Quality Assurance Report
National Atmospheric Deposition Program
2011

Laboratory Operations
Central Analytical Laboratory

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Acknowledgments

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Introduction

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

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

AMoN passive sampler extracts are measured for ammonium ions, which are used to calculate ambient gaseous ammonia concentrations.

The CAL is directed by guidelines specified in the NADP Network Quality Assurance Plan (QAP), which is available on the NADP website (http://nadp.isws.illinois.edu/lib). The CAL uses specific Data Quality Indicators (DQIs) detailed in the CAL operations QAP for all of its internal operations throughout the year. These documents are available from the CAL's website (http://nadp.isws.illinois.edu/CAL). The analytical methods used for each ion are shown in Table 1.

Table 1. CAL analytical methods

Ion	Method
pH	Ion-Specific Electrode
Specific Conductance	Electrical Conductivity Cell
Bromide	Ion Chromatography (IC)
Chloride	Ion Chromatography (IC)
Nitrate	Ion Chromatography (IC)
Sulfate	Ion Chromatography (IC)
Ammonium	Flow Injection Analysis (FIA) Colorimetry
Orthophosphate	Flow Injection Analysis (FIA) Colorimetry
Calcium	Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)
Magnesium	Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)
Sodium	Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)
Potassium	Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

Significant Developments in 2011

- Methods for calculating MDLs were modified to include filtration for NTN samples. (January 2011)
- Research continues on methods for measuring particulate carbon and total phosphorus in wet deposition samples. (see References)
- NTN filters are pre-conditioned with sample. (January 24, 2011)
- NTN split sample procedure was modified. Samples were split at the filtration step and analyzed sequentially. (February 23, 2011)
- New FIA (Lachat Instruments QuikChem 8500 Series 2; Omnion 3.0.223.2 software) was approved for analysis of NTN and AIRMoN samples. (April 1, 2011)
- Former NTN/AIRMoN FIA (QuikChem 8000) was transitioned to special project use (April 1, 2011)
- Orthophosphate measurements were discontinued for AMoN samples. (April 1, 2011)
- Cleaning procedure was modified to include triple rinses for AMoN diffusive bodies. (July 15, 2011)
- CAL review was conducted the week of July 18-21, 2011.
- New IC (Dionex ICS-5000, Chromeleon 7 software) was received for NTN and AIRMoN analysis. (July 2011) Installed by Dionex. (August 2011)
- Tanya Grandt was qualified as back-up ICP-OES analyst. (August 2011)
- Performance Test (PT) samples were analyzed only one time for reporting in response to findings from the July 2011 review. (September 2011)
- Bromide was approved as official NTN and AIRMoN analyte. (October 2011)
- AMoN diffusive bodies were placed in dessicator following triple rinse and sonication. (October 24, 2011)
- Autosampler for new IC (Dionex AS-DV) was installed and instrument evaluation commenced, with approval still pending. (November 2011)
- Kim Attig was qualified as analyst for AMoN samples. (November 2011)

Quality Assurance/Quality Control

Objectives

Quality Assurance (QA)/ Quality Control (QC) is an “all-hands” effort at the CAL. The CAL team members work together to maintain compliance 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 reproducible. The overall quality of NADP data is assessed through DQIs, including precision, accuracy, and comparability.

Precision is a measure of data reproducibility and random error. The CAL's analytical precision is assessed by the use of control charts and blind, split, and replicate samples. Control charts are used to evaluate long-term instrument precision and any drifts in the data. Blind samples are used to evaluate the detection limits. Sample processing precision is evaluated by split samples. Replicate samples are used to evaluate instrument precision throughout the duration of the analytical run.

Accuracy is a measure of correctness and how closely the data represent the true value. Accuracy is evaluated through the use of blind samples and participation in external laboratory comparison studies.

Comparability is measured by comparing the variability of one set of data with respect to another. Comparability is evaluated through daily control charts, internal blind data, and external laboratory comparison studies.

Summary

SOPs, control charts, internal blind samples, split/replicate, reanalysis samples, and supply blank tests are used by the CAL to maintain consistent data. Both data variability and deviation from target specifications are monitored daily using control charts. Supply cleanliness is monitored weekly. New supplies are evaluated before they are introduced for site or laboratory use. Internal blind samples (i.e., samples not readily identifiable to the analyst) are evaluated monthly.

The CAL prepares an internal verification standard termed "faux rain" (FR) as a dedicated matrix spike solution with target concentrations that represent the 50^{th} percentile level of analytes measured in NTN rain water samples (designated as FR50). This solution contains all CAL analytes except for orthophosphate, and is used for quality control. Orthophosphate standards are purchased from the Environmental Resource Associates[1] , and are diluted as necessary.

Two solutions are prepared and used to evaluate MDLs for each analyte. These solutions, labeled Cation MDL and Anion MDL, are prepared at concentrations that are approximately one to five times the projected MDL for each analyte. An external certified reference standard (AES-05) is purchased from RTC[2]. The target concentrations are shown in Table 2 for orthophosphate and Table 3 for all other analytes. Each analyst purchases second source standards to prepare two or three calibration check standards. The number of calibration check standards depends

[1] Environmental Resource Associates, 5540 Marshall Street, Arvada, CO 80002, Simple Nutrients, catalog number 584.
[2] RTC, 2931 Soldier Springs Road, Post Office Box 1346, Laramie, WY 82070.
Disclaimer: The use of trade or manufacturer's names does not constitute an endorsement by the University of Illinois, NADP, or project sponsors.

upon the calibration range. The target concentrations for the calibration check standards are determined by each analyst and confirmed by the QA chemist.

To set annual control chart limits, internal blind samples are measured a minimum of seven times. The average of these results is the target value for the control chart. Control limits are calculated using twice the standard deviation (2σ) for the warning limits, and 3σ for the control limits. Control chart limits are monitored daily using FR50 and calibration check standard solutions. When results for daily control solutions fall outside of control limits, analysis of the affected samples is repeated.

Five different solutions are used for the internal blind study: deionized water (DI), Anion MDL, Cation MDL, FR50, and AES-05. For NTN, internal blind samples are submitted weekly by the QA chemist at an interval of approximately one set per every 75 samples and include all five internal blind solutions. For AIRMoN, one internal blind sample is analyzed per week. That solution is always the FR50 solution. Blind samples have unique laboratory identification numbers. Internal blind unfiltered samples are submitted in standard NTN 60 mL bottles. These samples are not blind for pH and conductivity, but are blind to all other analysts. Internal blind filtered samples are submitted in standard 1 L NTN bottles. These samples are considered blind to the analysts. Control limits are used by the QA chemist to evaluate the instruments and analysts' performance when analyzing internal blind samples.

Each analyst selects two to three samples at random per week as a replicate sample. These samples are analyzed once sequentially and an additional one to two times later in the sample sequence. The analyst calculates a relative percentage difference to determine if the sample results are within control. If any of the results fall out of control, evaluation and corrective actions will be determined by the analyst. All replicate results are evaluated monthly by the QA chemist.

Approximately 1 out of every 100 samples is selected for duplication during the filtration process. The filtration technician selects a sample of volume greater than 500 mL nearest to the 100^{th} sample. The sample is split and filtered through two different filters. One sample is labeled with the NTN laboratory number, and the duplicate sample is labeled with the NTN laboratory number, but with a "Q" replacing "S" (e.g., NTN laboratory number TJ0123SW duplicate sample TJ0123QW). The two samples are placed on the tray sequentially. The sample labeled with the "Q" is added to the sample queue for pH and conductivity. Hence pH and conductivity analyses are performed after filtration for the "Q" sample. The percentage difference is evaluated between the duplicate samples by the analyst. Corrective actions are determined by the analysts when the differences are out of control. The QA chemist checks results for all duplicate samples monthly.

Table 2. Orthophosphate control solutions concentrations

	Low standard	High standard
Orthophosphate (mg/L)	0.011	0.100

Table 3. Target concentrations for control and internal blind solutions for NTN/AIRMoN

	50th percentile Target concentration	Cation MDL Target concentration	Anion MDL Target concentration	AES-05 Target concentration
CAL Designation	FR50	LV110001	LU110001	AES-05
pH	4.80	5.56	5.60	4.90
Specific Conductance (µS/cm)	10.6	1.5	1.1	10.8
Calcium (mg/L)	0.123	0.007	0.001	0.187
Magnesium (mg/L)	0.023	0.004	0	0.037
Sodium (mg/L)	0.049	0.005	0.008	0.181
Potassium (mg/L)	0.021	0.005	0.034	0.028
Chloride (mg/L)	0.098	0.061	0.021	0.225
Sulfate (mg/L)	0.828	0.019	0.018	1.28
Nitrate (mg/L)	0.958	0.042	0.024	1.15
Ammonium (mg/L)	0.227	0.031	0.005	0.312
Orthophosphate(mg/L)	NA	NA	0.030	NA

New supplies are checked according to the schedule in Table 4. Supplies that are washed daily and checked weekly are shown in Table 5. The test solution and contact time for each solution are included in the tables.

Table 4. New NTN/AIRMoN supply checks

Supply	Frequency	Test Solution	Volume	Contact Time	Label
new buckets	1 per 16	DI	150 mL	24 hours	CB
new bucket lids	1 per 32	DI	50 mL	24 hours	CC
new 1 L bottles	1 per 24	DI	150 mL	24 hours	CN
250 mL AIRMoN bottles	1 per 24	FR50	50 mL	24 hours	CN
bucket bags	1 per 200	DI	50 mL	24 hours	CF
lid bags	1 per 100	DI	50 mL	24 hours	CF
bottle bags	1 per lot	DI	50 mL	24 hours	CF
filters	2 per lot and weekly	DI/FR50	50 mL	NA	CD/BB/BC
polisher water all labs	Monthly	NA	50 mL	NA	CA

Table 5. Summary of NTN/AIRMoN weekly supply checks

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

Quality Control Discussion

Method Detection Limits

Method Detection Limits (MDLs) are defined by the U.S. Environmental Protection Agency (EPA) 40 CFR 136.2 document as the "minimum concentration of analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero." The EPA provides guidelines for calculating MDLs. Two standards are used to determine MDLs for sodium, calcium, magnesium, potassium, ammonium, nitrate, chloride, sulfate, and orthophosphate. Conductivity and pH do not have defined MDLs; instead, the value is calculated based on a measure of long-term variability. MDL samples used to determine MDLs are blind to the analyst, with the exception of the analyst for pH and conductivity.

MDL study results are compiled at the end of the year, and are used to compute the method detection limit for the upcoming year. The solutions measured during 2010 are used to calculate MDLs for 2011. Standard deviations for the MDL samples are multiplied by the Student's t value for the 99 percent confidence interval to compute the MDLs. The MDLs for 2011 are shown in Table 6 and were provided to the NADP Program Office. See Table 1 for methods.

Table 6. NTN/AIRMoN MDLs for 2011

Ion	MDL (mg/L)
Calcium	0.002
Potassium	0.001
Magnesium	0.001
Sodium	0.001
Chloride	0.005
Nitrate	0.004
Sulfate	0.003
Ammonium	0.006
Orthophosphate	0.008

Control Charts

In 2011, Data Quality Objectives (DQOs) as defined in the CAL QAP were met.

Weekly Blank Results

Target levels are based on historic and current MDLs for deionized water blanks and the historic precision measured in blanks for the 50th percentile solution. Box and whisker plots, as shown in Figure 1, can be used to identify outliers. The box identifies the 1st, median, and 3rd quartiles of the data. The whisker illustrates 1.5 times the interquartile range (box length). "X" designates points that are outside 1.5 times the interquartile range and are considered statistical outliers. When shaded areas are all gray, there is no difference between the 1st quartile and median. When shaded areas are all blue, the 3rd quartile and median are the same.

Polisher and Reverse Osmosis (RO) DI Blanks

The polisher and RO DI water blanks met all acceptance criteria for 2011 (Table 7). No measurements were observed to be outside the target limits.

Table 7. Number of samples outside the target limits for polisher and RO blanks in 2011

Parameter	Polisher DI N=55	RO Water N=52
pH	0	0
Specific Conductance	0	0
Calcium	0	0
Potassium	0	0
Magnesium	0	0
Sodium	0	0
Chloride	0	0
Sulfate	0	0
Nitrate	0	0
Ammonium	0	0
Orthophosphate	0	0

NTN Sample Filters: DI Water and FR50

Low levels of sodium and chloride were detected in DI water eluent from NTN sample filter supply tests (Table 8). The concentrations of sodium and chloride were typically less than the 5th percentile of NTN sample concentrations for the five-year period from 2005 to 2009. The median concentration of sodium found on filters was 0.001 mg/L, and the median concentration of chloride found on filters was 0 mg/L. Box and whisker plots for sodium and chloride are shown in Figure 1.

There was one outlier noted for calcium (Table 8), where the median concentration was equivalent to the target concentration (Figure 2) during two periods, and within expected variability from April to July. The levels of sodium, chloride, and calcium found when leaching filters with both DI and FR50 are small. When sample volume allows, filters are rinsed with sample prior to sample collection. (See SOP PR-1055.14 for details.) The CAL started this in November 2010 as a precautionary measure. Initially, filters were rinsed with 10 to 20 mL of sample, but results indicated small concentrations of calcium, sodium, and chloride. The rinse was increased to 50 mL for samples of volume greater than 200 mL. For samples of volume between 100 mL and 200 mL, 20 mL of sample is used as the rinse. In many cases low-volume samples have higher concentrations of analytes and therefore mask any filter contamination.

Table 8. Number of results outside of target limits in 2011 for filter blanks

Parameter	DI N=52	FR50 N=52
pH	0	0
Specific Conductance	0	0
Calcium	0	1
Potassium	0	0
Magnesium	0	0
Sodium	3	0
Chloride	4	0
Sulfate	0	0
Nitrate	0	0
Ammonium	0	0
Orthophosphate	NA	NA

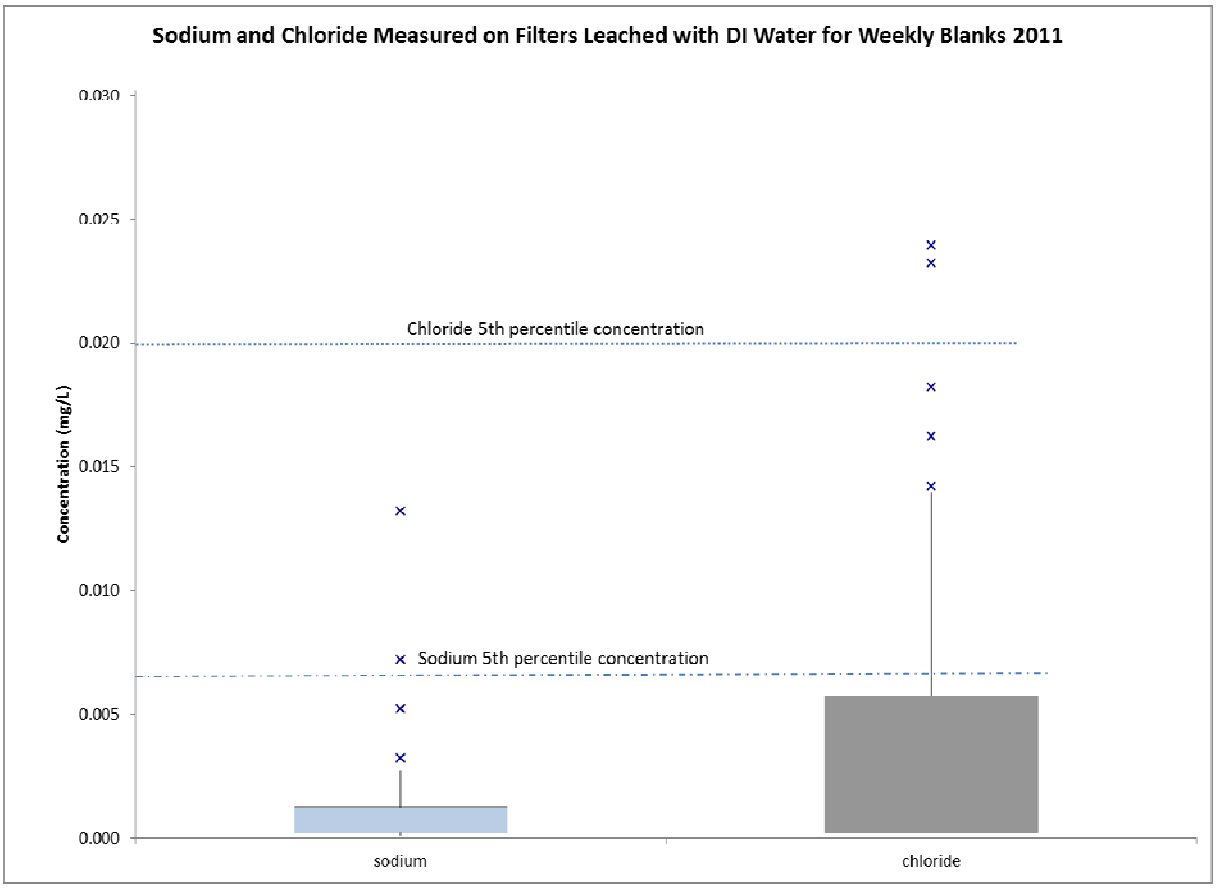

Figure 1. Box and whisker plot of sodium and chloride measured in DI used to leach filters for weekly blanks in 2011

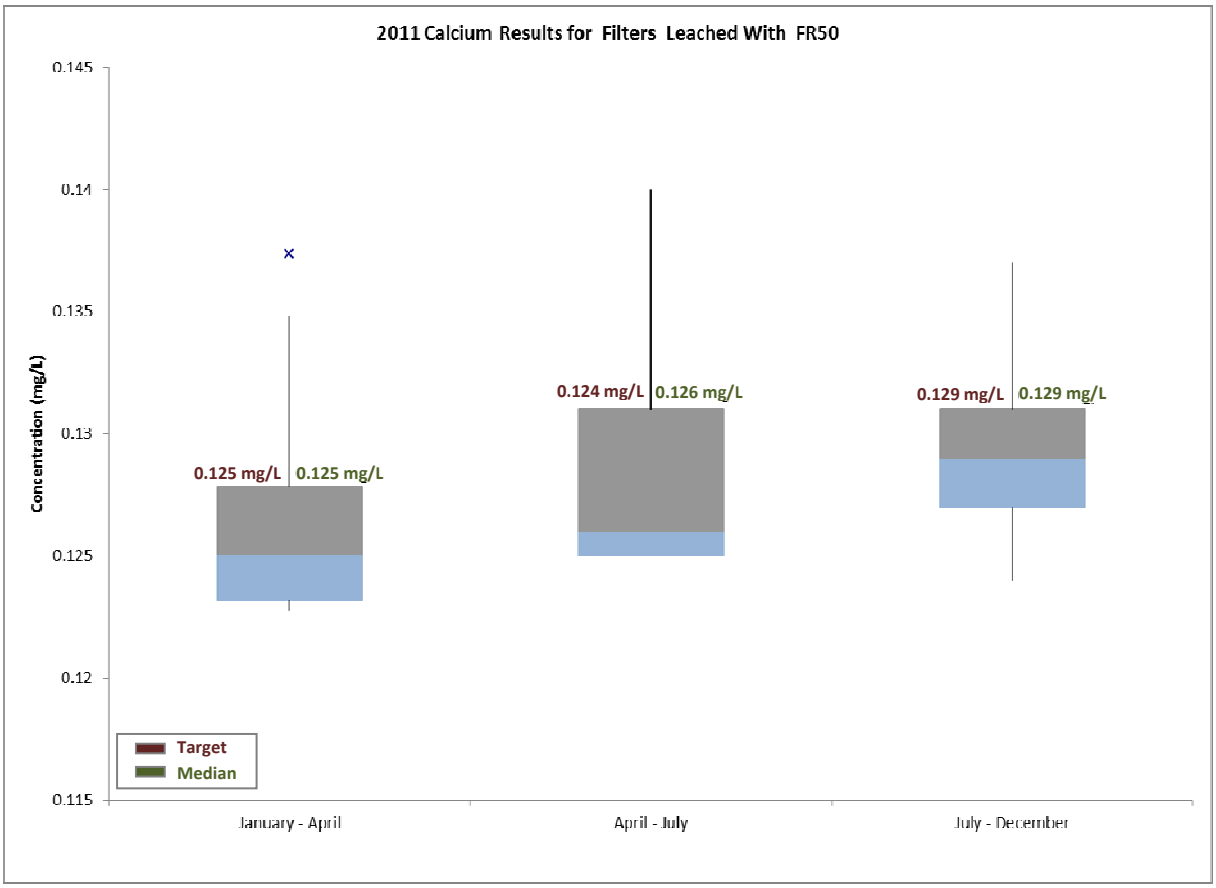

Figure 2. Box and whisker plot of calcium measured in FR50 used to leach filters for weekly blanks in 2011

Buckets, Bottles, and Lids

For supplies that are washed and reused (e.g., buckets, lids, and standard NTN 1 L bottles), when the analyte concentrations exceed target levels, the supply is rewashed and rechecked. If the supply does not pass the second check, it is discarded. Supplies are discarded in cases in which ammonium is below the control limits.

The same buckets are used for both NTN and AIRMoN sample collection. Changes implemented in 2011 include setting the test volume at 150 mL and using FR50 as the sole test solution. Blanks are set for a week to mimic the maximum exposure that may occur in the field. It is likely that contamination will dissolve in the test solution immediately if it is present. An evaluation comparing week-long blanks to 24-hour blanks was conducted in 2011. Late in 2011, an FR50 solution was spiked with orthophosphate to evaluate its usefulness as an additional control for the FIA instrument. Results were unexpected, in that orthophosphate concentrations were non-detectable, and the addition of the nutrient appeared to influence other measurements. As such, DI water was used for five weeks of weekly blank testing until a new FR50 solution without orthophosphate was prepared.

Results of bucket blanks exceedences during 2011 are shown in Table 9. The FR50, 24-hour outliers for potassium and chloride occurred in the same bucket. This particular bucket was rewashed and tested and found to be within control limits. One bucket tested with DI water for 24 hours had outliers for chloride, nitrate, and sulfate; it was also rewashed and tested and found to be within control limits.

Table 9. Number of results outside of target limits in 2011 for bucket blanks

Parameter	FR50 24 Hours N=210	FR50 1 Week N=210	DI 24 Hours N = 15	DI 1 Week N = 15
pH	0	0	0	0
Specific Conductance	0	0	0	0
Calcium	0	5	0	0
Potassium	1	0	0	0
Magnesium	0	0	0	0
Sodium	0	0	0	0
Chloride	1	0	1	0
Sulfate	0	0	1	0
Nitrate	0	0	1	0
Ammonium	8	6	1	0
Orthophosphate	NA	NA	0	0

There were five FR50 outliers for calcium in the one-week leach samples. Calcium is used during bucket manufacturing for extrusion and as a filler. Calcium has been measured in new buckets. As a result, new buckets are leached with nitric acid to remove the calcium. The levels detected routinely are low and are within the allowable control limits. Outliers are detected occasionally. Results for the year are shown in Figure 3.

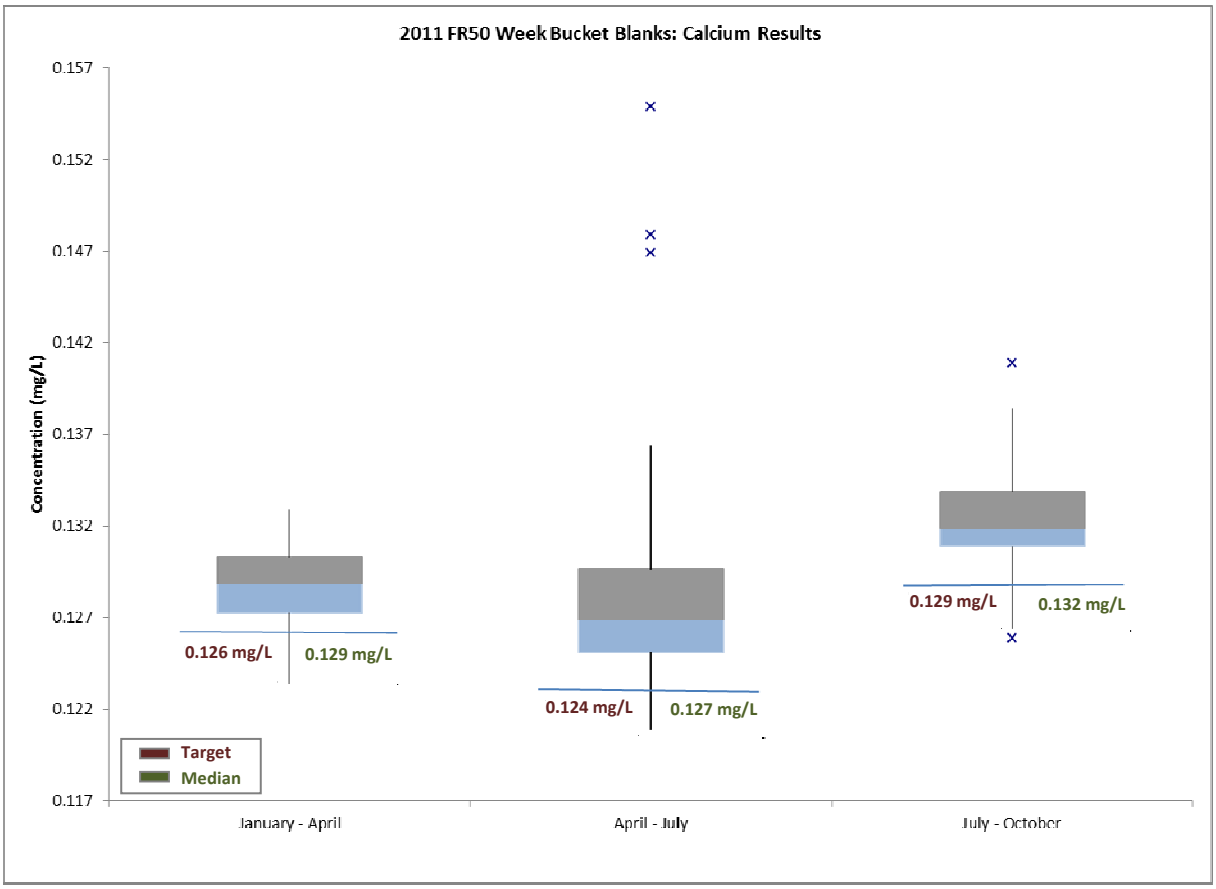

Figure 3. Box and whisker plot showing calcium results in buckets throughout 2011

Ammonium exceeded control limits 15 times throughout the year. Figure 4 shows the ammonium results measured in both 24-hour and weekly blanks. The variability in the ammonium results is due to absorption from the ambient air and biological processes. Results of buckets evaluated with the FR50 containing orthophosphate support the notion that a loss is due to the biological process.

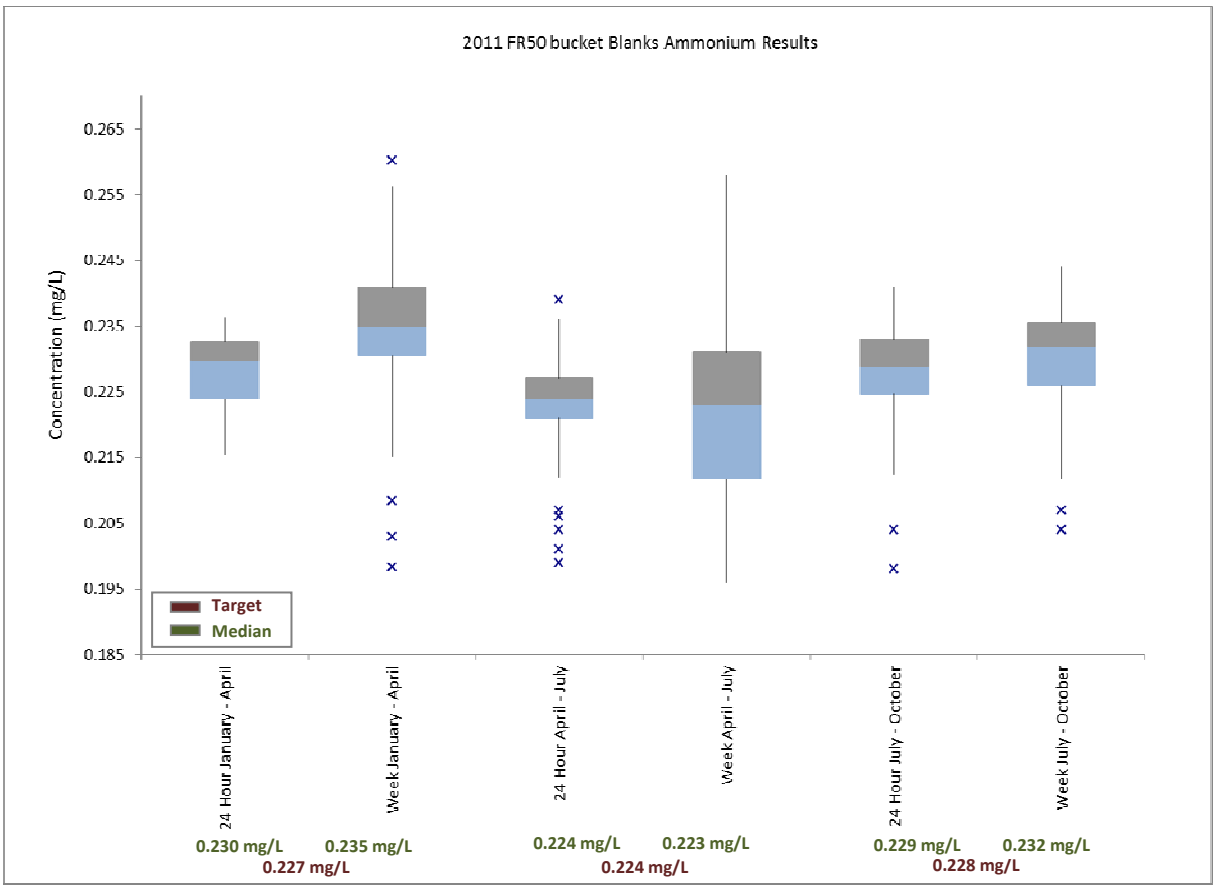

Figure 4. Box and whisker plot of ammonium concentrations measured in bucket blanks throughout 2011

The number of bottle blanks outside of control limits during 2011 is shown in Table 10. There were two outliers for potassium; these two bottles also had the most significant decreases for ammonium. Since potassium is a nutrient, this loss is likely due to biological activity. Figure 5 compares the FR50 blank data for both 24-hour and week-long samples. There appears to be a consistent negative deviation from the target concentrations. It is likely that ammonium is decreasing due to a biological process.

Table 10. Number of results outside of target limits in 2011 for bottle blanks

Parameter	FR50 24 Hours N=210	FR50 1 Week N=210	DI 24 Hours N = 15	DI 1 Week N = 15
pH	0	0	0	0
Specific Conductance	0	0	0	0
Calcium	0	0	0	0
Potassium	2	0	0	0
Magnesium	0	0	0	0
Sodium	0	0	0	0
Chloride	0	0	0	0
Sulfate	0	0	0	0
Nitrate	0	0	0	0
Ammonium	8	3	0	0
Orthophosphate	NA	NA	0	0

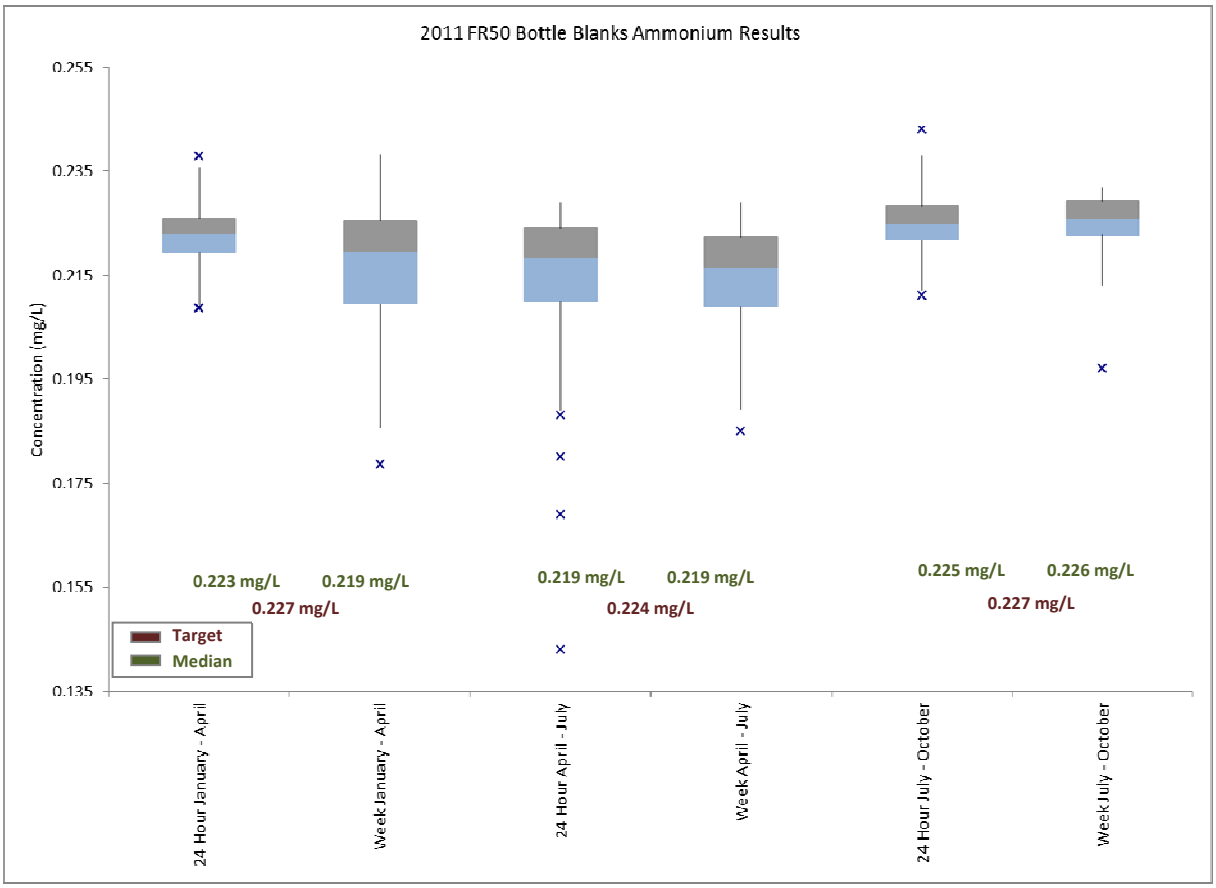

Figure 5. Box and whisker plot of ammonium concentrations measured in bottle blanks throughout 2011

Small amounts of sodium were detected in lid blanks (Table 11). Sodium was detected in lid bag blanks. This is likely the origin of sodium found on lids. Sodium in lid bags was also reported in 2010. Alternate bags were investigated, but they showed more contamination than the current bags. The 2011 median was slightly above the target concentration for sodium throughout the year but decreased halfway through the year (Figure 6). The elevated background in bags is not constant and seems to vary between individual packages. The CAL has continued to use lid bags. If levels were above the limits, the CAL could use bucket bags until a suitable replacement was found.

Table 11. Number of results outside of target limits in 2011 for bucket lids

Parameter	DI N=76	FR50 N=110
pH	0	0
Specific Conductance	0	0
Calcium	0	0
Potassium	0	0
Magnesium	0	0
Sodium	3	14
Chloride	0	0
Sulfate	0	0
Nitrate	0	0
Ammonium	1	2
Orthophosphate	0	NA

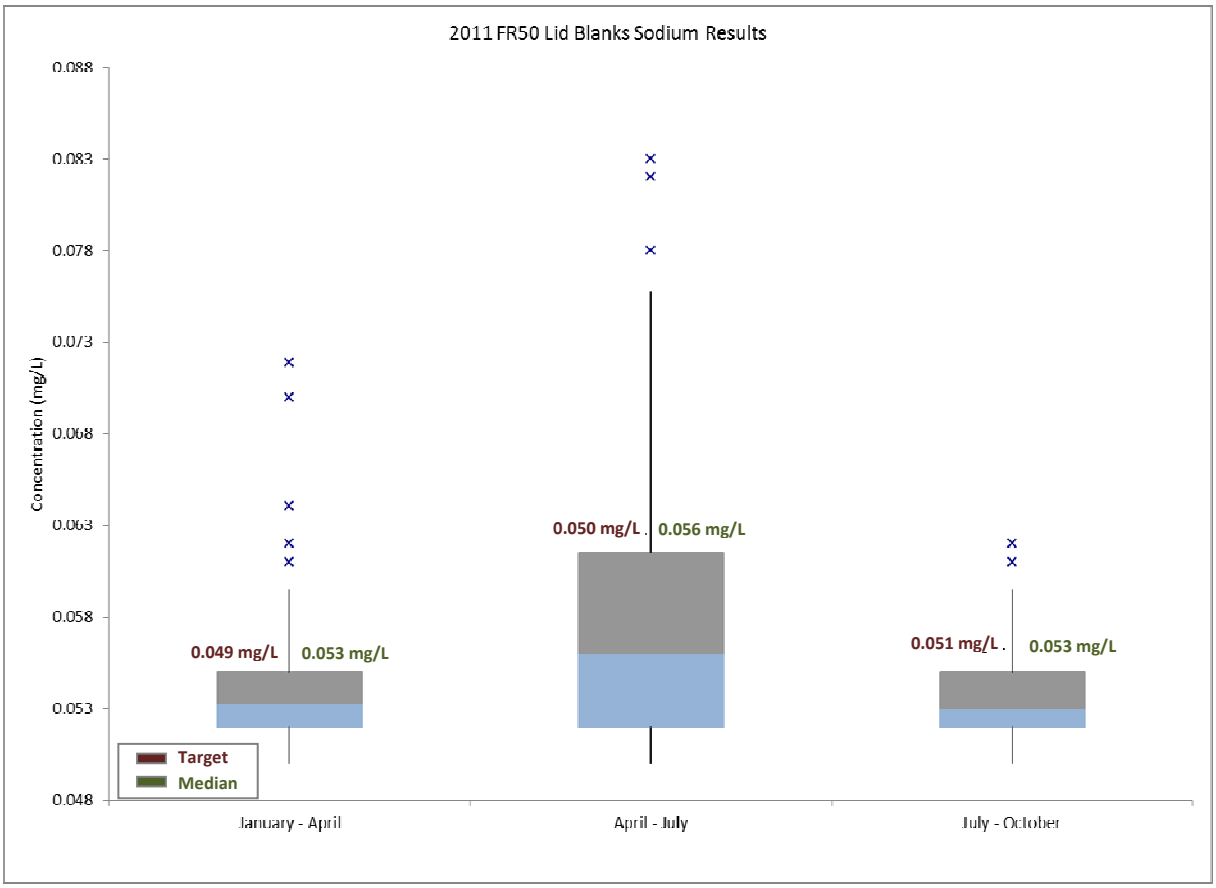

Figure 6. Box and whisker plot showing sodium measured in FR50 lid blanks throughout 2011

The median concentration of ammonium from lid blanks is slightly higher throughout the year for both DI Lid blanks (Figure 7) and FR50 Lid blanks (Figure 8). It is speculated that ambient concentrations of ammonia in the laboratory air are the cause of the elevated concentrations.

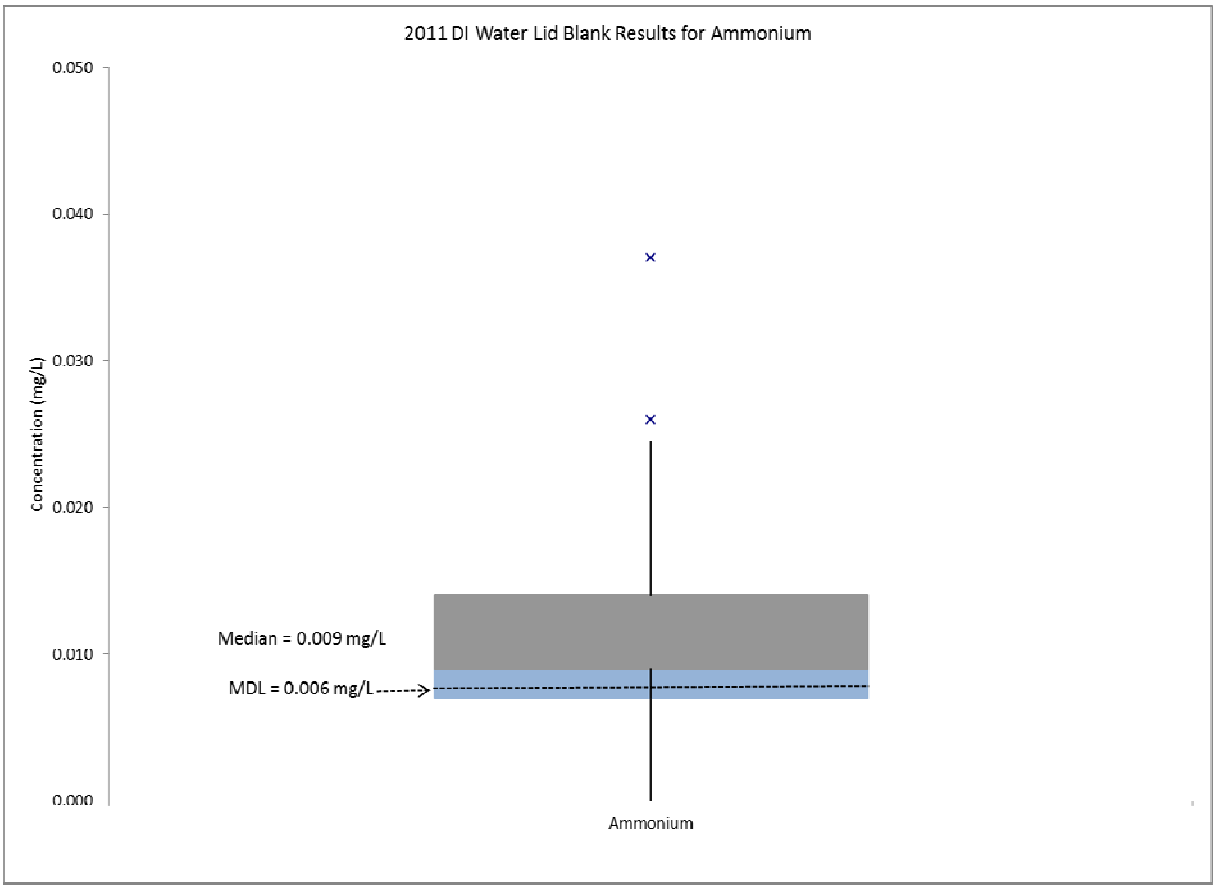

Figure 7. Box and whisker plot showing ammonium measured in DI water lid blanks throughout 2011

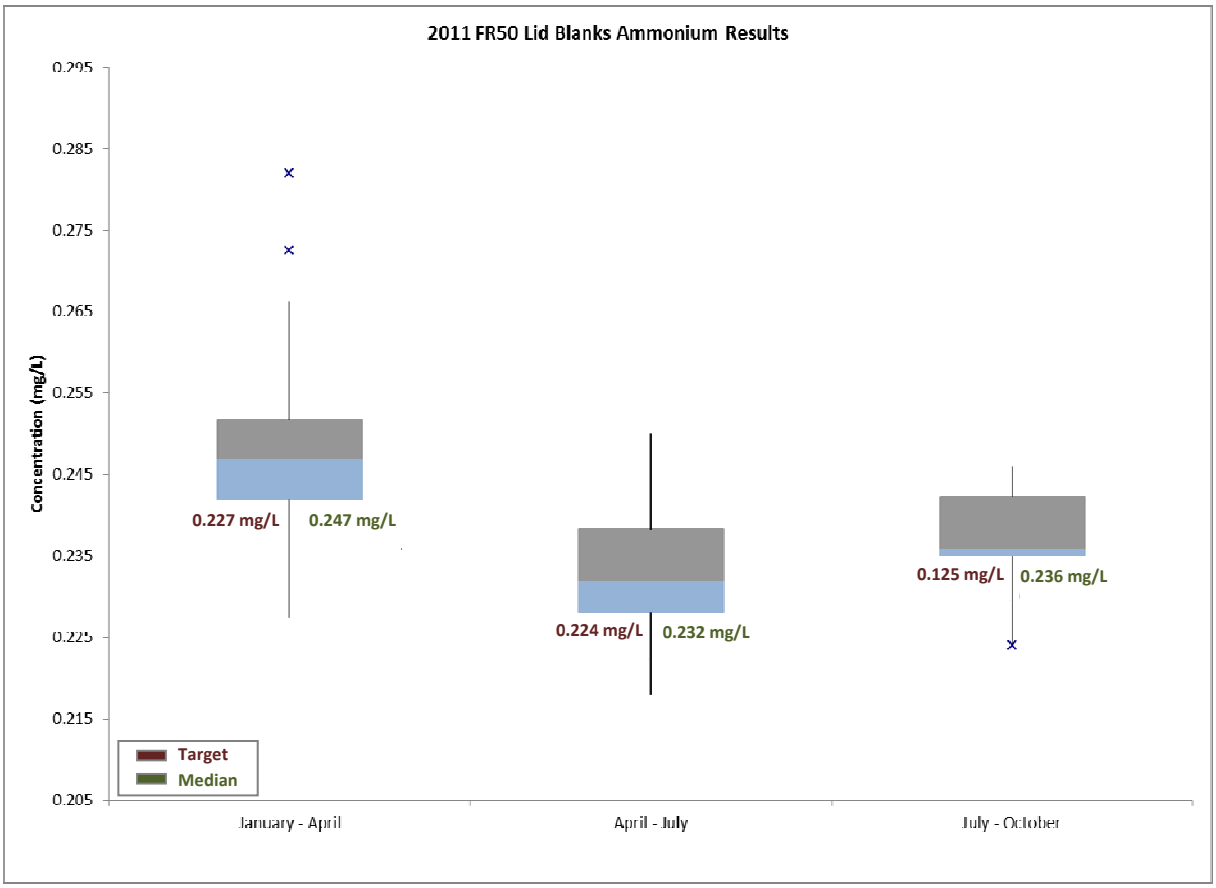

Figure 8. Box and whisker plot showing ammonium measured in FR50 lid blanks throughout 2011

AIRMoN bottles are single-use 250 mL Nalgene bottles that are not rewashed or reused. AIRMoN bottles were within the acceptable limits for all analytes throughout 2011.

Lid Bags

Lid bags are acceptance tested whenever a new shipment of bags is received. If a bag fails the acceptance test, one to two additional bags from the lot are tested. When sodium in additional bags exceeded limits, the lid bags are evaluated by placing clean lids into the bags. The lids remained in the bags for at least 24 hours and are tested following the weekly blank protocol. If these results do not exceed limits, the bags are used; if they fail, the bags are rejected. New lid bags from another manufacturer were evaluated, but these bags were found to contain even higher levels of sodium.

Bucket Bags

New bucket bags are acceptance tested whenever a new shipment of bags is received. All bucket bag results were within the acceptable target limits for all analytes throughout 2011.

Quality Assurance Discussion

Internal Blind Results

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

IDL and MDL Results

The MDL study conducted during 2011 was modified from previous years to incorporate the results from filtered samples. Analyses of filtered blind samples were used to calculate MDLs for NTN. Analyses of unfiltered samples were used to calculate MDLs for AIRMoN. Blind DI water samples were used to calculate IDLs. Results from the 2011 MDL and IDL studies are shown in Table 12.

Table 12. 2012 MDLs and IDLs

Ion	MDL for 2012		IDL for 2012 NTN & AIRMoN (mg/L)
	NTN (mg/L)	AIRMoN (mg/L)	
Calcium	0.005	0.002	0.001
Potassium	0.003	0.001	0.001
Magnesium	0.002	0.001	0.001
Sodium	0.002	0.001	0.001
Chloride	0.009	0.006	0.001
Nitrate	0.010	0.007	0.001
Sulfate	0.010	0.007	0.001
Ammonium	0.009	0.008	0.005
Orthophosphate	0.005	0.005	0.005

AES-05 and FR50 Solution Results

The RSDs and accuracy met the acceptance criteria for the AES-05 in 2011 (Table 13).

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

Parameter	Target	RSD Unfiltered N = 25 (%)	RSD Filtered N = 9 (%)	Recovery Unfiltered N = 25 (%)	Recovery Filtered N = 9 (%)
pH	4.90	.7	NA	99.6	NA
Specific Conductance	10.8 µS/cm	1.9	NA	105.0	NA
Calcium	0.187 mg/L	3.0	2.0	104.9	109.9
Potassium	0.037 mg/L	2.8	4.3	95.7	93.2
Magnesium	0.181 mg/L	2.4	2.4	104.5	103.1
Sodium	0.028 mg/L	2.1	1.8	101.0	99.6
Chloride	0.225 mg/L	4.2	2.4	105.1	103.7
Sulfate	1.28 mg/L	2.1	1.1	101.0	99.5
Nitrate	1.15 mg/L	1.9	1.2	101.6	100.5
Ammonium	0.312 mg/L	1.2	6.7	100.4	96.1

The recovery and RSDs for the internal blind FR50 met all acceptance criteria in 2011 (Table 14).

Table 14. RSDs and recoveries for internal blind FR50 solution

Parameter	Target	RSD Unfiltered N = 24 (%)	RSD Filtered N = 11 (%)	Recovery Unfiltered N = 24 (%)	Recovery Filtered N = 11 (%)
pH	4.80	0.9	NA	100.0%	NA
Specific Conductance	10.6 µS/cm	2.0	NA	100.3%	NA
Calcium	0.123 mg/L	1.8	1.6	101.2	102.1
Potassium	0.023 mg/L	3.2	3.3	97.3	97.4
Magnesium	0.049 mg/L	2.4	3.5	101.2	99.7
Sodium	0.021 mg/L	2.1	2.1	99.0	99.8
Chloride	0.098 mg/L	7.4	2.6	100.8	100.3
Sulfate	0.828 mg/L	2.7	1.2	100.1	99.2
Nitrate	0.958 mg/L	1.9	1.0	99.6	99.0
Ammonium	0.227 mg/L	1.1	2.7	100.7	100.1

Split, Replicate, and Reanalysis Samples

The flow of data from the CAL to the Program Office is shown in Figure 9. Chemistry results are reviewed by the analysts on a weekly basis for data completeness before they are released to the data manager. The data manager calculates the Ion Percent Difference (IPD) and Conductivity Percent Difference (CPD) to identify samples for reanalysis. An additional 2 percent of samples are selected at random for reanalysis. Generally, the reanalysis results are targeted for a reproducibility of 10 percent, but this can be extended if the concentration is near the MDL for a particular analyte. If samples fall outside the 10 percent difference windows, analysts try to determine the cause and analyze additional samples within the run. The results are reviewed by the QA Chemist and required edits are made. A total of 82 edits were made for NTN samples and 12 edits were completed for AIRMoN samples.

The CAL processed 164 pairs of split samples in 2011. The median percent difference was less than 1 percent for each analyte.

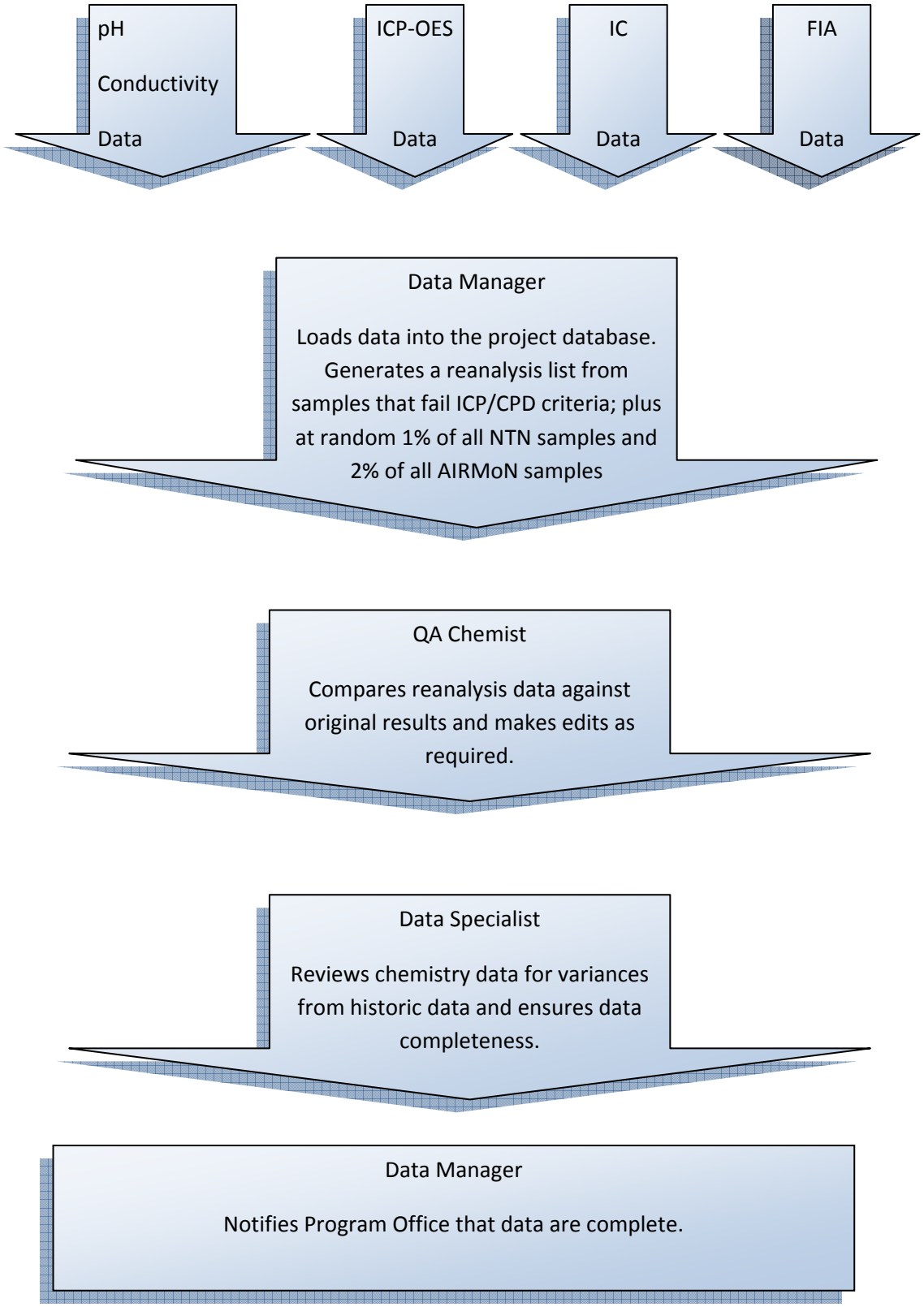

Figure 9. Flow of data from the CAL to the Program Office

The total number of samples with complete analysis and total number of QC samples are listed in Table 15. The total number of control chart checks includes all samples that the analysts check against control charts during an analytical run.

Table 15. Number of real and Quality Control (QC) samples analyzed during 2011

Network	Number Of Samples Analyzed	Number Of Reanalysis Samples	Number Of Split Samples	Number Of Blind Samples	Number of Control Chart Checks (percentage of samples analyzed)
NTN	10223	1100	145	163	pH/conductivity = 5174 (34%) ICP/OES = 4156 (29%) FIA = 5990 (37%) IC = 4431 (30%)
AIRMoN	1014	231	19	59	

Replicate results were within allowable precision for all samples tested. The allowable bias at 10 to 100 times the MDL is ± 20 percent (Table 16). There is no practical MDL for pH; hence the results for all of the pH replicates are also shown in Table 16. The allowable bias at 100 times the MDL is ± 10 percent (Table 17). CAL met requirements for analytical precision for all analytes, but the maximum RPD for calcium was at the allowable limit.

Table 16. Replicate samples, concentrations 10 to 100 times the MDL

Parameter	10 to 100 x MDL	n	Average RPD %	Maximum RPD %	Minimum RPD %
pH	NA	398	1.2	9.9	0
Specific Conductance	>3 µS/cm	273	5.6	18.6	0
Calcium	0.020 – 0.200 mg/L	165	5.3	20.4	0.2
Potassium	0.010 – 0.100 mg/L	175	3.4	11.9	0
Magnesium	0.010 – 0.100 mg/L	169	3.1	15.3	0
Sodium	0.010 – 0.100 mg/L	116	2.9	19.2	0
Chloride	0.050 – 0.500 mg/L	200	1.7	17.9	0.1
Sulfate	0.030 – 0.300 mg/L	64	1.6	8.2	0.1
Nitrate	0.040 – 0.400 mg/L	73	1.1	6.4	0.1
Ammonium	0.060 – 0.600 mg/L	135	2.0	10.2	0.4

Table 17. Replicate samples, concentrations greater than 100 times the MDL

Parameter	10 to100 x MDL	n	Average RPD %	Maximum RPD %	Minimum RPD %
Specific Conductance	>15 µS/cm	73	3.5	10.4	0
Calcium	> 0.200 mg/L	87	2.5	7.5	0
Potassium	> 0.100 mg/L	23	2.8	7.1	0.7
Magnesium	> 0.100 mg/L	25	1.9	4.2	0.2
Sodium	> 0.100 mg/L	103	2.3	7.1	0.2
Chloride	> 0.500 mg/L	47	1.0	9.9	0
Sulfate	> 0.300 mg/L	265	1.0	5.5	0
Nitrate	> 0.400 mg/L	275	0.8	4.9	0
Ammonium	> 0.600 mg/L	70	0.9	2.6	0.2

AMoN

Samples for the AMoN network are frozen upon receipt at the CAL. Samples are extracted and analyzed in batches on a weekly basis. During the extraction process, four additional samples are created to evaluate the background levels. These samples include:

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

The results for these samples for 2011 are shown in Figure 10. Acceptable limits are 0.200 mg/L. All DI water, new core blanks, and hood blanks were below the acceptable limits. Numerous travel blanks sent with deployed samples to field sites exceeded the limits throughout the year (Figure 10). The reason for the numerous exceedances continues to be investigated.

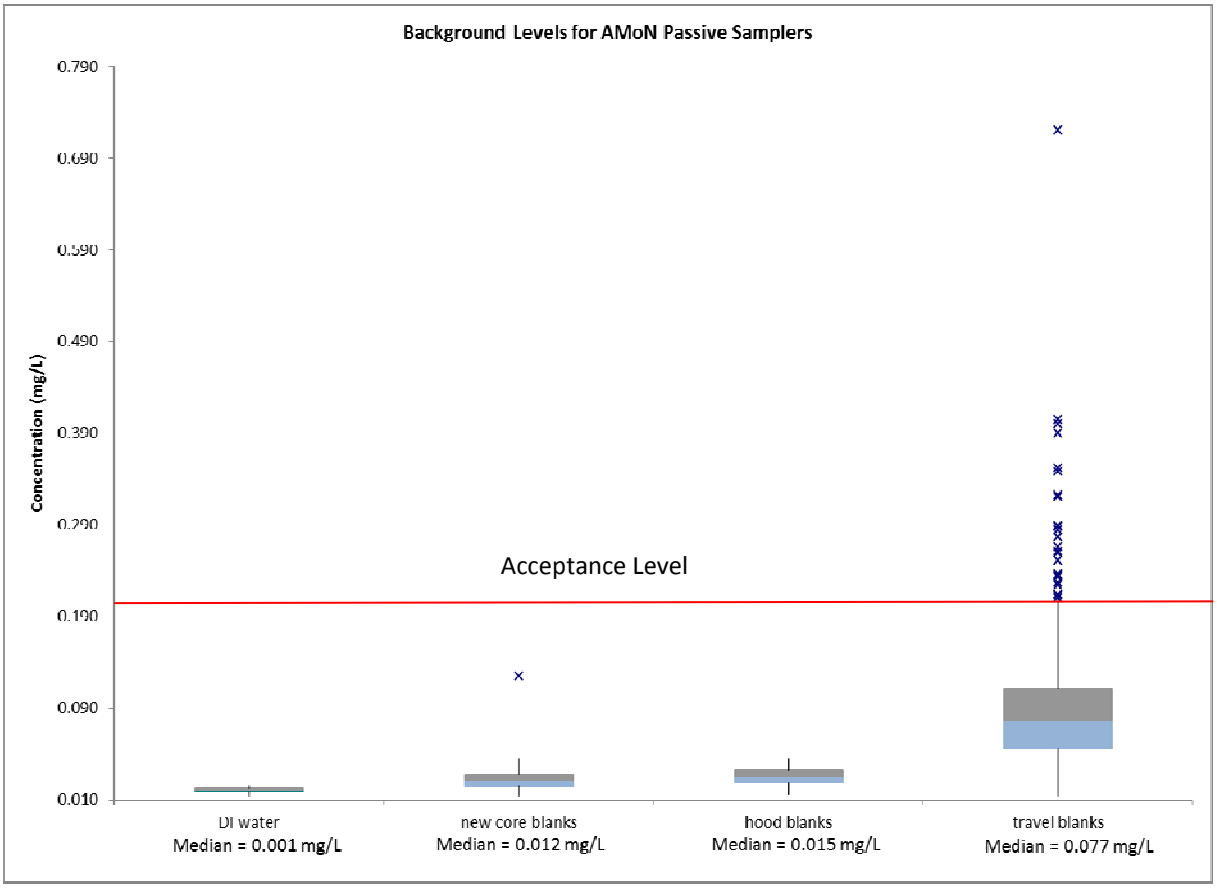

Figure 10. Box and whisker plot for ammonium ion concentrations in lab DI blanks, new core blanks, hood blanks, and travel blanks in sampler extracts in 2011

In order to understand why travel blank data exceeded the limits, the CAL staff began troubleshooting efforts in June 2011. The first efforts focused on isolating the problem. Two sets of three travel blanks with cores in sampler bodies and three travel blanks with cores only and no sampler bodies were prepared for storage at the Bondville, Illinois site and in the CAL laboratory. Measurable differences between travel blanks containing only cores and travel blanks with cores placed in sampler bodies were observed (Figure 11).

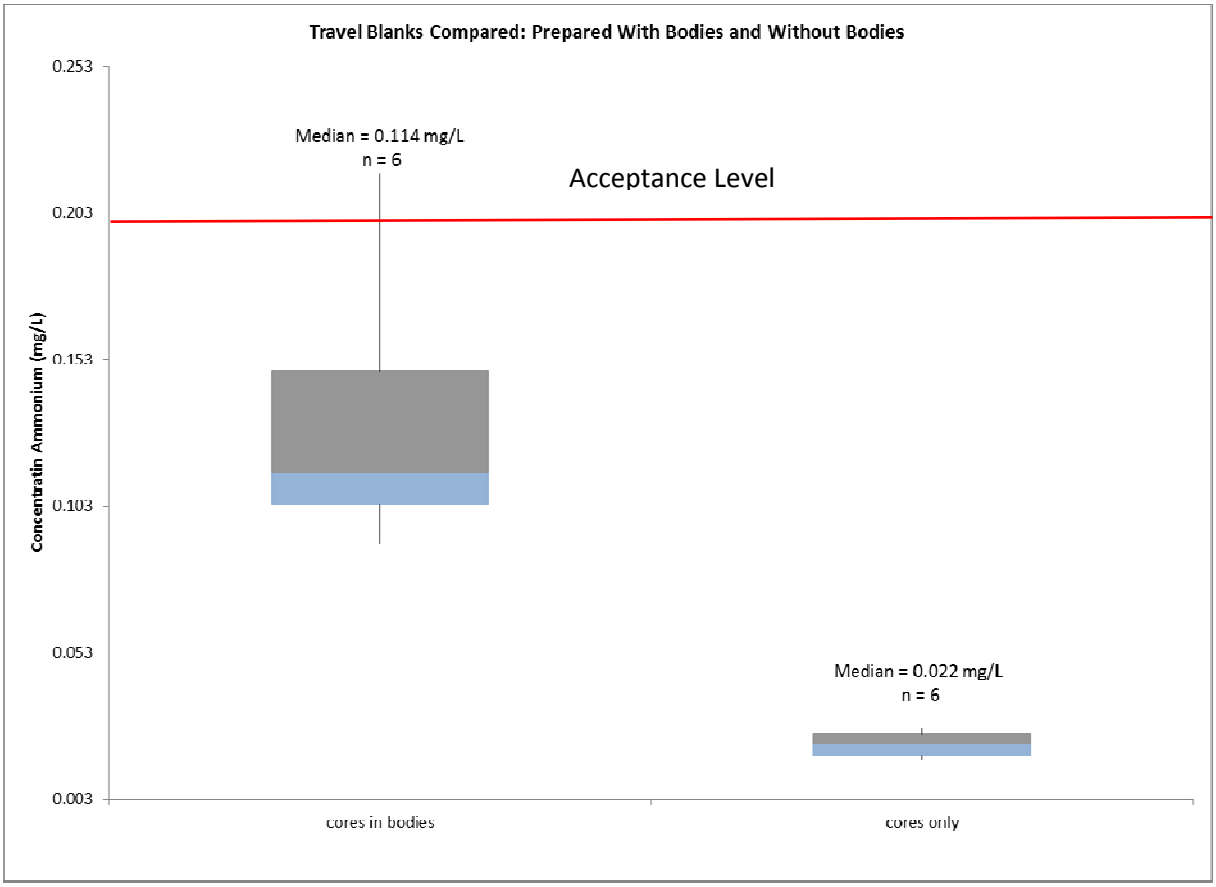

Figure 11. Box and whisker plot for ammonium ion concentrations in travel blanks prepared with and without bodies

Additional efforts focused on alternate methods for cleaning the sampler bodies. The standard cleaning procedure consisted of rinsing the sampler bodies and sonicating them fully submerged in a heated bath with polisher water for three one-hour periods. Beginning in July, the water was changed and the sampler bodies rinsed between each of the three one-hour sonication periods. In October CAL staff begin placing the cleaned sampler bodies in a vacuum desiccator. The sampler bodies were removed from the desiccator when they were to be prepared for deployments. A list of dates and changes are documented in Table 18. These changes did not significantly reduce the background levels detected in travel blanks (Figure 12). The evaluation of cleaning methods will continue.

Table 18. History of changes in cleaning procedures for AMoN sampling devices

Date	Change
7/15/2011	Triple rinse
10/10/2011	Vacuum Desiccator
10/10/2011	2 citric acid filters in vacuum desiccator
10/24/2011	2 citric acid filters + 2 AMoN cores in vacuum desiccator
12/05/2011	New core only in vacuum desiccator
12/12/2011	Replaced core in vacuum desiccator

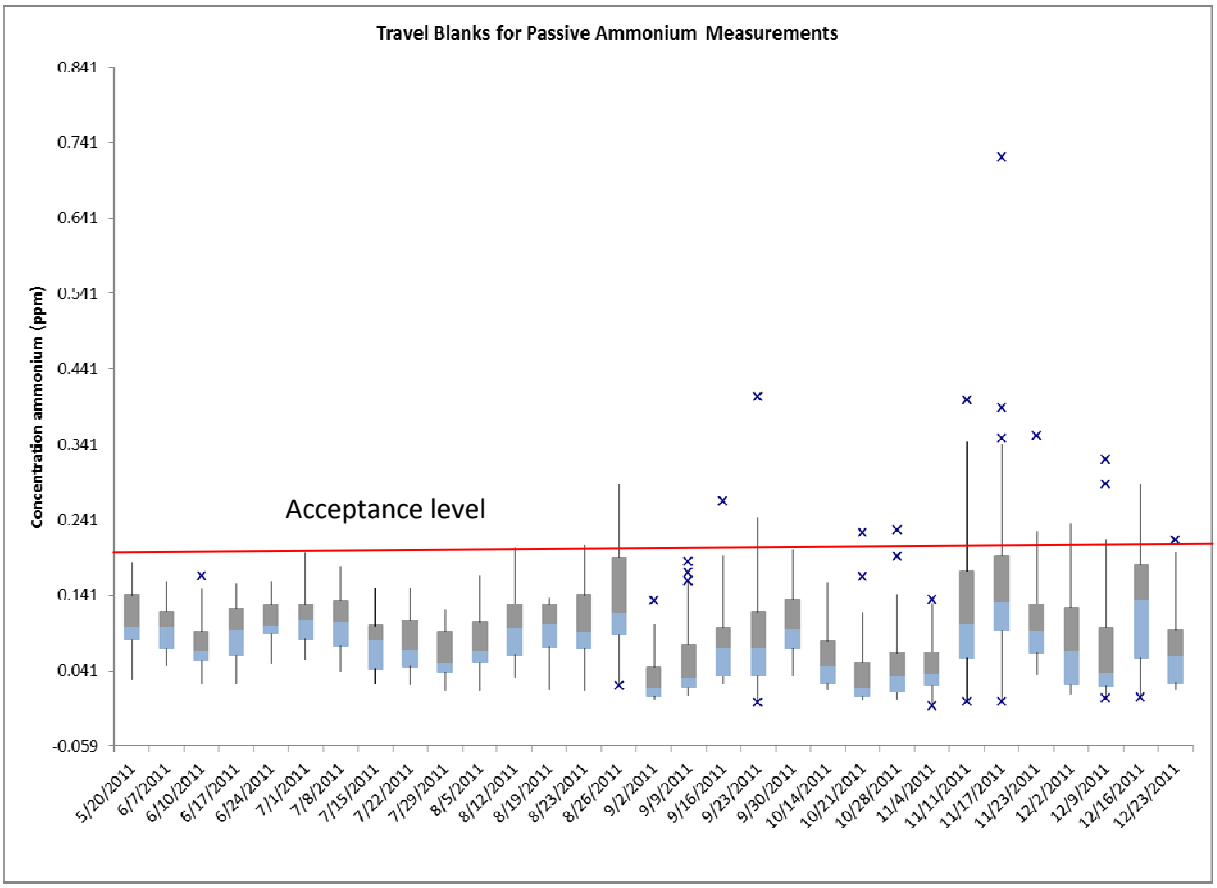

Figure 12. Box and whisker plot for ammonium ion concentrations in travel blanks shown from May 2011 through December 2011. Dates represent sample end.

The precision of triplicate measurements increased a little in 2011 compared to 2010 and 2009. However, the overall number of samples dramatically decreased. The relative percentage differences (RPDs) were calculated using the range divided by the average of the triplicate results. The average and median RPDs are shown in Table 19.

Table 19. Average and median RPDs for triplicate AMoN samples

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

External Quality Assurance

The CAL participated in four external proficiency testing studies throughout 2011. The study identifier and websites with study details and results are shown in Table 20. The CAL's performance was consistent with that of other top-performing laboratories participating in each of the studies.

Table 20. 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 45 and 46	World Meteorological Organization/Global Atmospheric Watch (WMO/GAW)	http://www.qasac-americas.org/
Study 98 and 99	Environment Canada Proficiency Testing Program	Available upon request
Study 28	Norwegian Institute for Air Research (NILU)	Available upon request

Conclusions

The CAL performed consistently throughout 2011 and met the guidelines as specified in the NADP Network Quality Assurance Plan (QAP).

References

Central Analytical Laboratory SOPs available upon request.

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

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

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

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

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