Quality Assurance Report
National Atmospheric Deposition Program
2016

Laboratory Operations
Central Analytical Laboratory

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List of Abbreviations

AIRMoN	Atmospheric Integrated Research Monitoring Network
AMoN	Ammonia Monitoring Network
APD	Absolute percent difference
ASTM	American Society for Testing and Materials
CAL	Central Analytical Laboratory
CALNAT	Natural rainwater samples prepared by the Central Analytical Laboratory
CEAC	Centro de Estudios Ambientales de Cienfuegos - Center of Environmental Studies of Cienfuegos, Cuba
DI	Deionized Water
DQIs	Data Quality Indicators
DQOs	Data Quality Objectives
FB	Deionized Water Quality Control Internal Blank
FH	High Concentration Quality Control Internal Blank
FHN	High Orthophosphate Internal Verification Standards
FIA	Flow Injection Analysis
FL	Low Concentration Quality Control Internal Blank
FLN	Low Orthophosphate Internal Verification Standards
FR50	A synthetic rainwater solution formulated to approximate the 50th percentile concentrations of NADP/NTN
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
IDL	Instrument Detection Limit
ISWS	Illinois State Water Survey
MDL	Method Detection Limit
NADP	National Atmospheric Deposition Program
NTN	National Trends Network
PO	Program Office
PRI	Prairie Research Institute
QA	Quality Assurance
QAP	Quality Assurance Plan
QC	Quality Control
RAIN-12	External Rain Water Certified Reference Standard
RO	Reverse Osmosis
SOP	Standard Operating Procedure

UIUC	University of Illinois at Urbana-Champaign
UNAM	Universidad Nacional Autónoma de México - the National Autonomous University of Mexico

Introduction

The Central Analytical Laboratory (CAL), located in Champaign, Illinois, on the campus of the University of Illinois at Urbana-Champaign (UIUC), has analyzed and processed data on wet deposition samples for the National Atmospheric Deposition Program (NADP) since 1978. The CAL also analyzes trace-level samples for atmospheric studies, in addition to the NADP. The CAL is within the Illinois State Water Survey of the Prairie Research Institute (PRI) 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. Figure 1 shows the CAL's organization. It is important to note that the QA chemist works independently of the Laboratory and Data Managers and reports directly to the CAL director.

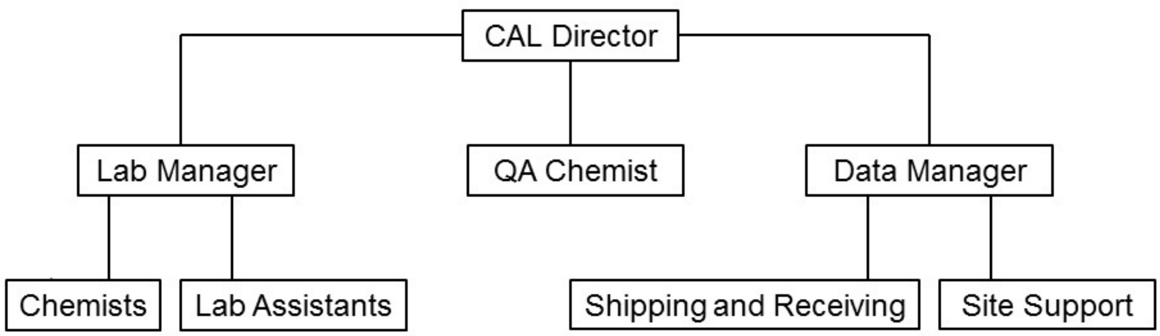

Figure 1. CAL's organization

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 wet deposition 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 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^+) concentrations (reported as mg/L), which are used to calculate the corresponding ambient gaseous ammonia (NH_3) concentrations (reported as µg/m^3).

The CAL follows guidelines specified in the NADP Network Quality Assurance Plan (QAP), which is available on the NADP website (see Reference 1). A list of CAL standard operating procedures (SOPs) is available on the CAL website (see Reference 2). The analytical method used for each ion is shown in Table 1.

Table 1. CAL Analytical Methods

Analyte	**Analytical Method/**Instrument/*Vendor*	CAL SOP #
pH	**Electrometric Method of pH Measurement with a Glass Electrode** / Ion-Selective Glass Electrode / *Broadley-James Corporation* / Seven Multi pH-Meter / *Mettler Toledo*	CAL SOP AN-0023
Specific Conductance	**Conductance by Conductivity Meter** / Electrical Conductivity Cell YSI 3253 K=1.0/cm; YSI 3200 Conductivity Instrument / *YSI Inc*	CAL SOP AN-0019
Bromide (Br^-) **Chloride** (Cl^-) **Nitrate** (NO_3^-) **Sulfate** (SO_4^{2-})	**Ion Chromatography (IC)** / Dionex ICS 2000 and Dionex ICS 5000 / *Thermo*	CAL SOP AN-0018
Ammonium (NH_4^+)	**Flow Injection Analysis (FIA) Colorimetry** / QuikChem 8500/ *HACH/Lachat Instruments*	CAL SOP AN-0014 CAL SOP AN-4022
Orthophosphate (PO_4^{3-})	**Flow Injection Analysis (FIA) Colorimetry** / QuikChem 8500/ *HACH/Lachat Instruments*	CAL SOP AN-0021
Calcium (Ca^{2+}) **Magnesium** (Mg^{2+}) **Sodium** (Na^+) **Potassium** (K^+)	**Inductively Coupled Plasma-Optical Emission Spectroscopy** (ICP-OES) / VISTA-PRO / Agilent Technology **Inductively Coupled Plasma-Optical Emission Spectroscopy** (ICP-OES) / 5100 / Agilent Technology	CAL SOP AN-0016

Significant Changes in 2016

- New equipment:
  - Mettler-Toledo Precision Balance ML802T (for weighing chemicals in the FIA lab, room 306) was received in April 2016.
  - Sartorius Signum Supreme Application Level 1 Balance (for weighing new supplies in the washing room 311) was received in July 2016.
  - In May 2016, the CAL received a new Flow Injection Analysis (FIA) automated colorimeter HACH Lachat QuikChem 8500 Series 2 for determination of total dissolved nitrogen in precipitation samples. The instrument is expected to be approved for NADP use in 2017.
  - In June 2016, the CAL received two new YSI 3200 Conductivity Instruments. One of the meters was approved in July 2016. The second instrument is stored as a spare. Instrument usage is tracked in the CAL's Laboratory Information Management System (LIMS).
  - Bench Top Analog Sterilizer Series "M" was received in July 2016. The sterilizer is designated for special projects. In 2016 it was used for manual digestion for determination of Total Phosphorous by Semi-Automated Colorimetry.
  - BreathEasy Pro, BP Series Air Filtration System from Quatro Air Technology, Inc. was installed in the FIA room in July 2016.
  - Fisher Scientific General Purpose Series ISOTEMP Lab Refrigerator was received in July 2016 for storing samples in the FIA lab, room 306.
- Within the Interlaboratory Comparison Program, the CAL started preparing additional CALNAT rainwater samples for CEAC laboratory, Cuba (since April 2016) and for the UNAM laboratory in Mexico (since June 2016). Participation by CEAC ended in September 2016.
- Testing of a new Automated pH and Specific Conductivity Instrument (TitrEc) began in 2016. A report was presented at the 2016 Fall NADP meeting, and the instrument was approved for pH measurement starting in January 2017.
- Starting October 2016, new plastic bucket lids are soaked in ~ 0.1% solution of Alconox, a liquid citric acid-based laboratory cleaner and detergent from Fisher Scientific (Cat. # 16000-136), before washing. This change in the cleaning method decreased calcium and ammonium in tested supplies.
- In November 2016 NTN bottles were tracked and discarded after 10 uses (versus 13 uses in the past). This has reduced the incidence of sample leakage noted upon receipt of samples.
- At the end of December 2016 the laboratory stopped using custom-made lid bags (DegageCorp™) due to Ca^{2+}contamination, and new lid bags were purchased from ULINE Corporation (S-10835, 16"x16" 3 Mil Slider Zip Bags). The ULINE bags show lower level of contamination.
- AMoN laboratory detection limit, network detection limit, and network uncertainty values were calculated and reported to NADP.
- New Special Projects:
  - Total Phosphorous Determination by Semi-Automated Colorimetry in precipitation samples from four NTN sites (CO96, IL11, MT05 and WI31), collected in August – September 2016.
  - Weekly versus biweekly AMoN Sampling Project started 2/16/2016.
  - Special study was initiated to track pollen in NTN sample filters.

- New SOPs:
  - DA-4084. Ammonia Monitoring Network (AMoN) Laboratory Blank and Travel Blank Data Exports.
  - DA-4085. Standard Definitions for Ammonia Monitoring Network (AMoN) Statistical Uncertainty and Detection Limits.
  - PR-0087. New NTN and AIRMoN Supplies Preparation.
  - PR-0088. CAL Labware Washers.
  - PR-2083. Preparation of AIRMoN Field Blank Solutions.
- Staff changes:
  - Christine Atkinson was hired as a CAL Accreditation Specialist (Hourly) in June 2016.
  - Kristina Bruhn was hired as a Supplies Preparation Assistant in August 2016.
  - Jeff Pribble, a Site Communication Specialist, retired in November 2016. Site support moved from the CAL to the Program Office.

Quality Assurance/Quality Control Overview

Objectives

Quality Assurance (QA)/Quality Control (QC) within the CAL is an "all-hands" effort to ensure that data products from the CAL are of documented high quality and reproducibility. 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 updated, maintained and followed to ensure adherence to the objective.

Definitions

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% when the value is ≥ 100 times the MDL, or ± 20% when the value is between 10 and 100 times MDL. When the value is less than 10 times MDL, a maximum allowable bias shall not exceed ± MDL [2014 CAL QAP Section B-4.2.2]. When 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 standardized again. 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 samples (i.e., samples not readily identifiable to the analysts) 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.

- **Instrument Detection Limit.** Blank samples without analytes (e.g., deionized water) are analyzed to evaluate false positive results for each instrument. The results are used to calculate the *Instrument Detection Limit* (**IDL**). The IDL is the constituent concentration that produces a signal greater than three standard deviations of the mean noise level [4].
- **Method Detection Limit (MDL)** [QAP Section B-4.2] is defined by the U.S. Environmental Protection Agency (EPA) in 40 CFR 136.2 as the "minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero". The EPA provides guidelines for calculating MDLs [5].

Summary of QA/QC procedures

IDLs are established by analyzing blank samples (see section "Reverse Osmosis (RO) Deionized and Polisher Deionized Water blanks) to evaluate false positive results for each analyte.

MDLs are established by analyzing a low concentration standard, that is approximately three to five times the projected MDL for each analyte, throughout the year on all instruments. Conductivity and pH do not have defined MDLs. Those values are calculated based on a measure of long-term variability. Samples used to determine MDLs are blind to the analysts. In addition to regular MDL blind samples, samples prepared from the MDL standards were submitted weekly for both NTN and AIRMoN networks. These blind samples were processed in the same way as field samples, including exposure to sampling buckets (sampling bags for AIRMoN) and lids used for each of the networks

In 2016, three MDL blind samples were sent each week to the laboratory for analysis. These samples included:

- one MDL sample;
- one MDL sample processed as an NTN sample;
- one MDL sample processed as an AIRMoN sample.

MDL study results are compiled at the end of each calendar year and are used to compute the MDLs for the upcoming year. Thus, the IDLs and MDLs for 2016 (Table 2) were calculated using results of analysis performed in 2015. The calculated MDLs are provided to the NADP Program Office for use when releasing data to the public.

Table 2. 2016 IDLs and MDLs

Ion	IDL (mg/L)	Laboratory MDL (mg/L)	AIRMoN MDL* (mg/L)	NTN MDL** (mg/L)
Calcium	0.0006	0.001	0.001	0.009
Potassium	0.0007	0.001	0.001	0.004
Magnesium	0.0007	0.001	0.001	0.002
Sodium	0.0004	0.001	0.001	0.003
Chloride	0.000	0.003	0.003	0.005
Nitrate	0.000	0.003	0.004	0.005
Sulfate	0.000	0.003	0.004	0.004
Bromide	0.000	0.003	0.003	0.004
Ammonium	0.006	0.008	0.008	0.019
Orthophosphate	0.002	0.003	0.003	0.005

* For AIRMoN sample range AD0662L – AD1607L

** For NTN sample range TP0370SW - TQ4117SW

Methods for each ion are found in Table 1 of this document.

During 2016, MDL values were also calculated every three months in order to determine how they could change during the year (see Appendix A).

Daily quality control is assured through the use of QC check samples, replicate samples, and split samples. Details are presented in the Quality Assurance Plan, Section B.

Variability and bias of analytical results for internal QC check solutions are monitored daily using control charts. These solutions are prepared by analysts and are termed "faux rain" (**FR**) samples, instrument specific low and high concentration control solutions (**FL** and **FH**), and DI water (**FB**).

"Faux rain" **FR50** is a dedicated matrix spike solution with target concentrations that represent the 50th percentile level of analytes measured in NTN rainwater samples. This solution contains all CAL analytes except for PO_4^{3-}, as it can affect the stability of NH_4^+ concentrations. Instrument specific control solutions are prepared from certified standards or chemicals, purchased from alternative sources than those standards and chemicals used for preparing calibration standards. The list of certified standards, reference solutions and chemicals, used for preparing calibration standards and QC standards in 2016 is shown in Appendix B.

To define annual control chart limits, all internal standards are analyzed a minimum of seven times at the end of the previous year. Target values for FR50 and NH_4^+ instrument specific standards are defined as the mean values of the analyses. For the other analytes, target values are established based on the supplier values. Limits are established at twice the standard deviation (2σ) for warning limits, and 3σ for control limits (Table 3). Target values are verified as described in Section B-4.5 of the CAL QA Plan.

Table 3. Target concentrations and acceptable ranges (± 3σ) for QC check solutions in 2016

Parameter	FR50	FL	FH	FB
pH (units)	4.79 ± 0.10	4.30 ± 0.10	6.96 ± 0.10	5.63 ± 0.27
Specific Conductance (µS/cm)	10.6 ± 0.9	5.3 ± 0.3	20.3 ± 1.5	1.0 ± 0.6
Calcium (mg/L)	0.132 ± 0.009	0.040 ± 0.004	2.500 ± 0.150	0.000 ± 0.001
Magnesium (mg/L)	0.024 ± 0.004	0.010 ± 0.002	1.000 ± 0.072	0.000 ± 0.001
Sodium (mg/L)	0.056 ± 0.005	0.040 ± 0.004	2.500 ± 0.150	0.000 ± 0.001
Potassium (mg/L)	0.021 ± 0.004	0.010 ± 0.002	2.000 ± 0.144	0.000 ± 0.001
Chloride (mg/L)	0.103 ± 0.015	0.025 ± 0.005	3.000 ± 0.150	0.000 ± 0.003
Sulfate (mg/L)	0.971 ± 0.050	0.500 ± 0.030	5.000 ± 0.210	0.000 ± 0.003
Nitrate (mg/L)	0.909 ± 0.050	0.500 ± 0.030	5.000 ± 0.210	0.000 ± 0.003
Bromide (mg/L)	0.020 ± 0.005	0.025 ± 0.005	3.000 ± 0.150	0.000 ± 0.003
Ammonium (mg/L)	0.239 ± 0.012	0.050 ± 0.010	1.500 ± 0.060	0.000 ± 0.008
Orthophosphate (mg/L)	N/A	0.015 ± 0.004	0.100 ± 0.010	0.000 ± 0.004

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

Table 4. Target concentrations and acceptable ranges for orthophosphate QC solutions in 2016

Parameter	Low standard (FLN)	High standard (FHN)
Orthophosphate (mg/L)	0.031 ± 0.005	0.155 ± 0.016

Internal blind samples [QAP Section B-9.2]. Internal blind samples are evaluated monthly. Four different solutions were used for the internal blind study in 2016: deionized water (DI), MDL standard, FR50 and RAIN-12 (Table 5). RAIN-12 is an external rain water certified reference standard purchased from *Environment and Climate Change Canada's National Water Research Institute* (https://www.ec.gc.ca/).

Table 5. Control internal blind samples target concentrations in 2016

Parameter	DI Water Target Concentration	FR50 Target Concentration	MDL standard Target Concentration	RAIN-12 Target Concentration
pH (units)	5.63	4.79	5.57	4.71
Specific Conductance (µS/cm)	1.0	10.6	1.4	17.0
Calcium (mg/L)	<0.003*	0.132	0.009	0.691
Magnesium (mg/L)	<0.001*	0.024	0.005	0.260
Sodium (mg/L)	<0.002*	0.056	0.006	0.076
Potassium (mg/L)	<0.002*	0.021	0.005	0.041
Chloride (mg/L)	<0.005*	0.103	0.015	0.190
Sulfate (mg/L)	<0.005*	0.971	0.015	2.900
Nitrate (mg/L)	<0.005*	0.909	0.014	1.399
Bromide (mg/L)	<0.005*	0.020	0.015	NA
Ammonium (mg/L)	<0.008*	0.239	0.023	0.126
Orthophosphate (mg/L)	<0.005*	N/A	0.010	NA

* The average historic (2011 – 2015) MDL value

Reanalysis Samples [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). An additional two percent of samples are selected at random for reanalysis. The results are reviewed by the QA Chemist and required edits are made.

Split Samples. Approximately every 100th NTN sample is split before filtering. Both samples are filtered and sent to the lab for analysis. Approximately every 50th AIRMoN sample is split, without filtering, and sent to the lab for analysis.

Quality Control Discussion

Control Charts

In 2016, all analytical values for FR50, FL /FH specific instrument control solutions and FB were within control for final NTN, AIRMoN and AMoN data submitted to the Program Office [QAP Section C-5.6.3]. The number of analyzed QC samples (FR50, FL, FH and FB) for each analyte and the number and percentage of measurements within the warning and control ranges (± 2σ to ± 3σ) are presented in Table 6. The mean percentage of measurements within the warning range was 2.9% and the median percentage was 1.9% in 2016. The Data Quality Objectives (DQOs) as defined in the CAL QAP were met.

When QC measurements exceed warning limits over two times in a row, the instrument is standardized again. If that does not resolve the problem, further corrective actions are taken as described in the QAP, Sections C- 5.6.3.2 – 5.6.3.4.

An example control chart is shown in Figure 2.

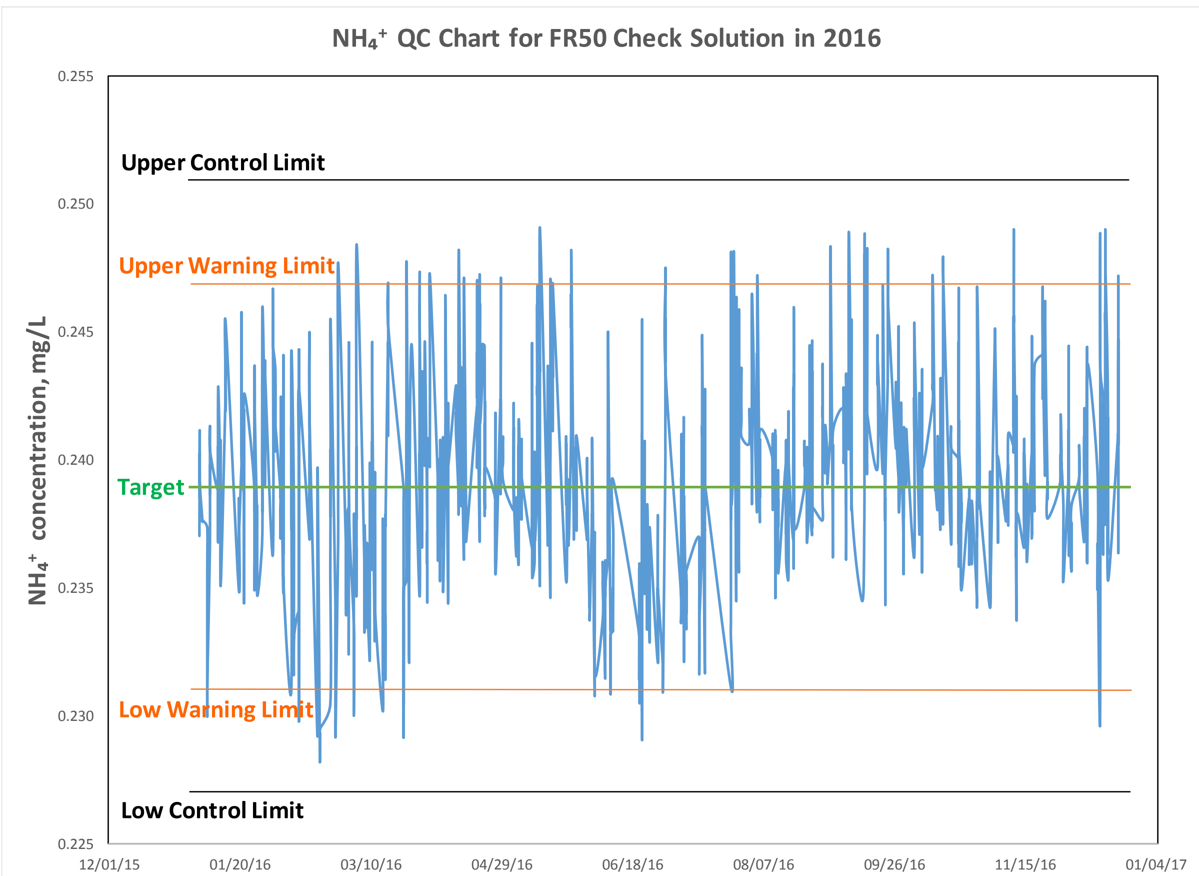

Figure 2. Example control chart for 2016

Table 6. Number of analyzed QC samples (FR50, FL, FH and FB), and number and percentage of QC values exceeding the warning limits (± 2σ) in 2016 (see target limits for solutions in Table 3)

Parameter	FR50			FL			FH			FB		
	N	Number of values exceeding warning limits	% of values exceeding warning limits	N	Number of values exceeding warning limits	% of values exceeding warning limits	N	Number of values exceeding warning limits	% of values exceeding warning limits	N	Number of values exceeding warning limits	% of values exceeding warning limits
pH	1065	61	5.7	1419	9	0.6	1580	1	0.1	1172	13	1.1
Specific Conductance	789	33	4.2	1344	32	2.4	1370	0	0	810	0	0
Calcium	819	0	0	1050	1	0.1	1116	40	3.6	363	4	1.1
Magnesium	835	2	0.2	1049	0	0	1115	29	2.6	373	6	1.6
Sodium	827	16	1.9	1051	4	0.4	1110	101	9.1	362	7	1.9
Potassium	837	4	0.5	1046	23	2.2	1112	69	6.2	350	47	13.4
Chloride	1315	19	1.4	1185	23	1.9	1092	4	0.4	745	0	0
Sulfate	1301	59	4.5	1186	64	5.4	1094	60	5.5	744	0	0
Nitrate	1309	59	4.5	1183	121	10.2	1093	30	2.7	745	0	0
Bromide	1317	48	3.6	1185	14	1.2	1084	30	2.8	745	0	0
Ammonium	1115	40	3.6	1201	1	0.1	1041	42	4.0	861	0	0
Orthophosphate	NA	NA	NA	916	28	3.1	795	97	12.2	602	51	8.5

Split Samples

Approximately every 100th NTN sample is split before filtering. Both samples are filtered and sent to the lab for analysis. Approximately every 50th AIRMoN sample is split, without filtering, and sent to the lab for analysis.

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

If samples fall outside the allowable variability, analysts investigate the cause and analyze additional samples within the run.

There were 140 pairs of split samples processed for NTN and AIRMoN in 2016. Variability for split chemical analyses is calculated as the Absolute Percent Difference (APD) *. The minimum, mean, maximum and median APDs are shown in Table 7. Only sample pairs with concentrations of analytes higher than 10 times the MDL were evaluated.

Since 95% of all NTN samples for the five-year period (2011 -2015) have PO_4^{3-} and Br^- concentrations lower than 10 times the MDL, results for orthophosphate and bromide are not shown. Only internal QC solutions are used to evaluate precision and accuracy for PO_4^{3-} and Br^- analysis.

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* APD =[abs (value1-value2) / 0.5 (value1+value2)] x 100%

Table 7. Minimum, mean, maximum, 25th, median and 75th absolute percent differences (APDs) for 140 split NTN and AIRMoN samples in 2016

Parameter	Minimum APD, %	Mean APD, %	Maximum APD, %	25th percentile APD, %	Median APD, %	75th percentile APD, %
pH	0	0.7	3.4	0.2	0.5	0.9
Specific Conductance	0	1.8	14.3	0.0	1.3	2.7
Calcium	0	2.5	24.8 *	0.5	1.1	2.8
Potassium	0	2.8	24.3 *	1.0	1.8	3.4
Magnesium	0	2.2	8.8	0.8	1.7	2.6
Sodium	0	2.7	57.0 *	0.6	1.4	2.5
Chloride	0	2.4	47.6 *	0.3	0.8	1.8
Sulfate	0	1.0	5.3	0.2	0.6	1.3
Nitrate	0	0.9	6.6	0.1	0.5	1.1
Ammonium	0	0.9	5.1	0.4	0.6	1.2

* The high APD values were detected for three pairs of NTN split samples for lab ID TP9524SW (K^+, Na^+ and Cl^-), TQ0659SW (Ca^{2+}) and TQ1384SW (Cl^-). Upon reanalysis the same results were obtained for each split portion of these samples. This may be due to the presence of particulate matter in the original unfiltered solution, or handling contamination during the splitting process.

The results of split samples met the DQOs in 2016 as specified in the CAL Quality Assurance Plan.

Replicate Samples

Analytical replicates are used by analysts daily. Random samples are selected for reanalysis at least twice following the original analysis during the same day. Precision for the replicates is calculated as the percent relative standard deviation (RSD) **.

Table 8 shows the relative standard deviations for replicate samples. Only values with concentrations ≥ 10 times MDL were evaluated.

Table 8. Minimum, mean, median and maximum relative standard deviations (RSDs) for replicate NTN and AIRMoN samples with concentrations ≥ 10 times the MDL in 2016

Parameter	N	Minimum RSD %	Mean RSD %	Median RSD %	Maximum RSD %
pH	103	0	0.5	0.4	5.1
Specific Conductance	102	0	1.3	1.1	6.0
Calcium	151	0	0.8	0.5	5.3
Potassium	116	0	1.7	1.5	5.1
Magnesium	116	0.1	1.4	1.3	5.3
Sodium	134	0	1.4	1.2	5.6
Chloride	213	0	1.1	0.5	24.7
Sulfate	261	0	0.9	0.5	4.7
Nitrate	266	0	0.9	0.4	5.3
Ammonium	106	0.1	0.9	0.7	8.1

** RSD (%) = (standard deviation of three or more values/average of three or more values) ·100

The results of replicate samples met the DQOs as specified in the QAP Sections B-4.2 – B-4.4.

Quality Assurance Discussion

Internal Blind Samples Results

Results for internal RAIN-12*, FR50 and MDL blind samples were used to assess post-analysis accuracy and precision of the laboratory throughout the year. The relative standard deviation (RSD) ** and mean percent recovery*** were calculated. The results are presented in Table 9.

Table 9. Relative standard deviations (RSDs) and mean percent recoveries for internal RAIN-12, FR50 and MDL blind samples in 2016

Parameter	RAIN-12 (N=14)			FR50 (N=12)			MDL (N= 27)		
	Target, mg/L	RSD, %	Mean Recovery, %	Target, mg/L	RSD, %	Mean Recovery, %	Target, mg/L	RSD, %	Mean Recovery, %
pH (units)	4.71	0.4	99.6	4.87	0.5	98.6	5.57	1.4	99.5
Specific Conductance	17.0 µS/cm	1.7	110.6	9.7 µS/cm	2.6	112.8	1.8 µS/cm	8.2	101.9
Calcium	0.691	1.2	98.1	0.131	1.3	99.5	0.009	6.8	100.8
Potassium	0.041	3.1	101.5	0.021	5.7	101.7	0.005	10.4	98.0
Magnesium	0.260	1.9	110.8	0.024	3.3	98.1	0.005	8.1	101.7
Sodium	0.076	2.0	98.3	0.057	4.5	98.5	0.005	5.0	105.2
Chloride	0.190	1.9	100.7	0.105	3.1	96.7	0.015	6.8	101.4
Sulfate	2.900	2.1	97.5	0.951	1.4	101.3	0.015	10.9	95.7
Nitrate	1.399	1.8	99.5	0.893	1.9	102.1	0.015	9.4	106.1
Bromide	NA	NA	NA	0.020	6.0	104.6	0.015	4.4	98.3
Orthophosphate	NA	NA	NA	NA	NA	NA	0.010	13.5	92.4
Ammonium	0.126	6.0	91.5	0.236	1.9	100.4	0.015	19.1	98.2

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* Certified Matrix Reference Material **RAIN-12** purchased from Environment and Climate Change Canada

* RSD (%) = (standard deviation/mean value) · 100

** Mean Recovery (%) = (mean 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) for wet NTN and AIRMoN samples (fully analyzed) to identify samples for reanalysis (SOP DA-0067). An additional one percent of NTN samples and two percent of AIRMoN samples are selected at random for reanalysis (QAP Section C-2.0).

AMoN samples are reanalyzed once a week. Two AMoN samples from a previous week batch are selected at random for reanalysis. The reanalysis occurs the same day when the current week batch is analyzed.

The results of reanalysis are reviewed by the QA Chemist, and required edits are made.

Based on the results of reanalysis review in 2016, a total of 121 edits (0.09% of all analytical values) were made for NTN samples and 15 edits (0.16% of all analytical values) were made for AIRMoN samples. Changes are documented in the database. No edits were made for AMoN samples based on reanalysis.

The number of field NTN, AIRMoN and AMoN samples analyzed in 2016, and number of quality assurance (reanalysis, blind and split) samples are shown in Table 10.

Table 10. Number of field and quality assurance (QA) samples, analyzed during 2016

Network	Number of field samples analyzed	Number of QA Samples		
		Reanalysis samples	Blind samples	Split samples
NTN	11405 wet samples	1637	32	125
AIRMoN	778 wet samples	187	32	15
AMoN	4003 (including replicates and travel blanks)	124	NA	NA

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

Deionized water generated through CAL's Reverse Osmosis (RO) System is used for washing supplies (buckets, lids, bottles, AMoN glass jars). The RO deionized water, passed through additional point of use polishers, is used for analysis, standards and reagents preparation.

RO DI water is tested weekly. The resistivity of RO DI is monitored throughout the day using inline meters while operations are taking place. A minimum 12.5 MΩ resistivity of RO water is required for use. Polisher DI water is tested once a month. The resistivity of polisher DI is monitored continuously. A minimum of 18.0 MΩ resistivity of polisher DI is required (Type I of reagent water) as specified in the ASTM D1193-99e1 - Standard Specification for Reagent Water.

Table 11 shows the number of exceedances (values higher the average historic MDL) for the RO and polisher DI water blanks.

Table 11. Number of results outside of control limits for RO and polishers DI water blanks in 2016

Parameter	Average Historic MDL , mg/L (2012-2016)	RO Water N = 51	Polisher DI N = 60
Calcium	0.003	0	0
Potassium	0.002	1	0
Magnesium	0.001	0	0
Sodium	0.002	0	0
Chloride	0.005	0	0
Sulfate	0.005	1	0
Nitrate	0.005	0	0
Bromide	0.004	0	0
Ammonium	0.008	0	0
Orthophosphate	0.004	0	0

Supplies

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. New polyethersulfone filters are tested using both DI water and MDL solution.
New brushes and gloves for cleaning buckets and bottles are soaked in 6L jars with DI water (changed daily) until no contaminants are detected in the soak water.

Table 12. Summary of NTN, AIRMoN and AMoN new supply checks

Supply Type	Test Frequency	Test Solution	Test Volume	Contact Time	N of tests in 2016
new buckets	1 per 8	DI	150 mL	24 hours	84
new bucket lids	2 per wash load	DI	50 mL	2 hours	22
new NTN 1-L bottles	1 per 24	DI	150 mL	24 hours	63
new 250 mL AIRMoN bottles	1 per 24	DI	50 mL	24 hours	5
new 60 mL bottles	1 per daily batch rinsed	DI	50 mL	24 hours	136
NTN bucket bags	1 per box (200)	DI	150 mL	24 hours	65
AIRMoN sampling bags	1 per box (250)	DI	150 mL	24 hours	3
lid bags	1 per box (100) *	DI	150 mL	24 hours	332 *
filters	2 per lot and weekly	DI/MDL solution	50 mL	N/A	114
Bucket/bottle brushes and gloves	each brush and each pair of gloves	DI	6L	Until the soak water is clean	64
AMoN Radiello™ cores	2 per each new lot and 1 per the extraction day	DI	10 mL	24 hours	71

* Lid bags, purchased from DegageCorp™ occasionally had elevated concentrations for Ca^{2+} in 2016, thus they were tested more frequently

NTN and AIRMoN washed and reused supplies cleanliness is monitored daily, using MDL solution (Table 13). All new and reused AMoN supplies are tested with DI water.

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

Supply Type	Test Frequency	Test Solution	Test Volume	Contact Time	N of tests in 2016
buckets	1/day	MDL solution	150 mL	24 hours	245
NTN 1-L bottles	1/day	MDL solution	150 mL	24 hours	195
bucket lids	1/day	MDL solution	50 mL	2 hours	242
AMoN glass jars	1 per each new lot	DI	20 mL	24 hours	48

For new NTN and AIRMoN supplies (i.e., buckets, lids, bottles, bags and filters) target levels are based on mean 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 2011 to 2015.

For used supplies, target levels are based on the mean values ± 3σ for concentration in specially prepared internal laboratory MDL solution.

The CAL used the following target values for new and used supply blanks in 2016 (Table 14):

Table 14. Target concentrations and acceptable ranges for new and used supply blanks in 2016

Parameter	New Supply Blanks (prepared with DI Water) Target Concentration (mg/L)	Used and Rewashed Supply Blanks (prepared with MDL Solution) Target Concentration (mg/L)
pH	5.65 ± 0.3	5.50 ± 0.3
Specific Conductance (µS/cm)	1.2 ± 0.5	1.7 ± 0.5
Calcium	<0.004	0.010 ± 0.003
Magnesium	<0.002	0.005 ± 0.003
Sodium	<0.002	0.005 ± 0.003
Potassium	<0.002	0.005 ± 0.003
Chloride	<0.005	0.015 ± 0.005
Sulfate	<0.005	0.015 ± 0.005
Nitrate	<0.005	0.015 ± 0.005
Bromide	<0.005	0.015 ± 0.005
Ammonium	<0.009	0.017 ± 0.007
Orthophosphate	<0.005	0.008 ± 0.004

NTN Sample Filters: DI Water and MDL Solution Checks

Polyethersulfone Supor® Membrane Disk filters (47 mm diameter/0.45 µm pore size) from VWR International (Cat. # 28147-640) are used to separate the dissolved and suspended fractions found in NTN precipitation samples [2014 QAP Section B6.2]. When sample volume allows, filters are rinsed with a small amount of sample 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 2016, concentrations of analytes in DI water eluents from NTN sample filters were lower than target concentrations presented in Table 14. Five exceedances were detected: Ca^{2+} (1), Na^{+} (1), Cl^{-}(1) and NH_4^{+} (2). Three outliers were detected in MDL solution eluents: Ca^{2+} (2) and SO_4^{2-} (1) – see Table 15.

Table 15. Number of results outside of control limits for filters, leached with DI water and MDL solution in 2016

Parameter	DI Water N = 57	MDL N = 57
pH	0	0
Specific Conductance	0	0
Calcium	1	2
Potassium	0	0
Magnesium	0	0
Sodium	1	0
Chloride	1	0
Sulfate	0	1
Nitrate	0	0
Bromide	0	0
Ammonium	2	0
Orthophosphate	0	0

Buckets, Bottles and Lids

New Buckets

Calcium is used in the manufacture of plastic buckets. Occasionally it has been detected in new buckets used to collect NTN wet deposition samples. New buckets are leached with hydrochloric acid to remove Ca^{2+}, and then washed and tested (see SOP PR-0009). One bucket per each set of eight new leached buckets is tested. 78 blanks, representing 624 new leached buckets were tested in 2016.
In 2016, the median concentration of Ca^{2+} in new leached and washed buckets was lower than the upper acceptable limit for new supplies (0.004 mg/L Ca^{2+}) (Figure 3). The median concentration of Ca^{2+} found in new buckets was ~ 0.001 mg/L.

A few NH_4^+ exceedances were detected in new buckets (Figure 4). 48 buckets (six sets of eight buckets each) were rewashed and then retested, and all of them were found to be lower than the acceptable limit (0.009 mg/L NH_4^+).

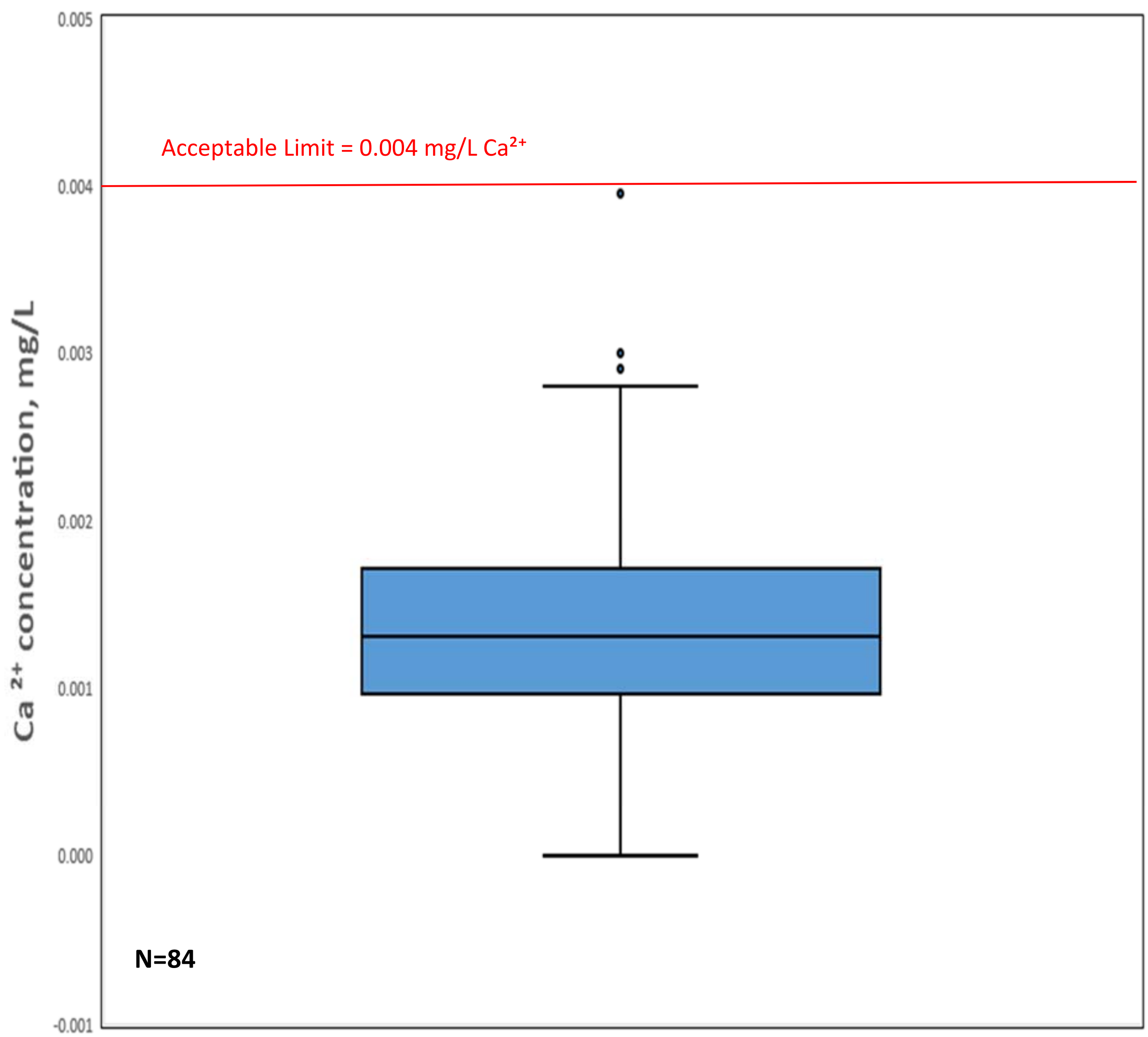


Figure 3. Box and whisker plot showing Ca^{2+} concentrations for new buckets, tested with DI water in 2016

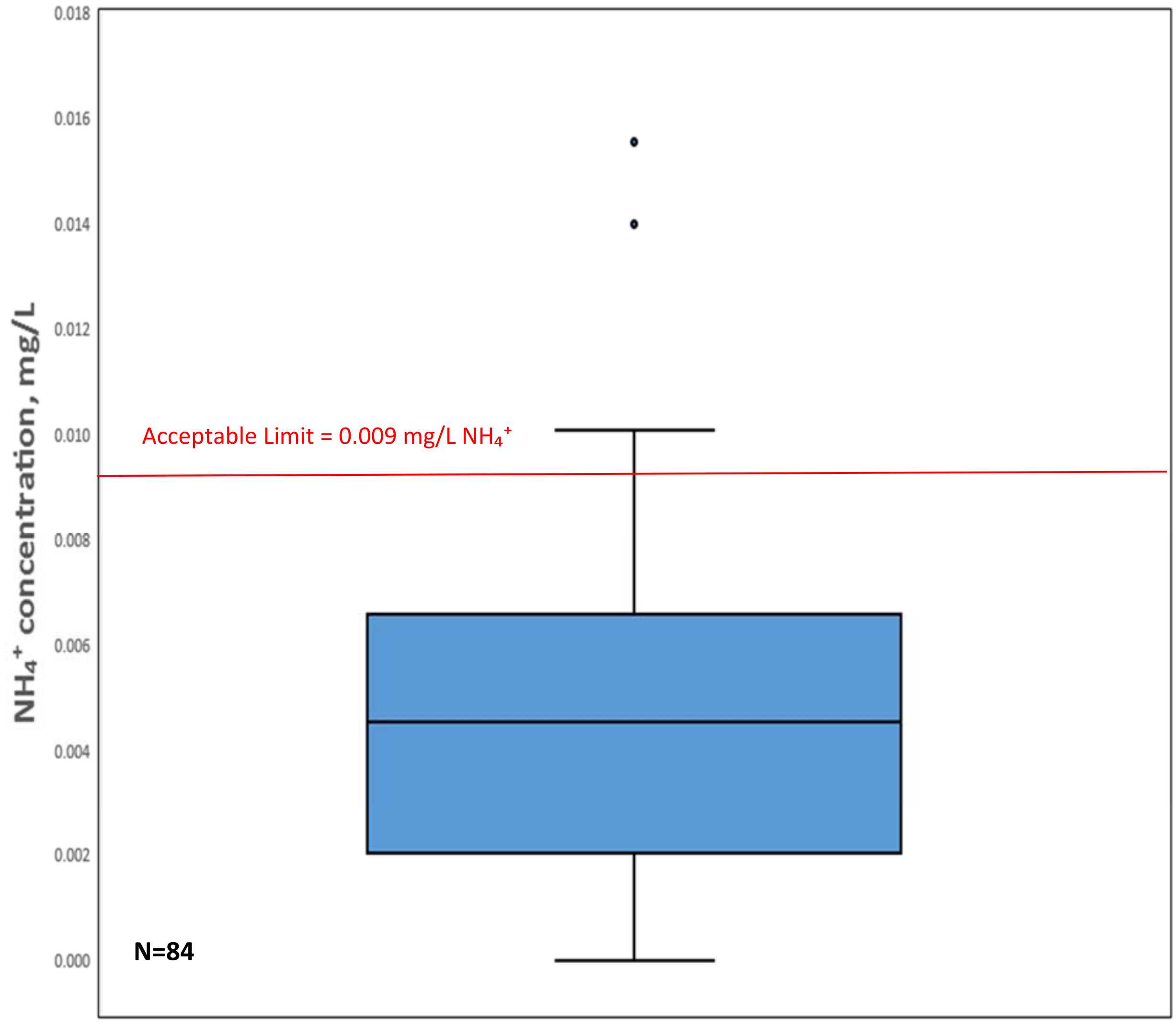


Figure 4. Box and whisker plot showing NH_4^+ concentrations for new buckets, tested with DI water in 2016

Washed and Reused Buckets. There were 245 washed and reused bucket blank samples prepared and analyzed in 2016. When analyte concentrations exceed target limits 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. Results outside of target limits are shown in Table 16. Seventeen buckets were responsible for the thirty three exceedances. All buckets were rewashed and retested, and twelve of them were found to be within control limits. Five buckets were discarded. A number of buckets were also discarded for other reasons including breakage, stains and scratched interior surfaces.

Table 16. Number of results outside of control limits for 245 washed and reused buckets, contacted with MDL solution for 24 hours and tested in 2016

Parameter	Number of results outside of control limits
pH	0
Specific Conductance	2
Calcium	12
Potassium	1
Magnesium	0
Sodium	2
Chloride	3
Sulfate	1
Nitrate	0
Ammonium	11
Bromide	0
Orthophosphate	0

The levels of main contaminants (Ca^{2+} and NH_4^+), detected routinely in washed and reused buckets, were low in 2016 and mostly were within allowable control limits for the MDL solution. Twelve exceedances for calcium and eleven exceedances for ammonium were detected (Table 16, Figures 5 and 6).

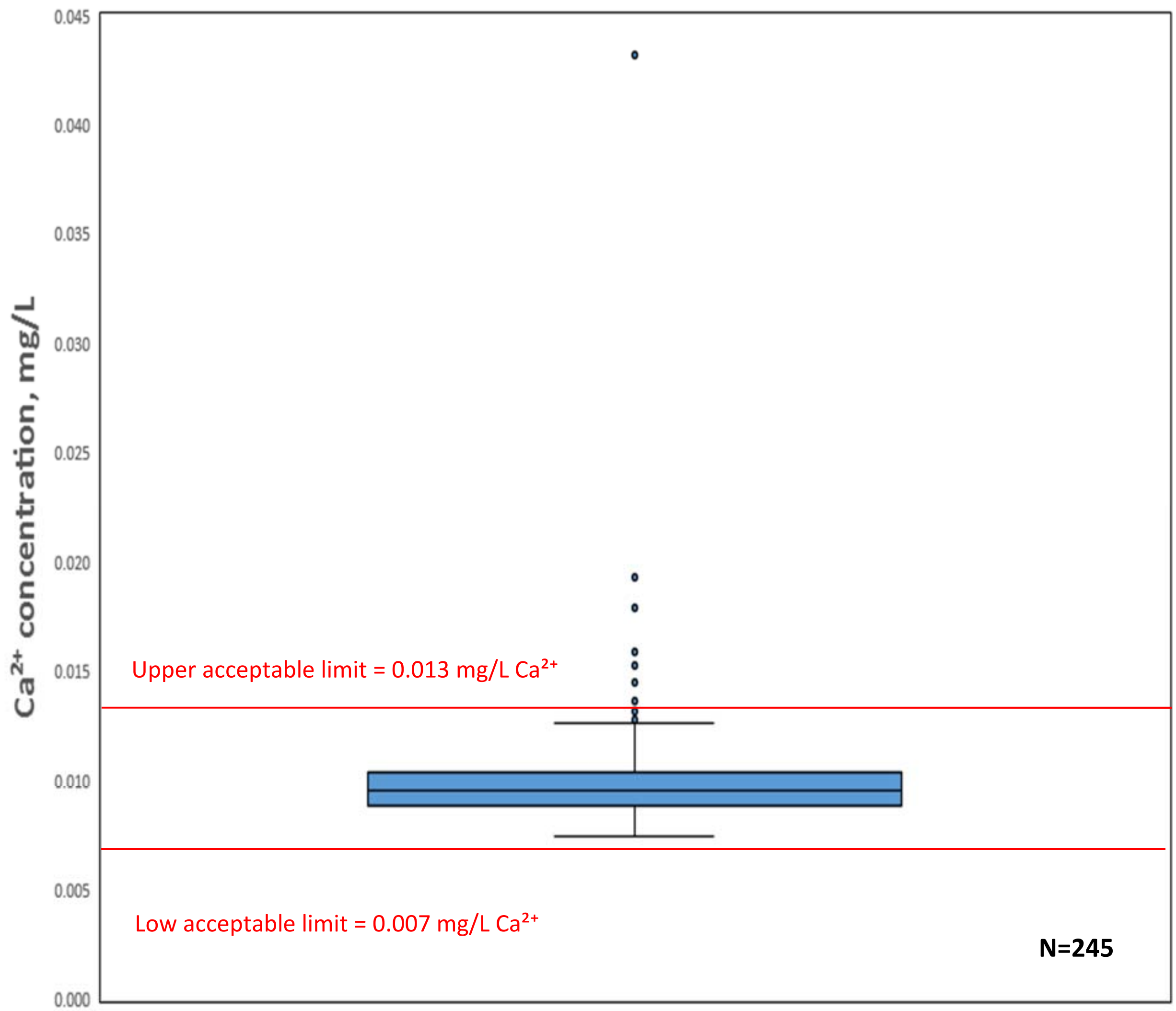


Figure 5. Box and whisker plot showing Ca^{2+} concentrations for washed and reused buckets, tested with MDL solution in 2016

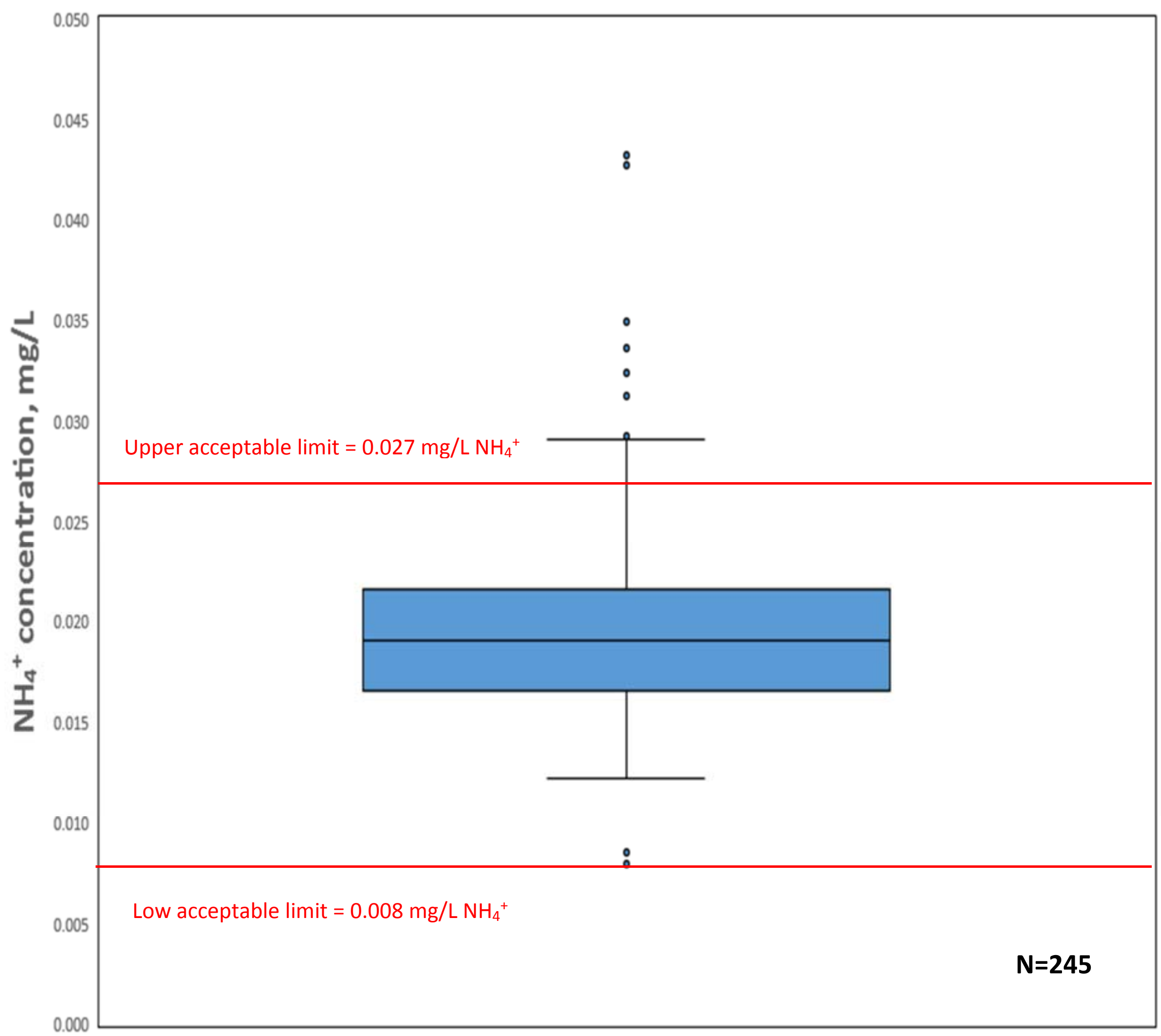


Figure 6. Box and whisker plot showing NH_4^+ concentrations for washed and reused buckets, tested with MDL solution in 2016

New NTN 1-L bottles, new AIRMoN 250-mL bottles and new 60 mL HDPE Nalgene™ bottles. New NTN, AIRMoN and 60 mL bottle blank results were within the acceptable limits for all analytes throughout 2016. There were no exceedances.

Washed and Reused NTN 1-L Bottles. During 2016, one NTN bottle was selected daily from the washed bottles and tested. Results outside of target limits are shown in Table 17. All contaminated bottles were rewashed and retested, and were subsequently found to be within control limits.
NTN 1-L bottles are discarded after 13 uses. A number of bottles were also discarded for changes in integrity (leakage, etc.).

Table 17. Number of results outside of control limits for 195 washed and reused NTN 1-L bottles, contacted with MDL solution for 24 hours and tested in 2016

Parameter	Number of results outside of control limits
pH	0
Specific Conductance	2
Calcium	1
Potassium	1
Magnesium	0
Sodium	0
Chloride	1
Sulfate	0
Nitrate	0
Ammonium	4
Bromide	0
Orthophosphate	0

New Lids. Ca^{2+} and NH_4^+ are traditionally the highest contaminants in new lids. To get rid of Ca^{2+} and NH_4^+, new lids are soaked for 24 hours in ~ 0.1% solution of Alconox (a liquid citric acid-based laboratory cleaner and detergent from Fisher Scientific, Cat. # 16000-136) before washing. If lid blanks have Ca^{2+} and NH_4^+ concentrations higher than acceptable limits, the whole set of new lids, represented by those blanks, is rewashed and retested. If the second test is outside of control limits, this set of lids is resoaked, washed and tested. Twenty two blanks, representing 227 new lids were tested in 2016 (see Table 18). Box and whisker plots showing Ca^{2+} and NH_4^+ concentrations measured in new lids in 2016 are shown in Figures 7 and 8. All contaminated new lids were rewashed and retested, and they all were found to be within control limits.

Washed and Reused Lids. Twenty seven bucket lids were responsible for the sixty three exceedances shown in Table 18. Those lids were rewashed and retested for all analytes. Two of them did not pass the second check and were discarded. The highest contaminants were Ca^{2+} (thirteen exceedances) and NH_4^+ (twenty nine exceedances). Box and whisker plots showing Ca^{2+} and NH_4^+ concentrations measured in washed and reused lids in 2016 are shown in Figures 9 and 10. Few exceedances were detected for pH, conductivity, Na^+, Mg^+, Cl^-, SO_4^{2-} and NO_3^-.

Table 18. Number of results outside of control limits for 22 new and 245 reused bucket lids, contacted with DI (new lids) or MDL solution (reused lids) for 24 hours and tested in 2016

Parameter	Number of results outside of control limits (new lids)	Number of results outside of control limits (washed and reused lids)
pH	0	2
Specific Conductance	0	6
Calcium	5	13
Potassium	0	0
Magnesium	0	1
Sodium	0	4
Chloride	0	4
Sulfate	0	3
Nitrate	0	1
Ammonium	9	29
Bromide	0	0
Orthophosphate	0	0

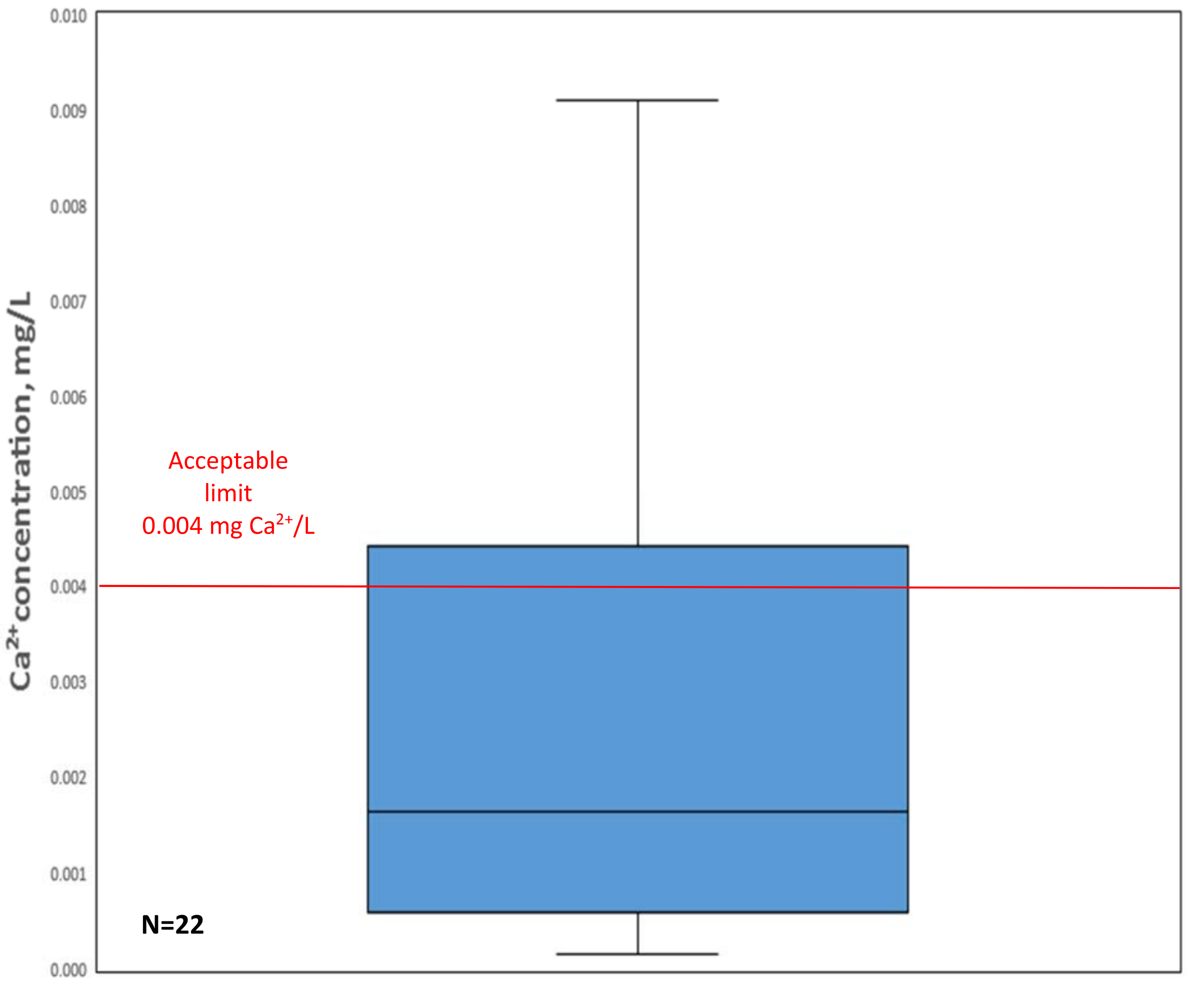


Figure 7. Box and whisker plot showing Ca^{2+} concentrations for new lids, tested with DI water in 2016

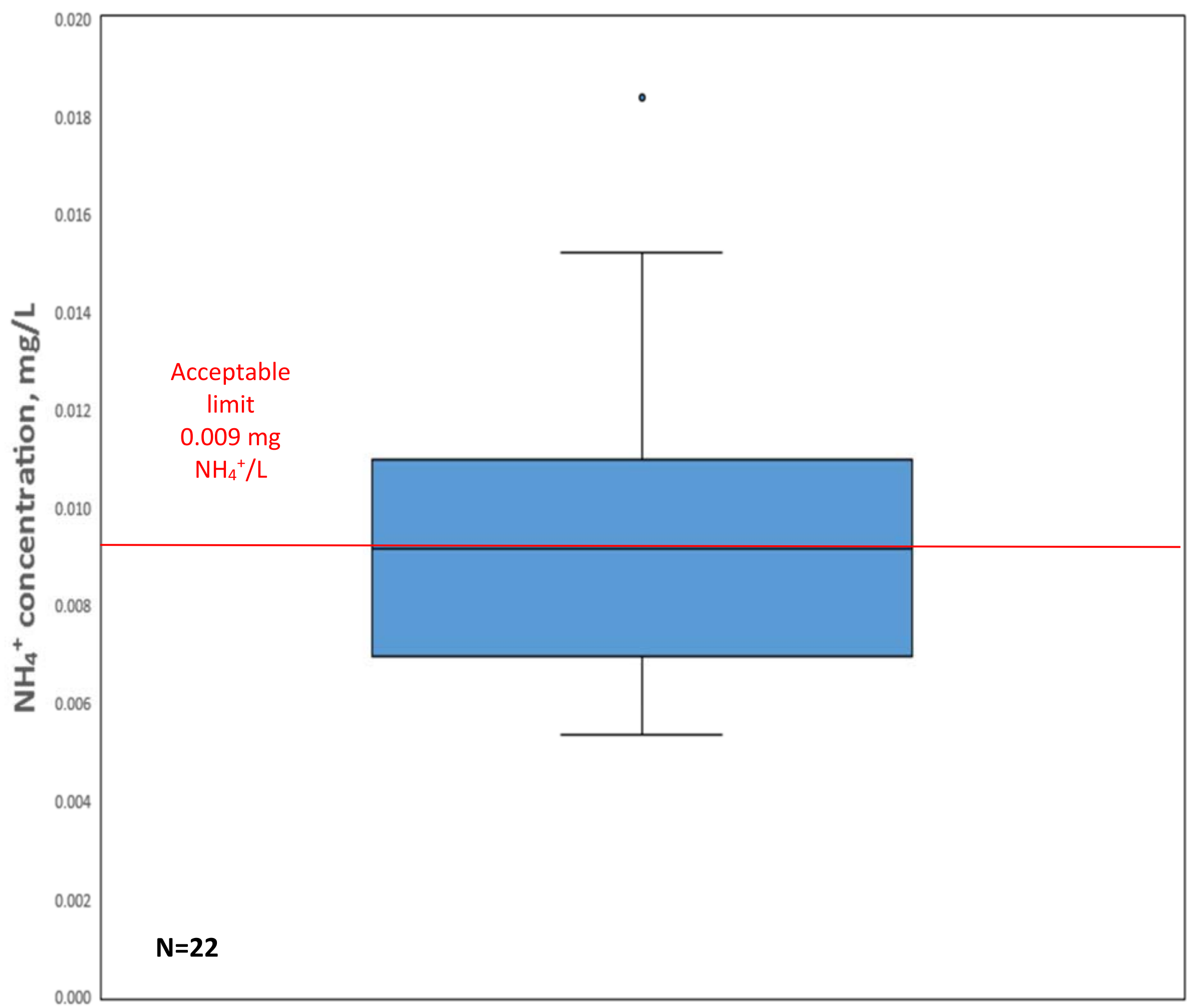


Figure 8. Box and whisker plot showing NH_4^+ concentrations for new lids, tested with DI water in 2016

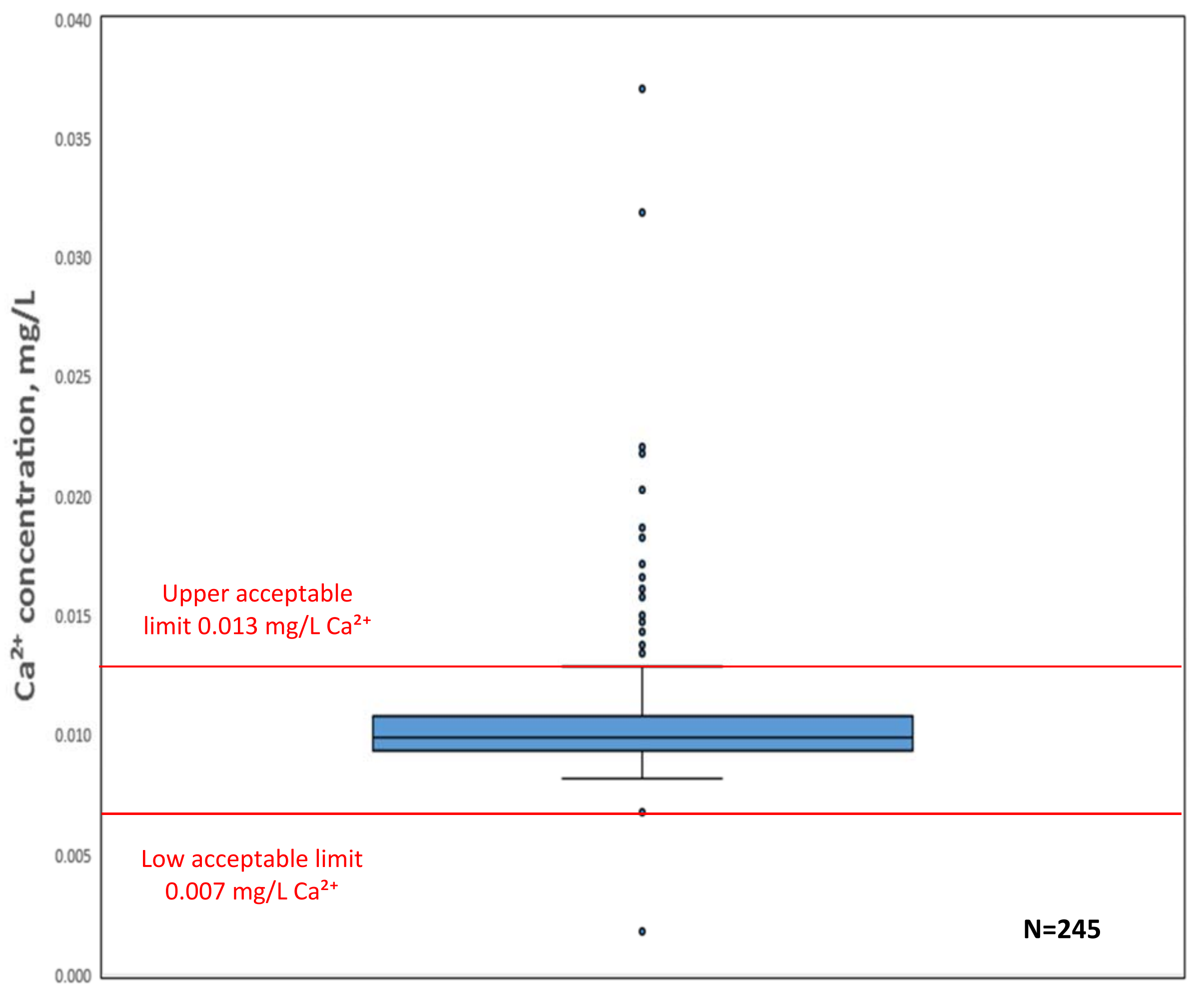


Figure 9. Box and whisker plot showing Ca^{2+} concentrations for washed and reused bucket lids, tested with MDL solution in 2016

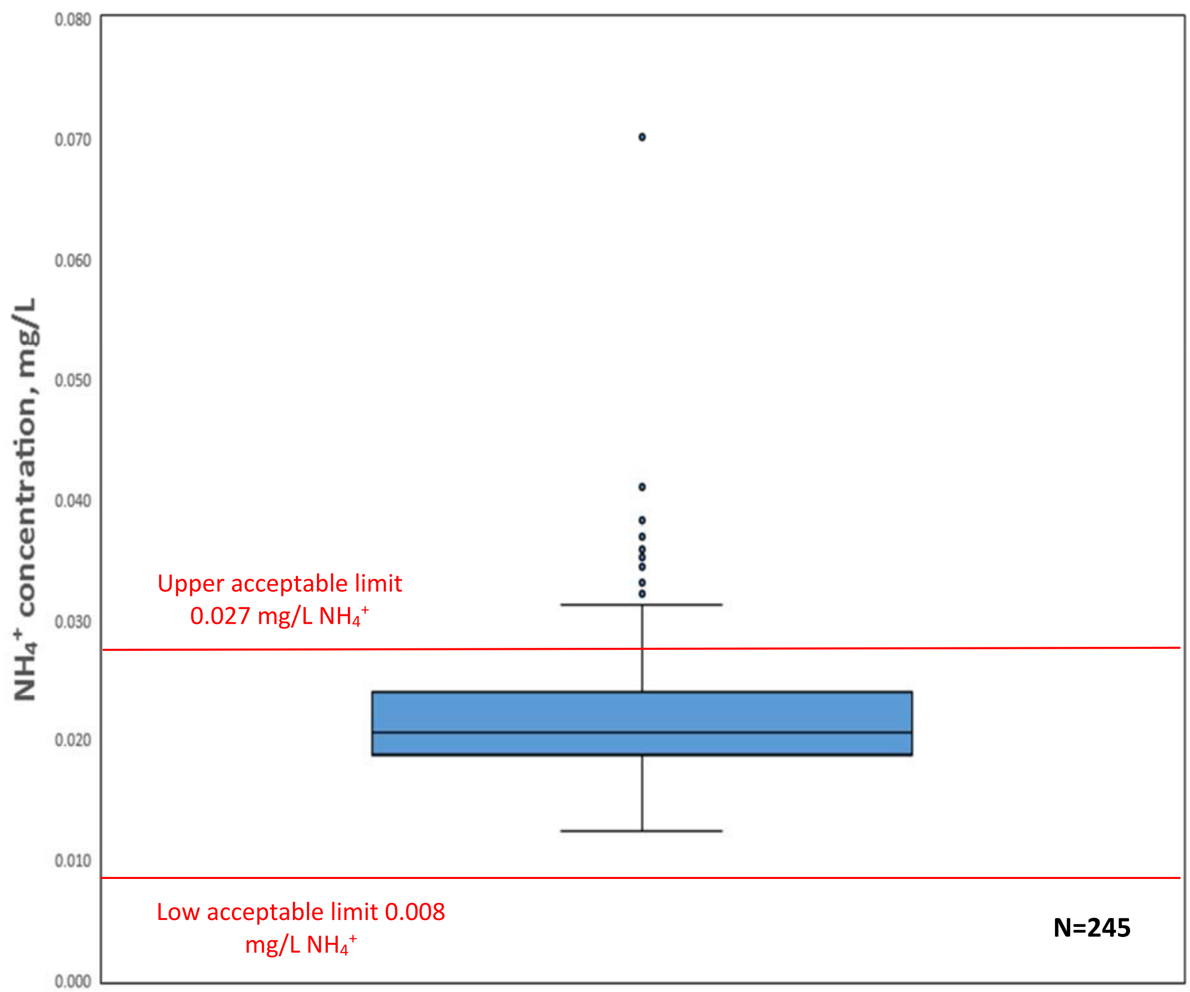


Figure 10. Box and whisker plot showing NH_4^+ concentrations for washed and reused bucket lids, tested with MDL solution in 2016

Bags

Lid bags, bucket bags and bags used to collect AIRMoN samples 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. Lid bags, purchased from DegageCorp™ occasionally had the elevated concentrations for Ca^{2+} in 2016 due to contaminated zipper material. 21 boxes of these bags were rejected and were not used. At the end of 2016 the laboratory stopped using DegageCorp™ bags. New lid bags were purchased from ULINE Corporation (S-10835, 16”x16” 3 Mil Slider Zip Bags). The ULINE bags have less contamination.

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 2016.

AMoN

The CAL assembles and ships the Sigma-Aldrich Radiello™ passive-type air samplers to sites (104 sites in 2016) and, when returned, analyzes, quality assures, and provides the analytical data to the NADP. Twenty five percent of Sigma-Aldrich Radiello™ passive-type air samplers are deployed in triplicates. Also, URG™ (University Research Glass) denuders are deployed in triplicates at the Bondville Station (IL11) during the year. Travel blanks are shipped to field sites along with regular samplers but are not opened or deployed.
Upon receipt at the CAL, samplers are stored in a freezer (at -17.5 °C). Samplers 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 2016.

For each extraction batch, six samples are generated for Quality Control/Quality Assurance. This set includes:

- one lab air QA sample (sampler deployed in the lab for a two week period);
- one hood air QA sample (sampler deployed in the positive flow hood during a two week period);
- one extraction hood air QA sample (sampler, deployed in the hood during the 1 – 3 hour 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);
- one glass jar blank.

The results of the lab AMoN QA samples for 2016 are shown in Figures 11 and 12.

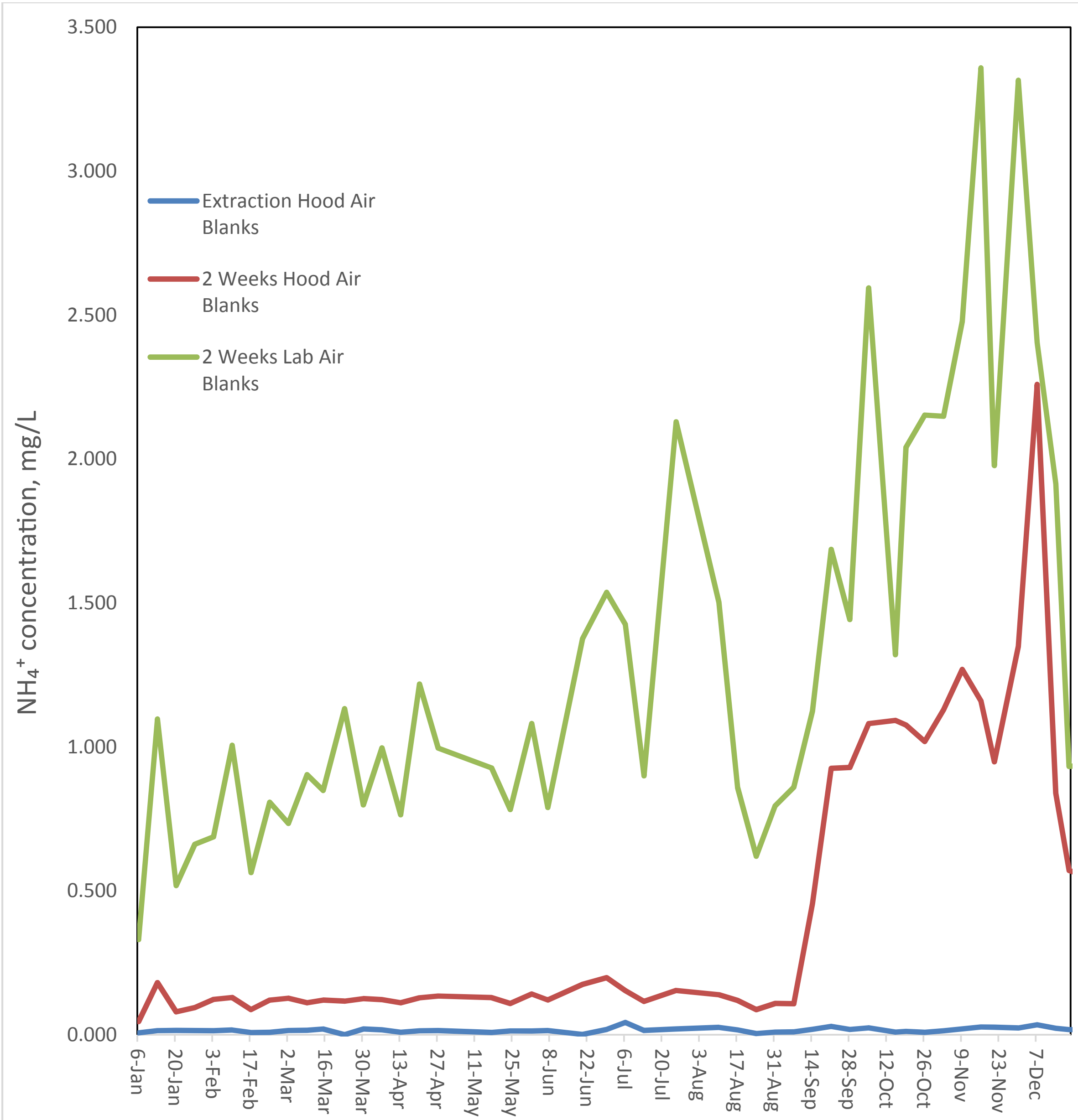


Figure 11. Comparison of lab air blanks (NH_4^+ concentrations, measured in 2016 in hood air blanks during extraction, two week hood air blanks and two week lab air blanks)

In September – December 2016, the NH_4^+ concentrations for two week hood air and two week lab air blanks significantly increased following replacement of the hood's activated carbon filters. The reasons for these spikes in concentration are being investigated.

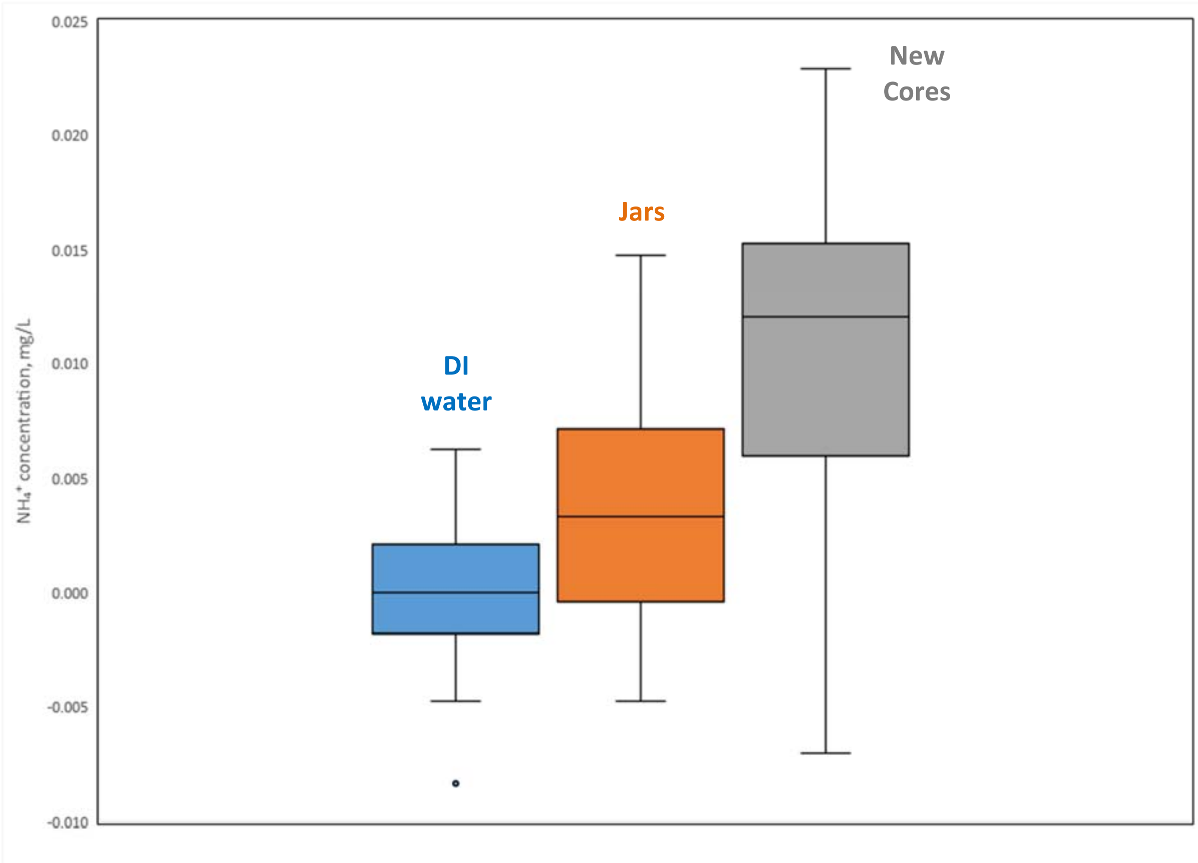


Figure 12. Comparison of AMoN supplies blanks (NH_4^+ concentrations, measured in DI water blanks, in washed and reused glass jars blanks and in new Radiello™ cores blanks) in 2016

Triplicate Samplers. The variability of Radiello™ and URG™ (University Research Glass) denuders triplicate results was quantified as the absolute percent difference (APD*) of valid deployed samplers measurements. Precision was quantified as the relative standard deviation (RSD**) (Table 19).

Table 19. Median and mean absolute percent differences (APDs) and relative standard deviations (RSDs) for triplicate Radiello™ samplers and URG™ (University Research Glass) denuders in 2016

	Number of triplicate sets	Median APD * (%)	Mean APD * (%)	Median RSD ** (%)	Mean RSD ** (%)
Radiello™	282	2.8	4.8	4.3	6.5
URG™ denuders	26	3.5	4.4	4.9	6.1

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

** RSD (%) = (stdev/average of the triplicate values) · 100

The CAL compares measurements of co-located Radiello™ passive-type air samplers (in triplicates) and URG™ (University Research Glass) active flow denuders (in triplicates) operated at the Bondville Station (IL11) (SOP DA-4065).

The APDs and RPDs of NH_3 results for co-located Radiello™ samplers and URG™ denuders during 2016 are shown in Figure 13. The mean and median APDs and RPDs of the results converted to NH_3 are shown in Table 20.

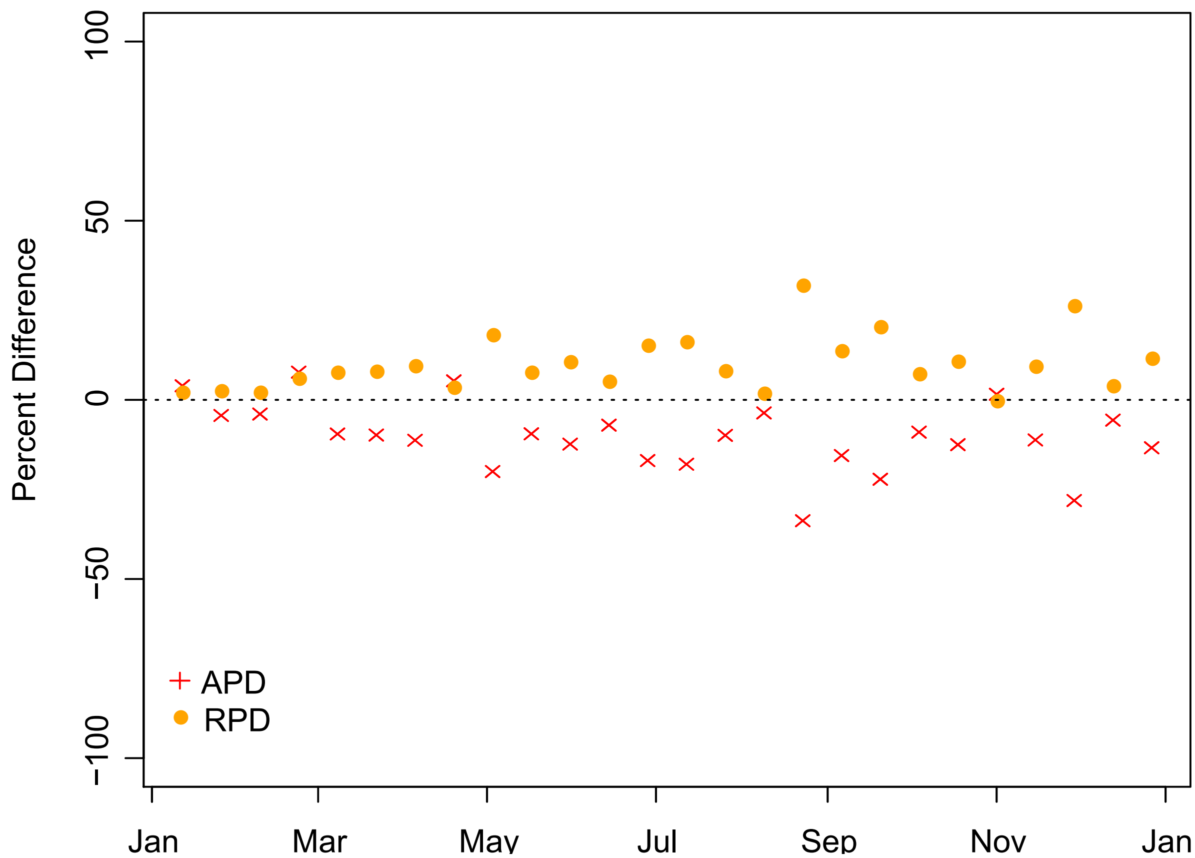


Figure 13. Absolute percent differences (APDs) and relative percent differences (RPDs) for co-located Radiello ™ and URG™ samplers operated at the IL11 site in 2016

Table 20. Median and mean absolute percent differences (APDs *) and relative percent differences (RPDs) for ammonia measured at IL 11 using Radiello™ passive-type air samplers and URG™ denuders in 2016**

Year	Count	Median APD * (%)	Mean APD * (%)	Median RPD** (%)	Mean RPD** (%)
2016	26	9.9	11.8	-9.9	-10.3

$$* \quad \text{APD (\%)} = abs\,\frac{\text{Radiello value} - \text{URG denuder value}}{\text{URG denuder value}} \cdot 100$$

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

Ambient NH_3 measurements using Radiello™ samplers and URG™ denuders at IL11 during 2016 are compared in Figure 14.

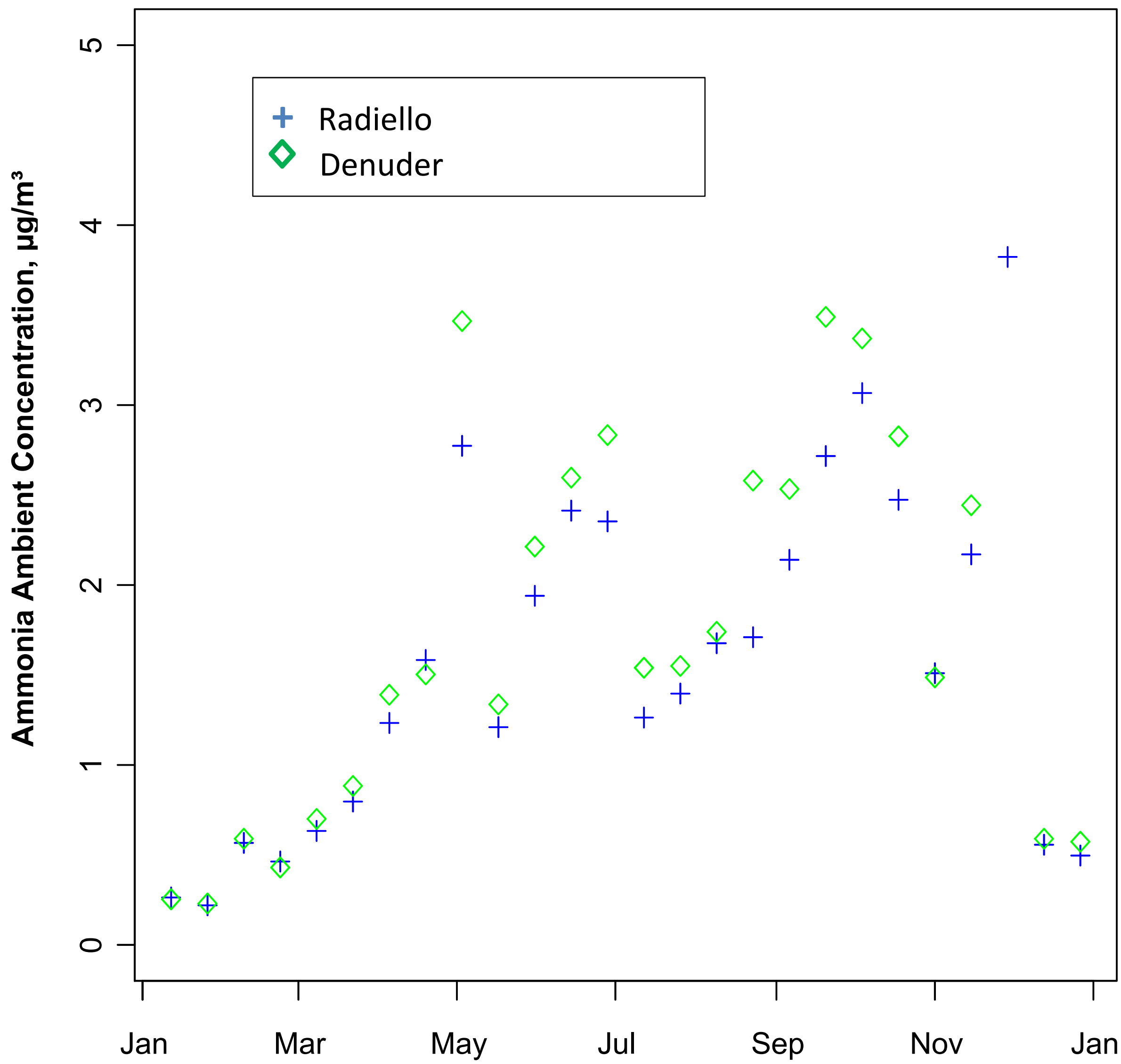


Figure 14. Ambient air concentrations of ammonia, measured at IL11 during 2016 using co-located Radiello™ passive samplers and URG ™ denuders

AMoN travel blanks

The AMoN travel blank acceptance limit is 0.200 mg/L of NH_4^+ in 10 mL of sampler extract. Three exceedances were observed in 2016. The median and mean NH_4^+ concentrations for travel blanks in 2016 are shown in Table 21. The table includes data for the whole year, and, separately, data for the January – August period (no issues with hood and lab air ammonia concentration) and for the September – December period (issues with hood and lab air ammonia concentration started – see Figure 11). There is a 7-10% increase in NH_4^+ concentrations in travel blanks in September – December 2016, probably associated with elevated hood and lab background ammonia level. The CAL continues to investigate improvements in clean air bench removal efficiency.

Table 21. Median and mean ammonium (NH_4^+) concentrations in travel blanks extracts, and percentage of exceedances (> 0.200 mg NH_4^+ /L)

Period	N	Median NH_4^+ concentration, mg/L	Mean NH_4^+ concentration, mg/L	% of exceedances
2016	**851**	**0.044**	**0.047**	**0.35**
Jan - Aug	577	0.042	0.048	0.35
Sept - Dec	274	0.045	0.053	0.36

The results of the travel sampler blanks for 2016 are shown in Figure 13.

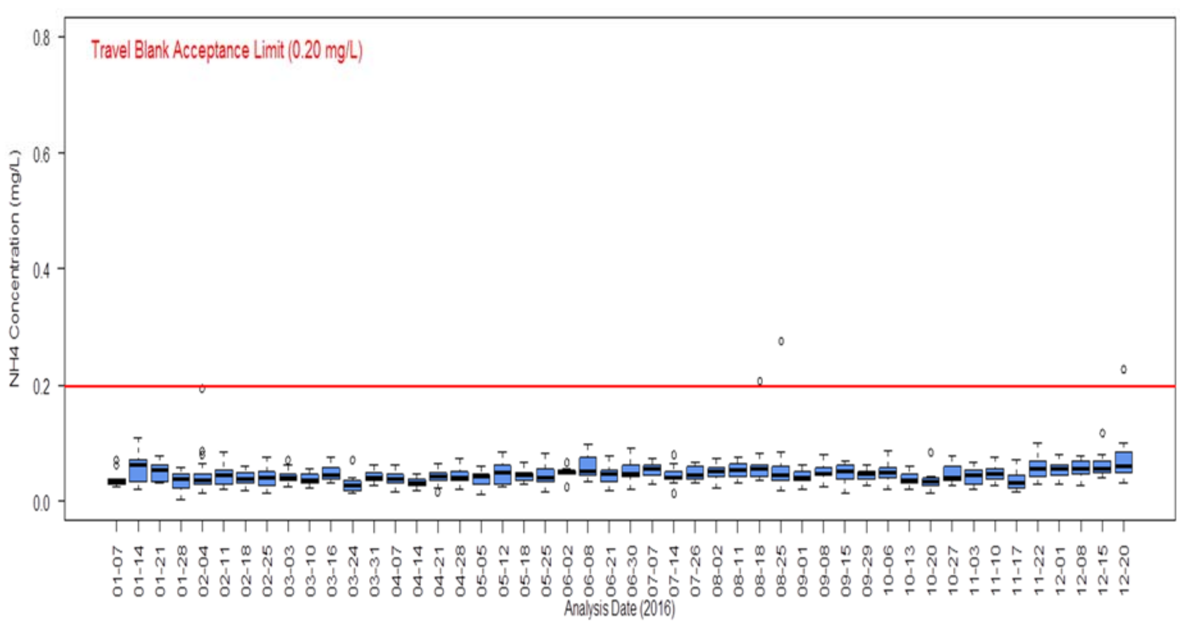


Figure 15. Box and whisker plot showing ammonium (NH_4^+) concentrations in extracts of AMoN travel blanks in 2016, grouped by analysis date

AMoN statistical uncertainty and detection limits

The calculations of statistical uncertainty and detection limits for ambient ammonia gas concentrations measured by NADP/AMoN are performed following CAL SOP DA-4085.

AMoN uncertainty

AMoN uncertainty for ambient NH_3 measurements (Table 22 and Figure 16) is calculated annually from valid replicate values for each quartile of data based on the prior three years of ambient concentration data.

$$\boldsymbol{u_{N_Q}} = \text{median}(\mathbf{2} \times \boldsymbol{\sigma_a})$$

where: $\boldsymbol{u_{N_Q}}$ = annual AMoN uncertainty based on concentration quartiles, µg/m^3

$$\boldsymbol{\sigma_a} = \sqrt{\frac{\sum(x_i - \bar{x})}{(n-1)}}$$

where: $\boldsymbol{\sigma_a}$ = standard deviation of valid individual field-exposed replicate measurements, µg/m^3

$\boldsymbol{x_i}$ = individual valid field-exposed replicate concentrations, µg/m^3

$\boldsymbol{\bar{x}}$ = arithmetic mean of individual valid field-exposed replicate concentrations, µg/m^3

$\boldsymbol{n}$ = number of individual valid field-exposed samples ($n \geq 2$)

For example, the 2016 AMoN uncertainty is calculated for replicate samples deployed in 2016, using data quartiles calculated from all samples collected during 2013 – 2015.

Table 22. AMoN 3-year moving uncertainty for ambient air ammonia (NH_3) concentration quartiles for 2010 - 2016

Year		n	1st Quartile	n	2nd Quartile (Median)	n	3rd Quartile	n	4th Quartile (Maximum)
			µg/m^3		µg/m^3		µg/m^3		µg/m^3
2010	Concentration range	101	≤ 0.42	146	> 0.42 ≤ 0.94	138	> 0.94 ≤ 1.99	133	> 1.99
	Uncertainty		**± 0.058**		**± 0.076**		**± 0.126**		**± 0.234**
2011	Concentration range	25	≤ 0.42	23	> 0.42 ≤ 0.93	16	> 0.93 ≤ 1.97	18	> 1.97
	Uncertainty		**± 0.081**		**± 0.121**		**± 0.190**		**± 0.270**
2012	Concentration range	13	≤ 0.35	28	> 0.35 ≤ 0.79	27	> 0.79 ≤ 1.73	22	> 1.73
	Uncertainty		**± 0.031**		**± 0.052**		**± 0.193**		**± 0.295**
2013	Concentration range	37	≤ 0.39	32	> 0.39 ≤ 0.80	37	> 0.80 ≤ 1.79	13	> 1.69
	Uncertainty		**± 0.028**		**± 0.048**		**± 0.095**		**± 0.234**
2014	Concentration range	58	≤ 0.40	37	> 0.40 ≤ 0.77	44	> 0.77 ≤ 1.73	17	> 1.73
	Uncertainty		**± 0.035**		**± 0.061**		**± 0.074**		**± 0.221**
2015	Concentration range	115	≤ 0.45	43	> 0.45 ≤ 0.83	51	> 0.83 ≤ 1.75	30	> 1.75
	Uncertainty		**± 0.042**		**± 0.060**		**± 0.083**		**± 0.167**
2016	Concentration range	62	≤ 0.42	65	> 0.42 ≤ 0.77	79	> 0.77 ≤ 1.59	66	> 1.59
	Uncertainty		**± 0.031**		**± 0.053**		**± 0.092**		**± 0.149**

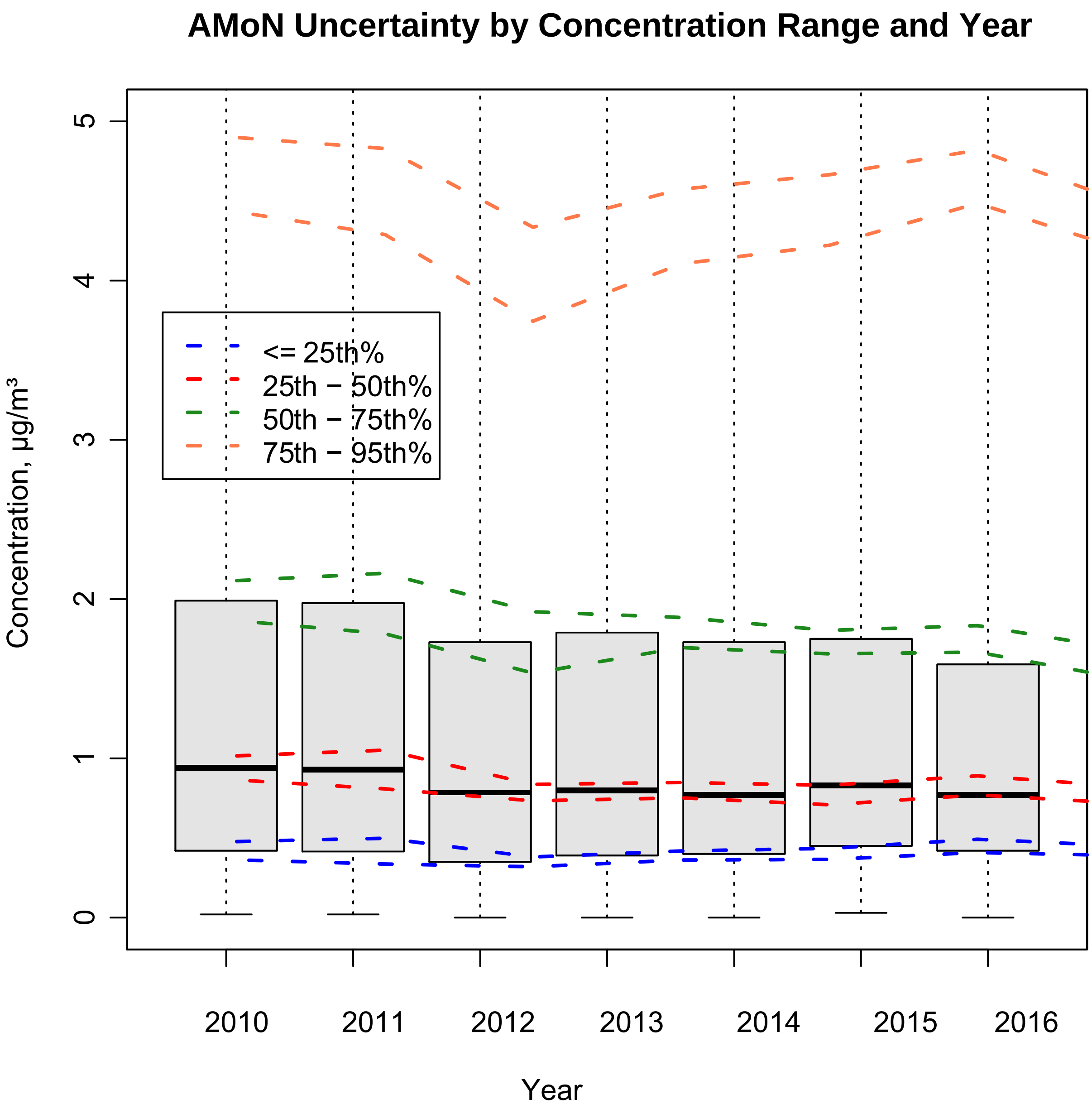


Figure 16. Annual AMoN ambient air ammonia (NH_3) measurements, and annual AMoN uncertainties by quartile based on 3-year moving data distribution for 2010 - 2016

AMoN detection limits

The AMoN laboratory detection limit (L_D) is calculated annually from unexposed passive sampler cores (i.e., "new core blanks"), extracted and analyzed at the Central Analytical Laboratory (CAL) with each sampling batch.

The AMoN network detection limit (L_N) is calculated quarterly and annually (see CAL SOP DA-4085) from values of valid travel blanks shipped to individual stations but not exposed following standard AMoN field procedures:

$$\boldsymbol{L_N} = \boldsymbol{\bar{x}_t} + \left(\mathbf{2} \times \boldsymbol{t}_{(95\text{th}\%, \boldsymbol{n_t}-\mathbf{1})} \times \boldsymbol{\sigma_t}\right)$$

where: $\boldsymbol{L_N}$ = annual AMoN detection limit, mg/L

$\boldsymbol{\bar{x}_t}$= annual arithmetic mean of valid travel blank concentrations, mg/L

$\boldsymbol{t}_{(95\text{th}\%, \boldsymbol{n_t}-\mathbf{1})}$ = student's *t*-distribution at the 95th% confidence interval and (n_t – 1) degrees of freedom, unitless

n_t = number of valid travel blanks deployed during the year

σ_t = standard deviation of annual valid travel blank concentrations, mg/L

Table 23 shows annually calculated AMoN laboratory and network detection limits.

Table 23. AMoN laboratory and network detection limits for 2010 – 2016

Year	Laboratory Detection Limit (L_D)			Network detection Limit (L_N)		
	n	NH_4^+, mg/L	NH_3, µg/m^3	n	NH_4^+, mg/L	NH_3, µg/m^3
2010	100	0.012	0.024	496	0.282	0.560
2011	100	0.012	0.023	1078	0.280	0.557
2012	101	0.016	0.032	1402	0.326	0.647
2013	74	0.010	0.019	410	0.395	0.785
2014	66	0.006	0.011	408	0.368	0.731
2015	68	0.010	0.019	562	0.183	0.363
2016	69	0.011	0.022	799	0.118	0.235

AMoN Special Study

The purpose of this study is to identify differences between various Radiello™ passive-type air samplers exposure times. Results will be used to develop DQOs and DQIs for AMoN.

During 2016 two separate deployment time studies were performed at IL11 using AMoN's Radiello™ samplers. For twelve weeks during February - April, triplicate Radiello™ samplers were deployed at 1-, 2-, 3- and 4- week intervals. Ammonia concentrations for the non-standard 1-, 3- and 4-week intervals were compared with the normal 2-week IL11 results. Preliminary results are shown in Table 24.

Table 24. Preliminary results for AMoN Radiello™ air sampler exposure time study at site IL11, 2016.

<table>
<tr><th rowspan="2">Sampling interval Start</th><th rowspan="2">Sampling interval End</th><th colspan="4">Ammonia concentrati0ns ($\mu g/m^3$) for sampler exposures periods (weeks)</th></tr>
<tr><th>1 week</th><th>2 week</th><th>3 week</th><th>4 week</th></tr>
<tr><td>2/9/2016</td><td>2/16/2016</td><td>0.21</td><td rowspan="2">0.46</td><td rowspan="3">0.55</td><td rowspan="4">0.59</td></tr>
<tr><td>2/16/2016</td><td>2/23/2016</td><td>0.76</td></tr>
<tr><td>2/23/2016</td><td>3/1/2016</td><td>0.83</td><td rowspan="2">0.63</td></tr>
<tr><td>3/1/2016</td><td>3/8/2016</td><td>0.56</td><td rowspan="3">0.71</td></tr>
<tr><td>3/8/2016</td><td>3/15/2016</td><td>0.81</td><td rowspan="2">0.80</td><td rowspan="4">1.05</td></tr>
<tr><td>3/15/2016</td><td>3/22/2016</td><td>0.89</td></tr>
<tr><td>3/22/2016</td><td>3/29/2016</td><td>1.67</td><td rowspan="2">1.23</td><td rowspan="3">1.25</td></tr>
<tr><td>3/29/2016</td><td>4/5/2016</td><td>0.95</td></tr>
<tr><td>4/5/2016</td><td>4/12/2016</td><td>1.17</td><td rowspan="2">1.58</td><td rowspan="4">2.05</td></tr>
<tr><td>4/12/2016</td><td>4/19/2016</td><td>2.15</td><td rowspan="3">2.51</td></tr>
<tr><td>4/19/2016</td><td>4/26/2016</td><td>3.90</td><td rowspan="2">2.77</td></tr>
<tr><td>4/26/2016</td><td>5/3/2016</td><td>2.06</td></tr>
<tr><td colspan="2">Average</td><td>1.33</td><td>1.25</td><td>1.25</td><td>1.23</td></tr>
</table>

This study resumed using just single 1-week exposure starting on the May 31st deployment and continued through the end of 2016. For this period, the average 1-week concentration (single sampler) was 2.13 $\mu g/m^3$ and the 2-week concentration (triplicate samplers) was 1.99 $\mu g/m^3$. This study is ongoing at the IL11 site.

Special Studies

AIRMoN Field DF/DK Blanks Study

Since 1993 the CAL performs AIRMoN field blank study to evaluate wind-blown dry deposition contaminants. AIRMoN field blanks are collected monthly. The CAL sends a field blank solution (in 2016 it was DI water) to each AIRMoN site where half of the a volume (approximately 125 mL) is poured into AIRMoN sampling bag installed in a bucket that was deployed to the field during a dry (non-precipitation) period. The solution is allowed to reside in the bag preferably overnight but at least two hours. This solution is then decanted into 250 mL clean shipping bottle (DF sample), and is returned to the CAL along with the other half of the unexposed original field blank solution remaining in the original bottle (DK sample) for complete chemical analysis of both sample (see SOP PR-2083 and Instruction SM-5026). Results of analysis of the field blank study during 2016 are presented in Appendix C.

External Quality Assurance

The CAL participated in four external proficiency testing studies throughout 2016. The study identifiers and URLs for websites with study details and results are shown in Table 25. The CAL's performance was consistent with that of other top-performing laboratories participating in each of the studies.

Table 25. Interlaboratory comparison studies

Study Identifier	Managing Agency	Details and Results
Interlaboratory Comparison Program	U.S. Geological Survey	https://bqs.usgs.gov/PCQA/Interlaboratory_Comparison/index.php?page=start
Study 54 and 55	World Meteorological Organization/Global Atmospheric Watch (WMO/GAW)	http://www.qasac-americas.org/
Study 108 and 109	Environment and Climate Change Canada Proficiency Testing Program	Available upon request
Study 34	Norwegian Institute for Air Research (NILU)	Available upon request

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. 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 equipment stations.

In 2016, maintenance for each instrument was performed as described in the CAL's SOPs.

Unscheduled maintenance in 2016 included:

- Three pH electrodes and one conductivity cell were replaced during the year;
- In March 2016 and in May 2016, the peristaltic pump was replaced on the Agilent Technologies 5100 ICP-OES instrument.
- In May 2016, a new software version 7.2.1 was installed on the Agilent Technologies 5100 ICP-OES instrument.
- In May 2016 the pump for the QuikChem 8500 FIA instrument was repaired by the manufacturer.

In March 2016 pipette calibration was performed by Calibrate, Inc. (see Appendix D).
Preventative maintenance of the balances is performed annually at the Illinois State Water Survey.
In November 2016 basic preventive maintenance and calibration were performed by Central Illinois Scale Company for six CAL balances (see Appendix E). No problems were found.

Conclusions

The CAL performed consistently throughout 2016 and met all guidelines specified in the NADP CAL Quality Assurance Plan (2014 QAP). Compliance with Data Quality Objective (DQO) requirements was maintained. The elevated levels of NH_4^+ in the hood air are currently under investigation.

References

1. National Atmospheric Deposition Program/Central Analytical Laboratory Quality Assurance Plan, Version 7.0 May 2014: http://nadp.isws.illinois.edu/lib/qaplans/qapCal2014.pdf.
2. Central Analytical Laboratory SOPs: http://nadp.isws.illinois.edu/cal/PDF/NADPCAL-StandardOperatingProcedures_10-15.pdf
3. NADP Network Quality Assurance Plan 2014: http://nadp.isws.illinois.edu/lib/qaplans/NADP_Network_Quality_Assurance_Plan.pdf
4. Standard Methods for the Examination of Water and Wastewater, 22nd Edition.
5. Title 40 Code of Federal Regulations Part 136 - GUIDELINES ESTABLISHING TEST PROCEDURES FOR THE ANALYSIS OF POLLUTANTS, Appendix B – Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11, July 1, 2011.
6. Guidance for the Data Quality Objectives Process, EPA QA/G-4, 2000.
7. Review of the Central Analytical Laboratory for the National Atmospheric Deposition Program, June 3 -5, 2014 (available upon request from NADP QA manager).

APPENDIX A

MDLs, calculated quarterly in 2016

Ion	Type of MDL	MDL, mg/L based on results of the 1st quarter of 2016	n	MDL, mg/L based on results of the 2nd quarter of 2016	n	MDL, mg/L based on results of the 3rd quarter of 2016	n	MDL, mg/L based on results of the 4th quarter of 2016	n
Calcium	Lab MDL	**0.001**	10	**0.004**	7	**0.001**	7	**0.001**	7
	AIRMoN MDL	**0.002**	9	**0.001**	9	**0.003**	9	**0.002**	9
	NTN MDL	**0.007**	9	**0.006**	9	**0.005**	9	**0.008**	9
Potassium	Lab MDL	**0.002**	10	**0.001**	7	**0.003**	7	**0.002**	7
	AIRMoN MDL	**0.002**	9	**0.001**	9	**0.002**	9	**0.002**	9
	NTN MDL	**0.002**	9	**0.001**	9	**0.001**	9	**0.002**	9
Magnesium	Lab MDL	**0.001**	10	**0.002**	7	**0.001**	7	**0.001**	7
	AIRMoN MDL	**0.001**	9	**0.001**	9	**0.001**	9	**0.002**	9
	NTN MDL	**0.002**	9	**0.002**	9	**0.002**	9	**0.003**	9
Sodium	Lab MDL	**0.001**	10	**0.001**	7	**0.001**	7	**0.001**	7
	AIRMoN MDL	**0.002**	9	**0.001**	9	**0.002**	9	**0.002**	9
	NTN MDL	**0.003**	9	**0.002**	9	**0.001**	9	**0.002**	9
Chloride	Lab MDL	**0.005**	10	**0.002**	7	**0.003**	7	**0.002**	7
	AIRMoN MDL	**0.003**	9	**0.002**	9	**0.004**	9	**0.005**	9
	NTN MDL	**0.002**	9	**0.003**	9	**0.004**	9	**0.004**	9
Nitrate	Lab MDL	**0.006**	10	**0.006**	7	**0.005**	7	**0.004**	7
	AIRMoN MDL	**0.005**	9	**0.005**	9	**0.005**	9	**0.004**	9
	NTN MDL	**0.005**	9	**0.005**	9	**0.006**	9	**0.004**	9
Sulfate	Lab MDL	**0.005**	10	**0.006**	7	**0.006**	7	**0.005**	7
	AIRMoN MDL	**0.005**	9	**0.005**	9	**0.005**	9	**0.004**	9
	NTN MDL	**0.006**	9	**0.004**	9	**0.008**	9	**0.007**	9
Bromide	Lab MDL	**0.002**	10	**0.000**	7	**0.002**	7	**0.002**	7
	AIRMoN MDL	**0.002**	9	**0.002**	9	**0.004**	9	**0.003**	9
	NTN MDL	**0.003**	9	**0.003**	9	**0.004**	9	**0.007**	9
Ammonium	Lab MDL	**0.009**	10	**0.008**	7	**0.007**	7	**0.013**	7
	AIRMoN MDL	**0.012**	9	**0.008**	9	**0.007**	9	**0.008**	9
	NTN MDL	**0.014**	9	**0.018**	9	**0.021**	9	**0.023**	9
Orthophosphate	Lab MDL	**0.003**	10	**0.003**	7	**0.004**	7	**0.006**	7
	AIRMoN MDL	**0.004**	9	**0.004**	9	**0.004**	9	**0.006**	9
	NTN MDL	**0.005**	9	**0.004**	9	**0.010**	9	**0.011**	9

APPENDIX B

Standards, reference solutions and chemicals, used for calibration and QC/QA in 2016

Method/ Equipment	**Chemical/ Standards**	**Manufacturer/ Supplier**	**Use**	**Catalog #**	**Notes**
Inductively Coupled Plasma-Optical Emission Spectroscopy: ICP-OES/Vista-PRO/Agilent Technology ICP-OES/5100/ Agilent Technology	Calcium 10000 µg/mL	*SPEXCertiPrep*	Calibration	PLCA2-3Y	Accredited to ISO/IES 17025 ISO Guide 34
	Calcium 1000 µg/mL	*SPEXCertiPrep*	Calibration	PLCA2-2Y	Accredited to ISO/IES 17025 ISO Guide 34
	Calcium 1000 µg/mL	*SCP Science (Canada)*	Reference	140-051-201	NIST Standard Reference Material
	Potassium 1000 µg/mL	*SPEXCertiPrep*	Calibration	PLK2-2Y	Accredited to ISO/IES 17025 ISO Guide 34
	Potassium 1000 µg/mL	*SCP Science (Canada)*	Reference	140-051-191	NIST Standard Reference Material
	Magnesium 1000 µg/mL	*SPEXCertiPrep*	Calibration	PLMG2-2Y	Accredited to ISO/IES 17025 ISO Guide 34
	Magnesium 1000 µg/mL	*SCP Science (Canada)*	Reference	140-051-121	NIST Standard Reference Material
	Sodium 10000 µg/mL	*SPEXCertiPrep*	Calibration	PLNA2-3Y	Accredited to ISO/IES 17025 ISO Guide 34
	Sodium 1000 µg/mL	*SPEXCertiPrep*	Calibration	PLNA2-2Y	Accredited to ISO/IES 17025 ISO Guide 34
	Sodium 1000 µg/mL	*SCP Science (Canada)*	Reference	140-051-111	NIST Standard Reference Material

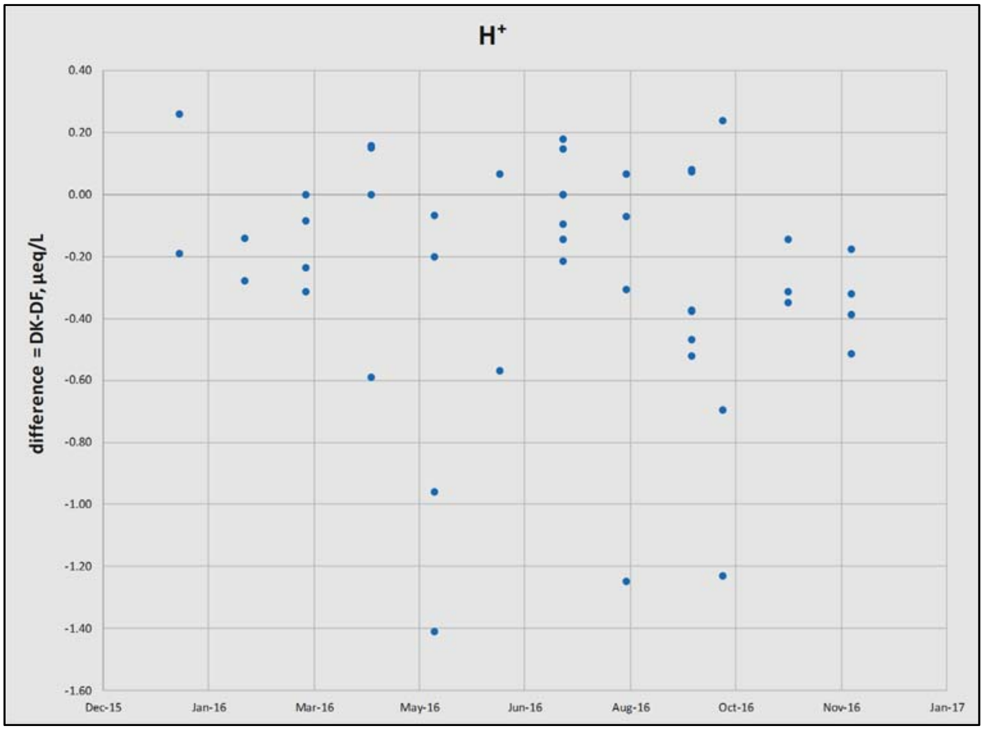
Method/ Equipment	Chemical/ Standards	Manufacturer/ Supplier	Use	Catalog #	Notes
Ion Chromatography: IC/Dionex ICS 2000/Thermo IC/Dionex ICS 5000/Thermo	Anion Standard 1000 µg/mL Chloride	*SPEXCertiPrep*	Calibration	AS-CL9-2X	Accredited to ISO/IES 17025 ISO Guide 34
	Chloride 1000 µg/mL	*Alfa Aesar*	Reference	35551	Manufactured and certified under an ISO 9001, ISO/IEC 17025, and ISO Guide 34
	Anion Standard 1000 µg/mL Nitrate	*SPEXCertiPrep*	Calibration	AS-NO39-2X	Accredited to ISO/IES 17025 ISO Guide 34
	Nitrate 1000 µg/mL	*Alfa Aesar*	Reference	35549	Manufactured and certified under an ISO 9001, ISO/IEC 17025, and ISO Guide 34
	Anion Standard 1000 µg/mL Sulfate	*SPEXCertiPrep*	Calibration	AS-SO49-2X	Accredited to ISO/IES 17025 ISO Guide 34
	Sulfate 1000 µg/mL	*Alfa Aesar*	Reference	35547	Manufactured and certified under an ISO 9001, ISO/IEC 17025, and ISO Guide 34
	Anion Standard 1000 µg/mL Bromide	*SPEXCertiPrep*	Calibration	AS-BR9-2X	Accredited to ISO/IES 17025 ISO Guide 34
	Bromide 1000 µg/mL	*Alfa Aesar*	Reference	35552	Manufactured and certified under an ISO 9001, ISO/IEC 17025, and ISO Guide 34

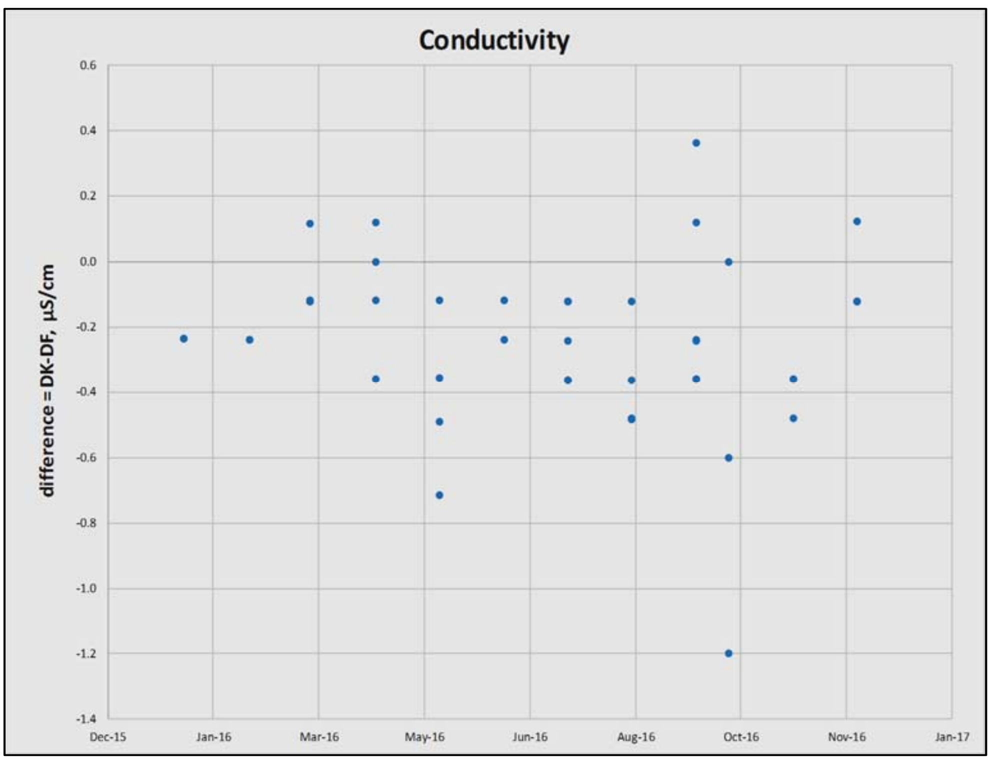
Method/ Equipment	Chemical/ Standards	Manufacturer/ Supplier	Use	Catalog #	Notes
Flow Injection Analysis (FIA) Colorimetry: QuickChem8500/HACH/ Lachat instruments	Ammonium Chloride Certified ACS	*Fisher Scientific*	Calibration	A661-500	
	Ammonium Sulfate Certified ACS	*Fisher Scientific*	Reference	A702-500	
	Phosphate as PO4 1000 mg/L	*ERA*	Calibration	994	Traceable to NIST
	o-Phosphate Nutrients	*VHG*	Reference	HG-QWSONUT-15	
	Phosphate 100.0 ± 1.0 mg/L as PO4	*HACH*	Reference	1436832	NIST
Conductivity measurement: YSI 3200 Conductivity Instrument/YSI Inc Electrical Conductivity Cell YSI 3253 K=1.0/cm	Conductivity standard 84 µS/cm	*Reagecon (Ireland)*	Calibration	CSKC84	Manufactured under an NSAI registered I.S EN ISO9001:2008 Quality System, registration no:19.2769
	Conductivity standard 5 µS/cm	*Reagecon (Ireland)*	Reference	CSKC5	Manufactured under an NSAI registered I.S EN ISO9001:2008 Quality System, registration no:19.2769
	Conductivity standard 20 µS/cm	*Reagecon (Ireland)*	Reference	CSKC20	Manufactured under an NSAI registered I.S EN ISO9001:2008 Quality System, registration no:19.2769
pH measurement: Seven Multi pH-Meter/Mettler Toledo Automater pH and specific conductivity instrument/SCP Science Ion-Selective Glass Electrode/Broadley-James Corporation	Buffer solution pH 10.00	*Fisher Scientific*	Calibration	SB116-500	
	Buffer solution pH 7.00	*Fisher Scientific*	Calibration	SB107-500	
	Buffer solution pH 4.00	*Fisher Scientific*	Calibration	SB101-500	
	Low ionic Strength pH Buffer pH 6.97	*ThermoFisher Scientific*	Reference	700702	
	Low pH Standard Solution		Reference	NA	Solution is prepared in CAL from Nitric Acid Optima Grade (Fisher Scientific Cat. # A467-500)

Method/ Equipment	Chemical/ Standards	Manufacturer/ Supplier	Use	Catalog #	Notes
All methods and instruments	Certified Matrix Reference Material **RAIN-12**	*ECCC*	Reference	NA	
	FR50 and **MDL** Matrix Reference Solutions, prepared from:		Reference	NA	Solutions are prepared in CAL
	Ammonium Bicarbonate	*Fisher Scientific*		A643-500	Certified
	Ammonium Chloride	*Fisher Scientific*		A702-500	Certified ACS
	Ammonium Sulfate	*Fisher Scientific*		A661-500	Certified ACS
	Calcium Hydroxide	*Fisher Scientific*		C97-500	Certified
	Calcium Nitrate Tetrahydrate	*Fisher Scientific*		C109-500	Certified ACS
	Magnesium Chloride Hexahydrate	*Fisher Scientific*		M35-500	Certified ACS
	Magnesium Sulfate	*Fisher Scientific*		M65-500	Certified
	Potassium Chloride	*Fisher Scientific*		P217-500	Certified ACS
	Sodium Fluoride	*Fisher Scientific*		S-299-100	Certified ACS
	Sodium Nitrate	*Fisher Scientific*		S343-500	Certified ACS
	Hydrochloric Acid	*Fisher Scientific*		A508-P500	Tracemetal Grade
	Nitric Acid	*Fisher Scientific*		A467-500	Optima™, for Ultra Trace Elemental Analysis
	Sulfuric Acid	*Fisher Scientific*		A510-P500	Tracemetal Grade

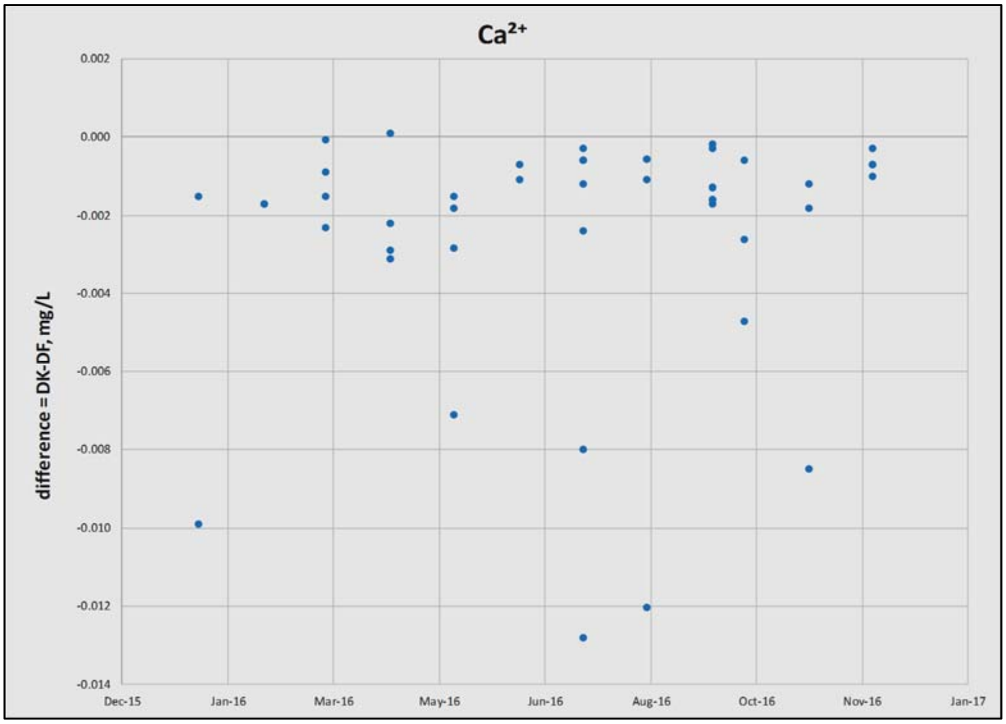
APPENDIX C

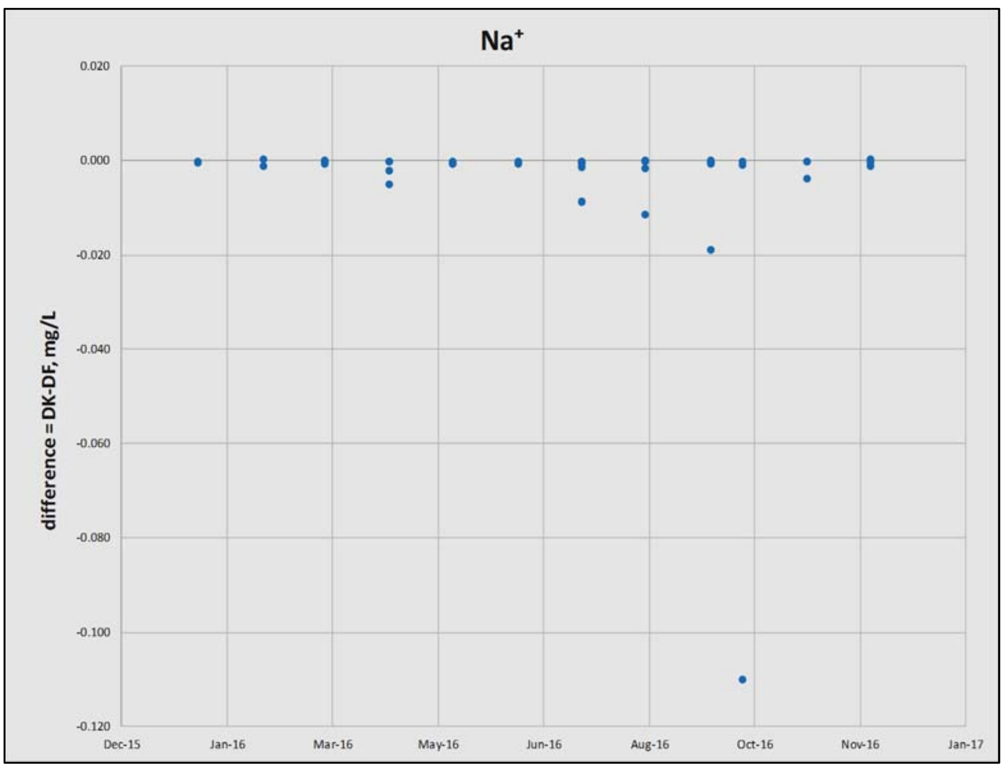
AIRMoN DF/DK Study Data





DF: Field Bag Exposed sample
DK: Original Bottle Sample





DF: Field Bag Exposed sample
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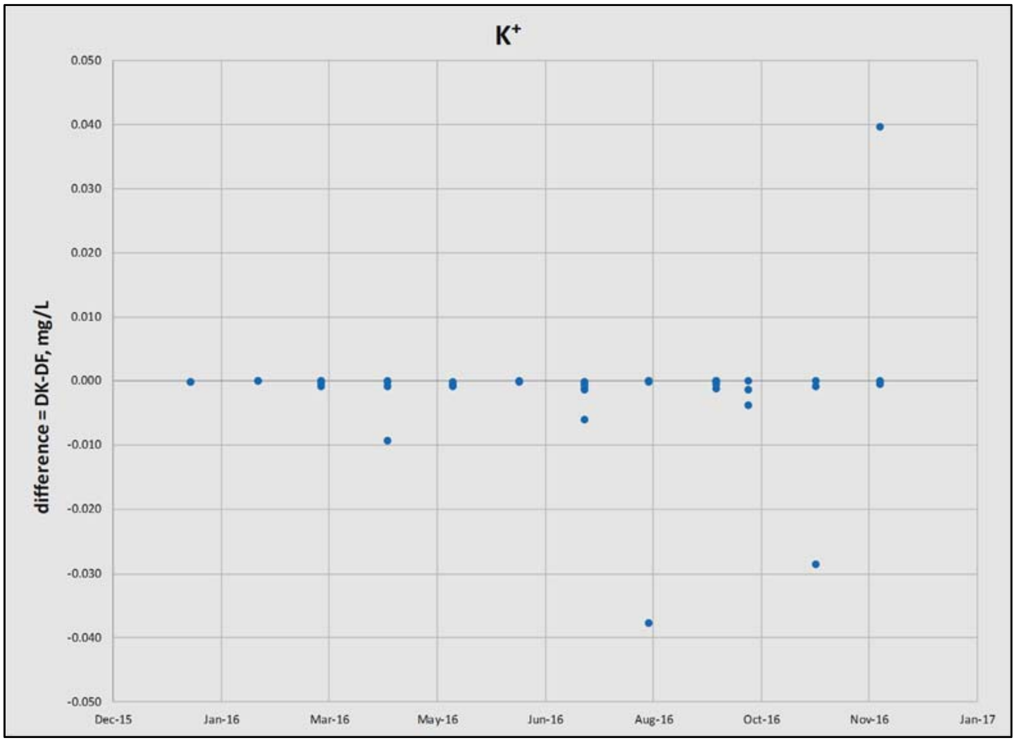

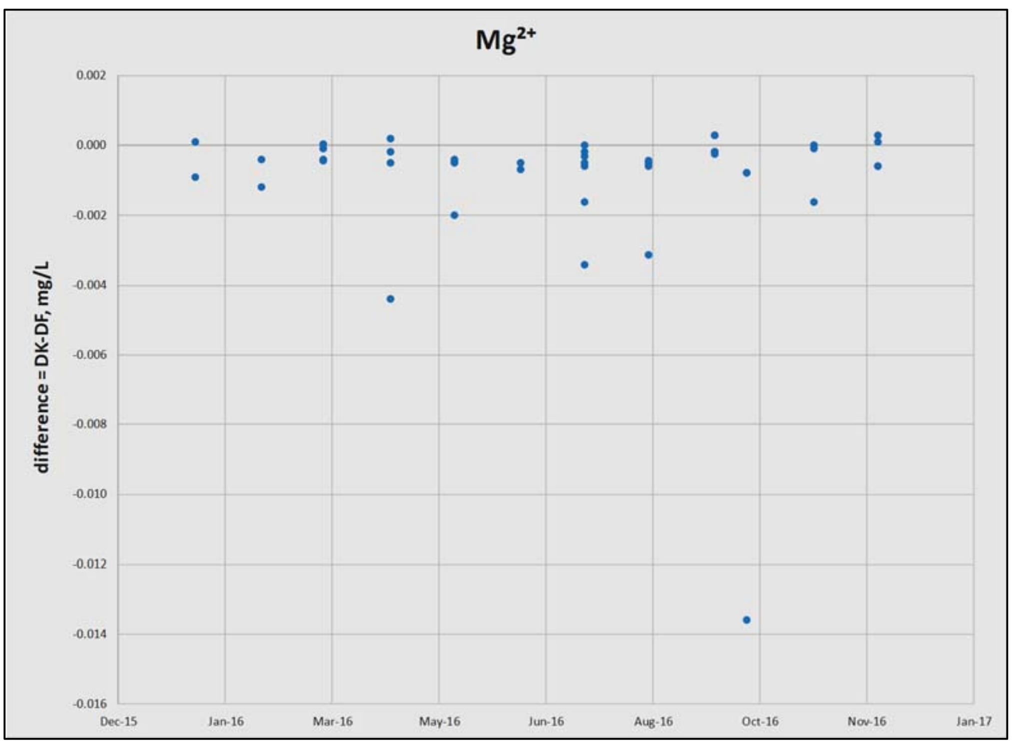

DF: Field Bag Exposed sample
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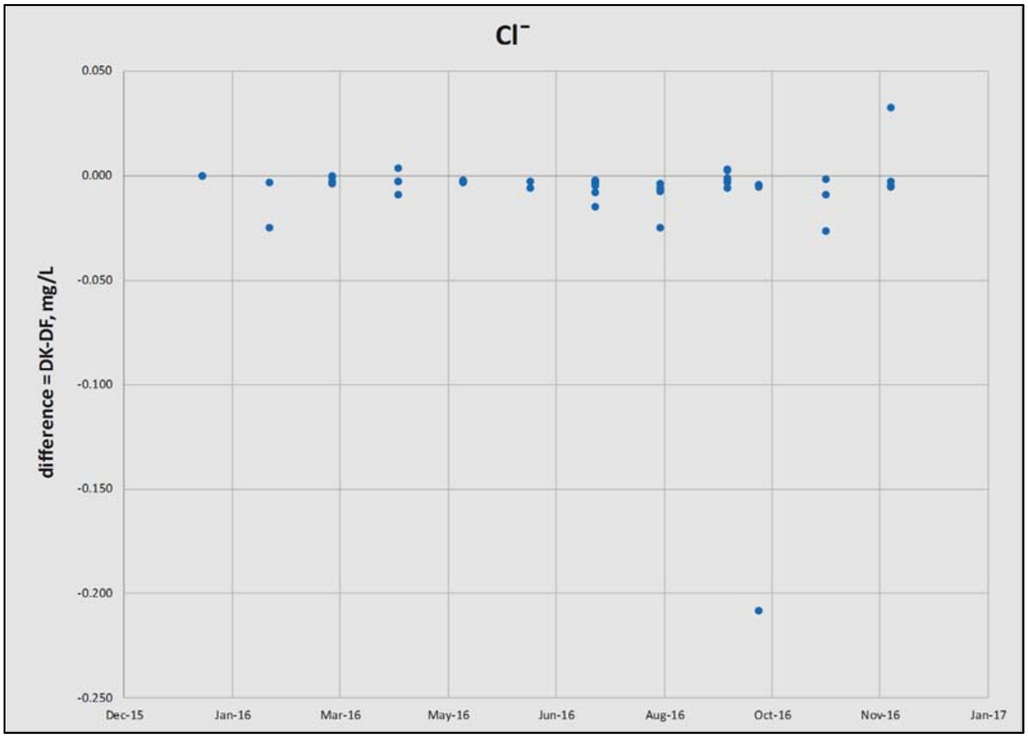
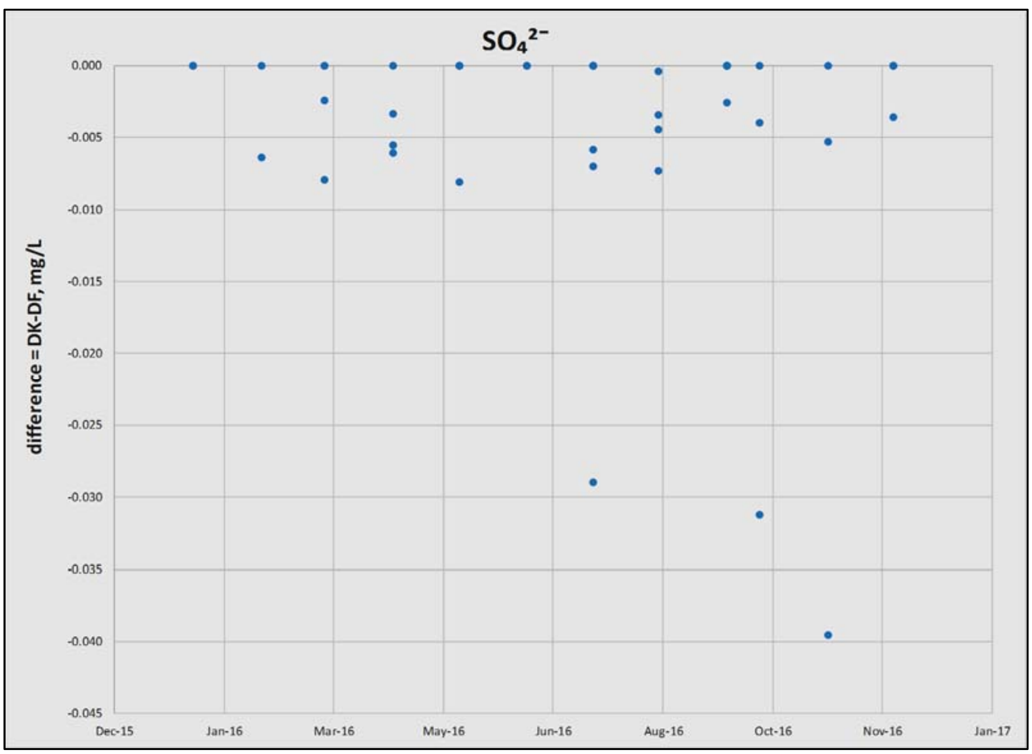
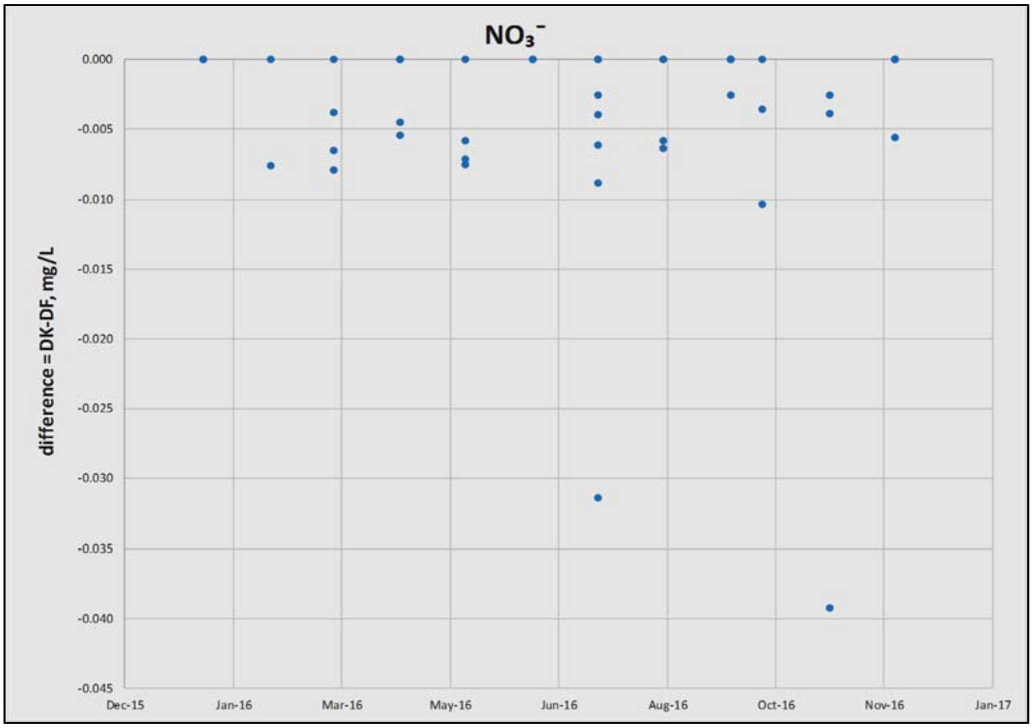
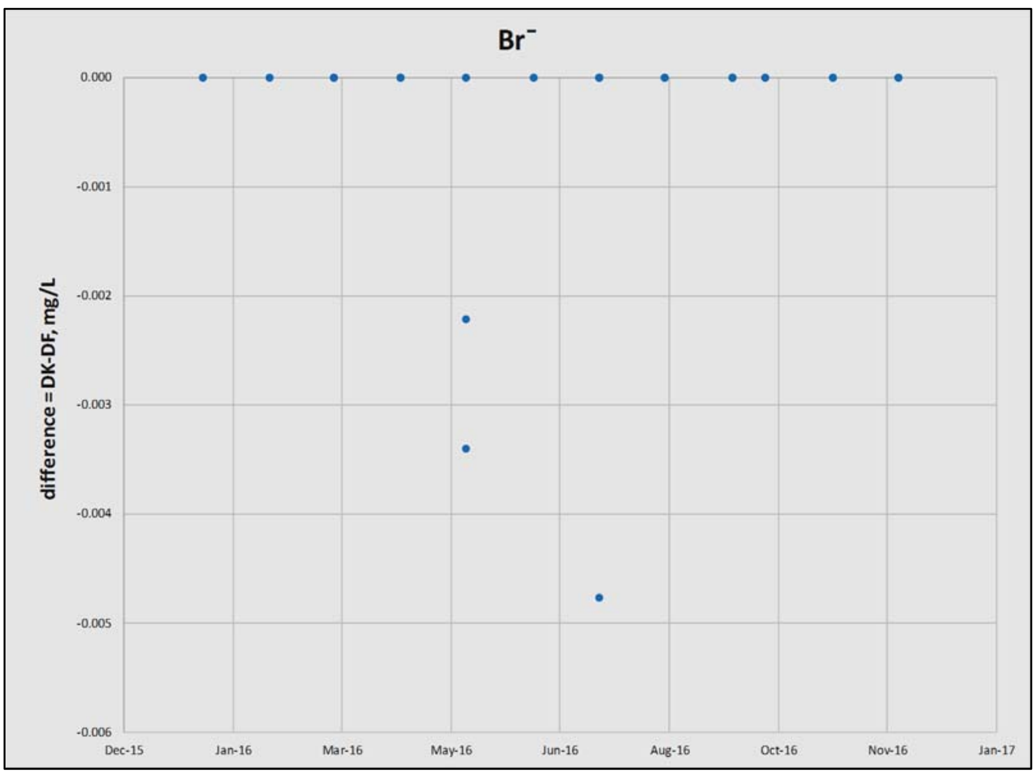


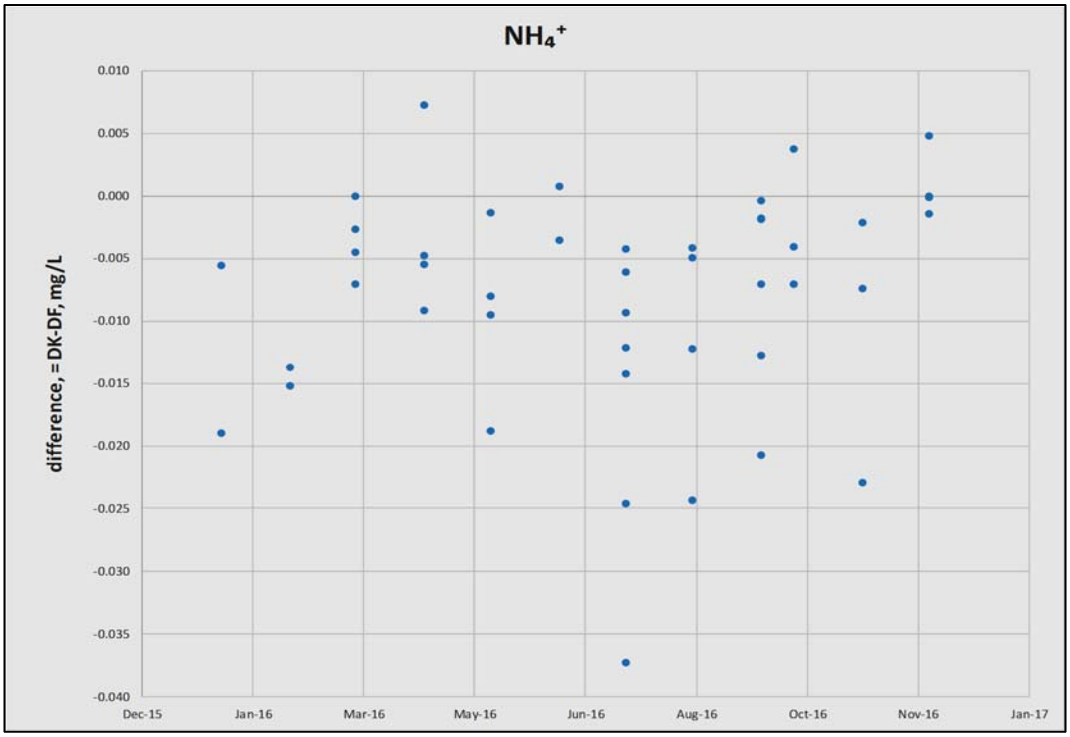


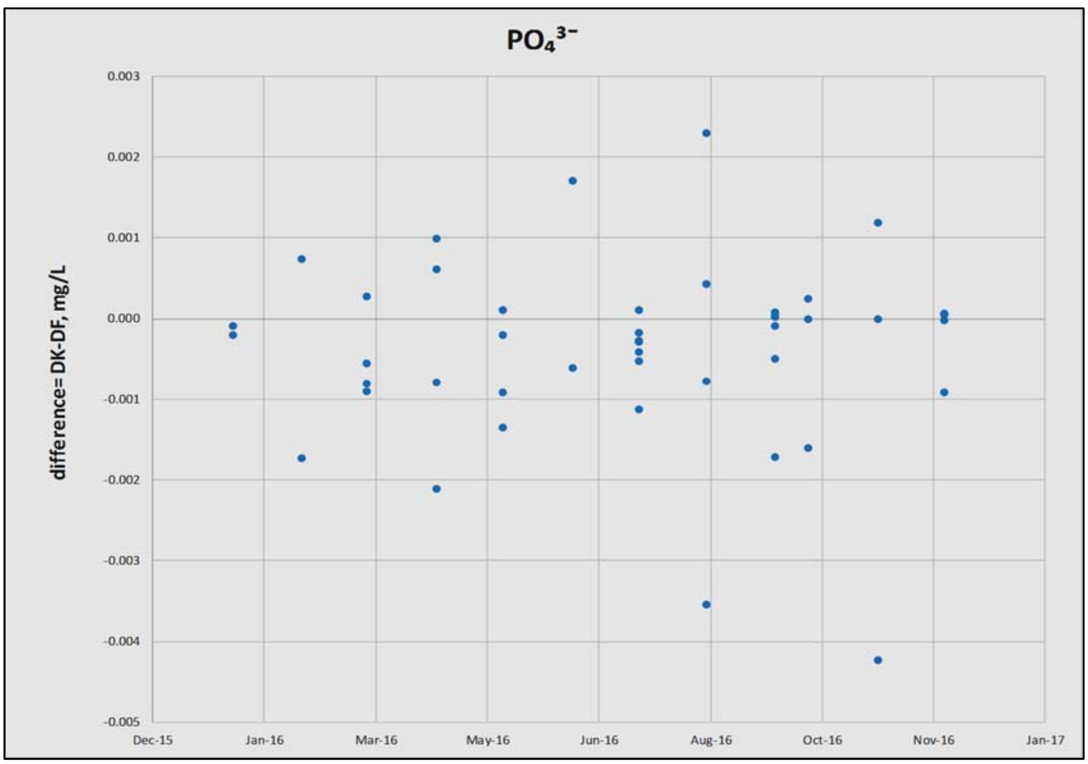
DF: Field Bag Exposed sample
DK: Original Bottle Sample





DF: Field Bag Exposed sample
DK: Original Bottle Sample





DF: Field Bag Exposed sample
DK: Original Bottle Sample

APPENDIX D

Pipettes Calibration Service Sheet in 2016

Calibrate, Inc.
The Pipet People

Work Order #: BK16031801

Client: ILLINOIS STATE WATER SURVEY:WEBB

ISO/IEC 17025 Accredited
Level 5 and 6 Service

Next Service Due: Mar-2017

LIST

Total # of Pipettes: 46

Pipette #	Size	Manufacturer	Type	Part / Part Number / Repairs	Parts/Repairs	Certification	Service	Total
215774	1000	Eppendorf	Single				$25.00	$25.00
215824	1000	Eppendorf	Single				$25.00	$25.00
KH02808	10000	Finnpipette	Single				$25.00	$25.00
KH02806	10000	Finnpipette	Single				$25.00	$25.00
431093Z	50000	Eppendorf Rep	Single				$25.00	$25.00
431110Z	50000	Eppendorf Rep	Single				$25.00	$25.00
A1416733U	200	Rainin	Single				$25.00	$25.00
H1401397U	1000	Rainin	Single				$25.00	$25.00
B1435388U	5000	Rainin	Single				$25.00	$25.00
017201	5000	Eppendorf	Single				$25.00	$25.00
4506655	1000	Eppendorf	Single				$25.00	$25.00
3491005	100	Eppendorf	Single				$25.00	$25.00
3492165	5000	Eppendorf	Single				$25.00	$25.00
2028121	1000	Eppendorf	Single				$25.00	$25.00
027565	100	Eppendorf	Single				$25.00	$25.00
J1414537U	10000	Rainin	Single				$25.00	$25.00
I1404705U	5000	Rainin	Single				$25.00	$25.00
L1440016U	1000	Rainin	Single				$25.00	$25.00
F89613	10000	Finnpipette	Single				$25.00	$25.00
AA90210	10000	Finnpipette	Single				$25.00	$25.00
H45296	5000	Finnpipette	Single				$25.00	$25.00
148352	1000	Eppendorf	Single				$25.00	$25.00
K1302176U	5000	Rainin	Single				$25.00	$25.00
A1417210U	1000	Rainin	Single				$25.00	$25.00
A1416777U	200	Rainin	Single				$25.00	$25.00
322476A	1000	Eppendorf	Single				$25.00	$25.00
O21978B	1000	Eppendorf	Single				$25.00	$25.00
313982Z	100	Eppendorf	Single				$25.00	$25.00
A1430084U	5000	Rainin	Single				$25.00	$25.00
A1417215U	1000	Rainin	Single				$25.00	$25.00
A1416739U	200	Rainin	Single				$25.00	$25.00
G1255851T	5000	Rainin	Single				$25.00	$25.00
B541546856	2000	Rainin	Single				$25.00	$25.00
E1516127U	1000	Rainin	Single				$25.00	$25.00
C1577645U	100	Rainin	Single				$25.00	$25.00
D0761414B	1000	Rainin	Single				$25.00	$25.00
A07149668	100	Rainin	Single				$25.00	$25.00
029662	1000	Eppendorf	Single				$25.00	$25.00
1784586	1000	Eppendorf	Single				$25.00	$25.00
1783386	1000	Eppendorf	Single				$25.00	$25.00
1290265	1000	Eppendorf	Single				$25.00	$25.00
269198	100	Eppendorf	Single				$25.00	$25.00
472058	100	Eppendorf	Single				$25.00	$25.00
1713856	100	Eppendorf	Single				$25.00	$25.00
382567	1000	Eppendorf	Single				$25.00	$25.00
1690348	100	Eppendorf	Single				$25.00	$25.00

APPENDIX E

Basic preventive maintenance and balance calibration in 2016

CENTRAL ILLINOIS SCALE COMPANY

2560 Parkway Court Decatur, IL 62526
(217) 428-0923 • (800) 234-5880
lab@CentralIllinoisScale.com

CALIBRATION CERTIFICATE

DANVILLE DECATUR PEORIA SPRINGFIELD

17025 Accredited

Certificate No: 411111601

PJLA Calibration
Accreditation #: 59078

Customer: IL. Water Survey
2204 Griffith Dr
Champaign, IL 61820

Device Calibration Date: November 11, 2016
Next Calibration Due: November 30, 2017
Listing: N/A

MAKE	MODEL	SERIAL NO.	CUSTOMER NO.	LOCATION	INDICATION
Mettler Toledo	XS204	11262292194	N/A	302	220g. X 0.0001g

Shift Test

	Initial Test				Final Test		
Point	Weight	Reading	Error	Tolerance	Weight	Reading	Error
C	100g	0.0000g	N/A	0.0008g	100g	0.0000g	0.0000g
1	100g	0.0001g	0.0001g	0.0008g	100g	0.0000g	0.0000g
2	100g	0.0000g	0.0000g	0.0008g	100g	0.0000g	0.0000g
3	100g	0.0001g	0.0001g	0.0008g	100g	0.0000g	0.0000g
4	100g	0.0000g	0.0000g	0.0008g	100g	0.0000g	0.0000g

Load Test

	Initial Test				Final Test		
Offset Wt.	Offset	Weight	Error	Tolerance	Offset	Weight	Error
0g	0.0000g	49.9999g	N/A	0.0003g	0.0000g	50.0000g	0.0000g
50g	49.9999g	99.9999g	0.0000g	0.0003g	50.0000g	100.0000g	0.0000g
100g	99.9999g	149.9999g	0.0000g	0.0003g	100.0000g	150.0000g	0.0000g
150g	149.9999g	199.9999g	0.0000g	0.0003g	150.0000g	200.0000g	0.0000g

Cal Span

	Initial Test				Final Test		
Test Wt.	Zero Load	Test Wt.	Error	Tolerance	Zero Load	Test Wt.	Error
220.0000g	0.0000g	219.9998g	-0.0002g	0.0004g	0.0000g	220.0000g	0.0000g

Quality : *The device listed has been adjusted / calibrated in accordance with NIST HB44 methods and specifications under Quality Procedure QAP-119 and Quality Work Instructions QAPI-120 as found in Central Illinois Scale Company ANSI/ ISO/IEC 17025 -2005 Quality System.*

Weight Standards

The listed device has been adjusted and calibrated with test weights certified by an authorized agency of the Bureau of Weights and Measures and issued NIST Traceable Numbers as documented in Central Illinois Scale Company Weight Traceability Record Book.

	ID Number	Date Certified	Next Due Date
Wt. Set 1	54890	4-Apr-2016	30-Apr-2017
Wt. Set 2	66507	N/A	N/A
Wt. Set 3	N/A	N/A	N/A

The tolerances listed are Maintenance Tolerances. Acceptance Tolerances are ½ Maintenance and will be applied when applicable. The results contained herein relate only to the item being calibrated. A Test Uncertainty Ratio of at least 4:1 of the standards used for calibration activities is maintained unless otherwise noted. This Calibration Certificate has been prepared for the expressed use by the customer whose name appears at the top and shall not be reproduced or distributed, except in full, outside of the customer's control without prior written consent of Central Illinois Scale Company.

Notes: **Cleaned and calibrated**

Customer: ____________________ Technician: Cory Mundwiler Date: November 11, 2016