 mg/L.

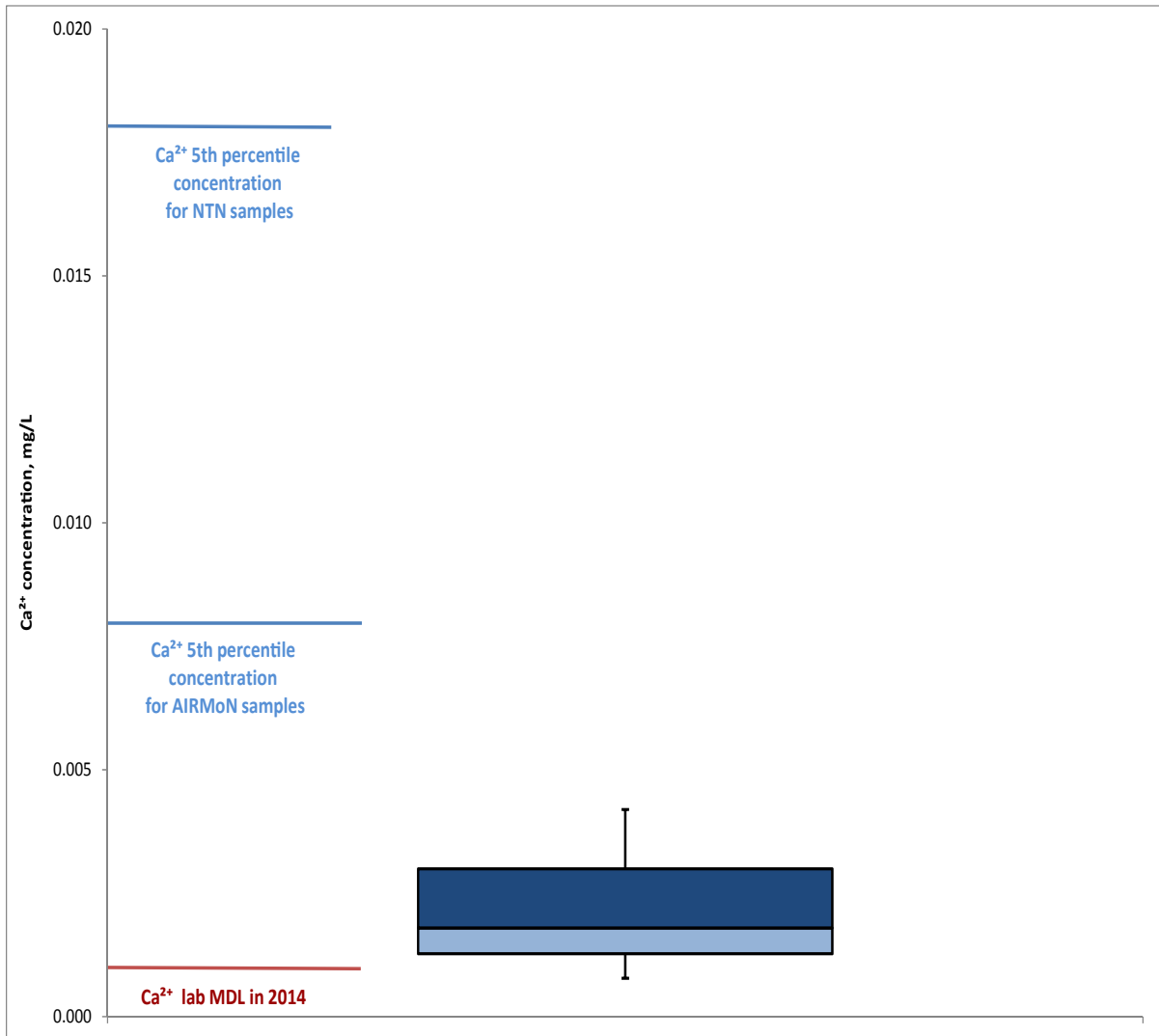


Figure 4. Box and whisker plot showing Ca^{2+} concentrations measured in new buckets blanks in 2014.

Washed and Reused Buckets. When analyte concentrations exceed target limits for supplies that are washed and reused, the supply is rewashed and rechecked in order to be sure that the source of contamination is not the supply's issue (temperature or mechanical deformation, etc.). 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. Results outside of target limits are shown in Table 14. Fourteen buckets were responsible for the twenty two exceedances. All buckets were rewashed and retested, and twelve of them were found to be within control limits. Two buckets were discarded. A number of buckets were also discarded for other reasons including breakage, stains, scratched interior surfaces, etc.

Table 14. Number of results outside of target limits in 2014 for washed and reused buckets tested with FR50 solution

Parameter	FR50 24 Hours N=251
pH	1
Specific Conductance	2
Calcium	9
Potassium	0
Magnesium	1
Sodium	1
Chloride	0
Sulfate	1
Nitrate	1
Ammonium	6
Bromide	0
Orthophosphate	NA

The levels of Ca^{2+} and NH_4^+ , detected routinely in washed and reused buckets, were low in 2014 and mostly were within historic allowable control limits for FR50 solution. Nine outliers for calcium and six outliers for ammonium were detected. Ca^{2+} results for each batch of FR50 solution are shown in Figure 5. NH_4^+ results are shown in Figure 6.

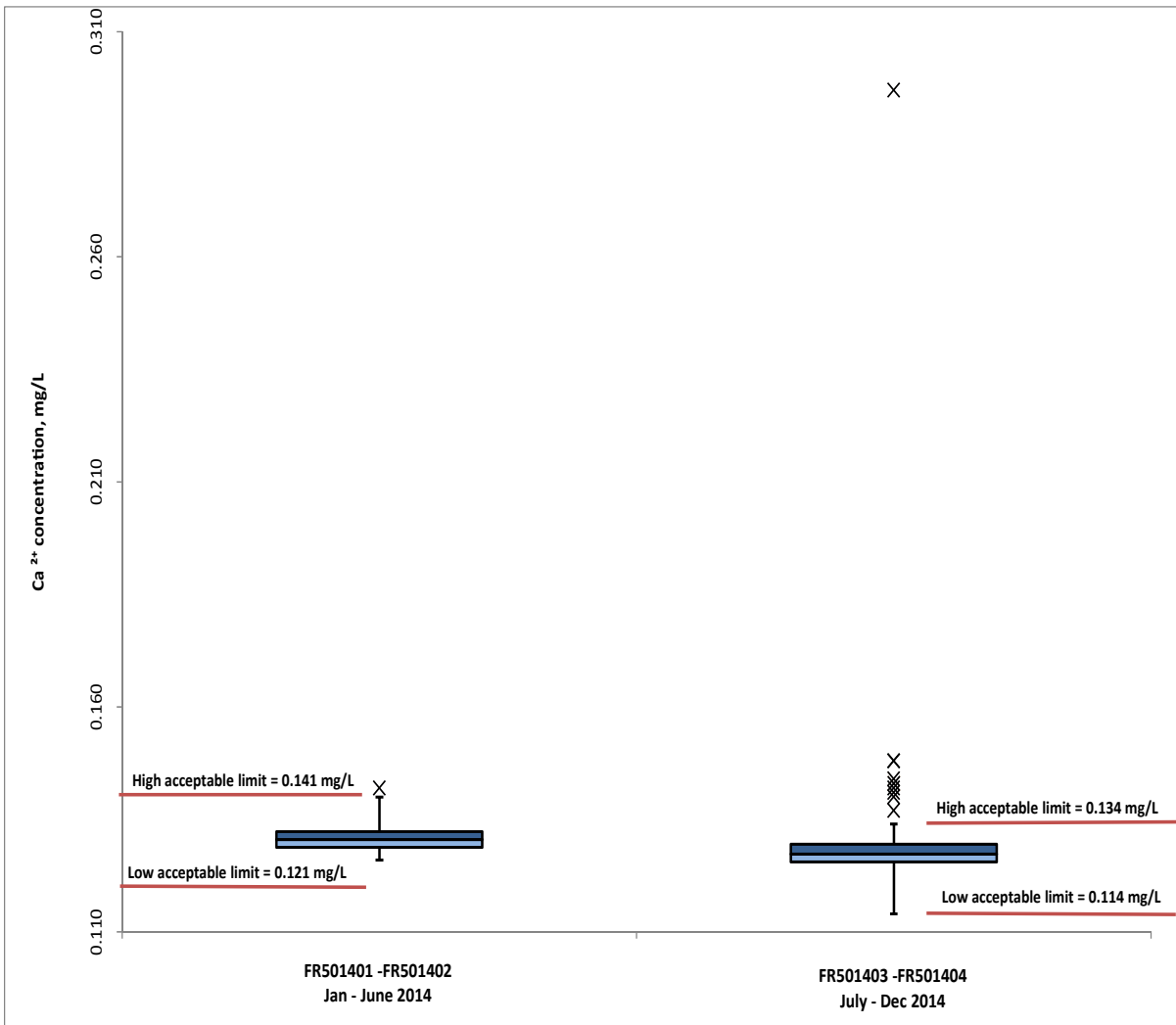


Figure 5. Box and whisker plot showing Ca^{2+} concentrations for washed and reused buckets tested with FR50 solution* in 2014

* In 2014 the CAL prepared four batches of FR50 solution. The first two (FR501401 and FR501402), used in January – June, had the same target and acceptable limits values for Ca^{2+} . Two other batches (FR501403 and FR501404), prepared from a new stock and used in July – December, had a slightly different target and acceptable limits values for Ca^{2+} .

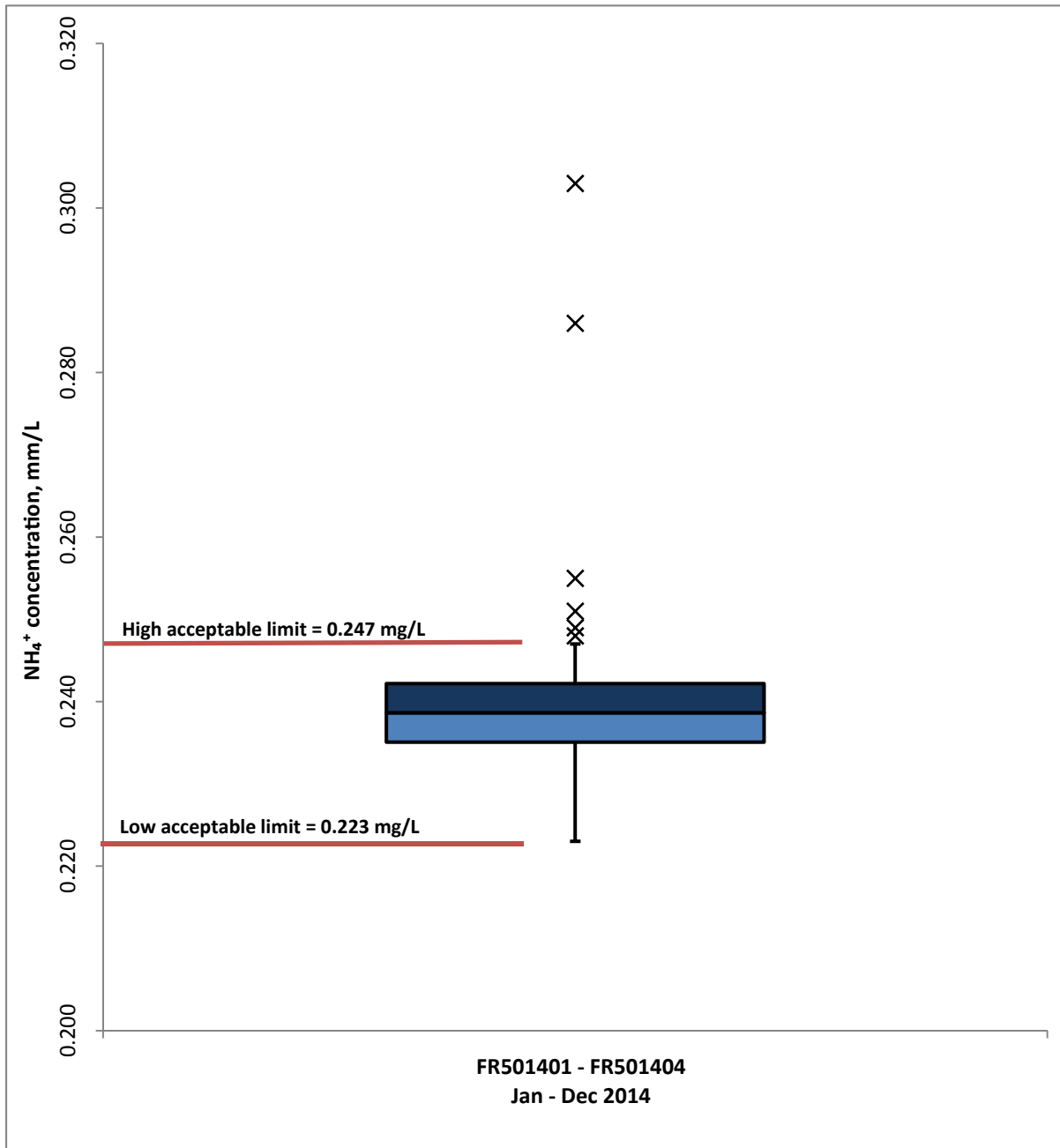


Figure 6. Box and whisker plot showing NH_4^+ concentrations for washed and reused buckets tested with FR50 solution in 2014

AIRMoN sample bottles are single-use Thermo-Fisher 250-mL Nalgene™ bottles. They are not rewashed or reused. NTN 1-L sample bottles are Nalgene™ bottles that are rewashed and reused. After filtering, NTN samples are collected in single-use new Thermo Fisher 60 mL HDPE bottles.

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 2014. There were no outliers.

New 60 mL bottles. Several cartons of 60 mL Nalgene analytical bottles used for NTN samples were inadvertently contaminated with domestic tap water at the CAL. The affected samples included those filtered between 8 October – 15 October, 2014 (NTN LABNO TN3482SW – TN3764SW). The problem supplies were discovered during a routine internal filter blank study. The samples were all rerun with the exception of a few low-volume samples. The unused contaminated bottles were sequestered and discarded.

Washed and Reused NTN 1-L Bottles. During 2014, one NTN bottle was selected from the bottles washed each day and tested. Results outside of target limits are shown in Table 15. The outliers for NH₄⁺ occurred in twelve bottles. Each of these bottles was rewashed and retested, and all of them were subsequently found to be within control limits.

Figure 7 shows NH₄⁺ results measured in FR50 bottle tests in 2014.

Table 15. Number of results outside of target limits in 2014 for washed and reused NTN 1-L bottles tested with FR50 solution

Parameter	FR50 24 Hours N=147
pH	0
Specific Conductance	0
Calcium	2
Potassium	0
Magnesium	0
Sodium	0
Chloride	0
Sulfate	0
Nitrate	0
Ammonium	12
Bromide	0
Orthophosphate	NA

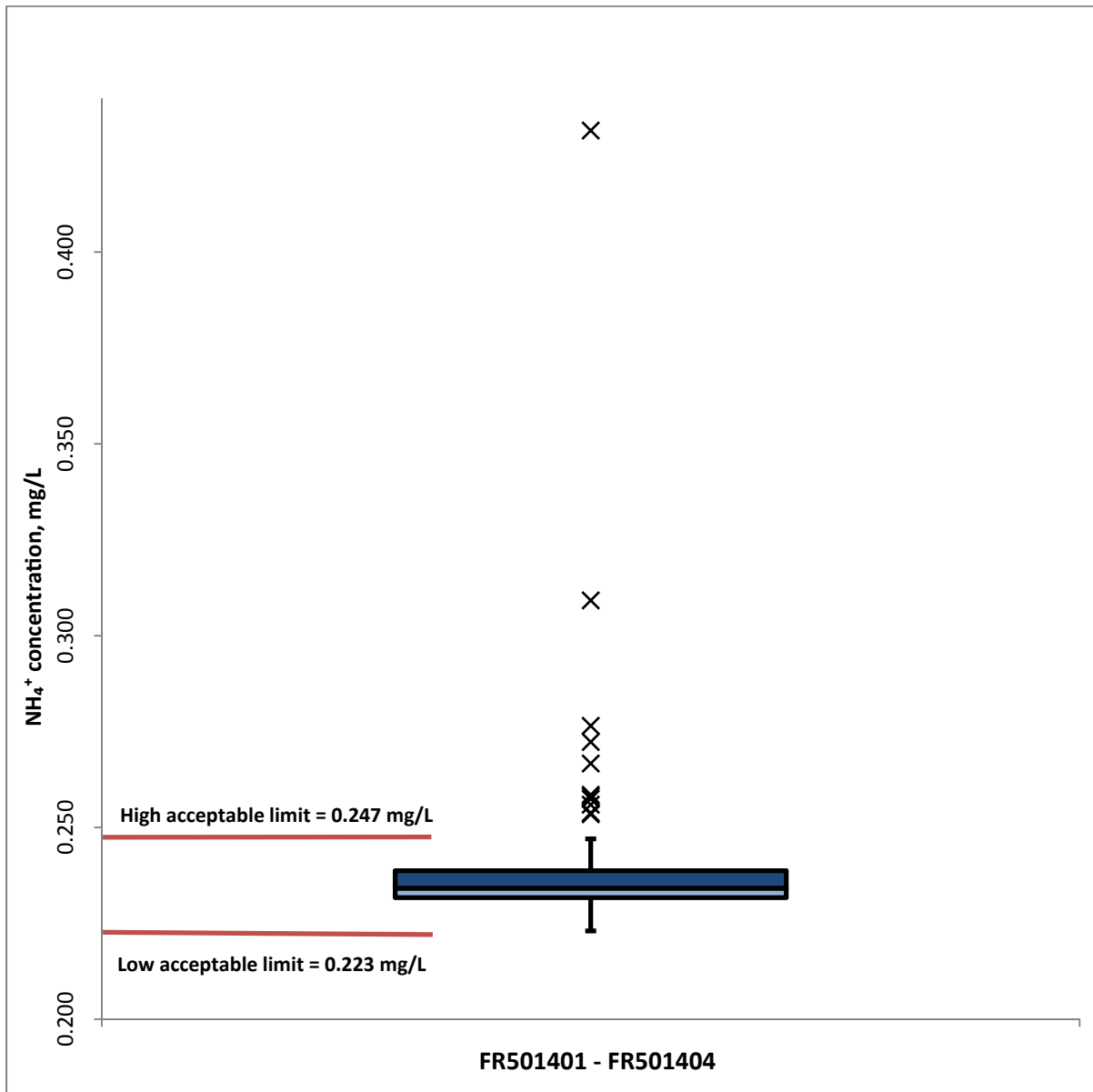


Figure 7. Box and whisker plot showing NH_4^+ concentrations for washed and reused NTN 1-L bottles tested with FR50 solution in 2014

New Lids. No new bucket lids were purchased or tested in 2014.

Washed and Reused Lids. Lid blanks tested with FR50 in 2014 indicated six outliers for Na⁺ and seven outliers for NH₄⁺ (Table 16). Those lids were rewashed and retested. They passed the second check. The single Ca²⁺ outlier was 0.144 mg/L versus a target concentration of 0.132 mg/L and a median concentration of 0.132 mg/L. One K⁺ outlier was 0.026 mg/L versus a target concentration of 0.021 mg/L and a median concentration of 0.022 mg/L. Three Cl⁻ outliers were 0.139, 0.124 and 0.139 mg/L versus a target concentration of 0.106 mg/L and a median concentration of 0.106 mg/L. Box and whisker plots showing Na⁺ and NH₄⁺ concentrations measured in washed and reused lids in 2014 are shown in Figures 8 and 9.

Table 16. Number of results outside of target limits in 2014 for washed and reused bucket lids tested with FR50 solution

Parameter	FR50 N=246
pH	0
Specific Conductance	0
Calcium	1
Potassium	1
Magnesium	0
Sodium	6
Chloride	3
Sulfate	0
Nitrate	0
Ammonium	7
Bromide	0
Orthophosphate	NA

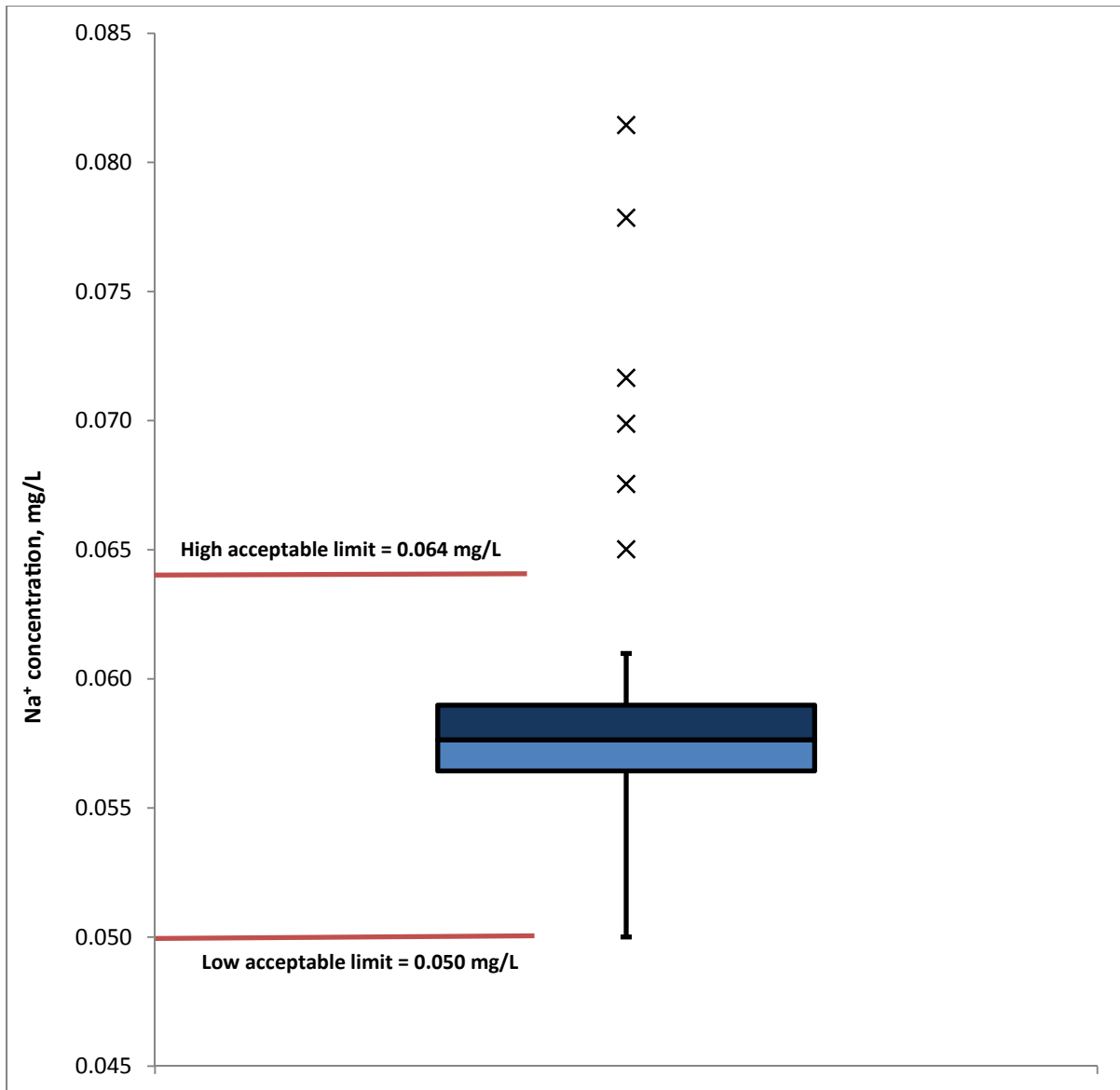


Figure 8. Box and whisker plot showing Na⁺ concentrations for washed and reused lids tested with FR50 solution in 2014

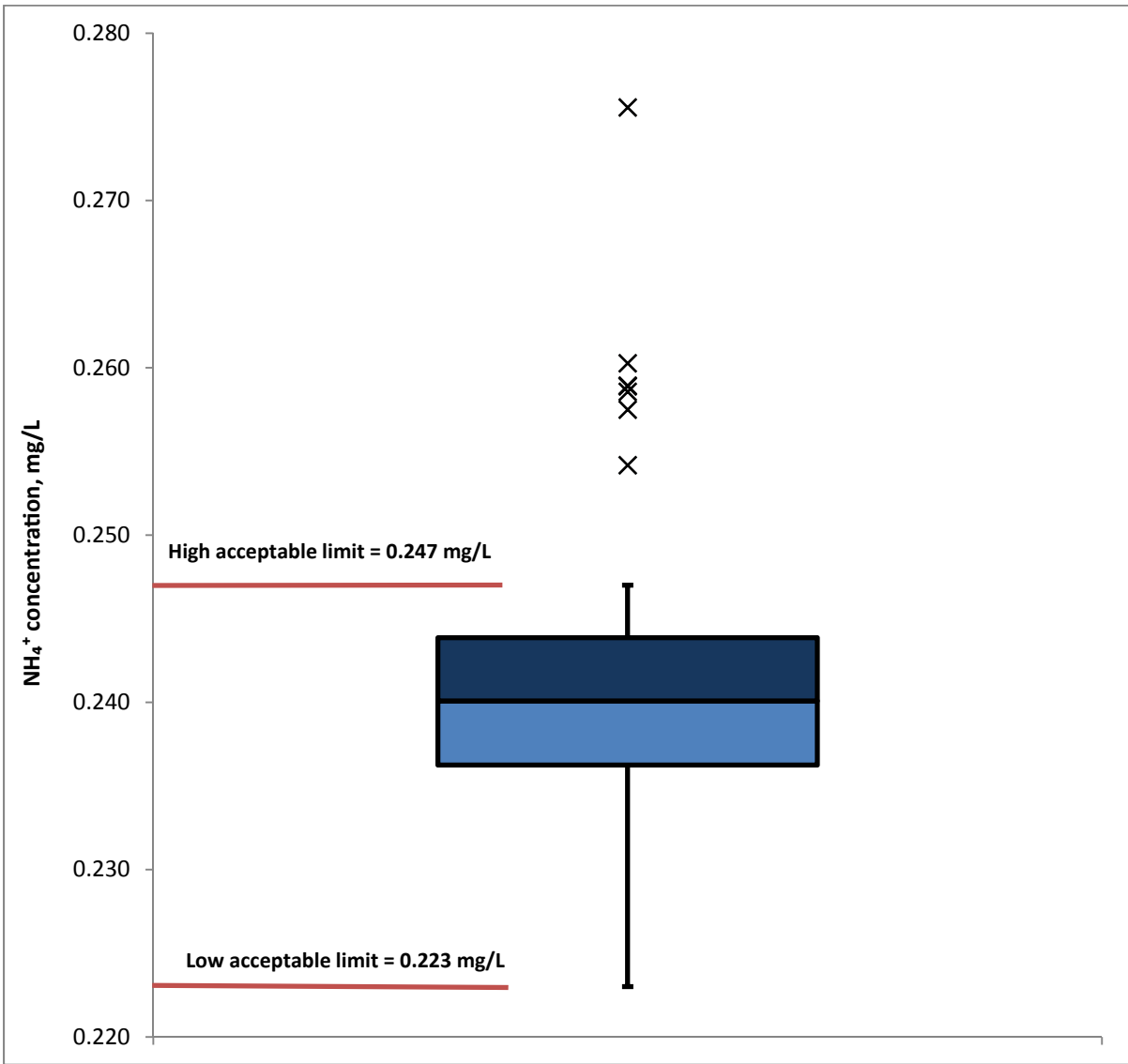


Figure 9. Box and whisker plot showing NH_4^+ concentrations for washed and reused lids tested with FR50 solution in 2014

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. In October 2014, similar tests were added for bags used to collect AIRMoN samples.

Lid Bags. A single lid bag had the elevated concentrations for Na^+ , K^+ and Cl^- . Additional bags from this box passed checks, and no bags were rejected.

Bucket Bags. All bags used to store/ship clean buckets, and bags used to collect AIRMoN samples were within the acceptable target limits for all analytes in 2014.

Internal Blind BIGMOOSE-02 and FR50 Results

Results for internal BIGMOOSE-02 and FR50 blind samples were used to assess post-analysis accuracy and precision of the laboratory throughout the year. In 2014 blind samples were processed as NTN samples and as AIRMoN samples, and then analyzed. The relative standard deviation (RSD)* and percent recovery** were calculated to evaluate precision and accuracy. The results are presented in Tables 17 and 18.

Table 17. Relative Standard Deviations (RSDs) and mean percent recoveries for internal blind BIGMOOSE-02 solution

Parameter	Target	RSD Unfiltered N = 7 (%)	RSD Filtered N = 7 (%)	Recovery Unfiltered N = 7 (%)	Recovery Filtered N = 7 (%)
pH	6.02	1.0	NA	99.6	NA
Specific Conductance	21.2 µS/cm	2.1	NA	101.0	NA
Calcium	2.010 mg/L	5.9	4.8	96.0	93.0
Potassium	0.326 mg/L	2.4	1.2	101.2	101.4
Magnesium	0.327 mg/L	2.7	3.0	100.8	97.9
Sodium	0.731 mg/L	1.3	2.9	97.9	97.8
Chloride	0.462 mg/L	1.0	2.6	103.0	103.1
Sulfate	5.080 mg/L	0.6	1.2	97.7	97.0
Nitrate	0.792 mg/L	1.2	0.8	100.4	99.5
Ammonium	0.034 mg/L	18.1	17.5	138.4	136.6

Table 18. Relative Standard Deviations (RSDs) and mean percent recoveries for internal blind FR50 solution

Parameter	Target	RSD Unfiltered (%) N = 10	RSD Filtered (%) N = 10	Recovery Unfiltered (%) N = 9	Recovery Filtered (%) N = 9
pH	4.88	0.5	NA	99.7	NA
Specific Conductance	9.7 µS/cm	2.2	NA	99.7	NA
Calcium	0.132 mg/L	1.9	3.2	101.2	103.6
Potassium	0.021 mg/L	4.4	4.3	100.1	98.6
Magnesium	0.024 mg/L	2.4	2.6	98.3	111.3
Sodium	0.057 mg/L	1.5	3.0	107.8	101.7
Chloride	0.106 mg/L	2.3	2.9	100.2	99.2
Sulfate	0.861 mg/L	1.0	1.0	100.2	98.0
Nitrate	0.986 mg/L	0.7	1.2	99.7	97.7
Ammonium	0.235 mg/L	3.1	2.9	103.9	103.8
Bromide	0.019 mg/L	5.0	13.4	100.2	95.4

*RSD (%) = (standard deviation/mean value) · 100; **Recovery (%) = (lab value/target value) · 100

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 two percent of samples are selected at random for reanalysis. The results of reanalysis are reviewed by the QA Chemist, and required edits are made.

In 2014, a total of 155 edits were made for NTN samples and 37 edits were made for AIRMoN samples. Changes are documented in the database.

In October 2014 additional samples were reanalyzed due to contamination of several cartons of 60 mL Nalgene bottles used for NTN samples. The affected sample range included 236 analyzed samples. 208 of those samples had an uncontaminated refrigerated archive split. Those archive samples were reanalyzed, and analytical values of all affected samples were edited. The remaining 28 affected samples, which did not have archive splits, were invalidated as having a “significant laboratory analytical issue” (i.e., Screening Level/SL code of L).

The number of field NTN, AIRMoN and AMoN samples analyzed in 2014, and counts of reanalysis, split and blind samples are shown in Table 19.

Table 19. Number of field and Quality Assurance (QA) samples analyzed during 2014

Network	Number of field samples analyzed	Number of QA Samples	
		Reanalysis samples	Blind samples
NTN	11281	1265	90
AIRMoN	779	212	92
AMoN	2641	99	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 FB standards are analyzed during the run for quality control. The analyst also selects 1-2 random samples per batch as replicate samples. All NH_4^+ values for QC standards were within allowable limits in 2014.

During the extraction process, five samples are generated for Quality Control/Quality Assurance. This set includes:

- one lab air QA sample (sampler deployed in the lab for two week period);
- one hood air QA sample (sampler deployed in the passive hood during two week period);
- one extraction hood QA sample (sampler, deployed in the passive hood during the 1 – 3 hours extraction period);
- one lab DI blank (DI water used for extractions, 1 per extraction batch);
- one new core blank (unused cartridge core as received from supplier).

The results of the lab AMoN QA samples for 2014 are shown in Figure 10.

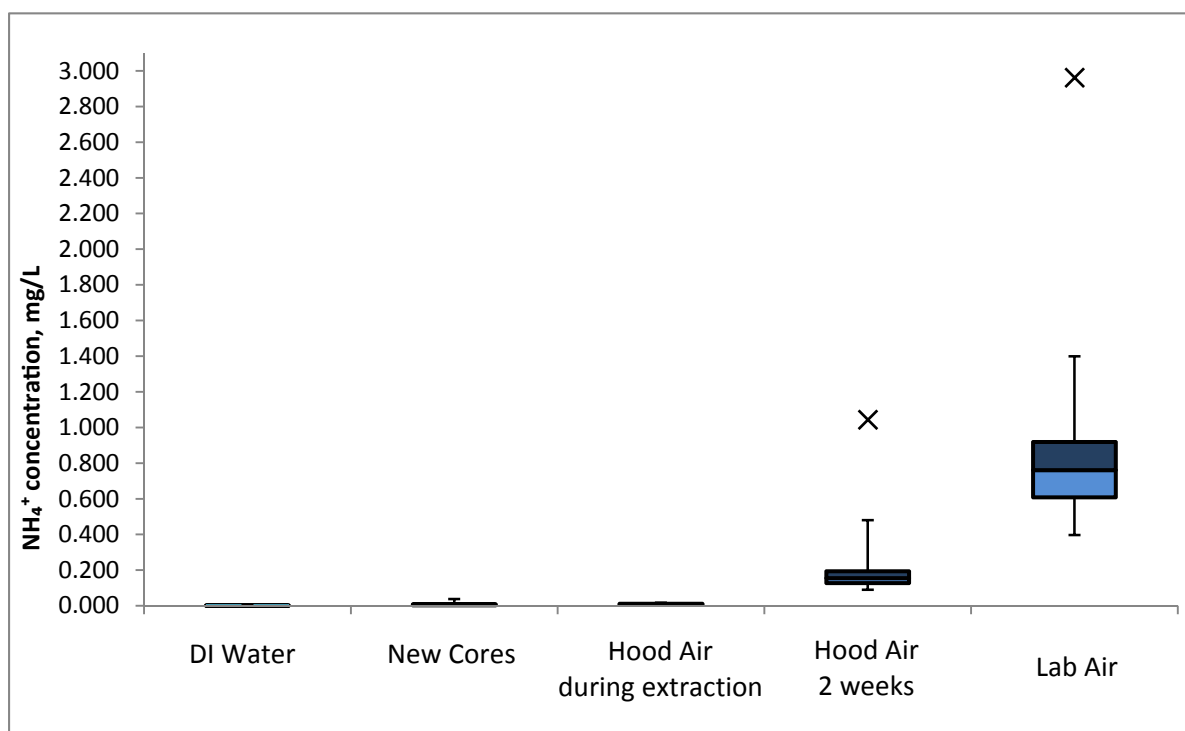


Figure 10. Box and whisker plot showing NH_4^+ concentrations, measured in 2014 in AMoN QA samples: laboratory DI water, 10 mL blank extracts of new cores, hood air blanks and laboratory air blanks

The precision of AMoN triplicate results were calculated as the median absolute percent difference (APD*) of valid deployed samplers measurements, and as the relative standard deviation (RSD**) (see Table 20). Because these results have not been presented in previous reports, data for previous years is presented for comparison.

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

Year	Count	Median ARPD (%)	Mean RSD (%)
2007	59	7.3	11.5
2008	370	7.3	11.5
2009	528	6.8	9.9
2010	521	6.0	10.1
2011***	82	10.5	22.4
2012	90	6.4	12.5
2013	138	4.1	5.3
2014	170	4.7	7.4

* $APD (\%) = ABS \frac{\text{triplicate value} - \text{average of the triplicate values}}{\text{average of the triplicate values}} \cdot 100$

** $RSD (\%) = (\text{stdev}/\text{average of the triplicate values}) \cdot 100$

*** Triplicate measurement frequency was decreased from one in every deployment to one in every 4th deployment in 2011

The CAL compares measurements between Radiello™ passive-type air samplers (in triplicates) and URG™ (University Research Glass) denuders (in triplicates), exposed side by side at the Bondville Station (IL11) during a year. The average and median RPDs**** of NH₃ results from IL11 measured using Radiello™ samplers and URG™ denuders are shown in Table 21. Because these results have not been presented in previous reports, data for previous years (starting with 2009 when the CAL started deploying denuders in triplicate) is presented for comparison. Based on the median RPD, the Radiello™ passive samplers tend to produce slightly lower estimates of NH₃ in ambient air compared to the denuders, but the bias has decreased every year since 2009. The median Radiello™ bias was low in 2014 (-1.2%), and the mean bias was elevated (+12.5%).

Table 21. Median and mean RPDs** for NH₃ measured at IL 11 using Radiello™ passive-type air samplers and URG denuders in 2014**

Year	Count	Median RPD (%)	Mean RPD (%)
2009	25	-22.0	-21.1
2010	25	-13.3	10.8
2011	22	-7.9	-5.4
2012	26	-5.5	-4.0
2013	27	-3.8	-3.24
2014	25	-1.2	12.5

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

Strong agreement between ambient NH₃ measurements using Radiello™ samplers and URG denuders at IL11 during 2014 is shown in Figure 11.

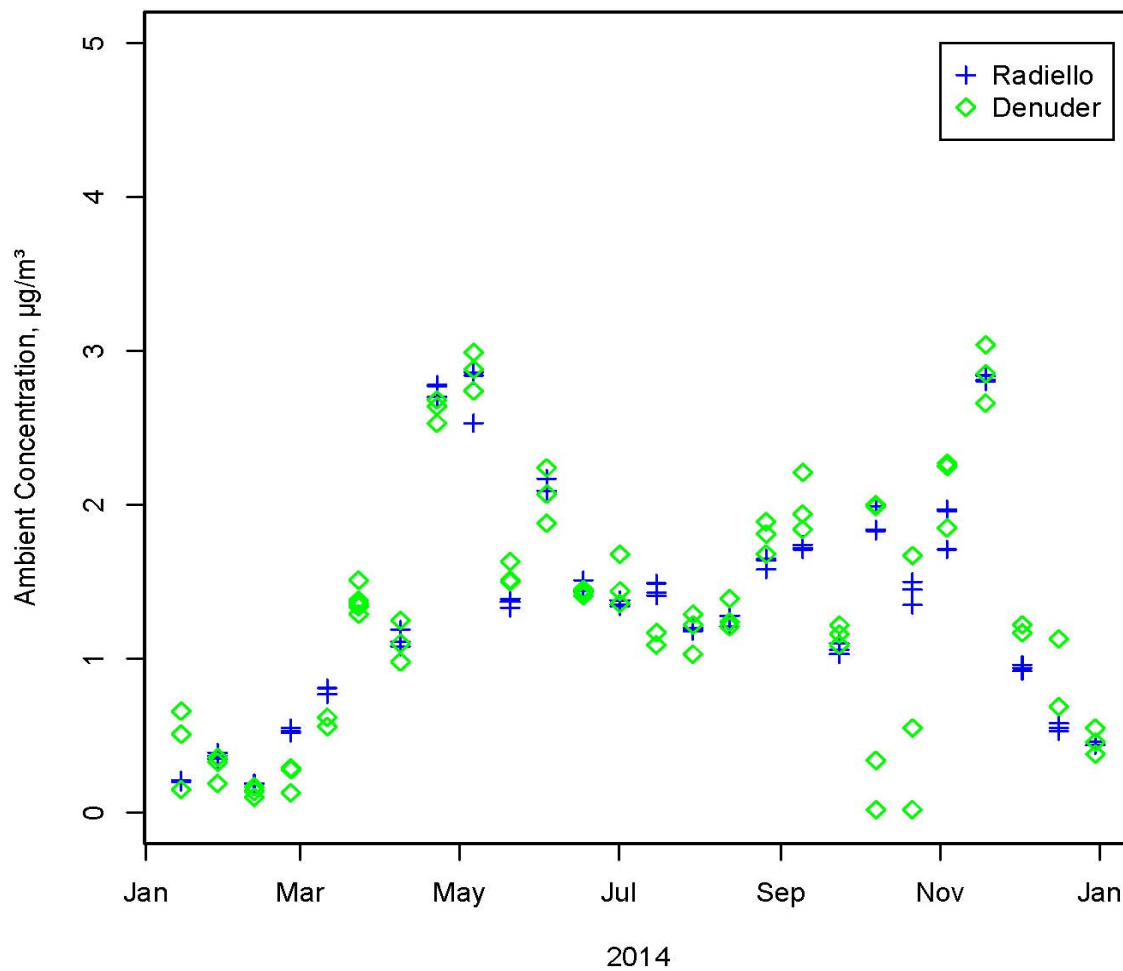


Figure 11. Ambient concentrations of ammonia measured at IL11 during 2014 using co-located Radiello™ passive samplers and URG denuders

AMoN Travel Blank Study Results

The results of the travel sampler blanks for 2014 are shown in Figure 12. Travel blanks are shipped to field sites along with regular samplers but are not opened or deployed.

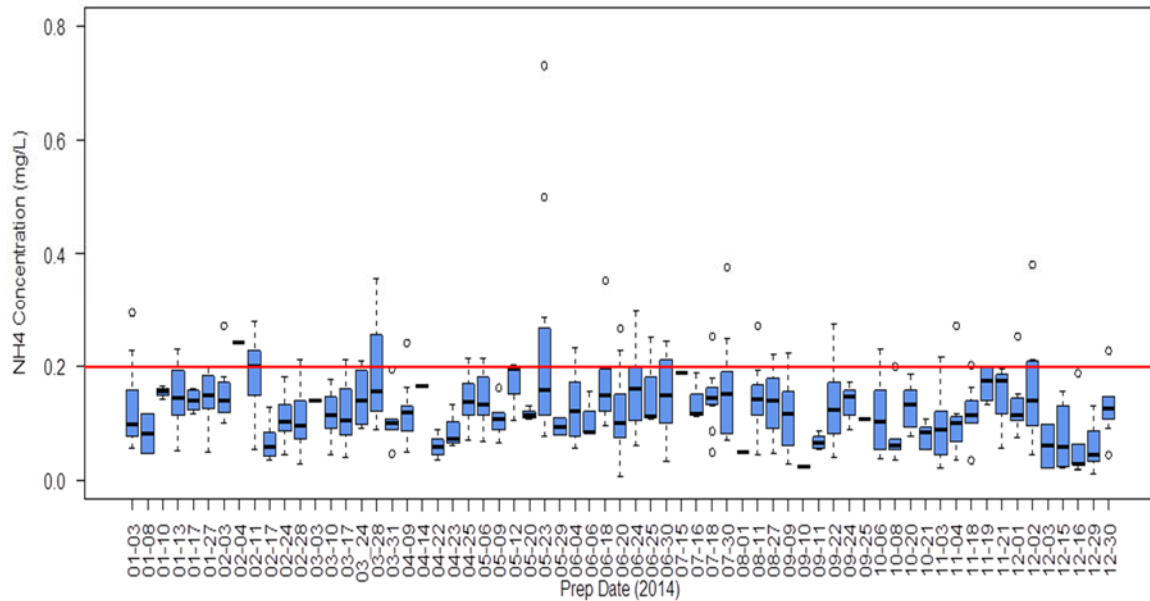


Figure 12. Box and whisker plot showing NH₄⁺ concentrations in 10 mL extracts of AMoN passive travel blanks in 2014, grouped by preparation date

The AMoN travel blank acceptance limit is 0.200 mg/L of NH₄⁺ in the 10 mL sampler extract. In 2014 the median NH₄⁺ concentration for travel blanks was 0.121 (0.107 mg/L in 2013). Like in previous years, numerous travel blanks exceeded acceptable limits throughout the year (Figure 11), and the frequency of exceedances was still high - at 14.4 % (during 2014) versus 14.9% (during 2013). The reason for the numerous travel blank exceedances continues to be investigated. In 2014 efforts were focused on testing the glass jars, PTFE-cap liners and polypropylene caps. No consistent cause for the elevated concentrations of NH₄⁺ was found. The problem will continue to be investigated in 2015.

Special Studies

The study as a part of a wider initiative sponsored by U.S. EPA’s National Risk Management Research Laboratory to better quantify total dissolved nitrogen (TDN) in wet deposition samples. The study was conducted in 2014. An overview of this study, including an evaluation of quality assurance and quality control, was presented in a poster at the Fall 2014 NADP Scientific Symposium. The title of the poster is “Determination of Total Dissolved Nitrogen (TDN) in AIRMoN Wet Deposition Samples”. It is available on the NADP website (<http://nadp.isws.illinois.edu/nadp2014>).

External Quality Assurance

The CAL participated in four external proficiency testing studies throughout 2014. 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 50 and 51	World Meteorological Organization/Global Atmospheric Watch (WMO/GAW)	http://www.qasac-americas.org/
Study 104 and 105	Environment Canada Proficiency Testing Program	Available upon request
Study 32	Norwegian Institute for Air Research (NILU)	Available upon request

The external review of the CAL was conducted June 3 - 5, 2014. The results are available upon request. No findings were identified for Quality Assurance during that Review.

Equipment Maintenance Summary

An internal maintenance schedule is established for each instrument and is included in individual SOPs. Each maintenance schedule is based on corresponding methods requirements and chemist's long-term observations. When needed, additional internal and external (manufacturer) maintenance is performed.

In 2014 internal maintenance for each instrument was performed as it was described in the internal SOPs.

Unscheduled maintenance in 2014 included:

- four pH electrodes and three conductivity cells were replaced during the year;
- one repair for the ICP (Varian Vista Pro) was made on 3/18/2014: an Agilent field engineer installed new RF coils, cone, and replaced tubing.

Preventative maintenance on balances is performed annually at the Illinois State Water Survey. In August 2014, scheduled basic preventive maintenance and calibration were performed by Mettler Toledo for seven CAL balances (see Appendix A). No problems were found.

All scheduled and unscheduled maintenance operations are recorded in the analysts' logbooks. The analysts' logbooks are stored at the workstations for each instrument. The balance and polisher logbooks are stored at corresponding appliances.

Conclusions

The CAL performed consistently throughout 2014 and met all the guidelines as specified in the NADP Network Quality Assurance Plan (2014 QAP). Compliance with Data Quality Objective (DQO) requirements was maintained.

Though no findings were identified for Quality Assurance during the external review, there were 8 recommendations. The CAL is addressing these recommendations.

The problem with AMoN travel blanks will continue to be investigated.

References

1. National Atmospheric Deposition Program/Central Analytical Laboratory Quality Assurance Plan, Version 7.0 May 2014 can be found at http://nadp.isws.illinois.edu/cal/PDF/QAP-2014_FINAL.pdf.
2. Central Analytical Laboratory SOPs can be found at http://nadp.isws.illinois.edu/cal/PDF/NADPCAL-StandardOperatingProcedures_10-15.pdf
3. NADP Network Quality Assurance Plan 2014 can be found at http://nadp.isws.illinois.edu/lib/qaplans/NADP_Network_Quality_Assurance_Plan.pdf
4. 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.
5. Guidance for the Data Quality Objectives Process, EPA QA/G-4, 2000.
6. Review of the Central Analytical Laboratory for the National Atmospheric Deposition Program, June 3 -5, 2014 (available upon request at NADP QA manager).
7. Determination of Total Dissolved Nitrogen (TDN) in AIRMoN Wet Deposition Samples. N.Gartman, L.Green, A.Wells, S.Anderson, K.Blaydes, C.Lehmann, M.Rhodes and J.Walker. Poster, presented at the Annual Meeting and Scientific Symposium of the National Atmospheric Deposition Program, Indianapolis, IN, October 20 - 24, 2014.

APPENDIX A

Basic preventive maintenance and balance calibration in 2014