Quality Assurance Report
National Atmospheric Deposition Program
2015

Laboratory Operations
Central Analytical Laboratory

Prepared by Nina Gartman
CAL Quality Assurance Lab Project Specialist
National Atmospheric Deposition Program
Illinois State Water Survey
Prairie Research Institute
University of Illinois at Urbana-Champaign
2204 Griffith Drive
Champaign, IL 61820
September 2016

Acknowledgments

Many individuals deserve a thank you and credit for their contributions to this report, which summarizes the quality assurance measures at the Central Analytical Laboratory (CAL). The CAL provides analytical support for the National Atmospheric Deposition Program (NADP) National Trends Network (NADP/NTN), Atmospheric Integrated Research Monitoring Network (NADP/AIRMoN), and Ammonia Monitoring Network (NADP/AMoN). The dedication of the highly skilled staff at the CAL is very much appreciated. Their expertise and contributions were critical to the success of quality assurance measures throughout the year. In addition, credit is also given to the site operators for their hard work and perseverance; the staff at the U.S. Geological Survey (USGS) Branch of Quality Systems for coordinating the external QA program for NADP; and to the reviewers for the final report, including Pam Bedient (NADP/CAL), Christopher Lehmann (NADP/CAL), Mark Rhodes (NADP), Melissa Puchalski (USEPA), Greg Wetherbee (USGS), and Dennis Jackson (Savannah River National Laboratory), for their insight and suggestions.

Table of Contents

Tables

Figures

List of Abbreviations

AES-07	External Rain Water Certified Reference Standard
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
DI	Deionized Water
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 50^{th} 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
QA	Quality Assuranse
QAP	Quality Assurance Plan
QC	Quality Control
PO	Program Office
RO	Reverse Osmosis
SOP	Standard Operating Procedure

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 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 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 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 for 2015 are provided in Table 2.

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 / *Broadley-James Corporation* / Seven Multi pH-Meter / *Mettler Toledo*	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 / *YSI Inc*	EPA Method 120.1 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*	EPA Method 300.1 ASTM Method D-5085-95 CAL SOP AN-0018
Ammonium (NH_4^+)	**Flow Injection Analysis (FIA) Colorimetry** / QuikChem 8500/ *HACH/Lachat Instruments*	EPA Method 350.1 Lachat Method 10-107-06-1B CAL SOP AN-0014 CAL SOP AN-4022
Orthophosphate (PO_4^{3-})	**Flow Injection Analysis (FIA) Colorimetry** / QuikChem 8500/ *HACH/Lachat Instruments*	EPA Method 365.1 Lachat Method 10-115-01-1B 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	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 the QA chemist works independently, and reports to the CAL director.

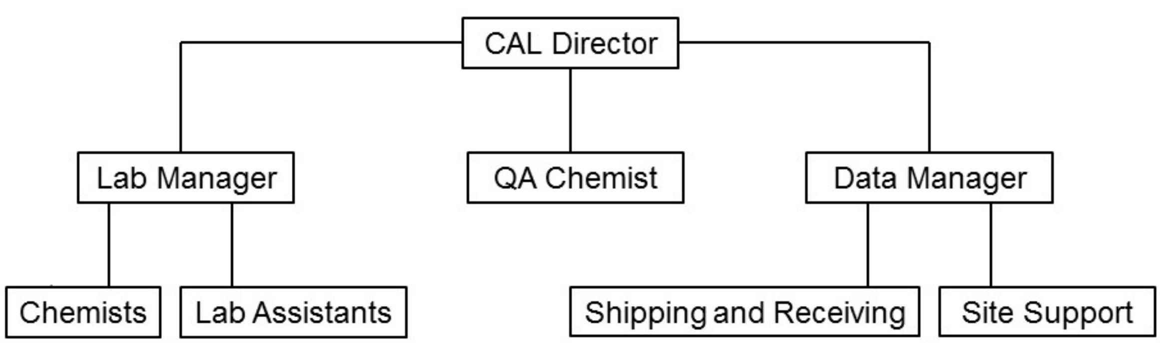


Figure 1. CAL's organization

Significant Changes in 2015

- January 1, 2015, the NTN initiated a new protocol for low-volume sample analysis, affecting samples starting with LABNO TN6575SW. For more information, see the Network Operations Subcommittee Meeting minutes from October 21, 2014.
- March 1, 2015, the AIRMoN has a new prioritization of sample analysis, affecting samples starting with LABNO AC9835L.
- Testing of a new Agilent Technologies 5100 ICP-OES was completed, and the instrument was approved March 1, 2015. The first data reported were for TN9608SW and AC9908L NTN and AIRMoN samples, respectively. The prior instrument, a Varian Vista Pro, continues for use, and the instrument used for analysis is tracked in the CAL's LIMS.
- In May 2015 the use of ULINE and Kimtech Kimwipe wipers ceased for AMoN preparation and extraction due to suspected cross contamination in handling AMoN samples, and Fisher Absorbent Surface Liners (Catalog # 14-127-46) were tested and selected for use.
- In June 2015 the new building-wide argon gas distribution system Bulk Argon Dewar was installed at ISWS to supply all ICP instruments.
- In September 2015 the CAL received delivery of an automated pH and specific conductivity instrument developed by SCP Science of Montreal, Quebec. Testing of new instrument started in October 2015. Once approved, this instrument will be used for analysis of NTN and AIRMoN samples.
- A new Miele dishwasher was installed in room 306. This dishwasher is designated for washing new 1-L NTN bottles and AMoN glass jars only.
- During 2015, MDL values were checked quarterly in order to determine whether they change during the year.
- In 2015, QA tests of washed and reused supplies changed from FR50 solution to the lower concentration MDL solution.
- Staff changes:
  - Kristina Freeman was hired as a Sample Processing Assistant in January 2015.
  - Wyatt Sherlock was hired as a Technician (Hourly) in February 2015
  - Anita Brown was hired as a Shipping/Receiving Clerk in May 2015.
  - Phyllis Ballard, a Shipping/Receiving Clerk, retired in June 2015.
  - Kevin Schoening was hired as a Shipping/Receiving Clerk in July 2015.
  - Sybil Anderson was hired as a CAL Project Coordinator in July 2015.

Quality Assurance/Quality Control Overview

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 ±10% if the value is ≥ 100 times the MDL, or ± 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 ± MDL [2014 CAL 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 standardized again, 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 [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) [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.

The low concentration standard, that is approximately three to five times the projected MDL for each analyte, is measured 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 2015, a QA specialist sent approximately three MDL blind samples to the laboratory for analysis each week:

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

Deionized (DI) water blind samples were also analyzed every week.
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 IDL and MDLs for 2015 (Table 2) were calculated using the results of analysis in 2014. The calculated MDLs are provided to the NADP Program Office for data released to the public.

Table 2. 2015 IDLs and MDLs

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 AC9682L - AD0661L

** For NTN sample range TN6516SW - TP0369SW

However, during 2015, MDL values were also calculated every three months in order to determine how they could change during the year (see Appendix A). The table shows the values of MDLs, calculated for each quarter in 2015.

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. 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 3). "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 PO_4^{3-} , as PO_4^{3-} can affect the NH_4^+ concentration.

Table 3. Target concentrations and acceptable ranges (± 3 x stdev) for QC check solutions in 2015

Parameter	FR50 (mg/L)	FL (mg/L)	FH (mg/L)	FB (mg/L)
pH	4.87 ± 0.10	4.34 ± 0.10	6.96 ± 0.10	5.63 ± 0.27
Specific Conductance (µS/cm)	9.7 ± 0.9	5.3 ± 0.3	20.3 ± 1.5	1.0 ± 0.6
Calcium	0.1300 ± 0.0090	0.0400 ± 0.0030	2.500 ± 0.150	0.0000 ± 0.0009
Magnesium	0.0230 ± 0.0040	0.0100 ± 0.0012	1.000 ± 0.060	0.0000 ± 0.0009
Sodium	0.0560 ± 0.0045	0.0400 ± 0.0030	2.500 ± 0.150	0.0000 ± 0.0009
Potassium	0.0215 ± 0.0037	0.0100 ± 0.0015	2.000 ± 0.135	0.0000 ± 0.0009
Chloride	0.104 ± 0.015	0.025 ± 0.006	3.000 ± 0.120	0.000 ± 0.004
Sulfate	0.955 ± 0.040	0.500 ± 0.030	5.000 ± 0.210	0.000 ± 0.002
Nitrate	0.893 ± 0.040	0.500 ± 0.030	5.000 ± 0.180	0.000 ± 0.004
Bromide	0.020 ± 0.004	0.025 ± 0.005	3.000 ± 0.150	0.000 ± 0.004
Ammonium	0.237 ± 0.012	0.050 ± 0.008	1.500 ± 0.060	0.000 ± 0.008
Orthophosphate	N/A	0.015 ± 0.003	0.100 ± 0.009	0.000 ± 0.004

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 2015

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

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 [QAP Section B-9.2]. Internal blind samples are evaluated monthly. Four different solutions were used for the internal blind study in 2015: deionized water (DI), MDL standard, FR50 and AES-07 (Table 5). AES-07 is an external rain water certified reference standard purchased from Environment Canada (https://www.ec.gc.ca/).

Along with regular blind samples, additional samples, prepared from the MDL standard, were submitted weekly for both NTN and AIRMoN networks. These blind samples were processed in the same way as field samples, including exposure to sample buckets (sample bags for AIRMoN) and lids used for each of the networks.

Table 5. Control internal blind samples target concentrations

Parameter	DI Water Target Concentration (mg/L)	FR50 Target Concentration (mg/L)	MDL standard Target Concentration (mg/L)	AES-07 Target Concentration (mg/L)
pH	5.63	4.87	5.57	5.42
Specific Conductance (µS/cm)	1.0	9.7	1.4	7.8
Calcium	<0.003*	0.131	0.009	0.224
Magnesium	<0.001*	0.024	0.005	0.048
Sodium	<0.002*	0.057	0.006	0.225
Potassium	<0.002*	0.021	0.005	0.041
Chloride	<0.005*	0.105	0.015	0.283
Sulfate	<0.005*	0.951	0.015	1.110
Nitrate	<0.005*	0.893	0.014	0.881
Bromide	<0.005*	0.020	0.015	NA
Ammonium	<0.008*	0.236	0.023	0.328
Orthophosphate	<0.005*	N/A	0.010	NA

* The average historic (2010 – 2014) 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.

Quality Control Discussion

Control Charts

In 2015, 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 [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 6. The Data Quality Objectives (DQOs) as defined in the CAL QAP were met.

If 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 5.6.3.2 – 5.6.3.4.

An example control chart is shown in Figure 2.

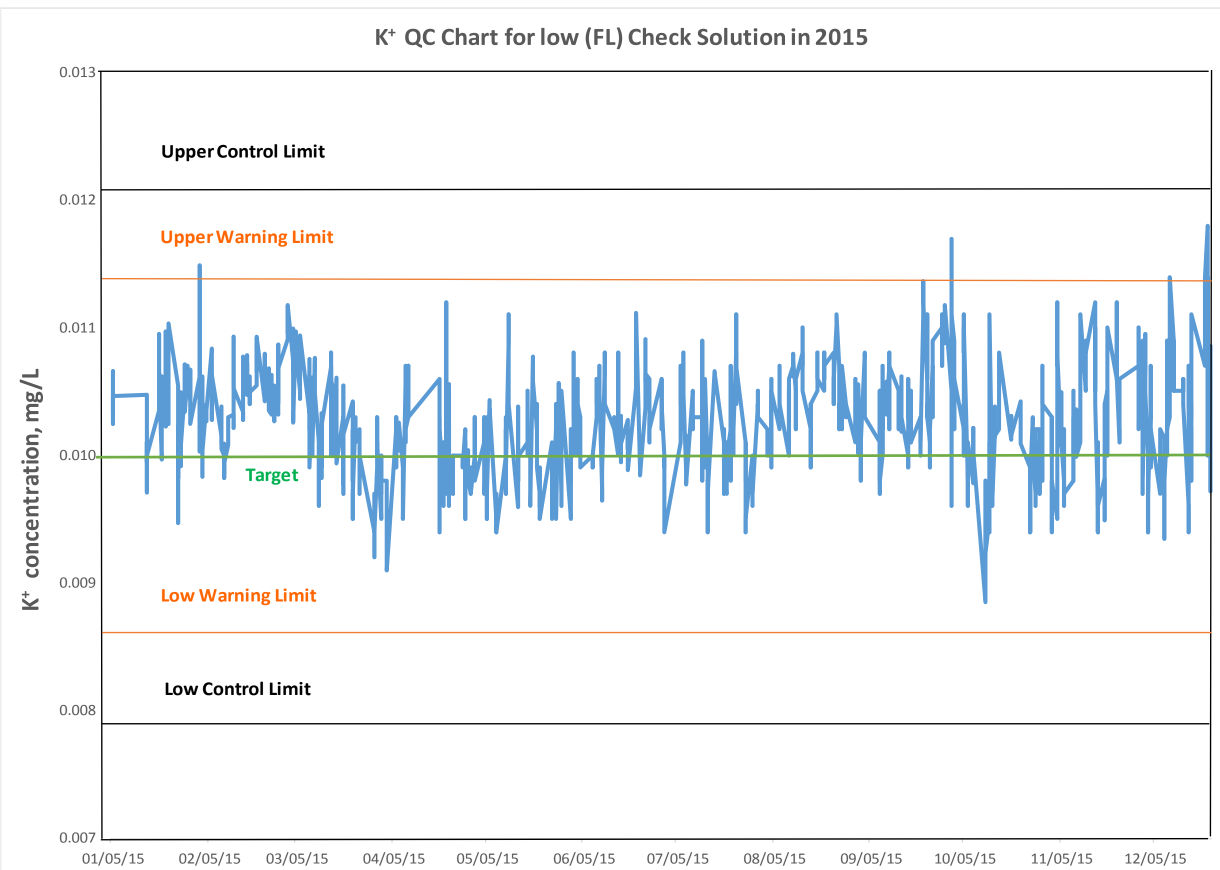


Figure 2. Example control chart in 2015

Table 6. Number of analyzed QC samples (FR50, FL, FH and FB), and number and percentage of QC values exceeding the warning limits in 2015 (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	1166	14	1.2	1465	5	0.3	1713	21	1.2	1320	12	0.9
Specific Conductance	884	3	0.3	1396	23	1.6	1403	1	0.1	907	14	1.5
Calcium	888	3	0.3	1053	5	0.5	1186	54	4.6	404	2	0.5
Magnesium	888	0	0.0	1054	7	0.7	1191	45	3.8	404	0	0.0
Sodium	884	19	2.1	1053	17	1.6	1184	154	13.0	404	0	0.0
Potassium	887	3	0.3	1050	3	0.3	1188	69	5.8	403	72	17.9
Chloride	1227	16	1.3	1272	19	1.5	1100	15	1.4	758	0	0.0
Sulfate	1211	48	4.0	1272	29	2.3	1103	63	5.7	761	0	0.0
Nitrate	1213	28	2.3	1273	61	4.8	1091	87	8.0	762	0	0.0
Bromide	1228	14	1.1	1276	8	0.6	1103	53	4.8	762	0	0.0
Ammonium	1059	17	1.6	1304	87	6.7	1147	53	4.6	932	1	0.1
Orthophosphate	NA	NA	NA	1002	11	1.1	878	29	3.3	629	39	6.2

Split Samples

Approximately every 100th NTN sample is split before filtering; then both samples are filtered and sent to the lab for analysis. Approximately every 50th AIRMoN sample is split, without filtering, and sent to 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 for the Absolute Percent Difference (APD) *, analysts investigate the cause and analyze additional samples within the run.

There were 137 pairs of split samples processed for NTN and AIRMoN in 2015. Variability for split chemical analyses is calculated as the Absolute Percent Differences (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 (2010 -2014) have PO_4^{3-} and Br^- concentrations lower than 10 times the MDL, the 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.

The results of split samples met the DQOs in 2015 as specified in the CAL Quality Assurance Plan.

---

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

Table 7. Minimum, mean, median and maximum absolute percent differences (APDs) for split samples in 2015

Parameter	Minimum APD (%)	Mean APD (%)	Median APD (%)	Maximum APD (%)
pH	0.0	0.6	0.4	2.8
Specific Conductance	0.0	1.7	1.4	13.3
Calcium	0.0	1.8	0.7	29.0 *
Potassium	0.0	2.2	1.6	22.9 *
Magnesium	0.0	1.8	1.3	9.9
Sodium	0.0	1.3	0.9	6.8
Chloride	0.0	2.1	0.7	13.1
Sulfate	0.0	1.0	0.4	6.7
Nitrate	0.0	0.9	0.4	6.4
Ammonium	0.0	1.2	0.7	6.9

* The high Ca^{2+} APD value (29.0%) was detected for the pair of NTN split samples for lab ID TO7288SW. The high K^+ APD value (22.9%) was detected for the pair of AIRMoN split samples for lab ID AC9778L. Upon reanalysis the same results were obtained for each split portion of these samples. This may due to the presence of particulate matter in the original unfiltered solution. The fact that Ca^{2+} and K^+ concentrations in those solutions were very low (0.033 and 0.026 mg/L Ca^{2+} in TO7288SW splits, and 0.023 and 0.018 K^+ in AC9778L splits) caused the large percent difference.

Replicate Samples

Analytical replicates are used by analysts daily. The chosen sample is reanalyzed 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. The table includes samples with concentrations ≥ 10 times MDL.

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

Table 8. Minimum, mean, median and maximum relative standard deviations (RSDs) for replicate samples with concentrations ≥ 10 times the MDL in 2015

Parameter	N	Minimum RSD %	Mean RSD %	Median RSD %	Maximum RSD %
pH	140	0.0	0.6	0.5	5.1
Specific Conductance	137	0.0	1.2	1.0	6.0
Calcium	178	0.0	0.6	0.4	5.3
Potassium	134	0.0	1.6	1.3	5.1
Magnesium	131	0.0	1.2	1.0	5.3
Sodium	158	0.1	1.3	1.1	5.6
Chloride	194	0.0	1.2	0.6	24.7 *
Sulfate	262	0.0	1.0	0.6	4.7
Nitrate	262	0.0	0.9	0.5	5.3
Ammonium	129	0.0	1.1	0.8	8.1

* The single high maximum RSD was due to random instrument analytical error unnoticed by the analyst

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 AES-07, FR50, 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 AES-07, FR50 and MDL blind solutions in 2015

Parameter	AES-07 (N=15)			FR50 (N=17)			MDL (N= 41)		
	Target, mg/L	RSD, %	Mean Recovery, %	Target, mg/L	RSD, %	Mean Recovery, %	Target, mg/L	RSD, %	Mean Recovery, %
pH	5.42	0.9	94.3	4.87	0.6	100.0	5.57	1.4	100.9
Specific Conductance	7.8 µS/cm	1.6	117.4	9.7 µS/cm	2.1	101.9	1.4 µS/cm	7.2	120.8
Calcium	0.224	1.4	98.4	0.131	1.3	100.1	0.009	2.7	99.7
Potassium	0.041	2.0	101.8	0.021	3.2	100.2	0.005	6.3	98.1
Magnesium	0.048	3.0	97.5	0.024	2.8	98.3	0.005	6.7	103.7
Sodium	0.225	2.1	100.7	0.057	2.6	98.5	0.006	4.2	90.3
Chloride	0.283	4.3	102.2	0.105	2.4	100.2	0.015	6.1	102.3
Sulfate	1.110	2.3	99.2	0.951	2.2	99.8	0.015	7.7	94.3
Nitrate	0.881	1.9	99.7	0.893	2.0	100.0	0.014	7.5	112.8
Bromide	NA	NA	NA	0.020	3.2	99.1	0.015	6.7	101.4
Orthophosphate	NA	NA	NA	NA	NA	NA	0.010	10.1	93.5
Ammonium	0.328	4.5	71.0 ***	0.236	1.5	99.8	0.023	15.4	80.3

---

*RSD (%) = (standard deviation/mean value) · 100
**Recovery (%) = (lab value/target value) · 100
***Ammonium values for AES-07 were low throughout the year (mean value = 0.233 mg/L). Testing throughout the year suggests that the ammonia concentration for the AES-07 solution changed.

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). An additional two percent of samples are selected at random for reanalysis (QAP Section 2.0). The results of reanalysis are reviewed by the QA Chemist, and required edits are made.

In 2015, a total of 111 edits (0.1% of all values) were made for NTN samples and 19 edits (0.2% of all values) were made for AIRMoN samples. Changes are documented in the database.

The number of field NTN and AIRMoN samples analyzed in 2015, and counts of reanalysis, split and blind samples are shown in Table 10.

Table 10. Number of field and Quality Control/Quality Assurance (QC/QA) samples analyzed during 2015

Network	Number of field samples analyzed	Number of QA Samples		
		Reanalysis samples	Blind samples	Split samples
NTN	11617	1369	41	121
AIRMoN	847	237	40	27

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 preparation, etc.

RO DI water is tested weekly. A resistivity of RO DI is monitored continuously using inline meters during the day when 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. A resistivity of polisher DI also 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 2015

Parameter	RO Water N=52	Polisher DI N=60
pH	1	0
Specific Conductance	1	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 polishers and RO DI water blanks met the acceptance criteria in 2015.

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 MDL 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, AIRMoN and AMoN 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
NTN bucket bags	1 per box (50)	DI	150 mL	24 hours
AIRMoN sampling bags	1 per box (250)	DI	150 mL	24 hours
lid bags	1 per box (100)	DI	150 mL	24 hours
filters	2 per lot and weekly	DI/MDL solution	50 mL	N/A
bucket and bottle brushes	each	DI	6L	Until DI water is clean
AMoN Radiello® cores	2 per each new lot and 1 per the extraction day	DI	10 mL	24 hours

Washed and reused supplies cleanliness is monitored daily (Table 13), using MDL solution.

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

Supply Type	Test Frequency	Test Solution	Test Volume	Contact Time
buckets	1/day	MDL solution	150 mL	24 hours
NTN 1-L bottles	1/day	MDL solution	150 mL	24 hours
bucket lids	1/day	MDL solution	50 mL	24 hours

For new supplies, 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 2010 to 2014.

For used supplies, target levels are based on the mean ± 3 standard deviations of the MDL solution results.

The CAL used the following target values for new and used supply blanks in 2015 (Table 14):

Table 14. Target concentrations and acceptable ranges for new and used supplies blanks in 2015

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	5.65 ± 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 ± 0.002
Sodium	<0.002	0.005 ± 0.002
Potassium	<0.002	0.005 ± 0.002
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	<0.008	0.027 ± 0.010
Orthophosphate	<0.005	0.008 ± 0.003

NTN Sample Filters: DI Water and MDL 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 2015, concentrations of analytes in DI water eluents from NTN sample filters were lower than target concentrations presented in Table 14. A few outliers were detected for Ca^{2+} (2), Na^{+} (1) and NH_4^{+} (1).

No outliers were detected in MDL solution eluents.

Table 15. Number of results outside of control limits for filters leached with DI water and MDL solution in 2015

Parameter	DI Water N=52	MDL N=52
pH	0	0
Specific Conductance	0	0
Calcium	2	0
Potassium	0	0
Magnesium	0	0
Sodium	1	0
Chloride	0	0
Sulfate	0	0
Nitrate	0	0
Bromide	0	0
Ammonium	1	0
Orthophosphate	0	0

Bucket, Bottle and Lid Checks

New Buckets. Calcium is used in the manufacture of plastic buckets and sometimes 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 8 new leached buckets is tested. 39 blanks, representing 312 new buckets, were tested during 2015.

In 2015, the concentration of Ca^{2+} in new leached and washed buckets was lower than the 5^{th} percentile Ca^{2+} concentration for NTN samples (Figure 3). The median concentration of Ca^{2+} found in new buckets was ~ 0.001 mg/L.

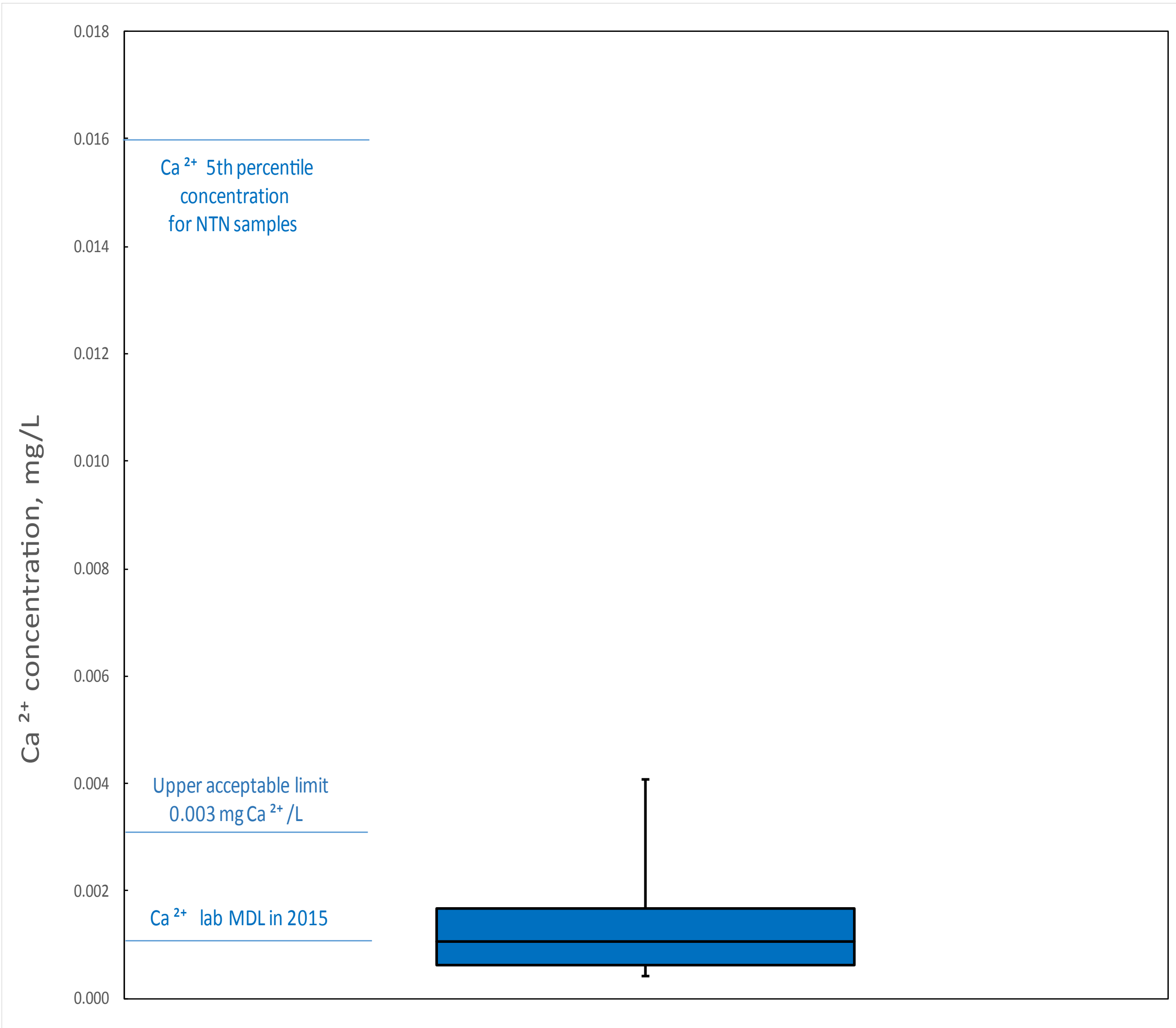


Figure 3. Box and whisker plot showing Ca^{2+} concentrations measured in new buckets blanks in 2015.

Washed and Reused Buckets. There were 245 washed and reused bucket blank samples prepared and analyzed in 2015. 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. Supplies are also discarded in cases when NH_4^+ concentrations are below the control limits. Results outside of target limits are shown in Table 16. Twenty two buckets were responsible for the twenty six exceedances. All buckets were rewashed and retested, and twenty 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 16. Number of results outside of control limits for washed and reused buckets tested with MDL solution in 2015

Parameter	MDL solution 24 Hours N=245
pH	2
Specific Conductance	3
Calcium	13
Potassium	1
Magnesium	0
Sodium	3
Chloride	4
Sulfate	0
Nitrate	0
Ammonium	3
Bromide	0
Orthophosphate	NA

The levels of Ca^{2+} and NH_4^+, detected routinely in washed and reused buckets, were low in 2015 and mostly were within allowable control limits for MDL solution. Thirteen outliers for calcium and 3 outliers for ammonium were detected. Ca^{2+} results are shown in Figure 4.

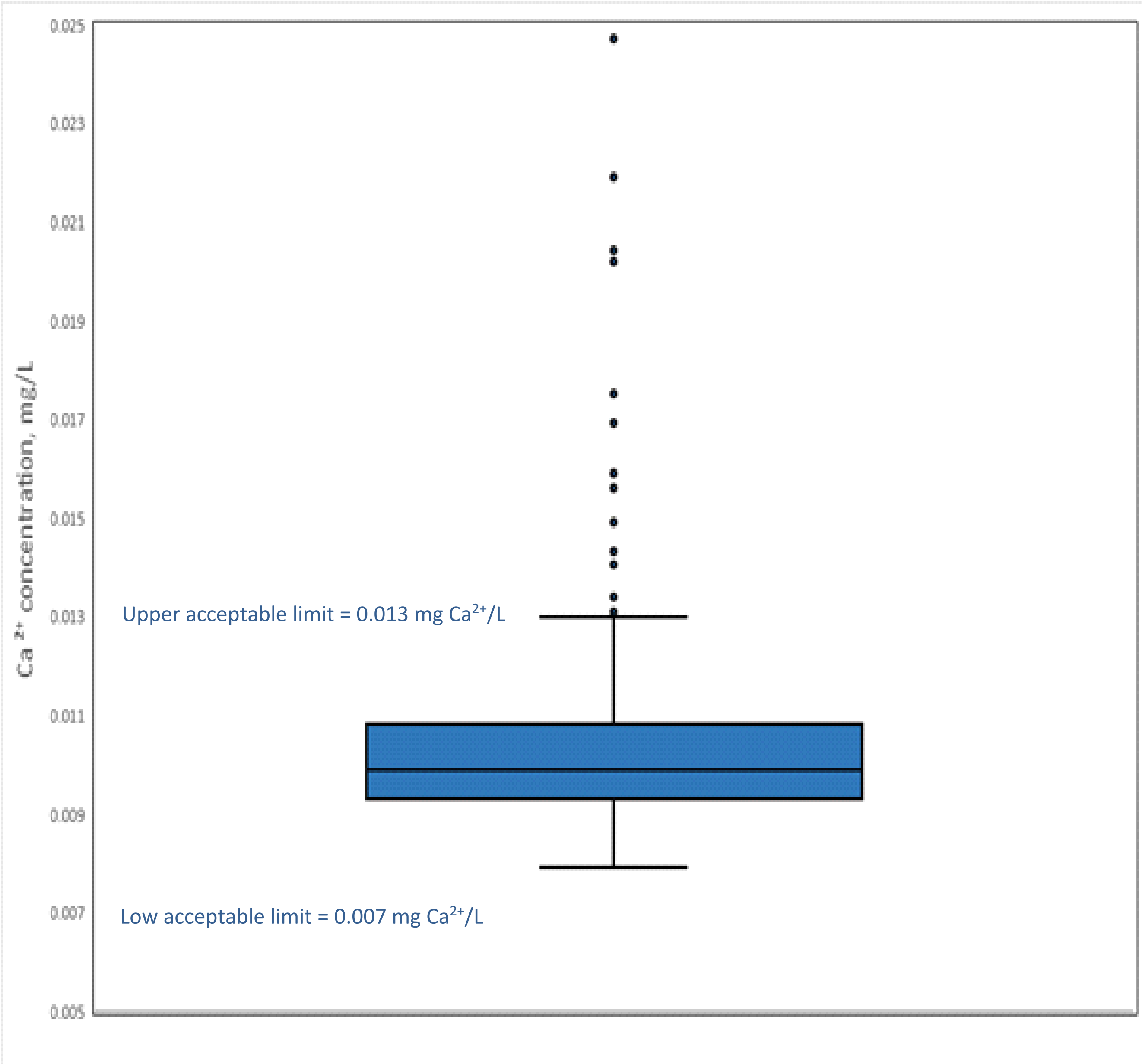


Figure 4. Box and whisker plot showing Ca^{2+} concentrations for washed and reused buckets tested with MDL solution in 2015

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 2015. There were no outliers.

Washed and Reused NTN 1-L Bottles. During 2015, one NTN bottle was selected daily from the washed bottles and tested. Results outside of target limits are shown in Table 17. The outliers for NH_4^+ occurred in eight bottles. Each of these bottles was rewashed and retested, and all of them 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.).

Figure 5 shows NH_4^+ results measured in used bottles in 2015.

Table 17. Number of results outside of control limits for washed and reused NTN 1-L bottles tested with MDL solution in 2015

Parameter	MDL solution 24 Hours N=147
pH	0
Specific Conductance	0
Calcium	1
Potassium	0
Magnesium	0
Sodium	0
Chloride	0
Sulfate	0
Nitrate	0
Ammonium	8
Bromide	0
Orthophosphate	NA

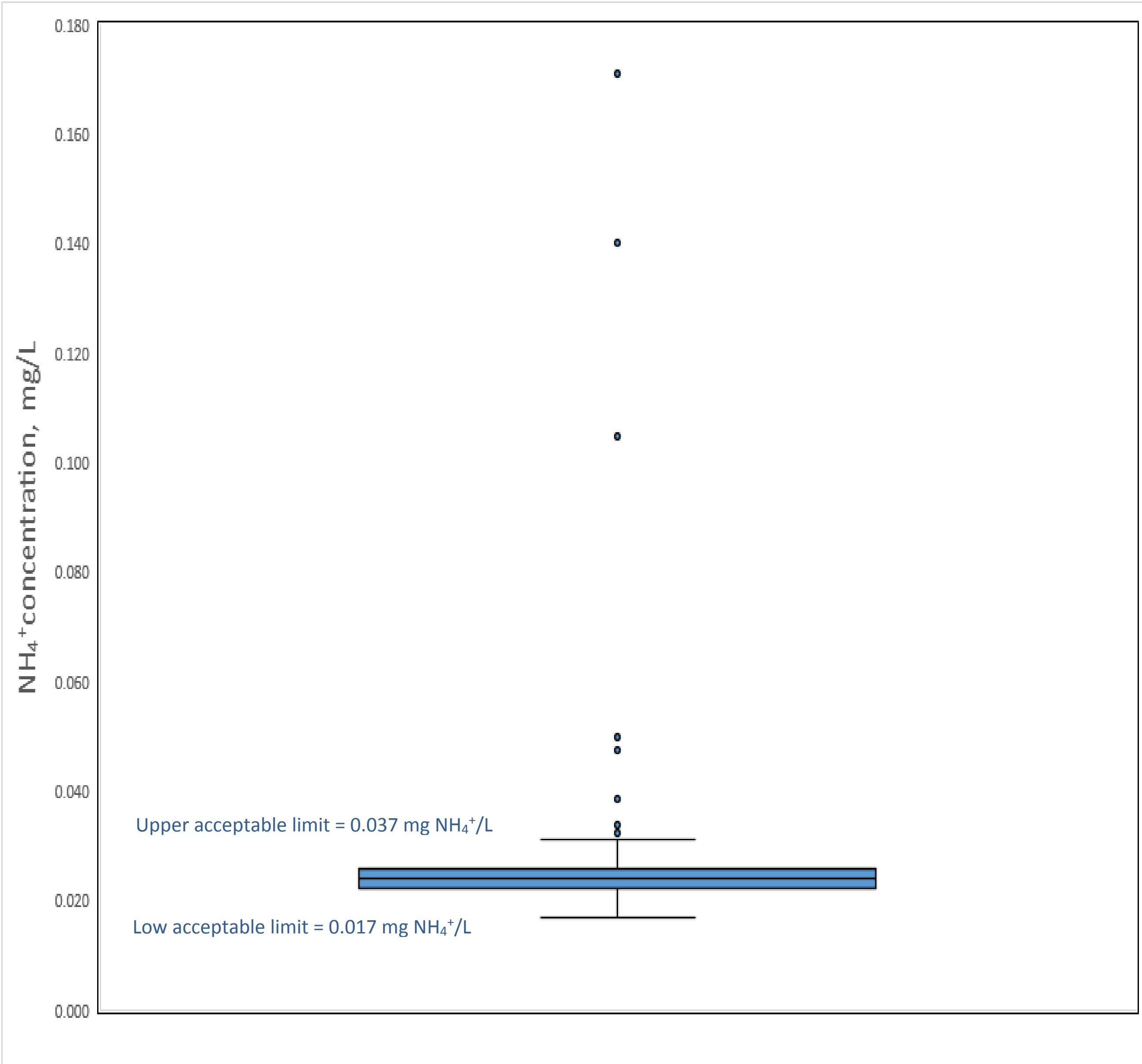


Figure 5. Box and whisker plot showing NH_4^+ concentrations for washed and reused NTN 1-L bottles tested with MDL solution in 2015

New Lids. No new bucket lids were purchased or tested in 2015.

Washed and Reused Lids. Twenty one bucket lids were responsible for thirty three exceedances (Table 18). Those lids were rewashed and retested. Two of them did not pass the second check and were discarded. The highest contaminants were: Ca^{2+} (nine outliers) and NH_4^+ (twelve outliers). Box and whisker plots showing Ca^{2+} and NH_4^+ concentrations measured in washed and reused lids in 2015 are shown in Figures 6 and 7. Also, a few outliers were detected for conductivity, K^+, Na^+, Cl^- and SO_4^{2-}

Table 18. Number of results outside of control limits for washed and reused bucket lids tested with MDL solution in 2015

Parameter	MDL solution N=250
pH	0
Specific Conductance	3
Calcium	9
Potassium	1
Magnesium	0
Sodium	4
Chloride	3
Sulfate	1
Nitrate	0
Ammonium	12
Bromide	0
Orthophosphate	NA

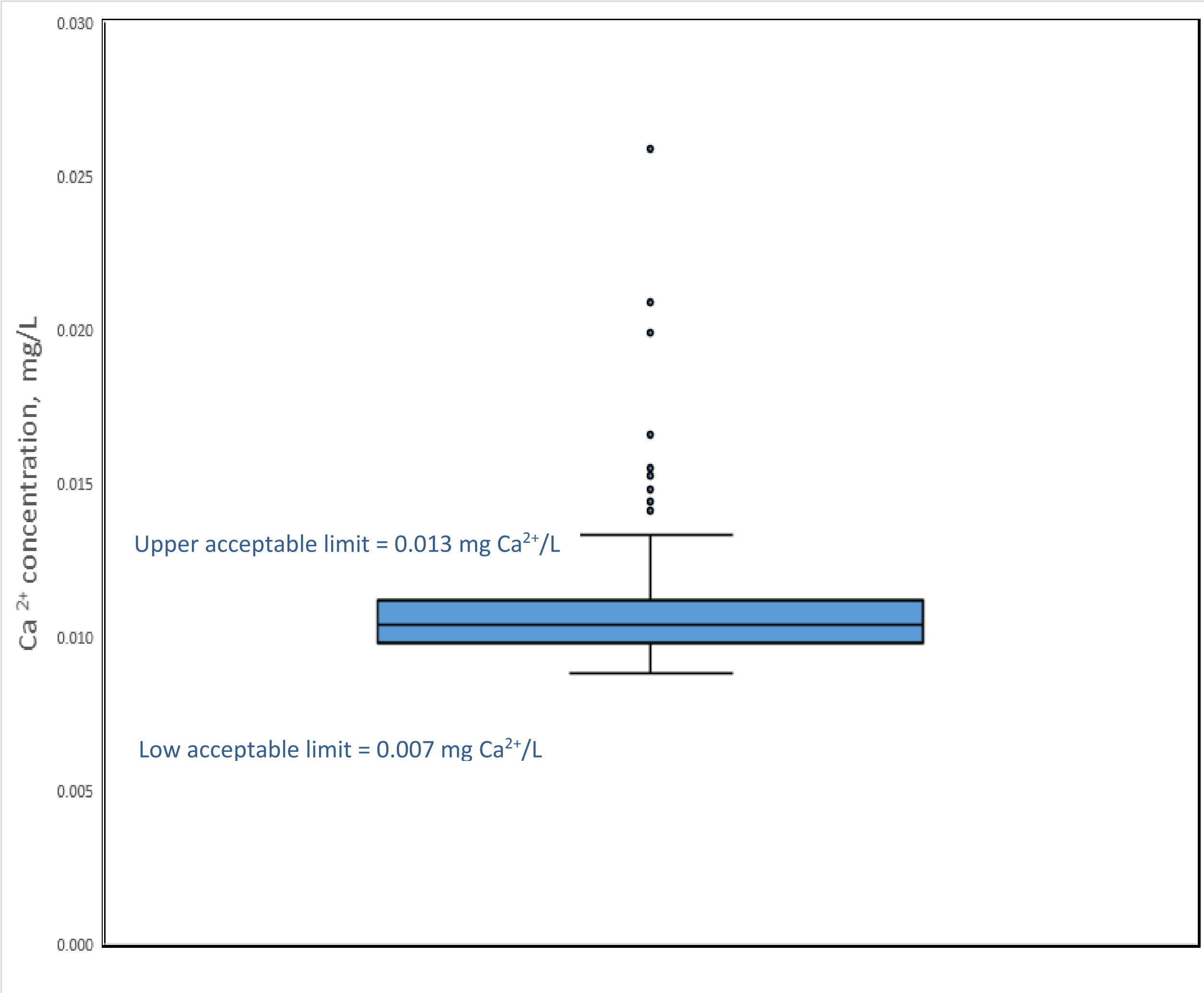


Figure 6. Box and whisker plot showing Ca^{2+} concentrations for washed and reused bucket lids tested with MDL solution in 2015

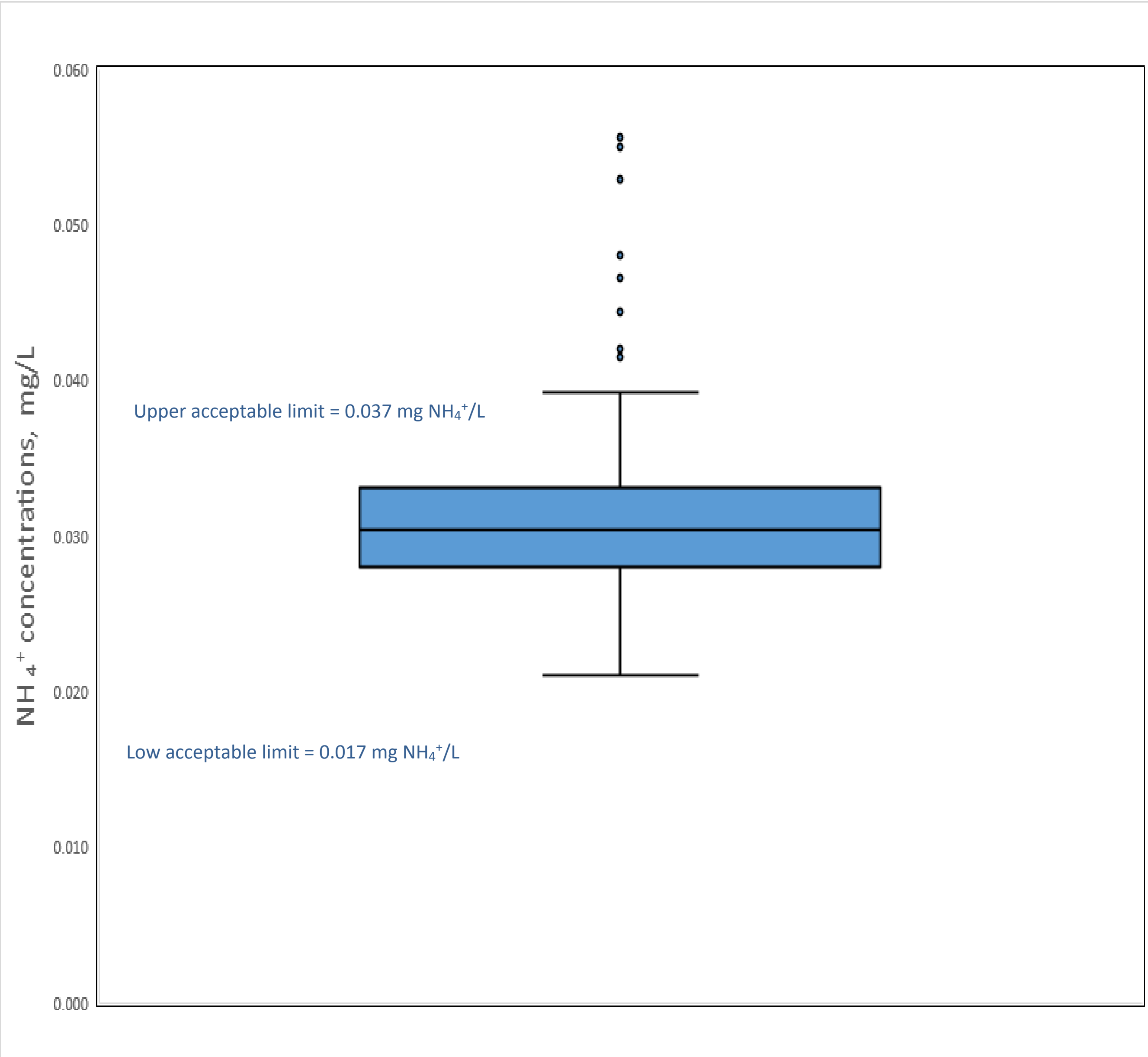


Figure 7. Box and whisker plot showing NH_4^+ concentrations for washed and reused bucket lids tested with MDL solution in 2015

Bags Checks

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. Starting June 2015 lid bags, purchased from ULINE Corporation, had the elevated concentrations for Na^{+}. Those bags (7 boxes) were rejected and not used. New lid bags were purchased from DegageCorp™. Starting November 2015 these new Degage bags occasionally had elevated concentrations for Ca^{2+}. All contaminated bags (11 packages) 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 2015.

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 2015.

For each extraction batch, 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 2015 are shown in Figure 8.

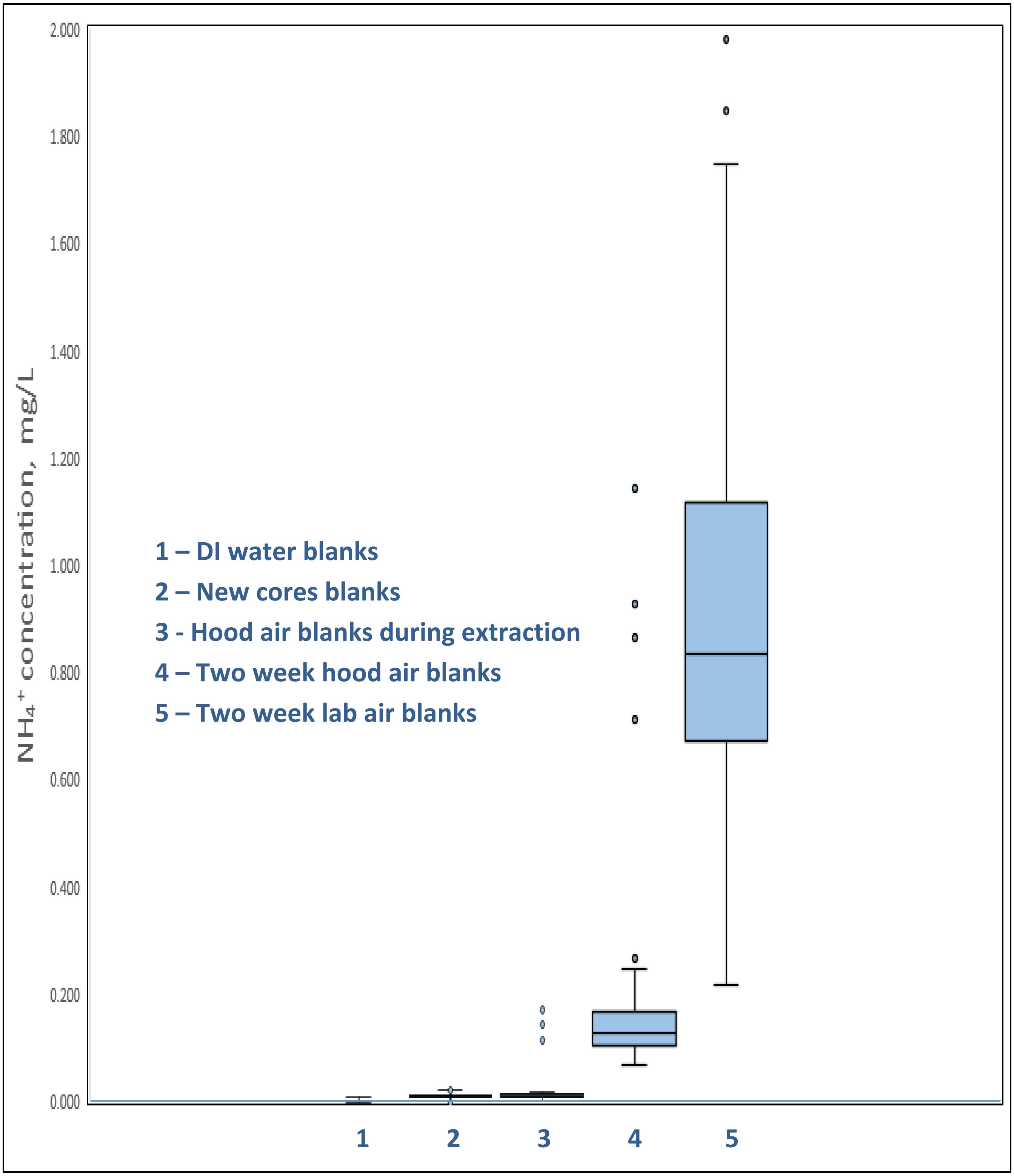


Figure 8. Box and whisker plot showing NH_4^+ concentrations, measured in 2015 in AMoN QA samples: laboratory DI water, 10 mL blank extracts of new cores, hood air blanks (during extraction and 2 weeks) and laboratory air blanks

The variability of AMoN triplicate results was quantified as the median absolute percent difference (APD*) of valid deployed samplers measurements, and the precision was quantified as the relative standard deviation (RSD**) (Table 19). Data for previous years are presented for comparison.

Table 19. Median absolute percent differences (APDs) and mean relative standard deviations (RSDs) for triplicate AMoN samples

Year	Count	Median APD * (%)	Mean RSD ** (%)
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
2015	241	4.0	5.0

* 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

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

The CAL also 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 mean and median APDs and RPDs of NH_3 results from IL11 measured using Radiello™ samplers and URG™ denuders are shown in Table 20. Based on the median RPD, the Radiello™ passive samplers tend to produce slightly lower estimates of NH_3 in ambient air compared to the denuders.

Table 20. Median and mean APDs * and RPDs for NH_3 measured at IL 11 using Radiello™ passive-type air samplers and URG denuders*****

Year	Count	Median APD * (%)	Mean APD * (%)	Median RPD** (%)	Mean RPD** (%)
2010	25	17.7	35.7	-13.5	9.6
2011	22	19.5	32.8	-8.8	-6.8
2012	26	8.3	16.3	-5.8	-4.5
2013	27	10.9	12.9	-5.0	-3.9
2014	25	11.7	19.2	-1.4	4.1
2015	26	13.3	21.0	-8.7	-2.9

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

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

*** The data for 2010 – 2014 were updated in 2015 after the 2014 CAL QA report was released

4

The agreement between ambient NH_3 measurements using Radiello™ samplers and URG denuders at IL11 is shown in Figure 9.

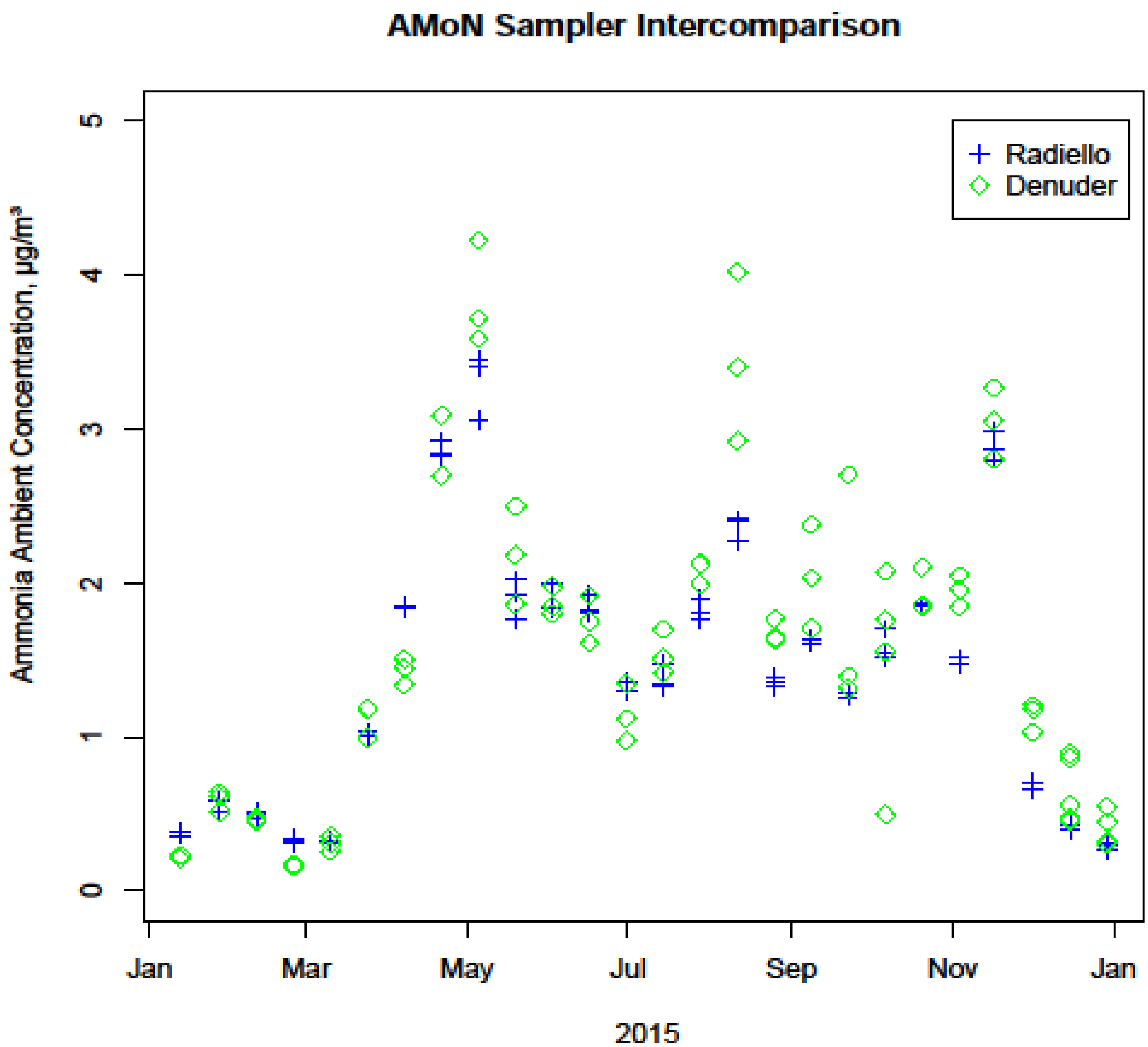


Figure 9. Ambient concentrations of ammonia measured at IL11 during 2015 using co-located Radiello™ passive samplers and URG denuders

AMoN Travel Blank Study Results

The AMoN travel blank acceptance limit is 0.200 mg/L of NH_4^+ in the 10 mL sampler extract. In previous years, numerous travel blanks exceeded acceptable limit. The reason for the numerous travel blank exceedances continued to be investigated through spring 2015 (see reference 7 - Protocol Changes to Address Low Level Contamination of Passive Sampler Bodies in NADP's Ammonia Monitoring Network). Laboratory paper (ULINE wipers), used during preparation of supplies, was found to have a high concentration of NH_4^+, and Kimtech Kimwipe wipers were found to have an elevated concentration of NH_4^+. In May 2015 the use of those wipers ceased, and Fisher Absorbent Surface Liners (Catalog No. 14-

127-46) were used instead. The median and mean NH_4^+ concentrations for travel blanks in 2008 – 2015 are shown in Table 21.

Table 21. Median and mean NH_4^+ concentrations in the 10 mL travel blanks extracts, and % of exceedances (> 0.200 mg NH_4^+ /L)

Year	N	Median NH_4^+ concentration, mg/L	Mean NH_4^+ concentration, mg/L	% of exceedances
2010	519	0.089	0.100	4.4
2011	1138	0.078	0.086	3.3
2012	1415	0.104	0.116	8.9
2013	430	0.108	0.131	17.2
2014	430	0.117	0.131	12.1
2015	625	0.054	0.059	1.0

The results of the travel sampler blanks for 2015 are shown in Figure 10. Travel blanks are shipped to field sites along with regular samplers but are not opened or deployed.

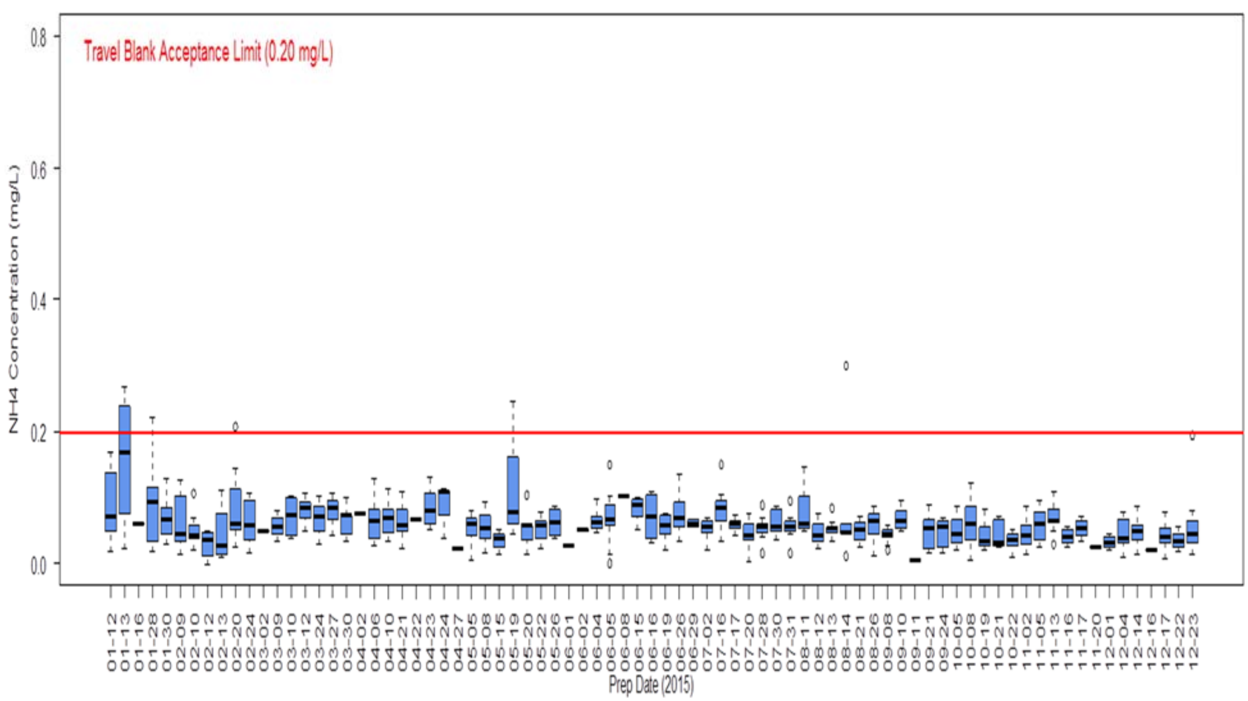


Figure 10. Box and whisker plot showing NH_4^+ concentrations in 10 mL extracts of AMoN passive travel blanks in 2015, grouped by preparation date

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 11) is calculated annually from valid replicate values for each quartile of data based on the prior three years of ambient concentration data. For example, the 2015 AMoN uncertainty is calculated for replicate samples deployed in 2015, using data quartiles calculated from all samples deployed during 2012 – 2014.

Table 22. AMoN 3-year moving uncertainty for ambient NH_3 measurement data quartiles for 2010 - 2015

Year		n	1st Quartile	n	2nd Quartile (Median)	n	3rd Quartile	n	4th Quartile (Maximum)
			µg/m³		µg/m³		µg/m³		µg/m³
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**

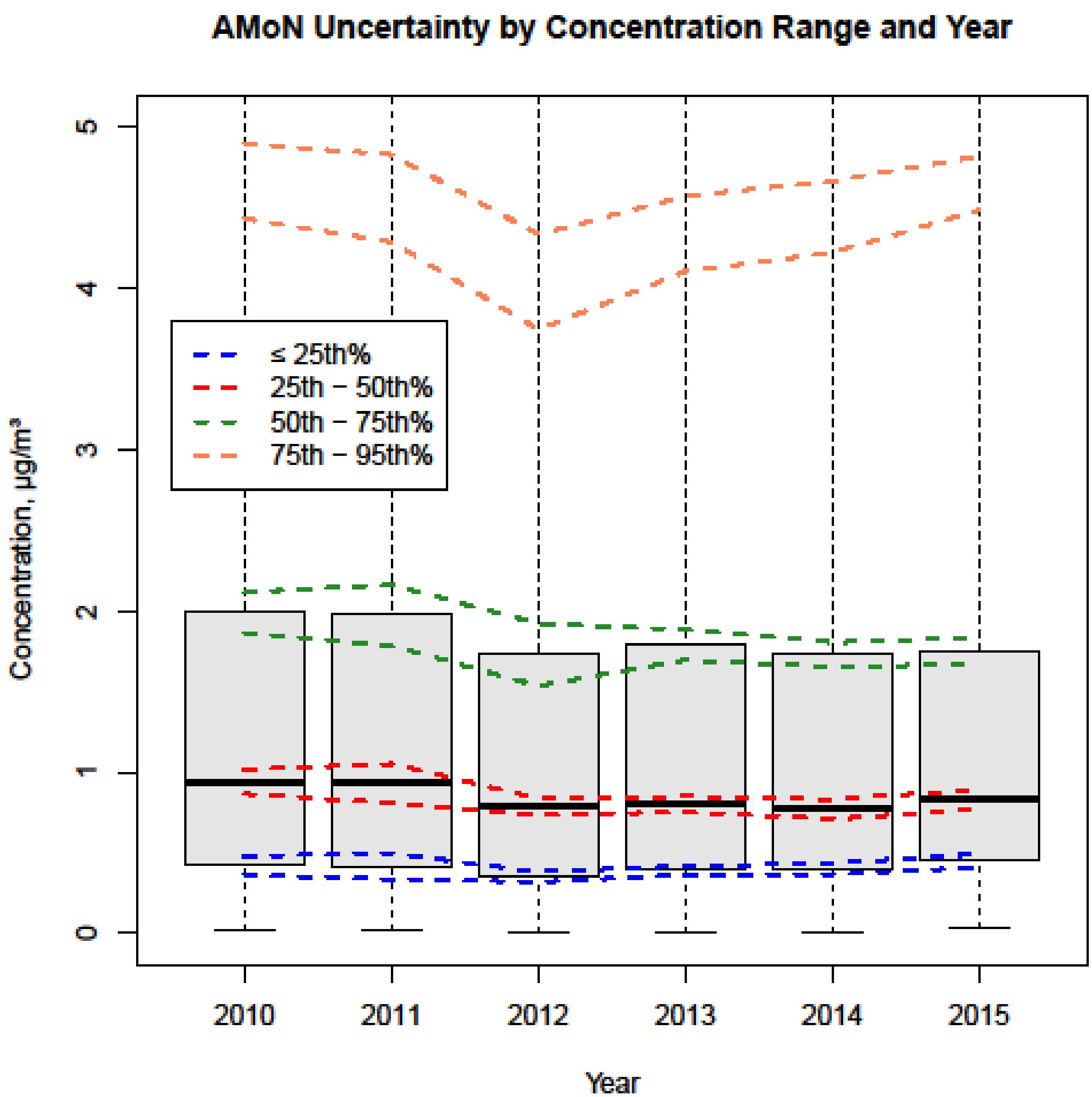


Figure 11. Annual AMoN ambient NH_3 measurements, and annual AMoN uncertainties by quartile based on 3-year moving data distribution for 2010 - 2015

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, following CAL SOP AN-4028.

The AMoN network detection limit (L_N) is calculated quarterly and annually from valid travel blanks shipped to individual stations but not exposed, following standard AMoN field procedures.

Table 23 shows AMoN laboratory and network detection limits. The network detection limit decreased significantly in 2015 due to changes in laboratory protocols that eliminated the NH_4^+ contaminated laboratory wipers.

Table 23. AMoN laboratory and network detection limits for 2010 – 2015

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

External Quality Assurance

The CAL participated in four external proficiency testing studies throughout 2015. The study identifier and websites with study details and results are shown in Table 24. The CAL's performance was consistent with that of other top-performing laboratories participating in each of the studies.

Table 24. 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 52 and 53	World Meteorological Organization/Global Atmospheric Watch (WMO/GAW)	http://www.qasac-americas.org/
Study 106 and 107	Environment Canada Proficiency Testing Program	Available upon request
Study 33	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.

In 2015, maintenance for each instrument was performed as described in the CAL's SOPs.

Unscheduled maintenance in 2015 included:

- Six pH electrodes and three conductivity cells were replaced during the year;
- In January 2015 the gas board, gas connectors, torch clamp, coils, electron (power) tube and ignitor were replaced for the Vista Pro ICP-OES instrument.
- In March 2015 the firmware was reinstalled on the Agilent Technologies 5100 ICP-OES instrument.
- In June 2015 a new board was installed on the Agilent Technologies 5100 ICP-OES instrument.
- In July 2015 the degas unit on IC (system 1) was replaced.

In June 2015 pipette calibration was performed by NOVAMED, INC. (see Appendix B).
Two electronics pipettes were purchased – LTS E-4-1000XLS+ (June 2015) and LTS E4 -200XLS+ (November 2015).
Preventative maintenance on balances is performed annually at the Illinois State Water Survey. In October 2015, basic preventive maintenance and calibration were performed by Central Illinois Scale Company for seven CAL balances (see Appendix B). 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 equipment stations.

Conclusions

The CAL performed consistently throughout 2015 and met all guidelines specified in the NADP Network Quality Assurance Plan (2014 QAP). Compliance with Data Quality Objective (DQO) requirements was maintained.

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/lib/qaplans/qapCal2014.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 from NADP QA manager).
7. Protocol Changes to Address Low Level Contamination of Passive Sampler Bodies in NADP's Ammonia Monitoring Network. N.Gartman, M.Rhodes, M.Puchalski, B.Riney, A.Wells, C.Lehmann, D.Gay and T.Dombek. Poster, presented at the Fall Meeting and Scientific Symposium / 9th International Conference on Acid Deposition. Rochester, New York, Oct.19-23, 2015.

APPENDIX A

MDLs, calculated quarterly in 2015

Ion	Type of MDL	MDL, mg/L based on results of the 1st quarter of 2015	n	MDL, mg/L based on results of the 2nd quarter of 2015	n	MDL, mg/L based on results of the 3rd quarter of 2015	n	MDL, mg/L based on results of the 4th quarter of 2015	n
Calcium	Lab MDL	**0.000**	10	**0.000**	12	**0.001**	10	**0.001**	9
	AIRMoN MDL	**0.000**	9	**0.001**	12	**0.001**	11	**0.001**	9
	NTN MDL	**0.007**	9	**0.007**	12	**0.015**	11	**0.008**	9
Potassium	Lab MDL	**0.001**	10	**0.001**	12	**0.001**	10	**0.001**	9
	AIRMoN MDL	**0.001**	9	**0.001**	12	**0.002**	11	**0.001**	9
	NTN MDL	**0.001**	9	**0.001**	12	**0.001**	11	**0.010**	9
Magnesium	Lab MDL	**0.000**	10	**0.001**	12	**0.001**	10	**0.001**	9
	AIRMoN MDL	**0.000**	9	**0.001**	12	**0.001**	11	**0.001**	9
	NTN MDL	**0.002**	9	**0.003**	12	**0.002**	11	**0.004**	9
Sodium	Lab MDL	**0.001**	10	**0.001**	12	**0.001**	10	**0.000**	9
	AIRMoN MDL	**0.001**	9	**0.001**	12	**0.003**	11	**0.001**	9
	NTN MDL	**0.006**	9	**0.001**	12	**0.002**	11	**0.004**	9
Chloride	Lab MDL	**0.003**	10	**0.003**	12	**0.003**	10	**0.003**	9
	AIRMoN MDL	**0.002**	9	**0.003**	12	**0.004**	11	**0.002**	9
	NTN MDL	**0.009**	9	**0.003**	12	**0.005**	11	**0.008**	9
Nitrate	Lab MDL	**0.004**	10	**0.003**	12	**0.004**	10	**0.003**	9
	AIRMoN MDL	**0.006**	9	**0.002**	12	**0.005**	11	**0.005**	9
	NTN MDL	**0.005**	9	**0.004**	12	**0.007**	11	**0.006**	9
Sulfate	Lab MDL	**0.004**	10	**0.002**	12	**0.004**	10	**0.004**	9
	AIRMoN MDL	**0.008**	9	**0.004**	12	**0.004**	11	**0.004**	9
	NTN MDL	**0.005**	9	**0.003**	12	**0.004**	11	**0.004**	9
Bromide	Lab MDL	**0.001**	10	**0.002**	12	**0.002**	10	**0.006**	9
	AIRMoN MDL	**0.003**	9	**0.004**	12	**0.003**	11	**0.003**	9
	NTN MDL	**0.003**	9	**0.006**	12	**0.005**	11	**0.004**	9
Ammonium	Lab MDL	**0.011**	10	**0.007**	12	**0.009**	10	**0.006**	9
	AIRMoN MDL	**0.007**	9	**0.008**	12	**0.009**	11	**0.009**	9
	NTN MDL	**0.034**	9	**0.016**	12	**0.021**	11	**0.028**	9
Orthophosphate	Lab MDL	**0.002**	10	**0.003**	12	**0.003**	10	**0.003**	9
	AIRMoN MDL	**0.004**	9	**0.003**	12	**0.004**	11	**0.003**	9
	NTN MDL	**0.006**	9	**0.002**	12	**0.004**	11	**0.010**	9

APPENDIX B

Pipettes Calibration Service Sheet in 2015

novamed
Your Reliable Pipette Connection™

NOVAMED, INC. – (FEIN): 36-3750788
8136 N. Lawndale Ave. Skokie, IL 60076-3413
Tel: 1-800-354-6676 • Fax: (847) 675-3322
Order Online at www.novamed1.com

ISO IEC An ISO 17025 Accredited Laboratory

• Pipettes
• Pipette Calibration & Repair
• Pipette Parts & Accessories

SERVICE SHEET

INSTITUTION (UIUC) WATER SURVEY LABS

SERVICE DATE: 06/03/15 Work Order # [illegible]

ORDERED BY
(Person Authorizing Service)

PURCHASE ORDER #

CREDIT CARD DETAILS MC ☐ VISA ☐ OTHER
CARD OWNER
CARD# EXP.DATE / /
SECURITY or CUSTOMER CODE ZIP CODE

LABORATORY ADDRESS
DEPARTMENT LAB
ROOM # 309/306 BUILDING NAME # BLDG. 3
STREET ADDRESS 2204 GRIFFITH DRIVE
CITY / STATE / ZIP CHAMPAIGN, IL
ATTN LEE ANN GREEN
TEL # (217) 244-5437

No. of Pipettes Received: 10
No. of Pipettes Returned: 10

BILLING ADDRESS ACCOUNTS PAYABLE
DEPARTMENT
ROOM # BUILDING NAME #
STREET ADDRESS
CITY / STATE / ZIP
ATTN TEL#

NO.	SERIAL # /PIPETTE #	MAKE	MODEL	PRE-CAL READING	CALIBRATED AT	CHECKED AT	PARTS REQUIRED / COMMENTS
1	W-7359	epp. Reference	100	–	10	100	
2	W-7358	" "	100	–	10	100	
3	W-7356	" "	100	–	10	100	
4	W-7357	" "	1000	–	100	1000	
5	W-7351	" "	1000	–	100	1000	RECEIVED MICROMETER PLASTIC WINDOW MISSING
6	W-7352	" "	1000	–	100	1000	
7	W-7350	" "	100	–	10	100	
8	W-7355	epp. Research Pro	1000	–	50	1000	eP
9	W-7353	Pipet Plus	RL 100	–	10	100	TSR
10	W-7354	" "	RL 1000	–	100	1000	TSR
	9 PIPETTS	CLEAN	CHECK &	CALIBRATE	10	@ $26.00	150.00
	1 EP				20	@ $35.00	35.00
	2 SEAL	REPLACED			30	@ $7.00	14.00

ACCEPTED BY: [signature] SERVICE TECHNICIAN INITIALS: [illegible]

TOTAL
$ 229.00

TERMINOLOGY EXPLAINED: TSR - Teflon Seal Replaced, FRR - Friction ring replaced, SR - Shaft replaced, PBR - Plunger button replaced, EAR - Ejector arm replaced, PREP - Pipette repaired, SCR - Shaft coupling replaced, ORR - O-ring replaced, PLR - Plunger replaced, PAR - Piston assembly replaced, SAHR - Seal assembly holder replaced, SSR - Small spring replaced, LSR - Large spring replaced, SPR - Spring positioner replaced, NCAR - Nose cone Assembly replaced, NIR - Nozzle insert replaced, BR - Battery replaced. EP- Electronic Pipette. MCP- Multi-Channel Pipette.
NOTE: Calibration warranty is valid if pipettes are not abused (physical or chemical trauma), & are used in accordance with the instructions contained in the manufacturer's operating manual. The above pipettes meets or exceeds Manufacturer's recommended specifications. They have been calibrated using "Gravimetric Methodology", checked at the specific points.

APPENDIX C

Basic preventive maintenance and balance calibration in 2015

Central Illinois Scale Company
Multiple Balance Test Confirmation Certificate

IL. State Water Survey
2204 Griffith Dr.
Champaign, IL 61820 Date: 10/20/15 Due: 10/31/2016

Manufacturer	Model	Serial Number	Room	Calibration Span "As Found"	Calibration Span "As Left"	Weight set Used
Mettler Toledo	XS204	1126292194	302	200.0002g	200.0000g	1
Denver	P4002D	P4K2D128001	302	4000.1g	4000.0g	2
Mettler Toledo	PB602-S	1128041572	306	600.03g	600.00g	2
Denver	S-8001	22450551	632	7999.5g	8000.0g	2
Ohaus	B5000	10562	632	5001.6	5000.0g	2
Sartorius	IB12EDEP	50511901	224A	11999.4g	12000.0g	2
Denver	P4002D	P4K2D126007	209	3999.6g	4000.0g	2
Mettler Toledo	PR8002	1119500563	1120	7999.93g	8000.00g	2
Mettler Toledo	AG204	1115210859	1120	199.9997g	200.0000g	1
Mettler Toledo	XP8002-S	1127021794	1120B	7999.97g	8000.00g	2
Mettler Toledo	AG204	1122050968	1120B	199.9997g	200.0000g	1
Sartorius	3102-1S	29001925	320	3000.04g	3000.00g	2
Mettler Toledo	XS204	1129110785	320	199.9994g	200.0000g	1
Mettler Toledo	MS304S	B311137255	316	300.0007g	300.0000g	1
Mettler Toledo	MS3002S	B207710989	316	2999.97g	3000.00g	2
Sauter	RE1614	B882198	316	159.9994g	160.0000g	1
Mettler Toledo	AX304	1121171614	312	300.0004g	300.0000g	1

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: 410201501

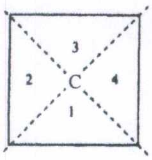
PJLA Calibration
Accreditation #: 59078

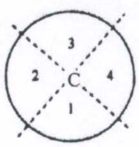
Customer: IL. Water Survey
2204 Griffith Dr
Champaign, IL 61820

Device Calibration Date: October 20, 2015
Next Calibration Due: October 31, 2016
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	0.0000g	0.0000g	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	200.0000g	0.0001g	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	220.0002g	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	31-Mar-2015	31-Mar-2016
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: October 20, 2015